Understanding the Thermodynamics at the LaMnO$_3$–YSZ Interface in SOFC

A dissertation submitted to the
SWISS FEDERAL INSTITUTE OF TECHNOLOGY
ZURICH

for the degree of
Doctor of Sciences

presented by
Ming Chen
Dipl. Ing. SICCAS
born on June 30, 1973
citizen of China

accepted on the recommendation of
Prof. Dr. Ludwig J. Gauckler, examiner
Prof. Dr. Hans Christian Oettinger, co-examiner
Dr. Bengt Hallstedt, co-examiner

Zurich, 2005
Acknowledgements

I am very grateful to Professor Dr. Ludwig J. Gauckler for giving me this opportunity to enter into the field of thermodynamic modeling and for invaluable support during this thesis. He gave me many opportunities to present my work at international conferences.

I am highly indebted to Dr. Bengt Hallstedt who brought me into the CALPHAD world, taught me the basics of the thermodynamic modeling, and guided me through my whole PhD study.

I wish to thank Dr. A. Nicholas Grundy for many helpful scientific discussions and for improving the quality of this thesis.

I would like to express my thanks to my colleagues at the Institute of Nonmetallic Inorganic Materials for helping me with everything. Special thanks go to Dr. David Sager for his great help in the beginning of my PhD study, Irene Urbanek for administrative work, Erwin Povoden for proof reading of this thesis, and my office mates, Dr. Elena Tervoort, Dr. André Studart, Dr. Kurosch Rezwan, Dr. Carlos Pagliosa Neto, Dr. Michel Prestat for many amusing conversations.

Many thanks go to my friends who used to live at Justinus-Heim for the enjoyable time we spent together and to my German teacher Harri Seidmann.

Finally I thank my parents and Yuehua for their continuous support and encouragement.
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Summary

This study presents a consistent thermodynamic description of the La–Mn–Y–Zr–O system. Based on crystal structure and chemical information, suitable models are chosen to reproduce the Gibbs energies of the phases. The Gibbs energy of each phase is represented as a function of temperature and - in the case of a solution phase - composition with adjustable parameters. The adjustable parameters are optimized using critically assessed thermodynamic data and phase diagram data. The whole procedure is called the CALPHAD (CALculation of PHAse Diagrams) method. A short introduction to this method is given in the first chapter.

In the La–Mn–Y–Zr–O system, the LaMnO₃ perovskite phase and the c-ZrO₂ (cubic fluorite) phase are of great importance. Yttria stabilized zirconia (YSZ, cubic fluorite) and Sr-doped LaMnO₃ perovskite (LSM) have been widely used as electrolyte and cathode materials in solid oxide fuel cells (SOFCs). Under certain conditions, highly electrically resistive phases (La₃Zr₂O₇ and/or SrZrO₃) are formed at the cathode–electrolyte interface, leading to degradation of the SOFC performance. This thesis is part of the project “Thermodynamic modeling of the LSM–YSZ interface reactions in SOFCs”.

This work starts with the Y–Zr–O system, in which the thermodynamic descriptions of the two binary systems Y–O and Zr–O and that of the ternary Y–Zr–O system are assessed (Chapter 2). By including the existing thermodynamic descriptions of the La–Mn–O and Mn–Y–Zr systems, 4 ternary systems Mn–Y–O (Chapter 3), Mn–Zr–O (Chapter 4), La–Y–O (Chapter 5), La–Zr–O (Chapter 6) and 1 quaternary system Mn–Y–Zr–O (Chapter 4) are assessed. The thermodynamic description of the La–Mn–Y–Zr–O system (Chapter 7) is obtained by an ideal extrapolation of the descriptions of the assessed sub-systems.

The most interesting part of this thesis is on the LaMnO₃–YSZ reactions (Chapters 7–9). Chapter 7 presents the calculated equilibrium phase relations in the LaO₁.₅–MnOₓ–YO₁.₅–ZrO₂ system. Calculations show that the thermodynamic origin of the La₃Zr₂O₇ formation at the LaMnO₃–YSZ interface is due to the high stability of the La₃Zr₂O₇ phase. Thermodynamically, increasing the La deficiency in LaMnO₃ cannot prevent the La₃Zr₂O₇ formation. This differs from the previous calculations from the literature. We
evaluate both the current thermodynamic description and the one from the literature (Chapter 8). The discrepancy is mainly ascribed to a difference in the Gibbs energy function of La$_2$Zr$_2$O$_7$. The current description reproduces the experimental data more satisfactorily and is shown to be the best description available till now.

In Chapter 9, previous experimental investigations on the LaMnO$_3$–YSZ reactions are reviewed. Local equilibrium calculations at the LaMnO$_3$–YSZ phase interface are conducted. The driving forces of the La$_2$Zr$_2$O$_7$ formation and of the La and Mn diffusion (from LaMnO$_3$ into YSZ) are related to the chemical potentials of metal elements. The factors influencing the La$_2$Zr$_2$O$_7$ formation and the La and Mn diffusion are clarified. It is shown that the driving force of the La$_2$Zr$_2$O$_7$ formation is mainly determined by the cation stoichiometries of LaMnO$_3$ and YSZ. Increasing the La deficiency in LaMnO$_3$ or the yttria content in YSZ decreases the driving force. In certain cases, the La$_2$Zr$_2$O$_7$ formation can be kinetically hindered. The driving force of the La or Mn diffusion strongly depends on the cation stoichiometry of LaMnO$_3$. Increasing the La deficiency in LaMnO$_3$ decreases the driving force of the La diffusion but increases that of the Mn diffusion. These calculations clarify the discrepancies between different experimental observations.

In conclusion, by applying the CALPHAD method, a consistent thermodynamic description of the La–Mn–Y–Zr–O system is obtained. The current description offers a better and thorough understanding of the thermodynamics at the LaMnO$_3$–YSZ interface. Measures are outlined to retard the zirconate formation by proper choice of the stoichiometries of the phases involved.
Zusammenfassung


Nach diesen Grundlagen kann die Bildungsbedingungen der wichtigen Phase La₂Zr₂O₇ als Produkt der Reaktion von LaMnO₃ mit YSZ diskutiert werden (Kapitel 7–9). Kapitel 7 zeigt die gleichgewichts Phasenbeziehungen im System LaO₁,₅–MnOₓ–YO₁,₅–ZrO₂ auf. Die
Berechnungen zeigen, dass die Ursache für die La$_3$Zr$_2$O$_7$ Bildung an der LaMnO$_3$–YSZ Grenzfläche die hohe Stabilität der La$_3$Zr$_2$O$_7$ Phase ist. Thermodynamisch betrachtet kann eine Erhöhung der La Unterstöchiometrie in der Phase LaMnO$_3$ die La$_3$Zr$_2$O$_7$ Bildung nicht verhindern. Dieser Befund weicht von bestehenden thermodynamischen Berechnungen in der Literatur ab, beschreibt aber sehr gut die experimentellen Befunde. Wir vergleichen dann eingehend die thermodynamischen Berechnungen aus der Literatur mit unserer eigener Modellierung (Kapitel 8). Die Abweichungen zwischen den beiden Beschreibungen lassen sich eindeutig auf die Differenz der Gibbschen Energie der La$_3$Zr$_2$O$_7$ Phase zurückführen. Die vorliegende Beschreibung gibt die experimentellen Befunde zufriedenstellender wieder als die der bisherigen Modelle. Der neu vorgestellte Satz an thermodynamischer Funktionen der Phasen im System stellt die beste heute erhältliche thermodynamische Beschreibung dar.

In Kapitel 9 werden die experimentellen Untersuchungen der LaMnO$_3$–YSZ Reaktionen evaluiert. Berechnungen des lokalen Gleichgewichts an der LaMnO$_3$–YSZ Grenzfläche werden durchgeführt. Die Triebkraft für die La$_3$Zr$_2$O$_7$ Bildung und die La und Mn Diffusion (von LaMnO$_3$ in YSZ) hängen mit dem chemischen Potential der Metall-Elemente zusammen. Die Faktoren, die die La$_3$Zr$_2$O$_7$ Bildung und die La und Mn Diffusion beeinflussen werden aufgeklärt. Es wird gezeigt, dass die Triebkraft für die La$_3$Zr$_2$O$_7$ Bildung hauptsächlich von der Kationen Stöchiometrie von LaMnO$_3$ und YSZ abhängt. Wenn die La Unterstöchiometrie in LaMnO$_3$ oder der Yttriumgehalt in YSZ erhöht wird, kann die La$_3$Zr$_2$O$_7$ Bildung kinetisch hinauszögert werden. Die Triebkraft für die La oder Mn Diffusion wird stark von der Kationen Stöchiometrie in LaMnO$_3$ beeinflusst. Wenn die La Unterstöchiometrie in LaMnO$_3$ erhöht wird, wird die Triebkraft für die La Diffusion erhöht, die Triebkraft für die Mn Diffusion hingegen erniedrigt. Diese Ergebnisse erklären die Diskrepanzen zwischen verschiedenen experimentellen Befunden in der Literatur.

Aim of the Study

Fuel cells are electrochemical devices that convert chemical energy into electrical energy without the restrictions of the Carnot law. In a solid oxide fuel cell (SOFC), oxide ceramics are used as the electrolytes. The first SOFC was demonstrated by Baur and Preis in 1937 (cited by Ormerod [1]) operated at 1273 K. In the last two decades, significant advances have been made in both material’s development and cell design and manufacturing. SOFCs are now approaching commercial reality [2].

The state of the art SOFC uses yttria-stabilized zirconia (YSZ, cubic fluorite) as electrolyte, Ni-YSZ cermet as anode, Sr-substituted LaMnO$_3$ perovskite (LSM) as cathode, and LaCrO$_3$-based perovskite as interconnects. It is normally operated at 1173–1273 K. High preparation temperatures of the components and high operation temperatures promote unwanted interface reactions in the SOFC, especially at the cathode–electrolyte interface where the oxygen reduction is supposed to take place. Lau and Singhal [3] first reported the formation of La$_2$Zr$_2$O$_7$ between diffusion couples of LSM and YSZ. The La$_2$Zr$_2$O$_7$ formation has been reported to be influenced by a few factors, e.g. the cation stoichiometries of LSM and YSZ, the ratio between LSM and YSZ, the nanostructure of the interface and temperature to name just a few of them [4, 5, 6]. The cation stoichiometry of LSM is reported to be a decisive controlling factor. By increasing the A-site deficiency in LSM, the La$_2$Zr$_2$O$_7$ formation is retarded or even prevented during high temperature treatment. Partially substituting La with Sr inhibits the La$_2$Zr$_2$O$_7$ formation [7, 8]. However, high Sr content may also lead to SrZrO$_3$ formation. Both La$_2$Zr$_2$O$_7$ and SrZrO$_3$ are highly electrically resistive and their formation at the LSM–YSZ interface is at least partly responsible for the long-term degradation of the SOFC performance. Understanding the factors influencing the zirconate formation is obviously advantageous not only for improving the performance of the state of the art SOFC but also for developing the SOFC operated at intermediate temperature (873–1073 K). For this purpose, the thermodynamics and phase equilibria in the La–Mn–Sr–Y–Zr–O system are of particular importance. The aim is to answer the question whether the zirconate formation is thermodynamically inevitable and if so, which kinetic factors govern the zirconate nucleation and growth.
The thermodynamics of the LSM–YSZ reactions has been studied by Yokokawa et al. [9]. They evaluated or estimated the thermodynamic properties of solid solution phases and stoichiometric compounds in the La–Mn–Sr–Y–Zr–O system. The high stability of the La$_2$Zr$_2$O$_7$ phase was excluded to be the thermodynamic origin of the La$_2$Zr$_2$O$_7$ formation. Instead, they stated that the La$_2$Zr$_2$O$_7$ formation was due to the destabilization of the valence state of Mn$^{3+}$ in the perovskite phase in the presence of ZrO$_2$. According to their calculations, the La$_2$Zr$_2$O$_7$ formation can be thermodynamically prevented by increasing $x$ in La$_{1-x}$MnO$_{3-\delta}$ to a certain extent ($x = 0.14$ at 1573 K in air). Yokokawa et al.’s phase equilibrium calculations give a good explanation of the formation mechanism of La$_2$Zr$_2$O$_7$ at the LSM–YSZ interface. However, there still exist open questions, like the disagreement on the observed inter-diffusion between LSM and YSZ and the effect of the yttria content in YSZ. Until now, no other effort has been conducted on modeling the thermodynamics of the LSM–YSZ reactions. Instead, quite a lot of measurements have been done on the thermodynamic properties of stoichiometric compounds and solution phases in the La–Mn–Sr–Y–Zr–O system. In Yokokawa et al.’s database, the thermodynamic descriptions of certain phases were obtained from estimations. It is hence necessary to re-evaluate the thermodynamic description of the La–Mn–Sr–Y–Zr–O system and to reconsider the thermodynamic origin of the zirconate formation at the LSM–YSZ interface.

This thesis is part of the project “Thermodynamic modeling of the LSM–YSZ interface reactions in SOFCs”, in which the CALPHAD method is employed. The CALPHAD method is nowadays a standard technique in phase equilibrium studies. CALPHAD is an acronym for CAULculation of PHAse Diagrams. The aim of the CALPHAD method is to derive a consistent thermodynamic description for the Gibbs energies of all the phases in a certain system and also to reproduce all sorts of thermodynamic properties and phase diagrams in a reasonable and reliable manner. The thermodynamic description obtained by the CALPHAD method is in general more reliable than one derived from a sum of individual measurements.

The aim of this thesis is to obtain a consistent thermodynamic description of the La–Mn–Y–Zr–O (without Sr) system and to verify the thermodynamics at the LaMnO$_3$–YSZ interface serving as a prototype of the LSM–YSZ interface. Both thermodynamic and kinetic factors influencing the La$_2$Zr$_2$O$_7$ formation will be clarified.
Aim of the Study

References

1 Introduction

1.1 Solid oxide fuel cell

A fuel cell is an electrochemical device that can directly convert chemical energy into electrical energy. It consists of two electrodes (the anode and the cathode) separated by an electrolyte. Figure 1.1 is a schematic diagram of the fuel cell. When the fuel cell is in operation, fuel and oxidant are fed to the anode and the cathode, respectively. At the anode, the fuel is oxidized and electrons are then released to the external circuit. At the cathode, the oxidant receives electrons from the external circuit and is reduced. The electrolyte conducts ions between the cathode and the anode. The direct-current (DC) electricity is produced by the electron flow through the external circuit [1]. Compared with conventional power generation, the fuel cell technology offers several advantages: substantially higher energy conversion efficiency, much lower production of pollutants, modular construction, siting flexibility and so on [1]. The concept of the fuel cell was first demonstrated by William Grove in 1839 [2]. For more details on fuel cells, the readers are referred to [3, 4, 5].

Solid oxide fuel cells (SOFCs) use solid oxide ceramics as the electrolyte and are operated at elevated temperatures, typically 1073–1273 K. The high operating temperature results in high reaction rates. No expensive catalysts are thus needed. Another advantage of SOFCs is that it can use natural gas directly. Following the discovery of solid oxide electrolytes by Nernst in 1899 [6], Baur and Preis (cited by Ormerod [7]) demonstrated the first SOFC running at 1273
K in 1937. Due to significant achievements in both material developing and cell manufacturing in the last two decades, the SOFC is now approaching commercial reality.

A single cell of a SOFC delivers a maximum of 1 V when hydrogen and air are used as the fuel and the oxidant, respectively [8]. To produce larger quantities of power, multiple cells are stacked in series connected by metallic conducting interconnects. The main components of a SOFC stack are the electrolyte, the cathode, the anode, and the interconnect. Each component serves several functions and therefore has to meet certain requirements. All the components must possess proper electrical conductivity and must be chemically and physically stable in an oxidizing and/or reducing atmosphere. Each component must be chemically compatible with the other components and its thermal expansion coefficient should be similar to those of the others. The anode and the cathode are porous to allow fuel or oxidant gas to be transported to the reaction sites, while the interconnect and the electrolyte are dense to prevent gas mixing. The state of the art SOFC uses yttria-stabilized zirconia (YSZ, cubic fluorite) as electrolyte, Ni-YSZ cermet as anode, Sr-doped perovskite-type La$_{1-x}$MnO$_{3-x/2}$ ((La$_{1-y}$Sr$_y$)$_{1-x}$MnO$_{3-x/2}$, LSM) as cathode, and LaCrO$_3$-based perovskite as interconnects. It is normally operated at 1173–1273 K. A further reduction of the operating temperature preferably to 873–1073 K would allow the use of ferritic steel (instead of expensive lanthanum chromite) as interconnects and would significantly reduce material costs and increase lifetime for the SOFC [9]. New materials with improved properties and new fabrication processes are being developed for this purpose.

A detailed review on the SOFC technology was given by Minh in 1993 [1]. For recent developments on SOFCs, the readers are referred to [7, 8, 10, 11].

1.2 The LSM–YSZ interface reactions

The oxygen reduction at the cathode–electrolyte interface can be written as (using Kröger–Vink notation):

\[ \text{O}_2 + 2 \text{V}^{**} + 4 e^- = 2 \text{O}_o^x \quad \text{Eq. 1.1} \]

The reduction is supposed to take place at or near the cathode–electrolyte–gas triple-phase boundary (tpb) [9]. At the LSM–YSZ interface, in which LSM is a pure electronic conductor and YSZ is an oxygen ion conductor, oxygen adsorbs on the surface of LSM and diffuses over
its surface towards the \( tpb \) where it becomes charged and is incorporated into the electrolyte. Figure 1.2a is a schematic representation of the oxygen reduction mechanism at the LSM–YSZ interface modified after Mitterdorfer and Gauckler [9]. It has been generally accepted that the electrochemical performance of the LSM cathode is mainly determined by the nanostructure and the phase assemblage at the LSM–YSZ interface, rather than by the microstructure of the LSM layer [9]. Under certain conditions, highly electrically resistive phases (La\(_2\)Zr\(_2\)O\(_7\) and/or SrZrO\(_3\)) are formed at the interface. Both La\(_2\)Zr\(_2\)O\(_7\) and SrZrO\(_3\) were reported to exhibit mixed \( p \)-type and ionic conduction at 1173–1373 K in air and their electrical conductivities are of several magnitudes lower than those of LSM and YSZ [12, 13, 14]. The zirconate formation at the interface leads to an increase in both the resistance and the over-potential of the LSM cathode, which is explained in Figure 1.2b. A detailed review on the LSM–YSZ reactions is given in Chapter 9. The formation of zirconates at the LSM–YSZ interface is at least partly responsible for the long-term degradation of the SOFC performance.

Understanding the factors influencing the zirconate formation at the LSM–YSZ interface is obviously advantageous for improving the performance of the state of the art SOFC and is also instructive for developing the SOFC operated at intermediate temperature (873–1073 K). For this purpose, the thermodynamics and the phase equilibria in the La–Mn–Sr–Y–Zr–O system are of particular importance. This work focuses on developing a consistent thermodynamic description of the La–Mn–Y–Zr–O system using the CALPHAD method. A short introduction on the CALPHAD methodology is given in the next section.

Figure 1.2 Model of the oxygen reduction at the LSM–YSZ interface modified after Mitterdorfer and Gauckler [9] (a) before and (b) after the La\(_2\)Zr\(_2\)O\(_7\) formation at the interface.
Chapter 1

(a) Oxygen adsors on the LSM surface and dissociates into \( \text{O}^{2-} \). Both the adsorption and the dissociation are coupled with charge transfer. \( \text{O}^{2-} \) is then transported to the interface by surface diffusion and is finally electronated and incorporated into YSZ at the tpb; (b) The formed \( \text{La}_2\text{Zr}_2\text{O}_7 \) phase at the tpb hinders both the dissociation and the final electronation. The surface diffusion of \( \text{O}^{2-} \) is also considerably retarded.

1.3 The CALPHAD methodology

Phase diagrams are graphical representations of the stability domains of the phases in a system. If the Gibbs energies of these phases are known, the phase diagrams can then be calculated. Due to the complex relations between thermodynamics and phase equilibria, the calculations applied to real systems were however practically impossible. For well over 100 years, phase diagrams have been constructed empirically based on experiments. The first computer calculated phase diagram was published by Kaufman and Bernstein [15]. With the developments of computers, the computation of phase equilibria spreads out rapidly. Nowadays it has established itself as a research activity with an annual conference and a journal called CALPHAD. CALPHAD is an acronym for CALculation of PHAse Diagrams. The CALPHAD methodology is rather aptly defined by the subtitle of the CALPHAD journal: “Computer Coupling of Phase Diagrams and Thermochemistry”.

The aim of the CALPHAD method is to derive a consistent thermodynamic description for the Gibbs energies of all the phases in a certain system and also to reproduce all sorts of thermodynamic quantities and phase diagrams in a reasonable and reliable manner. In a first stage of CALPHAD modeling, an appropriate thermodynamic model based on crystal structure and chemistry information has to be chosen for each phase. The Gibbs energy of a certain phase is then written as a function of temperature, composition, and pressure with adjustable parameters. In a second stage, those adjustable parameters are optimized using both thermodynamic data and phase diagram data. During this stage, the inconsistency between various kinds of experimental data can be easily identified and possibly resolved. This is actually the special strength of the CALPHAD method. A critical evaluation on the available experimental data is often necessary. The optimized thermodynamic description is in general more reliable than the one derived from a sum of individual measurements. With the optimized thermodynamic description, phase diagrams and thermodynamic properties can be calculated using various software packages. Nowadays the CALPHAD method has become a standard technique in phase equilibrium studies. Figure 1.3 is a schematic diagram for the
CALPHAD methodology, in which Thermo-Calc is a software package developed by Thermo-Calc Software AB, Stockholm, Sweden [16] and is used in the present work. Parrot and POLY_3 are modules included in the Thermo-Calc software package.

In the present work, the Gibbs energies of all phases in the La–Mn–Y–Zr–O system are described as functions of temperature and composition. For pure elements or stoichiometric compounds, the Gibbs energy is a function of the temperature only and can be obtained by integrating the heat capacity $C_p$. From room temperature upwards, $C_p$ can be well represented by the following equation:

$$C_p = -c - 2dT - 6eT^2 - 2fT^{-2}$$  \[\text{Eq. 1.2}\]

where $-c$ should be close to the Dulong-Petit value, $d$ and $e$ are corrections due to anharmonic and electronic contributions, and $f$ is a parameter allowing to describe the decrease of the heat capacity at lower temperatures [17]. The Gibbs energy can then be written as:

$$^oG_i - H_i^{\text{SER}} = a + bT + cT \ln T + dT^2 + eT^3 + fT^{-1} + jT^{-7} + kT^{-9}$$  \[\text{Eq. 1.3}\]

In the present work, all $^oG$ values are referred to the enthalpy of selected stable states for pure elements at 298.15 K and 1 bar. This state is denoted SER (Stable Element Reference). Different sets of the parameters $a$ to $k$ are used in different temperature ranges. The parameters $j$ and $k$ are for metastable ranges only, i.e. liquid below the melting temperature or solid above the melting temperature, respectively [18]. For pure elements, we take the thermodynamic descriptions from the SGTE (Scientific Group Thermodata Europe) database.
[19]. For stoichiometric compounds, here we use α-Mn₃O₄ as an example; the molar Gibbs energy is given by:

\[
GMN304A = \delta G_{Mn3O4} - 3 H_{Mn}^{SER} - 4 H_{O}^{SER} = a + bT + cT \ln T + dT^2 + eT^3 + fT^{-1} \quad \text{Eq. 1.4}
\]

The \( C_p \) parameters \( c-f \) can be optimized using experimentally measured heat capacity and enthalpy increment, while the parameters \( a \) and \( b \) can be optimized using enthalpy of formation, entropy, Gibbs energy of formation, dissociation temperature or oxygen partial pressure and so on.

All solid solution phases in the La–Mn–Y–Zr–O system are modeled using the compound energy model, in which the concept of sublattice is introduced. According to the compound energy model formalism, the structure of an ionic solid solution phase is split into at least two sublattices, one for cations and one for anions. The species within the same sublattice are allowed to mix randomly. We choose the m-ZrO₂ solution phase as an example. In this work, we model m-ZrO₂ as \((Y^{3+}, Zr^{4+})(O^{2-}, Va)₂\). The cations, \(Y^{3+}\) and \(Zr^{4+}\), mix randomly in the first sublattice and \(O^{2-}\) ions and oxygen vacancies (Va) in the second sublattice. The oxygen vacancies are introduced to maintain charge neutrality when \(Zr^{4+}\) is substituted by \(Y^{3+}\). The phase is well defined in the composition square shown in Figure 1.4. The Gibbs energy of m-ZrO₂ is given by:

\[
G_m = y_{Y^{3+}}, y_{O^{2-}}, y_{Zr^{4+}}, y_{Va} \sum_{i=0}^{n} I_{Y^{3+}, Zr^{4+}, O^{2-}, Va} \ln \left( y_{Y^{3+}} - y_{Zr^{4+}} \right) + y_{Zr^{4+}}, y_{Va} \sum_{i=0}^{n} I_{Y^{3+}, Zr^{4+}, Va} \ln \left( y_{Zr^{4+}} - y_{Va} \right) + RT \ln \left[ y_{Y^{3+}} + y_{Zr^{4+}} \ln y_{Zr^{4+}} + 2(y_{O^{2-}} \ln y_{O^{2-}} + y_{Va} \ln y_{Va}) \right] \quad \text{Eq. 1.5}
\]

where \(y_s\) is the fraction of the species \(s\) in a particular sublattice and colons are used to separate species in different sublattices. The molar Gibbs energy of m-ZrO₂ is a sum of the molar Gibbs energies of the corner compounds \((Y^{3+})(O^{2-})₂\), \(Y^{3+}(Va)₂\), \(Zr^{4+}(O^{2-})₂\), \(Zr^{4+}(Va)₂\) weighted by their respective site fractions plus the ideal entropy of mixing and the excess Gibbs energy. The excess Gibbs energy arises from the interactions between species within the same sublattice. For m-ZrO₂, the excess Gibbs energy is given by:

\[
\Delta G_m = y_{Y^{3+}}, y_{Zr^{4+}}, y_{O^{2-}}, y_{Va} \sum_{i=0}^{n} I_{Y^{3+}, Zr^{4+}, O^{2-}, Va} \ln \left( y_{Y^{3+}} - y_{Zr^{4+}} \right) + y_{Zr^{4+}}, y_{Va} \sum_{i=0}^{n} I_{Y^{3+}, Zr^{4+}, Va} \ln \left( y_{Zr^{4+}} - y_{Va} \right) \quad \text{Eq. 1.6}
\]
Introduction

The parameters to be determined are the $\delta G$ s of the four corner compounds and the interaction parameters. Among the four corner compounds, $(Zr^{4+})_1(O^{2-})_2$ represents stoichiometric m-ZrO$_2$ and the parameters for its $\delta G$ value ($\delta G_{Zr^{4+}O^{2-}}$) can be optimized using the thermodynamic properties of stoichiometric m-ZrO$_2$.

$$\delta G_{Zr^{4+}O^{2-}} - H_{Zr}^{\text{SER}} - 2 H_{O}^{\text{SER}} = \delta G_{ZrO2} \quad \text{Eq. 1.7}$$

The other three corner compounds are not neutral and can therefore not exist on their own. Only compounds along the neutral line in Figure 1.4 can exist. As nothing is known on the energy of the charged compounds, an arbitrary reference state has to be chosen. We choose $\delta G_{Zr^{4+}Va}$ as a reference and set it as:

$$\delta G_{Zr^{4+}Va} - H_{Zr}^{\text{SER}} = \delta G_{ZrO2} - 2 \delta G_{HSEROO} \quad \text{Eq. 1.8}$$

where $\delta G_{HSEROO}$ is the molar Gibbs energy of oxygen taken from Dinsdale [20]. We relate $\delta G_{Y^{3+}O^{2-}}$ and $\delta G_{Y^{3+}Va}$ to the Gibbs energy of the neutral end-member $(Y^{3+})_1((O^{2-})_{0.75}(Va)_{0.25})_2$ as:

$$GYO15 = \frac{3}{4}(\delta G_{Y^{3+}O^{2-}} - H_{Y}^{\text{SER}} - 2 H_{O}^{\text{SER}}) + \frac{1}{4}(\delta G_{Y^{3+}Va} - H_{Y}^{\text{SER}}) + 2[\frac{3}{4}\ln \frac{3}{4} + \frac{1}{4}\ln \frac{1}{4}]RT \quad \text{Eq. 1.9}$$

where $R$ is the gas constant and is equal to 8.31451 J/(mol K).
A reciprocal relation was used:

\[ ^0G_{Y^{3+};Va} + ^0G_{Zr^{4+};O^{2-}} - ^0G_{Y^{3+};O^{2-}} - ^0G_{Zr^{4+};Va} = \Delta G_i \]  
Eq. 1.10

In this work, we in general choose \( \Delta G_i = 0 \) and optimize the interaction parameters. This is due to the fact that reciprocal relations and interaction parameters are not independent from each other. They can have a similar influence on the Gibbs energy or even be identical in certain cases [21]. With interaction parameters, composition dependence can also be introduced.

By choosing \( \Delta G_i = 0 \), we obtain:

\[ ^0G_{Y^{3+};O^{2-}} - 2^0H_{Y}^{\text{SER}} = \text{GYO15} + 0.5 \text{GHSEREO} + 1.12467 RT \]  
Eq. 1.11

\[ ^0G_{Y^{3+};Va} - ^0H_{Y}^{\text{SER}} = \text{GYO15} - 1.5 \text{GHSEREO} + 1.12467 RT \]  
Eq. 1.12

The parameters for GYO15 and the interaction parameters are derived from the experimental data in the ZrO\(_2\)-YO\(_{1.5}\) system. The details of the parameter optimization can be found in Chapter 2. More information about the compound energy model formalism can be found in [21, 22].

The two-sublattice model for ionic liquids [23, 24] is used to model the liquid phase. For the La–Mn–Y–Zr–O system, we use the model \((\text{La}^{3+}, \text{Mn}^{2+}, \text{Mn}^{3+}, \text{Y}^{3+}, \text{Zr}^{4+})_p(\text{O}^{2-}, \text{Va}^\text{aq})_q\) where

\[ p = 2y_{O^{2-}} + qy_{Va^{\text{aq}}} \]  
Eq. 1.13

\[ q = 3y_{La^{3+}} + 2y_{Mn^{2+}} + 3y_{Mn^{3+}} + 3y_{Y^{3+}} + 4y_{Zr^{4+}} \]  
Eq. 1.14

Charged vacancies are introduced into the anion sublattice to ensure a continuous description from the metal liquid to the oxide liquid. The description for the molar Gibbs energy of the liquid phase is derived in a similar manner as for the solid solution phase using the compound energy model (Eqs. 1.5 and 1.6). More details on the two-sublattice model for ionic liquids can be found in the literature [23, 24].

### 1.4 Organization of the work

This work starts with the Y–Zr–O system, in which the thermodynamic descriptions of the two binary systems Y–O and Zr–O and that of the ternary Y–Zr–O system are assessed (Chapter 2). Chapters 3–6 present the assessments of other four ternary systems (Mn–Y–O,
Introduction

Mn–Zr–O, La–Y–O, La–Zr–O) and one quaternary system (Mn–Y–Zr–O). The thermodynamic description of the La–Mn–Y–Zr–O system is presented in Chapter 7 together with the calculated phase relations in the LaO$_{1.5}$–MnO$_x$–YO$_{1.5}$–ZrO$_2$ system. In Chapter 8, we evaluate the Gibbs energy functions of stoichiometric compounds in the La–Mn–Zr–O system from both literature and this work. The final chapter is dedicated to the thermodynamics at the LaMnO$_3$–YSZ interface, in which the previous experimental investigations on the LaMnO$_3$–YSZ reactions are reviewed and the La$_2$Zr$_2$O$_7$ formation mechanism is discussed in detail. In the appendix, the thermodynamic description of the La–Mn–Y–Zr–O system (the database) is given.

Chapters 2–9 have been either published [25, 26, 27] or submitted for publication in scientific journals and they are almost independent from each other. The readers can start with the Introduction (this chapter) and then jump to any chapter they are interested in. For the SOFC people, Chapters 8 and 9 are the most important.

1.5 References

Chapter 1


2 Thermodynamic Modeling of the ZrO$_2$–YO$_{1.5}$ System


**Abstract**

In the present work, an optimized set of Gibbs energy functions is proposed for the Y–Zr–O ternary system. We focus on the ZrO$_2$–YO$_{1.5}$ quasi-binary system, but reoptimizations of the Zr–O and Y–O binary systems are included as well. The parameters for the Y–Zr binary system were taken from a previous assessment.

The ZrO$_2$–YO$_{1.5}$ system was treated as a quasi-binary section of the Y–Zr–O ternary system. The existing experimental data on the ZrO$_2$–YO$_{1.5}$ system were carefully reviewed. The related parameters were optimized using both thermodynamic data and phase diagram data. A calculated phase diagram of the ZrO$_2$–YO$_{1.5}$ system is presented. Our optimization agrees well with most experimental data. Two calculated isothermal sections of the Y–Zr–O system at 1500 K and 2000 K are also included.

2.1 Introduction

Due to the disruptive monoclinic ↔ tetragonal martensitic phase transformation, pure ZrO$_2$ is of little use. However, found by Ruff and Ebert [1], this phase transformation can be suppressed by doping certain amount of MgO, CaO, Sc$_2$O$_3$, Y$_2$O$_3$ or CeO$_2$ into zirconia, and a metastable cubic fluorite solid solution can be obtained at room temperature. It has been generally recognized that the doping with lower valence oxides introduces oxygen vacancies into the ZrO$_2$ crystal lattice. When doping with a smaller amount than needed to produce fully stabilized zirconia, partially stabilized zirconia (PSZ) or tetragonal zirconia polycrystals (TZP) can be obtained. PSZ consists of fine (<1 μm) precipitates of tetragonal zirconia in a cubic matrix. PSZ is obtained by sintering in the tetragonal+cubic two-phase field at relatively high temperature. Garvie et al. [2] discovered that PSZ possesses a very high fracture toughness and Porter and Heuer [3] explained the mechanism of toughing. When the tetragonal precipitates are in the correct size range they will transform martensitically to the monoclinic
phase under volume increase on crack propagation, resulting in a closing force on the crack and absorbing energy. Gupta et al. [4] discovered that very fine grained (0.2–1.0 \(\mu\)m) single phase tetragonal zirconia, TZP, exhibits similar properties. Yttria TZP typically contains 3–6 mol\% \(\text{YO}_{1.5}\), where some amount of cubic zirconia will be present in the microstructure if the amount of yttria exceeds about 4 mol\% [5]. Among other useful properties, yttria stabilized zirconia (YSZ) exhibits high oxygen ion conductivity at elevated temperatures. Nowadays YSZ is of great importance in many applications, like electrolytes for solid oxide fuel cells (SOFCs) and oxygen sensors, refractory materials for high temperature furnaces as well as protective coatings for metals. Obviously the knowledge of the phase equilibria in the \(\text{ZrO}_2-\text{YO}_{1.5}\) system is essential for these applications.

Our interest in the \(\text{ZrO}_2-\text{YO}_{1.5}\) system mainly concerns SOFC applications and in particular we want to predict at what conditions insulating phases such as \(\text{La}_2\text{Zr}_2\text{O}_7\) and \(\text{SrZrO}_3\) are stable between a YSZ electrolyte and a \(\text{La}_{1.2}\text{Sr}_x\text{Mn}_{1.5}\text{O}_{3+δ}\) electrode. A description of the quasi-binary \(\text{ZrO}_2-\text{YO}_{1.5}\) system is probably adequate for this purpose, but we would prefer a description of the complete \(\text{Y}-\text{Zr}-\text{O}\) system if possible. At least we would like to use solution models which are based on the actual defect chemistry of the solid solution phases.

The first phase diagram for the \(\text{ZrO}_2-\text{YO}_{1.5}\) system was published in 1951, by Duwez et al. [6]. Since then, extensive research has been done on this system. 50 years later, however, some parts of the phase diagram are still not well established. The experimental information is full of controversy.

As phase diagrams are graphical representations of the stability domains of the phases in a system, they can be directly calculated from the thermodynamic properties of these phases. In the CALPHAD (CALculation of PHAse Diagrams) method, both phase diagram data and thermodynamic data are assessed together. An optimized set of Gibbs energy functions is obtained. Using these functions, a phase diagram can be calculated, which fits both the phase diagram data and the thermodynamic data. The CALPHAD method has been successfully applied to many systems. The first thermodynamic assessment on the \(\text{ZrO}_2-\text{YO}_{1.5}\) system was done by Degtyarev and Voronin [7]. Their assessment was based on very few experimental data. Du et al. [8] reassessed this system. Their assessment was mainly based on the available phase diagram data. Using different sets of liquidus data, two different optimized versions
were presented. The optimization based on the liquidus data by Noguchi et al. [9] (Optimization B) was suggested to be the best one. For most parts the assessment by Du et al. [8] is reasonable, but there are a number of points that could be improved. One obvious point is to use more physical models for the solid solution phases, where Du et al. [8] used a simple substitutional model with ZrO$_2$ and YO$_{1.5}$ as constituents. Including the formation of oxygen vacancies should result in a better description of the configurational entropy. Recently this system has been reassessed by Yokokawa [10], Fabrichnaya and Aldinger [11], and Jacobson et al. [12].

Originally we had planned to base our assessment on the Zr–O assessment by Liang et al. [13] and the Y–O assessment by Swamy et al. [14], but it turned out to be necessary to change the description of pure ZrO$_2$ in order to get a reasonable description of the ZrO$_2$–YO$_{1.5}$ system. The most important problem is that Liang et al. [13] chose an about 100 K too high temperature for the monoclinic to tetragonal transition, not compatible with data for pure ZrO$_2$ and ZrO$_2$–YO$_{1.5}$. This choice has been made in all thermodynamic evaluations of pure ZrO$_2$ so far and is based on enthalpy increment measurements. More detail is given later in the paper. Individual heat capacity functions for monoclinic, tetragonal, and cubic ZrO$_2$ have been used and the functions for tetragonal and cubic have an unrealistic strong temperature dependence resulting in unreliable extrapolations (cf Figure 2.1 (b)). The heat capacity function for monoclinic ZrO$_2$ does not reproduce experimental data well, but could in principle be accepted. The enthalpy of the tetragonal to cubic transition is too large, resulting in a too wide tetragonal+cubic two-phase field in the ZrO$_2$–YO$_{1.5}$ system. These three points make it necessary to reevaluate pure ZrO$_2$. Changing pure ZrO$_2$ also makes it necessary to reoptimize the complete Zr–O system. In this process we also changed all solid solution models and also reoptimized Y–O using models compatible with those in the Zr–O and ZrO$_2$–YO$_{1.5}$ systems. Also calculations in the complete Y–Zr–O ternary system are presented. The description of Y–Zr is taken from Flandorfer et al. [15] without change. The symbols, m, t, c, L, are used to denote the monoclinic phase, the tetragonal phase, the cubic fluorite ZrO$_2$-rich phase, and the liquid phase.
Chapter 2

2.2 Zr–O

Due to the wide range of technological applications of ZrO$_2$-based ceramics, the Zr–O binary system is of great importance. The most complete review on the experimental information of the Zr–O system was given by Abriata et al. [16].

Pure zirconium exists in two allotropic modifications, α-Zr (hcp) and β-Zr (bcc). At $1139 \, \text{K}$, α-Zr transforms to β-Zr and β-Zr melts at $2128 \, \text{K}$ [17]. Both α-Zr and β-Zr dissolve oxygen interstitially. The maximum solubility of oxygen in α-Zr has been reported to be $35 \, \text{at.\%}$ [18]. Domagala and McPherson [19] found that β-Zr dissolves $10.5 \, \text{at.\%}$ of oxygen maximally. At low temperature, the dissolved oxygen in the hcp phase tends to partially order. Three possible ordered phases, centered around $16, 25, 33.3 \, \text{at.\%}$ of oxygen, have been identified by Hirabayashi et al. [20].

The solid zirconium oxide, ZrO$_2$, has three modifications. The low-temperature phase, m-ZrO$_2$, has monoclinic crystal symmetry. The intermediate-temperature phase, t-ZrO$_2$, is tetragonal. The high-temperature phase, c-ZrO$_2$, has a fluorite structure isostructural with CaF$_2$.

The three solid ZrO$_2$ phases show different degrees of nonstoichiometry. The monoclinic phase has been observed to be nearly stoichiometric and no reliable information exists on its maximum degree of nonstoichiometry. The tetragonal phase has some degree of nonstoichiometry. The reported low limit of homogeneity range varies from 65.7 to 66.5 at.\% O [21, 22, 23]. The high-temperature fluorite phase shows a high degree of nonstoichiometry. The homogeneity region of fluorite ZrO$_2$ extends from 61 to 66.7 at.\% O, showing a high concentration of oxygen vacancies [18, 19, 21, 24]. None of these three phases have been observed to oxidize beyond stoichiometry.

The first thermodynamic assessment on the Zr–O system was done by Kaufman and Clougherty [25]. They only included α-Zr, β-Zr, the liquid phase, and the tetragonal ZrO$_{2-x}$ nonstoichiometric phase. Chevalier and Fischer [26] reassessed this system as one part of their modeling of the O–U–Zr system. They did not consider the low temperature ordering in the hcp phase and the liquid phase was described as a mixture of O, Zr, and ZrO$_2$ species. Later on, two groups, Liang et al. [13] and Arroyave et al. [27], assessed this system almost at the
same time. They both modeled the low-temperature ordering in the hcp phase. For the hcp phase (α-Zr), Liang et al. used a model of (Zr)$_1$(O, Va)$_1$. In Arroyave et al.’s work, the hcp phase was modeled as (Zr)$_1$(O, Va)$_{0.5}$. As Arroyave et al. mentioned, it is impossible to use this model to represent the maximum oxygen solubility in α-Zr. High priority was given to the compatibility of their model with the models used for other systems. In Liang et al.’s work, the maximum oxygen solubility also did not exceed $x_0 = 1/3$, although it would have been possible with their model. For stoichiometric ZrO$_2$, almost the same experimental information was used by these two groups.

As mentioned in the Introduction (Section 2.1), we could not use the description of stoichiometric ZrO$_2$ from Liang et al. [13]. In order to be compatible with the earlier description of the La–O system from our group [28], we changed the interstitial solution models for hcp and bcc from (Zr)$_1$(O, Va)$_1$ and (Zr)$_1$(O, Va)$_3$ [13] to (Zr)$_1$(O, Va)$_{0.5}$ and (Zr)$_1$(O, Va)$_{1.5}$. We also changed the solution model for cubic ZrO$_{2-x}$. This will be discussed further in Section 2.2.2.

2.2.1 Stoichiometric ZrO$_2$

The heat capacity of m-ZrO$_2$ was first measured by Kelley [29], in the temperature range of 54–295 K. Nevitt et al. [30] measured the heat capacity of m-ZrO$_2$ between 2.75 and 350 K. Using adiabatic calorimetry, Tojo et al. [31] measured the heat capacity of pure ZrO$_2$ at temperatures between 13 K and 300 K. All these measurements agree well. Arthur [32] measured mean heat capacity of zirconia from 293 K to 1073 K. Three data points of true heat capacity at 473 K, 623 K, and 773 K were determined from these measurements. No heat capacity measurement was done on t-ZrO$_2$ and c-ZrO$_2$. From the heat capacity measurement, Kelley [29] derived the standard entropy of ZrO$_2$ as $^\circ S$(ZrO$_2$, 298.16 K) = 50.33±0.33 J/(mol K). Based on this, the JANAF tables [33] give a value of $^\circ S$(ZrO$_2$, 298.15 K) = 50.359±0.33 J/(mol K). Tojo et al. [31] derived the standard entropy as $^\circ S$(ZrO$_2$, 298.15 K) = 49.79 J/(mol K).

Enthalpy increment measurements of ZrO$_2$ were made by Coughlin and King in the temperature range of 397–1841 K [34], by Kirilllin et al. [35] in the range of 1000–2400 K and by Chekhovskoi et al. [36] in the range of 1100–2400 K. Using combustion calorimetry,
Huber et al. [37] and Kornilov et al. [38] determined the standard enthalpy of formation of m-ZrO$_2$ as $-1100.8 \pm 2.1$ kJ/mol and $-1100.6 \pm 0.7$ kJ/mol, respectively. The value from the JANAF tables is $-1097.463 \pm 1.7$ kJ/mol, based on data from Humphrey [39] and Huber et al. [37].

The m-ZrO$_2$ $\rightarrow$ t-ZrO$_2$ transition invariably occurs as a martensitic transformation with a hysteresis of about 200 K. According to Kaufman and Cohen [40], the equilibrium temperature ($T_{o \rightarrow m}$) can be calculated as an average of the starting transition temperature of tetragonal $\rightarrow$ monoclinic during cooling ($M_s$) and the starting transition temperature of monoclinic $\rightarrow$ tetragonal during heating ($A_s$).

$$
T_{o \rightarrow m} = \frac{M_s + A_s}{2}
$$

Eq. 2.1

This equation was used to calculate $T_{o \rightarrow m}$ temperatures from reported $M_s$ and $A_s$ values.

The m-ZrO$_2$ $\rightarrow$ t-ZrO$_2$ transition has been investigated by many authors, both on heating and cooling [6, 41, 42, 43, 44, 45, 46, 47], using differential thermal analysis (DTA), thermal dilatometry and Raman spectroscopy. When adding YO$_{1.5}$, the $T_{o \rightarrow m}$ temperature decreases linearly with composition and also the hysteresis decreases drastically. Yashima et al. [48] analyzed the available data for pure ZrO$_2$ and YO$_{1.5}$-containing ZrO$_2$ and found the equilibrium temperature to be 1387 K for pure ZrO$_2$, in excellent agreement with our own analysis of the primary data. Coughlin and King [34] and Kirillin et al. [35] used enthalpy increment measurements to study the m-ZrO$_2$ $\rightarrow$ t-ZrO$_2$ transition. They found the transition temperature ($A_s$) to be 1478 and 1420 K, respectively, and the transition enthalpy to be 5.9 and 7.8 kJ/mol, respectively. The JANAF tables [33] and Liang et al. [13] adopted the transition temperature from Coughlin and King [34] and erroneously interpreted it as the equilibrium temperature.

The transition temperature of t-ZrO$_2$ $\rightarrow$ c-ZrO$_2$ was first reported by Smith and Cline [49] as 2558 K, using high-temperature X-ray diffraction. Later they redetermined the transition temperature as $2645 \pm 50$ K [50]. It has been suggested that the t-ZrO$_2$ $\rightarrow$ c-ZrO$_2$ transition is second order rather than first order [51, 52]. We have, however, not considered this possibility further.
Using high-temperature solution calorimetry, Molodetsky et al. [53] determined the transition enthalpy of m-ZrO₂ ← c-ZrO₂ as 13.5±2.2 kJ/mol, very close to the value estimated by Ackermann, 12.24 kJ/mol [54].

The available data on the melting temperature of ZrO₂ have been analyzed by an IUPAC (International Union of Pure and Applied Chemistry) commission [55]. They recommend a melting temperature of 2983±35 K.

In the present optimization, the molar Gibbs energy of solid ZrO₂ (m-, t-, and c-ZrO₂) is described as:

\[
G_{ZrO_2}^{\text{SER}} = T_{Zr}^{\text{SER}} - H_{O}^{\text{SER}} - 2 H_{Zr}^{\text{SER}} = A + B T + C T \ln T + D T^2 + E T^{-1}
\]

Eq. 2.2

Different sets of the parameters \( A \) and \( B \) are used for m-, t- and c-ZrO₂, but the \( C_p \) terms of all these phases are kept the same. The Gibbs energy of liquid ZrO₂ is described as:

\[
G_{ZrO_2}^{\text{LIQ}} = T_{Zr}^{\text{LIQ}} - H_{O}^{\text{LIQ}} - 2 H_{Zr}^{\text{LIQ}} = A + B T + C T \ln T
\]

Eq. 2.3

In the present work, all \( \delta G \) values are referred to the enthalpy of selected stable states for pure elements at 298.15 K and 1 bar (10⁵ Pa). This state is denoted SER (Stable Element Reference).

The \( C_p \) terms for the Gibbs energy functions of solid ZrO₂ (m-, t-, and c-ZrO₂), i.e. the parameters \( C, D, \) and \( E \) in Eq. 2.2, were determined using the heat capacity data (m-ZrO₂) from Kelley [29], Nevitt et al. [30], and Tojo et al. [31], Arthur [32], and the enthalpy increment data (m- and t-ZrO₂) [34, 35, 36] at temperatures above 200 K. The heat capacity data evaluated from enthalpy increment data at high temperature scatter too much to allow the evaluation of individual \( C_p \) functions for the solid forms of ZrO₂. The most reasonable approximation is then to use the same \( C_p \) function for all three forms, in contrast to Liang et al. [13]. Following the JANAF tables [33], a constant heat capacity of 90 J/(mol K) was used for liquid ZrO₂. The standard entropy of m-ZrO₂ at 298.15 K (49.8 J/(mol K)) was taken from Tojo et al. [31] and the enthalpy of formation at 298.15 K (−1100.7 kJ/mol) as the mean of the values from Huber et al. [37] and Kornilov et al. [38]. Entropy and heat capacity data at 298.15 K are given in Table 2.1 and enthalpy of formation data in Table 2.2. Figure 2.1 shows the calculated heat capacity of ZrO₂ compared with experimental data. The data points from
Coughlin and King [34], Kirillin et al. [35], and Chekhovskoi et al. [36] are the average heat capacities calculated from the measured enthalpy increments, using the equation:

\[ C_p(T) = \frac{H(T_2) - H(T_1)}{T_2 - T_1} \]  

Eq. 2.4

where \( T = (T_2 + T_1)/2 \). Enthalpy increment data are shown in Figure 2.2. The present description gives a very reasonable account of available data.

Table 2.1  Entropy and heat capacity of ZrO\(_2\) at 298.15 K

<table>
<thead>
<tr>
<th>Reference</th>
<th>( S(\text{ZrO}_2) ) J/(mol K)</th>
<th>( C_p(\text{ZrO}_2) ) J/(mol K)</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kelley, 1944 [29]</td>
<td>50.33</td>
<td></td>
<td>Calorimetry (54 to 295 K)</td>
</tr>
<tr>
<td>Nevitt et al., 1990 [30]</td>
<td>56.50</td>
<td></td>
<td>Calorimetry (2.75 to 350 K)</td>
</tr>
<tr>
<td>Tojo et al., 1999 [31]</td>
<td>49.79</td>
<td>56.14</td>
<td>Calorimetry (13 to 300 K)</td>
</tr>
<tr>
<td>Ackermann et al., 1975 [54]</td>
<td>50.71</td>
<td>56.02</td>
<td>Assessed</td>
</tr>
<tr>
<td>JANAF, 1985 [33]</td>
<td>50.359</td>
<td>56.191</td>
<td>Assessed</td>
</tr>
<tr>
<td>Liang et al., 2001 [13]</td>
<td>50.72</td>
<td>63.43</td>
<td>Assessed</td>
</tr>
<tr>
<td>This work</td>
<td>49.8</td>
<td>57.21</td>
<td>Assessed</td>
</tr>
</tbody>
</table>

Table 2.2  Enthalpy of formation of ZrO\(_2\) at 298.15 K

<table>
<thead>
<tr>
<th>Reference</th>
<th>( \Delta H(\text{ZrO}_2) ), kJ mol</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Huber et al., 1964 [37]</td>
<td>-1100.8</td>
<td>Combustion calorimetry</td>
</tr>
<tr>
<td>Kornilov et al., 1967 [38]</td>
<td>-1100.6</td>
<td>Combustion calorimetry</td>
</tr>
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Figure 2.1  Calculated heat capacity of ZrO$_2$ compared with experimental data and the previous assessment from Liang et al., 2001 [13], (a) 0–1000 K, (b) 0–4000 K. The experimental data are the measured heat capacity from Kelley, 1944 [29], Arthur, 1950 [32], Nevitt et al., 1990 [30], Tojo et al., 1999 [31], and the evaluated average heat capacity (calculated by the present authors using Eq. 2.4) from the measured enthalpy increment from Coughlin and King, 1950 [34], Kirillin et al., 1966 [35], and Chekhovskoi et al., 1979 [36].
Figure 2.2  Calculated enthalpy increment of ZrO₂ compared with experimental data and the previous assessment from Liang et al., 2001 [13]. The experimental data are from Coughlin and King, 1950 [34], Kirillin et al., 1966 [35], Chekhovskoi et al., 1979 [36], and Lee et al., 2003 [56].

The A and B parameters for t-ZrO₂ were determined from the temperature and the enthalpy of the m-ZrO₂ ↔ t-ZrO₂ transition. A transition temperature of 1387 K from Yashima et al. [48] and a transition enthalpy of 6.0 kJ/mol from Coughlin and King [34] were used in the present work. There was no reported transition enthalpy of t-ZrO₂ ↔ c-ZrO₂. Based on the transition enthalpy of m-ZrO₂ ↔ c-ZrO₂ from Molodetsky et al. [53], we set the transition enthalpy of t-ZrO₂ ↔ c-ZrO₂ as 7.5 kJ/mol. Liang et al. [13] used a considerably larger transition enthalpy (21.7 kJ/mol). This may be motivated by the enthalpy increment data, although no clear interpretation of these data is possible. It gives a somewhat better description of the nonstoichiometry of c-ZrO₂ in the Zr–O system but a worse description of the t+c two-phase field in the ZrO₂–YO₁.₅ system. Recent calorimetric data from Lee et al. [56] suggest that the transition enthalpy may be even considerably lower than the presently selected 7.5 kJ/mol.

The transition temperature was taken as 2645 K from Smith and Clyne (cited by Viechnicki and Stubican [50]). The melting temperature, 2983 K, was taken from Hlavac [55]. The enthalpy of melting has not been measured. We apply Richards rule to the entropy of melting of m-ZrO₂ (metastable). For m-ZrO₂, the entropy of melting is then about 30 J/(mol K) and for c-ZrO₂ about 23 J/(mol K). The enthalpy of melting of c-ZrO₂ then becomes 68.6 kJ/mol,
in reasonable agreement with the estimation in the JANAF tables [33]. Transition data are
given in Table 2.3 and the obtained Gibbs energy functions for m-, t-, c-, and liquid ZrO₂ are
given in Table 2.4.

Table 2.3 Transition temperatures and enthalpies of ZrO₂

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<th>Transition type</th>
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<th>Transition temperature, K</th>
<th>Transition enthalpy, kJ/mol</th>
<th>Method</th>
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<td>m-ZrO₂ ↔ t-ZrO₂</td>
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<td>DTA &amp; Dilatometry</td>
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Chapter 2

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### 2.2.2 Solution phases and phase diagram

Because of the changes in the description of pure ZrO$_2$, it also became necessary to revise the complete Zr–O description. We have essentially followed the work by Liang et al. [13], but changed all solution models. For the hcp and bcc phases we have reduced the number of interstitial sites to be compatible with the models used in the La–O system [28], to better reflect the expected maximum solubilities and to avoid that bcc becomes stable on the oxygen-rich side of ZrO$_2$. For hcp we use the model (Zr)$_i$(O, Va)$_{0.5}$, and for bcc the model (Zr)$_i$(O, Va)$_{1.5}$. We did not consider the ordering at low temperature in the hcp phase. For the liquid we use the ionic liquid model [57, 58] as Liang et al. [13], but without neutral oxygen; (Zr$^{4+}$)$_i$(O$^{2-}$, Va$^{r-}$)$_i$. As Liang et al. [13] we model m-ZrO$_2$ and t-ZrO$_2$ as stoichiometric phases. Some nonstoichiometry has been measured for t-ZrO$_2$, but it is fairly small and not very precisely known. The choice of model for c-ZrO$_2$ caused considerable problems. Liang et al. [13] used the model (Zr)$_i$(O, Va)$_2$. This is incompatible with our model for the ZrO$_2$–YO$_{1.5}$ system where we need to use the model (Y$^{3+}$, Zr$^{4+}$)$_i$(O$^{2-}$, Va)$_{2.5}$, i.e. with explicit charge included. Liang et al.’s [13] model is equivalent to the model (Zr$^{4+}$)$_i$(O$^{2-}$, Va$^{2-r-}$)$_i$ which is used by Arroyave et al. [27]. This would be compatible with our model for the ZrO$_2$–YO$_{1.5}$ system, but we do not find it reasonable to use charged vacancies in solid solution models, in particular not when there are neutral vacancies present in the same model. From a physical point of view it seems reasonable that some Zr take an effective charge of +3 or possibly +2 in nonstoichiometric ZrO$_{2-x}$. The existence of Zr$^{3+}$ in reduced yttria and calcia stabilized zirconia has been suggested by e.g. Orera et al. [59]. This would lead to the models (Zr$^{3+}$, Zr$^{4+}$)$_i$(O$^{2-}$, Va)$_2$ or (Zr$^{2+}$, Zr$^{4+}$)$_i$(O$^{2-}$, Va)$_2$. From a modeling point of view these models did not work since they lead to a sharp increase of the melting temperature when going from stoichiometric ZrO$_2$ towards Zr. The reason for this is that the configurational entropy and, thus, the stability increase much more rapidly for these models than for the ionic liquid model when removing
oxygen. A possible remedy would be to add \( \text{Zr}^{3+} \) or \( \text{Zr}^{2+} \) to the ionic liquid model, but it does not seem possible to find reasonable parameters for such a liquid model. It seems reasonable, though, to assume that the local atomic environment in solid and liquid \( \text{ZrO}_2 \) should be similar and that large differences in configurational entropy of mixing are not expected. The solution that we have chosen is to use the model \((\text{Zr}, \text{Zr}^{4+})(\text{O}^{2-}, \text{Va})_2\) for \( \text{c-ZrO}_2 \) with neutral \( \text{Zr} \). This is more compatible with the ionic liquid model, but physically doubtful since neutral \( \text{Zr} \) is much too large to fit in the fluorite structure. There is still a tendency of increasing melting temperature when going nonstoichiometric, but this can be suppressed to some extent. Even the model of Liang et al. [13], \((\text{Zr})(\text{O, Va})_2\), shows this tendency. To conclude, it seems that the ionic liquid model cannot be used in conjunction with sublattice models for the solids to predict solidus and liquidus close to stoichiometric compositions.

For the optimization, data on the bcc+hcp equilibria from Domagala and McPherson [19] and Gebhardt et al. [21], data on the hcp composition in equilibrium with \( \text{ZrO}_2 \) from Gebhardt et al. [21] and Ackermann et al. [18], data on the c-\( \text{ZrO}_2 \) composition in equilibrium with liquid or hcp from Gebhardt et al. [21] and Ackermann et al. [18, 24], and data on oxygen chemical potentials in the hcp phase field from Komarek and Silver [60] were used. Also used were data on the liquid+bcc+hcp [18], hcp+liquid+c-\( \text{ZrO}_2 \) [18], hcp+c-\( \text{ZrO}_2 \)+t-\( \text{ZrO}_2 \) [21] equilibria and the congruent melting point of hcp [18]. For the hcp, bcc and c-\( \text{ZrO}_2 \) phases we needed the same set of parameters as Liang et al. [13]. For the liquid phase we removed the temperature dependence of the interaction parameters and instead used a subsubregular parameter. The optimized parameters are listed in Table 2.4 and the calculated \( \text{Zr–O} \) phase diagram is shown in Figure 2.3. The hcp and bcc phase fields and invariant equilibria are very similar to those of Liang et al. [13], but the c-\( \text{ZrO}_2 \) field is somewhat different. The oxygen content of c-\( \text{ZrO}_2 \) in equilibrium with hcp and t-\( \text{ZrO}_2 \) is too high. This is related to the smaller enthalpy of the t-\( \text{ZrO}_2 \) \( \leftrightarrow \) c-\( \text{ZrO}_2 \) transition used in our work. This could be improved by treating also t-\( \text{ZrO}_2 \) as a solution phase. A rather large temperature dependence of the subregular interaction parameter was needed to decrease the congruent melting temperature to an acceptable level.
Chapter 2

2.3 Y–O

The main features of the Y–O phase diagram were established by Tucker et al. [61]. Carlson et al. [62] reviewed the experimental information on this system and published an assessed phase diagram [63].

Yttrium has two allotropic modifications, α-Y (hcp) and β-Y (bcc). At 1751 K, α-Y transforms into β-Y, which melts at 1795 K [17]. Both α-Y and β-Y can dissolve considerable amounts of oxygen [61].

α-Y2O3 and β-Y2O3 are the only known stable solid oxides in the Y–O system. α-Y2O3 (cubic, space group $Ia\bar{3}$) is stable from room temperature up to about 2600 K where it transforms into β-Y2O3. It is commonly believed that β-Y2O3 is hexagonal with a space group of $P\bar{3}m1$ [14]. Katagiri et al. [64] reported another high-temperature form of Y2O3, a cubic form with the fluorite-type structure (space group $F\bar{3}m$). This was confirmed by Swamy et al. [65]. It is still uncertain if the thermodynamically stable phase at high temperature is hexagonal or fluorite-type cubic, but we assume it to be fluorite-type cubic in this work and use a common model.
for β-Y2O3 and c-ZrO2. Ackermann et al. [66] reported a limited nonstoichiometry of α-Y2O3 in the temperature range of 1830–2075 K. No information exists on the nonstoichiometry of β-Y2O3. The melting temperature of Y2O3 has been determined in a round robin investigation involving ten laboratories [67]. Their result was 2712±12 K. They also discussed the possibility of using the melting point of Y2O3 as a secondary temperature standard, but found that the accuracy is not yet quite good enough [67].

The Y–O system has been thermodynamically assessed by Ran et al. [68], Gröbner et al. [69], Lysenko [70], and Swamy et al. [14]. We essentially accepted the assessment by Swamy et al. [14] and adopted their description of pure Y2O3 with minimal change. As in the Zr–O system we changed all solution models. For the hcp and bcc phases we used the models (Y)i(O, Va)_{0.5} and (Y)i(O, Va)_{1.5}, respectively. For the liquid phase we use the ionic liquid model [57, 58] as Swamy et al. [14], but without neutral oxygen: (Y^{3+})p(O^{2−}, Va^{q+})q. For the Y2O3 phases, it is necessary to consider the ZrO2–YO1.5 system, where, at least, α-Y2O3 shows a considerable solubility of ZrO2. α-Y2O3 has a cubic fluorite-related structure with ordered vacancies (Mn2O3 bixbyite type). We choose the model (Y, Y^{3+}, Zr^{4+})2(O^{2−}, Va)3(O^{2−}, Va)1 for α-Y2O3. This model allows both oxygen nonstoichiometry and ZrO2 dissolution, and honors the vacancy ordering. For pure α-Y2O3, the model reads (Y^{3+})2(O^{2−}, Va)3(O^{2−}, Va)1 and at perfect ordering second sublattice is filled and the third is empty. Perfectly ordered α-Y2O3 is described by the parameter $\delta G_{Y^{3+}, O^{2−}, Va}$. At increasing temperature α-Y2O3 will tend to disorder and the other extremum, with the third sublattice filled, is described by the expression:

$$
G_{\text{disorder}} = \delta G_{Y^{3+}, O^{2−}, Va} + \Delta G_{\text{nuc}} = \frac{2}{3} \delta G_{Y^{3+}, O^{2−}, Va} + \frac{1}{3} \delta G_{Y^{3+}, Va, O^{2−}} + 3RT \left( \frac{2}{3} \ln \frac{2}{3} + \frac{1}{3} \ln \frac{1}{3} \right)
$$

Eq. 2.5

The amount of disordering is given by $\Delta G_{\text{nuc}}$ and we use $\Delta G_{\text{nuc}} = 100$ kJ. This gives about 6% O^{2−} on the third sublattice at 2500 K. The drawback of this model is that it is not possible to give a closed expression for the Gibbs energy of α-Y2O3, at least not at high temperature. For β-Y2O3 we use a disordered fluorite model (Y, Y^{3+})2(O^{2−}, Va)2. As in the Zr–O system we use neutral Y instead of the more realistic Y^{2+}, since Y^{2+} is not present in the liquid model. In order to reproduce the properties of pure α-Y2O3, β-Y2O3, liquid Y2O3, and their transition data from Swamy et al. [14], it was necessary to adjust the parameters given by them somewhat.
As Swamy et al. [14] we mostly used phase diagram data from Tucker et al. [61], with additional data at low temperature from Carlson et al. [62] and data on the nonstoichiometry of α-Y₂O₃ from Ackermann et al. [66] for the optimization. The number of optimized parameters was about the same as in Swamy et al. [14], but the set of parameters was somewhat different. The parameters for the Y–O system are given in Table 2.4 and the Y–O phase diagram is shown in Figure 2.4. This phase diagram is very similar to that of Swamy et al. [14], except for β-Y₂O₃ which shows much less nonstoichiometry in our phase diagram.

2.4 Y–Zr

Palenzona and Cirafici [71] reviewed the Y–Zr phase diagram. Accordingly, this system is a simple eutectic system. No compounds and intermediate phases were found in this system. The mutual solubility of the elements is not extensive. Flandorfer et al. [15] published an optimized set of Gibbs energy functions for the Y–Zr system. Their calculated Y–Zr phase diagram keeps the basic shape of the diagram from Palenzona and Cirafici [71]. A few differences exist on the temperatures and the compositions of invariant reactions. We include their description of Y–Zr without change in the present work.

![Figure 2.4](image)

Figure 2.4 Calculated Y–O phase diagram from the present work.
2.5 Experimental data on the ZrO$_2$–YO$_{1.5}$ system

The ZrO$_2$–YO$_{1.5}$ phase diagram is always very close to the ZrO$_2$–YO$_{1.5}$ section as long as the atmosphere is not strongly reducing. c-ZrO$_2$ is strongly stabilized relative to m-ZrO$_2$ and t-ZrO$_2$ by the addition of YO$_{1.5}$ and dissolves up to about 70 mol% YO$_{1.5}$. t-ZrO$_2$ dissolves up to 5–6 mol% YO$_{1.5}$ and m-ZrO$_2$ dissolves only a very small amount of YO$_{1.5}$ (at equilibrium). α-Y$_2$O$_3$ dissolves up to about 14 mol% ZrO$_2$, but the solubility of ZrO$_2$ in β-Y$_2$O$_3$ is not well known. There is one confirmed intermediary phase, Zr$_3$Y$_4$O$_{12}$, with an ordered fluorite structure. We will generally use the abbreviations m, t, and c for m-ZrO$_2$, t-ZrO$_2$, and c-ZrO$_2$.

The ZrO$_2$-rich part of the system is of particular technical importance. Because of the slow cation diffusion, equilibrium phase boundaries can only be established above about 1500 K [48]. Also, a number of complex phase transformations take place in this part of the system, depending strongly on the thermal history and the grain size or particle size of the material. Metastable states are very common. A very good and clear overview of these phase transformations can be found in the papers of Rühle, Heuer and coworkers [5, 72, 73]. For a different interpretation of the phase transformations in the (stable and metastable) t+c two-phase region, the paper by Sakuma [51] can be consulted.

Below about 4 mol% YO$_{1.5}$, t-ZrO$_2$ transforms martensitically to m-ZrO$_2$ on cooling and back to t-ZrO$_2$ (also martensitically) on heating with a certain hysteresis. If the grain size is small enough (0.2–1.0 μm), material with 3–4 mol% YO$_{1.5}$ does not transform spontaneously to m-ZrO$_2$ at room temperature, but only on strong mechanical load, e.g. crack propagation.

In the range of 4–13 mol% YO$_{1.5}$ single phase c-ZrO$_2$ cooled quickly from the c-ZrO$_2$ phase field transforms to t-ZrO$_2$ by a massive transformation, i.e. a partitionless non-martensitic transformation. t-ZrO$_2$ formed in this way is usually called t’–ZrO$_2$, which is also called untransformable since it does not transform to m-ZrO$_2$. On increasing YO$_{1.5}$ content the tetragonality decreases and a possible t-ZrO$_2$ with cubic lattice parameters, but tetragonal symmetry is sometimes called t”–ZrO$_2$. Massive transformations are quite well-known in metallic systems [74, 75]. The transformation is essentially controlled by the migration rate of the phase interface. There has been much discussion if the massive transformation can take place in the two-phase field (below the $T_c$-line) or only in the single phase field (stable or
metastable). According to the current understanding [75], this will depend on the atomic mobility (diffusion rate), i.e. temperature. Different growth modes may be possible at a particular temperature. At relatively high mobilities a composition spike may form adjacent to the interface and control the migration rate. In this mode one may approach local equilibrium at the interface. At intermediate mobilities solutes may become trapped in the interface and dragged along with it. This is called solute drag. At even lower mobilities the migration rate will be controlled by the intrinsic mobility of the interface. In the case of ZrO$_2$–YO$_{1.5}$ the massive c → t transformation clearly takes place in the (metastable) t+c two-phase region.

Above 15 mol% YO$_{1.5}$, c-ZrO$_2$ becomes completely stabilized and does not transform further. The oxygen ion conductivity of c-ZrO$_2$ has a maximum at 15–20 mol% YO$_{1.5}$. The decrease of the conductivity at high YO$_{1.5}$ contents can probably be explained by short range ordering on the anion sublattice, leading to a decrease of the O$^{2-}$ mobility [76]. Bogicevic and Wolverton [76] used first-principle calculations to study defect interactions and ordering on the ZrO$_2$–YO$_{1.5}$ and ZrO$_2$–ScO$_{1.5}$ fluorite lattices. They found that vacancy–vacancy interactions dominate and that both elastic and electrostatic contributions to the interactions are important and form a delicate balance. They also explained the stability of the Zr$_3$Y$_4$O$_{12}$ ordered phase.

It is our intention to describe the equilibrium thermodynamic properties and equilibrium phase boundaries as well as possible. This does not necessarily correspond to where the different phases are found in practice. It is, however, a necessary basis to rationally interpret observed phase transformations and, in the end, to model them quantitatively. It also forms a necessary basis for extrapolations to higher order systems.

2.5.1 The cubic ZrO$_2$-rich phase (c-ZrO$_2$) and the cubic YO$_{1.5}$-rich phase (α-Y$_2$O$_3$)

Pure c-ZrO$_2$ (fluorite) has a face-centered cubic lattice and is isostructural with CaF$_2$. Pure α-Y$_2$O$_3$ (cubic) has a body-centered lattice and is isostructural with Mn$_2$O$_3$. The Mn$_2$O$_3$ type of structure could be obtained from the CaF$_2$ structure by removing one quarter of non-metallic atoms [7]. Both Degtyarev and Voronin [7] and Du et. al. [8] treated c-ZrO$_2$ and α-Y$_2$O$_3$ as one cubic solution phase having the fluorite structure. The c-ZrO$_2$+α-Y$_2$O$_3$ two-phase region was therefore regarded by them as a miscibility gap. We model c-ZrO$_2$ and α-Y$_2$O$_3$ as two
Modeling of the Y–Zr–O System

separate phases. Instead, we consider β-Y₂O₃ to have the fluorite structure and model c-ZrO₂ and β-Y₂O₃ as one phase.

2.5.2 Zr₃Y₄O₁₂, ZrY₆O₁₁, and Zr₂Y₂O₇

The existence of Zr₃Y₄O₁₂ was first reported by Ray and Stubican [77] and Scott [78], and was later confirmed by Stubican et al. [79, 80, 81], Pascual and Duran [82], and Jayaratna et al. [83]. Ray and Stubican [77] identified Zr₃Y₄O₁₂ as an ordered fluorite-related phase, isostructural with M₇O₁₂ type of compounds. They estimated the upper limit of existence of Zr₃Y₄O₁₂ as 1523±60 K. Scott [78] reported that Zr₃Y₄O₁₂ has a narrow homogeneity range and it disorders at about 1643 K into the fluorite phase. Pascual and Duran [82] found that at 1648 K, a few hours were necessary to complete the order–disorder process of Zr₃Y₄O₁₂ into the fluorite solid solution. They took this temperature as the decomposition temperature of Zr₃Y₄O₁₂. Stubican et al. [79] suggested that Zr₃Y₄O₁₂ has rhombohedral symmetry (space group R3) and is isostructural with UY₆O₁₂ and it decomposes incongruently at 1523±50 K. Later on, they [80, 81] reinvestigated this ordered phase and suggested that Zr₃Y₄O₁₂ decomposes congruently at 1655±5 K. In the present work, Zr₃Y₄O₁₂ was included into the ZrO₂–YO₁.₅ system. A decomposition temperature of 1643 K was used in the optimization.

Pascual and Duran [82] reported another ordered phase, with the formula ZrY₆O₁₁. They suggested that ZrY₆O₁₁ decomposes at >2023 K into the fluorite phase and the cubic phase. This was contradicted by Jayaratna et al. [83] and Stubican et al. [79, 80, 81]. Stubican et al. annealed several mixtures of reactive powders containing 71.0, 78.8, 85.7, 91.9 mol% YO₁.₅ at 1573 K for 6 months, only mixtures of Zr₃Y₄O₁₂ and the YO₁.₅-rich cubic phase (α-Y₂O₃) were detected. Fan et al. [84] detected a Zr₂Y₂O₇ compound with a pyrochlore type structure. Its stable temperature range extends from 1373 to 2803 K. However, the existence of Zr₂Y₂O₇ was contradicted by many other authors [8]. These two phases (ZrY₆O₁₁ and Zr₂Y₂O₇) were hence, excluded from the ZrO₂–YO₁.₅ system.
2.5.3 Phase boundaries of the monoclinic+tetragonal two-phase region

Due to the complicacy and the sluggishness of the tetragonal ↔ monoclinic diffusional phase transition, it is impossible to determine the equilibrium phase boundaries of the m+t two-phase region. Pascual and Duran [82] claimed to have determined the m+t/t boundary from DTA and thermal expansion measurements. However, these measurements are directly related to the \( T_{o-t}^{m} \) line, not the equilibrium phase boundary. They also found a value of 3.0 mol% \( \text{YO}_{1.5} \) for the first appearance of c-ZrO\(_2\) in their quenched samples. This value was proposed as the solubility limit of \( \text{YO}_{1.5} \) in the monoclinic phase. Using X-ray phase identification and lattice parameter techniques, Ruh et al. [43] investigated phase relations at low \( \text{YO}_{1.5} \) contents. They confirmed that approximately 3.0 mol% \( \text{YO}_{1.5} \) is soluble in monoclinic ZrO\(_2\). These data were not used in our optimization.

The \( T_{o-t}^{m} \) temperature is defined as the temperature where, for a certain composition, the Gibbs energy of the tetragonal phase, and that of the monoclinic phase are equal.

\[
G^{m} = G^{t} \quad \text{Eq. 2.6}
\]

The \( T_{o-t}^{m} \) temperatures can be used to optimize the parameters for the Gibbs energy functions of the monoclinic phase. \( T_{o-t}^{m} \) was calculated according to Eq. 2.1. Investigations on the t-m phase transition have been done on samples prepared from mixed oxides, using different techniques (DTA, thermal dilatometry, and acoustic emission techniques) [6, 41, 42, 43, 82, 85]. Yoshikawa and Suto [46] prepared samples from co-precipitated powders and investigated the t-m phase transition using thermal dilatometry. Using Raman spectroscopy, Perry et al. [45] investigated the t-m transition on single ZrO\(_2\) crystals containing 0–21.4 mol% \( \text{YO}_{1.5} \). The single crystals were prepared using the skull melting method. The same samples were also studied by Adams et al. [44] using thermal dilatometry. Yashima and Yoshimura [47] studied the thermal expansion behavior of arc-melted samples. The t-m transition temperatures were determined for samples containing 0, 2, and 4 mol% \( \text{YO}_{1.5} \).

Later on, Yashima et al. [48] evaluated previously reported \( T_{o-t}^{m} \) data of compositionally homogeneous samples and obtained an equation for the \( T_{o-t}^{m} \) line using a least-square fit. The equation is given as
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\[ T_{o^{t-c}} = 1387 - 159.44X \]  \hspace{1cm} \text{Eq. 2.7}

where \( X \) is the concentration of \( \text{YO}_{1.5} \) in mol\% , \( T_{o^{t-c}} \) is in Kelvin. In the present work, 4 data points of \( T_{o^{t-c}} \) temperatures from Yashima et al. [48] (calculated using Eq. 2.7 at \( X = 1, 2, 3, 4 \)) were used in the optimization.

2.5.4 Phase boundaries of the tetragonal+cubic two-phase region

The phase boundaries of the tetragonal+cubic two-phase region have been investigated by many authors. Different methods were used to prepare the samples. The samples were prepared from mixed oxides [6, 42, 79, 82, 86, 87, 88, 89, 90], from co-precipitates [79, 83, 87, 91, 92, 93], and from melts [87, 94, 95]. Different techniques were used to determine the phase boundaries. Most people used X-ray diffraction (XRD) and lattice parameter techniques [6, 42, 43, 79, 82, 83, 87]. Duwez et al. [6] determined that at 2273 K, the right boundary \((t+c/c)\) is at 13.1 mol\% \( \text{YO}_{1.5} \) and the same at 1648 K. Srivastava et al. [42] investigated the subsolidus phase relationships on the \( \text{ZrO}_2 \)-rich side. At 2273 K, the \( t+c \) two-phase region extends from 3–4 to 10–13 mol\% \( \text{YO}_{1.5} \). Scott [87] prepared samples containing from 3 to 25 mol\% \( \text{YO}_{1.5} \) by arc-melting, by co-precipitation, and by mixing oxides. Identical results were obtained with samples prepared from co-precipitates and those from mixed oxides. Ruh et al. [43] suggested that the \( t+c \) two-phase region exists from \(-3.0 \) to 14.0 mol\% \( \text{YO}_{1.5} \) and from 773 to 1873 K.

Analytical electron microscopy was also used to determine the \( t+c \) phase boundaries [5, 86, 91, 93, 94, 95]. Strickler and Carlson [86] determined that at 2073 K, the right boundary \((t+c/c)\) lies between 16.5 and 17.4 mol\% \( \text{YO}_{1.5} \) (between 13.1 and 16.5 mol\% \( \text{YO}_{1.5} \) from XRD measurements). Lanteri et al. [94] reported that at 1873 K, the \( t+c \) two-phase region extends from 4.4±0.1 to 11.5±0.1 mol\% \( \text{YO}_{1.5} \). Rühle et al. [5], Chaim et al. [91], Yoshikawa et al. [93], Yagi et al. [95] also investigated the \( t+c \) phase boundaries.

Lange [92] measured the average grain size of samples sintered at 1673 K and suggested that at this temperature, the left boundary \((t/t+c)\) lies between 1.6 and 2.8 mol\% \( \text{YO}_{1.5} \). Suzuki and Kohzaki [88, 89, 90] determined the phase transition temperatures of the tetragonal+cubic \( \rightarrow \) tetragonal and the cubic \( \rightarrow \) tetragonal+cubic transitions, from
electrical conductivity measurements on sintered samples. It is open to question if these measurements can be related to the equilibrium phase boundaries of the t+c two-phase region.

In the present work, the data from Lanteri et al. [94] and Rühle et al. [5] were used.

2.5.5 Phase boundaries of the cubic+\textit{Zr}_3\textit{Y}_4\textit{O}_{12} two-phase region

The phase boundaries of the cubic+ \textit{Zr}_3\textit{Y}_4\textit{O}_{12} two-phase region have been determined by Pascual and Duran [82] using XRD, and by Suzuki and Kohzaki [88, 89] based on electrical conductivity measurements. The experimental data above 1200 K [82, 89] were used in the optimization.

2.5.6 Phase boundaries of the cubic+\textit{a-Y}_2\textit{O}_3 two-phase region

The phase boundaries of the cubic+ \textit{a-Y}_2\textit{O}_3 two-phase region have been investigated by many authors, using XRD and/or lattice parameter techniques. The samples were prepared from mixed oxides [6, 42, 78, 79, 80, 81, 82, 86], from melts [9, 78], and from co-precipitates [79, 80, 81, 83]. Two different geometries were proposed for this region. The main difference lies in the position of the right boundary, i.e. the solubility of \textit{ZrO}_2 in \textit{a-Y}_2\textit{O}_3. Duwez et al. [6], Stubican et al. [79, 80, 81], and Pascual and Duran [82] detected an increasing solubility of \textit{ZrO}_2 in \textit{a-Y}_2\textit{O}_3 with increasing temperature; while Scott [78] and Jayaratna et al. [83] reported a decreasing solubility. Strickler and Carlson [86] determined that at 2073 K, the left boundary (c/c+\textit{a-Y}_2\textit{O}_3) lies between 62.1 and 66.7 mol% \textit{YO}_{1.5}. Srivastava et al. [42] reported that the left boundary (c/c+\textit{a-Y}_2\textit{O}_3) at 2273 K lies between 66.6 and 71 mol% \textit{YO}_{1.5}.

It is not clear which one of the two possibilities for the temperature dependence of the \textit{ZrO}_2 solubility in \textit{a-Y}_2\textit{O}_3 is the correct one. One difficulty lies in identifying which of the previous researches has been done on samples reaching equilibrium. As stated before, the structural similarity between \textit{ZrO}_2 and \textit{Y}_2\textit{O}_3 and the extrapolations of the liquidus and the solidus for the cubic phase make it possible to form a metastable \textit{YO}_{1.5}-rich phase with disordered fluorite structure. Even after high-temperature annealing, it is still open to question if these samples have reached equilibrium. This is due to the low cation mobility in the \textit{ZrO}_2-\textit{YO}_{1.5} system. Beside the samples, the phase discrimination method also plays a role. The previous
researches are mainly based on the conventional X-ray diffraction method. The XRD patterns of c-ZrO₂ and α-Y₂O₃ are very similar. The difference can only be found in the secondary features of the patterns. This may also cause a lot of discrepancies in the determined phase boundaries. During the optimization, we first tried two different versions, using different sets of data for the phase boundaries of the cubic+α-Y₂O₃ two-phase region. One includes the data from Stubican et al. [79, 81], the other includes the data from Scott [78] and Jayaratna et al. [83]. The second version leads to less realistic parameters for the cubic phase and α-Y₂O₃, and was hence disregarded. In the present work, we only include the data from Stubican et al. [79, 81].

2.5.7 Phase boundary of the Zr₃Y₄O₁₂+α-Y₂O₃ two-phase region

Based on lattice parameter measurements, Scott [78] derived the Zr₃Y₄O₁₂+α-Y₂O₃/α-Y₂O₃ phase boundary at 1473 K to be at 75 mol% YO₁.₅. No other investigations have confirmed this. On the contrary, Baldinozzi et al. [96] reported that the solubility of ZrO₂ in α-Y₂O₃ is lower than 1.4 mol%. Their samples were annealed at 1773 K for 2 hours. Recently, Calderon-Moreno and Yoshimura [97] prepared arc-melted YO₁.₅-rich samples. Based on Raman spectroscopy results, they suggested that the substitution of yttria by zirconia in the yttria lattice is very limited. In the present work, none of the above was taken into consideration.

2.5.8 Eutectoid reactions

2.5.8.1 Tetragonal → monoclinic + cubic

Based on DTA and XRD measurements, Srivastava et al. [42] determined that the eutectoid point of the tetragonal → monoclinic + cubic reaction is at ~7.5 mol% YO₁.₅ and ~838 K. Pascual and Duran [82] located the eutectoid point at 8.6 mol% YO₁.₅ and 763 K. Srikanth and Subbarao [85] detected an intense acoustic emission activity starting at 843±5 K on heating and cooling samples containing 3.9–11.3 mol% YO₁.₅. They attributed this temperature as the eutectoid temperature of the tetragonal → monoclinic + cubic reaction. Based on electrical conductivity measurements, Suzuki [89] reported the eutectoid temperature to be at ~872 K. These results are most probably not related to the
tetragonal → monoclinic + cubic reaction, but may be related to the massive transformation of cubic to t'\textsuperscript{−}ZrO\textsubscript{2}.

2.5.8.2 Cubic → monoclinic + Zr\textsubscript{3}Y\textsubscript{4}O\textsubscript{12}

Stubican et al. [79] suggested that this eutectoid point may be at a temperature < 673 K and at a composition between 33.3 and 46.2 mol% YO\textsubscript{1.5}. Suzuki [89] determined the eutectoid point at 692 K and 30 mol% YO\textsubscript{1.5}.

2.5.8.3 Cubic → Zr\textsubscript{3}Y\textsubscript{4}O\textsubscript{12} + α-Y\textsubscript{2}O\textsubscript{3}

Scott [78] determined this eutectoid point at 1573 K and 63 mol% YO\textsubscript{1.5}. Stubican et al. [80] reported a eutectic temperature of 1650±5 K.

These data were not used in our optimization, as most of them are questionable.

2.5.9 Melting relations

The liquidus was first measured by Rouanet [98] in the whole composition range. He reported a eutectic reaction at 90.6 mol% YO\textsubscript{1.5} and 2643 K. His reported melting temperatures of pure ZrO\textsubscript{2} and pure Y\textsubscript{2}O\textsubscript{3} are 2983 K and 2712 K respectively. Noguchi et al. [9] measured the cooling curves of samples containing 0-100 mol% YO\textsubscript{1.5}. They located the eutectic point at 86.4 mol% YO\textsubscript{1.5} and 2603 K. The melting temperatures of pure ZrO\textsubscript{2} and pure Y\textsubscript{2}O\textsubscript{3} were measured as 2979 K and 2649 K. Their measured melting temperature of pure Y\textsubscript{2}O\textsubscript{3} is too low. The measured liquidus is lower than the one from Rouanet [98] and seems less reliable. Skaggs et al. [99] reported a peritectic isotherm from 73.4 to 90.1 mol% YO\textsubscript{1.5} at 2756 K. The peritectic composition is 85.7 mol% YO\textsubscript{1.5}. Stubican et al. [79] determined the liquidus on the YO\textsubscript{1.5}-rich side. They located the eutectic point at 90.7±1 mol% YO\textsubscript{1.5} and 2633±20 K and the peritectic point at 86.4±1 mol% YO\textsubscript{1.5}. The melting temperature of pure Y\textsubscript{2}O\textsubscript{3} was determined as 2775 K, obviously too high. In our optimization, the liquidus data from Rouanet [98] for the c+L and the β-Y\textsubscript{2}O\textsubscript{3}+L two-phase regions and the data from Stubican et al. [79] for the c+L two-phase region were used. The reported temperatures and compositions of the eutectic and the peritectic reactions were not included.
2.5.10 Thermodynamic data

Vintonyak et al. [100] determined the yttria activity in the ZrO$_2$-rich solid solutions at 1300 K, using an EMF (electromotive force) method. Based on the calculated partial Gibbs energies of yttria, they concluded that at 1300 K, samples with a YO$_{1.5}$ content of 5.8–16.5 mol% are in the tetragonal+cubic two-phase region. Zaitseva and coworkers [101, 102, and 103] published a few papers on the thermodynamic properties of solid solutions in the ZrO$_2$–YO$_{1.5}$ system. Zaitseva and Granovskaya [101] used an EMF method to determine the activity ratios of ZrO$_2$ (cubic) in the solid solutions containing 46.2 and 51.8 mol% YO$_{1.5}$ at different temperatures. X-ray phase analyses confirmed their samples to be homogeneous and have fluorite structure. Also using an EMF method with an F-ion electrolyte, Zaitseva and Skolis [102] determined the partial thermodynamic properties of yttrium oxide in $\alpha$-Y$_2$O$_3$ solid solutions. Their samples (containing 82.4, 88.9, 91.9, 97.4 mol% YO$_{1.5}$) were held at 1673 K for 12 days and then at 1273 K for four months. The partial thermodynamic functions of Y$_2$O$_3$ in the cubic+$\alpha$-Y$_2$O$_3$ two-phase region and in the $\alpha$-Y$_2$O$_3$ one-phase region at 1273 K were reported. They also commented that the data from Vintonyak et al. [100], for samples with low contents of YO$_{1.5}$ (≤16.5 mol%) should be treated as erroneous. Later on, Zaitseva and Dobrokhotova [103] determined the partial thermodynamic properties of zirconia in c-ZrO$_2$ solid solutions at 1273 K. Belov and Semenov [104] studied the evaporation behavior of the ZrO$_2$–YO$_{1.5}$ solid solutions at 2773 K. The activities of ZrO$_2$ in the cubic phase were determined within the whole composition range. According to the measured liquidus in the ZrO$_2$–YO$_{1.5}$ system [9, 79, 98], there should be a cubic+liquid two-phase interval and a liquid single-phase interval on the yttria-rich side at 2773 K. The results from Belov and Semenov [104] did not show this. Marushkin and Alikhanyan [105] also studied the partial pressures of the vapour above the ZrO$_2$–YO$_{1.5}$ system at $T = 2800$ K.

Several groups measured the heat capacity of c-ZrO$_2$ with different yttria content. Hasselman et al. [106] measured the specific heat of a series of high density, yttria stabilized, polycrystalline ZrO$_2$ samples, with YO$_{1.5}$ content ranging from 2.6 to 18.2 mol%. Only the samples with a YO$_{1.5}$ content of ≥9.8 mol% were found to be single phase (cubic). They concluded that the specific heat of c-ZrO$_2$ was not significantly affected by the amount of yttria. Using adiabatic calorimetry, Tojo et al. [31, 107] measured the heat capacity of c-ZrO$_2$ at 3 different compositions ($x_{YO_{1.5}} = 0.144, 0.1768, 0.2039$, where $x_{YO_{1.5}}$ is the mole fraction of
YO1.5) between 13 and 300 K. Tanaka et al. [108] measured the specific heat of yttria stabilized zirconia with a composition of \((\text{ZrO}_2)_{0.942}(\text{YO}_{1.5})_{0.058}\) from 540 K to 840 K by quasi-static thermal radiation calorimetry. These heat capacity measurements were all done on sintered samples. Lee et al. [56] very recently measured enthalpies of formation of c-ZrO\(_2\) solid solutions and Zr\(_3\)Y\(_4\)O\(_{12}\) relative to pure m-ZrO\(_2\) and pure \(\alpha\)-Y\(_2\)O\(_3\) using solution calorimetry. These measurements indirectly give information on the enthalpy of mixing in c-ZrO\(_2\) and are the only ones to do that so far.

In our optimization, the thermodynamic data from Belov and Semenov [104], Vintonyak et al. [100], Zaitseva and coworkers [102, 103], and Lee et al. [56] were used.

### 2.6 Thermodynamic models

#### 2.6.1 Solid solution phases

Four solid solution phases were included into the present description: m-ZrO\(_2\), t-ZrO\(_2\), c-ZrO\(_2\), and \(\alpha\)-Y\(_2\)O\(_3\). \(\beta\)-Y\(_2\)O\(_3\) was included in the c-ZrO\(_2\) phase. The same formula, \((Y^{3+},Zr^{4+})_2(O^{2-},Va)_3\), was used for m-ZrO\(_2\), t-ZrO\(_2\), and c-ZrO\(_2\). For \(\alpha\)-Y\(_2\)O\(_3\) the formula \((Y^{3+},Zr^{4+})_2(O^{2-},Va)_2(O^{2-},Va)_1\) was used.

The Gibbs energies of the m, t and c solution phases are given by:

\[
G_m = y_{Y^{3+}}y_{O^{2-}}^oG_{Y^{3+},O^{2-}} + y_{Zr^{4+}}y_{O^{2-}}^oG_{Zr^{4+},O^{2-}} + y_{Y^{3+}}y_{Va}^oG_{Y^{3+},Va} + y_{Zr^{4+}}y_{Va}^oG_{Zr^{4+},Va} + RT\left(y_{Y^{3+}}\ln y_{Y^{3+}} + y_{Zr^{4+}}\ln y_{Zr^{4+}} + 2y_{O^{2-}}\ln y_{O^{2-}} + y_{Va}\ln y_{Va}\right) + \epsilon \tag{2.8}
\]

where \(y_s\) is the fraction of the species \(s\) in a particular sublattice.

The Gibbs energy of ZrO\(_2\) is given by the parameter \(oG_{Zr^{4+},O^{2-}}\):

\[
oG_{Zr^{4+},O^{2-}} - H_{Zr}^{SER} - 2H_{O}^{SER} = GZRO2 \tag{2.9}
\]

The parameter \(oG_{Zr^{4+},Va}\) is set as:

\[
oG_{Zr^{4+},Va} - H_{Zr}^{SER} = GZRO2 - 2GHSEROO \tag{2.10}
\]

where GHSEROO is the molar Gibbs energy of oxygen taken from Dinsdale [17].
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The Gibbs energy of YO$_{1.5}$ (0.5 mole of Y$_2$O$_3$) is given by:

$$G_{YO1.5} = \frac{3}{4}(G_{Y^{3+},O^{2-}} - H_Y^{SER} - 2H_O^{SER}) + \frac{1}{4}(G_{Y^{3+},Va} - H_Y^{SER}) + 2[\frac{3}{4}\ln\frac{3}{4} + \frac{1}{4}\ln\frac{1}{4}]RT$$  

Eq. 2.11

A reciprocal relation was used:

$$^oG_{Y^{3+},Va} + ^oG_{Zr^{4+},O^{2-}} = ^oG_{Y^{3+},O^{2-}} - ^oG_{Zr^{4+},Va} = \Delta G_i$$  

Eq. 2.12

where $\Delta G_i = 0$ is chosen for convenience.

From Eqs. 2.10, 2.11, and 2.12, we get

$$^oG_{Y^{3+},O^{2-}} - H_Y^{SER} - 2H_O^{SER} = G_{YO15} + 0.5 \text{GHSEEROO + 1.12467 } RT$$  

Eq. 2.13

$$^oG_{Y^{3+},Va} = G_{YO15} - 1.5 \text{GHSEEROO + 1.12467 } RT$$  

Eq. 2.14

The excess Gibbs energy $E_G_m$ has the following form:

$$E_G_m = \sum y^{Y^{3+}}y^{Zr^{4+}}y^{Va}\sum_{i=0}^n L_{Y^{3+},Zr^{4+},O^{2-}}(y^{Y^{3+}} - y^{Zr^{4+}})$$  

Eq. 2.15

where we require $L_{Y^{3+},Zr^{4+},O^{2-}} = L_{Y^{3+},Zr^{4+},Va}$.

The Gibbs energy of $\alpha$-Y$_2$O$_3$ is given by ($y'$ denotes the second sublattice and $y''$ the third):

$$G_m = y^{Y^{3+}}y'^{Y^{3+}}y'^{Va}^yG_{Y^{3+},O^{2-}} + y^{Zr^{4+}}y'^{Zr^{4+}}y'^{Va}^zG_{Zr^{4+},O^{2-}} + y^{Y^{3+}}y'^{Va}y''^{Va}y''^{O^{2-}}^yG_{Y^{3+},Va}$$

$$+ y^{Y^{3+}}y'^{Va}y''^{Va}G_{Y^{3+},Va} + y^{Zr^{4+}}y'^{Zr^{4+}}y''^{Va}G_{Zr^{4+},Va} + y^{Zr^{4+}}y'^{O^{2-}}y''^{O^{2-}}^zG_{Zr^{4+},O^{2-}}$$

$$+ y^{Zr^{4+}}y'^{O^{2-}}y''^{Va}G_{Zr^{4+},Va} + RT[2(y^{Y^{3+}}y'^{Va}, y^{Zr^{4+}}y'^{Va}, y^{Zr^{4+}}y'^{Va}) + 3(y^{O^{2-}}y'^{Va}, y^{O^{2-}}y'^{Va}) + (y^{O^{2-}}y'^{Va}, y''^{Va}, y''^{Va})]^{E_{G_m}}$$  

Eq. 2.16

The individual parameter is derived in a similar manner as for the m, t, and c phases. The metastable end point of $\alpha$-Y$_2$O$_3$ at the ZrO$_2$ composition is given by the parameter $^oG_{Zr^{4+},O^{2-}}$. For the excess Gibbs energy, we apply the restriction:

$$L_{Y^{3+},Zr^{4+},O^{2-}} = L_{Y^{3+},Zr^{4+},Va} = L_{Y^{3+},Zr^{4+},Va} = L_{Y^{3+},Zr^{4+},Va}$$  

Eq. 2.17
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The Gibbs energies of stable stoichiometric ZrO$_2$ phases were taken from the present work (see Section 2.2.1). The Gibbs energy of the metastable end point (i.e. ZrO$_2$) of $\alpha$-Y$_2$O$_3$ is left to be determined. The Gibbs energies of the stable stoichiometric YO$_{1.5}$ phases were taken from Swamy et al. [14]. The Gibbs energies of the metastable end points (i.e. YO$_{1.5}$) of m-ZrO$_2$ and t-ZrO$_2$ are left to be determined.

2.6.2 Zr$_3$Y$_4$O$_{12}$

The ordered phase Zr$_3$Y$_4$O$_{12}$ was treated as a stoichiometric compound.

2.6.3 Liquid phase

The liquid phase was modeled as $(Y^{3+}, Zr^{4+})_p(O^{2-})_q$, using the two-sublattice model for ionic liquids [57, 58], where

\begin{align*}
  p &= 2y_{O^{2-}} \\
  q &= 3y_{Y^{3+}} + 4y_{Zr^{4+}}
\end{align*}

The molar Gibbs energy of the liquid is:

\begin{equation}
  G_m^L = \sum_{i=0}^1 L_{i}^{L_{Y^{3+},Zr^{4+},O^{2-}}} (y_{Y^{3+}} - y_{Zr^{4+}})
\end{equation}

The excess Gibbs energy $E^L_{m}$ is given by

\begin{equation}
  E^L_{m} = \sum_{i=0}^1 L_{i}^{L_{Y^{3+},Zr^{4+},O^{2-}}} (y_{Y^{3+}} - y_{Zr^{4+}})
\end{equation}

The parameter $L_{i}^{L_{Y^{3+},Zr^{4+},O^{2-}}}$ was optimized in the present work.

2.7 Optimization procedure

In the present work, the optimized parameters are mainly the interaction parameters for the solid solution phases and the liquid phase. The Gibbs energies of the metastable end points were fixed at an early stage of the optimization and not changed further, with the exception of
the YO\textsubscript{1.5} end point of m-ZrO\textsubscript{2} which was optimized. No interaction parameter was used for m-ZrO\textsubscript{2}.

The interaction parameters were described as

\[ L = A + BT, \quad i = 0, 1, 2 \quad \text{Eq. 2.22} \]

For the liquid a subsubregular interaction (\( ^2L \)) was used and for c-ZrO\textsubscript{2} a subregular interaction (\( ^1L \)) was used. For t-ZrO\textsubscript{2} a regular interaction (\( ^0L \)) was enough. For the liquid phase the interaction parameters were used without temperature dependence. For the Zr\textsubscript{3}Y\textsubscript{4}O\textsubscript{12} phase two parameters were optimized. In the present optimization, the thermodynamic data were used mainly to adjust the parameters for the fluorite phase. We found that it is almost impossible to get a satisfactory fit of both the selected phase diagram data and the available thermodynamic data. The difficulty lies in fitting those thermodynamic data measured at low temperatures (around 1300 K). They seem to be inconsistent with most of the phase diagram data and the ZrO\textsubscript{2} activities in the fluorite phase at 2773 K [104]. We used ZrO\textsubscript{2} and Y\textsubscript{2}O\textsubscript{3} activities at 2773 K [104], 1300 K [100], and 1273 K [102, 103], and the enthalpy of formation data from Lee et al. [56]. Because of the problems described above a careful balancing of the weights was needed to get a stable optimization and a reasonable description of most of the data.

### 2.8 Results and discussion

A complete thermodynamic description of the Y–Zr–O system, including the ZrO\textsubscript{2}–YO\textsubscript{1.5} system is given in Table 2.4.

#### Table 2.4 Thermodynamic description of the Y–Zr–O system

<table>
<thead>
<tr>
<th>Element</th>
<th>Element reference</th>
<th>Mass</th>
<th>(H_{298}-H_0)</th>
<th>(S_{298})</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>(\frac{1}{2}) mole O\textsubscript{2}</td>
<td>15.999</td>
<td>4341.0</td>
<td>102.52</td>
</tr>
<tr>
<td>Y</td>
<td>Y–hcp</td>
<td>88.906</td>
<td>5966.4</td>
<td>44.434</td>
</tr>
<tr>
<td>Zr</td>
<td>Zr–hcp</td>
<td>91.224</td>
<td>5566.3</td>
<td>39.181</td>
</tr>
</tbody>
</table>

HCP

\[
\begin{align*}
\Delta G_{YO} - H_{\text{SER}}^{\text{Y}} - 0.5 H_{\text{SER}}^{\text{O}} &= \text{GHERYY} + 0.5 \text{GHEROO} - 303600 + 37.5T \\
\Delta G_{Y,\text{Va}} - H_{\text{SER}}^{\text{Y}} &= \text{GHERYY} \\
\Delta G_{ZrO} - H_{\text{SER}}^{\text{Zr}} - 0.5 H_{\text{SER}}^{\text{O}} &= \text{GHERZr} + 0.5 \text{GHEROO} - 280300 + 41T
\end{align*}
\]
### Chapter 2

<table>
<thead>
<tr>
<th>Temperature Dependence</th>
<th>Monoclinic ZrO$_2$</th>
<th>Tetragonal ZrO$_2$</th>
<th>Cubic ZrO$_2$ (and β-Y$_2$O$_3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^0G_{Zr,Va} - H^{SER}_{Zr}$</td>
<td>GHSERZR</td>
<td>GZRBCC</td>
<td>GHSERZR</td>
</tr>
<tr>
<td>$^0L_{Y^3+,Va}$</td>
<td>$+3500$</td>
<td></td>
<td>$+3500$</td>
</tr>
<tr>
<td>$^0L_{Zr,Zr,Va}$</td>
<td>$-29100 + 15.5T$</td>
<td></td>
<td>$-29100 + 15.5T$</td>
</tr>
<tr>
<td>$^1L_{Zr,O,Va}$</td>
<td>$-9150 + 3T$</td>
<td>$-9150 + 3T$</td>
<td>$-9150 + 3T$</td>
</tr>
<tr>
<td>$^0L_{Y,Y,Va}$</td>
<td>$+50000$</td>
<td>$+50000$</td>
<td>$+50000$</td>
</tr>
</tbody>
</table>

#### BCC

$(Y, Zr)\,(O, Va)_{1.5}$

- $^0G_{Y^3+,O^2-} - H^{SER}_{Y} = 1.5 H^{SER}_{O} = GYYBCC + 1.5 \, \text{GHSEROO} - 899200 + 123T$
- $^0G_{Y^3+,Va} - H^{SER}_{Y} = GYYBCC$
- $^0G_{Zr,O} - H^{SER}_{Zr} = GZRBCC + 1.5 \, \text{GHSEROO}$
- $^0G_{Zr,Va} - H^{SER}_{Zr} = GZRBCC$
- $^0L_{Y^3+,Va} = -5000$
- $^0L_{Zr,Va} = -1102000 + 155.4T$
- $^1L_{Zr,O,Va} = -235000$
- $^0L_{Y,Y,Va} = +40000$
- $^1L_{Y,Y,Va} = -9000$

#### Monoclinic ZrO$_2$

$(Y^{3+}, Zr^{4+})\,(O^{2-}, Va)_2$

- $^0G_{Y^{3+},O^2-} - H^{SER}_{Y} - 2 H^{SER}_{O} = \text{GMMYO15} + 0.5 \, \text{GHSEROO} + 9.3511T$
- $^0G_{Y^{3+},Va} - H^{SER}_{Y} = \text{GMMYO15} - 1.5 \, \text{GHSEROO} + 9.3511T$
- $^0G_{Zr^{4+},O^2-} - H^{SER}_{Zr} - 2 H^{SER}_{O} = \text{GMMZRO2}$
- $^0G_{Zr^{4+},Va} - H^{SER}_{Zr} = \text{GMMZRO2} - 2 \, \text{GHSEROO}$

#### Tetragonal ZrO$_2$

$(Y^{3+}, Zr^{4+})\,(O^{2-}, Va)_2$

- $^0G_{Y^{3+},O^2-} - H^{SER}_{Y} - 2 H^{SER}_{O} = \text{GMTYO15} + 0.5 \, \text{GHSEROO} + 9.3511T$
- $^0G_{Y^{3+},Va} - H^{SER}_{Y} = \text{GMTYO15} - 1.5 \, \text{GHSEROO} + 9.3511T$
- $^0G_{Zr^{4+},O^2-} - H^{SER}_{Zr} - 2 H^{SER}_{O} = \text{GTTZRO2}$
- $^0G_{Zr^{4+},Va} - H^{SER}_{Zr} = \text{GTTZRO2} - 2 \, \text{GHSEROO}$
- $^0L_{Y^{3+,Zr^{4+}},O^2-} = ^0L_{Y^{3+,Zr^{4+}},Va} = -48800 + 18.4T$

#### Cubic ZrO$_2$ (and β-Y$_2$O$_3$)

$(Y, Y^{3+}, Zr, Zr^{4+})\,(O^{2-}, Va)_2$

- $^0G_{Y,O^2-} - H^{SER}_{Y} - 2 H^{SER}_{O} = +\text{GHSERYY} + 2 \, \text{GHSEROO} + 122800$
- $^0G_{Y, Va} - H^{SER}_{Y} = +\text{GHSERYY} + 122800$
- $^0G_{Y^{3+},O^2-} - H^{SER}_{Y} - 2 H^{SER}_{O} = \text{GHHYO15} + 0.5 \, \text{GHSEROO} + 9.3511T$
- $^0G_{Y^{3+},Va} - H^{SER}_{Y} = \text{GHHYO15} - 1.5 \, \text{GHSEROO} + 9.3511T$
- $^0G_{Zr,O^2-} - H^{SER}_{Zr} - 2 H^{SER}_{O} = +\text{GHSERZR} + 2 \, \text{GHSEROO} + 100000$
Modeling of the $Y-Zr-O$ System

\[ \begin{align*}
\sigma G_{\text{Zr}^{4+}, \text{Va}} - H_{\text{Zr}}^{\text{SER}} &= +\text{GHSERZR} + 100000 \\
\sigma G_{\text{Zr}^{3+}, \text{O}^{2-}} - H_{\text{Zr}}^{\text{SER}} - 2 H_{\text{O}}^{\text{SER}} &= \text{GFFZRO2} \\
\sigma G_{\text{Zr}^{4+}, \text{Va}} - H_{\text{Zr}}^{\text{SER}} &= \text{GFFZRO2} - 2 \text{GHSEROO} \\
0 L_{\text{Y}^{3+}, \text{Zr}^{4+}, \text{O}^{2-}, \text{Va}} &= -76000 + 31.7T \\
1 L_{\text{Y}^{3+}, \text{Zr}^{4+}, \text{O}^{2-}, \text{Va}} &= +34200 - 8.6T \\
0 L_{\text{Zr}^{3+}, \text{Zr}^{4+}, \text{O}^{2-}, \text{Va}} &= -66500 - 1.6T \\
1 L_{\text{Zr}^{3+}, \text{Zr}^{4+}, \text{O}^{2-}, \text{Va}} &= -20000 - 42T
\end{align*} \]

\[ \begin{align*}
\alpha Y_2O_3 \\
&\left(\text{Y}^{3+}, \text{Zr}^{4+}\right)_2\left(\text{O}^{2-}, \text{Va}\right)_3(\text{O}^{2-}, \text{Va})_1 \\
\sigma G_{\text{Y}^{3+}, \text{O}^{2-}, \text{Va}} - 2 H_{\text{Y}}^{\text{SER}} - 4 H_{\text{O}}^{\text{SER}} &= 2 \text{GHSERYY} + 4 \text{GHSEROO} + 345600 + 15.87691T \\
\sigma G_{\text{Y}^{3+}, \text{Zr}^{4+}, \text{O}^{2-}, \text{Va}} - 2 H_{\text{Y}}^{\text{SER}} - 3 H_{\text{O}}^{\text{SER}} &= 2 \text{GHSERYY} + 3 \text{GHSEROO} + 245600 \\
\sigma G_{\text{Y}^{3+}, \text{Va}, \text{O}^{2-}, \text{Va}} - 2 H_{\text{Y}}^{\text{SER}} - H_{\text{O}}^{\text{SER}} &= 2 \text{GHSERYY} + \text{GHSEROO} + 345600 + 15.87691T \\
\sigma G_{\text{Y}^{3+}, \text{Va}, \text{O}^{2-}, \text{Va}} - 2 H_{\text{Y}}^{\text{SER}} &= 2 \text{GHSERYY} + 245600 \\
\sigma G_{\text{Y}^{3+}, \text{O}^{2-}, \text{Va}} - \frac{2 H_{\text{Y}}^{\text{SER}}}{\text{Y}} - 4 H_{\text{O}}^{\text{SER}} &= 2 \text{GCCYO15} + \text{GHSEROO} + 100000 + 15.87691T \\
\sigma G_{\text{Y}^{3+}, \text{Va}, \text{O}^{2-}, \text{Va}} - 2 H_{\text{Y}}^{\text{SER}} - 3 H_{\text{O}}^{\text{SER}} &= 2 \text{GCCYO15} \\
\sigma G_{\text{Y}^{3+}, \text{Va}, \text{O}^{2-}, \text{Va}} - 2 H_{\text{Y}}^{\text{SER}} - H_{\text{O}}^{\text{SER}} &= 2 \text{GCCYO15} - 3 \text{GHSEROO} \\
\sigma G_{\text{Y}^{3+}, \text{Va}, \text{O}^{2-}, \text{Va}} - 2 H_{\text{Y}}^{\text{SER}} &= 2 \text{GCCYO15} - 2 \text{GHSEROO} \\
\sigma G_{\text{Zr}^{4+}, \text{O}^{2-}, \text{Va}} - 2 H_{\text{Zr}}^{\text{SER}} - 4 H_{\text{O}}^{\text{SER}} &= 2 \text{GMCZRO2} \\
\sigma G_{\text{Zr}^{3+}, \text{Zr}^{4+}, \text{O}^{2-}, \text{Va}} - 2 H_{\text{Zr}}^{\text{SER}} - 3 H_{\text{O}}^{\text{SER}} &= 2 \text{GMCZRO2} - 4 \text{GHSEROO} + 100000 - 15.87691T \\
\sigma G_{\text{Zr}^{3+}, \text{Zr}^{4+}, \text{O}^{2-}, \text{Va}} - 2 H_{\text{Zr}}^{\text{SER}} - H_{\text{O}}^{\text{SER}} &= 2 \text{GMCZRO2} - 3 \text{GHSEROO} \\
\sigma G_{\text{Zr}^{3+}, \text{Zr}^{4+}, \text{O}^{2-}, \text{Va}} - 2 H_{\text{Zr}}^{\text{SER}} &= 2 \text{GMCZRO2} - 4 \text{GHSEROO} - 100000 - 15.87691T \\
0 L_{\text{Y}^{3+}, \text{Zr}^{4+}, \text{O}^{2-}, \text{Va}} &= 0 L_{\text{Y}^{3+}, \text{Zr}^{4+}, \text{O}^{2-}, \text{Va}} = 0 L_{\text{Y}^{3+}, \text{Zr}^{4+}, \text{O}^{2-}, \text{Va}} = 0 L_{\text{Y}^{3+}, \text{Zr}^{4+}, \text{O}^{2-}, \text{Va}} = -88700 + 13T
\end{align*} \]

Zr$_3$Y$_4$O$_{12}$
\[\begin{align*}
&\left(\text{Zr}^{4+}\right)_3\left(\text{Y}^{3+}\right)_4(\text{O}^{2-})_4 \\
\sigma G_{\text{Zr}^{4+}, \text{Y}^{3+}, \text{O}^{2-}} - 3 H_{\text{Zr}}^{\text{SER}} - 4 H_{\text{Y}}^{\text{SER}} - 12 H_{\text{O}}^{\text{SER}} &= 7 \text{GYZ0} \\
\end{align*}\]

Liquid
\[\begin{align*}
\begin{align*}
&\left(\text{Y}^{3+}, \text{Zr}^{4+}\right)_p (\text{O}^{2-}, \text{Va}^{p+})_q \\
p &= 2 y_{\text{O}^{2-}} + q y_{\text{Va}^{p+}}, \quad q = 3 y_{\text{Y}^{3+}} + 4 y_{\text{Zr}^{4+}} \\
\sigma G_{\text{Y}^{3+}, \text{O}^{2-}} - 2 H_{\text{Y}}^{\text{SER}} - 3 H_{\text{O}}^{\text{SER}} &= \text{GY2O3LIQ} \\
\sigma G_{\text{Y}^{3+}, \text{Va}} - H_{\text{Y}}^{\text{SER}} &= \text{GYYLIQ} \\
\sigma G_{\text{Zr}^{4+}, \text{O}^{2-}} - 2 H_{\text{Zr}}^{\text{SER}} - 4 H_{\text{O}}^{\text{SER}} &= \text{GZRO2LIQ} \\
\sigma G_{\text{Zr}^{4+}, \text{Va}} - H_{\text{Zr}}^{\text{SER}} &= \text{GZRLIQ} \\
0 L_{\text{Y}^{3+}, \text{O}^{2-}, \text{Va}} &= +6900 \\
1 L_{\text{Y}^{3+}, \text{O}^{2-}, \text{Va}} &= -17000 \\
0 L_{\text{Zr}^{4+}, \text{O}^{2-}, \text{Va}} &= -26500
\end{align*}
\end{align*}\]
Chapter 2

\[
\begin{align*}
^{1}L_{Zr^{4+},O^{2-},V_a} &= +50000 \\
^{2}L_{Zr^{4+},O^{2-},V_a} &= +72000 \\
^{0}L_{Y^{3+},Zr^{4+},O^{2-}} &= +20100 \\
^{1}L_{Y^{3+},Zr^{4+},O^{2-}} &= -13000 \\
^{2}L_{Y^{3+},Zr^{4+},O^{2-}} &= -40000 \\
^{0}L_{Y^{3+},Zr^{4+},V_a} &= +24000 \\
^{1}L_{Y^{3+},Zr^{4+},V_a} &= +3000 \\
O_2 (g) \\
\delta G_{O_2} - 2H_{O}^{SER} &= 2 \text{GHSEROO} + RT \ln(1 \times 10^{-5} P) \\
\end{align*}
\]

**Functions**

\[
\begin{align*}
\text{GMMZRO2} &= -1125300 + 416.97T - 68.47\ln T - 0.003357T^2 + 586000T^{-1} \\
\text{GTTZRO2} &= +\text{GMMZRO2} + 6000 - 4.326T \\
\text{GFFZRO2} &= +\text{GMMZRO2} + 13500 - 7.159T \\
\text{GMNZRO2} &= +\text{GFFZRO2} + 45000 \\
\text{GZRO2LIQ} &= -1077400 + 561.1T - 90T \ln T \\
\text{GCCYO15} &= -990900 + 381.86T - 62.85\ln T - 0.0025T^2 + 1172000T^{-1} - 5.9 \times 10^7T^{-2} \\
\text{GHHYO15} &= +\text{GCCYO15} + 13630 - 5T - 0.0003T^2 \\
\text{GMMYO15} &= +\text{GCCYO15} + 32700 + 20T \\
\text{GMTOYO15} &= +\text{GCCYO15} + 15000 \\
\text{GY2O3LIQ} &= +2 \text{GYLIQ} + 3 \text{GHSEROO} - 1824600 + 246T \\
\text{GZO} &= +0.4286 \text{GFFZRO2} + 0.5714 \text{GCCYO15} - 15900 + 1T \\
\end{align*}
\]

Note: All parameters are in SI units: J, mol, K, Pa; R=8.31451 J/(mol K). GHSERZR, GZRBCC, GZRLIQ, and GHSEROO are the molar Gibbs energies of pure Zr and oxygen from Dinsdale, 1991 [17]. GHSERYY, GYYBCC, and GYYLIQ are the molar Gibbs energies of pure Y from SGTE Unary Database (1996) [109]. Parameters for Y–Zr are from Flandorfer et al., 1997 [15].

50
Figure 2.5 shows the calculated $T_{o}^{\text{m-c}}$ line together with the experimental data. The present $T_{o}^{\text{m-c}}$ line almost coincides with the line from Yashima et al. [48]. Figure 2.6 presents our calculated phase diagram. A list of invariant reactions is shown in Table 2.5.

![Diagram showing calculated $T_{o}^{\text{m-c}}$ line compared with experimental data.]

Table 2.5 Temperatures and compositions of invariant reactions, (a) $t \rightarrow m+c$ , (b) $c \rightarrow m + \text{Zr}_3\text{Y}_4\text{O}_{12}$, (c) $c \rightarrow \text{Zr}_3\text{Y}_4\text{O}_{12} + \alpha$-$\text{Y}_2\text{O}_3$, (d) $\text{L} \rightarrow \alpha$-$\text{Y}_2\text{O}_3 + \beta$-$\text{Y}_2\text{O}_3$, (e) $c + \text{L} \rightarrow \alpha$-$\text{Y}_2\text{O}_3$, (f) $\text{Zr}_3\text{Y}_4\text{O}_{12} \rightarrow c$

(a) $t \rightarrow m+c$

<table>
<thead>
<tr>
<th>Reference</th>
<th>Temperature, K</th>
<th>$x(\text{YO}_{1.5})$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$t$</td>
<td>$m$</td>
</tr>
<tr>
<td>Srivastava et al., 1974 [42]</td>
<td>~838</td>
<td>~0.075</td>
</tr>
<tr>
<td>Pascual and Duran, 1983 [82]</td>
<td>763</td>
<td>0.086</td>
</tr>
<tr>
<td>Srikanth and Subbarao, 1994 [85]</td>
<td>843</td>
<td></td>
</tr>
<tr>
<td>Suzuki, 1995 [89]</td>
<td>~872</td>
<td></td>
</tr>
<tr>
<td>Du et al., 1991 [8]</td>
<td>1279</td>
<td>0.058</td>
</tr>
<tr>
<td>This work</td>
<td>1194</td>
<td>0.051</td>
</tr>
</tbody>
</table>
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(b) \( c \rightarrow \text{m} + \text{Zr}_3\text{Y}_4\text{O}_{12} \)

<table>
<thead>
<tr>
<th>Reference</th>
<th>Temperature, K</th>
<th>( x(\text{YO}_1.5) )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>c</td>
</tr>
<tr>
<td>Stubican et al., 1978 [79]</td>
<td>&lt;673</td>
<td>0.333–0.462</td>
</tr>
<tr>
<td>Suzuki, 1995 [89]</td>
<td>692</td>
<td>0.3</td>
</tr>
<tr>
<td>Du et al., 1991 [8]</td>
<td>666</td>
<td>0.413</td>
</tr>
</tbody>
</table>

(c) \( c \rightarrow \text{Zr}_3\text{Y}_4\text{O}_{12} + \alpha - \text{Y}_2\text{O}_3 \)

<table>
<thead>
<tr>
<th>Reference</th>
<th>Temperature, K</th>
<th>( x(\text{YO}_1.5) )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>c</td>
</tr>
<tr>
<td>Scott, 1977 [78]</td>
<td>1573</td>
<td>0.63</td>
</tr>
<tr>
<td>Stubican et al., 1984 [80]</td>
<td>1650</td>
<td></td>
</tr>
<tr>
<td>Du et al., 1991 [8]</td>
<td>1623</td>
<td>0.617</td>
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<tr>
<td>This work</td>
<td>1627</td>
<td>0.603</td>
</tr>
</tbody>
</table>

(d) \( \text{L} \rightarrow \alpha - \text{Y}_2\text{O}_3 + \beta - \text{Y}_2\text{O}_3 \)

<table>
<thead>
<tr>
<th>Reference</th>
<th>Temperature, K</th>
<th>( x(\text{YO}_1.5) )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>L</td>
</tr>
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<td>Rouanet, 1968 [98]</td>
<td>2653</td>
<td>0.904</td>
</tr>
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<td>Noguchi et al., 1970 [9]</td>
<td>2603</td>
<td>0.864</td>
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<tr>
<td>Stubican et al., 1978 [79]</td>
<td>2633</td>
<td>0.907</td>
</tr>
<tr>
<td>Du et al., 1991 [8]</td>
<td>2679</td>
<td>0.902</td>
</tr>
<tr>
<td>This work</td>
<td>2692</td>
<td>0.973</td>
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</table>

(e) \( c + \text{L} \rightarrow \alpha - \text{Y}_2\text{O}_3 \)

<table>
<thead>
<tr>
<th>Reference</th>
<th>Temperature, K</th>
<th>( x(\text{YO}_1.5) )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>( \alpha - \text{Y}_2\text{O}_3 )</td>
</tr>
<tr>
<td>Skaggs et al., 1972 [99]</td>
<td>2756</td>
<td>0.857</td>
</tr>
<tr>
<td>Stubican et al., 1978 [79]</td>
<td></td>
<td>0.864</td>
</tr>
<tr>
<td>Du et al., 1991 [8]</td>
<td>2682</td>
<td>0.807</td>
</tr>
<tr>
<td>This work</td>
<td>2725</td>
<td>0.844</td>
</tr>
</tbody>
</table>

(f) \( \text{Zr}_3\text{Y}_4\text{O}_{12} \rightarrow c \)

<table>
<thead>
<tr>
<th>Reference</th>
<th>Temperature, K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ray and Stubican, 1977 [77]</td>
<td>1523</td>
</tr>
<tr>
<td>Scott, 1977 [78]</td>
<td>1643</td>
</tr>
<tr>
<td>Stubican et al., 1978 [79]</td>
<td>1523</td>
</tr>
<tr>
<td>Pascual and Duran, 1983 [82]</td>
<td>1648</td>
</tr>
<tr>
<td>Stubican et al., 1984 and 1988 [80, 81]</td>
<td>1655</td>
</tr>
<tr>
<td>Du et al., 1991 [8]</td>
<td>1659</td>
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<td>This work</td>
<td>1639</td>
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</tbody>
</table>
Figure 2.6  Calculated ZrO$_2$–YO$_{1.5}$ phase diagram from the present work.

The calculated subsolidus and liquidus are shown in Figures 2.7, 2.8, and 2.9 together with experimental data. In the present optimization, c-ZrO$_2$ is stable at room temperature around 30 mol% YO$_{1.5}$. The eutectoid temperature of cubic $\rightarrow$ monoclinic + Zr$_3$Y$_4$O$_{12}$ is calculated to be below 200 K and is not listed in Table 2.5 (b). The subsolidus on the ZrO$_2$-rich side is shown in Figure 2.7. Our calculated phase boundaries of the tetragonal+cubic two-phase region fit most of the experimental data well. Due to the metastability and the low cation mobility in the ZrO$_2$–YO$_{1.5}$ system, it is possible that the true equilibrium phase boundaries of the t+c two-phase region should shift a little bit towards the pure ZrO$_2$ side, compared to the experimentally determined boundaries. As Figure 2.8 shows, our calculated phase boundaries of the cubic+α-Y$_2$O$_3$ two-phase region fit the chosen experimental data well. The calculated right boundary (c+α-Y$_2$O$_3$/α-Y$_2$O$_5$) is still rather tentative. Raman spectroscopy or neutron diffraction will be helpful to verify this. Our calculated liquidus is compared with experimental data in Figure 2.9. The fit of the experimental data is good for most compositions. For YO$_{1.5}$-rich compositions it is unclear how the phase diagram should actually look.
Figure 2.7  Calculated subsolidus of the ZrO$_2$-rich side compared with experimental data. The experimental data are from Duwez et al, 1951 [6], Strickler and Carlson, 1964 [86], Srivastava et al., 1974 [42], Scott, 1975 [87], Stubican et al., 1978 [79], Pascual and Duran, 1983 [82], Jayaratna et al., 1984 [83], Lanteri et al., 1984 [94], Rühle et al., 1984 [5], Chaim et al., 1986 [91], Lange, 1986 [92], Yagi et al., 1986 [95], Suzuki and Kohzaki, 1993 [88], Suzuki, 1995 [89], and Suzuki, 1997 [90].

Figure 2.8  Calculated subsolidus of the YO$_{1.5}$-rich side compared with experimental data. The experimental data are from Duwez et al., 1951 [6], Strickler and Carlson, 1964 [86], Srivastava et al., 1974 [42], Scott, 1977 [78], Stubican et al., 1978 [79], Pascual and Duran, 1983 [82], Jayaratna et al., 1984 [83], Stubican et al., 1984 [80], Stubican, 1988 [81], Suzuki and Kohzaki, 1993 [88], Suzuki, 1995 [89].
Figure 2.9 Calculated liquidus compared with experimental data. The experimental data are from Rouanet, 1968 [98], Noguchi et al., 1970 [9], and Stubican et al., 1978 [79].

Figure 2.10 ZrO$_2$ activities in the c-ZrO$_2$ phase at 2773 K. The experimental data are from Belov and Semenov, 1985 [104]. The data points pointed with arrows were used in the present optimization.

Figure 2.10 shows the ZrO$_2$ activities in the cubic phase at 2773 K. Notice that the cubic phase in the YO$_{1.5}$-rich region is metastable at this temperature, according to the measured liquidus and our calculated phase diagram. Table 2.6 lists the calculated Y$_2$O$_3$ activities in the
ZrO$_2$–YO$_{1.5}$ solid solutions at 1300 K, compared with the data from Vintonyak et al. [100]. The reference state is pure fluorite yttria (metastable). Figure 2.11 shows the relative chemical potential of ZrO$_2$ in the c-ZrO$_2$ phase at 1273 K.

Table 2.6 Activities of Y$_2$O$_3$ in the ZrO$_2$–YO$_{1.5}$ solid solutions at 1300 K

<table>
<thead>
<tr>
<th>Mole Fraction of YO$_{1.5}$</th>
<th>0.058</th>
<th>0.113</th>
<th>0.165</th>
<th>0.261</th>
<th>0.4</th>
<th>0.461</th>
<th>0.518</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phase</td>
<td>tetragonal + cubic</td>
<td>cubic</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a(Y_2O_3)$</td>
<td>Vintonyak et al., 1984 [100]</td>
<td>2.1x10$^{-5}$</td>
<td>1.9x10$^{-5}$</td>
<td>2.0x10$^{-5}$</td>
<td>7.9x10$^{-4}$</td>
<td>0.022</td>
<td>0.082</td>
</tr>
<tr>
<td>This work</td>
<td>2.2x10$^{-5}$</td>
<td>1.1x10$^{-3}$</td>
<td>0.027</td>
<td>0.070</td>
<td>0.14</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 2.11 Relative chemical potential of ZrO$_2$ in the c-ZrO$_2$ phase at 1273 K. The experimental data are from Zaitseva and Dobrokhotova, 1994 [103].

The calculated enthalpy of formation of cubic solid solutions is compared with experimental data from Lee et al. [56] in Figure 2.12. There is a clear conflict between the enthalpy of formation data of Lee et al. [56] and the experimental data on the c/c+Zr$_3$Y$_4$O$_{12}$ phase boundary (see Figure 2.8). More precisely, if the enthalpy of formation of c-ZrO$_2$ and Zr$_3$Y$_4$O$_{12}$ from Lee et al. [56] is used, the c/c+Zr$_3$Y$_4$O$_{12}$ phase boundary becomes much to YO$_{1.5}$-rich. The enthalpy of formation of Zr$_3$Y$_4$O$_{12}$ needs to be considerably more negative relative to c-ZrO$_2$ than measured by Lee et al. [56] in order to fit the phase boundary.
reasonably. We chose to give relatively little weight to the enthalpy of formation of \( \text{Zr}_3\text{Y}_4\text{O}_{12} \) (\(-5.3 \text{ kJ/mol cations measured and } -10.3 \text{ kJ/mol cations calculated} \)) and instead describe the enthalpy of formation of c-\( \text{ZrO}_2 \) (Figure 2.12) and the c/c+\( \text{Zr}_3\text{Y}_4\text{O}_{12} \) phase boundary reasonably well.

![Figure 2.12](image)

Figure 2.12 Calculated enthalpy of formation of c-\( \text{ZrO}_2 \) relative to m-\( \text{ZrO}_2 \) and \( \alpha-\text{Y}_2\text{O}_3 \). The experimental data are from Lee et al., 2003 [56].

Figure 2.13 shows calculated heat capacities of the cubic phase at \( x_{\text{YO}_{1.5}} = 0.1768 \) and \( x_{\text{YO}_{1.5}} = 0.182 \) compared with experimental data from Tojo et al. [107] and Hasselman et al. [106]. Calculations and data at \( x_{\text{YO}_{1.5}} = 0.144 \) and \( x_{\text{YO}_{1.5}} = 0.2039 \) [31, 107] look very similar to those in Figure 2.13a. The fit of Tojo et al.’s [31, 107] is very good although we only use a simple linear combination of the heat capacities of pure \( \text{ZrO}_2 \) and \( \alpha-\text{Y}_2\text{O}_3 \) (Neumann–Kopp rule). The data of Hasselman et al. [106] are obviously at variance with the data of Tojo et al. [107]. Although the emphasis of the present work is on the \( \text{ZrO}_2-\text{YO}_{1.5} \) system it includes a complete description of the \( \text{Y}–\text{Zr–O} \) system. In Figure 2.14 calculated isothermal sections at 1500 K and 2000 K are shown. There are a few things to be noted. The solution phases stay close to the edges except in the Y corner. The system is dominated by the strong \( \text{Zr}–\text{Y}_2\text{O}_3 \) diagonal, and in particular by the high stability of \( \text{Y}_2\text{O}_3 \). There is a ternary miscibility gap in the liquid caused by the much higher stability of \( \text{Zr}+\text{Y}_2\text{O}_3 \) than \( \text{Y}+\text{ZrO}_2 \). According to
experience the ionic liquid model overestimates this reciprocal miscibility gap, but we have not tried to correct this since information on its real extension is lacking.

(a)

(b)

Figure 2.13  Heat capacities of c-ZrO$_2$ with different YO$_{1.5}$ contents, (a) $x_{\text{YO}_{1.5}} = 0.1768$, (b) $x_{\text{YO}_{1.5}} = 0.182$. The experimental data are from Tojo et al., 1999 [107] and Hasselman et al., 1987 [106].
Figure 2.14  Calculated isothermal sections of the Y–Zr–O system, (a) at 1500 K, (b) at 2000 K.
Chapter 2

2.9 Summary

In the present work, a thermodynamic description of the Y–Zr–O ternary system is proposed. The same models were used for binary and ternary systems. The parameters for the Zr–O and Y–O binary systems were reoptimized. The present Gibbs energy functions of stoichiometric ZrO$_2$ phases represent most of the experimental data well.

The ZrO$_2$–YO$_{1.5}$ system was treated as a quasi-binary section of the Y–Zr–O ternary system. In this quasi-binary system, only one ordered phase, Zr$_3$Y$_4$O$_{12}$, was included and treated as a stoichiometric compound. The cubic ZrO$_2$-rich phase (c-ZrO$_2$) and the cubic YO$_{1.5}$-rich phase (α-Y$_2$O$_3$) were treated as two different phases. The parameters related to the ZrO$_2$–YO$_{1.5}$ system were optimized using both the thermodynamic data and the phase diagram data. Our optimization agrees well with most experimental data. Two calculated isothermal sections of the Y–Zr–O system are presented.

2.10 References

Modeling of the Y–Zr–O System


3 Thermodynamic Assessment of the Mn–Y–O System


Abstract

The thermodynamic properties of two yttrium manganese complex oxides, h-YMnO₃ and YMn₂O₅, were assessed. They were both treated as stoichiometric compounds. An optimized set of parameters of Gibbs energy functions is proposed. According to our calculation, in air, YMn₂O₅ is stable from room temperature up to 1461 K. Then it decomposes into h-YMnO₃ and β-Mn₃O₄. h-YMnO₃ is stable above 1062 K. At lower temperature, it decomposes into YMn₃O₅ and α-Y₂O₃. At 2067 K, it melts incongruently. A complete thermodynamic description of the Mn–Y–O system is proposed. The MnOₓ–YO₁·₅ phase diagram in air and three isothermal sections of the Mn–Y–O system are presented.

3.1 Introduction

Yttrium manganese complex oxides are well known for their ferroelectric and magnetic behavior. Three complex oxides have been reported: YMnO₃, YMn₂O₅, and Y₂Mn₂O₇.

YMnO₃ has two modifications, a hexagonal non-perovskite phase (h-YMnO₃) and an orthorhombic perovskite-type phase (o-YMnO₃). h-YMnO₃ is known to be a so called ferroelectromagnetic material. Bertaut et al. discovered that it is both antiferromagnetic and ferroelectric [1]. Based on neutron diffraction data and magnetization measurements, Munoz et al. [2] reported that o-YMnO₃ becomes magnetically ordered below $T_N = 42$ K. Unlike h-YMnO₃, the o-YMnO₃ phase is metastable under normal synthesizing conditions. It can be prepared by either low-temperature [3] or high-pressure (hydrostatic) synthesis [4], or via epitaxial thin film growth techniques [5] and soft-chemistry procedures [2,6]. Upon annealing under high hydrostatic pressure, h-YMnO₃ can be converted to o-YMnO₃ [4]. Under ambient pressure, Prokudina et al. [6] reported that o-YMnO₃ converts to h-YMnO₃ at 1223–1273 K. Using first-principle calculations, Filippetti and Hill [7] verified that the
metastability of $\alpha$-YMnO$_3$ is simply the result of the smaller size of the Y$^{3+}$ ion which is unable to stabilize the perovskite structure.

YMn$_2$O$_4$ is known to show successive ferroelectric phase transitions slightly below the magnetic phase transition temperature ($T_N = 45$ K) [8]. It undergoes successive phase transitions at 39 K and 19 K, at which the dielectric constant shows anomalies.

$Y_2Mn_2O_7$ is also metastable under normal synthesizing conditions. The formation of $Y_2Mn_2O_7$ was reported by Fujinaka et al. [9] under a condition of 1273–1373 K and high oxygen pressure (3–4 GPa), and by Subramanian et al. [10] under hydrothermal conditions. Shimakawa et al. [11] synthesized $Y_2Mn_2O_7$ by solid state reaction, at 1273–1573 K and 40 MPa oxygen pressure (a mixture of 20% oxygen and 80% argon) in a hot-isostatic-press apparatus. Subramanian et al. [10] also reported that $Y_2Mn_2O_7$ does not decompose in air up to 1073 K. After heating at 1173 K, it decomposes into YMnO$_3$.

Until now, the phase equilibria in the Mn–Y–O system have not been well investigated. A few measurements have been done on the thermodynamic properties of two stable complex oxides (h-YMnO$_3$ and YMn$_2$O$_4$). The properties of the two phases, $\alpha$-YMnO$_3$ and $Y_2Mn_2O_7$, are not well known. In the present work, these two phases are not considered. They are probably stable at low temperature and/or high oxygen pressure, though. The thermodynamic properties of h-YMnO$_3$ and YMn$_2$O$_4$ were assessed. Based on the assessments of the Y–O system by Chen et al. [12], the Mn–O system by Grundy et al. [13], and the Mn–Y system by Flandorfer et al. [14], a thermodynamic description of the complete Mn–Y–O system is presented. A tentative MnO$_x$–YO$_{1.5}$ phase diagram in air and the isothermal sections of the Mn–Y–O system at different temperatures were calculated.

### 3.2 Experimental data

For the ternary Mn–Y–O system, no phase diagram data have been reported. The experimental data are mainly about the thermodynamic properties of the h-YMnO$_3$ and YMn$_2$O$_4$ compounds.
Kyomen et al. [15] measured the heat capacity of h-YMnO₃ in a temperature range of 2–300 K. The high-temperature heat capacity of h-YMnO₃ was measured by Satoh et al. [16] from room temperature to 850 K, using differential scanning calorimetry (DSC). They also measured the enthalpy increments in the range of 573–1373 K using drop calorimetry. Heat capacity measurements on h-YMnO₃ were also conducted by Tomuta et al. [17] at temperatures below 200 K and by Munoz et al. [18] in the range of 2–100 K. Yokokawa et al. [19] derived $C_p$ coefficients of the h-YMnO₃ phase from 298 to 2500 K, based on the thermogravimetric study of h-YMnO₃ at different oxygen partial pressures at 1473 K from Kamata et al. [20]. In the present work, the heat capacity data from Kyomen et al. [15] and Satoh et al. [16] above 200 K and the enthalpy increment data from Satoh et al. [16] were used.

Yokokawa et al. [19] estimated the entropy of h-YMnO₃ at 298.15 K as 116.4 J/(K mol). Based on the measured heat capacities of h-YMnO₃ from Kyomen et al. [15] (2–298.15 K), we derived the standard entropy of h-YMnO₃ at 298.15 K as 105.4 J/(K mol). This value was used in the present optimization.

Using high transposed temperature drop calorimetry and drop solution calorimetry, Laberty et al. [21] determined the enthalpy of formation of YMnO₃ at 298.15 K to be $-29.8\pm2.1$ kJ/mol (from oxides) and $-1461.9\pm2.1$ kJ/mol (from elements). YMnO₃ was prepared by heating stoichiometric mixtures of simple oxides at 1223 K for 12 h, and then ground and further heated for 24 h at the same temperature. The crystal structure of YMnO₃ was reported to be a cubic perovskite-type. No X-ray diffraction (XRD) spectrum of YMnO₃ was given in their paper. The reported crystal structure of YMnO₃ is quite questionable, as all other papers report that normally h-YMnO₃ is obtained by sintering mixed oxides at temperatures above 1200 K. In the present optimization, the value of $-29.8\pm2.1$ kJ/mol from Laberty et al. [21] was used and treated as the enthalpy of formation of h-YMnO₃ (from oxides). Yokokawa et al. [19] estimated the enthalpy of formation of h-YMnO₃ at 298.15 K to be $-1449.1$ kJ/mol (from elements).

Kamata et al. [20] derived the standard Gibbs energy of the reaction:

$$\frac{1}{2}Y_2O_3 + MnO + \frac{1}{4}O_2(101325 \text{ Pa}) = h - YMnO_3$$

\textit{Eq. 3.1}
Chapter 3

at 1473 K as $-47.7 \text{ kJ/mol}$. By means of electromotive force (e.m.f.), Atsumi et al. [22] measured the oxygen dissociation pressure of $h$-$\text{YMnO}_3$ at high temperature ($1178–1391 \text{ K}$). The decomposition reaction was expressed as:

$$h$-$\text{YMnO}_3 = \frac{1}{2}\text{Y}_2\text{O}_3 + \text{MnO} + \frac{1}{4}\text{O}_2$$  \hspace{1cm} \text{Eq. 3.2}

These data were used in the present work.

Satoh et al. [23] measured the decomposition temperature of $\text{YMn}_2\text{O}_5$ under various oxygen partial pressures ($p_{\text{O}_2} = 10^{-10^5} \text{ Pa}$), using thermogravimetry (TG) and differential thermal analysis (DTA). By identifying the decomposition products with powder X-ray diffractometry and determining weight loss from TG, the decomposition reaction was confirmed as:

$$\text{YMn}_2\text{O}_5 = \text{YMnO}_3 + \frac{1}{3}\text{Mn}_3\text{O}_4 + \frac{1}{3}\text{O}_2$$  \hspace{1cm} \text{Eq. 3.3}

Golikov et al. [24] determined the dissociation temperature of $\text{YMn}_2\text{O}_5$ in air as $1428\pm5 \text{ K}$. $\text{YMn}_2\text{O}_5$ was prepared by ceramic synthesis from $\text{Y}_2\text{O}_3$ and $\text{Mn}_2\text{O}_3$ (open-air sintering). These data were all used to determine the Gibbs energy function of $\text{YMn}_2\text{O}_5$.

3.3 Binary sub-systems

Based on an assessment of the Y–O system by Swamy et al. [25], we recently presented a new description of the Y–O system, included in an assessment of the Y–Zr–O system [12]. This description is also used in the present work.

For the Mn–O system, we accepted the description by Grundy et al. [13], but changed the model for $\beta$-$\text{Mn}_2\text{O}_3$. As described in our Y–Zr–O assessment [12], $\alpha$-$\text{Y}_2\text{O}_3$ has a cubic fluorite-related structure with ordered vacancies ($\text{Mn}_2\text{O}_3$ bixbyite type). It is hence necessary to describe $\beta$-$\text{Mn}_2\text{O}_3$ and $\alpha$-$\text{Y}_2\text{O}_3$ as one phase. We changed the model for $\beta$-$\text{Mn}_2\text{O}_3$, using $(\text{Mn}^{3+})_2(\text{O}^{2-}, \text{Va})_3(\text{O}^{2-}, \text{Va})_1$, to be compatible with our model for $\alpha$-$\text{Y}_2\text{O}_3$. Perfectly ordered $\beta$-$\text{Mn}_2\text{O}_3$, in which the second sublattice is filled and the third is empty, is described by the parameter $G_{\text{Mn}^{3+}, \text{O}^{2-}, \text{Va}}$, taken from Grundy et al.’s description [13]. According to the new
model of $\beta$-$\text{Mn}_2\text{O}_3$, at increasing temperature, $\beta$-$\text{Mn}_2\text{O}_3$ will tend to disorder and the other extremum, with the third sublattice filled, is described by the expression:

$$G_{\text{anti}} = G_{\text{Mn}^{3+}\text{O}^{2-}\text{Va}} + \Delta G_{\text{anti}} = \frac{2}{3}G_{\text{Mn}^{3+}\text{O}^{2-}\text{Va}} + \frac{1}{3}G_{\text{Mn}^{2+}\text{Va}\text{O}^{2-}} + 3RT\left(\frac{2}{3}\ln\frac{2}{3} + \frac{1}{3}\ln\frac{1}{3}\right)$$  Eq. 3.4

The amount of disordering is determined by $\Delta G_{\text{anti}}$. A value of 100 kJ/mol was given to $\Delta G_{\text{anti}}$, the same value as used in the Y–O system [12]. This gives about 3% $\text{O}^{2-}$ on the third sublattice at 2000 K. The new description of $\beta$-$\text{Mn}_2\text{O}_3$ fits the experimental data (heat capacity and enthalpy increment) as well as Grundy et al.’s description [13]. The calculated phase diagram is very similar to Figure 1 in their paper [13]. A minor difference can be found in the $\text{Mn}_2\text{O}_3$ liquidus, which corresponds to high oxygen partial pressure (> 1 MPa) and where no experimental information exists.

Flandorfer et al. [14] published an optimized set of Gibbs energy functions for the Mn–Y–Zr system. We simply accepted their description of the Mn–Y system, except for the Gibbs energy function of hcp-Mn (metastable). In their description, they used GHSERMN, the Gibbs energy function of $\alpha$-Mn (cbcc). Instead, we used GMNHCP, the Gibbs energy function of hcp-Mn (metastable) from Dinsdale [26]. This does not change the calculated Mn–Y phase diagram.

### 3.4 Thermodynamic models

#### 3.4.1 Ternary compounds

In the present work, we include two ternary compounds, h-YMnO$_3$ and YMn$_2$O$_5$.

##### 3.4.1.1 h-YMnO$_3$

h-YMnO$_3$ has an ilmenite-type structure (space group $P6_3cm$), isomorphic with LuMnO$_3$ [3,20]. Its crystal structure was investigated by van Aken et al. [27] at room temperature and at 180 K and by Katsufuji et al. [28] at high temperatures. In the crystal lattice, Mn$^{3+}$ ions lie within bi-pyramids and each Mn$^{3+}$ ion is coordinated by 5 oxygen ions; while Y$^{3+}$ ions reside between the layers of the bi-pyramids and each is coordinated by 7 oxygen ions [29].
h-YMnO$_3$ shows slight oxygen nonstoichiometry at low oxygen partial pressure. This was investigated by Kamata et al. [20] and Atsumi et al. [30]. Kamata et al. [20] reported that at 1473 K, the oxygen deficiency, $x$ in YMnO$_{3-x}$, is around 0.04 for $P_{O_2} = 1.5 \times 10^{-2}$ Pa and that h-YMnO$_3$ decomposes at $P_{O_2} = 1.1 \times 10^{-2}$ Pa. At high oxygen partial pressure, h-YMnO$_3$ exhibits little oxygen excess. A chemical formula of h-YMnO$_{3.009}$ was reported by Kamata et al. [20] at 1473 K and $P_{O_2} = 10^5$ Pa. In the present work, h-YMnO$_3$ is treated as a stoichiometric compound.

h-YMnO$_3$ belongs to the rather small group of materials known as ferroelectromagnets. At low temperature, it undergoes an antiferromagnetic-to-ferromagnetic phase transition. The Néel temperature, $T_N$, was determined by Munoz et al. [18], Kyomen et al. [15], and Tomuta et al. [17] at $\sim 71$ K, based on heat capacity measurements. Park et al. [31] made thermal expansion and Neutron diffraction studies on h-YMnO$_3$ and found anomalous behavior at $T_N = 80$ K. There is another reported ferromagnetic ordering at 42 K [32], or at 46 K [33], which is often seen in powder samples of h-YMnO$_3$. van Aken et al. [32] suggested that this magnetic transition probably originates from the impurity phase of the ferromagnetic spinel Mn$_3$O$_4$ ($T_C = \sim 42$ K). In the present work, no effort was made to model the magnetic ordering at $T_N = 71$ K.

At high temperatures, h-YMnO$_3$ undergoes ferroelectric transitions. Using high temperature X-ray diffraction, Ismailzade and Kizhaev (cited by Satoh et al. [16]) found a phase transition occurring near 473 K and a dielectric transition at 933 K. Lukaszewicz and Karut-Kalicinska [34] measured lattice constants and atomic parameters of h-YMnO$_3$ from room temperature up to 1283 K. In the region 893–953 K, small anomalies of lattice constants and reflection intensities were observed. This was ascribed to the ferroelectric phase transition. They also found another phase transition at 1273 K resulting in a crystal structure with a small hexagonal cell, which may be considered as a prototypic structure in relation to the ferroelectric structure of h-YMnO$_3$ at room temperature. Satoh et al. [16] measured the enthalpy increment of h-YMnO$_3$ from 573 K to 1373 K, no heat anomaly due to the dielectric transition was detected. They suggested that the polarization effect of h-YMnO$_3$ is too small to detect any heat anomaly. Recently, Katsufuji et al. [28] used synchrotron X-ray diffraction to investigate the crystal structure of h-YMnO$_3$ and its temperature dependence, particularly at
Modeling of the Mn–Y–O System

high temperature. No structural phase transition up to 1000 K was detected. Due to the controversy on the ferroelectric transitions of h-YMnO$_3$ at high temperature, no transition above room temperature was considered in the present work. The Gibbs energy of the h-YMnO$_3$ phase is given by:

\[
G_{YMnO_3H}^\circ = G_{h,YMnO_3} - H_Y^{SER} - H_{Mn}^{SER} - 3H_O^{SER} = A_1 + B_1T + C_1T \ln T + D_1T^2 + E_1T^{-1}
\]

Eq. 3.5

3.4.1.2 YMn$_2$O$_5$

YMn$_2$O$_5$ has an orthorhombic structure belonging to the space group $Pbam$. Each Y$^{3+}$ ion is in 8-fold oxygen coordination. The Mn$^{3+}$ ions have a slightly flattened square-pyramidal oxygen coordination ($CN = 5$), while the Mn$^{4+}$ ions are coordinated by a slightly flattened octahedron of oxygen ($CN = 6$) [35].

Prokudina et al. [6] detected the formation of YMn$_2$O$_5$ as a by-product in the system of Y$_2$O$_3$–Mn$_2$O$_3$ (1:1) in air at 1123–1373 K. According to them, YMn$_2$O$_5$ is thermally stable at 1073–1373 K. At higher temperatures, it decomposes into h-YMnO$_3$ and Mn$_3$O$_4$. Fu et al. [33] detected the formation of single-phase YMn$_2$O$_5$ in the powder prepared using an organometallic precursor with an Y:Mn ratio of 1:2 and calcined in air at 1273 K and then quenched. Only h-YMnO$_3$ and Mn$_2$O$_3$ were detected when the powder was quenched from 1573 K. They suggested that at 1473 K in air, YMn$_2$O$_5$ decomposed as follows:

\[
YMn_2O_5 = YMnO_3 + \frac{1}{2}Mn_2O_3 + \frac{1}{4}O_2
\]

Eq. 3.6

In the present work, YMn$_2$O$_5$ is included and treated as a stoichiometric compound. The Gibbs energy of YMn$_2$O$_5$ is given by:

\[
G_{YMn_2O_5}^\circ = G_{YMn_2O_5} - H_Y^{SER} - 2H_{Mn}^{SER} - 5H_O^{SER}
\]

\[
= GYMNO3H + 0.5GMN2O3 + 0.5GHSEROO + A_2 + B_2T
\]

Eq. 3.7

GMN2O3 is the molar Gibbs energy of $\beta$-Mn$_2$O$_3$ from Grundy et al. [13] and GHSEROO is the molar Gibbs energy of oxygen taken from Dinsdale [26].

3.4.2 Ternary solid solution phases

Our interest is mainly about the oxide part of the Mn–Y–O ternary system and the subsolidus behavior of the MnO$_x$–YO$_{1.5}$ pseudo-binary system. Until now, no experiments have been
conducted on phase equilibria in the Mn–Y–O ternary system. Nothing is known about the solubility of MnOx in Y2O3 and vice versa. In the present work, on the MnOx-rich side, we did not include any Y2O3 solubility, except for β-Mn2O3. As described before, we describe β-Mn2O3 and α-Y2O3 as one phase, using the model \( (\text{Mn}^{3+}, \text{Y}, \text{Y}^{3+})_2(\text{O}^{2-}, \text{Va})_3(\text{O}^{2-}, \text{Va})_1 \). To describe the high-temperature yttria phase (β-Y2O3), we use the model \( (\text{Mn}^{2+}, \text{Mn}^{3+}, \text{Y}, \text{Y}^{3+})_i(\text{O}^{2-}, \text{Va})_2 \). This is to be compatible with our descriptions of the Y–Zr–O and the Mn–Y–Zr–O systems. In our assessment of the Y–Zr–O system, we describe β-Y2O3 and the cubic fluorite ZrO2-rich phase as one phase. A few groups have reported Mn\(^{3+}\) solubilities in ZrO2 and yttria stabilized ZrO2 (YSZ) [36-39]. It is, therefore, also necessary to include Mn\(^{2+}\) and Mn\(^{3+}\) into β-Y2O3 in the Mn–Y–O ternary system. In the present work, only two ternary solid solution phases are included: the α-Y2O3 phase (also the β-Mn2O3 phase) and the β-Y2O3 phase. The Gibbs energy functions of these two phases are listed in Table 3.1. Four parameters for the β-Y2O3 phase, \( g \text{G}_{\text{Mn}^{3+}, \text{O}^{2-}} \), \( g \text{G}_{\text{Mn}^{2+}, \text{Y}^{3+}, \text{Va}} \), \( g \text{G}_{\text{Mn}^{3+}, \text{O}^{2-}} \), and \( g \text{G}_{\text{Mn}^{3+}, \text{Va}} \), are taken from our assessment of the Mn–Zr–O system [40]. In the present work, we try to keep MnOx solubility in α-Y2O3 and β-Y2O3 small. Two interaction parameters were adjusted during the optimization:

\[
0L_{\text{Mn}^{3+}, \text{Y}^{3+}, \text{O}^{2-}, \text{Va}} = 0L_{\text{Mn}^{3+}, \text{Y}^{3+}, \text{O}^{2-}, \text{Va}} = 0L_{\text{Mn}^{3+}, \text{Y}^{3+}, \text{Va}} = A_4 \tag{Eq. 3.8}
\]

for the α-Y2O3 phase (also the β-Mn2O3 phase)

\[
0L_{\text{Mn}^{3+}, \text{Y}^{3+}, \text{O}^{2-}, \text{Va}} = 0L_{\text{Mn}^{3+}, \text{Y}^{3+}, \text{O}^{2-}} = 0L_{\text{Mn}^{3+}, \text{Y}^{3+}, \text{Va}} = A_4 \tag{Eq. 3.9}
\]

for the β-Y2O3 phase.

### 3.4.3 Liquid phase

The liquid phase was modeled as \( (\text{Mn}^{2+}, \text{Mn}^{3+}, \text{Y}^{3+})_p(\text{O}^{2-}, \text{Va})_q \), using the two-sublattice model for ionic liquids [41, 42]. It was assumed that the Mn–O and Y–O liquids mix ideally. No extra interaction parameters were used, except those taken from binary sub-systems.

### 3.5 Optimization and results

The assessment was made using the software PARROT included in the Thermo-Calc Databank System [43]. The Gibbs energy function of h-YMnO3 was first determined. The
parameters $C_1$, $D_1$, and $E_1$ in Eq. 3.5 were optimized using the heat capacity data from Satoh et al. [16] and Kyomen et al. [15] and the enthalpy increment data from Satoh et al. [16]. The parameters $A_1$ and $B_1$ were determined using the standard enthalpy of formation from Laberty et al. [21], the entropy at 298.15 K derived from heat capacity data measured by Kyomen et al. [15], and the oxygen dissociation pressure data from Kamata et al. [20] and Atsumi et al. [22]. The Gibbs energy function of $\text{YMn}_2\text{O}_5$ was determined afterwards, using the data from Satoh et al. [23] and Golikov et al. [24].

Due to its higher oxygen content, $\text{YMn}_2\text{O}_5$ is more stable than $\text{h-MnO}_3$ at low temperature. Our calculated $\text{MnO}_x\text{–Y}_2\text{O}_{1.5}$ diagram shows that in air, the following reaction happens at temperatures below 1200 K.

$$\text{h-MnO}_3 + \frac{1}{8}\text{O}_2 = \frac{1}{2}\text{YMn}_2\text{O}_5 + \frac{1}{4}\alpha\text{-Y}_2\text{O}_3 \quad \text{Eq. 3.10}$$

No direct measurement in the literature was available to prove this. Some hints could be found in the reported synthesis conditions of $\text{h-MnO}_3$. Normally $\text{h-MnO}_3$ is synthesized at temperatures above 1200 K by sintering mixed oxides. Prokudina et al. [6] roasted a 1:1 mixture of Y and Mn oxides at 973–1673 K in air and in vacuum. $\text{h-MnO}_3$ is formed at 1073–1573 K. $\text{YMn}_2\text{O}_5$ is formed as a by-product in air at 1123–1373 K and decomposes at higher temperature. It is therefore probable that at low temperature, $\text{h-MnO}_3$ decomposes into $\text{YMn}_2\text{O}_5$ and $\text{Y}_2\text{O}_3$, but the decomposition temperature in air is probably lower than 1073 K. We included this assumed decomposition temperature when optimizing the parameters $A_2$ and $B_2$ in Eq. 3.7, and set it as 1050 K to keep the calculated decomposition temperature lower than 1073 K.

To keep the low solubility of $\beta\text{-Mn}_2\text{O}_3$ in $\alpha\text{-Y}_2\text{O}_3$ and vice versa, a value of 100,000 was given to $A_3$ in Eq. 3.8. The value of $A_4$ in Eq. 3.9 was set to 30,000.

A complete thermodynamic description of the Mn–Y–O system is listed in Table 3.1. Figure 3.1 shows the calculated heat capacity curves of $\text{h-MnO}_3$ together with the experimental data. Our $C_p$ curve fits the experimental data very well. There is also a good agreement at temperatures below 1000 K between our curve and the $C_p$ curve calculated using Neumann–Kopp rule (from oxides). The heat content data of $\text{h-MnO}_3$ is plotted in Figure
3.2. Figure 3.3 shows the oxygen potential diagram of the Mn–Y–O system together with the measured oxygen dissociation pressures of h-YMnO$_3$ and YMn$_2$O$_5$. The monovariant equilibria in Figure 3.3 are indicated by numbers and are listed in Table 3.2. The agreement between the experimental data and the present calculation is good. In the present work, the entropy of h-YMnO$_3$ at 298.15 K is calculated to be 105.6 J/(K mol), very close to the value of 105.4 J/(K mol) derived from heat capacity data measured by Kyomen et al. [15]. Our calculated standard enthalpy of formation of h-YMnO$_3$ is $-30.485$ kJ/mol (from oxides) and $-1477.8$ kJ/mol (from elements).

<table>
<thead>
<tr>
<th>Table 3.1 Thermodynamic description of the Mn–Y–O system</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCP</td>
</tr>
<tr>
<td>(Mn, Y)$<em>i$(O, Va)$</em>{0.5}$</td>
</tr>
<tr>
<td>$^\circ G_{MnO} - H_{Mn}^{SER} - 0.5 H_{O}^{SER} = GMNHCP + 0.5 GHSEROO$</td>
</tr>
<tr>
<td>$^\circ G_{Mn:Va} - H_{Mn}^{SER} = GMNHCP$</td>
</tr>
<tr>
<td>$^\circ G_{Y:O} - H_{Y}^{SER} - 0.5 H_{O}^{SER} = GHSERYY + 0.5 GHSEROO - 303600 + 37.5T$</td>
</tr>
<tr>
<td>$^\circ G_{Y:Va} - H_{Y}^{SER} = GHSERYY$</td>
</tr>
<tr>
<td>$^\circ L_{Y:O:Va} = +3500$</td>
</tr>
<tr>
<td>$^\circ L_{Mn:Y:Va} = +19000$</td>
</tr>
</tbody>
</table>

| BCC                                                      |
| (Mn, Y)$_i$(O, Va)$_{0.5}$                               |
| $^\circ G_{MnO} - H_{Mn}^{SER} - 1.5 H_{O}^{SER} = GMNBCC + 1.5 GHSEROO + 50T$ |
| $^\circ G_{Mn:Va} - H_{Mn}^{SER} = GMNBCC$               |
| $^\circ G_{Y:O} - H_{Y}^{SER} - 1.5 H_{O}^{SER} = GYYBCC + 1.5 GHSEROO - 899200 + 123T$ |
| $^\circ G_{Y:Va} - H_{Y}^{SER} = GYYBCC$                 |
| $p = 0.4$                                                |
| $^\circ T_{Mn}^{bec} = -580$                            |
| $^\circ \beta_{Mn}^{bec} = -0.27$                       |
| $^\circ L_{Y:O:Va} = -5000$                             |
| $^\circ L_{Mn:Y:Va} = +25000$                            |

| a-Mn (CBCC)                                              |
| (Mn)$_i$(Va)$_i$                                        |
| $^\circ G_{Mn:Va} - H_{Mn}^{SER} = GHSERMN$             |
| $p = 0.28$                                              |
| $^\circ T_{Mn}^{cub} = -285$                            |
| $^\circ \beta_{Mn}^{cub} = -0.66$                       |

| $\beta$-Mn (CUBIC)                                      |
| (Mn)$_i$(Va)$_i$                                        |
# Modeling of the Mn–Y–O System

\[ ^0G_{\text{Mn}-\text{Va}} - H_{\text{Mn}}^{\text{SER}} = \text{GMNCUB} \]

- \( \gamma \text{Mn (FCC)} \)
  \( (\text{Mn})_1(\text{Va})_1 \)
  \[ ^0G_{\text{Mn}-\text{Va}} - H_{\text{Mn}}^{\text{SER}} = \text{GMNFCC} \]
  \( p = 0.28 \)
  \[ ^0T_{\text{Mn}}^{\text{FCC}} = -1620 \]
  \[ ^0\beta_{\text{Mn}}^{\text{FCC}} = -1.86 \]

- \( \text{Mn}_{12}Y \)
  \( (\text{Mn})_{12}(Y)_1 \)
  \[ ^0G_{\text{Mn}-\text{Y}} - 12 H_{\text{Mn}}^{\text{SER}} - H_{\text{Y}}^{\text{SER}} = \text{GMN12Y} \]

- \( \text{Mn}_{23}Y_6 \)
  \( (\text{Mn})_{23}(Y)_6 \)
  \[ ^0G_{\text{Mn}-\text{Y}} - 23 H_{\text{Mn}}^{\text{SER}} - 6 H_{\text{Y}}^{\text{SER}} = \text{GMN23Y6} \]

- \( \text{Mn}_2Y \)
  \( (\text{Mn})_2(Y)_1 \)
  \[ ^0G_{\text{Mn}-\text{Y}} - 2 H_{\text{Mn}}^{\text{SER}} - H_{\text{Y}}^{\text{SER}} = \text{GMN2Y} \]

- \( \text{Mn}_{14}O \)
  \( (\text{Mn}^{2+}, \text{Mn}^{3+}, \text{Va})_1(\text{O}^{2-})_1 \)
  \[ ^0G_{\text{Mn}^{3+},\text{O}^{2-}} - H_{\text{Mn}}^{\text{SER}} - H_{\text{O}}^{\text{SER}} = \text{GMN1O1} \]
  \[ ^0G_{\text{Mn}^{3+},\text{O}^{2-}} - H_{\text{Mn}}^{\text{SER}} - H_{\text{O}}^{\text{SER}} = \text{GMN1O1} - 21884 - 22.1857 \]
  \[ ^0G_{\text{Va},\text{O}^{2-}} - H_{\text{O}}^{\text{SER}} = 0 \]
  \[ ^1L_{\text{Mn}^{3+},\text{Mn}^{3+},\text{O}^{2-}} = -42105 \]
  \[ ^1L_{\text{Mn}^{3+},\text{Mn}^{3+},\text{O}^{2-}} = +46513 \]

- \( \alpha-\text{Mn}_3\text{O}_4 \)
  \( (\text{Mn})_3(\text{O})_4 \)
  \[ ^0G_{\text{Mn},\text{O}} - 3 H_{\text{Mn}}^{\text{SER}} - 4 H_{\text{O}}^{\text{SER}} = \text{GMN3O4} \]

- \( \beta-\text{Mn}_3\text{O}_4 \)
  \( (\text{Mn})_3(\text{O})_4 \)
  \[ ^0G_{\text{Mn},\text{O}} - 3 H_{\text{Mn}}^{\text{SER}} - 4 H_{\text{O}}^{\text{SER}} = \text{GMN3O4B} \]

- \( \text{MnO}_2 \)
  \( (\text{Mn})(\text{O})_2 \)
  \[ ^0G_{\text{Mn},\text{O}} - H_{\text{Mn}}^{\text{SER}} - 2 H_{\text{O}}^{\text{SER}} = \text{GMN1O2} \]

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Chapter 3

$\alpha$-$Y_2O_3$ (and also $\beta$-$Mn_2O_3$)

\[(\text{Mn}^{3+}, Y, Y^{3+})_2(\text{O}^{2-}, \text{Va}), (\text{O}^{2-}, \text{Va})\]

$^{\circ}G_{\text{Mn}^{3+}, \text{O}^{2-}, \text{Va}} - 2H_{\text{Mn}}^{\text{SER}} - 4H_{\text{O}}^{\text{SER}} = \text{GMN}_2\text{O}_3 + \text{GHSEROO} + 100000 + 15.8769I^T$

$^{\circ}G_{\text{Mn}^{3+}, \text{O}^{2-}, \text{Va}} - 2H_{\text{Mn}}^{\text{SER}} - 3H_{\text{O}}^{\text{SER}} = \text{GMN}_2\text{O}_3$

$^{\circ}G_{\text{Mn}^{3+}, \text{Va}, \text{O}^{2-}} - 2H_{\text{Mn}}^{\text{SER}} - H_{\text{O}}^{\text{SER}} = \text{GMN}_2\text{O}_3 - 2 \text{GHSEROO} + 100000 + 15.8769I^T$

$^{\circ}G_{\text{Mn}^{3+}, \text{Va}, \text{O}^{2-}} - 2H_{\text{Mn}}^{\text{SER}} = \text{GMN}_2\text{O}_3 - 3 \text{GHSEROO}$

$^{\circ}G_{\text{Y}^{3+}, \text{O}^{2-}, \text{Va}} - 2H_{\text{Y}}^{\text{SER}} - 4H_{\text{O}}^{\text{SER}} = 2 \text{GHSERYY} + 4 \text{GHSEROO} + 345600 + 15.8769I^T$

$^{\circ}G_{\text{Y}^{3+}, \text{Va}, \text{O}^{2-}} - 2H_{\text{Y}}^{\text{SER}} - 3H_{\text{O}}^{\text{SER}} = 2 \text{GHSERYY} + 3 \text{GHSEROO} + 245600$

$^{\circ}G_{\text{Y}, \text{Va}, \text{O}^{2-}} - 2H_{\text{Y}}^{\text{SER}} - H_{\text{O}}^{\text{SER}} = 2 \text{GHSERYY} + \text{GHSEROO} + 345600 + 15.8769I^T$

$^{\circ}G_{\text{Y}, \text{Va}, \text{O}^{2-}} - 2H_{\text{Y}}^{\text{SER}} = 2 \text{GHSERYY} + 245600$

$^{\circ}G_{\text{Y}^{3+}, \text{O}^{2-}, \text{Va}} - 2H_{\text{Y}}^{\text{SER}} - 4H_{\text{O}}^{\text{SER}} = 2 \text{GCCYO15} + \text{GHSEROO} + 100000 + 15.8769I^T$

$^{\circ}G_{\text{Y}^{3+}, \text{Va}, \text{O}^{2-}} - 2H_{\text{Y}}^{\text{SER}} - 3H_{\text{O}}^{\text{SER}} = 2 \text{GCCYO15}$

$^{\circ}G_{\text{Y}^{3+}, \text{Va}, \text{O}^{2-}} - 2H_{\text{Y}}^{\text{SER}} - H_{\text{O}}^{\text{SER}} = 2 \text{GCCYO15} - 2 \text{GHSEROO} + 100000 + 15.8769I^T$

$^{\circ}G_{\text{Y}, \text{Va}, \text{O}^{2-}} - 2H_{\text{Y}}^{\text{SER}} = 2 \text{GCCYO15} - 3 \text{GHSEROO}$

$0I_{\text{Mn}^{3+}, \text{O}^{2-}, \text{Va}} - 2I_{\text{Mn}^{4+}, \text{Y}^{3+}, \text{O}^{2-}, \text{Va}} - 2I_{\text{Mn}^{3+}, \text{Y}^{3+}, \text{Va}, \text{O}^{2-}} = +100000$

$\beta$-$Y_2O_3$

\[(\text{Mn}^{3+}, \text{Mn}^{3+}, Y, Y^{3+})_2(\text{O}^{2-}, \text{Va})_2\]

$^{\circ}G_{\text{Mn}^{3+}, \text{O}^{2-}, \text{Va}} - H_{\text{Mn}}^{\text{SER}} - 2H_{\text{O}}^{\text{SER}} = \text{GMCMN1O1} + \text{GHSEROO} + 11.5264I^T$

$^{\circ}G_{\text{Mn}^{3+}, \text{Va}, \text{O}^{2-}} - H_{\text{Mn}}^{\text{SER}} - 2H_{\text{O}}^{\text{SER}} = 0.5 \text{GMCMN2O3} + 0.5 \text{GHSEROO} + 9.3511I^T$

$^{\circ}G_{\text{Mn}^{3+}, \text{Va}, \text{O}^{2-}} - H_{\text{Mn}}^{\text{SER}} = 0.5 \text{GMCMN2O3} - 1.5 \text{GHSEROO} + 9.3511I^T$

$^{\circ}G_{\text{Y}^{3+}, \text{O}^{2-}, \text{Va}} - H_{\text{Y}}^{\text{SER}} - 2H_{\text{O}}^{\text{SER}} = + \text{GHSERYY} + 2 \text{GHSEROO} + 122800$

$^{\circ}G_{\text{Y}, \text{Va}, \text{O}^{2-}} - H_{\text{Y}}^{\text{SER}} = + \text{GHSERYY} + 122800$

$^{\circ}G_{\text{Y}^{3+}, \text{O}^{2-}, \text{Va}} - H_{\text{Y}}^{\text{SER}} - 2H_{\text{O}}^{\text{SER}} = \text{GHHY015} + 0.5 \text{GHSEROO} + 9.3511I^T$

$^{\circ}G_{\text{Y}^{3+}, \text{Va}, \text{O}^{2-}} - H_{\text{Y}}^{\text{SER}} = \text{GHHY015} - 1.5 \text{GHSEROO} + 9.3511I^T$

$0I_{\text{Mn}^{3+}, \text{Y}^{3+}, \text{O}^{2-}, \text{Va}} - 2I_{\text{Mn}^{3+}, \text{Y}^{3+}, \text{Va}, \text{O}^{2-}} - I_{\text{Y}, \text{Mn}^{3+}, \text{Y}^{3+}, \text{O}^{2-}} = +30000$

$h$-$YMnO_3$

\[(\text{Y}^{3+})_3(\text{Mn}^{3+})_1(\text{O}^{2-})_3\]

$^{\circ}G_{\text{Y}^{3+}, \text{Mn}^{3+}, \text{O}^{2-}} - H_{\text{Y}}^{\text{SER}} - H_{\text{Mn}}^{\text{SER}} - 3H_{\text{O}}^{\text{SER}} = \text{GYMNO3H}$

$Y$-$Mn_2O_5$

\[(\text{Y}^{3+})_3(\text{Mn}^{3+})_1(\text{Mn}^{3+})_1(\text{O}^{2-})_5\]

$^{\circ}G_{\text{Y}^{3+}, \text{Mn}^{3+}, \text{Mn}^{3+}, \text{O}^{2-}} - H_{\text{Y}}^{\text{SER}} - 2H_{\text{Mn}}^{\text{SER}} - 5H_{\text{O}}^{\text{SER}} = \text{GYMN}_2\text{O}_5$

Liquid

\[(\text{Mn}^{2+}, \text{Mn}^{3+}, \text{Y}^{3+})_p(\text{O}^{2-}, \text{Va}^{2-})_q\]

$p = 2y_{\text{Mn}^{2+}} + qy_{\text{Va}^{2+}}$, $q = 2y_{\text{Mn}^{3+}} + 3y_{\text{Mn}^{2+}} + 3y_{\text{Y}^{3+}}$

$^{\circ}G_{\text{Mn}^{3+}, \text{O}^{2-}} - 2H_{\text{Mn}}^{\text{SER}} - 2H_{\text{O}}^{\text{SER}} = 2 \text{GMN}_1\text{O}_1\text{LIQ}$
Modeling of the Mn–Y–O System

\[ \Delta G_{Mn^{2+},Va} - H_{Mn}^{SER} = GMNLIQ \]
\[ \Delta G_{Mn^{3+},O} - 2 H_{Mn}^{SER} - 3 H_{O}^{SER} = GMN203LIQ \]
\[ \Delta G_{Mn^{3+},Va} - H_{Mn}^{SER} = 2 GMNLIQ + GMN2O3LIQ - 3 GMN101LIQ \]
\[ \Delta G_{Y^{3+},O} - 2 H_{Y}^{SER} - 3 H_{O}^{SER} = GY2O3LIQ \]
\[ \Delta G_{Y^{3+},Va} - H_{Y}^{SER} = GYYLIQ \]
\[ \Delta L_{Mn^{3+},O}^{0} + \Delta L_{Va}^{0} = +129519 \]
\[ \Delta L_{Mn^{3+},O}^{0} + \Delta L_{Va}^{0} = -45459 \]
\[ \Delta L_{Y^{3+},Mn^{3+},O}^{0} = -33859 \]
\[ \Delta L_{Y^{3+},O}^{0} + \Delta L_{Va}^{0} = +6900 \]
\[ \Delta L_{Y^{3+},O}^{0} + \Delta L_{Va}^{0} = -17684.14 + 2.38277T \]
\[ \Delta L_{Mn^{3+},Va}^{0} + \Delta L_{Va}^{0} = -12579.78 \]

\[ \Delta G_{O_{2}} - 2 H_{O}^{SER} = 2 GHSEROO + RT \ln(1 \times 10^{-5} P) \]

**Functions**

\[ GMCMN101 = +GMN101 + 20000 \]
\[ GMCMN203 = +GMN203 + 60000 \]
\[ GYMN03H = -1515274 + 61877 - 105.471T - 0.017T^2 + 669185T^{-1} \]
\[ GYMN205 = +GMN03H + 0.5 GMN203 + 0.5 GHSEROO - 100383 + 62.2T \]

**Notes:**

1. All parameters are in SI units: J, mol, K, Pa; R = 8.31451 J/(mol K).
2. GHSERYY, GYYBCC, and GYYLIQ are the molar Gibbs energies of pure Y from the SGTE unary database (1996) [44]. GHSERMN, GMNCUB, GMNFCC, GMNBCC, GMNHCp, GMNLIQ, and GHSEROO are the molar Gibbs energies of pure Mn and oxygen from Dinsdale, 1991 [26].
3. GMN101, GMN102, GMN203, GMN304, GMN304B, GMN101LIQ, and GMN203LIQ are the molar Gibbs energies of manganese oxides, taken from Grundy et al. [13].
4. GCCYO15, GHHYO15, and GY2O3LIQ are the molar Gibbs energies of yttrium oxides from Chen et al. [12].
5. GMN12Y, GMN23Y6, and GMN2Y are the molar Gibbs energies of manganese yttrium intermetallics from Flandorfer et al. [14].
6. Parameters for Mn–O are from Grundy et al. [13]. Parameters for Y–O are from Chen et al. [12]. Parameters for Mn–Y are from Flandorfer et al. [14].
Figure 3.1 Calculated heat capacity of h-YMnO₃ compared with experimental data and the previous assessment from Yokokawa et al. [19]. The experimental data are from Satoh et al. [16] and Kyomen et al. [15].

Figure 3.2 Calculated enthalpy increment of h-YMnO₃ compared with experimental data from Satoh et al. [16].
Figure 3.3  Calculated Mn–Y–O oxygen potential diagram compared with experimental data from Kamata et al. [20], Atsumi et al. [22], Satoh et al. [16], and Golikov et al. [24]. The monovariant equilibria are indicated by numbers and are listed in Table 3.2.

Figure 3.4  Calculated MnOₙ–YO₁.₅ phase diagram in air from the present work.
Table 3.2  Monovariant equilibria in Figure 3.3

<table>
<thead>
<tr>
<th>Label</th>
<th>Equilibrium</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( L_2 + \alpha - Y_2O_3 + h - YMnO_3 )</td>
</tr>
<tr>
<td>2</td>
<td>( Mn_{1-x}O + \alpha - Y_2O_3 + h - YMnO_3 )</td>
</tr>
<tr>
<td>3</td>
<td>( L_2 + Mn_{1-x}O + \alpha - Y_2O_3 )</td>
</tr>
<tr>
<td>4</td>
<td>( L_2 + Mn_{1-x}O + h - YMnO_3 )</td>
</tr>
<tr>
<td>5</td>
<td>( L_2 + Mn_{1-x}O + \beta - Mn_3O_4 )</td>
</tr>
<tr>
<td>6</td>
<td>( L_2 + \beta - Mn_3O_4 + h - YMnO_3 )</td>
</tr>
<tr>
<td>7</td>
<td>( \beta - Mn_3O_4 + h - YMnO_3 + YMn_2O_5 )</td>
</tr>
<tr>
<td>8</td>
<td>( \alpha - Mn_3O_4 + \beta - Mn_3O_4 + YMn_2O_5 )</td>
</tr>
<tr>
<td>9</td>
<td>( L_2 + \alpha - Y_2O_3 + \beta - Y_2O_3 )</td>
</tr>
<tr>
<td>10</td>
<td>( \beta - Mn_2O_3 + \alpha - Mn_3O_4 + YMn_2O_5 )</td>
</tr>
<tr>
<td>11</td>
<td>( \beta - Mn_2O_3 + \beta - Mn_3O_4 + YMn_2O_5 )</td>
</tr>
<tr>
<td>12</td>
<td>( L_1 + L_2 + \beta - Y_2O_3 )</td>
</tr>
<tr>
<td>13</td>
<td>( L_2 + \beta - Mn_3O_4 + YMn_2O_5 )</td>
</tr>
<tr>
<td>14</td>
<td>( L_1 + \alpha - Y_2O_3 + \beta - Y_2O_3 )</td>
</tr>
<tr>
<td>15</td>
<td>( L_1 + L_2 + \alpha - Y_2O_3 )</td>
</tr>
<tr>
<td>16</td>
<td>( L_1 + L_2 + Mn_{1-x}O )</td>
</tr>
<tr>
<td>17</td>
<td>( L_2 + h - YMnO_3 + YMn_2O_5 )</td>
</tr>
<tr>
<td>18</td>
<td>( \alpha - Mn_3O_4 + \beta - Mn_3O_4 + h - YMnO_3 )</td>
</tr>
<tr>
<td>19</td>
<td>( Mn_{1-x}O + \alpha - Mn_3O_4 + h - YMnO_3 )</td>
</tr>
<tr>
<td>20</td>
<td>( Mn_{1-x}O + \beta - Mn_3O_4 + h - YMnO_3 )</td>
</tr>
<tr>
<td>21</td>
<td>( \alpha - Mn_3O_4 + h - YMnO_3 + YMn_2O_5 )</td>
</tr>
<tr>
<td>22</td>
<td>( \alpha - Y_2O_3 + h - YMnO_3 + YMn_2O_5 )</td>
</tr>
<tr>
<td>23</td>
<td>( L_1 + Mn_{1-x}O + \alpha - Y_2O_3 )</td>
</tr>
</tbody>
</table>

Note:
L<sub>1</sub> is the metal liquid and L<sub>2</sub> is the oxide liquid.

The calculated MnO<sub>x</sub>-YO<sub>1.5</sub> phase diagram in air is shown in Figure 3.4. According to our calculation, YMn<sub>3</sub>O<sub>4</sub> is stable from room temperature up to 1461 K. At higher temperature, it decomposes into h-YMnO<sub>3</sub> and \( \beta \)-Mn<sub>3</sub>O<sub>4</sub>. The stable temperature range of h-YMnO<sub>3</sub> is between 1062 K and 2067 K. At 2067 K, it melts incongruently into liquid and \( \alpha \)-Y<sub>2</sub>O<sub>3</sub>. There is a eutectic reaction on the MnO<sub>x</sub>-rich side and the eutectic point is located at 1822 K and
5.83 cation% \( \text{YO}_{1.5} \). In the present calculation, the maximum solubilities of MnO in \( \alpha-\text{Y}_2\text{O}_3 \) and \( \beta-\text{Y}_2\text{O}_3 \) are all below 1 cation%.

Isothermal sections of the Mn–Y–O system at different temperatures are plotted in Figure 3.5. This system is dominated by the strong Mn–Y\(_2\)O\(_3\) diagonal, which actually divides the Mn–Y–O system into two ternary sub-systems: Mn–Y\(_2\)O\(_3\)–O and Mn–Y\(_2\)O\(_3\)–Y. There is already a liquid phase at 1273 K, due to the eutectic reaction of Mn\(_2\)Y and hcp-Y at 1152 K in the Mn–Y binary sub-system [14]. A ternary miscibility gap, extending from the binary Mn–O system, exists in the liquid phase at 2273 K.

It is important for the readers to notice that Figures 3.4 and 3.5 should be treated as tentative. Further experimental efforts are necessary to investigate the phase equilibria in the Mn–Y–O ternary system.
Figure 3.5  Calculated isothermal sections of the Mn–Y–O system in pure oxygen (10^5 Pa) from the present work, (a) at 1273 K, (b) at 1673 K, and (c) at 2273 K.
3.6 Conclusions

In the present work, the thermodynamic properties of two stable complex oxides, $h$-$\text{YMnO}_3$ and $\text{YMn}_2\text{O}_5$, were assessed. An optimized set of parameters of Gibbs energy functions is proposed. The present optimization agrees very well with most experimental data. A complete thermodynamic description of the Mn–Y–O system is proposed. The $\text{MnO}_x$–$\text{YO}_{1.5}$ phase diagram in air and three isothermal sections of the Mn–Y–O system were calculated. These phase diagrams should be treated as tentative.

3.7 References


Chapter 3


SGTE Unary Database (Version 1996), SGTE (Scientific Group Thermodata Europe), Grenoble, France, 1996.
4 Thermodynamic Modeling of Phase Equilibria in the Mn–Y–Zr–O System


**Abstract**

In the present work, a complete thermodynamic description of the Mn–Y–Zr–O system is presented, based on the experimental data on the Mn–Zr–O and the Mn–Y–Zr–O systems which were carefully reviewed. In t- and c-ZrO$_2$, the Mn ions dissolve in the form of Mn$^{2+}$ and/or Mn$^{3+}$. Their solubility limits in pure c-ZrO$_2$ at 1673 K are calculated and compared with those of other metal ions. The ZrO$_2$–MnO$_x$ phase diagram and three isothermal sections of MnO$_x$–YO$_{1.5}$–ZrO$_2$ in air at different temperatures are calculated. Our optimization fits most of the experimental data very well.

4.1 Introduction

Yttria stabilized zirconia (YSZ, cubic fluorite) exhibits high ionic conductivity at elevated temperatures (~1273 K). YSZ is chemically stable under both oxidizing and reducing conditions. Nowadays YSZ is widely used as electrolytes for solid oxide fuel cells (SOFCs) and oxygen sensors.

Solid oxide fuel cells are very attractive for power generation systems. The state of the art SOFC uses YSZ for electrolyte, Ni–YSZ cermet for anode, LaMnO$_3$-based perovskite (e.g. (La$_{1.3}$Sr$_{0.7}$)$_{1-x}$MnO$_{3+y}$, LSM) for cathode, and LaCrO$_3$-based perovskite for interconnects. It is normally operated at 1173–1273 K. High preparation temperatures of the components and high operation temperatures promote unwanted interface reactions in the SOFC, especially at the cathode–electrolyte interface.

The cathode–electrolyte interface reaction has been experimentally investigated by a number of groups [1, 2, 3, 4, 5, 6, 7]. It was found that under certain conditions (temperature, composition and nonstoichiometry of LaMnO$_3$-based perovskite and YSZ, and oxygen partial
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pressure), a highly insulating phase, La$_2$Zr$_2$O$_7$, can be formed at the interface [8]. The Mn diffusion from LaMnO$_3$-based perovskite into YSZ seems to play a critical role. Partially substituting La with Sr could inhibit the La$_2$Zr$_2$O$_7$ formation. However, excess Sr content may also lead to the formation of another insulating phase, SrZrO$_3$. On the other hand, the dissolution of MnO$_x$ in YSZ also changes the electrical properties of YSZ. At high temperature, the ionic conductivity of YSZ does not change appreciably over a large oxygen partial pressure range. Kawada et al. [9] reported an oxygen-pressure dependence of electrical conductivity in MnO$_x$-doped YSZ ((ZrO$_2$)$_{0.85}$Y$_{0.15}$)$_{0.148}$. At low oxygen partial pressure, MnO$_x$ doping decreases the ionic conductivity of YSZ and increases the electronic conductivity; while at high oxygen partial pressure, an increase in hole conductivity is obtained. This was attributed to a mixed valence state of Mn (+2 and +3) in YSZ. Compared to its ionic conductivity, the electronic (or hole) conductivity of MnO$_x$-doped YSZ is rather low. The oxygen ion transference number of 4 cat.% (cation%) MnO$_x$-doped YSZ at 1273 K was estimated to be higher than 0.99 over the oxygen partial pressure range of $10^{-15}$ – $10^5$ Pa [9].

The reactivity of LaMnO$_3$ and YSZ has been thermodynamically modeled by Yokokawa et al. [10, 11]. The calculation shows that the reactivity between La$_{1-x}$MnO$_{3-\delta}$ and YSZ varies with the nonstoichiometry of La in La$_{1-x}$MnO$_{3-\delta}$ and there is a composition range where no La$_2$Zr$_2$O$_7$ forms. This composition range corresponds to a La deficiency in La$_{1-x}$MnO$_{3-\delta}$ and it changes with temperature. Obviously the diffusion of Mn from La$_{1-x}$MnO$_{3-\delta}$ into YSZ changes the stoichiometry and the activity of La in La$_{1-x}$MnO$_{3-\delta}$. An excess of Mn in La$_{1-x}$MnO$_{3-\delta}$ could be helpful to inhibit the La$_2$Zr$_2$O$_7$ formation [12], but may also increase the dissolution of Mn in YSZ and hence change the electrical properties of YSZ.

To understand the interface reaction between LSM and YSZ and to predict at what conditions insulating phases will form, a thermodynamic description of the La–Mn–Sr–Y–Zr–O system would be necessary. Our group has recently finished a thermodynamic assessment of the La–Sr–Mn–O system [13] and an assessment of the Y–Zr–O system [14]. To reach the final goal, the following step is the thermodynamic assessment of the Mn–Y–Zr–O system.

Among all these sub-systems, only the Mn-Zr-O ternary system has not been assessed. In the present work, the available experimental data on the Mn-Zr-O and the Mn-Y-Zr-O systems are carefully reviewed. The parameters of the Gibbs free energies of the Mn-Zr-O and Mn-Y-Zr-O systems were optimized. Based on the previous assessments of Mn-Y-Zr from Flandorfer et al. [15], Y-Zr-O and Mn-Y-O from Chen et al. [14, 16], a complete thermodynamic description of the Mn-Y-Zr-O system is presented, including a description of the Mn-Zr-O system as well.

We will generally use the abbreviations m, t, and c for m-ZrO$_2$ (monoclinic), t-ZrO$_2$ (tetragonal), c-ZrO$_2$ (cubic), and YSZ for yttria stabilized zirconia (cubic fluorite).

4.2 Experimental data

So far, relatively few experiments have been done on phase equilibria of the Mn-Zr-O and the Mn-Y-Zr-O systems.

4.2.1 Mn-Zr-O

In the Mn-Zr-O system, no ternary compounds or complex manganese zirconium oxides have been reported. Experimental work has focused on the Mn$_x$ZrO$_y$ quasi-binary section.

Von Wartenberg and Gurr [17] investigated the liquidus of Mn$_x$O$_y$-ZrO$_2$ and reported the eutectic temperature to be at 1893 K. This eutectic temperature is probably wrong as it is even higher than both the measured and the assessed melting temperatures of β-Mn$_3$O$_4$ [18]. Shultz and Muan [19] studied the phase relations of the MnO-ZrO$_2$ system in the liquidus temperature region, using the quenching technique. They used a CO$_2$-CO mixture of 32:1, trying to keep all Mn ions in the divalent state. The eutectic point of MnO-ZrO$_2$ was located at 1803 K and 74.7 cat.% MnO. Just below the eutectic temperature, the maximum solubility of MnO in ZrO$_2$ was reported to be 34.2 cat.%, while 3.5 cat.% ZrO$_2$ can dissolve in MnO. The crystal structure of the ZrO$_2$ solid solution was not determined. Dravid et al. [20] investigated a directionally solidified eutectic of MnO-ZrO$_2$. An argon atmosphere was used to retain Mn ions as Mn$^{2+}$. The eutectic composition was suggested to be close to 75 cat.%
MnO, in good agreement with the one from Shultz and Muan [19]. They reported that below the eutectic temperature, less than 0.5 wt% ZrO$_2$ can be dissolved into MnO, while 22.2 cat.% MnO is soluble in ZrO$_2$. MnO-stabilized ZrO$_2$ was confirmed to have the cubic fluorite structure and Mn is present as Mn$^{2+}$. In the present work, the eutectic temperature of MnO–ZrO$_2$ from Shultz and Muan [19] and the eutectic composition and the maximum solubility of MnO in c-ZrO$_2$ from Dravid et al. [20] were included. The reported maximum solubility of MnO in c-ZrO$_2$ from Shultz and Muan [19] is too high to be compatible with the reported MnO$_x$ solubilities in c-ZrO$_2$ at lower temperatures and was hence excluded.

Kawashima [21] investigated the solubility of MnO$_x$ in tetragonal ZrO$_2$ (t-ZrO$_2$) at 1673 K in air, using high temperature X-ray diffraction (XRD). The solubility limit of MnO$_x$ in t-ZrO$_2$ was reported to be 7 cat.%. This data point was included in our optimization.

Recently Occhiuzzi et al. [22] used XRD and electron paramagnetic resonance (EPR) to investigate MnO$_x$-doped m-ZrO$_2$, t-ZrO$_2$, and YSZ ((ZrO$_2$)$_{0.83}$(YO$_1$_$5$)$_{0.17}$), where m-ZrO$_2$ and t-ZrO$_2$ were not yttria doped. The samples were heated in air at 1623 K for 5 h and the solubility limit of Mn$^{x+}$ in m-ZrO$_2$ was reported to be 0.2 wt.% Mn. No solubility of MnO$_x$ in m-ZrO$_2$ was therefore, considered in the present work.

### 4.2.2 Mn–Y–Zr–O

No quaternary compound was found in the Mn–Y–Zr–O system. The ternary compound, hexagonal YMnO$_3$ (h-YMnO$_3$), was reported to have some Zr solubility, which can be written as Y$_{1-x}$Zr$_x$MnO$_3$. van Aken et al. [23] synthesized Zr doped h-YMnO$_3$ by mixing pure oxides of ZrO$_2$, Y$_2$O$_3$, and MnO$_2$ and sintering at 1073–1673 K. Samples with $x < 0.3$ were single phase and no trace of ZrO$_2$ could be found with either XRD or energy-dispersive spectroscopy (EDS). By investigating electronic and magnetic properties of Zr doped h-YMnO$_3$, they reported that Zr substitution creates a mixed Mn$^{3+}$–Mn$^{2+}$ system. The refinement of the occupation of the Mn site shows no replacement of Mn with Zr. Using floating-zone method, Katsufuji et al. [24] also doped Zr$^{4+}$ into h-YMnO$_3$ and a single crystal was obtained with a formula of Y$_{0.95}$Zr$_{0.05}$MnO$_3$. They reported that about 10 mol% of Y$^{3+}$ ions can be replaced by Zr$^{4+}$ ions, much less than reported by van Aken et al. [23]. Due to the uncertainty on the reported solubility data, in the present work, we excluded any Zr solubility in h-YMnO$_3$. 

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In the Mn–Y–Zr–O quaternary system, the MnO$_x$ solubility in YSZ has been investigated by a few groups. Lau and Singhal (cited by Kawashima and Hishinuma [25]) determined that 10.7 cat.% MnO$_x$ is soluble in YSZ ((Y$_{0.15}$Zr$_{0.85}$)$_{0.50}$O$_{0.55}$) in air at 1673 K. Kawada et al. [9] measured the lattice parameters of MnO$_x$-doped YSZ ((Zr$_{0.85}$Y$_{0.15}$)$_{0.50}$O$_{0.55}$) samples prepared at 1773 K in air and annealed at different temperatures. The solubility limits of MnO$_x$ in YSZ were determined at different temperatures from 1273 to 1773 K. Kim and Choi [26] estimated the solubility of MnO$_{1.5}$ in YSZ ((Zr$_{0.85}$Y$_{0.15}$)$_{0.50}$O$_{0.55}$) in air to be 12 mol% from XRD lattice parameter measurements. Their samples were sintered at 1673 K and annealed at 1023 K for 3 days. Using high temperature X-ray diffraction, Kawashima [21] investigated the phase equilibria in the ZrO$_2$-rich part of the MnO$_x$-Y$_{0.15}$-ZrO$_2$ ternary system at 1673 K in air. A schematic diagram was made for the ZrO$_2$-rich corner. They concluded that MnO$_x$ dissolves more in YSZ than in pure c-ZrO$_2$. In the present work, the data from Kawada et al. [9] and from Kawashima [21] were used.

Using Knudsen effusion mass spectrometry, Matraszek et al. [27] determined thermodynamic activities of MnO in (Zr$_{0.85}$Y$_{0.15}$)$_{1-x}$Mn$_x$O$_{1.93-\delta}$ (0.02 ≤ $x$ ≤ 0.18) at 1700 K. The samples were prepared by mixing oxides and sintering at 1673 K for 48 h in air. Together with XRD and SEM/EDX (scanning electron microscope/energy dispersive X-ray) analyses, they concluded that 11 cat.% MnO$_x$ can be dissolved into YSZ ((Zr$_{0.85}$Y$_{0.15}$)$_{0.50}$O$_{0.55}$). The activity data were included into our optimization.

### 4.3 Binary and ternary sub-systems

In the present work, the descriptions of all metal sub-systems (Mn–Y, Mn–Zr, Y–Zr, and Mn–Y–Zr) are taken from Flandorfer et al. [15].

Among all oxygen-containing sub-systems, only the Mn–Zr–O system needs to be assessed. In the present work, the descriptions of Y–O, Zr–O, and Y–Zr–O were taken from our assessment of the Y–Zr–O system [14]. The description of Mn–Y–O was taken from our recent work [16], which includes the description of Mn–O as well. For the Mn–O system, we accepted the description by Grundy et al. [18], but changed the model for β-Mn$_2$O$_3$ from a stoichiometric compound to (Mn$^{3+}$)$_2$(O$_{2-}$, Va)$_3$(O$_{2-}$, Va). The β-Mn$_2$O$_3$ phase and the α-Y$_2$O$_3$...
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phase have the same crystal structure, Mn$_2$O$_3$ bixbyite type. We described these two phases as one phase and changed the model for $\beta$-Mn$_2$O$_3$. The calculated Mn–O phase diagram is very similar to the one from Grundy et al. [18].

4.4 Thermodynamic models

Compared to the previously assessed sub-systems (binary and ternary), in the present work, no new phase was included into the Mn–Y–Zr–O quaternary system. The models of a few solution phases will however, be changed, including t-ZrO$_2$, c-ZrO$_2$ (also $\beta$-Y$_2$O$_3$), $\alpha$-Y$_2$O$_3$ (also $\beta$-Mn$_2$O$_3$), and the liquid phase. We use the compound energy model for solid solution phases [28]. For the liquid phase, the two-sublattice model for ionic liquids was used [29, 30].

4.4.1 Solid oxide solution phases

In the Mn–Y–Zr–O system, there exist four solid oxide solution phases: m-ZrO$_2$, t-ZrO$_2$, c-ZrO$_2$ (also $\beta$-Y$_2$O$_3$), $\alpha$-Y$_2$O$_3$ (also $\beta$-Mn$_2$O$_3$).

In the present work, we did not include any ZrO$_2$ or Y$_2$O$_3$ solubility in MnO$_x$ oxides, except for the $\beta$-Mn$_2$O$_3$ phase. In our description of the Mn–Y–O system [14], we describe $\alpha$-Y$_2$O$_3$ and $\beta$-Mn$_2$O$_3$ as one phase, using the model $(\text{Mn}^{3+}, \text{Y}, \text{Y}^{3+})_2(\text{O}^{2-}, \text{Va})_3(\text{O}^{2-}, \text{Va})_1$. On the other hand, in the Y–Zr–O system, we include ZrO$_2$ solubility in $\alpha$-Y$_2$O$_3$ [14]. To reflect both, here we use a model $(\text{Mn}^{3+}, \text{Y}, \text{Y}^{3+}, \text{Zr}^{4+})_2(\text{O}^{2-}, \text{Va})_3(\text{O}^{2-}, \text{Va})_1$. To keep the ZrO$_2$ solubility in $\beta$-Mn$_2$O$_3$ low, we use a value of 100 kJ/mol for the interaction parameters between Mn$^{3+}$ and Zr$^{4+}$ ($L_{\text{Mn}^{3+},\text{Zr}^{4+}::\text{O}^{2-},\text{O}^{2-}}$, $L_{\text{Mn}^{3+},\text{Zr}^{4+}::\text{O}^{2-},\text{Va}}$, $L_{\text{Mn}^{3+},\text{Zr}^{4+}::\text{Va},\text{O}^{2-}}$, $L_{\text{Mn}^{3+},\text{Zr}^{4+}::\text{Va},\text{Va}}$). No other parameters were optimized for this phase.

For ZrO$_2$-rich phases (m-, t-, and c-ZrO$_2$), in the present work, we include MnO$_x$ solubility into t- and c-ZrO$_2$, but not in m-ZrO$_2$. The Mn ions in these two phases were treated as a mixture of Mn$^{2+}$ and Mn$^{3+}$, whereas Mn$^{4+}$ was not included.
The valence state of manganese ions in ZrO$_2$ was studied by Voigt and Feltz [31], Sasaki et al. [32], Appel et al. [33], and recently Occhiuzzi et al. [22], both in air and in reducing atmosphere.

Occhiuzzi et al. [22] used EPR to investigate the valence state of manganese ions in m-, t-, c-ZrO$_2$. The samples were prepared using soft chemistry method and were heated in air at various temperatures up to 1623 K for 5 h and then heated at 773–973 K in a silica tubular furnace with a flow of H$_2$ for 5 h. Mn$^{2+}$, Mn$^{3+}$, and Mn$^{4+}$ in m-ZrO$_2$ and Mn$^{2+}$ and Mn$^{3+}$ in t- and c-ZrO$_2$ were suggested. Decreasing the oxygen partial pressure leads to a reduction of Mn$^{3+}$ → Mn$^{2+}$. The valence state of manganese ions in ZrO$_2$ was suggested to be determined by both the crystal structure of ZrO$_2$ and the oxygen partial pressure.

Among Mn ions, Occhiuzzi et al. [22] stated that Mn$^{2+}$ (high spin 3d$^5$) can occupy cationic sites with 4-, 6-, and 8-fold coordination, while Mn$^{4+}$ (3d$^3$) has a strong preference for 6-fold coordination. No comment was given on Mn$^{3+}$. In ZrO$_2$, foreign metal ions occupy the cationic sites, substituting Zr$^{4+}$. For metal ions with a charge lower than +4, oxygen vacancies are created on doping. In m-ZrO$_2$, each cation is coordinated by 7 oxygen ions; while in t- and c-ZrO$_2$, this coordination number is 8 [34]. Occhiuzzi et al. [22] suggested that in t- and c-ZrO$_2$, due to the high crystal field stabilization energy (CFSE), Mn$^{4+}$ is destabilized and enters with lower valence states (Mn$^{2+}$ and/or Mn$^{3+}$). In m-ZrO$_2$, however, the MnO$_7$ polyhedron is probably distorted towards a MnO$_6$ octahedron, which partially stabilizes Mn$^{4+}$. This could explain why Mn$^{4+}$ can only be found in m-ZrO$_2$.

In the present work, we use a model (Mn$^{2+}$, Mn$^{3+}$, Y$^{3+}$, Zr$^{4+}$)$_1$(O$_{2-}$, Va)$_2$ for t-ZrO$_2$ and (Mn$^{2+}$, Mn$^{3+}$, Y, Y$^{3+}$, Zr, Zr$^{4+}$)$_1$(O$_{2-}$, Va)$_2$ for c-ZrO$_2$.

The Gibbs energy of t-ZrO$_2$ is given by:

$$
G_m = y_{Mn^{2+}}y_{O_2^2}G_{Mn^{2+},O_2^2} + y_{Mn^{3+}}y_{O_2^2}G_{Mn^{3+},O_2^2} + y_{V}_{Mn^{2+}}y_{O_2^2}G_{Mn^{2+},O_2^2} + y_{V}_{Mn^{3+}}y_{O_2^2}G_{Mn^{3+},O_2^2} + y_{Zr^{4+}}y_{O_2^2}G_{Zr^{4+},O_2^2}$$
$$+ y_{Mn^{2+}}y_{Va}G_{Mn^{2+},Va} + y_{Mn^{3+}}y_{Va}G_{Mn^{3+},Va} + y_{V}_{Mn^{2+}}y_{Va}G_{Mn^{2+},Va} + y_{V}_{Mn^{3+}}y_{Va}G_{Mn^{3+},Va} + y_{Zr^{4+}}y_{Va}G_{Zr^{4+},Va} + RT[y_{Mn^{2+}}ln y_{Mn^{2+}} + y_{Mn^{3+}}ln y_{Mn^{3+}} + y_{V}_{Mn^{2+}}ln y_{V}_{Mn^{2+}} + y_{V}_{Mn^{3+}}ln y_{V}_{Mn^{3+}} + 2(y_{O_2^2}ln y_{O_2^2} + y_{Va}ln y_{Va})] + RT \ln \gamma_0 G_m \tag{4.1}
$$

where $\gamma_0$ is the fraction of the species $s$ in a particular sublattice.
The excess Gibbs energy is given by (not including ternary and higher order interactions):

\[
\begin{align*}
E_{G_m} &= y_{\text{Mn}}^2, y_{\text{Zr}}^{2+}, y_{\text{O}_2} \sum_{i=0}^{n} L_{\text{Mn}^{2+}, \text{Zr}^{4+}, \text{O}_2} \left( y_{\text{Mn}}^2 - y_{\text{Zr}}^{2+} \right)^i + y_{\text{Mn}}^3, y_{\text{Zr}}^{4+}, y_{\text{O}_2} \sum_{i=0}^{n} L_{\text{Mn}^{3+}, \text{Zr}^{4+}, \text{O}_2} \left( y_{\text{Mn}}^3 - y_{\text{Zr}}^{4+} \right)^i \\
&+ y_{\text{Zr}}^{2+}, y_{\text{Zr}}^{4+}, y_{\text{O}_2} \sum_{i=0}^{n} L_{\text{Zr}^{2+}, \text{Zr}^{4+}, \text{O}_2} \left( y_{\text{Zr}}^{2+} - y_{\text{Zr}}^{4+} \right)^i + y_{\text{Zr}}^{3+}, y_{\text{Zr}}^{4+}, y_{\text{O}_2} \sum_{i=0}^{n} L_{\text{Zr}^{3+}, \text{Zr}^{4+}, \text{O}_2} \left( y_{\text{Zr}}^{3+} - y_{\text{Zr}}^{4+} \right)^i \\
&+ y_{\text{Mn}}^2, y_{\text{Zr}}^{3+}, y_{\text{O}_2} \sum_{i=0}^{n} L_{\text{Mn}^{2+}, \text{Zr}^{3+}, \text{O}_2} \left( y_{\text{Mn}}^2 - y_{\text{Zr}}^{3+} \right)^i + y_{\text{Mn}}^3, y_{\text{Zr}}^{3+}, y_{\text{O}_2} \sum_{i=0}^{n} L_{\text{Mn}^{3+}, \text{Zr}^{3+}, \text{O}_2} \left( y_{\text{Mn}}^3 - y_{\text{Zr}}^{3+} \right)^i
\end{align*}
\]

Eq. 4.2

The lattice stability parameters \( \theta_{G_{\text{Mn}^{2+}, \text{Zr}^{2+}, \text{O}_2}} \), \( \theta_{G_{\text{Mn}^{3+}, \text{Zr}^{2+}, \text{O}_2}} \), \( \theta_{G_{\text{Mn}^{2+}, \text{Zr}^{4+}, \text{O}_2}} \), and the interaction parameters \( L_{\text{Mn}^{2+}, \text{Zr}^{4+}, \text{O}_2} \), \( L_{\text{Mn}^{3+}, \text{Zr}^{4+}, \text{O}_2} \), \( L_{\text{Mn}^{3+}, \text{Zr}^{4+}, \text{Zr}^{4+}} \), \( L_{\text{Zr}^{2+}, \text{Zr}^{4+}, \text{Zr}^{4+}} \) in Eq. 4.1 and 4.2 need to be determined. For the interaction parameters, we set:

\[
L_{\text{Mn}^{2+}, \text{Zr}^{4+}, \text{O}_2} = L_{\text{Mn}^{3+}, \text{Zr}^{4+}, \text{O}_2} = L_{\text{Mn}^{3+}, \text{Zr}^{4+}, \text{Zr}^{4+}} = L_{\text{Zr}^{2+}, \text{Zr}^{4+}, \text{Zr}^{4+}}
\]

Eq. 4.3

The individual parameters for \( c\text{-ZrO}_2 \) are derived in a similar manner as for \( t\text{-ZrO}_2 \). Both the binary interaction parameters ( \( L_{\text{Mn}^{2+}, \text{Zr}^{4+}, \text{O}_2} \), \( L_{\text{Mn}^{3+}, \text{Zr}^{4+}, \text{O}_2} \), \( L_{\text{Mn}^{3+}, \text{Zr}^{4+}, \text{Zr}^{4+}} \) ) and the ternary interaction parameters ( \( L_{\text{Mn}^{2+}, \text{Y}^{3+}, \text{Zr}^{4+}, \text{O}_2} \), \( L_{\text{Mn}^{3+}, \text{Y}^{3+}, \text{Zr}^{4+}, \text{O}_2} \), \( L_{\text{Mn}^{3+}, \text{Y}^{3+}, \text{Zr}^{4+}, \text{Zr}^{4+}} \) ) for \( c\text{-ZrO}_2 \) were optimized. We also set:

\[
L_{\text{Mn}^{2+}, \text{Zr}^{4+}, \text{O}_2} = L_{\text{Mn}^{3+}, \text{Zr}^{4+}, \text{O}_2} = L_{\text{Mn}^{3+}, \text{Zr}^{4+}, \text{Zr}^{4+}} = L_{\text{Zr}^{2+}, \text{Zr}^{4+}, \text{Zr}^{4+}}
\]

Eq. 4.4

and

\[
L_{\text{Mn}^{2+}, \text{Y}^{3+}, \text{Zr}^{4+}, \text{O}_2} = L_{\text{Mn}^{3+}, \text{Y}^{3+}, \text{Zr}^{4+}, \text{O}_2} = L_{\text{Mn}^{3+}, \text{Y}^{3+}, \text{Zr}^{4+}, \text{Zr}^{4+}}
\]

Eq. 4.5

4.4.2 Liquid phase

The liquid phase was described using the model (\( \text{Mn}^{2+}, \text{Mn}^{3+}, \text{Y}^{3+}, \text{Zr}^{4+} \))(\( \text{O}^{2-}, \text{Va}^{q+} \))\( p \), where

\[
p = 2y_{\text{O}^{2-}} + qy_{\text{Va}^{q+}}
\]

Eq. 4.6

\[
q = 2y_{\text{Mn}^{2+}} + 3y_{\text{Mn}^{3+}} + 3y_{\text{Y}^{3+}} + 4y_{\text{Zr}^{4+}}
\]

Eq. 4.7

The interaction parameters \( L_{\text{Mn}^{2+}, \text{Zr}^{4+}, \text{O}^{2-}} \) and \( L_{\text{Mn}^{3+}, \text{Zr}^{4+}, \text{O}^{2-}} \) were optimized in the present work, where we set:

\[
L_{\text{Mn}^{2+}, \text{Zr}^{4+}, \text{O}^{2-}} = L_{\text{Mn}^{3+}, \text{Zr}^{4+}, \text{O}^{2-}}
\]

Eq. 4.8
4.5 Optimization

Our assessment was made using the software PARROT included in the Thermo-Calc Databank System [35]. In the present optimization, only some of the parameters for t-ZrO₂, c-ZrO₂, and the liquid phase were optimized. The parameters \( \Delta G_{\text{Mn}^{2+}O^2} \), \( \Delta G_{\text{Mn}^{3+}O^3} \), \( \Delta G_{\text{Mn}^{2+}Va} \), \( \Delta G_{\text{Mn}^{3+}Va} \) for t-ZrO₂ and c-ZrO₂ were fixed at an early stage of the optimization and not changed further. The interaction parameters of these three phases were optimized together, using the phase diagram data from Shultz and Muan [19], Kawada et al. [9], Dravid et al. [20], and Kawashima [21] and the MnO activities in MnOₓ-doped YSZ at 1700 K from Matraszek et al. [27].

During the optimization, we had difficulty in fitting the phase diagram data from Kawashima [21]. He found that at 1673 K in air, MnOₓ dissolves more in YSZ than in pure c-ZrO₂. Trying to fit this leads to a decrease in MnOₓ solubility both in pure c-ZrO₂ and in YSZ, and strongly negative interaction parameters for c-ZrO₂. Using ternary interaction parameters \( I_{\text{Mn}^{2+},\text{Y}^{3+},\text{Zr}^{4+}O^2} \), \( I_{\text{Mn}^{2+},\text{Y}^{3+},\text{Zr}^{4+}Va} \), \( I_{\text{Mn}^{2+},\text{Y}^{3+},\text{Zr}^{4+}O^2} \), and \( I_{\text{Mn}^{2+},\text{Y}^{3+},\text{Zr}^{4+}Va} \) improved the fitting somewhat. In the MnOₓ-ZrO₂ section, Kawashima [21] did not detect the formation of c-ZrO₂ at 1673 K in air with MnOₓ doping up to 15 cat.%. Only t-ZrO₂ and Mn₃O₄ were found in his MnOₓ-doped ZrO₂ samples. According to his proposed phase diagram, c-ZrO₂ probably decomposes into t-ZrO₂ and Mn₃O₄ in air at a temperature higher than 1673 K. We set this temperature as 1700 K and included it into the optimization, to keep the calculated decomposition temperature higher than 1673 K. The weights of experimental data were adjusted carefully at the end.

4.6 Results and discussion

The phase descriptions for the Mn–Y–Zr–O system are shown in Table 4.1. Table 4.2 lists the parameters optimized in the present work.
Table 4.1  Phase descriptions for the Mn–Y–Zr–O system

<table>
<thead>
<tr>
<th>Phase</th>
<th>Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCP</td>
<td>((\text{Mn}, \text{Y}, \text{Zr}), (\text{O}, \text{Va})_{0.5} )</td>
</tr>
<tr>
<td>BCC</td>
<td>((\text{Mn}, \text{Y}, \text{Zr}), (\text{O}, \text{Va})_{1.5} )</td>
</tr>
<tr>
<td>(\alpha)-Mn (CBCC)</td>
<td>((\text{Mn}), (\text{Va})_{1} )</td>
</tr>
<tr>
<td>(\beta)-Mn (CUBIC)</td>
<td>((\text{Mn}), (\text{Va})_{1} )</td>
</tr>
<tr>
<td>(\gamma)-Mn (FCC)</td>
<td>((\text{Mn}, \text{Zr}), (\text{Va})_{1} )</td>
</tr>
<tr>
<td>(\text{Mn}_{12}\text{Y})</td>
<td>((\text{Mn})<em>{1} (\text{Y})</em>{1} )</td>
</tr>
<tr>
<td>(\text{Mn}<em>{23}\text{Y}</em>{6})</td>
<td>((\text{Mn})<em>{2} (\text{Y})</em>{6} )</td>
</tr>
<tr>
<td>(\text{Mn}_{2}\text{Y})</td>
<td>((\text{Mn})<em>{2} (\text{Y})</em>{1} )</td>
</tr>
<tr>
<td>(\text{Mn}<em>{2}\text{Zr}</em>{1-x})</td>
<td>((\text{Mn})<em>{2} (\text{Zr}, \text{Va})</em>{1} )</td>
</tr>
<tr>
<td>(\text{Mn}_{1-x}\text{O})</td>
<td>((\text{Mn}^{2+}, \text{Mn}^{3+}, \text{Va})<em>{1} (\text{O}^{2-})</em>{1} )</td>
</tr>
<tr>
<td>(\alpha)-(\text{Mn}<em>{3}\text{O}</em>{4})</td>
<td>((\text{Mn}^{2+})<em>{1} (\text{Mn}^{3+})</em>{2} (\text{O}^{2-})_{4} )</td>
</tr>
<tr>
<td>(\beta)-(\text{Mn}<em>{3}\text{O}</em>{4})</td>
<td>((\text{Mn}^{2+})<em>{1} (\text{Mn}^{3+})</em>{2} (\text{O}^{2-})_{4} )</td>
</tr>
<tr>
<td>(\text{MnO}_{2})</td>
<td>((\text{Mn}^{4+})<em>{1} (\text{O}^{2-})</em>{2} )</td>
</tr>
<tr>
<td>(\alpha)-(\text{Y}<em>{2}\text{O}</em>{3}) (and also (\beta)-(\text{Mn}<em>{2}\text{O}</em>{3}))</td>
<td>((\text{Mn}^{2+}, \text{Y}, \text{Zr}^{4+})<em>{1} (\text{O}^{2-}, \text{Va})</em>{1} (\text{O}^{2-}, \text{Va})_{1} )</td>
</tr>
<tr>
<td>(m)-(\text{ZrO}_{2})</td>
<td>((\text{Y}^{3+}, \text{Zr}^{4+})<em>{1} (\text{O}^{2-}, \text{Va})</em>{2} )</td>
</tr>
<tr>
<td>(t)-(\text{ZrO}_{2})</td>
<td>((\text{Mn}^{2+}, \text{Mn}^{3+}, \text{Y}^{3+}, \text{Zr}^{4+})<em>{1} (\text{O}^{2-}, \text{Va})</em>{2} )</td>
</tr>
<tr>
<td>(c)-(\text{ZrO}<em>{2}) (and also (\beta)-(\text{Y}</em>{2}\text{O}_{3}))</td>
<td>((\text{Mn}^{2+}, \text{Mn}^{3+}, \text{Y}, \text{Y}^{3+}, \text{Zr}, \text{Zr}^{4+})<em>{1} (\text{O}^{2-}, \text{Va})</em>{2} )</td>
</tr>
<tr>
<td>(h)-(\text{YMnO}_{3})</td>
<td>((\text{Y}^{3+})<em>{1} (\text{Mn}^{3+})</em>{1} (\text{O}^{2-})_{5} )</td>
</tr>
<tr>
<td>(\text{YMn}<em>{2}\text{O}</em>{5})</td>
<td>((\text{Y}^{3+})<em>{1} (\text{Mn}^{4+})</em>{1} (\text{O}^{2-})_{5} )</td>
</tr>
<tr>
<td>(\text{Zr}<em>{2}\text{Y}</em>{4}\text{O}_{12})</td>
<td>((\text{Zr}^{4+})<em>{3} (\text{Y}^{3+})</em>{4} (\text{O}^{2-})_{12} )</td>
</tr>
<tr>
<td>Liquid</td>
<td>((\text{Mn}^{2+}, \text{Mn}^{3+}, \text{Y}^{3+}, \text{Zr}^{4+})<em>{p} (\text{O}^{2-}, \text{Va}^{q}</em>{m})_{q} )</td>
</tr>
<tr>
<td>(\rho)</td>
<td>(= 2y_{\text{O}^{2-}} + qy_{\text{Va}^{q}_{m}} )</td>
</tr>
<tr>
<td>(q)</td>
<td>(= 2y_{\text{Mn}^{2+}} + 3y_{\text{Mn}^{3+}} + 3y_{\text{Y}^{3+}} + 4y_{\text{Zr}^{4+}} )</td>
</tr>
</tbody>
</table>

Turning to the Mn–Zr–O ternary system, our calculated \(\text{ZrO}_{2}\text{–MnO}_{x}\) phase diagram in air is shown in Figure 4.1. As the diagram shows, there is a eutectic of \(c\)-\(\text{ZrO}_{2}\text{–}\beta\)-\(\text{Mn}_{3}\text{O}_{4}\) at 1770 K and 84 cat.% \(\text{MnO}_{x}\). The maximal solubilities of \(\text{MnO}_{x}\) in \(t\)- and \(c\)-\(\text{ZrO}_{2}\) are 5.9 and 16 cat.%, respectively. Our calculated \(\text{MnO}_{x}\) solubility in \(t\)-\(\text{ZrO}_{2}\) at 1673 K is slightly lower than the measured value from Kawashima [21]. The calculated \(\text{ZrO}_{2}\) solubility in \(\beta\)-\(\text{Mn}_{2}\text{O}_{3}\) is close to zero in the present work. According to our calculation, in air, \(c\)-\(\text{ZrO}_{2}\) is stable down to 1682 K. At lower temperature, it decomposes into \(t\)-\(\text{ZrO}_{2}\) and \(\beta\)-\(\text{Mn}_{3}\text{O}_{4}\). \(t\)-\(\text{ZrO}_{2}\) decomposes into \(m\)-\(\text{ZrO}_{2}\) and \(\alpha\)-\(\text{Mn}_{3}\text{O}_{4}\) at 1312 K. The decomposition temperatures of \(t\)- and \(c\)-\(\text{ZrO}_{2}\) decrease at low oxygen partial pressure.
Figure 4.2 shows the calculated MnO_x solubility in c-ZrO_2 at 1673 K versus oxygen partial pressure. The Mn^{2+} and Mn^{3+} solubilities are plotted as well, using dash and dot lines respectively. The stable regions of Mn oxides are also indicated. At low oxygen partial pressure, the total solubility keeps constant, around 15.7 cat.%. It starts to increase at $P_{O_2} = 10^{-5}$ Pa, reaches a maximum at $P_{O_2} = 630$ Pa and then decreases continuously. In the low $P_{O_2}$ region, mainly Mn^{2+} dissolves in ZrO_2. Increasing oxygen partial pressure leads to a decrease in Mn^{2+} solubility and an increase in Mn^{3+} solubility. The Mn^{3+} solubility reaches maximum at $P_{O_2} = 1.17 \times 10^{11}$ Pa and then decreases. According to Figure 4.2, the solubility limits of Mn^{2+} and Mn^{3+} in c-ZrO_2 at 1673 K are 15.7 and 6.6 cat.%, respectively. The actual amounts of dissolved Mn^{2+} and Mn^{3+} vary with oxygen partial pressure.

Table 4.2 Parameters optimized in the present work for the Mn–Y–Zr–O system

<table>
<thead>
<tr>
<th>t-ZrO_2</th>
<th>Parameters optimized in the present work for the Mn–Y–Zr–O system</th>
</tr>
</thead>
<tbody>
<tr>
<td>$G_{Mn^{2+},O_2} - H_{\text{SER}}^{\text{Zr}} = GMN101 + GHSEROO + 11.5264T$</td>
<td></td>
</tr>
<tr>
<td>$G_{Mn^{3+},O_2} - H_{\text{SER}}^{\text{Zr}} = GMN101 - GHSEROO + 11.5264T$</td>
<td></td>
</tr>
<tr>
<td>$G_{Mn^{3+},O_2} - H_{\text{SER}}^{\text{Zr}} = 0.5 GMN203 + 0.5 GHSEROO + 9.3511T$</td>
<td></td>
</tr>
<tr>
<td>$G_{Mn^{3+},O_2} - H_{\text{SER}}^{\text{Zr}} = 0.5 GMN203 - 1.5 GHSEROO + 9.3511T$</td>
<td></td>
</tr>
<tr>
<td>$L_{Mn^{2+,Zr^{4+},O_2}} = L_{Mn^{2+,Zr^{4+},Va}} = L_{Mn^{3+,Zr^{4+},O_2}} = L_{Mn^{3+,Zr^{4+},Va}} = +24317$</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>c-ZrO_2 (and also $\beta$-Y_2O_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$G_{Mn^{2+},O_2} - H_{\text{SER}}^{\text{Zr}} = GMCMN101 + GHSEROO + 11.5264T$</td>
</tr>
<tr>
<td>$G_{Mn^{3+},O_2} - H_{\text{SER}}^{\text{Zr}} = GMCMN101 - GHSEROO + 11.5264T$</td>
</tr>
<tr>
<td>$G_{Mn^{3+},O_2} - H_{\text{SER}}^{\text{Zr}} = 0.5 GMCMN203 + 0.5 GHSEROO + 9.3511T$</td>
</tr>
<tr>
<td>$G_{Mn^{3+},O_2} - H_{\text{SER}}^{\text{Zr}} = 0.5 GMCMN203 - 1.5 GHSEROO + 9.3511T$</td>
</tr>
<tr>
<td>$L_{Mn^{2+,Zr^{4+},Va}} = L_{Mn^{3+,Zr^{4+},Va}} = L_{Mn^{2+,Zr^{4+},O_2}} = L_{Mn^{3+,Zr^{4+},O_2}} = +44110$</td>
</tr>
<tr>
<td>$L_{Mn^{2+,Zr^{4+},Va}} = L_{Mn^{3+,Zr^{4+},Va}} = L_{Mn^{2+,Zr^{4+},O_2}} = L_{Mn^{3+,Zr^{4+},O_2}} = +31770$</td>
</tr>
<tr>
<td>$L_{Mn^{3+,Y^{3+},Zr^{4+},O_2}} = L_{Mn^{3+,Y^{3+},Zr^{4+},Va}} = L_{Mn^{3+,Y^{3+},Zr^{4+},O_2}} = L_{Mn^{3+,Y^{3+},Zr^{4+},Va}} = -157216$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Liquid</th>
</tr>
</thead>
<tbody>
<tr>
<td>$L_{Mn^{2+,Zr^{4+},O_2}} = L_{Mn^{3+,Zr^{4+},O_2}} = -23410$</td>
</tr>
</tbody>
</table>

**Functions**

- GMTMN101 = GMN101 + 40000
- GMTN203 = GMN203 + 100000
- GMCMN101 = GMN101 + 20000
- GMCMN203 = GMN203 + 60000

**Notes:**
1. All parameters are in SI units: J, mol, K, Pa; R=8.31451 J/(mol K).
2. GMN101 and GMN203 are the molar Gibbs energies of manganese oxides, taken from Grundy et al. [18]. GHSEROO is the molar Gibbs energy of oxygen from Dinsdale [36].
Figure 4.1  Calculated ZrO$_2$–MnO$_x$ phase diagram in air from the present work. The experimental data point is from Kawashima [21].

Figure 4.2  Calculated MnO$_x$ solubility in c-ZrO$_2$ at 1673 K from the present work. The stable regions of Mn oxides against oxygen partial pressure are indicated as well.

It is quite clear that the solubility limit of Mn$^{3+}$ in c-ZrO$_2$ is much lower than that of Mn$^{2+}$. This should be due to the difference in radius and valence state between Mn$^{2+}$ and Mn$^{3+}$. In a
fluorite-type solid solution, substituting the host cation with a foreign cation with different radius and valence state introduces strain. The extent of the solid solution is hence, governed by the elastic energy in the strained lattice. The smaller the energy, the wider the extent of the solid solution. Kim [37] related the strain energy to the Vegard’s slope \( \frac{da}{dx} \), where \( a \) is the lattice parameter and \( x \) the dopant concentration) and suggested a linear relation between the solubility limit and the square of Vegard’s slope for elements belonging to the same group in the periodic table. Figure 4.3 shows the solubility limits of metal ions in pure c-ZrO\(_2\) at 1673 K from literature and from the present work. For c-ZrO\(_2\) solid solutions, Kim [37] set Vegard’s slope as 

\[
\frac{da}{dx} = 0.0212 \Delta r + 0.00023 \Delta \varepsilon,
\]

where \( \Delta r \) is the difference in ionic radius of the metal ion and Zr\(^{4+}\) in 8-fold coordination \( (r_{Me^{x+}} - r_{Zr^{4+}}, \text{in nanometer}) \) and \( \Delta \varepsilon \) is the valence state difference \( (z_{Me^{x+}} - z_{Zr^{4+}}) \). No line was drawn in Figure 4.3 since the elements belong to different groups in the periodic table. It is, however, quite clear that the larger the square of Vegard’s slope, the lower the solubility limit. Our calculated Mn\(^{2+}\) and Mn\(^{3+}\) solubility limits are in a reasonable range.

Moving on to the Mn–Y–Zr–O quaternary system, the calculated MnO activity in YSZ ((ZrO\(_2\))\(_{0.852}\)(YO\(_{1.5}\))\(_{0.148}\)) at 1700 K is shown in Figure 4.4. A very good fit of the experimental data from Matraszek et al. [27] was achieved in the present work. Three isothermal sections of MnO\(_x\)–YO\(_{1.5}\)–ZrO\(_2\) at 1273, 1673, and 2073 K in air are shown in Figure 4.5. Our optimization fits the data from Kawada et al. [9] very well and the data from Kawashima reasonably well [21]. Kawashima [21] investigated MnO\(_x\) solubility in YSZ at two different yttria contents and concluded that the solubility of MnO\(_x\) is higher in YSZ than in pure c-ZrO\(_2\). More experimental investigations are necessary to verify this. According to our calculation, the MnO\(_x\) solubility in c-ZrO\(_2\) changes very little at low yttria content and decreases at high yttria content. Increasing the temperature enlarges the c-ZrO\(_2\) field. At 1673 K in air, only a small amount of yttria is necessary in order to stabilize MnO\(_x\)-doped c-ZrO\(_2\).
Figure 4.3 Solubility limits of metal ions in c-ZrO$_2$ at 1673 K from literature [38, 39, 40, 41, 42, 43] and the present work.

Figure 4.4 MnO activity in MnO$_x$-doped YSZ ((ZrO$_2$)$_{0.852}$(YO$_{1.5}$)$_{0.148}$) at 1700 K. The experimental data are from Matraszek et al. [27].
Modeling of the Mn-Y-Zr-O System

(a) Kawada et al., 1992

(b) Kawashima, 1999
Figure 4.5 Isothermal sections of the MnOₓ–YO₁.₅–ZrO₂ system in air, (a) at 1273 K, (b) at 1673 K, (c) at 2073 K. The experimental data are from Kawada et al. [9] and from Kawashima [21].

Figure 4.6 shows the calculated MnOₓ solubility in YSZ ((ZrO₂)₀.₈₅₂(YO₁.₅)₀.₁₄₈) in air at different temperatures. The solubility increases monotonously from 4 to 16 cat.% with an increase of temperature from 1200 to 1800 K. The relationship between the MnOₓ solubility and the oxygen partial pressure at 1273 K is plotted in Figure 4.7. Figure 4.7 is similar to Figure 4.2.

4.7 Conclusions

In the present work, we reviewed all the experimental data on the Mn–Zr–O and the Mn–Y–Zr–O systems. A complete description of the Mn–Y–Zr–O system is presented. In the Mn–Y–Zr–O system, we include MnOₓ solubility in t- and c-ZrO₂, but not in m-ZrO₂. Mn²⁺ and Mn³⁺ solubility limits in pure c-ZrO₂ at 1673 K were calculated and compared with those of other metal ions. Our calculated results are in a reasonable range. The ZrO₂–MnOₓ phase diagram and three isothermal sections of MnOₓ–YO₁.₅–ZrO₂ in air were calculated.
Figure 4.6 MnO$_x$ solubility in YSZ ((ZrO$_2$)$_{0.852}$($YO_{1.5}$)$_{0.148}$) in air. The experimental data are from Kawada et al. [9].

Figure 4.7 MnO$_x$ solubility in YSZ ((ZrO$_2$)$_{0.852}$($YO_{1.5}$)$_{0.148}$) at 1273 K versus oxygen partial pressure. The stable regions of Mn oxides against oxygen partial pressure are indicated.
4.8 References


[37] D.-J. Kim, "Lattice parameters, ionic conductivities, and solubility limits in fluorite-

[38] T. Y. Tien and E. C. Subbarao, "X-ray and electrical conductivity study of the fluorite

[39] Y. Du and Z. Jin, "Optimization and calculation of the ZrO₂-MgO system", 

[40] K. Sasaki, P. Bohac, and L. J. Gauckler, "Phase equilibria in the system ZrO₂-In₂O₃", 

[41] G. S. Corman and V. S. Stubican, "Phase equilibria and ionic conductivity in the


Kawada, and J. Mizusaki, "Phase diagram calculations of ZrO₂-based ceramics with an
emphasis on the reduction/oxidation equilibria of cerium ions in the ZrO₂-YO₁.₅-CeO₂-
5 CALPHAD Modeling of the La$_2$O$_3$–Y$_2$O$_3$ System


Abstract

Using the CALPHAD approach, we model the La$_2$O$_3$–Y$_2$O$_3$ system as a pseudo-binary section of the La–Y–O ternary system. The descriptions of two binary sub-systems, La–O and Y–O, are taken from previous assessments with revision. The experimental data on the La$_2$O$_3$–Y$_2$O$_3$ system are reviewed and the parameters related to the La$_2$O$_3$–Y$_2$O$_3$ section are optimized. Our calculated La$_2$O$_3$–Y$_2$O$_3$ phase diagram agrees well with most experimental data. Further experimental efforts are necessary to verify the phase relations at temperatures below 2000 K.

5.1 Introduction

The La$_2$O$_3$–Y$_2$O$_3$ system is of particular interest for applications in high refractory materials for optical devices, core materials for casting, and electrode materials for solid oxide fuel cells [1, 2]. Due to the isotropic cubic structure, high melting point (2712 K), and excellent light transmittance capability, yttria exhibits great potential as optical materials and is becoming competitive with other infrared materials like alumina [3]. A transient second-phase sintering technique based on the La$_2$O$_3$–Y$_2$O$_3$ phase diagram has been developed by Rhodes [4], which results in fully dense and transparent La$_2$O$_3$-doped yttria solid solution. There also exists a perovskite LaYO$_3$ in the La$_2$O$_3$–Y$_2$O$_3$ system. Sr-doped LaYO$_3$ was found to exhibit proton conduction, which makes it a potential candidate as anode materials for solid oxide fuel cells [2, 5]. Obviously the phase relations in the La$_2$O$_3$–Y$_2$O$_3$ system is of great importance for the above-mentioned applications. The high-temperature part of this system has been investigated by a few groups [1,6]. Controversy exists on the low temperature part of the phase diagram (below 2000 K), especially on the La$_2$O$_3$-rich side. No investigations have been done for temperatures below 1400 K. In the present work, the experimental information on the La$_2$O$_3$–Y$_2$O$_3$ system is reviewed. We model the La$_2$O$_3$–Y$_2$O$_3$ system as a pseudo-binary section of the La–Y–O ternary system. The parameters related to the La$_2$O$_3$–Y$_2$O$_3$ section are...
optimized and a calculated La$_2$O$_3$–Y$_2$O$_3$ phase diagram is presented and compared with experimental data.

**5.2 Experimental data**

No thermodynamic data are available on the La–Y–O system. The experimental information is mainly about phase boundaries in the La$_2$O$_3$–Y$_2$O$_3$ pseudo-binary system.

Five solid solution phases have been reported in the La$_2$O$_3$–Y$_2$O$_3$ system. These solution phases are based on the different polymorphs of binary rare earth sesquioxides (RE$_2$O$_3$, RE = rare earth element). Rare earth sesquioxides have been identified to have five distinct polymorphs, A, B, C, H, X. The A, B, C types are stable at low temperature and the H and X types are stable at temperatures above 2273 K [7]. Only few rare earth sesquioxides have all five polymorphs. However, these five types all appear in the La$_2$O$_3$–Y$_2$O$_3$ system, but as solution phases with extended solubilities. We also use A, B, C, H, X to name these solution phases. In the La$_2$O$_3$–Y$_2$O$_3$ system, the A, B, C phases, existing in different composition regions, are stable at low temperature. The A phase originates from A-La$_2$O$_3$ and the C phase originates from C-Y$_2$O$_3$ (α-Y$_2$O$_3$), while the B phase only appears in the middle of the composition range. With increasing temperature, they all transform to the H phase and later to the X phase (or melt directly for the Y$_2$O$_3$-rich side). The high-temperature phases, H and X, cannot be obtained at room temperature by quenching. However, the existence of these two phases has been confirmed by high temperature X-ray diffraction (XRD) [1,6]. Two ternary compounds, La$_3$YO$_6$ and LaYO$_3$ have been reported [8, 9], but only LaYO$_3$ was confirmed.

### 5.2.1 LaYO$_3$

LaYO$_3$ was first reported by Padurow and Schusterius [8]. LaYO$_3$ has a perovskite-type structure. Different distortions have been reported for LaYO$_3$, i.e. orthorhombic [1,6, 10, 11] and monoclinic [12]. The disagreement in distortions is probably due to different preparation methods and different interpretations of XRD data. Mizuno et al. [11] reported a high-temperature form of LaYO$_3$ with a monoclinic perovskite-type structure. It turns out later that the high-temperature form of LaYO$_3$ is actually the B solution phase, which has a monoclinic Sm$_2$O$_3$-type structure [1, 13], i.e. LaYO$_3$ transforms into the B phase at high temperature.
The transformation temperature of LaYO$_3$ into the B phase was determined to be 1823 K by Coutures and Foex [6] and 1858 K by Lopato et al. [1]. Based on conductivity measurements, Gorelov et al. [12] detected a phase transition of LaYO$_3$ at 1778±20 K on heating LaYO$_3$, at which temperature the conductivity of LaYO$_3$ decreases sharply. This phase transition was concluded to be the transformation from monoclinic LaYO$_3$ into the B solution phase, accompanied by structural disordering. Berndt et al. [14] reported that LaYO$_3$ dissociates into a mixture of the B and C phases at 1743±30 K (peritectoid). In the present work, the transition temperature from Lopato et al. [1] is used.

The composition range of LaYO$_3$ was investigated by a few groups [1, 10, 11, 15, 16]. Lopato et al. [1] detected a narrow homogeneity range (from 48 to 53 mol% Y$_2$O$_3$) at 1623 K. Yoshimura and Rong [16] reported that at 1673 K, LaYO$_3$ exists in a composition range of 52–53 mol% Y$_2$O$_3$. The off-stoichiometry of LaYO$_3$ was attributed to an incomplete ordering. In the present work, LaYO$_3$ is treated as a stoichiometric compound.

5.2.2 Phase diagram data

The phase diagram of La$_2$O$_3$–Y$_2$O$_3$ has been published by Cassedanne and Forestier [9], Coutures and his coauthors [6, 10, 15], and Lopato et al. [1]. Coutures and his coauthors [6, 10, 15] investigated the phase relations in the La$_2$O$_3$–Y$_2$O$_3$ system from 1673 K up to the melting point, using thermal analyses and high temperature XRD. The H single-phase region was suggested to occupy the whole composition range, while the X single-phase region stops somewhere close to pure Y$_2$O$_3$. Lopato et al. [1] reinvestigated this system in a temperature range of 1623–2723 K. The samples were prepared by co-precipitation of hydroxides. The phase boundaries were determined using differential thermal analysis (DTA), XRD (room temperature to 2273 K), and pétrographic analyses. Their diagram is quite similar to the one from Coutures and Foex [6]. Lopato et al. [1] detected a minimum on the phase boundary between the H phase and the A, B, and C phases at 45 mol% Y$_2$O$_3$ and 2003 K as a eutectoid point. At 1913 K, 30 mol% Y$_2$O$_3$ dissolves in A-La$_2$O$_3$, while the solubility of La$_2$O$_3$ in C-Y$_2$O$_3$ varies very little in the temperature range of 1623–2173 K and is 15 mol% La$_2$O$_3$ at 2173 K. Andrievskaya et al. [17] studied the liquidus surface in the HfO$_2$–Y$_2$O$_3$–La$_2$O$_3$ system by DTA in helium at temperatures up to 2773 K and in air at temperatures up to 3273 K.
The liquidus temperature of 50 mol% $Y_2O_3$ – 50 mol% $La_2O_3$ was determined to be at 2523 K.

The high-temperature $Y_2O_3$-rich part of the $La_2O_3$–$Y_2O_3$ system is of great technical importance and has been investigated by a few groups. Rhodes [4] sintered $La_2O_3$-doped yttria with 12 to 14 mol% $La_2O_3$ at 2343 to 2543 K for ≥6 h and quenched to 1673 K within 1 min. The H+C/C boundary at 2443 K was determined to be between 4.95 to 6.7 mol% $La_2O_3$ by ceramographic and grain-growth studies and 6.8 mol% $La_2O_3$ by microprobe. The determined H+C/C boundary agrees with the one from Coutures and Foex [10], while the H/H+C boundary shift towards the $La_2O_3$-rich side, almost coincident with the X+H two-phase region in the published diagram from Coutures and Foex [6]. Wei et al. [18] analyzed the structures and compositions in single-phase and two-phase $La_2O_3$-doped $Y_2O_3$ materials fabricated by the transient solid second-phase sintering, using analytical electron microscopy (AEM). The content of $La_2O_3$ in the C phase at 2223 K was detected to be 6.7 to 9.1 mol%. Horvath et al. [3] studied the precipitation reactions in sintered samples of 9 mol% $La_2O_3$-doped yttria up-quenched from the C single-phase region into the H+C two-phase region. The determined $La_2O_3$ concentration in the matrix C phase agrees with Rhodes [4]. These three papers [3,4, 18] all reported that the $La_2O_3$ concentration in the second-phase precipitates is far in excess of the published H/H+C boundary from Coutures and Foex [6]. This was believed to arise from a re-equilibration of the second phase in the C+B phase field during quenching.

Berndt et al. [14] and Yoshimura and Rong [16] investigated the low-temperature part of the $La_2O_3$–$Y_2O_3$ system (below 2000 K), both using XRD and lattice constant measurements. Berndt et al. [14] investigated the temperature region between 1523 and 1823 K. The samples were prepared by solid state reactions in air at temperatures up to 1823 K and up to 14 days. At 1823 K, 23.5 mol% $Y_2O_3$ is soluble in A-$La_2O_3$ and up to 16.3 mol% $La_2O_3$ is soluble in C-$Y_2O_3$. Yoshimura and Rong [16] investigated the phase relations at 1673 K, 1823 K, and 1973 K. The samples were prepared from melts and were annealed at lower temperatures. Their determined phase boundaries of B/C and LaYO$_3$+C/C are in reasonable agreement with the results from Berndt et al. [14] and Lopato et al. [1], while their A/B phase boundaries obviously disagree with other results.
5.3 Binary sub-systems

The descriptions of two binary sub-systems, La-O and Y-O are taken from previous assessments. The description of La-O is from Grundy et al. [19] and that of Y-O is from the present authors [20]. In the two previous assessments, different models which are not compatible with each other were used for La$_2$O$_3$ and Y$_2$O$_3$. Based on the crystal structures of different polymorphs of RE$_2$O$_3$, we change the models for La$_2$O$_3$ and β-Y$_2$O$_3$. This leads to a consistent description for all the binary oxides and also for all the solution phases in the La$_2$O$_3$–Y$_2$O$_3$ system. The thermodynamic descriptions of these two binary sub-systems are hence revised. No assessment is available for the La–Y system and this sub-system is not considered in our modeling.

5.3.1 Crystal structure of RE$_2$O$_3$

A large number of investigations have been done on the crystal structure of different polymorphs of RE$_2$O$_3$ and these were recently reviewed by Adachi and Imanaka [7]. Among the five polymorphs of RE$_2$O$_3$, the A form has a hexagonal structure of space group $P32/m$ and the metal atoms are in a seven-fold coordination. The B form is a monoclinic distortion of the A form with a space group $C2/m$ and the metal atoms are in a six- or seven-fold coordination. The C form is of the cubic bixbyite type with a space group $Ia3$, isostructural with Mn$_2$O$_3$. The metal atoms are six-coordinated. These three different structures can all be derived from the cubic fluorite structure (space group $Fm\overline{3}m$, isostructural with CaF$_2$). In the cubic fluorite structure, the metal atoms are eight-coordinated with cubic polyhedra sharing all edges to form a three-dimensional network. The C-type structure could be obtained by removing one quarter of oxygen atoms, while the A-type structure could be obtained by preserving the oxygen sublattice of the fluorite and move the metal atoms into interstitial sites [7]. The B-type structure is similar to the A-type one, but different in the coordination of metal atoms. The crystal structures of high-temperature forms, H and X, have been studied by neutron diffraction analysis [21]. The H form was reported to possess a hexagonal structure with a space group $P6_3/mmc$, closely related to the A-type structure. The X form was reported to be cubic ($I\overline{m}3m$). In the present work, the A-, B-, C-, H-forms are described using the same model $(\text{RE}^{3+})_2(\text{O}^{2-}, \text{Va})_3(\text{O}^{2-}, \text{Va})$. The X-form is modeled the same as cubic fluorite using the model $(\text{RE}^{3+})_1(\text{O}^{2-}, \text{Va})_2$.  

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5.3.2 Y–O

The description of the Y–O system is taken from our previous work on the Y–Zr–O system [20]. A little change is made on the model for the high-temperature yttria phase, β-Y_2O_3. It is still uncertain if the crystal structure of β-Y_2O_3 is hexagonal or cubic fluorite. In the description of the Y–Zr–O system, we assumed β-Y_2O_3 to be cubic fluorite. This turns out to be an elegant solution for modeling the ZrO_2–YO_1.5 system. Treating β-Y_2O_3 as cubic fluorite is unfortunately, not compatible with the published La_2O_3–Y_2O_3 phase diagrams. In the experimentally determined phase diagrams from Coutures and his co-authors [6, 10, 15] and Lopato et al. [1], the H single-phase region covers the whole composition range from pure La_2O_3 to pure Y_2O_3, while the X single-phase region starts from pure La_2O_3 and stops somewhere close to pure Y_2O_3. This implies that the high-temperature yttria phase should be hexagonal (H). It does not seem reasonable not to trust the published La_2O_3–Y_2O_3 phase diagrams. We therefore, have to change our model for β-Y_2O_3.

In the present work, β-Y_2O_3 is modeled as (Y, Y^{3+})_2(O^{2-}, Va)_3(O^{2-}, Va)_1. Neutral Y is included to model the nonstoichiometry of β-Y_2O_{x-y}, in the same way as for α-Y_2O_{x-y}. The parameter $^\circ G_{Y^{3+}O^{2-}:Va}$, which represents the Gibbs energy of stoichiometric β-Y_2O_3, is adjusted using the transition temperature and enthalpy between β-Y_2O_3 and α-Y_2O_3. The Gibbs energy functions of other end members for β-Y_2O_3 are obtained in the same way as for α-Y_2O_3. The Gibbs energy of liquid Y_2O_3 is also adjusted using a melting temperature of 2712 K and a melting enthalpy of 84 kJ/mol. No other parameters for the Y–O system are changed. The parameters for α-Y_2O_3, β-Y_2O_3, and liquid Y_2O_3 are listed in Table 5.1. The calculated Y–O phase diagram in the present work is very similar to Figure 4 in our previous paper [20]. Only a slight difference can be found in the β-Y_2O_3 liquidus.
5.3.3 La–O

For the La–O system, we accept the description by Grundy et al. [19], but change the model for La₂O₃. The model \((\text{La}, \text{La}^{3+})_2(O^{2-}, \text{Va})_3(O^{2-}, \text{Va})_1\) is used here for A- and H-La₂O₃. X-La₂O₃ is treated as cubic fluorite, using the model \((\text{La}, \text{La}^{3+})_1(O^{2-}, \text{Va})_2\). Neutral La is included to model the nonstoichiometry of La₂O₃₋ₓ. The models for the metal phases (dhcp-La, fcc-La, and bcc-La) and for the liquid are kept without change. The parameters for all the phases in the La–O system are re-optimized, following Grundy et al.’s work [19]. At the end, only the parameters of oxide phases and the Gibbs energy function of liquid La₂O₃ are changed. The parameters for A-, H-, X-, and liquid La₂O₃ are listed in Table 5.1. The calculated La–O phase diagram from the present work is shown in Figure 5.1. The La–O phase diagram from Grundy et al. [19] shows a sharp increase in the La₂O₃ melting temperature when going from stoichiometric La₂O₃ towards La. This does not exist in our diagram. Our La₂O₃ liquidus also shifts towards lower temperature, while the eutectic temperature of liquid → bcc-La + A-La₂O₃ increases from 1168 K [19] to 1175 K in the present work. Apart from this, there is no other change.

![Figure 5.1](image_url)  
Calculated La–O phase diagram from the present work.
5.4 Thermodynamic models

In the present work, we treat the La$_2$O$_3$–Y$_2$O$_3$ system as a pseudo-binary section of the La–Y–O system. The parameters related to the La$_2$O$_3$–Y$_2$O$_3$ section are optimized. This concerns the liquid phase, LaYO$_3$, and five solid oxide solution phases (A, B, C, H, X).

The liquid phase is modeled as $(\text{La}^{3+}, \text{Y}^{3+})_p(\text{O}^{2-}, \text{Va}^\theta)_q$, using the two-sublattice model for ionic liquids [22, 23]. We assume that the La$_2$O$_3$ and Y$_2$O$_3$ liquids mix ideally. No extra interaction parameters are used, except those taken from binary sub-systems. We model LaYO$_3$ as a stoichiometric compound and relate its Gibbs energy to the Gibbs energies of A-La$_2$O$_3$ and C-Y$_2$O$_3$:

$$GLAYO_3 = 0.5GLA2O3A + GCCYO15 + V_1 + V_2T \quad \text{Eq. 5.1}$$

$GLAYO_3$, $GLA2O3A$, and $GCCYO15$ are the molar Gibbs energies of LaYO$_3$, A-La$_2$O$_3$, and 0.5 mol C-Y$_2$O$_3$. The parameters $V_1$ and $V_2$ are optimized in the present work.

The five ternary solid oxide solution phases, A, B, C, H, X, are all treated as a mixture of the corresponding binary oxide solution phases. Here we use the A phase as an example. We model the A phase as $(\text{La}, \text{La}^{3+}, \text{Y}^{3+})_2(\text{O}^{2-}, \text{Va})_3(\text{O}^{2-}, \text{Va})_4$. The Gibbs energies of all end-members are taken from binary subsystems, i.e. from La–O and Y–O. The lattice stability of metastable A-Y$_2$O$_3$ is from Zinkevich (private communication). For the B, C, H phases, similar models are used. The lattice stabilities of metastable B-La$_2$O$_3$, B-Y$_2$O$_3$, and C-La$_2$O$_3$ are also from Zinkevich (private communication). The X phase is modeled as $(\text{La}, \text{La}^{3+}, \text{Y}^{3+})_i(\text{O}^{2-}, \text{Va})_j$. The Gibbs energy of metastable X-Y$_2$O$_3$ is given as:

$$GXXYO15 = GCCYO15 + V_3 + V_4T \quad \text{Eq. 5.2}$$

for 0.5 mol X-Y$_2$O$_3$. The parameters $V_3$ and $V_4$ are adjusted using an assumed transition temperature of 2900 K and an assumed transition enthalpy of 7.4 kJ/mol for the X<->H transition (metastable). For oxide solution phases, we include the interaction parameters between La$^{3+}$ and Y$^{3+}$:

$$^iI_{La^{3+},Y^{3+},O^{2-},Va} = ^iI_{La^{3+},Y^{3+},O^{2-},Va} = ^iI_{La^{3+},Y^{3+},Va,O^{2-}} = ^iI_{La^{3+},Y^{3+},Va,Va} = ^iV_5 + ^iV_6T, \quad i = 0, 1, 2 \quad \text{Eq. 5.3}$$

for the A, B, C, H phases and:

$$^iI_{La^{3+},Y^{3+},O^{2-}} = ^iI_{La^{3+},Y^{3+},Va} = ^iV_5 + ^iV_6T, \quad i = 0, 1, 2 \quad \text{Eq. 5.4}$$
for the X phase. These interaction parameters are optimized using experimental data related to the La$_2$O$_3$–Y$_2$O$_3$ pseudo-binary section.

5.5 Optimization and results

The assessment is made using the software PARROT included in the Thermo-Calc Databank System [24]. The interaction parameters for A, B, C, H, X and the lattice stability parameters for LaYO$_3$ are optimized in the present work.

For the liquidus, we use the data from both Coutures and Foex [6] and Lopato et al. [1]. The X/H and the H/A phase boundary data are from Coutures and Foex [6]. The H/B phase boundary data from Lopato et al. [1] are not used. These data points might also correspond to the low-temperature part of the H/H+C phase boundary, as shown in the published phase diagram of La$_2$O$_3$–Y$_2$O$_3$ from Coutures and Foex [6]. We include a 3-phase equilibrium of H+A+B from Lopato et al. [1]. The H/C phase boundary data are from Coutures and his coauthors [6, 10] and Lopato et al. [1]. Large scatter exists on the A/B phase boundary data. Those from Yoshimura and Rong [16] are obviously away from the others. Instead, we use the data from Berndt et al. [14] and Lopato et al. [1]. The B/C phase boundary data are from Berndt et al. [14] and Yoshimura and Rong [16]. For LaYO$_3$, we use the measured transition temperature of LaYO$_3$ → B from Lopato et al. [1], the B/B+LaYO$_3$ phase boundary data from Lopato et al. [1], the LaYO$_3$+C/C phase boundary data from Lopato et al. [1] and Yoshimura and Rong [16], and an assumed standard enthalpy of formation for LaYO$_3$ at 298.15 K (from oxides) from the present work. Cheng and Navrotsky [25] measured enthalpies of formation of LaBO$_3$ perovskites (B = Al, Ga, Sc, and In) at 298.15 K (from oxides), using high-temperature solution calorimetry. They found that the enthalpy of formation of LaBO$_3$ increases when the tolerance factor, $t$, increases. The tolerance factor, $t$, was first proposed by Goldschmidt (cited by Li et al. [26]) to correlate the stability of perovskites. For an ABO$_3$ perovskite, $t$ is defined as:

$$t = \frac{r_{AO}}{\sqrt{2}r_{BO}} = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)} \quad \text{Eq. 5.5}$$

where $r_{AO}$ and $r_{BO}$ are bond lengths calculated as sums of ionic radii $r_A$, $r_B$, and $r_O$. $t = 1$ corresponds to an ideal cubic perovskite structure, composed by corner-linked BO$_6$ octahedra with A cations 12-coordinated at the center of each unit cell. When $t$ deviates from 1, typically
in the range of 0.8–1.1, a distorted perovskite will form with lower symmetry than cubic. For LaBO\(_3\) perovskites, Cheng and Navrotsky [25] proposed a linear relation between the enthalpy of formation and the tolerance factor as:

\[
\Delta H_{\text{f,ox}} = -389.3t + 323.8 \quad \text{Eq. 5.6}
\]

where \(\Delta H_{\text{f,ox}}\) is in kJ/mol. Using Eq. 5.6, we get a standard enthalpy of formation of \(-6.7\) kJ/mol for LaYO\(_3\), implying that LaYO\(_3\) is not a very stable perovskite, compared with LaAlO\(_3\) which has an enthalpy of formation of \(-69.61\pm3.23\) kJ/mol measured by Cheng and Navrotsky [25]. According to the empirical structure map of ABO\(_3\) perovskites by Li et al. [26], LaYO\(_3\) is located very closely to the boundary between perovskites and non-perovskites. The assumed value of \(-6.7\) kJ/mol for LaYO\(_3\) should be qualitatively correct and we include it into the optimization.

It is quite probable that the B solution phase in the La\(_2\)O\(_3\)–Y\(_2\)O\(_3\) system will decompose at low temperature. However, the experimental phase boundary data are not conclusive in this regard. By changing the weights of the phase boundary data involving the B phase any decomposition temperature between about 300 K and 1500 K could be obtained. Since the B phase is clearly an entropy stabilized phase and not expected in the ground state of the La\(_2\)O\(_3\)–Y\(_2\)O\(_3\) system, we choose a relatively high, admittedly arbitrary, decomposition temperature of 1400 K and include this in the optimization. It would of course be possible to obtain the same result by changing the weights of the phase boundary data accordingly, but it appears more transparent to make an explicit choice of the decomposition temperature. Further experimental investigation is necessary to determine this temperature.

The parameters are first optimized in a sequence of X→H→A/B/C→LaYO\(_3\). To fit both the B/LaYO\(_3\) and B/C phase boundaries well, we use regular and sub-regular interaction parameters for the B phase, each including a temperature term. No temperature term is used for other solution phases and only a regular interaction parameter is used for the X phase. At the end all parameters are optimized together.

The thermodynamic description of the La\(_2\)O\(_3\)–Y\(_2\)O\(_3\) system is listed in Table 5.1.

| Table 5.1 | Thermodynamic description of the La\(_2\)O\(_3\)–Y\(_2\)O\(_3\) system |
 Modeling of the La-Y-O System

The A phase

\[(La, La^{3+}, Y^{3+})_2(O^{2-}, Va)_3(O^{2-}, Va)\]

\[G_{LaO^{2-}O^{2-}} - 2 H_{La}^{SER} - 4 H_{O}^{SER} = 2 \text{GHSERLA} + 4 \text{GHSEROO} + 304124 + 15.87691T\]

\[G_{LaO^{2-}Va} - 2 H_{La}^{SER} - 3 H_{O}^{SER} = 2 \text{GHSERLA} + 3 \text{GHSEROO} + 204124\]

\[G_{LaVaO^{2-}} - 2 H_{La}^{SER} - H_{O}^{SER} = 2 \text{GHSERLA} + \text{GHSEROO} + 304124 + 15.87691T\]

\[G_{La, Va, Va} - 2 H_{La}^{SER} = 2 \text{GHSERLA} + 204124\]

\[G_{La^{3+}O^{2-}O^{2-}} - 2 H_{La}^{SER} - 4 H_{O}^{SER} = GLA2O3A + \text{GHSEROO} + 100000 + 15.87691T\]

\[G_{La^{3+}O^{2-}Va} - 2 H_{La}^{SER} - 3 H_{O}^{SER} = GLA2O3A\]

\[G_{La^{3+}VaO^{2-}} - 2 H_{La}^{SER} - H_{O}^{SER} = GLA2O3A - 2 \text{GHSEROO} + 100000 + 15.87691T\]

\[G_{La^{3+}, Va, Va} - 2 H_{La}^{SER} = GLA2O3A - 3 \text{GHSEROO}\]

\[G_{Y^{3+}O^{2-}O^{2-}} - 2 H_{Y}^{SER} - 4 H_{O}^{SER} = 2 \text{GAAYO15} + \text{GHSEROO} + 100000 + 15.87691T\]

\[G_{Y^{3+}O^{2-}Va} - 2 H_{Y}^{SER} - 3 H_{O}^{SER} = 2 \text{GAAYO15}\]

\[G_{Y^{3+}VaO^{2-}} - 2 H_{Y}^{SER} - H_{O}^{SER} = 2 \text{GAAYO15} - 2 \text{GHSEROO} + 100000 + 15.87691T\]

\[G_{Y^{3+}, Va, Va} - 2 H_{Y}^{SER} = 2 \text{GAAYO15} - 3 \text{GHSEROO}\]

The B phase

\[(La^{3+}, Y^{3+})_2(O^{2-}, Va)_3(O^{2-}, Va)\]

\[G_{La^{3+}O^{2-}O^{2-}} - 2 H_{La}^{SER} - 4 H_{O}^{SER} = GLA2O3B + \text{GHSEROO} + 100000 + 15.87691T\]

\[G_{La^{3+}O^{2-}Va} - 2 H_{La}^{SER} - 3 H_{O}^{SER} = GLA2O3B\]

\[G_{La^{3+}VaO^{2-}} - 2 H_{La}^{SER} - H_{O}^{SER} = GLA2O3B - 2 \text{GHSEROO} + 100000 + 15.87691T\]

\[G_{La^{3+}, Va, Va} - 2 H_{La}^{SER} = GLA2O3B - 3 \text{GHSEROO}\]

\[G_{Y^{3+}O^{2-}O^{2-}} - 2 H_{Y}^{SER} - 4 H_{O}^{SER} = 2 \text{GBBYO15} + \text{GHSEROO} + 100000 + 15.87691T\]

\[G_{Y^{3+}O^{2-}Va} - 2 H_{Y}^{SER} - 3 H_{O}^{SER} = 2 \text{GBBYO15}\]

\[G_{Y^{3+}VaO^{2-}} - 2 H_{Y}^{SER} - H_{O}^{SER} = 2 \text{GBBYO15} - 2 \text{GHSEROO} + 100000 + 15.87691T\]

\[G_{Y^{3+}, Va, Va} - 2 H_{Y}^{SER} = 2 \text{GBBYO15} - 3 \text{GHSEROO}\]

The C phase

\[(La^{3+}, Y, Y^{3+})_3(O^{2-}, Va)_3(O^{2-}, Va)\]

\[G_{La^{3+}O^{2-}O^{2-}} - 2 H_{La}^{SER} - 4 H_{O}^{SER} = GLA2O3C + \text{GHSEROO} + 100000 + 15.87691T\]

\[G_{La^{3+}O^{2-}Va} - 2 H_{La}^{SER} - 3 H_{O}^{SER} = GLA2O3C\]
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\[
\begin{align*}
\Delta G_{La^{3+},Va^{3+},O^{2-}} & - 2 H_{La}^{SER} - H_{O}^{SER} = GLA2O3C - 2 GHSEROO + 100000 + 15.876917I \\
\Delta G_{La^{3+},Va^{3+},O^{2-}} & - 2 H_{La}^{SER} = GLA2O3C - 3 GHSEROO \\
\Delta G_{Y^{3+},O^{2-}} & - 2 H_{Y}^{SER} - 4 H_{O}^{SER} = 2 GHSERYY + 4 GHSEROO + 345600 + 15.876917I \\
\Delta G_{Y^{3+},O^{2-}} & - 2 H_{Y}^{SER} - 3 H_{O}^{SER} = 2 GHSERYY + 3 GHSEROO + 245600 \\
\Delta G_{YVa^{3+},O^{2-}} & - 2 H_{Y}^{SER} - H_{O}^{SER} = 2 GHSERYY + GHSEROO + 345600 + 15.876917I \\
\Delta G_{YVa^{3+},O^{2-}} & - 2 H_{Y}^{SER} = 2 GHSERYY + 245600 \\
\Delta G_{Y^{3+},O^{2-}} & - 2 H_{Y}^{SER} - 4 H_{O}^{SER} = 2 GCCYO15 + GHSEROO + 100000 + 15.876917I \\
\Delta G_{Y^{3+},O^{2-}} & - 2 H_{Y}^{SER} - 3 H_{O}^{SER} = 2 GCCYO15 \\
\Delta G_{Y^{3+},O^{2-}} & - 2 H_{Y}^{SER} - H_{O}^{SER} = 2 GCCYO15 + 2 GHSEROO + 100000 + 15.876917I \\
\Delta G_{Y^{3+},O^{2-}} & - 2 H_{Y}^{SER} = 2 GCCYO15 - 3 GHSEROO \\
\Delta G_{La^{3+},Y^{3+},O^{2-}} & - 2 H_{La}^{SER} - H_{O}^{SER} = GLA3O3C - 2 GCCYO15 - 3 GHSEROO + 345600 + 15.876917I \\
\Delta G_{La^{3+},Y^{3+},O^{2-}} & - 2 H_{La}^{SER} = GLA3O3C - 3 GCCYO15 - 3 GHSEROO + 245600 \\
\Delta G_{La^{3+},Y^{3+},O^{2-}} & - 2 H_{La}^{SER} = GLA3O3C - 4 GCCYO15 - 3 GHSEROO + 100000 + 15.876917I \\
\end{align*}
\]
Modeling of the La–Y–O System

The H phase

\[(La,La^{3+},Y,Y^{3+})_2(O^{2-},Va)_1(O^{2-},Va)_1\]

- \(G_{LaO^{2-},O^{2-},Va}^{SER} - 2H_{La}^{SER} - 4H_{O}^{SER} = 2\, GSER\, La + 4\, GSER\, O + 304124 + 15.87691T\)
- \(G_{LaO^{2-},Va}^{SER} - 2H_{La}^{SER} - 3H_{O}^{SER} = 2\, GSER\, La + 3\, GSER\, O + 204124\)
- \(G_{LaVaO^{2-},Va}^{SER} - 2H_{La}^{SER} - H_{O}^{SER} = 2\, GSER\, La + GSER\, O + 304124 + 15.87691T\)
- \(G_{La,La,La}^{SER} - 2H_{La}^{SER} = 2\, GSER\, La + 204124\)
- \(G_{La^{3+},O^{2-},Va}^{SER} - 2H_{La}^{SER} - 4H_{O}^{SER} = GLA2O3H + GSER\, O + 100000 + 15.87691T\)
- \(G_{La^{3+},Va,O^{2-}}^{SER} - 2H_{La}^{SER} - 3H_{O}^{SER} = GLA2O3H\)
- \(G_{La^{3+},Va,O^{2-}}^{SER} - 2H_{La}^{SER} - H_{O}^{SER} = GLA2O3H - 2\, GSER\, O + 100000 + 15.87691T\)
- \(G_{La^{3+},Va,Va}^{SER} = 2\, GSER\, La + 245600\)

The X phase

\[(La,La^{3+},Y^{3+})_1(O^{2-},Va)\]

- \(G_{LaO^{2-},Va}^{SER} - H_{La}^{SER} - 2H_{O}^{SER} = GSER\, La + 2\, GSER\, O + 102062\)
- \(G_{La,Va}^{SER} - H_{La}^{SER} = GSER\, La + 102062\)
- \(G_{La^{3+},O^{2-},Va}^{SER} - 2H_{La}^{SER} - 3H_{O}^{SER} = 0.5\, GLA2O3X + 0.5\, GSER\, O + 245600\)
- \(G_{La^{3+},Va,O^{2-}}^{SER} - 2H_{La}^{SER} - H_{O}^{SER} = 0.5\, GLA2O3X - 1.5\, GSER\, O + 245600\)
- \(G_{La^{3+},Va,Va}^{SER} = 0.5\, GLA2O3X + 0.5\, GSER\, O + 9.3511T\)
- \(G_{La^{3+},Va}^{SER} = 0.5\, GLA2O3X - 1.5\, GSER\, O + 9.3511T\)
- \(G_{La^{3+},Va}^{SER} = GXXYO15 + 0.5\, GSER\, O + 9.3511T\)
- \(G_{La^{3+},Va}^{SER} = GXXYO15 - 0.5\, GSER\, O + 9.3511T\)
- \(I_{La^{3+},Va}^{SER} = I_{La^{3+},Va}^{SER} + 0.5\, I_{La^{3+},Va}^{SER} + 0.5\, I_{La^{3+},Va}^{SER} = +27920\)
- \(I_{La^{3+},Va}^{SER} = I_{La^{3+},Va}^{SER} + 0.5\, I_{La^{3+},Va}^{SER} + 0.5\, I_{La^{3+},Va}^{SER} = +12879\)

LaYO3

\[(La^{3+})(Y^{3+})(O^{2-})_3\]

- \(G_{La^{3+},Y^{3+},O^{2-}}^{SER} - H_{La}^{SER} - 3H_{O}^{SER} = GLAYO3\)

Liquid

\[(La^{3+},Y^{3+})_p(O^{2-},Va^{2+})_q\]

- \(p = 2y^{O_{2-}} + qy^{Va_{2+}}, q = 3y^{La_{3+}} + 3y^{Y^{3+}}\)
- \(G_{La^{3+},O^{2-}}^{SER} - 2H_{La}^{SER} - 3H_{O}^{SER} = GLA2O3LIQ\)
Chapter 5

\[
\begin{align*}
\Delta G_{\text{La}^{3+}\text{Va}^{3+}} - H_{\text{La}}^{\text{SER}} &= \text{GLALIQ} \\
\Delta G_{\text{Y}^{3+}\text{O}^{2-}} - 2 H_{\text{Y}}^{\text{SER}} - 3 H_{\text{O}}^{\text{SER}} &= \text{GY2O3LIQ} \\
\Delta G_{\text{Y}^{3+}\text{Va}^{3+}} - H_{\text{Y}}^{\text{SER}} &= \text{GYYLIQ} \\
\Delta L_{\text{Y}^{3+}\text{O}^{2-}\text{Va}^{3+}} &= +6900 \\
\Delta L_{\text{Y}^{3+}\text{O}^{2-}\text{Va}^{3+}} &= -17000 \\
O_2 (g) \\
\Delta G_{O_2} - 2 H_{O}^{\text{SER}} &= 2 \text{GHSEROO} + RT \ln(1 \times 10^{-5}P) \\
\end{align*}
\]

Functions

\[
\begin{align*}
\text{GLA2O3A} &= -1835600 + 674.72T - 1187\ln T - 0.008T^2 + 620000T^{-1} \\
\text{GLA2O3H} &= +\text{GLA2O3A} + 46000 - 19.89T \\
\text{GLA2O3X} &= +\text{GLA2O3A} + 111160 - 48.11T \\
\text{GLA2O3LIQ} &= -1807513 + 1282.4877 - 20071nr \\
\text{GLA2O3B} &= +\text{GLA2O3A} + 6388 + 0.508T \\
\text{GLA2O3C} &= +\text{GLA2O3A} + 10586 + 5.938T \\
\text{GCCYO15} &= -990900 + 381.86T - 62.85\ln T - 0.0025T^2 + 1172000T^{-1} - 5.9 \times 10^7T^{-2} \\
\text{GHHYO15} &= +\text{GCCYO15} + 12500 - 4.808T \\
\text{GY2O3LIQ} &= +2 \text{GYYLIQ} + 3 \text{GHSEROO} - 1824330 + 245.9T \\
\text{GAAYO15} &= +\text{GCCYO15} + 10584 - 3.3T \\
\text{GBBYO15} &= +\text{GCCYO15} + 5654 - 2.034T \\
\text{GXXYO15} &= +\text{GCCYO15} + 20000 - 8.1T \\
\text{GLAYO3} &= +0.5 \text{GLA2O3A} + \text{GCCYO15} - 8517 - 0.75T \\
\end{align*}
\]

Note: All parameters are in SI units: J, mol, K, Pa; R=8.31451 J/(mol K). GHSERLA, GLALIQ, and GHSEROO are the molar Gibbs energies of pure La and oxygen from Dinsdale, 1991 [27]. GHSERYY and GYYLIQ are the molar Gibbs energies of pure Y from SGTE Unary Database (1996) [28].

Figure 5.2 shows the calculated La$_2$O$_3$–Y$_2$O$_3$ phase diagram from the present work. A comparison between our diagram and the experimental data is shown in Figure 5.3. The reported composition ranges of LaYO$_3$ are not included. Our calculated phase diagram fits the experimental data well. The Y$_2$O$_3$-rich side of the X/H phase boundary from the present work is somewhat lower than the data from Coutures and Foex [6]. At temperatures below 2200 K, our calculated H/H+C phase boundary deviates from the experimental data [6]. The low-temperature part of our La$_2$O$_3$–Y$_2$O$_3$ phase diagram (below 2000 K) fits the experimental data reasonably well. Our calculated A+B two-phase region is wider than those reported from the literature. Scatter also exists on the reported B/B+LaYO$_3$ phase boundary and the one from Yoshimura and Rong [16] obviously shifts too much towards the Y$_2$O$_3$-rich side. Including temperature terms for the interaction parameters of the A, H, and C phases could improve the fit somewhat, but not enough to motivate their use. A list of the temperatures and compositions of invariant equilibria is shown in Table 5.2. The transition temperature of
LaYO₃ → B is calculated to be 1862 K. The enthalpy of formation of LaYO₃ at 298.15 K (from oxides: A-La₂O₃ and C-Y₂O₃) is −8.5 kJ/mol from the present work as compared to the estimated value of −6.7 kJ/mol.

Figure 5.2 Calculated La₂O₃–Y₂O₃ phase diagram in air from the present work.

Figure 5.3 Calculated La₂O₃–Y₂O₃ phase diagram in air from the present work compared with experimental data from Coutures and his coauthors [6, 10], Berndt et al. [14], Rhodes [4].

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5.6 Conclusions

In this paper, the experimental data on the \( \text{La}_2\text{O}_3-\text{Y}_2\text{O}_3 \) system are critically reviewed. We treat the \( \text{La}_2\text{O}_3-\text{Y}_2\text{O}_3 \) system as a pseudo-binary section of the La–Y–O ternary system. A thermodynamic description of the \( \text{La}_2\text{O}_3-\text{Y}_2\text{O}_3 \) system is proposed. The \( \text{La}_2\text{O}_3-\text{Y}_2\text{O}_3 \) phase diagram in air is calculated and compared with experimental data. Our results fit the experimental data well. The present assessment is mainly based on the available phase diagram data. Experimental investigations on the thermodynamic properties of \( \text{LaYO}_3 \) and solution phases and on the low-temperature part of the system would be helpful to improve the present description.

Table 5.2: Calculated temperatures and compositions of invariant equilibria compared with experimental data

<table>
<thead>
<tr>
<th>Invariant equilibrium</th>
<th>Temp., K</th>
<th>( x(\text{Y}_2\text{O}_3) )</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid+H=X (peritectic)</td>
<td>2583</td>
<td>0.83 (Liquid)</td>
<td>[1]</td>
</tr>
<tr>
<td></td>
<td>2625</td>
<td>0.86 (Liquid), 0.90 (X), 0.92 (H)</td>
<td>This work</td>
</tr>
<tr>
<td>Liquid→X (congruent)</td>
<td>2483</td>
<td>0.35 (Liquid, X)</td>
<td>[6]</td>
</tr>
<tr>
<td></td>
<td>2488</td>
<td>0.3 (Liquid, X)</td>
<td>[1]</td>
</tr>
<tr>
<td></td>
<td>2487</td>
<td>0.4 (Liquid, X)</td>
<td>This work</td>
</tr>
<tr>
<td>X→H (congruent)</td>
<td>2213</td>
<td>0.4 (X, H)</td>
<td>[6]</td>
</tr>
<tr>
<td></td>
<td>2218</td>
<td>0.35 (X, H)</td>
<td>[1]</td>
</tr>
<tr>
<td></td>
<td>2221</td>
<td>0.36 (X, H)</td>
<td>This work</td>
</tr>
<tr>
<td>H+A=B (peritectoid)</td>
<td>2003</td>
<td>0.45 (H)</td>
<td>[1]</td>
</tr>
<tr>
<td></td>
<td>1996</td>
<td>0.45 (A), 0.516 (B), 0.532 (H)</td>
<td>This work</td>
</tr>
<tr>
<td>H=B+C (eutectoid)</td>
<td>2173</td>
<td>0.71 (B)</td>
<td>[1]</td>
</tr>
<tr>
<td></td>
<td>1993</td>
<td>0.592 (B), 0.597 (H), 0.78 (C)</td>
<td>This work</td>
</tr>
<tr>
<td>( \text{LaYO}_3 \leftrightarrow \text{B} ) (congruent)</td>
<td>1823</td>
<td></td>
<td>[6]</td>
</tr>
<tr>
<td></td>
<td>1858</td>
<td></td>
<td>[1]</td>
</tr>
<tr>
<td></td>
<td>1778</td>
<td></td>
<td>[12]</td>
</tr>
<tr>
<td></td>
<td>1862</td>
<td></td>
<td>This work</td>
</tr>
<tr>
<td>B=LaYO_3+C (eutectoid)</td>
<td>1843</td>
<td>0.55 (B)</td>
<td>[1]</td>
</tr>
<tr>
<td></td>
<td>1851</td>
<td>0.55 (B), 0.79 (C)</td>
<td>This work</td>
</tr>
<tr>
<td>B=A+LaYO_3 (eutectoid)</td>
<td>1400</td>
<td>0.033 (A), 0.25 (B)</td>
<td>This work</td>
</tr>
</tbody>
</table>
5.7 References


[8] N. N. Padurow and C. Schusteriuss, "New compositions of the perovskite-type and mixed crystals in the La_{2}O_{3}-In_{2}O_{3}-Y_{2}O_{3} system", *Ber. DKG* 32 (1955), p. 292 (in German).


6 Thermodynamics and Phase Equilibria in the ZrO$_2$–LaO$_{1.5}$ System

Ming Chen, Bengt Hallstedt, and Ludwig J. Gauckler, to be submitted.

Abstract

The knowledge on the thermodynamic properties of La$_2$Zr$_2$O$_7$ and the phase relations in the ZrO$_2$–LaO$_{1.5}$ system is important for many applications. We review both the thermodynamic and the phase diagram data on the ZrO$_2$–LaO$_{1.5}$ system. The thermodynamic properties of stoichiometric La$_2$Zr$_2$O$_7$ are reassessed. We model the ZrO$_2$–LaO$_{1.5}$ system as a pseudo-binary section of the La–Zr–O ternary system and describe the La$_2$Zr$_2$O$_7$ pyrochlore phase using a 4-sublattice model. Our calculated ZrO$_2$–LaO$_{1.5}$ phase diagram fits most of the experimental data well. The La$_2$Zr$_2$O$_7$ pyrochlore phase shows notable nonstoichiometry at temperatures above 1600 K.

6.1 Introduction

La$_2$Zr$_2$O$_7$ has attracted considerable interest for applications such as thermal barrier coating [1] and nuclear waste storage materials [2]. La$_2$Zr$_2$O$_7$ is also known as a phase with high electrical resistivity formed at the cathode-electrolyte interface in solid oxide fuel cells (SOFCs), in which yttria-stabilized zirconia (YSZ) and Sr-doped perovskite-type LaMnO$_{3-\delta}$ (LSM, (La$_{1-x}$Sr$_x$)$_{1+z}$MnO$_{3-\delta}$) are used as electrolyte and cathode, respectively [3]. The formation of La$_2$Zr$_2$O$_7$ is reported to strongly depend on the A site stoichiometry in the LaMnO$_{3-\delta}$ perovskite [4]. The thermodynamic properties of La$_2$Zr$_2$O$_7$ and the phase relations in the ZrO$_2$–LaO$_{1.5}$ system are obviously very important for the above-mentioned applications. In the present paper, the experimental information on the ZrO$_2$–LaO$_{1.5}$ system is reviewed. Based on an assessment of both the thermodynamic and the phase diagram data, we present a thermodynamic description of the ZrO$_2$–LaO$_{1.5}$ system, which is obtained using the CALPHAD (CALculation of PHAse Diagrams) approach.
6.2 Experimental information

In the ZrO$_2$–LaO$_{1.5}$ system, two intermediary compounds, La$_2$Zr$_2$O$_7$ and C$_2$, have been reported. Besides the liquid phase, there also exist 6 solid oxide solution phases (m-, t-, c-ZrO$_2$, and A-, H-, X-La$_2$O$_3$). The available experimental information is mainly about the phase diagram data and the thermodynamic properties of stoichiometric La$_2$Zr$_2$O$_7$.

6.2.1 Phase diagram data

The ZrO$_2$–LaO$_{1.5}$ phase diagram was first proposed by Brown and Duwez [5]. Rouanet [6] reported the high-temperature part of the ZrO$_2$–LaO$_{1.5}$ phase diagram, based on thermal analysis and high temperature X-ray diffraction (XRD). Later he revised the LaO$_{1.5}$-rich part and published a new diagram [7], which is till now still the most complete and the best available.

6.2.1.1 La$_2$Zr$_2$O$_7$

The existence of La$_2$Zr$_2$O$_7$ was established by Roth [8] and Jorba and Collongues [9]. La$_2$Zr$_2$O$_7$ crystallizes in a cubic pyrochlore-type structure. Rouanet [6] determined the melting temperature of La$_2$Zr$_2$O$_7$ to be 2553 K. Karyakina et al. [10] reported that in argon, La$_2$Zr$_2$O$_7$ melts congruently at 2503±20 K.

La$_2$Zr$_2$O$_7$ was reported to exhibit some nonstoichiometry of both ZrO$_2$ excess and LaO$_{1.5}$ excess at high temperature. Brown and Duwez [5] are the first who reported the composition ranges of La$_2$Zr$_2$O$_7$ at different temperatures, determined from lattice parameter measurements. But they interpreted this pyrochlore phase as the ZrO$_2$ cubic solution phase. The composition ranges of La$_2$Zr$_2$O$_7$ at different temperatures have also been investigated by Lefevre et al. [11], Collongues et al. [12], Rouanet [6], Zoz et al. [13], Zheng and West [14], Skapin et al. [15], and Tabira et al. [16]. A large scatter exists on the reported composition ranges. Early investigations reported a certain width for the La$_2$Zr$_2$O$_7$ single-phase field [6, 11, 12, 13, 14], while two recent investigations reported very narrow composition ranges, 49.7–50.5 cat.% (cation%) LaO$_{1.5}$ at 1623 K from Skapin et al. [15] and 49–51 cat.% LaO$_{1.5}$ at 1773 K from Tabira et al. [16].
6.2.1.2 The C2 phase

The C2 phase was proposed by Rouanet [6]. It has a cubic Tl2O3-type structure with a composition close to a 1:1 mixture of ZrO2+La2O3. The cubic Tl2O3-type structure does not exist at high temperature for La2O3, but it was suggested that the solution of ZrO2 can stabilize this structure [6]. A very limited stability range (both temperature and composition) was determined for the C2 phase from high temperature XRD. It melts incongruently (into liquid and La2Zr2O7) at about 2320 K. On cooling it decomposes into La2Zr2O7 and X-La2O3 at 2223 K. The eutectoid composition is at 68.4 cat.% LaO1.5. No other investigations have been conducted on this phase.

6.2.1.3 Phase boundary information

The liquidus of the ZrO2–LaO1.5 system was first measured by von Wartenberg and Eckhardt [17]. A minimum was reported to be at 75 cat.% LaO1.5 and about 2367 K. Rouanet [6] obtained the liquidus curve from cooling curves of thermal analyses. Two eutectic points were reported: one at 40 cat.% LaO1.5 and 2493 K and the other at 76.9 cat.% LaO1.5 and 2303 K. The ZrO2-rich liquidus shows an apparent inflection. Cabannes et al. [18] measured the eutectic temperature of c-ZrO2 and La2Zr2O7 in air to be 2497±10 K. In argon, the eutectic temperature decreases by 45 K and this was ascribed to the reduction of ZrO2.

The ZrO2-rich part of the subsolidus has been investigated by a few groups. Brown and Duwez [5] reported large solubilities of LaO1.5 in ZrO2, less than 7.7 cat.% LaO1.5 in m-ZrO2 at T < 1253 K and 9.5 cat.% LaO1.5 in t-ZrO2 at 1203 K. Zoz et al. [13] investigated the ZrO2–LaO1.5 system at 1273–2173 K and 1–66.7 cat.% LaO1.5. The solubility of LaO1.5 in m-ZrO2 was concluded to be less than 2 cat.% LaO1.5 due to the large ionic radius of La3+. Bastide et al. [19] studied the ZrO2–LaO1.5 system in 0–26.1 cat.% LaO1.5. The maximum solubility of LaO1.5 in m-ZrO2 at room temperature was reported to be 1 cat.% LaO1.5. The solubility of LaO1.5 in t-ZrO2 was determined to be 1.5 cat.% LaO1.5 in a temperature range of 1373–1773 K. The solubility of LaO1.5 in t-ZrO2 was also reported by Zheng and West [14] to be less than 2 cat.% LaO1.5 at 1773 K, by Andrievskaya and Lopato [20] to be 1.5 cat.% LaO1.5 at 1523 and 1723 K, and by Skapin et al. [15] to be less than 2 cat.% LaO1.5 at 1623 K. Rouanet [6] located the eutectoid point of c-ZrO2 (into t-ZrO2 and La2Zr2O7) at 9.5 cat.% LaO1.5 and 2123 K. Later he adjusted this eutectoid point to be at 13.1 cat.% LaO1.5 and 2223 K [7]. Bastide et al. [19] reported a eutectoid point of t-ZrO2 (into m-ZrO2 and La2Zr2O7) at
1373 K and 1.5 cat.% LaO$_{1.5}$. Andrievskaya and Lopato [20] determined this eutectoid point to be at 1.5 cat.% LaO$_{1.5}$ and 1383 K, in good agreement with the result from Bastide et al. [19].

ZrO$_2$ also exhibits some solubility in LaO$_{1.5}$. Brown and Duwez [5] found that the ZrO$_2$ solubility in LaO$_{1.5}$ increases with increasing temperature and was 5.3 cat.% ZrO$_2$ at 1253 K and 11.1 cat.% ZrO$_2$ at 2033 K. Zheng and West [14] reported that at 1773 K, 2 cat.% ZrO$_2$ dissolves in A-La$_2$O$_3$. Based on high-temperature XRD measurements, Rouanet [7] suggested a eutectoid point of X-La$_2$O$_3$ (into La$_2$Zr$_2$O$_7$ and H-La$_2$O$_3$) at 2173 K and 83.7 cat.% LaO$_{1.5}$. Due to the unquenchability of X- and H-La$_2$O$_3$ and the excessive vaporization of La$_2$O$_3$ at high temperature, the ZrO$_2$ solubility in La$_2$O$_3$ could not be determined accurately.

6.2.2 Thermodynamic data

The reported thermodynamic data concern stoichiometric La$_2$Zr$_2$O$_7$. The heat capacity of La$_2$Zr$_2$O$_7$ has been measured by Bolech et al. [21] from 4 to 400 K using adiabatic calorimetry and by Vassen et al. [1] from 373 to 1573 K using differential scanning calorimetry (DSC). From the measured heat capacities, Bolech et al. [21] determined the standard entropy of La$_2$Zr$_2$O$_7$ at 298.15 K to be 238.53±0.48 J/(mol K). The enthalpy increments of La$_2$Zr$_2$O$_7$ have been measured by Bolech et al. [21] from 500 to 900 K and by Sedmidubsky et al. [22] from 800 to 1600 K, both using drop calorimetry. Sedmidubsky et al. [22] derived a 3-parameter polynomial equation for the heat capacity of La$_2$Zr$_2$O$_7$ in a temperature range of 298.15–1550 K, based on the reported heat capacity and enthalpy increment data from Bolech et al. [21], Vassen et al. [1], and Sedmidubsky et al. [22].

The enthalpy of formation of La$_2$Zr$_2$O$_7$ at 298.15 K was first measured by Korneev et al. [23] as −125.9 kJ/mol (from oxides), using combustion calorimetry. Bolech et al. [24] measured the enthalpy of formation of La$_2$Zr$_2$O$_7$ at 974 K to be −135.8±6.4 kJ/mol (from oxides), by high-temperature solution calorimetry. The enthalpy of formation of La$_2$Zr$_2$O$_7$ at 298.15 K was reported to be −136.1±6.4 kJ/mol (from oxides), which is 10 kJ/mol more negative than the value reported by Korneev et al. [23]. Korneev et al. [23] also measured the enthalpy of formation of m-ZrO$_2$ as −1087.8 kJ/mol, >10 kJ less negative than both the measured values from Huber et al. [25] and Kornilov et al. [26] and the assessed values from the JANAF table.
Modeling of the La–Zr–O System

It is quite possible that in Korneev et al.’s experiments [23], incomplete combustion or formation of metastable products undetectable by XRD led to the less negative enthalpies of formation for both m-ZrO$_2$ and La$_2$Zr$_2$O$_7$.

The Gibbs energy of formation of La$_2$Zr$_2$O$_7$ from oxides was measured by Jacob et al. [29] in a temperature range of 870–1240 K and by Rog and Kozlowska-Rog [30] in a temperature range of 1073–1273 K, both using the electromotive force (EMF) method. Jacob et al. [29] derived the standard enthalpy of formation of La$_2$Zr$_2$O$_7$ (from oxides) at 298.15 K as $-134.4 \pm 8.5$ kJ/mol by the second-law method and $-133.8 \pm 5$ kJ/mol by the third-law method, in good agreement with the measured value from Bolech et al. [24].

6.2.3 Previous assessments

Yokokawa et al. [31] published a series of calculated phase diagrams for ZrO$_2$-based ceramics, based on evaluated or estimated thermodynamic properties of solid solution phases and stoichiometric compounds. For the ZrO$_2$–LaO$_{1.5}$ system, they did not include the C$_2$ phase and the La$_2$Zr$_2$O$_7$ pyrochlore phase was modeled as a stoichiometric compound. Du et al. [32] assessed this system using the CALPHAD method. All the solution phases were modeled using a simple substitutional model with ZrO$_2$ and LaO$_{1.5}$ as components. To describe the nonstoichiometry of La$_2$Zr$_2$O$_7$, they used a model (ZrO$_2$, LaO$_{1.5}$)$_i$(LaO$_{1.5}$, ZrO$_2$)$_j$. The C$_2$ phase was treated as a stoichiometric compound at a composition of 68.8 cat.% LaO$_{1.5}$, which is an average value of two reported compositions by Rouanet [6]. Both Yokokawa et al. [31] and Du et al. [32] used the measured enthalpy of formation of La$_2$Zr$_2$O$_7$ from Korneev et al. [23], which is probably too less negative. It is obviously necessary to reassess the thermodynamic properties of stoichiometric La$_2$Zr$_2$O$_7$. The nonstoichiometry of La$_2$Zr$_2$O$_7$ also needs to be remodeled using a more physical model, which can reflect the crystal chemistry of the La$_2$Zr$_2$O$_7$ pyrochlore phase.

6.3 Thermodynamic models

In the present work, we model the ZrO$_2$–LaO$_{1.5}$ system as a pseudo-binary section of the La–Zr–O ternary system. The descriptions of two binary sub-systems, Zr–O and La–O, are taken from previous assessments. The description of Zr–O is from our previous work on the
No assessment is available for the La–Y system and this sub-system is not considered in our modeling. For the ZrO$_2$–LaO$_{1.5}$ system, we need to model the liquid phase, 6 solid oxide solution phases, the La$_2$Zr$_2$O$_7$ pyrochlore phase and the C$_2$ phase. The La$_2$Zr$_2$O$_7$ pyrochlore phase is the key phase in our modeling.

6.3.1 La$_2$Zr$_2$O$_7$

The nonstoichiometry of La$_2$Zr$_2$O$_7$ is related to its crystal structure. La$_2$Zr$_2$O$_7$ crystallizes in the so-called pyrochlore-type structure. The general formula of an oxide pyrochlore structure can be written as A$_2$B$_2$O$_6$O'. Here we only consider the (A$^{3+}$)$_2$(B$^{4+}$)$_2$O$_7$ pyrochlore. In the pyrochlore lattice, four crystallographically unique atom positions, A, B, O, O', have been identified. The pyrochlore structure can then be described by fixing its origin at the B site with atoms located at the following positions (using Wyckoff notation): A at 16$d$, B at 16$c$, O at 48$f$, and O' at 8$b$ [34]. The pyrochlore structure can also be considered as an ordered, defective fluorite. Similarity exists between the pyrochlore and the fluorite structures. In the fluorite crystal lattice, the anions are sitting in the tetrahedral sites in a face-centered-cubic (fcc) cation array. In the pyrochlore lattice, the cations are also located at the fcc positions, but they are ordered in such a way that the A ions with larger radius sit at the position 16$d$ with 8-fold oxygen coordination and the smaller B ions sit at the position 16$c$ with seven-fold oxygen coordination. The tetrahedral sites for oxygen anions are hence also ordered with three crystallographically different sites (48$f$, 8$a$, and 8$b$) and one out of every eight oxygen ions at the position 8$a$ is missing [34].

Most of the experimental work concerning the nonstoichiometry of the A$_2$B$_2$O$_7$ pyrochlores is on determining their composition ranges at different temperatures, i.e. phase diagram determinations, while the defect chemistry behind stays unclear. The nonstoichiometry in the A$_3$B$_3$O$_7$ pyrochlores is controlled by the energetics associated with solution of excess AO$_{1.5}$ or BO$_2$. To accommodate excess AO$_{1.5}$ or BO$_2$, defects have to be introduced into the pyrochlore crystal lattice. For example, the BO$_2$ excess can be accommodated by replacing A$^{3+}$ cations with B$^{4+}$ cations (cation antisite defects) or by forming A$^{3+}$ cation vacancies, i.e. AO$_{1.5}$ deficiency. In the case of forming cation antisite defects, O$^{2-}$ anion interstitials or cation vacancies (A$^{3+}$ or B$^{4+}$) also need to be introduced to keep the compound neutral. The BO$_2$
excess can hence be realized by different defect reactions. Using an atomistic computer simulation method, Stanek et al. [34] calculated energies of different defect reactions which can be responsible for accommodating AO, or BO, excess for a large number of A2B2O7-type compounds. They found that for stable pyrochlores (like La2Zr2O7), the BO, excess is generally realized by the following reaction described using Kröger-Vink notation,

$$7BO_2 + 4A^x \rightarrow 3B^y + V^w_A + 2A_2B_2O_7 \quad \text{Eq. 6.1}$$

while the AO, excess is realized by

$$2A_2O_3 + 2B^z + O^z \rightarrow 2A^w_y + V^w_A + A_2B_2O_7 \quad \text{Eq. 6.2}$$

In the present work, we model the nonstoichiometric La2Zr2O7 pyrochlore phase as 

$$(\text{La}^{3+}, \text{Zr}^{4+}, \text{Va})_2(\text{Zr}^{4+}, \text{La}^{3+})_2(\text{O}^{2-}, \text{Va})_6(\text{O}^{2-})_8.$$ 

This model is based on the calculation results from Stanek et al. [34]. $$(\text{La}^{3+})_2(\text{Zr}^{4+})_2(\text{O}^{2-})_6(\text{O}^{2-})_8$$ represents stoichiometric La2Zr2O7 and $$(\text{Zr}^{4+})_2(\text{La}^{3+})_2(\text{O}^{2-})_6(\text{O}^{2-})_8$$ is the antisite pyrochlore (Zr2La2O7). This model allows both ZrO2 and LaO1,5 excess. The ZrO2 excess is fulfilled by introducing Zr4+ into the first sublattice. Vacancies also have to be introduced into the same sublattice to maintain charge balance. The LaO1,5 excess can be achieved by introducing both La3+ cations into the second sublattice and oxygen vacancies into the third sublattice. Stanek et al. [34] did not specify at which positions (48/ or 8b) the oxygen vacancies will form. According to the crystal structure of the A2B2O7 pyrochlores, the oxygen atom sitting at the position 48/ has two A and two B nearest neighbors and the one sitting at 8b has four A nearest neighbors. In La2Zr2O7, it is quite possible that when there is a LaO1,5 excess, i.e. La3+ cations enter into the position 16c to partially replace Zr4+ cations, the oxygen vacancies will form at both 48/ and 8b with high probability at 48/. To simplify the calculation, we assume that the oxygen vacancy will form only at the position 48/.

The Gibbs energy of the La2Zr2O7 pyrochlore phase can be written as:
\[
G_m = y_{La}^I y_{La}^I y_{O}^{III} \cdot G_{La:La:O:O} + y_{La}^I y_{La}^I y_{Va}^{III} \cdot G_{La:La:Va:O} + y_{La}^I y_{Zr}^I y_{O}^{III} \cdot G_{La:Zr:O:O} + y_{La}^I y_{Zr}^I y_{Va}^{III} \cdot G_{La:Zr:Va:O} + y_{Zr}^I y_{Zr}^I y_{O}^{III} \cdot G_{Zr:Zr:O:O} + y_{Zr}^I y_{Zr}^I y_{Va}^{III} \cdot G_{Zr:Zr:Va:O} + y_{Va}^I y_{La}^I y_{O}^{III} \cdot G_{Va:La:O:O} + y_{Va}^I y_{La}^I y_{Va}^{III} \cdot G_{Va:La:Va:O} + y_{Va}^I y_{Zr}^I y_{O}^{III} \cdot G_{Va:Zr:O:O} + y_{Va}^I y_{Zr}^I y_{Va}^{III} \cdot G_{Va:Zr:Va:O} + 6(y_{O}^{III} \ln y_{O}^{III} + y_{Va}^{III} \ln y_{Va}^{III}) + \frac{RT}{2}(y_{La}^I \ln y_{La}^I + y_{Zr}^I \ln y_{Zr}^I + y_{Va}^{III} \ln y_{Va}^{III}) + 2(y_{La}^I \ln y_{La}^I + y_{Zr}^I \ln y_{Zr}^I) + 6(y_{O}^{III} \ln y_{O}^{III} + y_{Va}^{III} \ln y_{Va}^{III}) + \frac{EG_m}{2} = 0
\]

where \(y_S\) is the fraction of the species \(S\) in a particular sublattice. The superscripts, I, II, III, denote the first, second, and third sublattice sites. \(\Delta G_m\) is the excess Gibbs energy and we set it to 0 as no interaction parameter will be used for the \(La_2Zr_2O_7\) pyrochlore phase.

According to the present model, for the \(La_2Zr_2O_7\) pyrochlore phase, we need to determine the Gibbs energy functions for the 12 end-members. Due to the limited experimental data, it is almost impossible to optimize parameters independently for each of the 12 \(\Delta G\)'s. Also most of the end-members correspond to charged compounds, which do not physically exist. Therefore, no experimental data can be used to optimize the parameters for the \(\Delta G\) values of those end-members. The strategy we hence used is to choose appropriate neutral end-points, whose Gibbs energies could be related to experimental data. All the 12 \(\Delta G\) values are then rewritten using the Gibbs energies of these neutral end-points plus a combination of reciprocal relations. The strategy will be explained below in details.

Figure 6.1 shows the composition space of the \(La_2Zr_2O_7\) pyrochlore phase. Besides the 12 end-members, 6 neutral end-points are identified with 2 sitting at the same position. The neutral end-points are connected by dotted lines to form a neutral plane. Among the six neutral end-points, \((La^{3+})_2(Zr^{4+})_2(O^{2-})_6(O^{2-})_2\) represents stoichiometric \(La_2Zr_2O_7\) and \((Zr^{4+})_2(La^{3+})_2(O^{2-})_6(O^{2-})_2\) represents \(Zr_2La_2O_7\) (antisite pyrochlore). These two also belong to the 12 end-members. The neutral end-point \(([Zr^{4+}]_{\frac{4}{4}},Va_{\frac{4}{4}})_{\frac{2}{2}}(Zr^{4+})_{\frac{4}{4}}(O^{2-})_{\frac{6}{6}}(O^{2-})_{\frac{6}{6}}\) sits at the same position as \((La^{3+})_2(Zr^{4+})_2(O^{2-})_6(O^{2-})_2\) in the composition space, corresponds to the maximum \(ZrO_2\) excess. \((La^{3+})_2(La^{3+})_2((O^{2-})_{\frac{6}{6}},Va_{\frac{4}{4}})_{\frac{2}{2}}(O^{2-})_{\frac{6}{6}}\) corresponds to the
maximum LaO$_{1.5}$ excess. Two other neutral end-points, $(\text{Va})_2(\text{La}^{3+})_2((\text{O}^{2-})_1, \text{Va}_2)_6(\text{O}^{2-})_1$ and $(\text{Va})_2(\text{Zr}^{4+})_2((\text{O}^{2-})_1, \text{Va}_2)_6(\text{O}^{2-})_1$, are not considered in the present work.

$$(\text{La}^{3+}, \text{Zr}^{4+}, \text{Va})_2(\text{La}^{3+}, \text{Zr}^{4+})_2(\text{O}^{2-}, \text{Va})_6\text{O}_1$$

Figure 6.1 Composition space for the La$_2$Zr$_2$O$_7$ pyrochlore phase. The numbers in parentheses are the net charges of the corresponding end-members.

We define the Gibbs energy function of the neutral end-point $(\text{La}^{3+})_2(\text{Zr}^{4+})_2(\text{O}^{2-})_6(\text{O}^{2-})_1$ (stoichiometric La$_2$Zr$_2$O$_7$) as:

$$G_{\text{LZO}} = ^\circ G_{\text{La}^{3+}, Zr^{4+}, O_2^-, O_2^-} - 2H_{\text{La}}^{\text{SER}} - 2H_{\text{Zr}}^{\text{SER}} - 7H_{\text{O}}^{\text{SER}}$$

$$= 2\text{GFFZRO2} + \text{GLA2O3X} + V_1 + V_2T + V_3T\ln T \quad \text{Eq. 6.4}$$

All the $^\circ G$ values in the present work are referred to the enthalpy of selected stable states for pure elements at 298.15 K and 1 bar (10$^5$ Pa). The state is denoted SER (Stable Element Reference). GLZO, GFFZRO2, and GLA2O3X are the molar Gibbs energies of stoichiometric La$_2$Zr$_2$O$_7$, c-ZrO$_2$ and X-La$_2$O$_3$. The parameters $V_1$, $V_2$, and $V_3$ are optimized using the reported thermodynamic properties of stoichiometric La$_2$Zr$_2$O$_7$.

The Gibbs energy of the end-point $(\text{Zr}^{4+})_2(\text{La}^{3+})_2((\text{O}^{2-})_1, \text{Si}_2)_6(\text{O}^{2-})_1$ (antisite pyrochlore) is related to the Gibbs energy of stoichiometric La$_2$Zr$_2$O$_7$ as
Chapter 6

\[ G_{\text{ZO}} = G_{\text{GR}^4+\text{La}^{3+} \cdot \text{O}^{2-} \cdot \text{O}^{2-}} - 2 \, H_{\text{La}}^{\text{SER}} - 2 \, H_{\text{Zr}}^{\text{SER}} - 7 \, H_{\text{O}}^{\text{SER}} = \text{GZO} + V_6 + V_8 T \quad \text{Eq. 6.5} \]

The Gibbs energy of the ZrO_2 excess neutral end-point, \( (\text{Zr}^{4+})_3^4 \cdot \text{Va}_1 \cdot (\text{Zr}^{4+})_2 \cdot (\text{O}^{2-})_6 \cdot (\text{O}^{2-})_6 \), is defined as

\[ G(Z_{0.75}V_{0.25})_{\text{ZO}} = 3.5 \, G\text{FFZRO2} + V_7 + V_8 T \quad \text{Eq. 6.6} \]

and the Gibbs energy of the LaO_{1.5} excess neutral end-point, \( (\text{La}^{3+})_2 \cdot (\text{La}^{3+})_2 \cdot (\text{O}^{2-})_5 \cdot \text{Va}_1 \cdot (\text{O}^{2-})_6 \), is defined as

\[ G_{\text{LL}}(O_{0.83}V_{0.167}) = 2 \, G\text{LA2O3X} + V_9 + V_{10} T \quad \text{Eq. 6.7} \]

We choose the end member \((\text{Va})_2(\text{Zr}^{4+})_2(\text{O}^{2-})_6(\text{O}^{2-})_6\) as a reference point and define its Gibbs energy as:

\[ \text{GVZO} = 2 \, G\text{FFZRO2} + 3 \, G\text{HSEREOO} \quad \text{Eq. 6.8} \]

The Gibbs energy functions of the other 9 end-members are then derived from these four neutral end-points and one reference end-member plus reciprocal relations. The following reciprocal relations are used:

\[ G(Z_{0.75}V_{0.25})_{\text{ZO}} = \frac{3}{4} \, G\text{ZZO} + \frac{1}{4} \, \text{GVZO} + 2RT(\frac{3}{4} \ln \frac{3}{4} + \frac{1}{4} \ln \frac{1}{4}) \quad \text{Eq. 6.9} \]

\[ \text{GLZO} + \text{GZLO} - \text{GZZO} - \text{GLLO} = 0 \quad \text{Eq. 6.10} \]

\[ G_{\text{LL}}(O_{0.83}V_{0.167}) = \frac{5}{6} \, \text{GLLO} + \frac{1}{6} \, \text{GLLV} + 6RT(\frac{5}{6} \ln \frac{5}{6} + \frac{1}{6} \ln \frac{1}{6}) \quad \text{Eq. 6.11} \]

\[ \text{GLLO} + \text{GZLV} - \text{GLLV} - \text{GZLO} = 0 \quad \text{Eq. 6.12} \]

\[ \text{GZZV} + \text{GZLO} - \text{GZZO} - \text{GZLV} = 0 \quad \text{Eq. 6.13} \]

\[ \text{GLZV} + \text{GLLO} - \text{GLZO} - \text{GLLV} = 0 \quad \text{Eq. 6.14} \]

\[ \text{GVZV} + \text{GLZO} - \text{GVZO} - \text{GLZV} = 0 \quad \text{Eq. 6.15} \]

\[ \text{GVLO} + \text{GLZO} - \text{GVZO} - \text{GLLO} = 0 \quad \text{Eq. 6.16} \]

\[ \text{GVLV} + \text{GVZO} - \text{GVLO} - \text{GVZV} = 0 \quad \text{Eq. 6.17} \]

The parameters, \( V_5 - V_{10} \) in Eqs. 6.5–7, are optimized using the phase boundary data for the \( \text{La}_2\text{Zr}_2\text{O}_7 \) single-phase field.

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6.3.2 The C2 phase

The existence of the C2 phase is actually not very certain, as only Rouanet [6] reported this phase and no further investigations have been conducted. Due to its limited stability range, excluding the C2 phase will not change the general shape of the ZrO2-LaO1.5 phase diagram, but we choose to include it into the present work. We model the C2 phase as a stoichiometric compound at a composition corresponding to a 1:1 mixture of ZrO2+La2O3. Its Gibbs energy is related to the Gibbs energies of c-ZrO2 and X-La2O3 as:

$$G_{C2} = G_{cZrO2} + GLA2O3X + V_{11} + V_{12}T$$  \hspace{1cm} \text{Eq. 6.18}

6.3.3 Other phases

We model the liquid phase as \((La^{3+}, Zr^{4+})_p(O^{2-}, Va^{2-})_q\), using the two-subliattice model for ionic liquids [35, 36]. The interaction parameters between La\(^{3+}\) and Zr\(^{4+}\) are optimized:

$$I_{La^{3+},Zr^{4+}O^{2-}} = V_{1i} + V_{14}T \quad i = 0, 1, 2$$  \hspace{1cm} \text{Eq. 6.19}

Due to the small LaO1.5 solubility in m-ZrO2, we model m-ZrO2 as a stoichiometric compound. We do include the LaO1.5 solubility in t- and c-ZrO2 and the ZrO2 solubility in A-, H-, and X-La2O3 as well. c-ZrO2 and X-La2O3 are treated as one phase. These 4 solid solution phases, t-ZrO2, c-ZrO2 (also X-La2O3), A-La2O3, H-La2O3, are all modeled as a mixture of the corresponding binary oxide solution phases. The values for the lattice stabilities of metastable phases (t-La2O3, A-ZrO2, and H-ZrO2) are similar to those we used for the Y–Zr–O system [28]. The interaction parameters between La\(^{3+}\) and Zr\(^{4+}\) are then optimized using phase diagram data related to the ZrO2–LaO1.5 pseudo-binary section.

6.4 Optimization procedure

The assessment is made using the software PARROT included in the Thermo-Calc Databank System [37]. The parameters for GLZO, the Gibbs energy function of stoichiometric La2Zr2O7, are optimized in the beginning and are fixed afterwards. The interaction parameters for all the solution phases and the parameters for nonstoichiometric La2Zr2O7 and the C2 phase are optimized using phase diagram data.
In the present work, we relate the Gibbs energy of stoichiometric $\text{La}_2\text{Zr}_2\text{O}_7$ to the Gibbs energies of $\text{c-ZrO}_2$ and $\text{X-La}_2\text{O}_3$. We could also give an independent description for the Gibbs energy function of stoichiometric $\text{La}_2\text{Zr}_2\text{O}_7$ as:

$$\text{GLZO} = A + BT + CT \ln T + DT^2 + ET^{-1}$$  \hspace{1cm} \text{Eq. 6.20}

This will not change our description essentially, but will make our description of the $\text{La}_2\text{Zr}_2\text{O}_7$ pyrochlore phase more complicated and is hence not considered in the present work. During the optimization, we found that the parameter $V_3$ in Eq. 6.4 could be set to 0, i.e. no extra $C_p$ term is needed for GLZO. This means that the heat capacity of stoichiometric $\text{La}_2\text{Zr}_2\text{O}_7$ almost equals to a sum of the heat capacities of its components ($\text{c-ZrO}_2$ and $\text{X-La}_2\text{O}_3$), which is known as the Neumann-Kopp rule. The parameters $V_1$ and $V_2$ in Eq. 6.4 for GZLO are optimized using the enthalpy of formation of $\text{La}_2\text{Zr}_2\text{O}_7$ at 298.15 K (from oxides) from Bolech et al. [24], the entropy at 298.15 K from Bolech et al. [21] and the Gibbs energy of formation (from oxides) from Jacob et al. [29]. These two parameters are then kept fixed.

For the phase diagram data, we use the liquidus data plus two eutectics from Rouanet [6]. The peritectic and eutectic temperatures of the $\text{C}_2$ phase from Rouanet [6] are also used to optimize the parameters for $\text{C}_2$. For the $\text{LaO}_{1.5}$ solubility in c-ZrO$_2$, we use the reported data from Bastide et al. [19] and Andrievskaya and Lopato [20]. The eutectoid temperature and composition of c-ZrO$_2$ (into m-ZrO$_2$ and $\text{La}_2\text{Zr}_2\text{O}_7$) from these two investigations are also used. The phase boundary data of t+c/c-ZrO$_2$, c-ZrO$_2$/c-ZrO$_2$+La$_2$Zr$_2$O$_7$, and the eutectoid temperature and composition of c-ZrO$_2$ are all from Rouanet [6, 7]. For the LaO$_{1.5}$-rich side, we use the reported ZrO$_2$ solubility in A-La$_2$O$_3$ from Zheng and West [14], the maximal solubility of ZrO$_2$ in H-La$_2$O$_3$ and the eutectoid point of X-La$_2$O$_3$ from Rouanet [6, 7]. The data on the composition range of the La$_2$Zr$_2$O$_7$ pyrochlore phase are from Collongues et al. [12] and Tabira et al. [16]. In our optimization, we set the parameters $V_6$, $V_8$, and $V_{10}$ in Eqs. 6.5–7 to 0 and optimize $V_5$, $V_7$, and $V_9$ to get a good fit of the selected La$_2$Zr$_2$O$_7$ nonstoichiometry data. In the present work, we describe c-ZrO$_2$ and X-La$_2$O$_3$ as one phase and both regular and subregular interaction parameters are used. For other solution phases, only regular interaction parameters are used. In the end, the interaction parameters for all the solution phases (including the liquid phase), the parameters for the La$_2$Zr$_2$O$_7$ pyrochlore phase and the lattice stability parameters for the C$_2$ phase are optimized together.
6.5 Results and discussion

The thermodynamic description of the ZrO$_2$–LaO$_{1.5}$ system is listed in Table 6.1. Figure 6.2 shows the calculated heat capacities of stoichiometric La$_2$Zr$_2$O$_7$ compared with experimental data. The heat capacities from the present work agree well with the measured ones from both Bolech et al. [21] and Vassen et al. [1]. The enthalpy increments of stoichiometric La$_2$Zr$_2$O$_7$ are plotted in Figure 6.3. An excellent agreement exists between our calculated values and the measured ones from Bolech et al. [21] and Sedmidubsky et al. [22]. The calculated heat capacity and enthalpy increment of stoichiometric La$_2$Zr$_2$O$_7$ from Yokokawa [38] are also quite close to ours. The entropy and enthalpy of formation of stoichiometric La$_2$Zr$_2$O$_7$ at 298.15 K from different sources are listed in Table 6.2. Our calculated standard entropy is 237.5 J/(K mol), slightly smaller than the measured value from Bolech et al. [21]. The enthalpy of formation of stoichiometric La$_2$Zr$_2$O$_7$ at 298.15 K from the present work is calculated to be $-4130.5$ kJ/mol (from elements) and $-133.6$ kJ/mol (from oxides). Yokokawa et al. [38] took the enthalpy of formation of La$_2$Zr$_2$O$_7$ (from elements) at 298.15 K from Korneev et al. [23] and derived his own value for the enthalpy of formation of La$_2$Zr$_2$O$_7$ (from oxides) at 298.15 K, which is much less negative than the measured values from both Korneev et al. [23] and Bolech et al. [24]. The calculated Gibbs energies of formation of stoichiometric La$_2$Zr$_2$O$_7$ (from oxides) are plotted in Figure 6.4, together with the experimental data from Jacob et al. [29] and Rog and Kozłowska-Rog [30]. There is a small shift between these two sets of experimental data. We only use the data from Jacob et al. [29] in our optimization.

| Table 6.1 | Thermodynamic description of the ZrO$_2$–LaO$_{1.5}$ system |
## Chapter 6

### Monoclinic ZrO$_2$

$^{8}G_{\text{Zr}^{4+},\text{O}^{2-}} - H_{\text{Zr}}^{\text{SER}} - 2 H_{\text{O}}^{\text{SER}} = \text{GMMZRO2}$

### Tetragonal ZrO$_2$

$^{8}G_{\text{La}^{3+},\text{Zr}^{4+},\text{ Va}} - H_{\text{La}}^{\text{SER}} - 2 H_{\text{O}}^{\text{SER}} = 0.5 \text{GMTLA2O3} + 0.5 \text{GHSEROO} + 9.3511T$

### Cubic ZrO$_2$ (and X-La$_2$O$_3$)

$^{8}G_{\text{La},\text{Zr},\text{Va}} - H_{\text{La}}^{\text{SER}} - 2 H_{\text{O}}^{\text{SER}} = \text{GHSERLA} + 2 \text{GHSEROO} + 102062$

### A-La$_2$O$_3$

$^{8}G_{\text{La},\text{Zr},\text{Va}} - H_{\text{La}}^{\text{SER}} - 2 H_{\text{O}}^{\text{SER}} = 2 \text{GHSERLA} + 4 \text{GHSEROO} + 304124 + 15.87691T$

### Table

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<td>$-\Delta H_{\text{La},\text{Zr}^{4+},\text{O}^{2-}} = 2 \text{GHSERLA} + 2 \text{GHSEROO} + 304124 + 15.87691T$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Energy (KJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I_{\text{La},\text{Zr}^{4+},\text{O}^{2-}}$</td>
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<td>$I_{\text{La},\text{Zr}^{4+},\text{O}^{2-}}$</td>
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<td>$-\Delta H_{\text{La},\text{Zr}^{4+},\text{O}^{2-}} = 2 \text{GHSERLA} + 2 \text{GHSEROO} + 304124 + 15.87691T$</td>
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<table>
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</tr>
</thead>
<tbody>
<tr>
<td>$I_{\text{La},\text{Zr}^{4+},\text{O}^{2-}}$</td>
<td>$-\Delta H_{\text{La},\text{Zr}^{4+},\text{O}^{2-}} = 2 \text{GHSERLA} + 2 \text{GHSEROO} + 304124 + 15.87691T$</td>
</tr>
</tbody>
</table>
Modeling of the La–Zr–O System

\[ G_{Zr^{4+}, Va^{5+}, O^{2-}} - 2 H_{Zr}^{\text{SER}} - H_{O}^{\text{SER}} = 2 \text{GMZRO2} - 3 \text{GHSEROO} \]

\[ G_{Zr^{4+}, Va^{5+}, Va^{5+}} - 2 H_{Zr}^{\text{SER}} = 2 \text{GMZRO2} - 4 \text{GHSEROO} - 100000 - 15.87691T \]

\[ V_{La^{3+}, Zr^{4+}, O^{2-}, O^{2-}, Va^{5+}, Va^{5+}} = V_{La^{3+}, Zr^{4+}, Va^{5+}, Va^{5+}, Va^{5+}, Va^{5+}} = V_{La^{3+}, Zr^{4+}, Va^{5+}, Va^{5+}, Va^{5+}, Va^{5+}} = -101793 \]

\[ H-La_2O_3 \]

\[ (La, La^{3+}, Zr^{4+})_2(O^{2-}, Va)_1(O^{2-}, Va)_1 \]

\[ G_{La^{3+}, O^{2-}} - 2 H_{La}^{\text{SER}} - 4 H_{O}^{\text{SER}} = 2 \text{GHSERLA} + 4 \text{GHSEROO} + 304124 + 15.87691T \]

\[ G_{La^{3+}, Va^{5+}} - 2 H_{La}^{\text{SER}} - 3 H_{O}^{\text{SER}} = 2 \text{GHSERLA} + 3 \text{GHSEROO} + 204124 \]

\[ G_{La^{3+}, Va^{5+}, Va^{5+}} - 2 H_{La}^{\text{SER}} = 2 \text{GHSERLA} + 3 \text{GHSEROO} + 304124 + 15.87691T \]

\[ G_{La^{3+}, Va^{5+}, Va^{5+}} - 2 H_{La}^{\text{SER}} = 2 \text{GHSERLA} + 204124 \]

\[ G_{La^{3+}, Zr^{4+}, O^{2-}, O^{2-}} - 2 H_{La}^{\text{SER}} - 4 H_{O}^{\text{SER}} = \text{GLA2O3H} + \text{GHSEROO} + 100000 + 15.87691T \]

\[ G_{La^{3+}, Zr^{4+}, Va^{5+}} - 2 H_{La}^{\text{SER}} - 3 H_{O}^{\text{SER}} = \text{GLA2O3H} \]

\[ G_{La^{3+}, Zr^{4+}, Va^{5+}, Va^{5+}} - 2 H_{La}^{\text{SER}} - 3 H_{O}^{\text{SER}} = \text{GLA2O3H} + 2 \text{GHSEROO} + 100000 + 15.87691T \]

\[ G_{La^{3+}, Zr^{4+}, Va^{5+}, Va^{5+}} - 2 H_{La}^{\text{SER}} = \text{GLA2O3H} + 3 \text{GHSEROO} \]

\[ G_{Zr^{4+}, Zr^{4+}, O^{2-}, O^{2-}} - 4 H_{Zr}^{\text{SER}} = 2 \text{GHSEROO} - 100000 - 15.87691T \]

\[ G_{Zr^{4+}, Zr^{4+}, Zr^{4+}, O^{2-}, O^{2-}} - 2 H_{Zr}^{\text{SER}} - 4 H_{O}^{\text{SER}} = 2 \text{GMHZRO2} \]

\[ G_{Zr^{4+}, Zr^{4+}, Va^{5+}} - 2 H_{Zr}^{\text{SER}} = 2 \text{GMHZRO2} + 2 \text{GHSEROO} \]

\[ G_{Zr^{4+}, Zr^{4+}, Va^{5+}, Va^{5+}} - 2 H_{Zr}^{\text{SER}} = 2 \text{GMHZRO2} + 4 \text{GHSEROO} - 100000 - 15.87691T \]

\[ V_{La^{3+}, Zr^{4+}, O^{2-}, O^{2-}, Va^{5+}, Va^{5+}} = V_{La^{3+}, Zr^{4+}, Va^{5+}, Va^{5+}, Va^{5+}, Va^{5+}} = V_{La^{3+}, Zr^{4+}, Va^{5+}, Va^{5+}, Va^{5+}, Va^{5+}} = -144923 \]

\[ C_2 \]

\[ (La^{3+})_2(Zr^{4+})_1(O^{2-})_5 \]

\[ G_{La^{3+}, Zr^{4+}, O^{2-}, O^{2-}} - 2 H_{La}^{\text{SER}} - H_{Zr}^{\text{SER}} - 5 H_{O}^{\text{SER}} = \text{GC2} \]

\[ The La$_2$Zr$_2$O$_7$ pyrochlore \]

\[ (La^{3+}, Zr^{4+}, Va^{5+})_2(La^{3+}, Zr^{4+})_2(O^{2-}, Va)_1(O^{2-})_1 \]

\[ G_{La^{3+}, La^{3+}, O^{2-}, O^{2-}} - 4 H_{La}^{\text{SER}} - 7 H_{O}^{\text{SER}} = 2 \text{GLA2O3X} + \text{GHSEROO} - 327772 + 91.332T \]

\[ G_{La^{3+}, La^{3+}, Va^{5+}, O^{2-}} - 4 H_{La}^{\text{SER}} - H_{O}^{\text{SER}} = 2 \text{GLA2O3X} - 5 \text{GHSEROO} + 2013420 - 321.636T \]

\[ G_{La^{3+}, Zr^{4+}, O^{2-}, O^{2-}} = 2 H_{La}^{\text{SER}} - 2 H_{Zr}^{\text{SER}} - 7 H_{O}^{\text{SER}} = \text{GLA2O3X} + 2 \text{GFFZR02} - 271791 + 51.9T \]

\[ G_{La^{3+}, Zr^{4+}, Va^{5+}, O^{2-}} = 2 H_{La}^{\text{SER}} - 2 H_{Zr}^{\text{SER}} = \text{GLA2O3X} + 2 \text{GFFZR02} - 6 \text{GHSEROO} + 2069401 - 361.068T \]

\[ G_{Zr^{4+}, La^{3+}, O^{2-}, O^{2-}} = 2 H_{Zr}^{\text{SER}} - 7 H_{O}^{\text{SER}} = \text{GLA2O3X} + 2 \text{GFFZR02} + 28209 + 51.9T \]

\[ G_{Zr^{4+}, La^{3+}, Va^{5+}, O^{2-}} = 2 H_{Zr}^{\text{SER}} - 2 H_{O}^{\text{SER}} = \text{GLA2O3X} + 2 \text{GFFZR02} - 6 \text{GHSEROO} + 2369401 - 361.068T \]

\[ G_{Zr^{4+}, Zr^{4+}, O^{2-}, O^{2-}} = 4 H_{Zr}^{\text{SER}} - 7 H_{O}^{\text{SER}} = 4 \text{GFFZR02} - \text{GHSEROO} + 84190 + 12.468T \]

\[ G_{Zr^{4+}, Zr^{4+}, Va^{5+}, O^{2-}} = 4 H_{Zr}^{\text{SER}} - H_{O}^{\text{SER}} = 4 \text{GFFZR02} - 7 \text{GHSEROO} + 2425381 - 400.5T \]

\[ G_{Va^{5+}, La^{3+}, O^{2-}, O^{2-}} = 2 H_{La}^{\text{SER}} - 7 H_{O}^{\text{SER}} = \text{GLA2O3X} + 4 \text{GHSEROO} - 55981 + 39.432T \]

\[ G_{Va^{5+}, La^{3+}, Va^{5+}, Va^{5+}} = 2 H_{La}^{\text{SER}} - H_{O}^{\text{SER}} = \text{GLA2O3X} - 2 \text{GHSEROO} + 2285211 - 373.536T \]

\[ G_{Va^{5+}, Zr^{4+}, O^{2-}, O^{2-}} = 2 H_{Zr}^{\text{SER}} - 7 H_{O}^{\text{SER}} = 2 \text{GFFZR02} + 3 \text{GHSEROO} \]
\begin{align*}
g^o_{Va^3+, Zr^{4+}, O_2^-} - 2 H^o_{Zr} - H^o_O = 2 GFFZRO2 - 3 GSEROO + 2341192 - 412.968T
\end{align*}

**Liquid**

\((La^{3+}, Zr^{4+}, O^{2-})_p \) \((O^{2-}, Va^{5+})_q\)

\(p = 2 y_{O^{2-}} + q y_{Va^{5+}} \quad q = 3 y_{La^{3+}} + 4 y_{Zr^{4+}}\)

\(g^o_{La^{3+}, O^{2-}} - 2 H^o_{La} - 3 H^o_O = GLA2O3LIQ\)

\(g^o_{La^{3+}, Va^{5+}} - H^o_{La} = GLALIQ\)

\(g^o_{Zr^{4+}, O^{2-}} - 2 H^o_{Zr} - 4 H^o_O = 2 GZRO2LIQ\)

\(g^o_{Zr^{4+}, Va^{5+}} - H^o_{Zr} = GZRLIQ\)

\(L_{Zr^{4+}, O^{2-}, Va^{5+}} = -26500\)

\(L_{Zr^{4+}, O^{2-}, Va^{5+}} = +50000\)

\(L_{Zr^{4+}, O^2-, Va^{5+}} = +72000\)

\(L_{La^{3+}, Zr^{4+}, O^2-} = -212088\)

**O2 (g)**

\(g^o_{O_2} - 2 H^o_O = 2 GSEROO + RT \ln(1 \times 10^{-5} P)\)

**Functions**

GLA2O3A = \(-1835600 + 674.72T - 11871nr - 0.008T^2 + 620000T^{-1}\)

GLA2O3H = \(+GLA2O3A + 46000 - 19.89T\)

GLA2O3X = \(+GLA2O3A + 111160 - 48.11T\)

GLA2O3LIQ = \(-1807513 + 1282.4877 - 20071nr\)

GMLA2O3 = \(+GLA2O3A + 30000\)

GMMZRO2 = \(-1125300 + 416.9T - 68.471nr - 0.00335T^2 + 586000T^{-1}\)

GTTZRO2 = \(+GMMZRO2 + 6000 - 4.326T\)

GFFZRO2 = \(+GMMZRO2 + 13500 - 7.159T\)

GZRO2LIQ = \(-1077400 + 561.17 - 9071nr\)

GMATZRO2 = \(+GMMZRO2 + 50000\)

GMHZRO2 = \(+GMMZRO2 + 58500 - 7.159T\)

GC2 = \(+GLA2O3X + GFFZRO2 - 94433 + 2.5T\)

GLZO = \(+GLA2O3X + 2 GFFZRO2 - 271791 + 51.9T\)

GZLO = \(+GLZO + 300000\)

GLL(O_{0.83} V_{0.17}) = \(+2 GLA2O3X + 62427\)

G(Z_{0.75} V_{0.25}) ZO = \(+3.5 GFFZRO2 + 63158\)

**Note:** All parameters are in SI units: J, mol, K, Pa; \(R=8.31451 \ J/(\text{mol} \ K)\). GSEROO, GLALIQ, GSERZ, GZRLIQ, and GSEROO are the molar Gibbs energies of pure La, Zr, and oxygen from Dinsdale, 1991 [39].
Figure 6.2 Calculated heat capacity of stoichiometric La$_2$Zr$_2$O$_7$ from the present work compared with experimental data and previous assessments from Bolech et al. [21], Vassen et al. [1], Yokokawa et al. [38], and Sedmidubsky et al. [22].

Figure 6.3 Calculated enthalpy increment of stoichiometric La$_2$Zr$_2$O$_7$ from the present work compared with experimental data from Bolech et al. [21] and Sedmidubsky et al. [22] and previous assessment from Yokokawa et al. [38].
Table 6.2 Enthalpy and entropy of formation of stoichiometric La$_2$Zr$_2$O$_7$ at 298.15 K

<table>
<thead>
<tr>
<th>$\Delta H$, kJ/mol</th>
<th>$S$, J/(mol K)</th>
<th>Method</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(from oxides)</td>
<td>(from elements)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-125.9 (measured)</td>
<td>-4081.9</td>
<td>Combustion calorimetry</td>
<td>[23]</td>
</tr>
<tr>
<td>-136.1 (measured)</td>
<td>-4130.4</td>
<td>Solution calorimetry</td>
<td>[24]</td>
</tr>
<tr>
<td></td>
<td>238.53</td>
<td>Calorimetry (4–400 K)</td>
<td>[21]</td>
</tr>
<tr>
<td>-88.08</td>
<td>-4082.9</td>
<td>Assessed</td>
<td>[38]</td>
</tr>
<tr>
<td>-134.4</td>
<td></td>
<td>$2^{nd}$-law analysis</td>
<td>[29]</td>
</tr>
<tr>
<td>-133.8</td>
<td></td>
<td>$3^{rd}$-law analysis</td>
<td>[29]</td>
</tr>
<tr>
<td>-4212.7</td>
<td></td>
<td>Assessed</td>
<td>[32]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(Optimization A)</td>
<td></td>
</tr>
<tr>
<td>-4145.2</td>
<td></td>
<td>Assessed</td>
<td>[32]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(Optimization B)</td>
<td></td>
</tr>
<tr>
<td>-133.6</td>
<td>-4130.5</td>
<td>Assessed</td>
<td>This work</td>
</tr>
</tbody>
</table>

Figure 6.4 Gibbs energy of formation of stoichiometric La$_2$Zr$_2$O$_7$ (from oxides). The experimental data are from Jacob et al. [29] and Rog and Kozlowska-Rog [30].

Our calculated ZrO$_2$–LaO$_{1.5}$ phase diagram in air is shown in Figure 6.5. A detailed comparison of our diagram with experimentally determined phase diagram data is shown in Figures 6.6–9. All the temperatures and compositions of invariant equilibria are listed in Table 6.3.
Our calculated liquidus fits most of the experimental data well. The reported liquidus data from von Wartenberg and Eckhardt [17] are qualitatively correct, though they detected only one minimum which is the eutectic on the LaO$_{1.5}$-rich side. Compared to the reported c-ZrO$_2$+La$_2$Zr$_2$O$_7$ eutectic from Rouanet [6] and Cabannes et al. [18], our calculated one shifts towards lower temperature and the ZrO$_2$-rich side. According to the present description, La$_2$Zr$_2$O$_7$ melts congruently at 2537 K and 50.4 cat.% LaO$_{1.5}$. We get an enthalpy of melting of 994.4 kJ/mol, much larger than the estimated value using the Richard’s rule. According to the Richard’s rule, the melting entropy is about 10 J/(K mol atoms). This gives a melting enthalpy of about 280 kJ/mol for La$_2$Zr$_2$O$_7$ at 2537 K. No measurements have been done on the enthalpy of melting of La$_2$Zr$_2$O$_7$. Trying to decrease the melting enthalpy leads to a worse fit of the liquidus data. Instead, we choose to fit the liquidus data well.

Table 6.3 Calculated temperatures and compositions of invariant equilibria compared with experimental data

<table>
<thead>
<tr>
<th>Invariant equilibrium</th>
<th>Type</th>
<th>Temp., K</th>
<th>x(LaO$_{1.5}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>L$\rightarrow$P</td>
<td>Congruent melting</td>
<td>2553</td>
<td></td>
<td>[6]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2503</td>
<td></td>
<td>[10]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2537</td>
<td>0.504 (L, P)</td>
<td>This work</td>
</tr>
<tr>
<td>c+L+P</td>
<td>Eutectic</td>
<td>2493</td>
<td>0.4 (L), 0.462 (P)</td>
<td>[6]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2497</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>2453</td>
<td>0.245 (c), 0.345 (L), 0.46 (P)</td>
<td>This work</td>
</tr>
<tr>
<td>P+C$_2$+L</td>
<td>Peritectic</td>
<td>2320</td>
<td>0.667 (C$_2$)</td>
<td>[6]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2316</td>
<td>0.573 (P), 0.753 (L)</td>
<td>This work</td>
</tr>
<tr>
<td>C$_2$+L+X</td>
<td>Eutectic</td>
<td>2303</td>
<td>0.707 (C$_2$), 0.769 (L)</td>
<td>[6]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2302</td>
<td>0.763 (L), 0.811 (X)</td>
<td>This work</td>
</tr>
<tr>
<td>P+C$_2$+X</td>
<td>Eutectoid</td>
<td>2223</td>
<td>0.684 (C$_2$)</td>
<td>[6]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2221</td>
<td>0.583 (P), 0.838 (X)</td>
<td>This work</td>
</tr>
<tr>
<td>P+X+H</td>
<td>Eutectoid</td>
<td>2173</td>
<td>0.837 (X), 0.889 (H)</td>
<td>[7]</td>
</tr>
<tr>
<td></td>
<td></td>
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<td>This work</td>
</tr>
<tr>
<td>t+c+P</td>
<td>Eutectoid</td>
<td>2123</td>
<td>0.095 (c)</td>
<td>[6]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2223</td>
<td>0.131 (c)</td>
<td>[7]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2175</td>
<td>0.058 (t), 0.108 (c), 0.443 (P)</td>
<td>This work</td>
</tr>
<tr>
<td>P+H+A</td>
<td>Eutectoid</td>
<td>2138</td>
<td>0.578 (P), 0.913 (H), 0.963 (A)</td>
<td>This work</td>
</tr>
<tr>
<td>m+t+P</td>
<td>Eutectoid</td>
<td>1373</td>
<td>0.015 (t)</td>
<td>[19]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1383</td>
<td>0.015 (t)</td>
<td>[20]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1332</td>
<td>0.014 (t), 0.486 (P)</td>
<td>This work</td>
</tr>
</tbody>
</table>

L: Liquid; P: the La$_2$Zr$_2$O$_7$ pyrochlore phase; C$_2$: the C$_2$ phase; X and H: X- and H-La$_2$O$_3$; m, t, c: m-, t-, c-ZrO$_2$. 

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Figure 6.5  Calculated ZrO₂–LaO₁.₅ phase diagram from the present work.

Figure 6.6  Calculated liquidus of the ZrO₂–LaO₁.₅ system from the present work compared with experimental data from von Wartenberg and Eckhardt [17], Rouanet [6], Cabannes et al. [18], and Karyakina et al. [10].
Figure 6.7  Calculated ZrO$_2$-rich subsolidus compared with experimental data from Brown and Duwez [5], Rouanet [6, 7], Bastide et al. [19], and Andrievskaya and Lopato [20].

Figure 6.8  Calculated LaO$_{1.5}$-rich subsolidus compared with experimental data from Brown and Duwez [5], Rouanet [6, 7], and Zheng and West [14].
Figure 6.9  Calculated composition ranges of the La$_2$Zr$_2$O$_7$ pyrochlore phase at different temperatures from the present work compared with experimental data from Brown and Duwez [5], Lefevre et al. [11], Collongues et al. [12], Rouanet [6], Zoz et al. [13], Zheng and West [14], Skapin et al. [15], and Tabira et al. [16].

Our calculated ZrO$_2$-rich subsolidus gives a reasonable fit of the experimental data (Figure 6.7). For the LaO$_{1.5}$-rich side (Figure 6.8), due to evaporation of La$_2$O$_3$ at high temperature, the experimental data are very limited. Further experimental investigations are necessary to clarify the phase relations on the LaO$_{1.5}$-rich side and the existence of the C$_2$ phase.

The composition range of the La$_2$Zr$_2$O$_7$ pyrochlore phase is shown in Figure 6.9. According to our calculations, La$_2$Zr$_2$O$_7$ stays close to stoichiometric at temperatures below 1000 K and exhibits notable nonstoichiometry at temperatures above 1600 K with the LaO$_{1.5}$ excess slightly larger than the ZrO$_2$ excess. In the optimization, we use the experimental data from Collongues et al. [12] and Zheng and West [14]. Interestingly, the reported values from Brown and Duwez [5] correlate well with the calculated maximum composition range. Due to the large scatter on the reported composition ranges of La$_2$Zr$_2$O$_7$, it is difficult to say how well our description represents the real nonstoichiometry of La$_2$Zr$_2$O$_7$. Instead, we try to correlate our optimized parameters ($V_5$, $V_6$, and $V_7$ in Eqs. 6.5–7) with the reported defect formation energies from literature and to check if our parameters are reasonable.
Sickafus et al. [2] calculated the formation energy of the cation antisite defect for a series of A$_2$B$_2$O$_7$ compounds. The formation of the antisite defect is described as:

\[ A^+_A + B^-_B \rightarrow A^-_B + B^+ \_A \quad \text{Eq. 6.21} \]

Sickafus et al. [2] found that the absolute values of their calculated isolated cation antisite formation energies are too high to be compatible with the large degrees of disorder found in some pyrochlores. Including the defect clustering can lower the reaction energies. Stanek et al. [34] calculated defect formation energies corresponding to both the BO$_2$ excess and the AO$_{1.5}$ excess for a series of A$_2$B$_2$O$_7$ pyrochlores. According to their calculated defect energies, they concluded that the ZrO$_2$ excess in La$_2$Zr$_2$O$_7$ is mainly due to the following reaction:

\[ 7\text{ZrO}_2 + 4\text{La}^+ \rightarrow 3\text{Zr}^+ \_\text{La} + \text{V}^+ + 2\text{La}_2\text{Zr}_2\text{O}_7 \quad \text{Eq. 6.22} \]

while the mechanism accounting for the LaO$_{1.5}$ excess can be described as:

\[ 2\text{La}_2\text{O}_3 + 2\text{Zr}^+ \_\text{La} + \text{O}^- \rightarrow 2\text{La}^+ \_\text{Zr} + \text{V}^- + \text{La}_2\text{Zr}_2\text{O}_7 \quad \text{Eq. 6.23} \]

Their calculated reaction energy for Eq. 6.23 is higher than that for Eq. 6.22. Including the effect of defect clustering lowers the absolute values for these two reaction energies, but the relation between them does not change. Based on this, they predicted that the phase field for La$_2$Zr$_2$O$_7$ should be asymmetric with greater ZrO$_2$ excess than LaO$_{1.5}$ excess.

We correlate the optimized parameters $V_5$, $V_7$, and $V_9$ in Eqs. 6.5–7 with the calculated defect energies from Sickafus et al. [2] and Stanek et al. [34]. The parameter $V_5$ in Eq. 6.5 is the energy difference between 1 mol Zr$_2$La$_2$O$_7$ and 1 mol La$_2$Zr$_2$O$_7$, which can be correlated to the formation energy of the antisite defect (Eq. 6.21). The parameters $V_7$ in Eq. 6.6 and $V_9$ in Eq. 6.7 correspond to the ZrO$_2$ excess and the LaO$_{1.5}$ excess, respectively, which, according to our model for the La$_2$Zr$_2$O$_7$ pyrochlore phase, can be correlated to the defect formation energies of Eqs. 6.22 and 6.23. To simplify the case, here we only consider isolated defects.

We simply convert the calculated isolated defect formation energies into the corresponding values for $V_5$, $V_7$, and $V_9$ and compare them with our optimized values based on reported phase diagram data. From the calculated isolated defect formation energies from Sickafus et al. [2] and Stanek et al. [34], we get $V_5 = 887.7$ kJ/mol, $V_7 = 38.6$ kJ/mol, and $V_9 = 115.8$ kJ/mol. The three optimized values are $V_5 = 300$ kJ/mol, $V_7 = 63.2$ kJ/mol, and $V_9 = 62.4$ kJ/mol. Our optimized values are of the same magnitude as the three values derived from calculated isolated defect energies. As expected, the value for $V_5$ derived from the calculated isolated antisite defect energy from Sickafus et al. [2] is much larger than our optimized value. The
parameters $V_7$ and $V_9$ control the extents of the $\text{ZrO}_2$ and the $\text{LaO}_{1.5}$ excess. The two values derived from calculated isolated defect energies are different from each other with a smaller value for $V_7$, while the two optimized values are quite close to each other. Putting $V_7 = 38.6$ kJ/mol and $V_9 = 115.8$ kJ/mol into our description gives a quite asymmetric $\text{La}_2\text{Zr}_2\text{O}_7$ single-phase field with almost no $\text{LaO}_{1.5}$ excess. Stanek et al. [34] predicted that the $\text{La}_2\text{Zr}_2\text{O}_7$ single-phase field should be asymmetric with greater $\text{ZrO}_2$ excess than $\text{LaO}_{1.5}$ excess. This is in contradiction with most of experimental investigations. In our calculated phase diagram (Figure 6.9), the extent of the $\text{ZrO}_2$ excess is greater than that of the $\text{LaO}_{1.5}$ excess only at $T < 1400$ K, where the whole composition range of $\text{La}_2\text{Zr}_2\text{O}_7$ is very narrow. Further investigations are necessary to verify the nonstoichiometry of $\text{La}_2\text{Zr}_2\text{O}_7$, both experimentally and theoretically.

### 6.6 Conclusions

We assessed the thermodynamic properties of stoichiometric $\text{La}_2\text{Zr}_2\text{O}_7$. The experimentally measured heat capacity and heat content data can be represented very well using the Neumann-Kopp rule. Our Gibbs energy function of stoichiometric $\text{La}_2\text{Zr}_2\text{O}_7$ differs from the previously assessed ones. This is mainly due to the more reliable enthalpy of formation of $\text{La}_2\text{Zr}_2\text{O}_7$ at 298.15 K used in our optimization. We present a thermodynamic description of the $\text{ZrO}_2$-$\text{LaO}_{1.5}$ system. A 4-sublattice model is used to describe the $\text{La}_2\text{Zr}_2\text{O}_7$ nonstoichiometry. The present description fits most of phase diagram data well. According to our calculations, the $\text{La}_2\text{Zr}_2\text{O}_7$ pyrochlore phase exhibits notable nonstoichiometry of both $\text{ZrO}_2$ and $\text{LaO}_{1.5}$ excess at temperatures above 1600 K. Our calculated $\text{ZrO}_2$-$\text{LaO}_{1.5}$ phase diagram shows a more or less symmetric $\text{La}_2\text{Zr}_2\text{O}_7$ single-phase field.

### 6.7 References


[3] A. Mitterdorfer and L. J. Gauckler, "$\text{La}_2\text{Zr}_2\text{O}_7$ formation and oxygen reduction kinetics of the $\text{La}_{0.85}\text{Sr}_{0.15}\text{Mn}_2\text{O}_3$, $\text{O}_2(\text{g})$/$\text{YSZ}$ system", Solid State Ionics 111 (1998), p. 185.
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[16] Y. Tabira, R. Withers, J. Thompson, and S. Schmid, "Structured diffuse scattering as an indicator of inherent cristobalite-like displacive flexibility in the rare earth zirconate pyrochlore La$_{16-\delta}$Zr$_{10}$O$_{28}$, 0.49$\delta$$<$0.51", J. Solid State Chem. 142 (1999), p. 393.


[22] D. Sedmidubsky, O. Benes, and R. J. M. Konings, "High temperature heat capacity of Nd$_2$Zr$_2$O$_7$ and La$_2$Zr$_2$O$_7$ pyrochlores", J. Chem. Thermodyn., in press.

Chapter 6


7 Thermodynamic Modeling of the La–Mn–Y–Zr–O System

Ming Chen, A. Nicholas Grundy, Bengt Hallstedt, and Ludwig J. Gauckler, to be submitted.

Abstract

Based on descriptions of the previously assessed sub-systems, we present a thermodynamic description of the La–Mn–Y–Zr–O system. Ideal extrapolations from ternaries to quaternaries and to La–Mn–Y–Zr–O are proved to be quite successful. The calculated isothermal sections of pseudo-ternaries at different temperatures in air are in good agreement with available experimental data.

The thermodynamics at the LaMnO$_3$–YSZ interface, which is of particular importance for SOFC applications, is discussed in detail. Based on phase equilibrium calculations, we conclude that La$_2$Zr$_2$O$_7$ forms at the LaMnO$_3$–YSZ interface due to its high stability. Thermodynamically, the La$_2$Zr$_2$O$_7$ formation cannot be prevented by increasing the La deficiency in La$_{1-x}$MnO$_3$ or by increasing the yttria content in YSZ. Increasing the yttria content in YSZ can suppress and in the end prevent the La$_2$Zr$_2$O$_7$ formation. Apart from the temperature and the oxygen partial pressure, other factors, like the phase assemblage at the interface, the La deficiency in La$_{1-x}$MnO$_3$, the yttria content in YSZ and so on, also influence the amount of LaO$_{1.5}$ or MnO$_x$ (from LaMnO$_3$) dissolved in YSZ.

7.1 Introduction

7.1.1 The LSM–YSZ interface reactions

Yttria-stabilized zirconia (YSZ, cubic fluorite) and Sr-doped perovskite-type La$_{1-x}$MnO$_{3-δ}$ ((La$_{1-y}$Sr$_y$)$_{1.83}$MnO$_{3-δ}$, LSM) are widely used as electrolyte and cathode materials in solid oxide fuel cells (SOFCs). Under certain conditions, highly electrically resistive phases La$_2$Zr$_2$O$_7$ and SrZrO$_3$ are formed at the LSM–YSZ interface, leading to degradation of the cell performance. Lau and Singhal [1] first reported the La$_2$Zr$_2$O$_7$ formation between diffusion couples of dense La$_{0.9}$Sr$_{0.1}$MnO$_3$ and (YO$_{1.5}$)$_{0.18}$(ZrO$_2$)$_{0.82}$ single crystals. The amount of the
formed La$_2$Zr$_2$O$_7$ phase has been found to increase with longer reaction time or higher sintering temperature, and to decrease with increasing Sr substitution for La [2, 3]. For heavily doped (La$_{1-y}$Sr$_y$)$_{1-x}$MnO$_{3-y}$ ($y \geq 0.3$), SrZrO$_3$ was also found to form at the LSM–YSZ interface [4, 5]. It has been reported that by increasing the A-site deficiency ($x$ in (La$_{1-y}$Sr$_y$)$_{1-x}$MnO$_{3-y}$) or introducing excess Mn oxide in LSM [2, 6, 7, 8, 9, 10], or increasing the yttria content in YSZ [2, 11], the zirconate formation can be retarded or even prevented during high temperature treatment.

The inter-diffusion of metal elements between LSM and YSZ has been observed in the LSM–YSZ interface region. It has been reported that Mn and La diffuse from LSM into YSZ, while Sr hardly diffuses into YSZ [12, 13]. The diffusion of Mn has generally been found to take place to a larger extent than that of La. van Roosmalen and Cordfunke [14] however, found no diffusion of Mn from La$_{1-y}$Sr$_y$MnO$_3$ ($y = 0, 0.15, 0.3, 0.5$) into YSZ from diffusion couple experiments. Instead, they observed diffusion of La and Sr from LSM into YSZ. Mitterdorfer and Gauckler [10] reported no Mn diffusion from La$_{0.85}$Sr$_{0.15}$Mn$_{0.95}$O$_3$ or La$_{0.85}$Sr$_{0.15}$Mn$_{0.08}$O$_3$ into 17 cation% (cat.%) YO$_{1.5}$ stabilized zirconia single crystal, but heavy Mn diffusion from Mn-rich perovskites such as La$_{0.85}$Sr$_{0.15}$Mn$_{1.02}$O$_3$ into YSZ. The La$_{0.85}$Sr$_{0.15}$Mn$_{1.02}$O$_3$ cathode was prepared from a mixture of La$_{0.85}$Sr$_{0.15}$Mn$_{0.08}$O$_3$ and MnO$_x$. The diffusion of Y and Zr from YSZ into LSM was reported to be very limited [1, 8, 12, 13].

7.1.2 Yokokawa et al.’s efforts

The LSM–YSZ interface reactions are obviously influenced by both thermodynamic and kinetic factors. The thermodynamics at the LSM–YSZ interface has been studied by Yokokawa et al. [15]. They evaluated or estimated the thermodynamic properties of solid solution phases and stoichiometric compounds in the La–Mn–Sr–Y–Zr–O system. According to their calculations, the Gibbs energy change for the following reaction is essentially positive under the SOFC fabrication and operation conditions:

$$\text{LaMnO}_x + \text{ZrO}_2 = \frac{1}{2} \text{La}_2\text{Zr}_2\text{O}_7 + \text{MnO}_x + \frac{3 - 2x}{4} \text{O}_2$$

Eq. 7.1

The driving force for the zirconate formation was hence attributed to the destabilization of the unusual valence state of Mn$^{3+}$ in the perovskite phase in the presence of ZrO$_2$. Their calculated chemical potential diagram for the La–Mn–Zr–O system at 1573 K in air (Figure 8
Modeling of the La–Mn–Y–Zr–O System

in [16]) indicates that lanthanum manganites having large lanthanum deficiency \(x > 0.14\) for \(x\) in \(\text{La}_{1-x}\text{MnO}_{3.8}\) can be in equilibrium with YSZ, those having small lanthanum deficiency will be in equilibrium with \(\text{La}_2\text{Zr}_2\text{O}_7\). This means that the \(\text{La}_2\text{Zr}_2\text{O}_7\) formation can be thermodynamically prevented by increasing \(x\) in \(\text{La}_{1-x}\text{MnO}_{3.8}\) to a certain extent \((x = 0.14\) at 1573 K in air). As a consequence, this would allow operating a SOFC for long time without degradation of the cathode by forming the insulating \(\text{La}_2\text{Zr}_2\text{O}_7\) phase at the cathode–electrolyte interface.

7.1.3 Aim of this study

Yokokawa et al.‘s phase equilibrium calculations give a good explanation on the formation mechanism of \(\text{La}_2\text{Zr}_2\text{O}_7\) at the LSM–YSZ interface. However, there are still some open questions, like the disagreement on the observed inter-diffusion between LSM and YSZ, the effect of the yttria content in YSZ and so on. Until now, no other effort has been conducted on the thermodynamics at the LSM–YSZ interface. Instead, quite a lot of measurements have been done on the thermodynamic properties of stoichiometric compounds and solution phases in the La–Mn–Sr–Y–Zr–O system. In Yokokawa et al.‘s database, the thermodynamic descriptions of certain phases were obtained from estimations. It is hence necessary to re-evaluate the thermodynamic description of the La–Mn–Sr–Y–Zr–O system and to reconsider the thermodynamic origin of the zirconate formation at the LSM–YSZ interface.

We assessed the thermodynamic properties of stoichiometric compounds and solution phases in the La–Mn–Sr–Y–Zr–O system. In this paper we present the thermodynamic description of the La–Mn–Y–Zr–O system.

7.2 The La–Mn–Y–Zr–O system

La–Zr, La– Mn–Y, La– Mn–Zr, La–Y–Zr, La– Mn–Y–Zr) are not considered in the present work. Based on the available experimental data, a modeling strategy for the La–Mn–Y–Zr–O system is designed. The thermodynamic description of the La–Mn–Y–Zr–O system is obtained by an ideal extrapolation of the thermodynamic descriptions of the previously assessed sub-systems with some revisions.

We will generally use the designations c-ZrO₂ for cubic fluorite zirconia, YSZ for yttria-stabilized cubic fluorite zirconia, LMO for La₁₋ₓMnO₃₋₆, LSM for (La₁₋ₓSrₓ)₁₋ₓMnO₃₋₆, and LZO for La₂Zr₂O₇.

### 7.3 Experimental data

#### 7.3.1 La–Y–Zr–O

Colombo [17] investigated the phase relations in the La₂Zr₂O₇–Y₂Zr₂O₇–ZrO₂ system using X-ray diffraction (XRD). The samples were prepared by hydrolyzing zirconium butoxide with solutions of Y and La nitrates, followed by drying, calcining, and sintering at 1723 K in air for 2 h. The lattice parameter of c-ZrO₂ was observed to decrease with increasing the LaO₁.₅ content (x) in (LaₓY₁₋ₓ)₀.₃₃Zr₀.₆₇O₁.₈₃₅. He suggested that the LaO₁.₅ solubility in the fluorite structure is proportional to the yttria content. An isothermal section of La₂Zr₂O₇–Y₂Zr₂O₇–ZrO₂ at 1723 K was proposed. According to the proposed diagram, c-ZrO₂ is the stable phase at the Y₂Zr₂O₇-rich corner while t-ZrO₂ is stable at the ZrO₂-rich corner. The LaO₁.₅ solubility in c-ZrO₂ increases from almost 0 cat.% LaO₁.₅ for about 15 cat.% YO₁.₅ stabilized ZrO₂ to 20 cat.% LaO₁.₅ for 50 cat.% YO₁.₅ stabilized ZrO₂. The phase boundaries close to the ZrO₂-rich and the La₂Zr₂O₇-rich corners are not well-determined. Mori et al. [11] measured the lattice parameters of quenched mixtures of YSZ+La₂O₃ (YSZ having 15–21 cat.% YO₁.₅), which were sintered at 1873 K for 68 h. La₂Zr₂O₇ was found in samples containing more than 7 cat.% LaO₁.₅. Below 7 cat.% LaO₁.₅, the lattice parameter increases linearly with increasing LaO₁.₅ content. Above 7 cat.% LaO₁.₅, the lattice parameter still increases with increasing LaO₁.₅ content, but with a different slope. They suggested that the solubility of LaO₁.₅ in YSZ is about 6.5 cat.% and is almost independent of the yttria content in YSZ. This is different from what Colombo [17] indicated in his proposed diagram of La₂Zr₂O₇–Y₂Zr₂O₇–ZrO₂ at 1723 K in air.
It has been reported that La$_2$Zr$_2$O$_7$ can dissolve some yttria [18, 19]. Poulsen and van der Puil [18] detected the La$_2$Zr$_2$O$_7$ formation by a solid state reaction between La$_2$O$_3$ and 15 cat.% YO$_{1.5}$ stabilized ZrO$_2$. The lattice parameter of the formed pyrochlore phase is -within the experimental error- the same as the reported value for pure La$_2$Zr$_2$O$_7$. The lattice parameter of YSZ increased after the solid state reaction and this was ascribed to an increase in the yttria content in YSZ. They concluded that the solubility of YO$_{1.5}$ in La$_2$Zr$_2$O$_7$ is low. Ota et al. [19] synthesized Y$_2$O$_3$-substituted La$_2$Zr$_2$O$_7$ ((La$_{0.83}$Y$_{0.17}$)$_2$Zr$_2$O$_7$) by the hydrazine method. The lattice parameter of (La$_{0.83}$Y$_{0.17}$)$_2$Zr$_2$O$_7$ is smaller than that of pure La$_2$Zr$_2$O$_7$, which was suggested to be due to the substitution of smaller Y$^{3+}$ for La$^{3+}$. It is probably true that Y can substitute La in La$_2$Zr$_2$O$_7$ to form a solid solution. The YO$_{1.5}$ solubility in La$_2$Zr$_2$O$_7$ is however not yet clarified and hence will not be considered in the present work.

7.3.2 La–Mn–Y–O

Hrovat et al. [20] investigated the subsolidus phase equilibria in the La$_2$O$_3$–Mn$_2$O$_3$–Y$_2$O$_3$ system. The samples were sintered at 1473 K with intermediate grinding. They proposed a phase diagram for the isothermal section of La$_2$O$_3$–Mn$_2$O$_3$–Y$_2$O$_3$ at 1473 K in air. 3 tie lines (LaMnO$_3$–LaYO$_3$, LaMnO$_3$–Y$_2$O$_3$, LaMnO$_3$–YMnO$_3$) are drawn. No information is given on the solubilities.

7.3.3 La–Mn–Zr–O

Kuscer et al. [21] investigated the phase relations in the La$_2$O$_3$–Mn$_2$O$_3$–ZrO$_2$ system between 1723 and 1773 K in air. A schematic phase diagram for the isothermal section of La$_2$O$_3$–Mn$_2$O$_3$–ZrO$_2$ is proposed. The tie lines between La$_2$Zr$_2$O$_7$ and LaMnO$_3$ and between La$_2$Zr$_2$O$_7$ and Mn$_2$O$_3$ are drawn.
7.4 Thermodynamic modeling

7.4.1 Strategy

Due to the oxidative atmosphere (often air) at the LMO–YSZ interface, the phase relations in the La–Mn–Y–Zr metal system are irrelevant to the LMO–YSZ interface reactions. In the present work, we include the descriptions of Mn–Y, Mn–Zr, Y–Zr, and Mn–Y–Zr from Flandorfer et al. [22]. No assessment is available for the other metal sub-systems and they are not considered in the present work.

Due to the limited experimental data, we conduct no assessment on the La–Y–Zr–O, La–Mn–Y–O, La–Mn–Zr–O, and La–Mn–Y–Zr–O systems. Instead, ideal extrapolations from the lower-order sub-systems are made. The strategy we developed for modeling the La–Mn–Y–Zr–O system is shown in Figure 7.1. Our description of the La–Mn–Y–Zr–O system is based directly on the descriptions of La–Mn–O [23], La–Y–O [24], La–Zr–O [25], and Mn–Y–Zr–O [26]. Figure 7.1 shows all the assessed sub-systems in La–Mn–Y–Zr–O. The descriptions of Mn–Y, Mn–Zr, Y–Zr, and Mn–Y–Zr are from Flandorfer et al. [22] and all the others are from the present authors.

7.4.2 Revisions of previously assessed sub-systems

In the previously assessed binary sub-systems (La–O, Mn–O, and Y–O), different models which are not compatible with each other have been used. This concerns A-La2O3, H-La2O3, X-La2O3, β-Mn2O3, and β-Y2O3. The original descriptions of La–O and Mn–O are from Grundy et al. [27, 28] and that of Y–O is from Chen et al. [29]. In our work on the Mn–Y–O system [30], we changed the model for β-Mn2O3 and revised the description of Mn–O. In our work on the La–Y–O system [24], we changed the models for A-, H-, X-La2O3, and β-Y2O3. The thermodynamic descriptions of the two binary sub-systems, La–O and Y–O, were hence revised. The thermodynamic descriptions of other sub-systems related to these three binaries (La–O, Mn–O, and Y–O) are revised in the present work. This includes La–Mn–O, Y–Zr–O, Mn–Y–O, and Mn–Y–Zr–O. The revision leads to a consistent description for all the binary oxides and the oxide solution phases in the La–Mn–Y–Zr–O system. For the sub-systems
revised in the present work, the calculated phase diagrams and thermodynamic properties are very similar to the previously published ones.

Figure 7.1 Strategy for modeling the La–Mn–Y–Zr–O system. The thermodynamic descriptions of Mn–Y, Mn–Zr, Y–Zr, and Mn–Y–Zr are from Flandorfer et al. [22]. The descriptions of other sub-systems are from the present authors: La–O [27], Mn–O [28], La–Mn–O [23], Y–O, Zr–O, and Y–Zr–O [29], Mn–Y–O [30], Mn–Zr–O and Mn–Y–Zr–O [26], La–Y–O [24], La–Zr–O [25].

The original thermodynamic description of the corresponding sub-system from the literature was revised in the present work.

7.4.3 Thermodynamic description of the La–Mn–Y–Zr–O system

The models for all the solid and liquid phases are listed in Table 7.1. A few phases are described as one phase, like β-Mn2O3 and C-Y2O3 (α-Y2O3), H-La2O3 and H-Y2O3 (β-Y2O3), and X-La2O3 and c-ZrO2. The thermodynamic descriptions of all the intermetallic compounds and ternary oxide phases are taken from the binary or ternary sub-systems without any change. In the present work, we did not include any YO1.5 or ZrO2 solubility in the LMO phase and no YO1.5 solubility in the LZO phase. Ideal extrapolations are used for some of the metal and oxide solution phases. Here we use the c-ZrO2 phase as an example. In the present work, we describe the c-ZrO2 phase and the X-La2O3 phase as one phase using the model (La,La3+,Mn2+,Mn3+,Y,Y3+,Zr,Zr4+)1(O2−,Va)2. The Gibbs energies of all end-members are taken from the binary sub-systems. The interaction parameters are from the ternary and quaternary (Mn–Y–Zr–O) sub-systems. To keep the MnOx solubility in X-La2O3 small, a value of 30 kJ/mol is given to the interaction parameters between La2+ and Mn2+/3+.
## Chapter 7

### Table 7.1 Phase descriptions for the La–Mn–Y–Zr–O system

<table>
<thead>
<tr>
<th>Phase</th>
<th>Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>DHCP (La)</td>
<td>(La)\textsubscript{1}(O, Va)\textsubscript{0.5}</td>
</tr>
<tr>
<td>HCP (Mn, Y, Zr)</td>
<td>(Mn, Y, Zr)\textsubscript{1}(O, Va)\textsubscript{0.5}</td>
</tr>
<tr>
<td>BCC (La, Mn, Y, Zr)</td>
<td>(La, Mn, Y, Zr)\textsubscript{1}(O, Va)\textsubscript{0.5}</td>
</tr>
<tr>
<td>CBCC (α-Mn)</td>
<td>(Mn)\textsubscript{1}(Va)\textsubscript{0}</td>
</tr>
<tr>
<td>FCC (La, Mn, Zr)</td>
<td>(La, Mn, Zr)\textsubscript{1}(O, Va)\textsubscript{0}</td>
</tr>
<tr>
<td>CUBIC (β-Mn)</td>
<td>(Mn)\textsubscript{1}(Va)\textsubscript{0}</td>
</tr>
<tr>
<td>Mn\textsubscript{12}Y</td>
<td>(Mn)\textsubscript{12}(Y)\textsubscript{1}</td>
</tr>
<tr>
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<td>(Mn)\textsubscript{23}(Y)\textsubscript{6}</td>
</tr>
<tr>
<td>Mn\textsubscript{2}Y</td>
<td>(Mn)\textsubscript{2}(Y)\textsubscript{1}</td>
</tr>
<tr>
<td>Mn\textsubscript{2}Zr\textsubscript{1}−x</td>
<td>(Mn)\textsubscript{2}(Zr, Va)\textsubscript{1}</td>
</tr>
<tr>
<td>Mn\textsubscript{1−x}O</td>
<td>(Mn\textsuperscript{3+}, Mn\textsuperscript{3+}, Va)\textsubscript{1}(O\textsuperscript{2−})\textsubscript{1}</td>
</tr>
<tr>
<td>α-Mn\textsubscript{3}O\textsubscript{4}</td>
<td>(Mn\textsuperscript{3+})\textsubscript{1}(Mn\textsuperscript{3+})\textsubscript{3}(O\textsuperscript{2−})\textsubscript{4}</td>
</tr>
<tr>
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<tr>
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<tr>
<td>B-La\textsubscript{2}O\textsubscript{3}</td>
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</tr>
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<td>C-Y\textsubscript{2}O\textsubscript{3} (α-Y\textsubscript{2}O\textsubscript{3}) and β-Mn\textsubscript{2}O\textsubscript{3}</td>
<td>(La, La\textsuperscript{3+}, Mn\textsuperscript{3+}, Y\textsuperscript{3+}, Zr\textsuperscript{4+})\textsubscript{1}(O\textsuperscript{2−}, Va)\textsubscript{3}(O\textsuperscript{2−}, Va)\textsubscript{3}</td>
</tr>
<tr>
<td>H-Y\textsubscript{2}O\textsubscript{3} (β-Y\textsubscript{2}O\textsubscript{3}) and H-La\textsubscript{2}O\textsubscript{3}</td>
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</tr>
<tr>
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</tr>
<tr>
<td>c-Zr\textsubscript{2}O\textsubscript{2} and X-La\textsubscript{2}O\textsubscript{3}</td>
<td>(La\textsuperscript{3+}, Mn\textsuperscript{3+}, Mn\textsuperscript{3+}, Y\textsuperscript{3+}, Zr, Zr\textsuperscript{4+})\textsubscript{1}(O\textsuperscript{2−}, Va)\textsubscript{2}</td>
</tr>
<tr>
<td>La\textsubscript{3}Mn\textsubscript{2}O\textsubscript{3}−δ</td>
<td>(La\textsuperscript{3+}, Mn\textsuperscript{3+}, Va)\textsubscript{1}(Mn\textsuperscript{2+}, Mn\textsuperscript{3+}, Mn\textsuperscript{4+}, Va)\textsubscript{1}(O\textsuperscript{2−}, Va)\textsubscript{3}</td>
</tr>
<tr>
<td>La\textsubscript{2}Mn\textsubscript{0}O\textsubscript{4}</td>
<td>(La\textsuperscript{3+})\textsubscript{2}(Mn\textsuperscript{3+})\textsubscript{1}(O\textsuperscript{2−})\textsubscript{4}</td>
</tr>
<tr>
<td>La\textsubscript{Y}O\textsubscript{3}</td>
<td>(La\textsuperscript{3+})\textsubscript{1}(Y\textsuperscript{3+})\textsubscript{1}(O\textsuperscript{2−})\textsubscript{3}</td>
</tr>
<tr>
<td>La\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7}</td>
<td>(La\textsuperscript{3+}, Zr\textsuperscript{4+}, Va)\textsubscript{2}(La\textsuperscript{3+}, Zr\textsuperscript{4+})\textsubscript{2}(O\textsuperscript{2−}, Va)\textsubscript{6}(O\textsuperscript{2−})\textsubscript{6}</td>
</tr>
<tr>
<td>C\textsubscript{2}</td>
<td>(La\textsuperscript{3+})\textsubscript{2}(Zr\textsuperscript{4+})\textsubscript{1}(O\textsuperscript{2−})\textsubscript{5}</td>
</tr>
<tr>
<td>h-YMn\textsubscript{3}O\textsubscript{5}</td>
<td>(Y\textsuperscript{3+})\textsubscript{1}(Mn\textsuperscript{3+})\textsubscript{3}(O\textsuperscript{2−})\textsubscript{3}</td>
</tr>
<tr>
<td>YMn\textsubscript{2}O\textsubscript{5}</td>
<td>(Y\textsuperscript{3+})\textsubscript{1}(Mn\textsuperscript{3+})\textsubscript{3}(O\textsuperscript{2−})\textsubscript{5}</td>
</tr>
<tr>
<td>Zr\textsubscript{2}Y\textsubscript{3}O\textsubscript{12}</td>
<td>(Zr\textsuperscript{4+})\textsubscript{3}(Y\textsuperscript{3+})\textsubscript{3}(O\textsuperscript{2−})\textsubscript{12}</td>
</tr>
<tr>
<td>Liquid</td>
<td>(La\textsuperscript{3+}, Mn\textsuperscript{3+}, Mn\textsuperscript{3+}, Y\textsuperscript{3+}, Zr\textsuperscript{4+})\textsubscript{1}(Zr\textsuperscript{4+})\textsubscript{2}(O\textsuperscript{2−}, Va\textsuperscript{−})\textsubscript{12}</td>
</tr>
</tbody>
</table>

We include the thermodynamic description of the La–Mn–Y–Zr–O system as a database file (see Appendix). The database file can be used directly as an input for the software.
“Thermo-Calc”. With the current description of the La–Mn–Y–Zr–O system, the phase relations in any of the sub-systems can be calculated. The readers should note however, that the sub-systems which are not listed in Figure 7.1 are not assessed in the present work, especially those of the metal sub-systems.

**7.5 Results and discussion**

7.5.1 \( \text{LaO}_{1.5}–\text{YO}_{1.5}–\text{ZrO}_2 \)

In the present work, we conduct no assessment on the La-Y-Zr-O system. The thermodynamic description of this quaternary system is obtained by an ideal extrapolation of the thermodynamic descriptions of La-Y-O [24], La-Zr-O [25], and Y-Zr-O [29]. Figure 7.2 shows the calculated isothermal sections of the \( \text{LaO}_{1.5}–\text{YO}_{1.5}–\text{ZrO}_2 \) pseudo-ternary system at 3 different temperatures in air. At 1273 K (Figure 7.2a), the c-ZrO\(_2\) phase exhibits almost no LaO\(_{1.5}\) solubility. The LZO phase is the most stable phase and tie lines exist between LZO and all the other phases. At 1723 K (Figure 7.2b), the c-ZrO\(_2\) phase exhibits visible LaO\(_{1.5}\) solubility only at high yttria content. The maximum solubility of LaO\(_{1.5}\) in c-ZrO\(_2\) is about 1 cat.% LaO\(_{1.5}\). Increasing temperature also leads to an increase in the LaO\(_{1.5}\) solubility in c-ZrO\(_2\). At 2073 K (Figure 7.2c), the maximum solubility of LaO\(_{1.5}\) in c-ZrO\(_2\) is about 10 cat.% LaO\(_{1.5}\). No liquid appears at this temperature.

Our calculated phase diagram is somewhat different from Colombo’s. This is mainly because in the present work, we did not include any \( \text{YO}_{1.5}\) solubility in LZO. Concerning the phase relations close to the \( \text{Y}_2\text{Zr}_2\text{O}_7–\text{ZrO}_2 \) side, there is not too much difference between Colombo’s diagram and ours, except that with increasing the yttria content in c-ZrO\(_2\), the increase of the LaO\(_{1.5}\) solubility in c-ZrO\(_2\) calculated from the present work is too slight compared to Colombo’s. This will be discussed in Section 7.5.4.

7.5.2 \( \text{LaO}_{1.5}–\text{MnO}_x–\text{YO}_{1.5} \)

Our description of La–Mn–Y–O is an ideal extrapolation from the descriptions of La–Mn–O [23], La–Y–O [24], and Mn–Y–O [30]. We present here the calculated isothermal sections of the \( \text{LaO}_{1.5}–\text{MnO}_x–\text{YO}_{1.5} \) pseudo-ternary system at 1273, 1473, and 2073 K in air (Figure 7.3).
Chapter 7

(a)

(b)
Figure 7.2 Calculated isothermal sections of the La$_{0.5}$–YO$_{1.5}$–ZrO$_2$ system in air from the present work, (a) at 1273 K, (b) at 1723 K, (c) at 2073 K.
Figure 7.3  Calculated isothermal sections of the LaO$_{1.5}$–MnO$_x$–YO$_{1.5}$ system in air from the present work, (a) at 1273 K, (b) at 1473 K, (c) at 2073 K.
At 1273 K (Figure 7.3a), tie lines are found between LMO and all the other phases. Between C-Y$_2$O$_3$ and LMO, tie lines exist only between LaO$_{1.5}$-doped C-Y$_2$O$_3$ and LMO with La excess. The calculated isothermal section of LaO$_{1.5}$-MnO$_x$-YO$_{1.5}$ at 1473 K in air (Figure 7.3b) is quite similar to the one proposed by Hrovat et al. [20]. The only difference is the tie line between LMO and B-La$_2$O$_3$. According to our calculated LaO$_{1.5}$-YO$_{1.5}$ phase diagram in air [24], the B-La$_2$O$_3$ phase is stable at 1473 K. Hrovat et al. [20] detected neither the B-La$_2$O$_3$ phase nor the tie line between LaMnO$_3$ and B-La$_2$O$_3$, as no composition inside the LaO$_{1.5}$-LaMnO$_3$-LaYO$_3$ triangle was investigated. According to Figure 7.3c, two liquid-phase regions appear at 2073 K. One is at the MnO$_x$-rich corner and the other is close to the LaO$_{1.5}$-LaMnO$_3$ side.

7.5.3 LaO$_{1.5}$-MnO$_x$-ZrO$_2$

The thermodynamic description of La–Mn–Zr–O is extrapolated from the descriptions of La–Mn–O [23], La–Zr–O [25], and Mn–Zr–O [26]. Figure 7.4 shows the calculated isothermal sections of LaO$_{1.5}$-MnO$_x$-ZrO$_2$ at 1273, 1673, and 2073 K in air from the present work.
Figure 7.4 Calculated isothermal sections of the $\text{LaO}_{1.5}-\text{MnO}_x-\text{ZrO}_2$ system in air from the present work, (a) at 1273 K, (b) at 1673 K, (c) at 2073 K.
At 1273 K (Figure 7.4a), m-ZrO$_2$ is the stable phase for ZrO$_2$. Tie lines exist between LZO and α-Mn$_3$O$_4$ and between LZO and LMO. In the present work, we include neither LaO$_{1.5}$ nor MnO$_x$ solubility in m-ZrO$_2$. Figure 7.4a indicates that m-ZrO$_2$ cannot be in equilibrium with LMO. At 1673 K (Figure 7.4b), t-ZrO$_2$ becomes stable and exhibits both MnO$_x$ and LaO$_{1.5}$ solubilities. There is still no tie line between t-ZrO$_2$ and LMO. Figure 7.4b is similar to the one proposed by Kuscer et al. [21]. At 2073 K (Figure 7.4c), c-ZrO$_2$ also appears. The solubility of MnO$_x$ in c-ZrO$_2$ decreases with increasing the LaO$_{1.5}$ content in c-ZrO$_2$, while the solubility of LaO$_{1.5}$ in c-ZrO$_2$ remains almost constant with increasing the MnO$_x$ content in c-ZrO$_2$. Two liquid-phase regions exist, one at the MnO$_x$-rich corner and the other close to the LaO$_{1.5}$-LaMnO$_3$ side.

7.5.4 LaO$_{1.5}$–MnO$_x$–YO$_{1.5}$–ZrO$_2$

The composition space of the LaO$_{1.5}$–MnO$_x$–YO$_{1.5}$–ZrO$_2$ pseudo-quaternary system can be represented by a tetrahedron as shown in Figure 7.5.

![Figure 7.5](image.png)

Figure 7.5 Composition space for the LaO$_{1.5}$–MnO$_x$–YO$_{1.5}$–ZrO$_2$ system.

In the SOFC, 15 cat.% YO$_{1.5}$ stabilized zirconia ((YO$_{1.5}$)$_{0.15}$(ZrO$_2$)$_{0.85}$) is normally used as the electrolyte. We hence calculate the isothermal section of LaO$_{1.5}$–MnO$_x$–(YO$_{1.5}$)$_{0.15}$(ZrO$_2$)$_{0.85}$ at 1273 K in air (Figure 7.6). Some of the regions in Figure 7.6 are labeled and the corresponding equilibrium phase assemblages are listed. The calculated phase diagram is not really very illustrative. Tie lines cannot be displayed since they are out of the plane. 11 phases,
A-La$_2$O$_3$, $\alpha$-Mn$_3$O$_4$, C-Y$_2$O$_3$, t-ZrO$_2$, c-ZrO$_2$, LMO, LaYO$_3$, LZO, h-YMn$_3$O$_5$, YMn$_2$O$_5$, and Zr$_3$Y$_4$O$_{12}$, are involved in this isothermal section. Some of the phases (C-Y$_2$O$_3$, t-ZrO$_2$, LaYO$_3$, h-YMn$_3$O$_5$, YMn$_2$O$_5$, and Zr$_3$Y$_4$O$_{12}$) have never been reported to appear at the LMO–YSZ interface. We can actually exclude these phases and calculate a metastable phase diagram. This is probably more useful for the SOFC applications. The calculated metastable phase diagram of the LaO$_{1.5}$–MnO$_x$–(YO$_{1.5}$)$_{0.15}$(ZrO$_2$)$_{0.85}$ isothermal section at 1273 K in air is shown in Figure 7.7a. The following phases are included in the calculation: A-La$_2$O$_3$, $\alpha$-Mn$_3$O$_4$, c-ZrO$_2$, LMO, and LZO. To investigate the effect of the yttria content in YSZ on the LMO–YSZ interface reactions, we calculate three other isothermal sections (metastable) with different Y:Zr ratios (Figure 7.7b–d). No tie lines are plotted in Figure 7.7 since they are still out of the plane. Figure 7.7a is actually not too much different from Figure 7.6 and it is more meaningful than Figure 7.6.

![Figure 7.6](image)

Figure 7.6 Calculated isothermal section of the LaO$_{1.5}$–MnO$_x$–(YO$_{1.5}$)$_{0.15}$(ZrO$_2$)$_{0.85}$ system at 1273 K in air from the present work. Equilibrium phase assemblages in different regions: I: t-ZrO$_2$, c-ZrO$_2$, and LZO; II: c-ZrO$_2$ and LZO; III: $\alpha$-Mn$_3$O$_4$, c-ZrO$_2$, and LZO; IV: $\alpha$-Mn$_3$O$_4$, c-ZrO$_2$, LZO, and YMn$_2$O$_5$; V: c-ZrO$_2$, LZO, and YMn$_2$O$_5$; VI: $\alpha$-Mn$_3$O$_4$, LMO, LZO, and YMn$_2$O$_5$; VII: A-La$_2$O$_3$, LMO, LaYO$_3$, and LZO; VIII: A-La$_2$O$_3$, LMO, and LZO; IX: A-La$_2$O$_3$ and LMO.
In Figure 7.7a, there exist 7 regions with different equilibrium phase assemblages. The LZO phase seems to be quite stable and is involved in almost all regions except Region VII. $\alpha$-Mn$_3$O$_4$ is only involved in Regions II and III. Figure 7.7a indicates that the LZO phase is quite stable at the LMO–YSZ interface. At 1273 K in air, increasing the La deficiency in La$_{1+x}$MnO$_{3+\delta}$ by its own cannot thermodynamically prevent the LZO formation (but can decrease the driving force of the LZO formation, so kinetically retard its formation. This will be discussed in Chapter 9). We can further draw a conclusion that the LZO formation at the LMO–YSZ interface is mainly due to the high stability of LZO, and that the LZO formation is not always accompanied with the formation of Mn oxide ($\alpha$-Mn$_3$O$_4$ at $T < 1443$ K and $\beta$-Mn$_3$O$_4$ at $T > 1443$ K in air [28]). We should also bear in mind that manganese from the formed Mn oxide at the interface or from LMO can evaporate at high temperatures. Kuscer et al. [21] observed that Mn oxide condenses as small crystals on the alumina substrate which was used to cover the crucible containing the LaMnO$_3$+YSZ samples. Figure 7.7b–d presents isothermal sections at fixed Y/Zr ratios of 20:80, 30:60, and 40:60. By increasing the Y/Zr ratio, the area of Region II ($\alpha$-Mn$_3$O$_4$, c-ZrO$_2$, and LZO) decreases and those of Regions III ($\alpha$-Mn$_3$O$_4$, c-ZrO$_2$, LZO, and LMO) and IV (c-ZrO$_2$, LZO, and LMO) increase. The boundary line between II and III shifts towards the MnO$_x$–YSZ side. In Figure 7.7d (Y/Zr = 40:60), Region II disappears and Region III changes to Region VIII ($\alpha$-Mn$_3$O$_4$, c-ZrO$_2$, and LMO). The c-ZrO$_2$ phase can then be in equilibrium with LMO (Region IX). We also calculate isothermal sections of LaO$_{1.5}$–MnO$_x$–(YO$_{1.5}$)$_{0.15}$(ZrO$_2$)$_{0.85}$ at different temperatures (1073–1673 K) and at different oxygen partial pressures (1–21278 Pa). MnO, MnO$_2$, Mn$_2$O$_3$, and $\beta$-Mn$_3$O$_4$ are included. The temperature and the oxygen partial pressure do not influence the calculated isothermal sections much and they are all very similar to Figure 7.7a.
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(a)

(b)
Figure 7.7 Calculated isothermal sections of LaO₁₅–MnOₓ–(YO₁₅)ₓ(ZrO₂)₁₋ₓ at 1273 K in air from the present work. (a) LaO₁₅–MnOₓ–(YO₁₅)₀.₁₅(ZrO₂)₀.₈₅; (b) LaO₁₅–MnOₓ–(YO₁₅)₀.₂(ZrO₂)₀.₈; (c) LaO₁₅–MnOₓ–(YO₁₅)₀.₃(ZrO₂)₀.₇; (d) LaO₁₅–MnOₓ–(YO₁₅)₀.₄(ZrO₂)₀.₆. Only the following phases are included in the calculations:
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A-La$_2$O$_3$, α-Mn$_3$O$_4$, c-ZrO$_2$, LMO, and LZO. Equilibrium phase assemblages in different regions: I: c-ZrO$_2$ and LZO; II: α-Mn$_3$O$_4$, c-ZrO$_2$, and LZO; III: α-Mn$_3$O$_4$, c-ZrO$_2$, LMO, and LZO; IV: c-ZrO$_2$, LMO, and LZO; V: A-La$_2$O$_3$, c-ZrO$_2$, LMO, and LZO; VI: A-La$_2$O$_3$, LMO, and LZO; VII: A-La$_2$O$_3$ and LMO; VIII: α-Mn$_3$O$_4$, c-ZrO$_2$, and LMO; IX: c-ZrO$_2$ and LMO.

No experimental investigation has been conducted on the phase equilibria in the La–Mn–Y–Zr–O system. Therefore cannot verify if Figures 7.6 and 7.7 are correct. As our calculated phase diagram of LaO$_{1.5}$–MnO$_x$–ZrO$_2$ is in good agreement with the experimentally determined phase diagram from Kuscer et al. [21], this convinces us that Figure 7.7 should not be too far away from reality. For the experimental investigations of the LMO–YSZ interface reactions, most of the previous studies cannot be treated as equilibrium phase studies. We therefore compare our calculations with the results from Yokokawa et al. [15, 16]. According to our calculations, the LZO phase is quite stable at the LMO–YSZ interface. Increasing the La deficiency in La$_{1-x}$MnO$_{5-y}$ by its own cannot thermodynamically prevent the LZO formation. This is in contradiction to Yokokawa et al.'s calculations. Their calculations show that by increasing the La deficiency in La$_{1-x}$MnO$_{5-y}$, the LZO formation can be thermodynamically stopped. We evaluated the thermodynamic descriptions of major phases in the La–Mn–Y–Zr–O system from both Yokokawa et al. and the present authors. We found that the main difference is the thermodynamic description of stoichiometric La$_2$Zr$_2$O$_7$, which was caused by the fact that different enthalpies of formation of La$_2$Zr$_2$O$_7$ from the literature have been used by Yokokawa et al. and the present authors. The value proposed by the present authors agrees well with experimental values from literature and is about 50 kJ/mol more negative than the value proposed by Yokokawa et al. The detail of this evaluation is described in Chapter 8.

To quantify the equilibrium phase relations, we conduct calculations along the composition lines of (YO$_{1.5}$)(ZrO$_2$)$_{1-x}$–LaMnO$_3$ (x = 0.15, 0.2, 0.3, 0.4). These four lines actually lie inside the isothermal sections shown in Figure 7.7. We only include A-La$_2$O$_3$, α-Mn$_3$O$_4$, c-ZrO$_2$, LMO, and LZO in the calculations, the same as in Figure 7.7. The equilibrium phase fractions are plotted against the mole fraction of LaMnO$_3$ in the system (Figure 7.8). The Roman letters on the top of each diagram indicate the regions which the lines cross in Figure 7.7. In the equilibrium phase assemblage, the ratio of La:Mn in LMO and that of La:Zr in LZO is not exactly 1:1, but quite close to. The c-ZrO$_2$ phase exhibits some LaO$_{1.5}$ and MnO$_x$ solubilities. As Figure 7.8a shows, the phase fraction of LZO in the equilibrium phase assemblage reaches
a maximum in the middle of the composition range \( x(\text{LaMnO}_3) = 0.514 \) in Figure 7.8a). The phase fraction of \( \alpha\)-Mn\(_3\)O\(_4\) is proportional to that of LZO in Regions II and III. In Regions I and IV, \( \alpha\)-Mn\(_3\)O\(_4\) does not exist. The phase fraction of LMO is zero in Regions I and II where the LMO phase totally react with the c-ZrO\(_2\) phase, while the c-ZrO\(_2\) phase stays in the equilibrium phase assemblage in the whole composition range and its fraction decreases with increasing \( x(\text{LaMnO}_3) \). By increasing the Y:Zr ratio, Regions II, III, and IV shift towards the left side of the diagram. The width of Region I decreases and that of Region III first increases then decreases, while the width of Region IV keeps increasing. In Figure 7.8d, only Regions I and IV exist. Obviously increasing the Y:Zr ratio suppresses the LZO formation heavily. This can explain why Yamamoto and his co-authors [2, 11] found that increasing the yttria content in YSZ can retard the LZO formation.

The concentration of La\(_{0.5}\) in the c-ZrO\(_2\) phase along the four composition lines in Figure 7.8 is very low, always less than 0.1 cat.\%. It seems that in an equilibrium state, La\(^{3+}\) and Zr\(^{4+}\) ions prefer to form an ordered pyrochlore phase (LZO), instead of a disordered cubic fluorite solid solution phase (c-ZrO\(_2\)). Figure 7.9 plots the MnO\(_x\) concentration in the c-ZrO\(_2\) phase versus \( x(\text{LaMnO}_3) \) along the composition lines in Figure 7.8. Along the composition line of (YO\(_{1.5}\))\(_{0.15}\)(ZrO\(_2\))\(_{0.85}\)-LaMnO\(_3\) (Figure 7.9a), with increasing \( x(\text{LaMnO}_3) \), the MnO\(_x\) concentration first increases in the c-ZrO\(_2\)+LZO two-phase region (Region I) and then decreases after \( \alpha\)-Mn\(_3\)O\(_4\) appears in the equilibrium phase assemblage (Regions II, III). The highest concentration of MnO\(_x\) in c-ZrO\(_2\) at 1273 K in air is about 4.5 cat.\%. Increasing the yttria content (Figure 7.9b) leads to a decrease in the MnO\(_x\) concentration in c-ZrO\(_2\).
Chapter 7

(a)

(b)
Figure 7.8  Equilibrium phase fractions at 1273 K in air from the present work calculated along the composition lines: (a) \((YO_{1.5})_{0.15}(ZrO_2)_{0.85}\)–\(LaMnO_3\); (b) \((YO_{1.5})_{0.2}(ZrO_2)_{0.8}\)–\(LaMnO_3\); (c) \((YO_{1.5})_{0.3}(ZrO_2)_{0.7}\)–\(LaMnO_3\); (d) \((YO_{1.5})_{0.4}(ZrO_2)_{0.6}\)–\(LaMnO_3\). Only the following phases are included in the calculations: \(\alpha-La_2O_3\), \(\alpha-Mn_3O_4\), \(c-ZrO_2\), LMO,
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and LZO. Equilibrium phase assemblages in different regions: I: c-ZrO$_2$ and LZO; II: \(\alpha\)-Mn$_3$O$_4$, c-ZrO$_2$, and LZO; III: \(\alpha\)-Mn$_3$O$_4$, c-ZrO$_2$, LMO, and LZO; IV: c-ZrO$_2$, LMO, and LZO.

We also investigate the effect of the La deficiency in the La$_{1+\delta}$MnO$_{3-\delta}$ phase on the LaO$_{1.5}$ or MnO$_x$ solubilities in (YO$_{1.5}$)$_0$J(\(\text{ZrO}_2\))$_{0.85}$. Figure 7.10 shows the calculated LaO$_{1.5}$ solubility in (YO$_{1.5}$)$_0$J(\(\text{ZrO}_2\))$_{0.85}$ in air. The calculations are done in the two-phase region where the c-ZrO$_2$ phase and one of A-La$_2$O$_3$, LMO or LZO are included. The compositions (cation ratios) of the system are indicated in the diagram. As previously said, when A-La$_2$O$_3$ or LMO is in contact with YSZ, the LZO phase will form. The equilibrium solubility of LaO$_{1.5}$ in c-ZrO$_2$ should be the one calculated in the c-ZrO$_2$+LZO two-phase region. The others should be treated as metastable. Figure 7.10 shows that before LZO forms, c-ZrO$_2$ can dissolve quite a lot of LaO$_{1.5}$ from A-La$_2$O$_3$ or LMO and decreasing the La deficiency in the La$_{1+\delta}$MnO$_{3-\delta}$ phase further increases the solubility. After the LZO phase forms, the LaO$_{1.5}$ solubility decreases to almost zero. The equilibrium solubility of LaO$_{1.5}$ in c-ZrO$_2$ is very small. In our work on the Mn–Y–Zr–O system [26], we discussed the solubility limits of metal cations in pure c-ZrO$_2$ at 1673 K (Figure 3 in [26]) based on the theory proposed by Kim [31]. He suggested a linear relation between the solubility limit and the square of Vegard’s slope ($\frac{da}{dx}$, where $a$ is the lattice parameter and $x$ the dopant concentration) for elements belonging to the same group in the periodic table, the larger the square of Vegard’s slope, the lower the solubility limit. By comparing the square of the Vegard’s slope of La$^{3+}$ with those of other metal cations, we come to the conclusion that the solubility limit of LaO$_{1.5}$ in pure c-ZrO$_2$ at 1673 K should be very small. Currently we cannot draw a definite conclusion on how the yttria content in YSZ influences the LaO$_{1.5}$ solubility, but we can probably expect that the LaO$_{1.5}$ solubility in YSZ should not be too much different from the one in pure c-ZrO$_2$. The reported high solubility of 6.5 cat.% LaO$_{1.5}$ in YSZ at 1873 K from Mori et al. [11] is probably metastable.
Figure 7.9 The MnO$_x$ concentration in c-ZrO$_2$ at 1273 K in air calculated from the present work along the composition lines: (a) (YO$_{1.5}$)$_{0.15}$(ZrO$_2$)$_{0.85}$-LaMnO$_3$; (b) (YO$_{1.5}$)$_x$(ZrO$_2$)$_{1-x}$-LaMnO$_3$ ($x = 0.15, 0.2, 0.3, 0.4$). Only the following phases are included in the calculations: A-La$_2$O$_3$, $\alpha$-Mn$_3$O$_4$, c-ZrO$_2$, LMO, and LZO. Equilibrium phase assemblages
in different regions: I: c-ZrO$_2$ and LZO; II: $\alpha$-Mn$_3$O$_4$, c-ZrO$_2$, and LZO; III: $\alpha$-Mn$_3$O$_4$, c-ZrO$_2$, LMO, and LZO; IV: c-ZrO$_2$, LMO, and LZO.

Figure 7.10 Calculated LaO$_{1.5}$ solubilities in (YO$_{1.5}$)$_{0.15}$(ZrO$_2$)$_{0.85}$ in air from the present work. Note that the lines involving c-ZrO$_2$+LMO and c-ZrO$_2$+A-La$_2$O$_3$ are metastable and only valid as long as LZO does not form.

Figure 7.11 Calculated MnO$_x$ solubility in (YO$_{1.5}$)$_{0.15}$(ZrO$_2$)$_{0.85}$ in air from the present work. The experimental data are from Kawada et al. [32]. Note that the lines involving c-ZrO$_2$+LMO are metastable.
The MnOₓ solubility in (YO₁.₅)₀.₁₅(ZrO₂)₀.₈₅ in air is calculated in a two-phase region where c-ZrO₂ and MnOₓ (or LMO) are included. The one calculated in the c-ZrO₂+MnOₓ two-phase region is the equilibrium solubility. Our calculated values are in good agreement with the measured ones from Kawada et al. [32]. At 1273K in air, about 5 cat.% MnOₓ can dissolve in (YO₁.₅)₀.₁₅(ZrO₂)₀.₈₅. In the c-ZrO₂+LMO two-phase region, the MnOₓ solubility is influenced by the La deficiency in the La₁₋ₓMnO₃₋ₓ phase. Increasing the La deficiency leads to an increase in the MnOₓ solubility. Based on Figures 7.9 and 7.11, we can conclude that at the LMO–YSZ interface, the amount of MnOₓ dissolved in YSZ is determined by factors including the La deficiency in the La₁₋ₓMnO₃₋ₓ phase, the LMO:YSZ ratio, the yttria content in YSZ, temperature and oxygen partial pressure. The most important one is probably the La deficiency in the La₁₋ₓMnO₃₋ₓ phase.

7.6 Conclusions

In the present work, we present a thermodynamic description of the La–Mn–Y–Zr–O system. Due to the limited experimental data on the high-order systems, the description of La–Mn–Y–Zr–O is obtained by the ideal extrapolation of the descriptions of the previously assessed sub-systems with revision. The ideal extrapolations from ternaries to quaternaries and to La–Mn–Y–Zr–O are proven to be quite successful. The calculated isothermal sections of pseudo-ternaries at different temperatures in air are in good agreement with experimental data. Further experimental investigations are however still necessary to verify the phase relations in the un-assessed sub-systems and to improve the current description of La–Mn–Y–Zr–O.

The thermodynamics at the LaMnO₃–YSZ interface is discussed in detail. Based on our calculations, we conclude that:

a. The La₂Zr₂O₇ formation at the LaMnO₃–YSZ interface is mainly due to the high stability of La₂Zr₂O₇.

b. The La₂Zr₂O₇ phase is stable at the LaMnO₃–YSZ interface. Increasing the La deficiency in La₁₋ₓMnO₃₋ₓ by its own cannot thermodynamically prevent the La₂Zr₂O₇ formation.

c. Increasing the yttria content in YSZ can suppress and in the end thermodynamically prevent the La₂Zr₂O₇ formation.
d. A certain amount of LaO$_{1.5}$ from LaMnO$_3$ can dissolve in YSZ before the La$_2$Zr$_2$O$_7$ phase forms at the interface. The equilibrium solubility of LaO$_{1.5}$ in YSZ is however very small at $T < 1673$ K.

e. The amount of MnO$_x$ from LaMnO$_3$ dissolved in YSZ is influenced by quite a few factors. The most important factor is the La deficiency in the La$_{1-x}$Mn$_{0.5}$O$_{3-\delta}$ phase.

### 7.7 References


[6] M. Mori, N. Sakai, T. Kawada, H. Yokokawa, and M. Dokiya, "A new cathode material (La,Sr)$_{1-x}$(Mn$_{1-y}$Cr$_y$)O$_3$ (0<=y<=0.2) for SOFC", *Denki Kagaku* 58 (1990), p. 528.


M. Chen, B. Hallstedt, and L. J. Gauckler, "Thermodynamics and phase equilibria in the ZrO₂-LaO₁.₅ system", to be submitted.


8 Evaluation of the Thermodynamics of La$_2$Zr$_2$O$_7$ Formation

Ming Chen, Bengt Hallstedt, and Ludwig J. Gauckler, to be submitted.

Abstract

Calculations of the phase relations in the La–Mn–Y–Zr–O system and of the LaMnO$_3$–YSZ reactions from both Yokokawa et al. (J. Electrochem. Soc. 138 (1991), 2719-2727) and the present authors are reviewed. The Gibbs energy functions of stoichiometric compounds from both sources are evaluated. The discrepancy between Yokokawa et al.’s calculations and those from the present authors is mainly ascribed to a large difference in the Gibbs energy of La$_2$Zr$_2$O$_7$, which is caused by the fact that different values for the enthalpy of formation of La$_2$Zr$_2$O$_7$ have been used by Yokokawa et al. and the present authors. The calculated enthalpy of formation and Gibbs energy of formation of La$_2$Zr$_2$O$_7$ from Yokokawa et al. are much less negative than the experimentally measured values, while those from the present authors are in good agreement with the measured ones.

8.1 Introduction

Solid oxide fuel cells are very attractive for power generation systems. The state of the art SOFC uses yttria-stabilized zirconia (YSZ, cubic fluorite) as electrolyte, Ni-YSZ cermet as anode, Sr-doped perovskite-type La$_{1+y}$MnO$_3$ (La$_{1-y}$Sr$_y$)$_{1.5}$MnO$_3$ (LSM) as cathode, and LaCrO$_3$-based perovskite as interconnects. It is normally operated at 1173–1273 K. High fabrication temperatures of the components and high operation temperatures promote unwanted interface reactions in the SOFC, especially at the cathode–electrolyte interface. Lau and Singhal [1] first reported the La$_2$Zr$_2$O$_7$ formation between diffusion couples of dense La$_{0.9}$Sr$_{0.1}$MnO$_3$ and (YO$_{1.5}$)$_{0.18}$(ZrO$_2$)$_{0.82}$ single crystals. The amount of the formed La$_2$Zr$_2$O$_7$ phase has been found to increase with longer reaction time or higher sintering temperature, and to decrease with increasing Sr substitution for La, respectively [2, 3]. For heavily doped (La$_{1-y}$Sr$_y$)$_{1.5}$MnO$_3$ (y ≥ 0.3), SrZrO$_3$ was also found to form at the LSM–YSZ interface [4, 5]. It has been reported that by increasing the A-site deficiency (x in (La$_{1-y}$Sr$_y$)$_{1-x}$MnO$_{3.5-x}$) [2, 6,
Chapter 8

7], the zirconate formation can be retarded or even prevented during high temperature treatment.

The thermodynamics at the LSM–YSZ interface has been studied by Yokokawa et al. [8, 9, 10]. They evaluated or estimated the thermodynamic properties of solid solution phases and stoichiometric compounds in the La–Mn–Sr–Y–Zr–O system. According to their calculations, by increasing $x$ in $\text{La}_{1-x}\text{MnO}_3$ to a certain extent, the $\text{La}_2\text{Zr}_2\text{O}_7$ formation can be thermodynamically prevented. At 1573 K in air, lanthanum manganites having large lanthanum deficiency ($x > 0.14$ for $x$ in $\text{La}_{1-x}\text{MnO}_3$) can be in equilibrium with YSZ without forming $\text{La}_2\text{Zr}_2\text{O}_7$ [10].

Using the CALPHAD (CALculation of PHAse Diagrams) method, we assessed the thermodynamic properties of stoichiometric compounds and solution phases in the La–Mn–Sr–Y–Zr–O system. Recently we finished a thermodynamic description of the La–Mn–Y–Zr–O system, which is presented elsewhere [11] (Chapter 7). According to our phase equilibrium calculations, at 1573 K in air, the thermodynamic prevention of the $\text{La}_2\text{Zr}_2\text{O}_7$ formation is not possible by increasing the La deficiency in $\text{LaMnO}_3$. Our calculations obviously differ from Yokokawa et al.’s. In the present work, the thermodynamic descriptions of La–Mn–Y–Zr–O from both sources are compared and evaluated.

8.2 Previous work by Yokokawa et al.

Yokokawa et al. [12, 13, 14] evaluated the thermodynamic properties of stoichiometric compounds and solid solution phases in the Ln–M–O (Ln = rare earth elements and M = transition metal elements) and the $\text{ZrO}_2$-based ceramic systems. Since experimental thermodynamic data were missing for many of the phases, a major effort was put on finding thermodynamic regularities in enthalpies of formation of perovskite- and pyrochlore-type compounds and in interaction parameters of the $\text{ZrO}_2$-based solid solutions (cubic fluorite). A linear relation between the enthalpy of formation of the $\text{LaMO}_3$ perovskite and the tolerance factor $t$ was proposed [12]. The tolerance factor, $t$, was first proposed by Goldschmidt to correlate the stability of perovskites [15]. For an $\text{ABO}_3$ perovskite, $t$ is defined as:

$$
\frac{r_{AO}}{\sqrt{2}r_{BO}} = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)}
$$

Eq. 8.1
where \( r_A \) and \( r_B \) are bond lengths calculated as sums of ionic radii \( r_A^+, r_B^+, \) and \( r_0 \). The interaction parameters of the ZrO\(_2\)-based solid solutions (cubic fluorite) were derived from experimentally measured phase diagram data in the ZrO\(_2\)-MO or ZrO\(_2\)-MO\(_{1.5}\) systems or from empirical correlations between the interaction parameters and the ionic radii of the dopants (M\(^{2+}\) or M\(^{3+}\)) [14].

For the LaMn\(_{0.7}\)YSZ reactions, Yokokawa et al. calculated the Gibbs energies for the following reaction at \( P(O_2) = 1 \) bar [9, 16]:

\[
\text{LaMnO}_3 + \text{ZrO}_2 = \frac{1}{2} \text{La}_2\text{Zr}_2\text{O}_7 + \text{MnO}_x + \frac{3-2x}{4} \text{O}_2
\]

Eq. 8.2

According to their calculations (Figure 2 in [9] and Figure 10 in [16]), at the SOFC fabrication and operation temperatures, the Gibbs energies of the above reaction are essentially positive. This is apparently in contradiction with the experimental observations which actually indicated or verified the formation of La\(_2\)Zr\(_2\)O\(_7\) at the LaMn\(_{0.7}\)-YSZ or the LSM-YSZ interface [1, 2]. Considering the discrepancy between the experimental observations and the thermodynamic calculations, they have discussed the possibility of “some of the thermodynamic data used in the considerations are invalid, resulting in a wrong value for the Gibbs energy change for reaction” [17]. This possibility was however excluded. The discrepancy was instead ascribed to the fact that lanthanum nonstoichiometry in LaMn\(_{0.7}\) was neglected in the previous calculations. An ideal associate solution model with La\(_{0.667}\)Mn(IV)O\(_3\), La\(_{0.667}\)Mn(III)O\(_{2.5}\), LaMn(III)O\(_3\), LaMn(II)O\(_{2.5}\) as components was used to model the nonstoichiometry in LaMn\(_{0.7}\). According to this model, the lanthanum deficiency in LaMn\(_{0.7}\) is realized by introducing relatively stable Mn\(^{4+}\) ions into the perovskite crystal lattice. The thermodynamic parameters for the components La\(_{0.667}\)Mn(IV)O\(_3\), La\(_{0.667}\)Mn(III)O\(_{2.5}\), LaMn(II)O\(_{2.5}\) were obtained from a trial-and-error fitting of thermogravimetric results [18]. Phase equilibrium calculations were conducted on the La–Mn–Y–Zr–O system. In the new calculations, instead of pure c-ZrO\(_2\), yttria stabilized zirconia with a fixed mole ratio of \( 15\% \) ZrO\(_2\) was included. The dissolution of MnO\(_x\) and/or LaO\(_x\) in YSZ was also taken into account. According to their calculated chemical potential diagram (Figure 8 in [10]), at 1573 K in air, at the La\(_{1-x}\)MnO\(_{3-\delta}\)–(YO\(_{1.5}\))\(_{0.15}\)(ZrO\(_2\))\(_{0.85}\) interface, the La\(_2\)Zr\(_2\)O\(_7\) formation should take place for \( x < 0.14 \), whereas the Mn dissolution from La\(_{1-x}\)MnO\(_{3-\delta}\) into YSZ may become significant for \( x > 0.14 \). 11.4 cat.% MnO\(_x\) can dissolve in (YO\(_{1.5}\))\(_{0.15}\)(ZrO\(_2\))\(_{0.85}\) at 1573 K while the LaO\(_{1.5}\) solubility is much lower, only about 1.5 cat.%.
They also investigated the reactions between LSM and YSZ. The calculations for the reactions between \((\text{La}_{1-y}\text{Sr}_y)\text{MnO}_3\) and \((\text{YO}_{1.5})_{0.17}\text{ZrO}_2_{0.83}\) at 1673 K in air [19] show that for heavily doped \((\text{La}_{1-y}\text{Sr}_y)\text{MnO}_3\) \((y \geq 0.3)\), \(\text{SrZr}_2\) will form. The maximum solubility of \(\text{SrO}\) in YSZ is about 4 cat.%. 

### 8.3 The CALPHAD methodology

CALPHAD is an acronym for Calculation of PHase Diagrams. The CALPHAD methodology is rather aptly defined by the subtitle of the CALPHAD journal: “Computer Coupling of Phase Diagrams and Thermochemistry”. The aim of the CALPHAD method is to derive a consistent thermodynamic description for the Gibbs energies of all the phases in a certain system and also to reproduce all sorts of thermodynamic properties and phase diagrams in a reasonable and reliable manner. In a first stage of the CALPHAD modeling, an appropriate thermodynamic model based on crystal structure and chemistry information has to be chosen for each phase. The Gibbs energy of a certain phase is then written as a function of temperature, composition, and pressure with adjustable parameters. In a second stage, those adjustable parameters will be optimized using both thermodynamic data and phase diagram data. During this stage, the inconsistency between various kinds of experimental data can be easily identified and possibly resolved. This is actually the special strength of the CALPHAD method. A critical evaluation of the available experimental data is often necessary. The optimized thermodynamic description is in general more reliable than the one derived from a sum of individual measurements. With the optimized thermodynamic description, phase diagrams and thermodynamic properties can be calculated using various software packages. Nowadays the CALPHAD approach has become a standard technique in phase equilibrium studies and is hence used in our modeling of the \(\text{La–Mn–Y–Zr–O}\) system. Figure 8.1 is a schematic diagram for the CALPHAD methodology, in which Thermo-Calc is a software package developed by Thermo-Calc Software AB, Stockholm, Sweden [20] and is used in the present work. Parrot and POLY_3 are modules included in the Thermo-Calc software package.
In our description of La–Mn–Y–Zr–O, we describe the Gibbs energies of all phases as functions of temperature and composition. For pure elements or stoichiometric compounds, the Gibbs energy is a function of the temperature only and can be obtained by integrating the heat capacity \( C_p \). From room temperature upwards, \( C_p \) can be well represented by the following equation:

\[
C_p = -c - 2dT - 6eT^2 - 2fT^{-2}
\]

where \(-c\) should be close to the Dulong–Petit value, \(d\) and \(e\) are corrections due to anharmonic and electronic contributions, and \(f\) is a parameter allowing to describe the decrease of the heat capacity at lower temperatures [21]. The Gibbs energy can then be written as:

\[
\Delta G^\circ - H^\circ_{\text{SER}} = a + bT + cT \ln T + dT^2 + eT^3 + fT^{-1}
\]

Eq. 8.4

where \(\Delta G^\circ - H^\circ_{\text{SER}}\) is referred to the enthalpy of selected stable states for pure elements at 298.15 K and 1 bar. This state is denoted SER (Stable Element Reference). Different sets of the parameters \(a\) to \(f\) are used in different temperature ranges. For pure elements, we take the thermodynamic descriptions from the SGTE (Scientific Group Thermodata Europe) unary database [22].

All solid solution phases in the La–Mn–Y–Zr–O system are modeled using the compound energy formalism [23, 24], in which the concept of sublattice is introduced. According to the compound energy formalism, the structure of an ionic solid solution phase is split into at least two sublattices, one for cations and one for anions. The species within the same sublattice are allowed to mix randomly. We choose the m-ZrO\(_2\) solution phase as an example. In the present work, we include the YO\(_{1.5}\) solubility in m-ZrO\(_2\) and model it as \((Y^{3+}, Zr^{4+})(O^{2-}, Va)_2\). The cations, \(Y^{3+}\) and \(Zr^{4+}\), mix randomly in the first sublattice and O\(^{2-}\) ions and oxygen vacancies...
(Va) in the second sublattice. The oxygen vacancies are introduced to maintain charge neutrality when Zr$^{4+}$ is substituted by Y$^{3+}$. The molar Gibbs energy of m-ZrO$_2$ is a sum of the molar Gibbs energies of corner compounds ((Y$^{3+}$)$_2$(O$^{2-}$)$_2$, (Y$^{3+}$)$_2$(Va)$_2$, (Zr$^{4+}$)$_2$(O$^{2-}$)$_2$, (Zr$^{4+}$)$_2$(Va)$_2$) weighted by their respective site fractions plus the ideal entropy of mixing and the excess Gibbs energy. The molar Gibbs energy can thus be written as:

$$G_m = y_{Y^{3+}}y_{O^{2-}}G^m_{Y^{3+}O^{2-}} + y_{Zr^{4+}}y_{O^{2-}}G^m_{Zr^{4+}O^{2-}} + y_{Va}y_{O^{2-}}G^m_{VaO^{2-}}$$

$$+ RT\left[y_{Y^{3+}}\ln y_{Y^{3+}} + y_{Zr^{4+}}\ln y_{Zr^{4+}} + 2(y_{Va}\ln y_{Va})\right]$$

Eq. 8.5

where $y_s$ is the fraction of the species $s$ in a particular sublattice and colons are used to separate species in different sublattices. The excess Gibbs energy arises from the interactions between species within the same sublattice. For m-ZrO$_2$, the excess Gibbs energy is given by:

$$\Delta G_m = y_{Y^{3+}}y_{Zr^{4+}}y_{O^{2-}}\sum_{i=0}^{n}L^m_{Y^{3+}Zr^{4+}O^{2-}}(y_{Y^{3+}} - y_{Zr^{4+}}^i) + y_{Y^{3+}}y_{Zr^{4+}}y_{Va}\sum_{i=0}^{n}L^m_{Y^{3+}Zr^{4+}Va}(y_{Va} - y_{Zr^{4+}}^i)$$

Eq. 8.6

The details of the parameter derivation can be found in our work on the Y–Zr–O system [25] (Chapter 2).

We model the liquid phase as (La$^{3+}$, Mn$^{2+}$, Mn$^{3+}$, Y$^{3+}$, Zr$^{4+}$)$_p$(O$^{2-}$, Va$^{2-}$)$_q$ using the two-sublattice model for ionic liquids [26, 27], where

$$p = 2y_{O^{2-}} + qy_{Va^{2-}}$$

Eq. 8.7

$$q = 3y_{La^{3+}} + 2y_{Mn^{2+}} + 3y_{Mn^{3+}} + 3y_{Y^{3+}} + 4y_{Zr^{4+}}$$

Eq. 8.8

Charged vacancies are introduced into the anion sublattice to ensure a continuous description from the metal liquid to the oxide liquid. The description for the molar Gibbs energy of the liquid phase is derived in a similar manner as for the solid solution phase using the compound energy formalism (Eqs. 8.5 and 8.6).

8.4 Our work on the LaMnO$_3$–YSZ reactions

Based on the current thermodynamic description of La–Mn–Y–Zr–O, we calculate the Gibbs energies of the reaction corresponding to Eq. 8.2 at $P$(O$_2$) = 1 bar. The results are plotted in Figure 8.2.
Evaluation of the Thermodynamics

Figure 8.2 Calculated Gibbs energies of reactions at \(P(O_2) = 1\) bar from the present work. For Reaction 2, \(\alpha\)-Mn\(_3\)O\(_4\) is included in the calculations at \(T < 1443\) K and \(\beta\)-Mn\(_3\)O\(_4\) is included at \(T > 1443\) K.

The Gibbs energies of the stoichiometric compounds are used in the calculations. Concerning the SOFC applications, Reaction 2 \(\text{LaMnO}_3 + c\text{-ZrO}_2 = \frac{1}{2}\text{La}_2\text{Zr}_2\text{O}_7 + \frac{1}{3}\text{Mn}_3\text{O}_4 + \frac{1}{12}\text{O}_2\) is probably more important than the other three, as Mn\(_3\)O\(_4\) is the stable Mn oxide in air at \(T > 1155\) K (until it melts). According to the thermodynamic assessment of the Mn–O system from Grundy et al. [28], Mn\(_3\)O\(_4\) has two polymorphs, the low temperature form \(\alpha\)-Mn\(_3\)O\(_4\) and the high temperature form \(\beta\)-Mn\(_3\)O\(_4\). \(\alpha\)-Mn\(_3\)O\(_4\) transforms into \(\beta\)-Mn\(_3\)O\(_4\) at \(T = 1443\) K. We hence use the Gibbs energy of \(\alpha\)-Mn\(_3\)O\(_4\) for \(T < 1443\) K and that of \(\beta\)-Mn\(_3\)O\(_4\) for \(T > 1443\) K in calculating the Gibbs energy of Reaction 2. According to Figure 8.2, the Gibbs energy of Reaction 2 is negative from room temperature up to 2000 K. Decreasing the oxygen partial pressure from 1 bar to 0.21 bar (air) will not change the Gibbs energy of Reaction 2 significantly. This means that the reaction between LaMnO\(_3\) and c-ZrO\(_2\) to form La\(_2\)Zr\(_2\)O\(_7\) and Mn\(_3\)O\(_4\) is thermodynamically favorable at the SOFC fabrication and operation temperatures.

Phase equilibrium calculations are conducted on the LaO\(_{1.5}\)–MnO\(_x\)–ZrO\(_2\) pseudo-ternary system. An isothermal section is calculated at 1273 K in air, to be compared with the one
published by Yokokawa et al. (Figure 3 in [8]). The phases A-La$_2$O$_3$, $\alpha$-Mn$_3$O$_4$, c-ZrO$_2$, LaMnO$_3$, and La$_2$Zr$_2$O$_7$ are included in the calculations. Only $\alpha$-Mn$_3$O$_4$ is modeled as a stoichiometric compound. The calculated phase diagram is shown in Figure 8.3. No tie line exists between c-ZrO$_2$ and LaMnO$_3$. According to our calculated phase diagram, at 1273 K in air, the LaMnO$_3$ phase will react with the c-ZrO$_2$ phase (without yttria doping) to form La$_2$Zr$_2$O$_7$ and $\alpha$-Mn$_3$O$_4$. Increasing the La deficiency in LaMnO$_3$ by its own cannot prevent the La$_2$Zr$_2$O$_7$ formation. Figure 8.4 shows the chemical potential diagram of LaO$_{1.5}$-MnO$_x$-ZrO$_2$ calculated at 1273 K in air. This is to be compared with Figure 5 in [10]. The different X and Y scales in the two diagrams (Figure 5 in [10] and Figure 8.4 in this work) are due to the fact that different reference states have been used by Yokokawa et al. and the present authors. We choose SER as the reference state. In Figure 5 [10], the LaMnO$_3$ and c-ZrO$_2$ single-phase regions have a common boundary line. In our calculated chemical potential diagram (Figure 8.4), the c-ZrO$_2$ single-phase region does not have a contact with the LaMnO$_3$ single-phase region. They are separated by the La$_2$Zr$_2$O$_7$ and $\beta$-Mn$_3$O$_4$ single-phase regions, which indicates that the LaMnO$_3$ phase cannot be in equilibrium with the c-ZrO$_2$ phase without forming La$_2$Zr$_2$O$_7$ and/or $\alpha$-Mn$_3$O$_4$.

Figure 8.3  Calculated isothermal section of LaO$_{1.5}$-MnO$_x$-ZrO$_2$ at 1273 K in air from the present work. The following phases are included in the calculation: A-La$_2$O$_3$, $\alpha$-Mn$_3$O$_4$, c-ZrO$_2$, LaMnO$_3$, and La$_2$Zr$_2$O$_7$. 

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Figure 8.4  Calculated chemical potential diagram of LaO$_{1.5}$-MnO$_x$-ZrO$_2$ at 1273 K in air from the present work. The following phases are included in the calculation: A-La$_2$O$_3$, α-Mn$_3$O$_4$, c-ZrO$_2$, LaMnO$_3$, and La$_2$Zr$_2$O$_7$.

Further calculations are conducted on the LaO$_{1.5}$-MnO$_x$-YO$_{1.5}$-ZrO$_2$ pseudo-quaternary system. An isothermal section of LaO$_{1.5}$-MnO$_x$-(YO$_{1.5}$)$_{0.15}$(ZrO$_2$)$_{0.85}$ was calculated at 1573 K in air (Figure 8.5). The phases A-La$_2$O$_3$, β-Mn$_3$O$_4$, c-ZrO$_2$, LaMnO$_3$, and La$_2$Zr$_2$O$_7$ are included in the calculations. No tie lines are plotted in Figure 8.5 since they are out of the plane. There exist 7 regions with different equilibrium phase assemblages. The La$_2$Zr$_2$O$_7$ phase seems to be quite stable and is involved in almost all regions except Region VII. According to our calculations (Figures 8.3–5), we conclude that the reaction between c-ZrO$_2$ and LaMnO$_3$ to form La$_2$Zr$_2$O$_7$ and α-Mn$_3$O$_4$ (or β-Mn$_3$O$_4$) is thermodynamically favorable and that increasing the La deficiency in LaMnO$_3$ by itself cannot thermodynamically prevent the La$_2$Zr$_2$O$_7$ formation. For more details on our calculations, the readers are referred to [11] (Chapter 7).
Figure 8.5 Calculated isothermal section of LaO$_{1.5}$-$\text{MnO}_x$-$\text{Y}_x\text{O}_{1.5}$($\text{ZrO}_2$)$_{0.85}$ at 1573 K in air from the present work. The following phases are included in the calculation: A-La$_2$O$_3$, $\beta$-Mn$_3$O$_4$, c-ZrO$_2$, LaMnO$_3$, and La$_2$Zr$_2$O$_7$. Equilibrium phase assemblages in different regions: I: c-ZrO$_2$ and La$_2$Zr$_2$O$_7$; II: $\beta$-Mn$_3$O$_4$, c-ZrO$_2$, and La$_2$Zr$_2$O$_7$; III: $\beta$-Mn$_3$O$_4$, c-ZrO$_2$, LaMnO$_3$, and La$_2$Zr$_2$O$_7$; IV: c-ZrO$_2$, LaMnO$_3$, and La$_2$Zr$_2$O$_7$; V: A-La$_2$O$_3$, c-ZrO$_2$, LaMnO$_3$, and La$_2$Zr$_2$O$_7$; VI: A-La$_2$O$_3$, LaMnO$_3$, and La$_2$Zr$_2$O$_7$; VII: A-La$_2$O$_3$ and LaMnO$_3$.

8.5 Evaluation and discussion

The Gibbs energies of reactions (Figure 8.2) and the phase relations in the LaO$_{1.5}$-$\text{MnO}_x$-$\text{ZrO}_2$ system (Figures 8.3–4) calculated in this work differ from the ones calculated by Yokokawa et al. [8, 10]. This leads to the different interpretations of the LaMnO$_3$–YSZ reactions. These discrepancies obviously originate from differences in the Gibbs energy functions of the stoichiometric compounds. Yokokawa et al. did not publish the Gibbs energy functions but the enthalpies of formation and entropies at 298.15 K and the $C_p$ coefficients [8, 9, 29]. These are enough for us to derive the Gibbs energy functions they used, which are listed in Table 8.1. Table 8.2 lists the Gibbs energy functions from the present authors. For the complete thermodynamic description of La–Mn–Y–Zr–O, the readers are referred to [11] (Appendix). The calculated enthalpies of formation, entropies and heat capacities at 298.15 K from both Yokokawa et al. and the present authors are listed in Table 8.3.
Table 8.1  Gibbs energy functions of stoichiometric compounds derived from the thermodynamic data published by Yokokawa et al. [8, 9, 29]

<table>
<thead>
<tr>
<th>Compound</th>
<th>Gibbs energy function</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-La2O3</td>
<td>GLA2O3 = -1834515 + 685.67T - 119.67lnT - 0.0072557^2 + 6725007^-1</td>
</tr>
<tr>
<td>MnO</td>
<td>GMN1O1 = -400673 + 256.17T - 46.48lnT - 0.00406T^2 + 1840007^-1</td>
</tr>
<tr>
<td>β-Mn2O3</td>
<td>GMN2O3 = -995817 + 597.87T - 103.06lnT - 0.01753T^2 + 6755007^-1</td>
</tr>
<tr>
<td>MnO2</td>
<td>GMN1O2 = -546634 + 424.27T - 69.45lnT - 0.005105T^2 + 8115007^-1</td>
</tr>
<tr>
<td>m-ZrO2</td>
<td>GZRO2M = -1125844 + 417.49T - 68.33lnT - 0.00454T^2 + 6720007^-1</td>
</tr>
<tr>
<td>t-ZrO2</td>
<td>GZRO2T = -1117444 + 411.68T - 68.33lnT - 0.00454T^2 + 6720007^-1</td>
</tr>
<tr>
<td>c-ZrO2</td>
<td>GZRO2C = -1104444 + 406.8T - 68.33lnT - 0.00454T^2 + 6720007^-1</td>
</tr>
<tr>
<td>LaMnO3</td>
<td>GLMO = -1466292 + 669.56T - 117.35lnT - 0.00825T^2 + 8155007^-1</td>
</tr>
<tr>
<td>La2Zr2O7</td>
<td>GLZO = -4174283 + 1510.7T - 256.27lnT - 0.01634T^2 + 20165007^-1</td>
</tr>
</tbody>
</table>

Table 8.2  Gibbs energy functions of stoichiometric compounds from this work

<table>
<thead>
<tr>
<th>Compound</th>
<th>Gibbs energy function</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-La2O3</td>
<td>GLA2O3 = -1835600 + 674.72T - 118l7lnT - 0.008T^2 + 6200007^-1</td>
</tr>
<tr>
<td>MnO</td>
<td>GMN1O1 = -402478 + 259.35T - 46.83T - 0.003857^2 + 212922T^-1</td>
</tr>
<tr>
<td>α-Mn3O4</td>
<td>GMN3O4A = -1437037 + 889.56T - 154.74T - 0.0174T^2 + 9861397^-1</td>
</tr>
<tr>
<td>β-Mn3O4</td>
<td>GMN3O4B = -1416189 + 875.12T - 154.74TlnT - 0.0174T^2 + 9861397^-1</td>
</tr>
<tr>
<td>β-Mn3O3</td>
<td>GMN2O3 = -998618 + 588.61T - 101.95TlnT - 0.01884T^2 + 589057^-1</td>
</tr>
<tr>
<td>MnO2</td>
<td>GMN1O2 = -545091 + 395.37T - 65.27TlnT - 0.007803T^2 + 6649557^-1</td>
</tr>
<tr>
<td>m-ZrO2</td>
<td>GZRO2M = -1125300 + 416.97T - 68.47TlnT - 0.00335T^2 + 5860007^-1</td>
</tr>
<tr>
<td>t-ZrO2</td>
<td>GZRO2T = -1111800 + 409.74T - 68.47TlnT - 0.00335T^2 + 5860007^-1</td>
</tr>
<tr>
<td>c-ZrO2</td>
<td>GZRO2C = -1111800 + 409.74T - 68.47TlnT - 0.00335T^2 + 5860007^-1</td>
</tr>
<tr>
<td>LaMnO3</td>
<td>GLMO = -1480476 + 683.44T - 117.16TlnT - 0.0134T^2 + 8374627^-1</td>
</tr>
<tr>
<td>La2Zr2O7</td>
<td>GLZO = -4219831 + 14987T - 254.87TlnT - 0.0147T^2 + 17920007^-1</td>
</tr>
</tbody>
</table>

For most of the compounds listed in Tables 8.1–3, the difference between Yokokawa et al.’s description and ours is not very large and is within a reasonable range. A large difference was however found in the enthalpy of formation of La2Zr2O7. Our calculated enthalpy of formation of La2Zr2O7 at 298.15 K is about 50 kJ/mol more negative than the one from Yokokawa et al. [9]. This is well above the uncertainty for the enthalpy of formation measurements. Figure 8.6 shows the Gibbs energy curves of La2Zr2O7 calculated using the functions listed in Tables 8.1 and 8.2. Our calculated Gibbs energy of La2Zr2O7 is more negative than Yokokawa et al.’s. The difference is about 47 kJ/mol at T = 300 K and 42 kJ/mol at T = 2000 K. Figure 8.7 plots the Gibbs energies of reactions calculated using the functions listed in Tables 8.1 and 8.2. For all the reactions, our calculated Gibbs energies of reactions are more negative than Yokokawa et al.’s. It is then clear that the discrepancies on the calculated Gibbs energies of reactions and the calculated phase relations in the
LaO$_{1.5}$–MnO$_x$–ZrO$_2$ system are mainly due to the difference in the Gibbs energy function of La$_2$Zr$_2$O$_7$, which is caused by the fact that different values for the enthalpy of formation of La$_2$Zr$_2$O$_7$ at 298.15 K were used by Yokokawa et al. and the present authors.

Table 8.3 Enthalpies of formation, entropies, and heat capacities of stoichiometric compounds at 298.15 K from Yokokawa et al. [8, 9] and this work

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta H_{298.15} \text{ kJ/mol (from elements)}$</th>
<th>$S_{298.15} \text{ J/(K mol)}$</th>
<th>$C_p_{298.15} \text{ J/(K mol)}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-La$_2$O$_3$</td>
<td>-1793.7</td>
<td>127.32</td>
<td>108.8</td>
<td>Yokokawa et al.</td>
</tr>
<tr>
<td></td>
<td>-1795.5</td>
<td>127.34</td>
<td>108.82</td>
<td>This work</td>
</tr>
<tr>
<td>MnO</td>
<td>-385.2</td>
<td>59.710</td>
<td>44.76</td>
<td>Yokokawa et al.</td>
</tr>
<tr>
<td></td>
<td>-386.7</td>
<td>59.017</td>
<td>44.34</td>
<td>This work</td>
</tr>
<tr>
<td>MnO$_2$</td>
<td>-520.0</td>
<td>53.05</td>
<td>54.24</td>
<td>Yokokawa et al.</td>
</tr>
<tr>
<td></td>
<td>-520.5</td>
<td>53.95</td>
<td>54.97</td>
<td>This work</td>
</tr>
<tr>
<td>Mn$_2$O$_3$</td>
<td>-959</td>
<td>110.5</td>
<td>98.32</td>
<td>Yokokawa et al.</td>
</tr>
<tr>
<td></td>
<td>-962.6</td>
<td>112.10</td>
<td>99.94</td>
<td>This work</td>
</tr>
<tr>
<td>$\alpha$-Mn$_3$O$_4$</td>
<td>-1382.7</td>
<td>168.34</td>
<td>142.94</td>
<td>Yokokawa et al.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>This work</td>
</tr>
<tr>
<td>c-ZrO$_2$</td>
<td>-1079.2</td>
<td>61.07</td>
<td>55.92</td>
<td>Yokokawa et al.</td>
</tr>
<tr>
<td></td>
<td>-1087.2</td>
<td>56.96</td>
<td>57.21</td>
<td>This work</td>
</tr>
<tr>
<td>LaMnO$_3$</td>
<td>-1425.1</td>
<td>130.5</td>
<td>103.92</td>
<td>Yokokawa et al.</td>
</tr>
<tr>
<td></td>
<td>-1438.7</td>
<td>118.73</td>
<td>106.33</td>
<td>This work</td>
</tr>
<tr>
<td>La$_2$Zr$_2$O$_7$</td>
<td>-4082.9</td>
<td>238.08</td>
<td>220.63</td>
<td>Yokokawa et al.</td>
</tr>
<tr>
<td></td>
<td>-4130.5</td>
<td>237.48</td>
<td>223.25</td>
<td>This work</td>
</tr>
</tbody>
</table>

Figure 8.6 Gibbs energy curves of stoichiometric La$_2$Zr$_2$O$_7$. 

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The calculated enthalpy of formation of $\text{La}_2\text{Zr}_2\text{O}_7$ at 298.15 K from Yokokawa et al. [9] and the present authors are listed in Table 8.4, together with measured values from the literature. Two kinds of enthalpy of formation, the enthalpy of formation from oxides ($\text{A-La}_2\text{O}_3$ and $\text{m-ZrO}_2$) and the enthalpy of formation from elements, have been reported in the literature. The enthalpy of formation from elements is a sum of the enthalpy of formation from oxides plus the enthalpies of formation of the corresponding oxides, which can be written as:

$$
\Delta_f H_{298.15} (\text{La}_2\text{Zr}_2\text{O}_7, \text{from elements}) = \Delta_f H_{298.15} (\text{La}_2\text{Zr}_2\text{O}_7, \text{from A-La}_2\text{O}_3 \text{ and m-ZrO}_2) \\
+ \Delta_f H_{298.15} (\text{A-La}_2\text{O}_3, \text{from elements}) \\
+ \Delta_f H_{298.15} (\text{m-ZrO}_2, \text{from elements})
$$  \text{Eq. 8.9}

Only the values determined directly from the measurements should be used in obtaining the Gibbs energy function of $\text{La}_2\text{Zr}_2\text{O}_7$, not the derived value. The enthalpy of formation of $\text{La}_2\text{Zr}_2\text{O}_7$ (from oxides) at 298.15 K was first measured by Korneev et al. [30] as $-125.9$ kJ/mol, using combustion calorimetry. Bolech et al. [31] measured the enthalpy of formation of $\text{La}_2\text{Zr}_2\text{O}_7$ (from oxides) at 974 K to be $-135.8\pm6.4$ kJ/mol, by high-temperature solution calorimetry. The enthalpy of formation of $\text{La}_2\text{Zr}_2\text{O}_7$ (from oxides) at 298.15 K was reported to be $-136.1\pm6.4$ kJ/mol, which is 10 kJ/mol more negative than the value reported by Korneev et al. [30]. Korneev et al. [30] also measured the enthalpy of formation of m-ZrO$_2$ as $-1087.8$ kJ/mol, $>10$ kJ less negative than both the measured values from Huber et al. [32] and Kornilov et al. [33] and the assessed values from the JANAF table [34] and the present authors [25]. It is quite possible that in Korneev et al.'s experiments [30], incomplete combustion or formation of metastable products undetectable by XRD leads to the less negative enthalpies of formation for both m-ZrO$_2$ and $\text{La}_2\text{Zr}_2\text{O}_7$. The enthalpy of formation of $\text{La}_2\text{Zr}_2\text{O}_7$ reported by Bolech et al. [31] is probably more reliable and was used by the present authors. Korneev et al. also reported the enthalpy of formation of $\text{La}_2\text{Zr}_2\text{O}_7$ (from elements) at 298.15 K as $-4081.9$ kJ/mol, which is a sum of their measured enthalpy of formation of $\text{La}_2\text{Zr}_2\text{O}_7$ (from oxides) and enthalpy of formation of m-ZrO$_2$ and the enthalpy of formation of A-La$_2$O$_3$ from an unknown source. This value ($-4081.9$ kJ/mol) is obviously unreliable, but was unfortunately used by Yokokawa et al. in determining the Gibbs energy function of $\text{La}_2\text{Zr}_2\text{O}_7$. The enthalpy of formation of $\text{La}_2\text{Zr}_2\text{O}_7$ (from oxides) at 298.15 K from Yokokawa et al. is then $-88.08$ kJ/mol, which is much less negative than the measured values from both Korneev et al. [30] and Bolech et al. [24]. The enthalpy of formation of stoichiometric
La$_2$Zr$_2$O$_7$ at 298.15 K from the present work is calculated to be $-4130.5$ kJ/mol (from elements) and $-133.6$ kJ/mol (from oxides).

Table 8.4  Enthalpy of formation of stoichiometric La$_2$Zr$_2$O$_7$ at 298.15 K.

<table>
<thead>
<tr>
<th>$\Delta H_{298.15}$, kJ/mol</th>
<th>Method</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(from oxides)</td>
<td>(from elements)</td>
<td></td>
</tr>
<tr>
<td>$-125.9$ (measured)</td>
<td>$-4081.9$</td>
<td>Komeev et al. [30]</td>
</tr>
<tr>
<td>$-136.1$ (measured)</td>
<td>$-4130.4$</td>
<td>Bolech et al. [31]</td>
</tr>
<tr>
<td>$-88.08$</td>
<td>$-4082.9$</td>
<td>Yokokawa et al. [9]</td>
</tr>
<tr>
<td>$-134.4$</td>
<td></td>
<td>Jacob et al. [35]</td>
</tr>
<tr>
<td>$-133.8$</td>
<td></td>
<td>Jacob et al. [35]</td>
</tr>
<tr>
<td>$-133.6$</td>
<td>$-4130.5$</td>
<td>This work</td>
</tr>
</tbody>
</table>

A comparison of the calculated Gibbs energies of formation of La$_2$Zr$_2$O$_7$ (from A-La$_2$O$_3$ and m-ZrO$_2$) from Yokokawa et al. and the present authors with the experimentally measured values is also conducted. The results are shown in Figure 8.8. The Gibbs energy of formation of La$_2$Zr$_2$O$_7$ from oxides has been measured by Jacob et al. [35] in a temperature range of 870–1240 K and by Rog and Kozlowska-Rog [36] in a temperature range of 1073–1273 K, both using the electromotive force (EMF) method. The data from Jacob et al. [35] were used in our optimization. It is then not surprising that our calculated Gibbs energy of formation agrees well with the experimental data. We can also check the compatibility between the measured enthalpy of formation data and the measured Gibbs energy of formation data. During the optimization, we found that it is impossible to reproduce both the measured enthalpy of formation of La$_2$Zr$_2$O$_7$ (from oxide) at 298.15 K from Komeev et al. [30] and the measured Gibbs energies of formation from Jacob et al. [35] and Rog and Kozlowska-Rog [36] well. In other words, the reported enthalpy of formation from Komeev et al. [30] is not compatible with the measured Gibbs energy of formation data. On the other hand, the enthalpy of formation from Bolech et al. [31] is compatible with the measured Gibbs energy of formation data. This is also indicated in Table 8.4. From the measured EMF data, Jacob et al. [35] derived the enthalpy of formation of La$_2$Zr$_2$O$_7$ (from oxides) at 298.15 K as $-134.4\pm8.5$ kJ/mol by the second-law method and $-133.8\pm5$ kJ/mol by the third-law method, in good agreement with the measured value from Bolech et al. [24]. The experimental data from Bolech et al. [31], Jacob et al. [35] and Rog and Kozlowska-Rog [36] were measured by different groups with different methods and they are compatible with each other. These data are till now the best available. The Gibbs energy function of La$_2$Zr$_2$O$_7$ derived from these
data should also be the best available. This convinces us that our Gibbs energy of function of La$_2$Zr$_2$O$_7$ should be more reliable, compared to the one from Yokokawa et al. (Table 8.1). The details on the parameter derivation for the Gibbs energy function of La$_2$Zr$_2$O$_7$ can be found in our work on the La–Zr–O system [37].

(a)

(b)
Figure 8.7  Gibbs energies of reactions at $P(O_2) = 1$ bar.

The discussion above however does not say that our Gibbs energy of $La_2Zr_2O_7$ is exactly correct. Since phase diagrams are very sensitive to relative differences in the Gibbs energies of different phases, energy differences of a few hundred Joules can be enough to drastically
change the phase relations in multi-component systems. Thermodynamic values on the other hand can be determined only in the best cases to an uncertainty below 1 kJ. We calculated how much less negative the enthalpy formation of La$_2$Zr$_2$O$_7$ has to be to get the geometry in Yokokawa et al.'s phase diagram of LaO$_{1.5}$–MnO$_x$–ZrO$_2$ at 1273 K in air. We got a phase diagram similar to Figure 3 in [8] when the enthalpy of formation of La$_2$Zr$_2$O$_7$ (from oxides) at 298.15 was increased by at least 25 kJ/mol, i.e. 25 kJ/mol less negative than our assessed value (−133.6 kJ/mol). This is well above the uncertainty for the enthalpy of formation measurements. We hence conclude that the geometry in our calculated phase diagram of LaO$_{1.5}$–MnO$_x$–ZrO$_2$ at 1273 K in air (Figure 8.3) is a realistic description.

![Gibbs energy of formation of stoichiometric La$_2$Zr$_2$O$_7$ from A-La$_2$O$_3$ and m-ZrO$_2$. The experimental data are from Jacob et al. [35] and Rog and Kozlowska-Rog [36].](image-url)

Figure 8.8 Gibbs energy of formation of stoichiometric La$_2$Zr$_2$O$_7$ from A-La$_2$O$_3$ and m-ZrO$_2$. The experimental data are from Jacob et al. [35] and Rog and Kozlowska-Rog [36].

For the other compounds or solution phases in the La–Mn–Y–Zr–O system, our Gibbs energy functions are derived also from critically assessed experimental data. The calculated phase relations in the low-order sub-systems are in good agreement with experimental data. This convinces us that our description of the La–Mn–Y–Zr–O system and our calculations on the LaMnO$_3$–YSZ reactions should be till now the best available.

Moving on to the LaMnO$_3$–YSZ reactions, according to our phase equilibrium calculations, the La$_2$Zr$_2$O$_7$ phase is quite stable and increasing the La deficiency in LaMnO$_3$ by its own
cannot thermodynamically prevent the La$_2$Zr$_2$O$_7$ formation. This seems to be in contradiction to some of experimental findings. By increasing the A-site deficiency in LaMnO$_3$ or in LSM, other groups actually observed no La$_2$Zr$_2$O$_7$ formation [2, 6, 38]. Before making any conclusion, we first have to verify if equilibrium has been reached in these experiments. It is however often not the case. A good example can be found in the experimental investigations by Yamamoto et al. [2] and Mori et al. [39]. They reported no La$_2$Zr$_2$O$_7$ formation between La$_{0.8}$MnO$_{3.8}$ (a mixture of La$_{0.9}$MnO$_{3.8}$ and Mn$_2$O$_3$) and (YO$_{1.3}$)$_{0.15}$(ZrO$_2$)$_{0.85}$ after a reaction time of 48 h at 1523 K. However, the La$_2$Zr$_2$O$_7$ phase did form after 96 h and the amount of La$_2$Zr$_2$O$_7$ increased with increasing reaction time. Obviously equilibrium was not reached in these experiments, as probably in many other experiments as well. It is then not a surprise that our phase equilibrium calculations differ from some of these experimental findings. On the other hand, based on the current thermodynamic description of the La–Mn–Y–Zr–O system, we conduct calculations on the local equilibrium phase relations at the LaMnO$_3$–YSZ interface. Our calculations are found to be in good agreement with most of the experimental findings. This will be discussed in Chapter 9.

8.6 Conclusions

In the present work, an evaluation was conducted on the Gibbs energy functions of stoichiometric compounds in the La–Mn–Zr–O system from both Yokokawa et al. and the present authors. The major difference was found in the Gibbs energy function of La$_2$Zr$_2$O$_7$, which is due to the fact that different values for the enthalpy of formation of La$_2$Zr$_2$O$_7$ have been used by Yokokawa et al. and the present authors. The calculated enthalpy of formation and Gibbs energy of formation of La$_2$Zr$_2$O$_7$ from Yokokawa et al. are much less negative than the experimentally measured values, while the corresponding values from the present authors are in good agreement with experiments. We conclude that our Gibbs energy function of La$_2$Zr$_2$O$_7$ and also our thermodynamic description of La–Mn–Y–Zr–O are till now the best available. Further experimental investigations are however still necessary to improve the current description.

8.7 References

Evaluation of the Thermodynamics


[6] M. Mori, N. Sakai, T. Kawada, H. Yokokawa, and M. Dokiya, "A new cathode material (La,Sr)_{1-x}(Mn_{1-y}Cr_y)O_3 (0<=y<=0.2) for SOFC", Denki Kagaku 58 (1990), p. 528.

[7] A. Mitterdorfer and L. J. Gauckler, "La$_2$Zr$_2$O$_7$ formation and oxygen reduction kinetics of the La$_{0.85}$Sr$_{0.15}$Mn$_{3/2}$O$_{3-0.5}$ system", Solid State Ionics 111 (1998), p. 185.


[37] M. Chen, B. Hallstedt, and L. J. Gauckler, "Thermodynamics and phase equilibria in the ZrO_2-LaO_1.5 system", to be submitted.
9 Understanding the Thermodynamics at the LaMnO$_3$–YSZ Interface

Ming Chen, A. Nicholas Grundy, Bengt Hallstedt, and Ludwig J. Gauckler, to be submitted.

Abstract

Experimental investigations on the reactions between Sr-substituted LaMnO$_3$ (LSM) and yttria stabilized zirconia (YSZ, cubic fluorite) are reviewed. Calculations of phase equilibria in the LaO$_{1.5}$–MnO$_x$–YO$_{1.5}$–ZrO$_2$ system and local equilibria at the LaMnO$_3$–YSZ phase interface are presented. We conclude that the La$_2$Zr$_2$O$_7$ formation at the LaMnO$_3$–YSZ interface is due to the high stability of La$_2$Zr$_2$O$_7$. Increasing the La deficiency in LaMnO$_3$ by its own cannot thermodynamically prevent the La$_2$Zr$_2$O$_7$ formation. The driving force of the La$_2$Zr$_2$O$_7$ formation is determined essentially by the chemical potential of La in LaMnO$_3$, $\mu$(LaMnO$_3$, La) and that of Zr in YSZ, $\mu$(YSZ, Zr). The driving force is influenced by cation stoichiometries in LaMnO$_3$ and YSZ, temperature and oxygen partial pressure, of which the cation stoichiometry in LaMnO$_3$ is the most important. Diffusion of La and/or Mn from LaMnO$_3$ into YSZ changes $\mu$(LaMnO$_3$, La) and $\mu$(YSZ, Zr) at the interface and hence also the driving force of the La$_2$Zr$_2$O$_7$ formation. By neglecting the La$_2$Zr$_2$O$_7$ nucleation kinetics, we define the induction period of the La$_2$Zr$_2$O$_7$ formation as the period for the driving force (from a negative value) to be above zero. Increasing either the La deficiency in LaMnO$_3$ or the yttria content in YSZ leads to a decrease in the driving force and therefore a longer induction period. Measures are outlined to retard the La$_2$Zr$_2$O$_7$ formation by properly adjusting the compositions of LaMnO$_3$ and YSZ.

9.1 Introduction

Solid oxide fuel cells (SOFCs) are very attractive for power generation systems. The state of the art SOFC uses yttria-stabilized zirconia (YSZ, cubic fluorite) for electrolyte, Ni-YSZ cermet for anode, Sr-substituted La$_{1-x}$MnO$_{3-\delta}$ perovskite ((La$_{1-y}$Sr$_y$)$_{1-x}$MnO$_{3-\delta}$, LSM) for cathode, and LaCrO$_3$-based perovskite for interconnects. It is normally operated at 1173–1273 K. A further reduction of the operating temperature preferably to 873–1073 K would allow
the use of ferritic steel (instead of expensive lanthanum chromite) as interconnects and would significantly reduce material costs and increase lifetime of the SOFC [1, 2]. The reduction in the operation temperature will however lead to an increase in the electrode and electrolyte resistances and hence a decrease in the overall output of the SOFC.

Among all the losses in the SOFC, the contribution from the cathode–electrolyte interface is of particular importance. The cathode–electrolyte interface, i.e. the triple phase boundary (tpb), is where the oxygen reduction is supposed to take place. At the LSM–YSZ interface, oxygen adsorbs on the surface of LSM and diffuses over the surface towards the tpb where it becomes charged and is incorporated into YSZ [2]. It has been generally accepted that the electrochemical performance of the LSM cathode is mainly determined by the microstructure and the phase assemblage at the LSM–YSZ interface, rather than by the microstructure of the LSM layer [1]. Under certain conditions, highly electrically resistive phases (La$_2$Zr$_2$O$_7$ and/or SrZrO$_3$) are formed at the LSM–YSZ interface [3, 4]. The conductivities of La$_2$Zr$_2$O$_7$ and SrZrO$_3$ were reported to be much lower than those of LSM and YSZ. La$_2$Zr$_2$O$_7$ was reported to be a mixed $p$-type and ionic conductor at 1173–1373 K in air [5]. The electrical conductivity of La$_2$Zr$_2$O$_7$ at 1273 K was reported to be 2×10$^{-4}$ S cm$^{-1}$ by Brugnoni et al. [6] and 2.4×10$^{-5}$ S cm$^{-1}$ by Lee and Oh [7], much lower than both the electrical conductivity of LSM (for La$_{0.95}$Sr$_{0.05}$MnO$_{3-\delta}$, $\sigma = 100$ S cm$^{-1}$ at 1273 K) and that of YSZ (for (YO$_{1.5}$)$_{0.5}$ZrO$_{2.5}$, $\sigma = 0.1$ S cm$^{-1}$ at 1273 K) [7]. Labrincha et al. [5] reported that SrZrO$_3$ also shows mixed $p$-type and ionic conduction at 1073–1373 K in air and the electrical conductivity at 1273 K is about 10$^{-4}$ S cm$^{-1}$. The zirconate formation at the LSM–YSZ interface leads to an increase in both the resistance and the over-potential of the LSM cathode [1], and hence a degradation of the SOFC performance. The thermal expansion coefficients of the zirconates were reported to be also lower than that of YSZ [5, 8]. The zirconate formation can thus introduce a mechanical mismatch at the LSM–YSZ interface. This increases the risk of mechanical failure of the SOFC during thermal cycling. Understanding the factors influencing the zirconate formation at the LSM–YSZ interface is obviously advantageous for improving the performance of the state of the art SOFC and is also instructive for developing the SOFC operated at intermediate temperature (873–1073 K).

In the following we use the shorthand LMO for the La$_{1-x}$MnO$_{3-\delta}$ perovskite phase and LSM for (La$_{1-x}$Sr$_{x}$)$_{1-x}$MnO$_{3-\delta}$, LZO for the La$_2$Zr$_2$O$_7$ phase, c-ZrO$_2$ for the cubic fluorite ZrO$_2$ phase,
and YSZ for the yttria-stabilized cubic fluorite ZrO₂ phase. 8YSZ will be used as an acronym for 8 mol% Y₂O₃-stabilized zirconia ((YO₁₅)₀₁₈(ZrO₂)₀₈₅), which is often used as the electrolyte for the SOFC.

9.2 Previous experimental investigations

The cathode–electrolyte interface reaction was first reported by Tedmon et al. [9] at the LaCoO₃–YSZ interface. Lau and Singhal [3] first reported the LZO formation in diffusion couples of dense La₀.₉Sr₀.₁Mn₀.₃O₅ and (YO₁₅)₀₁₈(ZrO₂)₀₈₂ single crystal. Till now, a great number of experimental investigations have been conducted on the LSM–YSZ reactions. Experiments have been done on diffusion couples and powder mixtures. For diffusion couples, both porous and dense LSM (including La₁₋ₓMnO₃) have been used as the cathode, while both single- and poly-crystalline YSZ have been used as the electrolyte. The zirconate formation (La₂Zr₂O₇ and/or SrZrO₃) has been reported to be influenced by a number of factors, e.g. the cation stoichiometry in LSM, the yttria content in YSZ, the ratio between LSM and YSZ, the microstructure at the interface and so on. Inter-diffusion of cations was detected in the LSM–YSZ interface region. Different mechanisms for the formation and the growth of La₂Zr₂O₇ have been proposed. Below is a collection of representative results from previous experimental investigations.

9.2.1 Reactivity between LSM and YSZ

9.2.1.1 Cation stoichiometry in LSM

The A-site stoichiometry in LSM (or the La deficiency in LMO) has been reported to be the major factor controlling the zirconate formation. By increasing the A-site deficiency, the zirconate formation can be retarded or even prevented during high-temperature treatment [10, 11, 12, 13, 14]. Yamamoto et al. [11, 14] studied the reactivity between La₁₋ₓMnO₃/LSM and YSZ. Powder mixtures of La₁₋ₓMn₀.₃O₅ (x = 0, 0.05, 0.1, 0.15, 0.2) or La₀.₉Sr₀.₁Mn₀.₃O₅ and (YO₁₅)₀₁₈(ZrO₂)₀₈₂ (x = 0.15, 0.17, 0.20, 0.21) were pressed into pellets and were annealed at 1473–1673 K for different periods. The LZO formation was confirmed by X-ray diffraction (XRD) measurements and the amount of the formed LZO phase was determined by the intensity ratio of the highest diffraction peak of LZO to that of YSZ. An induction period was observed for the LZO formation. Increasing the A-site deficiency led to an increase in the
induction period and a decrease in the amount of the formed LZO phase. For the reactivity
between $\text{La}_{0.9}\text{MnO}_3$ (a mixture of $\text{La}_{0.9}\text{Mn}_1\text{O}_3+\text{Mn}_2\text{O}_3$) and 8YSZ, LZO was observed after
annealing at 1523 K in air for about 100h. Kenjo and Nishiya [12] investigated the reactions at
the LMO–YSZ interface. The $\text{La}_{1-x}\text{Mn}_1\text{O}_3$ ($x = 0$ and 0.15) powder was dispersed using
turpentine oil. The obtained slurry was painted on a sintered 8YSZ pellet and was annealed at
1273–1573 K for 1h. The XRD peaks corresponding to LZO were observed at the
$\text{La}_1\text{Mn}_1\text{O}_3$–YSZ interface, while no peaks of LZO were observed at the $\text{La}_{0.85}\text{Mn}_1\text{O}_3$–YSZ
interface for the sample annealed at 1573 K for 1h.

Increasing Sr substitution for La also inhibits the LZO formation [4, 11, 13, 15, 16, 17]. For
heavily doped ($\text{La}_{1-y}\text{Sr}_y\text{Mn}_1\text{O}_3$ ($y \geq 0.3$), SrZrO$_3$ was found to form at the LSM–YSZ
interface [4, 13, 17]. Takeda et al. [17] investigated the reactivity between ($\text{La}_{1-y}\text{Sr}_y\text{Mn}_1\text{O}_3$
($y = 0$–0.8) and 8YSZ using XRD, scanning electron microscopy (SEM) and energy
dispersive X-ray (EDX). LSM was sputtered on the polished surface of a YSZ pellet. The
samples were annealed at 1473 K for 2 h. The LZO formation was detected for $y = 0$–0.2 and
the SrZrO$_3$ formation for $y = 0.6$–0.8. No zirconate formation was observed for $y = 0.3$–0.5.
At the $\text{La}_{0.5}\text{Sr}_{0.5}\text{Mn}_1\text{O}_3$–8YSZ interface, no reaction was observed after annealing at 1473 K
for 200 h. Stochniol et al. [13] studied the reactivity between $\text{La}_{1-x-y}\text{Sr}_y\text{Mn}_1\text{O}_3$ ($x = 0$ and 0.05,
$y = 0$–0.5) and 8YSZ. Powder mixtures and dense diffusion couples were annealed in air at
1470 K up to 400 h and at 1670 K up to 200 h. For the powder mixtures of
$\text{La}_{1-y}\text{Sr}_y\text{Mn}_1\text{O}_3$+8YSZ annealed at 1470 K, either $\text{La}_2\text{Zr}_2\text{O}_7$ for $y < 0.3$ or SrZrO$_3$ for $y > 0.3$
was detected. No reaction was detected for $y = 0.3$ at 1470 K up to 400 h. At 1670 K,
reactions were detected for all the $\text{La}_{1-y}\text{Sr}_y\text{Mn}_1\text{O}_3$+8YSZ samples. For the powder mixtures of
$\text{La}_{0.95-y}\text{Sr}_y\text{Mn}_1\text{O}_3$+8YSZ, no reaction was detected for $y = 0.2$–0.4 at 1470 K for 400 h and for
$y = 0.3$ at 1670 K for 200 h.

Mitterdorfer and Gauckler [1] investigated the influence of the Mn stoichiometry in LSM
upon the formation and the growth of LZO at the LSM–YSZ interface. The $\text{La}_{0.85}\text{Sr}_{0.15}\text{Mn}_1\text{O}_3$
($y = 0.95, 0.98, 1.02, 1.10, 1.16$) powders were screen-printed on (YO$_{1.5}$)$_{0.17}$(ZrO$_2$)$_{0.83}$ single
crystals. The samples were annealed at 1373 K for up to 12 h. The $\text{La}_{0.85}\text{Sr}_{0.15}\text{Mn}_1\text{O}_3$ ($y = 1.02,$
1.10, 1.16) cathodes were prepared from a mixture of $\text{La}_{0.85}\text{Sr}_{0.15}\text{Mn}_{0.98}$O$_3$ powder and
manganese nitrate. The sintered cathodes were reported to be single-phase perovskite with a
rhombohedral structure, except for $\text{La}_{0.85}\text{Sr}_{0.15}\text{Mn}_{1.16}$O$_3$ in which the presence of Mn$_2$O$_4$ was
detected by TEM. SEM and EDX measurements gave no indication of the zirconate formation. With the help of high resolution transmission electron microscopy (HRTEM) and atomic force microscopy (AFM), formation of LZO islands was detected at the La$_{0.85}$Sr$_{0.15}$Mn$_3$O$_7$–YSZ ($\gamma = 0.95, 0.98, 1.02$) interface. For $\gamma = 1.10$ and 1.16, no formation of La$_2$Zr$_2$O$_7$ was found.

9.2.1.2 Yttria content in YSZ
The effect of the yttria content in YSZ on the LZO formation was systematically studied by Yamamoto and his co-authors [11, 14]. Powder mixtures of La$_{0.9}$Mn$_3$O$_7$ and (YO$_{1.5}$)(ZrO$_2$)$_{1-x}$ ($x = 0.15, 0.17, 0.20, 0.21$) were annealed at 1473–1673 K for different periods. YSZ with higher yttria content was found to be less reactive with La$_{0.9}$Mn$_3$O$_7$. Increasing the yttria content leads to an increase in the induction period of the LZO formation and a decrease in the calculated activation energy, which was assumed to be the activation energy for the diffusion of La$^{3+}$ or Mn$^{4+}$ in YSZ.

9.2.1.3 LSM:YSZ ratio
The ratio between LSM and YSZ also has an influence on the LZO formation. Clausen and his co-authors [18, 19, 20, 21] studied the reactions between the amorphous La$_{0.85}$Sr$_{0.15}$Mn$_1$O$_3$ powder and the 8YSZ powder. Powder mixtures of 25wt.%LSM–75wt.%YSZ and 80wt.%LSM–20wt.%YSZ were pressed into pellets and sintered at 1573 K for 2 h. TEM and EDX measurements indicated LZO formation in the 25wt.%LSM–75wt.%YSZ sample. In the 80wt.%LSM–20wt.%YSZ sample, no LZO was found, while Mn oxide up to 1 μm in diameter was detected within LSM. Mn oxide was also observed in the pure LSM sample not mixed with YSZ. Obviously in Clausen et al.’s experiments, not all the Mn in La$_{0.85}$Sr$_{0.15}$Mn$_1$O$_3$ enters into the perovskite crystal lattice after sintering at 1573 K for 2 h. The excess Mn can exist as Mn oxide or dissolve in YSZ.

9.2.1.4 Other factors
The sintering or annealing temperature, the reaction time, and the interface microstructure also influence the reaction between LSM and YSZ. The amount of the formed LZO phase has been found to increase with longer reaction time or higher annealing temperature [11, 13, 14]. Kenjo and Nishiya [12] investigated the reactions between a composite cathode and YSZ. A slurry made from a mixture of La$_1$Mn$_3$O$_7$ and 8YSZ powders was screen-printed on a sintered
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8YSZ pellet. Annealing at 1473 K for 1 h led to LZO formation inside the composite cathode, while no LZO was observed at the cathode–electrolyte interface. The interface microstructure has been observed to influence the growth of the formed LZO layer. Kaneko and his co-authors [22, 23] investigated the microstructures at the La\textsubscript{1}\textsubscript{−}\textsubscript{x}Mn\textsubscript{x}O\textsubscript{3}−8YSZ interface. La\textsubscript{1}Mn\textsubscript{1}O\textsubscript{3} paste was smeared on an 8YSZ pellet. The sample was annealed at 1673 K for 144 h. A LZO layer was found to form at the interface. The LZO layer was thin where the La\textsubscript{1}Mn\textsubscript{1}O\textsubscript{3} cathode was densely sintered and bonded closely to the 8YSZ electrolyte and was thick where the La\textsubscript{1}Mn\textsubscript{1}O\textsubscript{3} cathode was very porous and had bridge-like connections with 8YSZ. The LZO layer was reported to grow only towards the YSZ phase. Clausen et al. [20] reported that the formed LZO grain grows into both YSZ and LSM in the 25wt.%La\textsubscript{0.85}Sr\textsubscript{0.15}Mn\textsubscript{0.975}O\textsubscript{3}−75wt.%8YSZ sample, while Mitterdorfer and Gauckler [1] found that at the La\textsubscript{0.85}Sr\textsubscript{0.15}Mn\textsubscript{0.975}O\textsubscript{3}−YSZ interface, the LZO layer grows almost exclusively towards LSM and only to a minor extent into YSZ.

9.2.2 Inter-diffusion

Inter-diffusion of cations between LSM and YSZ has been observed in the LSM–YSZ interface region. It has been reported that Mn and La diffuse from LSM into YSZ, while Sr hardly diffuses into YSZ [22, 23]. The diffusion of Mn has generally been found to take place to a larger extent than that of La. van Roosmalen and Cordfunke [24] however, found no diffusion of Mn from La\textsubscript{1−}\textsubscript{x}Sr\textsubscript{x}Mn\textsubscript{0.975}O\textsubscript{3} (x=0, 0.15, 0.3, 0.5) into YSZ from diffusion couple experiments. Instead, they observed diffusion of La and Sr from LSM into YSZ. Mitterdorfer and Gauckler [1] reported no Mn diffusion from La\textsubscript{0.85}Sr\textsubscript{0.15}Mn\textsubscript{0.975}O\textsubscript{3} or La\textsubscript{0.85}Sr\textsubscript{0.15}Mn\textsubscript{0.98}O\textsubscript{3} into YSZ ((YO\textsubscript{1.5})\textsubscript{0.17}(ZrO\textsubscript{2})\textsubscript{0.83} single crystal), but heavy Mn diffusion from Mn-rich perovskites such as La\textsubscript{0.85}Sr\textsubscript{0.15}Mn\textsubscript{0.98}O\textsubscript{3} into YSZ. The La\textsubscript{0.85}Sr\textsubscript{0.15}Mn\textsubscript{0.98}O\textsubscript{3} cathode was prepared from a mixture of La\textsubscript{0.85}Sr\textsubscript{0.15}Mn\textsubscript{0.98}O\textsubscript{3} and MnO. The diffusion of Y and Zr from YSZ into LSM was reported to be very limited [3, 20, 22, 23].

The diffusion coefficients of La and Mn in YSZ have been measured by a number of groups. Lau and Singhal [3] reported the diffusion coefficient of Mn in the (YO\textsubscript{1.5})\textsubscript{0.18}(ZrO\textsubscript{2})\textsubscript{0.82} single crystal to be $10^{-17}$ to $10^{-16}$ m\textsuperscript{2} s\textsuperscript{−1} at 1673 K and two orders of magnitude higher in polycrystalline YSZ. The higher diffusion coefficient in polycrystalline YSZ was attributed to fast diffusion paths along grain boundaries [22, 23]. Taimatsu et al. [23] estimated the
diffusion coefficient of La in the (YO\(_{1.5}\))\(_{0.19}\)(ZrO\(_2\))\(_{0.81}\) single crystal to be \(2 \times 10^{-18} \text{ m}^2 \text{ s}^{-1}\) at 1673 K and that of Mn to be \(4 \times 10^{-18} \text{ m}^2 \text{ s}^{-1}\).

### 9.2.3 Formation and growth mechanism of La\(_2\)Zr\(_2\)O\(_7\)

The formation and the growth mechanisms of LZO at the LSM–YSZ interface have been proposed by a few groups [1, 14, 18, 19, 20, 22, 23]. An induction period is generally needed until the LZO formation can be experimentally detected. Obviously the induction period reported from SEM/TEM interface analysis is shorter than the one from XRD measurements. The induction period can be increased by increasing the A-site deficiency or including extra Mn oxide in LSM [11, 18, 19, 20], by increasing the yttria content in YSZ [11], by decreasing the temperature [11]. Kaneko and his co-authors [22, 23] related this induction period to the diffusion of La and Mn from LMO into YSZ and proposed the following mechanism for the LZO formation: Mn was observed to diffuse to a larger extent than La. After a certain period, the LMO phase near the interface becomes La rich. La\(_2\)O\(_3\) might form at the interface and react with YSZ to form LZO. The La-deficient LaMnO\(_3\) obviously needs longer induction periods to form La\(_2\)O\(_3\). Clausen et al. [20] proposed that Mn is the controlling factor for the LZO formation (“the initiation of the pyrochlore formation”). The diffusion of Mn from LSM into YSZ causes a depletion of Mn in LSM. La\(_2\)O\(_3\) might form at the interface. Including excess Mn oxide within LSM can delay or impede the above process. A similar mechanism for the LZO formation has also been proposed by Mitterdorfer and Gauckler [1].

A conclusion on the LZO formation can be derived from the above-mentioned mechanisms: The reaction between LSM and YSZ might happen between La\(_2\)O\(_3\) and YSZ rather than directly between LSM and YSZ; the induction period of the LZO formation is the period for La\(_2\)O\(_3\) to form at the interface; this process is controlled by the compositions of LSM and YSZ and the La and/or Mn diffusion into YSZ. This would indicate that nucleation of LZO is very difficult, since the driving force for LZO formation is much larger than that for La\(_2\)O\(_3\) formation. It is however a question if La\(_2\)O\(_3\) actually forms at the interface, since no one has observed it.

The growth of the formed LZO phase seems to be rather complicated. LZO has been observed to grow into YSZ only [22, 23], into both YSZ and LSM [20], or mostly into LSM and only to a minor extent into YSZ [1]. The LZO growth is determined by the way how La and Zr are
supplied from LSM and YSZ. This is obviously a diffusion-controlled process and is
determined by the inter-diffusion across the LSM–YSZ interface and the formed LZO layer
and the diffusion inside LSM and YSZ (towards the interface). These diffusion processes are
further influenced by the compositions and the microstructures of LSM and YSZ, the
microstructure and the phase assemblage at the interface, temperature and oxygen partial
pressure. The LZO growth mechanism has been discussed by Taimatsu et al. [23] and
Mitterdorfer and Gauckler [1] and no agreement has been achieved.

9.3 Modeling of the LSM–YSZ reactions by Yokokawa et al.

The thermodynamics of the LSM–YSZ reactions has been studied by Yokokawa et al. [25, 26,
27, 28]. They evaluated or estimated the thermodynamic properties of solid solution phases
and stoichiometric compounds in the La–Mn–Sr–Y–Zr–O system. According to their
calculations, the Gibbs energy of the following reaction is essentially positive under the SOFC
fabrication and operation temperatures:

\[ \text{LaMnO}_3 + c \cdot \text{ZrO}_2 = \frac{1}{2} \text{La}_2\text{Zr}_2\text{O}_7 + \text{MnO}_x + \frac{3-2x}{4} \text{O}_2 \]  

Eq. 9.1

This is apparently in contradiction to the experimental observations which actually indicated
or verified the formation of LZO at the LMO–YSZ or the LSM–YSZ interface [3, 11]. The
discrepancy was ascribed to the fact that lanthanum non-stoichiometry in LMO was neglected
in the previous calculations. An ideal associate solution model with \( \text{La}_{0.667}\text{Mn(IV)O}_3 \),
\( \text{La}_{0.667}\text{Mn(III)O}_{2.5} \), \( \text{LaMn(III)O}_3 \), \( \text{LaMn(II)O}_{2.5} \) as components was used to model the non¬
stoichiometry in LMO. According to this model, the lanthanum deficiency in LMO is realized
by introducing relatively stable Mn\(^{4+}\) ions into the perovskite crystal lattice. The driving force
of the zirconate formation was hence attributed to the destabilization of the valence state of
Mn\(^{3+}\) in the perovskite phase in the presence of \( \text{ZrO}_2 \), which can be represented by the reaction:

\[ \text{LaMnO}_3 + x \cdot \text{c} \cdot \text{ZrO}_2 + \frac{3x}{4} \text{O}_2 = \frac{x}{2} \text{La}_2\text{Zr}_2\text{O}_7 + \text{La}_{1-x}\text{MnO}_3 \]  

Eq. 9.2

Their calculated chemical potential diagram for the La–Mn–(Y)–Zr–O system at 1573 K in
air (Figure 8 in [27]) shows that lanthanum manganites having small lanthanum deficiency (\( x < 0.14 \) for \( x \) in \( \text{La}_{1-x}\text{Mn}_3\text{O}_3 \)) will react with YSZ to form LZO, those having large lanthanum
deficiency can be in equilibrium with YSZ. This means that the LZO formation can be
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thermodynamically prevented by increasing $x$ in La$_{1-x}$Mn$_3$O$_5$ to a certain extent ($x = 0.14$ at 1573 K in air). They also investigated the reactions between LSM and YSZ. The calculations for the reactions between (La$_{1-y}$Sr$_y$)Mn$_3$O$_5$ and (YO$_{1.5}$)$_{0.17}$(ZrO$_2$)$_{0.83}$ at 1673 K in air [29] show that for heavily doped (La$_{1-y}$Sr$_y$)Mn$_3$O$_5$ ($y \geq 0.3$), SrZrO$_3$ will form.

9.4 Open questions and aim of the study

Though numerous investigations have been conducted on the LSM–YSZ reactions, the mechanism for the zirconate formation is not totally clarified. The remaining questions concern mainly the LZO formation, as very often only LZO forms at the interface. SrZrO$_3$ forms at high Sr substitution in LSM.

a. The most important question is about the thermodynamic origin and the driving force of the LZO formation. Yokokawa et al. stated that the zirconate formation was due to the destabilization of the valence state of Mn$^{3+}$ in LSM in the presence of ZrO$_2$. The high stability of the LZO phase was not considered as the thermodynamic origin.

b. The second question is about the controlling factor of the LZO formation. The cation stoichiometry in LSM was in general considered as the major factor controlling the LZO formation. According to Yokokawa et al. [27], by increasing the A-site deficiency in LSM to a certain extent, the LZO formation can be thermodynamically prevented. In reality, the LZO formation is controlled by both thermodynamic and kinetic factors. The experimental investigations clearly indicate an induction period for the LZO formation. This induction period is influenced by the cation stoichiometry in LSM, the yttria content in YSZ, and the inter-diffusion between LSM and YSZ and so on. It is quite possible that under certain conditions, the observed absence of LZO formation is actually due to kinetics (e.g. short annealing time and slow diffusion), i.e. thermodynamically LZO should form but the LZO formation is kinetically hindered. A good example can be found in Yamamoto et al.’s experiments [11]. The LZO formation between La$_{0.5}$Mn$_3$O$_5$ and 8YSZ was detected only after 100 h annealing at 1523 K. According to Yokokawa et al.’s calculations (Figure 8 in [27]), at 1573 K in air, there should be no LZO formation between La$_{1-x}$Mn$_3$O$_5$ and YSZ when $x > 0.14$. This is obviously in contradiction to Yamamoto et al.’s experiments and this cannot just be attributed to the temperature difference of 50 K. So the questions are: Which factors
control the LZO formation? How are thermodynamics and kinetics involved in the LZO formation?

c. The induction period of the LZO formation was suggested to be related to the formation of La$_2$O$_3$ at the interface [1, 23]. But no one has actually observed La$_2$O$_3$ at the interface. Is the formation of La$_2$O$_3$ at the interface a prerequisite for the LZO formation?

d. How does the yttria content in YSZ influence the LZO formation?

e. The controversy on the observed inter-diffusion remains unresolved. Is this just due to different experimental conditions or does thermodynamics also play a role?

The purpose of our work is to reconsider the thermodynamic origin of the zirconate formation at the LSM–YSZ interface and to clarify the thermodynamic and kinetic factors influencing the formation and the growth of zirconates. This paper focuses on the reactions between LMO and YSZ. Phase equilibrium calculations in the La$_{0.5}$Mn$_x$YO$_{1.5}$ZrO$_2$ system are conducted. The driving forces of the LZO formation and of the La and/or Mn diffusion are calculated. The LZO formation mechanism is discussed in detail. The influences of the La and/or Mn diffusion and of the Sr substitution for La are also investigated. The LZO growth mechanism is not discussed in this paper.

9.5 Equilibrium phase relations in the La$_{0.5}$Mn$_x$YO$_{1.5}$ZrO$_2$ system

Using the CALPHAD (CALculation of PHAse Diagrams) method, we are studying the thermodynamic properties of stoichiometric compounds and solution phases in the La–Mn–Sr–Y–Zr–O system. Recently we finished the thermodynamic description of the La–Mn–Y–Zr–O system. The thermodynamic description (the database) and the details of the thermodynamic modeling are presented elsewhere [30] (Chapter 7 and Appendix).

Here we first present the calculated phase relations in the La$_{0.5}$Mn$_x$ZrO$_2$ pseudo-ternary system. A calculated isothermal section of La$_{0.5}$Mn$_x$ZrO$_2$ at 1273 K in air is shown in Figure 9.1a. Figure 9.1b shows the corresponding chemical potential diagram. In the calculations, we include the following phases: A-La$_2$O$_3$, α-Mn$_3$O$_4$, c-ZrO$_2$, LMO, and LZO.
\(\alpha\)-Mn\(_3\)O\(_4\) is modeled as a stoichiometric compound and the other four phases all exhibit certain degrees of nonstoichiometry. According to our calculated equilibrium phase diagrams of LaO\(_{1.5}\)–MnO\(_x\)–ZrO\(_2\) [30], at 1273 K in air, the stable phase for pure ZrO\(_2\) should be m-ZrO\(_2\) instead of c-ZrO\(_2\). Figure 9.1 and the other phase diagrams presented in this paper are calculated for SOFC applications. Only the phases which can or might appear at the LMO–YSZ interface are included in the calculations, e.g. only the metastable c-ZrO\(_2\) and not the stable m-ZrO\(_2\) or t-ZrO\(_2\) is included. The phase diagrams presented in this paper can be treated as the “true” equilibrium phase diagram for the SOFC applications. In Figure 9.1a, tie lines exist between LZO and c-ZrO\(_2\), between LZO and \(\alpha\)-Mn\(_3\)O\(_4\), and between LZO and LMO. No tie line exists between c-ZrO\(_2\) and LMO, meaning that these two phases cannot be in equilibrium. The phase relations shown in Figure 9.1a can also be represented by a chemical potential diagram (Figure 9.1b). We choose SER (Stable Element Reference) as the reference state, i.e. all the Gibbs energies are referred to the enthalpy of selected stable states for pure elements at 298.15 K and 10\(^5\) Pa (1 bar). In Figure 9.1b, the c-ZrO\(_2\) single-phase region does not have a contact with the LMO single-phase region. They are separated by the LZO and \(\alpha\)-Mn\(_3\)O\(_4\) single-phase regions. Obviously the LMO phase cannot be in equilibrium with c-ZrO\(_2\) without forming LZO and/or \(\alpha\)-Mn\(_3\)O\(_4\). According to our calculations, at 1273 K in air, LMO reacts with c-ZrO\(_2\) to form LZO and \(\alpha\)-Mn\(_3\)O\(_4\). Increasing the La deficiency in LMO by itself cannot thermodynamically prevent the LZO formation.

We also calculate the Gibbs energies of the reactions corresponding to Eq. 9.1 at \(P(O_2) = 1\) bar. The results are plotted in Figure 9.2. The Gibbs energy of the reaction \(\frac{1}{2}A\cdot La_2O_3 + c\cdot ZrO_2 = \frac{1}{2}La_2Zr_2O_7\) is also included. The Gibbs energies of the stoichiometric compounds are used in the calculations. As Figure 9.2 shows, at the SOFC fabrication and operation temperature (1000–1800 K), the Gibbs energies of Reactions 2, 3, and 5 are negative. Figures 9.1 and 9.2 indicate that the thermodynamic origin of the LZO formation at the LMO–YSZ interface is due to the high stability of LZO.
Figure 9.1 Calculated phase relations in the LaO$_{1.5}$–MnO$_x$–ZrO$_2$ system at 1273 K in air from the present work, (a) isothermal section, (b) chemical potential diagram. The following phases are included in the calculation: A-La$_2$O$_3$, α-Mn$_3$O$_4$, c-ZrO$_2$, LaMnO$_3$, and La$_2$Zr$_2$O$_7$. 
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Figure 9.2  Calculated Gibbs energies of reactions at $P(O_2) = 1$ bar from the present work.

Figures 9.1 and 9.2 in this paper are different from those published by Yokokawa et al. (Figure 3 in [25], Figure 5 in [27], and Figure 10 in [28]). We evaluate the Gibbs energies of stoichiometric compounds from both Yokokawa et al. and the present authors. The discrepancy between Yokokawa et al.’s calculations and those from the present authors is mainly due to a large difference in the Gibbs energy of La$_2$Zr$_2$O$_7$, which is caused by the fact that different values for the enthalpy of formation of La$_2$Zr$_2$O$_7$ have been used by Yokokawa et al. and the present authors. The calculated enthalpy of formation and Gibbs energy of formation of La$_2$Zr$_2$O$_7$ from Yokokawa et al. are much less negative than the experimentally measured values, while those from the present authors are in good agreement with the measured ones. The details of the evaluation are presented elsewhere [31] (Chapter 8).

To properly account for the reactions between LMO and YSZ, yttria should also be included in the calculations. We calculate phase relations in the LaO$_{1.5}$–MnO$_x$–YO$_{1.5}$–ZrO$_2$ pseudoquaternary system. An isothermal section of LaO$_{1.5}$–MnO$_x$–(YO$_{1.5}$)(ZrO$_2$)$_{0.85}$ at 1273 K in air is plotted in Figure 9.3. No tie lines are plotted as they are out of the plane. In Figure 9.3, there exist 7 regions with different equilibrium phase assemblages. The LZO phase seems to be quite stable and it is involved in almost all regions except Region VII. α-Mn$_3$O$_4$ is only involved in Regions II and III. According to Figure 9.3, at 1273 K in air, increasing the La
deficiency in LMO by itself cannot thermodynamically prevent the LZO formation from LMO and YSZ. Isothermal sections of LaO$_{1.5}$–MnO$_x$–(YO$_{1.5}$)$_{0.15}$(ZrO$_2$)$_{0.85}$ at different temperatures (1073–1673 K) and oxygen partial pressures (1–21278 Pa) have also been calculated. They are all quite similar to Figure 9.3 and therefore are not presented here.

![Diagram of LaO$_{1.5}$–MnO$_x$–(YO$_{1.5}$)$_{0.15}$(ZrO$_2$)$_{0.85}$ at 1273 K]

Figure 9.3 Calculated isothermal section of LaO$_{1.5}$–MnO$_x$–(YO$_{1.5}$)$_{0.15}$(ZrO$_2$)$_{0.85}$ at 1273 K in air from the present work. The following phases are included in the calculations: A-La$_2$O$_3$, $\alpha$-Mn$_3$O$_4$, YSZ(c-ZrO$_2$), LaMnO$_3$, and La$_2$Zr$_2$O$_7$. Equilibrium phase assemblages in different regions: I: YSZ and La$_2$Zr$_2$O$_7$; II: $\alpha$-Mn$_3$O$_4$, YSZ, and La$_2$Zr$_2$O$_7$; III: $\alpha$-Mn$_3$O$_4$, YSZ, LaMnO$_3$, and La$_2$Zr$_2$O$_7$; IV: YSZ, LaMnO$_3$, and La$_2$Zr$_2$O$_7$; V: A-La$_2$O$_3$, YSZ, LaMnO$_3$, and La$_2$Zr$_2$O$_7$; VI: A-La$_2$O$_3$, LaMnO$_3$, and La$_2$Zr$_2$O$_7$; VII: A-La$_2$O$_3$ and LaMnO$_3$.

The Y:Zr ratio also influences the equilibrium phase relations. We have calculated isothermal sections of LaO$_{1.5}$–MnO$_x$–(YO$_{1.5}$)$_x$(ZrO$_2$)$_{1-x}$ with different Y:Zr ratios ($x = 0.2, 0.3, 0.4$). For the details, the readers are referred to [30] (Chapter 7). By increasing the yttria content, the amount of the formed LZO phase decreases. In the isothermal section of LaO$_{1.5}$–MnO$_x$–(YO$_{1.5}$)$_{0.4}$(ZrO$_2$)$_{0.6}$, tie lines even appear between La-deficient LMO and YSZ, i.e. La-deficient LMO can be in equilibrium with YSZ (with 40 mol% YO$_{1.5}$ or more) without forming LZO.
The LaO$_{1.5}$ and MnO$_x$ solubilities in YSZ may reflect the tendency for the La and/or Mn diffusion from LMO into YSZ. We conduct calculations along the composition line of (YO$_{1.5}$)$_{0.15}$(ZrO$_2$)$_{0.85}$-La$_1$Mn$_1$O$_3$, which lies inside the plane of LaO$_{1.5}$-MnO$_x$-(YO$_{1.5}$)$_{0.15}$(ZrO$_2$)$_{0.85}$. Along the line of (YO$_{1.5}$)$_{0.15}$(ZrO$_2$)$_{0.85}$-La$_1$Mn$_1$O$_3$, our calculated LaO$_{1.5}$ concentration in YSZ is very low, all less than 0.1 cat.%. This indicates that in an equilibrium state, La$^{3+}$ and Zr$^{4+}$ ions prefer to form an ordered pyrochlore phase (La$_2$Zr$_2$O$_7$), instead of a disordered cubic fluorite solid solution phase (c-ZrO$_2$). Figure 9.4 shows the MnO$_x$ concentration in YSZ versus $x$(LaMnO$_3$) along the line of (YO$_{1.5}$)$_{0.15}$(ZrO$_2$)$_{0.85}$-La$_1$Mn$_1$O$_3$. With increasing $x$(LaMnO$_3$), the MnO$_x$ concentration in 8YSZ first increases in the YSZ+LZO two-phase region (Region I) and then decreases after $\alpha$-Mn$_3$O$_4$ appears in the equilibrium phase assemblage (Regions II, III). At 1273 K in air, the highest concentration of MnO$_x$ in 8YSZ (along the line of (YO$_{1.5}$)$_{0.15}$(ZrO$_2$)$_{0.85}$-La$_1$Mn$_1$O$_3$) is about 4.5 cat.%. It is clear that the phase assemblage at the LMO–YSZ interface influences the diffusion of Mn from LMO into YSZ.

Figure 9.4 Calculated MnO$_x$ concentration in YSZ at 1273 K in air from the present work along the composition line of (YO$_{1.5}$)$_{0.15}$(ZrO$_2$)$_{0.85}$-LaMnO$_3$. Only the following phases are included in the calculations: A-La$_2$O$_3$, $\alpha$-Mn$_3$O$_4$, YSZ(c-ZrO$_2$), LaMnO$_3$, and La$_2$Zr$_2$O$_7$. Equilibrium phase assemblages in different regions: I: YSZ and La$_2$Zr$_2$O$_7$; II: $\alpha$-Mn$_3$O$_4$, YSZ, and La$_2$Zr$_2$O$_7$; III: $\alpha$-Mn$_3$O$_4$, YSZ, LaMnO$_3$, and La$_2$Zr$_2$O$_7$; IV: YSZ, LaMnO$_3$, and La$_2$Zr$_2$O$_7$. 

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The effect of the La deficiency in LMO on the LaO\textsubscript{1.5} and MnO\textsubscript{x} solubilities in YSZ is also investigated. Figure 9.5a shows the calculated LaO\textsubscript{1.5} solubility in 8YSZ in air. The calculations are done in the LMO+YSZ or LZO+YSZ two-phase region. Also the LMO/LZO:YSZ ratio influences the LaO\textsubscript{1.5} solubility in YSZ. We fixed the LMO/LZO:YSZ cation ratio. Note that the phase assemblage of LMO+YSZ is not an equilibrium phase assemblage as LZO should form when LMO is in contact with YSZ. The LaO\textsubscript{1.5} solubility calculated in the LMO+YSZ two-phase region is therefore metastable. The equilibrium solubility is the one calculated in the LZO+YSZ two-phase region. Figure 9.5a indicates that before LZO forms, YSZ could dissolve some LaO\textsubscript{1.5} (from LMO). Decreasing the La deficiency in LMO can further increase the LaO\textsubscript{1.5} solubility. After the LZO phase forms, the LaO\textsubscript{1.5} solubility decreases to almost zero (the dotted line in Figure 9.5a). Figure 9.5b shows our calculated MnO\textsubscript{x} solubilities in 8YSZ in air together with experimental data. The calculations are done in the LMO+YSZ or MnO\textsubscript{x}+YSZ two-phase region. The one calculated in the MnO\textsubscript{x}+YSZ two-phase region is the equilibrium solubility. Our calculated values are in good agreement with the measured ones from Kawada et al. [32]. At 1273K in air, about 5 cat.% MnO\textsubscript{x} can dissolve in 8YSZ. In the LMO+YSZ two-phase region, the MnO\textsubscript{x} solubility (metastable) is influenced by the La deficiency in LMO. Increasing the La deficiency leads to an increase in the MnO\textsubscript{x} solubility.

Based on the calculated phase relations in the LaO\textsubscript{1.5}–MnO\textsubscript{x}–YO\textsubscript{1.5}–ZrO\textsubscript{2} system, a few conclusions can be drawn on the equilibrium thermodynamics of the LMO–YSZ reactions:

a. LZO forms due to its high stability.

b. Increasing the La deficiency in LMO by itself cannot prevent the LZO formation. Increasing the yttria content in YSZ can suppress and in the end prevent the LZO formation.

c. The amount of LaO\textsubscript{1.5} or MnO\textsubscript{x} dissolved in YSZ is influenced by the cation stoichiometries of LMO and YSZ, the LMO:YSZ ratio, the phase assemblage, temperature and oxygen partial pressure. In general, the MnO\textsubscript{x} solubility in YSZ is higher than that of LaO\textsubscript{1.5}. Increasing the La deficiency in LMO can further increase the MnO\textsubscript{x} solubility. Before LZO forms, some amount of LaO\textsubscript{1.5} could be dissolved in YSZ. The LaO\textsubscript{1.5} solubility in YSZ decreases to almost zero after LZO forms.
Figure 9.5  Calculated (a) $\text{LaO}_{1.5}$ and (b) $\text{MnO}_x$ solubilities in 8YSZ in air from the present work. The experimental data are from Kawada et al. [32]. Note that all lines involving $\text{LaMnO}_3+\text{YSZ}$ are metastable and only valid as long as $\text{LZO}$ does not form.
9.6 LaMnO$_3$–YSZ phase interface

The calculated equilibrium thermodynamics in Section 9.5 clarified the thermodynamic origin of the LZO formation. But it cannot completely reflect the experimental observations on the LMO–YSZ reactions. Some of the questions in Section 9.4 remain unresolved. This is partly due to the fact that equilibrium thermodynamics does not consider kinetic effects (like diffusion), which actually play an important role in reality. Due to slow diffusion, it is normally not easy to reach global equilibrium in a ceramic system and global equilibrium is obviously not reached in a SOFC.

Here we apply chemical potentials to study the local equilibrium (stable or metastable) at the LMO–YSZ interface before the formation of LZO takes place. To simplify the discussion, LMO and YSZ are assumed to be stable under all conditions employed in the calculations. In the end, the stability of LMO and YSZ is discussed.

9.6.1 Chemical potential

Chemical potentials are often used in local equilibrium considerations. A short introduction to the concept of the chemical potential is given below. For more details, the readers are referred to e.g. [33].

The chemical potential is a measure of the change of the Gibbs energy on introducing a component into a phase. For a binary solution with two components A and B, the chemical potential of the component A in the $\alpha$ phase is given by

$$\mu(\alpha, A) = \frac{\partial G'}{\partial n(\alpha, A)}$$  \hspace{1cm} Eq. 9.3

where $G'$ is the Gibbs energy of the $\alpha$ phase and $n(\alpha, A)$ is the mole number of the component A in the $\alpha$ phase. The chemical potential has a unit of J/mol. The molar Gibbs energy of the $\alpha$ phase can then be written as

$$G_m(\alpha) = x(\alpha, A)\mu(\alpha, A) + x(\alpha, B)\mu(\alpha, B)$$  \hspace{1cm} Eq. 9.4

where $x(\alpha, A)$ is the mole fraction of the component A in the $\alpha$ phase.
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For a solution phase, the chemical potential is a function of temperature and composition. For a phase $\gamma$ of the pure element A, the chemical potential $\mu(\gamma, A)$ is a function of temperature only and is equal to the molar Gibbs energy of the $\gamma$ phase:

$$\mu(\gamma, A) = G_m(\gamma, A)$$  \hspace{1cm} \text{Eq. 9.5}

For a stoichiometric compound AB, we cannot really define the individual chemical potentials of A and B, as Eq. 9.3 is not applicable in this case. Eq. 9.4 is however still applicable and can be written as:

$$G_m(AB) = \mu(AB, A) + \mu(AB, B)$$  \hspace{1cm} \text{Eq. 9.6}

The molar Gibbs energy of AB is a function of temperature only. We can hence assume that at a fixed temperature, $\mu(AB, A)$ and $\mu(AB, B)$ are both variable, but the sum of $\mu(AB, A)$ and $\mu(AB, B)$ remains constant and is equal to the molar Gibbs energy of AB. As for the Gibbs energy, a reference state also has to be chosen for the chemical potential. In the present work, we choose SER as the reference state for all metal elements. For oxygen, the reference state is oxygen gas (O$_2$) at a fixed oxygen partial pressure (often 21278 Pa, i.e. air). The chemical potential of oxygen $\mu(O)$ is then set to zero in the calculations.

Now we assume that there is another phase $\beta$ also with two components A and B. The condition for the two phases $\alpha$ and $\beta$ to be in equilibrium can be expressed as:

$$\mu(\alpha, A) = \mu(\beta, A)$$  \hspace{1cm} \text{Eq. 9.7}

$$\mu(\alpha, B) = \mu(\beta, B)$$  \hspace{1cm} \text{Eq. 9.8}

In a global equilibrium, the chemical potential of each component is identical at the phase interface and also inside each phase of the system, i.e. everywhere inside the system. When there is a difference in chemical potential between these two phases, e.g. $\mu(\alpha, A) > \mu(\beta, A)$, there will be a tendency for the component A to move from high chemical potential (the $\alpha$ phase) to low chemical potential (the $\beta$ phase). If a chemical potential gradient exists inside one phase, the component also tends to move inside this phase from high chemical potential to low chemical potential. The movement (diffusion) stops when the chemical potential of each component is identical everywhere.

For a local equilibrium consideration, the equilibrium conditions (Eqs. 9.7 and 9.8) are required only at the phase interface between $\alpha$ and $\beta$. The chemical potentials may still vary inside each phase, causing the components to move towards or away from the phase interface.
9.6.2 Diffusion from LaMnO$_3$ into YSZ

In our description of the La–Mn–Y–Zr–O system, we include the LaO$_{1.5}$ and MnO$_x$ solubilities in the c-ZrO$_2$ phase but neglect any YO$_{1.5}$ or ZrO$_2$ solubility in the LMO phase. In this section we discuss the diffusion of La and/or Mn from LMO into YSZ. Local equilibrium at the LMO–YSZ phase interface is considered. We are mainly concerned with the diffusion across the phase interface from LMO into YSZ, but the influence of the diffusion inside LMO and YSZ is also discussed.

We start with the Mn diffusion. We calculate the chemical potentials of Mn in YSZ and in LMO. The results are shown in Figure 9.6. The solid line represents the relation between $\mu$(YSZ, Mn) (the left axis) versus the Mn concentration in YSZ (the bottom axis), while the dashed line represents the relation between $\mu$(LMO, Mn) (the right axis) versus the La stoichiometry in LMO (the top axis). The driving force of the Mn diffusion across the LMO–YSZ phase interface is given by

\[
\text{Driving force} = \mu(\text{LMO}, \text{Mn}) - \mu(\text{YSZ}, \text{Mn}) \quad \text{Eq. 9.9}
\]

When the driving force is positive, Mn diffuses from LMO into YSZ. The maximum driving force of the Mn diffusion is the one before any Mn diffusion takes place, i.e. when there is no Mn in YSZ. This driving force is infinite, since the chemical potential of Mn in YSZ then is infinitely negative.

As indicated in Figure 9.6, the driving force of the Mn diffusion decreases as the diffusion proceeds and becomes zero when $\mu(\text{LMO}, \text{Mn}) = \mu(\text{YSZ}, \text{Mn})$. An identical $\mu(\text{Mn})$ is obtained at the LMO–YSZ phase interface (Point A in Figure 9.6). Theoretically the position of Point A is determined by the cation stoichiometries of LMO and YSZ, the mole ratio between LMO and YSZ, temperature and oxygen partial pressure, and the diffusion rates of Mn inside LMO and YSZ. In an ideal case, we may assume that the diffusion rates of Mn inside LMO and YSZ are similar. In this case, local equilibrium may be close to Point A and the MnO$_x$ concentration in YSZ close to the phase interface (Point A) may be very close to the one shown in Figure 9.5b (the dashed curve). If the Mn diffusion is fast in LMO and slow in YSZ, Point A will move towards high MnO$_x$ concentration. In the opposite case, Point A will move towards low MnO$_x$ concentration. In reality, the Mn diffusion rate is influenced by both microstructure and temperature. In YSZ Mn diffuses through both grains and grain boundaries;
while in LMO it also diffuses over surfaces and through the vapor phase. The Mn diffusion at the LMO–YSZ interface in the SOFC is more complicated than what we calculate in this paper. Our calculations give a qualitative explanation of the experimentally observed Mn diffusion. To quantify it, the Mn diffusion both inside LMO and YSZ and across the phase interface has to be included. The discussion above can also be applied to the La diffusion, though probably less important than the Mn diffusion.

![Graph showing calculated chemical potential of Mn in 8YSZ and LaMnO$_3$ at 1273 K in air from the present work. For pure YSZ, $\mu$(YSZ, Mn) is minus infinity. A possible local equilibrium is indicated by Point A.]

9.6.3 Formation of La$_2$Zr$_2$O$_7$

In this section, we discuss the driving force of the LZO formation. We assume identical oxygen potential across the interface region. The Gibbs energy change of forming LZO at the LMO–YSZ phase interface is given by

$$\Delta G = [\mu(LZO, La) + \mu(LZO, Zr)] - [\mu(LMO, La) + \mu(YSZ, Zr)]$$

Eq. 9.10

The driving force of the LZO formation is then defined as

$$\text{Driving force} = -\Delta G = [\mu(LMO, La) + \mu(YSZ, Zr)] - [\mu(LZO, La) + \mu(LZO, Zr)]$$

Eq. 9.11
When the driving force in Eq. 9.11 is calculated to be above zero, formation of LZO at the LMO–YSZ phase interface is thermodynamically favorable.

In this work, \( \mu(\text{LZO}, \text{La}) + \mu(\text{LZO}, \text{Zr}) \) is calculated at a La:Zr ratio of 1:1. \( \mu(\text{LMO}, \text{La}) \) and \( \mu(\text{YSZ}, \text{Zr}) \) are calculated at indicated cation stoichiometries. In the following text, various factors influencing the driving force of the LZO formation are discussed in detail. Most of the calculations are done at 1273 K in air. The effects of temperature and oxygen partial pressure are discussed in Section 9.6.3.3. In Sections 9.6.3.1–4, we assume that no diffusion takes place. In Section 9.6.3.5, the La and/or Mn diffusion from LMO into YSZ is included and its influence on the LZO formation is discussed.

9.6.3.1 Cation stoichiometry in \( \text{LaMnO}_3 \)

In this section, we discuss the effect of the cation stoichiometry in LMO on the driving force of the LZO formation. The calculations are conducted at \( T = 1273 \) K in air. Figure 9.7 shows the calculated chemical potential of La against the cation stoichiometry in LMO (\( x \) in \( \text{La}_{1-x}\text{Mn}_x\text{O}_3 \), \( x \) can be both positive and negative) and the corresponding driving force of the LZO formation (from LMO and 8YSZ). By increasing the La deficiency, \( \mu(\text{LMO}, \text{La}) \) decreases, leading to a decrease in the driving force of the LZO formation. The driving force reaches 0 for \( \text{La}_{0.89}\text{Mn}_{0.11}\text{O}_3 \).

9.6.3.2 Yttria content in YSZ

Figure 9.8 shows the calculated chemical potential of Zr versus the yttria content in YSZ at 1273 K in air. Increasing the yttria content decreases \( \mu(\text{YSZ}, \text{Zr}) \). The driving force of the LZO formation (from YSZ and \( \text{La}_x\text{Mn}_{1-x}\text{O}_3 \)) hence decreases and it reaches zero at \( x(\text{YSZ}, \text{YO}_{1.5}) = 0.54 \). Concerning the effect in decreasing the driving force, it is clear that increasing the yttria content in YSZ is less effective than increasing the La deficiency in LMO.
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Figure 9.7 Calculated chemical potential of La in LaMnO$_3$ (the dashed line) and the corresponding driving force of the La$_2$Zr$_2$O$_7$ formation from LaMnO$_3$ and 8YSZ (the solid line) at 1273 K in air from the present work.

Figure 9.8 Calculated chemical potential of Zr in YSZ (the dashed line) and the corresponding driving force of the La$_2$Zr$_2$O$_7$ formation from La$_1$Mn$_1$O$_3$ and YSZ (the solid line) at 1273 K in air from the present work.
9.6.3.3 Temperature and oxygen partial pressure

We calculate the driving force of the LZO formation from 8YSZ and La\(_{1-x}\)Mn\(_x\)O\(_3\) (\(x = 0.1, 0, -0.1\)) at different temperatures and oxygen partial pressures. The results are shown in Figure 9.9.

The cation stoichiometry in LMO influences not only the driving force itself, but also the relations between the driving force and the temperature or the oxygen partial pressure. In the case of A-site deficient LMO (La\(_{0.9}\)Mn\(_{1}\)O\(_3\)), the driving force decreases with either increasing temperature or decreasing oxygen partial pressure, both slightly. At 1273 K in air, the driving force is close to 0. For La\(_{1}\)Mn\(_1\)O\(_3\), it is opposite. The driving force decreases with either decreasing temperature or increasing oxygen partial pressure. For La\(_{1.1}\)Mn\(_1\)O\(_3\), the driving force also decreases with either decreasing temperature or increasing oxygen partial pressure, but more strongly. The difference in the relations between the driving force and the temperature or the oxygen partial is due to antisite-site defects and various valence states of Mn\(^{\text{iv}}\) in LMO [34]. For the SOFC applications, normally the A-site deficient or the stoichiometric perovskite is used as cathode.

9.6.3.4 Sr substitution

Substituting La in LMO with Sr decreases the chemical potential of La and hence also the driving force of the LZO formation. Based on the thermodynamic description of the La–Sr–Mn–O system [35], we calculate the chemical potential of La in LSM and the driving force of the LZO formation from LSM and 8YSZ at 1273 K in air (Figure 9.10). For (La\(_{0.9}\)Sr\(_{0.1}\))Mn\(_1\)O\(_3\) and (La\(_{0.1}\)Sr\(_{0.9}\))Mn\(_1\)O\(_3\), both \(\mu\) (LSM, La) and the driving force decrease with increasing Sr concentration in LSM. For (La\(_{0.1}\)Sr\(_{0.9}\))Mn\(_1\)O\(_3\), \(\mu\) (LSM, La) and the driving force decrease with increasing Sr concentration in LSM at \(y < 0.1\) (\(y\) in (La\(_{1-y}\)Sr\(_y\))\(_{1+x}\)Mn\(_2\)O\(_5\)) and start to increase at \(y > 0.1\). The increase of \(\mu\) (LSM, La) is due to a miscibility gap in (La\(_{0.1}\)Sr\(_{0.9}\))Mn\(_1\)O\(_3\) at high Sr concentration (for detail, see [35]). It should be note that both (La\(_{0.9}\)Sr\(_{0.1}\))Mn\(_1\)O\(_3\) and (La\(_{0.1}\)Sr\(_{0.1}\))Mn\(_1\)O\(_3\) are metastable under these conditions.
Figure 9.9 Calculated driving force of the La$_2$Zr$_2$O$_7$ formation from LaMnO$_3$ and 8YSZ from the present work (a) at different temperatures in air and (b) at 1273 K with different oxygen partial pressures.
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(a)

![Graph](image1)

(b)

![Graph](image2)

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We calculate the driving force of the LZO formation from La$_{0.85}$Sr$_{0.15}$O$_3$ and (YO$_{1.5}$)$_{0.17}$(ZrO$_2$)$_{0.83}$ at 1373 K in air. The calculated driving forces are 67.2, 42.7, 6.6, -7.3 kJ/mol for $y = 0.95$, 0.98, 1.02, 1.10 respectively. According to our calculations, at 1373 K in air, it is thermodynamically favorable to form LZO at the LSM–YSZ interface for $y \leq 1.02$. This is exactly what Mitterdorfer and Gauckler reported [1]. They examined the LSM–YSZ interface by HRTEM and AFM after the samples were annealed at 1373 K up to 12 h. The experimental conditions are close to those employed in our local equilibrium considerations.

9.6.3.5 Diffusion from LaMnO$_3$ into YSZ

In this section, we discuss how the diffusion from LMO into YSZ influences the LZO formation at the LMO–YSZ phase interface. As in general Mn diffuses to a larger extent from LMO into YSZ than La, we hence consider only the Mn diffusion.
The Mn diffusion from LMO into YSZ changes both $\mu$(LMO, La) and $\mu$(YSZ, Zr) at the LMO–YSZ interface. With the proceeding of the Mn diffusion, $\mu$(LMO, La) increases while $\mu$(YSZ, Zr) decreases. But the decrease of $\mu$(YSZ, Zr) is much less compared to the increase of $\mu$(LMO, La). The driving force of the LZO formation therefore increases. For LMO with large La deficiency, e.g. $\text{La}_0.85\text{Mn}_0.3$, the driving force of the LZO formation at the $\text{La}_0.85\text{Mn}_0.3$–YSZ interface is calculated to be negative when no Mn diffuses from LMO into YSZ. The driving force increases with the proceeding of the Mn diffusion and reaches zero after certain time. Formation of LZO at the interface is then thermodynamically favorable. By neglecting the LZO nucleation kinetics, we define the induction period of the LZO formation as the period for the driving force of the LZO formation (from a negative value) to be above certain limit ($\geq 0$). To simplify the discussion, we put the limit at zero in this work. Without actual diffusion data, it is however not possible to quantify how the driving force of the LZO formation at the interface will change with time and how long the induction period is. The experimentally measured induction period should also include the period for the LZO nucleation. It is clear that increasing the La deficiency in LMO or the yttria content in YSZ decreases the driving force and therefore increases the induction period of the LZO formation. Temperature influences both the driving force itself and the diffusion rate. At low temperature, the diffusion becomes much slower. A longer induction period is needed for enough diffusion to take place.

9.6.4 Equilibrium phase assemblage at the LaMnO$_3$–YSZ phase interface

In the local equilibrium considerations, we assume that single-phase LMO and YSZ are stable under all the conditions employed in the calculations. According to the equilibrium phase diagrams, under certain conditions LMO and YSZ are metastable and in principle a transformation should happen. Here we include the equilibrium phase assemblage into our local equilibrium considerations to see how the LZO formation is influenced. The discussions are limited to 1273 K in air.

According to the equilibrium phase diagram of LaO$_{1.5}$–MnO$_x$ [34], at 1273 K in air, the composition range of the LMO single-phase region is between $\text{La}_0.94\text{Mn}_1\text{O}_3$ and $\text{La}_{1.14}\text{Mn}_1\text{O}_3$. Outside this range, either $\alpha$-$\text{Mn}_3\text{O}_4$ or A-$\text{La}_2\text{O}_3$ is stable. By including the equilibrium phase assemblage, we plot Figure 9.7 again as Figure 9.11. The difference only appears in the two-
phase regions. In an equilibrium state, on increasing La deficiency in LMO, the driving force of the LZO formation decreases continuously in the single-phase region and remains constant in the two-phase regions. In the $\alpha$-Mn$_3$O$_4$+LMO two-phase region, the driving force is still positive. Then the question is: Should we consider only the equilibrium phase assemblage and exclude the metastable one? The answer is obviously “no”. To reflect the reality at the LMO–YSZ interface, the phase metastability has to be considered. According to Figures 9.7 and 9.11, a single phase of La$_{0.88}$MnO$_3$ is metastable. As its composition is not far away from the stability region of single-phase LMO, it can be obtained experimentally without too much difficulty. When it is in contact with YSZ, the driving force of the LZO formation is negative in the very beginning. The LZO formation is then dependent on the following two processes: the transformation of La$_{0.88}$MnO$_3$ into a mixture of La$_{0.946}$MnO$_3$+$\alpha$-Mn$_3$O$_4$ and the Mn diffusion from LMO into YSZ. These two processes are both controlled by kinetics. If the transformation or the diffusion is retarded or kinetically blocked, the LZO formation can then be retarded or kinetically prevented.

The same discussion can be applied to YSZ. According to the equilibrium phase diagram of the ZrO$_2$–YO$_{1.5}$ system [36], the stability region of single-phase YSZ is quite wide and is within $0.156 < x$(YSZ, YO$_{1.5}$) $< 0.417$ at 1273 K in air. By including the equilibrium phase relation, we plot Figure 9.8 again as Figure 9.12. According to the equilibrium phase relation, 8YSZ should transform into a mixture of $\alpha$–ZrO$_2$ and (YO$_{1.5}$)$_{0.156}$(ZrO$_2$)$_{0.844}$. But the transformation rate is very slow. 8YSZ is well known for its high stability and has been widely used as the electrolyte for SOFCs and oxygen sensors. YSZ with more than 41.7 cat.% YO$_{1.5}$ should transform into a mixture of (YO$_{1.5}$)$_{0.147}$(ZrO$_2$)$_{0.583}$ and Zr$_3$Y$_4$O$_{12}$ at 1273 K in air. In reality, the formation of Zr$_3$Y$_4$O$_{12}$ is found to be very sluggish. It would not be too difficult to obtain single-phase (YO$_{1.5}$)$_{0.54}$(ZrO$_2$)$_{0.46}$. Using (YO$_{1.5}$)$_{0.54}$(ZrO$_2$)$_{0.46}$ as the electrolyte in the SOFC is however impractical, though the corresponding driving force of the LZO formation is zero. One reason is that the oxygen ion conductivity of YSZ has a maximum at 15–20 mol% YO$_{1.5}$. The mechanical compatibility between YSZ and LSM also has to be considered.
Figure 9.11  Calculated stable chemical potential of La in LaMnO₃ (the dashed line) and the corresponding driving force of the La₂Zr₂O₇ formation from LaMnO₃ and 8YSZ (the solid line) at 1273 K in air from the present work.

Figure 9.12  Calculated stable chemical potential of Zr in YSZ (the dashed line) and the corresponding driving force of the La₂Zr₂O₇ formation from La₁Mn₁O₃ and YSZ (the solid line) at 1273 K in air from the present work.
9.6.5 Retarding the $\text{La}_2\text{Zr}_2\text{O}_7$ formation at the LaMnO$_3$–YSZ phase interface

In the previous sections (9.6.3 and 9.6.4), we have discussed the influences of different factors on the driving force of the LZO formation. By combining these factors, it is possible to reach a condition that the driving force is negative, i.e. the LMO–YSZ phase interface is actually stable, at least as long as diffusion is not considered. Sr doping further decreases the driving force of the LZO formation and stabilizes the LSM–YSZ phase interface.

Unfortunately the Mn diffusion from LMO into YSZ will change this unfavorably. With the proceeding of the Mn diffusion, the driving force of the LZO formation at the LMO–YSZ interface increases, leading to LZO formation in a long time run. By retarding the Mn diffusion, it is possible to deaccelerate the increase in the driving force of the LZO formation and to stabilize the LMO–YSZ phase interface for an enough long period. Thermodynamically, the Mn diffusion can be retarded by decreasing its driving force. As Eq. 9.9 shows, the driving force of the Mn diffusion from LMO into YSZ can be decreased by decreasing the chemical potential of Mn in LMO, $\mu(\text{LMO}, \text{Mn})$ or increasing that in YSZ, $\mu(\text{YSZ}, \text{Mn})$. It is not worthwhile to decrease $\mu(\text{LMO}, \text{Mn})$, as very often a decrease in $\mu(\text{LMO}, \text{Mn})$ means an increase in $\mu(\text{LMO}, \text{La})$ and therefore also an increase in the driving force of the LZO formation. An increase in $\mu(\text{YSZ}, \text{Mn})$ has no essential influence on the driving force of the LZO formation and this can be easily achieved by doping Mn oxide into YSZ. Mn oxide can also be introduced into LMO. The Mn oxide then serves as a Mn reservoir for the neighboring LMO phase. As long as LMO is in equilibrium with the Mn oxide, the Mn diffusion from LMO into YSZ will not change the driving force of the LZO formation. The Mn diffusion can also be retarded by adjusting the Mn diffusion rates in LMO and in YSZ. This is however very difficult and obviously less feasible. To totally stop the Mn diffusion, a thin layer of conducting diffusion barrier has to be put between LMO and YSZ. The above discussions outline the measures to retard the LZO formation at the LMO–YSZ interface. For real SOFC applications, the electrical properties, the chemical and mechanical compatibilities of LMO and YSZ also have to be considered.
9.7 Conclusions

a. The thermodynamic origin of the LZO formation is due to the high stability of the LZO phase. Thermodynamically, increasing the La deficiency in LMO by itself cannot prevent the LZO formation.

b. The driving force of the La\(_2\)Zr\(_2\)O\(_7\) formation is determined essentially by the chemical potential of La in LaMnO\(_3\), \(\mu(\text{LaMnO}_3, \text{La})\) and that of Zr in YSZ, \(\mu(\text{YSZ}, \text{Zr})\). The driving force is influenced by the cation stoichiometries in LaMnO\(_3\) and YSZ, temperature and oxygen partial pressure, of which the cation stoichiometry in LaMnO\(_3\) is the most important. The La/Mn diffusion changes \(\mu(\text{LMO}, \text{La})\) and \(\mu(\text{YSZ}, \text{Zr})\) and hence also the driving force of the LZO formation.

c. By neglecting the LZO nucleation kinetics, we define the induction period of the LZO formation as the period for the driving force of the LZO formation to be above zero. The prerequisite for the LZO formation is a positive driving force at the interface. Forming La\(_2\)O\(_3\) at the interface is not necessary.

d. The yttria content in YSZ influences the chemical potential of Zr. With increasing yttria content, the driving force of the LZO formation decreases and the induction period increases.

e. The La and/or Mn diffusion from LMO into YSZ is influenced by cation stoichiometries of LMO and YSZ, temperature and oxygen partial pressure.

f. By properly adjusting the compositions of LMO and YSZ, it is possible to retard the LZO formation and to stabilize the LMO–YSZ interface for long time.

9.8 References

[1] A. Mitterdorfer and L. J. Gauckler, "La\(_2\)Zr\(_2\)O\(_7\) formation and oxygen reduction kinetics of the La\(_{0.85}\)Sr\(_{0.15}\)Mn\(_3\)O\(_8\), \(\text{O}_2(\text{g})\)/YSZ system", Solid State Ionics 111 (1998), p. 185.


Thermodynamics at the LaMnO$_3$–YSZ Interface


[10] M. Mori, N. Sakai, T. Kawada, H. Yokokawa, and M. Dokiya, "A new cathode material (La$_x$Sr$_{1-x}$)$_3$(Mn$_{1-y}$Cr$_y$)O$_3$ (0<y<0.2) for SOFC", Denki Kagaku 58 (1990), p. 528.


[22] H. Kaneko, H. Taimatsu, K. Wada, and E. Iwamoto, "Reaction of La$_{1-x}$Ca$_x$MnO$_3$ cathode with YSZ and its influence of the electrode characteristics", in Proceedings of
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Conclusions and Outlook

In this work a consistent thermodynamic description of the La–Mn–Y–Zr–O system is obtained by applying the CALPHAD method. It is shown that the CALPHAD method and the models used in this work (the compound energy model for solid solution phases and the two-sublattice model for ionic liquids for the liquid phase) are well suited to describe highly complex phases and heterogeneous phase equilibria. The current description reproduces both the thermodynamic data and the phase diagram data with high satisfaction. Ideal extrapolations from ternaries to quaternaries and to La–Mn–Y–Zr–O are proven to be quite successful. Numerous phase diagrams, many of which are presented for the first time, give invaluable insight for materials’ processing and use. The database is a very powerful tool which can be used to calculate thermodynamic properties and phase relations for any combination of temperature, oxygen partial pressure, composition and phase assemblage, regardless if the condition is stable or metastable.

The most significant result of this work concerns the LaMnO$_3$–YSZ interface reactions. We conclude that at the LaMnO$_3$–YSZ interface the La$_2$Zr$_2$O$_7$ phase forms due to its high stability. Thermodynamically, increasing the La deficiency in LaMnO$_3$ cannot prevent the La$_2$Zr$_2$O$_7$ formation. We clarify both the thermodynamic and the kinetic factors influencing the La$_2$Zr$_2$O$_7$ formation. The driving force of the La$_2$Zr$_2$O$_7$ formation is determined essentially by the chemical potential of La in LaMnO$_3$, $\mu$(LaMnO$_3$, La) and that of Zr in YSZ, $\mu$(YSZ, Zr). The driving force is influenced by the cation stoichiometries in LaMnO$_3$ and YSZ, temperature and oxygen partial pressure, of which the cation stoichiometry in LaMnO$_3$ is the most important. The La/Mn diffusion changes the chemical potentials $\mu$(LaMnO$_3$, La) and $\mu$(YSZ, Zr) and hence also the driving force of the La$_2$Zr$_2$O$_7$ formation. By neglecting the La$_2$Zr$_2$O$_7$ nucleation kinetics, we define the induction period of the La$_2$Zr$_2$O$_7$ formation as the period for the driving force of the La$_2$Zr$_2$O$_7$ formation from a negative value to be above zero. The prerequisite for the La$_2$Zr$_2$O$_7$ formation is a positive driving force instead of forming free La$_2$O$_3$ at the interface. Increasing the La deficiency in LaMnO$_3$ or the yttria content in YSZ decreases the driving force. In certain cases, the La$_2$Zr$_2$O$_7$ formation can be kinetically hindered. The La/Mn diffusion from LaMnO$_3$ into YSZ is influenced by the cation stoichiometries of LaMnO$_3$ and YSZ, the LaMnO$_3$:YSZ ratio, the temperature and oxygen partial pressure, and the diffusion inside LaMnO$_3$ and YSZ. Increasing the La deficiency in
LaMnO$_3$ decreases the driving force of the La diffusion but increases that of the Mn diffusion. These calculations clarify the discrepancies between different experimental observations.

This work offers a better and thorough understanding of the thermodynamics at the LaMnO$_3$–YSZ interface serving as a prototype of the LSM–YSZ interface. The next step is to include Sr. Two ternary systems (Sr–Zr–O and Sr–Y–O) have to be assessed. This will lead to a thermodynamic description of the La–Mn–Sr–Y–Zr–O system, not a complete one, but sufficient for SOFC applications. This description can then account for the thermodynamics at the LSM–YSZ interface in SOFCs.

The current description of the La–Mn–Y–Zr–O system is till now the best available. Further experimental efforts may improve the current description. Due to the limited experimental data, the thermodynamic properties of a few phases in the La–Mn–Y–Zr–O system are still based on estimations and lack verifications. Also experimental investigations on the phase relations in the higher order sub-systems (quaternaries and above) are extremely scarce. Uncertainties, which have been pointed out in each assessment, were hence introduced into the current description. The corresponding experimental investigations are therefore highly desirable.

To quantitatively represent the LSM–YSZ interface reactions in the SOFC, apart from the thermodynamic description of the La–Mn–Sr–Y–Zr–O system, a few things still have to be included. Of particular importance is the diffusion kinetics, which concerns the diffusion inside LSM and YSZ and across the interface. In this work, the influence of the La and/or Mn diffusion from LaMnO$_3$ into YSZ on the La$_2$Zr$_2$O$_7$ formation was discussed only in a semi-quantitative way. By including both, the diffusion kinetics and the La$_2$Zr$_2$O$_7$ nucleation kinetics, the La$_2$Zr$_2$O$_7$ formation at the LSM–YSZ interface can be quantitatively represented. To model the growth of La$_2$Zr$_2$O$_7$, local equilibria at the LaMnO$_3$–La$_2$Zr$_2$O$_7$ and the YSZ–La$_2$Zr$_2$O$_7$ phase boundaries and the diffusion inside the La$_2$Zr$_2$O$_7$ phase also needs to be included. To reflect the real condition in the SOFC, the influence of the electrical field has also to be considered. In the end this will lead to a complete modeling of the LSM–YSZ interface reactions in the SOFC. The basis for this is obviously a consistent thermodynamic description of the La–Mn–Sr–Y–Zr–O system.
Description of La–Mn–Y–Zr–O

$ La-Mn-Y-Zr-O database, created by Ming Chen 20041216, revised 20050423.
$ Changed model for La2O3 by Ming Chen 20040622 (see Chapter 5).
$ Changed model for Mn2O3 by Ming Chen 20040119 (see Chapter 3).
$ Changed high temperature stable Y2O3 from fluorite to hexagonal
$ by Bengt Hallstedt October 2004.
$ Revised by Bengt Hallstedt October 2004 and by Ming Chen 20050422.
$ Changed L(Mn3+,La3+:02-) and L(Mn3+,La3+:VA) for the liquid phase
$ by Nicholas Grundy 20040624, and again 20050128.
$ La-Y-O from Ming Chen December 2004
$ La-Zr-O from Ming Chen December 2004
$ TEMP-LIM 298.15 6000.00 !
$SELEMENT NAMEREF. STATE ATOMICMASS HO S0 !
ELEMENT /- ELECTRON_GAS 0.0000E+00 0.0000 0.0000 !
ELEMENT VA VACUUM 0.0000E+00 0.0000 0.0000 !
ELEMENT LA DOUBLE_HCP(ABAC) 1.3891E+02 6665.112 56.9024 !
ELEMENT MN CBCC_A12 54.938 4996 32.008 !
ELEMENT Y HCP_A3 8.8906E+01 5.9664E+03 44.434 !
ELEMENT ZR HCP_A3 9.1224E+01 5.5663E+03 39.181 !
ELEMENT O 1/2_MOLE_O2(G) 1.5999E+01 4.3410E+03 102.52 !
$ SPECIE LA+2 LA/+2 !
SPECIE LA+3 LA/+3 !
SPECIE LAO1 LAO1 !
SPECIE LAO2 LAO2 !
SPECIE LAO15 LAO1.5 !
SPECIE LA2O1 LA2O1 !
SPECIE LA2O2 LA2O2 !
SPECIE LA2O3 LA2O3 !
SPECIE MN+2 MN/+2 !
SPECIE MN+3 MN/+3 !
SPECIE MN+4 MN/+4 !
SPECIE MNO MNO !
SPECIE MNO2 MNO2 !
SPECIE MNO3 MNO3 !

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SPECIE MN3O4        MN3O4  !
SPECIE O-2          O/-2  !
SPECIE O2           O2   !
SPECIE O3           O3   !
SPECIE Y+3          Y/+3  !
SPECIE Y2O          O1Y2  !
SPECIE YO           O1Y1  !
SPECIE Y2O2         O2Y2  !
SPECIE YO2          O2Y1  !
SPECIE YO15         O15Y1  !
SPECIE Y2O3         O3Y2  !
SPECIE ZR+4         ZR1/+4  !
SPECIE ZR2         ZR2  !
SPECIE ZRO         O1ZR1  !
SPECIE ZRO2        O2ZR1  !
SPECIE LA2ZR2O7     LA207ZR2  !
SPECIE Y2ZR2O7      07Y2ZR2  !

$ DEFAULT-COM DEFINE_SYSTEM_ELEMENT VA /- !
TYPE-DEF Z SEQ * !
TYPE-DEF L GES AMEND_PHASE_DESCRIPTION IONIC_LIQ COMP_SET ., MN+2 : VA : !
TYPE_DEF B GES AMEND_PHASE_DESCRIPTION @ MAGNETIC -1 0.4 !
TYPE_DEF A GES AMEND_PHASE_DESCRIPTION @ MAGNETIC -3 0.28 !

PHASE IONIC_LIQUID: Y ZL 2 1 1 !
CONST IONIC_LIQUID: Y : LA+3 MN+2 MN+3 Y+3 ZR+4 : O-2 VA : !
PAR G(ION,LA+3,VA) 298.15 +GLALIQ; 3200 N !
PAR G(ION,LA+3,O-2) 298.15 +GLA2O3L IQ; 6000 N !
PAR G(ION,MN+2,VA) 298.15 +GMNLIQ; 3000 N !
PAR G(ION,MN+2,O-2) 298.15 +2*GL11; 3000 N !
PAR G(ION,MN+3,VA) 298.15 +2*GMNLIQ+GL23-3*GL11; 3000 N !
PAR G(ION,MN+3,O-2) 298.15 +GL23; 6000 N !
PAR G(ION,Y+3,VA) 298.15 +GYYLIQ; 6000 N !
PAR G(ION,Y+3,O-2) 298.15 +2*GYYLIQ+3*GHSEROO-1824330+245.9*T; 6000 N !
PAR G(ION,ZR+4,VA) 298.15 +GZRLI Q; 6000 N !
PAR G(ION,ZR+4,O-2) 298.15 +2*GZRO2LIQ; 6000 N !
PAR L(ION,MN+2,O-2,VA;0) 298.15 +129519; 6000 N !
PAR L(ION,MN+2,O-2,VA;1) 298.15 -45459; 6000 N !
PAR L(ION,MN+2,MN+3,O-2;0) 298.15 -33859; 6000 N !
PAR L(ION,Y+3,O-2,VA;0) 298.15 +6900; 6000 N !
PAR L(ION,Y+3,O-2,VA;1) 298.15 -17000; 6000 N !
PAR L(ION,ZR+4,O-2,VA;0) 298.15 -26500; 6000 N !
PAR L(ION,ZR+4,O-2,VA;1) 298.15 +50000; 6000 N !
PAR L(ION,ZR+4,O-2,VA;2) 298.15 +72000; 6000 N !
PAR L(ION,LA+3,MN+2,O-2;0) 298.15 -119062; 6000 N !
PAR L(ION,LA+3,MN+3,O-2;0) 298.15 -119062; 6000 N !
PAR L(ION,LA+3,ZR+4,O-2;0) 298.15 -212088; 6000 N !
PAR $L(ION,MN+2,Y+3;VA;0)$ 298.15 -26874.14+2.38277*T; 6000 N
PAR $L(ION,MN+2,Y+3;VA;1)$ 298.15 -12579.78; 6000 N
PAR $L(ION,MN+2,ZR+4;VA;0)$ 298.15 -45851.78+5.21718*T; 6000 N
PAR $L(ION,MN+2,ZR+4;VA;1)$ 298.15 -10658.06+9.26869*T; 6000 N
PAR $L(ION,MN+2,ZR+4;VA;2)$ 298.15 -11253.58; 6000 N
PAR $L(ION,MN+2,ZR+4;O-2;0)$ 298.15 -12579.78; 6000 N
PAR $L(ION,Y+3,ZR+4;VA;0)$ 298.15 +24000; 6000 N
PAR $L(ION,Y+3,ZR+4;VA;1)$ 298.15 +3000; 6000 N
PAR $L(ION,Y+3,ZR+4;VA;2)$ 298.15 -3000; 6000 N
$\$

PHASE LIQUID Z 1 1 1
CONST LIQUID : LA MN Y ZR : !
PAR $G(LIQUID,LA)$ 298.15 +GLALIQ; 3200 N
PAR $G(LIQUID,MN)$ 298.15 +GMNLIQ; 3000 N
PAR $G(LIQUID,Y)$ 298.15 +GYYLIQ; 6000 N
PAR $G(LIQUID,ZR)$ 298.15 +GZRLIQ; 6000 N
PAR $L(LIQUID,MN,Y;0)$ 298.15 -26874.14+2.38277*T; 6000 N
PAR $L(LIQUID,MN,Y;1)$ 298.15 -12579.78; 6000 N
PAR $L(LIQUID,MN,ZR;0)$ 298.15 -45851.78+5.21718*T; 6000 N
PAR $L(LIQUID,MN,ZR;1)$ 298.15 -10658.06+9.26869*T; 6000 N
PAR $L(LIQUID,MN,ZR;2)$ 298.15 -11253.58; 6000 N
PAR $L(LIQUID,Y,ZR;0)$ 298.15 +24000; 6000 N
PAR $L(LIQUID,Y,ZR;1)$ 298.15 +3000; 6000 N
$\$

PHASE DHCP Z 2 1 0.5
CONST DHCP : LA : VA% O : !
PAR $G(DHCP,LA:VA)$ 298.15 +GHSERLA; 3200 N
PAR $G(DHCP,LA:O)$ 298.15 +GHSERLA+0.5*GHSEROO-285000+42.4*T; 3200 N
$\$

PHASE HCP_A3 Z 2 1 0.5
CONST HCP_A3 : MN Y% ZR% : VA% O : !
PAR $G(HCP_A3,MN:VA)$ 298.15 +GMNHCP; 2000 N
PAR $G(HCP_A3,MN:O)$ 298.15 +GMNHCP+0.5*GHSEROO;
PAR $G(HCP_A3,Y:VA)$ 298.15 +GHSERYY; 3700 N
PAR $G(HCP_A3,Y:O)$ 298.15 +GHSERYY+0.5*GHSEROO-303600+37.5*T; 6000 N
PAR $G(HCP_A3,ZR:VA)$ 298.15 +GHSERZR; 6000 N
PAR $G(HCP_A3,ZR:O)$ 298.15 +GHSERZR+0.5*GHSEROO-280800+41*T; 6000 N
PAR $L(HCP_A3,Y:O,VA;0)$ 298.15 +3500; 6000 N
PAR $L(HCP_A3,ZR,O,VA;0)$ 298.15 -29100+15.5*T; 6000 N
PAR $L(HCP_A3,ZR,O,VA;1)$ 298.15 -9150+3*T; 6000 N
PAR $L(HCP_A3,MN,Y,VA;0)$ 298.15 +19000; 6000 N
PAR $L(HCP_A3,MN,ZR,VA;0)$ 298.15 -8123.31; 6000 N
PAR $L(HCP_A3,Y,ZR;VA;0)$ 298.15 +50000; 6000 N

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Appendix

$ PHASE BCC_A2 ZB 2 1 1.5 !
CONST BCC_A2 : LA MN Y ZR : VA% O : !
P A R G(BCC_A2,LA:VA) 298.15 +GLABCC; 3200 N !
P A R G(BCC_A2,LA:O) 298.15 +GLABCC+1.5*GHSEROO-855000+142.5*T; 3200 N !
P A R G(BCC_A2,MN:VA) 298.15 +GMNBCC; 2000 N !
P A R G(BCC,MN:O) 298.15 +GMNBCC+1.5*GHSEROO+50*T; 6000 N !
P A R TC(BCC_A2,MN:VA) 298.15 -580; 2000 N !
P A R BMAGN(BCC_A2,MN:VA) 298.15 -0.27; 2000 N !
P A R G(BCC_A2,Y:VA) 298.15 +GYYBCC; 3700 N !
P A R G(BCC_A2,Y:O) 298.15 +GYYBCC+1.5*GHSEROO-899200+123*T; 6000 N !
P A R G(BCC_A2,ZR:VA) 298.15 +GZRBCC; 6000 N !
P A R G(BCC_A2,ZR:O) 298.15 +GZRBCC+1.5*GHSEROO; 6000 N !
P A R L(BCC_A2,Y,O,VA;0) 298.15 -5000; 3300 N !
P A R L(BCC_A2,ZR,O,VA;0) 298.15 -1102000+155.4*T; 6000 N !
P A R L(BCC_A2,ZR,O,VA;1) 298.15 -235000; 6000 N !
P A R L(BCC_A2,MN,Y:VA;0) 298.15 +25000; 3300 N !
P A R L(BCC_A2,MN,ZR:VA;0) 298.15 +5059.03-0.40472*T; 6000 N !
P A R L(BCC_A2,MN,ZR:VA;1) 298.15 -26984.11+2.15873*T; 6000 N !
P A R L(BCC_A2,Y,ZR:VA;0) 298.15 +40000; 6000 N !
P A R L(BCC_A2,Y,ZR:VA;1) 298.15 -9000; 6000 N !
$ PHASE CBCC_A12 ZA 2 1 1 !
CONST CBCC_A12 : MN : VA : !
P A R G(CBCC_A12,MN:VA) 298.15 +GHSERMN; 2000 N !
P A R TC(CBCC_A12,MN:VA) 298.15 -285; 2000 N !
P A R BMAGN(CBCC_A12,MN:VA) 298.15 -0.66; 2000 N !
$ PHASE FCC_A1 ZA 2 1 1 !
CONST FCC_A1 : LA% MN% ZR : VA% O : !
P A R G(FCC_A1,LA:VA) 298.15 +GLAFCC; 3200 N !
P A R G(FCC_A1,LA:O) 298.15 +GLAFCC+GHSEROO-570000+91.4*T; 3200 N !
P A R G(FCC_A1,LA:O) 298.15 +GMNFCC; 2000 N !
P A R G(FCC_A1,MN:VA) 298.15 +GMNFCC+GHSEROO; 2000 N !
P A R TC(FCC_A1,MN:VA) 298.15 -1620; 2000 N !
P A R BMAGN(FCC_A1,MN:VA) 298.15 -1.86; 2000 N !
P A R G(FCC_A1,ZR:VA) 130.00 +GHSERZR+7600-0.9*T; 6000 N !
P A R G(FCC_A1,ZR:O) 130.00 +GHSERZR+7600-0.9*T+GHSEROO; 6000 N !
P A R L(FCC_A1,MN,ZR:VA;0) 298.15 +5059.03-0.40472*T; 6000 N !
P A R L(FCC_A1,MN,ZR:VA;1) 298.15 -26984.11+2.15873*T; 6000 N !
$ PHASE CUB_A13 Z 2 1 1 !
CONST CUB_A13 : MN : VA : !
P A R G(CUB_A13,MN:VA) 298.15 +GMNCUB; 2000 N !
Description of La–Mn–Y–Zr–O

$\text{PHASE Mn12YZ 2 12 1!}$
$\text{CONST Mn12YZ : MN : Y : !}$
$\text{PAR } G(\text{Mn12YZ},\text{MN}:\text{Y}) \quad 298.15 \ +GMn12YZ; \quad 2000 \ \text{N} \ !$

$\text{PHASE Mn23Y6Z 2 23 6!}$
$\text{CONST Mn23Y6Z : MN : Y : !}$
$\text{PAR } G(\text{Mn23Y6Z},\text{MN}:\text{Y}) \quad 298.15 \ +GMn23Y6; \quad 2000 \ \text{N} \ !$

$\text{PHASE Mn2YZ 2 2 1!}$
$\text{CONST Mn2YZ : MN : Y : !}$
$\text{PAR } G(\text{Mn2YZ},\text{MN}:\text{Y}) \quad 298.15 \ +GMn2Y; \quad 2000 \ \text{N} \ !$

$\text{PHASE Mn2ZrZ 2 2 1!}$
$\text{CONST Mn2ZrZ : MN : ZR% VA : !}$
$\text{PAR } G(\text{Mn2ZrZ},\text{MN}:\text{ZR}) \quad 298.15 \ +2^*\text{GHSERMN}+\text{GHSERZR}-120013.95+36.9305*T; \quad 6000 \ \text{N} \ !$
$\text{PAR } G(\text{Mn2ZrZ},\text{MN}:\text{VA}) \quad 298.15 \ +2^*\text{GHSERMN}+15000; \quad 6000 \ \text{N} \ !$
$\text{PAR } L(\text{Mn2ZrZ},\text{MN:Z},\text{VA};0) \quad 298.15 \ -2029.39+0.16235*T; \quad 6000 \ \text{N} \ !$

$\text{PHASE MnO:1Z 2 1 1!}$
$\text{CONST MnO:1 : MN+2% MN+3 VA : O-2 : !}$
$\text{PAR } G(\text{MnO:1},\text{MN+2:O-2}) \quad 298.15 \ +GMn1O1; \quad 6000 \ \text{N} \ !$
$\text{PAR } G(\text{MnO:1},\text{MN+3:O-2}) \quad 298.15 \ +GMn1O1-21884-22.185*T; \quad 6000 \ \text{N} \ !$
$\text{PAR } G(\text{MnO:1},\text{VA:O-2}) \quad 298.15 \ 0; \quad 6000 \ \text{N} \ !$
$\text{PAR } L(\text{MnO:1},\text{MN+2, MN+3:O-2:0}) \quad 298.15 \ -42105; \quad 6000 \ \text{N} \ !$
$\text{PAR } L(\text{MnO:1},\text{MN+2, MN+3:O-2:1}) \quad 298.15 \ +46513; \quad 6000 \ \text{N} \ !$

$\text{PHASE Mn3O4_ALPHA:1 Z 3 1 2 4!}$
$\text{PAR } G(\text{Mn3O4_ALPHA:1},\text{MN+2:MN+3:O-2}) \quad 298.15 \ +GMn3O4; \quad 6000 \ \text{N} \ !$

$\text{PHASE Mn3O4_BETA:1 Z 3 1 2 4!}$
$\text{CONST Mn3O4_BETA:1 : MN+2 : MN+3 : O-2 : !}$
$\text{PAR } G(\text{Mn3O4_BETA:1},\text{MN+2:MN+3:O-2}) \quad 298.15 \ +GMn3O4B; \quad 6000 \ \text{N} \ !$

$\text{PHASE MnO2:1 Z 2 1 2!}$
$\text{CONST MnO2:1 : MN+4 : O-2 : !}$
$\text{PAR } G(\text{MnO2:1},\text{MN+4:O-2}) \quad 298.15 \ +GMn1O2; \quad 6000 \ \text{N} \ !$

$\text{PHASE La2O3_A:1 Z 3 2 3 1!}$
$\text{CONST La2O3_A:1 : La LA+3% Y+3 ZR+4 : O-2% VA : O-2 VA% : !}$
$\text{PAR } G(\text{La2O3_A:1},\text{LA:VA:VA}) \quad 298.15 \ +2^*\text{GHSERLA}+204124; \quad 6000 \ \text{N} \ !$
$\text{PAR } G(\text{La2O3_A:1},\text{LA:O-2:O-2}) \quad 298.15 \ +2^*\text{GHSERLA}+4^*\text{GHSEROO}+304124+15.87691*T; \quad 6000 \ \text{N} \ !$
$\text{PAR } G(\text{La2O3_A:1},\text{LA:O-2:VA}) \quad 298.15 \ +2^*\text{GHSERLA}+3^*\text{GHSEROO}+204124; \quad 6000 \ \text{N} \ !$
$\text{PAR } G(\text{La2O3_A:1},\text{LA:VA:O-2}) \quad 298.15 \ +2^*\text{GHSERLA}+\text{GHSEROO}+304124+15.87691*T; \quad 6000 \ \text{N} \ !$
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PAR G(LA2O3_A,LA+3:VA) 298.15 +GLA2O3A; 6000 N!
PAR G(LA2O3_A,LA+3:VA:VA) 298.15 +GLA2O3A-3*GHSEROO; 6000 N!
PAR G(LA2O3_A,LA+3:VA:O-2) 298.15 +GLA2O3A-2*GHSEROO+100000+15.87691*T; 6000 N!
PAR G(LA2O3_A,LA+3:O-2:O-2) 298.15 +GLA2O3A+GHSEROO+100000+15.87691*T; 6000 N!
PAR G(LA2O3_A,Y+3:O-2:VA) 298.15 +2*GAAY015; 6000 N!
PAR G(LA2O3_A,Y+3:VA:VA) 298.15 +2*GAAY015-3*GHSEROO; 6000 N!
PAR G(LA2O3_A,Y+3:VA:O-2) 298.15 +2*GAAY015-2*GHSEROO+100000+15.87691*T; 6000 N!
PAR G(LA2O3_A,Y+3:0-2:0-2) 298.15 +2*GAAY015+GHSEROO+100000+15.87691*T; 6000 N!
PAR G(LA2O3_A,Y+3:VA:VA;0) 298.15 +2*GAAY015-3*GHSEROO; 6000 N!
PAR G(LA2O3_A,Y+3:VA:0-2;1) 298.15 +18981; 6000 N!
PAR G(LA2O3_A,La+3,Y+3:O-2:0-2;0) 298.15 +18981; 6000 N!
PAR G(LA2O3_A,La+3,Y+3:O-2:VA;0) 298.15 -101793; 6000 N!
PAR G(LA2O3_B,La+3,ZR+4:VA:VA) 298.15 -21475+26.2*T; 6000 N!
PAR L(LA2O3_A,LA+3,Y+3:O-2:O-2;0) 298.15 -21475+26.2*T; 6000 N!
PAR L(LA2O3_A,LA+3,Y+3:O-2:VA;0) 298.15 -21475+26.2*T; 6000 N!
PAR L(LA2O3_A,LA+3,Y+3:VA:O-2;1) 298.15 -21475+26.2*T; 6000 N!
PAR L(LA2O3_A,LA+3,Y+3:VA:VA;1) 298.15 -21475+26.2*T; 6000 N!
PAR L(LA2O3_B,La+3,ZR+4:VA:VA;0) 298.15 -21475+26.2*T; 6000 N!
PAR L(LA2O3_B,La+3,ZR+4:O-2:O-2;0) 298.15 -21475+26.2*T; 6000 N!
PAR L(LA2O3_B,La+3,ZR+4:O-2:VA;0) 298.15 -21475+26.2*T; 6000 N!
PAR L(LA2O3_B,La+3,ZR+4:VA:O-2;0) 298.15 -21475+26.2*T; 6000 N!

$ PHASE LA2O3_B:1 Z 3 2 3 !
CONST LA2O3_B:1: LA+3 Y+3 : O-2% VA : O-2 VA% : !
PAR G(LA2O3_B,LA+3:O-2:VA) 298.15 +GLA2O3B; 6000 N!
PAR G(LA2O3_B,LA+3:VA:VA) 298.15 +GLA2O3B-3*GHSEROO; 6000 N!
PAR G(LA2O3_B,LA+3:VA:O-2) 298.15 +GLA2O3B-2*GHSEROO+15.87691*T+100000; 6000 N!
PAR G(LA2O3_B,LA+3:O-2:O-2) 298.15 +GLA2O3B+GHSEROO+15.87691*T+100000; 6000 N!
PAR G(LA2O3_B,Y+3:O-2:VA) 298.15 +2*GBBY015; 6000 N!
PAR G(LA2O3_B,Y+3:VA:VA) 298.15 +2*GBBY015-3*GHSEROO; 6000 N!
PAR G(LA2O3_B,Y+3:VA:O-2) 298.15 +2*GBBY015-2*GHSEROO+100000+15.87691*T; 6000 N!
PAR G(LA2O3_B,Y+3:O-2:O-2) 298.15 +2*GBBY015+GHSEROO+100000+15.87691*T; 6000 N!
PAR L(LA2O3_B,LA+3,Y+3:O-2:O-2;0) 298.15 -21475+26.2*T; 6000 N!
PAR L(LA2O3_B,LA+3,Y+3:O-2:VA;0) 298.15 -21475+26.2*T; 6000 N!
Description of La–Mn–Y–Zr–O

PAR L(LA₂O₃, LA+3, Y+3, VA: O-2; 0) 298.15 -21475+26.2*T; 6000 N
PAR L(LA₂O₃, LA+3, Y+3, VA: VA; 0) 298.15 -21475+26.2*T; 6000 N
PAR L(LA₂O₃, LA+3, Y+3, O-2; O-2; 1) 298.15 -60190+31.5*T; 6000 N
PAR L(LA₂O₃, LA+3, Y+3, VA; VA; 1) 298.15 -60190+31.5*T; 6000 N
PAR L(LA₂O₃, LA+3, VA; VA; O-2; 1) 298.15 -60190+31.5*T; 6000 N
PAR L(LA₂O₃, LA+3, VA; O-2; O-2; 1) 298.15 -60190+31.5*T; 6000 N

$ PHASE Y₂O₃-CUB : I Z 3 2 3 1 !$  
$ CONST Y₂O₃_CUB : I : LA+3 MN+3% Y Y+3% ZR+4% O-2% VA : O-2 VA% : !$  
$ This is essentially an ordered fluorite structure$  
$ This is also Mn2O3$  
PAR G(Y₂O₃_CUB, LA+3: O-2: VA) 298.15 +GLA₂O₃C; 6000 N
PAR G(Y₂O₃_CUB, LA+3: VA: VA) 298.15 +GLA₂O₃C-3*GHSEROO; 6000 N
PAR G(Y₂O₃_CUB, LA+3: VA: O-2) 298.15 +GLA₂O₃C-2*GHSEROO+15.87691*T+100000; 6000 N
PAR G(Y₂O₃_CUB, LA+3: O-2: O-2) 298.15 +GLA₂O₃C+GHSEROO+15.87691*T+100000; 6000 N
PAR G(Y₂O₃_CUB, MN+3: O-2: VA) 298.15 +GMN₂O₃; 6000 N
PAR G(Y₂O₃_CUB, MN+3: VA: VA) 298.15 +GMN₂O₃-3*GHSEROO; 6000 N
PAR G(Y₂O₃_CUB, MN+3: VA: O-2) 298.15 +GMN₂O₃-2*GHSEROO+15.87691*T+100000; 6000 N
PAR G(Y₂O₃_CUB, MN+3: O-2: O-2) 298.15 +GMN₂O₃+GHSEROO+15.87691*T+100000; 6000 N
PAR G(Y₂O₃_CUB, Y: VA: VA) 298.15 +2*GHSERY+245600; 6000 N
PAR G(Y₂O₃_CUB, Y: O-2: O-2) 298.15 +2*GHSERY+245600+4*GHSEROO+100000+15.87691*T; 6000 N
PAR G(Y₂O₃_CUB, Y: O-2: VA) 298.15 +2*GHSERY+245600+3*GHSEROO; 6000 N
PAR G(Y₂O₃_CUB, Y: VA: O-2) 298.15 +2*GHSERY+245600+2*GHSEROO; 6000 N
PAR G(Y₂O₃_CUB, Y: VA: VA) 298.15 +2*GHSERY+245600+1*GHSEROO+100000+15.87691*T; 6000 N
PAR G(Y₂O₃_CUB, Y: O-2: VA) 298.15 +2*GHSERY+245600+1*GHSEROO; 6000 N
PAR G(Y₂O₃_CUB, Y: O-2: VA) 298.15 +2*GHSERY+245600+1*GHSEROO; 6000 N
PAR G(Y₂O₃_CUB, ZR+4: VA: VA) 298.15 +2*GCCYO15; 6000 N
PAR G(Y₂O₃_CUB, ZR+4: O-2: VA) 298.15 +2*GCCYO15-3*GHSEROO; 6000 N
PAR G(Y₂O₃_CUB, ZR+4: O-2: VA) 298.15 +2*GCCYO15-3*GHSEROO; 6000 N
PAR G(Y₂O₃_CUB, ZR+4: O-2: VA) 298.15 +2*GCCYO15-3*GHSEROO; 6000 N
PAR G(Y₂O₃_CUB, ZR+4: O-2: VA) 298.15 +2*GCCYO15-3*GHSEROO; 6000 N
PAR G(Y₂O₃_CUB, ZR+4: O-2: VA) 298.15 +2*GCCYO15-3*GHSEROO; 6000 N
PAR G(Y₂O₃_CUB, ZR+4: O-2: VA) 298.15 +2*GCCYO15-3*GHSEROO; 6000 N
PAR G(Y₂O₃_CUB, ZR+4: O-2: VA) 298.15 +2*GCCYO15-3*GHSEROO; 6000 N
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PAR L(Y2O3_CUB,LA+3,Y+3:VA:O-2:1) 298.15 +29838; 6000 N !
PAR L(Y2O3_CUB,LA+3,Y+3:VA:VA:1) 298.15 +29838; 6000 N !
PAR L(Y2O3_CUB,MN+3,Y+3:VA:VA:0) 298.15 +100000; 6000 N !
PAR L(Y2O3_CUB,MN+3,Y+3:O-2:O-2:0) 298.15 +100000; 6000 N !
PAR L(Y2O3_CUB,MN+3,Y+3:O-2:VA:0) 298.15 +100000; 6000 N !
PAR L(Y2O3_CUB,MN+3,Y+3:VA:O-2:0) 298.15 +100000; 6000 N !
PAR L(Y2O3_CUB,MN+3,ZR+4:VA:VA:0) 298.15 +100000; 6000 N !
PAR L(Y2O3_CUB,MN+3,ZR+4:O-2:O-2:0) 298.15 +100000; 6000 N !
PAR L(Y2O3_CUB,MN+3,ZR+4:O-2:VA:0) 298.15 +100000; 6000 N !
PAR L(Y2O3_CUB,MN+3,ZR+4:VA:O-2:0) 298.15 +100000; 6000 N !
PAR L(Y2O3_CUB,Y+3,ZR+4:VA:VA:0) 298.15 -88700+13*T; 6000 N !
PAR L(Y2O3_CUB,Y+3,ZR+4:O-2:O-2:0) 298.15 -88700+13*T; 6000 N !
PAR L(Y2O3_CUB,Y+3,ZR+4:O-2:VA:0) 298.15 -88700+13*T; 6000 N !
PAR L(Y2O3_CUB,Y+3,ZR+4:VA:O-2:0) 298.15 -88700+13*T; 6000 N !

$ PHASE Y2O3_HEX:1 Z 3 2 3 1 !
CONST Y2O3_HEX:1 : LA+3% MN+3 Y Y+3% ZR+4 : O-2% VA : O-2 VA% : !
$ This is beta-Y2O3 (alias H-Y2O3)
$ This is also H-La2O3
PAR G(Y2O3_HEX,LA:VA:VA) 298.15 +2*GHSERLA+204124; 6000 N !
PAR G(Y2O3_HEX,LA:O-2:O-2) 298.15 +2*GHSERLA+4*GHSEROO+304124+15.87691*T; 6000 N !
PAR G(Y2O3_HEX,LA:O-2:VA) 298.15 +2*GHSERLA+3*GHSEROO+204124; 6000 N !
PAR G(Y2O3_HEX,LA:VA:O-2) 298.15 +2*GHSERLA+204124+15.87691*T; 6000 N !
PAR G(Y2O3_HEX,LA+3:O-2:O-2) 298.15 +GLA2O3H+GHSEROO+100000+15.87691*T+100000; 6000 N !
PAR G(Y2O3_HEX,LA+3:O-2:VA) 298.15 +GLA2O3H-2*GHSEROO+100000+15.87691*T+100000; 6000 N !
PAR G(Y2O3_HEX,MN+3:O-2:VA) 298.15 +GMHN2O3; 6000 N !
PAR G(Y2O3_HEX,MN+3:VA:VA) 298.15 +GMHN2O3-3*GHSEROO; 6000 N !
PAR G(Y2O3_HEX,MN+3:VA:O-2) 298.15 +GMHN2O3-2*GHSEROO+15.87691*T+100000; 6000 N !
PAR G(Y2O3_HEX,MN+3:O-2:O-2) 298.15 +GMHN2O3+GHSEROO+15.87691*T+100000; 6000 N !
PAR G(Y2O3_HEX,Y:VA:VA) 298.15 +2*GHSERY+245600+4*GHSEROO+100000+15.87691*T; 6000 N !
PAR G(Y2O3_HEX,Y:O-2:O-2) 298.15 +2*GHSERY+245600+3*GHSEROO; 6000 N !
PAR G(Y2O3_HEX,Y:O-2:VA) 298.15 +2*GHSERY+245600+3*GHSEROO; 6000 N !
PAR G(Y2O3_HEX,Y:VA:O-2) 298.15 +2*GHSERY+245600+3*GHSEROO; 6000 N !
PAR G(Y2O3_HEX,Y+3:O-2:VA) 298.15 +2*GHHYO15; 6000 N !
PAR G(Y2O3_HEX,Y+3:VA:VA) 298.15 +2*GHHYO15-3*GHSEROO; 6000 N !
PAR G(Y2O3_HEX,Y+3:VA:O-2) 298.15
Description of La–Mn–Y–Zr–O

\[ +2*GHHYO_{15}-2*GHSEROO+15.87691*T+100000; \]

PAR G(Y2O3_HEX,Y+3:O-2,O-2) 298.15
+2*GHHYO_{15}+GHSEROO+15.87691*T+100000;

PAR G(Y2O3_HEX,ZR+4:VA:VA) 298.15
+2*GMMZR02*4*GHSEROO-100000-15.87691*T;

PAR G(Y2O3_HEX,ZR+4:O-2:VA) 298.15
+2*GMMZR02-GHSEROO-100000-15.87691*T;

PAR G(Y2O3_HEX,ZR+4:VA:O-2) 298.15
+2*GMMZR02-3*GHSEROO;

PAR L(Y2O3_HEX,LA+3,Y+3:O-2:O-2;0) 298.15 +27920; 6000 N
PAR L(Y2O3_HEX,LA+3,Y+3:O-2:VA;0) 298.15 +27920; 6000 N
PAR L(Y2O3_HEX,LA+3,Y+3:VA:O-2;0) 298.15 +27920; 6000 N
PAR L(Y2O3_HEX,LA+3,Y+3:VA:VA;0) 298.15 +27920; 6000 N
PAR L(Y2O3_HEX,LA+3,ZR+4:O-2:VA;1) 298.15 +12879; 6000 N
PAR L(Y2O3_HEX,LA+3,ZR+4:O-2:O-2;1) 298.15 +12879; 6000 N
PAR L(Y2O3_HEX,LA+3,ZR+4:VA:VA;0) 298.15 +12879; 6000 N
PAR L(Y2O3_HEX,LA+3,ZR+4:VA:O-2;0) 298.15 +100000; 6000 N
PAR L(Y2O3_HEX,MN+3,Y+3:O-2:O-2;0) 298.15 +12879; 6000 N
PAR L(Y2O3_HEX,MN+3,Y+3:O-2:VA;0) 298.15 +12879; 6000 N
PAR L(Y2O3_HEX,MN+3,Y+3:VA:O-2;0) 298.15 +100000; 6000 N
PAR L(Y2O3_HEX,MN+3,Y+3:VA:VA;1) 298.15 +100000; 6000 N
PAR L(Y2O3_HEX,MN+3,Y+3:VA:VA;0) 298.15 +100000; 6000 N
PAR L(Y2O3_HEX,MN+3,Y+3:VA:VA;1) 298.15 +100000; 6000 N
PAR L(Y2O3_HEX,MN+3,ZR+4:O-2:O-2;0) 298.15 +12879; 6000 N
PAR L(Y2O3_HEX,MN+3,ZR+4:O-2:VA;0) 298.15 +12879; 6000 N
PAR L(Y2O3_HEX,MN+3,ZR+4:VA:O-2;0) 298.15 +100000; 6000 N
PAR L(Y2O3_HEX,MN+3,ZR+4:VA:VA;0) 298.15 +100000; 6000 N
PAR L(Y2O3_HEX,MN+3,ZR+4:VA:VA;1) 298.15 +100000; 6000 N
PAR L(Y2O3_HEX,MN+3,ZR+4:VA:VA;0) 298.15 +100000; 6000 N
PAR L(Y2O3_HEX,MN+3,ZR+4:VA:VA;1) 298.15 +100000; 6000 N
$ PHASE ZRO2_MONO1 Z 2 1 2 !
CONST ZRO2_MONO1: Y+3 ZR+4%: O-2% VA: !
PAR G(ZRO2_MONO,Y+3:O-2) 298.15
+GMMYO_{15}+0.5*GHSEROO+9.3511*T;

PAR G(ZRO2_MONO,Y+3:VA) 298.15
+GMMYO_{15}-1.5*GHSEROO+9.3511*T;

PAR G(ZRO2_MONO,ZR+4:O-2) 298.15
+GMTMN101+GHSEROO+11.5264*T;

PAR G(ZRO2_MONO,ZR+4:VA) 298.15
+GMTMN101-GHSEROO+11.5264*T;

PAR G(ZRO2_MONO,MN+3,Y+3:O-2:O-2;0) 298.15 +12879; 6000 N
PAR G(ZRO2_MONO,MN+3,Y+3:O-2:VA;0) 298.15 +12879; 6000 N
PAR G(ZRO2_MONO,MN+3,Y+3:VA:O-2;0) 298.15 +100000; 6000 N
PAR G(ZRO2_MONO,MN+3,Y+3:VA:VA;0) 298.15 +100000; 6000 N
PAR G(ZRO2_MONO,MN+3,Y+3:VA:VA;1) 298.15 +100000; 6000 N
PAR G(ZRO2_MONO,MN+3,Y+3:VA:VA;0) 298.15 +100000; 6000 N
PAR G(ZRO2_MONO,MN+3,Y+3:VA:VA;1) 298.15 +100000; 6000 N
PAR G(ZRO2_MONO,MN+3,Y+3:VA:VA;0) 298.15 +100000; 6000 N
PAR G(ZRO2_MONO,MN+3,Y+3:VA:VA;1) 298.15 +100000; 6000 N

$ PHASE ZRO2_TETR:1 Z 2 1 2 !
CONST ZRO2_TETR:1: LA+3 MN+2 MN+3 Y+3 ZR+4%: O-2% VA : !
PAR G(ZRO2_TETR,LA+3:O-2) 298.15
+0.5*GMTLA2O3+0.5*GHSEROO+9.3511*T;

PAR G(ZRO2_TETR,LA+3:VA) 298.15
+0.5*GMTLA2O3-1.5*GHSEROO+9.3511*T;

PAR G(ZRO2_TETR,MN+2:O-2) 298.15
+GMTMN101+GHSEROO+11.5264*T;

PAR G(ZRO2_TETR,MN+2:VA) 298.15
+GMTMN101-GHSEROO+11.5264*T;

PAR G(ZRO2_TETR,MN+3:O-2) 298.15
+0.5*GMTMN2O3+0.5*GHSEROO+9.3511*T;

PAR G(ZRO2_TETR,MN+3:VA) 298.15

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$+0.5*\text{GMTMN2O3}-1.5*\text{GHSEROO}+9.3511*T; 6000 N$

PAR \text{G(ZRO2\_TETR,Y+3:O-2)} = 298.15

$+\text{GMTYO15}+0.5*\text{GHSEROO}+9.3511*T; 6000 N$

PAR \text{G(ZRO2\_TETR,Y+3:VA)} = 298.15

$+\text{GMTYO15}-1.5*\text{GHSEROO}+9.3511*T; 6000 N$

PAR \text{G(ZRO2\_TETR,ZR+4:O-2)} = 298.15 +\text{GTTZR02}; 6000 N$

PAR \text{G(ZRO2\_TETR,ZR+4:VA)} = 298.15 +\text{GTTZR02}-2*\text{GHSEROO}; 6000 N$

PAR \text{L(ZRO2\_TETR,LA+3,ZR+4:O-2;0)} = 298.15 -23609; 6000 N$

PAR \text{L(ZRO2\_TETR,LA+3,ZR+4:VA;0)} = 298.15 -23609; 6000 N$

PAR \text{L(ZRO2\_TETR,MN+2,ZR+4:O-2;0)} = 298.15 +20863; 6000 N$

PAR \text{L(ZRO2\_TETR,MN+2,ZR+4:VA;0)} = 298.15 +20863; 6000 N$

PAR \text{L(ZRO2\_TETR,MN+3,ZR+4:O-2;0)} = 298.15 +20863; 6000 N$

PAR \text{L(ZRO2\_TETR,MN+3,ZR+4:VA;0)} = 298.15 +20863; 6000 N$

PAR \text{L(ZRO2\_TETR,Y+3,ZR+4:O-2;0)} = 298.15 -48800+18.4*T; 6000 N$

PAR \text{L(ZRO2\_TETR,Y+3,ZR+4:VA;0)} = 298.15 -48800+18.4*T; 6000 N$

$\text{PHASE}\ ZRO2\_CUB:1Z 2 1 2 !$

\text{CONST}\ ZRO2\_CUB:1 : \text{LA LA}+3\% \text{MN}+2 \text{MN}+3 \text{Y Y}+3\% \text{ZR ZR}+4\% : \text{O}-2 \text{ VA} : !$

$\text{This is also X-La2O3}$

PAR \text{G(ZRO2\_CUB,LA:O-2)} = 298.15

$+\text{GHSERLA}+2*\text{GHSEROO}+102062; 6000 N$

PAR \text{G(ZRO2\_CUB,LA:VA)} = 298.15 +\text{GHSERLA}+102062; 6000 N$

PAR \text{G(ZRO2\_CUB,LA+3:O-2)} = 298.15

$+0.5*\text{GLA2O3X}+0.5*\text{GHSEROO}+9.3511*T; 6000 N$

PAR \text{G(ZRO2\_CUB,LA+3:VA)} = 298.15

$+0.5*\text{GLA2O3X}-1.5*\text{GHSEROO}+9.3511*T; 6000 N$

PAR \text{G(ZRO2\_CUB,MN+2:O-2)} = 298.15

$+\text{GMFMN101}+\text{GHSEROO}+11.5264*T; 6000 N$

PAR \text{G(ZRO2\_CUB,MN+2:VA)} = 298.15

$+\text{GMFMN101}-\text{GHSEROO}+11.5264*T; 6000 N$

PAR \text{G(ZRO2\_CUB,MN+3:O-2)} = 298.15

$+0.5*\text{GMFMN2O3}+0.5*\text{GHSEROO}+9.3511*T; 6000 N$

PAR \text{G(ZRO2\_CUB,MN+3:VA)} = 298.15

$+0.5*\text{GMFMN2O3}-1.5*\text{GHSEROO}+9.3511*T; 6000 N$

PAR \text{G(ZRO2\_CUB,Y:O-2)} = 298.15

$+\text{GHSERYY}+2*\text{GHSEROO}+122800; 6000 N$

PAR \text{G(ZRO2\_CUB,Y:VA)} = 298.15 +\text{GHSERYY}+122800; 6000 N$

PAR \text{G(ZRO2\_CUB,Y+3:O-2)} = 298.15

$+\text{GXXYO15}+0.5*\text{GHSEROO}+9.3511*T; 6000 N$

PAR \text{G(ZRO2\_CUB,Y+3:VA)} = 298.15

$+\text{GXXYO15}-1.5*\text{GHSEROO}+9.3511*T; 6000 N$

PAR \text{G(ZRO2\_CUB,ZR:O-2)} = 298.15

$+100000+\text{GHSERZR}+2*\text{GHSEROO}; 6000 N$

PAR \text{G(ZRO2\_CUB,ZR:VA)} = 298.15 +100000+\text{GHSERZR}; 6000 N$

PAR \text{G(ZRO2\_CUB,ZR+4:O-2)} = 298.15 +\text{GFFZR02}; 6000 N$

PAR \text{G(ZRO2\_CUB,ZR+4:VA)} = 298.15 +\text{GFFZR02}-2*\text{GHSEROO}; 6000 N$

PAR \text{L(ZRO2\_CUB,ZR+4:O-2;0)} = 298.15 -66500-1.6*T; 6000 N$

PAR \text{L(ZRO2\_CUB,ZR+4:VA;0)} = 298.15 -66500-1.6*T; 6000 N$

PAR \text{L(ZRO2\_CUB,ZR+4:O-2;1)} = 298.15 -20000-42*T; 6000 N$

PAR \text{L(ZRO2\_CUB,ZR+4:VA;1)} = 298.15 -20000-42*T; 6000 N$

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$ LaMnO_3$ perovskite

$ with vacancies on both cation sub-lattices and antisite defects

$ PHASE PEROV-XZ 3 1 1 3 !

CONST PEROV:1 : MN+3 LA+3% VA : MN+2 MN+3% MN+4 VA : O-2% VA : !

PAR G(PEROV,LA+3:MN+3:0-2) 298.15 +GL3O; 6000 N !
PAR G(PEROV,LA+3:MN+3:VA) 298.15 +GL3O-3*GHSEROO; 6000 N !
PAR G(PEROV,LA+3:MN+4:0-2) 298.15 +0.66667*GL4O+0.5*GV4O-1.5*GVVV+0.5*GHSEROO+1.41263*T; 6000 N !
PAR G(PEROV,LA+3:MN+4:VA) 298.15 +0.66667*GL4O-2.5*GHSEROO+11.2386*T; 6000 N !
PAR G(PEROV,LA+3:MN+4:O-2) 298.15 +0.66667*GL4O+0.5*GV4O-0.16667*GVVV-0.5*GHSEROO+5.76318*T; 6000 N !
PAR G(PEROV,LA+3:MN+4:VA) 298.15 +2*GL4O-1.5*GV4O+0.5*GVVV+1.5*GHSEROO+1.41263*T; 6000 N !

$ To keep no MnOx solubility in X-La$_2$O$_3$

PAR L(ZRO$_2$ CUB,LA+3,MN+2:O-2;0) 298.15 +30000; 6000 N !
PAR L(ZRO$_2$ CUB,LA+3,MN+2:VA;0) 298.15 +30000; 6000 N !
PAR L(ZRO$_2$ CUB,LA+3,MN+3:O-2;0) 298.15 +30000; 6000 N !
PAR L(ZRO$_2$ CUB,LA+3,MN+3:VA;0) 298.15 +30000; 6000 N !
PAR L(ZRO$_2$ CUB,LA+3,MN+2:O-2;1) 298.15 +141939; 6000 N !
PAR L(ZRO$_2$ CUB,LA+3,MN+2:VA;1) 298.15 +141939; 6000 N !
PAR L(ZRO$_2$ CUB,LA+3,MN+3:O-2;1) 298.15 +141939; 6000 N !
PAR L(ZRO$_2$ CUB,LA+3,MN+3:VA;1) 298.15 +141939; 6000 N !

$
PAR G(PEROV,LA+3:VA:VA) 298.15
+2*GL4O+0.5*GVVV-1.5*GV4O-1.5*GHSEROO+1.41263*T; 6000 N!

$ PAR G(PEROV,MN+3:MN+3:O-2) 298.15 +GL3O+ANTI; 6000 N!
PAR G(PEROV,MN+3:MN+3:VA) 298.15 +GL3O-3*GHSEROO+ANTI; 6000 N!
PAR G(PEROV,MN+3:MN+4:O-2) 298.15 +0.66667*GL4O+0.5*GV4O-0.16667*GVVV-0.5*GHSEROO+5.76318*T+ANTI; 6000 N!
PAR G(PEROV,MN+3:MN+4:VA) 298.15 +0.66667*GL4O+0.5*GV4O-0.16667*GVVV-3.5*GHSEROO+5.76318*T+ANTI; 6000 N!
PAR G(PEROV,MN+3:MN+2:O-2) 298.15 +GL2O+0.5*GHSEROO+11.2386*T+ANTI; 6000 N!
PAR G(PEROV,MN+3:MN+2:VA) 298.15 +GL2O-2.5*GHSEROO+11.2386*T+ANTI; 6000 N!
PAR G(PEROV,MN+3:VA:O-2) 298.15 +2*GL4O-1.5*GV4O+0.5*GVVV+1.5*GHSEROO+1.41263*T+ANTI; 6000 N!
PAR G(PEROV,MN+3:VA:VA) 298.15 +2*GL4O-0.5*GVVV-1.5*GV4O-1.5*GHSEROO+1.41263*T+ANTI; 6000 N!

$ PAR G(PEROV,VA:MN+3:O-2) 298.15 +GL3O+1.5*GV4O+0.5*GVVV-2*GL4O+1.5*GHSEROO-1.41263*T; 6000 N!
PAR G(PEROV,VA:MN+3:VA) 298.15 +GL3O+1.5*GV4O+0.5*GVVV-2*GL4O-1.5*GHSEROO-1.41263*T; 6000 N!
PAR G(PEROV,VA:MN+4:O-2) 298.15 +2*GV4O+0.33333*GVVV-1.33333*GL4O+GHSEROO+4.35056*T; 6000 N!
PAR G(PEROV,VA:MN+4:VA) 298.15 +2*GV4O+0.3333*GVVV-1.333*GL4O-2*GHSEROO+4.35056*T; 6000 N!
PAR G(PEROV,VA:VA:O-2) 298.15 +GVVV+3*GHSEROO; 6000 N!
PAR G(PEROV,VA:VA:VA) 298.15 +GVVV; 6000 N!

$ PHASE L2MNO4:1 Z 3 2 1 4 !
CONST L2MNO4:1; LA+3; MN+2; O-2; !
PAR G(L2MNO4,LA+3:MN+2:O-2) 298.15 +GL2MNO4; 6000 N!

$ PHASE LAY03:1 Z 3 1 1 3 !
CONST LAY03:1; LA+3; Y+3; O-2;!
PAR G(LAY03,LA+3:Y+3:O-2) 298.15 +GLAY03; 6000 N!

$ La2Zr2O7
PHASE L2Z2O7:1 Z 4 2 2 6 1 !
CONST L2Z2O7:1; LA+3%ZR+4 VA: ZR+4% LA+3; O-2% VA: O-2;!
PAR G(L2Z2O7,LA+3:LA+3:O-2:O-2) 298.15 +2*GLA2O3X+GHSEROO-327772+91.332*T; 6000 N!
PAR G(L2Z2O7,LA+3:LA+3:VA:O-2) 298.15 +2*GLA2O3X-5*GHSEROO+2013420-321.636*T; 6000 N!
PAR \( G(L_2Z_2O_7, LA^{+3}: ZR^{+4}: 0^{-2}: 0) \) 298.15
+2*GFFZRO2+GLA2O3X-271791+51.9*T; 6000 N !

PAR \( G(L_2Z_2O_7, LA^{+3}: ZR^{+4}: VA: 0^{-2}: 0) \) 298.15
+2*GFFZRO2+GLA2O3X-6*GHSEEROO+2069401-361.068*T; 6000 N !

PAR \( G(L_2Z_2O_7, ZR^{+4}: LA^{+3}: 0^{-2}: 0) \) 298.15
+2*GFFZRO2+GLA2O3X+28209+51.9*T; 6000 N !

PAR \( G(L_2Z_2O_7, ZR^{+4}: VA: 0^{-2}: 0) \) 298.15
+2*GFFZRO2+GLA2O3X-6*GHSEEROO+2369401-361.068*T; 6000 N !

PAR \( G(L_2Z_2O_7, ZR^{+4}: ZR^{+4}: 0^{-2}: 0) \) 298.15
+4*GFFZRO2-GHSEROO+84190+12.468*T; 6000 N !

PAR \( G(L_2Z_2O_7, ZR^{+4}: VA: 0^{-2}: 0) \) 298.15
+4*GFFZRO2-7*GHSEROO+2425381-400.5*T; 6000 N !

PAR \( G(L_2Z_2O_7, VA: LA^{+3}: 0^{-2}: 0) \) 298.15
+GLA2O3X+4*GHSEROO-55981+39.432*T; 6000 N !

PAR \( G(L_2Z_2O_7, VA: LA^{+3}: VA: 0^{-2}: 0) \) 298.15
+GLA2O3X-2*GHSEROO+2285211-373.536*T; 6000 N !

PAR \( G(L_2Z_2O_7, VA: ZR^{+4}: 0^{-2}: 0) \) 298.15
+2*GFFZRO2+3*GHSEROO; 6000 N !

PAR \( G(L_2Z_2O_7, VA: ZR^{+4}: VA: 0^{-2}: 0) \) 298.15
+2*GFFZRO2-3*GHSEROO+2341192-412.968*T; 6000 N !

$ C2
PHASE C2.1 Z 3 2 1 5 !
CONST C2.1 : LA^{+3} : ZR^{+4} : O^{-2} : !
PAR G(C2,LA^{+3}:ZR^{+4}:O^{-2}) 298.15 +GC2; 6000 N !$
Appendix

$ C-Y2O3
PHASE RY2O3:1 Z 2 2 3 !
PAR G(RY2O3,Y+3:O-2) 298.15 +2*GCCYO15; 6000 N !
$m-ZrO2
PHASE RMZRO2:1 Z 2 1 2 !
CONST RMZRO2:1: ZR+4 : O-2 : !
PAR G(RMZRO2,ZR+4:O-2) 298.15 +GMMZRO2; 6000 N !
$t-ZrO2
PHASE RTZRO2:1 Z 2 1 2 !
CONST RTZRO2:1: ZR+4 : O-2 : !
PAR G(RTZRO2,ZR+4:O-2) 298.15 +GTIZRO2; 6000 N !
$c-ZrO2 (fluorite)
PHASE RFZRO2:1 Z 2 1 2 !
CONST RFZRO2:1: ZR+4 : O-2 : !
PAR G(RFZRO2,ZR+4:O-2) 298.15 +GFFZRO2; 6000 N !
$ LaMn03
PHASE RLMN03:1 Z 3 1 3 !
PAR G(RLMN03,LA+3:MN+3:O-2) 298.15 +GL3O; 6000 N !
$ La2Zr207
PHASE RL2Z207:1 Z 3 2 7 !
PAR G(RL2Z207,LA+3:ZR+4:O-2) 298.15 +GL2Z207; 6000 N !
$ O2_GAS:G Z 1 1 1 !
CONSTITUENT O2_GAS:O2 : !
PAR G(O2_GAS,O2) 298.15 +2*GHSEROO+RTLNP; 6000 N !
$ PHASE GAS:G Z 1 1 !
CONST GAS:G : LA LA1O1 LA2O1 LA2O2 MN MNO MNO2 O O2 O3
  Y Y2O YO2 YO2 ZR ZR2 ZRO ZRO2 : !
PAR G(GAS,LA) 298.15 +F12026T+RTLNP; 6000 N !
PAR G(GAS,LA1O1) 298.15 +F12049T+RTLNP; 6000 N !
PAR G(GAS,LA2O1) 298.15 +F12085T+RTLNP; 6000 N !
PAR G(GAS,LA2O2) 298.15 +F12089T+RTLNP; 6000 N !
PAR G(GAS,MN) 298.15 +F12439T+RTLNP; 6000 N !
PAR G(GAS,MNO) 298.15 +F12454T+RTLNP; 6000 N !
PAR G(GAS,MNO2) 298.15 +F12461T+RTLNP; 6000 N !
PAR G(GAS,O) 298.15 +F7397T+RTLNP; 6000 N !
PAR G(GAS,O2) 298.15 +2*GHSEROO+RTLNP; 6000 N !
PAR G(GAS,O3) 298.15 +F7683T+RTLNP; 6000 N !
PAR G(GAS,Y) 298.15 +F14722T+RTLNP; 6000 N !
PAR G(GAS,Y2O) 298.15 +F12945T+RTLNP; 6000 N !
PAR G(GAS,YO) 298.15 +F12929T+RTLNP; 6000 N !
PAR G(GAS,Y2O2) 298.15 +F13270T+RTLNP; 6000 N !
PAR G(GAS,YO2) 298.15 +F13266T+RTLNP; 6000 N !
PAR G(GAS,ZR) 298.15 +GZRGAS+RTLNP; 6000 N !
PAR G(GAS,ZR2) 298.15 +F15702T+RTLNP; 6000 N !
PAR G(GAS,ZRO) 298.15 +F12964T+RTLNP; 6000 N !
Description of La–Mn–Y–Zr–O

PAR G(GAS,ZRO2) 298.15 +F13281T+RTLNP; 6000 N!

FUNCTION GHSERLA
298.15 -7968.403+120.284604*T-26.34*T*LN(T)-0.01295165*T**2;
550 Y -3381.413+59.06113*T-17.1659411*T*LN(T)-0.008371705*T**2
+6.8932E-07*T**3-399448*T**(-1);
2000 Y -15608.882+181.390071*T-34.3088*T*LN(T);
4000 N!

FUNCTION GLABCC
298.15 -3952.161+88.072353*T-21.7919*T*LN(T)-0.004045175*T**2
-5.25865E-07*T**3;
800 Y +321682.673-3656.08252*T+513.440708*T*LN(T)-0.387295093*T**2
+4.9547989E-05*T**3-36581228*T**(-1);
1134 Y -16377.894+218.492988*T-39.5388*T*LN(T);
1193 Y -136609.91+1123.34397*T-163.413074*T*LN(T)+0.053968535*T**2
-4.056395E-06*T**3+21167204*T**(-1);
2000 Y -8205.988+174.836315*T-34.3088*T*LN(T);
4000 N!

FUNCTION GLAFCC
298.15 -6109.797+89.878761*T-21.7919*T*LN(T)
-0.004045175*T**2-5.25865E-07*T**3;
1134 Y -124598.976+955.878375*T-139.346741*T*LN(T)+0.042032405*T**2
-3.066199E-06*T**3+20994153*T**(-1);
2000 Y -12599.386+178.54399*T-34.3088*T*LN(T);
4000 N!

FUNCTION GLALIQ
298.15 +5332.653+18.23012*T-11.0188191*T*LN(T)-0.020171603*T**2
+2.93775E-06*T**3-133541*T**(-1);
1134 Y -3942.004+171.018431*T-34.3088*T*LN(T);
4000 N!

FUNCTION GHSERMN
298.15 -8115.28+130.059*T-23.4582*T*LN(T)
-0.00734768*T**2+69827*T**(-1);
1519.00 Y -28733.41+312.2648*T-48*T*LN(T)+1.656847E+30*T**(-9);
2000.00 N!

FUNCTION GMNCUB
298.15 -5800.4+135.995*T-24.8785*T*LN(T)
-0.00583359*T**2+70269*T**(-1);
1519.00 Y +442.65-0.9715*T+GHSERMN+2.310723E+30*T**(-9);
2000.00 N!

FUNCTION GNMFCC
298.15 -3439.3+131.884*T-24.5177*T*LN(T)
-0.006*T**2+69600*T**(-1);
1519.00 Y +2663.31-2.5984*T+GHSERMN+2.205113E+30*T**(-9);
2000.00 N!

FUNCTION GMNBCC
298.15 -3235.3+127.85*T-23.7*T*LN(T)
-0.00744271*T**2+60000*T**(-1);
1519.00 Y +5544.58-4.5605*T+GHSERMN-3.91695E+29*T**(-9);
2000.00 N!
Appendix

FUNCTION GMNHCP 298.15 -4439.3+133.007*T-24.5177*T*LN(T)
-0.006*T**2+69600*T**(-1);
1519.00 Y +1663.31-1.4754*T+GHSERMN+2.205113E+30*T**(-9);
2000.00 N !
FUNCTION GMNLIQ 298.15 +17859.91-12.6208*T+GHSERMN-4.41929E-21*T**7;
1519.00 Y -9993.9+299.036*T-48*T*LN(T);
2000.00 N !

FUNCTION GHSEROO 298.15 -3480.87-25.503038*T-11.136*T*LN(T)
-0.005098888*T**2+6.61846E-07*T**3-38365*T**(-1);
1000.00 Y -6568.763+12.65988*T-16.8138*T*LN(T)
-5.95798E-04*T**2+6.781E-09*T**3+262905*T**(-1);
3300.00 Y -13986.728+31.259625*T-18.9536*T*LN(T)
-4.25243E-04*T**2+1.0721E-08*T**3+4383200*T**(-1);
6000.00 N !

FUNCTION GHSERYY 100.00 -8011.09379+128.572856*T-25.6656992*T*LN(T)
-0.0017571641*T**2+4.17561786E-07*T**3+26911.509*T**(-1);
1000.00 Y -7179.74574+114.497104*T-23.4941827*T*LN(T)
-0.0038211802*T**2-8.2534534E-08*T**3;
1795.15 Y -67480.7761+382.124727*T-56.9527111*T*LN(T)
+0.0023174739*T**2-7.22513088E-08*T**3+18077162.6*T**(-1);
3700.00 N !
FUNCTION GYYBCC 100.00 -833.658863+123.667346*T-25.5832578*T*LN(T)
-0.00237175965*T**2+9.10372497E-07*T**3+27340.0687*T**(-1);
1000.00 Y -1297.79829+134.528352*T-27.3038477*T*LN(T)
-5.41757644E-04*T**2-3.05012175E-07*T**3;
1795.15 Y +15389.4975+0.981325399*T-8.88296647*T*LN(T)
-0.00904576576*T**2+4.02944768E-07*T**3-2542575.96*T**(-1);
3700.00 N !
FUNCTION GYYLIQ 100.00 +2098.50738+119.41873*T-24.6467508*T*LN(T)
-0.00347023463*T**2-8.12981167E-07*T**3+23713.7332*T**(-1);
1000.00 Y +7386.44846+19.4520171*T-9.0681627*T*LN(T)
-0.0189533369*T**2+1.75953276E-06*T**3;
1795.15 Y -12976.5957+257.400783*T-43.0952*T*LN(T);
3700.00 N !

FUNCTION GHSERZR 130.00 -7827.595+125.64905*T-24.1618*T*LN(T)
-0.00437791*T**2+34971*T**(-1);
2128.00 Y -26085.921+262.724183*T-42.144*T*LN(T)-1.342896E+31*T**(-9);
6000.00 N !
FUNCTION GZRBCC 130.00 -525.539+124.9457*T-25.607406*T*LN(T)
-3.40084E-04*T**2-9.729E-09*T**3+25233*T**(-1)-7.6143E-11*T**4;
2128.00 Y -4620.034+1.55998*T+GHSERZR+1.4103476E+32*T**(-9);
6000.00 N !
FUNCTION GZRRLIQ 130.00 +18147.69-9.080812*T+GHSERZR+1.6275E-22*T**7;
2128.00 Y -8281.26+253.812609*T-42.144*T*LN(T);
6000.00 N !

FUNCTION GMN12Y 298.15
Description of La–Mn–Y–Zr–O

\[
+12*\text{GHSERMN} + \text{GHSERYY} - 142346.62 + 58.97073*T; \\
\text{FUNCTION GMN23Y6} \quad 298.15 \\
+23*\text{GHSERMN} + 6*\text{GHSERYY} - 334013.88 + 27.83478*T; \\
\text{FUNCTION GMN2Y} \quad 298.15 \\
+2*\text{GHSERMN} + \text{GHSERYY} - 41092.59 + 3.42435*T; \\
\text{FUNCTION GMN203L} \quad 298.15 \\
-1835600 + 674.72*T - 118*T*\ln(T) - 0.008*T**2 + 620000*T**(-1); \\
\text{FUNCTION GMN1O1} \quad 298.15 \\
-4.02478000*E+05 + 2.59356E+02*T - 4.6835E+01*T*\ln(T) - 3.8500E-03*T**2 + 2.12922E+05*T**(-1); \\
\text{FUNCTION GMN1O2} \quad 298.15 \\
-5.45091000*E+05 + 3.95379E+02*T - 6.5277E+01*T*\ln(T) - 7.803E-03*T**2 + 6.64955E+05*T**(-1); \\
\text{FUNCTION GMN203} \quad 298.15 \\
-9.98618000*E+05 + 5.88619E+02*T - 1.01956E+02*T*\ln(T) - 1.8844E-02*T**2 + 5.89055E+05*T**(-1); \\
\text{FUNCTION GMN3O4} \quad 298.15 \\
-1.43703700*E+06 + 8.89568E+02*T - 1.54748E+02*T*\ln(T) - 1.7408E-02*T**2 + 9.86139E+05*T**(-1); \\
\text{FUNCTION GMN3O4B} \quad 298.15 \\
-1.41618900*E+06 + 8.75120E+02*T - 1.54748E+02*T*\ln(T) - 1.7408E-02*T**2 + 9.86139E+05*T**(-1); \\
\text{FUNCTION GL11} \quad 298.15 \\
+GMN1O1 + 4.3947E+04*E+04 - 2.0628E+01*T; \\
\text{FUNCTION GL23} \quad 298.15 \\
+2*GMN1O1 + GHSEROO - 6.4953E+04 + 4.3144E+01*T; \\
\text{FUNCTION GMTMN1O1} \quad 298.15 \\
+GMN1O1 + 40000; \\
\text{FUNCTION GMFMN1O1} \quad 298.15 \\
+GMN1O1 + 20000; \\
\text{FUNCTION GMTMN2O3} \quad 298.15 \\
+GMN2O3 + 100000; \\
\text{FUNCTION GMFMN2O3} \quad 298.15 \\
+GMN2O3 + 60000; \\
\text{FUNCTION GMHMN2O3} \quad 298.15 \\
+GMN2O3 + 60000; \\
\text{FUNCTION GCCYO15} \quad 298.15 \\
-990900 + 381.86*T - 62.85*T*\ln(T) - 0.0025*T**2 + 1172000*T**(-1) - 59000000*T**(-2); \\
\text{FUNCTION GAAYO15} \quad 298.15 \\
+GCCYO15 + 10584 - 3.3*T; \\
\text{FUNCTION GBBYO15} \quad 298.15 \\
+GCCYO15 + 5654 - 2.034*T; \\
\text{FUNCTION GHHYO15} \quad 298.15 \\
+GCCYO15 + 12500 - 4.808*T; \\
\text{FUNCTION GXXYO15} \quad 298.15 \\
+GCCYO15 + 20000 - 8.1*T; \\
\text{FUNCTION GMMYO15} \quad 298.15 \\
+GCCYO15 + 32700 + 20*T; \\
\text{FUNCTION GMTYO15} \quad 298.15 \\
+GCCYO15 + 15000; \\
\text{FUNCTION GMMZRO2} \quad 298.15 \\
-1125300 + 416.9*T - 68.4*T*\ln(T) - 0.00335*T**2 + 586000*T**(-1); \\
\text{FUNCTION GTTZRO2} \quad 298.15 \\
+GMMZRO2 + 6000 - 4.326*T; \\
\text{FUNCTION GFFZRO2} \quad 298.15 \\
+GMMZRO2 + 13500 - 7.159*T;
Appendix

FUNCTION GZR02LIQ 298.15 -1077400+561.1*T-90*T*LN(T); 6000 N !
FUNCTION GMAZR02 298.15 +GMMZRO2+50000; 6000 N !
FUNCTION GMCZR02 298.15 +GFFZRO2+45000; 6000 N !
FUNCTION GMHZR02 298.15 +GFFZRO2+45000; 6000 N !

$ Ternary compounds

$ LaMnO3: (La+3, Mn+3, Va)(Mn+2, Mn+3, Mn+4, Va)(O-2, Va)3
FUNCTION GL3O 298.15
0.5*GLA2O3A+0.5*GMN2O3-63367+51.77*T-7.19*T*LOG(T)+232934*T**(-1);
6000 N !
FUNCTION GL2O 298.15 0.5*GLA2O3A+GMN1O1+27672; 6000 N !
FUNCTION GL4O 298.15
0.5*GLA2O3A+0.75*GMN1O2-91857+20.31*T; 6000 N !
FUNCTION GV4O 298.15 0.333333*GLA2O3A+GMN1O2-53760; 6000 N !
FUNCTION GVVV 298.15 +6*GL2O+4*GL4O+3*GV4O-12*GL3O-254212;
FUNCTION ANTI 298.15 +547422; 6000 N !
FUNCTION GL2MN04 298.15 +GLA2O3A+GMN1O1+47276-28.61*T; 6000 N !
FUNCTION GLA2MN04 298.15
+0.5*GLA2O3A+GCCYO15-8517-0.75*T; 6000 N !
FUNCTION GL2Z207 298.15 +GLA2O3X+2*GFFZR02-271791+51.9*T; 6000 N !
FUNCTION GC2 298.15 +GLA2O3X+GFFZR02-94433+2.5*T; 6000 N !
FUNCTION GYMN03H 298.15
-1515274+618*T-105.4*T*LN(T)+0.017*T**2+669185*T**(-1);
FUNCTION GYMN205 298.15
+GYMNO3H+0.5*GMN2O3+0.5*GHSEROO-100383+62.2*T;
FUNCTION GZYO 298.15
+0.4286*GFFZRO2+0.5714*GCCYO15-15900+1*T;
FUNCTION RTLNP 298.15 +8.31451*T*LN(1E-05*P); 6000 N !
FUNCTION F12026T 298.15 +422273.955-30.3347881*T-22.06299*T*LN(T)-0.005444405*T**2
+4.71447833E-07*T**3+102710.1*T**(-1);
FUNCTION F12026T 298.15
+426628.905-85.4786162*T-13.83676*T*LN(T)-0.011938995*T**2
+1.33826017E-06*T**3+2891891*T**(-1);
FUNCTION F12026T 298.15
+404460.17+114.016725*T+4226046*T*LN(T)+0.0037094435*T**2
-2.70261E-07*T**3+2891891*T**(-1);
FUNCTION F12026T 298.15
+497751.747+246.085237*T+2.791973*T*LN(T)-0.006002155*T**2
+1.30043383E-07*T**3+34158815*T**(-1);
FUNCTION F12026T 298.15
-92343.0441+773.338363*T-111.0188*T*LN(T)+0.0037862445*T**2
-2.82257667E-08*T**3+5.418475E+08*T**(-1);
10000 N!

$LaO(g)$

FUNCTION F12049T

298.15  \(-1.31496.968-24.5469483*T-31.53764*T*LN(T)-0.0051956*T**2\)
+7.6044233E-07*T**3+103677.85*T**(-1); 
900 Y -133112.849+7.93847638*T-36.65559*T*LN(T)+2.4937065E-04*T**2
-2.0568333E-07*T**3+5676870*T**(-1);
2500 Y -137735.323-23.9414477*T-31.58251*T*LN(T)-0.003177688*T**2
+6.84986667E-08*T**3+103677.85*T**(-1);
5400 Y -39118.6731-213.786313*T-10.21743*T*LN(T)+9.162985E-08*T**2
+9.162985E-08*T**3+103677.85*T**(-1);

$La2O(g)$

FUNCTION F12085T

298.15  \(-69316.3279+46.9195461*T-51.12563*T*LN(T)-0.005701935*T**2\)
+8.637425E-07*T**3+103677.85*T**(-1); 
1000 Y -73167.5826+93.9280358*T-58.13034*T*LN(T)+4.41584333E-10*T**2
-2.0568333E-07*T**3+103677.85*T**(-1);
6000 N!

$La2O2(g)$

FUNCTION F12089T

298.15  \(-64253.065+54.8487791*T-51.72813*T*LN(T)-0.0048452875*T**2\)
+4.99643833E-06*T**3+271002.95*T**(-1); 
700 Y -657497.385+256.452173*T-82.32033*T*LN(T)-1.8245965E-04*T**2
+0.0013469965*T**3+11187120*T**(-1);
5100 Y -672122.137+293.83814*T-85.09706*T*LN(T)+6.16730*T**(-1);

$Mn(g)$

FUNCTION F12439T 298.15  \(+27616.054-34.4987547*T-20.786*T*LN(T);\)
1575.00 Y +275547.585-29.2480566*T-21.52064*T*LN(T)
+3.819474E-04*T**2-3.66030333E-08*T**3+95180.95*T**(-1); 
2100.00 Y +274521.741-16.3844926*T-23.35302*T*LN(T)
+0.0013469965*T**2+1.18903067E-07*T**3;
2400.0 N!

$MnO(g)$

FUNCTION F12454T 298.15  \(+151356.092-24.1662496*T-31.02229*T*LN(T)\)
-0.00519525*T**2+8.47063667E-07*T**3+95180.95*T**(-1); 
900.00 Y +146503.882+29.4389965*T-38.90434*T*LN(T)
+4.8722855E-04*T**2-5.46958333E-08*T**3+687003.5*T**(-1); 
4100.00 Y +163891.797+1.24225715*T-35.94693*T*LN(T)
+6.220655E-04*T**2-7.949125E-08*T**3-12461235*T**(-1);
6000.0 N!

$MnO2(g)$

FUNCTION F12461T 298.15  \(+9095.11807-9.18675027*T-36.92694*T*LN(T)\)
-0.01944391*T**2+3.43552E-06*T**3+201368.45*T**(-1); 
700.00 Y +4061.05468+167.414546*T-63.68895*T*LN(T)
+0.004964408*T**2-7.80481667E-07*T**3+1423101*T**(-1); 
2000.00 Y +74138.9718-312.782575*T+1646534*T*LN(T)
-0.1801756*T**2+7.59669E-07*T**3-16355180*T**(-1);
Appendix

\[
3900.00 \text{ Y } -269662.307+860.503282*T-143.1466*T*LN(T) \\
+0.008591745*T**2-1.67854167E-07*T**3+1.388169E+08*T**(-1); \\
6000.00 \text{ N }
\]

$O(g)$:
FUNCTION F7397T 298.15 +243206.529-42897.0876*T**(-1)-20.7513421*T \\
-17.2118798*T*LN(T)-5.41356254E-04*T**2+7.64520703E-09*T**3; \\
6000.00 \text{ N }

$O3(g)$:
FUNCTION F7683T 298.15 +133772.042-11328.9959*T**(-1)-84.8602165*T \\
-51.8410152*T*LN(T)-0.039201569*T**2+120.679664*T**3; \\
1500.00 \text{ Y }

$Y(g)$:
FUNCTION F14722T 298.15 +413926.156+43.942359*T-34.19791*T*LN(T) \\
+0.0122297*T**2+7.90727187E-06*T**3; \\
700.00 \text{ Y }

$Y20(g)$:
FUNCTION F12945T 298.15 -18834.6011+47.2728187*T-49.14357*T*LN(T) \\
-0.007582635*T**2+1.20676-0.06*T**3+211591.5*T**(-1); \\
900.00 \text{ Y }

$Y0(g)$:
FUNCTION F12929T 298.15 -55980.1334-24.7804591*T-39.58571*T*LN(T) \\
-0.005797885*T**2+9.040075E-07*T**3+9295.75*T**(-1); \\
900.00 \text{ Y }

$Y2O2(g)$:
FUNCTION F13270T 298.15 -57573.712+51.4042333*T-49.55549*T*LN(T) \\
-0.030210885*T**2+5.2779667E-06*T**3+255509.3*T**(-1);
Description of La–Mn–Y–Zr–O

700.00 Y -591679.029+265.724012*T-82.06371*T*LN(T)
-2.6169375E-04*T**2+1.095265E-08*T**3+1742125.5*T**(-1);
4500.00 Y -594803.763+277.512452*T-83.52789*T*LN(T)
+4.9195245E-05*T**2-1.17628333E-09*T**3+3139224*T**(-1);
6000.00 N !

\$ \text{YO}_2(g)
\text{FUNCTION F13266T 298.15 -453353.172+38.0172466*T-44.87379*T*LN(T)
-0.011836705*T**2+2.00650833E-06*T**3+281931.45*T**(-1);
800.00 Y -459941.788+124.969156*T-58.0167*T*LN(T)
+4.9195245E-05*T**2-1.17628333E-09*T**3+3139224*T**(-1);
6000.00 N !

\$ \text{Gas Zr}
\text{FUNCTION GZRGAS 298.15 +586876.841+74.4171195*T-38.69111*T*LN(T)
+0.01152846*T**2-1.693255E-06*T**3+270638.8*T**(-1);
700.00 Y +595990.293-26.0530509*T-24.06106*T**LN(T)
+0.001743641*T**2-5.94312333E-07*T**3+749847.5*T**(-1);
1300.00 Y +593841.673-46.0204551*T-20.46361*T**LN(T)
-0.002961084*T**2+1.08391433E-07*T**3+526352.5*T**(-1);
2700.00 Y +630745.052-161.965371*T-6.647343*T**LN(T)
-0.0046738955*T**2+1.06833583E-07*T**3-15872340*T**(-1);
6000.00 N !

\$ \text{Gas Zr}_2 (ssub)
\text{FUNCTION F15702T 298.15 +892794.963-14.4120751*T-37.13672*T**LN(T)
-3.2039655*T**2-4.3065167E-09*T**3+85422.15*T**(-1);
3600.00 Y +874148.858+9.34917918*T-39.33356*T**LN(T)
-0.001019669*T**2-6.09799967E-08*T**3+14065805*T**(-1);
6000.00 N !

\$ \text{Gas ZrO (ssub)}
\text{FUNCTION F12964T 298.15 +84650.2479-322.816859*T+21.98592*T**LN(T)
-1.0713165*T**2+2.81704E-05*T**3-33363.5*T**(-1);
500.00 Y +42648.3264+404.464721*T-93.37933*T**LN(T)
+0.03332466*T**2-3.80849833E-06*T**3+2526299*T**(-1);
1100.00 Y +84838.707+11.527709*T-37.46259*T**LN(T)
+9.16682E-05*T**2-7.005105E-08*T**3-3491878*T**(-1);
4100.00 Y +106867.647-98.6658671*T-23.49987*T**LN(T)
-0.00315689*T**2+5.93994E-08*T**3-6661880*T**(-1);
9600.00 Y +255442.536-262.961955*T-6.281221*T**LN(T)
-0.0038787795*T**2+6.18786667E-08*T**3-2.24669256+08*T**(-1);
10000.00 N !

\$ \text{Gas ZrO}_2 (ssub)
\text{FUNCTION F13281T 298.15 -332610.845+3.22325893*T-38.10718*T**LN(T)
-0.01852473*T**2+3.29626E-06*T**3+2187210.5*T**(-1);
700.00 Y -342836.09+140.579945*T-58.93983*T**LN(T)
+6.65405E-04*T**2-8.1181216E-08*T**3+1173742*T**(-1);
2600.00 Y -272800.105-96.5265444*T-30.24766*T**LN(T)
-0.0038011495*T**2+1.83201667E-11*T**3-2.8436635*T**(-1);
4900.00 Y -36436.152-803.246487*T-54.45089*T**LN(T)
-0.017172935*T**2+3.92562833E-07*T**3-1.509956E+08*T**(-1);
Appendix

6000.00 N!

$
Curriculum Vitae

Personal
Name: Ming CHEN
Date and Place of Birth: June 30, 1973, Jiangsu, China
Nationality: China

Education
January 2001 – Present
Ph.D. Study at the Institute of Nonmetallic Inorganic Materials, Department of Materials, Swiss Federal Institute of Technology Zurich (ETH Zurich), Zurich, Switzerland
Thesis: “Understanding the Thermodynamics at the LaMnO₃–YSZ Interface in SOFC”
Supervisors: Professor Dr. Ludwig J. Gauckler and Dr. Bengt Hallstedt

September 1996 – June 1999
Master Study at Shanghai Institute of Ceramics, Chinese Academy of Sciences (SICCAS), Shanghai, China
Thesis: “Study on Tape-Casting Electrolyte Membranes for SOFCs”
Supervisor: Professor Dr. Ting-Lian Wen
MS in Material Science, SICCAS, July 1999

Undergraduate Study at University of Science and Technology of China (USTC), Hefei, Anhui, China
Supervisor: Professor Shu-Fen Li
BS in Chemical Physics, USTC, July 1996

High School Study at Gaoyou Middle School, Gaoyou, Jiangsu, China
Publications

1. Ming Chen, Bengt Hallstedt, and Ludwig J. Gauckler,
   “Thermodynamic Assessment of the Co–O System”,

2. Ming Chen, Bengt Hallstedt, A. Nicholas Grundy, and Ludwig J. Gauckler,
   “CeO₂–CoO Phase Diagram”,

3. Ming Chen, Bengt Hallstedt, and Ludwig J. Gauckler,
   “Thermodynamic Modeling of the ZrO₂–YO₁₅ System”,

4. Ming Chen, Bengt Hallstedt, and Ludwig J. Gauckler,
   “Thermodynamic Assessment of the Mn–Y–O System”,

5. A. Nicholas Grundy, Ming Chen, Bengt Hallstedt, and Ludwig J. Gauckler,
   “Assessment of the La–Mn–O System”,

6. Ming Chen, Bengt Hallstedt, and Ludwig J. Gauckler,

7. Ming Chen, Bengt Hallstedt, and Ludwig J. Gauckler,
   “CALPHAD Modeling of the La₂O₃–Y₂O₃ System”,

8. Ming Chen, Bengt Hallstedt, and Ludwig J. Gauckler,
   “Thermodynamics and Phase Equilibria in the ZrO₂–LaO₁₅ System”,
   to be submitted.

9. Ming Chen, A. Nicholas Grundy, Bengt Hallstedt, and Ludwig J. Gauckler,
   “Thermodynamic Modeling of the La–Mn–Y–Zr–O System”,
   to be submitted.

10. Ming Chen, Bengt Hallstedt, and Ludwig J. Gauckler,
    “Evaluation of the Thermodynamics of La₂Zr₂O₇ Formation”,
    to be submitted.

11. Ming Chen, A. Nicholas Grundy, Bengt Hallstedt, and Ludwig J. Gauckler,
“Understanding the Thermodynamics at the LaMnO$_3$–YSZ Interface”,
to be submitted.

Conference presentations

1. CALPHAD XXXI, Stockholm, Sweden, May 5–11, 2002,
   “Thermodynamic Assessment of the Co–O System” (contributed talk).
2. CALPHAD XXXII, Quebec, Canada, May 25–30, 2003,
   “Thermodynamic Modeling of the ZrO$_2$–Y$_2$O$_3$ System” (contributed talk).
3. CALPHAD XXXIII, Krakow, Poland, May 30–June 4, 2004,
4. GRC on High Temperature Materials, Processes & Diagnostics, Waterville, ME, USA,
   August 1–6, 2004,
   “Thermodynamic Modeling of the ZrO$_2$–Y$_2$O$_3$ System” (poster).
5. International Conference on Chemical Thermodynamics (ICCT-2004), Beijing, China,
   August 17–21, 2004,
   “CALPHAD Modeling of the ZrO$_2$–Y$_2$O$_3$ System” (contributed talk).
6. Thermodynamics 2005, Sesimbra, Portugal, April 6–8, 2005,
   “Understanding the Thermodynamics at the SOFC Cathode–Electrolyte Interface”
   (poster).