Doctoral Thesis

Thermodynamic optimization of the Ag-Bi-Sr-Ca-Cu-O system and application to the processing of Bi-2212 with silver

Author(s):
Assal, Jérôme

Publication Date:
1998

Permanent Link:
https://doi.org/10.3929/ethz-a-002030274

Rights / License:
In Copyright - Non-Commercial Use Permitted
Thermodynamic Optimization
of the Ag–Bi–Sr–Ca–Cu–O System
and Application to the Processing
of Bi-2212 with Silver

A dissertation submitted to the
SWISS FEDERAL INSTITUTE OF TECHNOLOGY
ZURICH

for the degree of
Doctor of Technical Science

presented by
Jérôme Assal
Dipl. Ing. EPFL
born on April 4, 1970
citizen of Treytorrens, VD

accepted on the recommendation of
Prof. Dr. L. J. Gauckler, examiner
Prof. Dr. P. Uggowitzer, co-examiner
Dr. B. Hallstedt, co-examiner

Zürich 1998
Acknowledgments

I wish to thank

Prof. L. J. Gauckler for this interesting project at the crossing of thermodynamics modeling and high-temperature superconducting materials. Prof. L. J. Gauckler also gave me many opportunities to present my work at international conferences, which I am grateful for.

Dr. B. Hallstedt for his very helpful teaching. His patience and great insight have enhanced both this work and my knowledge of thermodynamic modeling.

Prof. G. Bayer for significant improvements in the quality of this manuscript.

Dr. D. Risold, Dr. Th. Lang, Dr. D. Buhl, D. Schneider and S. Köbel for their many helps as well as for interesting discussions on the experimental aspects of the processing of superconducting materials.

other colleagues and co-workers at the Chair of Nonmetallic Materials for their various help and the very good time spent at the office as well as outside the office.

my family and my friends who encouraged me continuously and, sometimes, enthusiastically during these years.

COST 512 (Modeling in Materials Science and Processing), the Swiss National Science Foundation (NFS) and the Swiss Federal Institute of Technology (ETHZ) for their financial support.
# Table of content

Abstract / Zusammenfassung ......................................................... 5 / 6
Aim of the Study ................................................................. 7

## Chapter 1  Calculation of Phase Diagram

1.1 Overview: The CALPHAD Method ............................................. 10
1.2 Thermodynamic Modeling in Heterogeneous Systems ............... 12
   1.2.1 General Considerations ............................................. 12
   1.2.2 Ionic Solid Solutions .............................................. 13
   1.2.3 The Liquid Phase .................................................. 14
   1.2.4 Thermodynamic Optimization ..................................... 15
1.3 Conclusion .................................................................. 19
1.4 References ............................................................... 19

## Chapter 2  Substrate Materials for Superconductors

2.1 Overview ................................................................ 24
2.2 Influence of Silver on the Bi–Sr–Ca–Cu–O System .................. 25
2.3 Conclusion ................................................................ 29
2.4 References ............................................................... 30

## Chapter 3  Thermodynamic Study and Sintering in
the Mg–Cu–O System

3.1 Introduction ................................................................ 33
3.2 The Mg–Cu–O System .................................................... 34
3.3 Sintering of (Mg,Cu)O Powder Compacts ......................... 50
3.4 Conclusion ................................................................ 52
3.5 References ............................................................... 52
Abstract

This study presents a consistent thermodynamic description of the Ag–Bi–Sr–Ca–Cu–O (ABSCCO) system suitable for phase diagram calculations. Every phase of the system is modeled with its Gibbs energy and parameters are optimized based on both phase diagram data and thermodynamic data. This consistent method, which is known as the CALPHAD method, is described in the first chapter of this work.

The Bi–Sr–Ca–Cu–O (BSCCO) system contains three high-temperature superconducting phases (HTSC), i.e. the one-layer compound (1101), the two-layer compound (2212) and the three-layer compound (2223). HTSC have to be processed in the partially molten state in order to obtain high current densities. The choice of silver as the most adapted substrate for Bi-based HTSC is discussed in Chapter 2. MgO or CuO-doped MgO are also promising substrates when the substrate has to be an insulating material. The thermodynamic optimization of the Mg–Cu–O system and a discussion on results on (Mg,Cu)O sintering are given in Chapter 3.

Using the CALPHAD method, we extend the existent database by adding Ag to the BSCCO system. Experimental data are reviewed, phases are modeled and parameters are optimized in the Ag–O, Ag–Bi–O, Ag–Cu–O, Ag–Sr–Cu–O and Ag–Ca–Cu–O systems, as well as in the ABSCCO system around the 2212 compound, in Chapter 4. Silver is not incorporated in any solid phases of the BSCCO system, especially not in the superconducting 2212 and 2223 compound. For this reason, the modeling and the optimization focus on the liquid phase. The observed decrease of the melting temperature of 2212 by Ag addition is modeled in very good agreement, as well as the eutectic transformation between Ag and 2212.

In the last chapter we compare the calculations with the results obtained on partial melt-processing of 2212 thick films on silver substrates and of 2212 bulk material. The reactions are rather complex since equilibria in regard to the oxygen content and in regard to the cation redistribution are not always reached. Calculations agree, however, rather well with the partial melt-processing results. Further investigations on the possible existence of a miscibility gap in the oxide liquid are needed, as well as the extension of the system to Pb, which is used to stabilize the 2223 compound.

Zusammenfassung

Diese Studie stellt eine konsistente thermodynamische Beschreibung des Systems Ag–Bi–Sr–Ca–Cu–O (ABSCCO) vor, welche für Berechnungen von Phasendiagrammen verwendet wird. Jede Phase des Systems wird mittels der Gibbs Energie geschrieben, deren Parameter sowohl bezüglich experimenteller Phasendiagramme als auch thermodynami-
scher Eigenschaften optimiert werden. Diese in sich konsistente Methode, die als die CALPHAD-Methode bekannt ist, wird im ersten Kapitel dieser Arbeit vorgestellt.

Das System Bi–Sr–Ca–Cu–O (BSCCO) enthält drei hochtemperatursupraleitende Phasen (HTSC), den Einschichter (11905), den Zweischichter (2212) und den Dreischichter (2223). Die HTSC müssen im partiellen Schmelzzustand verarbeitet werden, um hohe spezifische Stromdichten zu erzielen. Die Wahl des Silbers als angepaßtestes Substrat an die Bi-basierten hochtemperatursupraleitenden Phasen wird im Kapitel 2 behandelt. Vielverprechende isolierende Substrate sind zum Beispiel MgO oder auch CuO-dotierte MgO. Die thermodynamische Optimierung des Mg–Cu–O Systems und die Anwendung der Optimierung auf den Sinterprozess von (Mg,Cu)O Pulver werden im Kapitel 3 beschrieben.

Mit der CALPHAD-Methode dehnen wir die bestehende BSCCO Datenbank aus, indem wir das Element Silber hinzufügen. In Kapitel 4 werden die experimentellen Daten zusammengefaßt, die Phasen modelliert und die Parameter in den Systemen Ag–O, Ag–Bi–O, Ag–Cu–O, Ag–Sr–Cu–O und Ag–Ca–Cu–O sowie im ABSICO System um die 2212-Phase Zusammensetzung optimiert. Silber befindet sich in keiner festen Oxidphase des BSCCO-Systems, insbesondere nicht in den supraleitenden 2212- und 2223-Phasen. Deshalb werden die Modellierung und die Optimierung an der Schmelzphase vorgenommen. Sowohl für die Abnahme der Schmelztemperatur von 2212-Phase durch Zufügung von Ag als auch für die eutektische Transformation zwischen Ag und 2212-Phase wird eine gute Übereinstimmung mit den experimentellen Daten erzielt.

**Aim of the study**

Since the discovery of the superconductivity of mercury at 4.2 K in 1911, there is a continuing, strong interest in compounds showing higher critical temperature ($T_c$). In spite of intensive research the highest known $T_c$ remained at a modest 30 K in certain alloys of niobium. With the discovery of cuprates with high $T_c$, a new class of materials came into focus and the research on superconducting materials exploded. Shortly afterwards, Maeda et al. found a compound with $T_c$ above 100 K in the Bi–Sr–Ca–Cu–O system.

*Evolution of the critical temperature $T_c$ with time from 1911 up to now.*

It turned out that this system contains several superconducting phases with critical temperatures ranging from 30 K to 110 K. There are the one layer compound Bi$_{11}$Sr$_9$Cu$_5$O$_x$ (11905) with $T_c = 30$ K, the two layer compound Bi$_2$Sr$_2$CaCu$_2$O$_y$ (2212) with $T_c = 95$ K, and the three layer compound Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_z$ (2223) with $T_c = 110$ K. The two latter compounds show superconductivity above the boiling point of nitrogen at 77 K and are therefore of interest for industrial applications.

For practical applications not only a high $T_c$ is important, but even more important is a high critical current density. In order to achieve high current density below $T_c$, these compounds have to be processed in the partially molten state. For many shapes of the compounds, whether film or wire, the substrate or sheath material is silver. Silver has been chosen among other metals or oxide ceramic materials, because it exhibits attractive prop-

erties such as high-temperature chemical stability, high oxygen diffusivity, and high ductility with adequate mechanical stability. In contrast to most other metals, silver is not incorporated into the 2212 and 2223 compounds and, thus, does not cause any detrimental effects on the superconducting properties. During partial-melt processing, silver dissolves into the oxide liquid and lowers the melting temperatures of 2212 by about 30 K. MgO is also considered as a promising substrate material for these superconductors since it does not influence the 2212 chemistry. In order to improve the sintering of MgO, CuO is used as dopant. This also prevents copper oxide from 2212 to dissolve into the MgO substrate.

Due to the complexity of the Ag–Bi–Sr–Ca–Cu–O system, and due to the many variables influencing the phase stability, i.e. composition, oxygen partial pressure, temperature, total pressure, processing time, cooling rates, an extremely large amount of experimental data would be necessary to completely study the phase equilibria of this system. Experimental results of the phase relations of such high a component system are moreover difficult to overview and to analyze.

A complete description of the thermodynamics in the Ag–Bi–Sr–Ca–Cu–O system is therefore desirable. The CALPHAD method allows to build databases for such complex systems, where the Gibbs energy of each phase is modeled. The phases of the lowest order systems have to be described first, the final system is reached by adding the elements one by one. The result is a consistent thermodynamic description of the Ag–Bi–Sr–Ca–Cu–O system. The description can e.g. be used as a guideline for the processing of 2212 compound on silver substrate. The Mg–Cu–O system was also consistently modeled and can help to understand the mechanisms and to improve the sintering of CuO doped MgO.
Chapter 1

Calculation of Phase Diagram
1.1 Overview: The CALPHAD Method

Phase diagrams show the phase stability domains graphically and are direct representations of the thermodynamic properties. Already at the beginning of the 1900's thermochemists, among them Van Laar, realized this connection. The understanding of thermochemistry at this time, however, did not allow them to demonstrate the practical possibilities. In the early fifties Meijering successfully conducted a theoretical and experimental treatment in binary and ternary systems, see the review of Meijering's works by Kaufman [81Kau].

A new impulse in the calculation of phase diagrams came with the advent of the computers. In 1970 Kaufman and Bernstein published the first computed phase diagrams, and initiated the calculation of phase diagrams as a research activity in itself [70Kau]. Seven years later the CALPHAD (CALculation of PHase Diagrams) conference and the journal which are devoted to the interrelation of phase diagrams and thermochemical properties were founded [77Kau]. Since then the scientific community has extended and further developed thermodynamic models and calculation methods, leading to several software packages and thermodynamic databases, as reviewed by Bale and coauthors [90Bal, 93Bal]. In the following figure a brief overview of the CALPHAD method is given.

**Figure 1.1: General principle of the CALPHAD method.**

In order to establish a database describing a system, the first stage is the description of each known phase \( \Phi \) by its Gibbs energy, \( G^{\Phi}(x_i,T) \), as function of temperature and composition. The choice of the model is determined by structural information such as the existence of sublattices, their numbers and occupancies and by phase diagram information on solution ranges. Adjustable parameters, which represent enthalpies and entropies of formation and mixing, are introduced in the Gibbs functions.

The second stage consists in the optimization of the adjustable parameters. First, experi-
mental data are "extracted" from the literature or are obtained from own experimental work when needed. One of the main problems here is the correct description of the experimental conditions and the evaluation of the measurements in terms of what was really measured and how accurate. Different sets of measurements can be given different weights of confidence. Adjustable parameters in the Gibbs functions are optimized by fitting thermodynamic and phase diagram experimental data. This procedure itself is in principle relatively easy but contradictions between experimental data, poor measurements, or lack of data can make it rather complex in practice. When the parameters are satisfactorily optimized in a defined system, one may speak of an optimized thermodynamic database.

The use of the same energy reference state for the elements suggested by the Scientific Group Thermodata Europe (SGTE) [91Din], as well as compatible thermodynamic models, led to important developments. In thermodynamic databases of multicomponent systems, e.g. for complex materials like steel, several groups have been working in parallel and standards were needed in order to make the different phase descriptions compatible.

The optimized thermodynamic data and phase diagrams may be used to critically assess the experimental data and can even lead to the rejection of some of them. A completely optimized system can also be used as guideline for the processing of materials, as well as for the development of new materials, as shown in Figure 1.2. In Chapter 5, we will compare the calculation of phase equilibria in the Ag–Bi–Sr–Ca–Cu–O system with results obtained from melt-processing of the 2212 compound with silver.

Figure 1.2: Application of a thermodynamic database.

A major limitation of the CALPHAD method is that it cannot predict any new phases. As mentioned above, the existence of each phase has to be known as well as a minimum of experimental data which allow its description. Another possibility to obtain phase equilibria is to use first-principle methods. These are based on calculations of the electronic energy distribution on the atomic scale. They are able in some cases to predict new phases in good agreement with experiments. Examples of these methods are reviewed by Wim-
However, the very high relative accuracy needed for phase diagram calculations and materials development and processing cannot be reached yet. Also, complex phases, like 2212, cannot be realistically treated with today’s first-principle methods.

1.2 Thermodynamic Modeling in Heterogeneous Systems

1.2.1 General Considerations

Thermodynamics describes the stability of phases, as functions of macroscopic variables like temperature, total pressure and chemical composition. In most cases the temperature, the total pressure and the chemical composition can be controlled and the description using Gibbs functions is thus appropriate. In this work, we describe the Gibbs energies of the phases as functions of temperature and composition. The pressure variable is not taken into account since all calculations are performed using $P = 1$ bar. The superconducting transitions in the Bi–Sr–Ca–Cu–O system are much below the temperatures we are interested in and, therefore, are already included in the enthalpies and entropies at 298 K.

**Temperature dependence**

The Gibbs energy of a stoichiometric phase is a function of the temperature only. The specific heat at constant pressure, $c_p$, which is defined for temperatures above 298 K, is well represented by the polynomial:

$$c_p = -c - 2dT - 6eT^2 - 2fT^{-2} \quad (1.1)$$

where $-c$ comes from the harmonic lattice vibrations, $d$ and $e$ are due to the anharmonic and electronic corrections respectively, and $f$ is a correction term for lower temperatures.

The Gibbs energy can be obtained by integrating $c_p$ from the reference state (298 K) to the desired temperature $T$:

$$G = H - TS = \int_{298}^{T} c_p \, dT$$

According to the standards prescribed by SGTE [87Ans, 91Din] the Gibbs energy of a stoichiometric phase $\Phi$ is referred to the enthalpy of the elements $i$ at 298 K (SER reference state) and to the entropy at 0 K. The Gibbs energy can be written as:

$$G^\Phi_i(T) - H^\text{SER}_i(298.15 \text{ K}) = a + bT + cT \ln(T) + dT^2 + eT^{-1} + fT^3 + jT^7 + kT^{-9} \quad (1.3)$$

The $T^7$ and $T^{-9}$ terms describe $G$ in metastable states, i.e. the liquid below the melting point and the solid above the melting point, respectively. They are sometimes used to
avoid that a liquid phase becomes stable below the melting point or a solid phase above
the melting point. They allow a smooth change of $c_p$ across the melting for both phases.

Composition dependence

When considering an ideal solution of $i$ components, the Gibbs energy of mixing, $G_m^{ideal}$, can be written as:

$$G_m^{ideal} = \sum x_i G_i^\Phi + RT \sum x_i \ln x_i$$

(1.4)

where $x_i$ is the mole fraction of component $i$. The term $RT \sum x_i \ln x_i$ is the contribution due to configurational entropy and $R$ is the universal gas constant. Equation 1.4 describes the case of ideal solutions. However, in real solutions, interactions between the species give rise to deviations from the ideal Gibbs energy. These deviations are taken care by the excess term, $E G_m$, which, in case of a simple A–B solution, can be written as a Redlich-Kister series:

$$E G_{AB} = x_A x_B \sum_{\nu=0}^{\nu} L_{AB}^{(\nu)} (x_A - x_B)^\nu$$

(1.5)

The interaction parameters $L_{AB}^{(\nu)}$ characterize the Gibbs energy of mixing. The first term of the series is $x_A x_B L_{AB}$ that is a regular solution parameter based on random mixing. Furthermore, each $L$ term can be written as the sum of an enthalpy and entropy of mixing, i.e. $L = a + bT$.

Phases which do not have very strong interactions can be described with this formalism. Long-range order can be treated by a similar formalism, which is an extension to two (or more) sublattices, developed in the next paragraph. The special case of the liquid phase is treated separately in the Paragraph 1.2.3.

1.2.2 Ionic Solid Solutions

The regular solution formalism developed in the previous section cannot model long-range order observed frequently in ionic solid solutions. Then a modification of this approach can be used which employs the concept of sublattices. A sublattice can represent any type of interstitial site, as well as the cationic site in a ionic solution for example, or any specific site in an ordered phase. The number of sublattices and their occupancy are derived directly from crystallographic data. The Gibbs energy for one mole formula unit of a phase with $n$ sublattices and $i_k$ species on sublattice $k$ is given by an expression of the type:

$$G_m = \sum_{i_1} \cdots \sum_{i_{n}} y_{i_1} \cdots y_{i_n} G_{i_1 \cdots i_n} - TS^{ideal} + E G_m$$

(1.6)
where $y_{i,k}$ is the site fraction of $i$, i.e. the mole fraction of $i$ in a given sublattice $k$. This formalism is called the Compound Energy Model (CEM) [86And], and allows a large flexibility in the treatment of multicomponent and multisublattice phases.

### 1.2.3 The Liquid Phase

The thermodynamic properties of liquids can be very different. Therefore, many models have been developed to describe different types of liquids. One recurrent problem to describe liquids of many systems, including the oxide systems, is the strong short-range ordering which is present even at temperatures above the melting point. Several models can describe such liquids with short-range order. One of them is the two-sublattice model for ionic liquids [85Hil, 91Sun] and the associated solution model (see Rannikko [95Ran]).

The associated solution model is particularly adapted to describe liquids with a strong negative deviation from ideality. The highly negative enthalpy suggests that there is formation of molecular associates in the liquid, even in cases without any experimental evidence. In the liquid phase of the Ag–Cu–O system for example, the associates are based on the existing solid compounds, i.e. $\text{Ag}_2\text{O}$, $\text{Cu}_2\text{O}$, and $\text{CuO}$, as well as on the two metallic elements Ag and Cu, see Section 3.3. In the general case, the Gibbs energy is then described by:

$$G_m^{\text{liq}} = \sum_i y_i G_i^{\text{liq}} + RT \sum_i y_i \ln y_i + \sum_{i,j} y_i y_j L_{i,j}$$

where $y_i$ are the fractions of the different associates. $L_{i,j}$ are the interaction energies between the associates $i$ and $j$. As the number of interaction parameters involving two associates increases with the square of the number of associates, the model can become rather difficult to handle in high-order systems. The use of the associated solution model is recommended for rather low-order systems with strong short-range ordering. In this study, the need for a more flexible model which allows a high degree of extrapolation, and which is consistent with the existing BSCCO database [96Ris] leads us to use the two-sublattice model for ionic liquids.

The two-sublattice model was developed by Hillert et. al. [85Hil] and Sundman [91Sun]. Based on the real or postulated behavior of the components, it assumes that cations can mix on a formal sublattice, and anions can mix on another formal sublattice. In order to describe the total compositional range in an oxide liquid, hypothetical vacancies with a negative charge are introduced in the anionic sublattice. These purely formal species $V_a^{-q}$ allow the model to describe the liquid phase continuously from the oxide-rich compositions to metallic compositions. The liquid phase of the Ag–Bi–Sr–Ca–Cu–O system is then described as $(\text{Ag}^{1+},\text{Bi}^{3+},\text{Sr}^{2+},\text{Ca}^{2+},\text{Cu}^{1+},\text{Cu}^{2+})_p (\text{O}^{2-},\text{V}_a^{-q})_q$ where $p$ and $q$ vary with composition in order to maintain electroneutrality. In this case, $p$ and $q$ are given by:

$$p = 2y_{\text{O}^{2-}} + q y_{\text{V}_a}$$

(1.8)
\[ q = y_{Ag^{+}} + 3y_{Bi^{3+}} + 2y_{Sr^{2+}} + 2y_{Ca^{2+}} + y_{Cu^{2+}} + 2y_{Cu^{2+}} \]  

(1.9)

The Gibbs energy of 1 mole liquid can be written for the general case:

\[
G_{m}^{\text{liq}} = \sum_{i = \text{cations}} q_{i} y_{i} y_{Va}^{\text{liq}} G_{i;Va}^{\text{liq}} + \sum_{i = \text{cations}} y_{i} y_{O^{2-}}^{\text{liq}} G_{i;O^{2-}}^{\text{liq}} + \frac{RT}{2} \left( \sum_{i = \text{cations}} p y_{i} \ln y_{i} + \sum_{j = \text{anions}} q y_{j} \ln y_{j} \right) + E_{G_{m}^{\text{liq}}} \]  

(1.10)

where the \( G_{i;Va}^{\text{liq}} \) are the Gibbs energy of the pure elements, and \( G_{i;O^{2-}}^{\text{liq}} \) of the pure oxide species. The colon is used to distinguish the two sublattices. The excess term \( E_{G_{m}^{\text{liq}}} \) is the sum of all contributions due to interactive parameters of the subsystems, and can be written as:

\[
E_{G_{m}^{\text{liq}}} = \sum_{i_{1} = \text{cations}} \sum_{i_{n} = \text{cations}} y_{i_{1}} \cdots y_{i_{n}} \cdot \sum_{j_{1} = \text{anions}} \sum_{j_{n} = \text{anions}} y_{j_{1}} \cdots y_{j_{n}} L_{i_{1},i_{2}, \ldots,i_{n};j_{1},j_{2}, \ldots,j_{n}} \]  

(1.11)

where a comma "\," is used between interacting species and a colon "\:" between species in different sublattices. Each interaction parameter can be expanded in a Redlich-Kister formalism. For \( L_{A^{+};B^{+};C^{-}} \) we can then write:

\[
L_{A^{+};B^{+};C^{-}}^{(v)} = \sum_{y = 0}^{(v)} L_{A^{+};B^{+};C^{-}}^{(y)} (y_{A^{+}} - y_{B^{+}})^{y} \]  

(1.12)

The largest contributions to the \( L \) term come from the binary subsystems since it is more probable that two species \( A^{2+} \) and \( C^{2-} \) interact predominantly, i.e. that two species are first neighbors, instead of three or more. The contributions from higher order system are further considered in this study but their influences on the deviation from the regular solution model are rather small.

### 1.2.5 Thermodynamic Optimization

**Experimental input**

Following the CALPHAD method (see Figure 1.1) the first step in the thermodynamic optimization concerns the experimental input. Experimental methods used to investigate the phase diagrams and the thermodynamics are numerous, and are the object of many papers.
and books. We do not want to get into the details of these techniques, or even to list them, since they represent research areas of their own. Measurements of phase diagram are presented in [84Ips,94Mor] and experimental techniques for thermodynamics are reviewed in [83Kom,90Pra,93Kub].

As mentioned in Section 1.2.2, crystallographic data are of very great help for the modeling of the solid phases. The superconducting compounds have been intensively studied by neutron and X-ray powder diffraction techniques in order to understand the phenomenon of superconductivity. The 2212 compound, which has a complex layered structure (see Figure 1.3) has been studied by many authors, e.g. [88Sun,89Bor,96Gla,96Gre].

Figure 1.3: Structure of the Bi$_2$Sr$_2$CaCu$_2$O$_y$ compound [89Bor].

Using this information, the 2212 compound can be modeled as:

$$(\text{Bi}^{3+},\text{Bi}^{5+})_2(\text{Sr}^{2+},\text{Ca}^{2+},\text{Bi}^{3+})_2(\text{Ca}^{2+})_1(\text{Cu}^{2+},\text{Cu}^{3+})_2(\text{O}^{2-})_8(\text{O}^{2-},\text{Va})_{1/3}$$

where each bracket represents one sublattice. The substitutions shown are only the most important ones and the model is, thus, a simplification. The first sublattice takes into account the mutual existence of Bi$^{3+}$ and Bi$^{5+}$. The second sublattice describes the partial substitution of Ca$^{2+}$ and Bi$^{3+}$ for Sr$^{2+}$. The fourth sublattice models the copper site, that contains Cu$^{2+}$ and the more oxidized Cu$^{3+}$. The fifth sublattice represents the stoichiometric eight O$^{2-}$ sites, i.e. when the cation sites are filled by Bi$^{3+}$, Sr$^{2+}$, Ca$^{2+}$ and Cu$^{2+}$ respectively. The last sublattice, which contains oxygen and vacancies, takes into account the charge balance for the partial oxidation of Bi$^{3+}$ to Bi$^{5+}$ and Cu$^{2+}$ to Cu$^{3+}$ as well as for the partial substitution of Bi$^{3+}$ for Sr$^{2+}$. The number of extra sites for oxygen (1/3) does not come from crystallographic data but from measurements on the oxygen content.
Phase diagram data and results from thermodynamic measurements for a system have to be rewritten in a useful file. This is then compiled and used for the optimization of the thermodynamic parameters. In the following we give two examples of such transcriptions. One concerns the incongruent melting of 2212 with 10 wt-% silver into liquid and secondary solid phases in air as found by Majewski et. al. [97Maj] (see Table 1.1). The second refers to calorimetric \( c_p \) measurements of Ag\(_2\)O in the Ag–O system [5IKob] (see Table 1.2). According to the phase rule, we need 8 boundary conditions in case of the Ag–Bi–Sr–Ca–Cu–O system, and 4 for the Ag–O system.

**Table 1.1: Example of transcription of experimental data into the Parrot program of the Thermo-Calc package. The eutectic temperature of Bi\(_2\)Sr\(_2\)CaCu\(_2\)O\(_y\) + Ag (w\(_{Ag}\) = 10 wt-%) in air from Majewski et. al. [97Maj].**

<table>
<thead>
<tr>
<th>Experimental input</th>
<th>Explanations</th>
</tr>
</thead>
<tbody>
<tr>
<td>SET-REFERENCE</td>
<td>The reference for oxygen is air (O(<em>2) with ( P</em>{O_2} = 21278 ) Pa or 0.21 bar) at all temperatures (“*”). The other elements have the defined SER reference state.</td>
</tr>
<tr>
<td>O2GAS * 21278</td>
<td></td>
</tr>
<tr>
<td>CHANGE-STATUS PHASE</td>
<td>All phases are suspended (=not allowed to be present) in the equilibrium per default. 2212 is fixed (=must be present), but with 0 mole since it is melting. The oxide liquid and Ag (fcc) are entered (=present) since they are both stable. The secondary phases (01<em>1, 014</em>24, ...) are allowed to take part in the equilibrium. The gas is pure O(_2) (necessary to calculate the reference for oxygen) and is present as a “dormant” phase.</td>
</tr>
<tr>
<td>BI(_2)2212=FIX 0</td>
<td></td>
</tr>
<tr>
<td>FCC ION#2=ENTER 1</td>
<td></td>
</tr>
<tr>
<td>SRCUO2 SR14CU24O41 SR2CUO3</td>
<td></td>
</tr>
<tr>
<td>HALITE BI2SR306=ENTER 0</td>
<td></td>
</tr>
<tr>
<td>O2GAS=DORMANT</td>
<td></td>
</tr>
<tr>
<td>SET-CONDITION</td>
<td>The experimental conditions are now fixed: the total pressure is 1 bar, ( \mu(\frac{1}{2}O_2) = 0 ) (air), and silver content is 10 wt-%. The three next conditions fix the 2212 cationic stoichiometry used in the experiment, i.e. Bi(<em>{2})Sr(</em>{1.7})Ca(<em>{1})Cu(</em>{2})O(_y).</td>
</tr>
<tr>
<td>P=1E+05 MUR(O)=0 W(AG)=0.1</td>
<td></td>
</tr>
<tr>
<td>N(BI)=2.1 N(SR)=1.7</td>
<td></td>
</tr>
<tr>
<td>N(CA)=1.0 N(CU)=2.0</td>
<td></td>
</tr>
<tr>
<td>EXPERIMENT</td>
<td>Measured by DTA, the melting temperature of 2212 was 1136 K (with an error of 5 K). The silver content in the liquid, ( x_{Ag} = 0.054 ), was obtained by extrapolation and is relatively uncertain (error of 0.02).</td>
</tr>
<tr>
<td>T=1136:5</td>
<td></td>
</tr>
<tr>
<td>X(ION#2,AG)=0.054:0.02</td>
<td></td>
</tr>
</tbody>
</table>
Table 1.2: Example of transcription of experimental data into the Parrot program of the Thermo-Calc package. The heat capacity $c_p$ measurements of Ag$_2$O in air by Kobayashi [51Kob].

<table>
<thead>
<tr>
<th>Experimental input</th>
<th>Explanations</th>
</tr>
</thead>
<tbody>
<tr>
<td>SET-REFERENCE O 02GAS * 21278</td>
<td>The same reference for oxygen is used as in Table 1.1.</td>
</tr>
<tr>
<td>CHANGE-STATUS PHASE</td>
<td>As the $c_p$ measurements were performed on Ag$_2$O, this phase has to be fixed as 1 (mole). The O$_2$ gas is present as a &quot;dormant&quot; phase.</td>
</tr>
<tr>
<td>AG2O=FIX 1</td>
<td></td>
</tr>
<tr>
<td>O2GAS=DORMANT</td>
<td></td>
</tr>
<tr>
<td>SET-CONDITION</td>
<td>The total pressure is fixed to 1 bar, 9μ(1/2 O2) is 0 (air), and the temperature of the measurement is 317.6 K</td>
</tr>
<tr>
<td>P=1E+05 MUR(O)=0 T=317.6</td>
<td></td>
</tr>
<tr>
<td>EXPERIMENT</td>
<td>The heat capacity, $c_p$ (H.T stands for δH/δT) of Ag$_2$O was measured by calorimetry and its value is 68.3 J/(mol K) ± 2 J/(mol K).</td>
</tr>
<tr>
<td>H.T=68.3:2</td>
<td></td>
</tr>
</tbody>
</table>

Computation of phase equilibria

The basic strategies of calculating phase equilibria have been discussed by many authors. We refer here to the papers of Hillert [79Hil, 80Hil, 81Hil] and Lukas et. al. [82Luk]. We will not try to sum up these studies here, but merely outline the basic strategy for computing phase equilibria in general.

It is convenient to approach the problem first by considering the calculation of a single equilibrium, and then carry out a so-called mapping along the phase boundaries. Under constant pressure and temperature, two equivalent formulations can be used to calculate a single equilibrium. The first one considers that the total Gibbs energy has a minimum at equilibrium ($dG = 0$ and $d^2G < 0$), and the second one assumes that equilibrium is reached when the chemical potentials $\mu$ are identical for each component in all the phases. These two formalisms are equivalent since $\mu_j = \partial G/\partial n_j$. The latter approach can be mathematically written as:

$$\mu^\alpha_i = \ldots = \mu^\theta_i ; \ldots = \ldots = \ldots ; \mu^\alpha_z = \ldots = \mu^\theta_z$$

(1.13)

and is, to our knowledge, the most effective method to solve equilibria in multicomponent multiphase systems. In Eq. 1.13, the $z$ (= components) sets of $\theta$ (= phases) non-linear equations must be solved simultaneously.

When the single equilibrium is calculated, one may also want to map a complete phase diagram. The program has then to calculate the phase boundaries, i.e. the limits of existence of the phases. To do that, the POLY3 program [84Jan] used in the Thermo-Calc package rewrites the starting equilibrium and fixes one of the phase as obligatory present...
(one phase is then fixed 0). Then, the program follows the phase boundary according to the axes variables and the step along these axes entered by the user.

**Thermodynamic optimization**

The programs for thermodynamic optimizations nowadays are able to compute simultaneously sets of phase diagram and thermodynamic data and obtain the best fitting parameters. Some problems remain concerning the experimental data and the choice of the parameters. Experimental data are normally not equally distributed across the system. Data points may be in contradiction, experimental errors are often unknown and have to be estimated. Sometimes there may be very few or even no data for a system. This was the case for two of the studied systems, Ag–Sr–Cu–O and Ag–Ca–Cu–O. Then experimental thermal analysis (DTA/TG) was performed which gave us few but enough data to optimize the liquid phase, as shown in Section 3.4.

Reliability of the experiments has to be carefully checked and then the sets of parameters have to be chosen and tested. By testing the systems, one may be tempted to add parameters for a better fitting of the calculation to the experimental data points. These additional parameters should be avoided, as their physical meaning are usually unclear, their numerical values are very uncertain and extrapolations may become unrealistic.

The most important difficulty is the inherent conflict between thermodynamic data and phase diagram data. Phase diagrams are very sensitive to relative differences in the Gibbs energies of different phases but are rather insensitive to the absolute energy of these phases. If thermodynamic parameters are optimized using only thermodynamic data, the resulting phase diagram is most generally not realistic. On the other hand, optimizations of the parameters using phase diagram datapoints only are not satisfactory and often lead to unrealistic extrapolations.

1.3 Conclusion

The CALPHAD method combines informations on phase equilibria and thermodynamic properties to model phase diagrams and thermodynamics. This results in a complete description of a system in the sense that any phase diagram or thermodynamic property of the system can be calculated from it. There now exists versatile models and powerful software packages so that this method can be applied to a wide range of materials. The so optimized thermodynamic descriptions can be used to e.g. understand phase transformations and improve materials processing.

1.4 References


Chapter 2

Substrate Materials for Superconductors
2.1 Overview

After the discovery of compounds with high-$T_c$ superconductivity (HTSC) in the Bi–Sr–Ca–Cu–O system (BSCCO) by Maeda et al. [88Mae], much research activity was directed towards the production of HTSC BSCCO phases (2212 and 2223). Most of the effort concerned thin films (below 1 μm), thick films or tapes (up to the mm scale), and wires by the powder-in-tube (PIT) technique. In order to obtain good superconducting properties, such as high critical temperature $T_c$, high critical current density $j_c$, and high critical magnetic field $B_c$, the HTSC materials must be dense and reasonable phase pure. Because of their extreme two-dimensionality they cannot be densified by conventional solid-state sintering, but can be densified by partial melting. At the temperatures needed to form a liquid phase the substrate may react with the processed materials. The BiSrCaCu-oxide liquid is also very reactive.

Depending on the processing, on the form, and on the applications of HTSC compounds, three main types of substrate materials are normally used. For thin films, where the thickness is in the range of several atomic layers, epitaxial growth is achieved on single crystal substrates with perovskite structure, like SrTiO$_3$ and BaTiO$_3$. Thick films or tapes can be processed on different substrates, which must not chemically interfere with 2212. Oxide ceramics that are non-reactive to alkaline earth metals, like MgO and (Mg,Cu)O, YSZ (yttrium stabilized ZrO$_2$) and Al$_2$O$_3$, are of interest. For thick films, tapes and wires, for which a mechanical deformation is needed after film deposition, metals with high ductility are needed. Among them silver and some silver alloys do not incorporate into the 2212 structure and, thus, do not cause any detrimental effects on the superconducting properties [93Nom]. Silver possesses further attractive properties such as high-temperature chemical stability and high oxygen diffusivity. More details on the choice of substrate material can be found in the review paper by Phillips [96Phi].

We will mention here only the superconducting properties $T_c$ and $j_c$ (and the thickness) of Bi$_2$Sr$_2$CaCu$_2$O$_y$ films measured on MgO, SrTiO$_3$, and Ag substrates.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>$T_c$ K</th>
<th>Ref.</th>
<th>$j_c$ a A/cm$^2$</th>
<th>Thickness μm</th>
<th>Ref.</th>
<th>Amount of publications$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>82</td>
<td>[91Shi]</td>
<td>$7 \cdot 10^4$</td>
<td>&lt; 1$^c$</td>
<td>[91Shi]</td>
<td>36</td>
</tr>
<tr>
<td>SrTiO$_3$</td>
<td>75</td>
<td>[90Bal]</td>
<td>$1 \cdot 10^7$</td>
<td>0.25</td>
<td>[91Zha]</td>
<td>3</td>
</tr>
<tr>
<td>Ag</td>
<td>80</td>
<td>[90Zha]</td>
<td>$1.7 \cdot 10^5$</td>
<td>50</td>
<td>[98Mia]</td>
<td>233</td>
</tr>
</tbody>
</table>

a. measured at $T = 4.2$ K.
b. for the period 1/95–7/98, from EI Compendex (© SilverPlatter).
c. the thickness was not indicated in the reference but can be estimated as below 1 μm since 2212 in an epitaxial film.
These data lead to the conclusion that $T_c$ does not depend much on the choice of the substrate, $T_c$ equals $-80$ K for the three substrate materials, and can be considered as an "intrinsic" value, in contrast to $j_c$. Two of the criteria that influences the critical current density dramatically are the grain alignment and the thickness of the sample. Table 2.1 indicates also the number of research papers published on the subject "2212 and (...) substrate materials" and clearly demonstrates that silver is still the most used substrate for 2212 films or 2212 wires. This table also shows that little work is done on 2212 thin films. The reason for this is that Y–Ba–Cu–O materials have superior properties, in particular $B_c$, for thin film technology.

2.2 Influence of Silver on the Bi–Sr–Ca–Cu–O System

Silver addition influences the BSCCO system in different ways. It modifies the microstructure of the 2212 and 2223 materials, and improves the mechanical properties of these materials. Furthermore, the superconducting properties of 2212 and 2223 materials may be modified by silver, as well as the thermodynamics of the whole Bi–Sr–Ca–Cu–O system.

Figure 2.1: Microstructure of 2212 + 2.7 wt-% Ag thick film (melted on Ag substrate at 1166 K in 1 bar O$_2$, cooled at a rate of 5 K/h to 1143 K, and then quenched at RT) [97Lan].

Similar to other oxide ceramics the superconducting compounds of the BSCCO system also have rather poor ductility, strength, and fracture toughness. Joo et. al. [94Joo] studied the influence of silver addition on the mechanical properties of 2212. The mechanical strength of 2212 increased from $\sigma_c = 58$ MPa without silver to $\sigma_c = 107$ MPa with 30 vol-% Ag. The fracture toughness $K_{IC}$ increased from 1.81 MPa to 2.79 MPa with the
same proportion of Ag. The same tendency was observed for the 2223 compound. These radical improvements are due to the presence of Ag particles that may induce compressive stresses in the superconducting matrix and resist crack propagation by pinning the crack. Figure 2.1 shows the microstructure of 2212 after partial melting, from Lang et. al. [97Lan]. The dark grey long grains are the 2212 platelets and the white phase in-between, as well as the light grey areas, are the liquid. Small white Ag-particles can be seen along the boundary between the two liquids. This will be discussed further in Chapter 5. The large faceted black particles are $\text{Sr}_{14-x}\text{Ca}_x\text{Cu}_2\text{O}_4$ and the faceted grey particles $\text{Bi}_9\text{Sr}_{11}\text{Ca}_5\text{O}_y$.

The influence of silver addition on the superconducting properties has been discussed by many authors, with the general conclusion that silver does not modify the critical temperature. This was confirmed by Jones et. al. [90Jon] who observed the effect of silver on the crystallographic structures of 2212 and 2223 compounds, and concluded that silver does not enter into any of the phases.

The critical current density, though, depends strongly on the maximum processing temperature. As the addition of silver is known to lower the melting point of 2212, it may allow higher $j_c$ than without silver. Figure 2.2 (from Lang et. al. [98Lan]) shows $j_c/j_{c,\text{max}}$ as a function of the maximum processing temperature, in pure oxygen. A maximum in $j_c/j_{c,\text{max}}$ is observed around 1165 K (892°C), which is just below the melting point of pure 2212 ($T_m = 1168$ K), but above the eutectic temperature of 2212 + Ag ($T_e = 1143$ K), for $P_{O_2} = 1$ atm.

**Figure 2.2: Influence of $T_{\text{max}}$ processing (in pure oxygen) on $j_c/j_{c,\text{max}}$ for 2212 from Lang et. al. [98Lan].**

![Graph showing $j_c/j_{c,\text{max}}$ vs. $T_{\text{max}}$](image)

Several authors [96Mar,97Lan1,97Lan2,97Maj] studied the Ag–Bi–Sr–Ca–Cu–O system (ABSCCO) by quantifying the influence of silver addition on the melting of 2212 (or
2223) and on the secondary phases that appear during the partial melting. By dissolving Ag, the liquid phase is stable at lower temperatures, i.e. silver lowers the melting point of 2212, by about 30 K to 1136 K (in 1 atm O$_2$), see DTA curves from Lang et. al. [97Lan2] (Figure 2.3). Silver and 2212 form a eutectic where the oxide liquid can dissolve up to 5.5% silver metallic ratio$^1$, see Figure 2.4 from Majewski et. al. [97Maj].

Figure 2.3: DTA curves of 2212 and 2212 + 5.2 wt-% Ag in 1 atm O$_2$

[98Lan].

---

$^1$ where the metallic ration is $u_{Ag} = \frac{n_{Ag}}{n_{Ag} + n_{Bi} + n_{Sr} + n_{Ca} + n_{Cu}}$. 
Figure 2.4: Part of the 2212–Ag phase diagram in air [97Maj]. The mol-% indicated on the x-axis must be normalized taking into account the seven cations present in 2212.

Larger discrepancies among the different studies concern the stability limits of secondary phases. A rather comprehensive study was published by Margulies et al. [96Mar] in which the stability limits of the secondary phases and of the liquid above the 2212 melting point were shown. Figure 2.5 presents a summary of these results obtained in pure oxygen.
Figure 2.5: Secondary phase stability in presence of liquid above the melting point of 2212, in 1 atm O$_2$, with 0 wt-%, 2 wt-%, and 10 wt-% Ag [96Mar].

In this figure, as well as in this work, phases are abbreviated according to their stoichiometry in the BSCCO system, i.e. 014x24 for Sr$_{14-x}$Ca$_x$Cu$_{24}$O$_{41}$, 91150 for Bi$_2$Sr$_{11}$Ca$_5$O$_y$, 02x1 for Sr$_{2-x}$Ca$_x$CuO$_3$, 01x1 for Sr$_{1-x}$Ca$_x$CuO$_2$, and 01x0 for Sr$_{1-x}$Ca$_x$O. Figure 2.5 shows that silver increases the stability of the liquid phase relative to the solid phases.

The influence of silver on the phase equilibria in the BSCCO system will be presented in Chapter V, giving a comparison between our calculations and the experimental processing of 2212 in presence of silver by Lang et. al. [97Lang1, 97Lang2].

2.3 Conclusion

Several substrates for BSCCO HTSC films have been reviewed in this Chapter. Among them, two are of special interest for us, MgO (doped with CuO) which will be discussed in Chapter III, and Ag. Silver substrate for films and silver tubes for wires is the most used material in the scientific community as well as for the first industrial developments. Silver does not dissolve into the solid phases of the BSCCO system, and in particular not into the superconducting compounds and, thus, does not deteriorate their properties. Silver modifies the phase equilibria, though, and decreases the melting temperature of 2212 by about 30 K. Silver dissolves into the BiSrCaCu-oxide liquid up to 5.5% of the metallic ratio and increases the relative stability of the liquid phase to the solid phases.
2.4 References


(1997).


Chapter 3

Thermodynamic Study and Sintering
in the Mg–Cu–O System
3.1 Introduction

The Mg–Cu–O system does not belong to the subsystems of the Ag + BSCCO series but it is included in this study since MgO is of interest as a potential substrate for Bi-based HTSCs. To produce large and dense substrates by sintering, 5 to 18 mol-% CuO is added to the MgO powder. This allows sintering at a much lower temperature than for pure MgO. A second reason to add CuO to the MgO substrate is that when the MgO substrate is saturated with respect to CuO there is no risk that it “steals” CuO from the BSCCO liquid.

This chapter contains a thermodynamic optimization of the Mg–Cu–O system in Section 3.2 and results on the sintering of (Mg,Cu)O powders in Section 3.3.
3.2 The Mg–Cu–O System

Published in Z. Metallkd 86(7), 568–573 (1996)

This paper is dedicated to Dr. rer. nat. Hans Leo Lukas on the occasion of his 65th birthday.

Thermodynamic Evaluation of the Mg–Cu–O System

Jérôme Assal, Bengt Hallstedt and Ludwig J. Gauckler
ETH Zürich, Department of Materials, Nonmetallic Materials, Swiss Federal Institute of Technology, Sonneggstr. 5, 8092 Zurich, Switzerland

Abstract

A thermodynamic evaluation of the ternary Mg–Cu–O system has been made and a set of parameters consistently describing the system has been determined. Guggenite is the only ternary solid phase within the system and its stoichiometry is close to MgCu$_2$O$_3$. The MgO phase can dissolve considerable amount of CuO and is described with a simple model which allows Mg$^{2+}$ substitution by Cu$^{2+}$. Phase diagrams are given for the MgO–CuO$_x$ system at 0.21 and 1 bar oxygen partial pressures as well as a potential diagram. An isothermal section at 1423 K is also presented. Available experimental data are rather limited and most of them are well described by the calculation. There are still uncertainties on the CuO solubility in MgO and on the Cu$^{1+}$/Cu$^{2+}$ ratio present in MgO.

3.2.1 Introduction

Pure magnesium oxide has to be sintered at rather high temperatures, i.e. about 1873 K or higher [85Rys]. Some additives such as copper oxide can drastically decrease the sintering temperature of MgO.

The phase relations in the Mg–Cu–O system are characterised by the high stability of the magnesium oxide, which is in equilibrium with virtually all other phases. Magnesium oxide itself shows a considerable solid solubility of copper oxide with a mole fraction of about 0.2 at 1273 K [64Sch1,64Sch2,74Nav,63Nit]. As the oxygen partial pressure changes drastically when crossing the equilibria between MgO–Cu$_2$O and MgO–Cu, the system can be divided in three parts which can be treated almost separately. This work will mainly concern the oxide part of the system, i.e. the triangle MgO–CuO–Cu$_2$O.
Güggenite is the only ternary solid phase known and has a slightly variable stoichiometry about 0.725 as mole fraction of CuO [64Sch1,64Gad,68Ust,74Nav,94Win].

The present evaluation is based on previous assessments of the Mg–O system by Hallstedt [93Hal], the Cu–O system by Hallstedt et. al. [94Hal] and the Mg–Cu system by Ansara [92Ans].

3.2.2 Experimental Data

The Phase Diagram

The phase diagram of MgO–CuO$_x$, with $0.5 \leq x \leq 1$ where CuO$_{0.5}$ is equivalent to $\frac{1}{2}$ Cu$_2$O, has been systematically studied by Schmahl and Minzl [64Sch1] and by Gadalla and White [64Gad]. The latter used thermo-gravimetry (TG) to measure oxygen content as function of temperature for different Mg / Cu molar ratios in air (0.21 bar O$_2$), in 0.41, 0.61 and in 1.01 bar O$_2$. From their experimental data they could construct various phase diagrams and gain information on the CuO solubility in MgO and on the compositions of güggenite and of the liquid phase. They concluded that MgO dissolves considerable amounts of CuO$_x$, mainly CuO but also Cu$_2$O. The uncertainties in the CuO$_x$ solubility in MgO as well as the composition of the liquid phase are quite high though.

Schmahl and Minzl [64Sch1] measured isothermally the oxygen partial pressure as function of the oxygen content for various Mg / Cu ratios. Most of the measurements were made at 1273 K and some additional experiments were done at 1308 K and 1333 K. The liquid phase was not present in their equilibria. By extrapolating their data to lower temperatures they concluded that güggenite should decompose at 1131 K. Although the methods used by Schmahl and Minzl [64Sch1] and by Gadalla and White [64Gad] are different, the nature of their data is similar and they agree fairly well on the temperatures of the three-phase equilibria as function of oxygen partial pressure.

Schmahl et. al. [64Sch2] used X-ray diffraction (XRD) on quenched samples to determine the solubility of CuO in MgO at 1273 K in an oxygen gas flow, and found $x_{\text{CuO}} = 0.21$. Navrotsky [74Nav] measured CuO activity and oxygen partial pressure for MgO–CuO mixtures at 1273 K and found the same CuO solubility in MgO in air. Nitzsche [63Nit] investigated the microstructures of CuO-containing MgO in air with different cooling rates after heat treatments. His investigations give approximate indications on the CuO solubility in MgO at high temperatures, e.g. $x_{\text{CuO}} \approx 0.05$ at temperatures in the range 1623 to 1673 K. These data and the MgO–CuO$_x$ phase diagram are presented in Figure 3.1.

Güggenite

A ternary compound between MgO and CuO$_x$ was first described in 1947 by Rigamonti [47Rig] as stoichiometric MgCuO$_2$. Trojer [58Tro] found that MgCuO$_2$ is stable approximately below 1378 K in O$_2$ and named it güggenite. Gadalla and White [64Gad] described güggenite as stoichiometric MgCu$_2$O$_3$ while Schmahl and Minzl [64Sch1] described this phase as MgCu$_3$O$_4$ with an orthorhombic symmetry. Ust’yanntsev and Bes-
sonov [68Ust] concluded that güggenite shows a solid solution range and proposed that $x_{\text{CuO}}$ lies between 0.712 and 0.734. According to Drenkhahn and Müller-Buschbaum [75Dre] güggenite is described as stoichiometric MgCu$_2$O$_3$ and single-crystal XRD shows that its symmetry is orthorhombic with $Pmmn$ as space group. From neutron diffraction and single-crystal XRD Winkelmann and Graf [94Win] confirm the crystal structure described by Drenkhahn and Müller-Buschbaum and conclude that Mg-sites are partly occupied by Cu$^{2+}$ ions. Güggenite can then be written as Mg$_{1-x}$Cu$_{2+x}$O$_3$ where the excess of copper is $0.13 < x < 0.25$.

Güggenite is antiferromagnetic at low temperature with a Néel temperature ($T_N$) of 94.5 K [89Zei]. It appears that $T_N$ depends strongly on the CuO mole content. By slightly changing the composition $T_N$ decreases to 68 K [92Win].

### 3.2.3 Thermodynamic Models

**MgO**

MgO has a face-centred cubic structure (halite) dissolving a considerable amount of CuO$_2$. [64Schl, 64Sch2, 64Gad, 74Nav]. It is clear that Cu$^{2+}$ can substitute for Mg$^{2+}$ but Gadalla and White [64Gad] have indicated that MgO also dissolves CuO$_2$ in the form of Cu$^{1+}$ to a large extent. Their results are not very conclusive however. As a first approximation we have chosen the simple model ($\text{Mg}^{2+}, \text{Cu}^{2+}$)$_1$ ($\text{O}^{2-}$)$_1$ to describe the MgO phase, i.e. without any Cu$^{1+}$ ions. The molar Gibbs energy for MgO in presence of Cu$^{2+}$ and O$^{2-}$ is then given by

$$G_m^{\text{MgO}} = y_{\text{Mg}^{2+}} y_{\text{O}^{2-}} G_{\text{MgO}}^{\text{Mg}^{2+},\text{O}^{2-}} + y_{\text{Cu}^{2+}} y_{\text{O}^{2-}} G_{\text{Cu}^{2+},\text{O}^{2-}}^{\text{Cu}^{2+}}$$

$$+ RT (y_{\text{Mg}^{2+}} \ln y_{\text{Mg}^{2+}} + y_{\text{Cu}^{2+}} \ln y_{\text{Cu}^{2+}}) + E_m^{\text{MgO}}$$

Here a colon is used to separate species on different sublattices, $y_s$ is the site fraction of $s$, i.e. the fraction of the species $s$ in a particular sublattice. $G_{\text{MgO}}^{\text{Mg}^{2+},\text{O}^{2-}}$ represents the Gibbs energy of pure MgO and $G_{\text{Cu}^{2+},\text{O}^{2-}}^{\text{Cu}^{2+}}$ is the Gibbs energy of CuO in the MgO structure. $E_m^{\text{MgO}}$ represents the excess of the molar Gibbs energy for the phase MgO. We assume that $E_m^{\text{MgO}}$ is here equal to zero.

In order to dissolve Cu$^{1+}$ in MgO the difference in charge of the cations has to be compensated by either creating interstitial cations or oxygen vacancies. The Cu$^{1+}$ ion (0.77 Å) is somewhat larger than the Mg$^{2+}$ ion (0.72 Å) and the Cu$^{2+}$ ion (0.73 Å) [82Vai]. Calculations by Jacobs and Vernon [90Jac] indicate that the formation energy of cation (or anion) Frenkel defects in pure MgO is considerably higher than the formation energy of Schottky defects, i.e. over 12 eV compared with 8 eV. It seems more probable that Cu$^{1+}$ dissolves by creating oxygen vacancies than interstitial cations. This is also supported by measurements of diffusion in Li-doped MgO by Oishi et al. [87Ois] which indicate that
Li\textsuperscript{1+} dissolves in MgO by creation of oxygen vacancies. The dissolution of Cu\textsuperscript{1+} and Cu\textsuperscript{2+} in MgO could then be expressed by the model (Mg\textsuperscript{2+},Cu\textsuperscript{2+},Cu\textsuperscript{1+})\textsubscript{1} (O\textsuperscript{2-},Va\textsuperscript{1+})\textsubscript{1} which was tested to check if the calculation could be improved by allowing Cu\textsuperscript{1+} dissolution in the MgO phase in addition to Cu\textsuperscript{2+}.

\textit{Güggenite}

The solid solution range of güggenite is not known well enough to motivate the use of a solution model. We describe güggenite as a stoichiometric phase with the composition Mg\textsubscript{0.275}Cu\textsubscript{0.725}O, i.e. $x = 0.175$ in Mg\textsubscript{1-x}Cu\textsubscript{2+x}O\textsubscript{3}, which is about in the middle of the observed composition range, see Figure 3.2. The molar Gibbs energy is then given by

$$G_m^{\text{güg}} = 0.275 \cdot G_{\text{Mg}^{2+}:O^{2-}}^{\text{o}} + 0.275 \cdot G_{\text{CuO}}^{\text{o}} + K_1 + K_2 \cdot T \quad (3.2)$$

where $G_{i:O^{2-}}^{\text{o}}$ represent the Gibbs energy of pure $i$-oxide compounds, $K_1$ is the enthalpy of formation and $-K_2$ is the entropy of formation of güggenite.

\textit{The Liquid Phase}

The two-sublattice model for ionic liquid [85Hil,91Sun] describes the liquid phase continuously from metal to oxide liquid. This model assumes that cations and anions can mix freely in their respective sublattice. The liquid phase is written by the formula (Mg\textsuperscript{2+},Cu\textsuperscript{2+},Cu\textsuperscript{1+})\textsubscript{p} (O\textsuperscript{2-},Va\textsuperscript{1+})\textsubscript{q} where $p$ and $q$ vary with composition in order to maintain electroneutrality. Hypothetical vacancies with an induced minus charge are introduced in the second sublattice to make the model continuous to the metal liquid. In this case $p$ and $q$ are given by

$$p = 2y_{O^{2-}} + qy_{Va} \quad (3.3)$$

$$q = 2y_{Mg^{2+}} + y_{Cu^{1+}} + 2y_{Cu^{2+}} \quad (3.4)$$

where $y_s$ is the site fraction of $s$, i.e. the fraction of the species $s$ in a particular sublattice.
The molar Gibbs energy of the liquid is given by:

\[
G_{\text{liq}}^m = y_{\text{Mg}^{2+}} \cdot y_{\text{O}^{2-}} \cdot G_{\text{Mg}^{2+}:\text{O}^{2-}}^\text{liq} + y_{\text{Cu}^{1+}} \cdot y_{\text{O}^{2-}} \cdot G_{\text{Cu}^{1+}:\text{O}^{2-}}^\text{liq} \\
+ y_{\text{Cu}^{2+}} \cdot y_{\text{O}^{2-}} \cdot G_{\text{Cu}^{2+}:\text{O}^{2-}}^\text{liq} + q \left( y_{\text{Mg}^{2+}} \cdot y_{\text{Va}} \cdot G_{\text{Mg}^{2+}:\text{Va}}^\text{liq} \right) \\
+ q \left( y_{\text{Cu}^{1+}} \cdot y_{\text{Va}} \cdot G_{\text{Cu}^{1+}:\text{Va}}^\text{liq} + y_{\text{Cu}^{2+}} \cdot y_{\text{Va}} \cdot G_{\text{Cu}^{2+}:\text{Va}}^\text{liq} \right) \\
+ pRT \left( y_{\text{Mg}^{2+}} \cdot \ln \left( y_{\text{Mg}^{2+}} \right) + y_{\text{Cu}^{1+}} \cdot \ln \left( y_{\text{Cu}^{1+}} \right) + y_{\text{Cu}^{2+}} \cdot \ln \left( y_{\text{Cu}^{2+}} \right) \right) \\
+ qRT \left( y_{\text{O}^{2-}} \cdot \ln \left( y_{\text{O}^{2-}} \right) + y_{\text{Va}} \cdot \ln \left( y_{\text{Va}} \right) \right) \\
+ E_{\text{Mg-O}}^\text{liq} + E_{\text{Cu-O}}^\text{liq} + E_{\text{Cu-Mg}}^\text{liq} + E_{\text{ter}}^\text{liq}
\]

(3.5)

where \( G_{i}^\text{liq} \) represent the Gibbs energies of the pure liquid \( i \)-elements and \( G_{i:O^{2-}}^\text{liq} \) represent the Gibbs energies for the pure liquid \( i \)-oxide compounds. \( E_{i:O^{2-}}^\text{liq} \) represent the excess Gibbs energies of the liquid \( i-j \) subsystems and \( E_{\text{ter}}^\text{liq} \) is the excess Gibbs energy of the liquid ternary system. Gadalla and White [64Gad] measured the eutectic temperature between MgO and Cu2O in air slightly above the melting temperature of pure Cu2O in air calculated by Hallstedt et al. [94Hal]. The same observation can be made between CuO and guggenmite in 1.01 bar O2. These remarks lead to the conclusion that the ternary interactions in the liquid are slightly positive but cannot be quantified. We assume in this work that the ternary interactions can be then neglected, i.e. \( E_{\text{ter}}^\text{liq} = 0 \).

### 3.2.4 Optimisation of Parameters

The thermodynamic properties of the ternary Mg–Cu–O system are to a large extent determined by the binary edge systems, which have been studied in previous works. The assessments of Mg–O by Hallstedt [93Hal], Cu–O by Hallstedt et al. [94Hal] and Cu–Mg by Ansara [92Ans] are used in this work.

Two model parameters for the halite phase and two other for the ternary phase guggenite are to be determined, see Eq. 3.1 where \( G_{\text{Cu}^{2+}:O^{2-}}^{\text{MgO}} = G_{\text{Cu}^{2+}:O^{2-}}^{\text{CuO}} + K_{3} + K_{4} \cdot T \) and Eq. 3.2. As observed in Section 3.2.3, the liquid phase has no parameters to be optimised since the ternary interactions cannot be quantified.

The optimisation was carried out using the computer program PARROT [84Jan] included in the Thermo-Calc databank system [85Sun]. The program calculates the model parameters by minimising the squared error. Influence of experimental data can be enhanced or decreased by changing the weight of these data. The difficulty in the optimisation increas-
es when data are in contradiction or very inaccurate.

Experimental data from the isobaric dissociation curves of the \( \text{MgO} - \text{CuO} \) mixtures from Gadalla and White [64Gad] are considered here with a low weight since they show a relatively large uncertainty. Temperature measurements for the \( \text{MgO} - \text{CuO} - \text{güggenite} \) equilibrium are taken into consideration with a high weight. Temperature measurements for the three-phase equilibria where the liquid is present, i.e. liquid–\( \text{MgO} - \text{Cu}_2\text{O} \), liquid–\( \text{MgO} - \text{CuO} \) and liquid–\( \text{MgO} - \text{güggenite} \), are not considered since the liquid phase does not enter into the optimisation. Experimental data from the isothermal dissociation curves of the \( \text{MgO} - \text{CuO} \) mixtures from Schmahland Minzl [64Sch1] are considered here with a low weight and oxygen partial pressure measurements for the \( \text{MgO} - \text{Cu}_2\text{O} - \text{güggenite} \) and for the \( \text{MgO} - \text{CuO} - \text{güggenite} \) equilibria with a high weight. The XRD measurements of CuO solubility in MgO are considered with a high weight for the data from Schmahl et. al. [64Sch2] and from Navrotsky [74Nav]. Data from Nitzsche [63Nit] are taken into consideration with a relative low weight since the steps in temperature and in composition are quite coarse. From Ust'yansev and Bessonov [68Ust] two temperature measurements of the three-phase equilibria, i.e. the temperatures of \( \text{MgO} - \text{Cu}_2\text{O} - \text{güggenite} \) and liquid–\( \text{MgO} - \text{Cu}_2\text{O} \) equilibria, are considered with a low weight because the scale of their DTA curves was not properly defined and could not be read with enough precision.

### 3.2.5 Results and Discussion

The thermodynamic parameters optimised in the present work are listed in Table 3.1. The calculated \( \text{MgO} - \text{CuO}_x \) phase diagram in air is shown in Figure 3.1 and experimental and calculated data for the four invariant equilibria are given in Table 3.2. An enlargement around the composition of güggenite compared with experimental data is presented in Figure 3.2. The three invariant equilibria and the phase diagram in 1 bar oxygen are given in Table 3.3 and Figure 3.3, respectively. The \( \text{MgO} - \text{CuO}_x \) phase diagrams show that CuO solubility in MgO is about 0.2 mole fraction even at relative low temperatures, i.e. around 1000 K. The shape of the MgO-phase domain is in fact very uncertain at low temperatures due to the lack of data below 1273 K. Even at high temperatures, the few experimental data are somewhat uncertain except the XRD measurement by Schmahl et. al. [64Sch2] and by Navrotsky [74Nav]. Another reason for the uncertainties in the MgO-phase domain is the possible \( \text{Cu}_2\text{O} \) solubility which was not considered in the calculation. Figure 3.1 and Figure 3.3 show small differences in composition (< 0.02 CuO mole fraction) between our calculated curves and the experimental data for the CuO solubility in MgO since the weights on these data were rather large during the optimisation. Table 3.2 and Table 3.3 show larger differences between calculated and experimental invariant equilibria in air, e.g. for the liquid ↔ \( \text{MgO} + \text{Cu}_2\text{O} \) reaction, the experimental temperatures were measured at 1411 K [64Gad] and 1408 K [68Ust] and calculation shows 1386 K. These measured temperature (1411 K and 1408 K) are even slightly higher than the melting temperature of pure \( \text{Cu}_2\text{O} \) in air (1407 K) which shows the uncertainties of the measurements. The phase diagrams also show the calculated decomposition
temperature of güggenite at 1142 K which is 11 K higher than the only experimental da¬
tum [64Sch1]. This temperature is quite uncertain, though, since the datum from Schmahl
and Minzl relies on the extrapolation of two almost parallel lines. According to the calcu¬
lation güggenite is unstable below 10^{-2} \text{ bar} O_2.

The calculated potential phase diagram is shown in Figure 3.4. The lines represent
three-phase equilibria and the crossings four-phase (or invariant) equilibria. A magnifica¬
tion of the potential diagram is shown in Figure 3.5 in comparison with experimental data
from Table 3.2 and Table 3.3 included. The $L_2 + \text{MgO} + \text{Cu}_2\text{O}$ equilibrium shows a dif¬
ference of about 25 K between calculation and experimental data. A very good agreement
between experimental data and calculation is observed in the other equilibria. The list of
invariant equilibria is given in Table 3.4.

The calculated isothermal section of the $\text{MgO}-\text{CuO}-\text{Cu}_2\text{O}$ system at 1423 K is presented
in Figure 3.6. This ternary phasediagram shows that $L_2$, i.e. the oxide liquid phase, is sta¬
ble with a composition close to the $\text{Cu}_2\text{O}-\text{CuO}$ border. According to the calculation the
oxide liquid appears at around 1363 K. Below this temperature the oxide liquid is not sta¬
ble and two large three-phase fields appear, $\text{CuO}-\text{Cu}_2\text{O}$-güggenite and
$\text{MgO}-\text{Cu}_2\text{O}$-güggenite. As proposed in Section 3.1, MgO can be described with a model
which allows Cu$^{1+}$ dissolution. The only difference showed by this model is the narrow
Cu$^{1+}$ solubility in MgO, 0.02 in mole fraction at 1423 K, about one tenth of the assump¬
tion by Gadalla and White [64Gad]. As the MgO model $(\text{Mg}^{2+},\text{Cu}^{2+},\text{Cu}^{1+})_1
(O^{2-},V_a)_1$ shows no improvements in the description of the system from the $(\text{Mg}^{2+},\text{Cu}^{2+})_1
(O^{2-})_1$, we assume that Cu$_2$O solubility in MgO can be neglected and confirm the simple MgO
model.

Figure 3.7 shows the comparison between experimental isothermal decomposition curves
from Schmahl and Minzl [64Sch1] and our calculations. Experiments and calculations are
in relatively good agreement, especially for the equilibria MgO–Cu$_2$O–güggenite corre¬
sponding to the steps in oxygen pressure. At lower $x$ in CuO$_x$, that is concerning the MgO–
Cu$_2$O equilibria, a discrepancy in slope between the calculation and the experimental data
is observed. It could be reduced somewhat during the work of optimisation but not elimi¬
nated since the shape of these curves is independent from the choice of the MgO model.

Similar comparisons between experiments from Gadalla and White [64Gad] and calcula¬
tion are presented in Figure 3.8 which shows decomposition curves for different Mg/Cu
molar ratios in air. Gadalla and White considered the data for Mg/Cu = 9 to belong to the
MgO single-phase domain. As the value of $x$ in CuO$_x$ became smaller than 1, they con¬
cluded that MgO was able to dissolve Cu$_2$O as well as CuO. In contradiction with Gadalla
and White our calculation shows with the change in slope of the solid line that the liquid
phase appears at about 1480 K. The decrease of $x$ below 1 in CuO$_x$ is then due to the pres¬
ence of Cu$^{1+}$ cations within the liquid phase and not in the MgO solid solution phase. In
opposition to the solid line, the dashed curve represents the calculation for the Mg/Cu = 9
ratio with the MgO model which allows Cu$^{1+}$ solubility, i.e. $(\text{Mg}^{2+},\text{Cu}^{2+},\text{Cu}^{1+})_1
(O^{2-},V_a)_1$. The minimum value of $x$ in CuO$_x$ in solution in MgO reached by the dashed
curve is 0.91, that is approximately $\text{Cu}^{1+}/\text{Cu}^{2+} = 0.2$. As this MgO model does not fit the measurements better than the simple MgO model, our assumption that there is no Cu$_2$O solubility in MgO can be nevertheless considered as reasonable and the choice of $(\text{Mg}^{2+},\text{Cu}^{2+})_1(\text{O}^{2-})_1$ for model is so justified. The two other ratios, i.e. $\text{Mg}/\text{Cu} = 2.33$ and $\text{Mg}/\text{Cu} = 0.67$, show that experimental points and calculations are in relatively good agreement. The difference in temperature is about 15 K for güggenite decomposition and reaches 25 K for the eutectic temperature. This calculated temperature of 1386 K should depend strongly on the thermodynamic description of the liquid phase. As decisive experiments are nonexistent in literature, our optimisation may give a somewhat too low eutectic temperature.

3.2.6 Conclusion

A consistent set of thermodynamic parameters for the Mg–Cu–O system has been determined which describe the experimental data well. Due to the small amount of reliable experimental data the calculation is rather coarse. The major uncertainties concern the solid solution range of MgO and to what extent $\text{Cu}^{1+}$ is present, but the liquidus and minimum temperature of stability of güggenite are also uncertain. These uncertainties are mainly due to a lack of reliable experimental data and could not be eliminated by the use of another MgO model which allows $\text{Cu}^{1+}$ solubility.

3.2.7 Acknowledgement

The authors thank Dr. Claus Schüeler for initiating this work and many helpful discussions. Financial supporting of the Swiss National Science Foundation (NFP30) is gratefully acknowledged.

3.2.8 Literature


[58Tro] F. Trojer, “Güggenite, a New Crystal Type with the Composition CuMgO$_2$”, Radex-Rundschau, 7, 365–374 (1958) in German.


[64Sch2] N. G. Schmahl and E. Minzl, “Investigation of the Decomposition of Cop-
per(II) Oxide in the Presence of Magnesium Oxide”, Z. Phys. Chem. NF, 41, 66–77 (1964) in German.


Table 3.1: Thermodynamic parameters for the Mg–Cu–O system optimised in the present work.

MgO

\[ (\text{Mg}^{2+}, \text{Cu}^{2+})_1 (\text{O}^{2-})_1 \]

\[ \Delta G_{\text{MgO}}^{\text{Cu}^{2+}, \text{O}^{2-}} = \Delta G_{\text{Cu}^{2+}, \text{O}^{2-}}^{\text{Cu}^{2+}, \text{O}^{2-}} + 4120 + 9.2 \cdot T \]

Gügggenite

\[ G_m^{\text{g} \text{g}} = 0.275 \cdot \Delta G_{\text{Mg}^{2+}, \text{O}^{2-}}^{\text{Mg}^{2+}, \text{O}^{2-}} + 0.275 \cdot \Delta G_{\text{Cu}^{2+}, \text{O}^{2-}}^{\text{Cu}^{2+}, \text{O}^{2-}} + 4620 - 4.6 \cdot T \]

All parameter values are given in SI units (J, mol, K, R = 8.31451 J/mol K). For a complete set of parameters the reader is referred to Refs. [92Ans, 93Hal, 94Hal] concerning the binary subsystems.

Table 3.2: Experimental and calculated invariant equilibria in air (\(P_{O_2} = 0.21\) bar) of the Mg–Cu–O system.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>(T) K</th>
<th>Liquid composition</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(L \leftrightarrow \text{MgO} + \text{Cu}_2\text{O})</td>
<td>1411</td>
<td>0.62</td>
<td>[64Gad]</td>
</tr>
<tr>
<td></td>
<td>1408</td>
<td>–</td>
<td>[68Ust]</td>
</tr>
<tr>
<td></td>
<td>1386</td>
<td>0.971</td>
<td>This work</td>
</tr>
<tr>
<td>(\text{MgO} + \text{Cu}_2\text{O} \leftrightarrow G)</td>
<td>1317</td>
<td>–</td>
<td>[64Sch1]†</td>
</tr>
<tr>
<td></td>
<td>1333</td>
<td>–</td>
<td>[64Gad]</td>
</tr>
<tr>
<td></td>
<td>1318</td>
<td>–</td>
<td>[68Ust]</td>
</tr>
<tr>
<td></td>
<td>1321</td>
<td>–</td>
<td>This work</td>
</tr>
<tr>
<td>(\text{Cu}_2\text{O} \leftrightarrow \text{CuO})</td>
<td>1301</td>
<td>–</td>
<td>[64Sch1]†</td>
</tr>
<tr>
<td></td>
<td>1299</td>
<td>–</td>
<td>[64Gad]</td>
</tr>
<tr>
<td></td>
<td>1300</td>
<td>–</td>
<td>This work</td>
</tr>
<tr>
<td>(G \leftrightarrow \text{MgO} + \text{CuO})</td>
<td>1131</td>
<td>–</td>
<td>[64Sch1]‡</td>
</tr>
<tr>
<td></td>
<td>1142</td>
<td>–</td>
<td>This work</td>
</tr>
</tbody>
</table>

L is the liquid phase and G is gügggenite. † interpolated value, ‡ extrapolated value.
Table 3.3: Experimental and calculated invariant equilibria in 1.01 bar $O_2$ of the Mg–Cu–O system.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$T$ (K)</th>
<th>$x_{Cu^1} / (x_{Cu^2} + x_{Mg})$</th>
<th>$Cu^{1+} / Cu^{2+}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$L + MgO \leftrightarrow G$</td>
<td>1399</td>
<td>0.89</td>
<td>–</td>
<td>[64Gad]</td>
</tr>
<tr>
<td></td>
<td>1396</td>
<td>0.971</td>
<td>2.67</td>
<td>This work</td>
</tr>
<tr>
<td>$L + G \leftrightarrow CuO$</td>
<td>1380</td>
<td>0.98</td>
<td>–</td>
<td>[64Gad]</td>
</tr>
<tr>
<td></td>
<td>1374</td>
<td>0.981</td>
<td>2.51</td>
<td>This work</td>
</tr>
<tr>
<td>$G \leftrightarrow MgO + CuO$</td>
<td>1131</td>
<td>–</td>
<td>–</td>
<td>[64Sch1]‡</td>
</tr>
<tr>
<td></td>
<td>1142</td>
<td>–</td>
<td>–</td>
<td>This work</td>
</tr>
</tbody>
</table>

$L$ is the liquid phase and $G$ is güggenite. ‡ extrapolated value.

Table 3.4: Invariant equilibria in the Mg–Cu–O system calculated from the present set of parameters.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$T$ (K)</th>
<th>$\log(P_{O_2})$</th>
<th>Composition of the liquid phases</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>bar</td>
<td>$x_{Mg}$</td>
</tr>
<tr>
<td>$L_1 \leftrightarrow MgO + Cu_2O + Cu$</td>
<td>1340</td>
<td>–5.6</td>
<td>$L_1$</td>
</tr>
<tr>
<td>$L_1 + L_2 \leftrightarrow MgO + Cu_2O$</td>
<td>1479</td>
<td>–4.1</td>
<td>$L_1$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$L_2$</td>
</tr>
<tr>
<td>$G \leftrightarrow MgO + CuO + Cu_2O$</td>
<td>1142</td>
<td>–2.11</td>
<td>–</td>
</tr>
<tr>
<td>$L_2 \leftrightarrow MgO + Cu_2O + G$</td>
<td>1363</td>
<td>–0.39</td>
<td>$L_2$</td>
</tr>
<tr>
<td>$L_2 \leftrightarrow CuO + Cu_2O + G$</td>
<td>1354</td>
<td>–0.26</td>
<td>$L_2$</td>
</tr>
</tbody>
</table>

$L_1$ is the metal liquid, $L_2$ the oxide liquid and $G$ is güggenite.
Figure 3.1: Calculated MgO–CuO\textsubscript{x} phase diagram in air and experimental data [63Nit, 64Gad, 74Nav].

Figure 3.2: Experimental compositions of guggenite [64Gad, 64Sch1, 64Sch2, 68Ust, 74Nav, 94Win] in the calculated MgO–CuO\textsubscript{x} phase diagram in air.
Figure 3.3: Calculated MgO–CuO phase diagram in 1 bar O₂ and experimental datum [64Sch2].

Figure 3.4: Calculated Mg–Cu–O potential diagram. L₁, L₂ and G represent the metal liquid, the oxide liquid and guggenite, respectively.
Figure 3.5: Calculated Mg–Cu–O potential diagram with experimental data included [64Sch1,64Gad,68Ust,74Nav]. L₂ and G represent the oxide liquid and guggenite, respectively.

Figure 3.6: Calculated isothermal section at 1423 K of the MgO–CuO–Cu₂O system.
Figure 3.7: Isothermal decomposition curves of MgO–CuO\textsubscript{x} for Mg / Cu = 2 ratio, calculation compared with experimental data [64Sch1].

Figure 3.8: TG curves of MgO–CuO\textsubscript{x} in air, calculations compared with experimental data [64Gad]. The solid lines represent the calculation for (Mg\textsuperscript{2+},Cu\textsuperscript{2+})\textsubscript{1} (O\textsuperscript{2–})\textsubscript{1} MgO model and the dashed line for (Mg\textsuperscript{2+},Cu\textsuperscript{2+},Cu\textsuperscript{1+})\textsubscript{1} (O\textsuperscript{2–},Va)\textsubscript{1} MgO model.
3.3 Sintering of \((\text{Mg,Cu})\text{O}\) Powder Compacts

The sintering process consists of firing, consolidating, and densifying a body made out of powder particles. During this process, particles are brought into close contact and porosity is reduced. The driving force is the decrease of the total surface energy by increased grain contact and grain growth. The atoms in the small grains are transferred to the larger grains, and the pores are replaced by solid material. This mass transfer can be accomplished by four distinct but sometimes concurrent mechanisms, that are (i) plastic or viscous flow, (ii) solid-state diffusion, (iii) evaporation and condensation, and (iv) diffusion in a grain boundary liquid. Comprehensive reviews on sintering can be found in [97Chi] (pp. 392–428) and in [96Eis].

The atoms that diffuse from the particles to the pore-particle interface can come from the lattice, from the grain boundaries, and from the surface of the grains. The result on the powder compact is a shrinkage which is proportional to a power of the time as:

\[
\frac{\Delta L}{L} \propto t^\alpha
\]

where \(\Delta L\) is the shrinkage and \(L\) is the total length of the sample. The power \(\alpha\) is equal to 2/5 when lattice diffusion controls the process and can take another value when the process is controlled by another mechanism.

Improvement in the sintering of powder compacts can be achieved using additives, with the apparition of a eutectic liquid at the grain boundaries, and with the creation of crystallographic defects that increase the mobility of the atoms. The effects on sintering are the decrease of the sintering temperature and the increase of the final density. During the sintering of MgO with 5–18 mol-% CuO additive, the main mechanism for sintering is solid-state diffusion (or simply diffusion). Liquid phase may appear in samples sintered above 1678 K. This temperature depends on the CuO content and is higher for well-homogenized powders with low CuO content. In the case of MgO doped with Li\(_2\)O, it was found that dissolution of Li\(^{1+}\) into the interstitial sites of MgO creates oxygen vacancies. These vacancies increase the total diffusivity and improve the sintering of MgO, i.e. reduce the sintering temperature and increase the densification rate of the powder compact. The effect is measurable already at Li\(_2\)O concentrations that do not exceed 400 ppm [87Ois,90Jac]. Similarly one may conclude that any other monovalent dopant, like Cu\(^{1+}\), will enhance the sintering of MgO.

Experimental investigations of CuO-doped MgO sintering were conducted by Perednis (Nonmetallic Materials at ETHZ) in association with Schüller (ABB Corporate Research Center) in 1995. These reports were not published but we will describe their experiments briefly. The goal was to produce MgO substrates for BSCCO HTSC at lower temperature than necessary for pure MgO, with a high density (>95% theoretical density, i.e. closed porosity), and to avoid dopants like lithium or silicates since these additives dissolve in
BiSrCaCu-oxide liquid and deteriorate the superconducting properties of the HTSCs. Using copper oxide as dopant for the sintering of magnesia is a challenge since investigations on this topic were not reported elsewhere.

Perednis and Schüler used in-house prepared powders that were obtained by coprecipitating magnesium hydroxide and copper acetate in water at the desired composition, followed by a calcination in air at 973 K for 2 h. The initial Mg-based powder had an average particle size of 1 μm. X-ray diffraction of the calcinated samples showed the peaks of the magnesia structure only. Powder compacts were made by uniaxial cold pressing under 100 MPa. The powders with 6 mol-% CuO were then sintered in air at different temperatures between 1279 K and 1671 K, and their relative shrinkage was measured with a dilatometer (Bachr-Dil802).

Figure 3.9: Logarithm of relative shrinkage as a function of logarithm of time.

According to Equation 3.6, the slopes of the Log(ΔL/L) vs. Log(t) curves indicate the limiting diffusion path during sintering. Figure 3.9 shows different slopes for the curves, 0.4 for the sintering at T = 1279 K, from which one conclude that lattice diffusion controls the process. At T = 1671 K, the slope is equal to 0.62 and one can conclude that another mechanism becomes active. The phase diagram indicates that MgO containing 6 mol-% CuO starts to melt at T = 1678 K (calculated solidus line with an estimated error of ± 10 K). At T = 1671 K the sintering may be partly achieved by a reactive liquid, especially if one consider that inhomogeneities in the composition are present. As for the highest temperature, the slope of the log-log curves indicate that another process is active during the sintering at intermediate temperatures.

In air the phase diagram shows that above 1300 K, CuO is reduced to Cu₂O. If we assume
that Cu$_2$O is partly substituted into MgO, Cu$^{1+}$ dissolves similarly to Li$^{1+}$ according to Oishi et. al. [87Ois]:

$$\text{Cu}_2\text{O (in MgO)} \rightarrow \text{Cu}^+_{\text{Mg}} + \text{Cu}^{*} + \text{O}^{*} \quad (3.7)$$

where the copper cations in the interstitial positions are in equilibrium with copper substituted on Mg positions as:

$$\text{Cu}^{*} \leftrightarrow \text{Cu}^+_{\text{Mg}} + \text{V}^{**} \quad (3.8)$$

and create oxygen vacancies. These defects increase the mobility of the ions dramatically and improve the whole sintering process. The model used to describe the MgO solid solution, (Mg$^{2+}$,Cu$^{2+}$)$_1$ (O$^{2-}$)$_1$, in the thermodynamic optimization (see previous section 3.2) is not invalidated by the presence of a small portion of Cu$^{1+}$, though, since 400 ppm (in the case of Li-dopant) is very efficient for the sintering but is definitely too small to influence the phase relations.

Sintering of MgO doped with 18 mol-% CuO was also made and a density of ~100% was reached at $T = 1323 \text{ K}$ for 10 h in air. The microstructure was then checked by light microscopy and XRD which showed a monophased (MgO) structure. To obtain such high density, the initial powders were ground after the calcination step in a ball mill in order to break down residual large particles, especially those of CuO. Since CuO dissolves in MgO, the pores created by the vanishing of CuO particles are finer, and the densification higher. In this experiment, copper oxide was added to MgO progressively, which allowed CuO to dissolve within the MgO grains and not to concentrate along the grain boundaries. This conclusion was confirmed by XRD.

### 3.4 Conclusion

Experimental investigations on sintering of MgO doped with CuO up to 18 mol-% have been reviewed and improvements of sintering explained. Several mechanisms were evaluated. The possible existence of Cu$^{1+}$ in MgO creates oxygen vacancies which increase the mobility of the atoms. This mechanism is probably the most efficient one in order to improve the sintering and densification of (Mg,Cu)O powder compact. Finally the formation of a small amount of liquid phase also would have a possible effect on the sintering at high temperature. This latter mechanism could be predicted by the phase diagram study.

### 3.5 References


Chapter 4

The Ag–Bi–Sr–Ca–Cu–O System
4.1 Overview

In this Chapter we will apply the CALPHAD method to the thermodynamic descriptions of the Ag–Bi–Sr–Ca–Cu–O subsystems, as well as to the entire system. Our study is based on an existing description of the Bi–Sr–Ca–Cu–O system developed and published by Hallstedt, Risold, and Gauckler (for references, see Table 4.1 in the next section). This overview summarizes the results obtained in the system containing the superconducting phases.

The ABSCCO system contains many solid phases which are usually written in abbreviated form, derived from the cationic stoichiometry in the BSCCO system. Following this rule, 014x24 and 2212 represent the compounds \( \text{Sr}_{14-x}\text{Ca}_x\text{Cu}_{24}\text{O}_{41} \) and \( \text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_2\text{O}_x \), respectively. The studies of the ABSCCO subsystems showed that silver does not form any solid compounds with elements of the BSCCO system at 1 bar total pressure, except \( \text{Ag}_2\text{O} \). Furthermore, Ag does not substitute into the lattice of the oxide phases of BSCCO. All solid phases that are stable under atmospheric conditions are listed in Table 4.1 and more details on their denomination, structure, and composition can be found in the references. The systems with silver contain (Ag) as solid phase below its melting point in which the solubilities of the other elements are in the range of \( \sim 10 \text{ mol}-% \) for Cu, \( 0.1 \text{ mol}-% \) for O, and even less for Bi, Sr, and Ca. Above the melting temperature of Ag, two liquids are usually present, an oxide-rich liquid and a metal Ag-rich liquid, which are immiscible. Silver and the oxide compounds form a eutectic, where the oxide liquid contains Ag in the range of 5 to 10 cation-%. This result confirms the observations made in the Ag–Cu–O and Ag–Bi–O systems, and during partial melt-processing of 2212 with silver.

4.1.1 The Bi–Sr–Ca–Cu–O System

Thermodynamic modelling and optimization of the BSCCO subsystems were mainly carried out by Hallstedt, Risold, and Gauckler, see Table 4.1, except for the Ca–O system [93Sel]. These very comprehensive studies are reported and described in the dissertation of Risold [96Ris3]. Under normal conditions the BSCCO system can be considered as an oxide system, i.e. the metallic phases are less stable than the oxide phases for 1 bar total pressure, \( T = 1000–2000 \text{ K} \), and \( P_{\text{O}_2} = 10^{-3}–1 \text{ bar} \). Knowledge of the metallic system is thus generally of little interest but may be needed in the case of the precursor oxidation technique. This method was applied to mixed metallic powders in order to form the 2223 compound by controlled oxidation and annealing, see [90Gao,95Ott]. But even in this special case, it appeared that the metallic phases had a very narrow range of stability and that the oxide system was predominant which explains the formation of the 2223 compound. In the BSCCO system only a few metallic subsystems were optimized for which experimental data were available, Bi–Cu [89Tep], Sr–Ca [86Alc], Sr–Cu and Ca–Cu [96Ris1]. The Bi–Sr and Bi–Ca systems have also been experimentally investigated and compounds determined (see pp. 302–303 and 339 in [58Han]).
Table 4.1: The subsystems and oxide phases of the Ag–Bi–Sr–Ca–Cu–O system.

<table>
<thead>
<tr>
<th>System</th>
<th>Phases (which do not belong already to the lower-order subsystems)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag–O</td>
<td>(Ag), Ag₂O</td>
<td>Section 4.2</td>
</tr>
<tr>
<td>Bi–O</td>
<td>α-Bi₂O₃, δ-Bi₂O₃</td>
<td>[95Risl]</td>
</tr>
<tr>
<td>Sr–O</td>
<td>SrO, SrO₂</td>
<td>[96Risl2]</td>
</tr>
<tr>
<td>Ca–O</td>
<td>CaO</td>
<td>[93Sel]</td>
</tr>
<tr>
<td>Cu–O</td>
<td>(Cu), Cu₂O, CuO</td>
<td>[94Hal]</td>
</tr>
<tr>
<td>Ag–Bi–O</td>
<td></td>
<td>Section 4.3</td>
</tr>
<tr>
<td>Ag–Sr–O</td>
<td></td>
<td>Section 4.5</td>
</tr>
<tr>
<td>Ag–Ca–O</td>
<td></td>
<td>Section 4.5</td>
</tr>
<tr>
<td>Ag–Cu–O</td>
<td></td>
<td>Section 4.4</td>
</tr>
<tr>
<td>Bi–Sr–O</td>
<td>β-phase, γ-phase, Bi₂SrO₄, Bi₂Sr₂O₅, Bi₂Sr₃O₆, Bi₄Sr₆O₁₅, Bi₂Sr₆O₁₁</td>
<td>[97Hal1]</td>
</tr>
<tr>
<td>Bi–Ca–O</td>
<td>β-phase, γ-phase, Bi₁₄Sr₅O₂₆, Bi₂SrO₄, Bi₆Sr₄O₁₃, Bi₂Sr₂O₅</td>
<td>[97Hal2]</td>
</tr>
<tr>
<td>Bi–Cu–O</td>
<td>Bi₂CuO₄</td>
<td>[96Hal]</td>
</tr>
<tr>
<td>Sr–Cu–O</td>
<td>Sr₂CuO₃, SrCuO₂, Sr₁₄Cu₂₄O₄₁, SrCu₂O₂</td>
<td>[97Risl1]</td>
</tr>
<tr>
<td>Ca–Cu–O</td>
<td>Ca₂CuO₃, Ca₁₋ₓCuO₂₋₇, CaCu₂O₃</td>
<td>[95Risl2]</td>
</tr>
<tr>
<td>Sr–Ca–O</td>
<td></td>
<td>[97Risl2]</td>
</tr>
<tr>
<td>Ag–Bi–Sr–O</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag–Bi–Ca–O</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag–Bi–Cu–O</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag–Sr–Ca–O</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag–Sr–Cu–O</td>
<td></td>
<td>Section 4.5</td>
</tr>
<tr>
<td>Ag–Ca–Cu–O</td>
<td></td>
<td>Section 4.5</td>
</tr>
<tr>
<td>Bi–Sr–Ca–O</td>
<td>Bi₂SrCaOₓ, Bi₉Sr₁₁Ca₅Oₓ</td>
<td></td>
</tr>
<tr>
<td>Bi–Sr–Cu–O</td>
<td>Bi₁₁Sr₆Cu₅Oₓ, Bi₂Sr₂CuOₓ, Bi₂Sr₃Cu₂Oₓ, Bi₁₄Sr₈Cu₅Oₓ</td>
<td></td>
</tr>
<tr>
<td>Bi–Ca–Cu–O</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sr–Ca–Cu–O</td>
<td>SrₓCa₁₋ₓCuO₂</td>
<td>[97Risl2]</td>
</tr>
<tr>
<td>Ag–Bi–Sr–Ca–O</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag–Bi–Sr–Cu–O</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag–Bi–Ca–Cu–O</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag–Sr–Ca–Cu–O</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bi–Sr–Ca–Cu–O</td>
<td>Bi₂Sr₂CaCu₂Oₓ, Bi₂Sr₂Ca₂Cu₃Oᵧ</td>
<td>[96Risl3]</td>
</tr>
<tr>
<td>Ag–Bi–Sr–Ca–Cu–O</td>
<td></td>
<td>Section 4.6</td>
</tr>
</tbody>
</table>
The melting behavior of the BSCCO system is much influenced by the Cu–O and Bi–O
binary systems. On one hand, there is a miscibility gap in the liquid phase between metal-
lic Cu and CuO which extends to the higher-order systems. The relative amounts of Cu
ions with valence +1 and +2 is determined by the oxygen partial pressure and influences
the liquid composition also in higher-order systems. On the other hand, Bi₂O₃ has the
lowest melting point compared to the other oxides, therefore, the oxide liquid that forms
in the BSCCO system is rich in Bi. The two other binaries, Sr–O and Ca–O, are very simi-
lar to each other. The oxides SrO and CaO have high melting temperatures and a com-
plete mutual solubility at high temperature. Furthermore, the similarity of Sr and Ca (both
alkaline earth metals) means that they can substitute for each other in many oxide com-
pounds of the higher order systems, for example in Sr₁₄Cu₂₄O₄₁ which becomes
Sr₁₄₋ₓCaₓCu₂₄O₄₁ with 0 ≤ x ≤ 7.8.

Two families of secondary phases appear during the partial melt-processing of 2212, the
so-called Bi-free and the Cu-free compounds, which belong to the Sr–Ca–Cu–O and
Bi–Sr–Ca–O systems respectively. When heating pure 2212 in air, Margulies et. al.
[96Mar] observed the formation of 91150 (Cu-free) and 01x1 (Bi-free) compounds and,
at higher temperature, of 02x1 and of 01x0. These results are in agreement with other ex-
perimental investigations.

The 11905 (or 2201) superconducting compound appears in the Bi–Sr–Cu–O system
and the 2212 and 2223 HTSC phases in the Bi–Sr–Ca–Cu–O system. These phases belong to
the same structure family and can be written as Bi₂Sr₂Caₙ₋₁CuₙO₄₊₂n₊x (n = 1,2,3), the
so-called n-layer compounds. Experimental investigations revealed that these phases are
not stoichiometric. Considering the most important substitutions, the 2212 phase can be
modeled as:

\[(Bi^{3+},Bi^{5+})_2(Sr^{2+},Ca^{2+},Bi^{3+})_2(Ca^{2+})_1(Cu^{2+},Cu^{3+})_2(O^{2-})_8(O^{2-},Va)_{1/3}\]

where the last sublattice containing oxygen and vacancies compensates the excess charge
due to partial oxidation of Bi³⁺ and Cu²⁺. Figure 4.1 shows the single-phase field allowed
by the model, and the calculated single-phase field of 2212. Experimental data are also
presented [93Kni] and the agreement is generally good.

4.1.2 The Liquid Phase in the Ag–Bi–Sr–Ca–Cu–O System

As already mentioned, silver dissolves in the BiSrCaCu-oxide rich liquid during 2212
partial melt-processing and precipitates during solidification. The solubility of silver in
the oxide liquid and the presence of a metallic liquid at high temperatures and for high Ag
contents must be described by one model. In this study, we use the two-sublattice model
for ionic liquids which was described in Section 1.2.3. During the assessment of the
Ag–Cu–O system we compared this model with the associated model which can be seen
in Section 4.4.
Figure 4.1: a) Experimental results on the single phase field of 2212 summarized by Knizek et. al. [93Kni], b) Single-phase field allowed by the model (dashed line) and the calculated single phase field of 2212 at 800°C in air (solid line).

Fig 5. Comparison of single-phase compositions found in our work (•) with single-phase regions determined in refs. [17,21]. Ref. [17] (---) 850°C, air, XRD, EMA; Ref. [18] (-----) 860°C, air, XRD, EMA; Ref. [19] (----) varying T, air, XRD, EMA; Ref. [20] (-----) 830°C, air, XRD, EMA; Ref. [21] (-----) 865°C, oxygen, TEM.
4.1.3 References


[96Ris2] D. Risold, B. Hallstedt, and L. J. Gauckler, “The Strontium–Oxygen Sys-


4.2 The Ag–O System


**Thermodynamic Assessment of the Silver–Oxygen System**

Jérôme Assal, Bengt Hallstedt and Ludwig J. Gauckler
ETH Zürich, Department of Materials, Nonmetallic Materials,
Swiss Federal Institute of Technology, Sonneggstr.5, 8092 Zurich, Switzerland

**Abstract**

An assessment of the silver–oxygen system has been made, and a consistent set of thermodynamic parameters has been optimized. The calculated thermodynamic properties and phase relations are in good agreement with the experimental data. Ag₂O is the only phase that is commonly found within the system. In air, it decomposes to silver and oxygen gas at 462 K. There is a eutectic between silver and Ag₂O at a temperature of 804 K, an oxygen partial pressure ($P_{O_2}$) of 526 bar (5.26 x 10⁷ Pa), and an oxygen mole fraction in the liquid phase of 0.25. Uncertainties remain on the Ag₂O liquidus for $P_{O_2} > 10^8$ Pa. An ionic two-sublattice model has been used to describe the liquid phase. This work is part of a study of interactions between compounds from the bismuth–strontium–calcium–copper–oxygen system and silver.

**4.2.1 Introduction**

The present evaluation is the first step in a study of the interactions between compounds from the bismuth–strontium–calcium–copper–oxygen system, where several superconducting phases are found, and the substrate material silver. The silver–oxygen system contains one stable oxide phase at ambient pressure, Ag₂O, which is usually described as stoichiometric. However, Wöhnke et al. [94Woh] reported the existence of silver excess in Ag₂+δO where $δ < 2.2 \cdot 10^{-3}$. The crystal structure of Ag₂O is cubic with $Pn\bar{3}m$ as space group [92Kar]. A high-pressure modification with a hexagonal structure has been reported [64Kab].

Higher-valence silver oxides such as AgO, Ag₃O₄, and Ag₂O₃ have been synthesized by anodic oxidation of aqueous Ag(I)-solution at low temperatures [90Fis]. These higher-valence silver oxides are stable at low temperature ($T$) and high oxygen partial pressure ($P_{O_2}$). The existence of the silver suboxide Ag₄O was reported by Guntz [1899Gun] as an intermediate compound that formed during the reduction of Ag₂O. Lewis [06Lew] re-
peated the experiments but concluded that Ag$_2$O directly decomposed to silver and O$_2$.

Karakaya and Thompson [92Kar] assessed the silver–oxygen system and described the phase relations and the thermodynamics of the system. However, they observed large deviations between their description and the experimental data at high $P_{O_2}$ values ($> 5 \cdot 10^5$ Pa O$_2$).

We shall describe silver as a solid solution phase and Ag$_2$O as a stoichiometric phase. The two-sublattice model for ionic liquids [85Hil, 91Sun] will be used for the liquid phase. Higher-valence silver oxides and Ag$_4$O will not be considered further in this work.

**4.2.2 Experimental Data**

*Phase Diagram*

The equilibria between solid silver and the liquid phase have been investigated several times. Allen [32All] measured the melting temperature of silver as a function of $P_{O_2}$. His results show that the liquidus temperature decreases from 1234 K in an oxygen-free atmosphere to 1224 K in air and to 1211 K in 0.99 bar O$_2$ (9.9 $\cdot 10^4$ Pa). Johnstone and his coworkers [65Joh, 65Bak] used thermogravimetry (TG) and differential thermo analysis (DTA) to describe the liquidus up to 1.52 $\cdot 10^7$ Pa. Baker and Talukdar [68Bak] extended this study to 5.23 $\cdot 10^7$ Pa, which was consistent with other experimental works. In the latter investigation, the composition of the liquid was measured up to 1.01 $\cdot 10^7$ Pa along the liquidus.

Baker and Talukdar [68Bak] also measured the Ag$_2$O–liquid and silver–Ag$_2$O phase equilibria. The use of a high-pressure TG balance led to good precision in the temperature measurements. Characterization of the melting of Ag$_2$O was conducted for $P_{O_2}$ values in the range of 6.28 $\cdot 10^7$–8.27 $\cdot 10^7$ Pa. Using the silver–Ag$_2$O equilibrium measurements from Keyes and Hara [22Key] they could calculate the eutectic point (i.e. the intersection of these three equilibria) and found $T = 803$ K and $P_{O_2} = 5.37 \cdot 10^7$ Pa. By extrapolating the oxygen solubility along the liquidus, Baker and Talukdar [68Bak] estimated the oxygen mole fraction in the liquid phase, $x_O$, to be 0.22. Also by extrapolating the silver–Ag$_2$O equilibrium for high $P_{O_2}$ values, Allen [32All] estimated the eutectic reaction to occur at $T = 780$ K and $P_{O_2} = 4.19 \cdot 10^7$ Pa.

The oxygen solubility in solid silver was measured by several authors, mainly at $\leq 10^5$ Pa O$_2$. Using the absorption-desorption method from Sieverts and Hagenacker [09Sie], Steacie and Johnson [26Ste] found a minimum in the oxygen solubility in silver at ~ 673 K. However, Eichenauer and Müller [62Eic] later showed that the increase of the oxygen solubility at low temperature was due to adsorption. The use of a modified absorption-desorption technique [62Eic, 64Pod] or coulometric titration [72Ram] led to consistent results.
**Thermodynamic Data**

**A) Liquid Phase**

Several experimental data exist on the solubility of oxygen in liquid silver. The absorption-desorption technique from Sieverts and Hagenacker [09Sie] was used for low $P_{O_2}$ values ($\leq 10^5$ Pa) and gave consistent results [10Don,63Miz,65Par1,65Par2,67Sha, 68Kna, 68Lup]. Emf measurements of the thermodynamic properties of the liquid phase were made at low oxygen contents [66Dia,66Fis,81Ots,88Mag], and the results were in reasonable agreement. The studied temperatures were in the range of 1250–1673 K and the values of $x_O$ did not exceed 0.001. TG measurements at low $P_{O_2}$ values led to compatible results [70Bou]. Lower $x_O$ values were reported by Besson et al. [66Bes], using TG in an ambient atmosphere. Baker and Talukdar [68Bak] measured the value of $x_O$ in the liquid silver as a function of $P_{O_2}$. They used high-pressure TG, up to 101 bar $O_2$ $(1.01\times10^7$ Pa $O_2)$ at 1223 K and 1323 K, and found $x_O = 0.1$ for this $P_{O_2}$ value. Data on the Gibbs energy of the dissolution of oxygen in liquid silver, $\frac{1}{2}O_2 \leftrightarrow O$, are given in Table 4.2.

**B) Ag$_2$O Phase**

The dissociation pressures of Ag$_2$O, into silver and oxygen gas, have been studied over a large range of temperatures [06Lew,22Key,32Ben,65Bak,66Ott, 68Bak]. All the results are in good agreement.

The heat capacity ($C_P$) of Ag$_2$O has been measured over the temperature ranges 13–285 K [37Pit] and 318–502 K [51Kob]. A small discontinuity between the two sets of data of $\sim 1.2$ J/(mol·K)$^{-1}$ at 298.15 K is observed. With the help of their $C_P$ measurements, Pitzer and Smith [37Pit] calculated the entropy ($S$) of Ag$_2$O at 298.15 K and found $S_{298.15} = 121.7$ J/(mol·K)$^{-1}$. Using solution calorimetry in nitric acid (HNO$_3$), they also measured the enthalpy at 298.15 K of the reaction Ag$_2$O + 2H$^+$ → H$_2$O + 2Ag$^+$ and found $\Delta H$ value of $-43.65$ kJ/mol. With the help of data on the enthalpy for a chain of other reactions, Pitzer and Smith [37Pit] evaluated the enthalpy at 298.15 K of the reaction Ag + H$^+$ → Ag$^+$ + $\frac{1}{2}$H$_2$ to be $-105.82$ kJ/mol. Because the enthalpy of the reaction H$_2$O → H$_2$ + $\frac{1}{2}$O$_2$ is known to be 285.83 kJ/mol at 298.15 K (see Pitzer and Smith [37Pit]), the enthalpy of formation of Ag$_2$O at 298.15 K was calculated as $\Delta_f H = -30.54$ kJ/mol. Lewis [06Lew] reviewed older calorimetric data and found $\Delta_f H$ values of Ag$_2$O at 298.15 K to range between $-23.44$ kJ/mol and $-28.88$ kJ/mol, with an average $\Delta_f H$ value of $-26.53$ kJ/mol. Mixter [11Mix] used reaction calorimetry and found a $\Delta_f H_{298.15}$ value of $-22.6$ kJ/mol. No later measurements of $\Delta_f H_{298.15}$ were found. From the measurements of dissociation pressures of Ag$_2$O by Lewis [06Lew], Benton and Drake [32Ben], and Keyes and Hara [22Key], Pitzer and Smith gave the enthalpy of formation of Ag$_2$O in the temperature range of 446–773 K as being $\Delta_f H = -29.04$ kJ/mol.
4.2.3 Thermodynamic Models

Unary Phases

The descriptions from Dinsdale [91Dm] for the Gibbs energies of solid and liquid silver and for gaseous oxygen are used in this work. They are given as polynomials of the form:

\[ ^\circ G - H_{SER}^\circ = A + B T + C T \ln T + D T^2 + E T^3 + F T^{-1} \]  \hspace{1cm} (4.1)

where \( H_{SER}^\circ \) is the enthalpy for each pure element at 298.15 K and 10^5 Pa. These conditions define the Stable Element Reference (SER).

Liquid Phase

The two-sublattice model for ionic liquids [85Hil,91Sun] describes the liquid phase continuously from liquid silver to liquid Ag_2O. This model assumes that cations and anions can mix freely in their respective sublattices. The liquid phase is then written by \((\text{Ag}^{1+})_p (\text{O}^{2-}, \text{Va}^{q-})_q\) where \(p\) and \(q\) vary with composition, to maintain electroneutrality. Hypothetical negative vacancies are introduced in the anionic sublattice to make the model continuous from the metal to the oxide liquid. In this case, \(p\) and \(q\) are given by

\[ p = 2y_{O^{2-}} + qy_{\text{Va}} \] \hspace{1cm} (4.2)

\[ q = y_{\text{Ag}^{1+}} \] \hspace{1cm} (4.3)

where \(y_s\) is the site fraction of \(s\), i.e. the fraction of the species \(s\) in a particular sublattice. In this particular case, where \(\text{Ag}^{1+}\) is the only cation, \(y_{\text{Ag}^{1+}} = 1\) and the model can then be expressed by \((\text{Ag}^{1+})_p (\text{O}^{2-}, \text{Va}^{q-})_q\) with \(p = 2y_{O^{2-}} + y_{\text{Va}}\).

The molar Gibbs energy of the liquid is

\[ G_{\text{liq}}^\circ = y_{O^{2-}} G_{\text{Ag}^{1+},O^{2-}}^\circ + y_{\text{Va}} G_{\text{Ag}^{1+},\text{Va}}^\circ \]

\[ +RT(y_{O^{2-}} \ln(y_{O^{2-}}) + y_{\text{Va}} \ln(y_{\text{Va}})) \]

\[ +y_{O^{2-}} y_{\text{Va}} L_{\text{Ag}^{1+},O^{2-}, \text{Va}} \] \hspace{1cm} (4.4)

where \(G_{\text{Ag}^{1+},\text{Va}}^\circ\) is the Gibbs energy of pure liquid silver, as given by Dinsdale [91Dm].

The Gibbs energy of liquid Ag_2O, \(G_{\text{Ag}^{1+},O^{2-}}^\circ\), is given by

\[ G_{\text{Ag}^{1+},O^{2-}}^\circ = 2H_{\text{SER}}^\circ - H_{O}^\circ \]

\[ = A + BT + CT \ln T \] \hspace{1cm} (4.5)
where $C$ is the heat capacity of liquid Ag$_2$O. Because liquid Ag$_2$O is stable only at very high $P_O$ values, there are no measurements available. We have chosen to use the same heat capacity for liquid Ag$_2$O as for liquid Cu$_2$O [94Hal]. $L_{\text{Ag}^{+\cdot}O^{2-}}$, $v_a$ is the interaction parameter and can be described by a linear temperature dependence.

**Binary Solid Phases**

Solid silver has a face-centered cubic (fcc) structure and shows a small solubility of oxygen, in the order of $10^{-4}$--$10^{-3}$ mole fraction. We describe this with a substitutional solution model. The molar Gibbs energy is

$$G_m^{\text{fcc}} = x_{Ag} \cdot G_{Ag}^{\text{fcc}} + x_O \cdot G_{O}^{\text{fcc}} + RT \cdot (x_{Ag} \cdot \ln x_{Ag} + x_O \cdot \ln x_O)$$  \hspace{1cm} (4.6)

$$+ L_{\text{Ag},O}^{\text{fcc}}$$

where the Gibbs energy of pure silver is given by Dinsdale [91Din] and the Gibbs energy of fcc oxygen is expressed by $G_{O}^{\text{fcc}} - \frac{1}{2} G_{O^2} = 1000 \text{ kJ/mol}$. This value, which is greater than the 30 kJ/mol value that was suggested by Dinsdale [91Din], prevents the appearance of fcc oxygen. The oxygen solubility is then described by the interaction parameter $L_{\text{Ag},O}^{\text{fcc}}$.

Below the calculated melting temperature of Ag$_2$O ($T_m = 1060$ K), stoichiometric Ag$_2$O is described by

$$oG_{\text{Ag}_2O}^{\text{Ser}} - 2H_{\text{Ag}}^{\text{Ser}} - H_{\text{O}}^{\text{Ser}} = A + BT + CT\ln T + DT^2 + FT^{-1}$$  \hspace{1cm} (4.7)

where $C$, $D$ and $F$, which represent the heat capacity for solid Ag$_2$O, are taken from Kubaschewski [93Kub]. Above the melting temperature, solid Ag$_2$O is described by:

$$oG_{\text{Ag}_2O}^{\text{Ser}} - 2H_{\text{Ag}}^{\text{Ser}} - H_{\text{O}}^{\text{Ser}} = A + BT + CT\ln T$$  \hspace{1cm} (4.8)

where the same $C_P$ value as for liquid Ag$_2$O is used. The parameters of Eq. 8 prevent solid Ag$_2$O from reappearing at high temperature. A discontinuity in the $C_P$ value for Ag$_2$O at $T_m$, is predicted by Eqs. 7 and 8; however, because the melting of pure Ag$_2$O occurs at very high $P_O$ values, we have accepted this discontinuity and not considered, for example, the additions of a $T^7$ term at $T < T_m$ and a $T^{-5}$ term at $T > T_m$ as suggested Andersson et.al. [87And].

Small deviations from stoichiometry in Ag$_{2+\delta}$O were reported by Wöhnke et.al. [94Woh]. At $T = 443$ K they gave a maximum $\delta$ value of $2.2 \times 10^{-3}$. These small deviations
have a negligible influence on the thermodynamic properties of Ag₂O, and we choose not to model them.

4.2.4 Results and Discussion

The thermodynamic parameters that have been optimized in the present work are listed in Table 4.3.

Phase Diagram

The calculated silver–Ag₂O phase diagram is shown in Fig. 4.2 and the special points of the system can be found in Table 4.4, where they are compared with experimental data. The agreement is generally good. In the phase diagram (Fig. 4.2), the Ag₂O liquidus and the melting temperature of Ag₂O ($T_m = 1060$ K) are drawn with a dashed line to show that the extrapolation at $P_{O_2} > 10^3$ bar $O_2 (> 10^8$ Pa $O_2)$ are rather uncertain.

The calculated eutectic point is at $T = 803.6$ K, $P_{O_2} = 5.26 \cdot 10^7$ Pa, and $x_O = 0.2514$. The values of $T$ and $P_{O_2}$ are in good agreement with the measured values ($T = 803$ K, $P_{O_2} = 5.37 \cdot 10^7$ Pa) from Baker and Talukdar [68Bak]. However, the difference in the composition between their extrapolated value ($x_O = 0.22$) and our calculation is larger. The optimization has shown that the measurements along the liquidus from Baker and Talukdar [68Bak], and the extrapolated oxygen composition of the eutectic, contradict the large amount of data on the oxygen solubility in the liquid [09Sie, 10Don, 65Parl, 66Bes, 66Dia, 67Sha, 68Bak, 68Kna, 68Lup].

Figure 4.3 shows the calculated potential phase diagram, which is in good agreement with experimental data. However, the Ag₂O–liquid line is somewhat uncertain, because there are only a few experimental points from one reference [68Bak].

The oxygen solubility in solid silver is shown in Fig. 4.4. Our calculation fits the experimental data well and also is in good agreement with the assessment of Karakaya and Thompson [92Kar].

Thermodynamics

A) Liquid Phase

The calculated oxygen isobars in the liquid phase are compared to the experimental data in Fig. 4.5. The agreement is generally good except for the data of Besson et al. [66Bes] which seem unrealistic at high temperature. Table 4.2 shows the Gibbs energy of dissolution of oxygen in liquid silver and the first-order interaction parameter, $\varepsilon_O^0$, which is evaluated as the slope of the logarithm of the activity coefficient of oxygen, $\ln y_O$, in the $x_O$ range of 0–0.001. Our calculated $\Delta^O G$ value shows a small temperature dependence in the entropy range of 5.8 and 6.0 J·(mol·K)$^{-1}$. When compared with experimental evaluations, these values are at the lower end of the scatter band, which is very large (5.4–21.7 J·(mol·K)$^{-1}$).
B) $\text{Ag}_2\text{O}$ Phase

The heat capacity of $\text{Ag}_2\text{O}$ as a function of the temperature is shown in Fig. 4.6. Data on the heat capacity and the entropy of $\text{Ag}_2\text{O}$ at $T = 298.15 \text{ K}$ are listed in Table 4.5. The values of $C_p$ that have been used in this study are from Kubaschewski et al. [93Kub], because we assessed and accepted their $C_p$ description.

The enthalpy of formation of $\text{Ag}_2\text{O}$ at $298.15 \text{ K}$ in the temperature range of 446–773 K is listed in Table 4.6. Our calculated value of $\Delta_f H_{298.15}$ is very similar to the experimental data of Pitzer and Smith [37Pit], as compared to the assessed data of Kubaschewski et al. [93Kub]. Also, by calculation, we find that $\Delta_f H$ is equal to $-29.99 \text{ kJ/mol}$ at $T = 446 \text{ K}$ and $-25.81 \text{ kJ/mol}$ at $T = 773 \text{ K}$. These values can be compared to the average enthalpy of formation that was calculated by Pitzer and Smith [37Pit] for $446 \text{ K} < T < 773 \text{ K}$, i.e. $\Delta_f H = -29.04 \text{ kJ/mol}$.

The calculated and measured Gibbs energies of the reaction $2\text{Ag} + \frac{1}{2}\text{O}_2 \rightarrow \text{Ag}_2\text{O}$ are shown in Table 4.7. Our calculation agrees well with the experimental data as well as with the assessment of Karakaya and Thompson [92Kar]. This latter expression has been calculated by us from their $T-P_{O_2}$ relation for silver–$\text{Ag}_2\text{O}$. The reason for doing so is that, later in their work, Karakaya and Thompson indicated the Gibbs energy of formation of $\text{Ag}_2\text{O}$ with an error that corresponded to a factor of $2/\ln(10)$.

4.2.5 Conclusion

A consistent set of thermodynamic parameters that describe the experimental data on the silver–oxygen system very well has been obtained. However, some uncertainties on the properties of the liquid phase remain, for very high oxygen partial pressures $P_{O_2}$. To extend the assessment to higher $P_{O_2}$, the higher-valence silver oxides must be included and the pressure dependance of the condensed phases must be modeled.

4.2.6 Acknowledgement

Financial support from COST 512 (European Co-operation in the Field of Scientific and Technical Research, Modelling in Materials Science and Processing) is gratefully acknowledged.

4.2.7 References


[10Don] F. G. Donnan and T. W. A. Shaw, “The Solubility of Oxygen in Molten Sil-


Table 4.2: Gibbs energy dissolution of oxygen in liquid silver and first-order interaction parameter $\varepsilon_O^0$.

<table>
<thead>
<tr>
<th>$\Delta^0G$, J/mol</th>
<th>$\varepsilon_O^0$</th>
<th>Temperature, K</th>
<th>Method</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>-7028; -6887</td>
<td>—</td>
<td>1348; 1398</td>
<td>Absorption</td>
<td>[09Sie]</td>
</tr>
<tr>
<td>-6975</td>
<td>—</td>
<td>1348</td>
<td>Absorption</td>
<td>[10Don]</td>
</tr>
<tr>
<td>-13904+5.41·$T$</td>
<td>—</td>
<td>1284–1475</td>
<td>Absorption</td>
<td>[65Par]</td>
</tr>
<tr>
<td>-14145+21.22·$T$</td>
<td>—</td>
<td>1240–1490</td>
<td>Emf (O$_2$, 1 bar)</td>
<td>[66Dia]</td>
</tr>
<tr>
<td>-10463+18.04·$T$</td>
<td>—</td>
<td>1273–1673</td>
<td>Emf (air)</td>
<td>[66Fis]</td>
</tr>
<tr>
<td>-14473+5.98·$T$</td>
<td>—</td>
<td>1204–1492</td>
<td>Absorption</td>
<td>[67Sha]</td>
</tr>
<tr>
<td>-17872+8.0·$T$</td>
<td>6.92–1901/$T$</td>
<td>1223–1323</td>
<td>High-pressure (TG)</td>
<td>[68Bak]</td>
</tr>
<tr>
<td>-14940+21.68·$T$</td>
<td>3.9</td>
<td>1250–1420</td>
<td>Absorption</td>
<td>[68Lup]</td>
</tr>
<tr>
<td>-16140+6.52·$T$</td>
<td>—</td>
<td>1353–1573</td>
<td>Emf (air)</td>
<td>[81Ots]</td>
</tr>
<tr>
<td>-15614+6.76·$T$</td>
<td>—</td>
<td>1273–1323</td>
<td>Emf (air)</td>
<td>[88Mag]</td>
</tr>
<tr>
<td>-14759+5.79·$T$</td>
<td>7.32–3406/$T$</td>
<td>1200–1353</td>
<td>Calculated</td>
<td>This work</td>
</tr>
<tr>
<td>-15004+5.97·$T$</td>
<td>7.32–3406/$T$</td>
<td>1353–1673</td>
<td>Calculated</td>
<td>This work</td>
</tr>
</tbody>
</table>

Note: The Gibbs energy of dissolution is at infinite dilution using a standard state of 1 at.%. The reference state for oxygen is O$_2$ at 10$^5$ Pa. For emf measurements, the electrode reference is given in parentheses.
Table 4.3: Thermodynamic description the silver–oxygen system.

**Liquid**

\((\text{Ag}^{1+})_p (\text{O}^{2-}, \text{Va}^{1-})_1\)

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

\[ \Delta G_{\text{liq}, \text{Ag}^{1+}, \text{Va}}^{\text{SER}} = \Delta G_{\text{liq}} \]

\[ \Delta G_{\text{liq}, \text{Ag}^{1+}, \text{O}^{2-}}^{\text{SER}} = \Delta G_{\text{liq}} - 2\Delta H_{\text{Ag}^{1+}, \text{O}^{2-}}^{\text{SER}} = -40980 + 431.5 \cdot T - 84 \cdot T \cdot \ln T \]

\[ L_{\text{Ag}^{1+}, \text{O}^{2-}, \text{Va}} = 13806 - 13.17 \cdot T \]

**Solid Ag (fcc)**

\((\text{Ag}_2\text{O})\)

\[ \Delta G_{\text{fcc}, \text{Ag}}^{\text{SER}} - \Delta H_{\text{fcc}, \text{Ag}}^{\text{SER}} = \Delta G_{\text{fcc}} \]

\[ \Delta G_{\text{fcc}, \text{O}}^{\text{SER}} - \Delta H_{\text{fcc}, \text{O}}^{\text{SER}} = \Delta G_{\text{fcc}} + 1000000 \]

\[ L_{\text{fcc}, \text{Ag}_2\text{O}} = -945666 + 16.25 \cdot T \]

**Ag_2O**

\[ \Delta G_{\text{Ag}_2\text{O}}^{\text{SER}} - 2\Delta H_{\text{Ag}}^{\text{SER}} - \Delta H_{\text{O}}^{\text{SER}} = \]

\[ 298.15 < T < 1060 \]
\[ -51729 + 291.2 \cdot T - 59.33 \cdot T \cdot \ln T + 230000T^{-1} - 0.020395 \cdot T^2 \]

\[ 1060 < T < 3000 \]
\[ -51491 + 441.6 \cdot T - 84 \cdot T \cdot \ln T \]

**O_2 gas**

\[ \Delta G_{\text{O}_2}^{\text{gas}} - 2\Delta H_{\text{O}_2}^{\text{SER}} = 2\Delta G_{\text{O}_2} + RT \ln (9.8692327 \cdot 10^{-6} \cdot P) \]

(continued)
Functions
GAGLIQ\(\Phi\) =
\[\begin{align*}
298.15 & < T < 1235.08 \\
11025.293 - 8.890146 \cdot T & - 1.0322 \cdot 10^{-20} \cdot T^7 + \text{GHSERAG}
\end{align*}\]

\[\begin{align*}
1235.08 & < T < 3000 \\
11507.972 - 9.300495 \cdot T & - 1.412186 \cdot 10^{29} \cdot T^{-9} + \text{GHSERAG}
\end{align*}\]

GHSERAG\(\Phi\) =
\[\begin{align*}
298.15 & < T < 1235.08 \\
-7209.512 + 118.200733 \cdot T & - 23.8463314 \cdot T \cdot \ln T - 0.001790585 \cdot T^2 - 3.98587 \cdot 10^{-7} \cdot T^3 - 12011 \cdot T^{-1}
\end{align*}\]

\[\begin{align*}
1235.08 & < T < 3000 \\
-15095.314 + 190.265169 \cdot T & - 33.472 \cdot T \cdot \ln T + 1.412186 \cdot 10^{29} \cdot T^{-9}
\end{align*}\]

GHSEROO\(\Phi\) =
\[\begin{align*}
298.15 & < T < 1000 \\
-3480.87 - 25.503038 \cdot T & - 11.136 \cdot T \cdot \ln T - 0.005098888 \cdot T^2 + 6.61846 \cdot 10^{-7} \cdot T^3 - 38365 \cdot T^{-1}
\end{align*}\]

\[\begin{align*}
1000 & < T < 3300 \\
-6568.763 + 12.659888 \cdot T & - 16.8138 \cdot T \cdot \ln T - 5.95798 \cdot 10^{-4} \cdot T^2 + 6.781 \cdot 10^{-9} \cdot T^3 + 262905 \cdot T^{-1}
\end{align*}\]

\[\begin{align*}
3300 & < T < 6000 \\
-13986.728 + 31.259625 \cdot T & - 18.9536 \cdot T \cdot \ln T - 4.25243 \cdot 10^{-4} \cdot T^2 + 1.078 \cdot 10^{-8} \cdot T^3 + 4383200 \cdot T^{-1}
\end{align*}\]

All parameter values are given in SI units (mol, J, K, Pa, \(R = 8.31451\) J/(mol·K)\(^{-1}\)).

\(\Phi\) All expressions for the functions are from Dinsdale [91Din]
Table 4.4: Special points in the silver–oxygen system.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$T$</th>
<th>$x_O$ in liquid</th>
<th>$P_{O_2} \cdot 10^5$, Pa</th>
<th>Method</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>L $\leftrightarrow$ Ag + Ag$_2$O (eutectic)</td>
<td>780</td>
<td>—</td>
<td>420</td>
<td>Extrapolated</td>
<td>[32All]</td>
</tr>
<tr>
<td></td>
<td>803</td>
<td>0.22</td>
<td>537</td>
<td>High-pressure TG</td>
<td>[68Bak]</td>
</tr>
<tr>
<td></td>
<td>803.5</td>
<td>0.2514</td>
<td>526.0</td>
<td>Calculated</td>
<td>This work</td>
</tr>
<tr>
<td>L $\leftrightarrow$ Ag$_2$O</td>
<td>1060.2</td>
<td>0.3333</td>
<td>$\infty$</td>
<td>Calculated</td>
<td>This work</td>
</tr>
<tr>
<td>L $\leftrightarrow$ Ag + O$_2$ $\leftrightarrow$ Ag (in air)</td>
<td>1224</td>
<td>—</td>
<td>0.21</td>
<td>Cooling curve</td>
<td>[32All]</td>
</tr>
<tr>
<td></td>
<td>1223</td>
<td>—</td>
<td>0.21</td>
<td>TG</td>
<td>[65Bak,68Bak]</td>
</tr>
<tr>
<td></td>
<td>1219</td>
<td>0.0099</td>
<td>0.21</td>
<td>TG</td>
<td>[66Bess]</td>
</tr>
<tr>
<td></td>
<td>1223</td>
<td>0.0087</td>
<td>0.21</td>
<td>TG</td>
<td>[68Kna]</td>
</tr>
<tr>
<td></td>
<td>1226</td>
<td>0.0097</td>
<td>0.21</td>
<td>Assessed</td>
<td>[92Kar]</td>
</tr>
<tr>
<td></td>
<td>1224.2</td>
<td>0.00981</td>
<td>0.21</td>
<td>Calculated</td>
<td>This work</td>
</tr>
<tr>
<td>L $\leftrightarrow$ Ag + O$_2$ $\leftrightarrow$ Ag (in O$_2$)</td>
<td>1228</td>
<td>0.0204</td>
<td>1.01</td>
<td>Absorption</td>
<td>[09Sie]</td>
</tr>
<tr>
<td></td>
<td>1211</td>
<td>—</td>
<td>1.01</td>
<td>Cooling curve</td>
<td>[32All]</td>
</tr>
<tr>
<td></td>
<td>1210</td>
<td>—</td>
<td>1.01</td>
<td>TG</td>
<td>[65Bak,68Bak]</td>
</tr>
<tr>
<td></td>
<td>1212</td>
<td>0.021</td>
<td>1.01</td>
<td>Absorption</td>
<td>[67Sha]</td>
</tr>
<tr>
<td></td>
<td>1212</td>
<td>0.0195</td>
<td>1.01</td>
<td>TG</td>
<td>[68Kna]</td>
</tr>
<tr>
<td></td>
<td>1212</td>
<td>0.0209</td>
<td>1.01</td>
<td>Assessed</td>
<td>[92Kar]</td>
</tr>
<tr>
<td></td>
<td>1224.2</td>
<td>0.02053</td>
<td>1.01</td>
<td>Calculated</td>
<td>This work</td>
</tr>
</tbody>
</table>

Note: "L" represents the liquid phase.

Table 4.5: Heat capacity ($C_p$) and entropy ($S$) of Ag$_2$O at 298.15 K.

<table>
<thead>
<tr>
<th>$C_p$, J·(mol·K)$^{-1}$</th>
<th>$S$, J·(mol·K)$^{-1}$</th>
<th>Method</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>65.6</td>
<td>121.7</td>
<td>Calorimetry (13–285 K)</td>
<td>[37Pit]</td>
</tr>
<tr>
<td>66.8</td>
<td>—</td>
<td>Calorimetry (318–502 K)</td>
<td>[51Kob]</td>
</tr>
<tr>
<td>66.3</td>
<td>120.9</td>
<td>Assessed</td>
<td>[93Kub]</td>
</tr>
<tr>
<td>66.3</td>
<td>120.9</td>
<td>Calculated</td>
<td>This work</td>
</tr>
</tbody>
</table>
Table 4.6: Enthalpy of formation ($\Delta_f^H$) of Ag$_2$O at 298.15, 446, and 773 K.

<table>
<thead>
<tr>
<th>$T$, K</th>
<th>$-\Delta_f^H$, kJ/mol</th>
<th>Method</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>298.15</td>
<td>26.53</td>
<td>Reviewed</td>
<td>[06Lew]</td>
</tr>
<tr>
<td>298.15</td>
<td>22.60</td>
<td>Reaction calorimetry</td>
<td>[11Mix]</td>
</tr>
<tr>
<td>298.15</td>
<td>30.54</td>
<td>Solution calorimetry</td>
<td>[37Pit]</td>
</tr>
<tr>
<td>298.15</td>
<td>31.10</td>
<td>Assessed</td>
<td>[93Kub]</td>
</tr>
<tr>
<td>446–773</td>
<td>29.44</td>
<td>Calculated from</td>
<td>[06Lew,22Key,32Ben]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>298.15</td>
<td>30.68</td>
<td>Calculated</td>
<td>This work</td>
</tr>
<tr>
<td>446; 773</td>
<td>29.99; 25.81</td>
<td>Calculated</td>
<td>This work</td>
</tr>
</tbody>
</table>

Table 4.7: Gibbs energy change of the reaction $2\text{Ag} + \frac{1}{2} \text{O}_2 \rightarrow \text{Ag}_2\text{O}$.

<table>
<thead>
<tr>
<th>$\Delta^\circ G$, J/mol</th>
<th>Temperature, K</th>
<th>Method</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$-27766+60.9 \cdot T$</td>
<td>575–718</td>
<td>Dissociation pressure</td>
<td>[06Lew]</td>
</tr>
<tr>
<td>$-27263+60.1 \cdot T$</td>
<td>647–773</td>
<td>Dissociation pressure</td>
<td>[22Key]</td>
</tr>
<tr>
<td>$-29673+64.1 \cdot T$</td>
<td>446–464</td>
<td>Dissociation pressure</td>
<td>[32Ben]</td>
</tr>
<tr>
<td>$-29917+64.8 \cdot T$</td>
<td>447–554</td>
<td>Dissociation pressure</td>
<td>[66Ott]</td>
</tr>
<tr>
<td>$-28687+62.1 \cdot T$</td>
<td>446–773</td>
<td>Assessed</td>
<td>[92Kar]</td>
</tr>
<tr>
<td>$-28532+61.7 \cdot T$</td>
<td>446–773</td>
<td>Calculated</td>
<td>This work</td>
</tr>
</tbody>
</table>

Note: The reference pressure for O$_2$ is $10^5$ Pa.
Figure 4.2: Calculated Ag–Ag₂O phase diagram and experimental data [68Bak] (1 bar = 10⁵ Pa).

Figure 4.3: Calculated potential phase diagram of the silver–oxygen system compared with experimental data [06Lew, 22Key, 32All, 32Ben, 65Joh, 65Bak, 66Ott, 68Bak] (1 bar = 10⁵ Pa).
Figure 4.4: Calculated solubility of oxygen in solid silver (fcc) for $P_{O_2} = 1$ bar and $P_{O_2} = 0.5$ bar ($10^5$ and $0.5 \cdot 10^5$ Pa, respectively) compared with experimental data [09Sie,26Ste,62Eic,64Pod,72Ram] and the assessment by Karakaya and Thompson [92Kar].

![Graph showing calculated solubility of oxygen in solid silver.](image)

Figure 4.5: Calculated oxygen isobars in the liquid phase compared with experimental data [09Sie,10Don,65Parl,66Bes,66Dia,67Sha,68Bak,68Kna,68Lup] (1 bar = $10^5$ Pa).

![Graph showing calculated oxygen isobars in the liquid phase.](image)
Figure 4.6: Calculated heat capacity of Ag$_2$O compared with experimental data [37Pit, 51Kob].
4.3 The Ag–Bi–O System

Experimental Phase Diagram Study and Thermodynamic Optimization of the Ag–Bi–O System

Jérôme Assal, Bengt Hallstedt and Ludwig J. Gauckler
ETH Zürich, Department of Materials, Nonmetallic Materials, Swiss Federal Institute of Technology, Sonneggstr. 5, 8092 Zurich, Switzerland

Abstract

The Ag–Bi–O system has been experimentally studied using differential thermal analysis (DTA) and scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDX), and thermodynamically optimized. The temperatures of the eutectic, monotectic and Bi$_2$O$_3$ allotropic transformations have been measured in N$_2$, in air and in O$_2$ by DTA. There is no ternary phase. Presently measured transformation temperatures have been combined with existing oxygen activity measurements in the metal liquid to optimize thermodynamic parameters describing the liquid phase. The resulting fit is excellent. EDX measurements of the composition in the oxide liquid have a rather low precision but confirm the thermodynamic optimization. However, some uncertainties remain concerning the liquid composition at the eutectic transformation and the shape of the miscibility gap at higher temperatures.

4.3.1 Introduction

The Bi–Sr–Ca–Cu–O system contains several superconducting phases, including Bi-2212 and Bi-2223. These phases are of large technological interest since they have high critical temperatures ($T_c \approx 95$ K for Bi-2212 and $T_c \approx 115$ K for Bi-2223) and can be relatively easy synthesized. They are usually processed on silver substrate since silver is chemically stable at high temperature and has no detrimental effect on the superconducting properties. During processing of Bi-2212 thick films on silver substrate, it has been observed that Ag lowers the melting temperature of the 2212 phase of about 30 K [97Lan,97Maj]. This work is part of a project to evaluate the thermodynamics and the phase relations in the Ag–Bi–Sr–Ca–Cu–O system.

Very few experimental studies exist on the Ag–Bi–O system. The oxygen activity has been measured in the Ag–Bi metal liquid at $T = 1273$ K [84Ots] and $T = 1373$ K [88Yao].
using electrochemical force method (emf) with the cell: O / ZrO2 (+ CaO) / air, Pt. The measurements are fully consistent with each other. Several ternary compounds have been characterized but they are all stable at very high oxygen partial pressures only. Ag3BiO3 (tetragonal structure, space group: P4_1/n) and Ag5BiO4 (monoclinic structure, space group: P2_1/n) were produced either by a solid reaction between Ag2O and Bi2O3 under \( P_{O_2} = 100 \text{ MPa} \) and \( T \approx 800 \text{ K} \) or by a hydrothermally activated reaction between Ag2O and Ag3BiO3 under \( P_{O_2} = 10 \text{ MPa} \) and \( T = 620 \text{ K} \) [41Sch,93Bor]. Single crystals of Ag18Bi4O12 were obtained by dissolving Bi2O3 in molten AgNO3 at \( T = 573 \text{ K} \) and have an orthorhombic structure with space group Cmcm [86Mas]. Ag25Bi3O18 which belongs to the \( P\overline{3} \) space group of the trigonal symmetry was produced by hydrothermal reaction of Ag2O and AgBiO3 in \( P_{O_2} = 10 \text{ MPa} \) and \( T = 623 \text{ K} \). These ternary compounds will not be considered further in this study.

Since the phase relations in the Ag–Bi–O system have not been characterized yet, we studied Ag–BiO1.5 by differential thermal analysis (DTA). Extrapolations from the binaries in the ternary Ag–Bi–O system show in air a eutectic between fcc (Ag) and \( \delta\)-Bi2O3 at 997 K, a monotectic between fcc (Ag) and the oxide liquid at 1224 K, and the \( \alpha/\delta\)-Bi2O3 allotropic transformation at 1002 K. The similarities with the Ag–Cu–O system previously assessed [97Ass2] were also very helpful to start the experimental study. Eutectic, monotectic and Bi2O3 allotropic transformation temperatures have been measured for several compositions (between \( u_{Ag} \) values of 0.026 and 0.67) in three oxygen partial pressures, \( P_{O_2} = 200 \text{ Pa} \) (in N2), \( P_{O_2} = 2.1 \times 10^4 \text{ Pa} \) (air) and \( P_{O_2} = 1.01 \times 10^5 \text{ Pa} \) (in O2). In air and in O2, the silver content in the bismuth oxide-rich liquid was measured using energy dispersive X-ray spectrometry (EDX) and shows \( u_{Ag} \) values close to 0.11 in air and 0.15 in O2.

The Ag–Bi–O system was subsequently optimized using oxygen activity measurements in the metal liquid and invariant transformation temperatures measured by DTA. Previous assessments of Ag–O by Assal et.al. [97Ass1], Bi–O by Risold et.al. [95Ris] and Ag–Bi by Karakaya and Thompson [93Kar] have been used in this work.

### 4.3.2 Experimental Ag–BiO1.5 Phase Diagram

Appropriate amounts of Ag2O powder² and Bi2O3 powder³ were dry-mixed for 3 h in a ball mill. The compositions of the mixtures correspond to the following metallic ratio: \( u_{Ag} = 0.026, 0.05, 0.07, 0.11, 0.25 \) and 0.67. The temperatures of the invariant transformations were investigated by DTA⁴. During these measurements samples of approximately 100 mg were heated in Al2O3 crucibles at rates of \( dT/dt = 1 \text{ K/min} \), 2 K/min or 5 K/min in O2 (\( P_{O_2} = 1.01 \times 10^5 \text{ Pa} \) in O2), in air (\( P_{O_2} = 2.1 \times 10^4 \text{ Pa} \) in air) and in N2 (\( P_{O_2} = 200 \text{ Pa} \) in N2). The total gas pressure was \( 1.01 \times 10^5 \text{ Pa} \) (1.01 bar) and the gas flow 3 l/h. During the heat-

---

1. where \( u \) is the metallic ratio, i.e. \( u_{Ag} = n_{Ag}/(n_{Ag} + n_{Bi}) \)
2. CERAC, 99.0%  
3. Fluka Chemika, 99.9%  
4. STA 501, Bähr, Germany
ing a step of 2 h at 873 K allows the complete reduction of Ag₂O into Ag. The use of Ag₂O as starting powder leads to a fine distribution of Ag particles. The oxygen partial pressure was continuously measured with a ZrO₂-oxygen sensor when an N₂ atmosphere was used and the step at 873 K was lengthened to 32 h to reach a constant P₀₂. In O₂, the first peak measured by DTA was Tₑ = 959 ± 2 K and corresponds to the (Ag) + α-Bi₂O₃ ↔ L₂ eutectic reaction. For uₐg ≤ 0.11, the α-Bi₂O₃ ↔ δ-Bi₂O₃ transformation in presence of L₂ was measured at Tₐδ = 1004 ± 3 K and corresponds to the allotropic transformation in the Bi–O system. For uₐg ≥ 0.25, the monotectic reaction (Ag) + L₂ ↔ L₁ was determined at Tₘ = 1210 ± 4 K, very close to the melting temperature of silver (Tₘ = 1212 K in O₂). In air, the sequence of reactions is the same but the temperatures are Tₑ = 984 ± 2 K for the eutectic transformation, Tₐδ = 1002 ± 3 K for the Bi₂O₃ allotropic transformation and Tₘ = 1223 ± 4 K for the monotectic reaction. In N₂, P₀₂ changes with the reactions. After 32 h at T = 873 K, the oxygen partial pressure is constant, P₀₂ ≈ 10 Pa, and does not change during the α-Bi₂O₃ ↔ δ-Bi₂O₃ allotropic transformation measured at Tₐδ = 1005 ± 4 K. When the (Ag) + δ-Bi₂O₃ ↔ L₂ eutectic reaction starts, oxygen is produced and P₀₂ reaches 200 Pa, the eutectic temperature is then measured at Tₑ = 1050 ± 5 K. The monotectic transformation takes place in P₀₂ = 200 Pa at Tₘ = 1233 ± 5 K. All DTA results can be found in Tables 4.8–10, and in Figures A.1–A.9. No DTA peaks showing the presence of a ternary phase could be detected.

Two samples with initial composition corresponding to uₐg = 0.25 were melted in a vertical furnace in air and in oxygen and the silver contents of the bismuth rich oxide liquid were analysed by EDX. The samples were first heated to 873 K and kept at this temperature during 2 h, allowing the reduction of Ag₂O, and then heated and kept at 1136 K for 3 h, to homogenize the microstructure and the composition. They were then quenched in oil at room temperature (dT/dt > 100 K/sec). Because of its high thermal conductivity, silver was chosen as crucible material, which lead to reasonable homogeneity in composition and microstructure. It also modified the composition of the samples but with no influence on the silver content of the Bi-rich oxide liquid. In flowing oxygen (P₀₂ = 1.0×10⁵ Pa) the measured silver content in the oxide liquid was uₐg = 0.15 ± 0.04 and in air uₐg = 0.11 ± 0.03. The EDX measurements are shown in Figures 4.7 and 4.8.

4.3.3 Thermodynamic Models

Solid Phases

The Gibbs energies for pure Ag and Bi are taken from Dinsdale [91Din] and the descriptions of the oxides come from previous assessments, i.e. Ag₂O is from Assal et.al. [97Ass1] and α- and δ-Bi₂O₃ are from Risold et.al. [95Ris]. These compounds are considered as stoichiometric.

The fcc phase (Ag) in the Ag–Bi system shows a small solubility x₂Bi = 0.03 well fitted by the calculation of Karakaya and Thompson [93Kar]. When we tested the parameter of the

1. Type FCX-MW-FL, Pewatron, Switzerland
fcc phase, it turned out that the fitting was not satisfactory, though, see Figure 4.10 where the dotted line represents the limit of solubility calculated with $L_{\text{Ag, Bi}}^{\text{fcc}}$ given by Karakaya and Thompson. This interaction parameter between Ag and Bi was recalculated using experimental data taken from the phase diagram shown in Karakaya and Thompson's paper. The parameter is then $L_{\text{Ag, Bi}}^{\text{fcc}} = 24300 - 10.5 \cdot T$ and the reassessed fcc phase (Ag) can be seen in Figure 4.10 in very good agreement with the experimental data [40Chi, 46Rau, 83Ako, 88Sch].

Since the oxygen solubility in the fcc (Ag) is small, $x_0 < 5.8 \cdot 10^{-4}$ in O$_2$ for $T = 1212$ K, the extrapolation into the ternary system is expected to be reasonably accurate and there is no need to introduce a ternary interaction parameter in the description of (Ag). Solid bismuth (rhombohedral structure) is described as a stoichiometric phase.

**Liquid Phase**

The two-sublattice model for ionic liquids [85Hil, 91Sun] can continuously describe the liquid phase from the metal to the oxide compositions. It is assumed that cations and anions mix randomly in their respective sublattices. To describe the liquid phase to the metallic composition, formal negatively charged vacancies are added on the anionic sublattice and the model can be written as $(\text{Ag}^{1+}, \text{Bi}^{3+})_p (\text{O}^{2-}, \text{Va}^{q-})_q$. The indices $p$ and $q$ vary with composition in order to maintain electroneutrality and are given by:

$$
p = 2y_{O^{2-}} + qy_{Va^{q-}} \quad \text{(4.9)}$$
$$
q = y_{\text{Ag}^{1+}} + 3y_{\text{Bi}^{3+}} \quad \text{(4.10)}$$

where $y_s$ are the site fractions of $s$, i.e. the fractions of the species $s$ in each sublattice. The molar Gibbs energy of the liquid phase is given by:

$$
G_l^{\text{liq}} = y_{\text{Ag}^{1+}} \cdot y_{O^{2-}} \cdot G_{\text{Ag}^{1+}, O^{2-}}^{\text{liq}} + y_{\text{Bi}^{3+}} \cdot y_{O^{2-}} \cdot G_{\text{Bi}^{3+}, O^{2-}}^{\text{liq}} + q(y_{\text{Ag}^{1+}} \cdot y_{\text{Va}^{q-}} \cdot G_{\text{Ag}^{1+}, \text{Va}^{q-}}^{\text{liq}} + y_{\text{Bi}^{3+}} \cdot y_{\text{Va}^{q-}} \cdot G_{\text{Bi}^{3+}, \text{Va}^{q-}}^{\text{liq}}) + pRT[y_{\text{Ag}^{1+}} \cdot \ln y_{\text{Ag}^{1+}} + y_{\text{Bi}^{3+}} \cdot \ln y_{\text{Bi}^{3+}}] + qRT[y_{O^{2-}} \cdot \ln(y_{O^{2-}}) + y_{\text{Va}^{q-}} \cdot \ln(y_{\text{Va}^{q-}})] + E_m^{\text{liq}}$$

where $G_{i, Va^{q-}}^{\text{liq}}$ are the Gibbs energies, given by Dinsdale [91Din], of the pure liquid $i$ elements and $G_{i, O^{2-}}^{\text{liq}}$ are the Gibbs energies, previously assessed [95Ris, 97Ass1], for the pure liquid $i$ oxides. The molar excess Gibbs energy of the liquid, $E_m^{\text{liq}}$, is given by:

$$
G_m^{\text{liq}} = G_{\text{Ag-Bi}}^{\text{liq}} + G_{\text{Ag-O}}^{\text{liq}} + G_{\text{Bi-O}}^{\text{liq}} + G_{\text{Ag-Bi-O}}^{\text{liq}} \quad \text{(4.12)}$$
where the $E_{\text{liq}}^{i,j}$ represent the excess terms in the binary subsystems and were given in previous assessments [93Kar,95Ris,97Assl]. $E_{\text{Ag-Bi-O}}^{\text{liq}}$ is the molar excess Gibbs energy due to ternary interactions and is to be optimized:

$$E_{\text{Ag-Bi-O}}^{\text{liq}} = \gamma_{\text{Ag}^{1+}} \cdot \gamma_{\text{Bi}^{3+}} \cdot \gamma_{\text{O}^{2-}} \cdot L_{\text{Ag}^{1+}, \text{Bi}^{3+}, \text{O}^{2-}}^{\text{liq}}$$

$$+ \gamma_{\text{Ag}^{1+}} \cdot \gamma_{\text{Bi}^{3+}} \cdot \gamma_{\text{O}^{2-}} \cdot \gamma_{\text{Va}^{2-}} \cdot L_{\text{Ag}^{1+}, \text{Bi}^{3+}, \text{O}^{2-}, \text{Va}^{2-}}^{\text{liq}}$$

where each $L$ interaction parameter can be written as a Redlich-Kister polynomial. A colon is used to separate species on different sublattices and a comma to separate species on the same sublattice.

### 4.3.4 Optimization of Parameters

The program PARROT [84Jan] included in the Thermo-Calc databank system [85Sun] was used for the optimization of the interaction parameters. The program calculates the model parameters by minimising the sum of squared errors. The influence of each experimental data can be enhanced or decreased by changing its weight.

In the Ag–Bi–O system, the optimization could be achieved in a simple way. First $L_{\text{Ag}^{1+}, \text{Bi}^{3+}, \text{O}^{2-}, \text{Va}^{2-}}^{\text{liq}}$ is optimized using the thermodynamic data points in the metal liquid, with an equal weight, see Equation 5. A composition dependence could be introduced as [91Sun]:

$$L_{\text{Ag}^{1+}, \text{Bi}^{3+}, \text{O}^{2-}, \text{Va}^{2-}}^{\text{liq}} = 0L + (y_{\text{O}^{2-}} - y_{\text{Va}^{2-}}) \cdot 1L + (y_{\text{Ag}^{1+}} - y_{\text{Bi}^{3+}}) \cdot 2L$$

where $0L$ and $2L$ could be optimized but not $1L$ since $(y_{\text{O}^{2-}} - y_{\text{Va}^{2-}})$ is always close to (-1) in the metal liquid, and the influence of $1L$, thus, cannot be separated from that of $0L$. No temperature dependence could be introduced.

The DTA experimental data were used to optimize $L_{\text{Ag}^{1+}, \text{Bi}^{3+}, \text{O}^{2-}}^{\text{liq}}$ which describes the interactions in the oxide part of the liquid phase. It was not reasonable to consider neither a temperature nor a composition dependence in $L_{\text{Ag}^{1+}, \text{Bi}^{3+}, \text{O}^{2-}}^{\text{liq}}$. However, it turned out that this single parameter could describe the experimental results remarkably well. The EDX measurements were not included in the optimization because of their large relative uncertainties even if they were in very good agreement with the calculation.
4.3.5 Results and Discussion

The parameters optimized in the present work are listed in Table 4.11.

The Ag–BiO$_{1.5}$ calculated phase diagram in 1 atm O$_2$ ($P_{O_2} = 1.01 \times 10^5$ Pa) is presented in Figure 4.7 and invariant temperatures are listed in Table 4.8. Figure 4.8 and Table 4.9 show the Ag–BiO$_{1.5}$ calculated phase diagram in air ($P_{O_2} = 2.1 \times 10^4$ Pa) and Table 4.10 the invariant equilibria in the Ag–BiO$_{1.5}$ phase diagram in N$_2$ ($P_{O_2} = 200$ Pa). The measured temperatures are very well fitted by the calculation but some uncertainties remain. The composition of the eutectic liquid, both Ag and O content, is somewhat uncertain, even though the calculation is in good agreement with the EDX measurements. The $\alpha$-Bi$_2$O$_3$ and $\delta$-Bi$_2$O$_3$ liquidii could not be detected by DTA, but they are relatively well fixed by the system. The main uncertainties, though, are to be found in the liquid phase where the shape and the maximum temperature of the miscibility gap are extrapolated by the parameters. This is shown in Figures 4.7 and 4.8 by the use of dashed lines. In order to clarify the shape of the miscibility gap, further investigations at higher temperatures are needed.

The calculated oxygen potential phase diagram is shown in Figure 4.9 in comparison with DTA experimental data. The agreement is excellent but concerns only a rather limited range of oxygen partial pressure. The four phase invariant equilibria are marked with capital letters in Figure 4.11 and listed in Table 4.12.

Data on the oxygen activity coefficient in metallic Ag–Bi liquid, are presented in Figure 4.11. The few experimental points at $T = 1373$ K [84Ots] and at $T = 1273$ K [88Yao] are very well fitted by the calculation.

4.3.6 Conclusion

Thermodynamic parameters describing the Ag–Bi–O system have been optimized using oxygen activity measurements from the literature and experimental phase diagram data presented in this work. The combination of a few experimental measurements in the Ag–Bi–O phase diagram and thermodynamic measurements in the metal liquid associated with thermodynamic modelling of the phases lead to a consistent description of the whole system. The resulting fit is excellent. However, some uncertainties remain, mainly on the composition of the eutectic liquid and on the shape and the maximum temperature of the miscibility gap.

4.3.7 Acknowledgement

Financial support from the Swiss National Science Foundation and from COST 512 (European Co-operation in the Field of Scientific and Technical Research, Modelling in Materials Science and Processing) are gratefully acknowledged.
4.3.8 Literature


Table 4.8: Measured temperatures of reaction (DTA) in $P_{O_2} = 1 \cdot 10^5$ Pa (in $O_2$) compared with the calculation.

<table>
<thead>
<tr>
<th>Composition $u_{Ag}$</th>
<th>$dT/dt$ K/min</th>
<th>$(Ag) + \alpha \leftrightarrow L_2 \quad \alpha \leftrightarrow \delta \quad (Ag) + L_2 \leftrightarrow L_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.026</td>
<td>2</td>
<td>962 $\pm$ 5 K $\quad$ 1004 $\quad$ -</td>
</tr>
<tr>
<td>0.05</td>
<td>2</td>
<td>958 $\quad$ 1003 $\quad$ -</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>951 $\quad$ 1005 $\quad$ -</td>
</tr>
<tr>
<td>0.11</td>
<td>5</td>
<td>957 $\quad$ 1004 $\quad$ -</td>
</tr>
<tr>
<td>0.25</td>
<td>1</td>
<td>959 $\quad$ - $\quad$ -</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>958 $\quad$ - $\quad$ -</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>961 $\quad$ - $\quad$ -</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>959 $\quad$ - $\quad$ 1209</td>
</tr>
<tr>
<td>0.67</td>
<td>5</td>
<td>961 $\quad$ - $\quad$ -</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>959 $\quad$ - $\quad$ 1211</td>
</tr>
<tr>
<td>Mean values</td>
<td>Experimental (DTA)</td>
<td>959 $\pm$ 2 $\quad$ 1004 $\pm$ 3 $\quad$ 1210 $\pm$ 4</td>
</tr>
<tr>
<td></td>
<td>Calculated</td>
<td>959.5 $\quad$ 1002.1 $\quad$ 1211.6</td>
</tr>
</tbody>
</table>

Note: $\alpha$ and $\delta$ represent $\alpha$-$Bi_2O_3$ and $\delta$-$Bi_2O_3$

Table 4.9: Measured temperatures of reaction (DTA) in $P_{O_2} = 2.1 \cdot 10^4$ Pa (in air) compared with the calculation.

<table>
<thead>
<tr>
<th>Composition $u_{Ag}$</th>
<th>$dT/dt$ K/min</th>
<th>$(Ag) + \alpha \leftrightarrow L_2 \quad \alpha \leftrightarrow \delta \quad (Ag) + L_2 \leftrightarrow L_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.026</td>
<td>2</td>
<td>- $\quad$ 1006 $\quad$ -</td>
</tr>
<tr>
<td>0.05</td>
<td>5</td>
<td>981 $\quad$ 997 $\quad$ -</td>
</tr>
<tr>
<td>0.07</td>
<td>2</td>
<td>982 $\quad$ 1003 $\quad$ -</td>
</tr>
<tr>
<td>0.11</td>
<td>5</td>
<td>986 $\quad$ - $\quad$ -</td>
</tr>
<tr>
<td>0.25</td>
<td>2</td>
<td>986 $\quad$ - $\quad$ 1223</td>
</tr>
<tr>
<td>0.67</td>
<td>5</td>
<td>985 $\quad$ - $\quad$ 1223</td>
</tr>
<tr>
<td>Mean values</td>
<td>Experimental (DTA)</td>
<td>984 $\pm$ 2 $\quad$ 1002 $\pm$ 3 $\quad$ 1223 $\pm$ 4</td>
</tr>
<tr>
<td></td>
<td>Calculated</td>
<td>984.0 $\quad$ 1002.1 $\quad$ 1224.1</td>
</tr>
</tbody>
</table>
Table 4.10: Measured temperatures of reaction (DTA) in $N_2$
($P_{O_2} = 200$ Pa) compared with the calculation.

<table>
<thead>
<tr>
<th>Composition</th>
<th>$\frac{dT}{dt}$</th>
<th>$\alpha \leftrightarrow \delta$</th>
<th>$(Ag) + \delta \leftrightarrow L_2$</th>
<th>$(Ag) + L_2 \leftrightarrow L_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu_{Ag}$</td>
<td>K/min</td>
<td>$T_{\alpha/\delta} \pm 5$ K</td>
<td>$T_\alpha \pm 5$ K</td>
<td>$T_m \pm 5$ K</td>
</tr>
<tr>
<td>0.25</td>
<td>2</td>
<td>1002</td>
<td>1040$^b$</td>
<td>1230$^b$</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>1007</td>
<td>1050</td>
<td>1233</td>
</tr>
<tr>
<td>Mean values</td>
<td>Experimental (DTA)</td>
<td>1005 $\pm 4$</td>
<td>1050 $\pm 5$</td>
<td>1233 $\pm 5$</td>
</tr>
<tr>
<td>Calculated</td>
<td></td>
<td>1002.1</td>
<td>1050.3</td>
<td>1231.5</td>
</tr>
</tbody>
</table>

a. The oxygen partial pressure is measured as $P_{O_2} = 10$ Pa.

b. The oxygen partial pressure is not well defined and may be higher than 200 Pa. For this reason, the measurements are not included in the calculations of the mean values.

---

Table 4.11: Optimized thermodynamic parameters in the Ag–Bi and Ag–Bi–O systems.

Ag–Bi

Fcc phase: (Ag,Bi)

$L_{Ag,Bi}^{fcc} = +24300 - 10.5 \cdot T$

Ag–Bi–O

Two-sublattice model for ionic liquids: $(Ag^{1+},Bi^{3+})_p (O^{2-},Va^{q-})_q$

with $p = 2y_{O^{2-}} + qy_{Va^{q-}}$ and $q = y_{Ag^{1+}} + 3y_{Bi^{3+}}$

$L_{Ag^{1+},Bi^{3+}:O^{2-}}^{liq} = -5410$

$L_{Ag^{1+},Bi^{3+}:O^{2-},Va^{q-}}^{liq} = +32255 + (y_{Ag^{1+}} - y_{Bi^{3+}}) \cdot 39415$

All parameter values are given in SI units (mol, J, K, Pa, $R = 8.31451$ J/mol K). Binary parameters have been previously assessed, see [97Ass1] for Ag–O, [95Ris] for Bi–O and [93Kar] for Ag–Bi.
### Table 4.12: Calculated invariant equilibria in the Ag–Bi–O system.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$T$ (K)</th>
<th>$\log(P_{O_2})$</th>
<th>$x_{\text{Ag}}$</th>
<th>$x_{\text{Bi}}$</th>
<th>$x_{\text{O}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A: $\alpha$-Bi$_2$O$_3 \leftrightarrow \delta$-Bi$_2$O$_3$ (+ (Ag) + L$_1$)</td>
<td>1002.1</td>
<td>-9.12</td>
<td>L$_1$</td>
<td>0.818</td>
<td>0.182</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(Ag)</td>
<td>0.981</td>
<td>0.019</td>
</tr>
<tr>
<td>B: $\delta$-Bi$_2$O$_3$ + L$_1$ $\leftrightarrow$ (Ag) + L$_2$</td>
<td>1089.6</td>
<td>-7.21</td>
<td>L$_1$</td>
<td>0.884</td>
<td>0.116</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>L$_2$</td>
<td>0.001</td>
<td>0.400</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(Ag)</td>
<td>0.988</td>
<td>0.012</td>
</tr>
<tr>
<td>C: $\alpha$-Bi$_2$O$_3$ $\leftrightarrow$ $\delta$-Bi$_2$O$_3$ (+ (Ag) + L$_2$)</td>
<td>1002.1</td>
<td>-1.45</td>
<td>L$_2$</td>
<td>0.033</td>
<td>0.380</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(Ag)</td>
<td>1.000</td>
<td>$3 \cdot 10^{-8}$</td>
</tr>
<tr>
<td>D: Ag$_2$O + $\alpha$-Bi$_2$O$_3$ $\leftrightarrow$ L$_2$ (+ (Ag))</td>
<td>699.4</td>
<td>2.21</td>
<td>L$_2$</td>
<td>0.357</td>
<td>0.186</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(Ag)</td>
<td>1.000</td>
<td>$5 \cdot 10^{-18}$</td>
</tr>
<tr>
<td>E: Ag$_2$O + L$_2$ + (Ag) $\leftrightarrow$ L$_1$</td>
<td>803.6</td>
<td>2.72</td>
<td>L$_1$</td>
<td>0.749</td>
<td>$1 \cdot 10^{-7}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>L$_2$</td>
<td>0.446</td>
<td>0.133</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(Ag)</td>
<td>0.999</td>
<td>$8 \cdot 10^{-16}$</td>
</tr>
</tbody>
</table>

$L_1$ is the metal liquid and $L_2$ is the oxide liquid. The calculated invariant equilibria below the dotted line are only tentative because of the very high oxygen partial pressures.
Figure 4.7: Calculated Ag–BiO$_{1.5}$ phase diagram in 1 atm O$_2$, where the calculation is compared with experimental DTA and EDX data. The uncertainties in the miscibility gap due to the lack of experimental data at high temperatures are represented by a dashed line.

Figure 4.8: Calculated Ag–BiO$_{1.5}$ phase diagram in air, where the calculation is compared with experimental DTA and EDX data. The uncertainties in the miscibility gap due to the lack of experimental data at high temperatures are represented by a dashed line.
Figure 4.9: Ag–Bi–O oxygen potential diagram, where four-phase invariant equilibria are indicated with the letters A, B, C, D and E according to Table 4. The calculation is compared with DTA experimental data.
Figure 4.10: Calculated Ag–Bi phase diagram. The parameter describing the Bi solubility in fcc (Ag) has been reoptimized and the calculation is compared with the $L_{\text{Ag, Bi}}^{\text{fcc}}$ given by Karakaya and Thompson \cite{93Kar} (dashed line) and with experimental data \cite{40Chi, 46Rau, 83Ako, 88Sch}.

Figure 4.11: Logarithm of O activity coefficient at $x_O = 0.01$ in the metal liquid along the Ag–Bi composition. The calculation is compared with experimental data at $T = 1273 \text{ K}$ \cite{84Ots} and at $T = 1373 \text{ K}$ \cite{88Yao}.
4.4 The Ag–Cu–O System

Published in J. Phase Equilib., 19 (4), 351-360 (1998)

Thermodynamic Assessment of the Ag–Cu–O System

Jérôme Assal, Bengt Hallstedt and Ludwig J. Gauckler
ETH Zürich, Department of Materials, Nonmetallic Materials,
Swiss Federal Institute of Technology, Sonneggstr. 5, 8092 Zurich, Switzerland

Abstract

Available experimental data on the Ag–Cu–O system have been reviewed and an optimised thermodynamic description is presented. The Ag–Cu–O system does not contain any ternary solid phases and is characterised by a miscibility gap between the liquid metal phase and the liquid oxide phase. The few experimental data are well described by the thermodynamic assessment. The liquid phase is described by the two-sublattice model for ionic liquids and a comparison is made with the associated solution model.

4.4.1 Introduction

The present work is part of a project to evaluate the phase equilibria and the thermodynamics of the system formed by Ag and by the Bi–Sr–Ca–Cu–O system. Ag is commonly used as sheathing material during the processing of high-\(T_c\) superconducting phases, such as Bi\(_2\)Sr\(_2\)CaCu\(_2\)O\(_{8+\delta}\) (Bi-2212) or Bi\(_2\)Sr\(_2\)Ca\(_2\)Cu\(_3\)O\(_{10+\delta}\) (Bi-2223). In the case of Bi-2212 thick films on a silver substrate, it has been observed that silver lowers the melting temperature by about 30 K [97Lan,97Maj] without any detrimental effect on the superconducting properties. In this work, we model the phase relations and the thermodynamics of the Ag–Cu–O system using experimental data from the literature.

The ternary system Ag–Cu–O has been studied experimentally in two ways: the phase diagram between Ag and CuO\(_x\), where \(x\) can vary between 0.5 and 1, in a given atmosphere (usually air) and the oxygen activity in the metal liquid across the whole Ag–Cu composition range. In air, the Ag–CuO\(_x\) subsystem shows a eutectic reaction between the metal liquid, CuO and solid Ag at \(T = 1215\) K and a monotectic reaction between the metal liquid, the oxide liquid and CuO at \(T = 1242\) K [95Suz].

The presence of a miscibility gap in the liquid phase can already be observed in the Cu–O system, between Cu and Cu\(_2\)O. The Cu–O system contains two solid oxides, Cu\(_2\)O and CuO [94Hal]. The Ag–O system, which shows a eutectic reaction between Ag and Ag\(_2\)O [97Ass], is characterised by the high stability of the non-oxide phases at ambient oxygen
partial pressures.

The present evaluation is based on previous assessments of the binary subsystems, Ag–Cu by Hayes et al. [86Hay], Ag–O by Assal et al. [97Ass] and Cu–O by Hallstedt et al. [94Hal]. The two-sublattice model for ionic liquids [85Hil,91Sun] is used to describe the liquid phase. This model will be compared with the associated solution model, based on the description of the Cu–O system by Ranniko [95Ran], using Ag, Ag₂O, Cu, Cu₂O and CuO as associates.

4.4.2 Experimental Data

The Phase Diagram

Leroux and Fröhlich [31Ler] used thermal analysis to determine the phase relations between Ag and Cu₂O and found a eutectic reaction Ag + Cu₂O ↔ L₁ to be at T = 1214 K and a monotectic reaction Cu₂O + L₁ ↔ L₂ at T = 1407 K where L₁ and L₂ are the metal and the oxide liquids, respectively. This experimental study was conducted under purified nitrogen without any indication of the residual oxygen pressure. The oxygen partial pressure can nevertheless be estimated to be below 10⁻⁴ bar (10 Pa).

Shao et al. [93Sha] studied the Ag–CuO phase diagram in air using thermogravimetry (TG) and differential thermal analysis (DTA) and found the monotectic reaction, i.e. CuO + L₁ ↔ L₂, to take place at T = 1237 K with the miscibility gap extending from u_{Ag} = 0.31 to u_{Ag} = 0.98 where u is the metal ratio; u_{Ag} = x_{Ag} / (x_{Ag} + x_{Cu}). They indicated the eutectic reaction Ag + CuO ↔ L₁ to take place at T = 1205 K with u_{Ag} = 0.99 for L₁ and the Cu₂O–CuO transformation in presence of L₂ at T = 1300K with u_{Ag} = 0.19. This study is in good agreement with the one by Suzuki et al. [95Suz] except for the Cu₂O liquidus, where the results of [93Sha] are about 100 K too high. These data points would lead to a melting temperature of pure Cu₂O in air of 1505 K instead of 1397 K [94Hal]. An explanation for this could not be found.

Takeda and Roghani [93Tak] studied the miscibility gap in the liquid phase at T = 1523 K. They measured the compositions of both liquid phases (oxide and metal) in equilibrium as well as the oxygen partial pressure, from the Cu–O binary, at about 1.6 · 10⁻⁴ bar O₂, up to 1.01 bar O₂ (1 atm). At this oxygen partial pressure liquid Ag, containing small amounts of Cu and O, is in equilibrium with an oxide liquid with u_{Ag} ≈ 0.3. Unfortunately, very little detail of the experimental technique used is given. At T = 1523 K the miscibility gap extends from the Cu–O binary without any interference from the solid phases.

The most recent and complete work on the Ag–Cu–O system is the phase equilibria study of the Ag–Cu₂O–CuO system by Suzuki et al. [95Suz]. They investigated the Ag–CuO₃ phase diagram across the whole Ag–Cu composition range and from 3 · 10⁻⁵ bar O₂ to 1.01 bar O₂. The temperatures of transformation were measured using TG and DTA. For some quenched samples, the compositions of the liquids were analysed by emission dispersion X-ray spectrometry (EDX). In air, they determined the monotectic reaction CuO + L₁ ↔ L₂ to be at T = 1242 K where the miscibility gap extends from u_{Ag} = 0.36
to $u_{\text{Ag}} = 0.98$. The eutectic reaction $\text{Ag} + \text{CuO} \leftrightarrow L_1$ was found to be at $T = 1215$ K with $u_{\text{Ag}} = 0.99$. The $\text{Cu}_2\text{O} - \text{CuO}$ transformation was measured to be at $T = 1302$ K in presence of the oxide liquid ($L_2$) containing some Ag ($u_{\text{Ag}} = 0.10$) and with $\text{Cu}_2\text{O}$ containing a small amount of $\text{Ag}_2\text{O}$ ($u_{\text{Ag}} = 0.03$). However, some uncertainties remain in their study, as shown by the large scatter in their data for both the CuO liquidus and for the miscibility gap in the liquid phase, as well as for the $\text{Ag}_2\text{O}$ solubility in $\text{Cu}_2\text{O}$.

**Thermodynamic Data**

There are several experimental studies of oxygen activities in the metal liquid across the whole Ag–Cu composition range. The majority of these studies were conducted at $T = 1373$ K and some at $T = 1473$ K. Modified coulometric titration [69Fru, 73Jac, 78Fit, 88Yao], oxygen absorption-desorption technique [67Par, 69Blo] and gas phase equilibria measurements using a $\text{H}_2\text{O}/\text{H}_2$ mixture [72Tan] lead to similar results for the oxygen activities.

**4.4.3 Thermodynamic Models**

**Solid Phases**

Dinsdale’s values [91Din] for the Gibbs energies of solid Ag and Cu are used in this work. The common structure ($Pn3m$) and the relatively small difference in the cell parameters of $\text{Ag}_2\text{O}$ and $\text{Cu}_2\text{O}$, i.e. $a = 4.728$ Å for $\text{Ag}_2\text{O}$ and $a = 4.261$ Å for $\text{Cu}_2\text{O}$ [73Don], lead us to describe $\text{Cu}_2\text{O}$, whose structure is also called cuprite, by a substitutional solution model where the interaction parameter $L_{\text{Ag}^{1+}, \text{Cu}^{1+}, \text{O}^{2-}}$ has to be determined. The descriptions of pure $\text{Ag}_2\text{O}$ and $\text{Cu}_2\text{O}$, i.e. end points of cuprite, and CuO are taken from previous assessments [97Ass, 94Hal].

The Ag–Cu system shows a eutectic between fcc-Ag and fcc-Cu. These two fcc solid solutions are described as one phase with a miscibility gap using a substitutional solution model. Since oxygen solubility in pure silver and in pure copper is small, the extrapolation into the ternary system is expected to be reasonably accurate and there is no need to introduce a ternary interaction parameter.

**Liquid Phase**

The liquid phase is described by the two-sublattice model for ionic liquids [85Hil, 91Sun] which allows a continuous description from the metal liquid to the oxide liquid. The two-sublattice model for ionic liquids assumes that cations and anions mix randomly in their respective sublattice. The liquid phase is then written as $(\text{Ag}^{1+}, \text{Cu}^{1+}, \text{Cu}^{2+})_p (\text{O}^{2-}, \text{Va}^{q+})_q$ where $p$ and $q$ vary with composition in order to maintain electroneutrality. Hypothetical negative vacancies are introduced into the anionic sublattice in order to extend the model continuously to the metal liquid. In this case, $p$ and $q$ are given by:
\[ p = 2y_{O^2} + qy_{Va} \quad (4.15) \]
\[ q = y_{Ag^{1+}} + y_{Cu^{1+}} + 2y_{Cu^{2+}} \quad (4.16) \]

where \( y_s \) is the site fraction of \( s \), i.e. the fraction of the species \( s \) in a particular sublattice. The molar Gibbs energy of the liquid is:

\[
G_{m}^{\text{liq}} = y_{Ag^{1+}} \cdot y_{O^2} \cdot G_{Ag^{1+}:O^2}^{\text{liq}} + y_{Cu^{1+}} \cdot y_{O^2} \cdot G_{Cu^{1+}:O^2}^{\text{liq}} + y_{Cu^{2+}} \cdot y_{O^2} \cdot G_{Cu^{2+}:O^2}^{\text{liq}} \\
+ q \left( y_{Ag^{1+}} \cdot y_{Va} \cdot G_{Ag^{1+}:Va}^{\text{liq}} + y_{Cu^{1+}} \cdot y_{Va} \cdot G_{Cu^{1+}:Va}^{\text{liq}} + y_{Cu^{2+}} \cdot y_{Va} \cdot G_{Cu^{2+}:Va}^{\text{liq}} \right) \\
+ pRT \left[ y_{Ag^{1+}} \cdot \ln(y_{Ag^{1+}}) + y_{Cu^{1+}} \cdot \ln(y_{Cu^{1+}}) + y_{Cu^{2+}} \cdot \ln(y_{Cu^{2+}}) \right] \\
+ qRT \left[ y_{O^2} \cdot \ln(y_{O^2}) + y_{Va} \cdot \ln(y_{Va}) \right] + G_m^{\text{liq}} \quad (4.17) 
\]

where the species \( Va \) represents the charged vacancies \( V_{Ag^{1+}} \). \( G_{i:Va}^{\text{liq}} \) is the Gibbs energy of the pure liquid element \( i \), see [91Din], and \( G_{i:O^2}^{\text{liq}} \) is the Gibbs energy for the pure liquid oxide \( i \), given in previous assessments [86Hay,94Hal,97Ass]. \( G_m^{\text{liq}} \) is the molar excess Gibbs energy of the liquid phase and is given by:

\[
E_{G_m^{\text{liq}}} = E_{G_{Ag-Cu}}^{\text{liq}} + E_{G_{Ag-O}}^{\text{liq}} + E_{G_{Cu-O}}^{\text{liq}} + E_{G_{Ag-Cu-O}}^{\text{liq}} \quad (4.18) 
\]

where the \( E_{G_{i:j}}^{\text{liq}} \) represent the excess terms in the binary subsystems and were assessed previously [86Hay,94Hal,96Ass2]. \( E_{G_{Ag-Cu-O}}^{\text{liq}} \) is the excess Gibbs energy of the ternary system and can be written as the summation of interaction parameters between the species, i.e.:

\[
E_{G_{Ag-Cu-O}}^{\text{liq}} = y_{Ag^{1+}} \cdot y_{Cu^{1+}} \cdot y_{O^2} \cdot L_{Ag^{1+},Cu^{1+}:O^2}^{\text{liq}} \\
+ y_{Ag^{1+}} \cdot y_{Cu^{2+}} \cdot y_{O^2} \cdot L_{Ag^{1+},Cu^{2+}:O^2}^{\text{liq}} \\
+ y_{Ag^{1+}} \cdot y_{Cu^{1+}} \cdot y_{O^2} \cdot y_{Va} \cdot L_{Ag^{1+},Cu^{1+}:O^2,Va}^{\text{liq}} \quad (4.19) 
\]

where each interaction parameter, \( L \), can be written as a Redlich-Kister polynomial. A comma is used to separate species on the same sublattice and a colon to separate species on different sublattices.
4.4.4 Optimization of Parameters

The optimization was performed using the computer program PARROT [84Jan] included in the Thermo-Calc databank system [85Sun]. The program calculates the model parameters by minimising the sum of squared errors. The influence of each experimental data point can be enhanced or decreased by changing its weight.

The optimization of the interaction parameter describing the solubility of Ag$_2$O in Cu$_2$O (or cuprite) was made possible with the help of one experimental data point ($u_{Ag} = 0.03$, $T = 1302$ K) from [95Suz]. This small solubility has only a minor influence on the rest of the system.

The optimization for the liquid phase could be separated into two parts: the metal liquid can be described by the oxygen activity coefficient measurements along the Ag–Cu composition. Coulometric titration measurements at $T = 1373$ K and $T = 1473$ K [69Fru, 73Jac, 88Yao], gas phase equilibria measurements using H$_2$O/H$_2$ gas mixture at $T = 1373$ K [72Tan] and oxygen absorption-desorption data at $T = 1473$ K [69Blo] are used to optimise $L_{Ag^{1+},Cu^{1+}:O^{2-},V_a}$ and $L_{Ag^{1+},Cu^{2+}:O^{2-}}$. As these data are generally in good agreement we chose to apply the same weight to each of them. Since the large majority of these experiments were performed at $T = 1373$ K, it is not reasonable to introduce a temperature dependence for this parameter, but a composition dependence can be introduced as [91Sun]:

$$L_{Ag^{1+},Cu^{1+}:O^{2-},V_a}^{\text{liq}} = L + \left( y_{O^{2-}} - y_{V_a} \right) \cdot L + \left( y_{Ag^{1+}} - y_{Cu^{1+}} \right) \cdot 2L \quad (4.20)$$

where $L$ can be calculated but not $2L$ since $\left( y_{O^{2-}} - y_{V_a} \right)$ is always close to -1 in the metal liquid, and the influence of $L$, thus, cannot be separated from that of $L$.

The parameters describing the oxide liquid could be optimised using the data from experimental phase diagram investigations. We only considered the study from [95Suz] because the experimental oxygen partial pressures used by [31Ler] could not be deduced with any certainty and because the phase diagram from [93Sha] shows unexplained discrepancies in the temperature measurements of the Cu$_2$O liquidus. The experimental temperatures of the monotectic and eutectic transformations, i.e. $T = 1215$ K and $T = 1242$ K, respectively, from [95Suz], were used with a high weight since they represent the average values from a large number of DTA/TG measurements made over a wide composition range. Measurements of the Cu$_2$O and CuO liquidus and the miscibility gap were also used but with a lower weight. The compositions of the oxide liquid indicated in their phase diagrams were used with a low weight since the scatter is rather large. In all cases the experimental compositions were more difficult to fit than the experimental temperatures. The Cu$^{1+}$/Cu$^{2+}$ ratios from Suzuki et.al. [95Suz] evaluated at different oxygen partial pressures allow, in principle, the optimization of $L_{Ag^{1+},Cu^{1+}:O^{2-}}^{\text{liq}}$ and $L_{Ag^{1+},Cu^{2+}:O^{2-}}^{\text{liq}}$. 
(see Eq. 5), but it turned out that $L_{\text{Ag}^{1+},\text{Cu}^{1+}:\text{O}^2-}^{\text{liq}}$ and $L_{\text{Ag}^{1+},\text{Cu}^{2+}:\text{O}^2-}^{\text{liq}}$ could not be optimised independently, and, thus, were made equal. During the optimization, it became clear that neither temperature nor composition dependence could be introduced into these parameters.

The work of Takeda and Roghani [93Tak] on the isothermal section at $T = 1523$ K was found after the present optimization was completed. However, including their measurements in the optimization did not change the parameters appreciably.

4.4.5 Results and Discussion

The optimised thermodynamic parameters from the present work are listed in Table 4.13. The calculated phase diagram of the Ag–CuO$_2$ system in air is shown in Figure 4.12 in comparison with the experimental data from [93Sha] and [95Suz]. Experimental and calculated data for the three-phase equilibria in air are given in Table 4.14. It is important to note that there is a large difference between DTA and TG measurements from [95Suz] on the CuO liquidus. This difference, around 20 K in temperature or 0.07 in $u_{\text{Ag}}$, is about the same as the difference between the calculations and the data themselves. The measurements of the Cu$_2$O liquidus by [93Sha] are about 100 K higher than our calculations, and are in contradiction with the melting temperature of pure Cu$_2$O in air, as mentioned in Section 4.4.1. Above 1700 K, the calculated phase diagram becomes increasingly incorrect because of an instability in the description of the binary Cu–O system. This instability is a narrow miscibility gap just below $x_{\text{O}} = 0.33$ with a minimum at 1914 K.

Figures 4.13 and 4.14 represent the calculated isothermal sections at $T = 1173$ K and at $T = 1273$ K. The lower temperature is very close to the temperature usually reached during processing of Bi-2212 thick films on silver, see [97Lan], and gives a good view of the phase relations that apply during processing. In Figure 4.15, the calculated isothermal section at $T = 1523$ K is compared with the experimental data from [93Tak]. The agreement with the compositions of the two liquids and with the oxygen partial pressures is generally good. The experimental oxide liquid phase boundary has a rather peculiar shape with two minima in oxygen content. The first of these minima (close to the Cu–O edge) is to some extent reproduced by the calculation but the second is not. The second minimum cannot be described using the present model, except, perhaps, by introducing higher order interaction parameters. This might indicate that the interactions in the oxide liquid are more complex than assumed in this work.

Figure 4.16 shows the oxygen potential diagram, where the lines represent three-phase equilibria and the intersections four-phase (or invariant) equilibria. These equilibria are listed in Table 4.15. This diagram is a projection (along Cu or Ag potential) so that not all apparent intersections represent four-phase equilibria. This kind of diagram gives an efficient overview of the phase relations in the system in addition to giving the stability limits of the various phase assemblages. An enlargement of the oxygen potential diagram is
shown in Figure 4.17 where the experimental data from [95Suz] and our calculation are compared. The calculation shows good agreement with the experimental data except at the two lowest oxygen partial pressures. In particular, the calculation of the Cu$_2$O–L$_1$–L$_2$ equilibrium differs substantially from two of the measured data points. The end point of this equilibrium ($T = 1498$ K, Log($P_{O_2}$, bar) = -3.9) corresponds to the monotectic reaction Cu$_2$O + L$_1$ $\leftrightarrow$ L$_2$ in the binary Cu–O system. As this monotectic equilibrium has been measured many times, see [94Hal], the measurements by [95Suz] are obviously in error. It is possible that their measurements do not belong to the monotectic Cu$_2$O–L$_1$–L$_2$ equilibrium but rather to the Cu$_2$O liqudus. It is also possible that the effective oxygen partial pressures during the measurements were much higher than indicated in their work.

A more detailed comparison between experiments and calculation is given in Table 4.16.

Figure 4.18 shows the calculated liquidus projection in the Ag–Cu–O system in comparison with experimental data [95Suz]. The lines indicate the calculated compositions of the liquid phases and the arrows give the direction of decreasing temperature. The four experimental data points [95Suz] shown in this plot are composition measurements made on the liquid phase in ternary equilibria. The measured temperatures corresponding to these data points are shown in Figure 4.17 and are fitted very well by the calculation. As mentioned in Section 4.4.4, it turned out to be relatively easier to fit the measured temperatures than the compositions. It is also to be expected that the temperature can be more accurately measured than the oxygen content.

The thermodynamics of oxygen dissolution in liquid Ag–Cu alloys can be seen in Figure 4.19, where the activity coefficient of oxygen for $x_A$ = 0.01 is shown. For $x_A <$ 0.5, the fit is very good but for $x_A$ > 0.5 there is a difference between calculation and experiment which is somewhat larger than the experimental uncertainty.

### 4.4.6 The Associated Solution Model

At higher temperatures, the Ag–Cu–O system is dominated by a liquid miscibility gap. Since a miscibility gap is determined by the curvature of the Gibbs energy surface small changes in Gibbs energy might already lead to large changes in the shape and extent of the miscibility gap. It is therefore to be expected that the calculated miscibility gap will also depend critically on the choice of model. The Ag–Cu–O system is thus very well suited for a comparison between the ionic liquid model, which we use in this work, and the associated solution model, which also has been used to model Cu–O based liquids [92Bou, 95Ran].

The present associated solution model is based on [95Ran] for the Cu–O part of the system and [97Ass] for the Ag–O part. The choice of [95Ran] for Cu–O is motivated by the use of Cu, Cu$_2$O and CuO as associated species that are comparable with the ions in the two-sublattice model for ionic liquids. Assuming that no ternary species are formed, the liquid phase can be written as (Ag,Ag$_2$O,Cu,Cu$_2$O,CuO). In this case, the number of possible parameters in the excess term of the Gibbs energy is larger than for the ionic liquid model, and the choice of relevant parameters is less obvious. Two pairs of identical
parameters, \( L_{\text{Ag,} \text{Cu}_2 \text{O}}^{\text{liq}} = L_{\text{Ag,} \text{CuO}}^{\text{liq}} \) and \( L_{\text{Ag}_2 \text{O,} \text{Cu}_2 \text{O}}^{\text{liq}} = L_{\text{Ag}_2 \text{O,} \text{CuO}}^{\text{liq}} \), without temperature or composition dependence, were optimised. We consider here the parameters as equal since experimental data studies do not allow us to make any difference between the valence of the copper oxides. This is equivalent with the choice of the parameters in the two-sublattice model for ionic liquids in Section 4.4.2. In order to be consistent with [95Ran], we used the same descriptions for the solids \( \text{Cu}_2 \text{O} \) and \( \text{CuO} \), which come from Boudene et al. [92Bou]. These descriptions are nevertheless very close to those from Hallstedt et al. [94Hal]. The description of the solid \( \text{Ag}_2 \text{O} \) [97Ass] and the fcc phase [86Hay] are the same as those already used in this work. The optimization procedure and the weights used are the same as for the ionic liquid model described in Section 4.4.4. All optimised parameters are listed in Table 4.13.

In Figure 4.20 and Table 4.14 the two calculations are compared with the experimental data for the phase diagram of the Ag–CuO system in air. The calculated temperatures of the three-phase equilibria are very close but the corresponding compositions show some differences. The associated solution model generally shows better agreement with the measured compositions. Both models give similar results for all equilibria except for those involving the miscibility gap, i.e. where \( L_1 \) and \( L_2 \) are both present. For those equilibria, the two calculations are close to each other only in air (\( \log(P_{O_2}, \text{bar}) = -0.67 \)), see Figure 4.21. Otherwise the ionic liquid model shows good agreement with the experimental data, except at the lowest oxygen partial pressures as discussed in the previous section, whereas the associate model does not. Figure 4.19 shows the calculated logarithm of the \( O \) activity coefficient in the metal liquid according to the two models and compared with experimental data. The agreement between the two calculations and the data points is very good for the Cu-rich part of the metal liquid. For \( x_{\text{Ag}} > 0.5 \), the associate model fits the experimental data slightly better.

To get an idea of the extrapolative capabilities of the two models it is of interest to compare them without using any ternary parameters, i.e. the state before the optimization. With the ionic liquid model the miscibility gap comes out to be too dominating, the monotectic temperatures are too high by up to about 100 K, but the phase relations are essentially the same as after the optimization and the eutectic temperatures, involving the metal liquid only, change by less than 1 K. With the associated solution model on the other hand, the miscibility gap is almost completely missing; it appears only close to the Cu–O edge. The liquid is stable at lower temperatures by more than 100 K than after optimization. This behaviour is in agreement with the general tendency of the ionic liquid model to overestimate miscibility gaps and of the associate model to underestimate them.

To summarize, one single model is not superior in all cases, but a choice has to be based on what one wants to achieve. Also of importance is of course which models have been used for other systems with which the present one is going to be combined to describe higher order systems. The ionic liquid model appears to give more reasonable extrapolations to higher order systems than the associated solution model, at least when miscibility
gaps are involved. The number of possible interaction parameters is rather limited with the ionic liquid model, but can become large with the associate model. The ionic liquid model might, thus, be preferable when rather few experimental data are available, but the associate model might, thanks to its higher flexibility, give a more accurate description when detailed experimental data are available.

4.4.7 Conclusions

A consistent set of thermodynamic parameters describing the Ag–Cu–O system have been optimised, using three interaction parameters for the liquid phase. There is no known ternary phase. Available experimental data are generally fitted well, although some uncertainty remains concerning the exact composition of the oxide liquid. A comparison between the ionic liquid model with an associated solution model shows that both models in principle can be used, but that the ionic liquid model gives more reliable extrapolations.

4.4.8 Acknowledgement

Financial support from COST 512 (Modelling in Materials Science and Processing) and from the Swiss National Fund (NF) is gratefully acknowledged.

4.4.9 Literature


Table 4.13: Optimized thermodynamic parameters of cuprite and of the liquid phase according to the two models.

<table>
<thead>
<tr>
<th>Model</th>
<th>Expression</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cuprite</strong></td>
<td></td>
</tr>
<tr>
<td>((\text{Ag}^{1+},\text{Cu}^{1+})_2(\text{O}^2^-)_1)</td>
<td></td>
</tr>
<tr>
<td>(L_{\text{cuprite}}^{\text{Ag}^{1+},\text{Cu}^{1+}:0^2^-} = +14680 )</td>
<td></td>
</tr>
<tr>
<td><strong>Ionic liquid model</strong></td>
<td></td>
</tr>
<tr>
<td>((\text{Ag}^{1+},\text{Cu}^{1+},\text{Cu}^{2+})<em>p(\text{O}^2^-</em>\text{Va}^q)_q)</td>
<td>with (p = 2y_{\text{O}^2^-} + qy_{\text{Va}}; q = y_{\text{Ag}^{1+}} + y_{\text{Cu}^{1+}} + 2y_{\text{Cu}^{2+}})</td>
</tr>
<tr>
<td>(L_{\text{liq}}^{\text{Ag}^{1+},\text{Cu}^{1+}:0^2^-} = -46610 )</td>
<td></td>
</tr>
<tr>
<td>(L_{\text{liq}}^{\text{Ag}^{1+},\text{Cu}^{1+}:0^2^-} = -22660 + (y_{\text{Cu}^{1+}} - y_{\text{Ag}^{1+}}) \cdot 41210 )</td>
<td></td>
</tr>
<tr>
<td><strong>Associated solution model</strong></td>
<td></td>
</tr>
<tr>
<td>((\text{Ag},\text{Ag}_2\text{O},\text{Cu},\text{Cu}_2\text{O}, \text{CuO}))</td>
<td></td>
</tr>
<tr>
<td>(G_{\text{liq}}^{\text{Ag}<em>2\text{O}} - 2G</em>{\text{fcc}}^{\text{Ag}} - G_{\text{O}}^{1/2} = -40980 + 431.5 \cdot T - 84 \cdot T \cdot \ln(T))</td>
<td></td>
</tr>
<tr>
<td>(G_{\text{liq}}^{\text{Cu}<em>2\text{O}} - 2G</em>{\text{fcc}}^{\text{Cu}} - G_{\text{O}}^{1/2} = +2 \cdot G_{\text{ULIQ}} + G_{\text{HSEROO}} - 115379.42 + 43.8808 \cdot T)</td>
<td></td>
</tr>
<tr>
<td>(G_{\text{liq}}^{\text{CuO}} - G_{\text{fcc}}^{\text{Cu}} - G_{\text{O}}^{1/2} = +G_{\text{ULIQ}} + G_{\text{HSEROO}} - 91195.72 + 48.2323 \cdot T)</td>
<td></td>
</tr>
<tr>
<td>(L_{\text{liq}}^{\text{Ag,Ag}<em>2\text{O}} = +17534.6 - 4.454797 \cdot T + (y</em>{\text{Ag}} - y_{\text{Cu}})(2251.3 - 2.6733 T) + (y_{\text{Ag}} - y_{\text{Cu}})^2 492.7)</td>
<td></td>
</tr>
<tr>
<td>(L_{\text{liq}}^{\text{Ag,Ag}_2\text{O}} = +13806 - 13.17 \cdot T)</td>
<td></td>
</tr>
<tr>
<td>(L_{\text{liq}}^{\text{Ag,Ag}_2\text{O}} = +40225)</td>
<td></td>
</tr>
<tr>
<td>(L_{\text{liq}}^{\text{Ag,Ag}_2\text{O}} = -72450)</td>
<td></td>
</tr>
<tr>
<td>(L_{\text{liq}}^{\text{Cu,Cu}<em>2\text{O}} = +41940.93 - 8.0407 \cdot T + (y</em>{\text{Cu}} - y_{\text{Cu}_2\text{O}})(16175.83 - 4.832 \cdot T))</td>
<td></td>
</tr>
<tr>
<td>(L_{\text{liq}}^{\text{Cu,Cu}<em>2\text{O}} = -17867.14 + (y</em>{\text{Cu}} - y_{\text{Cu}_2\text{O}}) \cdot 27787.02)</td>
<td></td>
</tr>
<tr>
<td>(L_{\text{liq}}^{\text{Cu,Cu}<em>2\text{O}} = -43181.68 + 20.1294 \cdot T + (y</em>{\text{Cu}<em>2\text{O}} - y</em>{\text{Cu}_2\text{O}}) \cdot 14532.61)</td>
<td></td>
</tr>
</tbody>
</table>

All parameter values are given in SI units (mol, J, K, Pa, \(R = 8.31451 \text{ J/mol K}\)).

*: optimized in this work. Other parameters have been previously optimized, see [97Ass] for Ag–O, [94Hal] for Cu–O and [86Hay] for Ag–Cu.
Table 4.14: Experimental and calculated invariant equilibria in air ($P_{O_2} = 2.1 \times 10^4 \text{ Pa}$) of the Ag–Cu–O system for the ionic and the associate model.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$T$ (K)</th>
<th>$x_{Ag}^{/(x_{Ag}+x_{Cu})}$</th>
<th>$x_O$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuO ↔ (Cu$_2$O) (in presence of L$_2$)</td>
<td>1300</td>
<td>0.19</td>
<td>—</td>
<td>[93Sha]</td>
</tr>
<tr>
<td></td>
<td>1302</td>
<td>0.10</td>
<td>—</td>
<td>[95Suz]</td>
</tr>
<tr>
<td></td>
<td>1298.1</td>
<td>0.155</td>
<td>0.379</td>
<td>This work $^i$</td>
</tr>
<tr>
<td></td>
<td>1295.4</td>
<td>0.181</td>
<td>0.385</td>
<td>This work $^a$</td>
</tr>
<tr>
<td>CuO + L$_1$ ↔ L$_2$ (monotectic reaction)</td>
<td>1237</td>
<td>0.98</td>
<td>0.307</td>
<td>[93Sha]</td>
</tr>
<tr>
<td></td>
<td>1242</td>
<td>0.98</td>
<td>0.36</td>
<td>[95Suz]</td>
</tr>
<tr>
<td></td>
<td>1241.9</td>
<td>0.988</td>
<td>0.318</td>
<td>This work $^i$</td>
</tr>
<tr>
<td></td>
<td>1241.5</td>
<td>0.982</td>
<td>0.348</td>
<td>This work $^a$</td>
</tr>
<tr>
<td>(Ag) + CuO ↔ L$_1$ (eutectic reaction)</td>
<td>1205</td>
<td>0.986</td>
<td>—</td>
<td>[93Sha]</td>
</tr>
<tr>
<td></td>
<td>1215</td>
<td>0.99</td>
<td>—</td>
<td>[95Suz]</td>
</tr>
<tr>
<td></td>
<td>1219.5</td>
<td>0.989</td>
<td>0.011</td>
<td>This work $^i$</td>
</tr>
<tr>
<td></td>
<td>1215.1</td>
<td>0.988</td>
<td>0.016</td>
<td>This work $^a$</td>
</tr>
</tbody>
</table>

L$_1$ is the metal liquid and L$_2$ is the oxide liquid.

$^i$, resp. $^a$, refers to the use of the ionic, resp. the associate, model for the liquid phase.
Table 4.15: Calculated invariant equilibria in the Ag–Cu–O system.
The liquid phase is described with the ionic model.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$T$ (K)</th>
<th>$\log(P_{O_2})$</th>
<th>Composition of the phases</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$x_{Ag}$</td>
</tr>
<tr>
<td>a: $(Ag) + (Cu) + (Cu_2O)$</td>
<td>1055.7</td>
<td>-8.978</td>
<td>L$_1$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$(Ag)$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$(Cu)$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$(Cu_2O)$</td>
</tr>
<tr>
<td>b: $(Ag) + (Cu_2O)$</td>
<td>1221.7</td>
<td>-1.390</td>
<td>L$_1$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$(Ag)$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$(Cu_2O)$</td>
</tr>
<tr>
<td>c: $(Ag) + (Cu_2O) + CuO$</td>
<td>1214.3</td>
<td>-1.357</td>
<td>L$_2$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$(Ag)$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$(Cu_2O)$</td>
</tr>
<tr>
<td>d: $(Ag) + CuO$</td>
<td>1221.6</td>
<td>-1.183</td>
<td>L$_1$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$(Ag)$</td>
</tr>
<tr>
<td>e: $(Ag) + (Ag_2O) + CuO$</td>
<td>803.6</td>
<td>2.718</td>
<td>L$_1$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$(Ag)$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$(Ag_2O)$</td>
</tr>
<tr>
<td>f: $(Ag_2O) + CuO$</td>
<td>857.6</td>
<td>3.613</td>
<td>L$_1$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$(Ag_2O)$</td>
</tr>
</tbody>
</table>

L$_1$, resp. L$_2$, for metal, resp. oxide liquids. The calculated invariant equilibria below the dotted line are more uncertain because of the very high oxygen partial pressures.
Table 4.16: Temperature (in Kelvin) for experimental and calculated invariant equilibria of the Ag–Cu–O system in $P_{O_2} = 0.21$ bar ($2.1 \cdot 10^4$ Pa). The liquid is described with the ionic liquid model.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$P_{O_2}$ bar</th>
<th>Experimental $T$, K (DTA/TG) [95Suz]</th>
<th>Calculated $T$, K This work</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Ag) + CuO $\leftrightarrow$ L$_1$</td>
<td>1.01</td>
<td>1201</td>
<td>1209</td>
</tr>
<tr>
<td></td>
<td>0.10</td>
<td>1215</td>
<td>1221</td>
</tr>
<tr>
<td>CuO + L$_1$ $\leftrightarrow$ L$_2$</td>
<td>1.01</td>
<td>1265</td>
<td>1264</td>
</tr>
<tr>
<td></td>
<td>0.10</td>
<td>1228</td>
<td>1229</td>
</tr>
<tr>
<td>CuO $\leftrightarrow$ (Cu$_2$O) $^\dagger$</td>
<td>0.10</td>
<td>1261</td>
<td>1257</td>
</tr>
<tr>
<td>(Ag) + (Cu$_2$O) $\leftrightarrow$ L$_1$</td>
<td>0.02</td>
<td>1218</td>
<td>1222</td>
</tr>
<tr>
<td></td>
<td>0.01</td>
<td>1220</td>
<td>1221</td>
</tr>
<tr>
<td></td>
<td>$3 \cdot 10^{-4}$</td>
<td>1218</td>
<td>1211</td>
</tr>
<tr>
<td></td>
<td>$3 \cdot 10^{-5}$</td>
<td>1219</td>
<td>1197</td>
</tr>
<tr>
<td>(Cu$_2$O) + L$_1$ $\leftrightarrow$ L$_2$</td>
<td>0.02</td>
<td>1280</td>
<td>1292</td>
</tr>
<tr>
<td></td>
<td>0.01</td>
<td>1323</td>
<td>1341</td>
</tr>
<tr>
<td></td>
<td>$3 \cdot 10^{-4}$</td>
<td>1371</td>
<td>1473</td>
</tr>
<tr>
<td></td>
<td>$3 \cdot 10^{-5}$</td>
<td>1386</td>
<td>1498 $^\ddagger$</td>
</tr>
</tbody>
</table>

L$_1$ is the metal liquid and L$_2$ is the oxide liquid.

$^\dagger$: The reaction takes place in presence of L$_2$.

$^\ddagger$: Calculated end point of the $(Cu_2O) + L_1 \leftrightarrow L_2$ equilibrium at $P_{O_2} = 1.2 \cdot 10^{-4}$ bar ($12$ Pa $O_2$).
Figure 4.12: Calculated Ag–CuO$_x$ phase diagram in air and comparison with experimental data [93Sha, 95Suz].
Figure 4.13: Calculated isothermal section at $T = 1173$ K.

Figure 4.14: Calculated isothermal section at $T = 1273$ K.
Figure 4.15: Calculated isothermal section at $T = 1523$ K and comparison with experimental data [93Tak].

Figure 4.16: Ag–Cu–O oxygen potential diagram: the four-phase invariant equilibria are indicated with the letters a, b, c and d according to Table 4.15.
Figure 4.17: Part of the Ag–Cu–O oxygen potential diagram and comparison with experimental data [95Suz]. Four-phase invariant equilibria are indicated with the letters b, c and d according to Table 4.15.

Figure 4.18: Calculated projection of the liquidus equilibria compared with experimental data [95Suz].
Figure 4.19: Logarithm of O activity coefficient at $x_O = 0.01$ as a function of Ag content in the metal liquid at $T = 1373 \text{ K}$ and $T = 1473 \text{ K}$. The associated solution model and the ionic liquid model for the liquid phase are compared with experimental data [69Fru, 69Blo, 72Tan, 73Jac, 88Yao].
Figure 4.20: Calculated Ag–CuO$_x$ phase diagram in air: comparison between the ionic liquid model, the associated solution model for the liquid phase and the experimental data [93Sha, 95Suz].
Figure 4.21: Part of the Ag–Cu–O oxygen potential diagram: comparison of the results from the two models with experimental data [95Suz].
4.5 The Ag–Sr–Cu–O and Ag–Ca–Cu–O Systems


Experimental Phase Diagram Study and Thermodynamic Optimization of the Ag–Sr–Cu–O and Ag–Ca–Cu–O Systems

Jérôme Assal, Bengt Hallstedt and Ludwig J. Gauckler
ETH Zürich, Department of Materials, Nonmetallic Materials
Swiss Federal Institute of Technology, Sonneggstr. 5, CH-8092 Zurich, Switzerland

Abstract

The phase relations in the Ag–Sr–Cu–O and Ag–Ca–Cu–O systems are studied in O₂, in air and in N₂ using differential thermal analysis and energy dispersive spectrometry. Silver lowers the melting point of the oxide liquid to a monotectic in the Sr- and Ca-containing system by 62 K and 82 K to 1222 K and 1244 K respectively in O₂. The oxide liquid dissolves Ag up to 0.17 metallic ratio in the Ag–Sr–Cu–O system in O₂ at a temperature slightly above the monotectic reaction (silver content in the oxide liquid is measured as 0.29 in the Ag–Ca–Cu–O system). The two oxide systems are optimized by the CALPHAD method using these experimental data from monotectics and with the lower-order systems, that were previously published. This work is part of a project to evaluate the phase relations within the Ag–Bi–Sr–Ca–Cu–O, and in particular to focus on the influence of silver on the phase equilibria around the superconducting phases during the partial melt-processing.

4.5.1 Introduction

The Bi–Sr–Ca–Cu–O system contains three superconducting phases, the one-layer compound (11905 for Bi₁₁Sr₃Ca₉Cu₂Oₓ), the two-layer compound (2212), and the three-layer compound (2223). For most applications they are partially melt-processed on silver substrates or in silver tubes. Silver possesses attractive properties such as high-temperature chemical stability, high oxygen diffusivity, and high ductility with good enough mechanical stability. Silver does not dissolve into the superconducting phases and, thus, does not cause any detrimental effects on the superconducting properties [93Nom]. Silver dissolves into the oxide liquid and lowers the melting temperatures of the superconducting phases by about 30 K during the partial melt-processing of 2212 on silver [97Lan,97Maj]. This work is part of a project to evaluate the thermodynamic properties and the phase re-

lations in the Ag–Bi–Sr–Ca–Cu–O system, especially to quantify the influence of silver on the phase equilibria relevant for the processing of the 2212 and 2223 compounds.

This work is based on the optimizations of the systems Sr–Cu–O [97Ris], Ca–Cu–O [95Ris], and Ag–Cu–O [98Ass]. The two missing ternaries, Ag–Sr–O and Ag–Ca–O, could not be experimentally studied nor optimized because silver does not modify perceptibly the phase relations in the Sr–O and Ca–O binaries. In the Sr–Cu–O and Ca–Cu–O systems, extrapolations by the CALPHAD method show that monotectic temperatures might decrease significantly by the addition of silver. Therefore, experimental investigations and thermodynamic optimizations of the Ag–Sr–Cu–O and Ag–Ca–Cu–O systems are needed.

Neither phase diagram nor thermodynamic studies in these systems have been reported in the literature. No quaternary compounds were found in these systems to our knowledge and it is probable that there are no compounds stable at ambient pressure. Differential thermal analyses (DTA) are conducted in three controlled oxygen atmospheres: in O₂, in air, and in N₂ (with 85 Pa ≤ P₉₂ ≤ 400 Pa); where the temperatures of the monotectic transformation (T_{mono}), i.e. the emergence of the oxide liquid, and of the melting of silver (T_{m,(Ag)}) are determined. These experiments are described in Section II.1. The cationic compositions of the oxide liquid phases are determined by energy dispersive X-ray spectrometry (EDX), see Section II.2.

The optimizations of the Ag–Sr–Cu–O and Ag–Ca–Cu–O systems are based on the DTA measured monotectic temperatures, T_{mono}, and concern the liquid phases. In both cases, the two-sublattice model for ionic liquids is used.

4.5.2 Experimental Phase Diagram Study

DTA measurements

In order to select sample compositions and starting materials to investigate the Ag–Sr–Cu–O and Ag–Ca–Cu–O systems, we extrapolated from the known lower-order systems Ag–Cu–O [98Ass], Sr–Cu–O [97Ris], and Ca–Cu–O [95Ris] and calculated equilibria just below the monotectic temperature at the monotectic composition. In the first system, Ag (s), CuO, and Sr₁₄Cu₂₄O₄₁ are in equilibrium in P₀₂ = 10⁵ Pa; Ag (l), CuO, and Sr₁₄Cu₂₄O₄₁ in P₀₂ = 0.21·10⁵ Pa; and Ag (l), Cu₂O, and SrCu₂O₂ for P₀₂ < 500 Pa. In the second system, Ag (s), CuO, and Ca₂CuO₃ are in equilibrium in P₀₂ = 10⁵ Pa and in P₀₂ = 0.21·10⁵ Pa; and Ag (s), Cu₂O, and CaO for P₀₂ < 500 Pa.

To prepare Sr₁₄Cu₂₄O₄₁, we mixed SrCO₃(¹) and CuO(²) in a 14:24 molar ratio, calcined the mixture for 2 h in air at T = 1223 K followed by grinding, and sintering two times 12 h in air at T = 1203 K, each time followed by grinding. The same method was used to prepare Ca₂CuO₃ (with CaCO₃(³) and CuO in a 2:1 molar ratio) and CaO. X-ray diffraction

1. CERAC, 99.5%
2. CERAC, 99.9%
(XRD) patterns showed excellent phase purity on these powders.

Powder samples for the DTA were prepared with these powders at compositions that correspond to the extrapolated monotectics. This procedure resulted in DTA\(^{(1)}\) curves with large and clear peaks. In the Ag–Sr–Cu–O system, appropriate amounts of Ag\(_2\)O\(^{(2)}\), CuO, and Sr\(_{14}\)Cu\(_{24}\)O\(_{41}\) were dry-mixed for 3 h in a ball mill. For the DTA measurement in low oxygen partial pressures, in which SrCu\(_2\)O\(_2\) is stable below \(T_{\text{mono}}\) \(\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}\) was used since SrCu\(_2\)O\(_2\) is not stable in air. During the measurements, a holding time of 2 h at 1163 K was used to allow the two-step reduction of Sr\(_{14}\)Cu\(_{24}\)O\(_{41}\) into SrCu\(_2\)O\(_2\) via SrCuO\(_2\). The exact compositions of the DTA samples are given in Table 4.17. The same method was used to prepare the samples in the Ag–Ca–Cu–O system, with Ag\(_2\)O, CuO, Ca\(_2\)CuO\(_3\), and/or CaO and the compositions are given in Table 4.18.

Samples of approximately 100 mg were heated in Al\(_2\)O\(_3\) crucibles at rates of \(dT/dt = 1 \text{ K/min}, 2 \text{ K/min}, 3 \text{ K/min or 5 K/min in } \text{O}_2 (P_{\text{O}_2} = 1.01 \cdot 10^5 \text{ Pa}),\) in air \((P_{\text{O}_2} = 0.21 \cdot 10^5 \text{ Pa})\), and in \(N_2 (85 \text{ Pa} \leq P_{\text{O}_2} \leq 400 \text{ Pa})\). At low oxygen partial pressures, i.e. in flowing \(N_2\) gas, \(P_{\text{O}_2}\) was continuously measured with a ZrO\(_2\)–oxygen sensor\(^{(3)}\) and recorded, and a holding time between 2 h and 10 h at 873 K was added to reach low \(P_{\text{O}_2}\). The total gas pressure was 1 atm \((1.01 \cdot 10^5 \text{ Pa})\) and the gas flow rate 3 l/h. During heating, the Ag\(_2\)O and CuO particles reduced into Ag and Cu\(_2\)O, respectively, leading to fine dispersions. Each experiment was repeated at least once and the results showed satisfactory reproducibility. The normal error on the temperature measurements was estimated to be ±5 K, but in some indicated cases, though, the error was larger and is given below.

The DTA results for the Ag–Sr–Cu–O system are listed in Table 4.19. In \(\text{O}_2\), silver melts in presence of CuO and Sr\(_{14}\)Cu\(_{24}\)O\(_{41}\) at \(T_{m(\text{Ag})} = 1209 \text{ K}\). The monotectic transformation, i.e. \(L_1 + \text{CuO} + \text{Sr}_{14}\text{Cu}_{24}\text{O}_{41} \rightarrow L_2\), where \(L_1\) is the metallic liquid (rich in Ag) and \(L_2\) the oxide liquid, was measured at \(T_{\text{mono}} = 1226 \text{ K}\). In air the monotectic transformation \((\text{Ag}) + \text{CuO} + \text{Sr}_{14}\text{Cu}_{24}\text{O}_{41} \rightarrow L_2\) was measured at \(T_{\text{mono}} = 1198 \text{ K}\). At low oxygen partial pressures, \((\text{Ag}) + \text{Cu}_2\text{O} + \text{SrCu}_2\text{O}_2 \rightarrow L_2\) was measured in \(P_{\text{O}_2} = 90 \text{ Pa} \pm 50 \text{ Pa}\) at \(T_{\text{mono}} = 1209 \text{ K} \pm 10 \text{ K}\), and in \(P_{\text{O}_2} = 220 \text{ Pa} \pm 50 \text{ Pa}\) at \(T_{\text{mono}} = 1181 \text{ K} \pm 32 \text{ K}\). The large error on the last measured temperature was due to the difficulty to evaluate properly the beginning of the monotectic transformation since the peak overlapped with that of the solid transformation of Sr\(_{14}\)Cu\(_{24}\)O\(_{41}\) into SrCu\(_2\)O\(_2\). In the Ag–Ca–Cu–O system, the DTA curves showed two peaks for all the oxygen partial pressures: the first one was attributed to the melting of silver in presence of secondary phases, and the second one to the monotectic transformation. In \(\text{O}_2\), silver melting was measured at \(T_{m(\text{Ag})} = 1196 \text{ K}\), and the monotectic transformation, i.e. \(L_1 + \text{CuO} + \text{Ca}_2\text{CuO}_3 \rightarrow L_2\) at \(T_{\text{mono}} = 1245 \text{ K}\). In air the reactions are identical but the temperatures were measured as \(T_{m(\text{Ag})} = 1208 \text{ K}\) and \(T_{\text{mono}} = 1219 \text{ K}\).

---

3. AnalytiCals, 99.5%
1. STA 501, Bähr, Germany
2. CERAC, 99.0%
3. Type FCX-MW-FL, Pewatron, Switzerland
temperatures were the same. For measured oxygen partial pressures between 85 Pa ±50 Pa and 400 Pa ±50 Pa, silver melted in presence of Cu$_2$O and CaO at $T_{m}(Ag) = 1215$ K, and $L_1 + Cu_2O + CaO \rightarrow L_2$ took place at $T_{mono} = 1307$ K. Since low $P_{O_2}$ were rather difficult to determine precisely, these measurements must be considered with caution. The results are listed in Table 4.20.

**EDX measurements**

The metallic ratios, $\nu$, were determined in the oxide liquid phase of two samples with EDX coupled to a scanning electron microscope (SEM). The starting powders were prepared as for the DTA experiments. The samples, whose starting compositions were $\nu_{Ag} = 0.40$, $\nu_{Cu} = 0.48$, and $\nu_M = 0.12$ where M = Sr or Ca, were first pressed into pellets and put in alumina crucibles. They were heated in pure O$_2$ in a vertical furnace, homogenized at constant $T_{max}$ (1244 K for Ag–Sr–Cu–O and 1253 K for Ag–Ca–Cu–O) and rapidly cooled in oil at room temperature ($|dT/dt| > 100$ K/sec). An error of ±0.05 was estimated on the composition measurements. In the Ag–Sr–Cu–O system, the metallic ratios were measured as $\nu_{Ag} = 0.17$, $\nu_{Cu} = 0.62$, and $\nu_{Sr} = 0.22$. In the Ag–Ca–Cu–O system, we found $\nu_{Ag} = 0.29$, $\nu_{Cu} = 0.56$, and $\nu_{Ca} = 0.15$. No trace of aluminum coming from the crucibles was found in the samples.

### 4.5.3 Thermodynamic Models

**Solid Phases**

The Gibbs energies for pure elements are taken from Dinsdale [91Din]. The descriptions of the oxide compounds and of the fcc structure (Ag and Cu) come from previous assessments [95Ris,97Ris,98Ass].

**Liquid Phase**

The liquid phase is modeled by the two-sublattice model for ionic liquids [85Hil,91Sun] which allows a continuous description from the oxide to the metal side of the liquid. We wanted also these descriptions to be consistent with our existing database of the Ag–Bi–Sr–Ca–Cu–O system, where this model has been successfully used. The model assumes that cations and anions mix randomly in their respective sublattices, and negatively charged vacancies, $V_{a^{2-}}$, are added in order to reach the pure metallic composition. The model can be written as $(Ag^{1+},M^{2+},Cu^{1+},Cu^{2+})_p (O^{2-},V_{a^{2-}})_q$ with $M = Sr$ or Ca, where the indices $p$ and $q$ vary with composition in order to maintain electroneutrality as:

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

$$
q = y_{Ag^{1+}} + 2y_{M^{2+}} + y_{Cu^{1+}} + 2y_{Cu^{2+}}
$$

where $y_s$ are the site fractions of $s$, i.e. the fractions of the species $s$ in each sublattice. The molar Gibbs energy of the liquid phase is given by:
\[ G_{m}^{\text{liq}} = q \cdot \sum_{i = \text{cations}} y_{i} \cdot y_{VA} \cdot ^{\circ}G_{i,VA}^{\text{liq}} + \sum_{i = \text{cations}} y_{i} \cdot y_{O^{2-}} \cdot ^{\circ}G_{i,O^{2-}}^{\text{liq}} \]
\[ + R \cdot T \cdot \left( p \cdot \sum_{i = \text{cations}} y_{i} \cdot \ln y_{i} + q \cdot \sum_{j = \text{anions}} y_{j} \cdot \ln y_{j} \right) + E_{G_{m}}^{\text{liq}} \]  
(4.23)

where \(^{\circ}G_{i,VA}^{\text{liq}}\) are the Gibbs energies of the pure liquid \(i\) elements, given by Dinsdale [91Din], and \(^{\circ}G_{i,O^{2-}}^{\text{liq}}\) are the Gibbs energies of the pure liquid \(i\) oxides, previously assessed [95Ris,97Ris,98Ass]. The molar excess Gibbs energy of the liquid, \(E_{G_{m}}^{\text{liq}}\), is given by:

\[ E_{G_{m}}^{\text{liq}} = \sum_{\text{binaries}} E_{G_{\text{binaries}}}^{\text{liq}} + \sum_{\text{ternaries}} E_{G_{\text{ternaries}}}^{\text{liq}} + E_{G_{\text{Ag-M-Cu-O}}}^{\text{liq}} \]  
(4.24)

where the \(E_{G_{\text{binaries}}}^{\text{liq}}\) and \(E_{G_{\text{ternaries}}}^{\text{liq}}\) represent the excess terms in the binary and in the ternary subsystems, respectively, and were given, except for Ag–Sr–O and Ag–Ca–O, in previous assessments [95Ris,97Ris,98Ass]. \(E_{G_{\text{Ag-M-Cu-O}}}^{\text{liq}}\) is the molar excess Gibbs energy due to quaternary interactions.

### 4.5.4 Parameter Optimization

The program PARROT included in the Thermo-Calc databank system [85Sun] was used for the optimization of the interaction parameters. Since there is no quaternary compounds in the two systems, parameters describing the liquid phases only must be optimized. Equation 4.24 showed that two different excess Gibbs energies could be optimized, i.e. the ternary terms \(E_{G_{\text{Ag-M-O}}}^{\text{liq}}\) and the quaternary terms \(E_{G_{\text{Ag-M-Cu-O}}}^{\text{liq}}\). We tested these two parameters for each system and concluded that the results were nearly identical. For this reason, we decided to use the ternary terms \(E_{G_{\text{Ag-M-O}}}^{\text{liq}}\) in both Ag–M–Cu–O systems and not the quaternary terms. These excess terms of the Gibbs energies can be written as:

\[ E_{G_{\text{Ag-M-O}}}^{\text{liq}} = y_{Ag^{1+}} \cdot y_{M^{2+}} \cdot y_{O^{2-}} \cdot L_{Ag^{1+},M^{2+},O^{2-}}^{\text{liq}} \]
\[ + y_{Ag^{1+}} \cdot y_{M^{2+}} \cdot y_{O^{2-}} \cdot y_{VA} \cdot L_{Ag^{1+},M^{2+},O^{2-},VA}^{\text{liq}} \]  
(4.25)

where the \(L_{Ag^{1+},M^{2+},O^{2-}}^{\text{liq}}\) parameter describes the interactions in the liquid between the oxide species only, whilst \(L_{Ag^{1+},M^{2+},O^{2-},VA}^{\text{liq}}\) describes the interactions on both oxide and metal sides. These interaction parameters, \(L\), can be written as Redlich-Kister polynomials,
and a temperature dependence can be added.

During the preliminary optimization of the Ag–Sr–Cu–O system, we tested if the interaction parameter $L_{Ag, Sr, O, V}^{\text{liq}}$ could be used to influence the calculated $T_m(Ag)$. However, the calculated solubility of Sr in Ag (l) is so small, $y_{Sr} \leq 10^{-16}$, see Table 4.22, that the $L_{Ag, Sr, O, V}^{\text{liq}}$ parameter becomes inefficient and impossible to optimize. The same comment can be made for the parameter $L_{Ag, Ca, O, V}^{\text{liq}}$ in the Ag–Ca–Cu–O system. In other words, the calculated $T_m(Ag)$ in the Ag–M–Cu–O systems are very close to the $T_m(Ag)$ in the Ag–Cu–O system [98Ass].

These considerations imposed the optimization to the parameters $L_{Ag, M, O}^{\text{liq}}$ only, that can be optimized using the DTA measured $T_{\text{mono}}$ in different oxygen partial pressures. The small amount of data did not allow the use of a temperature or composition dependence in $L_{Ag, M, O}^{\text{liq}}$.

4.5.5 Results and Discussion

The Ag–Sr–Cu–O system

The optimized parameter is $L_{Ag, Sr, O}^{\text{liq}} = -39000$. The calculated values of $T_{\text{mono}}$ and $T_m(Ag)$ are compared with extrapolations, i.e. calculations with $L_{Ag, Sr, O}^{\text{liq}} = 0$, and with DTA experiments for the three studied atmospheres, see Table 4.19.

A graphic comparison between DTA experiments and calculations is presented in the oxygen potential diagram, which is a projection along the composition axes, see Fig. 4.22. Lines represent four-phase equilibria, numbered from 1 to 22, and intersections five-phase equilibria, labelled from A to K, see the legends in Tables 4.21 and 4.22. The calculation fits the experimental $T_{\text{mono}}$ very well, for the different monotectic transformations taking place in the different oxygen partial pressures. However, the calculated $T_m(Ag)$ for $P_{O_2} = 10^5$ Pa, is 13 K too high. Because of the small solubility of Sr in Ag (l), the presently calculated $T_m(Ag)$ is identical to $T_m(Ag)$ in the Ag–Cu–O system. In that system the calculated $T_m(Ag)$ was 8 K higher than the measurement in $P_{O_2} = 10^5$ Pa [98Ass]. In order to improve the agreement in the present system, adjustments must be made in the Ag–Cu–O system.

Figure 4.23 shows the calculated Ag–SrO–CuO isotherm for $T = 1244$ K and $P_{O_2} = 10^5$ Pa, and the EDX measured composition of the oxide liquid. In comparison with experimental value, the calculated composition is somewhat too rich in silver, too poor in strontium, and in good agreement in regard to the copper content. In the Sr–Cu–O system [97Ris], the inverse tendency was observed for $T < 1500$ K, where the calculated composition of the liquid was shifted towards the strontium composition.

Figure 4.24 shows the calculated $(CuO)_{0.8}(SrO)_{0.2}$ isopleth in $P_{O_2} = 10^5$ Pa as well
as the experimental $u_{Ag}$. The silver content in L$_2$, that is in equilibrium with Sr$_{14}$Cu$_2$O$_{41}$ and L$_1$, is satisfactorily fitted by the calculation when considering the large experimental error.

**The Ag–Ca–Cu–O system**

The parameter optimized in the liquid phase, $L_{Ag^{1+},Ca^{2+},O^{2-}}^{liq} = +10000$, reveals the small magnitude of the interactions between the species in the liquid. On one hand the two $T_{mono}$ measured in $P_{O_2} = 10^5$ Pa and in $P_{O_2} = 400$ Pa tend to push $L_{Ag^{1+},Ca^{2+},O^{2-}}^{liq}$ to positive values, on the other hand $T_{mono}$ measured in air leads to negative value of the interaction parameter. Using more parameters to describe the interactions in the liquid would lead to a better agreement with the experimental data but is not acceptable because of the very few experimental data. The optimized temperatures are compared with experimental values and extrapolated data in Table 4.20.

Figure 4.25 shows the calculated Ag–Ca–Cu–O oxygen potential phase diagram in comparison with the DTA experiments. The agreement with $T_{mono}$ is generally good, except for the lowest $P_{O_2}$. During this experiment, we had some difficulties to measure $P_{O_2}$ with high accuracy and estimate the experimental error to ±50 Pa. The measured temperature is the same as that measured in $P_{O_2} = 220$ Pa, but the calculation reveals a relatively strong dependence of $T_{mono}$ on $P_{O_2}$ in this region. Thus, we conclude that the measured $P_{O_2}$ for this point is probably incorrect. The experimental melting temperatures of silver, $T_{m,(Ag)}$, are not very well fitted by the calculation, which is explained similarly as in the Ag–Sr–Cu–O system since $u_{Ca}$ in L$_1$ is very small, see Table 4.24.

The calculated Ag–CaO–CuO phase diagram at $T = 1253$ K and for $P_{O_2} = 10^5$ Pa is shown in Fig. 4.26, in comparison with the experimental composition of L$_2$. The agreement is rather poor (similar to that in the Ag–Sr–Cu–O system), except for the silver ratio, and confirms the larger difficulty to fit the compositions as compared to the transformation temperatures.

Figure 4.27 shows the calculated isopleth between $(CuO)_{0.8}$(CaO)$_{0.2}$ and Ag in $P_{O_2} = 10^5$ Pa. The calculated composition of L$_2$ lays inside the experimental error of the measured $u_{Ag}$.

**4.5.6 Conclusion**

The monotectic temperatures in the Ag–Sr–Cu–O and Ag–Ca–Cu–O systems have been measured using DTA. These experiments were made in $P_{O_2} = 10^5$ Pa, 0.21·$10^5$ Pa, and in N$_2$. In the latter case, $P_{O_2}$ was continuously measured using an ZrO$_2$-oxygen sensor between 85 Pa and 400 Pa. At very low oxygen pressures, the measurements of $P_{O_2}$ are relatively uncertain, and data have to be used with caution. The experimental temperatures of the monotectic transformations could be used to optimize thermodynamics of the two systems. As they do not contain any new phases, interaction parameters in the liquid
phases are considered only. The cationic compositions of the oxide liquid were measured by EDX and agreement with calculations is acceptable, when considering the relatively large error of the measurements.

4.5.7 Acknowledgements

Supported by the Swiss National Science Foundation, under Grant No. 43199, and by COST 512 (European Co-operation in the Field of Scientific and Technical Research, Modeling in Materials Science and Processing).

4.5.8 Literature


Table 4.17: Compositions in the Ag–Sr–Cu–O system used for DTA.

<table>
<thead>
<tr>
<th>Mix No.</th>
<th>$P_{O_2}$</th>
<th>Compositions in $u^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>($10^5$ Pa)</td>
<td>Ag</td>
</tr>
<tr>
<td>S1</td>
<td>1.01</td>
<td>0.252</td>
</tr>
<tr>
<td>S2</td>
<td>0.21</td>
<td>0.188</td>
</tr>
<tr>
<td>S3</td>
<td>0.001</td>
<td>0.053</td>
</tr>
</tbody>
</table>

1. oxygen partial pressures used to calculate the extrapolated monotectic compositions
2. where $u$ is the metallic ratio, i.e. $u_j = n_j / \sum_{i=cations} n_i$

Table 4.18: Compositions in the Ag–Ca–Cu–O system used for DTA.

<table>
<thead>
<tr>
<th>Mix No.</th>
<th>$P_{O_2}$</th>
<th>Compositions in $u^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>($10^5$ Pa)</td>
<td>Ag</td>
</tr>
<tr>
<td>C1</td>
<td>1.01</td>
<td>0.314</td>
</tr>
<tr>
<td>C2</td>
<td>0.21</td>
<td>0.264</td>
</tr>
<tr>
<td>C3</td>
<td>0.001</td>
<td>0.074</td>
</tr>
</tbody>
</table>

1. oxygen partial pressures used to calculate the extrapolated monotectic compositions
2. where $u$ is the metallic ratio, i.e. $u_j = n_j / \sum_{i=cations} n_i$
Table 4.19: DTA measured temperatures of reaction, $T_{m,(Ag)} \pm 5$ K and $T_{mono} \pm 5$ K, in the Ag–Sr–Cu–O system compared with the calculations before and after the optimization (extrapolated and optimized values, respectively).

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>$dT/dt$ (K/min)</th>
<th>$P_{O_2}$ (Pa)</th>
<th>$T_{m,(Ag)}$ (K)</th>
<th>$T_{mono}$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1a</td>
<td>1</td>
<td>$1.01 \cdot 10^5$</td>
<td>1196</td>
<td>1226</td>
</tr>
<tr>
<td>S1b</td>
<td>3</td>
<td>$1.01 \cdot 10^5$</td>
<td>1196</td>
<td>1226</td>
</tr>
<tr>
<td>S2c</td>
<td>1</td>
<td>$0.21 \cdot 10^5$</td>
<td>-</td>
<td>1197</td>
</tr>
<tr>
<td>S2d</td>
<td>1</td>
<td>$0.21 \cdot 10^5$</td>
<td>-</td>
<td>1198</td>
</tr>
<tr>
<td>S3e</td>
<td>5</td>
<td>220 ± 50</td>
<td>-</td>
<td>1174 ± 24</td>
</tr>
<tr>
<td>S3f</td>
<td>3</td>
<td>220 ± 50</td>
<td>-</td>
<td>1199 ± 7</td>
</tr>
<tr>
<td>S3g</td>
<td>3</td>
<td>220 ± 50</td>
<td>-</td>
<td>1169 ± 43</td>
</tr>
<tr>
<td>S3h</td>
<td>3</td>
<td>90 ± 50</td>
<td>-</td>
<td>1209 ± 10</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Mix No.</th>
<th>Mean values</th>
<th>$P_{O_2}$ (Pa)</th>
<th>$T_{m,(Ag)}$ (K)</th>
<th>$T_{mono}$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>measured</td>
<td>$1.01 \cdot 10^5$</td>
<td>1196</td>
<td>1226</td>
</tr>
<tr>
<td>S1</td>
<td>extrapolated</td>
<td>$1.01 \cdot 10^5$</td>
<td>1209</td>
<td>1234</td>
</tr>
<tr>
<td>S1</td>
<td>optimized</td>
<td>$1.01 \cdot 10^5$</td>
<td>1209</td>
<td>1222</td>
</tr>
<tr>
<td>S2</td>
<td>measured</td>
<td>$0.21 \cdot 10^5$</td>
<td>-</td>
<td>1198</td>
</tr>
<tr>
<td>S2</td>
<td>extrapolated</td>
<td>$0.21 \cdot 10^5$</td>
<td>-</td>
<td>1211</td>
</tr>
<tr>
<td>S2</td>
<td>optimized</td>
<td>$0.21 \cdot 10^5$</td>
<td>-</td>
<td>1202</td>
</tr>
<tr>
<td>S3</td>
<td>measured</td>
<td>220 ± 50</td>
<td>-</td>
<td>1181 ± 32</td>
</tr>
<tr>
<td>S3</td>
<td>extrapolated</td>
<td>220</td>
<td>-</td>
<td>1200</td>
</tr>
<tr>
<td>S3</td>
<td>optimized</td>
<td>220</td>
<td>-</td>
<td>1184</td>
</tr>
<tr>
<td>S3</td>
<td>measured</td>
<td>90 ± 50</td>
<td>-</td>
<td>1209 ± 10</td>
</tr>
<tr>
<td>S3</td>
<td>extrapolated</td>
<td>90</td>
<td>-</td>
<td>1218</td>
</tr>
<tr>
<td>S3</td>
<td>optimized</td>
<td>90</td>
<td>-</td>
<td>1208</td>
</tr>
</tbody>
</table>
Table 4.20: DTA measured temperatures of reaction, $T_{m(\text{Ag})} \pm 5$ K and $T_{\text{mono}} \pm 5$ K, in the Ag–Ca–Cu–O system compared with the calculations before and after the optimization (extrapolated and optimized values, respectively).

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>$dT/dt$ (K/min)</th>
<th>$P_{O_2}$ (Pa)</th>
<th>$T_{m(\text{Ag})}$ (K)</th>
<th>$T_{\text{mono}}$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1a</td>
<td>3</td>
<td>$1.01 \times 10^5$</td>
<td>1197</td>
<td>-</td>
</tr>
<tr>
<td>C1b</td>
<td>3</td>
<td>$1.01 \times 10^5$</td>
<td>1196</td>
<td>1245</td>
</tr>
<tr>
<td>C1c</td>
<td>1</td>
<td>$1.01 \times 10^5$</td>
<td>1196</td>
<td>1244</td>
</tr>
<tr>
<td>C2d</td>
<td>3</td>
<td>$0.21 \times 10^5$</td>
<td>1208</td>
<td>1219</td>
</tr>
<tr>
<td>C2e</td>
<td>3</td>
<td>$0.21 \times 10^5$</td>
<td>1209</td>
<td>1219</td>
</tr>
<tr>
<td>C2f</td>
<td>1</td>
<td>$0.21 \times 10^5$</td>
<td>1208</td>
<td>1220</td>
</tr>
<tr>
<td>C3g</td>
<td>2</td>
<td>400 ±50</td>
<td>1215</td>
<td>1308</td>
</tr>
<tr>
<td>C3h</td>
<td>1</td>
<td>350 ±50</td>
<td>1214</td>
<td>1306</td>
</tr>
<tr>
<td>C3i</td>
<td>3</td>
<td>85 ±50</td>
<td>1215</td>
<td>1308</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Mix No.</th>
<th>Mean values</th>
<th>$P_{O_2}$ (Pa)</th>
<th>$T_{m(\text{Ag})}$ (K)</th>
<th>$T_{\text{mono}}$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>measured</td>
<td>$1.01 \times 10^5$</td>
<td>1196</td>
<td>1245</td>
</tr>
<tr>
<td>C1</td>
<td>extrapolated</td>
<td>$1.01 \times 10^5$</td>
<td>1209</td>
<td>1242</td>
</tr>
<tr>
<td>C1</td>
<td>optimized</td>
<td>$1.01 \times 10^5$</td>
<td>1209</td>
<td>1243</td>
</tr>
<tr>
<td>C2</td>
<td>measured</td>
<td>$0.21 \times 10^5$</td>
<td>1208</td>
<td>1219</td>
</tr>
<tr>
<td>C2</td>
<td>extrapolated</td>
<td>$0.21 \times 10^5$</td>
<td>1220</td>
<td>1225</td>
</tr>
<tr>
<td>C2</td>
<td>optimized</td>
<td>$0.21 \times 10^5$</td>
<td>1220</td>
<td>1225</td>
</tr>
<tr>
<td>C3</td>
<td>measured</td>
<td>400 ±50</td>
<td>1215</td>
<td>1307</td>
</tr>
<tr>
<td>C3</td>
<td>extrapolated</td>
<td>400</td>
<td>1220</td>
<td>1299</td>
</tr>
<tr>
<td>C3</td>
<td>optimized</td>
<td>400</td>
<td>1220</td>
<td>1301</td>
</tr>
</tbody>
</table>
Table 4.21: Ag–Sr–Cu–O system; calculated four-phase equilibria in Figure 4.22.

<table>
<thead>
<tr>
<th>Equil. No.</th>
<th>Phases</th>
<th>Equil. No.</th>
<th>Phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:</td>
<td>SrO - 2 1 - L₁ - L₂</td>
<td>12:</td>
<td>(Ag) - 1 1 - 14 24 - CuO</td>
</tr>
<tr>
<td>2:</td>
<td>SrO - 2 1 - 1 2 - L₂</td>
<td>13:</td>
<td>2 1 - 1 1 - L₁ - L₂</td>
</tr>
<tr>
<td>3:</td>
<td>SrO - 1 2 - L₁ - L₂</td>
<td>14:</td>
<td>1 1 - 14 24 - L₁ - L₂</td>
</tr>
<tr>
<td>4:</td>
<td>SrO - 2 1 - 1 2 - L₁</td>
<td>15:</td>
<td>14 24 - CuO - L₁ - L₂</td>
</tr>
<tr>
<td>5:</td>
<td>1 2 - (Cu₂O) - L₁ - L₂</td>
<td>16:</td>
<td>2 1 - 1 2 - L₁ - L₂</td>
</tr>
<tr>
<td>6:</td>
<td>(Ag) - SrO - 2 1 - L₁</td>
<td>17:</td>
<td>(Ag) - 1 1 - 1 2 - L₂</td>
</tr>
<tr>
<td>7:</td>
<td>(Ag) - 2 1 - 1 2 - L₁</td>
<td>18:</td>
<td>(Ag) - 1 2 - (Cu₂O) - L₂</td>
</tr>
<tr>
<td>8:</td>
<td>(Ag) - 1 2 - (Cu₂O) - L₁</td>
<td>19:</td>
<td>(Ag) - 1 1 - (Cu₂O) - L₂</td>
</tr>
<tr>
<td>9:</td>
<td>(Ag) - 2 1 - 1 1 - 1 2</td>
<td>20:</td>
<td>(Ag) - (Cu₂O) - CuO - L₂</td>
</tr>
<tr>
<td>10:</td>
<td>(Ag) - 1 1 - 1 2 - (Cu₂O)</td>
<td>21:</td>
<td>(Ag) - 1 1 - CuO - L₂</td>
</tr>
<tr>
<td>11:</td>
<td>(Ag) - 1 1 - (Cu₂O) - CuO</td>
<td>22:</td>
<td>(Ag) - 1 1 - CuO - L₂</td>
</tr>
</tbody>
</table>

where 2 1 is the abbreviation for Sr₂CuO₃, 1 1 for SrCuO₂, 14 24 for Sr₁₄Cu₂₃O₄₁, 1 2 for SrCu₂O₂, L₁ for the metal liquid (close to the Ag corner), and L₂ for the oxide liquid.
Table 4.22: Ag–Sr–Cu–O system: calculated five-phase equilibria in Figure 4.22. Compositions are given for the liquid phases.

<table>
<thead>
<tr>
<th>Equ. Label</th>
<th>Present phases</th>
<th>T (K)</th>
<th>Log($P_{O_2}$)</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>SrO - 2 1 - 1 2 - L$_1$ - L$_2$</td>
<td>1324</td>
<td>-3.45</td>
<td>L$_1$ 0.95 10$^{-16}$ 0.05</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>L$_2$ 0.03 0.32 0.65</td>
</tr>
<tr>
<td>B</td>
<td>(Ag) - 1 2 - (Cu$_2$O) - L$_1$ - L$_2$</td>
<td>1215</td>
<td>-3.17</td>
<td>L$_1$ 0.96 10$^{-19}$ 0.04</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>L$_2$ 0.06 0.17 0.77</td>
</tr>
<tr>
<td>C</td>
<td>(Ag) - 2 1 - 1 1 - 1 2 - L$_1$</td>
<td>1225</td>
<td>-2.39</td>
<td>L$_1$ 0.98 10$^{-19}$ 0.02</td>
</tr>
<tr>
<td>D</td>
<td>(Ag) - 1 1 - 1 2 - (Cu$_2$O) - L$_2$</td>
<td>1158</td>
<td>-2.34</td>
<td>L$_2$ 0.10 0.15 0.75</td>
</tr>
<tr>
<td>E</td>
<td>2 1 - 1 1 - 1 2 - L$_1$ - L$_2$</td>
<td>1240</td>
<td>-2.23</td>
<td>L$_2$ 0.07 0.23 0.69</td>
</tr>
<tr>
<td>F</td>
<td>(Ag) - 1 1 - 1 2 - L$_1$ - L$_2$</td>
<td>1224</td>
<td>-2.23</td>
<td>L$_2$ 0.08 0.21 0.71</td>
</tr>
<tr>
<td>G</td>
<td>(Ag) - 1 1 - (Cu$_2$O) - CuO - L$_2$</td>
<td>1148</td>
<td>-2.02</td>
<td>L$_2$ 0.12 0.13 0.74</td>
</tr>
<tr>
<td>H</td>
<td>(Ag) - 1 1 - 14 24 - CuO - L$_2$</td>
<td>1165</td>
<td>-1.60</td>
<td>L$_2$ 0.14 0.13 0.73</td>
</tr>
<tr>
<td>J</td>
<td>(Ag) - 1 1 - 14 24 - L$_1$ - L$_2$</td>
<td>1220</td>
<td>-0.62</td>
<td>L$_2$ 0.19 0.14 0.67</td>
</tr>
<tr>
<td>K</td>
<td>(Ag) - 14 24 - CuO - L$_1$ - L$_2$</td>
<td>1215</td>
<td>-0.27</td>
<td>L$_2$ 0.24 0.11 0.65</td>
</tr>
</tbody>
</table>

where 2 1 is the abbreviation for Sr$_2$CuO$_3$, 1 1 for SrCuO$_2$, 14 24 for Sr$_{14}$Cu$_{24}$O$_{41}$, 1 2 for SrCu$_2$O$_2$, L$_1$ for the metal liquid (close to the Ag corner), and L$_2$ for the oxide liquid.
Table 4.23: Ag–Ca–Cu–O system; calculated four-phase equilibria in Figure 4.25.

<table>
<thead>
<tr>
<th>Equil. No.</th>
<th>Phases</th>
<th>Equil. No.</th>
<th>Phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CaO - (Cu₂O) - L₁ - L₂</td>
<td>9</td>
<td>2₁ - CuO - L₁ - L₂</td>
</tr>
<tr>
<td>2</td>
<td>(Ag) - CaO - (Cu₂O) - L₂</td>
<td>10</td>
<td>2₁ - 1₂ - CuO - L₂</td>
</tr>
<tr>
<td>3</td>
<td>(Ag) - CaO - 2₁ - (Cu₂O)</td>
<td>11</td>
<td>CaO - 2₁ - L₁ - L₂</td>
</tr>
<tr>
<td>4</td>
<td>(Ag) - 2₁ - (Cu₂O) - CuO</td>
<td>12</td>
<td>1₂ - (Cu₂O) - CuO - L₂</td>
</tr>
<tr>
<td>5</td>
<td>(Ag) - 2₁ - 1₅₁₈ - CuO</td>
<td>13</td>
<td>CaO - 2₁ - (Cu₂O) - L₂</td>
</tr>
<tr>
<td>6</td>
<td>(Ag) - 1₅₁₈ - CuO - L₁</td>
<td>14</td>
<td>2₁ - (Cu₂O) - CuO - L₂</td>
</tr>
<tr>
<td>7</td>
<td>(Ag) - CaO - 2₁ - L₁</td>
<td>15</td>
<td>(Ag) - 2₁ - (Cu₂O) - L₂</td>
</tr>
<tr>
<td>8</td>
<td>2₁ - 1₅₁₈ - CuO - L₁</td>
<td>16</td>
<td>(Ag) - 2₁ - CuO - L₂</td>
</tr>
</tbody>
</table>

where 2₁ is the abbreviation for Ca₃CuO₅, 1₂ for CaCu₂O₃, 1₅₁₈ for Ca₁₅Cu₁₈O₃₅, L₁ for the metal liquid (close to the Ag corner), and L₂ for the oxide liquid.
Table 4.24: Ag–Ca–Cu–O system; calculated five-phase equilibria in Figure 4.26. Compositions are given for the liquid phase.

<table>
<thead>
<tr>
<th>Equ. Label</th>
<th>Present phases</th>
<th>$T$ (K)</th>
<th>$\log(P_{O_2})$ (bar)</th>
<th>Composition</th>
<th>$\mu_{Ag}$</th>
<th>$\mu_{Ca}$</th>
<th>$\mu_{Cu}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>(Ag) - CaO - (Cu$_2$O) - L$_1$ - L$_2$</td>
<td>1222</td>
<td>-1.75</td>
<td>L$_1$ 0.98 $10^{-20}$ 0.02</td>
<td>L$_2$ 0.17 0.07 0.76</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>(Ag) - CaO - 21 - (Cu$_2$O) - L$_2$</td>
<td>1210</td>
<td>-1.68</td>
<td>L$_2$ 0.18 0.07 0.76</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>(Ag) - 21 - (Cu$_2$O) - CuO - L$_2$</td>
<td>1194</td>
<td>-1.55</td>
<td>L$_2$ 0.19 0.06 0.75</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>(Ag) - CaO - 21 - L$_1$ - L$_2$</td>
<td>1222</td>
<td>-1.38</td>
<td>L$_1$ 0.99 $10^{-21}$ 0.01</td>
<td>L$_2$ 0.19 0.07 0.74</td>
<td></td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>21 - 12 - (Cu$_2$O) - CuO - L$_2$</td>
<td>1255</td>
<td>-1.03</td>
<td>L$_2$ 0.05 0.12 0.83</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>(Ag) - 21 - CuO - L$_1$ - L$_2$</td>
<td>1221</td>
<td>-0.84</td>
<td>L$_1$ 0.99 $10^{-21}$ 0.01</td>
<td>L$_2$ 0.23 0.06 0.71</td>
<td></td>
<td></td>
</tr>
<tr>
<td>G</td>
<td>(Ag) - 21 - 15 18 - CuO - L$_1$</td>
<td>1188</td>
<td>+0.60</td>
<td>L$_1$ 1.00 $10^{-21}$ 2.10$^{-3}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>21 - 15 18 - CuO - L$_1$ - L$_2$</td>
<td>1248</td>
<td>+0.97</td>
<td>L$_1$ 1.00 $10^{-19}$ 4.10$^{-3}$</td>
<td>L$_2$ 0.39 0.05 0.56</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

where 21 is the abbreviation for Ca$_2$CuO$_3$, 12 for CuCu$_2$O$_2$, 15 18 for Ca$_{15}$Cu$_{18}$O$_{33}$, L$_1$ for the metal liquid (close to the Ag corner), and L$_2$ for the oxide liquid.
Figure 4.22: Calculated Ag–Sr–Cu–O oxygen potential phase diagram compared with DTA measurements. The four-phase equilibria are numbered from 1 to 22 according to Table 4.21, and the five-phase equilibria are labeled from A to K according to Table 4.22.
Figure 4.23: Calculated Ag–CaO–CuO phase diagram in $P_{O_2} = 10^5$ Pa and $T = 1253$ K where the dotted lines represent the tie-lines. EDX measurement of the composition in the oxide liquid is indicated.

Figure 4.24: Calculated Ag–(CuO)0.8(SrO)0.2 phase diagram in $P_{O_2} = 10^5$ Pa. The EDX measurement of the Ag content is indicated. Note that the experimental data is not in the calculated section (see Fig. 4.23).
Figure 4.25: Calculated Ag–Ca–Cu–O oxygen potential phase diagram compared with DTA measurements (experiments in parenthesis are uncertain). The four-phase equilibria are numbered from 1 to 16 according to Table 4.23, and the five-phase equilibria are labeled from A to H according to Table 4.24.
Figure 4.26: Calculated Ag–CaO–CuO phase diagram in \( P_{O_2} = 10^5 \) Pa and \( T = 1253 \) K where the dotted lines represent the tie-lines. EDX measurements of the composition in the oxide liquid and sample composition are indicated.

Figure 4.27: Calculated Ag–\((\text{CuO})_{0.8} \cdot (\text{CaO})_{0.2}\) phase diagram in \( P_{O_2} = 10^5 \) Pa. The EDX measurement of the Ag content is indicated.
4.6 The Ag–Bi–Sr–Ca–Cu–O System

4.6.1 Introduction

The present evaluation is the final stage in the thermodynamic optimization of the Ag–Bi–Sr–Ca–Cu–O system. The BSCCO system contains three superconducting compounds, and we will focus on one of these, the Bi$_2$Sr$_2$CaCu$_2$O$_y$ compound, and its interactions with Ag. It has been observed that silver does not form any compounds with the Bi, Sr, Ca, and Cu oxides, but that it lowers the melting point of 2212 by having a solubility in the BiSrCaCu oxide rich liquid up to 5 mol-%.

This work follows the optimization of the Bi–Sr–Ca–Cu–O system, as described comprehensively in the thesis of Risold [96Risl], and extends to the Ag–Bi–Sr–Ca–Cu–O system as mentioned in the preceding sections.

4.6.2 Experimental Data

Many studies have been reported in the literature concerning a change in the phase relations in the Bi–Sr–Ca–Cu–O system due to Ag addition, particularly around the 2212 compound. We summarize here the most important and comprehensive contributions to this subject, which focus on the eutectic between Ag and 2212 [94Mcc,96Mar, 97Lan,97Maj], on the modification of the stability of the secondary phases due to the presence of Ag in samples of 2212 [96Mar, 97Maj,98Won], and on the composition of the oxide and metal liquids at high temperatures [94Mcc]. No thermodynamic data on the liquid phase in the Ag–Bi–Sr–Ca–Cu–O system have been reported yet.

Lang et. al. [97Lan] used differential thermal analysis (DTA) and determined the melting temperature of Bi$_{2.2}$Sr$_{2.05}$Ca$_{0.95}$Cu$_2$O$_y$ mixed with Ag in the range of $w_{Ag} = 0$ to 15 wt-% at three oxygen partial pressures, $P_{O_2} = 1$ bar, 0.21 bar, and 0.001 bar. They reported a decrease of the melting temperature of 2212 with increasing Ag content to a eutectic temperature at $w_{Ag} = 5$ wt-%. In pure oxygen the decrease was from 1166 K to 1141 K, in air from 1153 K to 1133 K, and at 0.001 bar $O_2$ from 1107 K to 1098 K. The usual accuracy of DTA measurements is ±5 K but, for the measurements at low $P_{O_2}$, an error of ±10 K seemed to be more reasonable.

Majewski et. al. [97Maj] studied the melting behavior of Bi$_{2.1}$Sr$_{1.7}$CaCu$_2$O$_y$ + Ag in the range of $u_{Ag} = 0$ to 0.07 $^1$ in air. Using DTA they measured the temperature of the 2212 + Ag eutectic at $T_e = 1136$ K ±3 K as well as the limit of the miscibility gap on the oxide side for two silver contents. From these measured temperatures, they could evaluate the silver content in the oxide liquid phase to be $u_{Ag} = 5.4\%$ at the eutectic. Majewski et. al. also determined the secondary phases by X-ray diffraction (XRD) and their composition by energy dispersive spectrometry (EDS). The decomposition pathway of 2212 was not modified by silver addition but the temperatures were decreased. For silver contents be-

\[ u_{Ag} = \frac{n_{Ag}}{n_{Ag} + n_{Bi} + n_{Sr} + n_{Ca} + n_{Cu}} \]

1. where $u_{Ag}$ is the silver fraction.
low the eutectic composition, they described the decomposition pathway of 2212 as:

$$
\begin{align*}
2212 + Ag & \rightarrow \\
2212 + 2O_2 + 0O_1 + L & \rightarrow \\
23x0 + 0O_1 + L & \rightarrow \\
23x0 + 2O_2 + 0O_1 + L & \rightarrow \\
\end{align*}
$$

The effects of the silver content and of the oxygen partial pressure on the decomposition pathway of the Bi$_2$O$_{1.1}$Sr$_{2.04}$Ca$_{0.98}$Cu$_2$O$_y$ compound were investigated very carefully by Margulies et al. [96Mar]. They used EDS coupled to scanning electron microscopy (SEM) and microprobe analysis on quenched samples of 2212 with 0, 2 and 10 wt-% Ag, at $P_{O_2} = 1$, 0.21, and 0.01 bar. The secondary phases that first appeared in pure oxygen above the eutectic were 014$_{24}$ and 91150. In air these were 91150 and 01x1, and at 0.01 bar $O_2$ 23x0, 01x1 and 02x1. Using DTA, they determined the temperatures of the 2212 + Ag eutectic and found $T_e = 1145$ K at $P_{O_2} = 1$ bar (to be compared with the melting temperature of 2212 without Ag, $T_m = 1172$ K), $T_e = 1140$ K (1160 K) in air, and $T_e = 1107$ K (1118 K) at 0.01 bar $O_2$. The accuracy on these temperatures can be estimated to be ±5 K and the agreement with the measurements by Lang et al. [97Lan] and by Majewski et al. [97Maj] is good.

Wong-Ng and Cook [98Won] comprehensively studied the initial melting of four-phase fields containing the 2212 compound (and three secondary phases) in air, with and without silver. They used DTA to measure the thermal events, XRD, SEM and X-ray mapping on quenched samples to characterize the phases, as well as SEM coupled to quantitative EDS to determine the composition of the oxide liquid. The initial melting temperatures of the four-phase fields were generally decreased by about 4 K to 22 K with silver addition of $\omega_{Ag} = 30$ wt-%, where the correspondent oxide liquid showed a silver content, $\omega_{Ag}$, between 0.031 and 0.078, depending on the initial equilibria. The lowest melting point was found for the 2212–119x5–2110–CuO equilibrium at $T = 1098$ K without Ag and at $T = 1088$ K with 30 wt-% Ag, where the liquid composition is $\omega_{Ag} = 0.078$, $\omega_{Bi} = 0.385$, $\omega_{Sr} = 0.131$, $\omega_{Ca} = 0.204$, and $\omega_{Cu} = 0.202$.

McCallum et al. [94Mcc] studied by DTA the melting properties of Bi$_{1.88}$Sr$_2$CaCu$_2$O$_y$ in air with a silver content of 20 wt-%. They measured the eutectic temperature at 1128 K ±10 K and the melting point of silver at 1206 K ±5 K. Using inductively coupled plasma and atomic emission spectrometry (ICP-AES) they investigated the composition of the oxide liquid as well as the metal liquid on quenched samples held at temperatures between 1173 K and 1473 K. At 1473 K for example, the miscibility gap extended from $\omega_{Ag} = 0.10$ to $\omega_{Ag} = 0.97$.

4.6.3 Thermodynamic Models

The Gibbs energies for pure solid, liquid and gaseous elements are taken from Dinsdale [91Din]. The descriptions of the oxide compounds and of the fcc structure (Ag) come
from previous assessments [93Sel,94Hal,95Ris1,95Ris2,96Hal,96Ris1,96Ris2,97Ass1, 97Ass2,97Hal1,97Hal2,97Ris1,97Ris2,98Ass1,98Ass2].

The liquid phase is described by the two-sublattice model for ionic liquids [85Hil,91Sun] that allows a continuous description from the metal liquid to the oxide liquid, as well as the miscibility gap between them. The cationic sublattice contains all metallic species present with their usual valencies and the anionic sublattice contains the oxygen anions, as well as negatively charged vacancies that allows the description to the metallic side also. The model is then \((\text{Ag}^{1+},\text{Bi}^{3+},\text{Sr}^{2+},\text{Ca}^{2+},\text{Cu}^{1+},\text{Cu}^{2+})_p (\text{O}^{2-},\text{Va}^{q-})_q\) with \(p\) and \(q\) which vary in order to maintain electroneutrality. The molar Gibbs energy of the liquid phase is given by:

\[
G_{m}^{liq} = q \cdot \sum_{i = \text{cations}} y_i \cdot y_{Va} \cdot G_{i;Va}^{liq} + \sum_{i = \text{cations}} y_i \cdot y_{O^{2-}} \cdot G_{i;O^{2-}}^{liq} + R \cdot T \cdot \left( p \cdot \sum_{i = \text{cations}} y_i \cdot \ln y_i + q \cdot \sum_{j = \text{anions}} y_j \cdot \ln y_j \right) + E_{G_{m}}^{liq}
\]

where \(y_s\) are the site fractions. The molar Gibbs energies of the pure liquid \(i\) elements, \(G_{i;Va}^{liq}\), are given by Dinsdale [91Din], and the Gibbs energies of the pure liquid \(i\) oxides, \(G_{i;O^{2-}}^{liq}\), have been previously assessed [93Sel,94Hal,95Ris2,96Ris2,97Ass2]. The molar excess Gibbs energy of the liquid, \(E_{G_{m}}^{liq}\), is given by:

\[
E_{G_{m}}^{liq} = \sum E_{G_{m}}^{liq, \text{binaries}} + \sum E_{G_{m}}^{liq, \text{ternaries}} + \sum E_{G_{m}}^{liq, \text{quaternaries}}
\]

where \(E_{G_{m}}^{liq, \text{binaries}}\), \(E_{G_{m}}^{liq, \text{ternaries}}\), \(E_{G_{m}}^{liq, \text{quaternaries}}\) and \(E_{G_{m}}^{liq, \text{quinary}}\) represent the excess terms in the binary, ternary, quaternary and in the quinary subsystems, respectively. \(E_{G_{m}}^{ABSCCO}\) is the molar excess Gibbs energy due to interactions in the Ag–Bi–Sr–Ca–Cu–O system and can be written as the sum of an oxide contribution (first term), and an oxide and metal contribution (second term):

\[
E_{G_{m}}^{liq, \text{ABSCCO}} = y_{\text{Ag}}y_{\text{Bi}}y_{\text{Sr}}y_{\text{Ca}}y_{\text{Cu}}y_{\text{O}}L_{\text{Ag,Bi,Sr,Ca,Cu,O}}^{liq} + y_{\text{Ag}}y_{\text{Bi}}y_{\text{Sr}}y_{\text{Ca}}y_{\text{Cu}}y_{\text{O}}y_{\text{Va}}L_{\text{Ag,Bi,Sr,Ca,Cu,O, Va}}^{liq}
\]

with \(y_{\text{Cu}^{1+}} = y_{\text{Cu}^{2+}}\) and \(L_{\text{Cu}^{1+}}^{liq} = L_{\text{Cu}^{2+}}^{liq}\). The interaction parameters, \(L\), can be written with a linear temperature dependence but not as a Redlich−Kister polynomials as for low-
er-order system, though, since the second and higher-order parts of such parameters with so many species have no physical meaning.

4.6.4 Optimization

If we consider the above Equation 4.28, there is a maximum of four parameters to optimize (pure oxide and oxide-metal interactions, each of them can be written as an "A + BT" expression). In this case, however, the L parameter taking into account the interactions between oxide and metallic species could not be optimized since the solubilities of some species, i.e. Bi, Sr, and Ca, are too small in the metal liquid. Furthermore, the temperature dependence of the pure oxide interaction parameter could not be calculated since there are few experimental data available. There is finally only one parameter to optimize, $L_{Ag,Bi,Sr,Ca,Cu}^{\text{liq}}$.

The optimization of the parameter was carried out using the PARROT program included in the Thermo-Calc package [85Sun]. In this program the parameters are fitted to the experiments by minimizing the squared error.

The experiments which were used for the optimization have been described previously and concern phase equilibria around 2212 with silver only, i.e. the eutectic temperatures of 2212 + Ag in pure oxygen [96Mar,97Lan], in air [94Mcc,96Mar,97Lan,97Maj], at 0.01 bar O$_2$ [96Mar], and at 0.001 bar O$_2$ [97Lan]. Composition of the eutectic liquid by Majewski et al. [97Maj] and of the oxide liquid in the miscibility gap by McCallum et al. [94Mcc] were compared later. The secondary phases that appear at higher temperatures during 2212 decomposition described by Margulies et al. [96Mar] were compared after the optimization. The melting temperatures determined by Wong-Ng and Cook [98Won] in four-phase fields containing 2212 were not taken into account at all in the optimization.

4.6.5 Results and Discussion

During the optimization the parameter $L_{Ag,Bi,Sr,Ca,Cu}^{\text{liq}}$ converged to a value close to $-10^7$ J·mol$^{-1}$. By changing the weight on the experiments, the parameter varied slightly. As these variations did not modify the calculated temperatures of equilibria much, we chose the value $L_{Ag,Bi,Sr,Ca,Cu}^{\text{liq}} = -10^7$ J·mol$^{-1}$.

The 2212–Ag phase diagram in air is presented in Figure 4.28 with the eutectic transformation at $T_e = 1145$ K and $u_{Ag} = 0.038$. This silver ratio is not the effective silver content in the liquid phase but is a projection on the 2212–Ag line. The calculated silver ratio for the eutectic is $u_{Ag} = 0.064$ and is rather close to the experimental value. Furthermore, the secondary phases are mentioned in the calculated phase diagram and one may be surprised to find O14xCu stable in air, in disagreement with experimental investigations [96Mar,97Maj]. It can be seen, though, that O14xCu is stable in a very narrow range of temperatures and, furthermore, calculations show that it appears in a very low proportion (phase fraction < 5%). Previous calculations showed that O14xCu was not stable in air without Ag.
A comparison between calculated and measured eutectic transformations at different oxygen partial pressures is given in Table 4.25. Compared with experimental data, the calculated values seem to be too high in air, but the agreement can still be considered as generally good since errors are in the range of 10 K.

Figure 4.29 shows the 2212 phase stability in an oxygen potential diagram, without silver addition and with 10 wt-% Ag. Here again, calculation and experimental data show a rather good agreement. The limit of stability of 2212 in regard to the liquid phase (melting of 2212) is a curve whose maximum corresponds to $\log(P_{O_2} \text{ bar}) = -0.62$, which is very close to $\log(P_{O_2 = \text{ air bar}}) = -0.67$. Moving the curve to the right (to higher oxygen partial pressures) would lead to a better agreement with experimental data. This shifting may only be obtained by modifying the thermodynamic description of the liquid phase in the subsystems of Bi–Sr–Ca–Cu–O. Experimental data at higher oxygen partial pressures would also increase the reliability of the optimization.
Table 4.25: Eutectic transformations between 2212 and Ag for different $P_{O_2}$, comparison between experimental data and calculation.

<table>
<thead>
<tr>
<th>$P_{O_2}$, bar</th>
<th>$T$, K</th>
<th>$u_{Ag}$ in L$_2$ a</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1145</td>
<td>—</td>
<td>[96Mar]</td>
</tr>
<tr>
<td>1</td>
<td>1141</td>
<td>—</td>
<td>[97Lan]</td>
</tr>
<tr>
<td>1</td>
<td>1140</td>
<td>0.077</td>
<td>This work</td>
</tr>
<tr>
<td>0.21</td>
<td>1128</td>
<td>—</td>
<td>[94Mcc]</td>
</tr>
<tr>
<td>0.21</td>
<td>1140</td>
<td>—</td>
<td>[96Mar]</td>
</tr>
<tr>
<td>0.21</td>
<td>1133</td>
<td>—</td>
<td>[97Lan]</td>
</tr>
<tr>
<td>0.21</td>
<td>1136</td>
<td>0.054</td>
<td>[97Maj]</td>
</tr>
<tr>
<td>0.21</td>
<td>1145</td>
<td>0.038</td>
<td>This work</td>
</tr>
<tr>
<td>0.01</td>
<td>1107</td>
<td>—</td>
<td>[96Mar]</td>
</tr>
<tr>
<td>0.01</td>
<td>1122</td>
<td>0.039</td>
<td>This work</td>
</tr>
<tr>
<td>0.001</td>
<td>1098</td>
<td>—</td>
<td>[97Lan]</td>
</tr>
<tr>
<td>0.001</td>
<td>1099</td>
<td>0.028</td>
<td>This work</td>
</tr>
</tbody>
</table>

a. along the 2212–Ag line.

Figure 4.29: Calculated 2212 phase stability with 10 wt-% Ag and without Ag compared with experimental data [96Mar, 97Lan, 97Maj].
Figure 4.30: Calculated molar phase fraction of the decomposition pathway of 2212 with 10 wt-% Ag, at $P_{O_2} = 1$ bar.

Figure 4.30 shows the decomposition pathway of 2212 with 10 wt-% Ag in pure oxygen. The melt appears at $T_e = 1136$ K as well as two secondary phases, $014x24$ and $91150$, that make up close to 50% of the mixture. The fraction of the secondary phases decreases with increasing the temperature. At the eutectic temperature, the fraction of solid silver is reduced since Ag dissolves in the liquid. At $T_{m,Ag} = 1213$ K, the silver solid solution melts. At higher temperatures, $02x1$ appears and $014x24$ and $91150$ vanish, and, just below 1300 K, $02x1$ is replaced by $01x0$. Margulies et. al. [96Mar] investigated experimentally the decomposition of 2212 which is relatively well confirmed by the calculation, see Table 4.26.

Comparison of the initial melting temperature in the four-phase fields (containing 2212) based on experiments of Wong-Ng and Cook [98Won] and the calculation is rather difficult. This is due to the relative stability of the secondary phases with respect to the liquid which is critical. For the equilibrium $2212-x19x5-x2110-CuO-Ag$ ($w_{Ag} = 30$ wt-%), the initial melting is calculated in air at $T_m = 1035$ K, i.e. 53 K lower than the measured temperature by Wong-Ng and Cook. At this temperature, the liquid has the calculated composition $u_{Ag} = 0.032$, $u_{Bi} = 0.527$, $u_{Sr} = 0.045$, $u_{Ca} = 0.228$, and $u_{Cu} = 0.169$, where the measurement indicated $u_{Ag} = 0.078$, $u_{Bi} = 0.385$, $u_{Sr} = 0.131$, $u_{Ca} = 0.204$, and $u_{Cu} = 0.202$. In this case the agreement is not very satisfactory. This is probably due to mismatch in the stability of the secondary phases in the calculation.
**Table 4.26: Calculated decomposition pathway of 2212 with 10 wt-% Ag in pure oxygen compared with results of Margulies et. al. [96Mar].**

<table>
<thead>
<tr>
<th>Margulies et. al. [96Mar]a</th>
<th>This work</th>
<th>T, K</th>
</tr>
</thead>
<tbody>
<tr>
<td>2212 →</td>
<td>2212 + Ag →</td>
<td>1145±5</td>
</tr>
<tr>
<td>014x24 + 91150 + L2 →</td>
<td>014x24 + 91150 + Ag + L2 →</td>
<td>1182±9</td>
</tr>
<tr>
<td>014x24 + 91150 + 02x1 + L2 →</td>
<td>014x24 + 91150 + 02x1 + Ag + L2 →</td>
<td>1199±4</td>
</tr>
<tr>
<td>91150 + 02x1 + 01x1 + L2 →</td>
<td>91150 + 02x1 + Ag + L2 →</td>
<td>1207±5</td>
</tr>
<tr>
<td>91150 + 02x1 + 01x1 + 01x0 + L2 →</td>
<td>02x1 + Ag + L2 →</td>
<td>1213±1</td>
</tr>
<tr>
<td>91150 + 02x1 + 01x0 + L2 →</td>
<td>02x1 + L1 + L2 →</td>
<td>1220±3</td>
</tr>
<tr>
<td>91150 + 01x0 + L2 →</td>
<td>02x1 + 01x0 + L1 + L2 →</td>
<td>1226±3</td>
</tr>
</tbody>
</table>
| 01x0 + L2                | 01x0 + L1 + L2 → | 1390  
|                           | L1 + L2     |

a. Margulies did not mention the presence of silver (solid and liquid, L1).  

### 4.6.6 Conclusion

A consistent description of the liquid phase in the Ag–Bi–Sr–Ca–Cu–O system has been given with the two-sublattice model for ionic liquids. By optimizing one parameter of interaction between all the species present in the oxide liquid, the calculation shows good agreement with the experimental data. The eutectic between 2212 and Ag is well reproduced for different oxygen partial pressures and the secondary phases appearing agree rather well with experimental investigations. Thermodynamic data, as well as phase diagram experiments at higher oxygen partial pressure, would improve the quality of this optimization and are therefore much needed.

### 4.6.7 References


D. Risold, B. Hallstedt, and L. J. Gauckler, “Thermodynamic Assessment of


Chapter 5

Application of the CALPHAD Method
to the Processing of 2212 with Silver
5.1. Overview

In this Chapter, we summarize the experimental results of Lang et. al. [97Lan1,97Lan2] and those of Heeb et. al. [92Hee] relevant for the partial melt-processing of 2212 with silver and without silver. These studies were performed at the Chair of Nonmetallic Materials between 1992 and 1998. Using the thermodynamic optimizations of the Ag–Bi–Sr–Ca–Cu–O system (see previous Chapter), we compare the calculations with the experimental investigations.

Heeb et. al. [92Hee] investigated the partial melt-processing of 2212 bulk material without silver in air. They showed the influence of the maximum temperature and cooling rate on the formation of 2212 and secondary phases after cooling. When $T_{\text{max}}$ exceeded 1223 K, 2212 was not formed.

Lang and coauthors published two comprehensive papers on the partial melt-processing of Bi-2212 with silver. They first showed that Ag lowered the melting point of 2212 of about 25 K in pure oxygen, reaching a eutectic temperature at $T_e = 1141$ K for 4 wt-% Ag [97Lan1]. In the same publication, they reported that Ag addition decreased the weight loss during heating, i.e. that the presence of Ag limited the oxygen loss in the liquid phase. In their second paper, Lang et. al. [97Lan2] investigated the phase relations and microstructure during partial melting of 2212 on Ag. Using X-ray diffraction they showed that two classes of secondary phases appeared during partial melting of 2212 in pure oxygen, the Bi-free phases (mainly $\text{O}_{14x24}$) and the Cu-free phase ($\text{Cu}_{1150}$). The composition of the Bi-free phases was determined using energy dispersive spectrometry coupled to a scanning electron microscope (EDS/SEM). They also reported that some amount of the liquid phase and the secondary compounds remained at low temperatures after slow cooling. In a complementary paper, Lang et. al. [98Lan] reported the influence of the processing temperature on the microstructure of 2212 thick films and on the critical current density $j_c$ at 77 K.

5.2 The Calculation Applied to Partial Melt-Processing of 2212 with Silver

We reported in Chapter IV the measured eutectic of 2212 and Ag at $T_e = 1141$ K, 1133 K, and 1098 K at $P_{\text{O}_2} = 1$ bar, 0.21 bar, and 0.001 bar, respectively, by Lang et. al. [97Lan1]. Furthermore, they investigated the influence of silver on the oxygen content in the liquid using thermogravimetry (TG). The use of a low heating rate (1 K/min) allowed the powder samples to reach (or come close to) thermodynamic equilibrium. They compared the TG curves obtained for pure 2212 and for 2212 + 5 wt-% Ag in the three mentioned oxygen atmospheres and found that Ag limited the oxygen loss in the liquid phase. The effect of Ag is larger in high oxygen partial pressure. In pure oxygen, 2212 + 5 wt-% Ag lost 0.7 wt-%, and pure 2212 1.1 wt-%, where the weights are compared between $T_e$ and $T_e + 100$ K. Finally they observed a slight gain in weight in 2212 + Ag just when the sample started to melt (see Figure 5.1).

The calculated "TG curves" are shown in Figure 5.2. In these plots, the calculated phases
are in equilibrium at each temperature. The first plot (A) presents the equilibrium state, where $0_{14}x_{24}$ is present. Using the same definition as Lang et al., we calculated that pure 2212 without Ag loses 1.0 wt-% between $T_e = 1166$ K and $T_e + 100$ K = 1266 K (1.1 wt-% according to experiments), and 0.6 wt-% between $T_e = 1140$ K and 1240 K (0.7 wt-% according to experiments) in presence of Ag. The agreement is excellent. At the melting point, the two curves show an increase in weight which is accentuated by silver addition. It was first thought that this increase was only due to Ag solubility which increased the oxygen content in the liquid. If we consider the plot (B), where the $0_{14}x_{24}$ compound is not present, the weight gain at the melting is annihilated. At higher temperatures, the curves from (B) are identical to the curves from (A). From these curves, we can conclude that Ag retains oxygen in the 2212 liquid phase in excellent agreement with the experiments. Furthermore, the weight gain at the melting of 2212 is mostly due to the presence of the $0_{14}x_{24}$ secondary phase whose oxygen content is high (41 oxygen instead of 38 for 100% Cu$^{2+}$). This effect is accentuated by Ag since the phase fraction of $0_{14}x_{24}$ is increased by the presence of silver.

Figure 5.1: Experimental TG curves of 2212 and 2212 + 5 wt-% Ag in pure oxygen (heating rate is 1 K/min). The short curve is a three times enlarged (in y-direction) section of a slow TG scan with a three times the usual amount of powder, from Lang et al. [97Lan1].
Figure 5.2: Calculated TG curves of 2212 and 2212 + 5 wt-% Ag in pure oxygen, (A) 014x24 is present in the calculation, and (B) 014x24 is not present.

(A)

(B)

In their second paper, Lang et. al. [97Lan2] investigated the phase relations and microstructure during partial melt of 2212 on Ag in pure oxygen. They heated thick films of Bi$_{2.2}$Sr$_{2.05}$Ca$_{0.95}$Cu$_2$O$_y$ on silver substrates at a rate of 1 K/min up to 1203 K, and quenched the samples in oil at a rate of −100 K/min, as shown in Figure 5.3 (A).

Figure 5.3: Schematic heat treatment schedules used by Lang et. al. [97Lan2]. The atmosphere is pure oxygen.
Figure 5.4: Volume fractions of the phases of 2212 thick film heated on a silver substrate in pure oxygen as a function of temperature (from Lang et al. [97Lan2]). Bi-free phases changed from 014x24 to 01x1, 02x1 and 01x0 at $T = 1184$ K.

The experimental phase fraction (in volume) as function of temperature is shown in Figure 5.4. During the experimental processing, silver diffused from the substrate into the liquid and the silver content increased. The plot shows that 2212 started to melt at 1159 K and disappeared at 1163 K. At this temperature, two secondary phases appeared, 91150 and 014x24, whose amount decreased with the heating temperature. At 1184 K 014x24 transformed into 01x1, 02x1 and 01x0.

The calculated phase fractions (in mole) of 2212 + Ag with $x_{Ag} = 0, 0.02, 0.06$ are shown in Figure 5.5 (A), (B) and (C), respectively. If we consider the beginning of the experimental processing, see Figure 5.4, 2212 starts to melt at 1159 K which is higher than the eutectic temperature of 1141 K. In the sample the eutectic composition is reached at the 2212/Ag interface only and the measured temperature (1159 K) is between the eutectic temperature (1141 K) and the melting temperature of pure 2212 (1166 K). The experiment showed that 2212 disappeared at 1163 K, in good agreement with the 2212 liquidus at $T = 1160$ K calculated for $x_{Ag} = 0.01$ (see plot (B) of Figure 5.5). This calculated plot shows the two secondary phases 91150 and 014x24 in smaller amounts than in plot (A). Further heating led to an increase of the silver content of the liquid phase, and to a decrease of the secondary phase presence. Figure 5.5 (C) shows the calculated phase fractions for $x_{Ag} = 0.06$ (close to the eutectic composition). At 1200 K, 91150 is still present, as well as 02x1, in rather good agreement with the experimental results.
Figure 5.5: Molar fractions of the phases of 2212 melting calculated in pure oxygen with \( x_{Ag} = 0 \) (A), \( x_{Ag} = 0.01 \) (B), and \( x_{Ag} = 0.06 \) (C).
Lang et al. [97Lan2] also determined the composition of the Bi-free secondary phases by EDS/SEM. Table 5.1 contains these data compared with the calculations in the ABSCCO system with $x_{Ag} = 0.06$. In the calculated system, $01x1$ does not appear as the experimental results showed. It can be seen that the agreement in the composition is rather good, particularly at low temperatures for the $014x24$ compound.

**Table 5.1: Measured and calculated stoichiometries of the Bi-free phases. The calculations were achieved with $x_{Ag} = 0.06$.**

<table>
<thead>
<tr>
<th>Phase</th>
<th>$T$ K</th>
<th>Phase fractions</th>
<th>Composition $u_{Sr}$</th>
<th>$u_{Ca}$</th>
<th>$u_{Ca}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>014x24</td>
<td>1159-1184</td>
<td>0.17</td>
<td>0.22</td>
<td>0.15</td>
<td>0.63</td>
<td>[97Lan2]</td>
</tr>
<tr>
<td>014x24</td>
<td>1153</td>
<td>0.26</td>
<td>0.26</td>
<td>0.11</td>
<td>0.63</td>
<td>This work</td>
</tr>
<tr>
<td>02x1</td>
<td>1195-1203</td>
<td></td>
<td>0.15</td>
<td>0.52</td>
<td>0.33</td>
<td>[97Lan2]</td>
</tr>
<tr>
<td>01x1</td>
<td>1195-1203</td>
<td>$\Sigma = 0.03$</td>
<td>0.26</td>
<td>0.21</td>
<td>0.52</td>
<td>[97Lan2]</td>
</tr>
<tr>
<td>01x0</td>
<td>1195-1203</td>
<td></td>
<td>0.02</td>
<td>0.98</td>
<td>0</td>
<td>[97Lan2]</td>
</tr>
<tr>
<td>02x1</td>
<td>1188</td>
<td>0.11</td>
<td>0.32</td>
<td>0.35</td>
<td>0.33</td>
<td>This work</td>
</tr>
<tr>
<td>01x0</td>
<td>1323</td>
<td>0.02</td>
<td>0.07</td>
<td>0.93</td>
<td>0</td>
<td>This work</td>
</tr>
</tbody>
</table>

a. The phase fractions indicated by Lang et al. were measured according to the volume fractions, and those calculated in this work are calculated according to the mole fractions.

Lang et al. [97Lan2] studied the phase assemblage during cooling and annealing after partial melting of 2212 on silver substrate in pure oxygen. The heat treatment is shown in Figure 5.3 (B). The fractions of the phases (in volume) as a function of the temperature are shown in Figure 5.6. It can be seen that even at low temperatures and for long annealing time, a small amount of liquid and secondary phases was still present. As the experiments were done on a film of about 60 $\mu$m, two limiting factors have to be considered. First, the slow oxygen diffusion from the atmosphere into the samples can limit the formation of 2212. Second, the slow cationic diffusion from the secondary phases into 2212 can also explain the partial recovery of 2212, especially at low temperatures.

Figure 5.7 shows the calculation where there is no cation diffusion from the secondary phases. In this calculation, we used the composition of the liquid phase at 1193 K as the overall composition. It can be seen that the liquid phase remains at rather low temperatures also, as well as the usual secondary phases. The one-layer compound (11905) is present in a large proportion also since the composition of the liquid is between those of 11905 and of 2212. The one-layer compound was not observed by Lang and coauthors. In agreement with the experiments, however, the calculation shows that 2212 does not recover totally. This calculation is an extreme case where no diffusion from the secondary...
phases can happen.

Figure 5.6: Volume fractions of the phases in a 2212 film on Ag substrate in pure oxygen. Measurements were made during cooling at a rate of 5 K/min from 1166 K to 1123 K and annealing at 1123 K for 48 h, from Lang et al. [97Lan2].

Figure 5.7: Molar fractions of the phases calculated for a composition fixed at the cationic ratio of the liquid phase, i.e. Ag:Bi:Sr:Ca:Cu is 0.62:2.76:1.73:1.07:2 at 1193 K in pure oxygen. The starting composition is 2212 with $x_{Ag} = 0.06$. 
Figure 5.8 shows the case where the oxygen diffusion is hindered. In this figure, the phase fractions are modeled for a fixed oxygen content that is calculated at 1193 K in $P_{O_2} = 1$ bar. As the oxygen content is smaller at 1193 K than at lower temperatures, the effective oxygen partial pressure in the sample decreases with decreasing the temperature. This extreme case where the diffusion of oxygen from the atmosphere into the sample is not allowed, models the very slow oxygen diffusion in thick films and in bulk materials.

**Figure 5.8: Molar fractions of the phases calculated for a oxygen content fixed at 1193 K in pure oxygen. The starting composition is 2212 with $x_{Ag} = 0.06$.**

Figure 5.9 shows the volume fractions during cooling of 2212 bulk material after partial melting without Ag from Heeb et al. [92Hee]. The cooling rate of $-7$ K/min is rather high and equilibrium is not reached, neither with respect to oxygen nor with respect to cations. The very slow cooling used for the processing of thick films combined with the relatively short diffusion distances mean that the material is basically in equilibrium with the surrounding atmosphere. In the early stages of 2212 formation cations can redistribute by diffusion in the liquid phase, which is quite fast. Only at later stages, when cations must diffuse through already formed 2212, larger deviations from equilibrium are expected. For bulk material the situation is quite different. A relatively high cooling rate combined with large diffusion distances mean that the material can be expected to be deficient in oxygen. Also there will not be enough time for cation redistribution. The calculation (Figure 5.7) shows that the composition of the liquid is somewhere between 11905 and 2212. When the cation redistribution is insufficient, formation of 11905 is expected as in Figure 5.9. This is further accentuated by the oxygen deficiency since 11905 is stable at
lower \( P_{O_2} \) than 2212. The oxygen deficiency also stabilizes the liquid phase towards low temperature (Figure 5.8).

**Figure 5.9: Volume fractions of the phases measured in a bulk sample of 2212, from Heeb et. al. [92Hee].**

5.3 Conclusion

We have shown that thermodynamic modeling of a complex system like Ag–Bi–Sr–Ca–Cu–O can be compared with experimental results of partial melting of 2212 in presence of silver with a high degree of satisfaction. During the slow heating of 2212 on a silver substrate, partial melting occurs and secondary phases are formed. Our calculation fits these results very well, as well as the amount of lost oxygen in the melt during further heating. Experimental results during cooling are more difficult to interpret since the equilibrium state is not reached. The causes are multiple but two of them have been presented. First the slow cation rearrangement between the liquid and the secondary phases into the 2212 compound plays an important role during 2212 formation from the melt and secondary phases in thick films and in bulk materials. Second the slow diffusion of oxygen from the atmosphere into the 2212 compound is probably important during the 2212 formation in bulk materials.

5.4. Outlook

The modeling and optimization of such a complex system like the Ag–Bi–Sr–Ca–Cu–O system can be considered for several reasons as a neverending story. The first reason is
that some phases or some parts of the system are not well defined and new experimental
data may become available in the future. These existing deficits in consistent data (lack
of data or non-satisfying data) can be in the future replaced by new data that will allow a
new and better optimization. The second reason is oriented towards the processing of ma¬
terials. Processing of such complex compounds are continuously the subject of new re¬
searches and new substrates or doping elements can become interesting. In the case of
processing of the three-layer compound (2223) it is known that addition of Pb increases
the stability of this phase. Extension of the modeling and optimizations must then be di¬
rected to additional elements. The thermodynamic modeling of Pb–Bi–Sr–Ca–Cu–O sys¬
tem has been started by the Pb–O system [98Ris].

Figure 5.10: Microstructure of 2212 + 2.7 wt-% Ag thick film (melted
on Ag substrate at 1166 K in 1 bar O2, cooled at a rate of 5 K/h to
1143 K, and then quenched at RT, from Lang et. al. [97Lan2].

Concerning the system presented in this work, Ag–Bi–Sr–Ca–Cu–O, one experimental
observation has not been explained yet. During partial melt-processing of 2212 with silver
2212 first transforms into an oxide liquid and two major remaining solid phases, 91150
and 014x24. Silver can dissolve into the liquid phase as well. During cooling, the cations
from the liquid and from the secondary phases rearrange and lead to the formation of the
2212 compound, with the help of oxygen from the atmosphere. During this process, silver
is expelled from the liquid and precipitates. It has been observed that silver particles grow
not at the 2212/liquid interface but between two oxide liquids. When considering
Figure 5.10 by Lang et al. [97Lan2], one observes the dark grey platelets of 2212, the white small spheres of silver, and two liquids that are the white long area along the 2212 grains (or "bright cloud"), and the light grey large area, which can be clearly seen at the bottom of the SEM picture.

Transmission electron microscopy (TEM) showed that these two phases are amorphous, i.e. that they are two liquid phases. Chemical analyses of these two liquids using EDS/SEM showed:

\[
\begin{array}{cccccc}
\text{Phase} & \text{Composition} \\
& u_{\text{Ag}} & u_{\text{Bi}} & u_{\text{Sr}} & u_{\text{Ca}} & u_{\text{Cu}} \\
\text{liquid} & 0.03 & 0.38 & 0.27 & 0.05 & 0.26 \\
\text{"bright cloud"} & 0.02 & 0.42 & 0.30 & 0.05 & 0.21 \\
\end{array}
\]

The difference in the compositions between the liquid and the "bright cloud" is rather small but is significant. Further experimental investigations are needed to confirm the existence of this second oxide liquid as a stable phase, or as a transient liquid that appears in metastable equilibrium. From a modeling point of view, further work will be necessary in order to confirm a miscibility gap in the oxide liquid.

5.5 References


List of Publications

Papers


Proceedings


Abstracts


Curriculum Vitae

Personal data

Date and place of birth: April 4, 1970, Lausanne, Switzerland
Citizenship: Switzerland

Education


Professional experience

7/1994 to 12/1994 Practical at the Laboratory for High-Temperature Materials and Process Technology, Prof. J. Rösler, ABB Corporate Research Center, Dättwil, Switzerland.