Comparative pressure-dependent structural studies of titanite (CaTiOSiO$_4$) and malayaite (CaSnOSiO$_4$)

Author(s):
Rath, Stephanie

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Comparative Pressure-Dependent Structural Studies of Titanite (CaTiOSiO$_4$) and Malayaite (CaSnOSiO$_4$)

Dissertation

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Presented by

Stephanie Rath
Dipl. Mineralogin (University of Hannover)
born 2 September 1973 in Germany

Accepted on the recommendation of

Prof. Dr. Walter Steurer
Laboratorium für Kristallographie, ETH Zürich
examiner

PD Dr. Martin Kunz
Universität Basel und Naturhistorisches Museum, Basel
co-examiner

Prof. Dr. Ulrich Bismayer
Mineralogisch-Petrographisches Institut, Universität Hamburg
co-examiner

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Meiner Familie..... und John

Aus meiner tiefsten Seele zieht
Mit Nasenflügelbeben
Ein ungeheurer Appetit
Nach Frühstück und nach Leben.

aus "Morgenwonne" von J. Ringelnatz
Summary

The aim of this thesis was to improve our knowledge of the influence of electronically driven structural distortions on stability and phase transitions of crystal structures. Structural distortions induced by electronic distortions observed around octahedrally coordinated $d^0$ transition metals influence the behavior in inorganic materials and can modulate physical properties, e.g. non-linear optical properties. The effect of electronically driven distortions on physical properties depends on the mutual orientation of these distortions, which can also affect the crystal structure and vice versa. Comparing isostructural compounds with and without $d^0$ transition metals can elucidate the specific influence of such distortions on the crystal structure. A most useful model material for this is the mineral titanite, $\text{CaTiOSiO}_4$, as it shows a rich phase diagram in the P - T space. When the $d^0$ transition metal atom Ti in titanite is replaced by the main group element Sn, the isostructural mineral malayaite, $\text{CaSnOSiO}_4$, is obtained.

Isothermal high-pressure experiments of monoclinic $A2/a$ single-crystal malayaite $\text{CaSnOSiO}_4$ and monoclinic $P2_1/a$ titanite $\text{CaTiOSiO}_4$ are analyzed in this thesis and provide information about compressibility and structural changes in titanite-type crystals. As samples natural single-crystals of malayaite were used, whereas for titanite a synthetic sample ensured chemical purity. The synthesis of single-crystals was optimized by nucleated melt crystallization. The modular ETH diamond-anvil high-pressure cell was used to collect isothermal compressibility data as well as intensity data sets of the samples from room-pressure to 7.3 GPa for malayaite and room-pressure to 10.5 GPa for titanite.

The single-crystal high-pressure diffraction study on malayaite ($\text{CaSnOSiO}_4$) showed a transformation of monoclinic malayaite into a triclinic high-pressure polymorph at a pressure $P_c = 4.87(8)$ GPa. No discontinuity was seen, neither for the individual crystallographic axes nor the volume. Instead, the $A2/a$ - $A\bar{1}$ phase transition was observed through significant deviations of the $\alpha$ and $\gamma$ angles from 90°. Calculations of the 3rd order Birch-Murnaghan Equation of State resulted in a bulk modulus for malayaite with $V_0 = 389.68(3)$ Å$^3$, $K_0 = 121(1)$ GPa and $K' = 4.2(5)$ for data with $P < P_c$. Structure refinements at 4 different pressures revealed the structural details of the monoclinic $A2/a$ and triclinic $A\bar{1}$ phase. Below the transition pressure the $\text{SiO}_4$ polyhedra showed non-rigid distortion, whereas the $\text{SnO}_6$ polyhedra remained almost unchanged. At the phase transition, the $\text{SiO}_4$ tetrahedra showed
further angular twisting while the SnO$_6$ chains shift parallel [101] inducing a reduction in symmetry. Furthermore, the Ca atoms move almost parallel [100] within their framework cavity, causing a polymerization of CaO$_7$-polyhedra to sheets of CaO$_8$ parallel [111] at pressures above 5.8 GPa. The phase transition could be identified as second-order transition with a critical exponent $\beta = 0.4(1)$ and $P_c = 4.87(8)$ GPa. A kink in the angular evolution at 5.8 GPa indicates a second isosymmetric A1 – A1 transition within the triclinic phase.

The single-crystal high-pressure study of titanite (CaTiOSiO$_4$) reconfirmed the monoclinic – monoclinic P2$_1$/a - A2/a phase transition. This transition is controlled by the centering of the formerly off-centered Ti atom in the octahedra. Calculations of the critical exponent $\beta$ to determine the order of the phase transition resulted in $\beta = 0.46(3)$ and $P_c = 4.3(2)$ GPa indicating a second-order phase transition. 3$^{rd}$ order Birch-Murnaghan EoS fits yield a bulk modulus for titanite in the A2/a phase with $V_0 = 368.750(9)$ Å$^3$, $K_0 = 126.87(8)$ GPa and $K' = 4.77(4)$. A second phase transition above 10 GPa from monoclinic A2/a to triclinic A1 in titanite is indicated by large deviation of the $\alpha$ and $\gamma$ angles from 90º. Above 10.2 GPa reversible twinning of the sample was observed.

Comparison of the bulk moduli of malayaite and titanite showed that malayaite behaves softer under pressure than titanite as indicated by the smaller bulk modulus. This difference is caused by a higher flexibility of the slightly larger Sn – Si framework in malayaite.

The difference in the monoclinic – triclinic transition pressure of titanite and malayaite (~10.2 GPa vs. ~5 GPa) can be explained by the influence of the off-centered Ti-atom. Up to 4.4 GPa the Ti out-of-center distortion remains in the P2$_1$/a phase and thus permits an increased compressibility. Interestingly, the A2/a phase in both crystals is stable over a pressure range of around 5 GPa.
Zusammenfassung


In dieser Arbeit wurden isotherme Hochdruckexperimente an einkristallinem, monoklinen A2/a Malayait und einkristallinem, monoklinen P21/a Titanit durchgeführt, um Informationen über die Kompressibilität und das strukturelle Verhalten in Kristallen mit Titanit-artigen Strukturen zu erhalten.


Berechnungen nach der Birch-Murnaghan Zustandsgleichung dritter Ordnung ergaben ein Kompressionsmodul für Daten mit P < Pc von V0 = 389.68(3)Å3, K0 = 121(1) GPa und K’ = 4.2(5). Strukturverfeinerungen bei 4 verschiedenen Drücken zeigten strukturelle Details in der

Die Einkristallhochdruckmessungen von Titanit CaTiOSiO₄ bestätigten die P2₁/a -A2/a Phasenumwandlung. Dieser Übergang wird durch das Zentrieren der vorher dezentrierten Titanatome im Oktaeder kontrolliert. Die Phasenumwandlung konnte als Übergang zweiter Ordnung mit einem kritischen Exponenten β = 0.46(3) und einem P_c = 4.3(2) GPa identifiziert werden. Die Bestimmung der Birch-Murnaghan Zustandsgleichung dritter Ordnung ergab Werte von V₀ = 368.750(9) Å³; K₀ = 126.87(8) GPa und K’ = 4.77(4) für Titanit. Eine zweite Phasenumwandlung oberhalb von 10 GPa von monoklin A2/a zu triklin A₁ in Titanit zeigte sich in starken Abweichungen der α und γ Winkel von 90°. Oberhalb von 10.2 GPa wurde reversible Verzwillingung der Probe beobachtet.

Vergleiche der Kompressionmodule von Malayaite und Titanit zeigten, dass sich Malayait weicher verhält als Titanit, wie durch das kleinere Kompressionmodul angedeutet wird. Dieser Unterschied wird verursacht durch die höhere Flexibilität des leicht vergrößerten Sn – Si Gerüstes. Die Differenz im Umwandlungsdruck von der monoklinen in die trikline Phase in Titanit und Malayaite (~10.2 GPa vs. ~5 GPa) kann mit dem Einfluß des dezentrierten Ti-Atoms erklärt werden. Bis 4.4 GPa bleibt die Verzerrung des Titanatoms aus dem Zentrum in der P2₁/a Phase bestehen und erlaubt daher eine erhöhte Kompressibilität/ Interesanterweise scheint die A2/a Phase in beiden Kristallen über einen Druckbereich von 5 GPa stabil zu bleiben.
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1. Introduction

The aim of this thesis is to better understand the relation between the structure of a crystal and its resulting physical properties to facilitate the search for new and optimized materials with defined physical features. One of the many interesting physical properties accessible is the so-called non-linear optical (NLO) behavior, which is industrially important as it is utilized for optical information transfer, information processing and laser frequency mixing in second-harmonic generation lasers, infrared (IR) wavelength generation and other wavelength-transmutation methods (Hansson et al. 2000) and recently also in third-harmonic generation lasers (Mu & Ding 2001).

The materials that exhibit non-linear behavior can either be organic or inorganic. The organic crystals such as NLO chromophores (Nordmann & Roehl 1993) or amino-nitropyridines (Küpfer et al. 1993) to name just a few have the advantage of growing quite fast, and a multitude of different components can be tested and most importantly defined thin films can be structured. The disadvantage of organic crystals is their poor damage threshold of temperature or water. Inorganic non-linear optical materials are dominated by the XYO\textsubscript{4} family, where X can be potassium (K), rubidium (Rb) or cesium (Cs), the Y site is occupied by d\textsuperscript{0} transition metals atoms, mainly titanium (Ti) and Z can be phosphorus (P) or arsenic (As). The advantages of these materials are the high non-linearity, their high damage threshold and their thermal stability, which make the crystals interesting for the laser industry. KTiOPO\textsubscript{4} (KTP) plays the most important role among the KTP analogues because it shows the best damage thresholds, highest efficiency and crystal homogeneity (Wang et al. 2000). The disadvantage is the slow and quite complicated growth of these materials (Hansson et al. 2000).

The reason for these interesting physical properties can be found in the structural arrangement of the crystal and the properties of the d\textsuperscript{0} cation on the octahedral site. The noncentrosymmetric orthorhombic Pna\textsubscript{2}\textsubscript{1} crystal structure of all members of this chemical family are characterized by ZO\textsubscript{4} tetrahedra and distorted YO\textsubscript{6} octahedra that form a three-dimensional network with channels along the c-axis. The large X atom occupies the high coordination site along the channels and is only weakly bonded to the tetrahedra and octahedra. The distorted TiO\textsubscript{6} octahedra are corner-linked and form twisted chains with alternating long and short O–Ti=O bonds unidirectional along the chains. The short titanyl bond Ti=O creates a local dipole moment and is thus mainly responsible for the observed
non-linearity. Hansen et al. (1988) showed that the short Ti-O bond causes a build-up of charge density between the two atoms and thus leading to a hyperpolarization. Kunz & Brown (1995) examine the relationship between $d^0$ transition metal and out-of-center distortion more precisely. They found that the size and charge of the cation are correlated to the energy-level of the $d$ orbitals. These orbitals interact with the $p$ orbitals of the oxygen ligand. Therefore, the occurrence and extent of an off-centering in octahedrally coordinated atoms depend on the ionic charge and ionic size of the transition metal cation. The orientation of the structural distortion depends on the direction of cation - cation repulsion as well as bond networks and/or lattice stress effects.

Aside from KTP other inorganic compounds with the same $XYOZO_4$ stoichiometry and $d^0$ transition metal atoms in linear chains exist, e.g. the mineral titanite $CaTiOSiO_4$. However, titanite does not exhibit any interesting optical properties. The Ti atoms are off-centered as well but the vectors of this off-centering are antiparallel between neighboring chains resulting in a centrosymmetric $P2_1/a$ structure. Hence, the local dipole moments are cancelled on a global scale. The aim of this thesis is to elucidate the question why off-centering is supported in one structure and suppressed in another. Information on this can be expected by investigating phase transitions that involve changes in the off-centering of the octahedral atom. The question is whether phase transitions in titanite are restricted only by order/disorder phenomena, i.e. the presence/absence of the off-centering. Therefore, a comparison of the structural behavior between titanite and a topological similar material, where the $d^0$ transition metal is exchanged by main group elements, is done. Experiments with the replacement of Ti against the main group element tin (Sn) in KTP (Thomas et al. 1990) and in titanite (Kunz et al. 1997) showed that a complete chemical exchange is possible. The mineral malayaite $CaSnOSiO_4$ is therefore the ideal candidate to differentiate between topological and chemical influences on phase transitions in titanite. A phase transition under high-pressure is known for titanite (Kunz et al. 1996, Angel et al. 1999) and hence it is most interesting to examine the behavior of malayaite under high-pressure as well. Furthermore, preliminary information on titanite under high-pressure, gained from powder diffraction experiments, need to be complemented and extended by single-crystal high-pressure experiments.
1.1 Titanite

The mineral titanite CaTiOSiO$_4$ is a natural antiferroelectric material, i.e. a material with a spontaneous sublattice polarization with alternating signs in the sublattices. The monoclinic structure of titanite is characterized by TiO$_6$ octahedra forming chains parallel [100] through shared *trans* corners. These chains are mutually connected via SiO$_4$- tetrahedra. CaO$_7$ polyhedra occupy cavities in this rigid framework and form chains parallel [101] (Fig. 1).

![Polyhedral model of titanite CaTiOSiO$_4$ and malayaite CaSnOSiO$_4$](image)

**Figure 1**: Polyhedral model of titanite CaTiOSiO$_4$ and malayaite CaSnOSiO$_4$ (a) along the [001] direction and (b) along the [100] direction. The solid line represents the unit cell.

At ambient conditions the Ti atoms exhibit out-of-center distortions with parallel displacement vectors within a single TiO$_6$ chain and antiparallel orientation between neighboring chains (Fig. 2). This displacement leads to the above mentioned polarized
sublattices, which are related by the two-fold screw axis in space group P2\textsubscript{1}/a (Zhang et al. 1995).

High-temperature investigations of titanite showed an antiferrodistorsive phase transition from P2\textsubscript{1}/a to A2/a symmetry (\(\alpha - \beta\) transition) at 496 K (Taylor and Brown 1976, Kek et al. 1997, Salje et al. 1993b). The transition at 496 K is driven by the loss of the long range coherence of the out-of-center dipoles between neighboring chains but not within a TiO\textsubscript{6} chain (Malcherek et al. 2001). Therefore, on average the structure shows A2/a symmetry. A second, isosymmetric phase transition is observed at 825 K and ambient pressure (\(\beta - \gamma\) transition) (Kek et al. 1997, Zhang et al. 1997, Chrosch et al. 1997). Malcherek (2001) used spontaneous strains calculated from high-temperature powder data to show that the intermediate phase between 496K and 825K is characterized by shearing. High-pressure powder experiments (Angel et al. 1999, Kunz et al. 1997) also revealed a phase transition around 3.5 GPa corresponding to a symmetry change from P2\textsubscript{1}/a to A2/a. Kunz et al. (2000) related the 825 K phase transition to the 3.5 GPa phase transition based on their in situ powder diffraction study under simultaneous high-pressure and high-temperature. The high-pressure phase as well as the high-temperature \(\gamma\)-phase were assumed to be induced by local symmetrization of the Ti octahedra, i.e. a disappearance of its out-of-center distortion. There are indications for a second high-pressure phase transition of titanite around 10 GPa (Kunz, pers. comm.), but the data available could not be interpreted satisfactorily.

Diffuse scattering of titanite has been investigated as a function of chemical exchange and temperature. Impurities over 4 mol% on the octahedral site lead to domains parallel to the b axis (Fig. 2), especially if Al and/or Fe are present in the structure and act as boundary for the domains (Speer & Gibbs 1976, Taylor & Brown 1976, Oberti et al. 1991). The existence of diffuse scattering in titanite was first published by Higgins and Ribbe (1976). They showed by means of X-ray precession photographs that reflections with \(k + l = \text{odd}\) become diffuse with increasing chemical exchange in synthetic titanite leading to A2/a symmetry in natural titanite. Diffuse scattering has also been observed in titanite under high temperature. Bismayer et al. (1992) followed the evolution of diffuse scattering as a function of temperature and found anisotropic diffuse scattering for the 40\(\bar{3}\) reflection streaked along b* even above 496 K. Malcherek et al. (2001) described a two-step pathway from the ordered
to the disordered titanite phase using synchrotron radiation and Monte Carlo spin calculations. In the intermediate phase between 496K and 850K they found planar lens shaped diffuse intensities normal to [100] and concluded that the lateral correlation of the linearly off-centered Ti atoms leads to this diffuse feature. Above 825K the diffuse scattering disappears completely (Kek et al. 1997).

**Figure 2**: Domain model of titanite in the ab plane modified after Taylor & Brown (1976). The arrows represent the off-center distortion of the Ti atom inside the octahedra in each chain. The domains are shown by opposing arrows at the boundary (solid line) and the off-centering of the Ti atom is shifted about b/2.

Schmidt (1993) expected an alternating Ti off-centering in titanite under an AC electric field up to 35 kV/cm as a function of frequency and high-temperature as evidence for an antiferroelectric double hysteresis. Typical for an antiferroelectric, the integration of the dielectric constant $\varepsilon'$ increases up to the critical temperature $T_c \approx 490K$ but no sharp maximum was detected. Therefore, Schmidt (1993) interpreted this behavior as fluctuating anti-phase domains, which build randomly induced fields and therefore weaken the temperature dependency of $\varepsilon'$. The lack of the sharp maximum indicated a strong coupling between the sublattices. This phenomenon has already been observed in so-called "dirty ferroelectrics" (Burns & Scott 1973, Westphal 1992).
1.2 Malayaite

The mineral malayaite, CaSnOSiO₄, was first described in 1960 on Perak, Malay Peninsula by Ingham and Bradford (1960). The structure of the colorless to yellowish mineral was solved by Higgins and Ribbe (1977) reporting monoclinic space group symmetry A2/a. The structure of malayaite is equivalent to the aristotype of titanite CaTiOSiO₄ with SnO₆ octahedra chains linked by SiO₄ tetrahedra and large cavities filled with CaO₇ polyhedra (Fig. 1). Investigations of malayaite under high temperature using synchrotron radiation, high-resolution transmission electron microscopy, X-ray powder diffraction and Raman spectroscopy by Groat et al. (1996) revealed a structural anomaly around 500 K. The authors correlated this anomaly with the thermal parameter of the Ca position indicating a maximum elongation along the a axis. Nevertheless, they found no deviations from the A2/a symmetry, nor any structural domains or antiphase boundaries with a reduced symmetry. Meyer et al. (1998b) reinvestigated the 500K anomaly using single-crystal X-ray diffraction and powder IR spectroscopy at different temperatures. They confirmed the strong increase of the anisotropic thermal parameter U₁₁ for Ca as a function of temperature and concluded a partial collapse of the CaO₇ polyhedra around 500K. Both Bismayer et al. (1999) and Zhang et al. (1999) described another important behavior with respect to the 500 K anomaly: Single-crystal X-ray diffraction and powder hard mode IR studies showed a weak tilting of the SnO₆ octahedra. These displacements change the oxygen environment around the Ca atoms where one oxygen moves closer to the calcium atom. Zhang et al. (1999) also reported a change in the coordination of the Ca atom and described the structural anomaly at 500K as an isosymmetric second-order phase transition. No diffuse scattering occurs in malayaite. So far, neither powder nor single-crystal high-pressure experiments were done on malayaite. However, it is interesting to see how this structure type behaves under pressure in the absence of a d⁰ transition metal. Also, the slightly larger ionic radius of Sn might cause further interesting features as a function of pressure. Takenouchi (1971) showed that malayaite and the topologically identical titanite CaTiOSiO₄ have a complete solid solution above 888 ± 15 K. Kunz et al. (1997) investigated the join along CaSnOSiO₄ – CaTiOSiO₄ in more detail and found on quenched samples that already a small substitution (10 mol%) of Sn changes the titanite space group symmetry from P2₁/a to A2/a.
2. Theoretical background

2.1 Linear Equation of State (EoS)

In general an equation of state is the mutual relation between pressure, volume and temperature in a system.

The best known equation of state is the Boyle-Mariotte law for ideal gases

\[ PV = nRT \]  

with \( n \) = the number of atoms in the system and \( R \) = gas constant. This equation of state is only valid for gases. The P-V-T- relationship in condensed matter is complicated through the strong non-linear interactions between neighboring atoms. As the temperature in these high-pressure experiments is constant the volume of the crystal only depends on the given pressure.

Therefore, the isothermal bulk modulus \( K \) of a crystal (in GPa) can be defined as:

\[ K_{0,T} = -V \ast \left( \frac{dP}{dV} \right) = \frac{dP}{dlnP} = \frac{1}{\beta} \]  

\( K_0 \) can be interpreted as the slope of a P-V curve. From this equation one can read the bulk modulus as the inverse compressibility \( \beta \), which describes the “softness” of the crystal. This means that a soft material with high compressibility \( \beta \) will have a small bulk modulus \( K_0 \) and vice versa. For example, the hardest material, diamond, has a bulk modulus \( K_0 \) of 444(3) GPa (Knittle 1995) in contrast to SiO\(_2\) with a \( K_0 \) of 37.99 GPa (Angel et al. 1997b). Murnaghan (1967) defined a first order equation of state, where \( K' \) is constant and the bulk modulus varies linearly with pressure

\[ K = K_0 + K'P \]  

The pressure derivate of \( K_0 \), and therefore the curvature of the slope of the P-V plot, is the nondimensional \( K' \)

\[ K' = \left( \frac{dK}{dP} \right)_T \]  

The integration shows the relation between pressure \( P \) and volume \( V \) with \( V_0 \) being the volume at room pressure:

\[ V = V_0 \ast \left( 1 + \frac{K'P}{K_0} \right)^{-1/K'} \]  

This so called Murnaghan linear Equation of State can be used only for a narrow pressure range (Knittle, 1995) or for elastic solids (Poirier, 1999).
2.2 Birch-Murnaghan Equation of State

In contrast to high-temperature experiments, the variation of the crystal volume and cell parameters under pressure is mostly non-linear. As mentioned above, this behavior is caused by the inter-atomic forces in a solid material. Thus, this non-linearity has to be taken into account when calculating the EoS of a crystal. Birch and Murnaghan introduced the so-called 3\textsuperscript{rd} order Equation of State in 1967. This formula is based on the Eulerian strain $\varepsilon^E$ for an isotropic (negative) compression

$$
\varepsilon^E = \frac{1}{2} \left( \frac{V_0}{V} \right)^3 - 1 = -f_e
$$

After solving the equation for constant temperature and zero pressure after Poirier (1999) the following expression is obtained

$$
p = 3K_0 f_e^e \left( 1 + 2f_e^e \right)^3 \left( \frac{3}{2} K' - 4 \right)
$$

If equation (6) is inserted into equation (7) the following equation, known as the 3\textsuperscript{rd} order Birch - Murnaghan Equation of State, is obtained.

$$
p = \frac{3}{2} K_0 \left[ \left( \frac{V_0}{V} \right)^3 - \left( \frac{V_0}{V} \right)^5 \right] \left[ 1 - \frac{3}{4} (4 - K') \left( \frac{V_0}{V} \right)^2 - 1 \right]
$$

Based on calculations of many materials the most common $K'$ seems to be 4. If $K'$ is therefore kept constant to this number, the second bracket in equation (8) will become zero. This reduced equation is known as the 2\textsuperscript{nd} order Birch - Murnaghan Equation of State.

The formula for the axial equation of state is given in table 7 Appendix B.

2.3. Spontaneous strain $e_{ij}$ (Carpenter et al. 1998; Nye 1995)

Under non-ambient conditions every crystal shows some lattice strain in form of macroscopic relaxation or distortions that is caused by microscopic reasons such as displacements or ordering on the atomic site. The excess distortion caused by a phase transition can be expressed by the spontaneous strain $e_s$ (Aizu 1970, Newham 1974). The spontaneous volume strain is calculated from the relative difference between the volume of the low symmetry phase and the volume of the high symmetry phase extrapolated to the low symmetry conditions (Fig. 3).
Figure 3: Illustration of the definition of spontaneous strain. This principle holds for volume strain as well as tensile and shear strains. (a) a phase transition occurs at a pressure P2 and the evolution of the volume deviates from the previous trend. The excess volume between V1 and V2 can be expressed as the spontaneous strain. Therefore, the data points between P1 and P2 are fitted with an equation of state and are extrapolated into the region of P > P2. The resulting relative difference below and above P2 as a function of pressure is shown in (b).

The strain can be described by a second-rank tensor which has an ellipsoid as its representation quadric:

$$
\begin{bmatrix}
e_{11} & e_{12} & e_{13} \\
e_{21} & e_{22} & e_{23} \\
e_{31} & e_{32} & e_{33}
\end{bmatrix}
$$

(9)

It can be visualized most clearly by referring it to the principal axes, which is achieved through a principal axis transformation:

$$
\begin{bmatrix}
e_1 & 0 & 0 \\
0 & e_2 & 0 \\
0 & 0 & e_3
\end{bmatrix}
$$

(10)

To visualize the strains the following definitions in combination with Fig. 4 are important.

In general, strains are described in a Cartesian reference system, where Z is parallel to the normal to the (001) plane, Y parallel to the crystallographic y-axis and X is perpendicular to Z and Y. A change in the extension of a line along the three reference axes is identified by $e_{11}$, $e_{22}$ and $e_{33}$. These are called the tensile strains $e_{ij}$ (with $i = j$). The change in the angle spanned
by two lines originally parallel to two reference axes is expressed by the spontaneous strain $e_{12}, e_{23}, e_{13}$. This strain is called the *shear strain* $e_{ij}$ (with $i \neq j$).

**Figure 4.** Sketch to visualize the effect of spontaneous strain at a given pressure. The outer cube represents the experimentally measured crystal unit cell. The inner cube shows the extrapolated unit cell at the same pressure condition if the phase transition had not taken place.

When a phase transition is observed, the spontaneous strain can be calculated depending on the original and the transformed symmetry. The strain is always calculated from the high-symmetry into the low symmetry phase. Any excess values can be seen as deviation from the zero line (Fig. 3). In our study the symmetries of malayaite and titanite changed from monoclinic to triclinic, therefore, the following formulas had to be used to calculate the spontaneous strains. $X_0$ is the extrapolated value of the respective axis or angle if the phase transition had not taken place (Fig. 4), $\beta^*$ is the reciprocal angle ($180^\circ - \beta$).

\[
e_{11} = \frac{a}{a_0} \sin \gamma - 1 \quad (11)
\]

\[
e_{22} = \frac{b}{b_0} - 1 \quad (12)
\]

\[
e_{33} = \frac{c \sin \alpha \sin \beta^*}{c_0 \sin \beta^*_0} - 1 \quad (13)
\]

For the monoclinic – monoclinic phase transition in titanite around 3.5 GPa reduced formulas are used as the $\alpha$ and $\gamma$ angles remain $90^\circ$. 
A shear strain is given if the distortion is reached by a shear through an angle $\theta$ (Fig. 5). In principal the shear is defined as $\tan \theta = \frac{x}{x_0} \cos \phi$. The shear strain is positive if the involved angle gets smaller and negative if the angle gets larger.

![Figure 5: Sketch of the shear strain modified after Carpenter et al. (1998)](image)

Therefore the formulas for the shear strain comprise the enclosed angles of the axes (Fig. 4).

\[
e_{12} = \frac{1}{2} \left( \frac{a}{a_0} \sin \gamma \cos \beta^* - \frac{c \sin \alpha \cos \beta^*}{c_0 \sin \beta_0^*} \right)
\]

\[
e_{13} = \frac{1}{2} \left( \frac{a \sin \gamma \cos \beta_0^*}{a_0 \sin \beta_0^*} + \frac{c \cos \alpha \cos \gamma}{c_0 \sin \beta_0^*} \right)
\]

\[
e_{23} = \frac{1}{2} \left( \frac{c \cos \alpha}{c_0 \sin \beta_0^*} + \frac{a \cos \beta_0^* \cos \gamma}{a_0 \sin \beta_0^*} \right)
\]

It results from these equations that $e_{12}$ and $e_{23}$ deviate from zero if the angle $\alpha$ and $\gamma$ are $\neq 90^\circ$.

### 2.4 Volume strain

The general volume strain is defined as
A symmetry-breaking strain “transforms as any irreproducible representation of the point-group of the high-symmetry phase, other than the identity representation” (Carpenter et al. 1998). The symmetry-breaking strain has to be a shear strain which excludes a change in molar volume as $\varepsilon_1 + \varepsilon_2 + \varepsilon_3 = 0$. All “non-symmetry breaking” strains contribute to a change in volume and volume strain will be detected. Analogous to the tensile and shear strain the volume strain can be calculated by the simple equation

$$V_s = \varepsilon_1 + \varepsilon_2 + \varepsilon_3$$

(20)

with $V_0$ being the extrapolated volume at room pressure and $V$ being the volume at measured pressure.

### 2.5 Order parameter

A phase transition can be thermodynamically described by the order parameter $Q$. The basic relation between the Gibbs Free Energy $G$ of a crystal and the order parameter $Q$ is the Landau potential of the order parameter $L(Q)$ which can be described as a Taylor expansion of $G$ in $Q$. The thermodynamic nature of such a phase transition is reflected in the evolution of the order parameter with pressure. Therefore, the order parameter is proportional to $\Delta p$

$$Q \propto (P - P_{\text{trans}})^\beta$$

(22)

with $P_{\text{trans}}$ being the transition pressure. The so-called critical exponent $\beta$ specifies the type of phase transition. A second-order phase transition has the critical exponent $\beta = 1/2$, tricritical transitions yield a value of $\beta = 1/4$. First order phase transitions are always accompanied by a discontinuity and show a more complicated behavior, which can be described as:

$$Q \sim \frac{2}{3} \Delta \left\{ 1 + \left[ 1 - \frac{3}{4} \frac{(P - P_c)}{(P_{\text{tr}} - P_c)} \right]^{0.5} \right\}$$

(23)

with $P_{\text{tr}}$ = pressure of the phase transition, $P_c$ = fitted critical pressure for $V_s = 0$ if no discontinuity would exist and $\Delta = \text{discontinuity in volume strain at } P_{\text{trans}}$.

The order parameter $Q$ cannot be measured directly, therefore it has to be determined indirectly by a measurable variable, e.g. some geometrical change under non-ambient conditions. Most phase transitions are correlated with a deformation of the unit cell. The
spontaneous strain $e_{ij}$ described in chapter 2.3. is a structural quantity that measures the deformation of the unit cell and can be used to quantify $Q$. Hence, a coupling of strain and the order parameter has to be found to correlate these features. The relation between the Gibbs Free Energy $G$ of a crystal and the two thermodynamic variables $Q$ and $e_{ij}$ is given by (a) the Landau-potential $L(Q)$ for the order parameter $Q$, (b) the elastic energy due to a phase transition $\frac{1}{2} \sum C_{ik} e_i e_k$ with the coefficient $C_{ik}^0$ for the elastic constants and the elastic energy $e_i e_k$ from the relaxation of the unit cell that is described by the spontaneous strain, and finally (c) the coupling energy for the order parameter $(Q^n)$ and the spontaneous strain $(e^m)$ with $\xi_{imn}$ being a coupling constant between $Q^n$ and $e^m$. These factors form the general relation:

$$G(Q, e) = L(Q) + \frac{1}{2} \sum C_{ik} e_i e_k + \sum \xi_{imn} e^m Q^n$$  \hspace{1cm} (24)

Hence, the calculation of the spontaneous strain allows the determination of the order parameter $Q$ and therefore the thermodynamic characteristics of the phase transition.

The theory of the coupling between order parameters $Q$ and spontaneous strains $e_{ij}$ is rather complex and an extensive description would go beyond the scope of this thesis. For a more detailed insight into this subject the following literature is recommended: Salje (1993a), Carpenter et al. (1998) and Price & Ross (1992).

2.6 Polarization (Kittel 1993)

The polarization $P$ of a crystal is defined as the dipole moment per volume unit averaged over the volume of the unit cell. The electric field $E$ in a distance $r$ from this dipole with the momentum $p$ is described by

$$E(r) = \frac{3(p \cdot r) - r^2 p}{r^5}$$  \hspace{1cm} (25)

The local electric field $E_{\text{loc}}$ at a position in any crystal system is the sum over the electric field $E_0$, which is the inner field induced by an applied outer field, and the sum of all dipoles in the sample.

$$E_{\text{loc}} = E_0 + E(r)$$  \hspace{1cm} (26)

To see what influences the dipole moment and thus the local electric field, $E(r)$ can be split into three different terms $E_1$, $E_2$ and $E_3$: 
E_{\text{loc}} = E_0 + E_1 + E_2 + E_3  \tag{27}

E_1 \text{ is the depolarization field which counteracts to the applied external field; } E_2 \text{ is the Lorentz cavity field that is the field on the surface of a spherical cavity with its center on the reference atom and } E_3 \text{ gives the field inside that cavity.}

On an atomic level the polarization can be split into 3 terms:
(a) the electronic polarization. This is caused by the displacement of the electrons relative to the atomic nucleus.
(b) the ionic polarization, which is due to the field induced relative shift of the cations and anions.
(c) the orientation polarization. This is based on the parallel orientation of already existing dipoles within the crystal structure.

\textbf{Figure 6:} Different contributions of polarization } \alpha \text{ as a function of frequency (after Kittel 1993).

These 3 mechanisms show different flexibility upon the application of an external field. This is reflected by the frequency dependency on their contribution to the total polarization. We
can understand this frequency dependency by the different shifts necessary to induce the respective polarization. While the electronic and ionic polarization rely on only small and hardly detectable movement of electrons and ions, the orientation polarization can involve significant rearrangement of structural units.

Orientation polarization is frequently observed in molecular crystals. On the other hand the strong ionic and covalent bonds of extended, inorganic crystals make a field induced rearrangement of structural units with a dipole moment very difficult. The asymmetric O-Ti=O bonding is one of the few structural units that allows orientation polarization also in inorganic extended crystals. This is even more the case if, as in titanite there exists an order/disorder phase transition influencing the orientation of these dipole moments. As will be described in the experimental part of this thesis (chapter 3.5.1), the crystal structure of titanite is supposed to remain monoclinic when heated up to 500K and cooled down to room temperature under an electric field. If the off-centering of the Ti atoms is influenced by a directed electric field, all Ti atoms will move into one direction along the a-axis. This movement will violate the two-fold axis from the high temperature A2/a phase, as well as the two-fold screw axis of the P21/a phase at room temperature. It should be possible to detect a change of the space-group into Aa depending on temperature and electric field amplification.
3. Materials and Methods

In this chapter, the synthesis of a single-crystal titanite, the principle of the high-pressure diamond anvil cells, as well as the samples used in this thesis are introduced. The data collection, reduction and analysis for high-pressure compressibility and intensity data, Image Plate data and the experiment in the electric field are described.

3.1 Synthesis of single-crystal titanite CaTiOSiO₄

So far, all experiments on high-pressure titanite were done on powder samples (Angel et al. 1999, Kunz et al. 1996, Kunz et al. 2000). Single-crystal experiments may provide more information about crystal structures since there is no peak overlap as in powder experiments. One aspect of this thesis was to grow single-crystal titanites in a suitable size of around 100 μm to collect compressibility and intensity data sets. Different synthesis techniques were used to obtain single-crystal titanite. The results of these experiments were tested afterwards with a STOE powder diffractometer. If single-crystals were obtained, these were checked with a Nonius CAD4 diffractometer and SEM (scanning electron microscopy) technique.

The most common method to grow single-crystal titanite is the hydrothermal synthesis. A defined mixture of oxide powders is filled into a gold capsule together with a variable amount of water. This capsule is loaded into a high-pressure furnace and the pressure around the capsule is increased by gas or water. After a variable experiment time the sample is quenched by rapidly releasing the pressure medium. The capsule is then carefully opened and the sample can be extracted.

This technique has been successfully used by several authors (e.g. Xirouchakis, 1997, Hollabaugh, 1983). After the first unsuccessful attempts of strictly following the literature prescriptions (see Appendix A), a series of experiments was done with different relative amounts of the commercially available oxide powders, water content or with the addition of a nucleus. The results varied from almost unreacted starting substances, titanite powder with a large amount of excess SiO₂, cubic schorlomite Ca₃(Fe,Ti)₂[(Si,Ti)O₄]₃ or bluish colored crystallites that were not titanite crystals. For more details see Appendix A. Possible explanations for these problems might be: (a) in the powder diffractograms a certain amount of excess SiO₂ was always present indicating incomplete reaction. Xirouchakis (pers. communication) recommended excess initial SiO₂, but even after the synthesis with only stoichiometric oxide mixture an amount of excess SiO₂ was present; (b) the P – T conditions
in the furnace might not have been stable during the synthesis time; (c) nucleation problems. Since these problems could not be solved, an alternative method had to be found. A mixture of powdered SiO₂, Ca(OH)₂ and TiO₂ were melted and cooled down in an inert crucible in air as described by Brower & Robbins (1969) and Robbins (1968). Again, several starting mixtures of the oxides were tested. The powders were mixed in an Agate Mortar and filled into a Pt crucible. A small wire of PtRh (⌀ = 100 μm) was looped around the crucible to fix it and the end was hung into the crucible slightly touching the powder sample as support for nucleation (Fig. 7b). A Linn HT1800 Vac oven was used for the synthesis. The temperature path given by Robbins (1968) was modified: The sample was heated in 30 minutes up to 1400°C to melt the oxides. In steps of 8°C per hour the melt was cooled to 1000°C and kept at this temperature for 5 hours. Afterwards the integrated cooling program of the Linn oven was used to reach room temperature after altogether 70 h (Fig. 7a).

![Figure 7](image)

Figure 7: (a) P-t path used for single crystal titanite growth in the Linn oven and (b) sketch of the Pt crucible and the sample touching PtRh wire looped around the crucible.

The best result was obtained by a stoichiometric mixture of Ca(OH)₂, SiO₂ and TiO₂ and the above described temperature curve. This resulted in different sizes of crystals. The largest crystal (250 x 175 x 60 μm³) was first analyzed with SEM for its composition, followed by X-ray diffraction for cell parameters and space group and showed to be suitable as a basis for smaller crystals. The results verified the crystal as pure titanite CaTiOSiO₄ with the space group P2₁/a. A small cut-off single crystal was loaded into the DAC (Fig. 9) for compressibility and intensity data collections as described in paragraph 3.3.
3.2. High - Pressure Generation

There are many ways to generate pressure over a large range by piston cylinder cells, hydrothermal techniques, multi anvil cells or gas pressure cells. The largest pressure is reached by the shock-wave technique where pressures up to 50TPa (50*10^3 GPa) are achieved. In order to investigate the behavior of materials in situ with X-ray diffraction or spectroscopic techniques, the Diamond Anvil Cell (DAC) proves to be the most efficient device.

**Figure 8:** (a) Sketch of the X-ray beam pathway through the cell. The beam goes through the upper diamond anvil, diffracts at the sample and is detected after its way through the second diamond anvil as a function of the respective angle. The ruby is excited by a laser light for in situ pressure measurement and the fluorescence is detected (Ruby signal). (b) the principle of pressure generation: the diamonds are pushed together, the sample chamber get smaller and the medium transmits the pressure to the sample. The gasket also extrudes while the diamonds are pressed towards each other.

Between two opposed tip-cut diamonds a hardened metal foil ("gasket") with a small hole drilled at its center serves as sample chamber. It is filled with powder or single crystal sample, a pressure transmitting medium and a pressure calibrant (Fig. 8a). The pressure-transmitting medium can be an inert gas (such as Ar or N\textsubscript{2}), a fluid or an oil, providing hydrostaticity during the experiment. Ruby, quartz, NaCl or SiO\textsubscript{2} powder and other well investigated materials are used as pressure calibrants. To generate pressure, the diamonds are pushed closer together, which causes the gasket in between to extrude (Fig. 8b). This results in a decreased chamber volume and therefore an increased pressure in the sample chamber. For
review and discussion of different types of Diamond Anvil Cells see Jayaraman (1983) and Miletich et al. (2000).

3.2.1 The ETH Diamond Anvil Cell (ETH – DAC)
At the ETH an improved modular diamond anvil cell based on the BGI (“Bayerisches Geoinstitut”) cell type has been developed (Miletich et al. 2000).

One of the new features of this DAC are four surface treated guide pins in one part of the cell. These guarantee a controlled opening and closing of the cell as well as an additional stability of the corpus. Because of its modular design several inner modules, e.g. for spectroscopic or high-pressure high-temperature measurements, can replace the standard room temperature high-pressure module shown in Fig. 9b. The diamonds itself are held by a new spring-leaf bayonet mount that allows easy exchange of the diamonds. The diamonds are placed on beryllium backing plates with a conical hole at the center. Beryllium is used as backing plate since it is hard enough to transmit the force of the surrounding metal corpus to the diamonds (Miletich et al. 2000) and its transparency for the incoming and diffracted X-ray beam. The disadvantage of Be is the diffraction signal contribution to the background and its high toxicity. The incoming X-ray beam has to travel through the Beryllium part before diffracting at the sample. To obtain a defined absorption for the in- and outgoing beam, Be plugs are
mounted into the opening hole of the cell for structure measurements to define a plain disk of Beryllium. The cell fits on a conventional goniometer head and can therefore be used on different diffractometers with reproducible alignment and quick exchange.

3.2.2 Accessibility of reciprocal space (Miletich et al. 2000)

The accessibility of the reciprocal space is limited by the diamond anvil cell's design. In contrast to a single crystal on a glass needle, most of the reciprocal space of a crystal in the DAC is shadowed by the metal components of the cell in the transmission mode. The accessible reciprocal space is limited to only 1/4 to 1/3 of a full sphere to satisfy Bragg's law. The limiting factor is the opening angle $\alpha$ of the cell as shown in Fig. 10.

Figure 10: Schematic view of the diffraction geometry in the DAC in transmission mode. The angles $\psi_1$ and $\psi_D$ are defined by the cell axis CA and the incident and diffracted beam. They cannot exceed one half of the opening angle $2\alpha$ (modified after Miletich et al. 2000).

The maximal accessible $2\theta$ angle is given relative to the opening angle $2\alpha$ by $2\theta \leq (\alpha + \psi_1)$ where $\psi_1$ is the angle of the DAC relative to the incident beam. In reciprocal space the maximum length of the reciprocal space vector $k$ is therefore given by

$$k_{\text{max}} = \frac{2}{\lambda} \sin \frac{\alpha + \psi_1}{2}$$

(28)

As the DAC is rotated the crystal rotates in its center S and along with it the reciprocal space around $0^*$, which brings the $k$ vector to the Ewald sphere surface and into diffraction condition (Fig. 11).
21

Figure 11: (a) Ewald construction and reciprocal lattice. The origin S of the crystal is in the center of the Ewald sphere ES, and O* labels the origin in reciprocal space. If the crystal is rotated the reciprocal space around O* will rotate likewise. (b) Scattering takes place when the reciprocal lattice point P_{hkl} passes through the Ewald sphere. The diffraction angle 2\theta is specified by the angle between SP_{hkl} and SO*. The dashed lines show the limitation of the diffracted beam by the angle 2\alpha. The dumb-bell like areas describe the accessible reciprocal space (after Miletich et al. 2000).

Because of the restrictions described above, only a dumb-bell like shaped fraction of the reciprocal space can be passed through the Ewald sphere. The opening windows of the DAC are conical, hence the limits in the accessible reciprocal space in three dimensions can be described as a toroidally shaped surface by rotating the dumb-bell like two-arc segments around 360°.

In the ETH-DAC the opening angle \alpha is 45° and \psi is for example 30°. Thus, the maximal 2\theta value is 75°.

3.2.3 Gasket

A hole of ~ 1/3 to ~ 1/2 the culet diameter has to be drilled with the BETSA electroerosion device into the gasket to serve as sample chamber. The diamonds used in this study have a culet of 600 \mu m thus an appropriate size for the experiments is a hole of 200 \mu m to 250 \mu m.

Under pressure the gasket undergoes a plastic deformation. However, if the gasket collapses, the diamonds will not only break the sample in between but might also strike each other and in the worst case break apart. A pre-indentation limits the plastic behavior and the accessible pressure range is therefore increased. A T301 foil (tempered steel) is used as gasket for the
malayaite and titanite experiments. For titanite structure data measurements at 1 bar and 10 GPa a tungsten gasket was used because the absorption edge of tungsten is close to the energy of the Mo radiation and hence gasket absorption is maximized. The pre-indentation in these experiments were between 70 \mu m and 107 \mu m.

### 3.2.4 Pressure Medium

A 4:1 methanol-ethanol mixture is used as pressure medium for both titanite and malayaite experiments. This medium is filled into the gasket hole on the lower part of the cell. The sample crystal, the quartz and the ruby are placed on the upper diamond of the cell. The 4:1 methanol-ethanol mixture remains quasi-hydrostatic up to 10.4 GPa (Piermarini et al. 1975), which can be confirmed by the full width at half maximum (FWHM) of quartz. In our experiments the quartz FWHM remained constant (around 0.050°) up to 10.51(1) GPa in the titanite measurements. This improved quasi-hydrostatic behavior might be explained by a certain water content in the pressure medium, as Fujishiro et al. (1981) report hydrostaticity with a 16:3:1 methanol:ethanol:water mixture up to 14.5 GPa.

### 3.2.5 Pressure Calibration

In contrast to large volume pressure cells where the pressure can be calculated to the applied load, an internal pressure standard in the DAC is necessary. The use of small ruby crystals as pressure calibrants was first reported by Barnett et al. (1973) and King & Prewitt (1979). In our experiments ruby balls were used with a size of 10 to 30 \mu m, doped with 3000 to 5500 ppm Cr\textsuperscript{3+}. A blue-green laser light is microfocused on the ruby ball in the DAC by a microscope with long working-length objective. The $^2E \rightarrow ^4A_2$ electronic transition of the excited Cr\textsuperscript{3+} can be measured as intense R\textsubscript{1} – R\textsubscript{2} doublet (at 6942 Å and 6928 Å, respectively). The wavelength of these bands shift with increasing pressure to higher values (Hanfland, 1989) (Fig. 12). This shift was calibrated against the Decker equation of state for NaCl up to 19.5 GPa (Barnett et al. 1973, Piermarini et al. 1975) and later by Mao & Bell (1978) and Mao et al. (1986) also against the equation of state of several metals such as Cu, Mo, Ag and Pb up to 1.8 Mbar. The relation between the wavelength $\lambda$ of the ruby fluorescence and pressure $p$ is given by

$$p(\lambda) = \frac{B_0}{B'} \left( \frac{\lambda}{\lambda_0} \right)^{B'} - 1$$  \hspace{1cm} (29)
with $\lambda_0$ being the wavelength of $R_1$ peak at room pressure, $B_0 = \lambda_0 \left( \frac{dp}{d\lambda} \right)_{p=0} = 1904$ GPa

and $B' = \left( \frac{dB}{dp} \right)_{p=0} = 5$ (Mao & Bell 1978)

The advantages of the ruby fluorescence system are the small amount of space occupied in the pressure chamber by the ruby balls and the immediate, quick check of the pressure just after changing the applied pressure. The disadvantage of this system is the high temperature dependence of the band shifts. A change of 6K produces a change in pressure of around 1 kbar (Barnett et al. 1973, Vos & Schouten 1991). The accuracy of the pressure determination is in the order of 0.1 kbar (Vos & Schouten 1991). Therefore, the temperature must be controlled within the limits of 0.5K. In-house measurements with the ruby system gave an analytical precision of $\pm 0.03$kbar.

**Figure 12**: Sketch of the ruby fluorescence system. A blue laser light is focused on the ruby creating $P$ and $T$ dependent fluorescence peaks. From the position of the wavelength of these lines the pressure is calculated after equation (29) (modified after Miletich et al 2000).

Since the diffractometer and the ruby system are not in the same room and thus the temperatures are not the same, a second, more precise internal pressure calibrant had to be
used. Angel et al. (1997b) investigated the 3rd order EoS of quartz in great detail. The cell parameters of the quartz single-crystal were determined with the same routine like the cell parameters of the sample as described in chapter 3.3. The current pressure can be derived by inserting the measured volume of the quartz crystal into equation (8) with $K_0 = 37.12$ GPa and $K' = 5.99$. The analytical precision of ±0.08kbar of the in-house quartz volume determined pressure is in the region of the ruby fluorescence uncertainties, but the reproducibility of the quartz measured pressure is much higher. The quartz crystals used in this study are oriented (100) plates and are obtained from the same batch used by Angel et al. (1997b). The main disadvantage of quartz as internal standard is the required volume within the sample chamber. A comparison between in-house ruby and quartz determined pressure is shown in Fig 12. A clear deviation in the pressure region below 60 kbar and the good agreement above 70 kbar show that the equation for ruby fluorescence seems to be more accurate in the higher pressure regions.

![Figure 13](image-url)

Figure 13. Comparison between the pressures obtained by quartz volume (abscissa) and pressures obtained by ruby fluorescence (ordinate). The dashed line indicates the “ideal value” i.e. the quartz value at the respective pressure.

### 3.3. Data collection and analysis

In this chapter the theoretical and practical background for the data collection processes and reduction procedures for compressibility and intensity data are explained. For a more detailed instruction Angel et al. (2000) are recommended.
3.3.1 Compressibility data

Up to 31 reflections of the sample and 15 reflections of the quartz crystal for each pressure point were measured. From these reflections the unit cell parameters were obtained by constrained least square refinement. The $P - V$, $P - a$, $P - b$, $P - c$, $P - \alpha$, $P - \beta$ and $P - \gamma$ data were then used to calculate compressibility, spontaneous strains and equation of state according to equations (8), (11) – (19) and (23).

The changes in the unit cell parameters under non-ambient conditions are usually in the order of 0.05 – 0.5% for a change of 1 GPa or 100K. Thus, the precision of unit cell parameter measurement must be much better than these changes to detect any pressure or temperature induced modification. In this study the unit cell parameters were determined on an in-house HUBER 4-circle diffractometer with unfiltered and non-monomochromatized molybdenum X-ray radiation (50kV and 35 mA, and 45kV and 30mA, respectively) and a point-detector (Fig. 14). The omission of a monochromator is due to the fact that the graphite monochromator does not discriminate between the $\alpha_1$ and $\alpha_2$ lines. After monochromatization, these would have different directions leading to aberrant peak shapes and ill-defined peak positions.

The data itself was collected in the fixed - $\phi$ mode (Finger & King 1978) with the 8-position centering technique as implemented on the program SINGLE (Finger et al. 1999). In contrast to the bisecting mode the advantage of the fixed - $\phi$ mode is an increase in observable reflection numbers up to 40% because the opening angle $\alpha$ stays at its maximum value.

Hamilton (1974) first described the so-called 8 – position centering technique where each reflection is centered on eight different positions. These position settings had to be changed as given in Table 1 (Finger & Hadidiacos 1982) to be applicable to the fixed - $\phi$ technique. This modification also increased the efficiency of the centering procedure. The 8 - position centering technique not only yields highly accurate setting angles, but also enables to determine offsets of the crystal relative to the center of the diffractometer. This is a vital feature when doing experiments in a DAC, where optical centering of the crystal is strongly restricted.
Table 1: Reflection position with the 8-position centering technique after Hamilton (1974) modified for the program SINGLE by Finger and Hadidiacos (1982) with $D_i = (\omega + \Theta)$ and $A_i = \text{observed } \chi$ angle.

<table>
<thead>
<tr>
<th>position</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>Correction for setting angles</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2\Theta$</td>
<td>20</td>
<td>-20</td>
<td>-20</td>
<td>20</td>
<td>20</td>
<td>-20</td>
<td>-20</td>
<td>20</td>
<td>$(D_1-D_2-D_3+D_4+D_5-D_6-D_7+D_8)/4$</td>
</tr>
<tr>
<td>$\omega$</td>
<td>$\omega$</td>
<td>$-\omega$</td>
<td>$-\omega$</td>
<td>$-\omega$</td>
<td>$\omega$</td>
<td>$\omega$</td>
<td>$\omega$</td>
<td>$(D_1+D_2-D_3-D_4-D_5+D_6+D_7+D_8)/8$</td>
<td></td>
</tr>
<tr>
<td>$\chi$</td>
<td>$\chi$</td>
<td>$\pi+\chi$</td>
<td>$\pi+\chi$</td>
<td>$-\pi-\chi$</td>
<td>$-\pi-\chi$</td>
<td>$-\chi$</td>
<td>$-\chi$</td>
<td>$(A_1+A_2+A_3+A_4-A_5-A_6-A_7-A_8-4\pi)/8$</td>
<td></td>
</tr>
<tr>
<td>$\phi$</td>
<td>$\phi$</td>
<td>$\phi$</td>
<td>$\phi$</td>
<td>$-\phi$</td>
<td>$-\phi$</td>
<td>$-\phi$</td>
<td>$-\phi$</td>
<td>0 as $\phi$ is fixed</td>
<td></td>
</tr>
</tbody>
</table>

Figure 14: The in-house HUBER 4 - circle diffractometer with labeled setting angles. A large diffractometer geometry provides an improved peak - to - background ratio.

The measurement of the quartz crystal was performed in the same way as the measurement of the sample crystal with the 8 – position centering technique in fixed $\phi$ – mode. The $P – V$ equation of state of quartz was then used for pressure determination after equation (8).
3.3.2 Intensity data collection and structure refinement

All X-ray intensity data sets were collected on an in-house Enraf Nonius CAD4 diffractometer with graphite-monochromatized MoKα radiation (wavelength = 0.71073Å, 50 kV and 35 mA) and a point detector. In contrast to the compressibility measurements a monochromator can be used for intensity data collections since no high angular precision is necessary. The UB matrix of the sample was transferred from the UB matrix determined by the HUBER diffractometer to the CAD4 program by the following 3*3 matrix

\[
UB_{CAD4} = \begin{pmatrix}
0 & 1 & 0 \\
-1 & 0 & 0 \\
0 & 0 & 1
\end{pmatrix} UB_{HUBER}
\]

(30)

The reflections accessible were calculated with the program “lisgen” (David Allen pers. comm.), where the UB matrix of the sample and the opening angle of the DAC are used as input. Two or three strong reflections were selected as intensity and orientation standard reflection to observe possible sample shifts or decay of incident beam. The calculated reflections were scanned in the fixed – φ mode with an ω - scan (Fig. 15). Thereby, the smallest shadowing effects of the cell components are obtained. For both malayaite and titanite all intensity data sets were collected over the whole accessible reciprocal space including symmetry-forbidden reflections to receive information about possible symmetry violations. The measured reflections were treated by the program Integrate (R. Angel, pers. comm.), where each single reflection was surveyed in order to reject aberrant reflections, which were contaminated by signals from the cell components. Peak fits were performed by using the Lehmann-Larsen algorithm (Grant & Gabe, 1978). It is necessary to exclude aberrant scattering (e.g. from the diamond anvils), suppressed intensities (shadowing by the cell components) or asymmetric backgrounds (weak reflections) from averaging because these cannot be corrected. An analytical absorption correction for both sample and beam path through the cell (see chapter 3.2.1) was performed using the program Absorb modified after Burnham (1966). Averaging of the symmetry-equivalent reflections after Blessing (1987) based on the appropriate point symmetry provided the first internal R-values as validation of the data set quality. More details of the data collection are given in Appendix B Tables 2a and 2b.

With the remaining reflections with I > 4σ, the crystal structures were refined with Shelxl-97 (Sheldrick, 1997). Starting values for the refinement were taken from our own measurement
of the respective crystal on a glass needle in combination with data from literature (Bismayer et al. 1999, Kunz et al. 2000).

Figure 15: The in-house CAD4 diffractometer with labeled setting angles. The geometry of this diffractometer varies from the HUBER 4 - circle diffractometer in so far as the $\chi$ circle of the Eulerian cradle is replaced by a single axis $\kappa$ that is fixed inclined with respect to the angle $\omega$ with $\chi_E = 2\arcsin (\sin \alpha \sin \kappa/2)$. This set up has the advantage of more freedom of movement for $\chi < 90^\circ$. Therefore, smaller diffractometer sizes are possible and as a result higher intensity can be attained.

The refinement in the triclinic phase in malayaite and titanite was done in space-group A\(\bar{1}\). We chose space group A\(\bar{1}\) instead of standard P\(\bar{1}\) to enable easier comparison of the triclinic structure with the monoclinic A2/a structure. In order to transform coordinates from the A\(\bar{1}\) setting into P\(\bar{1}\), the following matrix has to be applied: \[
\begin{pmatrix}
1 & 0 & 0 \\
0 & 1 & 1 \\
0 & 1 & 1
\end{pmatrix}
\]. During refinement, the displacement parameters for the oxygen atoms were constrained to be equal. The bond length of Si – O were soft-constrained to a target value of 1.63 \(\text{Å}\) (weighting factor 0.006). The angles were kept free. The isotropic displacement parameters $U_{iso}$ were fixed at 0.010 \(\text{Å}^2\) for oxygen. For more details see Table 3a and 3b Appendix B.
There are several difficulties that degrade the quality of the structure refinement: The restricted accessible reciprocal space as described in chapter 3.2.2 provides only a small number of reflections compared to measurements on a glass needle. Also a disadvantageous position of the crystals cell axis with respect to the X-ray beam can result in a reduced number of measurable reflections. This leads to problems in the averaging as the background of the cell components can lead to intensity differences in equivalent reflections. All in all these factors affect the reflection to parameter ratio (overestimation) and in contrast to a data collection in air the overestimation in high-pressure experiments is only about a factor of 5 to 7. From these uncertainties the displacement factors and positional parameters are influenced. All this results in a deteriorated R-value that can be 2 to 3 times larger than for crystals in air.

3.3.3 Samples malayaite

The malayaite samples for the experiments were taken from the same sample batch used by Groat et al. (1996), Meyer et al. (1998b) and Bismayer et al. (1999). Its origin is a skarn north of Ash Mountain, British Columbia in Canada. The sample has the following chemical composition based on five oxygen atoms according to Bismayer et al. (1999): Ca$_{1.01}$ Sn$_{1.01}$ Fe$_{0.01}$ Si$_{0.98}$ O$_5$.

Two different single crystals of malayaite were used for the high-pressure experiments. The crystals had the dimensions of 100 x 80 x 80 $\mu$m$^3$ and 130 x 50 x 40 $\mu$m$^3$, respectively. The first crystal was pressurized from ambient conditions up to 7.394(4) GPa. At ~7.6 GPa the crystal bridged the diamond anvils and broke apart. The second crystal was loaded for both, intensity measurements and additional compressibility data points in the range of interest. In Appendix B Table 1a the unit cell parameters of the malayaite sample as function of pressure are listed. Intensity data were collected on a Enraf Nonius CAD4 diffractometer as described above at 1 bar, 4.238(4) GPa, 4.505(7) GPa, 5.769(5) GPa and 7.33(2) GPa. Details of the structure refinement and atom coordinates for the different data sets are given in Table 2a and 3a in Appendix B.

3.3.4 Sample titanite

The titanite sample was cut from the large crystal described in chapter 3.1 with the dimensions of 120 $\mu$m * 75 $\mu$m * 5 – 30 $\mu$m. The crystal was pressurized for compressibility data collection from room pressure up to 10.9 GPa until the pressure medium reached non-
hydrostaticity and the gasket extruded. For the next loading liquid nitrogen was tested as pressure medium as nitrogen is known to be quasi-hydrostatic up to 13.0 GPa (Le Sar et al. 1979). Nevertheless, the FWHM of titanite showed a large increase up to 200% at 2.8 GPa already. Le Sar et al. (1979) identify the freezing point of nitrogen at 2.4 GPa so titanite seems to be very sensitive to freezing of the pressure medium. Because of these results the following experiments were carried out with the 4:1 methanol:ethanol mixture again. In Appendix B Table 1b the unit cell parameters of the titanite sample as function of pressure are listed. Intensity data were collected on an Enraf Nonius CAD4 diffractometer as described above at 1 bar, 5.08(2) GPa, 6.99(2) GPa, 9.70(2) GPa, 10.20(2) GPa and 10.4(2) GPa. The measurement at 10.4 GPa could not be refined to satisfaction, the reason for this is discussed in chapter 4.6. Details of the structure refinement and atom coordinates for the different data sets are given in Table 2b and 3b in Appendix B.

3.4 Image plate data analysis

One goal of this thesis was (a) to test the compatibility of the ETH - DAC with the synchrotron device at the Swiss-Norwegian beam line (SNBL) and (b) to test for detectability of diffuse scattering.

The Diamond Anvil Cell proved to be perfectly suitable for the SNBL setup. Data processing was done with the program packages fit2d and KUMA. Problems occurred with fit2d in so far as the background could not be properly subtracted. This problem could however be solved using a self-learning algorithm (“Ewald explorer”) implemented in the KUMA software. The program scrolled through the images in given frames (10 images to learn the background of these images) and subtracted the background. Afterwards the UB matrix of the sample could be extracted and refined and subsequently the cell parameters were roughly obtained. Unit cell parameters are given in Table 1 in Appendix C.

3.4.1 Sample natural titanite

Small crystals were cut of a large greenish natural titanite mineral provided by the National Museum, Brazil. The crystal was loaded into the ETH - DAC together with a ruby ball and the 4:1 methanol:ethanol mixture. The single-crystal titanite was measured at various pressures in the range between 0.02 to 3.7 GPa with synchrotron radiation (wavelength = 0.72Å) at the Swiss Norwegian beamline SNBL at ESRF in Grenoble. The θ rotation varied from 335° to
55° in 5 seconds with a $\Delta \varphi = 1°$ per step (Fig. 2 Appendix C). The data was collected on a MAR Image Plate with a distance cell - image plate between 230 to 250 mm.

Two major problems occurred with this experiment. Firstly the contribution of the cell components and other phenomena such as Kossel lines and a high Compton background ratio can suppress or superimpose diffuse scattering of the sample. Secondly the knowledge about high-pressure single-crystal data detected by an Image Plate is small and thus the usual analysis procedures for Image Plate data for these specific measurements are in its infancy. Because of these two reasons the data obtained by this experiment could not be interpreted as desired. Nevertheless, it might be possible to qualitatively detect diffuse scattering but a quantitative statement can only be made if the background subtraction and the data analysis procedures are improved.

3.5 Electric field

Electric field experiments for various materials such as KDP, KTP and also titanite are reported in literature (e.g. Schmidt 1993, Sebastian & Klapper, 1992). There, the applied electric field was mostly an AC field. In this experiment a DC field with different field strength at different temperatures was applied. The idea for this experiment was to see whether the centering of the Ti atom could be influenced by an electric field. Therefore, the crystal was heated up to 520K to guarantee a loss of the off-center correlation of the Ti in the A2/a phase. From here an applied DC electric field might influence the Ti atoms in so far as they move unidirectional out of the octahedral center. This movement should lead to space group Aa as the 2-fold axis is removed by the off-centering.

The data was collected at ID 15C of the European Synchrotron Radiation (ESRF) in Grenoble, France, at different temperatures using a wavelength of 0.33Å (Fig. 16). The X-ray beam was monochromatized by a Si (111) monochromator crystal. The experimental setup has been described by van Reeuwijk et al. (2000) as a setup for alternating current AC measurement, where a beam chopper and a fast X-ray shutter were used.
We modified the setup for direct current measurement (DC) as there are neither chopper nor X-ray shutter necessary. The goniometer with the sample was mounted on a four-circle HUBER diffractometer and the electrodes were connected to the high-voltage supply. A gas blower which was assembled on top of the sample provided the required temperature of maximal 520K. An X-ray Image Intensifier XRII with a large input area and high sensitivity was coupled in front of the 1152 * 1242 charge coupled device (CCD camera).

As the XRII is almost spherical with respect to the sample, spatial distortion correction had to be made by defined calibration techniques. During the measurement of total 100 seconds the crystal was rotated from −10 to 10° in θ. This turn was repeated 50 times to get sufficient statistics. Also, the dark current (background without X-ray beam) was measured in order to subtract it from the images. The final data was scaled, averaged and spatial corrected by the
program fit2d and should be analyzed with the program “Denzo” normally used for data analysis of biomolecules.

3.5.1 Sample titanite for electric field

The single crystal of pure titanite for the electric field was provided by Prof. Hulliger, University of Berne. The crystal was grown by the Chrochalski method in the laboratory of Prof. Hulliger as described by Caprez (1997). The cell parameters and an intensity data set were performed by X-ray diffraction on the CAD4 and the Huber 4-circle diffractometer. A large single crystal was cut along the [100] direction with the dimension of \( \sim 4.5 \times 4.5 \times 0.57 \) mm\(^3\). A 1000 Å thin gold surface was sputtered onto each side of the crystal and the electrodes were glued on one edge of this area with gold paste, so that the electric field could be applied parallel to the a axis of the crystal. The crystal itself was mounted into the sample holder with a ceramic bond glue. The electrode connectors were kept safe from the temperature in a Teflon plate covered by aluminum foil (Fig 16 b). Different field strength between 0 and 3.5 kV/mm and temperatures from room temperature up to 520 K were applied.

The analysis of the data is still on-going but no qualitative results can be reported up to now. Therefore this experiment will be discussed in chapter 6.
4. Results and discussion

In this chapter the results of the crystallographic experiments on malayaite and titanite are discussed. Refinement details, tabulated bond length and polyhedral volumes are listed in Appendix A and B. Figure 17 shows a section of the structure with labeled atoms to follow the explanations given in the text.

![Figure 17](image)

**Figure 17**: Ball and stick model of a fragment of the malayaite and titanite structure.

### 4.1 Structural evolution of malayaite and titanite under high-pressure

#### 4.1.1 Malayaite

A structural phase transition accompanied by a symmetry reduction from monoclinic to triclinic reveals itself at $P_c = 4.87(8)$ GPa. Here the $\alpha$ and $\gamma$ angles start to deviate from $90^\circ$ up to $91.230(7)^\circ$ and $89.078(7)^\circ$, respectively, at $7.394(4)$ GPa (Fig. 18).
In order to correlate the monoclinic to triclinic phase transition with structural changes, diffracted intensities on either side of the phase transition were measured, namely at 1 bar, 4.238(4) GPa, 4.505(7) GPa, 5.769(5) GPa, and 7.33(2) GPa. The structure refinements reveal the following patterns:

**monoclinic A2/a**

Between room pressure and 4.5 GPa the Sn – O1 – Sn angle stays almost constant with a small decreasing trend from 133.2(6)° to 132.6(9)°. This is accompanied by an only very small internal distortion of the SnO₆ octahedron (Table 4a Appendix B). The Sn – O bond distances remain almost constant. This stiffness shows that the SnO₆ polyhedra act as rigid units inside the structure. Within the calcium polyhedra, only the expected shortening of the bond lengths can be seen. The largest change in the monoclinic structure is the decrease of the SiO₄ tetrahedral edges O3 - O3 and O2 - O2 with a decrease of 0.027Å and 0.029Å, respectively. In parallel, the Si – O bond distances decrease. The tetrahedral angles remain nearly constant suggesting an isotropic compression of the SiO₄ tetrahedra. The large volume...
reduction of the CaO$_7$ polyhedra in the monoclinic phase (3.4%) represents the softest structural unit. Remarkably, however, the SiO$_4$ tetrahedron is forced to reduce its volume by about 3%, which is mainly achieved by a decrease in bond lengths.

In all intensity data sets below 5 GPa no evidence for a structural change from A2/a to a different monoclinic structure was found. A search for forbidden reflections (0kl: k+l≠ 2n, h0l: h ≠ 2n and 0k0: k ≠2n) at 4.647 GPa on the 4 - circle diffractometers showed no evidence for any violation either.

![Figure 19](image.png)

**Figure 19**: Schematic sketch of the A1 (solid line) and P1 (dashed line) setting for malayaite and titanite viewed along [100]. The diamonds represent the octahedral chains projected parallel to the a - axis. The even-sided rhombohedral shape outlined by 4 neighboring chains becomes an uneven rhombus in the triclinic phase. The numbers denote the distances listed in Table 5a and 5b in Appendix B.

**triclinic A$_1$**

The structural differences between the triclinic and monoclinic phase are most clearly recognized when looking at cation-cation distances. As previously mentioned in chapter 1.2, the SnO$_6$ octahedra form linear chains parallel [100] in the monoclinic structure. When projected parallel [100], these chains are arranged on the corners of an even sided rhombus with 4 equivalent Sn-Sn distances parallel <011> (Fig.19). After the phase transition, the
distance between adjacent SnO$_6$ chains is stronger compressed parallel [011] than parallel [011], violating both the 2-fold screw axis as well as the glide plane (Table 5a Appendix B, Fig. 19). As a consequence, the Sn site splits into two symmetrically distinct sites occupying alternate positions along the octahedral chains. The asymmetric relative shift of the SnO$_6$ chains is also reflected in a twisting of the chain-linking SiO$_4$ tetrahedra. Their O2-O2 edge rotates relative to the O3-O3 edge towards a more parallel arrangement of these normally perpendicular tetrahedral edges.

The distortion of the SnO$_6$ - SiO$_4$ framework also affects the coordination of the Ca atom. As a response to the imposed constraint due to high-pressure, the CaO$_7$ polyhedra move closer together. This brings an eighth oxygen atom which is part of the neighboring CaO$_7$ polyhedra into the coordination sphere of the Ca atom (Fig. 20a and b). The bond valence of this new Ca – O2 bonds increase from 0.038 v.u. (at 1 bar) to 0.057 v.u. (at 5.7 GPa) to 0.095 v.u. (at 7.3 GPa) (Fig. 20c). Hence, the originally linear CaO$_7$ chains polymerize into CaO$_8$ sheets parallel $\langle 111 \rangle$ in the triclinic phase at 7.338 GPa (Fig. 20a, Table 4a Appendix B).

It is remarkable that this polymerization does not coincide with the phase transition at 4.87(8) GPa but occurs somewhere within the triclinic phase. Comparing the evolution of the $\alpha$ and $\gamma$ angles versus pressure (Fig. 18) with the evolution of the Ca - O2 bond valence and bond length (Fig. 20) suggests that this polymerization occurs at the same pressure where the angular evolution shows a change in slope. This could imply an isosymmetric phase transition above 5.77GPa.
Figure 20: (a) CaO$_7$ polyhedra of malayaite at room pressure and (b) at 7.33 GPa. The arrows indicate the oxygen atom, which at high pressure connects to the neighboring chain and thus helps to form sheets parallel [111].

(c) Range of Ca - O bonds for CaO$_7$ polyhedra (bars) in malayaite compared to the approaching Ca - O2 distance (open marks). Note that 8-fold coordination is only achieved between 5.7 GPa and 7.3 GPa. (d) Plot of bond valences vs. pressure for Ca-O2. Note the sharp kink at ~ 5.8 GPa, the same pressure where a change of slope is also noticed for the cell angles versus pressure. The lines are a guide to the eye.

The relative shift of the Ca atoms is again best described in terms of cation-cation distances (Table 6a Appendix B). Ca occupies a cavity within the SnO$_6$-SiO$_4$ framework. In the a-c plane, the size and geometry of this cavity is defined by the position of the SiO$_4$ tetrahedra, whereas it is limited in the [010] direction by the O1 oxygen. This on the other hand links two consecutive SnO$_6$ octahedra within their chain (Fig. 1, 17 & 21). At ambient conditions, the Ca atom is known to show an increased dynamic or static displacement within this cavity parallel [100] as indicated by a large value of U$_{11}$ (Groat et al. 1996, Meyer et al. 1998b). This
can be interpreted by either a flat Ca potential well parallel [100] (dynamic disorder) or two energy minima statistically occupied by the Ca atom (static disorder) (Fig. 24). From the interatomic distances between Ca and Si, we can see that this symmetric arrangement in the monoclinic phase is replaced by an asymmetric arrangement in the triclinic phase. This is evidenced by a shortening of one Si - Ca distance parallel approximately [100] (Table 6a Appendix B, Fig. 21 & 24). It is this movement that brings one additional O2, which is linked to the respective Si atom, into the coordination sphere of the Ca atom.

![Figure 21](image)

**Figure 21**: Sketch of the environment of the Ca atom in the a-c plane. The Si-labels refer to the numbers in Table 6a and 6b. The fifth SiO₄ tetrahedron is placed just below the Ca atom along [010].

### 4.1.2 Titanite

A pressure-dependent P2₁/a to A2/a transition was first revealed with high-pressure powder experiments by Kunz et al. (1996) and more precisely characterized by Angel et al. (1999b) and Kunz et al. (2000). In order to correlate the monoclinic to monoclinic phase transition as well as a possible monoclinic to triclinic phase transition (Kunz, pers. communication, chapter 1.1) with structural changes, diffracted intensities on either side of the phase transitions were measured at 1 bar, 5.08(2) GPa, 6.99(2) GPa, 9.70(2) GPa, 10.20(3) GPa and 10.4(2) GPa. The structure refinements reveal the following patterns:
The refinement results for the titanite structure at room pressure agree with previous results from powder and single-crystal refinements. The most noticeable feature in titanite is the off-centering of the Ti atom from the middle of the octahedron. In our study this off-centering could be refined (Table 4b Appendix B) and lies within the values described in literature (e.g. Taylor & Brown 1976, Kunz et al. 1996, Bismayer et al. 1999). The angle of 141.5(4)° between Ti - O1 - Ti confirms with the reports by these authors. Only small differences can be detected between our study and the study of Kunz et al. (1996) with a smaller O3 – Ti – O1 angle of 90.2° compared to 93° (Kunz et al. 1996). All other angles and bond lengths of the different polyhedra correspond to the data in the literature.

The relative position of the Ca atoms is again best described in terms of cation-cation distances (Table 6b Appendix B) as previously illustrated for malayaite. The interatomic distances between the Ca atom and its five surrounding Si atoms display an asymmetric vicinity. The distance between the Ca atom to the Si2 atom (Fig. 21) is with 3.759 Å the longest distance within this unequal surrounding area, the shortest distance is the Ca – Si4 with 3.311 Å.

The high symmetry A2/a phase is reached by a symmetrization of the titanium environment. The driving force for the P21/a – A2/a transition is the movement of the Ti atom into the middle of the octahedra and the formation of equal distances (1.842(4) Å) between the Ti and O1 atoms (Table 4b Appendix B). Within the A2/a phase previous experiments on titanite based on Rietveld refinements of high-pressure powder data suggest a straightening of the Ti-O1-Ti angle, whereas the O1-Ti-O3 angle does not vary significantly (Kunz et al. 1996, Kunz et al. 2000). This straightening of the octahedral chains and the subsequent movements of the SiO4 tetrahedra were not observed in our study neither for malayaite nor for titanite. In contrast to the observations of Kunz et al. (1996), we observed a decrease in the angle between Ti – O1 – Ti from 141.5(4) to 137.7(4) between 1 bar and 9.70 GPa (Table 4b Appendix B). The O3 - Ti - O1 angle opens up about 3 degrees so that the internal distortion slightly increases as the octahedra are moved closer together with pressure along [100]. The average <Ti-O> distance decreases as expected. The major contribution to the Ti - O bond distance decrease is the centering of the Ti atoms in the high-symmetry phase, whereas the Ti...
– O2 and Ti –O3 bond length remain constant. The relatively small movements in the A2/a phase indicate that the TiO6 octahedron acts as rigid unit within the structure. We suspect the difference in the pressure behavior for the TiO6 octahedron to the data reported by Kunz et al. (2000) to be due to the limited accuracy of the O-positions as determined from powder data, especially in the presence of strong scatterers such as Ca or Ti.

The symmetrization also affects the cation – cation surrounding: four TiO6 octahedra parallel [100] built an even rhombus akin to malayaite (Fig. 19). The TiO6 – TiO6 distance are equally compressed from 5.39Å at 5.08(2) GPa to 5.35Å at 9.70(2) GPa (Table 5b Appendix B). Alongside the centering of the Ti-atom the largest modification from the P21/a to the A2/a phase is the decrease in distance between Ca and Si2. As described for malayaite the Ca occupies a cavity within the TiO6-SiO4 framework. In the a-c plane, the TiO6 – SiO4 framework defines the size and geometry of this cavity just akin to malayaite. Between the P21/a and A2/a phase the interatomic Ca – Si distances in titanite change in so far as the respective opposing distances adopt the same value (Ca-Si1 = Ca-Si3, Ca-Si2 = Ca-Si4, Fig 21 and Table 6b Appendix B). Especially the distance between Ca and Si2 decreases from 3.759Å at 1 bar down to 3.471Å at 5.08(2) GPa. This declining trend continues up to 9.70(2) GPa where the distances between the Ca and the Si atoms reach 3.441Å and 3.426Å, respectively. The <Si-O> bond length remains nearly constant within the monoclinic phase (Table 4b Appendix B).

The reduction in polyhedral volume is strongest in the CaO7 polyhedra with 7.4% between 1 bar and 9.70(2) GPa and shows that it is the softest unit in the structure as expected. As expected the SiO4 tetrahedra behave rigidly and reduce their volume by only 1.57% for the same pressure range. Remarkably, in all polyhedra the highest reduction in volume is observed across the phase transition, whereas the volume reduction in the A/2a phase is slowed down.

The results presented in this chapter shall only be considered as trends of the structural evolution. The data refinement is already influenced by the relatively small amount of accessible reflections available for low triclinic symmetry. Additionally, the possible freezing of the pressure medium around 10.4 GPa might have affected the sample resulting in weak intensities of the reflections and large FWHM (0.5° in contrast to 0.05° at room conditions).
At 10.4 GPa some reflections showed double peaks so that a pressure induced twinning cannot be excluded. The occurrence of pressure twins for titanite has been mentioned by Klockmann (1978) and will be discussed later on in chapter 4.6.

**Figure 22**: Evolution of the $\alpha$ (squares) and $\gamma$ angle (diamonds) as a function of pressure between 9.6 and 10.6 GPa. Full symbols mark the angle before the phase transition, open symbols denote the angle after the phase transition.
The interatomic Ca - Si distances in titanite decrease approximately parallel [100] towards Si2 (Fig. 23, Table 6b Appendix B). No polymerization of CaO₈ sheets could be observed, although an additional oxygen O2 converges the coordination sphere of the Ca atom. The bond length within the CaO₇ polyhedra decreases quite rapidly under pressure as already observed in A2/a titanite by Kunz et al. (1996), so that the coordination sphere of the Ca atom is equally decreased. Therefore, the formation of a new Ca – O2 bond does not occur around 10 GPa, but it might appear at even higher pressures.
The Ca potential, which exhibits an increased displacement along [100] (e.g. Ghose et al. 1991, Groat et al. 1996, Kunz et al. 1999) seems to behave similarly to the Ca potential in malayaite. Here, the potential changed from the flat symmetric potential at ambient conditions into an asymmetric potential in the triclinic phase at high pressure (Fig. 24).

![Figure 24: Schematic sketch of possible potential energy curves of the Ca atom parallel [100] in (a) the monoclinic and (b) the triclinic phase. Note that the large displacement parameter parallel a at ambient conditions can be explained by either a dynamic or a static disorder expressing either a flat potential well or a multiple-minima energy curve.](image)

After the A2/a - A1 phase transition the even rhombus formed by the TiO$_6$ octahedral chains parallel [100] is altered into an uneven rhombus (Fig. 19, Table 5b Appendix B). The distances of the rhombus between the TiO$_6$ chains in the triclinic phase indicate a compression more strongly parallel [011] than parallel [011]. The chain-linking SiO$_4$ tetrahedra are not affected since the constant internal tetrahedra angles as well as the almost constant <Si – O> distances indicate no distortion of the SiO$_4$ tetrahedra up to 10.20(3) GPa.

4.2 Comparison and discussion of malayaite with titanite under non-ambient conditions

Comparing malayaite under high pressure with titanite under high pressure reveals some differences in the structural evolution. Malayaite does not exhibit a P2$_1$/a structure like titanite. This is due to the fact that the Ti$^{4+}$ cation in titanite is a d$^0$ transition metal ion and has therefore a different electron configuration than the Sn$^{4+}$ atom. As already explained in the
introduction the off-centering of the Ti atom is a consequence of this configuration. Therefore, malayaite and titanite can only be compared in the A2/a and rudimentarily in the A1 phase.

In the A2/a phase the behavior of titanite and malayaite is quite similar. The rhombi built by the SnO6 and TiO6 octahedra, respectively, and hence the adjacent octahedral chains are compressed into the preferred direction along [011]. Although the SiO4 tetrahedra behave as rigid unit in titanite as expected and act unusually softly in malayaite, the Sn/TiO6 – SiO4 framework distortion leads to a change of the Ca - Si environment in malayaite as well as in titanite. In both crystals the movement of the Ca atom towards the Si2 atom can be clearly seen. The resulting formation of CaO8 polyhedra sheets in the triclinic high-pressure phase occurs only in malayaite but should also be obtained in titanite at higher pressures as the O2 atoms seem to draw near the coordination sphere of the Ca atom.

Interestingly, the phase transitions from A2/a to A1 in malayaite and titanite do not occur at the same pressure. Although malayaite is more compressible than titanite (see chapter 4.4) the monoclinic – triclinic phase transition takes place at much lower pressures than in the relatively rigid titanite.

It is tempting to explain the differences in the macroscopic bulk modulus with the polyhedral behavior within the structure. However, we do not find any significant correlation between the changes in polyhedral volume and the evolution of the unit cell volume under pressure as expressed by the bulk modulus (Fig. 26). There are two possible explanations: (a) the volume reduction is achieved only by tilting and twisting of the semi-rigid structural units. Since the topology of titanite and malayaite cannot distort only by rigid rotation of the octahedra and tetrahedra (Hammonds et al. 1998) some internal distortion is required. Our data indicate that this internal distortion is mostly accommodated by an internal twisting of tetrahedra. (b) Our structural data collections at high-pressure may have to be interpreted with care due to possible limited accuracy of the positions of oxygen atoms in the presence of heavy scatters such as Ca and Ti also for single-crystal data at high-pressure.

Nevertheless, the TiO6 octahedra are able to buffer some of the pressure-imposed volume reduction by moving the Ti atoms into the center of the octahedron. Further on, with the adoption of the high-symmetry A2/a phase at 4 GPa titanite reacts similarly to malayaite under pressure. The second phase transition in titanite occurs after the crystal is pressurized by an additional 5.5 GPa after adopting A2/a symmetry. This roughly coincides with the behavior of malayaite which reduces its symmetry after 5 GPa.
Taking all these facts into account one can conclude that the Ti atom with its smaller size and its off-centering permits an increased compressibility over a larger pressure range and is therefore the reason for the monoclinic – triclinic phase transition to occur at higher pressure. In malayaite the larger and already centered Sn atom prevents such a buffering effect and thus the phase transition in malayaite takes place at lower pressures than in titanite.

4.2.1 Comparing the behavior of malayaite under pressure with other titanite-like structures

Troitzsch & Ellis (1999) report strongly distorted SiO₄ tetrahedra at ambient conditions for the CaTiOSiO₄ - CaAlFSiO₄ series. CaAlFSiO₄ is an Al - F analog to A2/a titanite. The Si - O2 bonds are shortened, Si - O3 bonds are elongated and the O2 – Si - O2 angle at 101.4° is very small. The authors explain this distortion with an improvement of the bond-valence sum of all tetrahedral atoms by an off-centering of the Si atom. Although the distortion of the tetrahedra is less pronounced in malayaite, it seems that in this structure type deviations from the ideal bond lengths and angles of SiO₄ tetrahedra are not so exceptional in order to balance external strain imposed either by chemical exchange or non-ambient conditions.

The montebrasite-amblygonite series Li[Al(PO₄)OH] – Li[Al(PO₄)F] is topologically identical to the malayaite structure (Groat et al. 1990). Interestingly, these are the only known naturally occurring minerals with the titanite structure-type crystallizing in triclinic structure. Groat et al. (1990) report them as triclinic C1. The transformation matrix

\[
\begin{pmatrix}
0 & 0 & 1 \\
0 & 1 & 0 \\
1 & 0 & 0
\end{pmatrix}
\]

reveals the identity of this structure with the triclinic high-pressure malayaite structure. The <P-O> distance in amblygonite – montebrasite remains constant across the series, but the angles deviate with increasing F/F + OH value. The PO₄ tetrahedra are flattened with increasing OH value similar to the SiO₄ tetrahedra in malayaite upon increasing pressure. Comparable to triclinic malayaite, the distances between the octahedral chains are different in distinct directions. These differences become more pronounced upon increasing OH content. This seems to indicate that chemically imposed structural strain has a similar effect on this structure type as pressure induced strain.

The structure of CaGe₂O₅ can be correlated with the high-temperature structure of titanite (Aust et al. 1976) and therefore also to malayaite. Here, the Ti and Si atoms are replaced by the larger Ge atom, which reduces the symmetry at ambient conditions to P1. At T > 600°C CaGe₂O₅ adopts the monoclinic space-group C2/c. Interestingly, the bond length of one
oxygen atom to the cations (Ca – O2 and Ge[6] – O2) seems to be shortened in the low symmetry as well as in the high symmetry phase leading to irregular, neighboring GeO6 octahedra.

Angel et al. (1996) describe a triclinic phase for CaSi2O5. This material contains 4-, 5- and 6-fold coordinated silicon and thus is distinctly different from the triclinic malayaite high-pressure phase. However, its structure type is very similar to the aristotype of malayaite. This relationship is confirmed by a high-pressure phase transition from triclinic to monoclinic CaSi2O5, where the A2/a structure of malayaite is adopted (Angel, 1997a).

4.3 Compressibility of malayaite and titanite

4.3.1. Malayaite

So far the compressional behavior of malayaite has neither been investigated by powder nor single crystal experiments. In this study single crystal malayaite has been pressurized with the ETH Diamond Anvil Cell from room pressure up to 7.394(5) GPa. The relative axis compressibility showed that the b axis is the least compressible axis in malayaite (Fig. 25) whereas the c axis is the softest axis in this system. No discontinuity was observed in the pressure dependence of axes and volume and the phase transition at P_c = 4.87(8) GPa is fully reversible. However, we observed a conspicuous, reproducible change in slope in the evolution of the $\alpha$ and $\gamma$ angle as a function of pressure within the triclinic phase around ~5.8 GPa. The bulk modulus of malayaite was determined by fitting a 3rd order Birch-Murnaghan equation of state after equation (8) to the $P - V$ data of the monoclinic phase. Least squares fits yield $V_0 = 389.68(3)Å^3$, $K_0 = 121(1)$ GPa and $K' = 4.2(5)$ for data with $P < P_c$ and $V_0 = 390.3(1) Å^3$, $K_0 = 118.3(7)$ GPa, $K' = 4$ (fixed) for data with $P > P_c$. This implies a softening of the structure under high-pressure, which is impossible from a thermodynamic point of view. As the difference of the fitted compressibility values is less than two standard deviations we conclude that the resolution of our data does not allow to detect any difference in the elastic properties between the monoclinic and triclinic phase. We therefore applied one single EoS to the full pressure range from room pressure to 7.3 GPa. Fitting a 3rd order Birch-Murnaghan equation of state to these data yields the following values: $V_0 = 389.64(3)Å^3$, $K_0 = 121.6(7)$ GPa and $K' = 4.6(2)$. $K_0$ of A2/a malayaite is smaller than $K_0$ of titanite (121(1) GPa vs. 131.4(7) GPa), which means, that malayaite is easier to compress than titanite (Table 5). Due to the above-mentioned kink in the $\alpha$ and $\gamma$ angles at 5.8 GPa we aimed to fit bulk and axial compressibilities as well as angle-polynomials separately to data sets measured above
and below 5.8 GPa. No significant difference was obtained for the bulk or axial values, whereas the observed angular kink is clearly reflected in the fitted polynomial for the angles (Table 7 Appendix B).

**Figure 25:** Normalized unit cell axes of malayaite and titanite as a function of pressure.

### 4.3.2 Titanite

The Equation of State of titanite has been published by Angel et al. (1999b) with a 2\(^{nd}\) order EoS with \(V_0 = 367.7(1) \text{ Å}^3\) and \(K_0 = 131.4(7)\) GPa calculated for powder samples and 6 data points between 3.58 and 7.61 GPa. In our study the 2\(^{nd}\) order EoS for the monoclinic A2/a phase yield \(V_0 = 368.76(4) \text{ Å}^3\) and \(K_0 = 129.3(4)\) GPa calculated from 19 data points between 3.966(6) GPa and 9.902(9) GPa. Furthermore, we could determine the 3\(^{rd}\) order Equation of State after equation (8) which results in \(V_0 = 368.750(9) \text{ Å}^3\), \(K_0 = 126.87(8)\) GPa and \(K' = 4.77(4)\). The relative axis progression shows that the b - axis is the stiffest axis in titanite as already shown by Angel et al. (1999b).
4.4 Comparison and discussion of the compressional behavior of malayaite and titanite

Although titanite and malayaite are closely related in their structure, some differences in the compressional behavior can be seen. In the A2/a phase the bulk modulus $K_0$ of malayaite is smaller than the bulk modulus $K_0$ in the same phase of titanite (119.29(7) GPa vs. 126.87(7) GPa), which means that malayaite is easier to compress than titanite. The relative volume change as a function of pressure shows that the unit cell volume of malayaite and titanite decrease to an equal relative amount (Fig. 26) as discussed in chapter 4.2. The comparison of the axial behavior shows that the $a$ and $c$ axis in titanite are almost similar in their compressional behavior as they decrease alike. Interestingly, the $a$ axis in malayaite is stiffer than the $a$ axis in titanite. This observation can only be explained by the different chemical composition of the crystals and the resulting structural differences. Under pressure the off-centering is lost as the Ti atom moves into the middle of the octahedra and facilitates a more regular compression of the $a$ axis. As the Sn atom is already positioned in the middle of the octahedra such a compensation is prevented and the $a$ axis in malayaite behaves more stiffly. The $c$ axis in malayaite is more compressible than the $c$ axis in titanite. The reason for this is not understood.

Viewed over the whole pressure range it is noteworthy that titanite reduces most of its TiO$_6$ octahedra volume in the P2$_1$/a phase where the Ti atom can compensate increased overbonding by moving into the center of the octahedron (Brown, 1992). The CaO$_7$ polyhedra volume in malayaite (20.75Å$^3$) is larger than the CaO$_7$ polyhedra volume in titanite (19.82Å$^3$). The change of CaO$_7$ volume in both malayaite and titanite is the largest change as it is the softest unit in the system. In malayaite the relatively soft behavior of the [SiO$_4$]$^4-$ complex anion relative to the other structural units shown in Table 4a Appendix B is unusual and surprising. But as already discussed in chapter 4.2.1 for CaAlFSiO$_5$ the SiO$_4$ tetrahedra show strong distortions. This may be a feature of structures, where no collective rigid-unit modes (Hamrnods et al. 1998) are possible.

Summarizing it can be said, that the softer behavior of malayaite in the A2/a phase is indicated by a smaller $K_0$ and can be explained by the higher flexibility of the Sn-Si framework. This, in turn is the consequence of the large volume of the SnO$_6$ octahedra since they define the difference in size of the framework.
4.5. Strain calculations

The calculations of the spontaneous strains $e_{ij}$ and the volume strain $V_s$ from our experiments followed the equations (11) to (19) and (23) given by Carpenter et al. (1998) for monoclinic to monoclinic and monoclinic to triclinic phase transitions. The determination of the thermodynamic nature of the phase transitions types was done by the calculation of the critical exponent $\beta$ after the description given in chapter 2.4.

4.5.1 Malayaite

In malayaite a phase transition from monoclinic to triclinic was found. Following the notation of Salje (1993a) a change of the monoclinic point-group 2/m into triclinic $\bar{1}$ corresponds to the active representation $B_g$. This means that only the symmetry-breaking strains $e_4$ and $e_6$ (Voigt notation, $e_4 = 2e_{23}$ and $e_6 = 2e_{12}$) are allowed for this transition, yet no volume strain $V_s$. From figure 28 one can see that only these two strains exist as a function of pressure in malayaite. The strains start to deviate at 5 GPa from zero to $-0.0096$ and $0.0037$ at 7.38 GPa, respectively, and follow the behavior of the $\alpha$ and $\gamma$ angles (Fig. 18) with a kink in the
evolution at around 5.8 GPa. The volume strain \( V_s \) is zero within the limits of measurement accuracy. Therefore the transition shows only proper symmetry-breaking strains. The only noticeable strains are the ones including the angles \( \alpha \) and \( \gamma \) as well as the \( a \) and \( c \) axes. The character of the transition is a shear movement of the cell. To determine the direction of the shears in the unit cell the orientation of the strain tensor representation quadric was calculated. The representation quadric is a 2D-circle oriented subparallel (19º) to (100).

To determine the pressure dependency of the order parameter \( Q \) the coupling between the order parameter \( Q \) and the measurable spontaneous strains \( e_{ij} \) had to be identified. Carpenter et al. (1998) summarized a scheme by which different kinds of strains \( e_{ij} \) and their coupling with the order parameter \( Q \) can be sorted by their behavior under non-ambient conditions. The lowest symmetry allowed coupling is the bilinear coupling between strains and order parameter with \( e_{ij} \propto Q \) and \( V \approx 0 \). Since only \( e_4 \) and \( e_6 \) are present there has to be a linear relation between \( e_6 \approx \cos \gamma \approx Q \) and \( e_4 \approx -\cos \alpha \approx Q \) or in other words, there has to be a linear relationship between \( e_{12} \) and \( e_{23} \) for this kind of coupling between spontaneous strain and order parameter. Figure 27 shows this linear relationship between the two shear strains.

![Figure 27: Relation between \(-\cos \alpha\) and \(\cos \gamma\) calculated for pressures from 4.99 GPa to 7.33 GPa.](image)
Following the explanation in chapter 2.4, there are three possible types of phase transition. A first order transition can be excluded as there is no discontinuity in the $e_{12}$ and $e_{23}$ strain behavior at the monoclinic - triclinic phase transition. For a second-order transition the critical exponent $\beta$ has to be 1/2 and therefore $Q \approx e_{ij} = (P - P_c)^{1/2}$. For tricritical transitions $\beta$ equals 1/4 and therefore $Q \approx e_{ij} = (P - P_c)^{1/4}$.

In order to calculate the critical exponent $\beta$ the data above 5 GPa had to be divided into two separate areas because of the above-mentioned kink in the strains. The fit included data points between 4.9 and 5.77 GPa, the second area included all data points above 5.77 GPa and was not fitted as it seems to belong to a second phase transition. The fits for the spontaneous strains $e_{12}$ and the $e_{23}$ in the first area result both in a critical exponent $\beta = 0.4(1)$ with transition pressures of $P_c = 4.84(2)$ GPa and 4.87(8) GPa, respectively (Fig. 28). These results correspond to the observed pressure dependent change in the angles (Fig. 18).

The second pressure area above 5.77 GPa can be addressed as “5.8 GPa anomaly” because the evolution of the spontaneous strains indicates a triclinic to triclinic change of the structure. Therefore the strains above 5.8 GPa may not be calculated on the basis of the angle evolution below 5 GPa (monoclinic) but on the basis of the angle evolution between 5 and 5.77 GPa (triclinic). Following the notation of Salje (1993a) a change of the triclinic point-group $\bar{1}$ into triclinic $1$ corresponds to the group-theoretical active representation $A_g$. This kind of transition allows all non-symmetry breaking strains $e_{ij}$ and the volume strain $V_s$. After Carpenter et al. (1998) the lowest symmetry coupling in the $\bar{1}$-$1$ transition is linear quadratic: $e_i \propto Q^2$ with $V_s \neq 0$. But neither for the volume strain $V_s$ nor for the $e_{11}$, $e_{22}$ and $e_{33}$ strains a fit was possible to determine a noticeable strain. Only the $e_{12}$ and $e_{23}$ strains continue their trend with a diminished evolution. This implies that spontaneous strains other than $e_4$ and $e_6$ at this isosymmetric anomaly are very small. A thermodynamic characterization of this anomaly based on strain analysis is thus not possible with the available data. In conclusion more data is necessary from both structural and thermodynamic measurements for a more precise characterization of the isosymmetric phase transition.

Summing up, the phase transition in malayaite at 5 GPa from monoclinic $A2/a$ to triclinic $A\bar{1}$ could be identified as second-order with a possible second isosymmetric phase transition at pressures above 5.77 GPa. It is tempting to speculate from the structural data described in
chapter 4.1.1 that the second isosymmetric phase transition above 5.77 GPa might coincide with the polymerization of the CaO$_8$ polyhedra. As we have only structural information at 5.77 GPa and 7.3 GPa further detailed structure analysis in the area of interest would reveal such a behavior.

**Figure 28:** (a) Variation of the strains $e_{12}$ (triangles) and $e_{23}$ (circles) as a function of pressure. Note the kink in the evolution around 5.8 GPa, which is in accordance with the angular evolution under pressure. (b) Fit of the critical exponent $\beta$ for both $e_{12}$ and $e_{23}$ in the triclinic phase for the pressure area between 5 and 5.77 GPa 5.8.
4.5.2 Titanite

The phase transition in titanite around 4 GPa does not change the point-group 2/m and thus correspond to the identity representation $A_u$. Hence, only non-symmetry breaking strains and volume strain $V_s = e_{11} + e_{22} + e_{33}$ are allowed. The lowest symmetry allowed coupling between strain and order parameter is linear-quadratic: $e_i \approx Q^2$ with $V_s \neq 0$. The volume strain $V_s$ should therefore be proportional to $Q^2$ and thus $V_s \approx (P_c - P)^{2b}$. The intensities of reflections forbidden in the high-symmetry phase are proportional to the squared order parameter $I \approx Q^2$ and would directly reflect the behavior of the order parameter (Ghose et al. 1991, Angel et al. 1999b). In this study only one data point in the low symmetry $P2_1/a$ phase was measured and the intensity evolution could not be followed. The assumptions given above, however, can be accepted for our data as well.

We observe only significant values for the non-symmetry breaking strain $e_{11}$ and the volume strain (Fig. 29). The change of the low symmetry phase $P2_1/a$ to the high symmetry phase $A2/a$ is reflected in the deviation of these strains from zero between 1 bar and 4 GPa. This has also been stated by Angel et al. (1999b) in their study of high-pressure titanite. The $e_{11}$ strain is the tensile strain affected most by pressure, the other tensile strains $e_{22}$ and $e_{33}$ deviate unnoticeable from the zero line. As already suggested by Kunz et al. (2000) and Angel et al. (1999b) the dilation of the a-axis by the Ti off-centering in the $P2_1/a$ phase is the reason for the $e_{11}$ strain to be the most dominant strain in titanite under high pressure. Angel et al. (1999b) have observed a similar evolution of spontaneous strains and volume strain with titanite high-pressure powder experiments. The spontaneous strains and the volume strain are shown in figures 29 and 30 in comparison with the strains calculated after Angel et al. (1999b) for their high-pressure powder experiment. The trend of the strains $e_{11}$ and $V_s$ of our study are in good agreement with the strains given by Angel et al. (1999b).

Angel et al. (1999b) tested two different critical exponents ($\beta = 1/2$ and $1/4$) for volume and $e_{11}$ strain for a fit of 8 data points, but both fits yield transition pressures higher than expected from the disappearance of the above mentioned superlattice reflections below 3.58 GPa. They show that a free refinement of the critical exponent results in $\beta = 0.13$ with a transition pressure of 3.4 GPa. In our study 14 data points could be fitted between 1 bar and 4 GPa (Fig. 29 and 30). The strain evolution of our data indicate a phase transition at increased pressures compared to Angel et al. (1999b) which was verified by the fit of the critical exponent. Free refinement of the critical exponent for our data resulted in $\beta = 0.46(3)$ and a transition
pressure $P_c = 4.3(2)$ GPa. In figure 30 the different fits for $V_s$ are shown. Since in this study the critical exponent is close to 0.5 we suggest a second-order transition of the $P2_1/a$ to $A2/a$ phase.

As previously mentioned, the spontaneous strain $e_{11}$ is the most significant one of the symmetry-allowed strains. Therefore, the coupling of $e_{11}$ with the order parameter follows the coupling of the volume strain and shows a linear quadratic coupling. The free refinement of the critical exponent for $e_{11}$ indicates a second-order transition with $\beta = 0.5(4)$ and $P_c = 4.4(4)$ GPa. This is in good accordance with the results received by calculations of the volume strain $V_s$.

Summing up, the $P2_1/a - A2/a$ phase transition in titanite could be identified as second-order transition with a transition pressure $P_c = 4.4$ GPa as concluded from free refinement of the critical exponents of the volume strain $V_s$ and the spontaneous strain $e_{11}$. The differences to the results reported by Angel et al. (1999b) are most likely due to the insufficiency of the powder data to determine the phase transition satisfactorily. In our study almost twice as much data points could be measured and therefore the accuracy of the fits was improved. Furthermore, the disappearance of forbidden reflections in powder data shows only the lower detection boundary, as the weak peaks might not be identified in the higher background.
Figure 29: (a) Variation with pressure of the spontaneous strains $e_{11}$ (full circles), $e_{12}$ (triangles) and $e_{23}$ (squares) in comparison with the $e_{11}$ strain (open circles) given by Angel et al. (1999b). (b) magnification of the pressure area from 1 bar to 6 GPa. The solid line represents the fits for $e_{11}$ of the critical exponent $\beta = 1/2$, the dashed line represents the fits for $e_{11}$ of the critical exponent $\beta = 1/4$. (c) magnification of the pressure area from 9.6 GPa to 10.6 GPa, the symmetry-breaking strain $e_{12}$ (triangles) and $e_{23}$ (squares) deviate from the zero line above 10 GPa.
Figure 30: (a) Variation of the volume strain $V_s$ (triangles) with pressure in comparison to the volume strain (open circles) given by Angel et al. (1999b). (b) Magnification of the pressure area from 1 bar to 6 GPa. The solid line represents the fits for $V_s$ of the critical exponent $\beta = 1/2$, the dashed line represents the fits for $V_s$ with the critical exponent $\beta = 1/4$.

As previously mentioned in chapter 4.1.2 the second phase transition in titanite from $A2/a$ to $\bar{A}1$ is indicated by the change of the $\alpha$ and $\gamma$ angles. The shear strains $e_{12}$ and $e_{23}$ should therefore follow this change in a deviation from the zero line around 10 GPa. These strains in fact deviate from zero starting at 10.23 GPa as presented in figure 30c. But for an adequate fit
of the critical exponent more than the available two data points in the triclinic phase are necessary. Hence only a prediction can be made on the basis of the results of the previously described monoclinic to triclinic transition and order coupling for malayaite. As described in the case of malayaite, the only symmetry-allowed strains are $e_4$ and $e_6$, which are also observed in titanite at 10.23 GPa. Whether the phase transition is first-order, second-order or tricritical has to be demonstrated by additional experiments above 10.5 GPa. By inference from the results of malayaite, however, one could assume that the $A2/a - A1$ phase transition in titanite might as well be second-order with a critical exponent $\beta$ around 0.5.

4.6 Comparison and discussion of the strains behavior of malayaite and titanite

The driving forces of the transitions are different in malayaite and titanite as shown in chapter 4.1 and thus a comparison between the phase transitions is not possible. In contrast to titanite malayaite does not exhibit any monoclinic – monoclinic transition under high-pressure. Unfortunately, the $A2/a - A1$ phase transition in titanite occurs in a pressure region, where the pressure medium is close to freezing. Hence, only trends of the spontaneous strains and volume strains can be taken into consideration. As described above, these strain trends indicate a possible transition with the same characteristics as in malayaite. Interestingly, the strains $e_{12}$ and $e_{23}$ in titanite are different in magnitude from the $e_{12}$ and $e_{23}$ in malayaite. The $e_{12}$ shear strain in titanite deviates largely from zero at 10.4 GPa as the phase transition takes place (Fig. 30). However, these data need to be interpreted with care. As previously mentioned in chapter 4.1.2, we observe peak splitting of most reflections at pressures higher than 10.2 GPa. The magnitude of the splitting increases with increasing pressure and decreases upon pressure release. A possible explanations for this observation might be the following:

Twinning can be induced by mechanical stress as known for some minerals such as calcite or uranium. Klassen-Neklyudova (1964) described detwinning of materials if the force is applied in the reverse direction, in our case this would be the release of pressure. The existence of a pressure-induced twinning could have led to erroneous cell parameters resulting in increased standard deviations of the cell parameters. Also the spontaneous strain values are simultaneously disproportional increased by the twinning of the crystal. The detwinning process upon pressure release could explain the disappearance of the doubled peaks.
5. Conclusions

The investigations of single-crystal titanite $\text{CaTiOSiO}_4$ and malayaite $\text{CaSnOSiO}_4$ with isothermal high-pressure X-ray diffractometry show that the behavior of these two minerals under high-pressure is somewhat different.

The $P2_1/a - A2/a$ phase transition in titanite is driven by the symmetrization of the off-centered Ti atoms into the middle of the octahedra, which reconfirms published powder data results by Kunz et al. (1996) and Angel et al. (2000). Furthermore, with our compressibility data the thermodynamic nature of the phase transition could be identified as being of second-order with a transition pressure $P_c = 4.3(2)$ GPa. A second phase transition from monoclinic $A2/a$ to triclinic $A\overline{1}$ takes place at around 10.2 GPa and the occurrence of ferroelastic switching (Salje 1993a) in titanite above 10 GPa might be possible.

The first high-pressure data of both compressibility and structural data for malayaite reveal a so far unknown phase transition at 5 GPa from monoclinic $A2/a$ to triclinic $A\overline{1}$. The phase transition is identified as a second-order phase transition. This transition is controlled by a twisting of the relatively rigid framework, in which the SiO$_4$ tetrahedra seem to experience a most pronounced internal rotation. A possible second isosymmetric phase transition occurs at pressures above 5.77 GPa regarded to as 5.8 GPa anomaly. This transition might coincide with the polymerization of CaO$_8$ polyhedra as observed at 7.3 GPa.

The comparison between titanite and malayaite shows that malayaite is easier to compress than titanite as indicated by a smaller bulk modulus. These differences cannot be seen directly in the polyhedral volumes. Therefore, relative softness is due rather to a more flexible framework, probably caused by the larger size of the SnO$_6$ octahedra compared to the TiO$_6$ octahedra.

The structural evolution of malayaite and titanite in the $A2/a$ phase is quite similar but, remarkably, the transition pressure from monoclinic $A2/a$ to triclinic $A\overline{1}$ of the two crystals is different. In malayaite the transition takes place at a much lower pressure than in titanite. The reason for this behavior is found in the structural differences between malayaite and titanite as well as the different cation size of the two elements Sn$^{4+}$ and Ti$^{4+}$. The Ti atom and its off-centering in the $P2_1/a$ phase enables an increased compressibility over a larger pressure range than in malayaite, where the Sn atom prevents such a buffering effect as it is already centered. Interestingly, the $A2/a$ phase remains stable in both crystals over a pressure range of approximately 5 GPa.
The aim of this thesis was to examine what role the octahedral framework atom plays under non-ambient conditions. By taking all observations into account one can conclude that within the examined pressure range, the structural differences between malayaite and titanite are controlled by the size and the electronic configuration of the octahedral cation.

6. Outlook

This study has suggested a number of future projects. The most important of these are discussed in this section.

(1) To extend the knowledge about the behavior of $\text{XYOZO}_4$ components titanite-related materials should be investigated under high-pressure. One possible crystal would be MnSi$_2$O$_4$, synthesized and described by Arlt et al. (1998) as titanite structure with space-group A2/a. Some single crystals were already quality checked for in-house high-pressure measurements but no data was collected up to now. Another possibility to obtain information about the influence of XO$_7$ polyhedra in these structures is to investigate the behavior of monoclinic P2$_1$/c NaTiOPO$_4$ (ICSD code 67538). Here, the Ca atom is replaced by the smaller Na atom and the XO$_7$ polyhedra might change its soft behavior under high-pressure.

(2) In malayaite the 5.8 GPa anomaly should be closely examined to determine the thermodynamical and structural driving forces for the proposed isosymmetric $\bar{1}$ - $\bar{1}$ phase transition. Therefore more intensity data must be collected and also calorimetric calculations after e.g. Hayward et al. (2000) should be done. The results of these measurements will help to understand more about the interplay between microscopic structural behavior under pressure (compressional behavior, tilting, etc.) and macroscopic thermodynamic properties (order parameter, spontaneous strain).

(3) Another interesting topic is the monoclinic – triclinic phase transition in titanite, which occurs around 10 GPa. Measurements of intensity data sets e.g. between 9.5 GPa and 13 GPa are capable of clarifying whether the observed monoclinic – triclinic phase transition around 10 GPa in titanite is due to a mechanism related to the A2/a – A1 phase transition in malayaite at 5 GPa. To avoid complications caused by non-hydrostatic twinning a pressure medium must be found that is still liquid at pressures higher than 10 GPa. Gases like helium (Bell & Mao, 1981) or xenon (Miletich et al. 2000) present an alternative to the 4:1 methanol:
ethanol mixture. These gases, however, are either impossible to load cryogenically due to their very low boiling point (-268.9°C for helium) or very expensive or both.

An alternative method is the calculation of the structure of titanite above 10 GPa using computational crystallography with the information gained by malayaite and the existing data of titanite at high-pressure. This is of particular interest if the search for an appropriate pressure medium fails. The result of these investigations will show to what extent the d⁰ transition metal Ti has an influence not only on the P2₁/a – A2/a but also on the A2/a - A1 transition.

(4) While titanite is well characterized by simultaneous variation of high-pressure and high-temperature (Kunz et al. 2000, Angel et al. 1999b), malayaite has only been investigated under high temperature (Meyer et al., 1998, Bismayer et al., 1999, Zhang et al.1999) or under high pressure (Rath et al. 2002). With this proposed experiment the structures and phase transitions of CaSnOSiO₄ as a function of combined pressure and temperature by means of powder diffraction using a heatable diamond anvil cell in combination with a 2-dimensional detector at the Swiss Norwegian Beamline SNBL, Grenoble, could be investigated. The p and T ranges are comparable to the ones in the titanite powder experiments and would also allow the extraction of P-V-T equations of state for this material. The DAC should be heated up from room temperature to 800 K and the pressure ought to be increased from room pressure up to 10 GPa. The aim of these experiments would be to elucidate the temperature behavior of the newly found high-pressure phases and to draw conclusions from these to a better understanding of the behavior of XYOZO₄ minerals on the whole and the driving force for physical anomalies in particular.

(5) Low temperature experiments on both titanite and malayaite could provide more information about the relationship between pressure-induced and temperature-induced effects on these two materials.

(6) The effect of a DC electric field as a function of temperature applied to a single-crystal titanite should be analyzed. The data has already been collected at ID15C, ESRF, Grenoble as described in chapter 3.5. If it could be shown that an electric DC field can influence titanite in so far as the Ti atoms are shifted cooperatively off-center parallel in all octahedral chains, a possible new non-linear optical material might be found.

(7) The measurement of resonance ultrasonic spectra (RUS) of titanite and maybe also malayaite could show the orientation of the elastic constants. This could provide new information about the independent elastic constants of the crystal as a function of temperature.
and frequency in order to compare these results with existing ones from high-temperature and high-pressure experiments or calculations. These experiments could be carried out with the in-house RUS apparatus if an appropriate single-crystal in a suitable size would be synthesized. Summarizing it can be said that if the experimental limits such as pressure medium or high background of the cell components are improved, the results of high-pressure single crystal experiments can contribute significantly to the understanding of crystal behavior under non–ambient conditions and furthermore improve the theoretical knowledge on physical and chemical aspects of phase transitions.
7. Literature


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8. Appendix

Appendix A: Synthesis protocols for single-crystal titanite

Appendix B: Details of the high-pressure experiments of malayaite and titanite

- Table 1a: Unit cell parameters of malayaite at various pressures
- Table 1b: Unit cell parameters of titanite at various pressures
- Table 2a: Structure refinement detail for malayaite
- Table 2b: Structure refinement detail for titanite
- Table 3a: Fractional atomic coordinates of malayaite
- Table 3b: Fractional atomic coordinates of titanite
- Table 4a: Selected interatomic distances (Å) and angles (°) for malayaite at 4 pressures
- Table 4b: Selected interatomic distances (Å) and angles (°) for titanite at 4 pressures
- Table 5a: Distances between Sn parallel <011> in malayaite
- Table 5b: Distances between Sn parallel <011> in titanite
- Table 6a: Distances between the Ca atom and its surrounding Si atoms in malayaite
- Table 6b: Distances between the Ca atom and its surrounding Si atoms in titanite
- Table 7: Comparison of equations of state between malayaite and titanite

Appendix C: Details of the high-pressure experiments of natural titanite

- Table 1: Unit cell parameters for natural titanite determined by Image Plate single-crystal analysis
- Figure 1: Unit cell parameters of natural titanite as a function of pressure
- Figure 2: Selected Image Plate pictures of natural titanite at 2.6 GPa
Appendix A

Robbins 9-1

Chemical composition
~ 54mg stoichiometric mixture of Ca(OH)$_2$, SiO$_2$, TiO$_2$ in Pt-crucible + PtRh-wire

Pressure & temperature/Synthesis time
Program Linn oven:
- 30 min to 1400°C – 50h down to 1000°C (8°C/h) – 5h at 1000°C – cooling to room temperature
- altogether 70h

Results

First inspection
- melt cake in the middle but a lot of smaller Xtals!
- translucent to green color
- partial defined habitus

STOE-powder
Grinded powder
- titanite lines, very slightly shifted
- 2 strong lines that are not from titanite
- maybe from wire? not directly from Pt or Rh

CAD 4 – single Xtal
Tit HT9
- relatively broad peaks, strong peaks
- 180 * 200 * ~50 μm
- monoclinic P
- a = 7.054 Å, b = 8.7170 Å, c = 6.553 Å, beta = 113.76°

Tit HT9_2
- low intensity
- 50 * 50 * 20 μm, too small
- monoclinic P
- a = 7.053 Å, b = 8.699 Å, c = 6.550 Å, beta = 113.82°

Tit HT9_3
- large xtal (visible to the naked eye), basis for smaller xtals
- strong peaks, very good FWHM
- Monoclinic P
- a = 7.052 Å, b = 8.710 Å, c = 6.552 Å, beta = 113.740°
SEM

Tit HT9_3
- contains only Ca, Ti and Si!

Huber
- smaller Xtals cut off Tit HT9_3 and loaded into DAC
- used for compressibility and intensity data sets

Special feature
## Hollabaugh 4-1

**Chemical composition**

1:1:1 Ca(OH)$_2$, SiO$_2$, TiO$_2$, ~ 40mg in platinum crucible

**Pressure & temperature/Synthesis time**

- Program Linn oven:
  - 30 min to 1412°C – 12 min at 1412°C – in 50h down to 1362°C (1°C/h) – 12 min at 1362°C – cooling to room temperature
  - altogether 50h 52min

**Results**

- First inspection
  - only melt cake, no Xtals

- STOE- powder
  - 

- CAD 4 – single Xtal
  - 

- SEM
  - 

- Special feature
  - 

# Hollabaugh 6-1

<table>
<thead>
<tr>
<th>Chemical composition</th>
<th>31 mol% Ca(OH)$_2$, SiO$_2$, TiO$_2$ + 17 wt% H$_2$O</th>
</tr>
</thead>
</table>
| Pressure & temperature/Synthesis time | Hydrothermal synthesis  
700°C, 2 kbar  
27 d |

## Results

### First inspection
- Capsule totally crumbled
- No water content
- White powder in flakes and yellowish powder
- No single Xtal

### STOE- powder
- Titanite lines, slightly shifted
- No complete reaction, too less water

### CAD 4 – single Xtal
- 

### SEM
- 

### Special feature
- 
**Hollabaugh 6-2**

<table>
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<th>Chemical composition</th>
<th>31 mol% Ca(OH)$_2$, SiO$_2$, TiO$_2$ + 17 wt% H$_2$O</th>
</tr>
</thead>
</table>
| Pressure & temperature/Synthesis time | Hydrothermal synthesis  
700°C, 2kbar  
13 d |

**Results**

**First inspection**
- 0.5mg lost because of hole in capsule
- no water
- white powder
- no single Xtals!

**STOE- powder**
- d-values show good agreement with titanite d-values of ICDS

**CAD 4 – single Xtal**
- 

**SEM**
- 

**Special features**
- Hole in capsule, water lost
Hollabaugh 6-3

Chemical composition
31 mol% Ca(OH)$_2$, SiO$_2$, TiO$_2$ + 17 wt% H$_2$O

Pressure & temperature/
Hydrothermal synthesis
700°C, 2 kbar

Synthesis time
41 d

Results

First inspection
- white powder
- big blue flakes – look like glass
- single Xtals → Tit_X5x
- white powder very hard, compact
- different blue colors from deep blue to light blue
- different sizes and shapes, plates, compact habitus

STOE- powder
(i) best correspondence with titanite d-values
(ii) CaCO$_3$ seems to be present
(iii) at small 2 values peaks from starting materials (~ 10%)

CAD 4 - single Xtal
Tit_X5.1 (lost)
- bad peaks
- twin or intergrowth?
- Glas more likely

SEM
Tit_X5.2
- No Ti present
- Na and Zn present besides Si and Ca

Special feature
- blue xtals described by Cerny (1972)
### Hollabaugh 6-4

<table>
<thead>
<tr>
<th>Chemical composition</th>
<th>31 mol% Ca(OH)$_2$, SiO$_2$, TiO$_2$ + 17 wt% H$_2$O + nucleii from synthetic titanite</th>
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<tbody>
<tr>
<td>Pressure &amp; temperature/</td>
<td>Hydrothermal synthesis</td>
</tr>
<tr>
<td>Synthesis time</td>
<td>700°C, 2 kbar</td>
</tr>
<tr>
<td></td>
<td>42 d</td>
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</tbody>
</table>

### Results

**First inspection**
- dark and white powder

**STOE- powder**
- divided in dark and white component
- **white**: large SiO$_2$-peak (up to 20%)
  - Titanite lines, unknown phase present
- dark: again SiO$_2$-peak, bit less pronounced than in white phase,
  - again Titanite lines more peaks of the unknown phase
- no single Xtls

**CAD 4 – single Xtal**
- 

**SEM**
- 

**Special feature**
- powder gets wet if grinded even without addition of fluid
Hollabaugh 6.5

<table>
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<tr>
<th>Chemical composition</th>
<th>31 mol% Ca(OH)$_2$, SiO$_2$, TiO$_2$ + 17 wt% H$_2$O (1mol% CsCl solution) + nuclei from synthetic titanite</th>
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<td>Hydrothermal synthesis 700°C, 2kbar 36 d</td>
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<td>Results</td>
<td></td>
</tr>
<tr>
<td>First inspection</td>
<td>- wet white powder, electrified - garnet or 1 twinned</td>
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<tr>
<td>STOE- powder</td>
<td>- clear titanite peaks - high background and SiO$_2$ peaks - unknown phase present</td>
</tr>
<tr>
<td>CAD 4 – single Xtal</td>
<td>-</td>
</tr>
<tr>
<td>SEM</td>
<td>-</td>
</tr>
<tr>
<td>Special feature</td>
<td>-</td>
</tr>
</tbody>
</table>
Hollabaugh 7a

### Chemical composition
31 mol% Ca(OH)$_2$, SiO$_2$, TiO$_2$ + 17 wt% H$_2$O -RbSO$_4$-(1%Lsg.)

### Pressure & temperature/
Hydrothermal synthesis
700°C, 2 kbar

### Synthesis time
40 d

### Results

#### First inspection
- dark grains in white powder
- amber colored grains under microscope
- elongated pentagonal
- between 50 and 150 µm
- intergrowth or twins?
- agglomerates with the white powder
- few colorless Xtals

#### STOE- powder
- 

#### CAD 4 – single Xtal
**Tit$_2$** (garnet)

- (iv) Too many reflections
- (v) Cubic!
- (vi) Unit cell: $a = 12.06$ Å, $b = 12.06$ Å, $c = 12.07$ Å
- (vii) $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 89.9^\circ$
- (viii) $V = 1756.94$ Å$^3$
- (ix) Sharp peaks
- (x) -Single crystal !!
- (xi) Ti- garnet ?

#### SEM
- Mn und Fe present besides Si, Ti and Ca

#### Special feature
**Schorlomite** $Ca_3(Fe,Ti)$_2[(Si,Ti)O$_4$]$_3$
- Unit cell and volume in good accordance
- Mn replaces Fe partly ?
**Takenouchi 12a**

**Chemical composition**

1:3:1 (Ca:Si:Ti) + 5 vol% H$_2$O-NaCO$_3$ solution.

**Pressure & temperature/ Synthesis time**

Hydrothermal synthesis

511°, 1 kbar

8 d

**Results**

**First inspection**

- no fluid
- white powder in large flakes
- yellow powder
- colorless Xtals grown on powder
- one blue Xtal (lost)
- one large light Xtal
- one dark Xtal →Tit$_3$
- other Xtals too small <100 μm, mostly around 20 – 50 μm

**STOE- powder**

Grenoble:

- Titanite powder, still rings from CaCO$_3$ and TiO$_2$
  - Synthese not completed

**CAD 4 – single Xtal**

**Tit$_3$**

- Large FWHM
- Orthorhombic C
- a = 10.52 Å, b = 10.52 Å, c = 8.58 Å, V = 950.83 Å$^3$

**SEM**

-  

**Special feature**

-
**Takenouchi 12b**

<table>
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<th>Chemical composition</th>
<th>1:3:1 (Ca:Si:Ti) + 2 vol% H₂O</th>
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<tbody>
<tr>
<td>Pressure &amp; temperature/ Synthesis time</td>
<td>Hydrothermal synthesis 700°C, 1kbar 10 d</td>
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</tbody>
</table>

**Results**

**First inspection**
- white powder
- yellowish powder under microscope
- many transparent Xtals in different sizes
- one transparent bar → Tit_X4
- many small Xtals ~ 50 μm

**STOE- powder**
- clear titanite lines, but contains a lot of starting materials (esp. CaCO₃)
- gets dark when grinded

**CAD 4 – single Xtal**

**Tit_X4**
- On the Huber diffractometer only 0kl reflections

**SEM**
- -

**Special feature**
- -
# Takenouchi 12b-2

<table>
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<tr>
<th>Chemical composition</th>
<th>1:3:1 (Ca:Si:Ti) + 2 vol% H₂O</th>
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<tbody>
<tr>
<td>Pressure &amp; temperature/ Synthesis time</td>
<td>Hydrothermal synthesis 700°C, 1kbar 12 d</td>
</tr>
</tbody>
</table>

## Results

**First inspection**
- just one big white nugget at the end of the crucible
- homogeneous powder, very wet

**STOE- powder**
- powder had to be dried before grinding
- still lines of starting components, but also lines from titanite

**CAD 4 - single Xtal**
- 

**SEM**
- 

**Special feature**
- starting compositions grinded with alcohol in Agate mortar dried at 80 C for 30 minutes before synthesis
**Chemical composition**

Stoichiometric mixture of Ca(OH)$_2$, SiO$_2$, TiO$_2$

**pressure & temperature/ Synthesis time**

- Program Linn oven:
  - 30 min to 1412°C – 12 min at 1412°C – in 50h down to 1362°C (1°C/h) – 12 min at 1362°C Grad – cooling to room temperature
  - altogether 50h 52min

**Results**

**First inspection**

- only melt cake, no single crystals

**STOE- powder**

- 

**CAD 4 -single Xtal**

- 

**SEM**

- 

**Special feature**

-
## Appendix B

### Table 1a: Unit cell parameters of malayaite CaSnOSiO$_4$ at various pressures

<table>
<thead>
<tr>
<th>P [GPa]</th>
<th>a [Å]</th>
<th>b [Å]</th>
<th>c [Å]</th>
<th>V [Å$^3$]</th>
<th>$\alpha$</th>
<th>$\beta$</th>
<th>$\gamma$</th>
<th>$N_{\text{refl}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0001$^*$</td>
<td>7.1529(5)</td>
<td>8.8901(5)</td>
<td>6.6667(5)</td>
<td>389.19(4)</td>
<td>90</td>
<td>113.359(4)</td>
<td>90</td>
<td>21</td>
</tr>
<tr>
<td>0.000(6)$^b$</td>
<td>7.1556(7)</td>
<td>8.897(1)</td>
<td>6.6697(8)</td>
<td>389.22(5)</td>
<td>90</td>
<td>113.352(8)</td>
<td>90</td>
<td>11</td>
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<tr>
<td>0.10(1)</td>
<td>7.1532(4)</td>
<td>8.8964(6)</td>
<td>6.666(3)</td>
<td>389.51(4)</td>
<td>90</td>
<td>113.348(4)</td>
<td>90</td>
<td>27</td>
</tr>
<tr>
<td>0.52(2)</td>
<td>7.1406(3)</td>
<td>8.8899(7)</td>
<td>6.6541(3)</td>
<td>387.96(4)</td>
<td>90</td>
<td>113.297(3)</td>
<td>90</td>
<td>30</td>
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<tr>
<td>0.645(7)</td>
<td>7.1400(4)</td>
<td>8.8907(6)</td>
<td>6.6517(3)</td>
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<td>90</td>
<td>113.287(4)</td>
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<tr>
<td>1.074(8)</td>
<td>7.1297(4)</td>
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<td>2.12(1)</td>
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<td>3.001(5)</td>
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<tr>
<td>3.987(5)</td>
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<td>4.505(4)$^*$</td>
<td>7.0498(4)</td>
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<td>90</td>
<td>112.916(4)</td>
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<td>Pressure (GPa)</td>
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<td>c</td>
<td>Alpha (deg)</td>
<td>Beta (deg)</td>
<td>Gamma (deg)</td>
<td>Volume (Å³)</td>
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**Note:**

Pressures are determined from unit-cell parameters from internal quartz standard after Angel et al. (1997b)

*a* = crystal in air  
*b* = crystal in DAC  
* = structural data have been collected at this pressure  
N_ref = number of reflections used for least square refinement of the samples unit-cell parameters
Table 1b: Unit cell parameters of titanite CaTiOSiO$_4$ at various pressures

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**Note:**

Pressures are determined from unit-cell parameters from internal quartz standard after Angel et al. (1997b)

\textsuperscript{a} = Crystal in air HT9\_3 (CAD4)

\textsuperscript{b} = Crystal in DAC without pressure transmitting fluid

\textsuperscript{c} = Crystal in DAC without pressure transmitting fluid, new loading with W gasket after experiment with cryogenic N\textsubscript{2} loading

\textsuperscript{*} : structural data have been collected at this pressure

\( N_{ref} \) = number of reflections used for least square refinement of the samples unit cell parameters
Table 2a: Structure refinement detail for malayaite CaSnOSiO$_4$

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<td>A2/$a$</td>
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Notes:
- $t_{\text{min}}$ and $t_{\text{max}}$ give the x-ray transmission percentage after its path through the cell and the sample
- $R_{\text{int}} = \Sigma |F_o|^2 - |F_c|^2 / \Sigma |F_o|^2$ ; $R_1 = \Sigma |F_o| - |F_c| / \Sigma |F_o|$
- GoF = $S = \{ \Sigma w(F_o)^2 - F_c^2 / n-p \}$ with $w =$ weights, $n =$ numbers of reflections and $p =$ total


Table 2b: Structure refinement detail for titanite CaTiOSiO₄

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<th>P [GPa]</th>
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Notes:
t_min and t_max give the x-ray transmission percentage after its path through the cell and the sample
R_int = \sum |F_o|^2 - |F_c|^2 / \sum |F_o|^2 ; R_1 = \sum |F_o| - |F_c| / \sum |F_o|
GoF = S = \sqrt{\sum [w(F_o^2 - F_c^2)]^2 / n-p} with w = weights, n = numbers of reflections and p = total number of parameters refined
Table 3a: Fractional atomic coordinates of malayaite CaSnSiO$_4$ at various pressures.

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Table 3b: Fractional atomic coordinates of titanite CaTiOSiO$_4$ at various pressures.

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10.4(2)

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Table 4a: Selected interatomic distances (Å) and angles (°) for malayaite CaSnOSiO₄ at 4 pressures

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<th>Pressure [GPa]</th>
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<th>4.238(7)</th>
<th>4.505(4)</th>
<th>5.769(6)</th>
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*Note: † the standard deviation of the average bond length is given in brackets*

*These values are calculated for CaO₈ polyhedra in triclinic structures.*
Table 4b: Selected interatomic distances (Å) and angles (°) for titanite CaTiOSiO$_4$ at 5 pressures

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<tr>
<th>Pressure [GPa]</th>
<th>0.000(4)</th>
<th>5.08(2)</th>
<th>6.99(2)</th>
<th>9.70(2)</th>
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Note: † the standard deviation of the average bond length is given in brackets

* These values are calculated for CaO₈ polyhedra in triclinic structures.
Table 5a: Distances between Sn atoms parallel <011> in malayaite. The numbers 1 – 4 refer to the labeling in Figure 19. Sn – Sn lists the distances within an octahedral chain. Note the stronger decrease parallel [011] (1 and 3) if compared to [011] (2 and 4).

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<tr>
<th>Pressure [GPa]</th>
<th>0.000(6)</th>
<th>4.238(7)</th>
<th>4.505(4)</th>
<th>5.769(6)</th>
<th>7.33(3)</th>
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<td>5.503 Å</td>
<td>5.485 Å</td>
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Table 5b: Distances between Ti atoms parallel <011> in titanite. The numbers 1 – 4 refer to the labeling in Figure 19. Ti – Ti lists the distances within an octahedral chain. Ti – Ti lists the distances within an octahedral chain.

<table>
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<th>Pressure [GPa]</th>
<th>0.000(4)</th>
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<td>1</td>
<td>5.436 Å</td>
<td>5.396 Å</td>
<td>5.376 Å</td>
<td>5.350 Å</td>
<td>5.350 Å</td>
<td>5.363 Å</td>
</tr>
<tr>
<td>2</td>
<td>5.436 Å</td>
<td>5.396 Å</td>
<td>5.376 Å</td>
<td>5.350 Å</td>
<td>5.351 Å</td>
<td>5.302 Å</td>
</tr>
<tr>
<td>3</td>
<td>5.436 Å</td>
<td>5.396 Å</td>
<td>5.376 Å</td>
<td>5.350 Å</td>
<td>5.350 Å</td>
<td>5.363 Å</td>
</tr>
<tr>
<td>4</td>
<td>5.436 Å</td>
<td>5.396 Å</td>
<td>5.376 Å</td>
<td>5.350 Å</td>
<td>5.351 Å</td>
<td>5.301 Å</td>
</tr>
</tbody>
</table>
Table 6a: Distances between the Ca atom and its surrounding Si atoms in malayaite. The numbers 1-4 refer to the Si-labeling in Figure 21. Note the large decrease of the distance to Si-2. This causes the O2-atom coordinated to Si-2 to come into the coordination sphere of Ca and thus form a CaO8 polyhedron.

<table>
<thead>
<tr>
<th>Pressure [GPa]</th>
<th>0.000(6)</th>
<th>4.238(7)</th>
<th>4.505(4)</th>
<th>5.769(6)</th>
<th>7.33(3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.609 Å</td>
<td>3.570 Å</td>
<td>3.561 Å</td>
<td>3.532 Å</td>
<td>3.484 Å</td>
</tr>
<tr>
<td>2</td>
<td>3.581 Å</td>
<td>3.538 Å</td>
<td>3.530 Å</td>
<td>3.490 Å</td>
<td>3.399 Å</td>
</tr>
<tr>
<td>3</td>
<td>3.609 Å</td>
<td>3.570 Å</td>
<td>3.560 Å</td>
<td>3.562 Å</td>
<td>3.594 Å</td>
</tr>
<tr>
<td>4</td>
<td>3.581 Å</td>
<td>3.538 Å</td>
<td>3.530 Å</td>
<td>3.543 Å</td>
<td>3.609 Å</td>
</tr>
</tbody>
</table>

Table 6b: Distances between the Ca atom and its surrounding Si atoms in titanite. The numbers 1-4 refer to the Si-labeling in Figure 21. Note the large decrease of the distance to Si-2. This causes the O2-atom coordinated to Si-2 to come into the coordination sphere of Ca and thus form a CaO8 polyhedron.

<table>
<thead>
<tr>
<th>Pressure [GPa]</th>
<th>0.000(4)</th>
<th>5.08(2)</th>
<th>6.99(2)</th>
<th>9.70(2)</th>
<th>10.20(2)</th>
<th>10.4(2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.559 Å</td>
<td>3.478 Å</td>
<td>3.459 Å</td>
<td>3.441 Å</td>
<td>3.451 Å</td>
<td>3.482 Å</td>
</tr>
<tr>
<td>2</td>
<td>3.759 Å</td>
<td>3.471 Å</td>
<td>3.451 Å</td>
<td>3.426 Å</td>
<td>3.422 Å</td>
<td>3.494 Å</td>
</tr>
<tr>
<td>3</td>
<td>3.496 Å</td>
<td>3.478 Å</td>
<td>3.459 Å</td>
<td>3.441 Å</td>
<td>3.433 Å</td>
<td>3.377 Å</td>
</tr>
<tr>
<td>4</td>
<td>3.311 Å</td>
<td>3.471 Å</td>
<td>3.451 Å</td>
<td>3.426 Å</td>
<td>3.426 Å</td>
<td>3.337 Å</td>
</tr>
</tbody>
</table>
Table 7: Comparison of equations of state between malayaite (CaSnOSiO₄) and titanite (CaTiOSiO₄). The axial compressibilities were fitted to the equation \( x = x_0 \ast (1 + 4P/K_0)^{-1/12} \), where \( x \) and \( x_0 \) denote the unit cell axes \( a, b \) and \( c \) at the measured and zero pressure, respectively. The monoclinic angle \( b \) was fitted to a second-degree polynomial. For the triclinic phase, only the \( \alpha \) and \( \gamma \) angles were fitted separately above and below 5.7 GPa.

<table>
<thead>
<tr>
<th></th>
<th>( K_0 ) (GPa)</th>
<th>( K' )</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Malayaite</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( A2/\alpha )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bulk compressibility</td>
<td>( V_0 = 389.68(3) \ \AA^3 )</td>
<td>121(1)</td>
</tr>
<tr>
<td>Axial compressibilities</td>
<td>( a_0 = 7.156(2) \ \AA )</td>
<td>93.0(5)</td>
</tr>
<tr>
<td></td>
<td>( b_0 = 8.8985(3) \ \AA )</td>
<td>226(3)</td>
</tr>
<tr>
<td></td>
<td>( c_0 = 6.6695(3) \ \AA )</td>
<td>79.3(4)</td>
</tr>
<tr>
<td>( \beta_0 = 113.361(2) – 0.122(3)P + 0.0037(1)P^2 )</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>A1</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bulk compressibility</td>
<td>( V_0 = 390.3(1)\ \AA^3 )</td>
<td>118.3(7)</td>
</tr>
<tr>
<td>Axial compressibilities</td>
<td>( a_0 = 7.154(1)\ \AA )</td>
<td>94.92(7)</td>
</tr>
<tr>
<td></td>
<td>( b_0 = 8.8985(1)\ \AA )</td>
<td>229.2(4)</td>
</tr>
<tr>
<td></td>
<td>( c_0 = 6.6697(1)\ \AA )</td>
<td>80.47(8)</td>
</tr>
<tr>
<td>( 5.2 – 5.76 \text{ GPa} )</td>
<td>( \alpha_0 = 90.001(5) + 0.23(6)\Delta P + 0.09(7)\Delta P^2 )</td>
<td>( \beta_0 = 112.896(4) – 0.08(1)\Delta P + 0.08(2)\Delta P^2 )</td>
</tr>
<tr>
<td>( 5.84 – 7.39 \text{ GPa} )</td>
<td>( \alpha_0 = 90.3(2) – 0.64(4)\Delta P + 0.070(2)\Delta P^2 )</td>
<td>( \beta_0 = 112.88(1) – 0.062(3)\Delta P + 0.002(1)\Delta P^2 )</td>
</tr>
<tr>
<td><strong>Titanite</strong></td>
<td>( \text{Angel et al. 1999} )</td>
<td></td>
</tr>
<tr>
<td>Bulk compressibility</td>
<td>( V_0 = 367.7(1) )</td>
<td>131.4(7)</td>
</tr>
<tr>
<td>Axial compressibilities</td>
<td>( a_0 = 7.046(1) )</td>
<td>89.9(9)</td>
</tr>
<tr>
<td></td>
<td>( b_0 = 8.707(5) )</td>
<td>229(1)</td>
</tr>
<tr>
<td></td>
<td>( c_0 = 6.5543(1) )</td>
<td>90.65(8)</td>
</tr>
<tr>
<td>( \beta_0 = 113.84(1) – 0.141(4)P + 0.0041(3)P^2 )</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Appendix C

Table 1: Unit cell parameters for natural titanite collected with Image Plate single-crystal analysis

<table>
<thead>
<tr>
<th>Pressure [GPa]*</th>
<th>a [Å]</th>
<th>b [Å]</th>
<th>c [Å]</th>
<th>V [Å³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02</td>
<td>7.06(2)</td>
<td>8.68(3)</td>
<td>6.55(2)</td>
<td>368.47</td>
</tr>
<tr>
<td>0.20</td>
<td>7.05(2)</td>
<td>8.69(2)</td>
<td>6.54(2)</td>
<td>365.24</td>
</tr>
<tr>
<td>1.50</td>
<td>6.99(1)</td>
<td>8.68(1)</td>
<td>6.50(1)</td>
<td>360.19</td>
</tr>
<tr>
<td>2.60</td>
<td>6.97(2)</td>
<td>8.65(1)</td>
<td>6.49(2)</td>
<td>359.01</td>
</tr>
<tr>
<td>3.20</td>
<td>6.97(2)</td>
<td>8.65(2)</td>
<td>6.47(2)</td>
<td>357.24</td>
</tr>
<tr>
<td>3.70</td>
<td>6.95(2)</td>
<td>8.66(1)</td>
<td>6.47(2)</td>
<td>356.15</td>
</tr>
</tbody>
</table>

* Pressures are determined by the ruby fluorescence method described in chapter 3.2.5

Figure 1: Unit cell parameters of natural titanite as a function of high-pressure
Figure 2: Selected Image Plate pictures of natural titanite at 2.6 GPa between 335° (a) and 55° (i) in φ with a step size of 10° per image. Note the artefact of the cell components Be and gasket and the gasket and the strong reflections of diamond in picture (g).
Thanx

Am Ende meiner Arbeit hier in Zürich gibt es eine Menge Menschen, denen mein Dank gilt:
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Curriculum Vitae

Date and place of birth  September 2\textsuperscript{th} 1973 in Hannover, Germany
Citizenship  German
Marital status  Single

Education

1979 – 1985  Primary school, Hannover
May 1992  School leaving exam

1992 – 1998  Student of Mineralogy at the University of Hannover
1995  Intermediate diploma
Oct. 1996 – May 1997  Diploma thesis with the collaboration of Institut für Siedlungswasserwirtschaft, University of Hannover
May 1998  Diploma in Crystallography
Subsidiary subject Petrology, Material Science and Jurisprudenz

1999 – 2002  Ph.D student at the Laboratory for Crystallography ETH Zürich, Switzerland, Supervisor PD Dr. Martin Kunz
June 24\textsuperscript{th} 2002  Defense of the Ph.D thesis