Top-seeded solution growth of SrTiO$_3$ crystals and phase diagram studies in the SrO–TiO$_2$ system

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The TiO$_2$ rich part of the (1–x) SrO + x TiO$_2$ phase diagram 0.5 ≤ x ≤ 1.0 was redetermined and the eutectic point between SrTiO$_3$ and TiO$_2$ was found at x$_{\text{eut}}$ = 0.7700 ± 0.0001; T$_{\text{eut}}$ = (1449 ± 3)°C. From TiO$_2$ rich melt solutions, x = 0.75 centimeter-sized single crystals could be grown. The best crystals with etch pit density < 2 × 10$^4$/cm$^2$ were obtained for growth directions (110) and (100). AFM investigation of the interface reveals layer-by-layer growth.

1 Introduction

Tausonite (SrTiO$_3$, STO) is a cubic perovskite and high quality single crystalline bulk crystals are attractive as substrates for oxide heterostructures. Two dimensional electron gases can be found at the interface between SrTiO$_3$ and TiO$_2$. The observation of the conducting interfaces has led to an increasing demand of high quality single crystals for fundamental research and devices having extraordinary properties and functionality. Most tausonite substrates which are used nowadays are grown by flame fusion growth with high dislocation densities typically between 10$^9$/cm$^2$. These Verneuil-grown crystals are produced at industrial scale and they are commercially available. When it comes to higher structural perfection only a few crystal growth methods are suitable to reach the high quality demands with a sufficient crystal size. One of the methods is optical floating zone which yields crystals with dislocation densities typically between (1–5) × 10$^5$/cm$^2$. With a cold crucible Czochralski technique (cold crucible pulling technique) etch pit densities of 10$^2$–10$^3$/cm$^2$ can be reached. SrTiO$_3$ with the lowest dislocation density can be grown from the flux (0–10$^2$/cm$^2$).

SrTiO$_3$ and TiO$_2$ are setting up a eutectic subsystem where top-seeded solution growth (TSSG) can be used for the growth of SrTiO$_3$ crystals at substantially lower temperature, compared to the growth from stoichiometric melts. However, there is a lack of thermodynamic data at this composition range in the literature. This work highlights the self-flux growth of SrTiO$_3$ single crystals in a cylindrical shape, the refinement of the SrO–TiO$_2$ phase diagram, which now includes the thermodynamic data of the melt, by means of DTA/DSC measurements and a description of typical growth surface morphologies when using different seed orientations by the AFM method.

2 Experimental

Thermal analysis of commercial SrTiO$_3$ crystals (CrysTec GmbH, Berlin) was performed up to the melting point beyond 2000°C in a NETZSCH STA 429 calorimeter. Lidded tungsten crucibles in 99.9999% pure static He atmosphere and W-W/Re thermocouples were used. The significant aging of these thermocouples that is shown under given conditions was accounted for by a subsequent calibration run with Al$_2$O$_3$ powder, where melting point $T_f$ and heat of fusion $\Delta H_f$ are known (Fig. 1).

![Fig. 1 DTA heating curves of 80.99 mg crystalline SrTiO$_3$ and Al$_2$O$_3$ powder standard. The latter melts at 2054°C with $\Delta H_f = 1161$ J/g.](image)

In addition, 23 different (1–x) SrO + x TiO$_2$ powder mix-
Figures with a representative EPD value of 1

Evaporation especially of strontium.

be obtained only with the STA 449 due to lower temperatures. Moreover, the oxygen atmosphere was expected to suppress evaporation especially of strontium.

A solution composition of 75 mol% TiO₂ and 25 mol% SrO was used for the self-flux growth experiments. For these experiments, the dried, mixed and pressed starting powders of SrCO₃ and TiO₂ with purities of 99.99%, were heated in platinum crucibles in MoSi₂ muffle furnaces at maximum temperatures of 1620°C.

Crystal growth was performed in a conventional rf-heated Czochralski setup (Cyberstar) with automatic diameter control. Verneuil-grown SrTiO₃ single-crystals seeds (supplied by Crystec GmbH, Berlin) with orientations of (100), (110) and (111) were used. The growth runs were carried out in air with use of a platinum crucible embedded in ZrO₂ and Al₂O₃ insulation. Most of the growth runs were performed using a pulling rate of 0.2 mm/h and with an additional actively heated Pt after heater on top of the crucible. Different growth conditions were tested, which are shown in table 1.

Crystals grown by self flux method with convex (a), W-shaped (b), nearly flat (c) and pronounced concave growth interfaces (d,e). Pulling directions of the crystals (a-d) were ⟨100⟩, ⟨110⟩, ⟨111⟩ and ⟨100⟩, respectively and the growth conditions (see table 1) were T₁, T₃, T₄, T₂, respectively. Interfaces are partially covered by the frozen melt solution (a–c) and by crystals grown from the vapor phase (a). A pulling rate of 0.2 mm/h was used for the crystals shown in a–c and mainly 0.35 mm/h was used for the crystal shown in d and e.

Growth interfaces between nearly flat (Fig. 2c), w-shaped (Fig. 2b) and concave (Fig. 2d–e) were observed, depending on the growth conditions (see table 1) and orientation of the crystals. Non-convex interfaces, especially strong pronounced concave growth interfaces (Fig 2e) lead to a formation of cavities in the central region of the crystal, where the melt can penetrate into the crystals core, causing the crystal to crack upon cooling, which can be seen in Fig. 3. The outer parts of the crystal retain the high crystal quality (EPD 1 \( \times 10^4 \) /cm²), which is similar to the crystals pulled in ⟨100⟩ direction without use of an additional after heater. The cracking can be explained by the deviations of thermal expansion properties of the two solid phases, taursonite and rutile, which crystallize
and (b) post-growth conditions have to be applied for different pulling directions which also may cause cracking. Appropriate growth and cave interface leads to a higher density of grown-in dislocations which is more than one order of magnitude \[4, 9\]. Moreover, a concentration of rutile at crystal surfaces and reduce the amount of frozen melt solution at the bottom of the crystal at the same time.

Figs. 3 and 4 show AFM pictures taken on the different growth facets at the central part of the melt-solid interfaces for different pulling directions. (a) \{100\} and (b) \{110\} direction.

Figs. 3 and 4 show AFM pictures taken on the different growth facets. The measurements were performed at melt droplet free regions. Step flow can be observed for the three surfaces with different step heights. On the one hand, step bunching is indicated in Fig. 3 for the \{110\} pulling direction with step heights between 5 and 31 unit cell distances \(a\) and average step distances of 136 ± 40 nm. On the other hand, step heights between 1−2\(a\) and step distances of 65 ± 12 nm were measured at the \{100\} facet in case of the pure step flow (Fig. 4a). Furthermore, we observed step meandering instabilities at \{111\} surfaces, which can be explained by the Bales-Zangwill mechanism \[2\]. Figs. 4 shows steps at the \{111\} surface with step heights between 44 and 418 nm.

Investigations of the dislocation densities of the grown crystals have shown, that the dislocation density is similar for crystals which were pulled in \{100\} and \{110\} direction (growth condition T1–T3, EPD ca. \(1−2\times10^4\) cm\(^{-2}\)). In contrast to that, a higher dislocation density \((8 \times 10^4\) cm\(^{-2}\)) was measured for the crystal which was pulled in \{111\} direction (T4). These results indicate that the \{110\} and \{100\} pulling directions are more favourable due to stable step flow growth and lower dislocation densities.

### 3.2 Thermal analysis

SrTiO\(_3\) shows one melting peak (Fig. 1), also during repeated DTA runs, which indicates congruent melting. If the measured onset temperature for SrTiO\(_3\) is compared to the Al\(_2\)O\(_3\) standard, a fusion point \(T_f = (2054 \pm 1922)\, ^\circ\)C + 1947 °C = (2079 ± 20) °C is obtained. The error is estimated from the fluctuation of results for these and other substances in this temperature range. Even if a DSC is not available for such high \(T\), the heat of fusion can be estimated by comparing the peak area with that of the standard. (One can assume that the sensitivity of the sample carrier is almost identical for SrTiO\(_3\) and Al\(_2\)O\(_3\) because their fusion points differ by only 25 K.) One finds \(\Delta H_f \approx 683\, J/g = 125.2\, kJ/mol\). Here a larger error of ca. ±20% must be assumed, derived from the insufficient reproducibility of this determination. At least this value seems not unrealistic: for the structurally similar CaTiO\(_3\) the FactSage \[24\] database gives at its melting point 1960 °C a \(\Delta H_f = 106.638\, kJ/mol\).

For the \((1−x)\) SrO + \(x\) TiO\(_2\) powder mixtures coming from the SrO rich side, \(x = 0.4270\) was the last composition not showing any sign of a eutectic peak (uppermost DTA curve in the insert of Fig. 5), and the next composition, \(x = 0.4533\) \(3^{rd}\) experimental point from the left in Fig. 5, already showed a minor eutectic peak \((A = 2.6\, J/g)\). The largest eutectic peak
was found for \( x = 0.7700 \) (\( A = 520.7 \) J/g). The extrapolated onsets of the eutectic peaks vary for all compositions in a small range of \((1449 \pm 3) \)°C, which is the eutectic temperature \( T_{\text{eut}} \).

It is obvious from the lever rule that the peak area \( A(x) \) varies linearly with \( x \), with a maximum at \( x_{\text{eut}} \). Fig. 5 shows such Tammann construction and from the intersection of linear fits \( A(x) \) from both sides one obtains \( x_{\text{eut}} = 0.7701 \), which almost coincides with the experimental point and the DTA curve that is marked by dashed lines.

### 3.3 Thermodynamic calculations

With the Schröder-van Laar equation one can calculate a pseudo-binary phase diagram \( \text{SrTiO}_3 - \text{TiO}_2 \) from the melting point and heat of fusion of both end members. Data for \( \text{SrTiO}_3 \) were estimated by the DTA measurements shown in Fig. 1 and reliable values for \( \text{TiO}_2 \) \((T_l = 1857 \)°C, \( \Delta H_f = 46024 \) J/mol) can be found in FactSage databases [24]. With these data a hypothetical eutectic point at \( x = 0.8053 \) (in scales of \( \text{SrO/ TiO}_2 \)) and \( T = 1652 \)°C can be calculated if the melt was ideal, which is far way from the measured values \( x = 0.7701, T_{\text{eut}} = 1449 \)°C. To reach such low \( T_{\text{eut}} \) for an ideal melt, \( \Delta H_f \) of \( \text{SrTiO}_3 \) would have to be only \( \frac{1}{2} \) of its measured value, which can be ruled out. Instead one can conclude that the melt is stabilized by a very large negative excess enthalpy, probably resulting from the strong chemical interaction between the Lewis base \( \text{SrO} \) and the Lewis acid \( \text{TiO}_2 \).

The excess Gibbs energy of the melt was expressed by

\[
\sum_{a,b} G_{\text{ex}} = \gamma^b \lambda^a (A + BT)
\]  

(1)

where \( y = 1 - x \) is the molar fraction of \( \text{SrO} \). Reasonable fits of the experimental data (\( T_l \) for \( \text{SrTiO}_3, T_{\text{eut}} \) and \( x_{\text{eut}} \), a few liquidus temperatures for compositions near \( x_{\text{eut}} \)) were obtained only if exponents \( a, b \) up to 4 were taken into consideration. The assessment was performed with FactSage [24] for compositions between \( \text{SrTiO}_3 \) and \( \text{TiO}_2 \) only, because only there experimental data were available. Results are given in Table 2. Even if not used in the assessment itself, it turned out the heat of fusion for \( \text{SrTiO}_3 \) that can be calculated from the difference of the enthalpy of the 1:1 composition directly below and above \( T_l \) \((126.24 \)kJ/mol) corresponds almost perfectly with the experimental value mentioned above \((\Delta H_f = 125.2 \)kJ/mol). Only Gibbs energy data for the melt were assessed here, and data for solid \( \text{SrTiO}_3 \) were taken from recent accurate galvanic measurements: \( \Delta H_f^{\text{ex}} = -1653.290 \)kJ/mol, \( S = 109.128 \) J/(mol·K), \( c_p = 137.09676 + 0.00323T - 456.7919T^{-0.5} - 1195220T^{-2} \) (in J/(mol·K)) [7].

Table 2: Assessed parameters for the description of melts from 0.5 \( \leq x \leq 1.0 \) by (1)

| \( a (\text{TiO}_2) \) | \( b (\text{SrO}) \) | \( A \) | \( B \) |
|----------------|----------------|------|------|
| 1              | 1              | -256452 | 44.6683 |
| 1              | 2              | -7038.11 | -19.2816 |
| 1              | 4              | -1042.50 | 7.01178 |
| 2              | 1              | 301.955  | -16.3740 |
| 4              | 1              | 1385.40  | 32.9610 |

![Fig. 5: Tammann plot of the eutectic peak area \( A \) vs. \( \text{TiO}_2 \) mole fraction \( x \). Full points left or right from \( x_{\text{eut}} \) were fitted by linear functions separately. A few DTA curves of the eutectic peaks are shown in the insert; the corresponding points in the plot are marked by an arrow. The dashed DTA curve is for \( x = 0.7700 \), which is almost the intersection of the linear fits at \( x_{\text{eut}} = 0.7701 \).](image)

![Fig. 6: Gibbs free energy of liquid \( \text{SrO/ TiO}_2 \) mixtures at the melting temperature of \( \text{SrTiO}_3 \). Solid line: real data (equation (1) and table 2), dashed line: ideal mixture for comparison. \( G_{\text{ex}} \) data for \( x < 0.5 \) are dotted because no experimental results were available.](image)
4 Discussion and conclusions

With the assessed thermodynamic data, equilibria between solids (SrTiO$_3$, TiO$_2$), liquids (SrO–TiO$_2$ melt with $G_{ex}$ described by (11)), and gas phase (SrO(g), TiO$_2$(g)) can be calculated, and the results are summarized in Fig. 7. It turns out that SrO has the highest vapour pressure, expressed by its fugacity $f$. $p_{SrO}$ is $\geq$ 3 mbar for pure SrTiO$_3$ at its melting point. Such high fugacity can lead to strontium loss of the melt, which could be accounted for by a slight SrO excess in the feedstock. Then, however, excess SrO might be dissolved in the solid e.g. under the formation of Ruddlesden-Popper (RP) phases impeding crystal quality [18]. Measurements with polycrystalline SrO(SrTiO$_3$)$_x$ up to 1000 K showed that the thermal conductivity $\kappa$ is maximum for the cubic perovskite SrTiO$_3$ ($n = \infty$) and significant lower for RP phases $n = 1$ (Sr$_2$TiO$_4$) and $n = 2$ (Sr$_3$Ti$_2$O$_7$) [23]. Oh et al. [13] pointed out that phonons with wavelengths in the order of 1 nm dominate heat transport. Sr$_2$TiO$_4$ has perpendicular to the SrO interlayers a lattice parameter $c = 1.259$ nm (cf. Fig. 3 top in Ref. [10]) and one can assume that phonon scattering at the SrO interlayers is responsible for the drop of $\kappa$. For crystal growth from the melt, too low $\kappa$ leads to insufficient heat flux through the crystal, and thus to unstable growth.

By using the TSSG method and TiO$_2$ rich melts, cylindrical SrTiO$_3$ single crystals were grown. In this study a starting composition $x_0 = 0.75$ was used, which is close to $x_{eut} = 0.77$. The proximity of $x_0$ to $x_{eut} = 0.77$ restricts crystal yield, but keeps strontium loss by SrO evaporation negligible ($p_{SrO} = 1.5 \times 10^{-3}$ bar at $T_{liq} = 1535^\circ$C, Fig. 7). Under the given experimental conditions (Pt crucible in air) $x_0$ could be shifted only slightly towards SrTiO$_3$ to increase yield, because then the liquidus temperature quickly exceeds the stability limit of platinum (e.g. $T_{liq} = 1725^\circ$C with $p_{SrO} = 7.5 \times 10^{-5}$ bar at $x = 0.70$).

In this study, even by using Verneuil-grown seeds, taursonite crystals with higher structural perfection were obtained. Special attention is necessary to avoid the growth of rutile (TiO$_2$) on the grown crystal surfaces, and to keep a convex growth interface at the same time. The avoidance of rutile growth and the minimization of frozen melt solution droplets at the growth interfaces reduce the risk of crystal cracking during cooling to room temperature.

AFM investigations have shown that the growth is dominated by the step flow growth mode. Pure step flow, step bunching and step meandering instabilities were observed at growth interface facets {100}, {110} and {111}, respectively. It can be concluded that {110} and {100} pulling directions from TiO$_2$ rich melts are favourable at low pulling speeds (0.2 mm/h), to establish stable step flow growth modes at the growth facets and low dislocation densities in the crystals.

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