Formation of BaTiO₃ thin films from (110) TiO₂ rutile single crystals and BaCO₃ by solid state reactions

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Received 6 July 2005; received in revised form 1 November 2005; accepted 21 December 2005

Abstract

The formation of BaTiO₃ thin films from (110) TiO₂ rutile single crystals and BaCO₃ was investigated experimentally by solid–solid and gas–solid reactions in vacuum. X-ray diffraction revealed the formation of an intermediate Ba₂TiO₄ phase before BaTiO₃ is formed. According to our calculations the formation of Ba₂TiO₄ is associated with a maximum decrease in the Gibbs energy at a CO₂ pressure lower than 10⁻⁴ mbar. Reactions at 600–900 °C showed different processes to occur in the solid–solid and gas–solid reactions. The observations are interpreted in terms of the different mass transport mechanisms involved. The results shed new light on the phase sequence during BaTiO₃ formation; in particular a dissociation of BaCO₃ prior to its participation in the reaction has become rather unlikely.

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Keywords: Solid state reactions; Barium orthotitanate; Barium metatitanate; Barium carbonate; XRD analyses

1. Introduction

The perovskite-type compound BaTiO₃ exhibits ferroelectric ordering at temperatures below 120 °C. Ferroelectric and dielectric ceramics based on BaTiO₃ are widely used for high-performance multilayer ceramic capacitors (MLCCs) and thermoresistors.

The common way to produce BaTiO₃ ceramics from BaCO₃ and TiO₂ powders is to make use of solid state reactions [1–6]. The mainly adopted mechanism to explain the sequence of forming phases during calcination of BaCO₃ and TiO₂ powders was proposed by Beauger et al. [5,6]. The formation processes that may occur during calcination under vacuum are described as follows:

First scheme:

a) Decomposition of BaCO₃ according to:

\[ \text{BaCO}_3 \rightarrow \text{“BaO”} + \text{CO}_2; \quad (1) \]

b) Formation of Ba₂TiO₄ by reaction between the two oxides:

\[ 2\text{BaO} + \text{TiO}_2 \rightarrow \text{Ba}_2\text{TiO}_4; \quad (2) \]

c) Finally, synthesis of BaTiO₃ according to:

\[ \text{Ba}_2\text{TiO}_4 + \text{TiO}_2 \rightarrow 2\text{BaTiO}_3. \quad (3) \]

Second scheme:

(a) Decomposition of BaCO₃ according to reaction (1);
(b) Formation of BaTiO₃ by direct reaction between the oxides:

\[ \text{BaO} + \text{TiO}_2 \rightarrow \text{BaTiO}_3; \quad (4) \]

(c) Formation of Ba₂TiO₄ at the expense of BaTiO₃ according to:

\[ \text{BaTiO}_3 + \text{BaO} \rightarrow \text{Ba}_2\text{TiO}_4; \quad (5) \]

d) Finally, the Ba₂TiO₄ reacts with the TiO₂ nucleus to form BaTiO₃ according to reaction (3).

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However, the experimental observations of Beauger et al. [5,6] did not allow to make a choice between these two schemes. Thus, the mechanism of BaTiO₃ formation from BaCO₃ and TiO₂ is still open. Hence, the selection of this rather complex system for a phase formation study in model experiments using single crystals as one reactant [7] should be a way to gain a better understanding of the process.

Tochitsky and Romanova [8] investigated solid state reactions in the multicomponent thin film systems TiO₂/BaO, TiO₂/BaCO₃, TiO₂/PbO, and TiO₂/Bi₂O₃. The thin film systems were prepared by a layer-by-layer thermal evaporation of metals onto alkali halide single crystal substrates in a vacuum of about 10⁻⁵ mbar followed by annealing in an O₂ ambient. The authors found that in the TiO₂/BaCO₃ system after annealing at 500–800 °C only the BaTiO₃ compound formed.

On the other hand, a topotaxial reaction can take place between BaTiO₃ and TiO₂ as shown in Ref. [9]. In contrast, topotaxy between TiO₂ and Ba₂TiO₄ has not been reported yet.

Therefore, the aim of the present study is to experimentally investigate the phase formation sequence during BaTiO₃ formation in model experiments. Titanium dioxide (rutile) (110) single crystals (the thermodynamically most stable crystal face) are used as substrates to provide a model system. The solid state reactions of the latter with BaCO₃ (solid and vapour, respectively) in high vacuum, and the orientation relationship of the final products with respect to the substrate are studied.

2. Experimental

In the reaction experiments, polished (110) surfaces of commercial rutile TiO₂ (T) single crystals (CrysTec GmbH, Berlin, Germany) were subjected to BaCO₃ vapour. The latter was obtained by electron-beam evaporation of a BaCO₃ layer target in a high-vacuum system. Before the experiments the (110) TiO₂ substrates were annealed in air at 1100 °C for 1 h. After this heat treatment the substrate surface involves terraces of about 150 nm in width with ordered steps of about 0.6 nm in height as shown by AFM.

The base pressure of the vacuum system was (1–2) × 10⁻⁵ mbar. During deposition, pure O₂ was introduced to establish a pressure of 1 × 10⁻⁴ mbar. The deposition rate (0.08 nm/s) and the thickness of the thin film (about 100 nm) were monitored in situ by a quartz microbalance. The substrates were heated in a tube furnace from 300 to 500 °C during deposition, followed by a solid–solid reaction at 575–900 °C between BaCO₃ and TiO₂ for 30 min; for the gas–solid reaction, the substrates were heated from 575 to 900 °C for one minute.

The phases present in the thin films after the reaction, and their orientation relationships were investigated by X-ray diffraction (XRD, Philips Xpert MRD) with CuKα radiation. θ–2θ and 2θ measurements were performed to identify the oriented and polycrystalline reaction products. The θ–2θ scans were taken after optimising φ and ψ for the (220) substrate plane. Pole figures (center: ψ = 0°, rim: ψ = 90°) were taken with ψ steps of 2° to determine the crystallographic orientation of the thin films relative to the rutile substrate. θ = 0° in all pole figures corresponds to the planes of the thin film being parallel to the substrate surface whereas ψ = 90° corresponds to the planes of the thin film being perpendicular to the substrate surface.

3. Results

3.1. Phase formation

3.1.1. Solid–solid reaction

The presence of BaCO₃ (JCPDS 45-1471, barium carbonate, BC), Ba₂TiO₄ (JCPDS 38-1481, barium orthotitanate, B2T) and BaTiO₃ (JCPDS 89-2475, barium metatitanate, BT) phases depending on the reaction temperature was investigated by XRD. After deposition at a temperature between 300 and 500 °C a single BaCO₃ phase was observed. At 500 °C the orientation relationship between the barium carbonate and the substrate is well-defined as indicated by the XRD θ–2θ scan (Fig. 1b) and a pole figure (Fig. 2). Most of the solid–solid reactions were conducted using BaCO₃ layers grown at 500 °C.

A deposition at 500 °C followed by solid–solid reaction at ≈75–600 °C for 30 min produced a single Ba₂TiO₄ phase (Fig. 1c). The Ba₂TiO₄ had an orthorhombic structure as indicated by pole figure analyses.

In order to evaluate the rate of the solid–solid reaction, the BaCO₃–TiO₂ system was annealed at constant temperature (≈75–600 °C) for different length of times. The reaction proceeds from a BaCO₃ layer to a mixture of BaCO₃ and Ba₂TiO₄. As soon as all the BaCO₃ has been consumed, the film consists only of Ba₂TiO₄. Both BaCO₃ and Ba₂TiO₄ phases were found immediately after heating the sample up to ≈75 °C (holding time null minutes) while only the Ba₂TiO₄ phase was observed after annealing at 600 °C for one minute. The effect of a short holding time is mainly given by the heating during ramp up and ramp down (∼5 K/min). Increasing the reaction time up to 180 min at 600 °C resulted, together with the Ba₂TiO₄ phase in the formation of BaTiO₃.

The reaction at temperatures between 625 and 825 °C leads to the formation of both Ba₂TiO₄ and BaTiO₃ phases (Fig. 1d, e). The barium orthotitanate was found to be a very unstable compound and to decompose entirely after a storage for two weeks in air, most probably by reaction with H₂O and CO₂ (see Fig. 3, the unidentified peaks at 2θ = 25.1° and 25.6° are assumed to arise from barium hydroxide hydrate (JCPDS 77-2334)). This observation is in good agreement with the data obtained in Refs. [10,11]. XRD pole figure measurements of the sample prepared after heating at 850 °C for 30 min showed the formation of BaTiO₃ without any evidence of remaining Ba₂TiO₄. After reaction for a short time (holding time null minutes at 850 °C) two phases (Ba₂TiO₄ and BaTiO₃) were identified. The solid state
reaction at 900 °C leads to the formation of BaTiO$_3$ (Fig. 1f). Additionally, the presence of Ti-rich phases was observed by pole figure measurements (not shown). It should be noted that after reaction at this temperature the samples became blue in colour. As was reported earlier [12], heating TiO$_2$ crystals in vacuum or under reducing conditions results in oxygen losses and corresponding change of the colour from yellowish to blue. The formation of the Ti-rich phase may thus be a result of a joint out-diffusion of oxygen and titanium from the substrate into the BaTiO$_3$ film.

3.1.2. Gas–solid reaction

The gas–solid experiments showed a reaction process that is similar to the solid–solid reaction with a shift of the temperatures of BaTiO$_3$ formation.

At a reaction temperature of $\approx$575 °C, only the Ba$_3$TiO$_4$ phase was identified, and between 600 and 850 °C two phases (Ba$_2$TiO$_4$ and BaTiO$_3$) were formed in contrast to the solid–solid reaction. But at 600 °C the BaTiO$_3$ phase is contained in the thin film in a small amount only as shown by the very weak intensity in the pole figures (not shown). As in the solid–solid reaction, the barium orthotitanate obtained after gas–solid reaction was also found to decompose when exposed to air for two weeks. Experiments at 900 °C show the presence of BaTiO$_3$ (see Fig. 4) and a Ti-rich phase (detected by pole figures) in the thin film.

3.2. Orientation relationships

3.2.1. Orientation of BaCO$_3$

The barium carbonate formed with a well-defined orientation with respect to the TiO$_2$ substrate. But the orientation relationship of the BaCO$_3$ phase was strongly dependent on the substrate temperature. Thus, at a substrate temperature of
300 °C the XRD θ–2θ results indicate that (111) BC || (110) T. XRD pole figure measurements recorded at 23.89° and 41.88° show, however, that no well-defined azimuthal orientation can be found at this temperature.

At 400 °C, BaCO₃ is crystallographically oriented according to the relation:

- main (101)BC || (110)T; [010]BC || [001]T,
- minor (100)BC || (110)T; [011]BC || [001]T.

Remarkably, the XRD pole figures display rather broad reflections of BaCO₃ both in φ and ψ directions (not shown). Fig. 1b indicates that at a substrate temperature of 500 °C (202) BC || (110) T. The in-plane orientation was determined by pole figures taken at 23.9°, 24.2° and 34.3° (one of them is shown in Fig. 2) and a φ scan of the TiO₂ (200) reflection taken at ψ=45° (not shown). The φ positions corresponding to the (001) and (001) substrate planes are denoted “A” and “B”, respectively (see Fig. 2). The main orientation relationship at 500 °C was derived as:

(101)BC || (110)T; [101]BC || [001]T.

A second orientation relation was determined as:

(211)BC || (110)T; [231]BC || [001]T.

3.2.2. Orientation of Ba₂TiO₄

The orientation of Ba₂TiO₄ after the solid–solid reaction was strongly dependent on the orientation quality of BaCO₃.

A deposition of BaCO₃ at 300 °C followed by solid–solid reaction at 575–700 °C for 30 min produced Ba₂TiO₄ with a low orientation quality (pole figures not shown). In contrast, a
deposition of BaCO$_3$ at 500–850 °C followed by solid–solid reaction at 575–850 °C for 30 min produced a well-oriented Ba$_2$TiO$_4$. The peak at $2\theta = 43.8°$ in Fig. 1c, d and e is from (330) Ba$_2$TiO$_4$. All results of solid–solid reactions presented in this paper use a BaCO$_3$ thin film deposited at 500–850 °C.

Several pole figures were recorded at different $2\theta$ values to find out which plane of Ba$_2$TiO$_4$ is parallel to the TiO$_2$ substrate. Fig. 5a shows a pole figure taken at $2\theta = 29.24°$ (Ba$_2$TiO$_4$ (031)/(002)) of the sample prepared after solid–solid reaction at a temperature of 700 °C. The orientation relationship of Ba$_2$TiO$_4$ with respect to the (110) rutile surface was found as follows:

$\langle 110 \rangle$B$_2$T $\parallel \langle 110 \rangle$T; $\langle 001 \rangle$B$_2$T $\parallel \langle 001 \rangle$T.

This orientation relationship was also found for the samples prepared after the reaction at temperatures between 575 and 850 °C.

After a gas–solid reaction, the orientation relationship of the Ba$_2$TiO$_4$ phase is different compared to the solid–solid reactions. Fig. 6 shows a pole figure taken at $2\theta = 29.24°$ of the sample prepared after gas–solid reaction at a substrate temperature of 700 °C. The orientation relationship of Ba$_2$TiO$_4$ with respect to the (110) rutile surface was found as follows:

$\langle 100 \rangle$B$_2$T $\parallel \langle 110 \rangle$T; $\langle 001 \rangle$B$_2$T $\parallel \langle 001 \rangle$T.

This orientation relationship was also observed for the samples prepared at 575–700 °C.

At a substrate temperature of 800 °C the reflections of the Ba$_2$TiO$_4$ phase in the pole figures are broad in $\varphi$ and $\psi$ directions and, thus, no well-defined orientation can be deduced.

### 3.2.3. Orientation of BaTiO$_3$

In this part we will present first the orientation relations of BaTiO$_3$ grains after gas–solid reaction because their tilt distribution is sharp compared to the solid–solid reaction.

A pole figure taken at $2\theta = 31.4°$ for the sample prepared after gas–solid reaction at 900 °C is presented in Fig. 4. The peaks from the BaTiO$_3$ {101} family in Fig. 4 are sharp and strong, indicating the growth of BaTiO$_3$ grains with well-defined orientation. The orientation relationships of BaTiO$_3$ were identified as:

**main** ($700–900°C$) $\langle 119 \rangle$BT $\parallel \langle 110 \rangle$T; $\langle 1\bar{1}0 \rangle$BT $\parallel \langle 001 \rangle$T,

**minor** ($800–900°C$) $\langle 331 \rangle$BT $\parallel \langle 110 \rangle$T; $\langle 1\bar{1}0 \rangle$BT $\parallel \langle 001 \rangle$T.

Both orientations can be understood as a result of a systematic tilt around a unique tilt axis starting from low index orientations with $\langle 001 \rangle$ BT $\parallel \langle 110 \rangle$ T and $\langle 110 \rangle$ BT $\parallel \langle 110 \rangle$ T, respectively. The common tilt axis is $\langle 1\bar{1}0 \rangle$ BT $\parallel \langle 001 \rangle$ T.
After the solid–solid reaction, the BaTiO₃ grains grown on (110) rutile show similar orientations. A pole figure after solid–solid reaction at 700 °C is presented in Fig. 5b. The figure displays extended reflections of the BaTiO₃ {101} family with a shape like a fin, which means that the BaTiO₃ film consists of several kinds of tilted grains with a common tilt axis. For this temperature most of the BaTiO₃ grains were grown with a mean orientation:

\[
(001)\text{BT} \parallel (110)\text{ T}; [1\bar{1}0]\text{BT} \parallel [001]\text{ T}.
\]

With increasing temperature the number of tilted grains is increasing with systematic tilting from (001) BT∥(110) T towards (119) BT∥(110) T. After reaction at 800–900 °C XRD θ–2θ scans (Fig. 1e and f) and pole figure measurements (not shown) revealed additional minor orientations of BaTiO₃ such as (110) BT∥(110) T and (331) BT∥(110) T. In contrast to the formation of Ba₂TiO₄, BaTiO₃ formed also with (001) BT∥(110) T if a BaCO₃ film with low orientation quality grown at 300 °C was used.

All the determined orientation relationships between the product phases and the substrate for the solid–solid (ss) and the gas–solid reaction (gs) are listed in Table 1.

### 4. Discussion

#### 4.1. Phase formation

A comparison of phase formation and orientation relationships in the solid–solid and gas–solid reactions enables us to discuss the mechanisms of BaTiO₃ and Ba₂TiO₄ formation. Notably, the processes to be considered occur under vacuum lower than 1 × 10⁻⁴ mbar.

In the solid–solid reactions the single intermediate Ba₂TiO₄ compound forms at the beginning of heating by reaction between barium carbonate grains and rutile single crystal. Whether step a) of the reaction according to Eq. (1) is really occurring is doubtful. The time required for the formation of Ba₂TiO₄ is low compared to the decomposition time of BaCO₃ reported by Judd and Pope [13] or by L’vov [14]. Thus we rather expect a direct reaction of BaCO₃ with TiO₂. It was shown that both BaCO₃ and Ba₂TiO₄ phases were found immediately after the reaction at 575 °C (holding time null minutes). For short reaction times at this temperature, a decomposition of BaCO₃ into BaO and CO₂ and a subsequent reaction of BaO with TiO₂ are unlikely. For the influence of the Gibbs energy in dependence on the CO₂ pressure, see below.

In the gas–solid reaction we expect barium oxide and titanium oxide as the reacting species. BaCO₃ evaporates by decomposition, the vapour consisting of BaO and CO₂. Thus first BaO is condensing on the surface. The formation of BaCO₃ by reaction with CO₂ vapour at a temperature of 575 °C is suppressed by a positive value of the Gibbs energy when the partial pressure of CO₂ is lower than 1 × 10⁻⁵ mbar (estimation see below). At a temperature of 500 °C the Gibbs energy of BaCO₃ formation is negative, consistent with the observation of BaCO₃ film growth.

According to our calculations, the formation of barium orthotitanate is accompanied by a maximum decrease in Gibbs energy. The results of these calculations are presented in Table 2. The ΔG₀ (standard Gibbs energy) values were taken from Ref. [15] at T = 1000 K (P_CO₂ = 1 bar) where two phases (Ba₂TiO₄ and BaTiO₃) were identified. The values of ΔG° and ΔG° were calculated for reactions occurring in air (where P_CO₂ = 0.3 mbar) and in vacuum (the absolute background

### Table 1

<table>
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<th>Phase</th>
<th>T, °C</th>
<th>Orientation relationship</th>
<th>Misfit</th>
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<td>4BaCO₃</td>
<td>400</td>
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<td>500</td>
<td>2 (100) BC∥[110] T</td>
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<td></td>
<td>3 (101) BC∥[110] T</td>
<td>(010), +12.4%</td>
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<td></td>
<td></td>
<td>4 (211) BC∥[110] T</td>
<td>(010), +34.4%</td>
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<td></td>
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<td></td>
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<td></td>
<td>(119) BT∥[110] T</td>
<td>(992), +100%</td>
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<td></td>
<td></td>
<td>(331) BT∥[110] T</td>
<td>(116), +100%</td>
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<td>4BaCO₃</td>
<td>700</td>
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### Table 2

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<th>N</th>
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<th>ΔG°, kJ/mol</th>
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<th>ΔG°, kJ/mol</th>
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<td>2BaCO₃ + TiO₂ → Ba₂TiO₄ + 2CO₂</td>
<td>+3.7</td>
<td>−131.1</td>
<td>−302.5</td>
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<tr>
<td>2</td>
<td>BaCO₃ + TiO₂ → BaTiO₃ + CO₂</td>
<td>−48.7</td>
<td>−11.6</td>
<td>−201.8</td>
</tr>
<tr>
<td>3</td>
<td>BaCO₃ + BaTiO₃ → Ba₂TiO₄ + CO₂</td>
<td>+52.1</td>
<td>−15.3</td>
<td>−101</td>
</tr>
<tr>
<td>4</td>
<td>BaCO₃ → BaO + CO₂</td>
<td>+101.8</td>
<td>+34.4</td>
<td>−51.3</td>
</tr>
</tbody>
</table>
pressure of the vacuum system was \( \leq 2 \times 10^{-5} \) mbar, thus the partial pressure of CO\(_2\) during our experiments was lower than \( 1 \times 10^{-5} \) mbar), respectively. In reaction nos (1)–(4) (see Table 2), the chemical potential of CO\(_2\) gas depends on its partial pressure and is described by [16]:

\[
\mu_{\text{CO}_2} = g_{\text{CO}_2}^0 + RT\ln P_{\text{CO}_2},
\]

where \( \mu \) is the chemical potential of CO\(_2\) and \( g_{\text{CO}_2} \) is the molar Gibbs free energy of CO\(_2\). For one mole, \( \mu_{\text{CO}_2} = g_{\text{CO}_2} \) and \( g_{\text{CO}_2}^0 = G_{\text{CO}_2}^0 \). As can be seen from Table 2, reaction no (4) in vacuum is relatively unfavourable compared to reaction nos (1) or (2) due to an only small decrease in the Gibbs energy. From a thermodynamical point of view, reactions nos (1), (3) and (4) are not sufficient at low temperatures.

Although thermodynamics describes whether or not a solid state reaction will occur, it does not give any information on the kinetics of such reactions. Thin film reactions are determined by processes at the reaction fronts, or by nucleation phenomena, whereas reactions in the bulk are controlled by diffusion. In our case, the initial formation of BaTiO\(_3\) during the solid–solid reaction at \( T = 575–600 \) °C may have been hindered due to a nucleation barrier, so that the first phase forming was Ba\(_2\)TiO\(_4\). In the gas–solid reaction, surface diffusion may be predominant, and independent nucleation events at surface defects may have occurred. Thus, a similar nucleation probability of BaTiO\(_3\) and Ba\(_2\)TiO\(_4\) in the gas–solid reaction may have facilitated the initial formation of both phases.

We can assume different formation mechanisms of Ba\(_2\)TiO\(_4\) and BaTiO\(_3\) based on the differences in the orientations of both phases in dependence on the orientation of BaCO\(_3\). The orientation of Ba\(_2\)TiO\(_4\) is strongly dependent on the orientation of BaCO\(_3\), while the orientation of BaTiO\(_3\) grains is independent of the BaCO\(_3\) orientation. The formation of Ba\(_2\)TiO\(_4\) might be the result from diffusion of Ti ions into the BaCO\(_3\) matrix. In contrast, BaTiO\(_3\) grains might be formed by diffusion of Ba ions into TiO\(_2\).

The formation temperatures of Ba\(_2\)TiO\(_4\) and BaTiO\(_3\) under our experimental conditions were substantially lower than those in bulk ceramic systems [17]. For an explanation one should consider that in ceramic samples the grain sizes (about 2–5 \( \mu m \)) are much larger compared to grain sizes in thin films (about 20–50 nm), so that mass transport in bulk ceramics is not sufficient at low temperatures.

### 4.2. Orientation relationships

Comparing the orientations of the phases formed on (110) TiO\(_2\) the similarities and differences become obvious. The orientations of BaTiO\(_3\) grains after two types of solid state reactions have similar features but with different sharpness of the tilt distributions. In contrary, the Ba\(_2\)TiO\(_4\) grains after solid–solid reaction show another orientation compared to the gas–solid reaction. This difference might be caused by different nucleation mechanisms. During the solid–solid reaction Ti ions seem to be diffusing into the BaCO\(_3\) film. The gas–solid reaction starts by surface diffusion of BaO on the TiO\(_2\) substrate. The relations [110] BT || [001] T and [001] B2T || [001] T are observed under different reaction conditions. This means that the [001] TiO\(_2\) axis is the tilt axis for compounds grown on (110) TiO\(_2\), independent of their crystallographic structure.

From Table 1 we see that the interplanar distances of barium carbonate and barium orthotitanate do not fit the respective ones in rutile in both directions (items 1–6). One interplanar distance of BaTiO\(_3\) matches with one of TiO\(_2\) in the [001] TiO\(_2\) direction giving a rather low lattice misfit of \( -4.1\% \) (items 7–10) but no match occurs in the perpendicular direction.

To explain the occurrence of interfaces with a rather large lattice misfit in Table 1, a near coincidence site lattice (NCSL) model [18,19] was applied for the thin films on the (110) rutile substrate. The model is a generalisation of the coincidence site lattice (CSL) theory. For heteroepitaxial interfaces, the non-commensurate relationship between the lattice parameters of the two materials means that exact coincidence cannot be found and hence a lattice misfit or “near coincidence” is introduced. We consider the interface between two crystalline materials with lattice parameters \( a \) and \( b \), respectively, as a two-dimensional rectangular lattice. Exact coincidence occurs when \( n \cdot a = m \cdot b \), where \( m \) and \( n \) are integers. The misfit is given by

\[
F = 2(na - mb)/(na + mb).
\]

In the NCSL theory, the smaller the misfit and the higher the periodicity \( (n,m) \) are, the lower is the interfacial energy. We calculated NCSL misfits for all index combinations \( (\pm 9, \pm h, \pm k, \pm l) \) using a computer program written in the Free Pascal programming language [20]. Although the observed orientation relations between BaCO\(_3\) and (110) TiO\(_2\) (Table 3) can be matched by choosing \( n \leq 8, m \leq 13 \) and \( |F_1| \leq 1\% \), there are much better matching orientation relations with \( m \leq 3, n \leq 2 \) and \( |F_1| \leq 0.9\% \) found by our program. One example is (025) BC || (001) T (\( n_1 = 2, m_1 = 1, F_1 = -0.04\% \)) and (100) BC || (110) T (\( n_2 = 1, m_2 = 2, F_2 = -0.9\% \)). Clearly, the NCSL theory based on a simple geometrical criterion cannot select the observed orientations of BaCO\(_3\) out of a larger set of low-misfit solutions.

As was mentioned above, the interplanar distances of BaTiO\(_3\) (items 7–10 in Table 1) do not fit those of TiO\(_2\) in

| Phase       | No | Film plane || (001) T | Film plane || (110) T |
|-------------|----|------------|----------------|----------------|
|             |    | \( n_1 \) | \( m_1 \) | \( F_1, \% \) | \( n_2 \) | \( m_2 \) | \( F_2, \% \) |
| BaCO\(_3\)  | 1  | 5         | 9         | -0.2          | 8   | 9         | 0.2 |
|             | 2  | 8         | 7         | +0.04         | 5   | 7         | +0.4 |
|             | 3  | 4         | 5         | -1            | 8   | 13        | +0.7 |
|             | 4  | 4         | 5         | +0.5          | 5   | 4         | -0.2 |
| Ba\(_2\)TiO\(_4\) | 5  | 1         | 2         | +3.1          | 3   | 4         | +0.4 |
|             | 6  | 1         | 2         | +3.1          | 3   | 10        | -2.6 |
| BaTiO\(_3\) | 7  | 1         | 1         | -4.1          | 8   | 7         | -0.2 |
|             | 8  |           |           |               | 4   | 5         | -1.2 |
|             | 9  |           |           |               | 10  | 1         | -4.3 |
|             | 10 |           |           |               | 5   | 1         | +0.3 |

Table 3: The misfit values between product phases and rutile substrate calculated by NCSL theory.
the [110] TiO2 direction but are well matched in the [001] TiO2 direction. The non-matching orientation relations of BaTiO3 can be matched using the NCSL model (see Table 3) with \( n \leq 10, m \leq 7 \) and \( |F| \leq 4.3\% \). The non-matching orientation relations for Ba2TiO4 in the [001] and [110] TiO2 directions (items 5–6 in Table 1) are fitted by choosing \( n/C20 \), \( m/C20 \), and \( F/C20 \)). The NCSL theory seems to be able to describe why a particular observed orientation relationship is a good one, but without predictive power.

5. Conclusions

The formation of BaTiO3 from BaCO3 and (110) rutile single crystals has been studied experimentally under vacuum by solid state reactions. A dissociation of BaCO3 prior to its participation in the reaction is rather unlikely. The formation of BaTiO3 was always preceded by an intermediate Ba2TiO4 compound that formed by direct reaction between BaCO3 and rutile single crystals. This is in contrast to the model of Beauger et al. [5,6]. The barium orthotitanate was found to be an unstable compound and to decompose entirely after a storage of two weeks in air, most probably by reaction with H2O and CO2.

According to our calculations the formation of the intermediate phase Ba2TiO4 is associated with a maximum decrease in the Gibbs energy. The formation temperatures of Ba2TiO4 and BaTiO3 under our experimental conditions were substantially lower than those in bulk ceramic samples. Different formation mechanisms of Ba2TiO4 and BaTiO3 are assumed. The formation of Ba2TiO4 is discussed as diffusion of Ti ions into BaCO3, while BaTiO3 might be formed by diffusion of Ba ions into TiO2.

Different orientation relations have been found for BaCO3, Ba2TiO4 and BaTiO3 depending on the reaction conditions, all of which imply, however, a common [001] TiO2 tilt axis. Although the observed orientations of BaCO3 on (110) TiO2 are in principal accordance with an NCSL model, this model did not allow to uniquely define the observed orientations. The orientation relations of the Ba2TiO4 and BaTiO3 phases, however, can be explained in terms of a good lattice fit (at least in one direction). A more detailed discussion of the type of the diffusing species and crystallographic details of these reactions, as well as related TEM investigations, is in progress.

Acknowledgement

Work supported by Deutsche Forschungsgemeinschaft (DFG) via SFB 418 at Martin-Luther-Universität Halle–Wittenberg.

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