

Solid state reactions in electroceramic systems

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Dedicated to my lovely wife Svitlana and my son Volodymyr

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1 Introduction

Solid state reactions in ceramic materials are investigated since many years under both fundamental and technological points of view.¹⁻⁴ Under working conditions, many devices consisting of multi-phase or multilayered ceramics are often subjected to high temperatures. As a result, interfacial solid state reactions may occur between the components. Such reactions occurring on the nanometer scale may affect the desired properties of the devices, because chemical and physical properties of interfaces are changed. Thus, in order to optimise the properties of the existing materials as well as to produce new materials with desired properties, advanced knowledge of thin film solid state reactions is required.

Model experiments are well suited to study various aspects of complex solid state reactions. In this approach, instead of using polycrystalline materials, one reactant is a bulk single crystal. In such model experiments, the formation and orientation of the reaction products can well be characterised by several structural techniques such as X-ray diffractometry (XRD) and transmission electron microscopy (TEM). This approach has successfully been used by several research groups to study interfacial reaction mechanisms and reaction kinetics in oxides.⁵⁻¹¹ In the present work, solid state reactions in different oxide systems, viz. $\text{BaCO}_3\text{-TiO}_2$, BaO-TiO_2 , SrO-TiO_2 , CaO-TiO_2 and MgO-TiO_2 , are investigated.

In the first two systems, $\text{BaCO}_3\text{-TiO}_2$ and BaO-TiO_2 , the solid state reaction of solid BaCO_3 and BaO vapour with TiO_2 substrates of different crystallographic structure (anatase and rutile) are studied in a thin film geometry. In particular, phase formation, phase sequence and orientation of the reaction phases are analysed. The main goal of this part of the Ph.D. work was to study the mechanism of BaTiO_3 formation in vacuum and in air. The solid state reaction between BaCO_3 and TiO_2 raw materials is still one of the main industrial ways for BaTiO_3 production. The BaTiO_3 forming process usually occurs via an intermediate Ba_2TiO_4 compound. There are many experimental works which describe the formation of BaTiO_3 . At the beginning of the 1990s, Niepce and Thomas¹² have proposed a model based on spherical TiO_2 particles surrounded by BaCO_3 . For this arrangement, they have predicted that it is possible to prevent the formation of the Ba_2TiO_4 phase by controlling the grain sizes of the initial powders. Such core-shell structured $\text{BaCO}_3\text{-TiO}_2$ substances were prepared by Gablenz *et al.*¹³ (BaCO_3 (shell)- TiO_2 (core), with diameters of the core-shell grains up to several μm) in the year 2001 and by Buscaglia *et al.*¹⁴ (BaCO_3 (core)- TiO_2 (shell), with sizes of the core-shell grains $\approx 100\text{ nm}$ - 500 nm in length and $\approx 50\text{ nm}$ in diameter) in the year 2007. Heating of the powders prepared by Gablenz *et al.*¹³ showed a modified sequence of phases.^{13,15,16} In addition to the intermediate Ba_2TiO_4 phase, different Ti-rich barium titanates were observed depending on the annealing temperature. On the other hand, heating of the powders prepared by Buscaglia *et al.*¹⁴ showed a formation of only the BaTiO_3 compound. The effect of the particle size of the initial reactants and of the gas pressure on the solid state synthesis of barium titanate was given by Hennings *et al.*¹⁷ and by Buscaglia *et al.*,¹⁸ respectively. Hennings *et al.* found

that the formation of the Ba_2TiO_4 compound in air can be suppressed in a reaction between submicrometer BaCO_3 ($0.17\ \mu\text{m}$) and fine TiO_2 ($0.2\ \mu\text{m}$). Buscaglia *et al.* reported that the calcination of nanocrystalline BaCO_3 and TiO_2 powders performed in flowing air at 1 bar (100 kPa) completely suppresses the formation of the Ba_2TiO_4 secondary phase. However, the decrease of pressure to 40 mbar induced the formation of Ba_2TiO_4 at a reaction temperature of $740\ ^\circ\text{C}$. Hence, the selection of this rather complex system for a phase formation study in model experiments should be a way to gain a better understanding of the processes. The commercial TiO_2 powder usually contains a mixture of TiO_2 rutile and TiO_2 anatase. Thus, in the present work TiO_2 rutile single crystals as well as epitaxial TiO_2 anatase single crystalline thin films are used as substrates to provide a model system. In this Ph.D. work, the phase formation sequences and orientation relationships during BaTiO_3 growth from BaCO_3 (solid film with a thickness of $\approx 50\ \text{nm}$) or BaO (vapour equivalent to a nominal BaO thickness up to $\approx 50\ \text{nm}$) and TiO_2 (substrate) are investigated using a combined application of XRD, TEM and high-resolution TEM (HRTEM).

In the next three systems, SrO-TiO_2 , CaO-TiO_2 and MgO-TiO_2 , the solid state reaction between TiO_2 (rutile) single crystals and SrO , CaO or MgO vapour was studied. The primary aims of this part of the Ph.D. thesis are: (1) To compare the orientation relationships found for the BaTiO_3 perovskite grown on TiO_2 (rutile) substrates with those for SrTiO_3 and CaTiO_3 perovskites as well as for the rhombohedral MgTiO_3 ; (2) To determine possible topotaxial orientation relationships between tetragonal TiO_2 (rutile) and the rhombohedral MgTiO_3 phase. As has been shown recently on the example of the non-cubic, corundum-type phases $\text{Mg}_4\text{Ta}_2\text{O}_9$ and $\text{Mg}_4\text{Nb}_2\text{O}_9$ growing topotaxially on cubic MgO single-crystal substrates, surprising topotaxial orientation relationships and corresponding reaction mechanisms can be found in case of non-cubic reactants and/or reaction products.^{19,20} (3) To study the role of crystallography in topotaxial first phase formation in the MgO-TiO_2 system, taking into account previous results of investigations of vapour-solid reactions obtained using MgO substrates.¹¹ The question which phase forms first in a thin-film solid state reaction, if the corresponding phase diagram permits the formation of several phases, is of considerable scientific and technological significance. However, the role of crystallography in topotaxial first-phase selection has not been sufficiently considered so far.

In thin film diffusion couples not all of the equilibrium phases may be observed which are stable in bulk. Various reasons have been given in the literature. The selective formation of phases has been attributed to thermodynamic factors,^{21,22} nucleation barriers²³ and kinetic factors.^{24–27} The main statements of these models are presented in **Chapter 2**. This chapter also gives an introduction to the crystal structure and some properties of the investigated compounds such as TiO_2 , BaTiO_3 , BaCO_3 , Ba_2TiO_4 and Ti-rich barium titanates. Experimental results on solid state reactions in the systems $\text{BaCO}_3\text{-TiO}_2$, BaO-TiO_2 , SrO-TiO_2 , CaO-TiO_2 and MgO-TiO_2 are also presented in **Chapter 2**. The experimental set-up and investigation techniques used in the present study are given in details in **Chapter 3**. The results of the experiments are presented in **Chapter 4**. The findings on the solid state reactions in the systems $\text{BaCO}_3\text{-TiO}_2$ (rutile) and BaO-TiO_2 (rutile) are given in **Section 4.1**. A study of solid state reactions in the systems $\text{BaCO}_3\text{-TiO}_2$ (anatase) and BaO-TiO_2 (anatase) is presented in **Section 4.2**. In the last two systems, epitaxial TiO_2 (anatase)

films were used as substrates. The growth of epitaxial TiO_2 anatase films on SrTiO_3 and LaAlO_3 substrates is described in **Subsection 4.2.1**. **Section 4.3** describes vapour-solid reactions of SrO vapour, CaO vapour and MgO vapour with the TiO_2 (rutile) substrates. **Chapter 5** is dedicated to the discussion of the experimental results obtained in this work. A summary is given in **Chapter 6**.

2 Literature review

2.1 Thin film solid state reactions

A solid state chemical reaction in the classical sense occurs when local transport of matter is observed in crystalline phases and new phases are formed.¹ This definition does not mean that gaseous or liquid phases may not take part in the solid state reactions. However, it does mean that the reaction product occurs as a solid phase. Thus, the tarnishing of metals during dry or wet oxidation is also considered to be a solid state reaction. Commonly, the solid state reactions are heterogeneous reactions. If after reaction of two substances one or more solid product phases are formed, then a heterogeneous solid state reaction is said to have occurred. Spinel- and pyrochlore-forming reactions are well-known examples of solid-state reactions where a ternary oxide forms.⁵⁻¹¹ In this Ph.D. thesis, heterogeneous solid state reactions are considered.

Extended crystal defects as high mobility paths for atoms are essential in the reactivity of solids. Furthermore, interfaces play an important role in the solid state reactions because during heterogeneous reactions interfaces move and mass transport occurs across them. The interfaces can be coherent, semicoherent or incoherent.²⁸ At the interface, chemical reactions take place between species and defects; they are often associated with structural transformations and volume changes.

The characteristics of thin film solid state reactions running on the nanometer scale are considerably different from solid state reactions proceeding in the bulk. During bulk reactions, the diffusion process is rate limiting and controls the growth. In this case, the thickness of the reaction layer (x) usually increases as a function of the square root of time (t), which is the well-known parabolic law of reaction kinetics and is characteristic of a diffusion controlled reaction:

$$x \sim \sqrt{t}. \quad (2.1)$$

During thin film solid state reactions, the diffusion paths of the reacting species are short and consequently the kinetics are determined by interfacial reactions. In this case, the thickness of the reaction layer typically increases linearly with time, which is known as linear reaction kinetics and is characteristic of an interface controlled reaction:

$$x \sim t. \quad (2.2)$$

Moreover, in thin film diffusion couples compared to bulk diffusion couples not all of the compound phases predicted by the equilibrium phase diagram have been observed to be present.²⁹ For example, nickel films deposited on silicon form an intermediate Ni_2Si compound at temperatures between 200 °C and 350 °C with no indication of the presence of other equilibrium phases as long as both unreacted nickel and silicon are still available.²³ Various reasons have been given in the lit-

erature as to why not all of the equilibrium phases may be observed in thin film diffusion couples. The selective formation of phases has been attributed to thermodynamic factors,^{21,22} nucleation barriers²³ and kinetic factors.^{24–27} The main ideas of the major models presented in the literature are given below.

2.1.1 Thermodynamic model

In several silicide systems it was well established that a layer of the most thermodynamically stable compound is the first phase to nucleate and grow. Pretorius *et al.*^{21,22} have proposed the so-called effective heat of formation (EHF) model and have shown that thermodynamic data could be directly used to predict first phase formation and phase formation sequence in thin film reaction couples. According to this model an effective heat of formation $\Delta H'$ is proposed, which is dependent on the concentrations of the reacting elements and is given by:

$$\Delta H' = \Delta H^\circ \times \frac{\text{effective concentration limiting element}}{\text{compound concentration limiting element}} = \Delta H^\circ \times \frac{ec'}{ec}, \quad (2.3)$$

where ΔH° is the standard heat of formation expressed in kJ/mole of atoms. If a compound $A_{1-ec}B_{ec}$ is to be formed for an effective concentration ec' of element B, then element B will be the limiting element if $ec' < ec$, the effective heat of formation being linearly dependent on the effective concentration of the limiting element ec' . By choosing the effective concentration of the interacting species at the growth interface during the solid phase reaction to be that of the liquidus minimum, the model correctly predicts first phase formation during formation of silicides, germanides, aluminides, and other metal-metal binary systems. The EHF model has also been used to describe amorphous and metastable phase formation as well as the effect of impurities and diffusion barriers on phase formation.

2.1.2 Nucleation-controlled model

The basic statements of a nucleation-controlled model for silicide formation have been given by d'Heurle *et al.*²³ Although in most cases there is a lack of knowledge of the material parameters which does not allow a quantitative description, it was shown that the classical theory of nucleation allows for a good qualitative description of the processes involved. In this theory, a phase AB that is formed at the interface between two phases A and B is considered. The driving force for the reaction between A and B is the difference in free energy ΔG_r between A+B and AB. However, because of the formation of AB, the system evolves from a situation with one interface A/B into a system with two interfaces A/AB and AB/B. This will usually result in an increase of the interfacial energy $\Delta\sigma$. For such a system, there is a competition between two mechanisms: on the one hand, the transformation of a volume of A+B into a nucleus AB with radius r results in an energy gain $\Delta G_v \sim r^3 \Delta G_r$. On the other hand the additional interfaces result in a surface energy

cost $\Delta\sigma \sim r^2\sigma$. The free energy change of the nucleus is thus given by:

$$\Delta G_N(r) = a_1 r^2 \sigma - a_2 r^3 \Delta G_r, \quad (2.4)$$

where a_1 and a_2 are geometrical terms that take into account the fact that if the nucleus is a crystal, it will generally not be spherical because of its anisotropic character; a_1 will then represent some averaged coefficient for different values of the surface and interface energies.

The scheme of the relation between the free energy change of a nucleus and its radius r is shown in Fig. 2.1. As can be seen from this figure, $\Delta G_N(r)$ passes through a maximum that corresponds

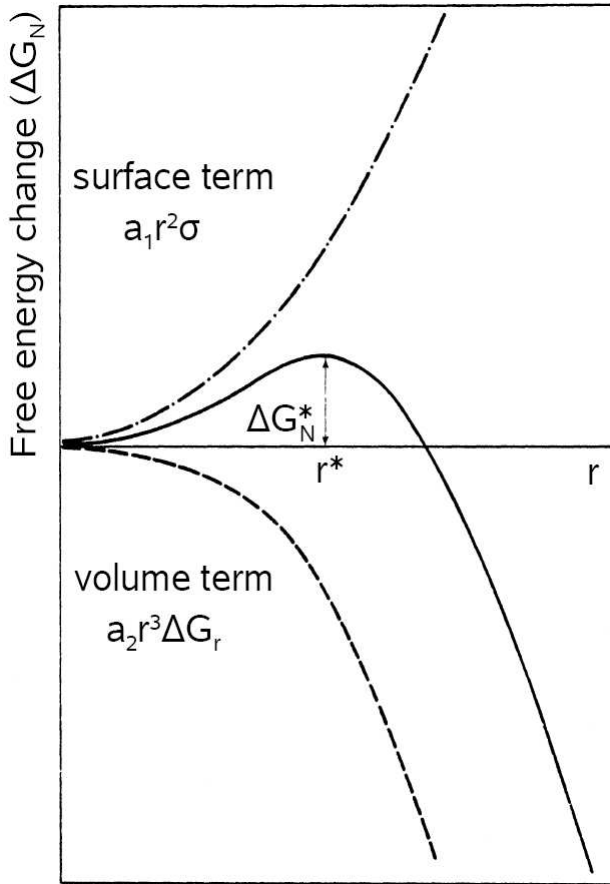


Fig. 2.1. The free energy change of a nucleus as a function of its radius (r), showing the surface and the volume contributions, and their sum.²³

to the critical size r^* of the nucleus. Only the population of nuclei bigger than r^* will tend to grow. Thus, $\Delta G_N(r)$ has a maximum value ΔG_N^* for a critical radius r^* :

$$r^* = \frac{2a_1\sigma}{3a_2\Delta G_r}, \quad (2.5)$$

$$\Delta G_N^* = \frac{4a_1^3\sigma^3}{27a_2^2\Delta G_r^2}. \quad (2.6)$$

ΔG_N^* can be regarded as the activation energy necessary for the nucleation of AB. From the formula, it is clear that nucleation phenomena will only be important if ΔG_r , the free energy of formation of AB, is small.

The rate of nucleation ρ^* is given by the product of the concentration of nuclei with a critical

size and some kinetic term Q , taking into account the local atomic rearrangement needed to form the nucleus:

$$\rho^* \sim e^{\frac{-\Delta G_N^*}{kT}} e^{\frac{-Q}{kT}}, \quad (2.7)$$

where k is the Boltzmann constant and T is the temperature. One should retain the great significance of the relative magnitudes of either the surface energy or the Gibbs energy change, since $\Delta G_N^* \sim \sigma^3/\Delta G_r^2$. Because the surface energy term is usually small, the activation energy for nucleation becomes significant only when the free energy change is also small.

2.1.3 Kinetic model

The concept based on a kinetic model is particularly attractive because it allows to discuss the general nature of thin film solid state reactions, viz. kinetics and phase formation sequence. The mostly adopted kinetic model was proposed by Gösele and Tu.²⁷ In this model, reaction barriers are generally introduced as purely phenomenological quantities, which limit the flux of atomic species through the interface or which otherwise restrict the rate of the interfacial reaction. The influence of such interfacial reaction barriers on the growth kinetics of single compound layers is shown in Fig. 2.2. A compound layer $A_\beta B$ of thickness x_β grows between two saturated phases

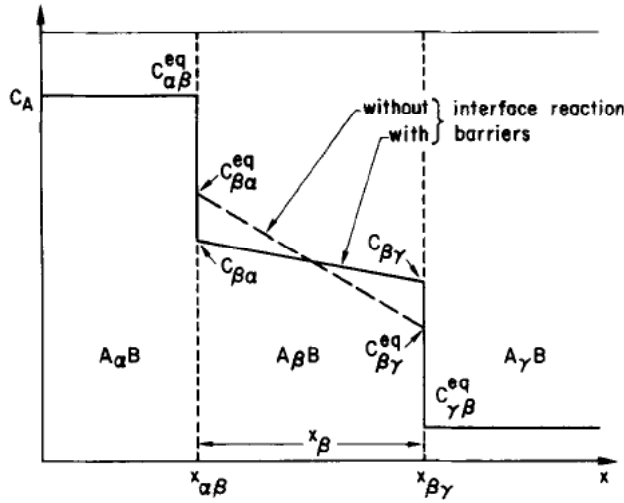


Fig. 2.2. Schematic of concentration profile of atoms A across an $A_\alpha B/A_\beta B/A_\gamma B$ diffusion couple with and without interface reaction barriers.²⁷

$A_\alpha B$ and $A_\gamma B$ where the subscripts $\alpha > \beta > \gamma$ characterise the composition of the compounds. The diffusion flux j_β^A of A atoms in the $A_\beta B$ phase is given by:

$$j_\beta^A = \Delta C_\beta^{eq} k_\beta^{eff} / (1 + x_\beta k_\beta^{eff} / \tilde{D}_\beta), \quad (2.8)$$

where ΔC_β^{eq} is the concentration difference of component A between the left and right sides of the reaction front of phase $A_\beta B$ in equilibrium state, \tilde{D}_β is the chemical interdiffusion coefficient for the $A_\beta B$ layer and k_β^{eff} is an effective interfacial reaction barrier for the $A_\beta B$ layer composed of the two interfacial reaction barriers $k_{\beta\alpha}$ and $k_{\beta\gamma}$ according to:

$$1/k_\beta^{eff} = 1/k_{\beta\alpha} + 1/k_{\beta\gamma}. \quad (2.9)$$

The change of the layer thickness x_β is given by:

$$dx_\beta/dt = [1/(C_{\alpha\beta}^{\text{eq}} - C_{\beta\alpha}) + 1/(C_{\beta\gamma} - C_{\gamma\beta}^{\text{eq}})]j_\beta^A. \quad (2.10)$$

By combining Eq. (2.9) with Eq. (2.10), the following equation can be written:

$$dx_\beta/dt = G_\beta \Delta C_\beta^{\text{eq}} k_\beta^{\text{eff}} / (1 + x_\beta k_\beta^{\text{eff}} / \tilde{D}_\beta), \quad (2.11)$$

where G_β is a constant determined by the composition of the three phases $A_\alpha B$, $A_\beta B$ and $A_\gamma B$. The growth kinetics described by the last equation are different below and above a change-over thickness x_β^* , defined by:

$$x_\beta^* = \tilde{D}_\beta / k_\beta^{\text{eff}}. \quad (2.12)$$

From Eq. (2.12) it follows that

$$x_\beta \sim \sqrt{t} \quad \text{for} \quad x_\beta \gg x_\beta^*, \quad (2.13)$$

and

$$x_\beta \sim t \quad \text{for} \quad x_\beta \ll x_\beta^*. \quad (2.14)$$

Eqs. (2.13) and (2.14) are identical to Eqs. (2.1) and (2.2) and show again the well-known result that interface controlled growth kinetics will change over to diffusion controlled growth kinetics if the layer has grown to a sufficiently thick thickness $x_\beta \gg x_\beta^*$.

If $A_\beta B$ grows in competition to other phases, certain of these phases will formally have negative growth rates, so that they are kinetically not stable.

2.2 Synthesis of BaTiO₃ ceramics

2.2.1 Crystal structure and some properties of TiO₂

There are at least five TiO₂ structures.³⁰ The naturally occurring TiO₂ polymorphs are rutile (tetragonal), anatase (tetragonal), brookite (orthorhombic) and TiO₂ (B) (monoclinic). Among these structural modifications, rutile and anatase are the most often encountered and technically utilised forms. Anatase TiO₂ has the same stoichiometry as rutile TiO₂ but a different crystal structure (see Figs. 2.3-2.4). The relevant crystallographic parameters of rutile and anatase are listed in Table 2.1.

In the rutile and anatase structures, the titanium cation is surrounded by six oxygen anions in more or less distorted octahedral configuration (Figs. 2.3(b)-2.4(b)). These octahedra are the basic building blocks of the various polymorphic structures of TiO₂ (rutile, anatase, brookite, TiO₂ (B)) that differ from each other by the distortion within the octahedra and by their coordination as well as by their linkage. The bond lengths for rutile and anatase are similar, but the anatase octahedra exhibit a greater distortion in bond angles (see Table 2.1). Consequently, the anatase structure has a somehow more open structure (higher molar volume, lower density). There are open channels in the two lattices. The channels in the rutile lie parallel to the *c* axis (perpendicular to the (001) plane) as shown in Fig. 2.3(b). In contrast, the channels in the anatase run perpendicular

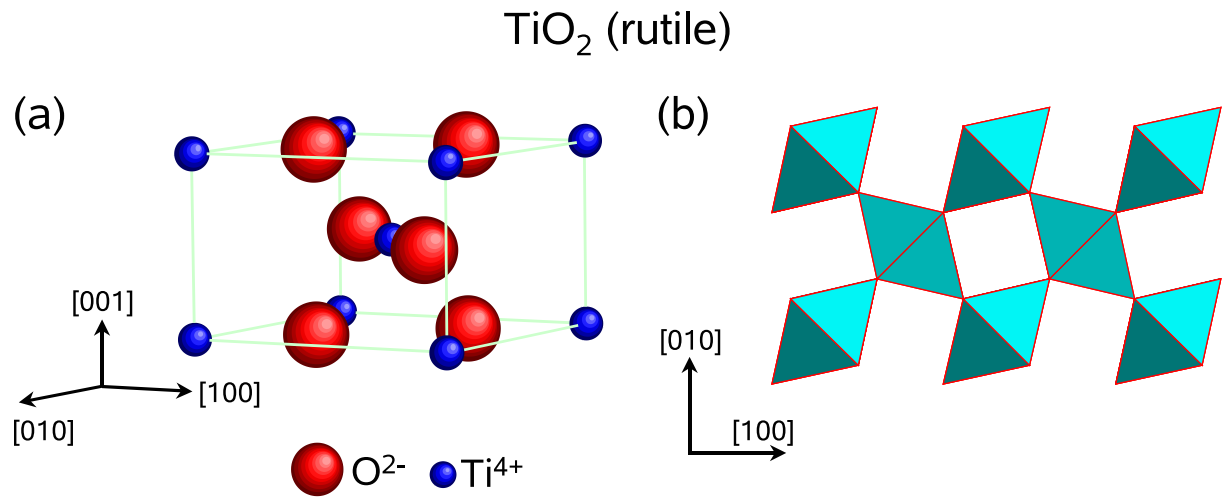


Fig. 2.3. (a) Unit cell of rutile TiO₂ ($a=b=0.459$ nm, $c=0.295$ nm; space group $P4_2/mnm$). (b) Representation of TiO₆ octahedra of rutile.

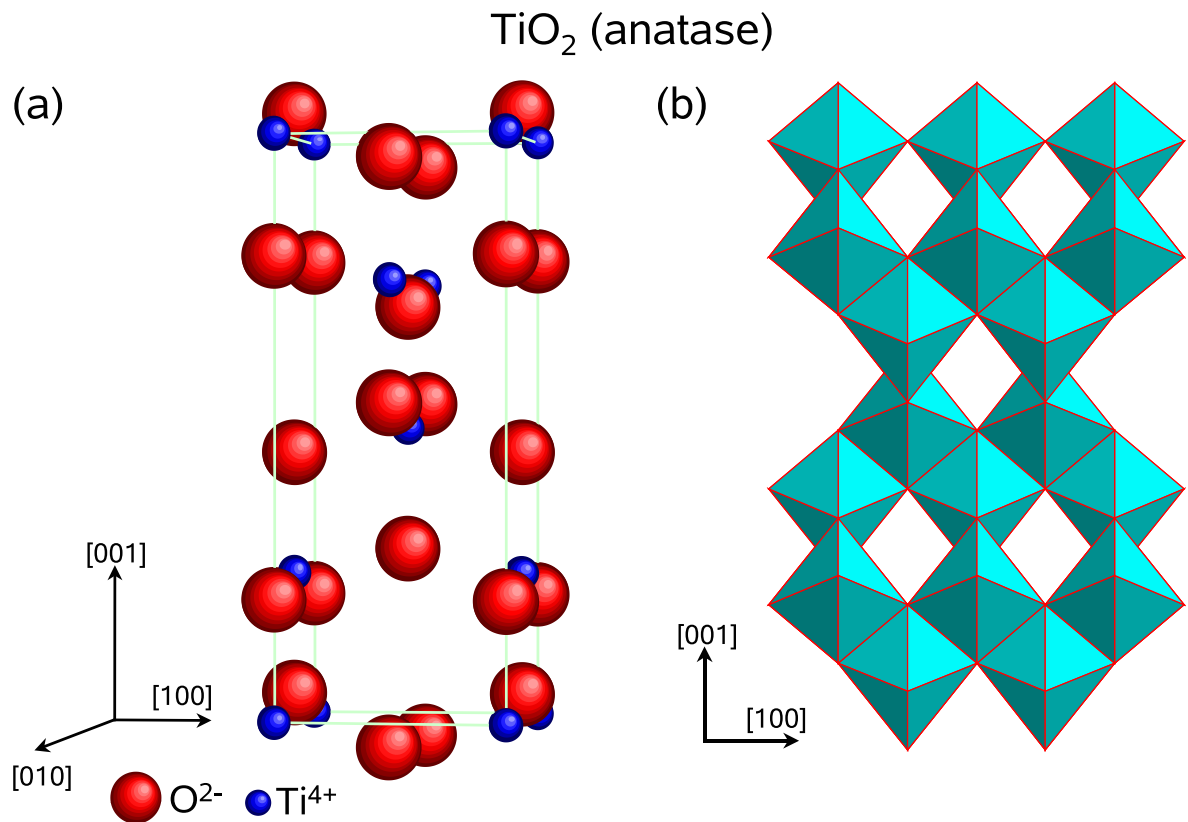


Fig. 2.4. a) Unit cell of anatase TiO₂ ($a=b=0.378$ nm, $c=0.951$ nm; space group $I4_1/amd$). b) Representation of TiO₆ octahedra of anatase.

Table 2.1. Crystallographic parameters for rutile and anatase.³¹

Rutile	<p>Unique Ti coordinates (0,0,0) and (1/2,1/2,1/2)</p> <p>Unique O coordinates ($\pm u, \pm u, 0$) and ($\pm(1/2+u), \pm(1/2-u), 1/2c$) where $u = 0.3048$</p> <p>Ti-O bond lengths: 0.195 nm (4 per octahedra) and 0.198 nm (2 per octahedra)</p> <p>O-Ti-O bond angles: 90°, 81.21° and 98.79°</p> <p>Molar volume: 18.80 cm³</p> <p>Density: 4.25 g/cm³</p> <p>$a=b= 0.459$ nm, $c= 0.295$ nm</p>
Anatase	<p>Unique Ti coordinates (0,0,0), (1/2,1/2,1/2), (1/2,0,1/4) and (0,1/2,3/4)</p> <p>Unique O coordinates (0,0,$\pm u$), (1/2,1/2,(1/2$\pm u$)), (1/2,0,(1/4$\pm u$)) and (0,1/2,(3/4$\pm u$)) where $u=0.2081$</p> <p>Ti-O bond lengths: 0.1934 nm (4 per octahedra) and 0.198 nm (2 per octahedra)</p> <p>O-Ti-O bond angles: 90°, 78.1° and 101.9°</p> <p>Molar volume: 20.52 cm³</p> <p>Density: 3.894 g/cm³</p> <p>$a=b= 0.378$ nm, $c= 0.951$ nm</p>

to the c axis (Fig. 2.4(b)).

Rutile is the most stable form of TiO₂ whereas anatase and brookite are metastable and transform to the rutile phase on heating. There is no well-defined temperature for these transformations. However, the anatase-rutile transition was observed at temperatures between 400 °C and 1000 °C, depending on many factors such as presence of dopants and size of corresponding precipitates, deviations from stoichiometry, surface area, particle size and surrounding atmosphere.^{32–38}

The two polymorphs rutile and anatase have also quite distinct crystal morphologies. Whereas rutile forms slender prismatic crystals,³⁹ anatase usually occurs in a bipyramidal shape.^{39,40} The surface energy of periodic TiO₂ rutile slabs was calculated by Ramamoorthy *et al.*⁴¹ using a self-consistent ab-initio method. The (110) surface has the lowest surface energy while the (001) surface has the highest. The thermodynamic stability of the (100) surface was also considered, and it was found to be stable with respect to forming (110) facets. The surface energies of TiO₂ anatase were estimated by Lazzeri *et al.*⁴² using an ab-initio density functional method. The (001) and (101) faces of anatase were found as the most stable faces. The calculations indicated that the average surface energy of an anatase crystal is lower than that of a crystal in the rutile phase.

2.2.2 Crystal structure of BaCO₃, BaTiO₃ and Ba₂TiO₄

A. BaCO₃

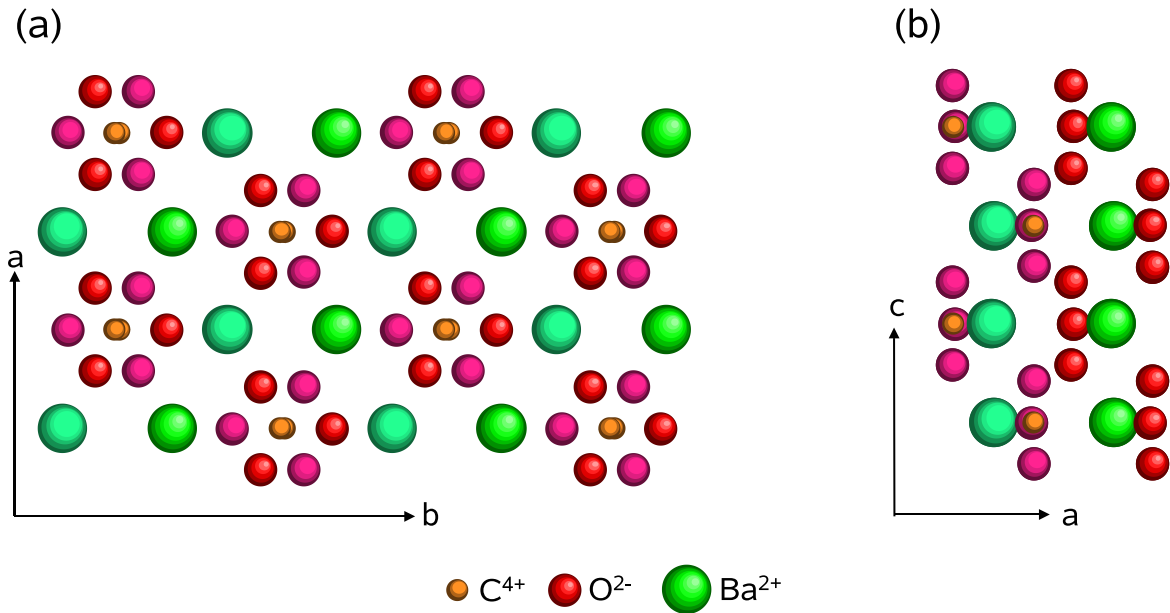
There are three modifications of BaCO₃. Crystallographic data for the room and high temperature forms of barium carbonate are listed in Table 2.2.

The aragonite-type modification is the only stable form under normal conditions at room temperature. Two other modifications of BaCO₃, of the calcite-type and of the NaCl-type, are reversibly formed above 830 °C and 960 °C, respectively.

The structure of aragonite-type BaCO₃ (mineral name is witherite) is illustrated in Fig. 2.5.

Table 2.2. Crystallographic data for different modifications of BaCO₃.⁴³

T, °C	Space group	Symmetry	a, nm	b, nm	c, nm	α , °	β , °	γ , °	Type
20	Pmcn	orthorhombic	0.53	0.888	0.642	90	90	90	aragonite
830	R3m	rhombohedral	0.52	0.52	1.055	90	90	120	calcite
960	Fm3m	cubic	0.696	0.696	0.696	90	90	90	NaCl

**Fig. 2.5.** Illustration of aragonite-type BaCO₃. (a) Top and (b) side view. Different colours for oxygen and barium ions used in (a) and (b) show different height levels of the ions in the projections.

In aragonite, each CO₃²⁻ ion is surrounded by six Ba ions and each Ba ion has nine nearest oxygen neighbours. The Ba ions in BaCO₃ are approximately hexagonally close-packed, alternating with layers of CO₃²⁻ ions perpendicular to the c-axis. The CO₃²⁻ ion deviates very slightly from planarity, but the O-Ba-O angles do not differ from 120°.

B. BaTiO₃

Several ferroelectrics crystallise in a perovskite structure with a general chemical formula ABO₃, where A and B are cations and O is an anion. Perovskite (calcium titanium oxide, CaTiO₃) is a relatively rare mineral occurring in orthorhombic crystals. Perovskite was discovered in the Ural mountains of Russia by Gustav Rose in the year 1839 and named after the Russian mineralogist, L. A. Perovski.⁴⁴

Barium titanate (BaTiO₃) is well-known to have several phase transitions, depending on temperature. Above the Curie temperature (≈ 120 °C), it has the cubic perovskite structure (with Ba²⁺ as A and Ti⁴⁺ as B, $a \approx 0.4$ nm, space group Pm3m). This is a centrosymmetric cubic structure with Ba at the corners, Ti at the center and the oxygens at the face centers (Fig.2.6). The ions are

in the following positions: Ba at (0,0,0), Ti at (1/2,1/2,1/2) and three oxygen ions at (1/2,1/2,0), (1/2,0,1/2), (0,1/2,1/2). The titanium ion is surrounded by six oxygen ions in octahedral configuration (Fig. 2.6) and lies in octahedral holes of the Ba-O packing. Each barium ion has twelve oxygen neighbours.

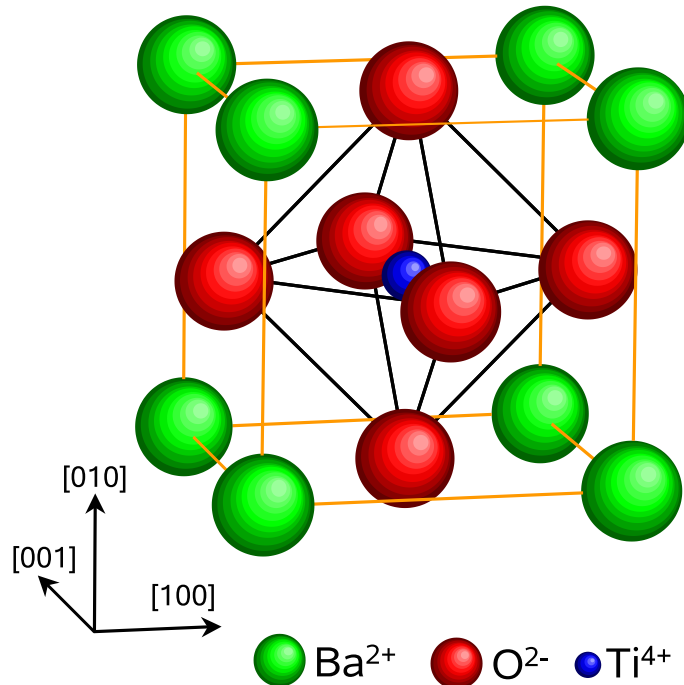


Fig. 2.6. Cubic unit cell of BaTiO₃.

However, there are two high temperature forms of BaTiO₃: cubic and hexagonal ($a = 0.57$ nm and $c = 1.405$ nm, space group C6/mmc). At temperatures above 1432 °C, the cubic form of BaTiO₃ transforms into the hexagonal form.^{45,46} These two modifications are built from close-packed (111) layers of composition BaO₃. In cubic BaTiO₃ there is repetition after every third layer as ABC....; in the hexagonal form repetition occurs along the c axis after every sixth layer as ABCACB.....⁴⁷

As the temperature is lowered, cubic BaTiO₃ goes through phase transitions to three different ferroelectric phases: cubic to tetragonal at 393 K, tetragonal to orthorhombic at 278 K, and orthorhombic to rhombohedral at 183 K. These three phases involve small distortions from the cubic symmetry.⁴⁸ At room temperature, BaTiO₃ is usually considered as tetragonal with $a = 0.3994$ nm and $c = 0.4038$ nm (space group P4mm). It should be noted that this Ph.D. thesis is mainly focused on phase formation sequences during BaTiO₃ synthesis. As shown below, the reaction experiments were performed at temperatures between 575 °C and 1000 °C, where BaTiO₃ is cubic and the question of phase transitions of BaTiO₃ will be not considered in detail. Consequently, the pseudocubic indexing for BaTiO₃ will be used ($a = 0.4$ nm).

C. Ba₂TiO₄

Ba₂TiO₄ (barium orthotitanate) is the most Ba-rich compound in the system BaO-TiO₂. It is formed as an intermediate phase during the synthesis of BaTiO₃ by solid state reaction between BaCO₃ and TiO₂. Ba₂TiO₄ exists in monoclinic^{49,50} and orthorhombic^{51–54} modifications. The orthorhombic form is stable at high temperatures while the monoclinic phase is stable at room

temperature.^{53,54} The orthorhombic Ba₂TiO₄ was observed to be a chemically unstable compound and it decomposed when exposed to air.^{55,56}

Monoclinic Ba₂TiO₄ has a β -Ca₂SiO₄ type structure. Its unit cell has the dimensions: $a = 0.612$ nm, $b = 0.77$ nm, $c = 1.05$ nm and $\beta = 92.99^\circ$. The orthorhombic modification of Ba₂TiO₄ has a distorted β -K₂SO₄ structure. Its unit cell has the dimensions: $a = 0.765$ nm, $b = 1.055$ nm, $c = 0.61$ nm (space group Pnam).⁵² The orthorhombic structure consists of tetravalent titanium cations in an unusual tetrahedral coordination (Fig. 2.7).

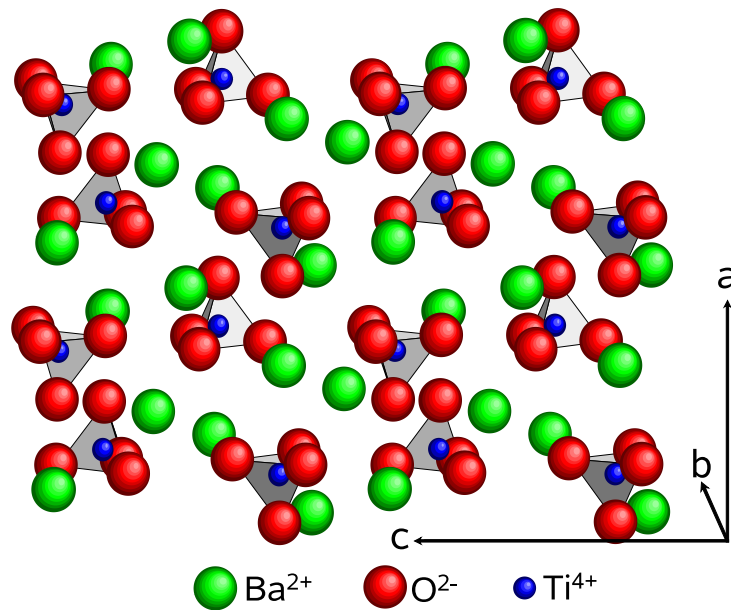
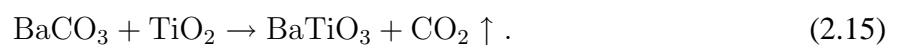


Fig. 2.7. Orthorhombic unit cell of Ba₂TiO₄. TiO₄ tetrahedra are shown with lines.

2.2.3 Formation of BaTiO₃ from BaCO₃ and TiO₂ by solid state reactions

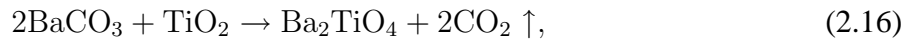
During the past decades, compounds in the BaO-TiO₂ system are of interest because many ternary barium titanates are used as electronic materials for capacitive and microwave devices. One of the most important compounds is BaTiO₃. Due to their ferroelectric and dielectric properties, the perovskite-type BaTiO₃-based materials have many applications in electronics devices such as high-performance multilayer ceramics capacitors (MLCCs), sensors and thermoresistors. The industrial way to produce BaTiO₃ is the solid state reaction between BaCO₃ and TiO₂ at temperatures as high as 1200 °C. This reaction can be described as follows:



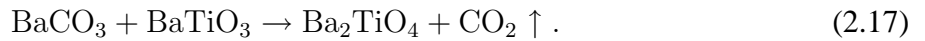
A lot of work has been devoted in order to understand details of reaction (2.15). The above reaction frequently occurs via an intermediate Ba₂TiO₄ compound. Even a few percent of this phase unfavourably affect the electrical properties of BaTiO₃ based ceramics.⁵⁷ In recent years a great

deal of attention has been given to the problem how to explain the formation of the two titanates (BaTiO₃ and Ba₂TiO₄). The main results and assumptions are summarised below.

In the 1950s, the formation of BaTiO₃ has been extensively studied by several groups.^{57–64} Tzebiatowski *et al.*^{58,59} and Kubo *et al.*^{60–62} studied the formation of BaTiO₃ from BaCO₃ and TiO₂ (mainly rutile) by heating the raw materials at certain temperatures and analysing the reaction mixtures by using selectively acting acids. They agree that some BaTiO₃ forms first according to reaction (2.15) and then Ba₂TiO₄, and finally Ba₂TiO₄ combines with the remaining TiO₂ to form BaTiO₃; but they do not agree on the way of Ba₂TiO₄ formation. Tzebiatowski *et al.* indicated that Ba₂TiO₄ is formed directly from BaCO₃ and TiO₂ according to the following reaction:



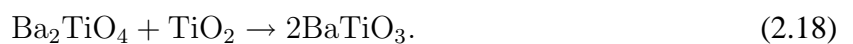
whereas Kubo *et al.* concluded that Ba₂TiO₄ can not be formed according to reaction (2.16) and is produced by reaction between BaTiO₃ and BaCO₃ according to the following reaction:



Templeton *et al.*⁶⁵ studied the formation of BaTiO₃ in air and CO₂ by differential thermal analysis. They found that a small amount of BaTiO₃ is formed first directly from BaCO₃ and TiO₂ (rutile). Then, Ba₂TiO₄ forms according to the reaction (2.17) and occurs in largest amounts until all the BaCO₃ is gone; now experiments confirmed the formation of an intermediate compound according to the reaction proposed by Kubo *et al.*. Ba₂TiO₄ was not at any time observed to form directly by the reaction (2.16). The authors found also that in 1 atmosphere (1 bar) of CO₂ gas, the intermediate Ba₂TiO₄ step was suppressed up to a temperature of about 1100 °C. But it was mentioned that Ba₂TiO₄ reacts fast within an atmosphere of 1 atmosphere of CO₂ below 1100 °C to produce BaTiO₃ and BaCO₃. In addition, the authors reported that a high pressure of oxygen (heating was performed in air) is not necessary for Ba₂TiO₄ formation. The results of Templeton *et al.*⁶⁵ performed with rutile TiO₂ powder are in agreement with findings of Syama *et al.*⁶⁶ who studied the formation of BaTiO₃ using TiO₂ anatase powder.

Later, the dependence of the reaction kinetics on P_{CO₂}, P_{N₂} and P_{O₂} for the reaction (2.15) with rutile TiO₂ have been investigated by Cournil *et al.*^{67,68} It was found that the formation rate of BaTiO₃ continuously decreases with increasing P_{CO₂} or P_{N₂} whereas P_{O₂} leads to a minimum rate under a certain condition (P_{O₂} = 112.5 mbar, T = 720 °C for a given partial pressure of carbon dioxide between 75 mbar and 112.5 mbar).

The quantitative aspects of the experiments performed at the beginning of the 1980s by Beauger *et al.*⁶⁹ have supplemented the data already obtained on the synthesis of BaTiO₃ in air and in the presence of CO₂ (1 bar). In air, BaTiO₃ is formed first according to reaction (2.15). Ba₂TiO₄ then forms at the expense of BaTiO₃ according to reaction (2.17). When all the BaCO₃ has been consumed, the reaction (2.17) stops and the final reaction occurs according to the following equation:



The authors described also the sequence of forming phases for the reaction (2.15) that may occur during heating in vacuum of about 10^{-3} mbar. Beauger *et al.* proposed two schemes.

First scheme:

a) Decomposition of BaCO₃ according to:



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



c) Finally, synthesis of BaTiO₃ according to the reaction (2.18).

Second scheme:

a) Decomposition of BaCO₃ according to reaction (2.19);

b) Formation of BaTiO₃ by direct reaction between the oxides:



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



d) Finally, Ba₂TiO₄ reacts with the TiO₂ nucleus to form BaTiO₃ according to the reaction (2.18).

However, the experimental observations of Beauger *et al.*⁶⁹ did not allow to make a choice between these two schemes.

Beauger *et al.*⁷⁰ have also carried out investigations on planar polycrystalline solid-solid reaction couples in air such as BaCO₃/TiO₂, BaCO₃/BaTiO₃/TiO₂ and Ba₂TiO₄/BaTiO₃/TiO₂. In the first reaction couples, a layer of BaTiO₃ was found after heat treatment at 750 °C for less than one hour inside the TiO₂ layer. With longer treatment times (24 h) at the same temperature, two layers were observed within TiO₂: the inner layer (in contact with TiO₂) consists of BaTiO₃ and the outer layer consists of Ba₂TiO₄. In the second reaction couples, a layer of Ba₂TiO₄ was formed after heat treatment at 850 °C for 3 days within the BaTiO₃ pellet. The formation of BaTiO₃ as well as Ba₂TiO₄ were explained by diffusion of barium through TiO₂ and BaTiO₃, respectively. In the third reaction couples, transformations were observed on both sides of the interface and near it. It was proposed that the conversion of Ba₂TiO₄ into BaTiO₃ occurred through an unidentified species of BaO stoichiometry which diffuses towards TiO₂ through the BaTiO₃ layer. Based on these experimental results, Mutin *et al.*⁷¹ proposed a model consisting of TiO₂ grains covered by BaCO₃.

At the beginning of the 1990s, Niepce *et al.*¹² summarised the main experimental results and suggested a model based on spherical TiO₂ particles surrounded by BaCO₃. From this arrangement, they deduced that it is possible to prevent the formation of the Ba₂TiO₄ phase by controlling

the grain sizes of the initial powders. They discussed also all the interfacial reactions at the various stages. It has been supposed that BaTiO₃ can be formed according to different processes: directly by barium and oxygen diffusion into TiO₂ and by degradation of Ba₂TiO₄. Such core-shell structured BaCO₃-TiO₂ substances were prepared by Gablenz *et al.*¹³ (BaCO₃ (shell)-TiO₂ (core), with diameters of core-shell grains up to several μm) in the year 2001 and by Buscaglia *et al.*¹⁴ (BaCO₃ (core)-TiO₂ (shell), with sizes of core-shell grains $\approx 100\text{ nm}$ -500 nm in length and $\approx 50\text{ nm}$ in width) in the year 2007. Heating of the core-shell powders prepared by Gablenz *et al.*¹³ showed a modified sequence of phases.^{13,15,16} The formation of BaTiO₃ besides remaining BaCO₃ and TiO₂ was observed after reaction at 800 °C (holding time 0 min). Further heating leads to the formation of the Ba₂TiO₄ phase (900 °C-1100 °C, holding time 0 min) and different Ti-rich phases with the general formula BaTi_xO_{1+2x} (x= 2, 4, 5) (850 °C-1050 °C, holding time 0 min). The formation of a single BaTiO₃ phase occurred during heating at 1200 °C for 2 h. On the other hand, heating of the core-shell powders prepared by Buscaglia *et al.*¹⁴ showed a complete formation of a single BaTiO₃ compound after heating at 600 °C for 1 h without formation of any intermediate phases.

The effect of particle size of the initial reactants and pressure on the solid state synthesis of barium titanate was given by Hennings *et al.*¹⁷ and by Buscaglia *et al.*,¹⁸ respectively. Hennings *et al.* found that the formation of the Ba₂TiO₄ compound in air can be suppressed in a reaction between submicrometer BaCO₃ (0.17 μm) and fine TiO₂ (0.2 μm). Thus, the predictions made by Niepce *et al.*¹² were confirmed. Buscaglia *et al.* reported that the calcination of nanocrystalline BaCO₃ and TiO₂ powders performed in flowing air at 1 bar (100 kPa) completely suppresses the formation of the Ba₂TiO₄ secondary phase. However, the decrease of pressure to 40 mbar induced the formation of Ba₂TiO₄ at a reaction temperature of 740 °C.

There was also one attempt to investigate the BaTiO₃ formation in a thin-film system. Tochitsky *et al.*⁷² have investigated solid state reactions in the multicomponent thin film systems TiO₂/BaO, TiO₂/BaCO₃, TiO₂/PbO, and TiO₂/Bi₂O₃. The 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 at constant temperature in a vacuum furnace under a pressure of about 10⁻⁴ mbar and in air. The authors found that in the TiO₂/BaCO₃ system after annealing between 500 °C and 800 °C only the BaTiO₃ compound formed whereas the synthesis of BaTiO₃ during annealing of the TiO₂/BaO system occurred through an intermediate Ba₂TiO₄ compound.

From the above, it is clearly seen that numerous factors influence the reaction (2.15), i.e. composition and pressure of the reaction atmosphere, and size and geometrical arrangement of the initial reactants. However, the mechanism of BaTiO₃ formation from BaCO₃ and TiO₂ in vacuum is still open. The results performed with rutile powders are consistent with those conducted with anatase powders.

2.2.4 Ti-rich barium titanates

A. Phase diagram

There are many compounds which form by a reaction between BaTiO₃ and TiO₂ as well as between BaO and TiO₂. Some of these compounds are of great interest and technological importance. Statton⁷³ has tried first to establish phase relations in the BaO-TiO₂ system. Later, this phase diagram was restudied and improved by many other works.⁷⁴⁻⁸¹

A high-temperature phase diagram constructed for the system BaTiO₃-TiO₂ is shown in Fig. 2.8.⁴⁵ The determination of the phase relations was based on X-ray diffraction and micro-

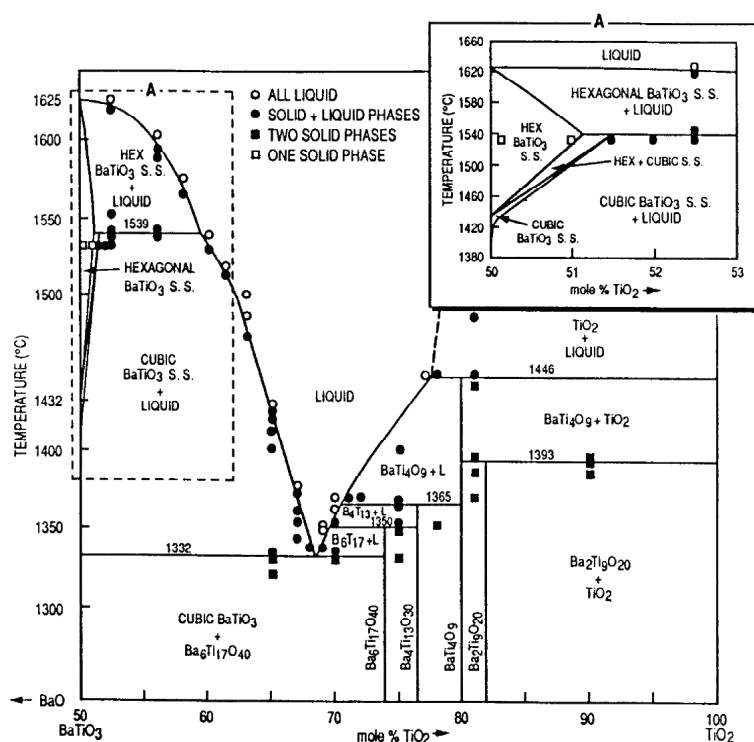


Fig. 2.8. BaTiO₃-TiO₂ equilibrium phase diagram,⁴⁵ see also Fig. A.1 in the appendix (magnified version of the diagram).

scopic visual analyses of the samples quenched from high temperature. In the Ti-rich region, the results of Kirby *et al.*⁴⁵ are in general agreement with those of Negas *et al.*⁷⁷ and O'Bryan *et al.*⁷⁶ As can be seen from the phase diagram, the formation of Ti-rich barium titanates is depending on the ratio of Ba to Ti and temperature.

The stable Ti-rich barium titanates which exist at high temperatures are Ba₆Ti₁₇O₄₀, Ba₄Ti₁₃O₃₀, BaTi₄O₉ and Ba₂Ti₉O₂₀.⁴⁵ The last two Ti-rich phases are used in microwave industry.⁸¹ Other supposedly possible Ti-rich barium titanates such as BaTi₅O₁₁ and BaTi₆O₁₃⁸² have not been observed in these studies. The compound BaTi₂O₅ was found in a sample with 65 mol% TiO₂ quenched from the liquid state. However, heating of this sample at 1320 °C for 64 h resulted in a mixture of BaTiO₃ and Ba₆Ti₁₇O₄₀ with no evidence of any remaining BaTi₂O₅. It was noted that these three Ti-rich barium titanates form only through a liquid intermediate.

However, Ritter *et al.*⁷⁸ obtained BaTi₂O₅ and BaTi₅O₁₁ phases using low-temperature alkoxide synthesis techniques. Fig. 2.9 shows their phase diagram constructed from the data obtained by X-ray diffraction analyses. In this diagram, both BaTi₂O₅ and BaTi₅O₁₁ phases crystallise

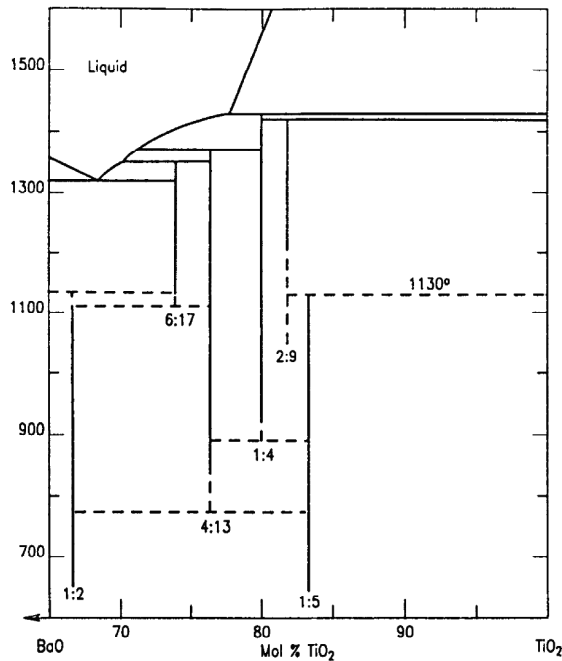


Fig. 2.9. Low temperature BaTiO₃-TiO₂ phase diagram,⁷⁸ see also Fig. A.2 in the appendix (magnified version of the diagram).

at ~ 700 °C. BaTi₂O₅ decomposes into Ba₆Ti₁₇O₄₀ and BaTiO₃ at ~ 1150 °C while BaTi₅O₁₁ decomposes to TiO₂, Ba₂Ti₉O₂₀ and/or BaTi₄O₉ at ~ 1200 °C. Thus, we can conclude that both these phases (BaTi₂O₅ and BaTi₅O₁₁) are either low-temperature stable phases or metastable phases obtained by crystallisation of an amorphous precursor.

B. Crystal structure

The crystal structures of Ti-rich barium titanates have been extensively studied. BaTi₄O₉ and BaTi₂O₅ have structures which can be described as cubic close-packed arrangements of Ba and O atoms. Both these compounds have one short cell constant of about 0.4 nm. These structures have often been referred to as Wadsley-Andersson type phases (also called tunnel structures).⁸³ The structures of other Ti-rich barium titanates, i.e. BaTi₆O₁₃, BaTi₅O₁₁, Ba₄Ti₁₃O₃₀, Ba₂Ti₉O₂₀, Ba₂Ti₁₃O₂₂ and Ba₆Ti₁₇O₄₀, are more complex but can be described as close packing of Ba and O atoms in which some of the octahedral O₆ interstices are occupied by Ti atoms.^{84,85} These structures can be illustrated as being made up of Ba-O close-packed layers with 4, 6, 8 or 10 layers per unit cell. The unit cell dimensions of Ti-rich barium titanates as well the number of layers per unit cell are given in Table 2.3.

The mean thickness of each close-packed layer of the Ti-rich barium titanates is ≈ 0.234 nm which is similar to the (111) interplanar spacing of BaTiO₃. The orientation of the close-packed layer is usually derived from the morphology of the crystals or from the diffraction pattern and gives substantial structural information. For example, in the case of Ba₆Ti₁₇O₄₀, the lattice constant $c = 1.892$ nm ($\approx 8 \times 0.234$ nm) leads to the conclusion that the unit cell contains eight close-packed layers perpendicular to the c axis. Despite one unit cell repeating itself after 8 layers, the real crystallographic identity period of the packing of the complete structure is 24 layers.⁹³ This is because the direction of packing is [103]. The angle between the [103] direction and the (001)

Table 2.3. Unit cell parameters of Ti-rich barium titanates.

Phase	Space group	Symmetry	a, nm	b, nm	c, nm	$\alpha, ^\circ$	$\beta, ^\circ$	$\gamma, ^\circ$	Number of layers	Ref.
<i>Wadsley-Andersson type</i>										
BaTi ₂ O ₅	A2/m	monoclinic	0.9409	0.393	1.69	90	103.5	90		86
BaTi ₄ O ₉	Pmmn	orthorhombic	1.452	0.379	0.629	90	90	90		87
<i>Close-packed type</i>										
BaTi ₆ O ₁₃	P $\bar{1}$	triclinic	0.751	0.985	0.746	105.38	118.9	72.58	4	82
Ba ₂ Ti ₉ O ₂₀	P $\bar{1}$	triclinic	0.747	1.408	1.434	89.94	79.43	84.45	6	88,89
BaTi ₅ O ₁₁	P2 ₁ /n	monoclinic	0.767	1.402	0.752	90	98.33	90	6	90
Ba ₂ Ti ₁₃ O ₂₂	Bmab	orthorhombic	1.165	1.410	1.005	90	90	90	6	91
Ba ₄ Ti ₁₃ O ₃₀	Cmca	orthorhombic	1.706	0.986	1.405	90	90	90	6	92
Ba ₆ Ti ₁₇ O ₄₀	C2/c	monoclinic	0.988	1.708	1.892	90	98.42	90	8	93
Ba ₂ Ti ₅ O ₁₂	Ammm	orthorhombic	0.99	1.14	2.35	90	90	90	10	94,95

plane in Ba₆Ti₁₇O₄₀ is $\approx 1.3^\circ$. The compositions of other Ti-rich barium titanates can be derived by analogy to the layers in Ba₆Ti₁₇O₄₀ and Ba₄Ti₁₃O₃₀ as was shown by Roth *et al.*⁹⁶ for the phases Ba₆Ti₁₄Nb₂O₃₉, Ba₁₄Ti₄₀Nb₂O₉₉ and Ba₁₈Ti₅₄Nb₂O₁₃₂.

Recently, a topotaxial orientation relationship between BaTiO₃ and Ba₆Ti₁₇O₄₀^{97–100} as well as between BaTiO₃ and Ba₄Ti₁₃O₃₀^{6,97} has been established. Despite the different procedure of sample preparation (solid state reaction of BaCO₃ and TiO₂ at high temperatures in air^{98,100} or chemical reaction of SiO₂ film with BaTiO₃ single crystals^{6,97,99}), the Ti-rich phases (TRP) grow in all cases according to the following orientation relationship:

$$(001) \text{ TRP} \parallel (111) \text{ BaTiO}_3; [010] \text{ TRP} \parallel [1\bar{1}0] \text{ BaTiO}_3. \quad (2.23)$$

Thus, the close-packed planes of Ba₆Ti₁₇O₄₀ and Ba₄Ti₁₃O₃₀ lie parallel to the close-packed planes of BaTiO₃. Crystallographically, Kraševac *et al.*⁹⁸ explained the orientation relationship between Ba₆Ti₁₇O₄₀ and BaTiO₃ phases by the similarity of the stacking sequence of (111) planes of BaTiO₃ and (001) planes of Ba₆Ti₁₇O₄₀, if the larger unit cell of the monoclinic Ba₆Ti₁₇O₄₀ phase was appropriately cut.⁹⁸ On the base of the above relationship a model of a topotactic boundary between Ba₆Ti₁₇O₄₀ and BaTiO₃ phases was constructed.

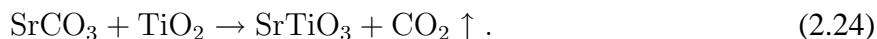
2.3 The system SrO-TiO₂

In the bulk phase diagram of the system SrO-TiO₂ (Fig. 2.10¹⁰¹), several compounds are known such as Sr₂TiO₄, Sr₃Ti₂O₇ and SrTiO₃. There is an eutectic at 1440 °C between SrTiO₃ and TiO₂.

Sr₂TiO₄ has a tetragonal structure with $a=b=0.388$ nm and $c=1.26$ nm (space group I4/mmm) while Sr₃Ti₂O₇ has also a tetragonal structure with $a=b=0.39$ nm and $c=2.038$ nm (space group

I4/mmm). SrTiO₃ has a cubic perovskite structure with $a = 0.39$ nm (space group Pm3m) at room temperature and higher.

Strontium titanate is commonly produced by a solid state reaction of SrCO₃ with TiO₂ at high temperatures (above 1000 °C):



No intermediate products were observed during SrTiO₃ synthesis by Tagawa and Igarashi¹⁰² as well as by Chang and Liu.¹⁰³ However, recent results suggested that the above reaction occurred via an intermediate Sr₂TiO₄ compound.¹⁰⁴

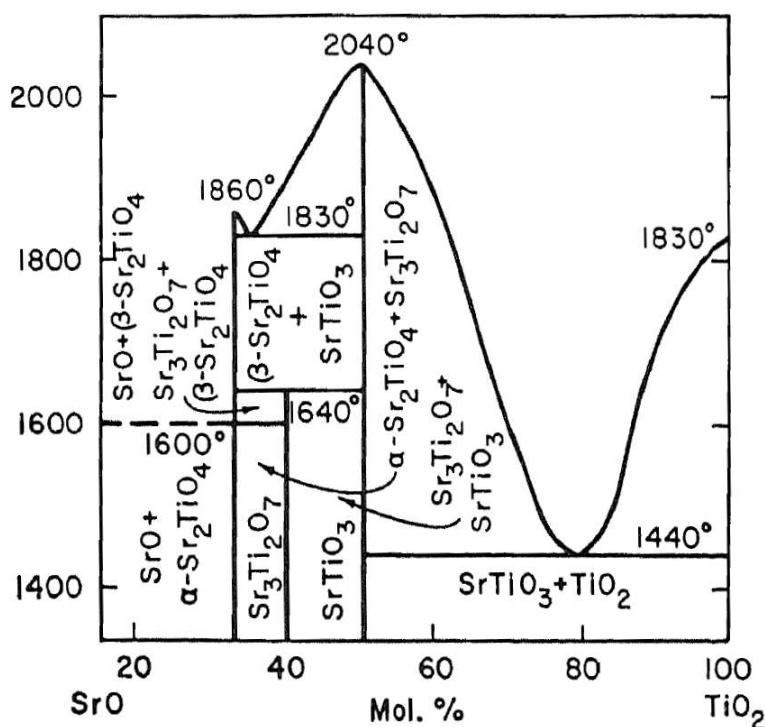


Fig. 2.10. Phase diagram of the system SrO-TiO₂ (Fig. 297 in Ref. ¹⁰¹), see also Fig. A.3 in the appendix (magnified version of the diagram).

SrTiO₃ is of technical significance. Owing to its high dielectric constant and large dielectric breakdown field, SrTiO₃ is a potential candidate for storage capacitor cells in dynamic random access memories.¹⁰⁵ SrTiO₃ single crystals and thin films are extensively used as substrates for high-T_c superconducting,¹⁰⁶ ferroelectric¹⁰⁷ and multiferroic¹⁰⁸ thin films. Suitably doped SrTiO₃ single crystals have been considered for non-volatile memories based on resistive switching.^{109,110}

2.4 The system CaO-TiO₂

Several investigations of the bulk phase diagram of the system CaO-TiO₂ (Fig. 2.11) predict the existence of three stable compounds such as Ca₃Ti₂O₇, Ca₄Ti₃O₁₀ and CaTiO₃. The first two phases peritectically decompose at 1750 °C and 1840 °C, respectively, whereas the CaTiO₃ melts congruently at 1960 °C. There is also a eutectic at 1450 °C between CaTiO₃ and TiO₂.

Ca₃Ti₂O₇ has an orthorhombic structure with $a = 0.541$ nm, $b = 1.94$ nm and $c = 0.542$ nm (space

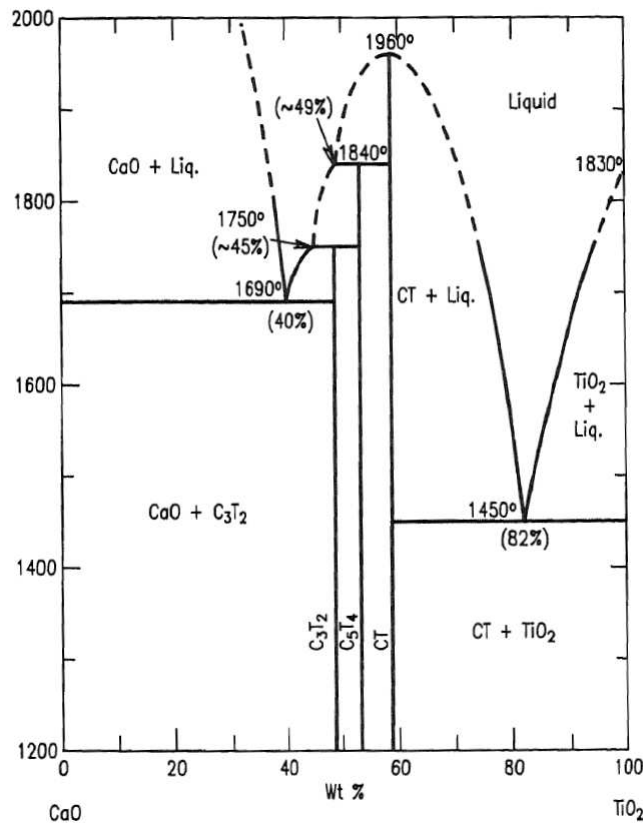


Fig. 2.11. Phase diagram of the system CaO-TiO₂ (Fig. 6385 in Ref.¹⁰¹), see also Fig. A.4 in the appendix (magnified version of the diagram). C= CaO, T= TiO₂.

group Ccm21) while Ca₄Ti₃O₁₀ has also an orthorhombic structure with $a = 0.54$ nm, $b = 2.714$ nm and $c = 0.543$ nm (space group Pcab). The mineral perovskite, CaTiO₃, has an orthorhombic structure at room temperature with $a = 0.538$ nm, $b = 0.544$ nm and $c = 0.7654$ nm (space group Pbnm). The orthorhombic distortion of CaTiO₃ decreases with increasing temperature. The phase transitions from the room temperature orthorhombic structure to a tetragonal ($a = b = 0.549$ nm and $c = 0.778$ nm, space group I4/mcm) polymorph occur at temperatures between 1373 K and 1423 K, followed by transformation to the cubic phase ($a = 0.38$ nm, space group Pm $\bar{3}$ m) at 1523 ± 10 K.¹¹¹ In this Ph.D. work, the pseudocubic indexing for CaTiO₃ will be used ($a = 0.38$ nm).

CaTiO₃ is mostly prepared by a solid state reaction of CaO or CaCO₃ with TiO₂ at high temperatures. The undoped CaTiO₃ is an incipient ferroelectric¹¹² with potential application in microwave-tunable devices,¹¹³ but on doping with Pb it becomes a true ferroelectric.¹¹⁴ The versatility of calcium titanate extends to its suitability as a material for the immobilization of radioactive waste¹¹⁵ and a biocompatible coating for medical Ti implants.¹¹⁶

2.5 The system MgO-TiO₂

In the system MgO-TiO₂, several compounds are known such as MgTi₂O₅, Mg₂TiO₄ and MgTiO₃ (Fig. 2.12). MgTi₂O₅ (armalcolite) has a pseudobrookite structure with $a = 0.97$ nm, $b = 1$ nm and $c = 0.37$ nm (space group Bbmm), while Mg₂TiO₄ (quandilite) has either a cubic structure with $a = 0.84$ nm at 700 °C (space group Fd3m, spinel) or a tetragonal structure with $a = 0.59$ nm and $c = 0.84$ nm (space group P4₁22, spinel) at 500 °C.¹¹⁷ MgTiO₃ (geikielite) has a rhombohedral

ilmenite structure with $a = 0.505$ nm and $c = 1.389$ nm (space group $R\bar{3}$).¹¹⁷

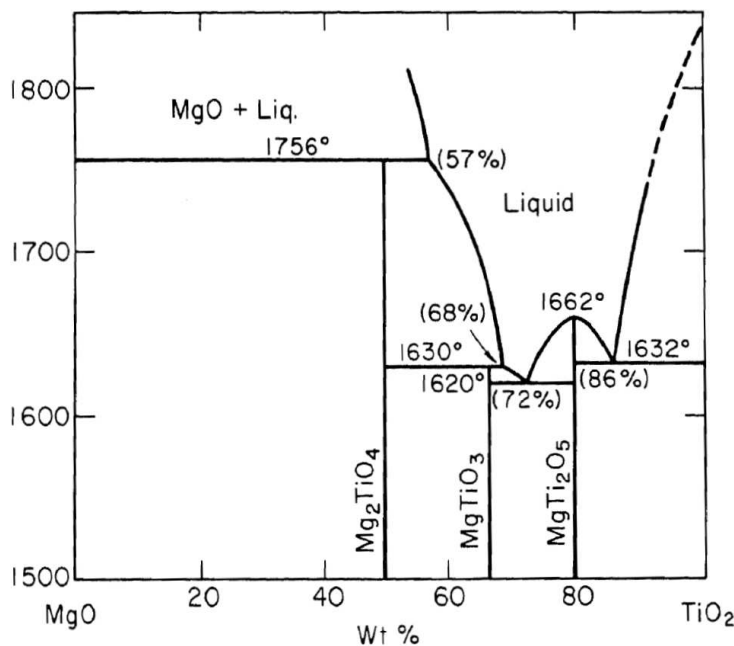
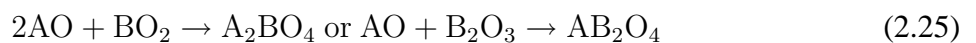


Fig. 2.12. Phase diagram of the system MgO-TiO₂ (Fig. 4336 in Ref.¹⁰¹), see also Fig. A.5 in the appendix (magnified version of the diagram).

Mg₂TiO₄ has attracted attention because of its optical properties to be used in integrated optics and as a dielectric material. Epitaxial layers of Mg₂TiO₄ grown by solid-state reaction between (001) MgO single crystals and TiO₂ have been used as buffer layers for growing high temperature superconducting thin films.^{118–120} On the other hand, MgTiO₃ is known as a dielectric material which has good dielectric properties at high frequencies as well as a high thermal stability. Bulk MgTiO₃ is used for microwave ceramic capacitors and resonators.^{121–124} MgTiO₃ has a refractive index of 1.95 which lies between that of LiNbO₃ (2.2) and Al₂O₃ (1.7).¹²⁵ Thus, MgTiO₃ thin films can be used as a cladding layer. Mostly, MgTiO₃ has been produced and studied in bulk ceramic form. However, there have been some reports on fabrication and properties of MgTiO₃ thin films.^{126,127}

Spinel-forming topotaxial solid state reactions like:



are prototypes of chemical reactions in complex oxides. Previously, a series of topotaxial reactions with (100) MgO single crystals were studied. Different spinels, such as Mg₂TiO₄, Mg₂SnO₄, MgIn₂O₄, MgAl₂O₄, MgCr₂O₄ and MgFe₂O₄, with different values of spinel/MgO lattice misfit were considered.^{6,11} In such cases of cube-on-cube orientation, the structure of the reaction fronts and the mechanism of the interfacial reaction were determined by the sign and amount of the lattice misfit. At positive misfit, the Burgers vector of the misfit dislocations present at the reaction front points out of the interface, enabling the dislocations to glide, when coping with the movement of the advancing reaction front. At negative misfit, the Burgers vector lies in the interface plane, so that a climb process is required for the movement of the dislocations. At very low misfit ($< \pm 0.2\%$), no misfit (interfacial) dislocations form and the misfit is accommodated by point defects and antiphase boundaries.

2.6 Modeling of powder reactions

In order to enhance the speed of reaction, solid state reactions are usually performed by mixing powders of the reactants followed by heating. A reaction between two phases A and B can be regarded as a reaction between two grains A and B.

Fig. 2.13 shows a schematic drawing of two particles which are in contact with each other. The solid state reaction of these two particles occurs by different mass transport mechanisms such as surface diffusion, grain boundary diffusion and volume diffusion. Coupled grain-boundary and surface diffusion is often the dominant mechanism for the reaction of a fine particle compact. The different mass transport mechanisms occurring during the reaction can be studied in model experiments. In this approach, instead of using polycrystalline materials, one reactant is a bulk single crystal. Surface diffusion is a mass flow along the particle surface or along pore walls. Thus, the surface diffusion can be modeled in the reaction between vapour and single crystals as shown in Fig. 2.13. The interface between two (crystalline) particles is a grain boundary. Grain boundary diffusion results in mass flow along the grain boundary while volume diffusion results in mass flow across the newly formed layer. Thus, to model such a situation, the solid-solid reaction between thin films and single crystals can be studied as given in Fig. 2.13. Although solid state reactions involve usually three-dimensional aggregates of particles, the pseudo-two-dimensional problem used in model experiments can give significant insights into the reaction mechanism.

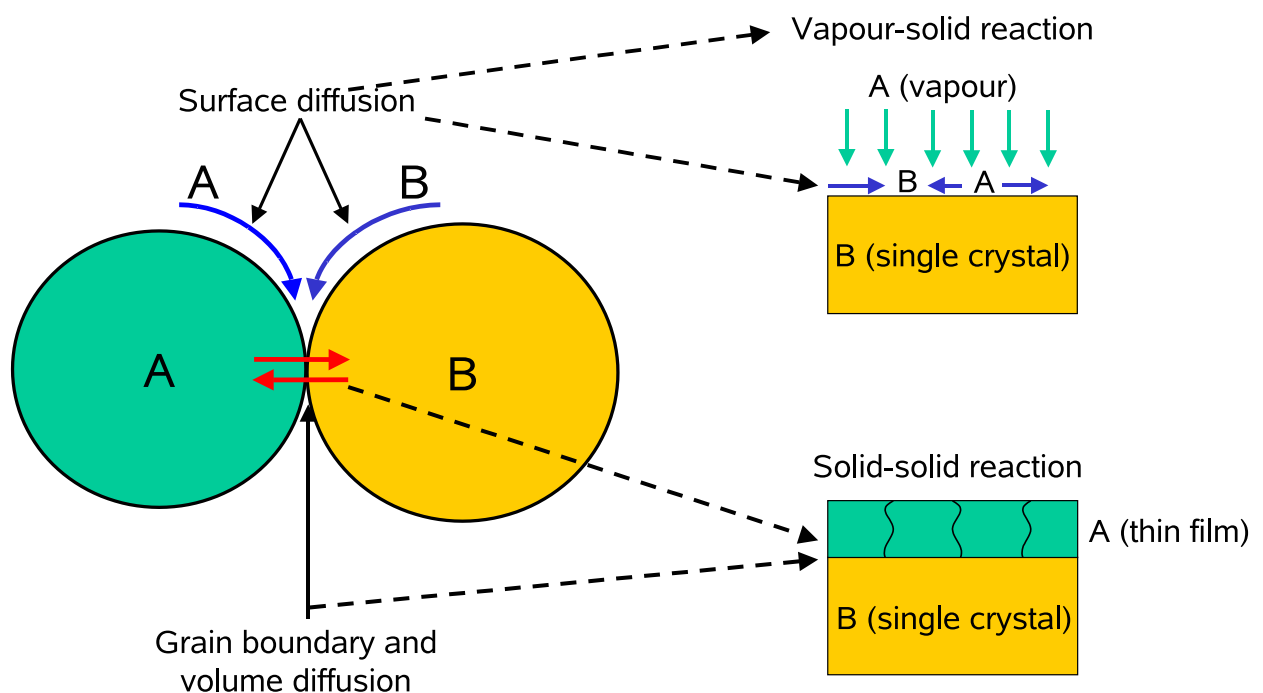


Fig. 2.13. Two different solid state reaction geometries which can be used to study the reaction of two particles in a powder.

3 Experimental and investigation procedures

3.1 Sample preparations

Titanium dioxide (TiO_2) with rutile and anatase structures was used. To provide a model system, single crystalline materials are usually used as one reactant. TiO_2 rutile single crystals are commercially available with different surface orientations. But anatase single crystals are more difficult to obtain with appropriate size and purity. This problem has been addressed by growing epitaxial anatase thin films.

Thus in the case of TiO_2 with rutile structure, polished (110) and (100) surfaces of commercial rutile TiO_2 single crystals (CrysTec GmbH, Berlin, Germany) were used as substrates. Before the experiments the rutile crystals were annealed in air at 1100 °C for 1 h. After this heat treatment the (110) rutile surfaces involved terraces of about 450 nm in width with ordered steps of about 0.26 nm in height as shown by AFM in Fig. 3.1(a). An annealing at 1100 °C for 1 h was found to be optimal for the (110) rutile substrates. The surface morphology of thermally treated (100) rutile surfaces was significantly different from (110) ones. The surface of (100) rutile substrates consisted of terraces of 450 nm to 800 nm in width. The height of the steps ranged from 0.6 nm to 0.96 nm (Fig. 3.1(b)). Extensive step bunching was also observed on (100) surfaces.

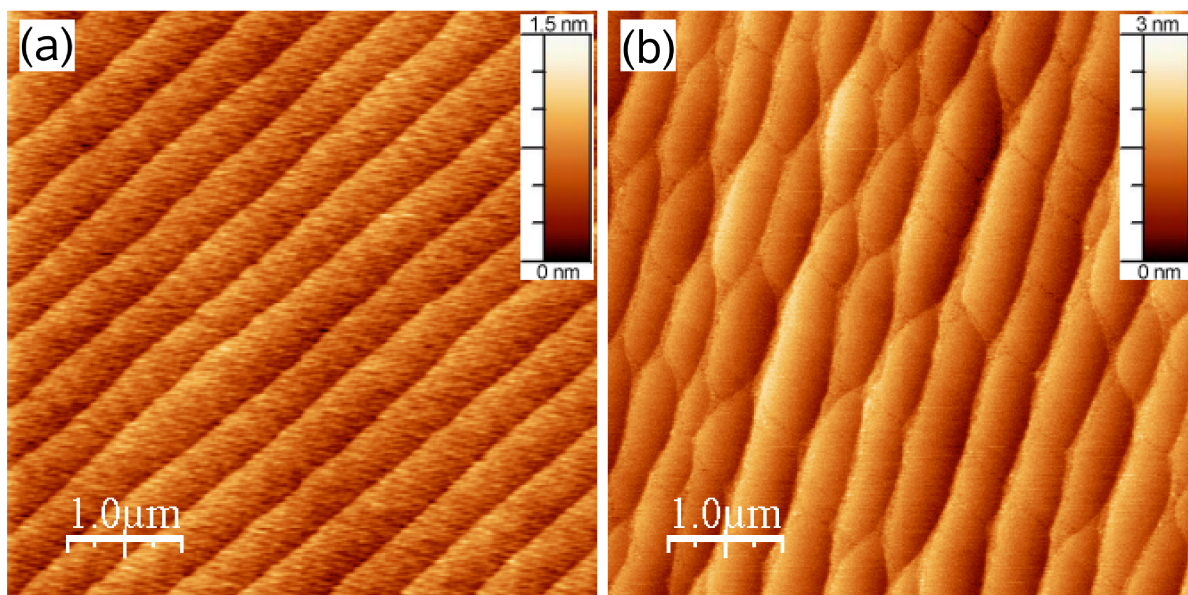


Fig. 3.1. AFM topography images after thermal treatment in air at 1100 °C for 1 h: (a) (110) rutile surface (root-mean-square roughness is 0.15 nm) and (b) (100) rutile surface (root-mean-square roughness is 0.25 nm).

In the case of TiO_2 with anatase structure, (001) and (012) surfaces of epitaxial TiO_2 anatase thin films were used for the reaction experiments. Epitaxial TiO_2 thin films with a good crystalline quality and microstructure were prepared on (100)-oriented SrTiO_3 and LaAlO_3 substrates as well

as on (110)-oriented SrTiO_3 and LaAlO_3 substrates. Details on epitaxial thin film growth are given in **Chapter 4 (Section 4.2)**.

Two reaction geometries were used to study the solid state reactions (Fig. 3.2). Fig. 3.2(a) shows the so-called solid-solid regime of the solid state reactions. The solid-solid reaction between BaCO_3 and TiO_2 was initiated by heating in a high-vacuum environment and in air. The second regime of the solid state reactions, the so-called vapour-solid reaction, was performed between TiO_2 and BaO vapour in a high-vacuum environment (Fig. 3.2(b)). For experiments with other vapours BaO was replaced by SrO , CaO and MgO .

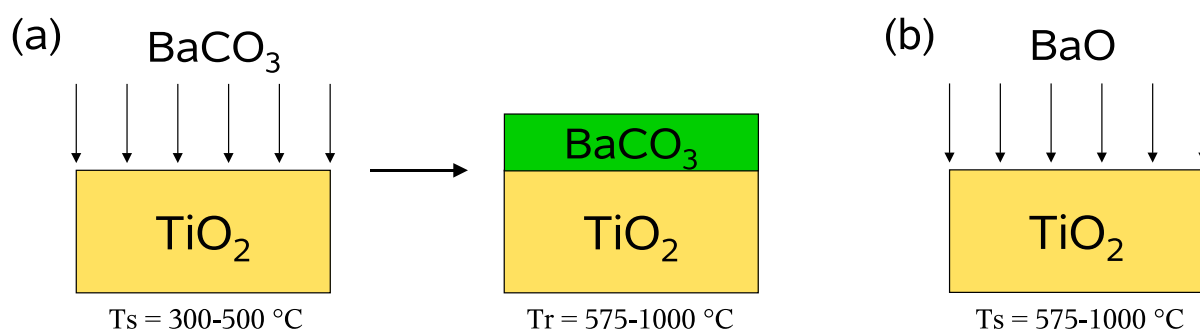


Fig. 3.2. Two solid state reaction geometries: (a) solid-solid reaction and (b) vapour-solid reaction. T_s is the substrate temperature during deposition while T_r is the annealing temperature.

A BaCO_3 thin film or BaO vapour was obtained in a high-vacuum chamber by evaporating a BaCO_3 powder target while SrO , CaO or MgO vapour was produced by electron-beam evaporation of either a SrCO_3 , a CaCO_3 or a MgO powder target. Fig. 3.3 gives a schematic drawing of the evaporation system used in this study. The distance between evaporator and the sample is approximately 20 cm, which is quite large. This minimises the heat load on the sample and thus prevents a rise in sample temperature during deposition. The base pressure of the vacuum system was less than 2×10^{-5} mbar. During deposition pure oxygen was introduced to establish a pressure of 1×10^{-4} mbar. The deposition rate and film thickness were in-situ monitored during deposition by a quartz crystal microbalance (INFICON, gold coated crystals, 6 MHz), positioned just a few centimeters away from the sample. The thickness of the BaCO_3 thin film was determined by cross-sectional transmission electron microscopy and it was found to be ≈ 50 nm thick. The substrates were heated in a tube furnace directly by thermal irradiation during deposition. They were put into a holder placed in the middle of the furnace and were hanging down with the polished surface pointing towards the electron-beam evaporator. The temperatures were measured by a Pt/PtRh10 thermocouple installed behind the substrate. After the solid state reactions the samples were kept in the vacuum chamber or in a laboratory furnace and allowed to cool to room temperature.

For the growth of BaCO_3 thin films, the substrate temperature was kept at $300\text{ }^\circ\text{C}$, $400\text{ }^\circ\text{C}$ or $500\text{ }^\circ\text{C}$. The solid-solid reactions in vacuum were performed directly after deposition (without cooling down to room temperature) by heating up to temperatures between $575\text{ }^\circ\text{C}$ and $1000\text{ }^\circ\text{C}$ for different length of time (0 min to 180 min holding time). For the solid-solid reaction experiments

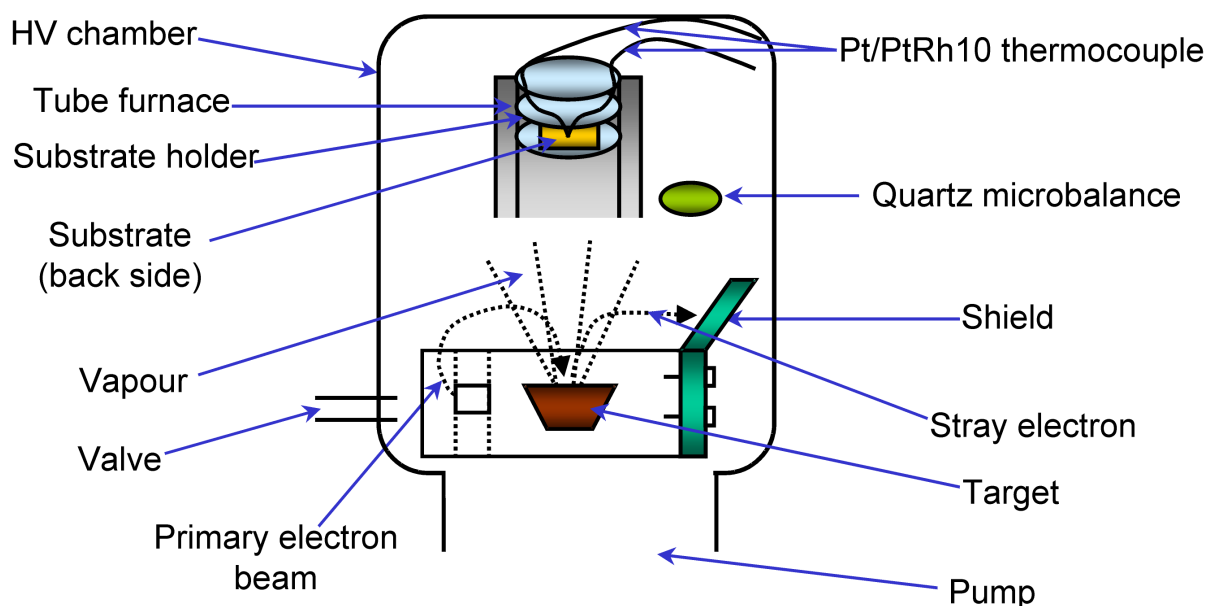


Fig. 3.3. Scheme of the electron beam evaporation system.

in air, the substrate with deposited BaCO_3 thin film was taken out from the vacuum chamber and annealed in a laboratory furnace at temperatures ranging from 575 °C to 1000 °C for different length of time (0 min to 30 min holding time).

For the vapour-solid reaction of BaO with TiO_2 , the substrate was heated to the reaction temperature (575 °C-1000 °C) and kept constant at a desired temperature during the reaction. A complete deposition/reaction experiment required about 35 min. It should be noted that BaCO_3 evaporates by decomposition, the vapour consists of BaO and CO_2 . In view of the high volatility (low sticking coefficient) of CO_2 at such high temperatures, the material reacting with the rutile substrate consists of BaO species. This is in agreement with thermodynamical calculations where the formation of BaCO_3 by a reaction between BaO and CO_2 at temperatures higher than 575 °C is suppressed by a positive value of Gibbs energy (Fig. 3.4).¹²⁸ The same conclusion is valid for the formation

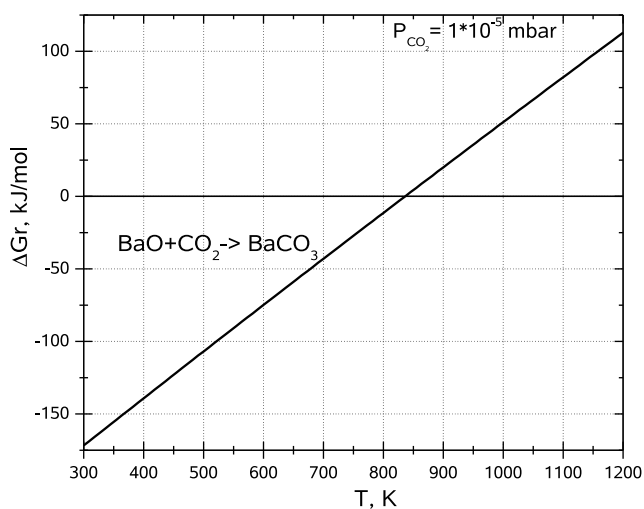


Fig. 3.4. The change in Gibbs free energy (ΔG_r) vs T for the formation of BaCO_3 in vacuum of 1×10^{-5} mbar. Calculated using data from I. Barin.¹²⁸

of SrCO_3 or CaCO_3 on hot TiO_2 substrates by a reaction between SrO or CaO and CO_2 since the thermodynamic estimations for the reactions $\text{SrO} + \text{CO}_2 \rightarrow \text{SrCO}_3$ and $\text{CaO} + \text{CO}_2 \rightarrow \text{CaCO}_3$ are close to the reaction $\text{BaO} + \text{CO}_2 \rightarrow \text{BaCO}_3$.

Several methods have been used to analyse the samples after solid state reactions. These methods are described in the next two chapters.

3.2 X-ray diffraction

Techniques based on X-ray probes dominate in the field of materials science mainly because of their simplicity, reliability, quantitative and nondestructive nature. Of these techniques, XRD plays a leading role, as a fundamental tool for material characterization.¹²⁹

3.2.1 Basic principles

X-rays are electromagnetic radiation with typical photon energies in the range of 100 eV-100 keV. For diffraction applications, mainly short wavelength X-rays (hard X-rays) in the range of a few angstroms to 0.1 Å (1 keV-120 keV) are used. Because the wavelength of X-rays is comparable to the size of atoms, they are ideally suited for probing the structural arrangement of atoms and molecules in a wide range of materials. X-rays primarily interact with electrons in atoms. When X-ray photons collide with electrons, some photons from the incident beam will be deflected away from the direction of their original travel. If the wavelength of these scattered X-rays did not change (meaning that the X-ray photons did not lose any energy), the process is called elastic scattering in that only momentum has been transferred in the scattering process. These are the X-rays that we measure in diffraction experiments, as the scattered X-rays carry information about the electron distribution in materials. Diffracted waves from different atoms can interfere with each other and the resultant intensity distribution is strongly modulated by this interaction. If the atoms are arranged in a periodic fashion, as in crystalline solids, the diffracted waves will consist of sharp interference maxima (peaks) with the same symmetry as the distribution of atoms. The angles of peaks in a XRD pattern are directly related to the atomic distances. For a given set of lattice planes with an inter-plane distance of d , the condition for diffraction to occur can be simply written as:

$$2d\sin\theta = n\lambda, \quad (3.1)$$

which is known as Bragg's law. In the above equation λ is the wavelength of the X-ray, θ is the scattering angle and n is an integer representing the order of the diffraction peak.

3.2.2 XRD analysis performed in this work

Powder XRD is perhaps the most widely used XRD technique for material characterisation. Powder diffraction data can be collected using either transmission or reflection geometry. Because

the particles in the powder sample are randomly oriented, these two methods will yield the same information.

Generally speaking thin film diffraction refers not to a specific technique but rather a collection of XRD techniques used to investigate thin film samples grown on single crystalline substrates. There are several special considerations for using XRD to characterise thin film samples. First, a reflection geometry is used for these measurements, as the substrates are generally too thick for transmission. Second, high angular resolution is required.

A four-circle Material Research Diffractometer was used in the present work (Philips X'Pert MRD, type 3050/65, 50 kV and 30 mA, CuK_α radiation). The axes of a four-circle diffractometer are shown in Fig. 3.5.

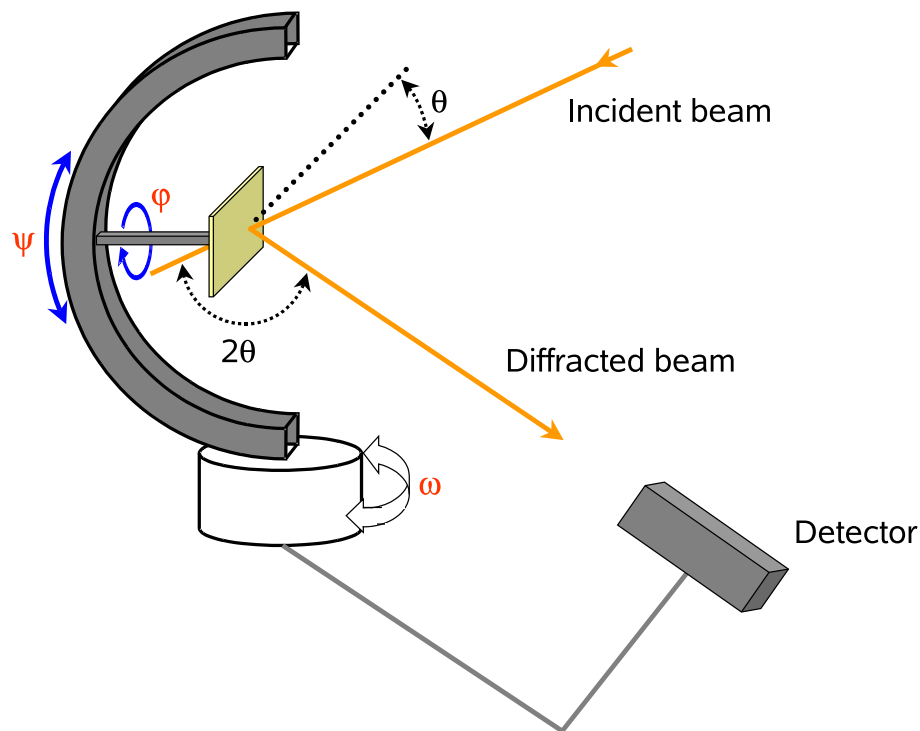


Fig. 3.5. Scheme of a four-circle diffractometer. The ϕ axis is always parallel to the sample surface normal. The ψ axis is always in the plane of diffraction.

A parallel-beam optics geometry was used for the investigations (Fig. 3.6). In this geometry, the diffracted-beam optics is modified to parallel-beam optics, and a flat plate graphite monochromator is incorporated in front of the detector.

Standard θ - 2θ scans were made for phase analysis and to investigate a preferential orientation of the films. The θ - 2θ scan is also called ω - 2θ scan. In a four-circle diffractometer, an ω - 2θ scan runs on two axes of the diffraction system which are driven by two different motors (ω motor: sample holder and 2θ motor: detector). In this Ph.D. work, the ω axis is referred to as θ one. In Fig. 3.5, θ (the angle of incidence) represents the angle between the incident X-ray beam and the plane of the sample holder while 2θ (the angle of reflection) is the angle between the viewing direction of the detector (or scattered X-ray beam) and the incident X-ray beam. In a normal θ - 2θ scan these two angles are varied simultaneously from θ_{\min} to θ_{\max} and $2\theta_{\min}$ to $2\theta_{\max}$. In this work, the samples

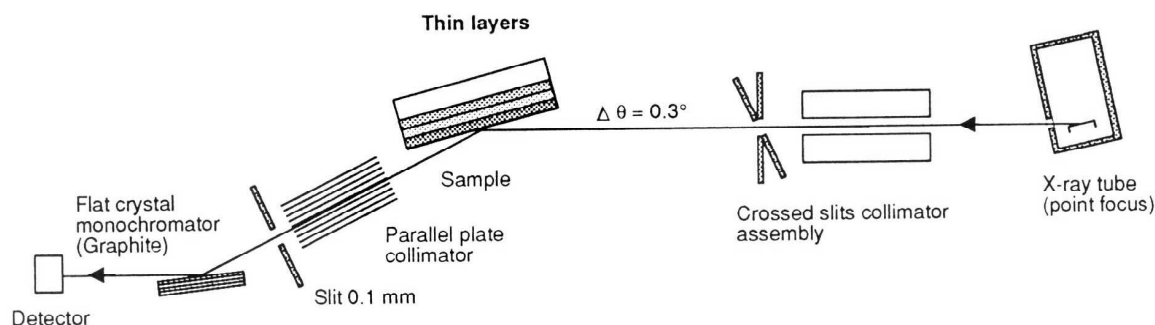


Fig. 3.6. Scheme of a parallel-beam optics geometry according to the User Guide for Philips X'Pert MRD Systems (1995). The 2θ resolution of the parallel plate collimator is 0.09° .

were mounted on a (001)-oriented silicon wafer in an open Eulerian cradle. After that, the ϕ and ψ angles were optimised for a weak reflection of the substrate (e.g. for a (110)-oriented TiO_2 (rutile) substrate the reflection (220) was used) in order to record the well-oriented contribution from the film. Fixing these two angles, the sample will then be rotated only in one direction by the variation of the θ angle. Thus, θ - 2θ scans are only scans along one direction in reciprocal space. It is therefore a one-dimensional scan in the reciprocal space. If a film that covers the substrate crystal was grown with a certain orientation (i.e. in the case of epitaxy or topotaxy), the diffractogram of the sample will show the reflections of the single crystal substrate and reflections of those film planes which are parallel to the sample holder plane (substrate surface).

A 2θ scan was performed to study the polycrystalline or unoriented reaction products. The θ - 2θ scan is not useful for the study of polycrystalline thin films on single crystalline substrates, because of the presence of the interfering effect of the strong substrate reflections. A useful geometry is a grazing-incidence diffraction that is based on a low angle of incidence of the X-rays. In this geometry, X-rays pass through a suitable slit system and are made to fall on the sample at a grazing angle while the detector on the 2θ axis scans the XRD pattern. In this work a fixed θ value of 5° was used to attenuate the substrate reflections (the ϕ and ψ angles were kept as optimised for the θ - 2θ scan).

Texture measurements are used to determine the orientation distribution of crystalline grains in the sample. In materials science, texture is the distribution of crystallographic orientations of a sample. A sample in which these orientations are fully random is said to have no texture. If the crystallographic orientations are not random, but have some preferred orientation, then the sample has a weak, moderate or strong texture. The degree is dependent on the percentage of crystals that have the preferred orientation. Texture measurements can provide a complete description of the preferred orientation of a material. This is because a texture scan is a two-dimensional scan in reciprocal space. The surface of a hemisphere in reciprocal space is scanned for the reflections $\{hkl\}$ off the sample/film. The possible reflections are selected by choosing the fixed value of 2θ . A texture measurement is also referred to as a pole figure (this definition is used in the present work) as it is plotted in polar coordinates consisting of the tilt and rotation angles with respect to a given orientation of the substrate surface. Thus, a pole figure is similar to a stereographic projection. This projection is used to represent graphically the orientation of planes in 3D space.

The pole figure analysis was performed using an open Eulerian cradle. A pole figure was measured at a fixed scattering angle 2θ (constant d spacing) and consists of a series of ϕ -scans (in-plane rotation around the center of the sample) at different tilt ψ angles. $\psi = 0^\circ$ (center of the plot) in the pole figures corresponds to the planes of the thin film being parallel to the substrate plane whereas $\psi = 90^\circ$ (rim of the plot) corresponds to the planes of the thin film being perpendicular to the substrate plane. The full determination of the texture requires at least the measurements of two pole figures corresponding to planes that are not parallel and that do not have the same diffraction angle (different interplanar distances). In this work, to identify the orientation relationship between reaction products and the substrate, a series of pole figures were recorded with different 2θ values. The Ca.R.Ine Crystallography software was used to draw stereographic projections and 3D crystal structures.¹³⁰

ϕ scans were performed in order to find-out the in plane orientation of the thin film with respect to the substrate. In this scan, the 2θ and ψ angles are fixed. For example, in the case of a (110) rutile TiO_2 substrate a ϕ scan with the TiO_2 (200) reflection ($2\theta = 39.2^\circ$) at $\psi = 45^\circ$ could be done to determine the in-plane orientation of the substrate.

The XRD investigations in this work were performed outside the growth chamber at room temperature. The transfers of the samples were made through air.

3.3 Transmission electron microscopy

The electron microscopy methods are powerful techniques in the nanoscience world. Among them, cross-sectional TEM is essential for characterising of interfaces between thin films and substrates. TEM investigations were a significant part of this work. A conventional TEM CM20 Twin (Philips, Netherlands) at primary beam energy of 200 keV (point resolution 2.7 Å) and a HRTEM JEOL 4010 (JEOL, Japan) at primary beam energy of 400 keV (point resolution 1.8 Å) were used to study the reactive interfaces.

3.3.1 Basic concepts

A transmission electron microscope works on the same basic principles as a light microscope but uses electrons instead of light. The main principles of electron microscopy can be understood by use of optical ray diagrams as shown in Fig. 3.7.¹³¹ As in the XRD, electron diffraction is an elastic scattering phenomenon with electrons being scattered by atoms in a regular array (crystal). When a crystal of lattice spacing d is irradiated with electrons of wavelength λ , diffracted waves will be produced at angles 2θ , satisfying the Bragg condition (3.1). The diffracted waves form diffraction spots on the back focal plane. In an electron microscope, the use of electron lenses allows the regular arrangement of the diffraction spots to be projected on a screen and the so-called electron diffraction pattern can then be observed. If the transmitted and the diffracted beams interfere on the image plane, a magnified image can be seen. The space where the diffraction pattern forms is called the reciprocal space, while the space at the image plane or at a specimen is called the real space.

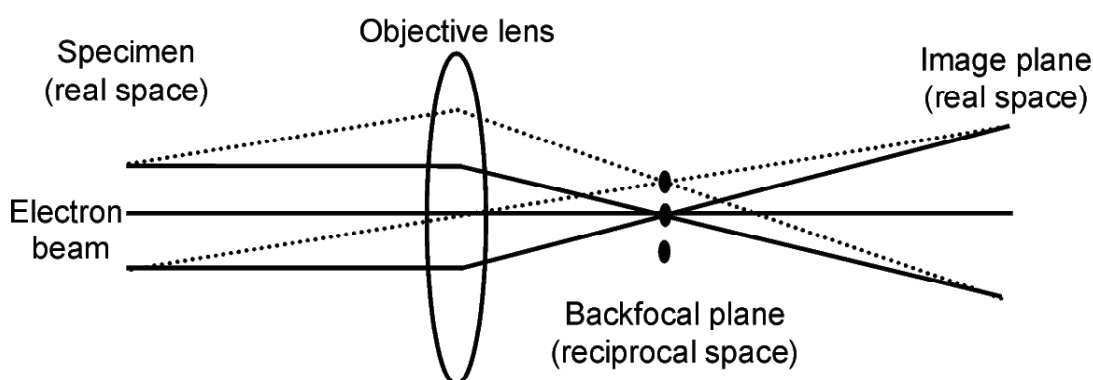


Fig. 3.7. Optical ray diagram with an optical objective lens showing the principle of the imaging process in a transmission electron microscope.

The transformation from the real space to the reciprocal space is mathematically given by the Fourier transform. By adjusting the electron lenses to obtain a diffraction image and inserting an aperture (selected area aperture) in a plane of the microscope containing an intermediate image, a specific area can be resolved and a diffraction pattern of the selected area (SAED) can be obtained. Because a SAED pattern can be obtained locally from different parts of the investigated material, crystal structure and mutual crystal orientation relationships of these parts can be identified.

Several types of observation modes in the electron microscope can be selected using an objective aperture. The observation mode using only the transmitted beam is called bright-field method and the image observed is a bright-field image (Fig. 3.8(a)). When one diffracted beam is selected, it is called dark-field method, and the image observed is a dark field image (Fig. 3.8(b)). It is also possible to form a TEM image by selecting multiple beams on the back focal plane using a large objective aperture. This observation is called high-resolution electron microscopy, and the image observed is a high-resolution image (HRTEM image) (Fig. 3.8(c)). HRTEM images can be classified into five groups: 1. lattice fringes; 2. one-dimensional structure images; 3. two-dimensional lattice images (showing the structural information at unit cell scale); 4. two-dimensional structure images (or crystal structure images, showing the structural information at atomic scale) and 5. special images.¹³³

3.3.2 TEM sample preparation

A cross-sectional TEM investigation can only be performed, if a specimen is sufficiently thin (thinner than ≈ 100 nm). The samples for these investigations were prepared by standard methods of mechanical polishing and ion milling.¹³⁴

The first step is to cut the substrate with the grown thin film into two parts of the same size using a diamond wire saw and then glue them face-to-face. In this work M-Bond 610 epoxy resin that has a very low viscosity was used. The glued sample is compressed by a uniformly distributed pressure during the curing time (1.5 h at curing temperature of 150 °C). The glue layer should be

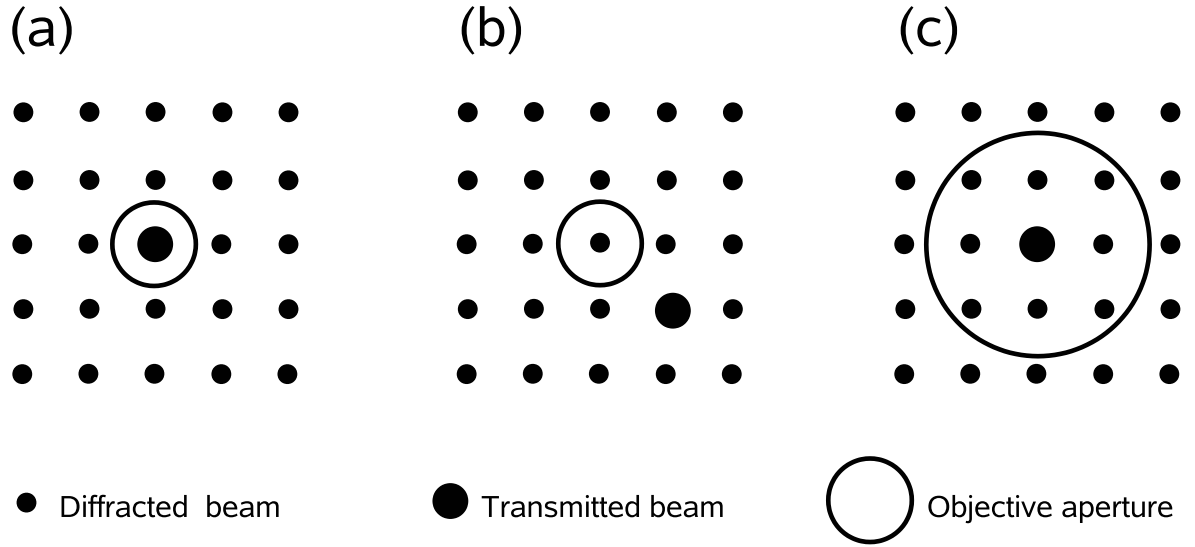


Fig. 3.8. Three observation modes in electron microscope using an objective aperture. The center of the objective aperture is on the optical axis. (a) Bright-field method, (b) Dark-field method and (c) High-resolution electron microscopy.¹³³

as thin as possible. The glued sample is cut into slices normal to the interfaces with a thickness of 0.5 mm. Then, this slice was polished manually on grinding and polishing paper until the thickness is less than 70 μm . A Gatan Model 656 dimple grinder was used to dimple and polish from one side at the center of the slice (the interface region) by a copper wheel with a radius of 15 mm. Hot wax was used to mount the slice onto a glass cylinder. After dimpling, the specimen was glued to a metallic Cu grid. The wax attached on the slice was cleaned by acetone. At the end of this step, the thickness at the dimpled area is in the range of 15 μm -20 μm .

The next step was thinning the slice at the center of the dimple by ion sputtering until a transparent hole is formed. A Gatan PIPS 691 was used to do the work. Two Ar^+ ion guns bombard the up- and down-side of the specimen alternatively. The incident angles were set to 6° . A varying ion energy method has been used to quicken the specimen preparation. At the beginning of the ion milling process, the ion energy was set to 4 keV. Several hours later when the specimen was nearly transparent, the ion energy was reduced to 3 keV. After the transparent hole was formed, the milling was terminated. After a careful investigation of the sample by an optical microscope, the last step consisted of a fine polish for several minutes at incident angles of 10° - 15° with respect to the surface using a decreasing accelerating voltage of 4 kV to 2 kV. A Duomill (Dual Ion Mill, Gatan) was used to perform the last step. This step completes the cross-section specimen preparation for TEM investigations.

3.4 Atomic force microscopy

An atomic force microscope (AFM) was used in this work to get information on the sample topography. AFM is a scanning probe microscope that probes the surface of a sample by moving the sample beneath a tip attached to a weak cantilever while the tip is in contact, or near contact,

with the surface. An AFM comprises two main components: the scanner and the AFM detection system. An AFM can operate in two principal modes, viz. tapping (non-contact) mode and contact mode, depending on the interaction between the tip and the sample.

In the contact mode, the tip adheres to the sample surface with a finite force as it is dragged across the surface. The finite adhesion forces deform the tip and sample so that contact occurs over a finite area. This area is greatly influenced by the tip sharpness and is increased by any additional spring force. In the tapping mode, long-range van der Waals forces deflect the tip. The strength of the van der Waals interaction depends on the tip sharpness and the amount of spring deflection is fixed by the spring constant. More information about AFM can be found in Ref.¹³⁵.

In this study, the surfaces of substrates and thin films were studied by a Digital Instruments 5000 microscope working in tapping mode and using ultrasharp Si tips.

4 Results

4.1 Solid state reactions of BaCO_3 and BaO with TiO_2 (rutile)

4.1.1 Solid-solid reaction of BaCO_3 with TiO_2 (rutile)

A. Some properties of BaCO_3 thin films

It is well-known that the substrate temperature has a primary role in controlling structure and composition of a growing thin film. Effects of the substrate temperature appear to be very important in obtaining a particular crystal structure and orientation of a thin film. A desired temperature should be below the temperature at which a reaction of the deposited film with the substrate occurs. The optimal temperature for BaCO_3 deposition was first found by using the (110) TiO_2 (rutile) substrates. Furthermore, this temperature was used for the deposition of BaCO_3 on (100) TiO_2 (rutile) substrates and TiO_2 (anatase) thin films.

Deposition of BaCO_3 at temperatures between 300 °C and 500 °C resulted in the growth of a single BaCO_3 phase (JCPDS 45-1471,[†] barium carbonate) as indicated by the XRD θ - 2θ , 2θ and pole figure measurements. However, the orientation relationship of the BaCO_3 with respect to the (110) rutile substrates was dependent on the substrate temperature. BaCO_3 films with a poor orientation quality were growing at a deposition temperature of 300 °C or 400 °C. The optimum temperature for the BaCO_3 deposition was found at 500 °C. At this temperature the orientation relationship between the barium carbonate and the substrate was well-defined. Fig. 4.1(left) shows a XRD θ - 2θ scan of a BaCO_3 thin film deposited at a substrate temperature of 500 °C. The peak position at $2\theta = 34.3^\circ$ in Fig. 4.1(left) is from the (202) reflection of BaCO_3 which means that the (101) plane of BaCO_3 is parallel to the (110) substrate plane. 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. 4.1(right)) and ϕ scans of the TiO_2 (200) reflection taken at $\psi = 45^\circ$. The ϕ positions corresponding to the (001) and (00 $\bar{1}$) substrate planes are denoted A and B, respectively. The main orientation relationship at 500 °C was derived as:

$$(101) \text{ BaCO}_3 \parallel (110) \text{ TiO}_2; [10\bar{1}] \text{ BaCO}_3 \parallel [001] \text{ TiO}_2. \quad (4.1)$$

A second orientation relation was determined as:

$$(21\bar{1}) \text{ BaCO}_3 \parallel (110) \text{ TiO}_2; [2\bar{3}1] \text{ BaCO}_3 \parallel [001] \text{ TiO}_2. \quad (4.2)$$

[†]Lattice parameters: a= 0.643 nm, b= 0.531 nm, c= 0.89 nm; space group Pnma (62).

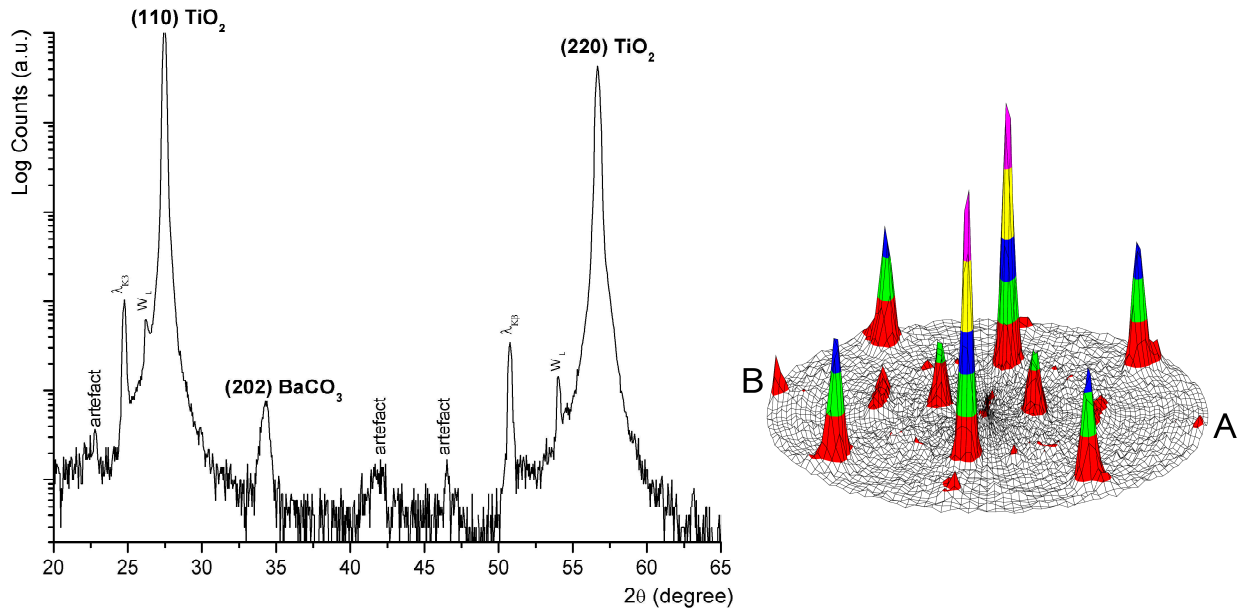


Fig. 4.1. (left) XRD θ - 2θ scan of a BaCO₃ thin film deposited at 500 °C on a (110) rutile substrate. The $\lambda_{K\beta}$ lines are the substrate peaks originating from the remaining Cu-K β radiation, and the W_L lines are coming from the tungsten contamination of the X-ray target by the tungsten cathode filament. The "artefact" peaks are substrate-induced artefacts. (right) BaCO₃ (111) ($2\theta = 23.9^\circ$) pole figure of a sample deposited on (110) TiO₂ at 500 °C. The positions of marks A and B correspond to the ϕ values of the (001) and (00 $\bar{1}$) substrate planes, respectively.

The crystallite size determined from the broadening of the (202) reflection of BaCO₃ using Scherrer's equation[‡] (see footnote) was ≈ 20 nm.

The BaCO₃ thin films were found to be unstable and decomposed when extensively exposed to the 200 keV electron beam for a few minutes, most probably to BaO and CO₂. Recently, a similar decomposition of BaCO₃ particles was observed in Ref. ¹³⁶.

The BaCO₃ thin films deposited on (100) TiO₂ at a substrate temperature of 500 °C formed also with a defined orientation to the substrate. A XRD θ - 2θ scan indicated that the (100) plane of BaCO₃ ($2\theta = 27.7^\circ$) is parallel to the (100) substrate surface (Fig. 4.2(left)). A pole figure recorded at $2\theta = 23.9^\circ$ of the sample prepared at a substrate temperature of 500 °C is shown in Fig. 4.2(right). This figure displays rather broad reflections of BaCO₃ both in ϕ and ψ directions. The X-ray intensity of this phase was also low in Fig. 4.2(left). In addition, some weak peaks were observed in a 2θ scan which means that the film contained unoriented parts. The mean orientation of most of the BaCO₃ grains determined by pole figure measurements and a ϕ scan of the (110) TiO₂ reflection ($\psi = 45^\circ$, $2\theta = 27.45^\circ$) was derived as:

$$(100) \text{ BaCO}_3 \parallel (100) \text{ TiO}_2; [001] \text{ BaCO}_3 \parallel [001] \text{ TiO}_2. \quad (4.3)$$

The crystallite size determined from the broadening of the (100) peak of BaCO₃ using Scherrer's

[‡] $D_v = 0.9\lambda/B\cos\theta$, where D_v - crystallite size, λ - wavelength of radiation, and B - FWHM of diffraction peak (in radians) and θ is the diffraction angle. This approach does, however, neglect the effect that strain and defects can have on the width of the diffraction peaks.

equation was ≈ 19 nm.

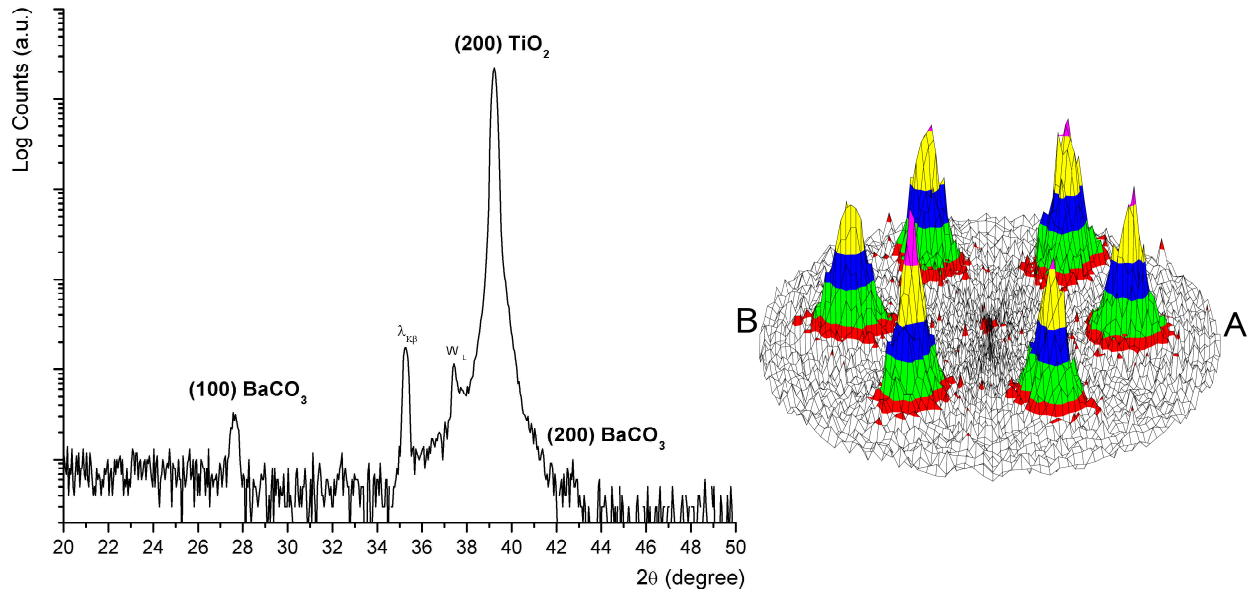


Fig. 4.2. (left) XRD θ - 2θ scan of a BaCO₃ thin film deposited at 500 °C on a (100) rutile substrate. The $\lambda_{K\beta}$ lines are the substrate peaks originating from the remaining Cu-K β radiation, and the W_L lines are coming from the tungsten contamination of the X-ray target by the tungsten cathode filament. (right) BaCO₃ (111) ($2\theta = 23.9^\circ$) pole figure of a sample deposited at 500 °C on (100) TiO₂. The positions of marks A and B correspond to the ϕ values of the (001) and (00 $\bar{1}$) substrate planes, respectively.

B. Phase formation

a. Reaction in vacuum ($P_{CO_2} = 10^{-5}$ mbar)

X-ray diffraction

Most of the solid-solid reactions presented in this work were conducted on (110) TiO₂ (rutile) substrates using BaCO₃ layers grown at 500 °C.

The presence of Ba₂TiO₄ (JCPDS 38-1481), BaTiO₃ (JCPDS 89-2475) and Ti-rich phases depending on the reaction temperature was first investigated by XRD. A deposition of BaCO₃ at 500 °C followed by solid-solid reaction at 575 °C-600 °C for 30 min produced a single Ba₂TiO₄ phase (Fig. 4.3(b)). The reaction at temperatures between 625 °C and 825 °C lead to the formation of both Ba₂TiO₄ and BaTiO₃ phases (Figs. 4.3(c)-(d)) while the reaction at 850 °C for 30 min resulted in the formation of BaTiO₃ without any evidence of remaining Ba₂TiO₄.

In order to evaluate the rate of the solid-solid reaction, the BaCO₃-TiO₂ system was annealed at constant temperature (575 °C-600 °C and 850 °C) for different length of times. The reaction proceeded 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 575 °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

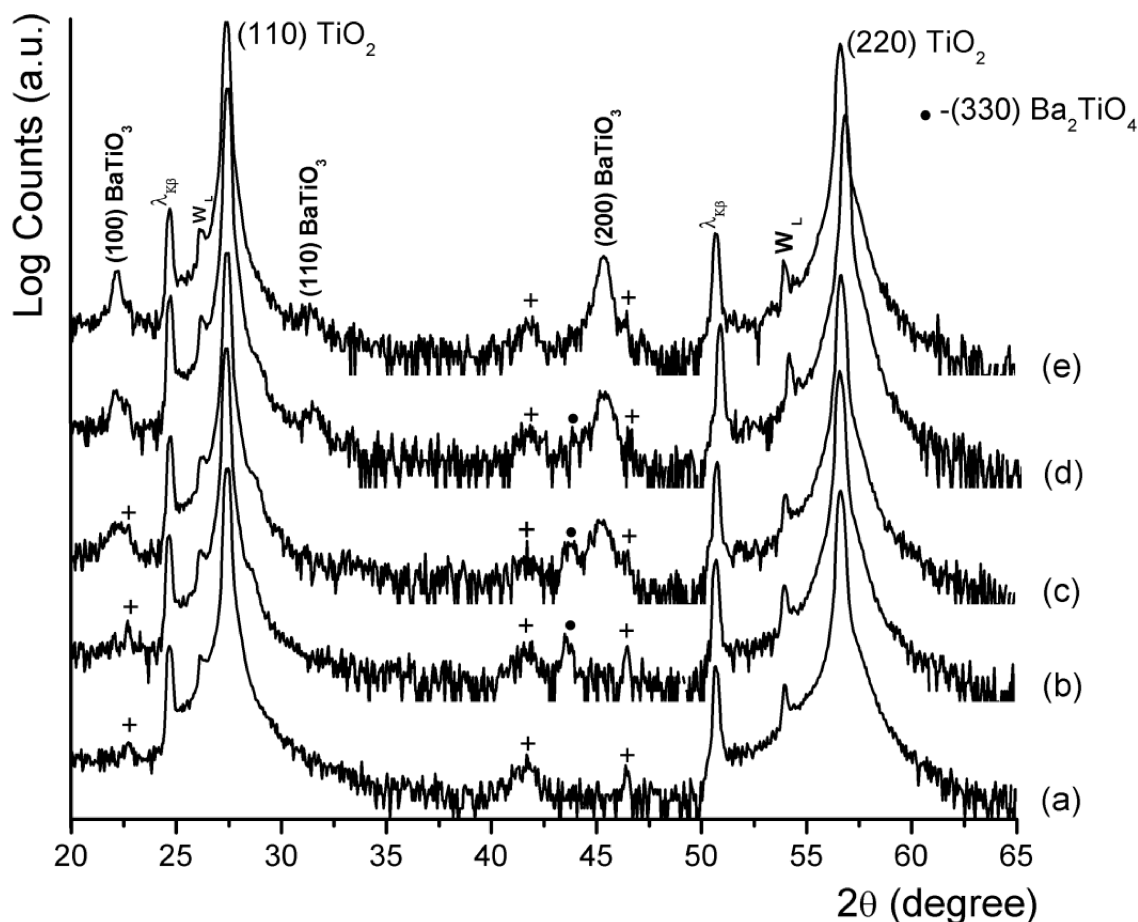


Fig. 4.3. XRD θ - 2θ scans for: (a) virgin (110) rutile substrate and for samples after solid-solid reaction of BaCO_3 thin film deposited at 500 °C with the (110) TiO_2 at (b) 600 °C, (c) 700 °C, (d) 800 °C and (e) 900 °C. The $\lambda_{K\beta}$ lines are the substrate peaks originating from the remaining $\text{Cu-K}\beta$ radiation, and the W_L lines are coming from the tungsten contamination of the X-ray target by the tungsten cathode filament. The peaks marked by "+" characters are substrate-induced artefacts.

reaction time up to 180 min at 600 °C resulted, together with the Ba_2TiO_4 phase, in the formation of BaTiO_3 . After the reaction at 850 °C for a short time (holding time null minutes), two phases (Ba_2TiO_4 and BaTiO_3) were identified.

The Ba_2TiO_4 had an orthorhombic structure as indicated by pole figure analyses. This phase was found to be a chemically unstable compound and to decompose entirely after a storage for two weeks in air, most probably by reaction with H_2O and CO_2 . This observation is in good agreement with the data obtained in Refs.^{55,56}.

After reaction at 900 °C, BaTiO_3 (Fig. 4.3(e)) and Ti-rich phases were observed on the (110) TiO_2 substrate (detected by pole figures) while after the reaction at 1000 °C, only the BaTi_4O_9 phase was detected by XRD. It should be noted that after reaction at 900 °C-1000 °C the samples became blue in colour. As was reported earlier,¹³⁹ 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 phase sequence during solid-solid reaction on (100) TiO_2 (rutile) substrates at temperatures between 600 °C and 1000 °C showed a process that is similar to the reaction on (110) TiO_2 . An

example of a sample prepared by a solid-solid reaction between a BaCO_3 film and (100) TiO_2 substrate at 1000 °C for 30 min is shown in Fig. 4.4.

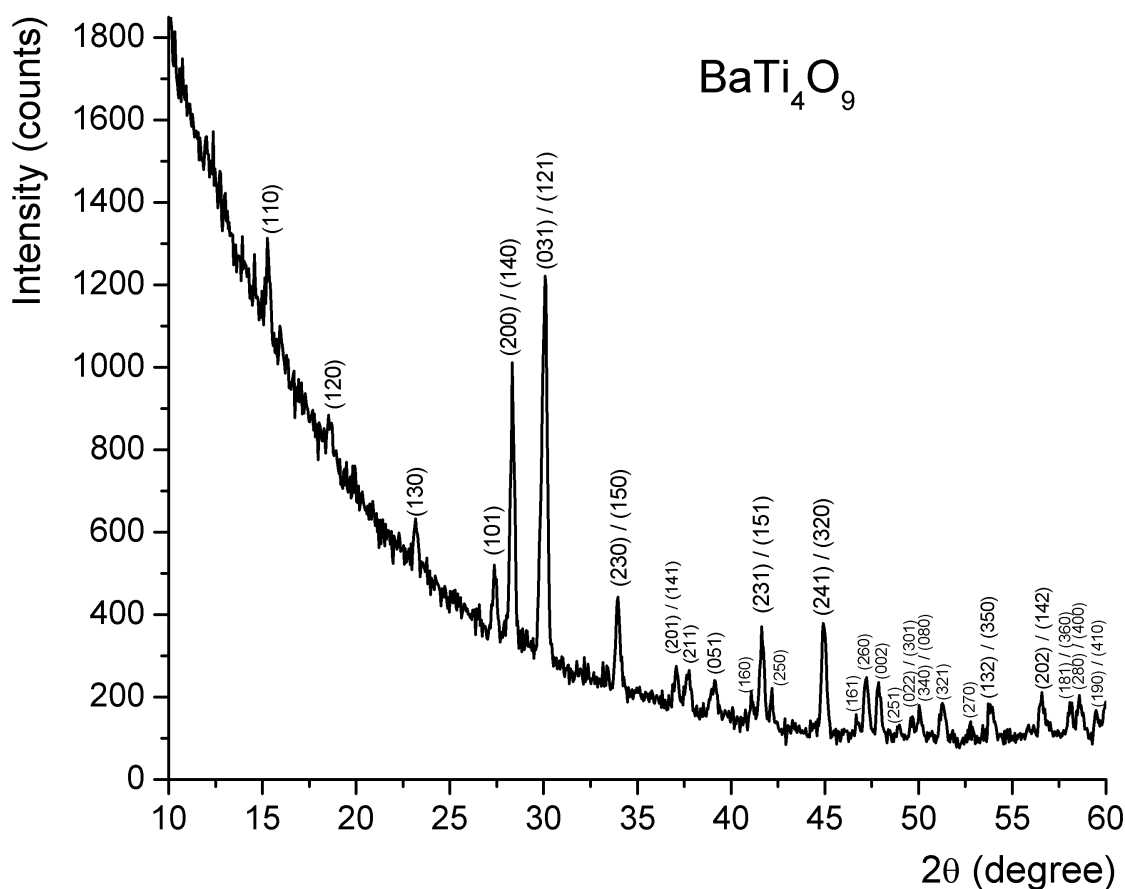


Fig. 4.4. XRD 2θ scan of a sample made by a solid-solid reaction in vacuum at 1000 °C for 30 min between a (100) TiO_2 substrate and a BaCO_3 thin film grown at 500 °C. The pattern was indexed according to JCPDS 77-1565. The scan speed was 0.0005 °/s.

TEM and HRTEM investigations

As was shown above, only the Ba_2TiO_4 phase was detected by XRD after solid-solid reaction at temperatures between 575 °C and 625 °C. To obtain more information about the presence of possible other phases formed in the films after the reactions on a nanometer scale, TEM and HRTEM were employed.

As was mentioned above, the Ba_2TiO_4 phase is a very unstable compound and decomposed when exposed to air by reaction with H_2O and CO_2 . To protect this phase, a SiO_2 film was deposited at room temperature after a solid-solid reaction. This film protected Ba_2TiO_4 from the influence of air and, thus, induced a stability of Ba_2TiO_4 for several weeks, as shown by repeated X-ray diffraction measurements in air. Using such protected samples, cross-sectional samples with the Ba_2TiO_4 phase were prepared for TEM investigations several times.

Fig. 4.5 shows a HRTEM image of a typical interface after solid-solid reaction of BaCO_3 with (110) TiO_2 in vacuum at 600 °C for 1 min. Small poorly-oriented BaTiO_3 grains separated from each other by large distances were observed on the substrate surface after the reaction. However,

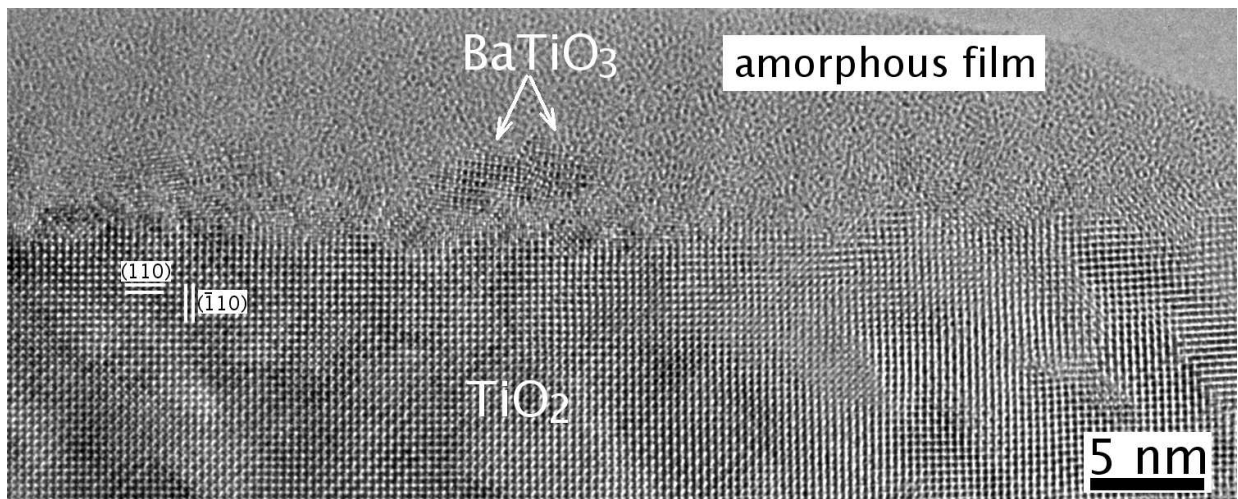


Fig. 4.5. Cross-sectional TEM image of the interface after solid-solid reaction of BaCO_3 with (110) TiO_2 in vacuum at 600 °C for 1 min. Viewing direction is $[001]$ TiO_2 .

their density was very low. The Ba_2TiO_4 phase was not found in the sample. Instead, an amorphous film on the TiO_2 substrate was observed in TEM. This film was converted into the crystalline BaTiO_3 phase when extensively exposed to the 400 keV electron beam for a few minutes.

Fig. 4.6 shows a HRTEM image of a typical interface after solid-solid reaction of BaCO_3 with (110) TiO_2 in vacuum at 700 °C for 30 min. A thin layer consisting of oriented BaTiO_3 grains was observed on the (110) TiO_2 substrate surface after the reaction. The interface between the film and the substrate is rough. In addition, misfit dislocations were found at the BaTiO_3 /(110) TiO_2 interface (Fig. 4.7).

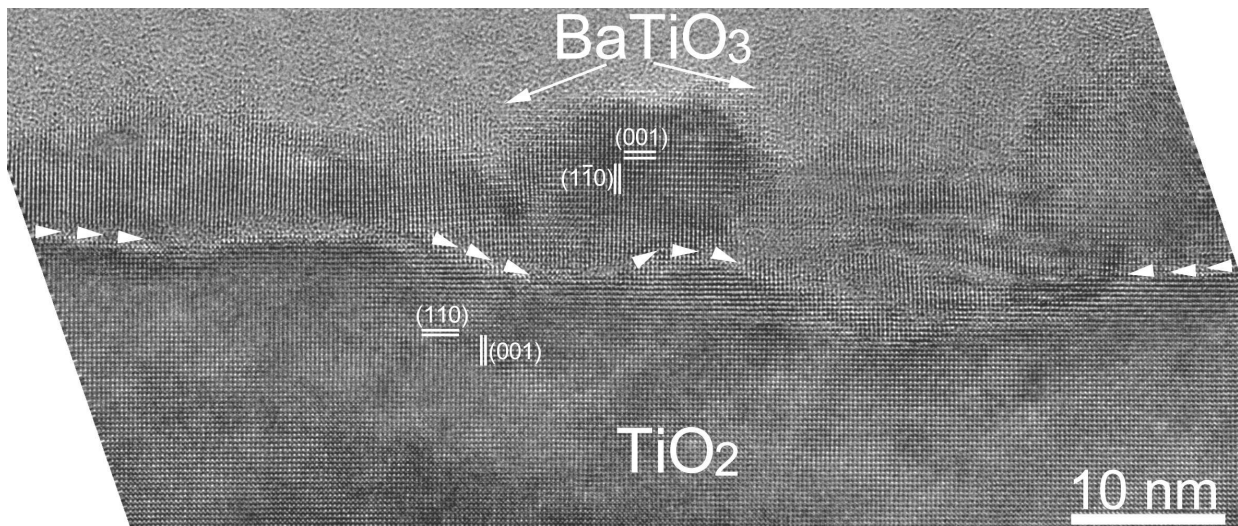


Fig. 4.6. Cross-sectional TEM image of a thin BaTiO_3 layer grown by a solid-solid reaction in vacuum at 700 °C for 30 min between a (110) TiO_2 (rutile) substrate and a BaCO_3 layer grown at 500 °C. The rutile surface is marked by arrows. Viewing direction is $[110]$ $\text{BaTiO}_3 \parallel [\bar{1}10]$ TiO_2 .

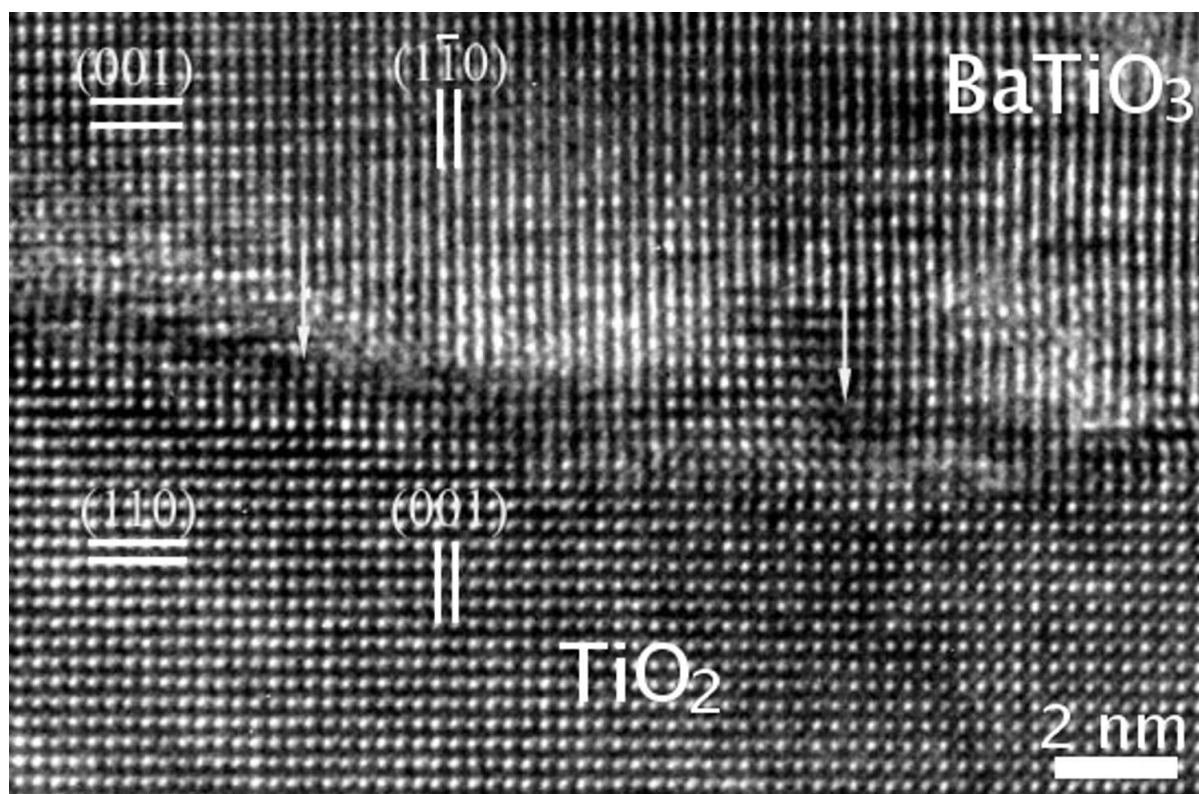


Fig. 4.7. Cross-sectional TEM image of the $\text{BaTiO}_3/\text{TiO}_2$ reaction front. Interfacial dislocations are marked by arrows. Viewing direction is $[110] \text{BaTiO}_3 \parallel [\bar{1}10] \text{TiO}_2$.

b. Reaction in air ($P_{\text{CO}_2} = 0.381 \text{ mbar}$)

The phase formation sequence after the solid-solid reaction of BaCO_3 with the (110) and (100) TiO_2 (rutile) substrates in air is different from the phase formation sequence in vacuum. Only the BaTiO_3 phase was detected by XRD measurements after solid-solid reaction in air on (110) rutile substrates at substrate temperatures between 575°C and 800°C for 30 min. Fig. 4.8 gives an XRD θ - 2θ scan of a sample made by a solid-solid reaction of a BaCO_3 thin film deposited at 500°C with the (110) TiO_2 substrate at 600°C for 30 min, revealing the formation of only BaTiO_3 . Ba_2TiO_4 was not found in the thin films also by pole figure measurements. Even after the reaction for a short reaction time (holding time null minutes at 575°C), BaTiO_3 and BaCO_3 phases were observed.

By contrast, BaTiO_3 and non-reacted BaCO_3 phases were found by XRD measurements after solid-solid reaction in air on (100) TiO_2 (rutile) at substrate temperatures between 575°C and 700°C for 30 min. The reaction at 800°C on (100) TiO_2 resulted in the formation of BaTiO_3 without any evidence of remaining BaCO_3 . After a reaction at 900°C , BaTiO_3 and Ti-rich barium titanates were observed on both (110) and (100) TiO_2 substrates while after reaction at 1000°C , the $\text{Ba}_4\text{Ti}_{13}\text{O}_{30}$ phase was formed on both substrates.

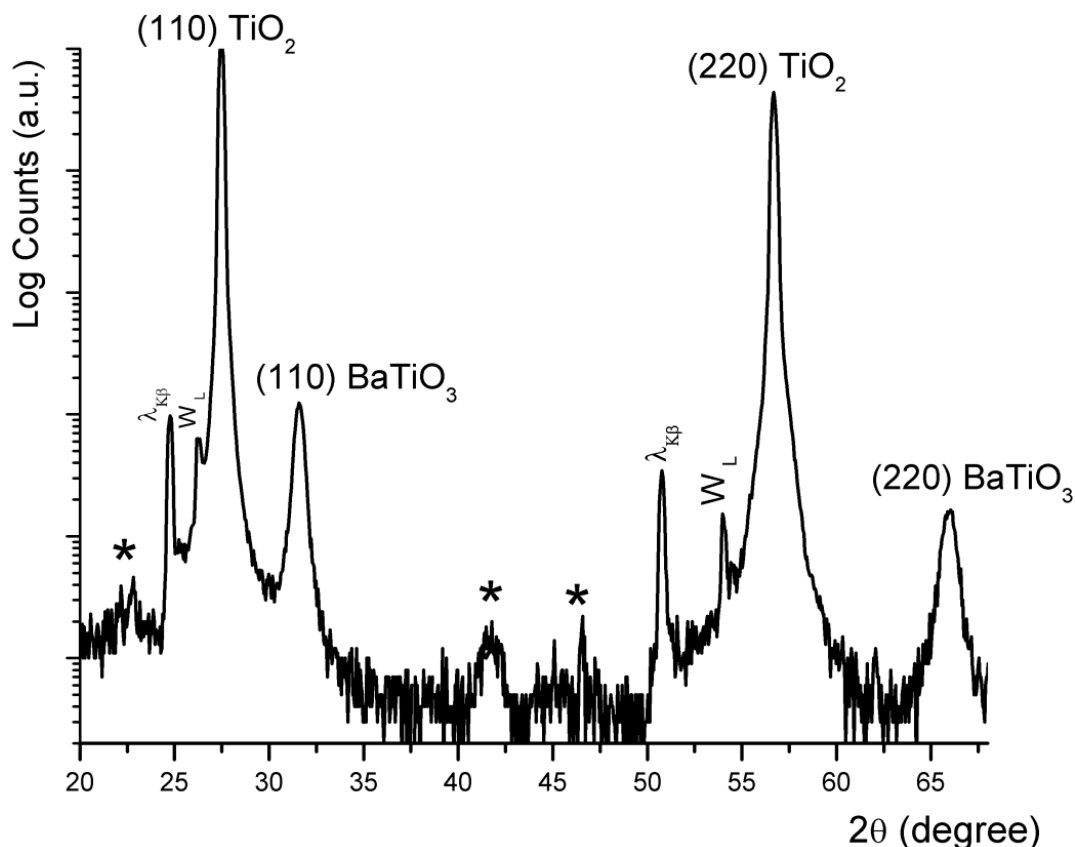


Fig. 4.8. XRD θ - 2θ scan of a sample made by a solid-solid reaction in air at 600 °C for 30 min between a (110) TiO_2 substrate and a BaCO_3 thin film deposited at 500 °C. The $\lambda_{K\beta}$ lines are the substrate peaks originating from the remaining Cu- K_β radiation, and the W_L lines are coming from the tungsten contamination of the X-ray target by the tungsten cathode filament. The peaks marked by "*" characters are substrate-induced artefacts.

4.1.2 Vapour-solid reaction of BaO with TiO_2 (rutile)

A. Phase formation

The vapour-solid experiments on (110) TiO_2 (rutile) 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 575 °C, only the Ba_2TiO_4 phase was identified, and between 600 °C and 850 °C two phases (Ba_2TiO_4 and BaTiO_3) were formed in contrast to the solid-solid reaction. But at 600 °C the BaTiO_3 phase was contained in the thin film in a small amount only as shown by the very weak intensity in the pole figures. As in the solid-solid reaction, the barium orthotitanate obtained after vapour-solid reaction was also found to decompose when exposed to air for two weeks. Experiments at 900 °C resulted in the formation of BaTiO_3 and Ti-rich grains in the thin film. Fig. 4.9 shows a cross-section HRTEM image of a typical reaction front developed after vapour-solid reaction of BaO with the (110) TiO_2 surface at 900 °C. A thin film consisting of BaTiO_3 and Ti-rich grains was formed after the reaction. The Ti-rich grains are located at the interface with the rutile substrate, whereas the BaTiO_3 grains are located on top of the Ti-rich layer. The reaction interface is rough. In addition, large pores have developed during the reaction,

at the interface with the (110) TiO_2 substrate. The walls of the pore in Fig. 4.9 are faceted by large $\{100\}$ and $\{110\}$ TiO_2 facets.

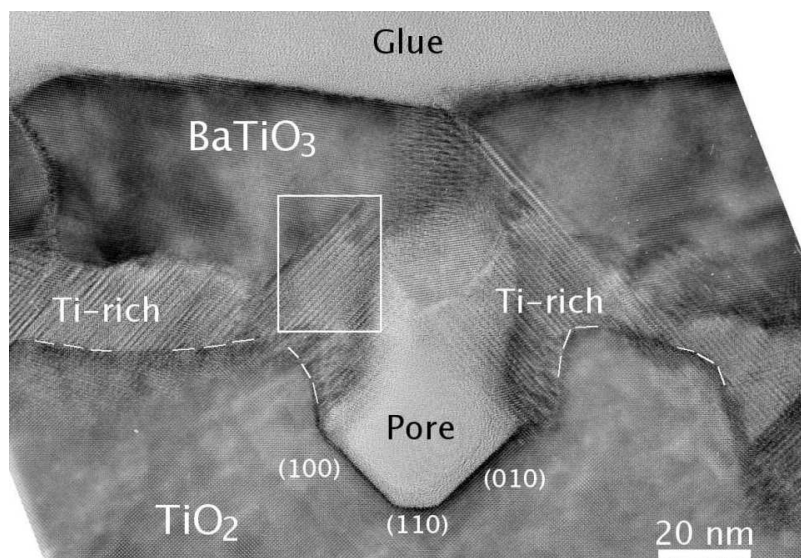


Fig. 4.9. TEM image of a typical reaction front after vapour-solid reaction of a BaO vapour with (110) TiO_2 at 900 °C. The dashes mark the rutile surface.

The Ti-rich phase $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ (marked by a white rectangle in Fig. 4.9) was characterised by HRTEM investigation shown in Fig. 4.10. In this figure, the $(\bar{2}00)$ and (002) interplanar distances of the Ti-rich phase are ~ 0.94 nm and ~ 0.49 nm (respectively), with an angle of 98.8° in between them. Thus, this Ti-rich grain was identified as the $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ phase. This phase was also found in other parts of the sample.

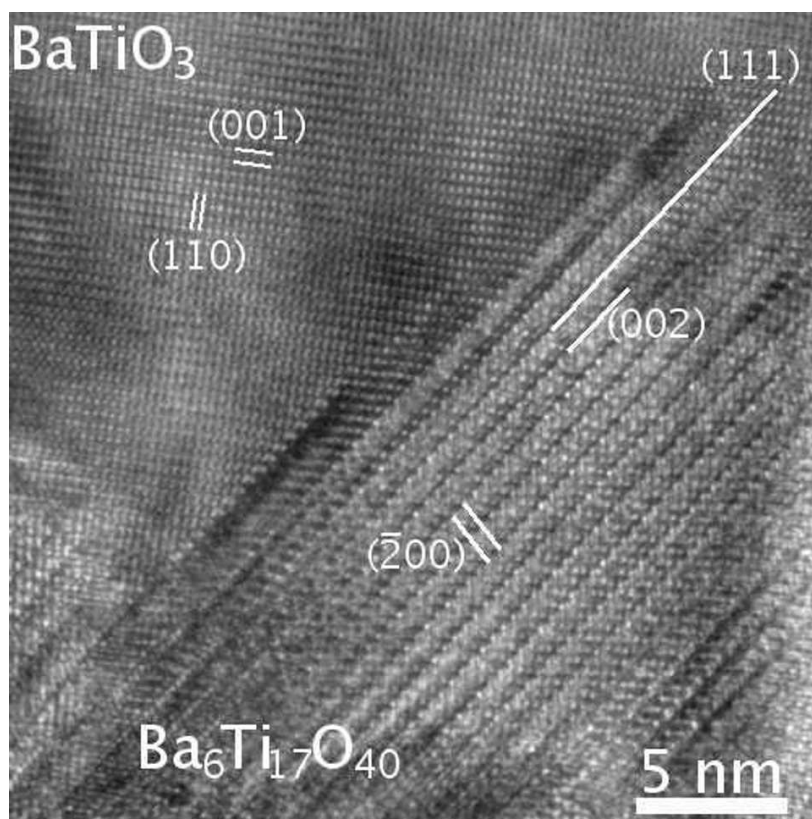


Fig. 4.10. Lattice plane image of $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ and BaTiO_3 (magnified image of the white box shown in Fig. 4.9). Viewing direction is $[010] \text{Ba}_6\text{Ti}_{17}\text{O}_{40} \parallel [110] \text{BaTiO}_3$.

After vapour-solid reaction at 1000 °C, only Ti-rich grains were found by XRD pole figure investigations. Fig. 4.11 shows a TEM image of the interface after reaction of BaO with (110) TiO_2

at 1000 °C. Several large holes with $\{100\}$ and $\{110\}$ TiO_2 facet walls were formed during the reaction.

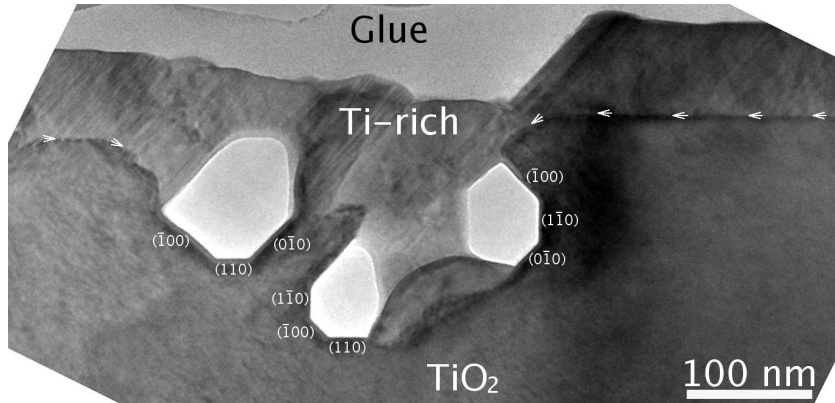


Fig. 4.11. Cross-sectional TEM image of a typical reaction front after vapour-solid reaction of BaO vapour with (110) rutile substrate at 1000 °C. Large holes with $\{100\}$ and $\{110\}$ TiO_2 facet walls are visible in the image. The arrows mark the rutile surface.

The phase sequence during vapour-solid reaction on (100) TiO_2 (rutile) substrates at temperatures between 600 °C and 1000 °C showed a process that is similar to the reaction on the (110) TiO_2 substrate. A summary of the phase sequences after both solid-solid and vapour-solid reactions is given in Fig. 4.12.

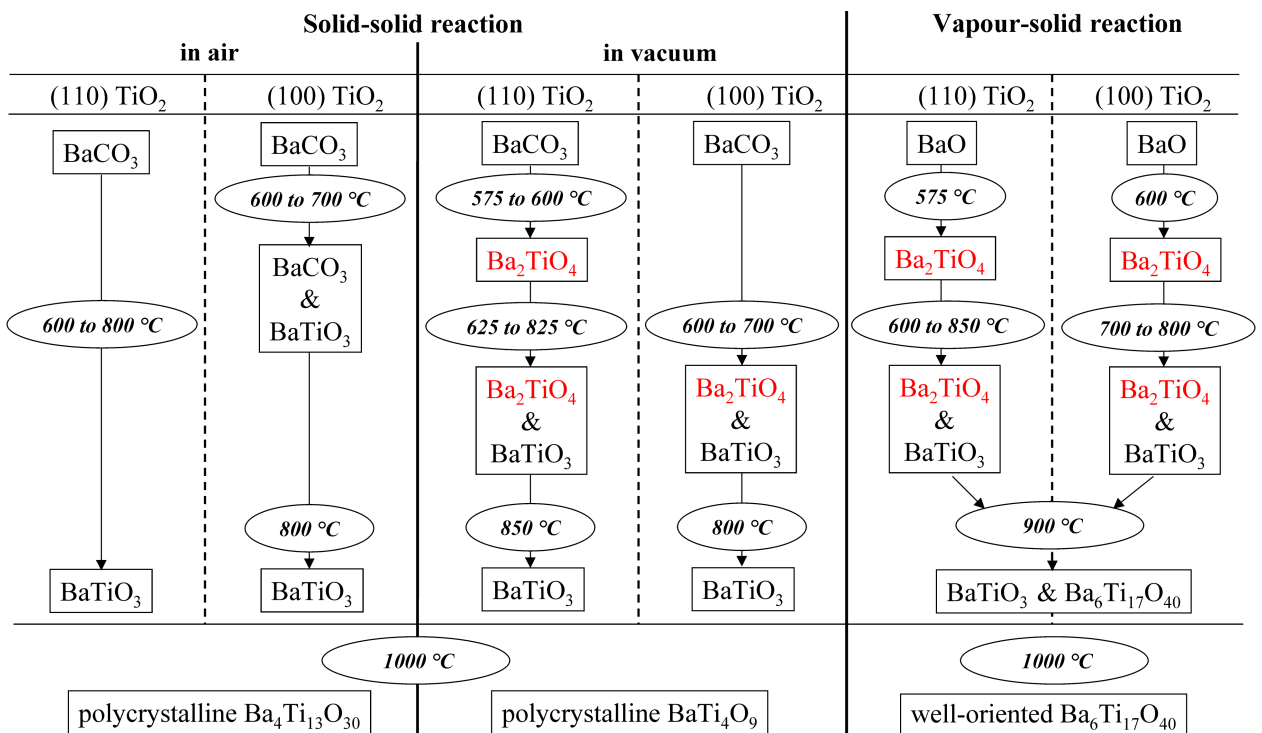


Fig. 4.12. Schematic representation of phase sequences after solid-solid (in air and in vacuum) and vapour-solid (in vacuum) reactions.

B. Initial stage of vapour-solid reaction at 900 °C

This part of the work was performed to define which phase is nucleated first during a vapour-solid reaction at high reaction temperature. A very low amount of BaO was deposited on a (110) TiO_2 substrate and on a (100) TiO_2 substrate, both at 900 °C. The nominal thickness of BaO was varied from ≈ 1 nm to ≈ 5 nm.

Fig. 4.13(a) shows a typical top-view AFM image and a line profile of Ba-Ti-O islands formed after vapour-solid reaction of a BaO quantity equivalent to a nominal film thickness of 1 nm with the (110) TiO_2 surface at 900 °C. The line profile in Fig. 4.13(b) is along the blue line in

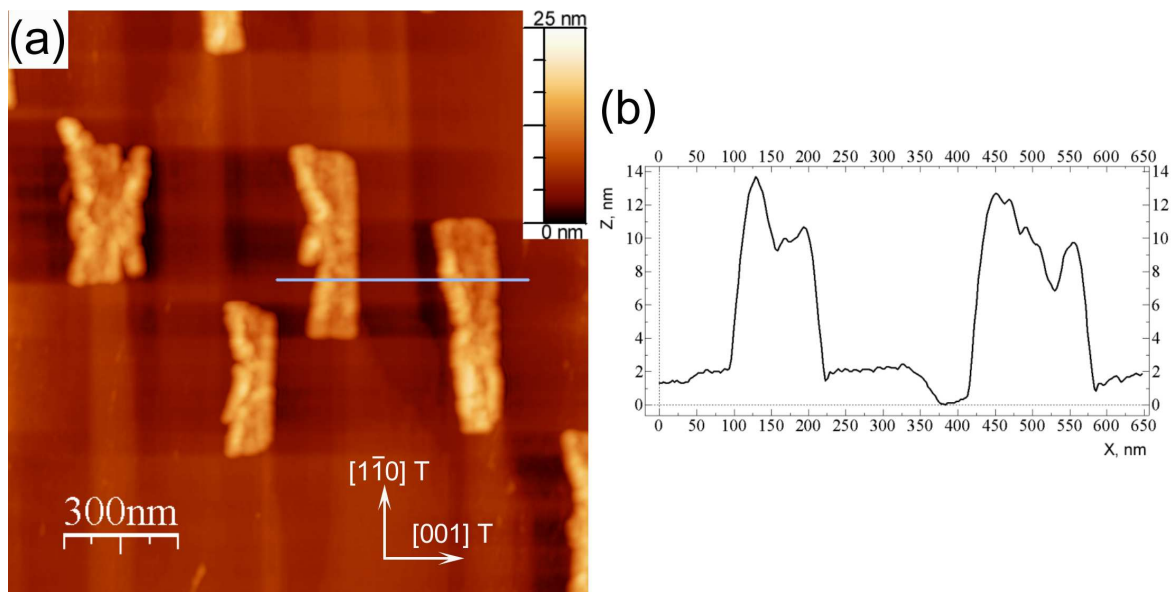


Fig. 4.13. (a) AFM image and (b) line profile of Ba-Ti-O islands formed by vapour-solid reaction on (110) TiO_2 (T) surface at 900 °C. The height profile is along the blue line in image (a).

Fig. 4.13(a). The islands in Fig. 4.13(a) are elongated along the $[1\bar{1}0]$ direction of TiO_2 (the orientation of the substrate was confirmed by X-ray diffraction). The lateral sizes of the islands are in the range of 400 nm-600 nm in the $[1\bar{1}0]$ direction of TiO_2 while in the range of 100 nm-200 nm in the $[001]$ direction of TiO_2 . Their height varies from 10 nm to 15 nm (Fig. 4.13(b)). Each big island in Fig. 4.13(a) consists of several small grains. HRTEM investigations showed that the Ba-Ti-O grains consist of Ti-rich barium titanates.

Fig. 4.14 gives a typical cross-section HRTEM image of the sample shown in Fig. 4.13(a) in the $[001]$ viewing direction of TiO_2 . The reaction interface is flat. The grain in Fig. 4.14 is characterised by a large lattice constant and by stacking faults which are typical for Ti-rich phases formed by solid state reactions. The $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ Ti-rich phase was identified by the Fast Fourier Transformation (FFT) of the corresponding HRTEM image (Fig. 4.14(b)). Similar grains were observed in other parts of the TEM sample. No BaTiO_3 grains or any wetting layer were found on the (110) TiO_2 surface.

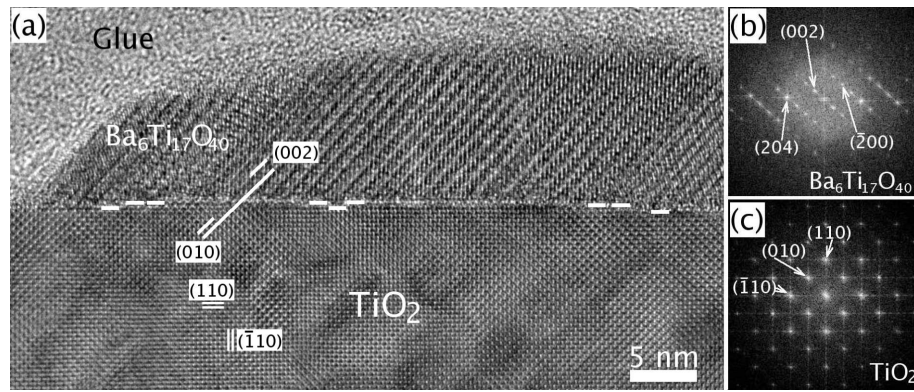


Fig. 4.14. HRTEM image of a sample after the reaction of a BaO vapour with a (110) TiO_2 substrate at 900 °C. The nominal thickness of BaO was ≈ 1 nm. (a) Part of a Ti-rich island on the rutile substrate. The long white line in the image indicates $(002) \text{Ba}_6\text{Ti}_{17}\text{O}_{40} \parallel (010) \text{TiO}_2$. The dashes show steps on the TiO_2 surface. (b) FFT image of a $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ Ti-rich grain. (c) FFT image of the rutile substrate. Viewing direction is $[010] \text{Ba}_6\text{Ti}_{17}\text{O}_{40} \parallel [001] \text{TiO}_2$. Magnified version of this figure see in the appendix, Fig. A.6.

Fig. 4.15 gives HRTEM images of the reaction products that have formed on the (100) rutile substrate after the initial stage of the reaction between a BaO vapour and the (100) TiO_2 substrate at 900 °C. The nominal thickness of BaO was ≈ 1 nm. BaTiO_3 and Ti-rich grains were found on

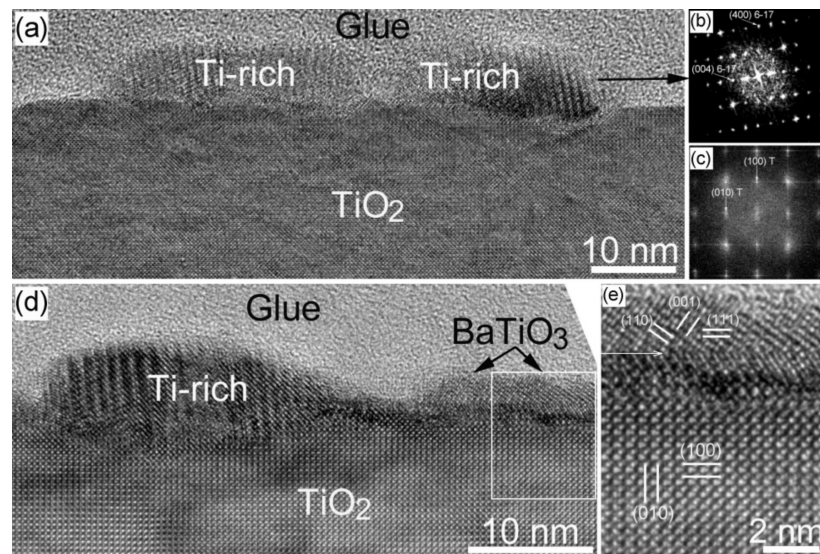


Fig. 4.15. HRTEM images of a sample after the reaction of a BaO vapour with a (100) TiO_2 substrate at 900 °C. The nominal thickness of BaO was ≈ 1 nm. (a) Ti-rich islands on the rutile substrate. (b) FFT image of a $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ (6-17) Ti-rich grain. (c) FFT image of the rutile substrate (T). Viewing direction is $[010] \text{Ba}_6\text{Ti}_{17}\text{O}_{40} \parallel [001] \text{TiO}_2$. (d) Ti-rich and BaTiO_3 grains on the rutile substrate. (e) Computer-processed lattice plane images of BaTiO_3 and the rutile substrate (magnified section of image (d)). The arrow in image (e) marks a (111) twin boundary in BaTiO_3 . Viewing direction is $[1\bar{1}0] \text{BaTiO}_3 \parallel [001] \text{TiO}_2$. Magnified version of the figure see in the appendix, Fig. A.7.

the substrate surface after the reaction. The Ti-rich islands have an average size of about 10 nm in height and 25 nm in width. The $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ Ti-rich phase was identified by the FFT of the corresponding HRTEM images (Figs. 4.15(b)-(c)). BaTiO_3 grains were also formed well-oriented with respect to the rutile substrate (Fig. 4.15(e)). They grew with a (111) orientation. However, their density was much lower than the density of the Ti-rich grains. Mainly, the (100) rutile surface

was covered by Ti-rich islands. No wetting layer was found on the substrate surface.

Increasing the nominal thickness of BaO up to ≈ 5 nm, the average size of the Ti-rich grains is increasing as shown in Fig. 4.16. In addition, cavities between the Ti-rich grains are formed (Fig. 4.16).

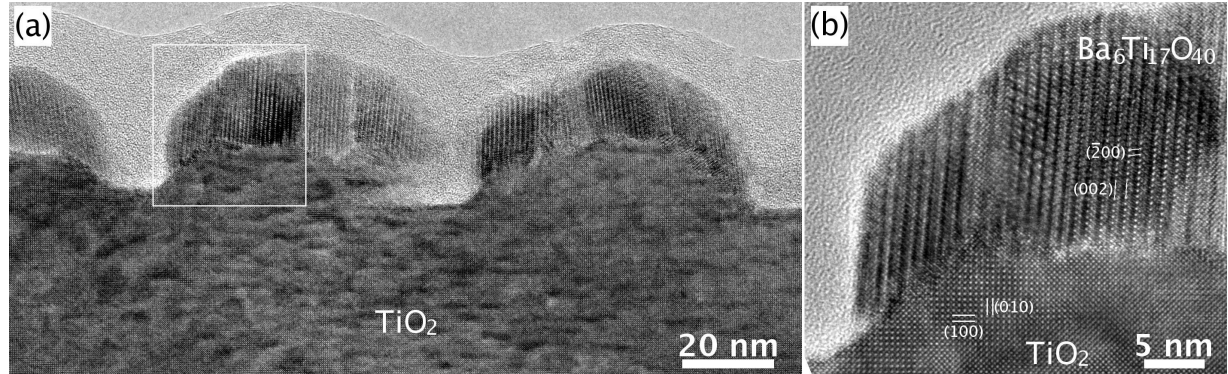


Fig. 4.16. HRTEM images of a sample made by a vapour-solid reaction on a (100) TiO_2 substrate at 900 °C. The nominal thickness of BaO was ≈ 5 nm. a) Overview and b) lattice plane images of $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ and the rutile substrate (magnified section of image (a)). Viewing direction is $[010] \text{Ba}_6\text{Ti}_{17}\text{O}_{40} \parallel [001] \text{TiO}_2$. Magnified version of image (b) see in the appendix, Fig. A.8.

4.1.3 Orientation relationships

A. Orientation of Ba_2TiO_4

Solid-solid reaction

The orientation of Ba_2TiO_4 after solid-solid reaction on (110) TiO_2 substrates was dependent on the orientation quality of BaCO_3 . A deposition of BaCO_3 at 300 °C followed by solid-solid reaction at 575 °C-700 °C for 30 min produced Ba_2TiO_4 with a low orientation quality (Fig. 4.17(left)).

On the other hand, a deposition of BaCO_3 at 500 °C followed by solid-solid reaction at 575 °C-850 °C for 30 min produced a well-oriented Ba_2TiO_4 . The peaks at $2\theta = 43.8^\circ$ in Figs. 4.3(b)-(d) are from (330) Ba_2TiO_4 . Several pole figures were recorded at different 2θ values to find out which plane of Ba_2TiO_4 is parallel to the TiO_2 substrate. Fig. 4.17(right) shows a pole figure taken at $2\theta = 29.24^\circ$ (Ba_2TiO_4 (031)/(002)) of the sample prepared after solid-solid reaction at 700 °C. The orientation relationship of Ba_2TiO_4 with respect to the (110) rutile surface was found as follows:

$$(110) \text{Ba}_2\text{TiO}_4 \parallel (110) \text{TiO}_2; [001] \text{Ba}_2\text{TiO}_4 \parallel [001] \text{TiO}_2. \quad (4.4)$$

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

The orientation quality of Ba_2TiO_4 after the solid-solid reaction on (100) rutile substrates was also dependent on the orientation quality of BaCO_3 . A deposition of BaCO_3 at 300 °C followed by solid-solid reaction at 700 °C for 30 min produced Ba_2TiO_4 with a poor orientation quality while a deposition of BaCO_3 at 500 °C followed by solid-solid reaction at 600 °C-700 °C for 30 min produced a well-oriented Ba_2TiO_4 .

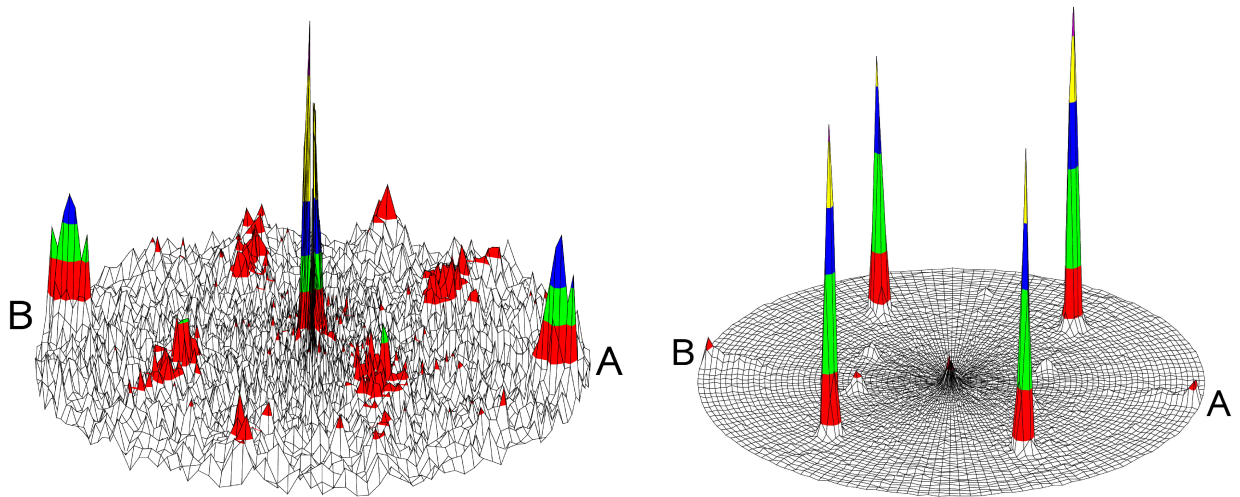


Fig. 4.17. Pole figures of samples grown by a solid-solid reaction recorded with $\{103\}/\{200\}$ Ba₂TiO₄ reflections ($2\theta = 29.24^\circ$). The samples were made by a reaction at 700 °C for 30 min between (110) TiO₂ substrate and BaCO₃ layer grown at: (left) 300 °C and (right) 500 °C. In the right figure, peaks are situated at $\psi = 0^\circ$, 60° and 90° and thus correspond to a (110) orientation of Ba₂TiO₄. Weak peaks situated at $\psi = 34^\circ$ are from $\{211\}$ and $\{21\bar{1}\}$ Ba₂TiO₄ which correspond to $2\theta = 28.78^\circ$ of Ba₂TiO₄. They appear in the figure because the intensity of these peaks are rather strong (Int= 82% according to JCPDS 38-1481) and they are very close to $2\theta = 29.24^\circ$ (Int= 100% according to JCPDS 38-1481).

Fig. 4.18 shows a pole figure recorded at $2\theta = 29.24^\circ$ (Ba₂TiO₄ (031)/(002)) of the sample made by solid-solid reaction at 700 °C for 30 min between (100) TiO₂ substrate and BaCO₃ layer grown at 500 °C. The orientation relationship of Ba₂TiO₄ with respect to the (100) rutile surface was found as follows:

$$(100) \text{ Ba}_2\text{TiO}_4 \parallel (100) \text{ TiO}_2; [001] \text{ Ba}_2\text{TiO}_4 \parallel [001] \text{ TiO}_2. \quad (4.5)$$

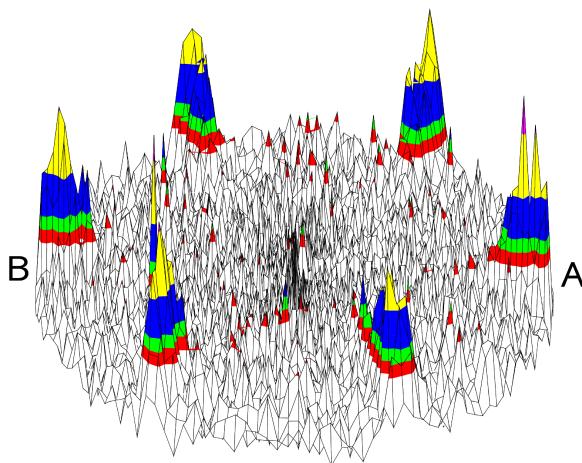


Fig. 4.18. Pole figure of a sample grown by a solid-solid reaction at 700 °C for 30 min between a (100) TiO₂ substrate and a BaCO₃ layer grown at 500 °C. The figure was recorded with $\{031\}/\{002\}$ Ba₂TiO₄ reflections ($2\theta = 29.24^\circ$). Peaks are situated at $\psi = 0^\circ$ and 90° and, thus, correspond to a (100) orientation of Ba₂TiO₄.

Vapour-solid reaction

After vapour-solid reaction on the (110) TiO₂ surface, the orientation relationship of the Ba₂TiO₄ phase is different compared to the solid-solid reactions. In the temperature range between 575 °C

and 700 °C, most of the Ba₂TiO₄ grains grew according to the following relation:

$$(100) \text{Ba}_2\text{TiO}_4 \parallel (110) \text{TiO}_2; [001] \text{Ba}_2\text{TiO}_4 \parallel [001] \text{TiO}_2. \quad (4.6)$$

At a substrate temperature of 800 °C no well-defined orientation was deduced because a XRD pole figure taken at $2\theta = 29.24^\circ$ showed broad reflections of Ba₂TiO₄ both in ϕ and ψ directions. On the other hand, the orientation relationship of the Ba₂TiO₄ phase after vapour-solid reaction on (100) TiO₂ did not change compared to the solid-solid reactions. In the temperature range between 575 °C and 800 °C, the Ba₂TiO₄ grains grew according to the relation (4.5).

B. Orientation of BaTiO₃

Solid-solid reaction

(110) TiO₂ (rutile)

After the solid-solid reaction in vacuum, BaTiO₃ grains were formed with a defined orientation with respect to the (110) TiO₂ substrates. Figs. 4.19(a)-(c) show typical pole figures taken at $2\theta = 31.4^\circ$ for samples prepared on (110) TiO₂ at 700 °C, 800 °C and 900 °C, respectively. The figures display 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.

A pole figure after solid-solid reaction at 700 °C is shown in Fig. 4.19(a). For this temperature most of the BaTiO₃ grains were grown with a mean orientation relationship (001) BaTiO₃ \parallel (110) TiO₂ (see also Figs. 4.6-4.7).

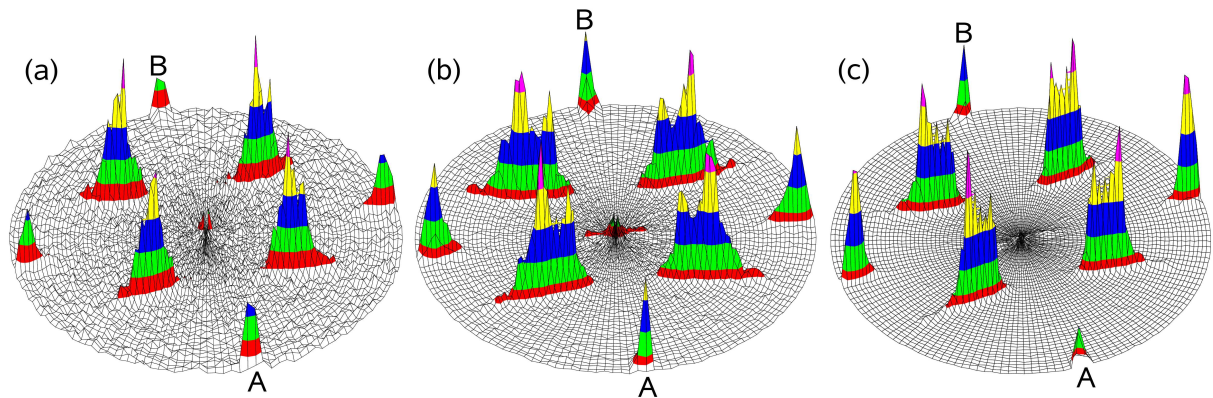


Fig. 4.19. Pole figures of samples produced on (110) TiO₂ substrates by a solid-solid reaction in vacuum at: (a) 700 °C, (b) 800 °C and (c) 900 °C. The figures were taken at $2\theta = 31.4^\circ$ (BaTiO₃ {101}). The peaks are situated at $\psi = 40^\circ$ to 60° and 90° in all the figures. Additional weak peaks in Figs. 4.16(b)-(c) are situated at $\psi = 0^\circ$, 11° and 82° . The ψ values of 40° , 50° , 82° and 90° correspond to a (119) orientation of BaTiO₃ while the ψ values of 11° , 50° , 70° and 90° correspond to a (441) orientation of BaTiO₃ and the ψ value of 45° corresponds to a (001) orientation of BaTiO₃.

With increasing reaction temperature, the number of tilted grains is increasing. After reaction between 800 °C and 900 °C XRD θ - 2θ scans (Figs. 4.3(d)-(e)) and pole figure measurements (Figs. 4.19(b)-(c)) revealed additional orientations of BaTiO₃ such as (110) BaTiO₃ \parallel (110) TiO₂,

(119) BaTiO₃ || (110) TiO₂ and (441) BaTiO₃ || (110) TiO₂. From a series of pole figures, ϕ scans and HRTEM investigations, the in-plane orientation was found to be $[1\bar{1}0]$ BaTiO₃ || $[001]$ TiO₂ for all orientations of BaTiO₃ grown by a solid-solid reaction in vacuum on (110) TiO₂ substrates.

In contrast to the formation of Ba₂TiO₄, BaTiO₃ formed also with (001) BaTiO₃ || (110) TiO₂ after reaction at 700 °C for 30 min if a BaCO₃ film with low orientation quality grown at 300 °C was used.

A deposition of BaCO₃ at 500 °C followed by the reaction in air produced well-oriented BaTiO₃. Fig. 4.20 shows a X-ray pole figure of a sample made on a (110) TiO₂ substrate by a solid-solid reaction in air at 700 °C for 30 min. The orientation relationship of BaTiO₃ was identified as:

$$(110) \text{ BaTiO}_3 \parallel (110) \text{ TiO}_2; [1\bar{1}0] \text{ BaTiO}_3 \parallel [001] \text{ TiO}_2. \quad (4.7)$$

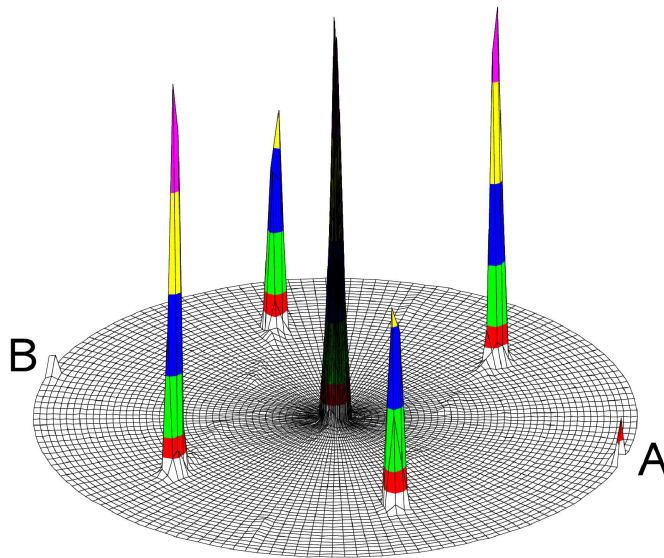


Fig. 4.20. Pole figure of a sample made on a (110) TiO₂ substrate by a solid-solid reaction in air at 700 °C for 30 min. The pole figure was recorded at $2\theta = 31.4^\circ$ (BaTiO₃ {101}). The peaks are situated at $\psi = 0^\circ, 60^\circ$ and 90° and thus correspond to a (110) orientation of BaTiO₃.

Such an orientation relationship was also observed for the samples after solid-solid reaction at temperatures between 600 °C and 900 °C in air. No tilted grains were found in the thin films. This is in contrast to the orientation of BaTiO₃ grains grown by solid-solid reaction on (110) rutile substrates in vacuum.

(100) TiO₂ (rutile)

The BaTiO₃ grains grown on (100) TiO₂ surfaces are also crystallographically well-oriented.

Fig. 4.21 gives the pole figure taken at $2\theta = 31.4^\circ$ of the sample prepared on (100) TiO₂ by a solid-solid reaction in vacuum at 700 °C for 30 min. The orientation relationship of BaTiO₃ was found as:

$$(111) \text{ BaTiO}_3 \parallel (100) \text{ TiO}_2; [1\bar{1}0] \text{ BaTiO}_3 \parallel [001] \text{ TiO}_2. \quad (4.8)$$

Such an orientation relationship was also observed for the samples after solid-solid reaction at temperatures between 600 and 900 °C in vacuum and in air. Noticeably, the (111) BaTiO₃ ($2\theta = 38.8^\circ$) reflection could not be detected in XRD θ - 2θ scans because it is completely hidden by the strong TiO₂ (200) peak ($2\theta = 39.2^\circ$).

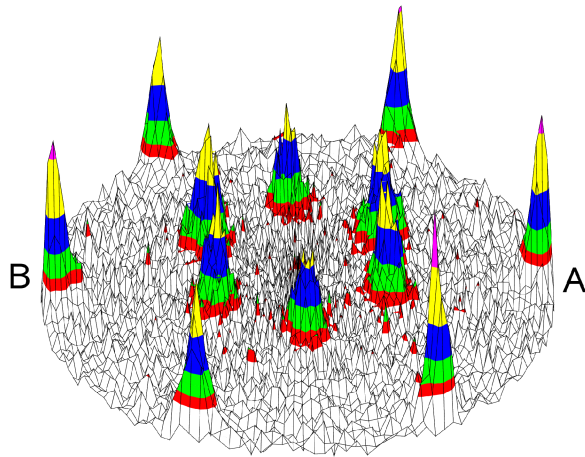


Fig. 4.21. Pole figure of a sample produced on a (100) TiO_2 substrate by a solid-solid reaction at 700 °C. The peaks are situated at $\psi = 35^\circ$ and 90° and thus correspond to a (111) orientation of BaTiO_3 .

Vapour-solid reaction

(110) TiO_2 (rutile)

After vapour-solid reaction, the BaTiO_3 grains grew with a well-defined orientation with respect to the (110) TiO_2 substrates. However, their tilt distribution is sharper compared to the solid-solid reaction in vacuum.

Figs. 4.22(a)-(b) give typical pole figures taken at $2\theta = 31.4^\circ$ for samples prepared on (110) TiO_2 at 800 °C and 900 °C, respectively. Compared to the reflections of BaTiO_3 in Figs. 4.19(a)-(c), the peaks from the BaTiO_3 {101} planes in Figs. 4.22(a)-(b) are stronger and sharper, indicating the growth of BaTiO_3 grains with well-defined orientations.

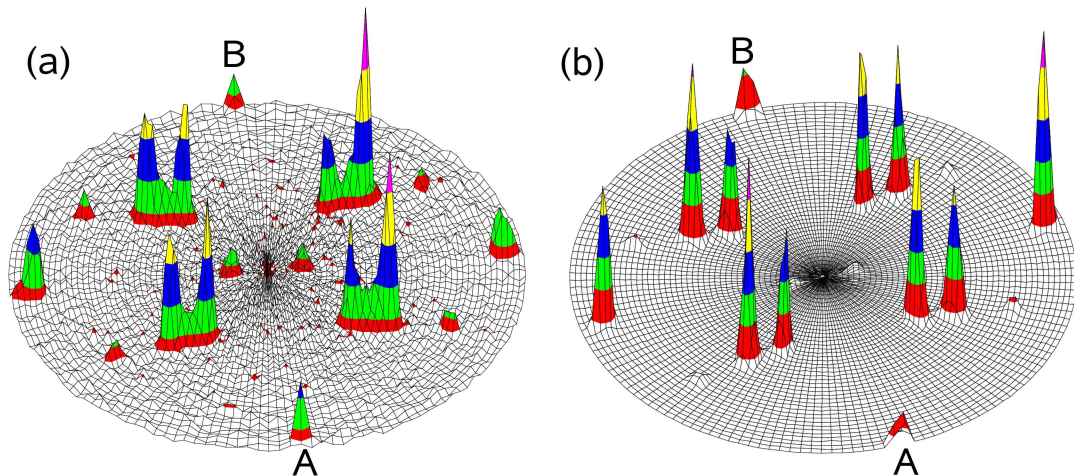


Fig. 4.22. Pole figures of samples made on (110) TiO_2 substrates by a vapour-solid reaction at: (a) 800 °C and (b) 900 °C. The figures were taken at $2\theta = 31.4^\circ$ (BaTiO_3 {101}). The peaks are situated at $\psi = 11^\circ, 40^\circ, 50^\circ, 70^\circ, 82^\circ$ and 90° in the Figs. (a)-(b), while there are additional reflections at $\psi = 45^\circ$ in Fig. (a). The ψ values of $40^\circ, 50^\circ, 82^\circ$ and 90° correspond to a (119) orientation of BaTiO_3 while the ψ values of $11^\circ, 50^\circ, 70^\circ$ and 90° correspond to a (441) orientation of BaTiO_3 and the ψ value of 45° corresponds to a (001) orientation of BaTiO_3 .

Fig. 4.23 gives a HRTEM image of an interface after vapour-solid reaction of BaO with (110) TiO_2 in vacuum at 800 °C. The reaction interface is rough. Looking along the [001] direction of

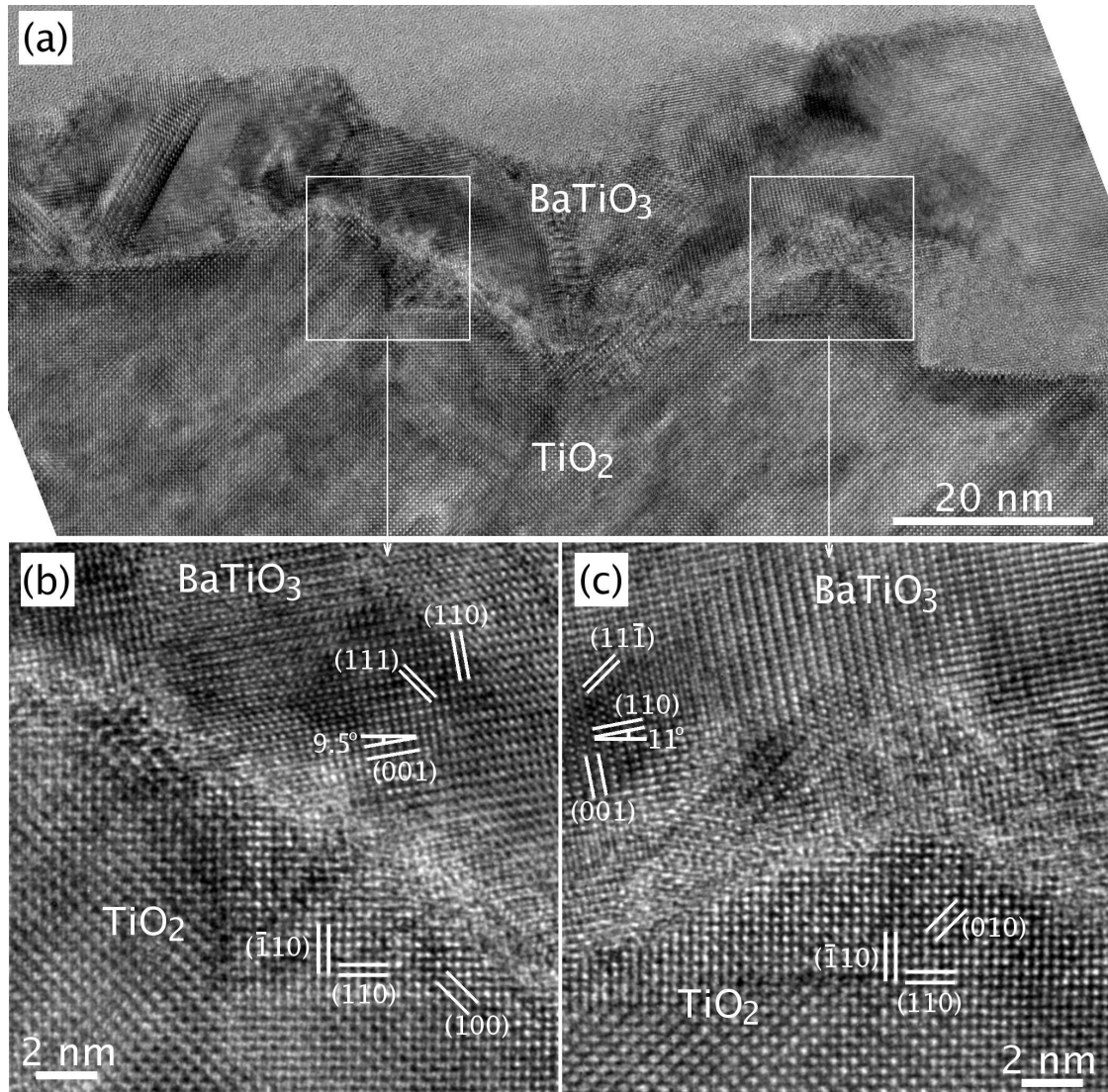


Fig. 4.23. HRTEM images of a sample made on a (110) TiO_2 substrate by a vapour-solid reaction at 800 °C: (a) thin film-substrate interface, (b) and (c) lattice plane images of BaTiO_3 grains and the substrate (magnified sections of image (a)). Viewing direction is $[1\bar{1}0]$ $\text{BaTiO}_3 \parallel [001]$ TiO_2 .

TiO_2 , (100), (010), (110) and $(\bar{1}10)$ TiO_2 facets are seen. The orientation relationships of BaTiO_3 found by HRTEM (Fig. 4.23) as well as by pole figure measurements (Fig. 4.22) are: (119) $\text{BaTiO}_3 \parallel (110)$ TiO_2 (major) and (441) $\text{BaTiO}_3 \parallel (110)$ TiO_2 (minor). It should be noted that the (441) orientation of BaTiO_3 is rather close to the (331) orientation of BaTiO_3 ($\angle(441); (331)$ $\text{BaTiO}_3 = 3.24^\circ$). HRTEM investigations (Figs. 4.23(b)-(c)) showed that (119)- and (441)-oriented BaTiO_3 grains are located on (100) and (010) facets of TiO_2 , respectively. Both orientations can be understood as a result of a systematic tilt around a unique tilt axis starting from low index orientations with (001) $\text{BaTiO}_3 \parallel (110)$ TiO_2 ($\angle \text{BaTiO}_3 (001); (119) = 8.9^\circ$, see also Fig. 4.23(b)) and (110) $\text{BaTiO}_3 \parallel (110)$ TiO_2 ($\angle \text{BaTiO}_3 (110); (441) = 10^\circ$, see also Fig. 4.23(c)), respectively. It is worth to note that the (119) and (441) orientations of BaTiO_3 have one of the $\{111\}$ BaTiO_3 planes almost parallel to one of the $\{100\}$ TiO_2 planes in the viewing direction $[1\bar{1}0]$ $\text{BaTiO}_3 \parallel [001]$ TiO_2 : $\angle \text{BaTiO}_3 (119); (111) = 45.8^\circ$ and $\angle \text{BaTiO}_3 (441); (11\bar{1}) = 45.3^\circ$ while $\angle \text{TiO}_2 (110); (100) = 45^\circ$ and $\angle \text{TiO}_2 (110); (010) = 45^\circ$. This is in agreement with HRTEM observations. The main (119)

orientation of BaTiO_3 deviates from the minor (441) one by a tilt of 71° around the $[\bar{1}\bar{1}0]$ $\text{BaTiO}_3 \parallel [001]$ TiO_2 tilt axis. In addition, pole figure measurements revealed a second minor orientation of BaTiO_3 at 800°C as (001) $\text{BaTiO}_3 \parallel (110)$ TiO_2 .

After vapour-solid reaction at 900°C , BaTiO_3 grains were found on top of $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ grains. They formed exactly with (119) $\text{BaTiO}_3 \parallel (110)$ TiO_2 (major) and (441) $\text{BaTiO}_3 \parallel (110)$ TiO_2 (minor) orientations as was found by pole figure measurements (Fig. 4.22(b)). The in-plane orientation relationship was found to be $[\bar{1}\bar{1}0]$ $\text{BaTiO}_3 \parallel [001]$ TiO_2 for all these orientations.

Fig. 4.9 shows a HRTEM image of the interface region after the reaction between a BaO vapour and a (110) TiO_2 (rutile) substrate of a sample prepared at a substrate temperature of 900°C . The reaction layer consisted of BaTiO_3 and $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ grains. The latter were located between the TiO_2 substrate and the BaTiO_3 phase. The crystallographic orientation relationship found by HRTEM (Fig. 4.10) between the BaTiO_3 and $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ grains was:

$$(001) \text{Ba}_6\text{Ti}_{17}\text{O}_{40} \parallel (111) \text{BaTiO}_3; [010] \text{Ba}_6\text{Ti}_{17}\text{O}_{40} \parallel [\bar{1}\bar{1}0] \text{BaTiO}_3. \quad (4.9)$$

This orientation relationship indicates a topotaxial reaction between BaTiO_3 and $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ and is in agreement to the relation (2.23).

(100) TiO_2 (rutile)

Fig. 4.24 shows a HRTEM image of the interface region between a BaTiO_3 thin film and a (100) TiO_2 substrate of a sample made after vapour-solid reaction at 700°C . In Fig. 4.24, the interface between the thin film and the substrate is not flat. Large (110) and $(\bar{1}\bar{1}0)$ rutile facets are clearly visible.

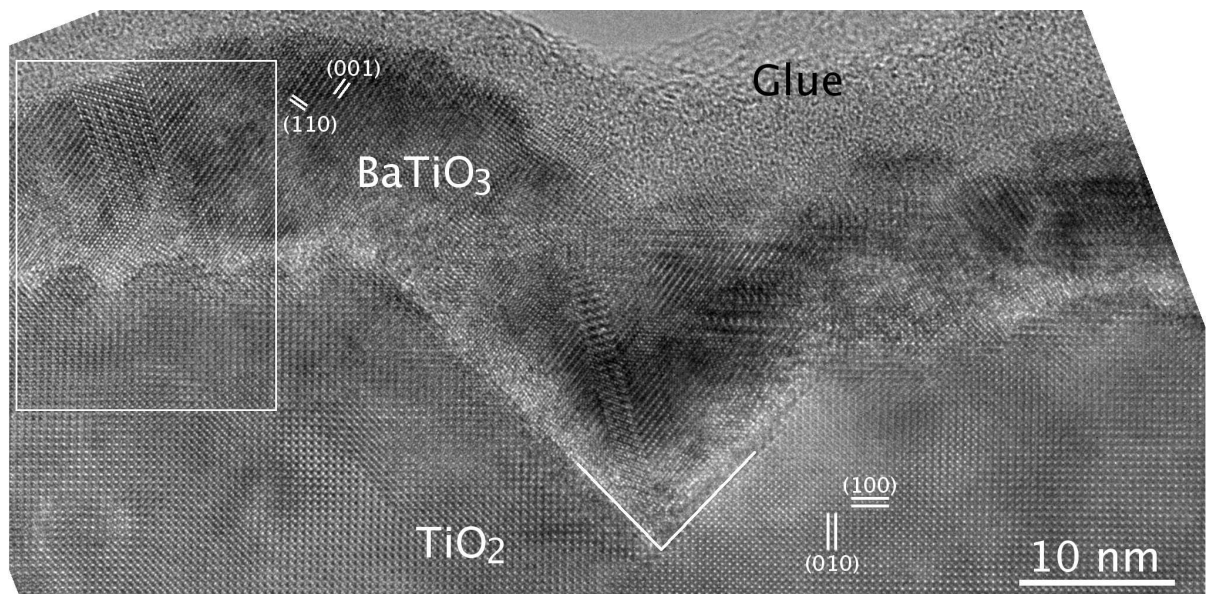


Fig. 4.24. HRTEM micrograph of a sample made after vapour-solid reaction on (100) TiO_2 at 700°C . Large (110) and $(\bar{1}\bar{1}0)$ TiO_2 facets were formed after the reaction (marked by white lines). Viewing direction is $[\bar{1}\bar{1}0]$ $\text{BaTiO}_3 \parallel [001]$ TiO_2 . A TEM image taken from a larger area by conventional TEM can be seen in the appendix, Fig. A.9.

Fig. 4.25 shows lattice plane images of BaTiO_3 grains and a TiO_2 substrate. From Fig. 4.25, it was found that the BaTiO_3 grains grew according to the relation (4.8). In addition, $(11\bar{1})$ twins were found within BaTiO_3 grains.

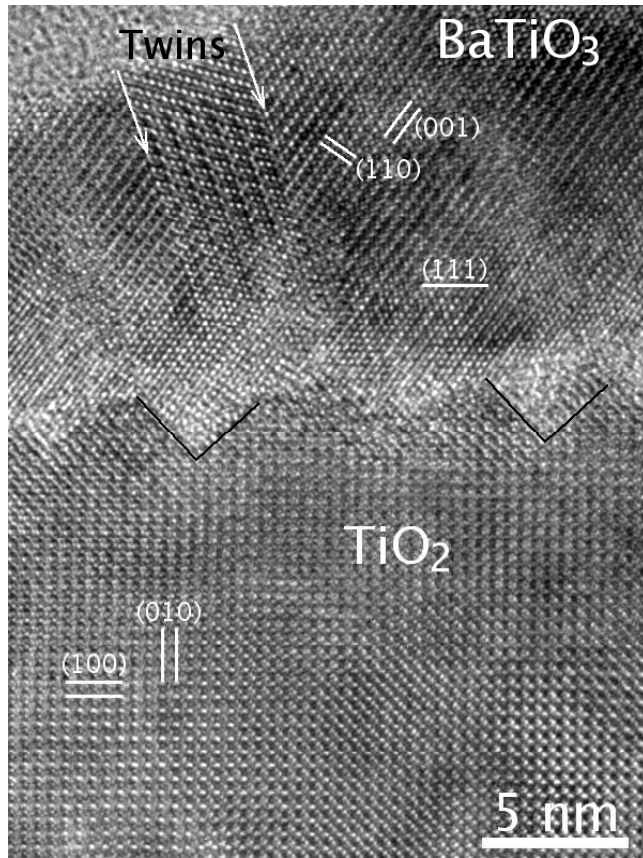


Fig. 4.25. Lattice plane images of BaTiO_3 in the $[1\bar{1}0]$ viewing direction and the TiO_2 substrate in the $[001]$ viewing direction (magnified image of the white box shown in Fig. 4.24). Small (110) and $(1\bar{1}0)$ TiO_2 facets are marked by black lines. $(11\bar{1})$ twins in BaTiO_3 were also observed.

A XRD θ - 2θ scan of the sample made on (100) TiO_2 substrate by vapour-solid reaction at 800°C showed the appearance of the characteristic reflection of (112) BaTiO_3 ($2\theta = 56.2^\circ$) beside the substrate reflections which means that the (112) plane of BaTiO_3 is parallel to the (100) substrate plane. Fig. 4.26 gives a pole figure for a sample prepared by vapour-solid reaction at 800°C using (100) TiO_2 substrate. At this temperature two orientation relations for BaTiO_3 were found.

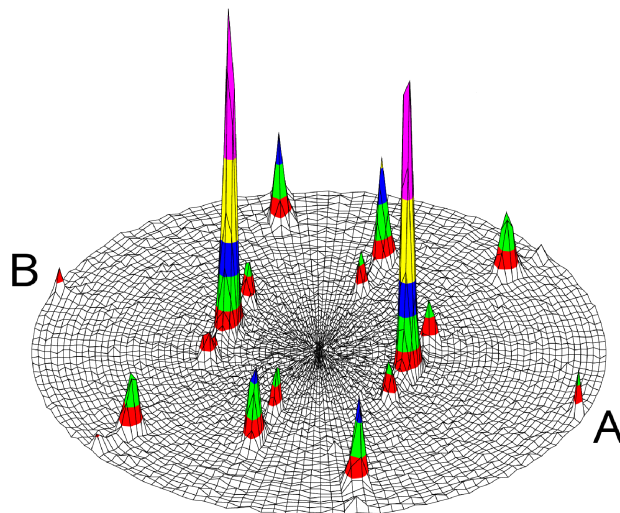


Fig. 4.26. Pole figure of a sample grown on a (100) TiO_2 substrate by a vapour-solid reaction at 800°C . The figure was recorded at $2\theta = 31.4^\circ$ ($\text{BaTiO}_3 \{101\}$). The peaks are situated at $\psi = 30^\circ, 55^\circ, 74^\circ$ and 90° .

While the peaks in Fig. 4.26 at $\psi = 30^\circ, 55^\circ, 74^\circ$ and 90° are from the major orientation relationship $(112) \text{BaTiO}_3 \parallel (100) \text{TiO}_2$ those at $\psi = 0^\circ, 35^\circ$ and 90° are from the minor orientation relationship $(111) \text{BaTiO}_3 \parallel (100) \text{TiO}_2$. The in-plane orientation relationship is found to be $[1\bar{1}0] \text{BaTiO}_3 \parallel [001] \text{TiO}_2$ for all these orientations. The main (112) orientation of BaTiO_3 deviates from the minor (111) one by a tilt of 19.5° around the $[1\bar{1}0] \text{BaTiO}_3 \parallel [001] \text{TiO}_2$ tilt axis.

Fig. 4.27(a) shows a cross sectional bright field TEM image of a reaction layer prepared by vapour-solid reaction on a $(100) \text{TiO}_2$ substrate at 800°C . In Fig. 4.27(a), the interface between the thin film and the substrate is rough and faceted. Well-oriented BaTiO_3 grains were formed after the reaction. This was confirmed by selected area electron diffraction (Fig. 4.27(b)). The (112) orientation relationship of BaTiO_3 found by XRD texture measurements is in agreement with the one deduced by selected area electron diffraction (Fig. 4.27(b)).

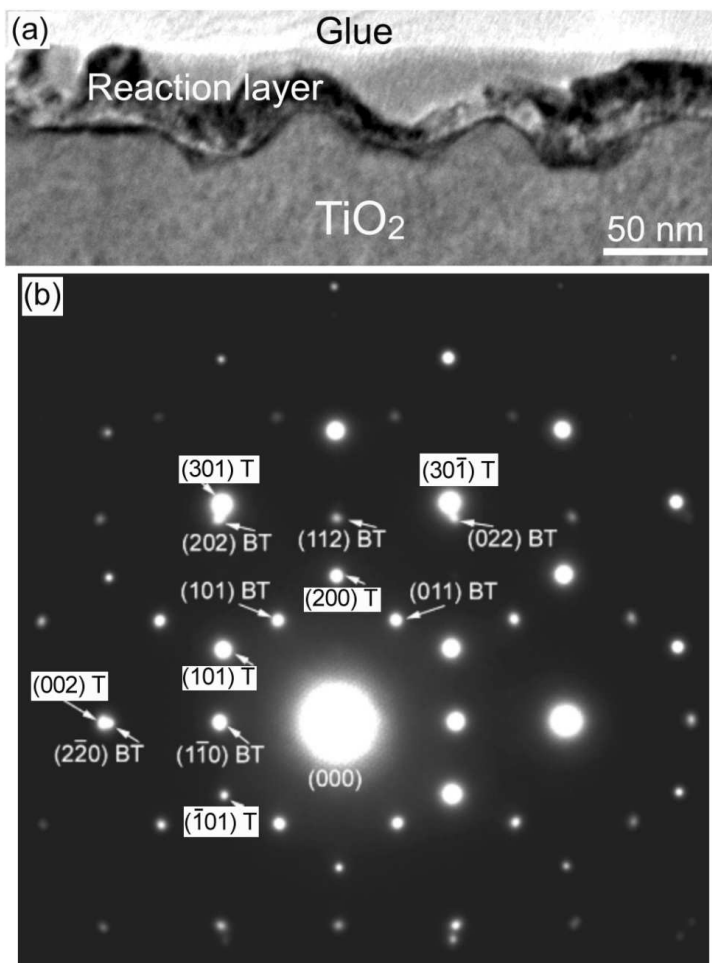


Fig. 4.27. (a) Bright-field TEM image of a reaction layer formed by vapour-solid reaction on the (100) rutile surface at 800°C , and (b) electron diffraction pattern taken from the surface region between the rutile substrate (T) and the reaction layer. Well-oriented BaTiO_3 (BT) grains were found in the thin film. Viewing direction is $[11\bar{1}] \text{BaTiO}_3 \parallel [010] \text{TiO}_2$.

Fig. 4.28 shows a HRTEM image of the interface region after the reaction between a BaO vapour and the $(100) \text{TiO}_2$ (rutile) single crystal of a sample prepared at a substrate temperature of 900°C . The reaction layer consists of BaTiO_3 and $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ grains. The latter were again observed between the TiO_2 substrate and the BaTiO_3 phase. The crystallographic orientation relationship found by HRTEM between the BaTiO_3 and $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ grains corresponds to the relation (4.9).

The BaTiO_3 grains have also a well-defined orientation to the $(100) \text{TiO}_2$ substrate. Several orientations of the BaTiO_3 phase were found by XRD pole figures and HRTEM investigations

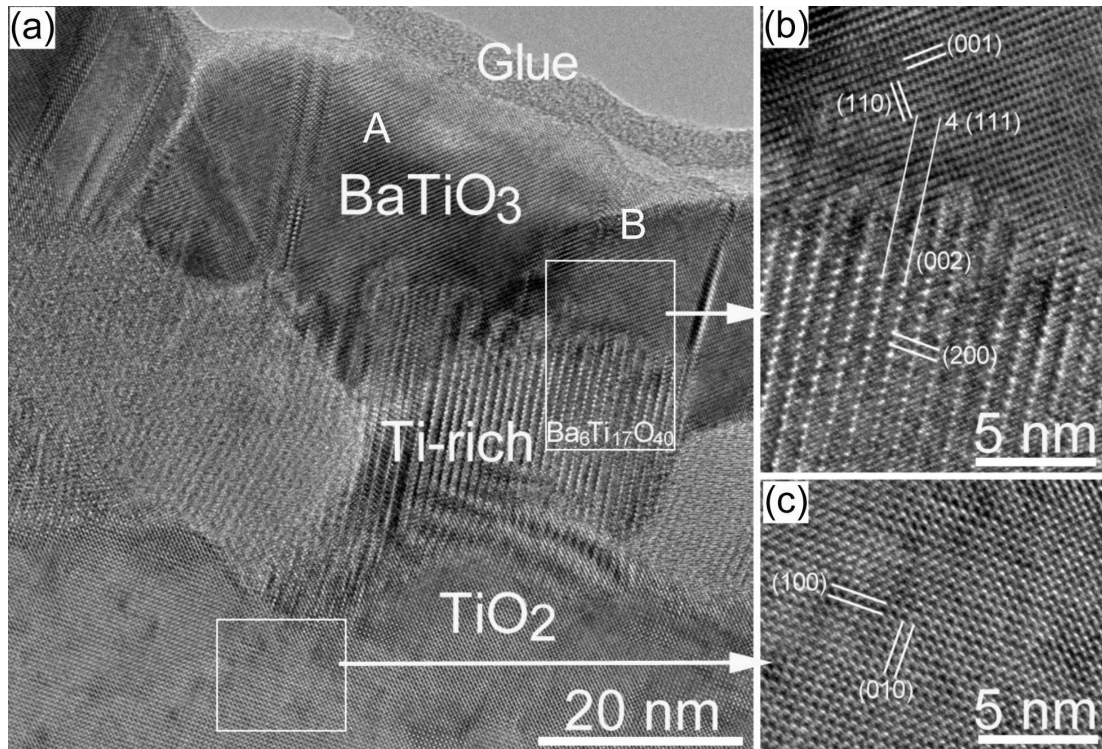


Fig. 4.28. HRTEM cross-section images of reaction products grown between BaO vapour and (100) TiO_2 at 900 °C: (a) thin film-substrate interface; (b) lattice plane images of BaTiO_3 and $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ grains and (c) the rutile substrate. The long white lines in image (b) mark the (001) $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ \parallel (111) BaTiO_3 lattice planes. Viewing direction is $[010]$ $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ \parallel $[1\bar{1}0]$ BaTiO_3 \parallel $[001]$ TiO_2 .

at 900 °C. Fig. 4.29 gives a pole figure for a sample made at a substrate temperature of 900 °C. The observed orientations of BaTiO_3 are: (223) BaTiO_3 \parallel (100) TiO_2 (grain A in Fig. 4.28);

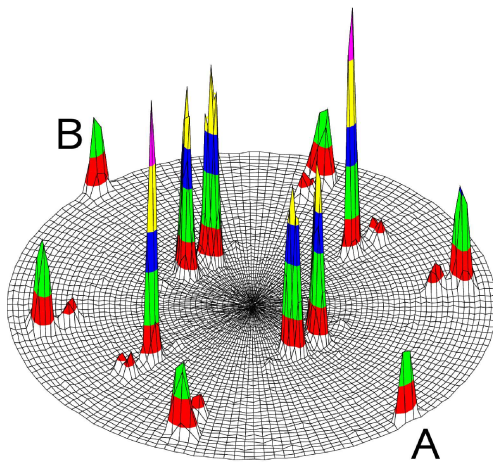


Fig. 4.29. Pole figure of a sample grown on a (100) TiO_2 substrate by a vapour-solid reaction at 900 °C. The figure was taken at $2\theta = 31.4^\circ$ (BaTiO_3 $\{101\}$). The peaks are situated at $\psi = 30^\circ, 35^\circ, 48^\circ, 60^\circ, 68^\circ, 78^\circ$ and 90° . The ψ values of $30^\circ, 48^\circ, 78^\circ$ and 90° correspond to a (223) orientation of BaTiO_3 while the ψ values of $30^\circ, 60^\circ, 68^\circ$ and 90° correspond to a (225) orientation of BaTiO_3 and the ψ values of 35° and 90° correspond to a (111) orientation of BaTiO_3 .

(335) BaTiO_3 \parallel (100) TiO_2 (grain B in Fig. 4.28); (225) BaTiO_3 \parallel (100) TiO_2 ; (111) BaTiO_3 \parallel (100) TiO_2 . The in-plane orientation relationship is found to be $[1\bar{1}0]$ BaTiO_3 \parallel $[001]$ TiO_2 for all these orientations. The (223) BaTiO_3 \parallel (100) TiO_2 and (335) BaTiO_3 \parallel (100) TiO_2 orientations can be understood as a result of a systematic tilt around the $[1\bar{1}0]$ BaTiO_3 \parallel $[001]$ TiO_2 tilt axis starting from the low-index orientation (111) BaTiO_3 \parallel (100) TiO_2 : $\angle \text{BaTiO}_3$ (111); (223) = 11.4° , $\angle \text{BaTiO}_3$ (111); (335) = 14.4° , $\angle \text{BaTiO}_3$ (111); (225) = 25.2° .

Table 4.1 summarises the orientation relationships and the misfit values for BaTiO₃ grown on the (100) and (110) TiO₂ substrates by solid-solid reaction in vacuum (ss(v)), solid-solid reaction in air (ss(a)) and vapour-solid reaction (vs) at different substrate temperatures. The misfits were calculated by using the equation adopted in the near-coincidence site lattice theory (NCSL):^{137,138}

$$F = 2(nd_1 - md_2)/(nd_1 + md_2), \quad (4.10)$$

where d₁ and d₂ are lattice spacings of the two materials in the interface plane and n and m are integers.

Table 4.1. Orientation relationships and NCSL misfit values (F₁ (in-plane) and F₂ (in-plane rotated by 90°)) for BaTiO₃ (BTO) thin films grown on (110) and (100) TiO₂ rutile (T) substrates at different temperatures.

T, °C	Parallel planes	Parallel direction	F ₁ , %	F ₂ , %
(110) TiO ₂ (rutile)				
ss(v)700–900& vs700 – 800	(001) BTO (110)T	[1 $\bar{1}$ 0] BTO [001] T	2(8d(001)BTO – 7d($\bar{1}$ 10)T)/ (8d(001)BTO + 7d($\bar{1}$ 10)T)=0.2	2(d(1 $\bar{1}$ 0)BTO – d(001)T)/ (d($\bar{1}$ 10)BTO + d(001)T)=4.1
ss(v)800–900& vs700 – 900	(119) BTO (110) T	[$\bar{1}$ 10] BTO [001] T	2(10d(99 $\bar{2}$)BTO – d($\bar{1}$ 10)T)/ (10d(99 $\bar{2}$)BTO + d($\bar{1}$ 10)T)=4.3	2(d(1 $\bar{1}$ 0)BTO – d(001)T)/ (d($\bar{1}$ 10)BTO + d(001)T)=4.1
ss(v)800–900& vs800 – 900	(441) BTO (110) T	[1 $\bar{1}$ 0] BTO [001] T	2(7d(11 $\bar{8}$)BTO – d($\bar{1}$ 10)T)/ (7d(11 $\bar{8}$)BTO + d($\bar{1}$ 10)T)=+6.1	2(d(1 $\bar{1}$ 0)BTO – d(001)T)/ (d($\bar{1}$ 10)BTO + d(001)T)=4.1
ss(v)800–900& ss(a)700 – 900	(110) BTO (110) T	[1 $\bar{1}$ 0] BTO [001] T	2(4d(001)BTO – 5d($\bar{1}$ 10)T)/ (4d(001)BTO + 5d($\bar{1}$ 10)T)=1.2	2(d(1 $\bar{1}$ 0)BTO – d(001)T)/ (d($\bar{1}$ 10)BTO + d(001)T)=4.1
(100) TiO ₂ (rutile)				
ss(v&a)&vs 700 – 900	(111) BTO (100) T	[1 $\bar{1}$ 0] BTO [001] T	2(3d(11 $\bar{2}$)BTO – d(010)T)/ (3d(11 $\bar{2}$)BTO + d(010)T)=+6.9	2(d(1 $\bar{1}$ 0)BTO – d(001)T)/ (d($\bar{1}$ 10)BTO + d(001)T)=4.1
vs800	(112) BTO (100) T	[1 $\bar{1}$ 0] BTO [001] T	2(2d(11 $\bar{1}$ 0)BTO – d(010)T)/ (2d(11 $\bar{1}$ 0)BTO + d(010)T)=+0.7	2(d(1 $\bar{1}$ 0)BTO – d(010)T)/ (d($\bar{1}$ 10)BTO + d(010)T)=4.1
vs900	(223) BTO (100) T	[1 $\bar{1}$ 0] BTO [001] T	2(7d(33 $\bar{4}$)BTO – d(010)T)/ (7d(33 $\bar{4}$)BTO + d(010)T)=+4.7	2(d(1 $\bar{1}$ 0)BTO – d(001)T)/ (d($\bar{1}$ 10)BTO + d(001)T)=4.1
	(335) BTO (100)T	[1 $\bar{1}$ 0] BTO [001] T	2(10d(55 $\bar{6}$)BTO – d(010)T)/ (10d(55 $\bar{6}$)BTO + d(010)T)=–6	2(d(1 $\bar{1}$ 0)BTO – d(001)T)/ (d($\bar{1}$ 10)BTO + d(001)T)=4.1
	(225) BTO (100) T	[1 $\bar{1}$ 0] BTO [001] T	2(9d(55 $\bar{4}$)BTO – d(010)T)/ (9d(55 $\bar{4}$)BTO + d(010)T)=–3.6	2(d(1 $\bar{1}$ 0)BTO – d(001)T)/ (d($\bar{1}$ 10)BTO + d(001)T)=4.1

Most remarkably, the relation [1 $\bar{1}$ 0] BaTiO₃ || [001] TiO₂ holds for all the different orientation relationships in Table 4.1, independently of the experimental conditions and substrate orientation. The various orientation relationships differ from each other by a tilt around the [1 $\bar{1}$ 0] BaTiO₃ || [001] TiO₂ axis. The parallel orientation of the (1 $\bar{1}$ 0) plane of BaTiO₃ to the (001) plane of TiO₂ (rutile) seems thus to be the principal orientation relation in this system.

C. Orientations of Ti-rich phases

Ti-rich phases were identified after both types of solid state reactions at high reaction temperatures in vacuum and in air but with quite different textures. At 1000 °C, a polycrystalline BaTi₄O₉ phase was formed after the solid-solid reaction in vacuum while a polycrystalline Ba₄Ti₁₃O₃₀ phase with fiber texture was grown after the reaction in air at temperatures between 900 °C (see Fig. A.10 in the appendix) and 1000 °C. The XRD pattern showed all reflections of the Ba₄Ti₁₃O₃₀ phase as in the standard powder diffractogram but the intensity relations of the peaks were changed due to a preferred orientation of the Ba₄Ti₁₃O₃₀ phase.

Contrary to the solid-solid reaction, a vapour-solid reaction at 900 °C and 1000 °C produced well-oriented Ba₆Ti₁₇O₄₀ grains on both (110) and (100) TiO₂ (rutile) surfaces. The examples for 900 °C are shown in Figs. 4.14-4.16, A.8 and 4.28. The crystallographic orientation relationship found by HRTEM between the TiO₂ substrates and the Ba₆Ti₁₇O₄₀ grains can be written as:

$$(001) \text{ Ba}_6\text{Ti}_{17}\text{O}_{40} \parallel (010) \text{ TiO}_2; [010] \text{ Ba}_6\text{Ti}_{17}\text{O}_{40} \parallel [001] \text{ TiO}_2, \quad (4.11)$$

which is, however, not exactly fulfilled. By analysing many HRTEM images, it was found that the (001) plane of Ba₆Ti₁₇O₄₀ can form an angle between 0° and ≈ 6° with the (010) plane of the substrate for Ti-rich grains grown on (110) TiO₂, and between 0° and ≈ 9° with the (010) plane of the substrate for Ti-rich grains grown on (100) TiO₂. Thus, a deviation (tilt) from 0° to ≈ 9° around the [010] Ba₆Ti₁₇O₄₀ \parallel [001] TiO₂ tilt axis is possible for Ba₆Ti₁₇O₄₀ grains in the above orientation.

Because of the monoclinic distortion of the Ba₆Ti₁₇O₄₀ unit cell, there is no low-index plane exactly parallel to the substrate surface plane (110) TiO₂. However, from HRTEM and FFT images it was found that the ($\bar{1}02$) plane of Ba₆Ti₁₇O₄₀ can approximately be parallel to (110) TiO₂. The angle between the ($\bar{1}02$) and (001) planes of Ba₆Ti₁₇O₄₀ is 47.88° in the [010] viewing direction of Ba₆Ti₁₇O₄₀, whereas the angle between (110) and (010) planes of TiO₂ is 45° in the [001] viewing direction of TiO₂. The orientation of the (001) Ba₆Ti₁₇O₄₀ plane parallel to one of the {010} TiO₂ planes in the viewing direction [010] Ba₆Ti₁₇O₄₀ \parallel [001] TiO₂ results in two positions (growth twins) of the Ba₆Ti₁₇O₄₀ grains on the (110) TiO₂ surface (see Fig. 4.9). Thus, there are two subsets of Ba₆Ti₁₇O₄₀ grains belonging to two different (010) and (100) planes of TiO₂, any of which has the ($\bar{1}02$) plane of Ba₆Ti₁₇O₄₀ almost parallel to (110) TiO₂. In the case of a (100) TiO₂ surface, it was found that the ($\bar{1}00$) plane of Ba₆Ti₁₇O₄₀ can approximately be parallel to the rutile surface.

4.2 Solid state reactions of BaCO₃ and BaO with TiO₂ (anatase)

4.2.1 Epitaxial growth of TiO₂ anatase thin films

TiO₂ (anatase) single crystals are more difficult to obtain with appropriate size than rutile.^{40,140–142} This problem has been addressed by growing epitaxial TiO₂ (anatase) thin films¹⁴³ or by using mineral samples.¹⁴⁴ Epitaxial TiO₂ (anatase) films could be prepared by several physical and chemical deposition techniques. Various substrates with different lattice misfits were used. Yamamoto *et al.* have used pulsed laser deposition (PLD) to grow TiO₂ thin films on SrTiO₃, LaAlO₃ and Y-stabilised ZrO₂ substrates.¹⁴⁵ They found that no epitaxial TiO₂ thin films can be obtained on (110) SrTiO₃ and (110) LaAlO₃. (001) TiO₂ (anatase) films can be grown on (100) SrTiO₃ even at a substrate temperature of 1000 °C.¹⁴⁶ Single crystal epitaxial (001) TiO₂ (anatase) films were also obtained on (100) LaAlO₃ by PLD.¹⁴⁷ Thus, only the (001) crystallographic surface of anatase can be grown by PLD with high quality.

The deposition of TiO₂ thin films on fused silica and titanium-coated fused silica by reactive electron beam evaporation has been reported previously.¹⁴⁸ The structure and properties of thin films under different conditions such as oxygen partial pressure and substrate temperature were investigated. The structure of the obtained film depends on the oxygen partial pressure and on the substrate used.

In this Ph.D. work, the growth of epitaxial TiO₂ thin films was carried out by reactive electron beam evaporation of titanium (IV) oxide (TiO₂) powder tablets (Merck, Germany) as described in **Chapter 3**. The influence of substrate orientation and substrate temperature on formation and phase contents of TiO₂ films is investigated. The typical thicknesses of the thin films were \approx 100 nm and \approx 200 nm. The substrates were heated to temperatures between 400 °C and 1200 °C during deposition. After deposition the samples were kept in the vacuum chamber and allowed to cool to room temperature.

One-side polished (100) and (110) surfaces of commercial SrTiO₃ as well as (100) and (110) surfaces of LaAlO₃ single crystals were used as substrate materials. Before the experiments the (100) SrTiO₃ substrates were chemically cleaned in buffered HF solution and thermally treated in air at 950 °C. (110) SrTiO₃ substrates were heated in air at 1100 °C for 60 min while (100) and (110) LaAlO₃ were thermally treated in air at 900 °C for 10 min.

A. TiO₂ film growth on (100) SrTiO₃ and (100) LaAlO₃

Pure TiO₂ (anatase) thin films were obtained on (100) SrTiO₃ and (100) LaAlO₃ substrates at substrate temperatures ranging from 500 °C to 1000 °C. XRD θ -2 θ scans (Fig. 4.30) and pole figure measurements revealed the epitaxial nature of the TiO₂ (anatase) films.

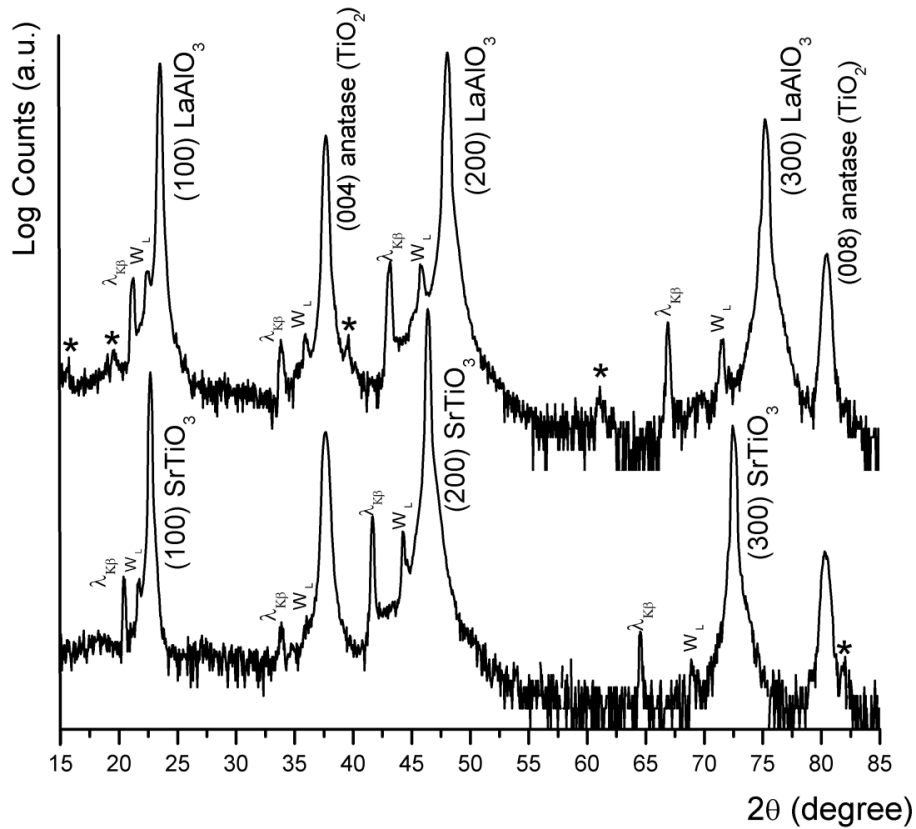


Fig. 4.30. XRD θ - 2θ scans of epitaxial TiO_2 (anatase) thin films grown on (100) SrTiO_3 and (100) LaAlO_3 substrates. The films were deposited at 700 °C. The $\lambda_{K\beta}$ lines are the substrate and thin film peaks originating from the remaining Cu- K_β radiation, and the W_L lines are coming from the tungsten contamination of the X-ray target by the tungsten cathode filament. The peaks marked by "*" characters are substrate-induced artefacts.

Fig. 4.31 shows a TEM micrograph of the film made on (100) SrTiO_3 at a substrate temperature of 600 °C. Columnar grains are clearly seen in the film.

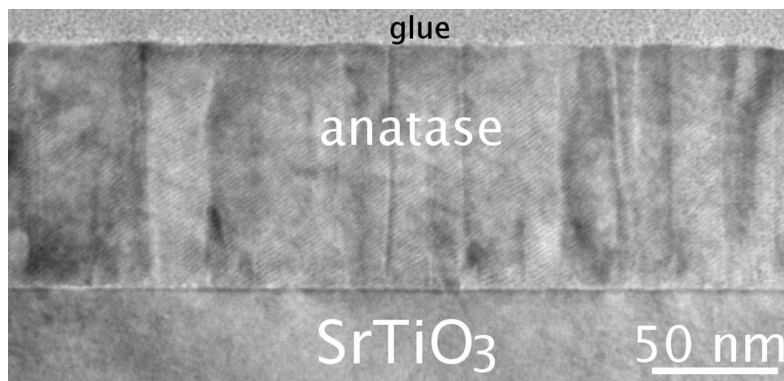


Fig. 4.31. Cross-sectional TEM micrograph of a TiO_2 (anatase) thin film grown on (100) SrTiO_3 at 600 °C.

HRTEM images of the TiO_2 (anatase)/ SrTiO_3 interface are shown in Fig. 4.32. The interface between substrate and film is sharp. Low angle grain boundaries are seen in the film showing a rather perfect microstructure of the TiO_2 (anatase) film (TiO_2 (a)). The epitaxial orientation relationship obtained from TEM and XRD investigations is:

$$(001) \text{TiO}_2 (\text{a}) \parallel (100) \text{SrTiO}_3; [100] \text{TiO}_2 (\text{a}) \parallel [001] \text{SrTiO}_3. \quad (4.12)$$

This orientation relationship was also observed on (100) LaAlO_3 .

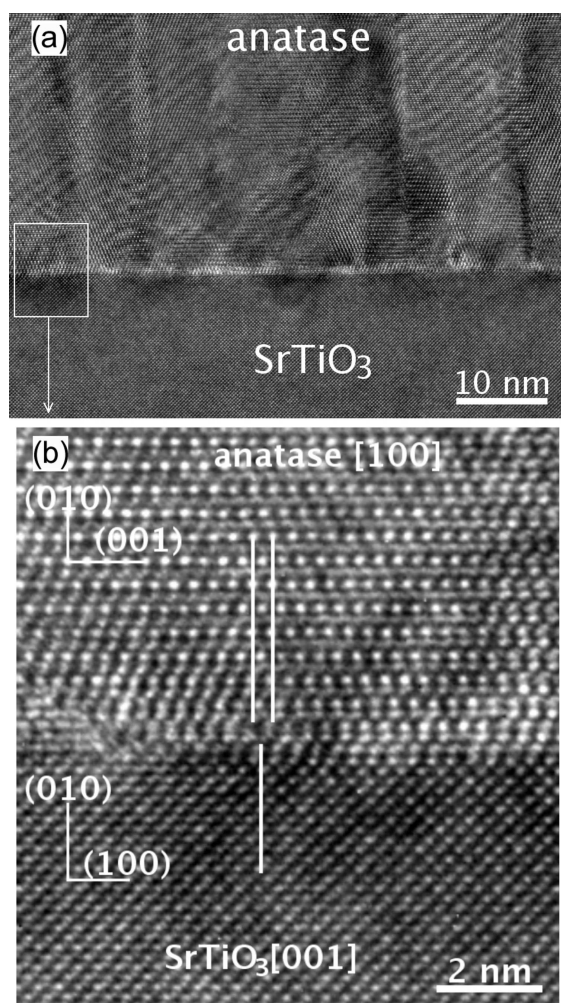


Fig. 4.32. HRTEM images of an anatase thin film grown at 600 °C: (a) overview of the (001) TiO_2 (anatase)/(100) SrTiO_3 interface and (b) lattice plane image of the TiO_2 (anatase) and the substrate. A misfit dislocation is marked by white lines.

The crystal quality of the prepared TiO_2 (anatase) thin films was analysed by rocking curves. The corresponding full-width at half maximum (FWHM) values of the (004) TiO_2 (anatase) peaks for the films prepared on (100) SrTiO_3 at substrate temperatures up to 900 °C ranged from 0.54° to 0.69°. The FWHM of the K_β line of the (100) SrTiO_3 substrate was 0.13°. At a substrate temperature of 1000 °C, a relatively broad peak, split into three peaks, was observed in the θ scan which means that the TiO_2 (anatase) film consisted of three kinds of tilted domains. For the thin films deposited on (100) LaAlO_3 , the FWHM values of the rocking curves were about 0.2° showing a better crystallinity of the TiO_2 (anatase) films grown on (100) LaAlO_3 compared to those on (100) SrTiO_3 . It should be noted that LaAlO_3 substrates usually consist of several twin domains. The rocking curve of the (200) LaAlO_3 peak measured by high-resolution XRD with a Ge (220) monochromator showed a broad peak and the FWHM was estimated to be about 0.1°.

AFM images of thin films deposited on (100) SrTiO_3 and (100) LaAlO_3 at a substrate temperature of 800 °C are shown in Figs. 4.33(a)-(b), respectively. The surface morphology shows an average island diameter of about 180 nm in Fig. 4.33(a), and of about 450 nm in Fig. 4.33(b). The islands in Figs. 4.33(a)-(b) are square-shaped. The surface of each island consists of spiral terraces due to a spiral growth mechanism.

To study the stability of TiO_2 (anatase) thin films made on (100) SrTiO_3 , a film deposited on

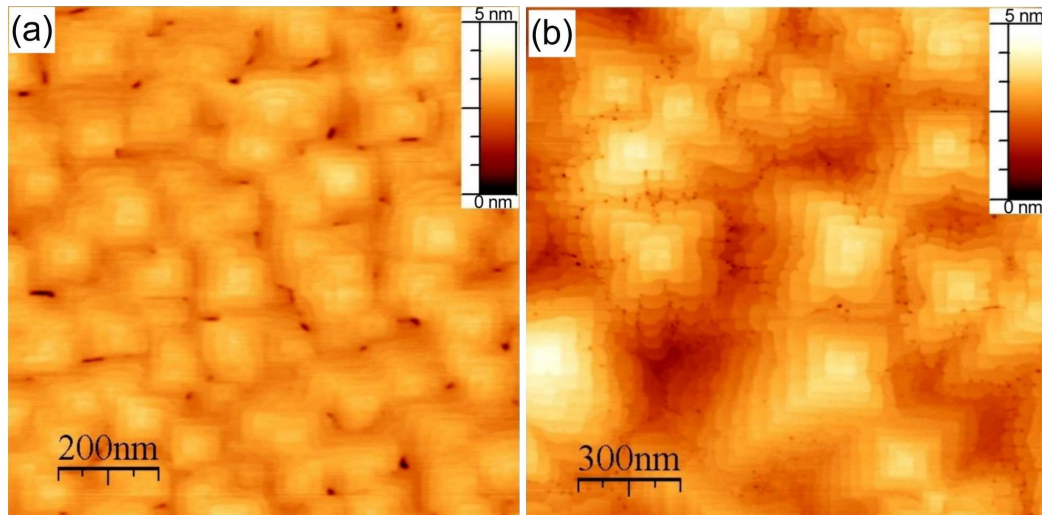


Fig. 4.33. AFM images of (001) TiO_2 (anatase) thin films grown on (a) (100) SrTiO_3 and (b) (100) LaAlO_3 at a substrate temperature of 800 °C.

the SrTiO_3 at a substrate temperature of 800 °C was annealed in air or in vacuum at 900 °C for 60 min. After this postannealing step, XRD analysis showed that no transformation from the anatase structure to the rutile structure had occurred.

At a substrate temperature of 1100 °C the films grown on (100) SrTiO_3 consisted of a mixture of (110) TiO_2 (rutile) and (001) TiO_2 (anatase) grains. A splitting of the {101} TiO_2 (anatase) peaks in pole figures into two peaks occurred, which means that the TiO_2 (anatase) film consisted of two kinds of tilted domains.

B. TiO_2 film growth on (110) SrTiO_3 and (110) LaAlO_3

In the case of (110) SrTiO_3 and (110) LaAlO_3 , pure epitaxial TiO_2 (anatase) films were obtained at substrate temperatures between 500 °C and 750 °C, and 500 °C and 900 °C, respectively.

Fig. 4.34(left) shows XRD θ - 2θ scans of epitaxial TiO_2 (anatase) films grown at 700 °C on (110) SrTiO_3 and (110) LaAlO_3 . The peaks at 62.6° in Figs. 4.34(a)-(b) correspond to (024) TiO_2 . Fig. 4.34(right) shows a pole figure recorded at fixed $2\theta = 25.3^\circ$ of the sample grown on (110) LaAlO_3 at a substrate temperature of 800 °C. The epitaxial orientation relationship between the thin film and (110) LaAlO_3 is:

$$(012) \text{TiO}_2 \text{ (a)} \parallel (110) \text{LaAlO}_3; [100] \text{TiO}_2 \text{ (a)} \parallel [001] \text{LaAlO}_3. \quad (4.13)$$

This orientation relationship was also observed on (110) SrTiO_3 .

In rocking curves of the TiO_2 (anatase) films grown on (110) SrTiO_3 the FWHM values of the (024) TiO_2 (anatase) peak varied from 0.56° to 0.72°. The crystal quality of the films obtained on (110) LaAlO_3 was better than on (110) SrTiO_3 . The FWHM values of the (024) TiO_2 (anatase) peak were 0.4° for the films prepared at substrate temperatures up to 700 °C and 0.2° for the films prepared at substrate temperatures higher than 800 °C, showing the good crystallinity of the thin films.

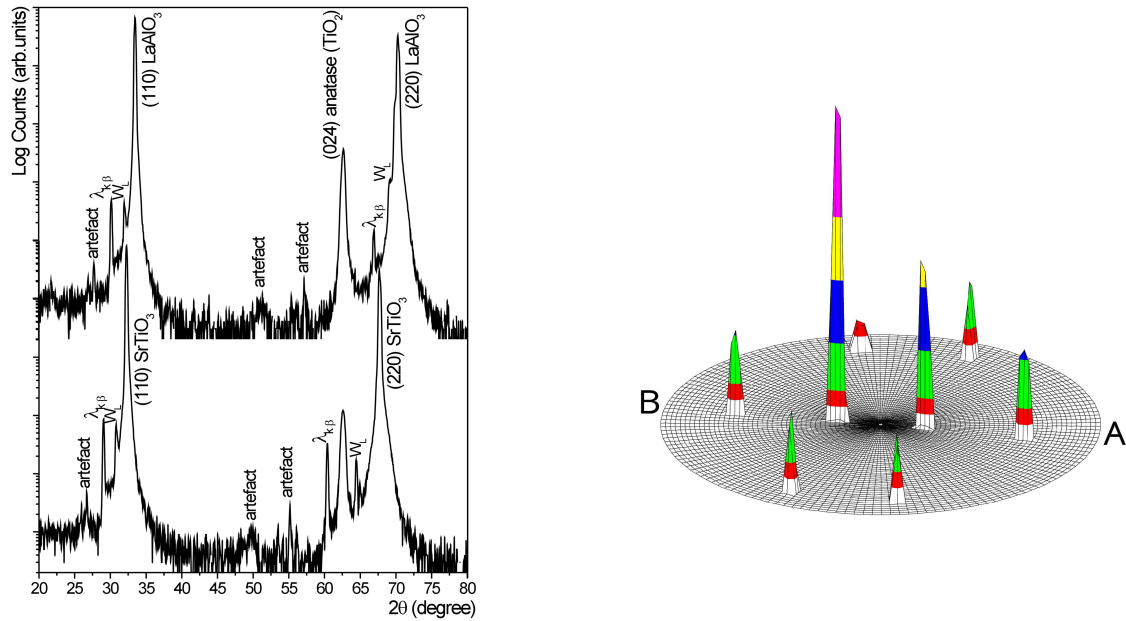


Fig. 4.34. (left) XRD θ - 2θ scans of epitaxial TiO_2 (anatase) thin films grown on (110) SrTiO_3 and (110) LaAlO_3 substrates. The films were deposited at 700 °C. The $\lambda_{K\beta}$ lines are the substrate and thin film peaks originating from the remaining Cu- K_β radiation, and the W_L lines are coming from the tungsten contamination of the X-ray target by the tungsten cathode filament. The "artefact" peaks are substrate-induced artefacts. (right) X-ray pole figure recorded at $2\theta = 25.3^\circ$ ($\{101\}$ TiO_2) of the TiO_2 (anatase) film deposited on (110) LaAlO_3 at 800 °C. Peaks are situated at $\psi = 16^\circ$, 61° and 75° and correspond to a (012) orientation of TiO_2 (anatase). The positions of marks A and B correspond to the ϕ values of the $(1\bar{1}0)$ and $(\bar{1}10)$ substrate planes, respectively.

Fig. 4.35 shows a HRTEM image of the film deposited on (110) SrTiO_3 substrate at a substrate temperature of 700 °C. The above orientation relationship is in good agreement with the one de-

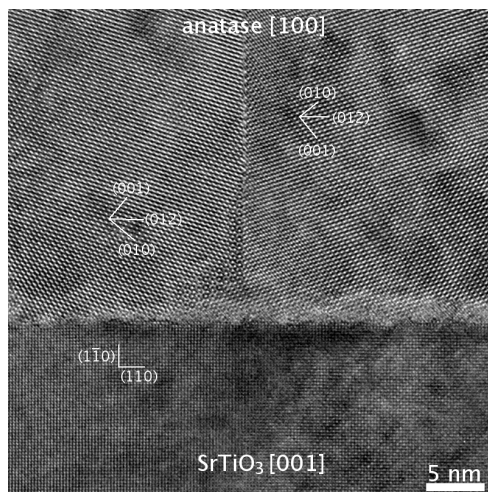


Fig. 4.35. HRTEM image of an epitaxial TiO_2 (anatase) thin film grown on (110) SrTiO_3 substrate at 700 °C. Magnified version of the image see in the appendix, Fig. A.11.

duced from HRTEM. Low angle grain boundaries are seen in the film showing a rather perfect microstructure of the anatase film.

The anatase film was converted into a cubic phase similar to TiO when extensively exposed to the 400 keV electron beam for a few minutes. Fig. 4.36 shows a HRTEM micrograph of a place after exposure of the anatase film under the electron beam for a few minutes. The film shows strong black and white contrast indicating the instability of the film under the electron beam.

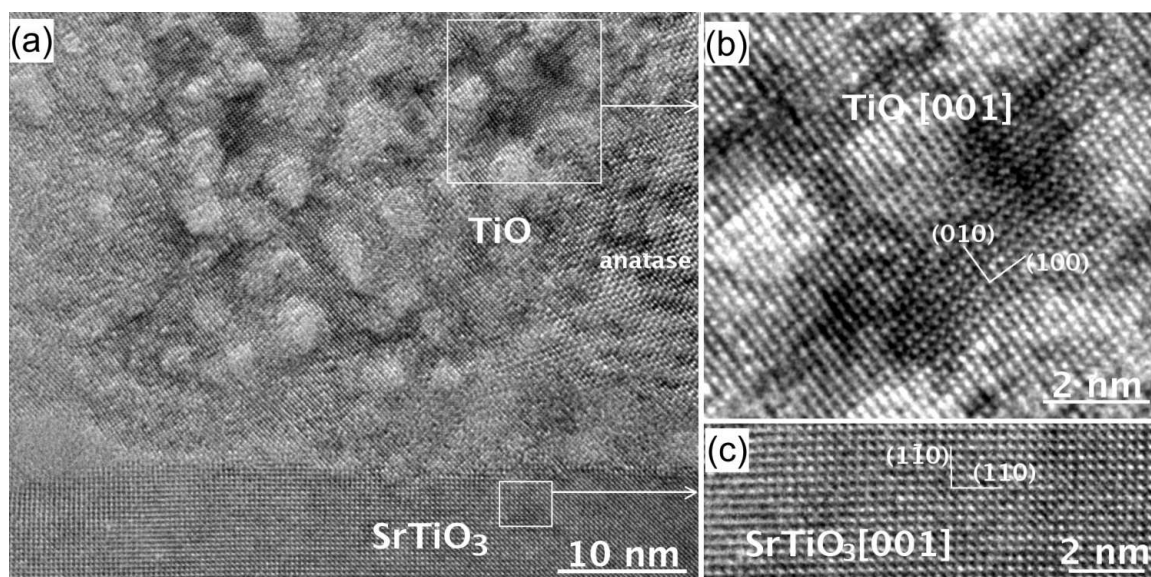


Fig. 4.36. TEM cross-section micrographs of TiO_2 (anatase) film and (110) SrTiO_3 substrate after extended exposure to the electron beam: (a) interface between the damaged film and (110) SrTiO_3 ; (b) and (c) lattice plane images of TiO and the SrTiO_3 substrate, respectively.

Damaged parts (white areas) are clearly seen in Fig. 4.36(a). At the same time, the contrast of the substrate is uniform showing that no distortions occur. Fig. 4.36(b) shows an enlarged image of the damaged part of Fig. 4.36(a). The angle between the lattice planes of the converted phase is 90° , with a spacing of 0.42 nm. This phase can thus be attributed to a cubic phase similar to titanium monoxide (TiO).

An AFM image of the thin film deposited on (110) LaAlO_3 at a substrate temperature of 800°C is shown in Fig. 4.37. The islands are elongated in the $[\bar{1}10]$ direction of LaAlO_3 (the orientation

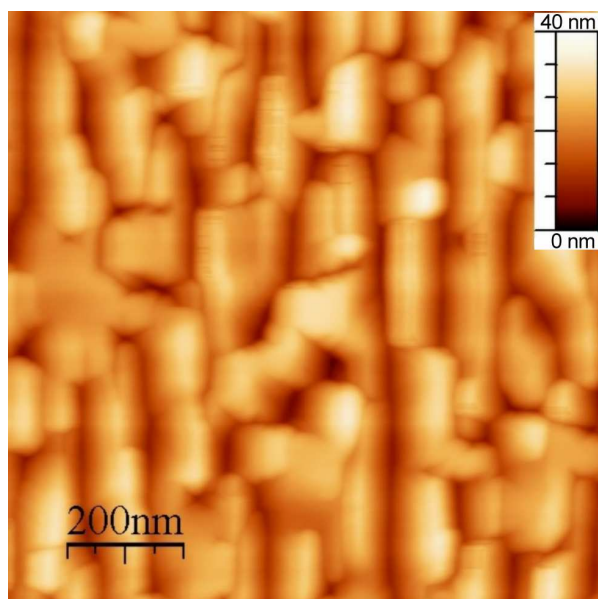


Fig. 4.37. AFM image of a (012)-oriented TiO_2 (anatase) thin film grown on a (110) LaAlO_3 substrate at a substrate temperature of 800°C .

of the substrate was confirmed by XRD), with an average grain size of about $100\text{ nm} \times 200\text{ nm}$. The same surface morphology of the anatase islands was observed on (110) SrTiO_3 . As shown by AFM, most of the surface of large (012)-oriented TiO_2 (anatase) grains is planar and parallel to the

substrate surface, so that it could represent a crystallographic (012) plane.

A small amount of the TiO_2 (rutile) phase was detected after deposition on (110) SrTiO_3 at temperatures of 800 °C and 900 °C, as shown by one very weak peak in the pole figures recorded at $2\theta = 27.4^\circ$. The amount of TiO_2 (rutile) grains was about the same at a temperature of 1000 °C but its orientation quality was improved. The maximum intensity of the TiO_2 (rutile) phase at this temperature taken from a pole figure with $2\theta = 27.4^\circ$ was 38 cps. This is a very low value compared to the intensity of TiO_2 (anatase) taken from a pole figure with $2\theta = 25.3^\circ$, which was 9216 cps. The orientation quality and the amount of the TiO_2 (anatase) phase decreased at a substrate temperature of 1100 °C. However, the total intensity obtained from TiO_2 (anatase) was 3516 cps while from rutile it was 85 cps. At a substrate temperature of 1200 °C the TiO_2 (anatase) phase was not present any more in the films. Now the film consisted mainly of tilted TiO_2 (rutile) grains.

C. Origin of the epitaxy between TiO_2 (anatase) and $\text{SrTiO}_3/\text{LaAlO}_3$

Although the growth of the TiO_2 (anatase) thin film was not the major aim of this Ph.D. work, it is worth to analyse the results on the epitaxial growth of TiO_2 (anatase) on the SrTiO_3 and LaAlO_3 substrates.

As was mentioned above, rutile is the most stable form of TiO_2 whereas anatase and brookite are metastable and transform to the rutile phase on heating. Experimental data¹⁴⁹ and theoretical analysis^{149,150} show that anatase becomes more stable with respect to rutile at very small crystallite sizes (10 nm - 14 nm). These findings are not directly applicable to the results shown above. The pure TiO_2 (anatase) films deposited on SrTiO_3 and on LaAlO_3 have an average grain size from 100 nm to 600 nm depending on the substrate temperature used. In addition, the stability of TiO_2 (anatase) depends strongly on the substrate temperature, the substrate orientation, and the kind of substrate used. Previous discussions on the stability of the TiO_2 (anatase) phase and on the epitaxial growth were focused on the similarities between the local atomic arrangements in the grown layer and the substrate materials.^{146,151} Here, we will apply a fundamental building block approach in order to better understand the epitaxial relations between TiO_2 (anatase) and the substrates - an approach that was formerly adopted by Banfield *et al.*¹⁵² to understand epitaxial relations among the TiO_2 minerals. TiO_2 and perovskite structures can be constructed from AO_6 octahedra (in our case A = Ti, Al). Figs. 4.38(a)-(b) show a schematic representation of building blocks (TiO_6 octahedra) for (001) TiO_2 (anatase)/(100) SrTiO_3 and (012) TiO_2 (anatase)/(110) SrTiO_3 interfaces, respectively. The similarities between the orientations of the TiO_6 octahedra of SrTiO_3 and TiO_2 (anatase) are clearly visible.

It should be noted that the (100) surface of SrTiO_3 presented in Fig. 4.38(a) is SrO-terminated. According to the work of Ohnishi *et al.*,¹⁵³ the experimental treatment of the (100) SrTiO_3 substrates performed in our work (heating in air and then in vacuum of 10^{-5} mbar), however, results in mixed SrO- and TiO_2 -terminated surfaces of SrTiO_3 . The substrate termination is important for the interface because the TiO_2 -terminated (100) SrTiO_3 surface contains truncated TiO_6 octahedra. On the other hand, the (100) surface of LaAlO_3 is terminated by a La-O layer at high temperatures (above 523 K)^{154,155} and thus contains complete AlO_6 octahedra. The AO_6 octahedra (A = Ti, Al)

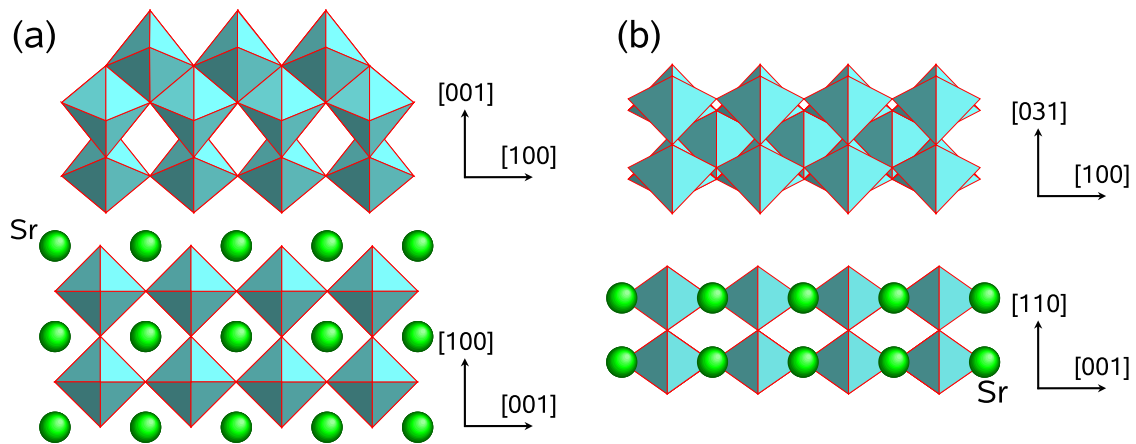


Fig. 4.38. Representation of the TiO_6 octahedra of (a) the (001) TiO_2 (anatase) (top)/(100) SrTiO_3 (bottom) interface and (b) the (012) TiO_2 (anatase) (top)/(110) SrTiO_3 (bottom) interface, respectively. Similarities can be found in the orientations of TiO_6 octahedra of SrTiO_3 and anatase structures.

are assumed to be important in determining the final phase formation and the epitaxial growth of the thin films. Moreover, the SrTiO_3 surfaces show a good lattice match with the TiO_2 (anatase) surfaces. The in-plane lattice mismatch between (100) TiO_2 (anatase) and (100) SrTiO_3 is -3.04 % while the lattice mismatch between (01 $\bar{3}$) TiO_2 ($d = 0.243$ nm) and (1 $\bar{1}0$) SrTiO_3 ($d = 0.275$ nm) is -11.6 %. It should be noted that the angle between the (01 $\bar{3}$) and (012) planes of anatase is not exactly 90° . A calculation results in the value of 88.5° . This means that the (01 $\bar{3}$) plane of a perfectly (012)-oriented anatase grain would deviate from the (1 $\bar{1}0$) SrTiO_3 plane by 1.5° , resulting in a kink by 1.5° at the anatase/ SrTiO_3 interface. In the same scenario the epitaxial formation of anatase films on (100) LaAlO_3 and (110) LaAlO_3 surfaces can be explained. The only difference is the better lattice match of (001)/(012) anatase with (100)/(110) LaAlO_3 surfaces. The lattice mismatch is -0.01 % between (100) TiO_2 (anatase) and (001) LaAlO_3 and -9.4 % between (01 $\bar{3}$) TiO_2 and (1 $\bar{1}0$) LaAlO_3 ($d = 0.268$ nm).

It was found that the irradiation of TiO_2 (anatase) cross-section TEM specimens by the electron beam results in a transformation into a cubic phase. A similar transformation was observed by Hengerer *et al.*^{40,156} by secondary-electron imaging and low energy electron diffraction. The authors found that sputtering with 500 eV Ne^+ ions of a (001) TiO_2 (anatase) surface leads to a transformation from tetragonal TiO_2 (anatase) to the face-centered cubic titanium monoxide (TiO). Our TEM investigations also showed this phenomenon. The new transformed structure is topotaxial with TiO_2 (anatase). A comparison of TiO_2 (anatase) and TiO is shown in Figs. 4.39(a)-(b). The building blocks of the TiO_2 (anatase) structure are distorted TiO_6 octahedra in a zig-zag alignment (Fig. 4.39(a)) whereas the TiO_6 octahedra in TiO are highly symmetric and without distortions (Fig. 4.39(b)). The cubic NaCl type lattice of TiO is known to be stable with very strong deviations from an ideal 1:1 stoichiometric ratio. Comparing one TiO_2 (anatase) unit cell with two TiO unit cells, the authors of Ref.¹⁵⁶ found that filling interstitial sites in the anatase structure with titanium ions would lead to the TiO structure (see Fig. 6 in Ref.¹⁵⁶). Thus, TiO_2 (anatase) can be considered as an ordered phase similar to $\text{Ti}_{0.5}\text{O}_{1.0}$ with missing octahedra. The electron beam induced disorder in TiO_2 (anatase) results in a cubic oxide with an intermediate composition in the

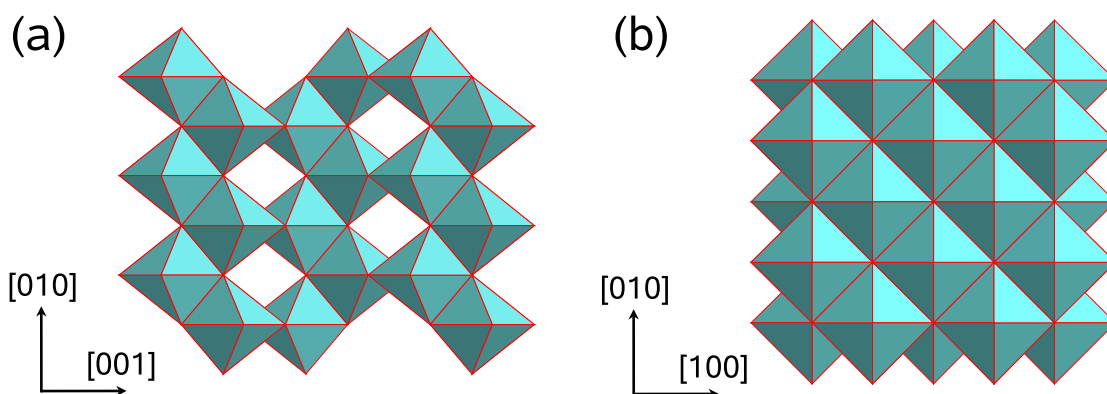


Fig. 4.39. Representation of the TiO_6 octahedra of (a) the TiO_2 (anatase) cell and (b) the TiO cell, respectively.

neighbourhood of $\text{Ti}_{0.5}\text{O}_{1.0}$. A transition from TiO_2 (anatase) to ideal TiO would require a strong shrinkage since the densities are very different ($\rho_{\text{anatase}} = 3.9 \text{ g/cm}^3$, $\rho_{\text{TiO}} = 5.84 \text{ g/cm}^3$).

4.2.2 Phase formation and orientation relationships

For the reaction experiments anatase thin films grown on SrTiO_3 and LaAlO_3 substrates at a substrate temperature of 800°C were used.

A. Phase formation

The phase sequences after solid-solid reactions in vacuum and in air at temperatures between 575°C and 900°C as well as after vapour-solid reaction at temperatures between 575°C and 900°C on epitaxial (001)- and (012)-oriented TiO_2 (anatase) thin films indicate a process that is similar to the reaction on the TiO_2 (rutile) substrates. It can be summarised as follows:

- At a substrate temperature of 500°C a single BaCO_3 phase is present, as detected by XRD.
- The formation of BaTiO_3 is always preceded by an intermediate Ba_2TiO_4 compound at temperatures between 575°C and 750°C in vacuum. After solid-state reaction in air, the Ba_2TiO_4 phase was not detected by XRD. Fig. 4.40 shows a HRTEM image of the interface region after the reaction between a BaCO_3 thin film and the epitaxial (012)-oriented anatase thin film of a sample after solid-solid reaction in air at 600°C for 30 min. The reaction layer consists of BaTiO_3 and BaCO_3 grains.
- After solid state reactions at 900°C Ti-rich phases were observed by XRD and TEM investigations in both types of the solid state reactions. Fig. 4.41 shows a TEM image of the interface region after the reaction between a BaO vapour and the epitaxial (001) anatase film of a sample prepared at a substrate temperature of 900°C . In Fig. 4.41 the reaction front is similar to the Ti-rich/(110) TiO_2 one (see Fig. 4.9). The Ti-rich grains were found at the interface with the anatase film and pores were formed during the reaction. HRTEM investigations revealed the presence of $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ in this sample.

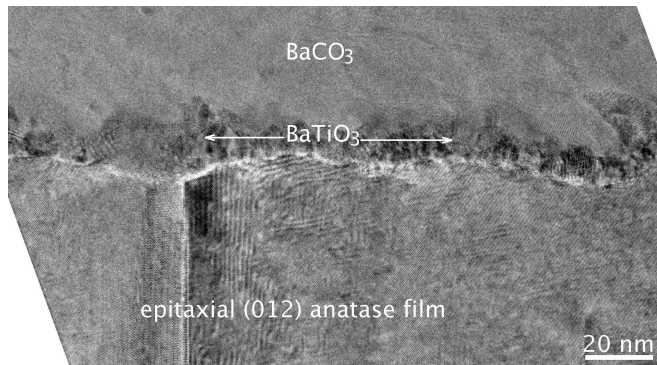


Fig. 4.40. Cross-sectional TEM image of the reaction front after solid-solid reaction of BaCO_3 with an epitaxial (012) TiO_2 (anatase) film. The reaction was performed in air at 600°C for 30 min.

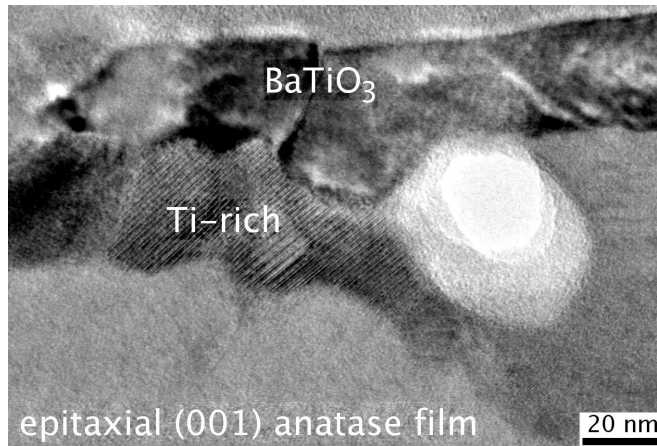


Fig. 4.41. Cross-sectional TEM image of the reaction front after vapour-solid reaction of BaO with an epitaxial (001) TiO_2 (anatase) film at 900°C .

B. Orientation relationships

Orientation of Ba_2TiO_4

The orientation quality of Ba_2TiO_4 grains after solid state reactions in vacuum with epitaxial anatase films is not as good as after the reactions with the rutile substrates. The solid state reactions with epitaxial anatase films lead to the formation of a polycrystalline Ba_2TiO_4 phase with fiber texture. An example for a sample prepared after solid-solid reaction of BaCO_3 with an epitaxial (001) anatase film is shown in Fig. 4.42.

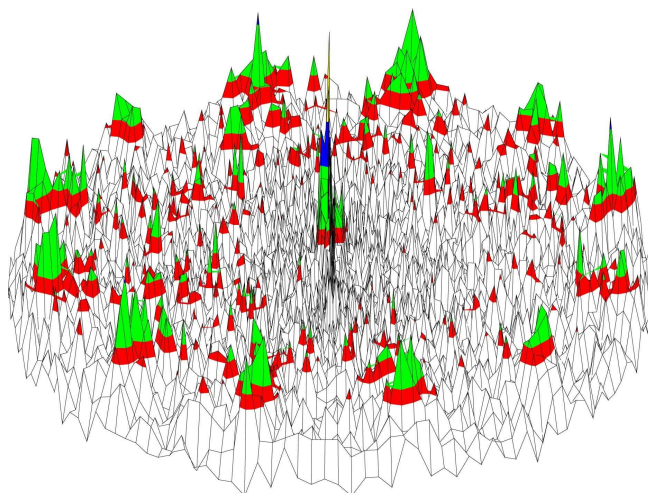


Fig. 4.42. Pole figure of a sample grown on an epitaxial (001) TiO_2 (anatase) film by a solid-solid reaction in vacuum at 700°C for 30 min. The pole figure was recorded at $2\theta = 29.34^\circ$ ($\{031\}/\{002\}$ Ba_2TiO_4).

Orientation of BaTiO_3

An X-ray pole figure analysis showed that the BaTiO_3 grains grown on epitaxial (001) and (012) TiO_2 (anatase) films after both types of the solid state reactions are crystallographically well-oriented.

Fig. 4.43 shows HRTEM images of the interface region after the reaction between a BaO vapour and the epitaxial (001) anatase film of a sample prepared at a substrate temperature of 900°C . The reaction layer consists of BaTiO_3 and $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ grains. The latter were observed between the epitaxial TiO_2 (anatase) film and the BaTiO_3 grains. The crystallographic orientation relationship found by HRTEM between the BaTiO_3 and $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ grains corresponds to relation (4.9). The orientation relationship of BaTiO_3 can be written from Fig. 4.43 as:

$$(001) \text{BaTiO}_3 \parallel (001) \text{TiO}_2 \text{ (a)}; [\bar{1}\bar{1}0] \text{BaTiO}_3 \parallel [\bar{1}\bar{1}0] \text{TiO}_2 \text{ (a)}. \quad (4.14)$$

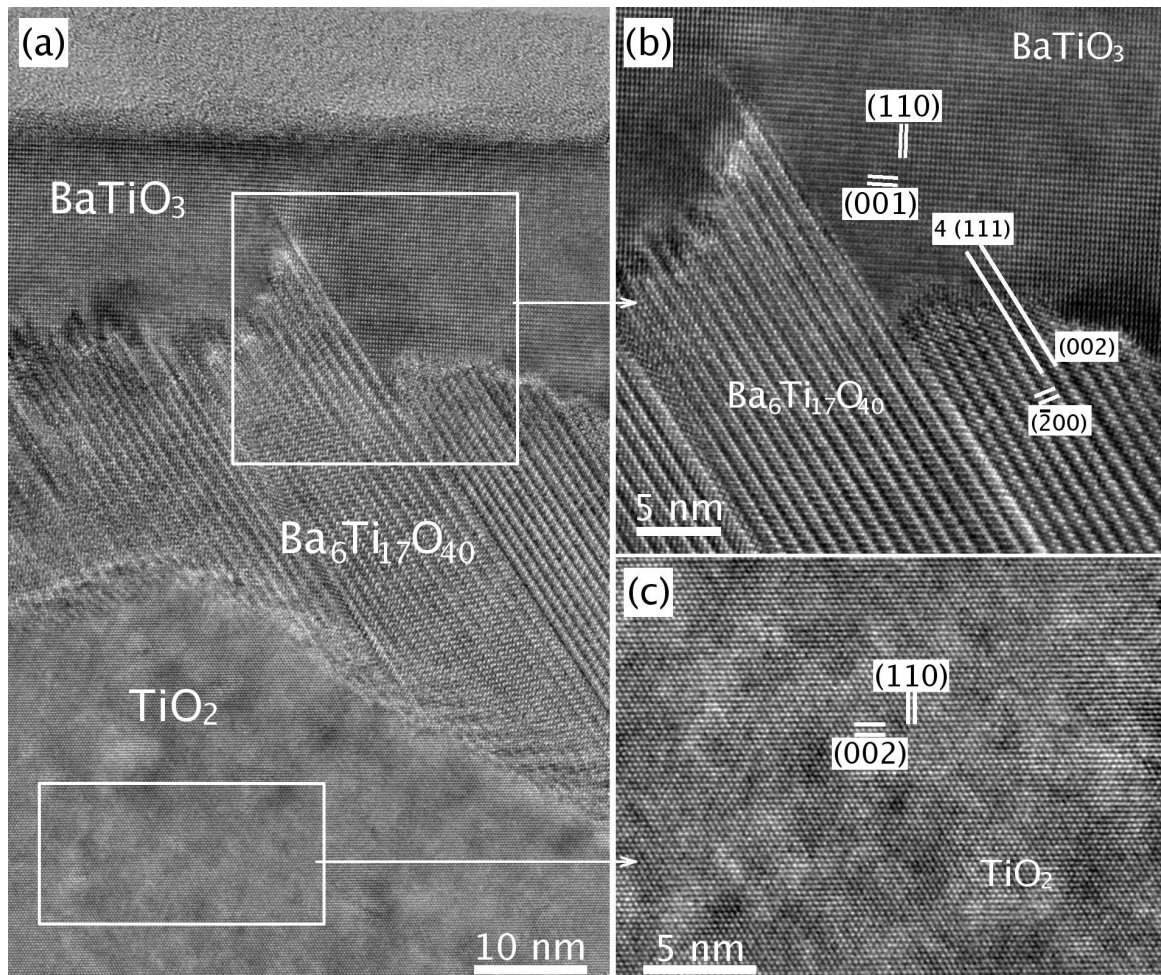


Fig. 4.43. HRTEM cross-section images of reaction products grown between a BaO vapour and an epitaxial (001) TiO_2 (anatase) film at 900°C : (a) thin film-substrate interface; (b) lattice plane images of BaTiO_3 and $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ grains and (c) the TiO_2 (anatase) film. The long white lines in the image (b) mark the $(001) \text{Ba}_6\text{Ti}_{17}\text{O}_{40} \parallel (111) \text{BaTiO}_3$ lattice planes. Viewing direction is $[010] \text{Ba}_6\text{Ti}_{17}\text{O}_{40} \parallel [\bar{1}\bar{1}0] \text{BaTiO}_3 \parallel [\bar{1}\bar{1}0] \text{TiO}_2$ (anatase).

However, BaTiO_3 grains show a small tilt of 0° to 4° around the $[\bar{1}\bar{1}0]$ $\text{BaTiO}_3 \parallel [\bar{1}\bar{1}0]$ TiO_2 (anatase) tilt axis in the above orientation as was found by analysing many HRTEM images. Such an orientation relationship was also observed for the samples after vapour-solid reaction at temperatures between 600°C and 900°C , as well as after solid-solid reaction at temperatures between 600°C and 900°C in vacuum and in air.

Fig. 4.44 shows a HRTEM image of the interface region of a sample prepared by a solid-solid reaction in air at 600°C for 30 min between a BaCO_3 film and the epitaxial (012) TiO_2 (anatase) film. The BaTiO_3 grains of Fig. 4.44 show the following orientation relationship:

$$(110) \text{BaTiO}_3 \parallel (012) \text{TiO}_2 \text{ (a)}; [001] \text{BaTiO}_3 \parallel [100] \text{TiO}_2 \text{ (a)}. \quad (4.15)$$

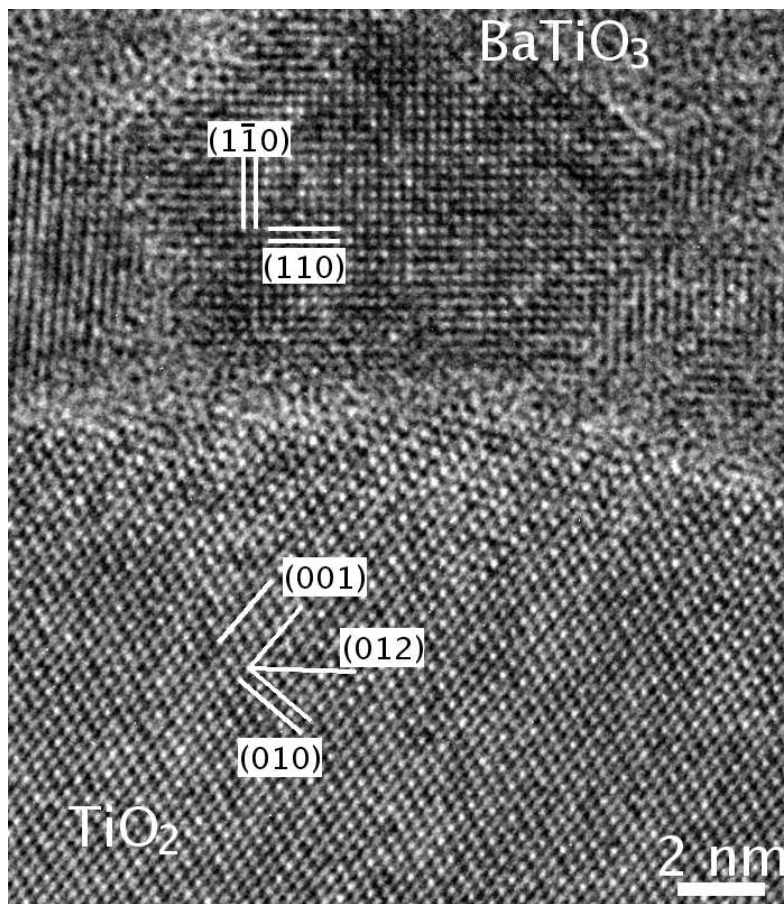


Fig. 4.44. Lattice plane image of an epitaxial (012) TiO_2 (anatase) film and BaTiO_3 grains. The sample was prepared by a solid-solid reaction in air at 600°C for 30 min. Viewing direction is $[001] \text{BaTiO}_3 \parallel [100] \text{TiO}_2$ (anatase).

HRTEM investigations showed that the BaTiO_3 grains were tilted by 0° to 3° around the $[001] \text{BaTiO}_3 \parallel [100] \text{TiO}_2$ (anatase) tilt axis in the above orientation. This orientation relationship was also found for the samples after solid-solid reaction at temperatures between 600°C and 900°C in vacuum and in air, as well as after vapour-solid reaction at temperatures between 600°C and 900°C .

Table 4.2 summarises the orientation relationships at different substrate temperatures and the misfit values found for BaTiO_3 films grown on epitaxial (001) and (012) TiO_2 (anatase) films by solid state reactions.

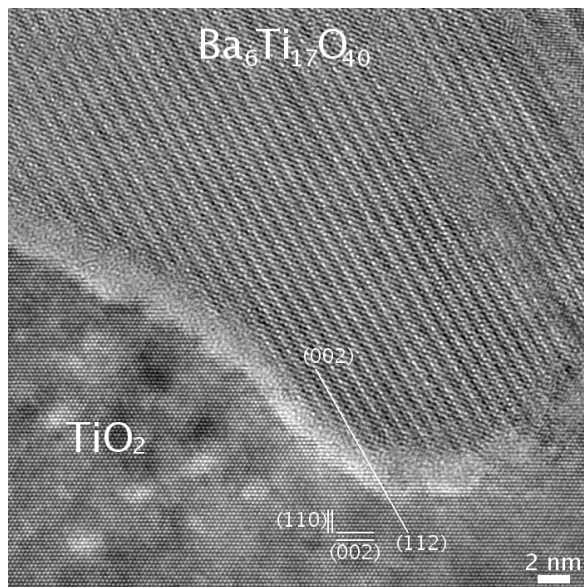
Table 4.2. Orientation relationships and NCSL misfit values (F_1 (in-plane) and F_2 (in-plane rotated by 90°)) for BaTiO₃ (BTO) thin films grown on epitaxial (001) and (012) TiO₂ (anatase) films (A) after solid state reactions in vacuum and in air.

$T, ^\circ\text{C}$	Parallel planes	Parallel direction	$F_1, \%$	$F_2, \%$
(001) TiO ₂ (anatase)				
600 – 900	(001) BTO (001) A	$[1\bar{1}0]$ BTO $[1\bar{1}0]$ A	$2(d(110)\text{BTO} - d(110)\text{A}) / (d(110)\text{BTO} + d(110)\text{A}) = +5.6$	$2(d(1\bar{1}0)\text{BTO} - d(1\bar{1}0)\text{A}) / (d(1\bar{1}0)\text{BTO} + d(1\bar{1}0)\text{A}) = +5.6$
(012) TiO ₂ (anatase)				
600 – 900	(110) BTO (012) A	$[001]$ BTO $[100]$ A	$2(5d(1\bar{1}0)\text{BTO} - 6d(01\bar{3})\text{A}) / (5d(1\bar{1}0)\text{BTO} + 6d(01\bar{3})\text{A}) = -3$	$2(d(001)\text{BTO} - d(100)\text{A}) / (d(001)\text{BTO} + d(100)\text{A}) = +5.6$

Orientation of Ti-rich phase

Fig. 4.43 shows a cross-section HRTEM image of a typical Ti-rich phase/BaTiO₃ reaction front. The interplanar distances of the Ti-rich phase measured from Fig. 4.43 are 0.94 nm and 0.49 nm with an angle of 98.8° in between them. They correspond to the ($\bar{2}00$) and (002) planes of the Ba₆Ti₁₇O₄₀ phase. In Fig. 4.43, the (002) plane of the Ba₆Ti₁₇O₄₀ Ti-rich phase is parallel to the (111) BaTiO₃ planes. The crystallographic orientation of the Ba₆Ti₁₇O₄₀ follows a relation similar to (4.8).

Fig. 4.45 shows a HRTEM image of the Ba₆Ti₁₇O₄₀/TiO₂ (anatase) interface of a sample prepared by vapour-solid reaction at 900 °C. The crystallographic orientation relationship found by

**Fig. 4.45.** Lattice plane image of an epitaxial (001) TiO₂ anatase film and a Ba₆Ti₁₇O₄₀ grain. The long white lines mark the (001) Ba₆Ti₁₇O₄₀ || (112) TiO₂ (anatase) planes. Viewing direction is $[010]$ Ba₆Ti₁₇O₄₀ || $[1\bar{1}0]$ TiO₂ (anatase). The sample was prepared by a vapour-solid reaction at 900 °C. Magnified version of the image see in the appendix, Fig. A.12.

HRTEM between the TiO₂ (anatase) and the Ba₆Ti₁₇O₄₀ grain in Fig. 4.45 can be written as:

$$(002) \text{Ba}_6\text{Ti}_{17}\text{O}_{40} \parallel (112) \text{TiO}_2 \text{ (a)}; [010] \text{Ba}_6\text{Ti}_{17}\text{O}_{40} \parallel [1\bar{1}0] \text{TiO}_2 \text{ (a)}. \quad (4.16)$$

HRTEM investigations of other parts of this sample showed that the Ba₆Ti₁₇O₄₀ grains were tilted by 0° to 3° around the $[010]$ Ba₆Ti₁₇O₄₀ || $[1\bar{1}0]$ TiO₂ tilt axis in the above orientation.

4.3 Solid state reactions of other alkaline-earth oxides with TiO₂ (rutile)

As was shown above, more than one orientation relationship was found for BaTiO₃ grown on the rutile substrates, depending on the reaction temperature. X-ray texture investigations and high-resolution TEM images showed that all observed orientations of BaTiO₃ grains on the TiO₂ (rutile) substrates have a common $[1\bar{1}0]$ BaTiO₃ \parallel $[001]$ TiO₂ tilt axis. In this part of the work, the experiments are extended to three other oxide systems, viz. SrO-TiO₂, CaO-TiO₂ and MgO-TiO₂ which involve product phases containing Sr²⁺ ($r_{\text{Sr}^{2+}} \approx 118$ pm), Ca²⁺ ($r_{\text{Ca}^{2+}} \approx 99$ pm) and Mg²⁺ ($r_{\text{Mg}^{2+}} \approx 75$ pm) ions (respectively), the ionic radii (r) of which are lower than that of Ba²⁺ ($r_{\text{Ba}^{2+}} \approx 138$ pm).

4.3.1 Vapour-solid reaction of SrO with TiO₂ (rutile)

The reaction of SrO vapour with TiO₂ (rutile) substrates was systematically investigated by XRD as a function of substrate temperature. Only SrTiO₃ was found after vapour-solid reaction at temperatures between 700 °C and 900 °C.

Fig. 4.46 gives typical pole figures taken at $2\theta = 32.4^\circ$ for samples prepared on (100) TiO₂ at 700 °C, 800 °C and 900 °C, respectively. Fig. 4.46(a) shows that at 700 °C, only the peaks

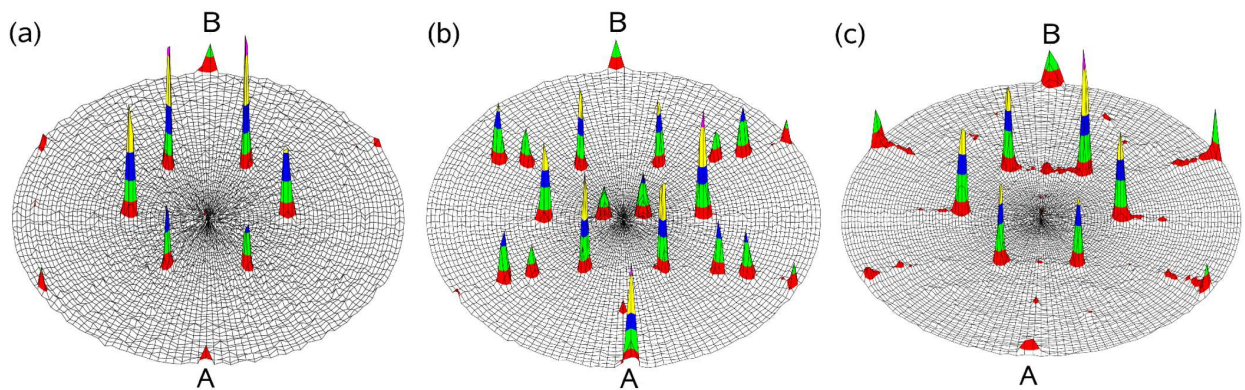


Fig. 4.46. Pole figures taken at $2\theta = 32.4^\circ$, corresponding to SrTiO₃ {101}, for samples made by vapour-solid reaction between SrO vapour and (100) TiO₂ (rutile) substrates at three different temperatures (a) 700 °C, (b) 800 °C and (c) 900 °C. For the full explanation see the text. Peaks situated at $\psi = 58^\circ$ are from {101} TiO₂. The positions of marks A and B correspond to the ϕ values of the (001) and (00 $\bar{1}$) substrate planes, respectively.

at $\psi = 35^\circ$ and 90° are present. This is due to the first orientation relationship (111) SrTiO₃ \parallel (100) TiO₂. In Fig. 4.46(b) for a sample made at 800 °C, in addition to the peaks at $\psi = 35^\circ$ and 90° , there are peaks at $\psi = 8^\circ$, 54° and 67° which are from the second orientation relationship (551) SrTiO₃ \parallel (100) TiO₂. Fig. 4.39(c) shows a pole figure of a sample made at a substrate temperature of 900 °C. In Fig. 4.46(c), the strong peaks at $\psi = 35^\circ$ and 90° are due to the (111) orientation of SrTiO₃, whereas the weak reflections at $\psi = 30^\circ$, 55° , 73° are coming from the third orientation relationship (112) SrTiO₃ \parallel (100) TiO₂ and those at $\psi = 30^\circ$, 48.5° , 79.5° are due to the

fourth orientation relationship (558) SrTiO₃ || (100) TiO₂.

The in-plane orientation was determined by pole figures recorded at $2\theta = 32.4^\circ$ and $2\theta = 46.5^\circ$ and a ϕ scan of the TiO₂ {110} reflections taken at $\psi = 45^\circ$. The ϕ positions corresponding to the (001) and (00 $\bar{1}$) substrate planes are denoted by marks A and B, respectively. Thus the in-plane orientation is always $[1\bar{1}0]$ SrTiO₃ || $[001]$ TiO₂ for all the orientations observed on the (100) rutile substrates. Notably, the (551) orientation of SrTiO₃ deviates from the (111) one by a tilt of 27.2° around the $[1\bar{1}0]$ SrTiO₃ || $[001]$ TiO₂ axis, while the (112) and (558) orientations of SrTiO₃ deviate from the (111) one by a tilt of 19.4° and 13.2° , respectively, around the same axis.

Fig. 4.47 shows typical pole figures taken at $2\theta = 32.4^\circ$ for samples prepared on (110) TiO₂ at 700 °C, 800 °C and 900 °C, respectively. Fig. 4.47(a) gives a pole figure for a sample made at

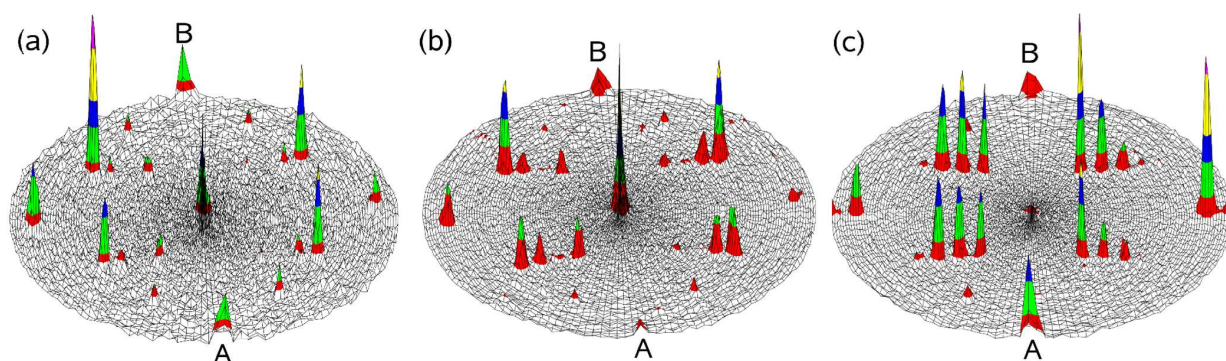


Fig. 4.47. Pole figures taken at $2\theta = 32.4^\circ$, corresponding to SrTiO₃ {101}, for samples after vapour-solid reaction of SrO with (110) TiO₂ (rutile) substrates made at three different temperatures (a) 700 °C, (b) 800 °C and (c) 900 °C. For more details see the text. Peaks situated at $\psi = 67.5^\circ$ are from {101} TiO₂. The positions of marks A and B correspond to the ϕ values of the (001) and (00 $\bar{1}$) substrate planes, respectively.

a substrate temperature of 700 °C. At this temperature two orientation relations for SrTiO₃ were found. Whereas the peaks in Fig. 4.47(a) at $\psi = 0^\circ, 60^\circ$ and 90° are from the first orientation relationship (110) SrTiO₃ || (110) TiO₂, those at $\psi = 38.5^\circ, 52^\circ, 79.4^\circ$ and 90° are from the second orientation relationship (118) SrTiO₃ || (110) TiO₂. For the samples made at temperatures between 800 °C and 900 °C, a third orientation relationship for this phase was found. The weak peaks situated at $\psi = 45^\circ$ in Fig. 4.47(b) for the sample made at a substrate temperature of 800 °C are due to the third orientation relationship (001) SrTiO₃ || (110) TiO₂. The peak intensity from this orientation becomes stronger at 900 °C (Fig. 4.47(c)). On the other hand, the peak intensity is getting much weaker for the first orientation.

From a series of pole figures and a ϕ scan of the TiO₂ {100} reflections taken at $\psi = 45^\circ$, the in-plane orientation was found to be $[1\bar{1}0]$ SrTiO₃ || $[001]$ TiO₂ for all the orientations observed on the (110) rutile substrates. It should be noted that the (118) orientation of SrTiO₃ deviates from the (110) one by a tilt of 79.8° around the $[1\bar{1}0]$ SrTiO₃ || $[001]$ TiO₂ axis, whereas the (001) orientation of SrTiO₃ deviates from the (110) one by a tilt of 90° around the same axis.

Table 4.3 summarises the orientation relationships and the misfit values for SrTiO₃ grown on the (100) and (110) TiO₂ (rutile) substrates by vapour-solid reaction in vacuum at different substrate temperatures. As in the case of BaTiO₃, the relation $[1\bar{1}0]$ SrTiO₃ || $[001]$ TiO₂ holds independently of the substrate orientation.

Table 4.3. Orientation relationships and NCSL misfit values (F_1 (in-plane) and F_2 (in-plane rotated by 90°)) for SrTiO₃ (STO) thin films grown on (100) and (110) TiO₂ (rutile) substrates (T) at different temperatures.

$T, ^\circ\text{C}$	Parallel planes	Parallel direction	$F_1, \%$	$F_2, \%$
(100) TiO ₂ (rutile)				
700 – 900	(111) STO (100) T	[1 $\bar{1}$ 0] STO [001] T	$2(3d(11\bar{2})\text{STO} - d(010)\text{T}) / (3d(11\bar{2})\text{STO} + d(010)\text{T}) = +3.8$	$2(10d(1\bar{1}0)\text{STO} - 9d(001)\text{T}) / (10d(1\bar{1}0)\text{STO} + 9d(001)\text{T}) = +3.5$
800	(551) STO (100) T	[1 $\bar{1}$ 0] STO [001] T	$2(12d(11\bar{1}0)\text{STO} - d(010)\text{T}) / (12d(11\bar{1}0)\text{STO} + d(010)\text{T}) = +0.9$	$2(10d(1\bar{1}0)\text{STO} - 9d(010)\text{T}) / (10d(1\bar{1}0)\text{STO} + 9d(010)\text{T}) = +3.5$
900	(112) STO (100) T	[1 $\bar{1}$ 0] STO [001] T	$2(2d(11\bar{1})\text{STO} - d(010)\text{T}) / (2d(11\bar{1})\text{STO} + d(010)\text{T}) = -1.9$	$2(10d(1\bar{1}0)\text{STO} - 9d(001)\text{T}) / (10d(1\bar{1}0)\text{STO} + 9d(001)\text{T}) = +3.5$
	(558) STO (100) T	[1 $\bar{1}$ 0] STO [001] T	$2(9d(44\bar{5})\text{STO} - d(010)\text{T}) / (9d(44\bar{5})\text{STO} + d(010)\text{T}) = +1.4$	$2(10d(1\bar{1}0)\text{STO} - 9d(001)\text{T}) / (10d(1\bar{1}0)\text{STO} + 9d(001)\text{T}) = +3.5$
(110) TiO ₂ (rutile)				
700 – 900	(110) STO (110) T	[1 $\bar{1}$ 0] STO [001] T	$2(5d(001)\text{STO} - 6d(\bar{1}10)\text{T}) / (5d(001)\text{STO} + 6d(\bar{1}10)\text{T}) = +0.06$	$2(10d(1\bar{1}0)\text{STO} - 9d(001)\text{T}) / (10d(1\bar{1}0)\text{STO} + 9d(001)\text{T}) = +3.5$
	(118) STO (110) T	[1 $\bar{1}$ 0] STO [001] T	$2(5d(44\bar{1})\text{STO} - d(\bar{1}10)\text{T}) / (5d(44\bar{1}) + d(\bar{1}10)\text{T}) = +4.4$	$2(10d(1\bar{1}0)\text{STO} - 9d(001)\text{T}) / (10d(1\bar{1}0)\text{STO} + 9d(001)\text{T}) = +3.5$
800 – 900	(001) STO (110) T	[1 $\bar{1}$ 0] STO [001] T	$2(7d(110)\text{STO} - 6d(\bar{1}10)\text{T}) / (7d(110)\text{STO} + 6d(\bar{1}10)\text{T}) = -0.9$	$2(10d(1\bar{1}0)\text{STO} - 9d(001)\text{T}) / (10d(1\bar{1}0)\text{STO} + 9d(001)\text{T}) = +3.5$

4.3.2 Vapour-solid reaction of CaO with TiO₂ (rutile)

A. Phase formation

Vapour-solid reactions between CaO vapour and (110) TiO₂ (rutile) substrates are different compared to the previous systems BaO-TiO₂ (rutile) and SrO-TiO₂ (rutile). CaTiO₃ and non-reacted CaO phases were found in the thin films after vapour-solid reactions at temperatures between 600 °C and 900 °C by XRD investigations. The reaction time was \approx 32 min.

Fig. 4.48 shows a XRD θ -2 θ scan of a sample prepared by vapour-solid reaction between CaO vapour and (110) TiO₂ substrate at a substrate temperature of 600 °C. In Fig. 4.48, beside the

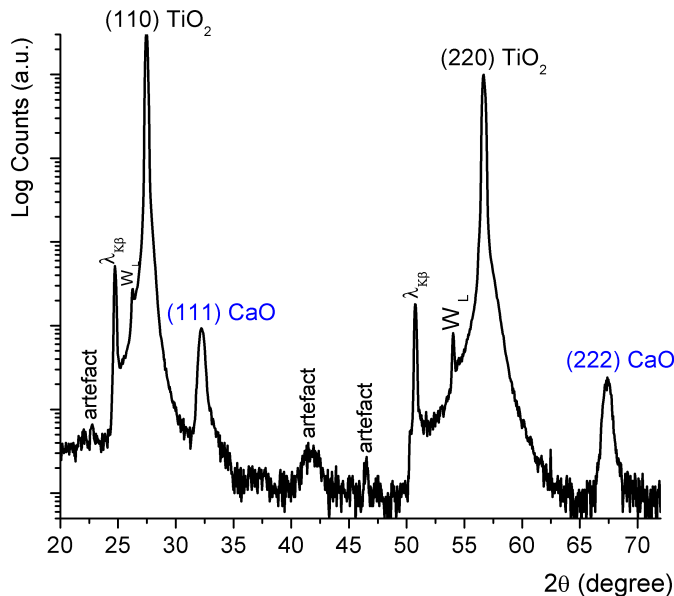


Fig. 4.48. XRD θ -2 θ scan of a sample made by vapour-solid reaction between CaO vapour and (110) rutile substrate at 600 °C. The $\lambda_{K\beta}$ lines are the substrate peaks originating from the remaining Cu-K β radiation, and the W_L lines are coming from the tungsten contamination of the X-ray target by the tungsten cathode filament. The "artefact" peaks are substrate-induced artefacts.

substrate reflections, there are peaks at $2\theta = 32.3^\circ$ and at $2\theta = 67.4^\circ$. They correspond to (111) and (222) reflections of CaO (JCPDS 78-0649), respectively. The CaTiO₃ phase is not seen in the XRD θ - 2θ pattern after the reaction at 600 °C because the phase was contained in the thin film in a small amount ($I = 25$ cps at $\psi = 60^\circ$) as was shown by the weak intensity in the pole figure taken at $2\theta = 33.1^\circ$ (CaTiO₃ (110)). With increasing reaction temperature the amount of the CaTiO₃ phase increased while the amount of CaO phase decreased. Fig. 4.49(a) gives a XRD θ - 2θ pattern of a sample made by vapour-solid reaction at 800 °C. While the peaks at $2\theta = 32.3^\circ$ and at $2\theta = 67.4^\circ$

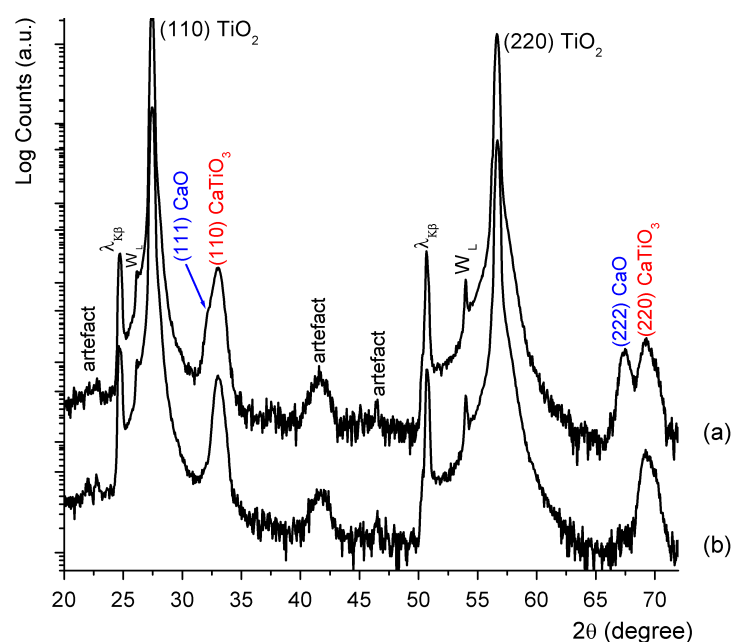


Fig. 4.49. XRD θ - 2θ scans of a sample made by vapour-solid reaction between CaO vapour and (110) rutile substrate at 800 °C: (a) as deposited and (b) after storage in air for two days. The $\lambda_{K\beta}$ lines are the substrate peaks originating from the remaining Cu-K β radiation, and the W_L lines are coming from the tungsten contamination of the X-ray target by the tungsten cathode filament. The "artefact" peaks are substrate-induced artefacts.

are from (111) and (222) reflections of CaO, those at $2\theta = 33.1^\circ$ and at $2\theta = 69.3^\circ$ correspond to (110) and (220) reflections of CaTiO₃. It is well-known that CaO is an unstable phase in air. In our work, the CaO phase was also found to be a very unstable compound and to react after storage for two days in air, most probably with H₂O and CO₂. Fig. 4.49(b) gives a XRD θ - 2θ scan which was taken from the sample shown in Fig. Fig. 4.49(a) after two days storage in air. The peaks at $2\theta = 32.3^\circ$ and at $2\theta = 67.4^\circ$ are not present any more in the XRD pattern, indicating the instability of the CaO phase in air. A vapour-solid reaction at 900 °C resulted in the formation of two phases (CaO and CaTiO₃).

To define which phase is formed first during a vapour-solid reaction between CaO vapour with (110) TiO₂ (rutile) substrates, a low amount of CaO was deposited on a hot (110) TiO₂ substrate at 700 °C. The nominal thickness of CaO was ≈ 3 nm. Only CaTiO₃ was found in the thin film after the reaction by XRD θ - 2θ measurements as well as by pole figures. This was also confirmed by TEM investigations shown in Figs. 4.50-4.51.

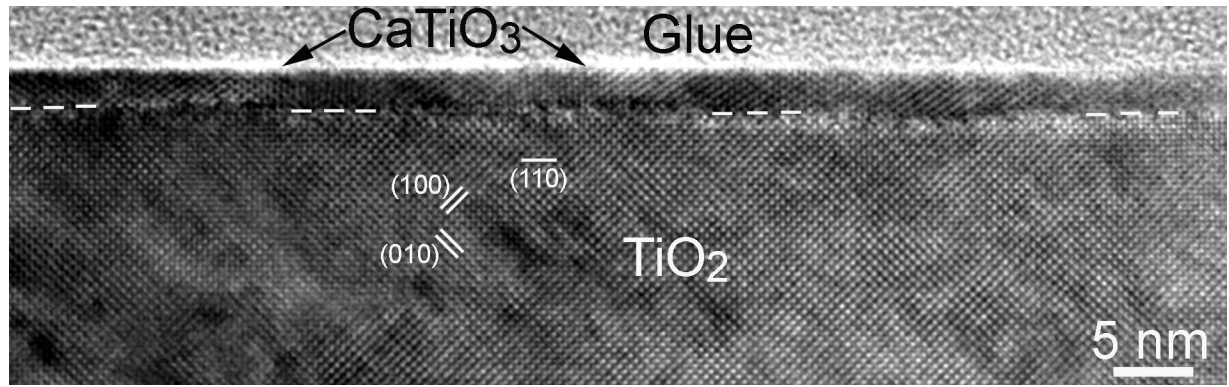


Fig. 4.50. Cross-sectional TEM image of a sample made by the reaction of CaO vapour with (110) TiO₂ (rutile) substrate at 700 °C. The dashes mark the rutile substrate. Viewing direction is [001] TiO₂.

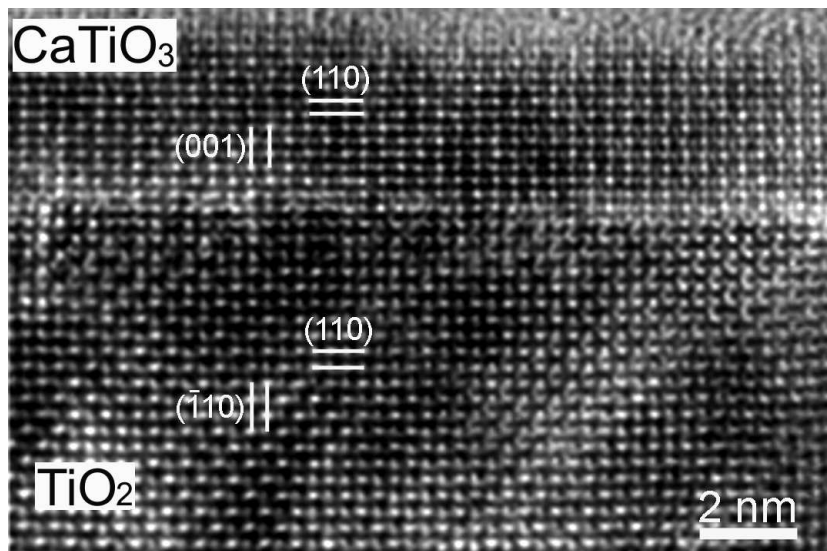


Fig. 4.51. Lattice plane image of the CaTiO₃/TiO₂ reaction front. Viewing direction is [1 $\bar{1}$ 0] CaTiO₃ || [001] TiO₂.

B. Orientation relationships

CaTiO₃ grew well-oriented with respect to the (110) rutile substrate. From Fig. 4.49 it can be concluded that the (110) plane of CaTiO₃ is parallel to the (110) TiO₂ surface. The orientation relationship of CaTiO₃ found by HRTEM (Fig. 4.51) as well as by pole figure measurements was:

$$(110) \text{ CaTiO}_3 \parallel (110) \text{ TiO}_2; [1\bar{1}0] \text{ CaTiO}_3 \parallel [001] \text{ TiO}_2. \quad (4.17)$$

This orientation relationship was observed for the samples made at temperatures between 600 °C and 900 °C. No other orientations of CaTiO₃ were found in the samples after the reaction. A rocking curve measurement with the (110) reflection of CaTiO₃ resulted in a tilting FWHM of $\approx 0.7^\circ$. The FWHM of the (110) TiO₂ substrate reflection was 0.1° .

To analyse the orientation of the CaO thin film, a number of pole figures were recorded at different 2θ values (32.2° , 37.4° and 53.9°). Fig. 4.52 gives a pole figure recorded at $2\theta = 37.4^\circ$ (CaO (200)). In the pole figure, six peaks are situated on the circle at $\psi = 55^\circ$ ($\Delta\phi = 60^\circ$) and correspond to the (111) orientation of CaO. For reasons of symmetry, these six reflection peaks can be related to two in-plane domain variants of the (111)-oriented CaO film, which are rotated in-

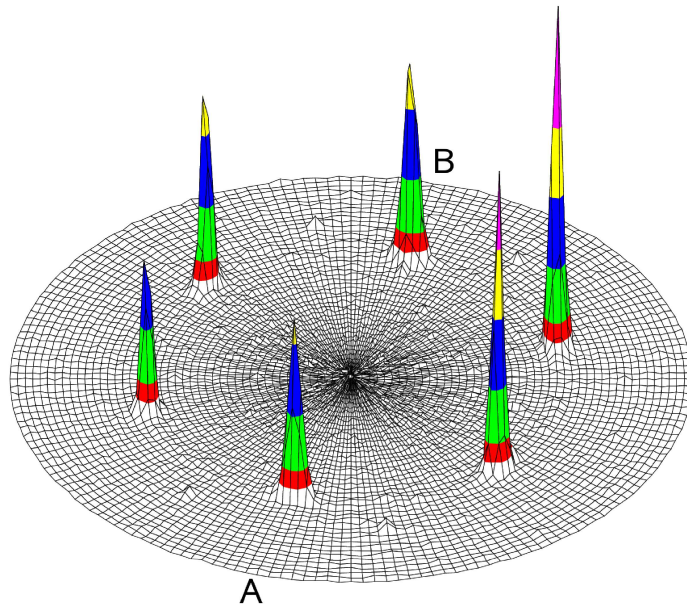


Fig. 4.52. Pole figure recorded with CaO (200) ($2\theta = 37.4^\circ$) of a sample made at 600 °C. The positions of marks A and B correspond to the ϕ values of the (001) and (00 $\bar{1}$) substrate planes, respectively.

plane by 90° relative to each other. From a series of pole figures, ϕ and θ - 2θ scans, the orientation relationship of CaO with respect to (110) TiO₂ was found to be:

$$(111) \text{ CaO} \parallel (110) \text{ TiO}_2; [11\bar{2}] \text{ CaO} \parallel [001] \text{ TiO}_2. \quad (4.18)$$

This orientation relationship was observed for the samples made at temperatures between 600 °C and 900 °C. A rocking curve measurement with the (111) planes of CaO resulted in a tilting FWHM of $\approx 1.7^\circ$. The FWHM of the (110) TiO₂ substrate reflection was 0.1° .

From Eqs. (4.17) and (4.18), the orientation relationship between CaO and CaTiO₃ can be written as follows:

$$(110) \text{ CaTiO}_3 \parallel (111) \text{ CaO}; [1\bar{1}0] \text{ CaTiO}_3 \parallel [11\bar{2}] \text{ CaO}. \quad (4.19)$$

Table 4.4 summarises the orientation relationships and NCSL misfit values observed for CaO and CaTiO₃ thin films on (110) TiO₂ substrates.

Table 4.4. Orientation relationships and NCSL misfit values (F_1 (in-plane) and F_2 (in-plane rotated by 90°)) for CaTiO₃ (CT) and CaO (CO) thin films grown on (110) rutile substrates (T).

$T, ^\circ\text{C}$	Parallel planes	Parallel direction	$F_1, \%$	$F_2, \%$
600 – 900	(110) CT \parallel (110) T	$[1\bar{1}0]$ CT \parallel $[001]$ T	$2(6d(001)CT - 5d(\bar{1}10)T) / (6d(001)CT + 5d(\bar{1}10)T) = -1.2$	$2(9d(1\bar{1}0)CT - 8d(001)T) / (9d(1\bar{1}0)CT + 8d(001)T) = +3.3$
600 – 900	(110) CT \parallel (111) CO	$[1\bar{1}0]$ CT \parallel $[11\bar{2}]$ CO	$2(8d(001)CT - 9d(1\bar{1}0)CO) / (8d(001)CT + 9d(1\bar{1}0)CO) = -0.5$	$2(3d(1\bar{1}0)CT - 4d(11\bar{2})CO) / (3d(1\bar{1}0)CT + 4d(11\bar{2})CO) = -2.7$

4.3.3 Vapour-solid reaction of MgO with TiO₂ (rutile)

Only the phase MgTiO₃ was observed after reaction of MgO vapour with the TiO₂ (rutile) substrates at temperatures between 600 °C and 800 °C. X-ray diffractometry and pole figure analysis showed that the MgTiO₃ films grown on (100) and (110) TiO₂ substrates were crystallographically well-oriented.

XRD θ - 2θ scans of the films produced on the (100) TiO₂ substrates showed the appearance of characteristic reflections of (11.0) MgTiO₃ at $2\theta = 35.5^\circ$ and (22.0) MgTiO₃ at $2\theta = 75.1^\circ$ beside the (200) and (400) substrate reflections. This means that the (11.0) plane of MgTiO₃ is parallel to the (100) surface of TiO₂. A rocking curve measurement with the planes (11.0) MgTiO₃ resulted in a tilting FWHM of 0.37° . The FWHM of the (200) TiO₂ (rutile) substrate reflection was 0.1° .

Fig. 4.53(a) shows a cross sectional transmission electron micrograph of a MgTiO₃ thin film grown by vapour-solid reaction on (100) TiO₂ (rutile) at a substrate temperature of 700 °C. The

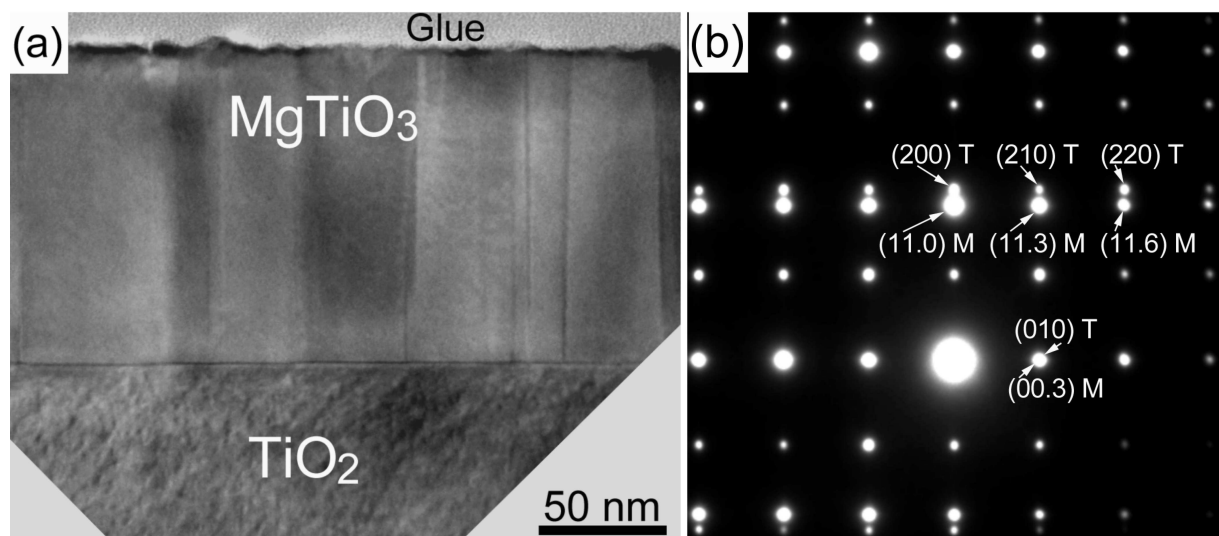


Fig. 4.53. (a) Bright field transmission electron micrograph of a MgTiO₃ thin film produced by vapour-solid reaction between MgO vapour and (100) TiO₂ at a substrate temperature of 700 °C. (b) Selected area electron diffraction pattern from the interface region between the MgTiO₃ film (M) and the substrate (T). Viewing direction is $[1\bar{1}.0]$ MgTiO₃ \parallel $[001]$ TiO₂.

interface between the thin film and the substrate is flat. This is in contrast to the interface after reaction of BaO vapour with (100) TiO₂, where large and small (110) and ($1\bar{1}0$) TiO₂ facets of the (100) rutile surface were observed. Fig. 4.53(b) shows a selected area electron diffraction pattern taken from the substrate/film interface region of Fig. 4.53(a). The complete orientation relationship can be derived from Fig. 4.53(b) as:

$$(11.0) \text{ MgTiO}_3 \parallel (100) \text{ TiO}_2; [1\bar{1}.0] \text{ MgTiO}_3 \parallel [001] \text{ TiO}_2.$$

Fig. 4.54 gives a pole figure recorded at $2\theta = 32.9^\circ$ ($\{10.4\}/\{\bar{1}1.4\}$ MgTiO₃) for a sample prepared on (110) TiO₂ at a substrate temperature of 600 °C. In Fig. 4.53, the peaks at $\psi = 21^\circ$, 56.5° and 80° are due to a $(22.\underline{11})$ orientation of MgTiO₃ (cf. $\angle \text{MgTiO}_3 (22.\underline{11}); (10.4) = 20.8^\circ$, $\angle \text{MgTiO}_3 (22.\underline{11}); (\bar{1}1.4) = 56.4^\circ$ and $\angle \text{MgTiO}_3 (22.\underline{11}); (0\bar{1}.4) = 80^\circ$). The $(22.\underline{11})$ orientation of MgTiO₃ is rather close to the (11.6) orientation of MgTiO₃ ($\angle \text{MgTiO}_3 (22.\underline{11}); (11.6) = 2.5^\circ$,

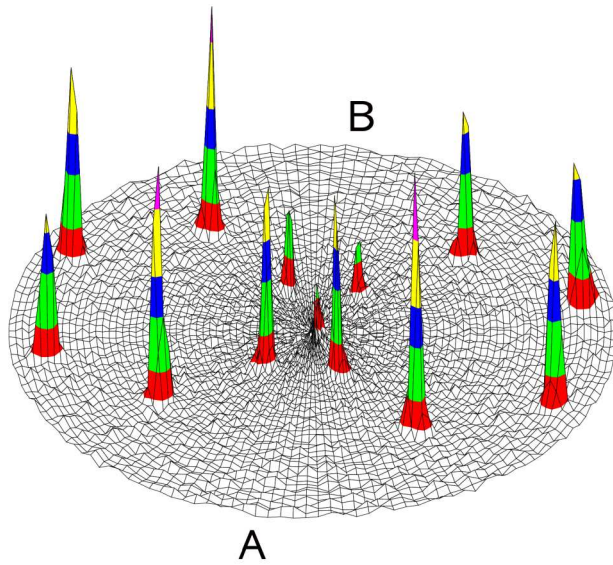


Fig. 4.54. X-ray pole figure measured at $2\theta = 32.9^\circ$ ($\{10.4\}/\{\bar{1}1.4\}$ MgTiO₃) of a sample prepared on (110) TiO₂ at a substrate temperature of 600 °C. Peaks are situated at $\psi = 21^\circ$, 56.5° and 80° . The peak in the middle of the figure at $\psi = 0^\circ$ marks the (110) TiO₂ substrate surface. The positions of labels A and B correspond to the ϕ values of the (001) and (00 $\bar{1}$) substrate planes, respectively.

however, $\angle \text{MgTiO}_3 (11.6); (10.4) = 19.8^\circ$, $\angle \text{MgTiO}_3 (11.6); (\bar{1}1.4) = 54.8^\circ$ and $\angle \text{MgTiO}_3 (11.6); (0\bar{1}.4) = 77.7^\circ$. The peak at the center ($\psi = 0^\circ$) in Fig. 4.54 is the (110) TiO₂ peak (not fully suppressed) that results from the non-optimum wavelength selectivity of the secondary monochromator. From a series of pole figures and a ϕ scan of the TiO₂ {200} reflections taken at $\psi = 45^\circ$, the in-plane orientation was found to be $[1\bar{1}.0] \text{ MgTiO}_3 \parallel [001] \text{ TiO}_2$. It should be noted that the (11.0) orientation of MgTiO₃ deviates from the (22.11) one by a tilt of 45° around the $[1\bar{1}.0] \text{ MgTiO}_3 \parallel [001] \text{ TiO}_2$ axis.

Table 4.5 summarises the orientation relationships at different substrate temperatures and NCSL misfit values observed for MgTiO₃ films on both (100) and (110) TiO₂ substrates.

Table 4.5. Orientation relationships and NCSL misfit values (F_1 (in-plane) and F_2 (in-plane rotated by 90°)) for MgTiO₃ (MTO) thin films grown on (100) and (110) TiO₂ (rutile) substrates (T).

T, °C	Parallel planes	Parallel direction	F_1 , %	F_2 , %
(100) TiO ₂ (rutile)				
600 – 800	(11.0) MTO \parallel (100) T	$[1\bar{1}.0] \text{ MTO} \parallel [001] \text{ T}$	$2(d(00.1)\text{MTO} - 3d(010)\text{T}) / (d(00.1)\text{MTO} + 3d(010)\text{T}) = +0.9$	$2(2d(1\bar{1}.0)\text{MTO} - 3d(001)\text{T}) / (2d(1\bar{1}.0)\text{MTO} + 3d(001)\text{T}) = -1.2$
(110) TiO ₂ (rutile)				
600 – 800	(22.11) MTO \parallel (110) T	$[1\bar{1}.0] \text{ MTO} \parallel [001] \text{ T}$	$2(7d(11.\bar{5})\text{MTO} - 4d(\bar{1}10)\text{T}) / (7d(11.\bar{5})\text{MTO} + 4d(\bar{1}10)\text{T}) = +1$	$2(2d(1\bar{1}.0)\text{MTO} - 3d(001)\text{T}) / (2d(1\bar{1}.0)\text{MTO} + 3d(001)\text{T}) = -1.2$

5 Discussion

5.1 The reaction systems $\text{BaCO}_3\text{-TiO}_2$ and BaO-TiO_2

5.1.1 Phase formation

A. Solid-solid reaction of BaCO_3 with TiO_2

a. Reaction at low temperature (575 °C-800 °C)

The solid-solid reactions in vacuum and in air showed different processes to occur during BaTiO_3 formation. The intermediate Ba_2TiO_4 phase was observed always after reaction in vacuum. However, Ba_2TiO_4 was not detected after a reaction in air. The formation of the observed phases was independent of the nature of TiO_2 (rutile or anatase).

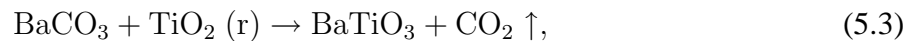
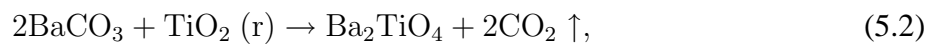
In the classical theory of nucleation, the rate of nucleation of a new nucleus is proportional to a term of the form $\exp(-\sigma^3/\Delta G_r^2 kT)$. Therefore, the nucleation of a new phase will occur rapid for compounds with high (more negative) values of ΔG_r (reaction Gibbs energy). The ΔG_r is usually defined as:

$$\Delta G_r = \sum G (\text{product}) - \sum G (\text{reactant}), \quad (5.1)$$

where G is the standard Gibbs energy of compound formation.

Thermodynamic analysis

The ΔG_r values were calculated for the following reactions:



where $\text{TiO}_2 (\text{r})$ is referred to the rutile modification of TiO_2 . The G values for $\text{TiO}_2 (\text{r})$, BaTiO_3 , Ba_2TiO_4 , BaCO_3 , and CO_2 were taken from I. Barin.¹²⁸ It should be noted that the G values for anatase TiO_2 are rather close to those of $\text{TiO}_2 (\text{r})$ and, thus, the calculations performed for reactions (5.2)-(5.5) with $\text{TiO}_2 (\text{r})$ can be extrapolated to the anatase TiO_2 . Below, the discussion will be always referred to $\text{TiO}_2 (\text{r})$.

ΔG_r values for reactions (5.2)-(5.5) are strongly dependent on the partial pressure of CO_2 (in air P_{CO_2} is 0.381 mbar, in vacuum P_{CO_2} during the experiments was lower than 1×10^{-5} mbar) which is described as:¹⁵⁷

$$G_{\text{CO}_2} = G + nRT \ln \frac{P_{\text{CO}_2}}{P_o}, \quad (5.6)$$

where G is the standard Gibbs energy of CO_2 gas at $P_{\text{CO}_2} = 1$ bar, n is the number of CO_2 molecules released, R is the gas constant, T is the temperature, P_{CO_2} is a partial pressure of CO_2 gas and P_o is the standard pressure of 1 bar. The results of the thermodynamic calculations for reactions (5.2)-(5.5) are shown in Figs. 5.1(a)-(d).

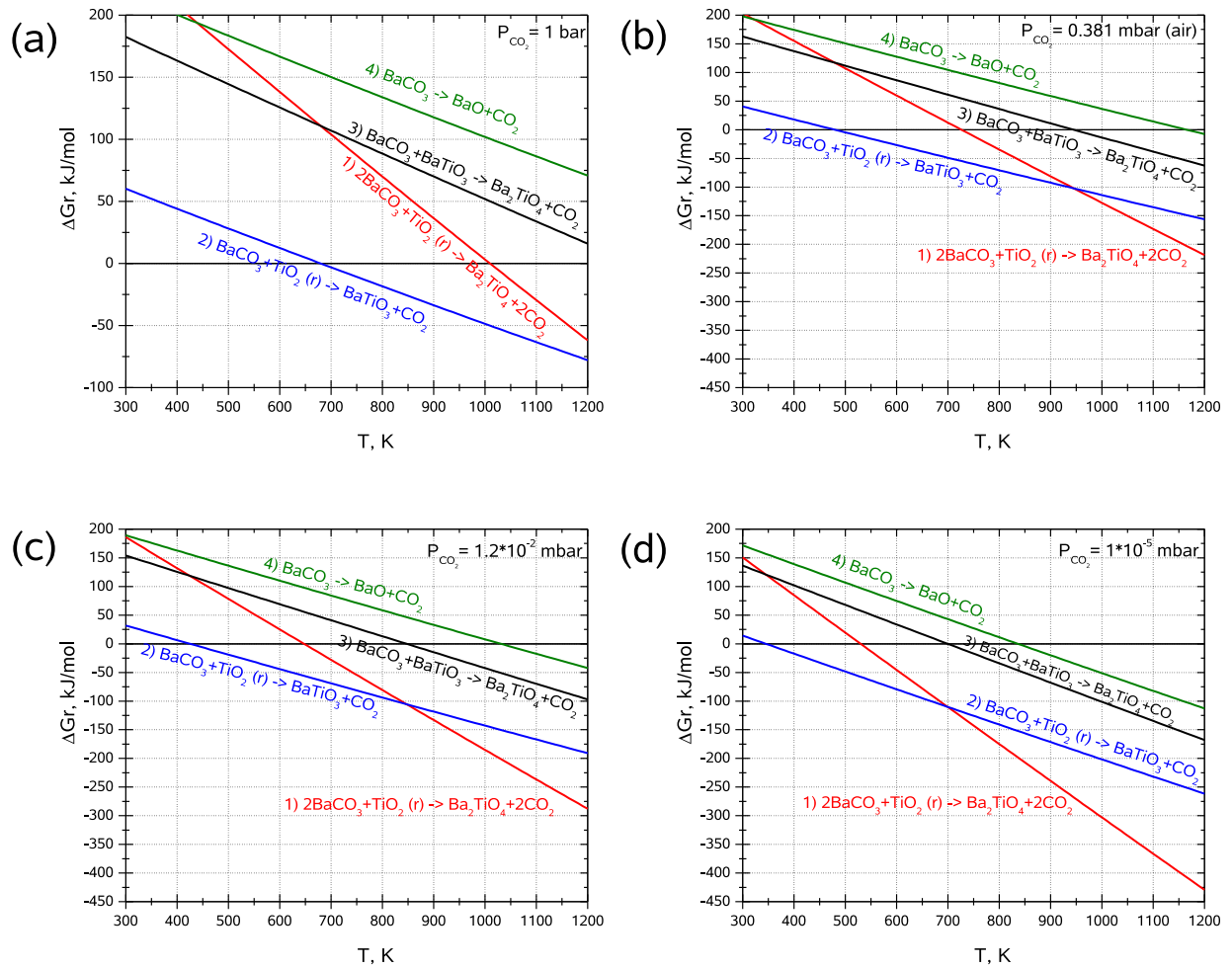


Fig. 5.1. Change in Gibbs free energy (ΔG_r) vs T during reactions under different partial pressures of CO_2 : (a) $P_{\text{CO}_2} = 1$ bar, (b) $P_{\text{CO}_2} = 0.381$ mbar, (c) $P_{\text{CO}_2} = 1.2 \times 10^{-2}$ mbar and (d) $P_{\text{CO}_2} = 1 \times 10^{-5}$ mbar. Calculated from values given in I. Barin.¹²⁸

As can be seen from Fig. 5.1, the preferred formation of either the Ba_2TiO_4 or BaTiO_3 phase by reaction between BaCO_3 and TiO_2 is a function of P_{CO_2} . The temperatures at which the formation of Ba_2TiO_4 is more likely compared to the formation of BaTiO_3 are lowered with a decreasing of P_{CO_2} .

A possible mechanism of BaTiO_3 formation in vacuum

During the solid-solid reactions in vacuum the intermediate Ba_2TiO_4 compound forms at the beginning of heating by direct reaction between barium carbonate grains and rutile single crystal. The time required for the formation of Ba_2TiO_4 observed in this work is low compared to the decomposition time of BaCO_3 reported by Judd *et al.*¹⁵⁸ or by L'vov.¹⁵⁹ Thus, a direct reaction of BaCO_3 with TiO_2 is expected. This is also supported by our thermodynamic calculations presented in Fig. 5.1(d). From these calculations, the decomposition of BaCO_3 into BaO and CO_2 (reaction (4) in Fig. 5.1(d)) or the formation of Ba_2TiO_4 by a reaction between BaTiO_3 and BaCO_3 in vacuum at 575 °C is relatively unfavourable compared to the formation of Ba_2TiO_4 or BaTiO_3 by a reaction between BaCO_3 and TiO_2 (reaction (1) or (2) in Fig. 5.1(d)) due to an only small decrease in the Gibbs energy. The ΔG_r values for the formation of Ba_2TiO_4 (-205.9 kJ/mol) and BaTiO_3 (-155.6 kJ/mol) at 575 °C are distinctly different, with a higher (more negative) value for Ba_2TiO_4 . Thus, the phase Ba_2TiO_4 will always nucleate and grow as the first phase in vacuum. This reaction will continue up to all BaCO_3 is consumed. The formation of BaTiO_3 by a direct reaction between BaCO_3 and TiO_2 in vacuum could be suppressed due to a Ba_2TiO_4 diffusion barrier. Thus, BaTiO_3 is formed by a reaction between Ba_2TiO_4 and TiO_2 .

Different formation mechanisms of Ba_2TiO_4 and BaTiO_3 can be assumed based on the differences in the orientations of both phases in dependence on the orientation of BaCO_3 grown on the rutile substrates. The orientation of Ba_2TiO_4 is strongly dependent on the orientation of BaCO_3 , while the orientation of BaTiO_3 grains is independent of the orientation of BaCO_3 . Thus, the formation of Ba_2TiO_4 might be dominated by diffusion of Ti ions into the BaCO_3 matrix. In contrast, BaTiO_3 grains might be formed by in-diffusion of Ba ions into the TiO_2 lattice.

From the above discussion, it is clearly seen that neither the first scheme nor the second scheme proposed by Beauger *et al.*⁶⁹ to describe the phase formation sequence during BaTiO_3 synthesis in vacuum is valid. The heating of nanocrystalline BaCO_3 and TiO_2 powders under pressure of 40 mbar at 740 °C performed by Buscaglia *et al.*¹⁸ showed a significant formation of Ba_2TiO_4 phase in the powder after the calcination. This results fits well to the description developed in this thesis.

A possible mechanism of BaTiO_3 formation in air

During the solid-solid reactions in air the BaTiO_3 compound forms at the beginning of heating (575 °C) by reaction between barium carbonate grains and rutile single crystal. Similar to the reaction in vacuum, a direct reaction between BaCO_3 and TiO_2 has occurred. The formation of BaTiO_3 in air by direct reaction between BaCO_3 and TiO_2 was also proposed by Beauger *et al.*⁶⁹ and by Buscaglia *et al.*¹⁸. Thermodynamic estimations showed that BaCO_3 is a stable phase in air until 880 °C due to positive values of the Gibbs free energy for the decomposition of BaCO_3 (Fig. 5.1(b)).

In air, the ΔG_r value for BaTiO_3 formation at 575 °C (-82.9 kJ/mol) is more negative than for Ba_2TiO_4 formation at 575 °C (-60.5 kJ/mol) while at temperatures higher than 657 °C the ΔG_r values for Ba_2TiO_4 formation become more negative than for BaTiO_3 formation. Consequently,

BaTiO_3 can be nucleated during heating at 575°C as the first phase in air. This description is supported by the results obtained by Buscaglia *et al.*¹⁴ Initial formation of BaTiO_3 was observed after heating of BaCO_3 (core) - TiO_2 (shell) powders at temperatures between 500°C and 550°C , in agreement with our observations and thermodynamic calculations (Fig. 5.1(b)). According to previous studies,^{12,18,69,70} the formation of a BaTiO_3 layer occurs at the interface $\text{BaCO}_3/\text{TiO}_2$ by in-diffusion of Ba ions into TiO_2 . In our case, the nucleation of BaTiO_3 might also have occurred by in-diffusion of Ba into TiO_2 .

The formation of the Ba_2TiO_4 compound by direct reaction of BaCO_3 with TiO_2 substrates in air at temperatures higher than 575°C may be suppressed due to a diffusion barrier induced by BaTiO_3 grains which are nucleated on heating at 575°C . However, the formation of Ba_2TiO_4 in air is considered possible by a reaction between BaCO_3 and beforehand formed BaTiO_3 at its expense at temperatures above 800°C . In this work, Ba_2TiO_4 was not observed to form by the reaction between BaCO_3 and BaTiO_3 after heating in air at temperatures between 600°C and 700°C (see Table 1). From a thermodynamical point of view, the formation of Ba_2TiO_4 by a reaction between BaCO_3 and BaTiO_3 up to temperatures 644°C is hindered due to positive values of ΔG_r . We used only a thin layer of BaCO_3 (50 nm) and at a temperature of 650°C this layer was reacted rapidly to BaTiO_3 .

b. Reaction at high temperature (1000°C)

Ti-rich barium titanates were observed after solid-solid reaction in vacuum and in air at high temperature. In the bulk phase diagram of the BaO-TiO_2 system, the compounds BaTi_4O_9 and $\text{Ba}_4\text{Ti}_{13}\text{O}_{30}$ exist between temperatures of about 900°C and 1400°C . The BaTi_4O_9 and $\text{Ba}_4\text{Ti}_{13}\text{O}_{30}$ compounds were observed in our experiments after reaction at 1000°C .

B. Vapour-solid reaction of BaO vapour with TiO_2

a. Reaction at low temperature (575°C - 800°C)

During the vapour-solid reaction, a reaction between BaO and TiO_2 has occurred. As can be seen from Fig. 5.2, the formation of BaTiO_3 by a reaction between BaO and TiO_2 at 575°C is relatively unfavourable compared to the formation of Ba_2TiO_4 by a reaction between BaO and TiO_2 due to an only small decrease in the values of ΔG_r with increasing temperature.

During the vapour-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_2TiO_4 during the vapour-solid reaction may have facilitated the initial formation of both phases at 600°C observed in this work.

b. Reaction at high temperature (900°C - 1000°C)

The $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ Ti-rich phase was found after vapour-solid reaction at high temperature. However, the BaO-TiO_2 phase diagram⁷⁸ permits the formation of several Ti-rich phases, some of which should form more easily than $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ at low temperatures. The occurrence and relative contribution of the different Ti-rich phases was investigated by Ritter *et al.*⁷⁸ who studied the

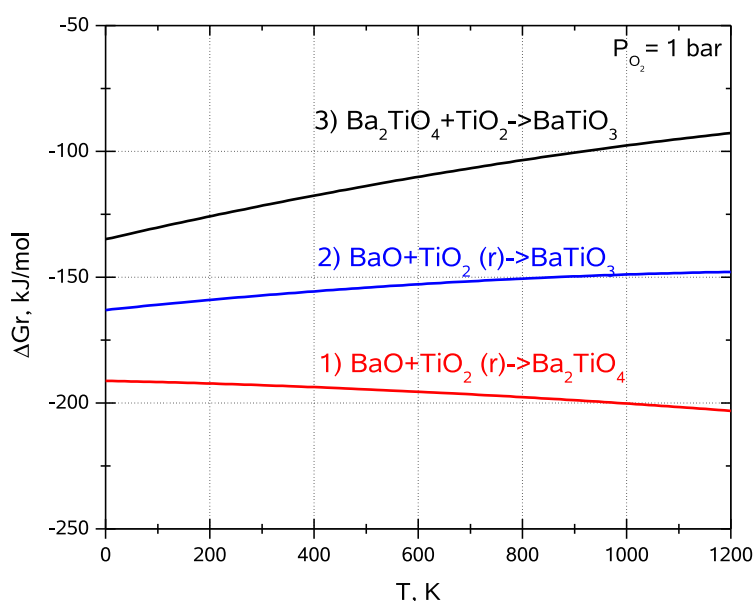


Fig. 5.2. Change in standard Gibbs free energy (ΔG_r) vs T during vapour-solid reaction. Calculated from values given in I. Barin.¹²⁸

crystallisation of amorphous Ba-Ti-O compounds prepared by a metalorganic chemical precursor method at temperatures between 600 °C and 1500 °C in air. They found that the $\text{Ba}_4\text{Ti}_{13}\text{O}_{30}$ phase is obtained most easily even at lower temperatures than the $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ phase. The latter crystallised only above ≈ 1100 °C and begins to decompose into BaTi_2O_5 and $\text{Ba}_4\text{Ti}_{13}\text{O}_{30}$ below ≈ 1100 °C. In the precursor prepared by Ritter *et al.*⁷⁸ the three elements Ba, Ti and O are already intermixed on an atomic scale and constraints for the nucleation of crystalline phases are quite different from a reaction between crystalline grains. Thus, the results obtained by Ritter *et al.*⁷⁸ do not fit directly to reactions between crystalline materials. In this work, the Ti-rich phases were formed always from crystalline phases. We have found that the BaTi_4O_9 and $\text{Ba}_4\text{Ti}_{13}\text{O}_{40}$ phases were formed after a solid-solid reaction in vacuum and in air (respectively) at 1000 °C for 30 min while $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ was found after a vapour-solid reaction at 900 °C-1000 °C. This difference might be explained by the geometrical nucleation conditions. The vapour-solid reaction allows a nucleation on the free surface of TiO_2 and obeys the thermodynamic model (EHF) proposed by Pretorius *et al.*^{21,22}. The $\text{BaTiO}_3\text{-TiO}_2$ phase diagram (Fig. 2.8 or Fig. A.1) shows the existence of the lowest eutectic at 1332 °C and an eutectic composition of 68.5 mole % TiO_2 . Two phases BaTiO_3 and $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ form an eutectic at this temperature. Thus, the $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ phase will be the first Ti-rich phase to grow at high temperature according to the EHF model. On the other hand, the reaction conditions during a solid-solid experiment are different. Ti diffuses out rapidly and nucleation of Ti-rich barium titanates occurred at BaCO_3 grain boundaries or at the surface of BaCO_3 . Unfortunately, the model of Pretorius *et al.*^{21,22} cannot explain the formation of BaTi_4O_9 or $\text{Ba}_4\text{Ti}_{13}\text{O}_{30}$ Ti-rich phases observed after solid-solid reaction at high temperature in vacuum and in air, respectively.

5.1.2 Orientation relationships

A. Orientation of Ba_2TiO_4 on TiO_2 (rutile)

The Ba_2TiO_4 phase grew well-oriented with respect to the (110) and (100) rutile substrates. However, the similarity between these two structures is not so obvious. The fundamental structural building elements of TiO_2 rutile are TiO_6 octahedra which lie along the $[001]$ TiO_2 direction while the basic building elements of Ba_2TiO_4 are TiO_4 tetrahedra which lie along the $[001]$ Ba_2TiO_4 direction. Thus, there are no common structural elements in the TiO_2 rutile and Ba_2TiO_4 structures. The projections of the (110) Ba_2TiO_4 /(110) TiO_2 and (100) Ba_2TiO_4 /(100) TiO_2 interfaces based on their structural elements in the $[001]$ $\text{Ba}_2\text{TiO}_4 \parallel [001]$ TiO_2 viewing direction are shown in Fig. 5.3. No features of the two lattices are recognisable that coincidence in this projection. Thus, the rutile structure cannot be taken over by the growing Ba_2TiO_4 .

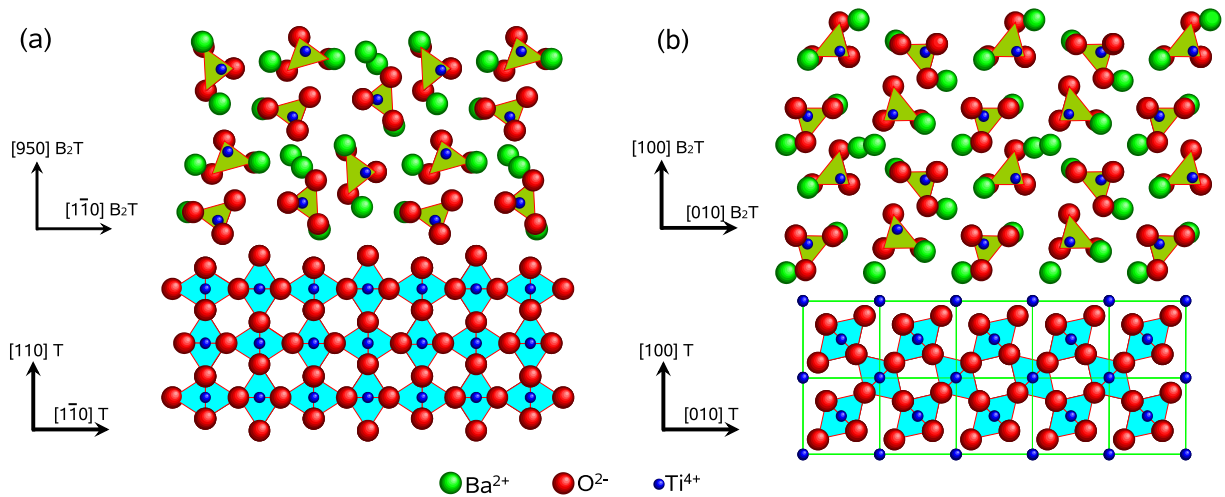


Fig. 5.3. Projections of the (110) Ba_2TiO_4 (B_2T)/(110) TiO_2 (T) and (100) Ba_2TiO_4 /(100) TiO_2 interfaces based on their structural elements. Viewing direction is $[001]$ $\text{Ba}_2\text{TiO}_4 \parallel [001]$ TiO_2 .

As was discussed above, Ba_2TiO_4 formed by direct reaction between BaCO_3 and TiO_2 . Thus, Ti ions seem to be diffusing into the BaCO_3 film. However, a transformation of BaCO_3 into Ba_2TiO_4 would require a strong shrinkage since the densities are different ($\rho_{\text{BaCO}_3} = 4.3 \text{ g/cm}^3$, $\rho_{\text{Ba}_2\text{TiO}_4} = 5.2 \text{ g/cm}^3$). The structural transformation could in principle occur through an intermediate phase like barium oxycarbonate¹⁶⁰ with a stoichiometry close to $\text{Ba}_2\text{Ti}_2\text{O}_5(\text{CO}_3)$. However, nothing is known about the crystal structure of the oxycarbonate phase. In addition, recently it was suggested that the phase commonly attributed in the literature to (Ba,Ti)-oxycarbonate is a barium oxycarbonate,¹⁶¹ containing no titanium.

B. Orientations of BaTiO_3 on TiO_2 (rutile)

It has been well established that the growth of films with preferred orientation on a substrate is closely related to surface free energy, film/substrate interface energy as well as misfit strain energy.^{162,163} However, during solid state reactions nucleation and diffusion take place so that the system cannot immediately reach thermodynamic equilibrium conditions. Thus, the kinetic

effect of nucleation of thin films with preferred orientation should also be taken into account. The two different solid state reaction geometries used in the present study may lead to two different nucleation conditions.

In the case of a solid-solid reaction, the nucleation of BaTiO_3 might have mainly occurred by diffusion of Ba ions into the TiO_2 lattice. On the other hand, in the case of a vapour-solid reaction, the orientations of the product phases are a complex function of the reaction conditions such as substrate temperature and deposition rate. Surface diffusion may be dominant in the vapour-solid reaction, and a direct nucleation of BaTiO_3 grains on the TiO_2 surface may occur.

One and the same orientation relation of BaTiO_3 on (100) TiO_2 was found after solid-state reactions in vacuum and in air. On the other hand, different orientation relations between the BaTiO_3 grains and the (100) TiO_2 (rutile) substrates were observed after vapour-solid reaction. The orientations of BaTiO_3 grains on the (110) TiO_2 after solid-solid and vapour-solid reaction have similar features but with different sharpness of the tilt distributions. After vapour-solid reaction the orientations of BaTiO_3 on (110) TiO_2 are sharper than after solid-solid reaction in vacuum. Below, we will discuss first the orientation relationships of BaTiO_3 after vapour-solid reaction.

a. Vapour-solid reaction

Growth at low temperatures (575 °C-800 °C)

The BaTiO_3 grains grew oriented with respect to the (110) and (100) TiO_2 substrates. Different orientations were found for BaTiO_3 depending on the substrate temperature and substrate orientation. However, the relation $[1\bar{1}0] \text{BaTiO}_3 \parallel [001] \text{TiO}_2$ is ever standing and independent of the orientation of the substrate surface and substrate temperature used. This means that the [001] TiO_2 axis is a common tilt axis for BaTiO_3 grown on (110) and (10) TiO_2 (rutile) surfaces. This is because the (110) and (100) planes of TiO_2 are connected by a tilt of 45° around the [001] TiO_2 axis. Thus, it is expected that the angles between crystal planes of BaTiO_3 grown on (110) and (100) TiO_2 substrates will also be close to 45° . The results of such a consideration are presented in Table 5.1. From Table 5.1, it can be seen that there are only small deviations from the value of 45° ($\pm 0.8^\circ$). Thus, the growth of some BaTiO_3 grains occurs with a three-dimensional orientation relationship with respect to the TiO_2 substrates, irrespective of the orientation of the substrate surface.

Table 5.1. Angles between crystal planes observed for BaTiO_3 thin films grown on (100) and (110) TiO_2 substrates. The major orientations are marked by bold font while minors are marked by italic font.

(hkl) BaTiO_3 (\mathbf{B}_1) \parallel (110) TiO_2	(hkl) BaTiO_3 (\mathbf{B}_2) \parallel (100) TiO_2	$\angle(\mathbf{B}_1); (\mathbf{B}_2), (^\circ)$
(119)	(111)	45.8
<i>(441)</i>	(112)	44.7

Below, we describe factors influencing the nucleation of BaTiO_3 on TiO_2 . First, the structural similarities between TiO_2 (rutile) and BaTiO_3 (perovskite) will be considered. The fundamental

structural building elements of both the TiO_2 and BaTiO_3 structures are TiO_6 octahedra linked in a three-dimensional network. The octahedra in the TiO_2 rutile structure are both corner- and edge-shared and lie along the $[001]$ TiO_2 direction while the octahedra in the perovskite structure are only corner-shared and lie along the $[1\bar{1}0]$ BaTiO_3 direction. The structural considerations given below are based on a surface of the TiO_2 (rutile) crystals obtained by simple cutting.

Fig. 5.4 shows a schematic projection of the $\text{BaTiO}_3/\text{TiO}_2$ interfaces constructed from TiO_6 octahedra for different orientations of BaTiO_3 grown on (110) TiO_2 surfaces looking along the $[1\bar{1}0]$ $\text{BaTiO}_3 \parallel [001]$ TiO_2 direction. The different types of linkage of TiO_6 octahedra in the two

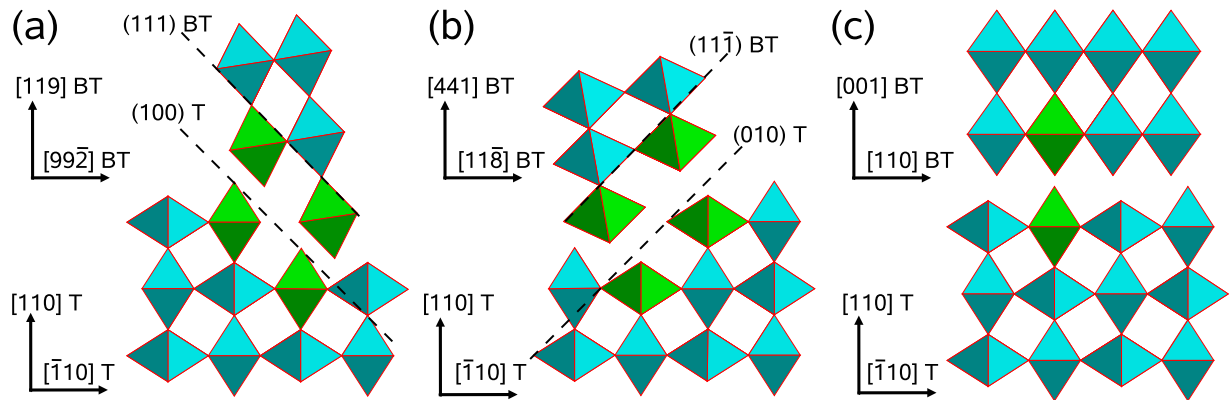


Fig. 5.4. Schematic representations of projections based on TiO_6 octahedra for (a) (119) BaTiO_3 (BT)/(110) TiO_2 (T), (b) (441) BaTiO_3 /(110) TiO_2 , (c) (001) BaTiO_3 /(110) TiO_2 . Viewing direction is $[1\bar{1}0]$ $\text{BaTiO}_3 \parallel [001]$ TiO_2 for all projections. The highlighted octahedra are octahedra required for the nucleation of BaTiO_3 (for more details see text). Both lattices are repeated perpendicular to the projection plane and thus the marked octahedra in 3D space make chains of octahedra parallel to the viewing direction.

structures are clearly seen in Fig. 5.4, making structural considerations easy. The presence of (119)- and (441)-oriented BaTiO_3 grains on (110) TiO_2 substrates can be explained by the fact that the surface of (110) TiO_2 substrates has terraces which are separated by monoatomic step edges running predominantly along $[001]$ TiO_2 and $[1\bar{1}0]$ TiO_2 directions.¹⁶⁴ The step edges lying along the $[001]$ TiO_2 direction may favour the nucleation of (119)-oriented BaTiO_3 grains as shown in Fig. 5.4(a) as well as nucleation of (441)-oriented BaTiO_3 grains as shown in Fig. 5.4(b). In both these cases, for the nucleation of (119)- and (441)-oriented BaTiO_3 grains only two chains of substrate octahedra will be required (the octahedra required for the nucleation are highlighted and small octahedra misorientations are ignored). The nucleation would occur more easily if $\{100\}$ or $\{010\}$ TiO_2 facets would be present on the rutile surface. In this case, more than two chains of substrate octahedra can be taken for the nucleation of BaTiO_3 . Such facets were observed after vapour-solid reaction at 800 °C by HRTEM investigations shown in Fig. 4.23. On these facets, (119)- and (441)-oriented BaTiO_3 grains are found, confirming our suggestions. As was already pointed out above, (119)- and (441)-orientations of BaTiO_3 have one of the $\{111\}$ BaTiO_3 planes almost parallel to one of the $\{100\}$ TiO_2 planes in the viewing direction $[1\bar{1}0]$ $\text{BaTiO}_3 \parallel [001]$ TiO_2 . The highlighted octahedra of BaTiO_3 in Fig. 5.4(a) show a (111) plane of BaTiO_3 which is almost parallel to the (100) plane of TiO_2 whereas the highlighted octahedra of BaTiO_3 in Fig. 5.4(b) show a $(11\bar{1})$ plane of BaTiO_3 which is almost parallel to the (010) plane of TiO_2 . Thus,

the growth of (119)- and (441)-orientations of BaTiO_3 is obviously determined by the condition that one of its close-packed $\{111\}$ planes of BaTiO_3 is parallel to one of the rather close-packed $\{100\}$ planes of the TiO_2 substrate. The (111) orientation of BaTiO_3 was observed on (100) TiO_2 surfaces, details will be discussed below. In addition, the octahedra of a [001] monoatomic step edge of the (110) TiO_2 surface are octahedra belonging to $\{100\}$ planes of TiO_2 . Consequently, the nucleation of (119)- and (441)-orientations of BaTiO_3 on the [001] steps of the (110) TiO_2 surface is plausible. However, the (001)-orientation of BaTiO_3 cannot be explained by the reasons shown above. This case is illustrated in Fig. 5.4(c). Only one octahedron of BaTiO_3 matches to the substrate octahedra. The nucleation of (001)-oriented BaTiO_3 grains will be possible only if one chain of octahedra of TiO_2 is taken over by the growing BaTiO_3 (the octahedra required for the nucleation are highlighted). The octahedra of BaTiO_3 belonging to the (111) plane of BaTiO_3 deviate from the octahedra of $\{100\}$ planes of TiO_2 by 9.7° ($\angle \text{BaTiO}_3 (001); (111) = 54.7^\circ$ while $\angle \text{TiO}_2 (110); (100) = 45^\circ$). It is worth to mention that the nucleation of BaTiO_3 on (110) TiO_2 substrates will occur as line only in one $[1\bar{1}0] \text{BaTiO}_3 \parallel [001] \text{TiO}_2$ direction. This is because TiO_6 octahedra in TiO_2 and BaTiO_3 are connected with different topology. In BaTiO_3 , the columns of edge-shared TiO_6 octahedra are missing.

Fig. 5.5 shows a schematic projection of the $\text{BaTiO}_3/\text{TiO}_2$ interfaces constructed from TiO_6 octahedra for different orientations of BaTiO_3 grown on (100) TiO_2 surfaces, looking along the $[1\bar{1}0] \text{BaTiO}_3 \parallel [001] \text{TiO}_2$ direction. Similarities in the alignment of the TiO_6 octahedra can be

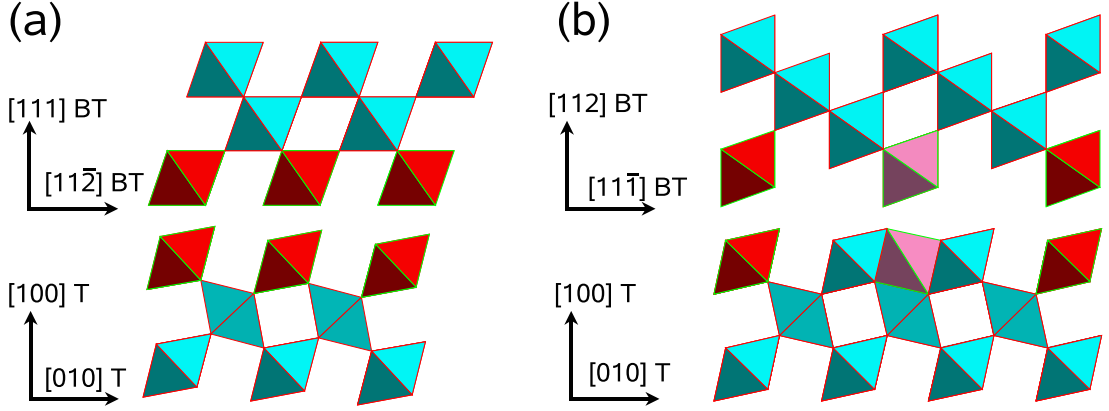


Fig. 5.5. Schematic representations of projections based on TiO_6 octahedra for (a) (111) BaTiO_3 (BT)/(100) TiO_2 (T) and (b) (112) BaTiO_3 (BT)/(100) TiO_2 (T). Viewing direction is $[1\bar{1}0] \text{BaTiO}_3 \parallel [001] \text{TiO}_2$ for all projections. The highlighted octahedra are octahedra required for the nucleation of BaTiO_3 (for more details see text).

seen in Fig. 5.5(a) for the (111) BaTiO_3 / (100) TiO_2 interface. Ignoring small misorientations of the octahedra, the (111)-oriented BaTiO_3 can be nucleated in such a way that the TiO_6 octahedra of rutile in the surface layer can be taken over by the growing BaTiO_3 (the octahedra required for the nucleation are highlighted). It should be noted that the situation illustrated in Fig. 5.5(a) is similar to that shown in Fig. 5.4(a). But compared to Fig. 5.5(a), the representation in Fig. 5.4(a) is rotated around the common $[001] \text{TiO}_2$ axis by 45° , showing the three-dimensional orientation relationship of BaTiO_3 with respect to the TiO_2 substrates in the case of (111)- and (119)-oriented

BaTiO_3 grains. The presence of (112)-oriented BaTiO_3 grains on (100) TiO_2 substrates can be explained by the fact that the surface of (100) TiO_2 reconstructs dramatically from (1×1) to (1×3) when heated in vacuum. However, the detailed surface geometry of the reconstruction is not well known. Two microfacet models are shown in Figs. A.13¹⁶⁵-A.14¹⁶⁶ (see appendix). In addition, adsorption of Ba may influence the surface geometry of (100) TiO_2 . Thus, one might speculate that the structural model of the (100) surface of TiO_2 shown in Fig. 5.5(b) could exist. This surface structure may favour the nucleation of (112)-oriented BaTiO_3 grains as shown in Fig. 5.5(b). It is worth to mention that the surface structure of the (100) TiO_2 presented in Fig. 5.5(b) can be simply obtained from Fig. A.14(b) (see appendix) by removal of the top chain of TiO_6 octahedra.

Thus, based on structural considerations the reasons for the nucleation of BaTiO_3 grains on the TiO_2 surfaces have been shown. On the other hand, the origin of all observed orientations of BaTiO_3 seems to be determined by the initial stage of the solid state reaction, where the surface morphology of the TiO_2 surfaces may influence the nucleation kinetics of the grains. As a model system, the (110) and (100) surfaces of TiO_2 (rutile) are very well investigated. The TiO_2 surfaces have been shown to exhibit various reconstructions upon annealing at elevated temperatures. The most commonly observed reconstruction of the (100) TiO_2 surface has a (1×3) structure along the [001] TiO_2 direction, which appears by annealing in ultrahigh vacuum ($<10^{-6}$ mbar) at temperatures above 750 °C,^{164,167} while the most frequently detected reconstruction on the (110) TiO_2 surface has a (1×2) superstructure with features along the [001] TiO_2 direction, which appear by annealing in ultrahigh vacuum ($\sim 10^{-7}$ mbar) at temperatures higher than 730 °C.^{164,168} These reconstructed surfaces are nonstoichiometric and oxygen-deficient. Our experiments were performed using an oxygen pressure of $(1\text{-}4) \times 10^{-4}$ mbar. Thus, we expect that the temperatures of oxygen losses of the surface are shifted to higher temperatures compared to heating in ultrahigh vacuum. The interaction of different metals and metal oxides with the single crystalline TiO_2 surfaces has also been investigated.¹⁶⁴ When a Ca overlayer formed by Ca metal vapour deposition (up to a monolayer (ML) coverage) or by precipitation from the bulk of (110) TiO_2 crystals is annealed at ~ 800 °C for several hours, well-ordered $c(6 \times 2)$ overlayers are formed.¹⁶⁹ At a calcium coverage of ≈ 1.2 ML, two coexisting structures (the ordered $c(6 \times 2)$ and a "disordered" structure) were observed. At higher calcium coverage, only a highly "disordered" structure was found and it completely covered the rutile substrate.¹⁶⁹ No experimental data on the influence of Sr or Ba on the reconstruction of rutile surfaces have been reported up to now. Since they are alkaline-earth metals, like Ca, the formation of various surface structures after adsorption of Ba or Sr on hot rutile substrates is expected. The nucleation kinetics and conditions on these changed TiO_2 surfaces may be different. As a consequence, a nucleation of differently oriented BaTiO_3 grains may occur with some of them being favoured during the initial stage of the nucleation.

Growth at high reaction temperature (900 °C)

After vapour-solid reaction of BaO with (100) TiO_2 substrates at 900 °C, BaTiO_3 of several different orientations was observed on top of the $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ phase. The investigation of the initial stage of the vapour-solid reaction of a 1 nm thick BaO layer with the (100) TiO_2 substrate at this

temperature showed that both BaTiO_3 and $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ phases nucleate during the initial stage of the reaction. However, the density of the Ti-rich grains was much larger than that of the (111)-oriented BaTiO_3 grains. Thus, with increasing reaction time (increasing amount of BaO), BaTiO_3 grains will nucleate on the as-formed $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ grains, which now play the role of a substrate for BaTiO_3 growth. Thus, the orientations of BaTiO_3 grains are mainly given by the orientation of the $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ grains. The topotaxial relationship of BaTiO_3 with respect to $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ results in the orientation $(111) \text{ BaTiO}_3 \parallel (001) \text{ Ba}_6\text{Ti}_{17}\text{O}_{40}$. The tilt of the (001) $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ plane can be calculated from the tilt of the (100) $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ plane using the angle $\beta = 98.7^\circ$ between them. The result of this calculation is a tilt of the (001) $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ plane around the $[010] \text{ Ba}_6\text{Ti}_{17}\text{O}_{40} \parallel [001] \text{ TiO}_2$ axis by 8.7° to 17.7° . Corresponding tilts of BaTiO_3 grains were indeed observed, confirming the above discussion.

b. Solid-solid reaction

One orientation of BaTiO_3 on (100) TiO_2 was observed after solid-state reactions in vacuum and in air. The BaTiO_3 grew with (111) orientation. It can be explained by the crystallographic reasons shown above.

The orientations of BaTiO_3 grains on the (110) TiO_2 surface after solid-solid reaction in vacuum were found to be similar to those observed after vapour-solid reaction. However, the tilt distributions of BaTiO_3 grains in the thin films after the reaction in vacuum were not sharp. The number of (001)-oriented BaTiO_3 grains in the thin films produced by a solid-solid reaction were higher than after a vapour-solid reaction. After vapour-solid reaction, (119)- and (441)-oriented BaTiO_3 grains were observed on $\{100\}$ facets of TiO_2 which favour the nucleation of these two orientations. On the other hand, the frequently observed facets on the (110) TiO_2 surface after solid-solid reaction are nearly $\{1\bar{1}0\}$ TiO_2 facets (see Fig. A.15 in the appendix). Thus, the nucleation of BaTiO_3 mainly occurred on $\{110\}$ surfaces of TiO_2 which favour the nucleation of (001)-oriented BaTiO_3 grains. The structural considerations for the nucleation of (001)-oriented BaTiO_3 grains as well as for the nucleation of (119)- and (441)-oriented BaTiO_3 grains on (110) TiO_2 were shown above (see Fig. 5.4). All observed orientation relationships of BaTiO_3 on TiO_2 (rutile) after both types of the solid state reactions can be explained in terms of a NCSL model (see Table 4.1).

C. Orientations of BaTiO_3 on TiO_2 (anatase)

The observed orientation relationships between BaTiO_3 and epitaxial TiO_2 (anatase) thin films can be explained in terms of their crystal structures. As was mentioned above, BaTiO_3 has a similar structure as SrTiO_3 . Epitaxial TiO_2 (anatase) thin films were obtained on SrTiO_3 substrates. Epitaxial formation of TiO_2 (anatase) on SrTiO_3 is a result of a similar orientation of TiO_6 octahedra at the $\text{TiO}_2/\text{SrTiO}_3$ interface (see Subsection 4.2.1c of Section 4.2). The same crystallographic reason is valid for BaTiO_3 produced by solid state reactions on epitaxial TiO_2 (anatase) thin films since BaTiO_3 has similar epitaxial orientation relationships with respect to TiO_2 (anatase). The epitaxial orientation relationship between BaTiO_3 and (001) TiO_2 (anatase) thin films observed in this work is in agreement with the epitaxial relation obtained for BaTiO_3 grown in alkaline

aqueous solutions using TiO_2 (anatase) powder¹⁷⁰ or for BaTiO_3 produced by solid-solid reaction between TiO_2 (anatase) single crystals and a barium salt.¹⁷¹ The observed orientation relationships of BaTiO_3 on TiO_2 (anatase) can be explained in terms of a NCSL model (see Table 4.2).

D. Orientations of Ti-rich phases on TiO_2 (rutile)

a. Solid-solid reaction

Ti-rich phases were grown in both types of solid state reactions at high reaction temperatures, but with quite different textures. Oriented $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ grains were formed after vapour-solid reaction at substrate temperatures between 900 °C and 1000 °C. Contrary to the vapour-solid reaction, polycrystalline BaTi_4O_9 and $\text{Ba}_4\text{Ti}_{13}\text{O}_{30}$ (with fiber texture) phases were found after the solid-solid reaction at 1000 °C in vacuum and in air, respectively. These differences are caused by the reaction conditions changing with reaction geometry. During the vapour-solid reaction, the BaO vapour directly reacts with the TiO_2 rutile surfaces. In this case, the orientations of the reaction products are determined only by the orientation of the substrate. Thus, the nucleation directly on the rutile single crystal surface results in well-oriented Ti-rich grains (details are shown below). The initial reaction during solid-solid experiments seems to be dominated by Ti out-diffusion. At low reaction temperatures, Ba_2TiO_4 with an orientation influenced by the orientation of BaCO_3 was observed. If this behaviour is extrapolated to high temperatures, we can expect a more rapid Ti out-diffusion that results in a high Ti concentration at BaCO_3 grain boundaries and on top of the BaCO_3 layer. The nucleation of Ti-rich phases now occurs without a direct interface to the substrate surface and thus results in a random orientation of the Ti-rich phases.

b. Vapour-solid reaction

$\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ grows well-oriented with respect to the (110) TiO_2 substrate as well as to the (100) TiO_2 substrate. This feature can be explained on the basis of the crystallographic similarity of the two lattices.

A schematic projection of the $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}/\text{TiO}_2$ interface for the observed orientation of the Ti-rich phase on a (110) TiO_2 substrate is shown in Fig. 5.6 looking along the $[010] \text{Ba}_6\text{Ti}_{17}\text{O}_{40} \parallel [001] \text{TiO}_2$ direction. Similarities can be found in the arrangements of oxygen sublattices of the $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ and TiO_2 (rutile) structure. However, small deviations of the oxygen positions in $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ (Fig. 5.6(a)) from those in TiO_2 (Fig. 5.6(b)) are seen. This is due to different types of linkage of the TiO_6 octahedra in the two structures. In addition, the (001) and $(\bar{1}02)$ planes of $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ are joined by a tilt of 47.88° around the $[010] \text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ axis, whereas the (010) and (110) planes of TiO_2 are aligned by a tilt of 45° around the $[001] \text{TiO}_2$ axis. Thus, from these considerations, it is very probable that the growth of $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ on TiO_2 rutile substrates is topotaxial. The small deviations from perfect orientation are a result of the monoclinic distortion of the $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ lattice.

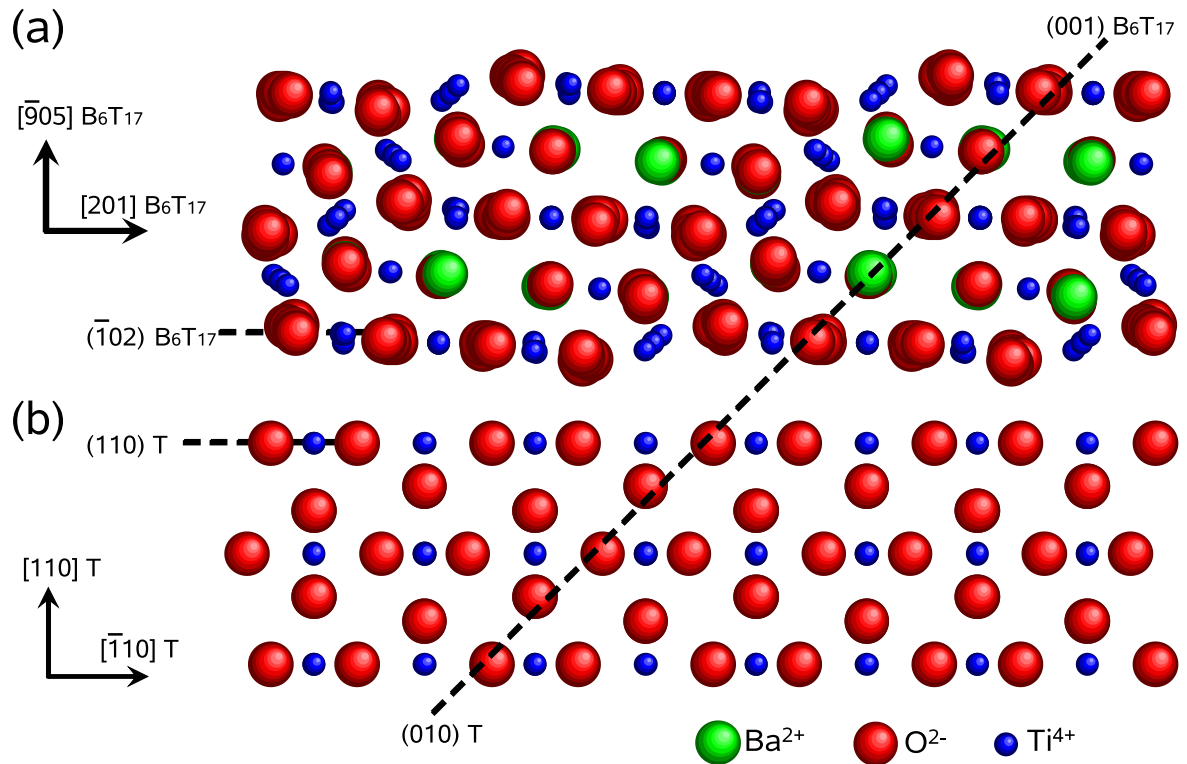


Fig. 5.6. Schematic cross-section representation of the interface between the $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ phase (B_6T_{17}) and TiO_2 (rutile) substrate (T) looking along the $[010]$ $\text{B}_6\text{T}_{17} \parallel [001]$ T direction. The orientation relationship is (001) $\text{B}_6\text{T}_{17} \parallel (010)$ T and $[010]$ $\text{B}_6\text{T}_{17} \parallel [001]$ T. The dashed line indicates (001) $\text{B}_6\text{T}_{17} \parallel (010)$ T.

5.1.3 Reaction of BaO vapour with TiO_2 surfaces at 900°C

A. Reaction mechanism

Based on TEM investigations and structural considerations, the following reaction mechanism between BaO vapour and TiO_2 surfaces at 900°C can be considered. The vapour-solid reaction starts with the surface diffusion of Ba-O species arriving on the hot TiO_2 surface. The reaction leads to the nucleation and formation of small $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ grains. It is reasonable to assume that steps on the TiO_2 surface (see the dashes in Fig. 4.14) are preferred sites for the nucleation of $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$. The height of one normal step of the (110) TiO_2 surface is 0.32 nm while the height of one step of the $(\bar{1}02)$ $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ surface (see Fig. 5.6(a)) is 0.17 nm . The nucleation could occur more easily if steps with lower heights would be present on the rutile surface. The presence of surface defects like crystallographic shear planes (CSPs) or added rows of Ti_2O_3 forming on the (110) TiO_2 surface after high-temperature annealing in ultrahigh-vacuum was reported by Bennet *et al.*¹⁷² The height of one CSP is $\approx 0.16\text{ nm}$ which fits well to the height of one step of the $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ surface. Thus, the nucleation of $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ phase might have been favoured due to surface defects created on the (110) rutile substrates by heating in our high-vacuum chamber. The Ti-rich phase nucleates by Ba in-diffusion while the film growth proceeds mainly by surface diffusion. With increasing amount of BaO, the Ti-rich islands coalesce and form a nearly continuous thin film. This film induces a diffusion barrier for Ti out-diffusion. Thus, the concentration

of Ti ions on top of the $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ layer decreases. As a consequence, BaTiO_3 grains nucleate on top of the film consisting of Ti-rich grains. Due to a certain similarity between the BaTiO_3 and $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ lattices, a definite crystallographic orientation of BaTiO_3 results. As is well-known, the (001) planes of $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ can be compatibly attached to the (111) planes of BaTiO_3 , forming a topotactic boundary.⁹⁸ Here, we observed a similar topotaxial orientation relationship as the one published in Ref.⁹⁸, confirming the above discussion. The topotaxial reaction involves the transformation of (111) planes of BaTiO_3 into (001) planes of the Ti-rich phase by removal of BaO and insertion of TiO_2 .

B. Void formation

Large pores have been observed after vapour-solid reaction of a BaO quantity equivalent to a nominal film thickness of 50 nm at the TiO_2 (rutile)/Ti-rich or TiO_2 (anatase)/Ti-rich interface at 900 °C in this work, as well as after vapour-solid reaction of a BaO quantity equivalent to a nominal film thickness of 100 nm at the TiO_2 (rutile)/Ti-rich interface at 900 °C in Ref.¹⁷³. The formation of voids is usually attributed to the Kirkendall effect.^{174,175} The latter was originally observed in bulk diffusion couples of Cu and CuZn (α -brass or Cu-30wt% Zn). Mo-wire markers which were placed at the original Cu/CuZn interface had moved into the α -brass, showing that the Zn flux was greater than that of Cu. Thus, different diffusion rates of the atoms moving in and out of the interface between two reacting materials caused a net flux of vacancies which may subsequently lead to the formation of voids at the interface of two materials. This phenomenon is completely general in metallic systems with a simple system of lattice sites. Recently, the Kirkendall effect was applied to explain the formation of hollow spherical nanocrystals¹⁷⁶ and monocrystalline ZnAl_2O_4 spinel nanotubes.¹⁷⁷ Thermodynamic and kinetic aspects of this effect which might contribute to the design, fabrication route, and materials choice of hollow nanostructures were given by Tu and Gösele.¹⁷⁸

Below, we propose a model describing the formation of void at the interface with the TiO_2 (rutile) surfaces. After the initial stage of a vapour-solid reaction with a BaO quantity equivalent to a nominal film thickness of 1 nm the formation of $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ islands was observed (Fig. 5.7(a), see also Figs. 4.14-4.15). No voids are formed at the TiO_2 (rutile)/Ti-rich interface at this stage of the reaction. The Ti-rich phase nucleates by Ba in-diffusion while the film growth proceeds mainly by surface diffusion. Thus, with increasing reaction time (amount of BaO), cavities are formed between neighbouring islands (Fig. 5.7(b), see also Fig. 4.16). Since surface diffusion of TiO_2 species along the TiO_2 surface is relatively easy and fast, the cavities are produced by out-diffusion of the TiO_2 . Further reaction leads to the coalescence of the Ti-rich islands over the cavities (Fig. 5.7(c)). Consequently, voids are formed. We conclude that in our case the pores are produced mainly by surface diffusion of TiO_2 .

When the reaction is continued, Ti is supplied to the surface by grain boundary diffusion. The concentration of Ti on the surface decreases and consequently BaTiO_3 is formed (see Fig. 4.9).

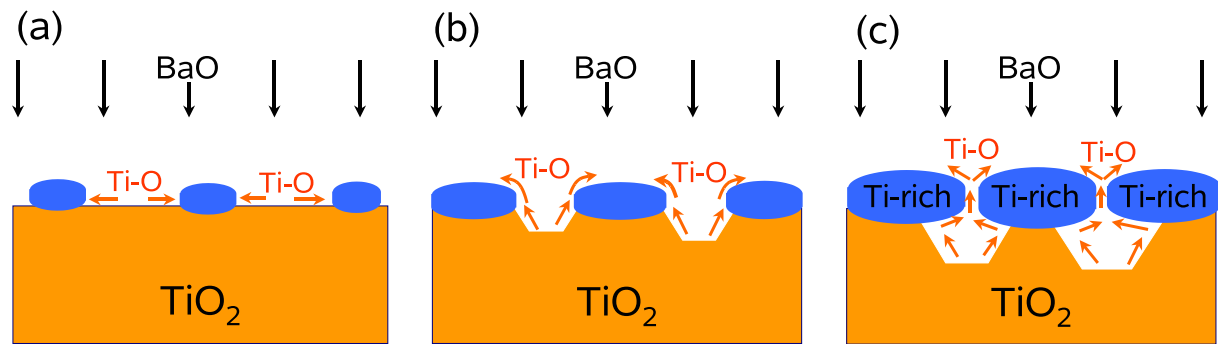


Fig. 5.7. Schematic diagram of void formation.

5.2 The reaction systems SrO-TiO_2 , CaO-TiO_2 and MgO-TiO_2

5.2.1 Orientation of SrTiO_3 on TiO_2 (rutile)

The orientations of SrTiO_3 after vapour-solid reaction on the TiO_2 substrates were found to be similar to those observed for BaTiO_3 . By comparing the orientation relationships found for BaTiO_3 with those observed for SrTiO_3 , it can be concluded that the $[001]$ TiO_2 axis is a unique tilt axis for BaTiO_3 and SrTiO_3 grains grown on (100) and (110) TiO_2 surfaces. The nucleation of SrTiO_3 on TiO_2 can be explained by the same scenario as was done above (Figs. 5.4-5.5) for BaTiO_3 on TiO_2 (rutile). This is because the crystal structures of BaTiO_3 and SrTiO_3 are very similar. All observed orientation relationships of SrTiO_3 on TiO_2 can be explained in terms of a NCSL model (see Table 4.3).

5.2.2 Orientation of CaTiO_3 on TiO_2 (rutile)

One orientation of CaTiO_3 on (110) TiO_2 was found after the reaction of CaO (vapour) with TiO_2 . This is in contrast to the results obtained in the previous two systems BaO (vapour)- TiO_2 and SrO (vapour)- TiO_2 where more than one orientation relationship was identified for BaTiO_3 as well as for SrTiO_3 on (110) TiO_2 . In addition, an unreacted CaO phase was observed in the thin films produced by vapour-solid reaction on (110) TiO_2 substrates at temperatures between 600°C and 900°C . This is a somewhat surprising result. It seems that the reactivity of CaO with TiO_2 is different from the reactivity of SrO or BaO with the rutile substrates.

Calcium is a common impurity of commercial TiO_2 single crystals. The segregation of Ca impurities from the bulk to the surface of rutile TiO_2 (110) has been previously studied by several groups.^{169,179,180} Zhang *et al.*¹⁷⁹ have proposed the formation of a (110) -oriented CaTiO_3 -like compound on the (110) TiO_2 surface after annealing of the fresh (110) surface of TiO_2 (rutile) at 700°C for several hours. In our work, we observed the growth of (110) -oriented CaTiO_3 on the (110) TiO_2 surface. CaTiO_3 was formed as the first phase on (110) TiO_2 substrates as was shown by HRTEM for sample prepared by vapour-solid reaction of a CaO quantity equivalent to a nominal film thickness of ≈ 3 nm. The observed orientation relationship of CaTiO_3 on the (110) TiO_2

can be explained in terms of a NCSL model (see Table 4.4).

The formation of an unreacted CaO phase can be explained as follows. Initial stage of the reaction between CaO vapour and (110) TiO_2 leads to the formation of a nearly continuous CaTiO_3 thin film. This film induces a diffusion barrier for Ti out-diffusion and Ca in-diffusion. As a consequence, an un-reacted CaO film is formed on top of the perovskite layer.

5.2.3 Orientation of MgTiO_3 on TiO_2 (rutile)

The vapour-solid reaction between MgO vapour and TiO_2 (rutile) substrates resulted in the nucleation and growth of well-oriented MgTiO_3 thin films. This feature can be explained on the basis of crystallographic similarity of the two lattices.

The ilmenite MgTiO_3 structure is based on a hexagonal close packing of oxygen ions with cations occupying two thirds of the available octahedral sites. This structure results from equal amounts of di- (Mg) and tetravalent (Ti) cations, which are ordered at the octahedral sites and alternate along the c axis of the unit cell. A pair of MgO_6 and TiO_6 octahedra share a (001) face. Each octahedron in the ilmenite structure shares an edge with the same type of octahedron and three edges with the other octahedra. On the other hand, the rutile TiO_2 structure is based on a hexagonal close packing of oxygen ions with Ti cations in octahedral interstitials. Each Ti cation has six octahedral neighbours and each octahedron is connected to two neighbouring octahedra via an edge and 8 octahedra via a corner.

A projection of the MgTiO_3 - TiO_2 interface based on the observed orientations of MgTiO_3 on (100) and (110) rutile substrates is shown in Fig. 5.8. Similarities can be found in the arrangements of oxygen sublattices of the MgTiO_3 and TiO_2 (rutile) structures. However, small deviations of the oxygen positions in TiO_2 from those in MgTiO_3 (Figs. 5.8(a)-(c)) are seen. This is due to different types of linkage of TiO_6 octahedra in the two structures. In addition, the (11.0) and (22.11) planes of MgTiO_3 are joined by a tilt of 45° around the $[\bar{1}1.0]$ MgTiO_3 axis, whereas the (100) and (110) planes of TiO_2 are aligned by a tilt also of 45° around the $[001]$ TiO_2 axis. Moreover, the TiO_2 rutile surfaces show a good lattice match with the MgTiO_3 (see Table 4.5). Thus, from these considerations, it can be concluded that the growth of MgTiO_3 on TiO_2 rutile substrates is topotaxial. The formation of MgTiO_3 from MgO vapour and TiO_2 crystals seems to have occurred via an in-diffusion of Mg cations into the TiO_2 lattice, so that the oxygen sublattice of TiO_2 (rutile) can be taken over by the growing MgTiO_3 (geikielite) phase.

Our results can be compared with earlier experiments in the system MgO-TiO_2 ^{11,118-120,181} where a MgO substrate was exposed to TiO_2 vapour. The result was a topotaxial formation of a cubic Mg_2TiO_4 spinel on the cubic rock-salt substrate. In this case the oxygen sublattice is also kept. Thus, a vapour-solid reaction in the system MgO-TiO_2 leads to two different phases, depending on the crystallographic structure of the substrate.

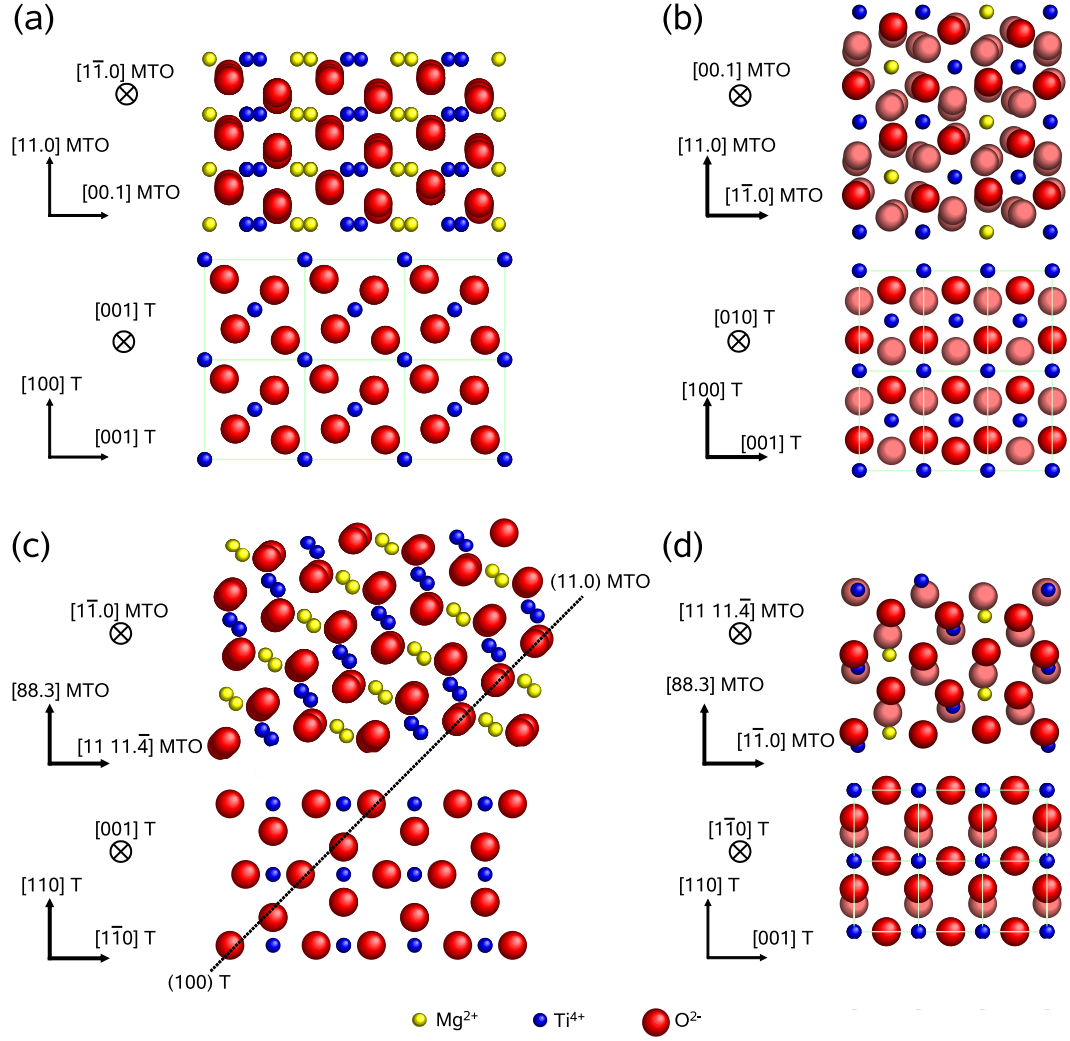


Fig. 5.8. Schematic cross-section representations of the interface between the MgTiO_3 phase (MTO) and TiO_2 (rutile) substrates (T). Orientation relationships are: (a)-(b) $(11.0) \text{MgTiO}_3 \parallel (100) \text{TiO}_2$ and (c)-(d) $(22.11) \text{MgTiO}_3 \parallel (110) \text{TiO}_2$. Viewing directions are: (a) and (c) $[11.0] \text{MgTiO}_3 \parallel [001] \text{TiO}_2$, (b) $[00.1] \text{MgTiO}_3 \parallel [010] \text{TiO}_2$ and (d) $[11 \ 11.4] \text{MgTiO}_3 \parallel [110] \text{TiO}_2$. The dashed line in (c) indicates $(11.0) \text{MgTiO}_3 \parallel (100) \text{TiO}_2$. Different colours for oxygen ions used in (b) and (d) show different height levels of the ions in the projections.

5.3 Factors influencing the first-phase selection in complex oxide thin film systems

The prediction of the first phase forming during a thin-film solid state reaction is of considerable interest since many years. Correspondingly, a number of models have been put forward, including kinetic, thermodynamic, and nucleation-controlled models. But these models mainly considered metal (thin film)-Si (substrate) systems. In the nucleation-controlled model,²³ it was shown that nucleation effects are dominant if ΔG_r is small. The estimated limit of nucleation dominance $\Delta g = \Delta G_r/V$ (V is the molar volume of the compound) is -400 J/cm^3 . Factors influencing the first-phase selection in oxide thin film systems have not been sufficiently considered so far. In this section, we analyse factors influencing the first-phase selection in complex oxides like BaCO_3 -

TiO₂, SrO-TiO₂, CaO-TiO₂ and MgO-TiO₂ on the base of experimental results obtained in this work.

In the system BaCO₃-TiO₂, the Δg values for the Ba₂TiO₄ and BaTiO₃ formation in air (see Fig. 5.9(a)) and in vacuum (see Fig. 5.9(b)) are beyond the limit. As was discussed above, the nucleation of the first phase in the system BaCO₃-TiO₂ is determined by ΔG_r values.

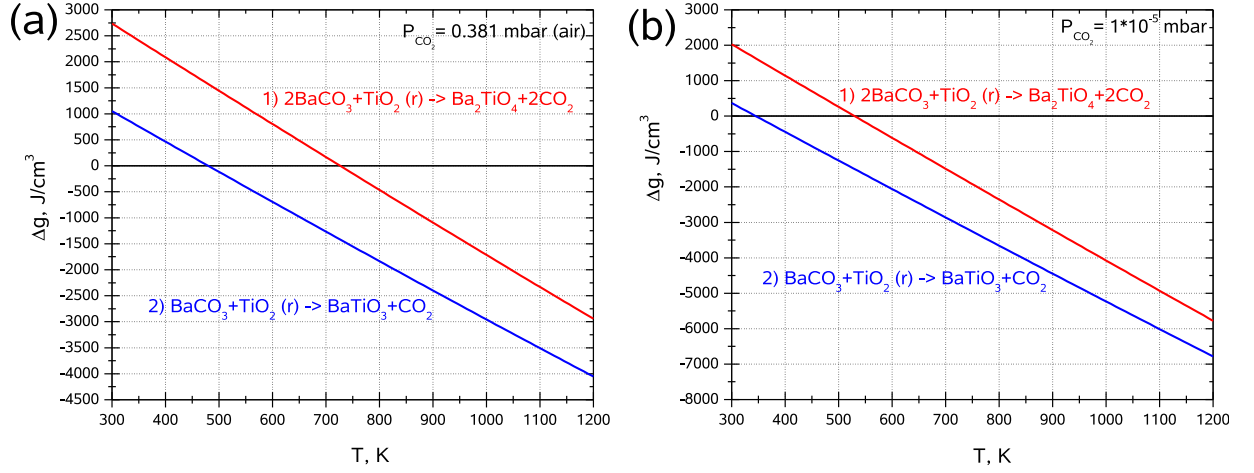
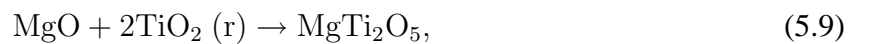
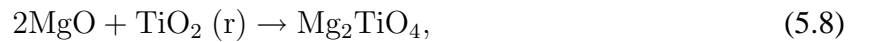


Fig. 5.9. a) Δg vs T for the formation of Ba₂TiO₄ and BaTiO₃ in air and (b) Δg vs T for the formation of Ba₂TiO₄ and BaTiO₃ in vacuum. Calculated from values given in I. Barin.¹²⁸

In the systems SrO-TiO₂ and CaO-TiO₂, the Δg values for the formation of SrTiO₃ (ranging from -3805 J/cm³ to -3875 J/cm³ at temperatures between 300 K and 1200 K) and CaTiO₃ (ranging from -2491 J/cm³ to -2690 J/cm³ at temperatures between 300 K and 1200 K) are beyond the limit. The formation of SrTiO₃ or CaTiO₃ as the first compound can be explained according to the EHF model.^{21,22} The SrO-TiO₂ phase diagram (Fig. 2.10 or Fig. A.3) and the CaO-TiO₂ phase diagram (Fig. 2.11 or Fig. A.4) show the existence of the lowest eutectic at 1440 °C and at 1450 °C, respectively. The two phases SrTiO₃ and TiO₂ form an eutectic at 1440 °C (Fig. 2.10 or Fig. A.3) while CaTiO₃ and TiO₂ form an eutectic at 1450 °C (Fig. 2.11 or Fig. A.4). Thus, the SrTiO₃ and CaTiO₃ phase will be the first phase to grow in the systems SrO-TiO₂ and CaO-TiO₂, respectively.

For the system MgO-TiO₂, ΔG_r was calculated for the following reactions:



where TiO₂ (r) is referred to the rutile modification of TiO₂. The G values for TiO₂ (r), MgTiO₃, Mg₂TiO₄ and MgTi₂O₅ were taken from I. Barin¹²⁸. The results of the thermodynamic calculations for reactions (5.7)-(5.9) are given in Fig. 5.10(a). As can be seen from Fig. 5.10(a), the ΔG_r values for compounds in the system MgO-TiO₂ are small and close to each other. The formation of MgTiO₃ from simple oxides is less likely at temperatures higher than 530 °C. In this work, MgTiO₃ was observed at temperatures between 600 °C and 800 °C. However, the formation of Mg₂TiO₄

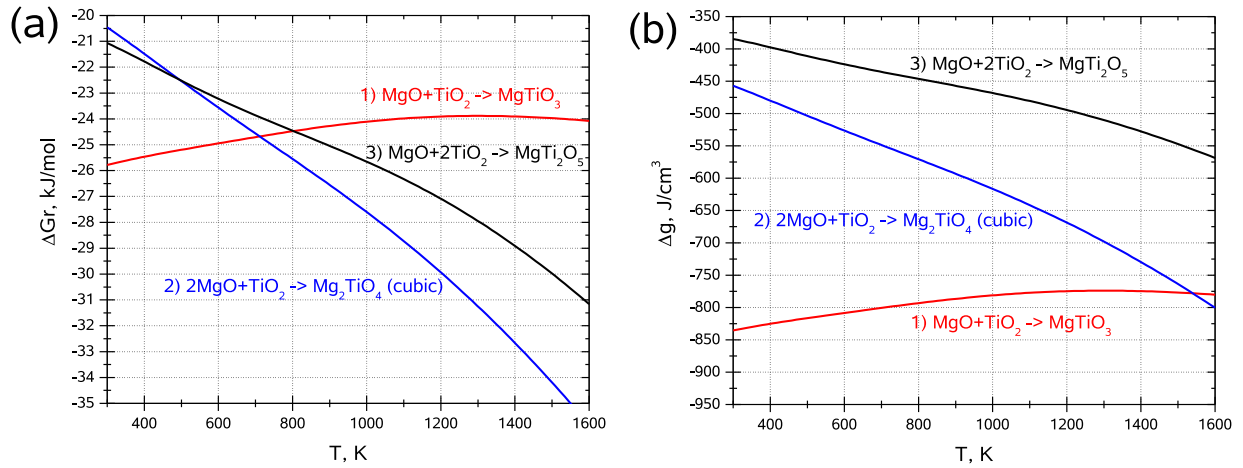


Fig. 5.10. a) ΔG_r vs T for the formation of compounds in the system MgO-TiO₂ and (b) Δg vs T for the formation of compounds in the system MgO-TiO₂. Calculated from values given in I. Barin.¹²⁸

at these temperatures is more likely as shown by thermodynamical estimations (Fig. 5.10(a)). The Δg values for the MgTiO₃, Mg₂TiO₄ and MgTi₂O₅ are presented in Fig. 5.10(b). They are also beyond the limit of -400 J/cm³.

Previous investigations of vapour-solid reactions in the system MgO-TiO₂ using (100) MgO substrates showed topotaxial formation of Mg₂TiO₄ on MgO.^{11,118–120,181} In this Ph.D. thesis, topotaxial formation of MgTiO₃ on TiO₂ (rutile) was found. Consequently, the choice in the nucleation and growth of the kind of first phase in the system MgO-TiO₂ is not determined by ΔG_r , but instead is given by the crystallography of the substrate serving as reactant: For MgO, it is Mg₂TiO₄, whereas for TiO₂ (rutile), it is MgTiO₃. Thus, crystallography obviously plays an important, if not dominant, role in the determination of the first growing phase in some topotaxial solid-state reactions. We propose the limit of Δg for oxides as -850 J/cm³. It should be noted that according to the EHF model,^{21,22} either MgTiO₃ or MgTi₂O₅ (see phase diagram in Fig. 2.12) should be the first phase forming in the system MgO-TiO₂. Consequently, the EHF model is not suitable for the system MgO-TiO₂. The phase MgTi₂O₅ has a pseudobrookite structure. Thus, we can assume that MgTi₂O₅ might be obtained using TiO₂ with brookite structure as substrate for the reaction.

6 Conclusions

In the present work, thin-film solid state reactions in the systems BaCO_3 (thin film)- TiO_2 (rutile or anatase, substrate), BaO (vapour)- TiO_2 (rutile or anatase, substrate), SrO (vapour)- TiO_2 (rutile, substrate), CaO (vapour)- TiO_2 (rutile, substrate) and MgO (vapour)- TiO_2 (rutile, substrate) were experimentally studied. The substrates were one-side polished (110) and (100) surfaces of commercial TiO_2 (rutile) (from CrysTec GmbH, Berlin, Germany) and (001) and (012) surfaces of epitaxial TiO_2 (anatase) thin films grown on SrTiO_3 or LaAlO_3 substrates. The main findings of this Ph.D. thesis are summarised below.

- The formation of BaTiO_3 thin films from BaCO_3 (thin film) and (110)/(100) TiO_2 (rutile) single crystals as well as from BaCO_3 (thin film) and (001)/(012) epitaxial TiO_2 (anatase) thin films by solid-solid reactions has been studied in vacuum and in air at temperatures between 575 °C and 1000 °C. The phase sequence during the reaction is independent of the structure of TiO_2 (i.e. rutile or anatase). The solid-solid reactions in vacuum and in air showed different processes to occur during BaTiO_3 formation. The Ba_2TiO_4 compound is formed as the first phase after the reaction in vacuum at 575 °C while BaTiO_3 is found as the first phase after a reaction in air at 575 °C. Thermodynamic factors favour the nucleation of Ba_2TiO_4 in vacuum and of BaTiO_3 in air. A mechanism of BaTiO_3 formation in vacuum is proposed. This mechanism is in contrast to the model of Beauger *et al.*.⁶⁹ Different formation mechanisms of Ba_2TiO_4 and BaTiO_3 are assumed. The Ba_2TiO_4 is formed mainly by in-diffusion of Ti ions into BaCO_3 , while BaTiO_3 is nucleated mainly by in-diffusion of Ba ions into TiO_2 .
- Ti-rich barium titanates were formed after solid-solid and vapour-solid reactions at high reaction temperatures, but with quite different textures. Oriented $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ phases were grown after vapour-solid reaction of BaO with the rutile substrates at temperatures between 900 °C and 1000 °C. Contrary to the vapour-solid reaction, polycrystalline BaTi_4O_9 and $\text{Ba}_4\text{Ti}_{13}\text{O}_{30}$ (with fiber texture) phases were found after the solid-solid reaction at 1000 °C in vacuum and in air, respectively. These differences are caused by the reaction conditions changing with reaction geometry.
- Vapour-solid reactions on the rutile surfaces at 900 °C were investigated at different reaction stages (using BaO vapour of different nominal thicknesses):
 - the initial stage of vapour-solid reaction of a BaO quantity equivalent to a nominal film thickness of 1 nm and 5 nm with the TiO_2 substrates showed the formation of well-oriented $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ islands. A topotaxial orientation relationship between $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ and TiO_2 was found. This topotaxy is facilitated by a certain similarity in the oxygen sublattices of TiO_2 and $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$. The nucleation of the Ti-rich phase most probably occurs at surface steps

of the (110) TiO_2 substrate via in-diffusion of Ba ions while the film growth proceeds mainly by surface diffusion.

-a thin film consisting of well-oriented BaTiO_3 and $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ grains was observed after vapour-solid reaction of a BaO quantity equivalent to a nominal film thickness of 50 nm with the rutile substrates. The Ti-rich grains are located at the interface with the rutile substrates, whereas the BaTiO_3 grains are located on top of the Ti-rich layer. Large pores were found after the reaction, at the interface with the TiO_2 substrates. The pores have been formed by surface diffusion of TiO_2 . The latter is the dominant diffusing species during vapour-solid reaction. Thus, the formation of the voids at the surface of the rutile substrates occurs by diffusion of one reactant, similar to the Kirkendall voids which are frequently observed after solid-solid reactions in planar reaction couples.

- More than one orientation relationship has been found for BaTiO_3 and SrTiO_3 after vapour-solid reaction of BaO (vapour) or SrO (vapour) with the TiO_2 (rutile) substrates depending on the reaction temperature and substrate orientation, all of which imply, however, a common [001] TiO_2 tilt axis. The crystallographic reason for the tilt axis are chains of TiO_6 octahedra oriented along the [001] direction of TiO_2 (rutile). Dominant orientations of BaTiO_3 as well as SrTiO_3 can be explained by common octahedra chains. The growth of the BaTiO_3 and SrTiO_3 grains with the observed various orientations are discussed in terms of the different nucleation kinetics and conditions which seem to be dependent on the surface structure and morphology of the TiO_2 substrates.
- Only one orientation relationship has been found for BaTiO_3 after vapour-solid reaction of BaO (vapour) with a TiO_2 anatase thin film. This can be explained by a similar orientation of TiO_6 octahedra in anatase and perovskite.
- Vapour-solid reaction between MgO (vapour) and TiO_2 (rutile) single crystals resulted in the growth and topotaxial formation of the MgTiO_3 phase. This is facilitated by similar oxygen sublattices of the MgTiO_3 and TiO_2 (rutile) structures. The nucleation of MgTiO_3 occurred via in-diffusion of Mg cations into the TiO_2 lattice, so that the oxygen sublattice of TiO_2 (rutile) can be taken over by the growing MgTiO_3 .
- Factors influencing the first-phase selection in complex oxide thin film systems are discussed. The nucleation of the first phase in the system $\text{BaCO}_3\text{-TiO}_2$ is determined by the free energy change of the reaction ΔG_r . The formation of SrTiO_3 and CaTiO_3 compounds in the systems SrO-TiO_2 and CaO-TiO_2 , can be explained according to the EHF model.^{21,22} On the other hand, in the system MgO-TiO_2 the phase forming first is neither determined by ΔG_r nor by the EHF model,^{21,22} but instead is determined by the crystallography of the substrate serving as reactant: For MgO, it is Mg_2TiO_4 , whereas for TiO_2 (rutile), it is MgTiO_3 . The model by d'Heurle²³ describes phase formation as a nucleation controlled process. For silicide formation a limit of nucleation dominance ($\Delta g = \Delta G_r/V$) was proposed as -400 J/cm^3 .²³ We propose the limit of Δg for oxides as -850 J/cm^3 .

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- Although, the growth of epitaxial anatase TiO_2 films on SrTiO_3 and LaAlO_3 substrates was not the main aim of the work, epitaxial (001)- and (012)-oriented TiO_2 anatase films with a good microstructure were prepared and used for the solid state reactions. The (012) orientation of the TiO_2 was most probably obtained for the first time. The mean orientation of the surface of (012)-oriented anatase grains is close to (012). The question, whether the (012) surface is stable or whether micro-faceting occurs, remains for further work. The similarities in the orientations of the AO_6 ($\text{A} = \text{Ti}, \text{Al}$) octahedra of $\text{SrTiO}_3/\text{LaAlO}_3$ and anatase structures determine the final phase formation and the epitaxial growth of the thin films. The anatase films were transformed into a cubic phase similar to TiO when in situ exposed to an electron beam.
 - It appears that solid state reactions in electroceramic systems as a rule are complex, and that their understanding requires the detailed consideration of thermodynamics, crystallographic, and nucleation-related conditions. As a rule, the oxygen sublattice, in particular the frame of octahedra of type AO_6 , plays a dominating role for the crystallographic orientation relationships that are found after phase formation by solid state reactions, but it can also have a considerable impact on the phase formation sequence including first-phase selection.

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Appendix

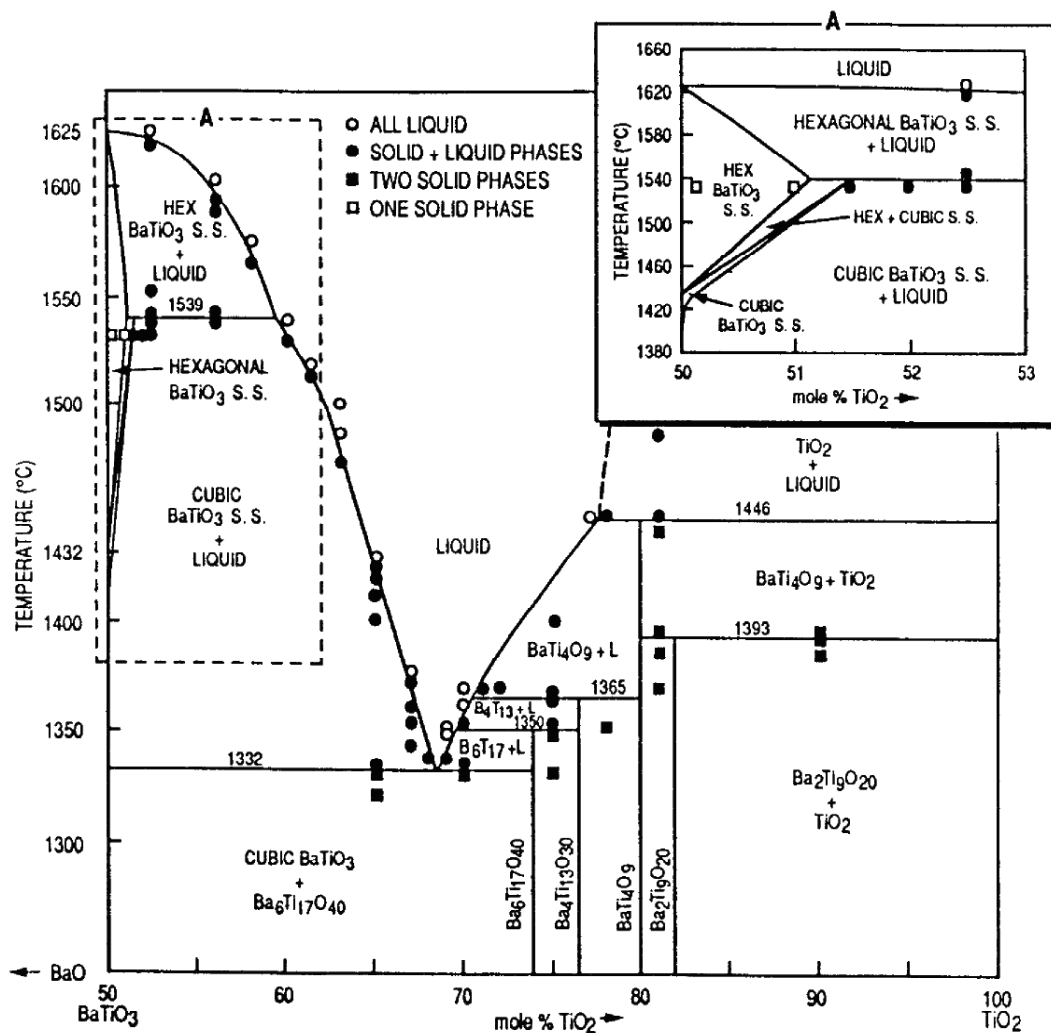


Fig. A.1. BaTiO₃-TiO₂ equilibrium phase diagram.⁴⁵

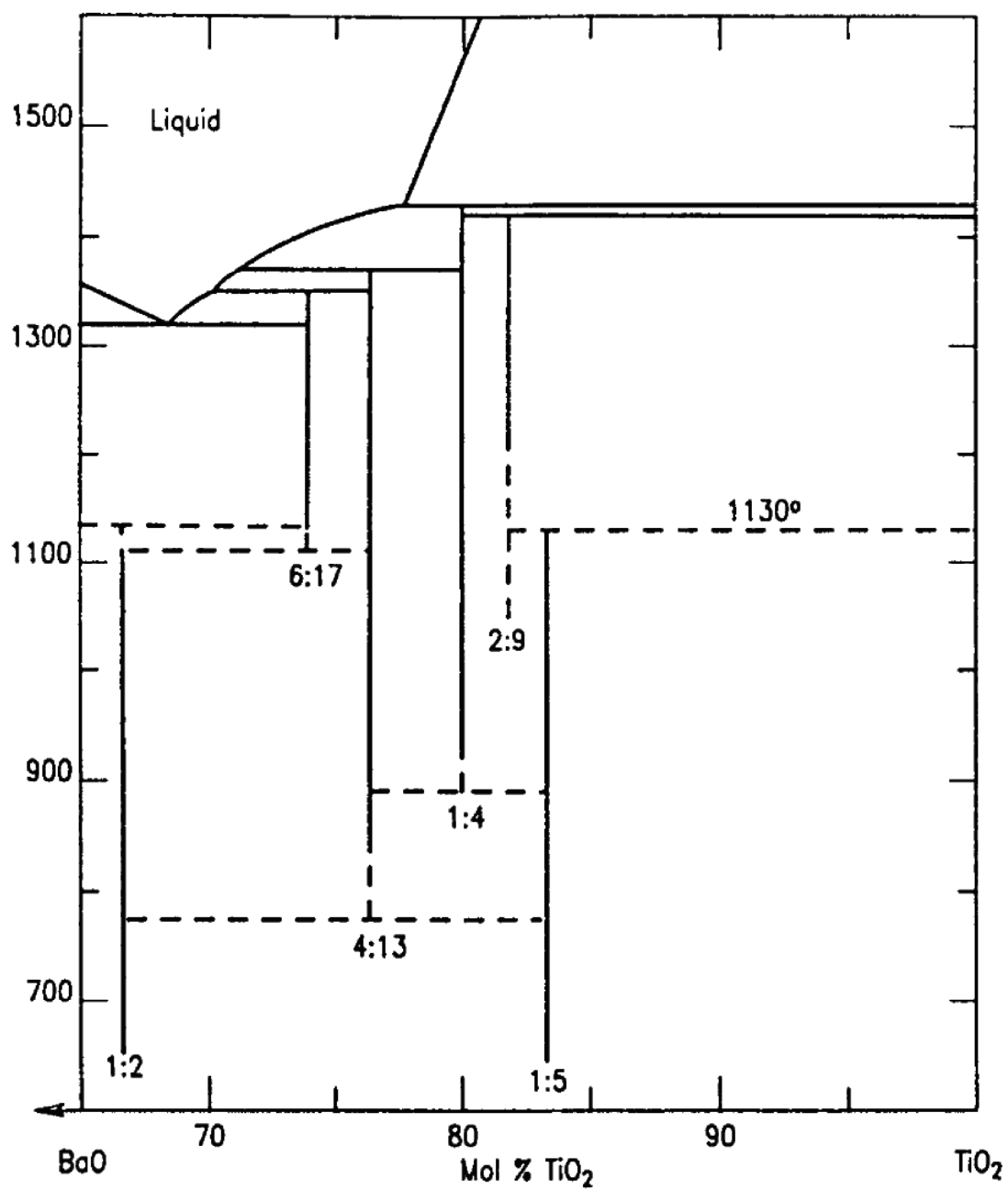


Fig. A.2. Low temperature BaTiO₃-TiO₂ phase diagram.⁷⁸

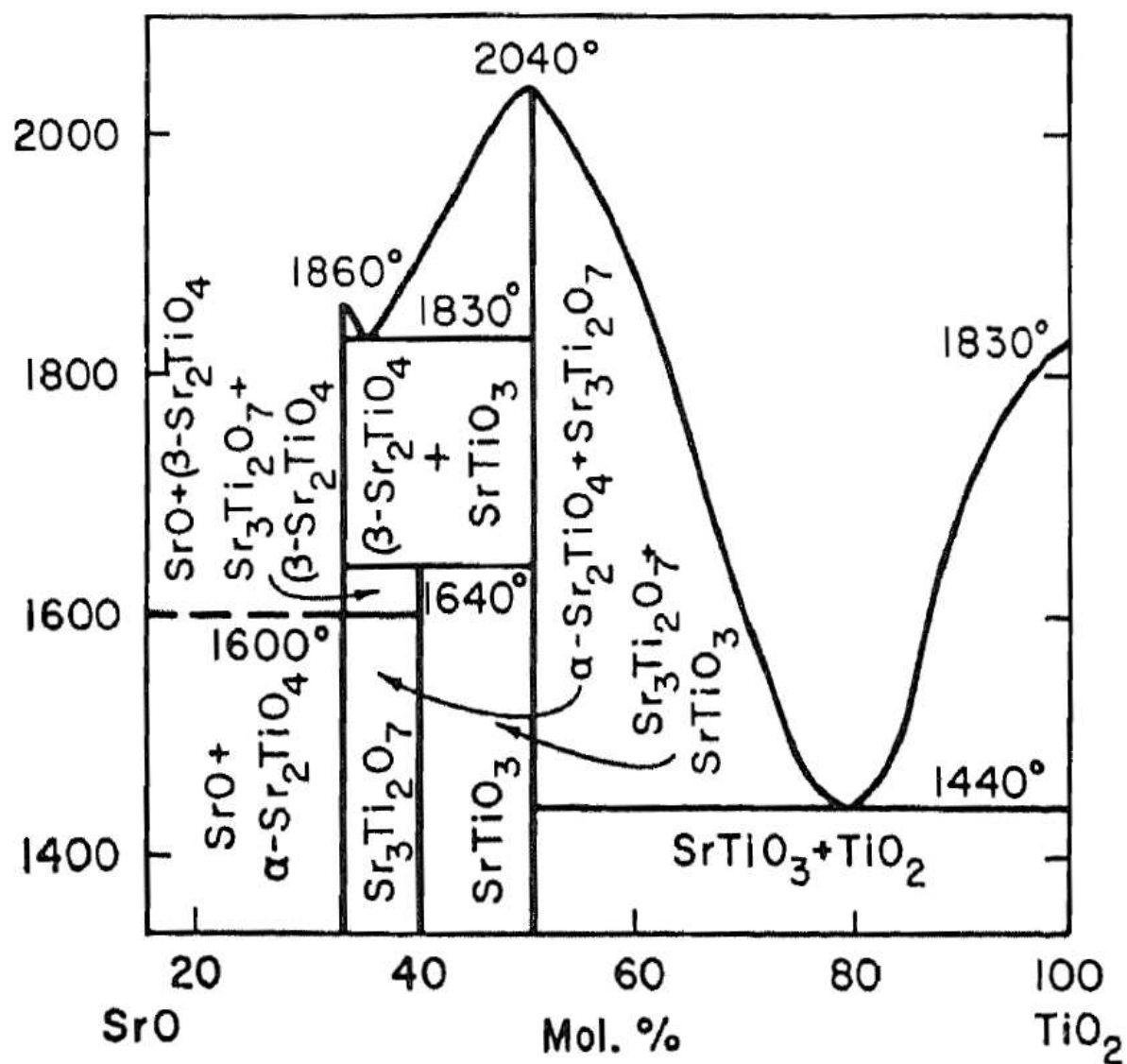


Fig. A.3. Phase diagram of the system SrO-TiO₂ (Fig. 297 in Ref.¹⁰¹).

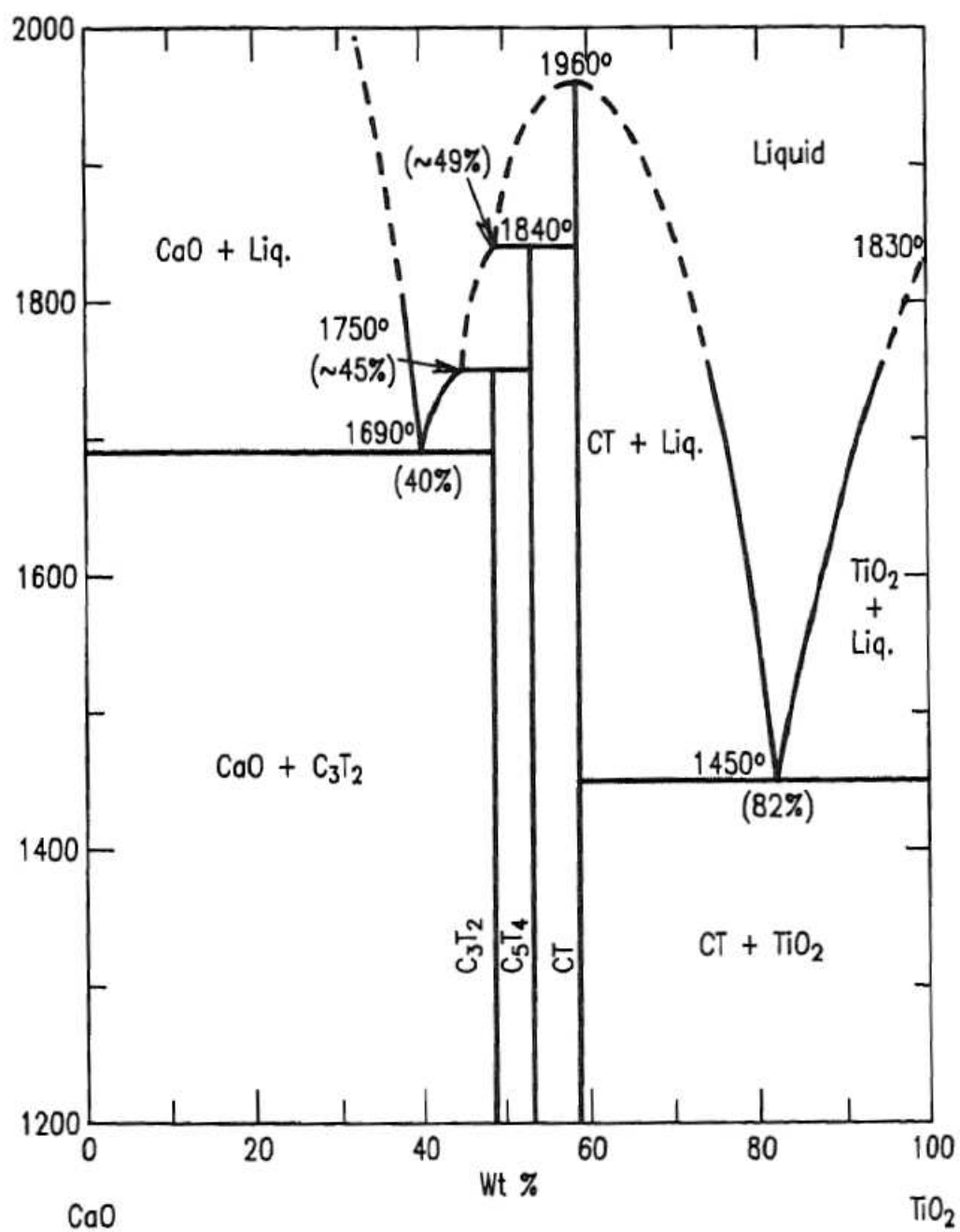


Fig. A.4. Phase diagram of the system CaO-TiO₂ (Fig. 6385 in Ref. ¹⁰¹). C= CaO, T= TiO₂.

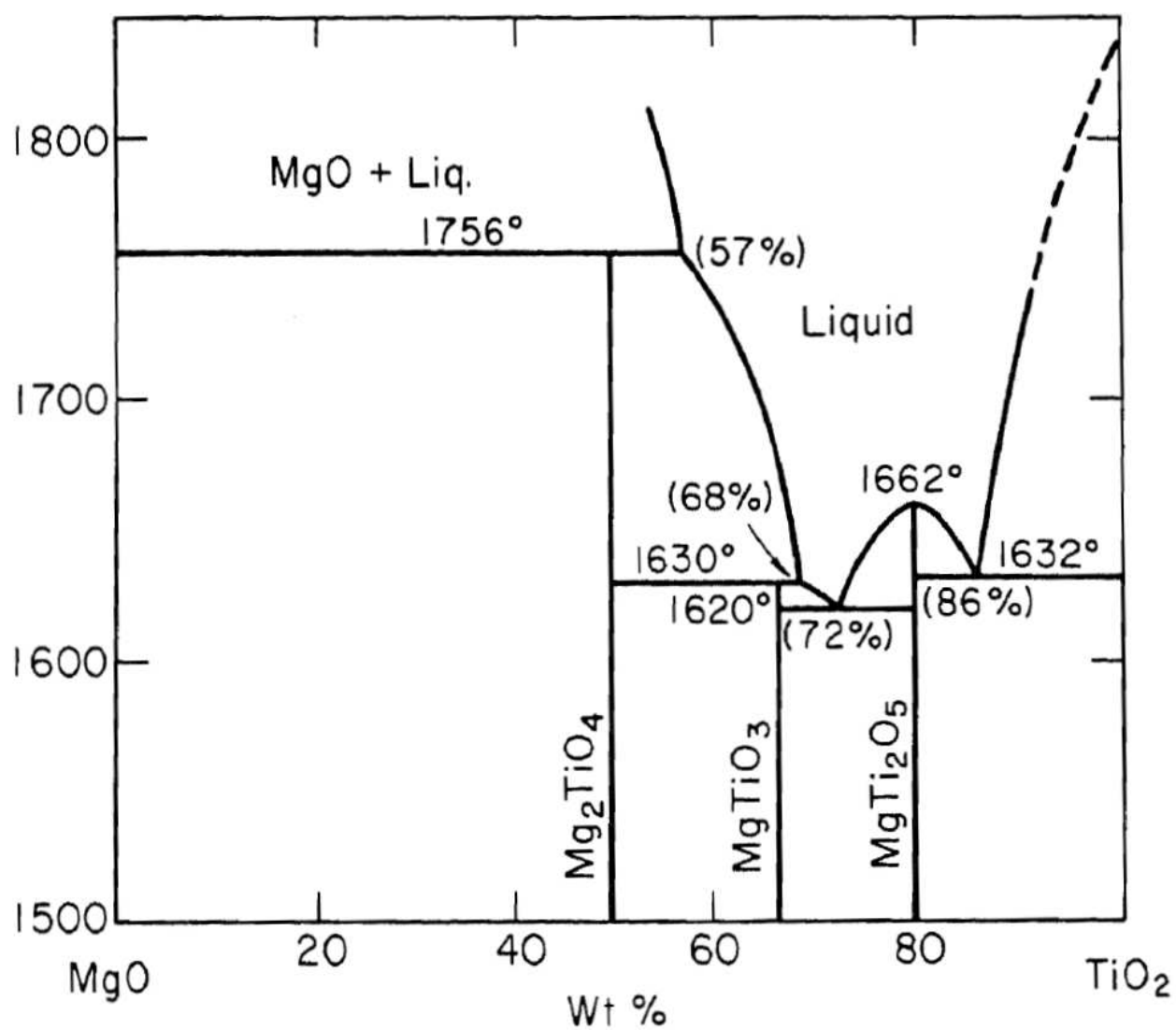


Fig. A.5. Phase diagram of the system MgO-TiO₂ (Fig. 4336 in Ref. ¹⁰¹).

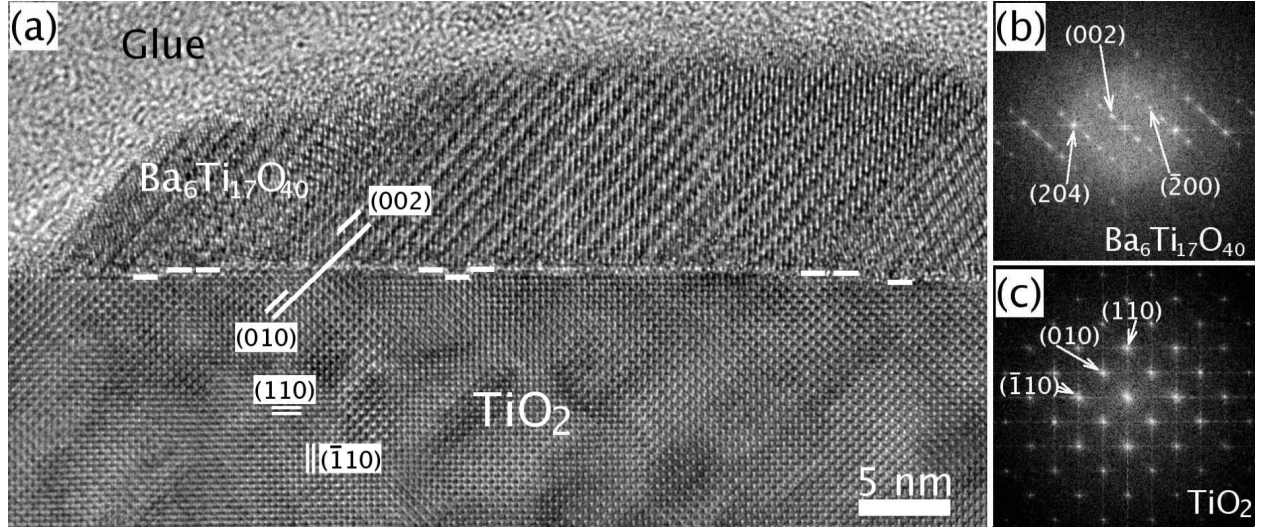


Fig. A.6. HRTEM image of a sample after the reaction of a BaO vapour with a (110) TiO_2 (rutile) substrate at 900 °C. The nominal thickness of BaO was ≈ 1 nm. (a) Part of a Ti-rich island on the rutile substrate. The long white line in the image indicates (002) $\text{Ba}_6\text{Ti}_{17}\text{O}_{40} \parallel (010) \text{TiO}_2$. The dashes show steps on the TiO_2 surface. (b) FFT image of a $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ Ti-rich grain. (c) FFT image of the rutile substrate. Viewing direction is $[010] \text{Ba}_6\text{Ti}_{17}\text{O}_{40} \parallel [001] \text{TiO}_2$.

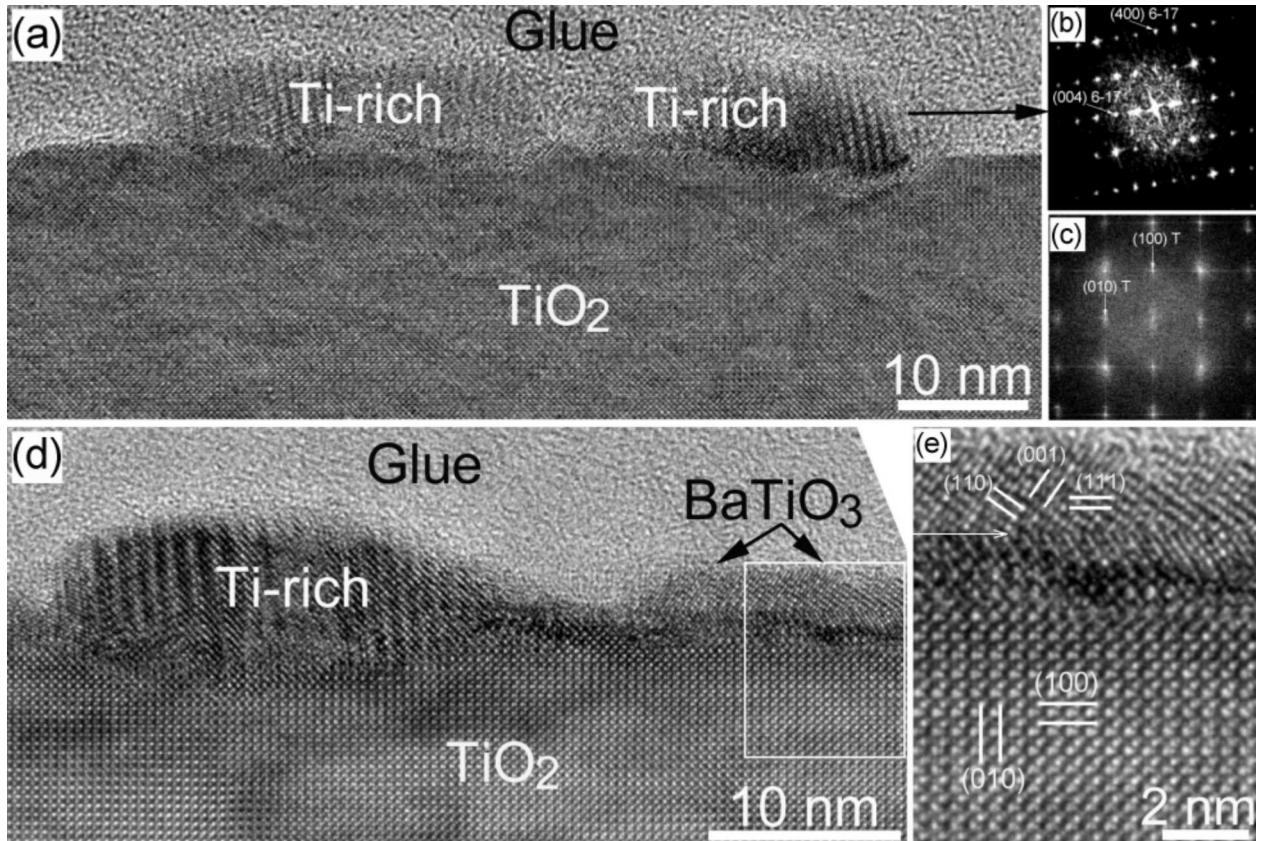


Fig. A.7. HRTEM images of a sample after the reaction of a BaO vapour with a (100) TiO_2 (rutile) substrate at 900 °C. The nominal thickness of BaO was ≈ 1 nm. (a) Ti-rich islands on the rutile substrate. (b) FFT image of a $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ (6-17) Ti-rich grain. (c) FFT image of the rutile substrate (T). Viewing direction is $[010] \text{Ba}_6\text{Ti}_{17}\text{O}_{40} \parallel [001] \text{TiO}_2$. (d) Ti-rich and BaTiO_3 grains on the rutile substrate. (e) Computer-processed lattice plane images of BaTiO_3 and the rutile substrate (magnified section of image (d)). The arrow in image (e) marks a (111) twin boundary in BaTiO_3 . Viewing direction is $[\bar{1}\bar{1}0] \text{BaTiO}_3 \parallel [001] \text{TiO}_2$.

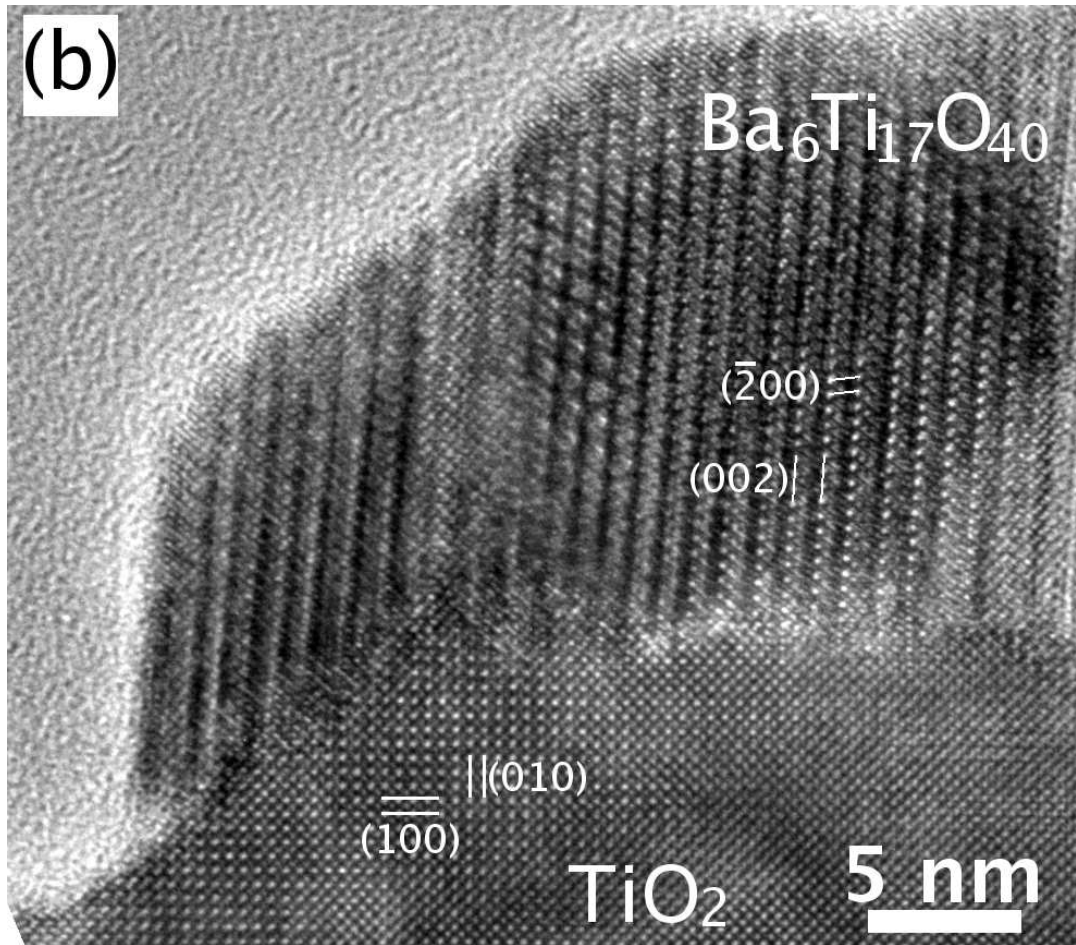


Fig. A.8. HRTEM image of a sample made by a vapour-solid reaction on a (100) TiO_2 (rutile) substrate at 900 °C. The nominal thickness of BaO was ≈ 5 nm. b) lattice plane images of $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ and the rutile substrate. Viewing direction is $[010] \text{Ba}_6\text{Ti}_{17}\text{O}_{40} \parallel [001] \text{TiO}_2$.

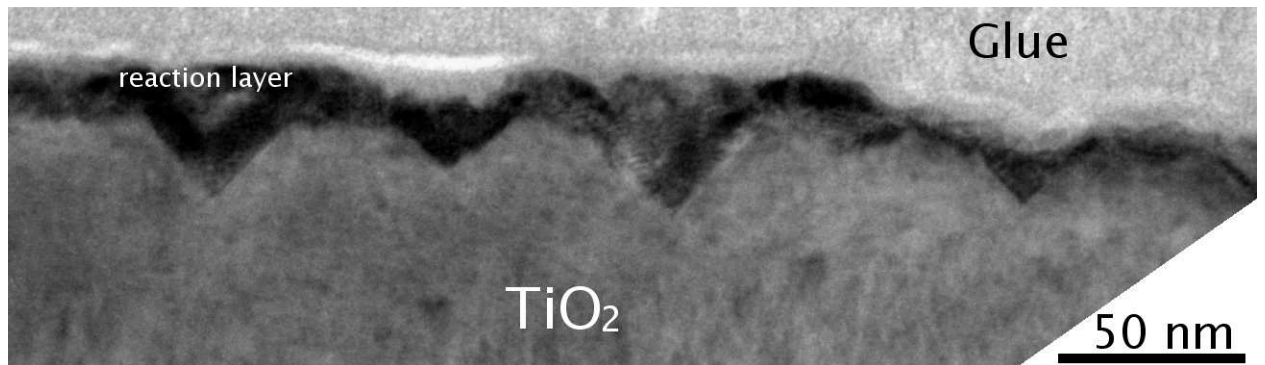


Fig. A.9. TEM image of a sample made by vapour-solid reaction of a BaO vapour with (100) TiO_2 (rutile) surface at 700 °C. Large (110) and $(\bar{1}\bar{1}0)$ TiO_2 facets have developed after the reaction.

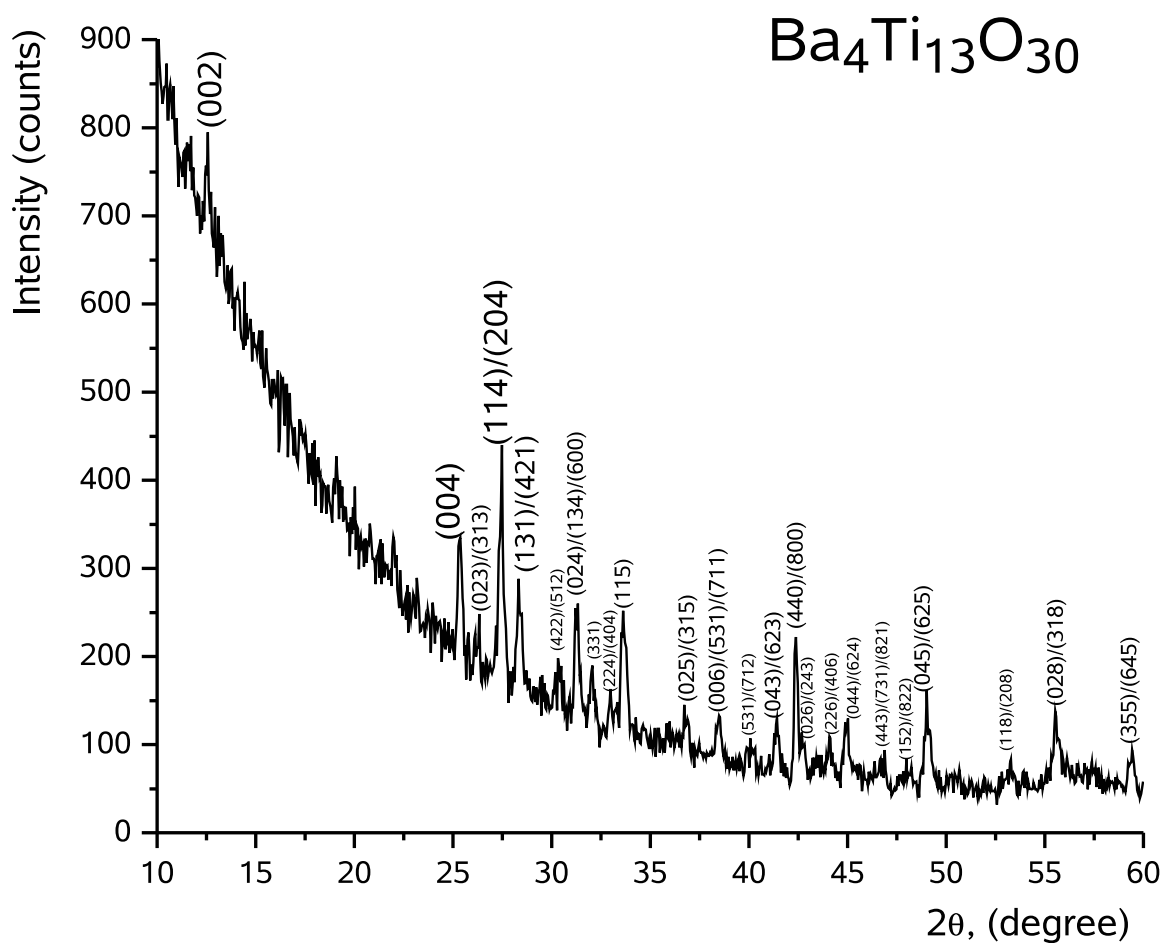


Fig. A.10. XRD 2θ scan of a sample made by a solid-solid reaction in air at 900 °C for 30 min between a (100) TiO_2 (rutile) substrate and a BaCO_3 thin film grown at 500 °C. The pattern was indexed according to JCPDS 84-2213. The scan speed was 0.001 °/s.

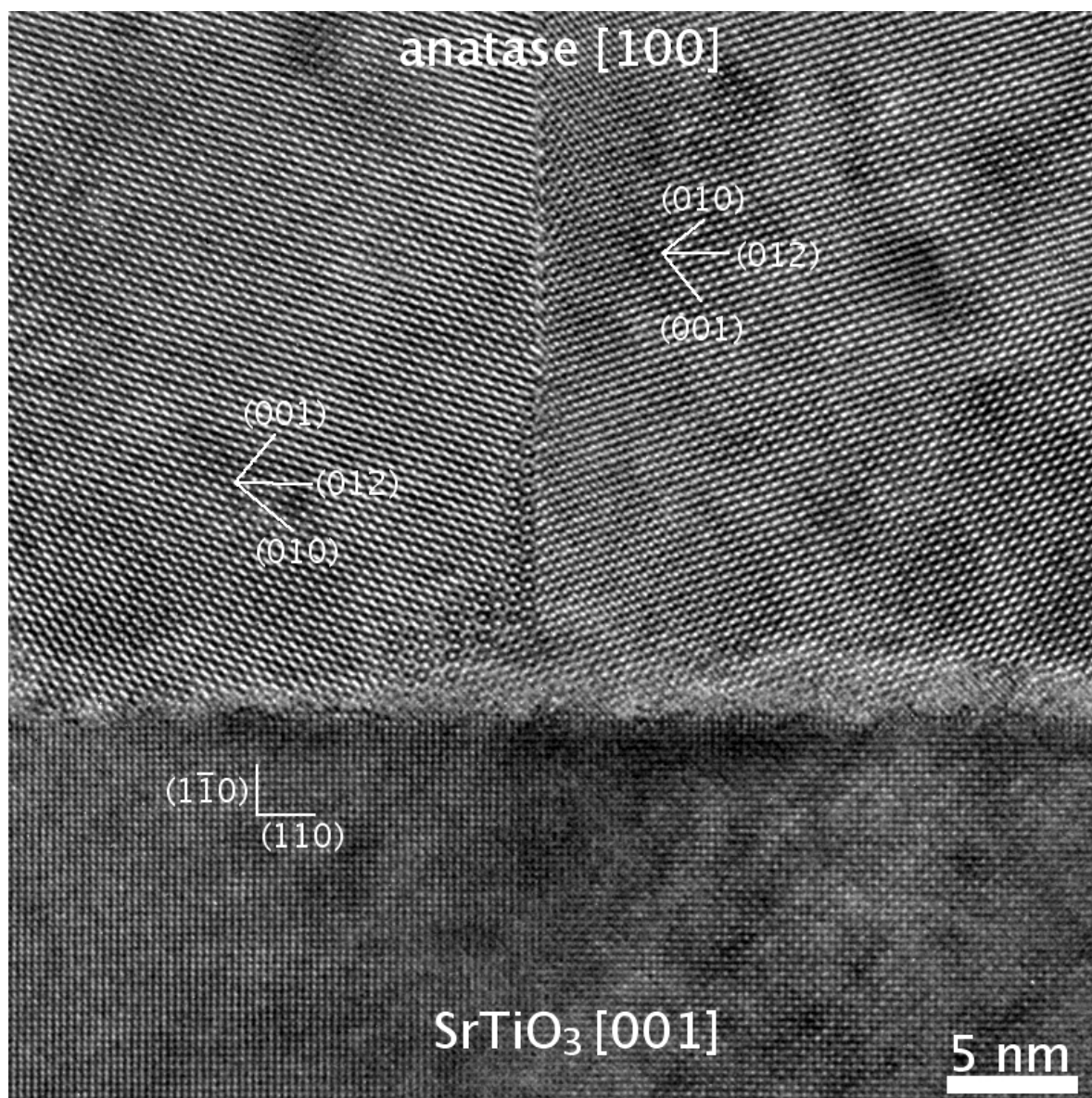


Fig. A.11. HRTEM image of an epitaxial TiO₂ (anatase) thin film grown on a (110) SrTiO₃ substrate at 700 °C.

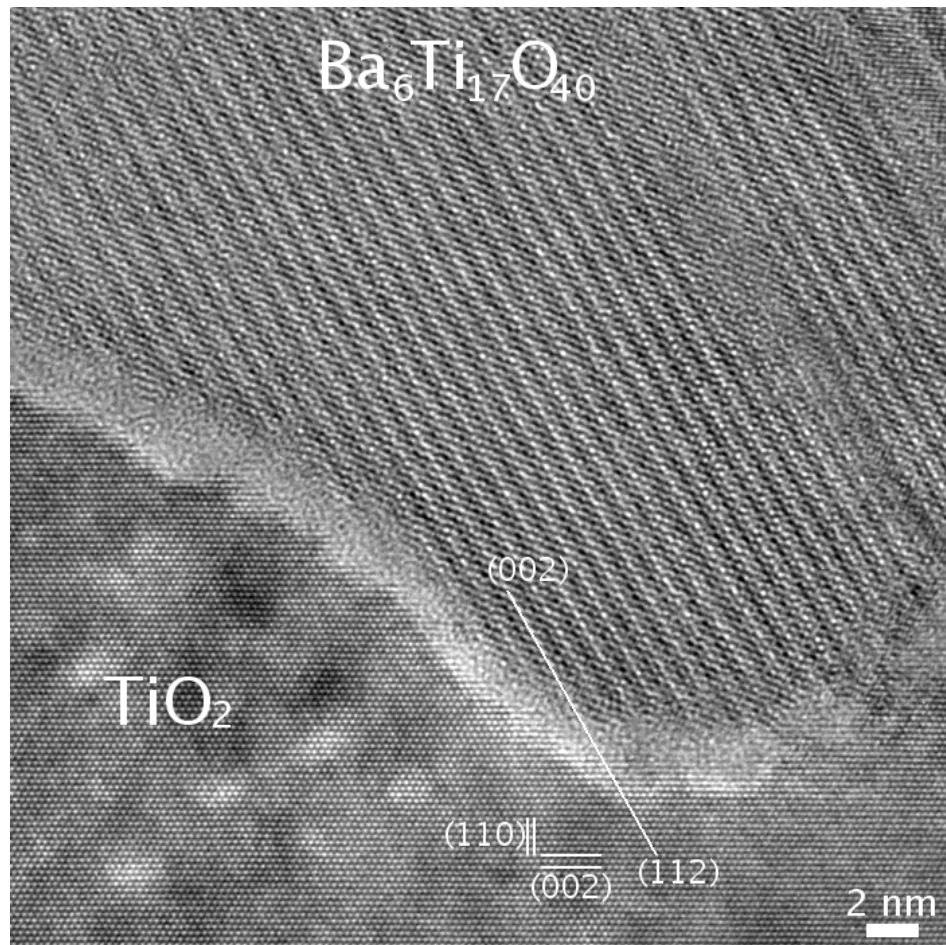


Fig. A.12. Lattice plane image of an epitaxial (001) TiO_2 (anatase) film and a $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ grain. The long white lines mark the $(001) \text{Ba}_6\text{Ti}_{17}\text{O}_{40} \parallel (112) \text{TiO}_2$ (anatase) planes. Viewing direction is $[010] \text{Ba}_6\text{Ti}_{17}\text{O}_{40} \parallel [1\bar{1}0] \text{TiO}_2$ (anatase).

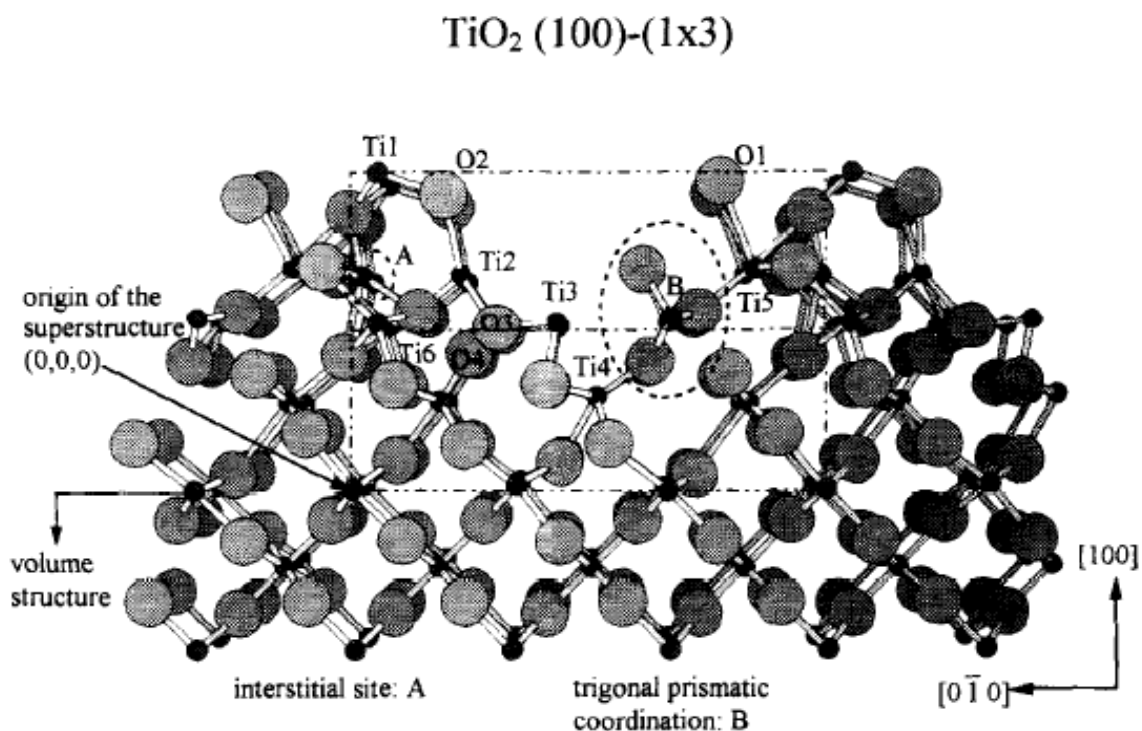


Fig. A.13. Structure model of the rutile (100)-(1x3) surface projected along [001]. The origin of the superstructure cell is indicated by an arrow. The titanium atoms labelled Ti1-Ti5 and A, B are coordinated by oxygen as follows: Ti1 three-fold; Ti2 five-fold; Ti3 bridge site; Ti4 six-fold; Ti5 six-fold; A five-fold (interstitial site); B six-fold (trigonal prismatic). This heavily relaxed model was proposed by Zajonz *et al.*¹⁶⁵

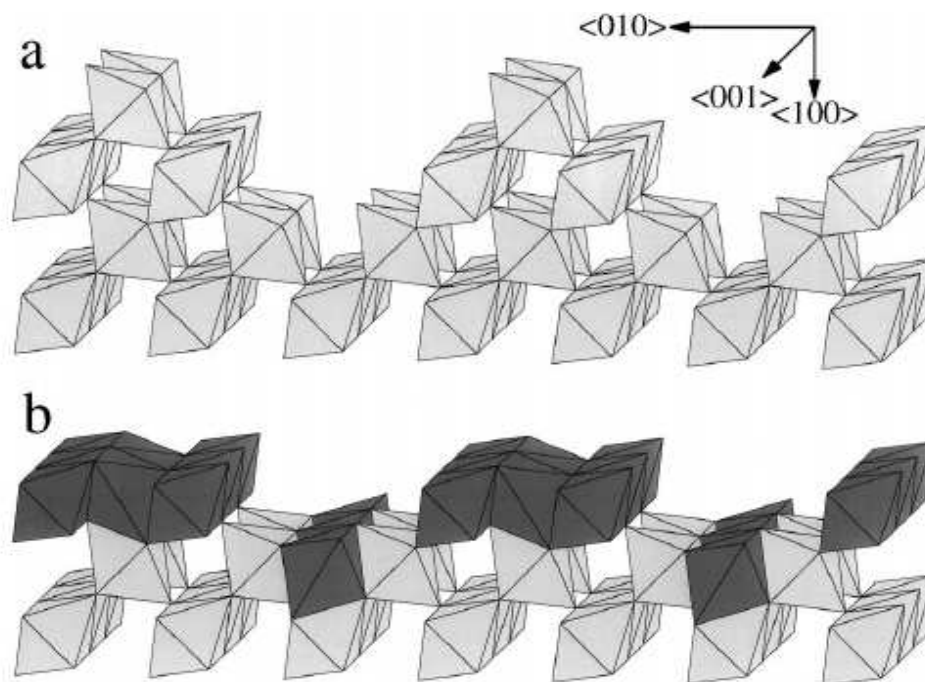


Fig. A.14. Octahedra models: schematic representation of (a) the microfacet model and (b) the model proposed by E. Landree *et al.*¹⁶⁶ At the center of each octahedron is a titanium atom and oxygen atoms are positioned at the corners. The darker shade is used to highlight the major differences between (a) and (b).

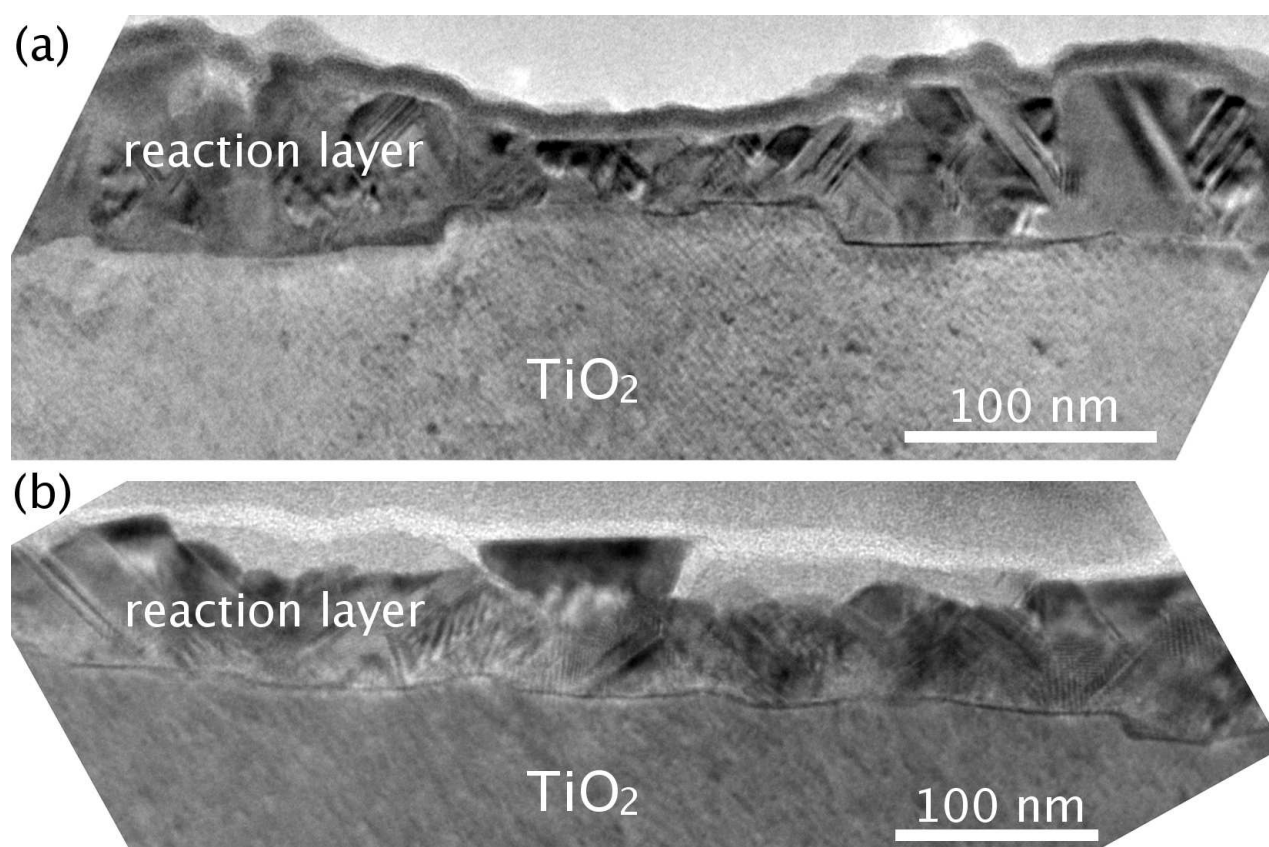


Fig. A.15. TEM images of a sample made by a solid-solid reaction between a BaCO_3 film and a (110) TiO_2 (rutile) surface at 800 °C for 30 min in vacuum. The BaCO_3 layer was grown at a substrate temperature of 500 °C.

Eidesstattliche Erklärung

Hiermit erkläre ich, dass ich meine Dissertation selbständig und ohne fremde Hilfe verfasst und keine anderen als die von mir angegebenen Quellen und Hilfsmittel zur Erstellung meiner Dissertation verwendet habe. Den benutzten Werken wörtlich oder inhaltlich entnommene Stellen sind als solche gekennzeichnet.

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Andriy Lotnyk,

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List of publications

1. A. Lotnyk, S. Senz, D. Hesse "BaTiO₃ formation by solid-state reactions on rutile single crystals", *Diffusion Fundamentals*, **2**, 51.1-51.2 (2005).
2. A. Lotnyk, S. Senz, D. Hesse "Formation of BaTiO₃ thin films from (110) TiO₂ rutile single crystals and BaCO₃ by solid state reactions", *Solid State Ionics*, **177**, 429-436 (2006).
3. A. Lotnyk, S. Senz, D. Hesse "Growth and characterization of (012)- and (001)-oriented epitaxial anatase thin films", *Advances in Science and Technology*, **46**, 146-151 (2006) (<http://www.scientific.net>, Trans Tech Publications).
4. A. Lotnyk, S. Senz, D. Hesse "Epitaxial growth of TiO₂ thin films on SrTiO₃, LaAlO₃ and yttria-stabilized zirconia substrates by electron beam evaporation", *Thin Solid Films*, **515**, 3439-3447 (2007).
5. A. Lotnyk, S. Senz, D. Hesse "Thin film solid state reactions of solid BaCO₃ and BaO vapor with (100) rutile substrates", *Acta Mater.*, **55**, 2671-2681 (2007).
6. A. Lotnyk, S. Senz, D. Hesse "Orientation relationships of SrTiO₃ and MgTiO₃ thin films grown by vapor-solid reactions on (100) and (110) TiO₂ (rutile) single crystals", *J. Phys. Chem. C*, **111**, 6372-6379 (2007).
7. A. Lotnyk, A. Graff, S. Senz, N. D. Zakharov, D. Hesse "Topotaxial formation of titanium-rich barium titanates during solid-state reactions on (110) TiO₂ (rutile) and (001) BaTiO₃ single crystals", *Solid State Sci.*, in press, doi:10.1016/j.solidstatesciences.2007.08.001, (2007).

Conference contributions

1. A. Lotnyk, S. Senz, A. Graff, D. Hesse "Phase formation and microstructure in the system BaO-TiO₂ during solid-state reactions on rutile single crystal surfaces", International Workshop on Nanoscale Structure and Dynamics, Leucorea, Lutherstadt, Wittenberg, Germany, 20.-22.09.2004, *Poster*.
2. A. Lotnyk, A. Graff, S. Senz, D. Hesse "Phase formation sequence during thin film solid-state reactions in the BaO-TiO₂ system", Frühjahrstagung des Arbeitskreises Festkörperphysik der Deutschen Physikalischen Gesellschaft, Berlin, Germany, 04.-09.03.2005, *Poster*.
3. A. Lotnyk, S. Senz, D. Hesse "BaTiO₃ formation by solid state reactions on rutile single crystals", Autumn School on Materials Science and Electron Microscopy "Microscopy of Tomorrow's Industrial Materials", Berlin, Germany, 03.-08.10.2005, *Poster*.
4. A. Lotnyk, S. Senz, D. Hesse "Epitaxial anatase (012) and (001) grown on (110) and (100) SrTiO₃", Frühjahrstagung des Arbeitskreises Festkörperphysik der Deutschen Physikalischen Gesellschaft, Dresden, Germany, 27.-31.03.2006, *Talk*.
5. A. Lotnyk, S. Senz, D. Hesse "Phase and microstructure evolution during BaTiO₃ formation by solid state reactions on TiO₂ surfaces", Frühjahrstagung des Arbeitskreises Festkörperphysik der Deutschen Physikalischen Gesellschaft, Dresden, Germany, 27.-31.03.2006, *Poster*.
6. A. Lotnyk, S. Senz, D. Hesse "Epitaxial growth of anatase thin films on (110) and (100) SrTiO₃", 11th International Ceramic Congress and 4th Forum on New Materials (CIMTEC 2006), Acireale, Italy, 04.-09.06.2006, *Talk*.
7. A. Lotnyk, S. Senz, D. Hesse "Role of crystallography in topotaxial first-phase selection", Frühjahrstagung des Arbeitskreises Festkörperphysik der Deutschen Physikalischen Gesellschaft, Regensburg, Germany, 26.-30.03.2007, *Talk*.