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:

\[
x \sim \sqrt{t}.
\]  

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:

\[
x \sim t.
\]  

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 \(\text{Ni}_2\text{Si}\) 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-
2.1 Thin film solid state reactions

Temperature 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 barriers\(^ {23}\) 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:

\[
\Delta H' = \Delta H^\circ \times \frac{\text{effective concentration limiting element}}{\text{compound concentration limiting element}} = \Delta H^\circ \times \frac{ec'}{ec},
\]

where \(\Delta H^\circ\) is the standard heat of formation expressed in kJ/mole of atoms. If a compound \(A_1-ecB_{ec}\) 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 \(\Delta G_v\) 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 \(\Delta G_v \sim r^3 \Delta G_v\). 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:

\[
\Delta G_N(r) = a_1 r^2 \sigma - a_2 r^3 \Delta G_r,
\]

(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 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 \( \Delta G_N^* \) for a critical radius \( r^* \):

\[
r^* = \frac{2a_1 \sigma}{3a_2 \Delta G_r},
\]

(2.5)

\[
\Delta G_N^* = \frac{4a_1^3 \sigma^3}{27a_2^2 \Delta G_r^2}.
\]

(2.6)

\( \Delta G_N^* \) 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 \( \Delta G_r \), the free energy of formation of AB, is small.

The rate of nucleation \( \rho^* \) 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:

\[
\rho^* \sim e^{-\frac{\Delta G^*}{kT}} e^{-\frac{Q}{kT}},
\]

(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 \( \Delta G_N^* \sim \sigma^3 / \Delta G_i^2 \). 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 \( x_\beta \) grows between two saturated phases \( A_\alpha B \) and \( A_\gamma B \) where the subscripts \( \alpha > \beta > \gamma \) characterise the composition of the compounds. The diffusion flux \( j_A^\beta \) of A atoms in the \( A_\beta B \) phase is given by:

\[
 j_A^\beta = \Delta C_{eq}^\beta k_{eff}^\beta / (1 + x_\beta k_{eff}^\beta / \tilde{D}_\beta),
\]

(2.8)

where \( \Delta C_{eq}^\beta \) 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, \( \tilde{D}_\beta \) is the chemical interdiffusion coefficient for the \( A_\beta B \) layer and \( k_{eff}^\beta \) 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:

\[
 1/k_{eff}^\beta = 1/k_{\beta \alpha} + 1/k_{\beta \gamma}.
\]

(2.9)
The change of the layer thickness $x_\beta$ is given by:

$$\frac{dx_\beta}{dt} = \left[ \frac{1}{(C_{\alpha\beta}^{eq} - C_{\beta\alpha})} + \frac{1}{(C_{\beta\gamma}^{eq} - C_{\gamma\beta}^{eq})} \right] j_A^\beta. \tag{2.10}$$

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

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

where $G_\beta$ 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 $x_\beta^*$, defined by:

$$x_\beta^* = \tilde{D}_\beta / k_{\beta}^{eff}. \tag{2.12}$$

From Eq. (2.12) it follows that

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

and

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

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 BaTiO$_3$ ceramics

### 2.2.1 Crystal structure and some properties of TiO$_2$

There are at least five TiO$_2$ structures.\(^{30}\) The naturally occurring TiO$_2$ polymorphs are rutile (tетрагональ), anatase (tetragonal), brookite (orthorhombic) and TiO$_2$ (B) (monoclinic). Among these structural modifications, rutile and anatase are the most often encountered and technically utilised forms. Anatase TiO$_2$ has the same stoichiometry as rutile TiO$_2$ 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 TiO$_2$ (rutile, anatase, brookite, TiO$_2$ (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
2.2 Synthesis of BaTiO$_3$ ceramics

Fig. 2.3. (a) Unit cell of rutile TiO$_2$ (a=b= 0.459 nm, c= 0.295 nm; space group P4$_2$/mnm). (b) Representation of TiO$_6$ octahedra of rutile.

Fig. 2.4. a) Unit cell of anatase TiO$_2$ (a=b= 0.378 nm, c=0.951 nm; space group I4$_1$/amd). b) Representation of TiO$_6$ octahedra of anatase.
Table 2.1. Crystallographic parameters for rutile and anatase.  

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

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

Rutile is the most stable form of TiO$_2$ 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.  

The two polymorphs rutile and anatase have also quite distinct crystal morphologies. Whereas rutile forms slender prismatic crystals, anatase usually occurs in a bipyramidal shape. The surface energy of periodic TiO$_2$ rutile slabs was calculated by Ramamoorthy et al.  

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 TiO$_2$ anatase were estimated by Lazzeri et al. 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 BaCO$_3$, BaTiO$_3$ and Ba$_2$TiO$_4$

A. BaCO$_3$

There are three modifications of BaCO$_3$. 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 BaCO$_3$, of the calcite-type and of the NaCl-type, are reversibly formed above 830 °C and 960 °C, respectively.

The structure of aragonite-type BaCO$_3$ (mineral name is witherite) is illustrated in Fig. 2.5.
Table 2.2. Crystallographic data for different modifications of BaCO$_3$.

<table>
<thead>
<tr>
<th>T, °C</th>
<th>Space group</th>
<th>Symmetry</th>
<th>a, nm</th>
<th>b, nm</th>
<th>c, nm</th>
<th>α, °</th>
<th>β, °</th>
<th>γ, °</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>Pmcn</td>
<td>orthorhombic</td>
<td>0.53</td>
<td>0.888</td>
<td>0.642</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>aragonite</td>
</tr>
<tr>
<td>830</td>
<td>R3m</td>
<td>rhombohedral</td>
<td>0.52</td>
<td>0.52</td>
<td>1.055</td>
<td>90</td>
<td>90</td>
<td>120</td>
<td>calcite</td>
</tr>
<tr>
<td>960</td>
<td>Fm3m</td>
<td>cubic</td>
<td>0.696</td>
<td>0.696</td>
<td>0.696</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>NaCl</td>
</tr>
</tbody>
</table>

Fig. 2.5. Illustration of aragonite-type BaCO$_3$. (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 CO$_3^{2-}$ ion is surrounded by six Ba ions and each Ba ion has nine nearest oxygen neighbours. The Ba ions in BaCO$_3$ are approximately hexagonally close-packed, alternating with layers of CO$_3^{2-}$ ions perpendicular to the c-axis. The CO$_3^{2-}$ ion deviates very slightly from planarity, but the O-Ba-O angles do not differ from 120°.

B. BaTiO$_3$

Several ferroelectrics crystallise in a perovskite structure with a general chemical formula ABO$_3$, where A and B are cations and O is an anion. Perovskite (calcium titanium oxide, CaTiO$_3$) 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.

Barium titanate (BaTiO$_3$) is well-known to have several phase transitions, depending on temperature. Above the Curie temperature ($\approx$ 120 °C), it has the cubic perovskite structure (with Ba$^{2+}$ as A and Ti$^{4+}$ 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.

However, there are two high temperature forms of BaTiO$_3$: 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 BaTiO$_3$ transforms into the hexagonal form.$^{45,46}$ These two modifications are built from close-packed (111) layers of composition BaO$_3$. In cubic BaTiO$_3$ 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 BaTiO$_3$ 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, BaTiO$_3$ 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 BaTiO$_3$ synthesis. As shown below, the reaction experiments were performed at temperatures between 575 °C and 1000 °C, where BaTiO$_3$ is cubic and the question of phase transitions of BaTiO$_3$ will be not considered in detail. Consequently, the pseudocubic indexing for BaTiO$_3$ will be used (a= 0.4 nm).

C. Ba$_2$TiO$_4$

Ba$_2$TiO$_4$ (barium orthotitanate) is the most Ba-rich compound in the system BaO-TiO$_2$. It is formed as an intermediate phase during the synthesis of BaTiO$_3$ by solid state reaction between BaCO$_3$ and TiO$_2$. Ba$_2$TiO$_4$ 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
2.2 Synthesis of BaTiO\textsubscript{3} ceramics

The orthorhombic Ba\textsubscript{2}TiO\textsubscript{4} was observed to be a chemically unstable compound and it decomposed when exposed to air.\textsuperscript{55,56} Monoclinic Ba\textsubscript{2}TiO\textsubscript{4} has a \( \beta \)-Ca\textsubscript{2}SiO\textsubscript{4} 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 Ba\textsubscript{2}TiO\textsubscript{4} has a distorted \( \beta \)-K\textsubscript{2}SO\textsubscript{4} structure. Its unit cell has the dimensions: a= 0.765 nm, b= 1.055 nm, c= 0.61 nm (space group Pnam).\textsuperscript{52} The orthorhombic structure consists of tetravalent titanium cations in an unusual tetrahedral coordination (Fig. 2.7).

![Orthorhombic unit cell of Ba\textsubscript{2}TiO\textsubscript{4}. TiO\textsubscript{4} tetrahedra are shown with lines.](image)

2.2.3 Formation of BaTiO\textsubscript{3} from BaCO\textsubscript{3} and TiO\textsubscript{2} by solid state reactions

During the past decades, compounds in the BaO-TiO\textsubscript{2} 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 BaTiO\textsubscript{3}. Due to their ferroelectric and dielectric properties, the perovskite-type BaTiO\textsubscript{3}-based materials have many applications in electronics devices such as high-performance multilayer ceramics capacitors (MLCCs), sensors and thermoresistors. The industrial way to produce BaTiO\textsubscript{3} is the solid state reaction between BaCO\textsubscript{3} and TiO\textsubscript{2} at temperatures as high as 1200 °C. This reaction can be described as follows:

\[
\text{BaCO}_3 + \text{TiO}_2 \rightarrow \text{BaTiO}_3 + \text{CO}_2 \uparrow. \tag{2.15}
\]

A lot of work has been devoted in order to understand details of reaction (2.15). The above reaction frequently occurs via an intermediate Ba\textsubscript{2}TiO\textsubscript{4} compound. Even a few percent of this phase unfavourably affect the electrical properties of BaTiO\textsubscript{3} based ceramics.\textsuperscript{57} In recent years a great
deal of attention has been given to the problem how to explain the formation of the two titanates (BaTiO$_3$ and Ba$_2$TiO$_4$). The main results and assumptions are summarised below.

In the 1950s, the formation of BaTiO$_3$ has been extensively studied by several groups. Tzebiatowski et al. and Kubo et al. studied the formation of BaTiO$_3$ from BaCO$_3$ and TiO$_2$ (mainly rutile) by heating the raw materials at certain temperatures and analysing the reaction mixtures by using selectively acting acids. They agree that some BaTiO$_3$ forms first according to reaction (2.15) and then Ba$_2$TiO$_4$, and finally Ba$_2$TiO$_4$ combines with the remaining TiO$_2$ to form BaTiO$_3$; but they do not agree on the way of Ba$_2$TiO$_4$ formation. Tzebiatowski et al. indicated that Ba$_2$TiO$_4$ is formed directly from BaCO$_3$ and TiO$_2$ according to the following reaction:

$$2\text{BaCO}_3 + \text{TiO}_2 \rightarrow \text{Ba}_2\text{TiO}_4 + 2\text{CO}_2 \uparrow,$$

(2.16)

whereas Kubo et al. concluded that Ba$_2$TiO$_4$ can not be formed according to reaction (2.16) and is produced by reaction between BaTiO$_3$ and BaCO$_3$ according to the following reaction:

$$\text{BaCO}_3 + \text{BaTiO}_3 \rightarrow \text{Ba}_2\text{TiO}_4 + \text{CO}_2 \uparrow.$$

(2.17)

Templeton et al. studied the formation of BaTiO$_3$ in air and CO$_2$ by differential thermal analysis. They found that a small amount of BaTiO$_3$ is formed first directly from BaCO$_3$ and TiO$_2$ (rutile). Then, Ba$_2$TiO$_4$ forms according to the reaction (2.17) and occurs in largest amounts until all the BaCO$_3$ is gone; now experiments confirmed the formation of an intermediate compound according to the reaction proposed by Kubo et al.. Ba$_2$TiO$_4$ 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 CO$_2$ gas, the intermediate Ba$_2$TiO$_4$ step was suppressed up to a temperature of about 1100 °C. But it was mentioned that Ba$_2$TiO$_4$ reacts fast within an atmosphere of 1 atmosphere of CO$_2$ below 1100 °C to produce BaTiO$_3$ and BaCO$_3$. In addition, the authors reported that a high pressure of oxygen (heating was performed in air) is not necessary for Ba$_2$TiO$_4$ formation. The results of Templeton et al. performed with rutile TiO$_2$ powder are in agreement with findings of Syama et al. who studied the formation of BaTiO$_3$ using TiO$_2$ anatase powder.

Later, the dependence of the reaction kinetics on $P_{\text{CO}_2}$, $P_{\text{N}_2}$ and $P_{\text{O}_2}$ for the reaction (2.15) with rutile TiO$_2$ have been investigated by Cournil et al.. It was found that the formation rate of BaTiO$_3$ continuously decreases with increasing $P_{\text{CO}_2}$ or $P_{\text{N}_2}$ whereas $P_{\text{O}_2}$ leads to a minimum rate under a certain condition ($P_{\text{O}_2} = 112.5$ 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. have supplemented the data already obtained on the synthesis of BaTiO$_3$ in air and in the presence of CO$_2$ (1 bar). In air, BaTiO$_3$ is formed first according to reaction (2.15). Ba$_2$TiO$_4$ then forms at the expense of BaTiO$_3$ according to reaction (2.17). When all the BaCO$_3$ has been consumed, the reaction (2.17) stops and the final reaction occurs according to the following equation:

$$\text{Ba}_2\text{TiO}_4 + \text{TiO}_2 \rightarrow 2\text{BaTiO}_3.$$

(2.18)
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 BaCO$_3$ according to:

$$\text{BaCO}_3 \rightarrow \text{BaO} + \text{CO}_2 \uparrow; \quad (2.19)$$

b) Formation of Ba$_2$TiO$_4$ by reaction between the two oxides:

$$2\text{BaO} + \text{TiO}_2 \rightarrow \text{Ba}_2\text{TiO}_4; \quad (2.20)$$

c) Finally, synthesis of BaTiO$_3$ according to the reaction (2.18).

Second scheme:

a) Decomposition of BaCO$_3$ according to reaction (2.19);

b) Formation of BaTiO$_3$ by direct reaction between the oxides:

$$\text{BaO} + \text{TiO}_2 \rightarrow \text{BaTiO}_3; \quad (2.21)$$

c) Formation of Ba$_2$TiO$_4$ at the expense of BaTiO$_3$ according to:

$$\text{BaTiO}_3 + \text{BaO} \rightarrow \text{Ba}_2\text{TiO}_4; \quad (2.22)$$

d) Finally, Ba$_2$TiO$_4$ reacts with the TiO$_2$ nucleus to form BaTiO$_3$ 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 BaCO$_3$/TiO$_2$, BaCO$_3$/BaTiO$_3$/TiO$_2$ and Ba$_2$TiO$_4$/BaTiO$_3$/TiO$_2$. In the first reaction couples, a layer of BaTiO$_3$ was found after heat treatment at 750 °C for less than one hour inside the TiO$_2$ layer. With longer treatment times (24 h) at the same temperature, two layers were observed within TiO$_2$: the inner layer (in contact with TiO$_2$) consists of BaTiO$_3$ and the outer layer consists of Ba$_2$TiO$_4$. In the second reaction couples, a layer of Ba$_2$TiO$_4$ was formed after heat treatment at 850 °C for 3 days within the BaTiO$_3$ pellet. The formation of BaTiO$_3$ as well as Ba$_2$TiO$_4$ were explained by diffusion of barium through TiO$_2$ and BaTiO$_3$, 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 Ba$_2$TiO$_4$ into BaTiO$_3$ occurred through an unidentified species of BaO stoichiometry which diffuses towards TiO$_2$ through the BaTiO$_3$ layer. Based on these experimental results, Mutin et al.$^{71}$ proposed a model consisting of TiO$_2$ grains covered by BaCO$_3$.

At the beginning of the 1990s, Niepce et al.$^{12}$ summarised the main experimental results and suggested a model based on spherical TiO$_2$ particles surrounded by BaCO$_3$. From this arrangement, they deduced that it is possible to prevent the formation of the Ba$_2$TiO$_4$ 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 BaTiO$_3$ can be formed according to different processes: directly by barium and oxygen diffusion into TiO$_2$ and by degradation of Ba$_2$TiO$_4$. Such core-shell structured BaCO$_3$-TiO$_2$ substances were prepared by Gablenz et al.\textsuperscript{13} (BaCO$_3$ (shell)-TiO$_2$ (core), with diameters of core-shell grains up to several $\mu$m) in the year 2001 and by Buscaglia et al.\textsuperscript{14} (BaCO$_3$ (core)-TiO$_2$ (shell), with sizes of core-shell grains $\approx$ 100 nm-500 nm in length and $\approx$ 50 nm in width) in the year 2007. Heating of the core-shell powders prepared by Gablenz et al.\textsuperscript{13} showed a modified sequence of phases.$^{13,15,16}$ The formation of BaTiO$_3$ besides remaining BaCO$_3$ and TiO$_2$ was observed after reaction at 800 °C (holding time 0 min). Further heating leads to the formation of the Ba$_2$TiO$_4$ phase (900 °C-1100 °C, holding time 0 min) and different Ti-rich phases with the general formula BaTi$_x$O$_{1+2x}$ ($x= 2, 4, 5$) (850 °C-1050 °C, holding time 0 min). The formation of a single BaTiO$_3$ 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.\textsuperscript{14} showed a complete formation of a single BaTiO$_3$ 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.\textsuperscript{17} and by Buscaglia et al.,\textsuperscript{18} respectively. Hennings et al. found that the formation of the Ba$_2$TiO$_4$ compound in air can be suppressed in a reaction between submicrometer BaCO$_3$ (0.17 $\mu$m) and fine TiO$_2$ (0.2 $\mu$m). Thus, the predictions made by Niepce et al.\textsuperscript{12} were confirmed. 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$_2$TiO$_4$ secondary phase. However, the decrease of pressure to 40 mbar induced the formation of Ba$_2$TiO$_4$ at a reaction temperature of 740 °C.

There was also one attempt to investigate the BaTiO$_3$ formation in a thin-film system. Tochitsky et al.\textsuperscript{72} have investigated solid state reactions in the multicomponent thin film systems TiO$_2$/BaO, TiO$_2$/BaCO$_3$, TiO$_2$/PbO, and TiO$_2$/Bi$_2$O$_3$. 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 TiO$_2$/BaCO$_3$ system after annealing between 500 °C and 800 °C only the BaTiO$_3$ compound formed whereas the synthesis of BaTiO$_3$ during annealing of the TiO$_2$/BaO system occurred through an intermediate Ba$_2$TiO$_4$ 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 BaTiO$_3$ formation from BaCO$_3$ and TiO$_2$ 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

The are many compounds which form by a reaction between BaTiO$_3$ and TiO$_2$ as well as between BaO and TiO$_2$. Some of these compounds are of great interest and technological importance. Statton$^{73}$ has tried first to establish phase relations in the BaO-TiO$_2$ system. Later, this phase diagram was restudied and improved by many other works.$^{74–81}$

A high-temperature phase diagram constructed for the system BaTiO$_3$-TiO$_2$ is shown in Fig. 2.8.$^{45}$ The determination of the phase relations was based on X-ray diffraction and microscopic 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 Ba$_6$Ti$_{17}$O$_{40}$, Ba$_4$Ti$_{13}$O$_{30}$, BaTi$_4$O$_9$ and Ba$_2$Ti$_9$O$_{20}$. The last two Ti-rich phases are used in microwave industry.$^{81}$ Other supposedly possible Ti-rich barium titanates such as BaTi$_5$O$_{11}$ and BaTi$_6$O$_{13}$ have not been observed in these studies. The compound BaTi$_2$O$_5$ was found in a sample with 65 mol% TiO$_2$ quenched from the liquid state. However, heating of this sample at 1320 °C for 64 h resulted in a mixture of BaTiO$_3$ and Ba$_6$Ti$_{17}$O$_{40}$ with no evidence of any remaining BaTi$_2$O$_5$. It was noted that these three Ti-rich barium titanates form only through a liquid intermediate.

However, Ritter et al.$^{78}$ obtained BaTi$_2$O$_5$ and BaTi$_5$O$_{11}$ 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 BaTi$_2$O$_5$ and BaTi$_5$O$_{11}$ phases crystallise.

---

**Fig. 2.8.** BaTiO$_3$-TiO$_2$ equilibrium phase diagram, see also Fig. A.1 in the appendix (magnified version of the diagram).
at ∼ 700 °C. BaTi$_2$O$_5$ decomposes into Ba$_6$Ti$_{17}$O$_{40}$ and BaTiO$_3$ at ∼1150 °C while BaTi$_5$O$_{11}$ decomposes to TiO$_2$, Ba$_2$Ti$_9$O$_{20}$ and/or BaTi$_4$O$_9$ at ∼1200 °C. Thus, we can conclude that both these phases (BaTi$_2$O$_5$ and BaTi$_5$O$_{11}$) 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. BaTi$_4$O$_9$ and BaTi$_2$O$_5$ 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. BaTi$_6$O$_{13}$, BaTi$_5$O$_{11}$, Ba$_4$Ti$_{13}$O$_{30}$, Ba$_2$Ti$_9$O$_{20}$, Ba$_2$Ti$_{13}$O$_{22}$ and Ba$_6$Ti$_{17}$O$_{40}$, are more complex but can be described as close packing of Ba and O atoms in which some of the octahedral O$_6$ 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 BaTiO$_3$. 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 Ba$_6$Ti$_{17}$O$_{40}$, the lattice constant $c$ = 1.892 nm (∼ 8×0.234 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.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Space group</th>
<th>Symmetry</th>
<th>a, nm</th>
<th>b, nm</th>
<th>c, nm</th>
<th>α, °</th>
<th>β, °</th>
<th>γ, °</th>
<th>Number of layers</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaTi$_2$O$_5$</td>
<td>A2/m</td>
<td>monoclinic</td>
<td>0.9409</td>
<td>0.393</td>
<td>1.69</td>
<td>90</td>
<td>103.5</td>
<td>90</td>
<td>86</td>
<td></td>
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<tr>
<td>BaTi$_4$O$_9$</td>
<td>Pmmm</td>
<td>orthorhombic</td>
<td>1.452</td>
<td>0.379</td>
<td>0.629</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>87</td>
<td></td>
</tr>
</tbody>
</table>

Close-packed type

<table>
<thead>
<tr>
<th>Phase</th>
<th>Space group</th>
<th>Symmetry</th>
<th>a, nm</th>
<th>b, nm</th>
<th>c, nm</th>
<th>α, °</th>
<th>β, °</th>
<th>γ, °</th>
<th>Number of layers</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaTi$<em>6$O$</em>{13}$</td>
<td>P1̅</td>
<td>triclinic</td>
<td>0.751</td>
<td>0.985</td>
<td>0.746</td>
<td>105.38</td>
<td>118.9</td>
<td>72.58</td>
<td>4</td>
<td>82</td>
</tr>
<tr>
<td>Ba$_2$Ti$<em>9$O$</em>{20}$</td>
<td>P1̅</td>
<td>triclinic</td>
<td>0.747</td>
<td>1.408</td>
<td>1.434</td>
<td>89.94</td>
<td>79.43</td>
<td>84.45</td>
<td>6</td>
<td>88,89</td>
</tr>
<tr>
<td>Ba$_4$Ti$<em>5$O$</em>{11}$</td>
<td>P2$_1$/n</td>
<td>monoclinic</td>
<td>0.767</td>
<td>1.402</td>
<td>0.752</td>
<td>90</td>
<td>98.33</td>
<td>90</td>
<td>6</td>
<td>90</td>
</tr>
<tr>
<td>Ba$<em>2$Ti$</em>{13}$O$_{22}$</td>
<td>Bmab</td>
<td>orthorhombic</td>
<td>1.165</td>
<td>1.410</td>
<td>1.005</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>6</td>
<td>91</td>
</tr>
<tr>
<td>Ba$<em>4$Ti$</em>{13}$O$_{30}$</td>
<td>Cmca</td>
<td>orthorhombic</td>
<td>1.706</td>
<td>0.986</td>
<td>1.405</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>6</td>
<td>92</td>
</tr>
<tr>
<td>Ba$<em>6$Ti$</em>{17}$O$_{40}$</td>
<td>C2/c</td>
<td>monoclinic</td>
<td>0.988</td>
<td>1.708</td>
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<td>90</td>
<td>98.42</td>
<td>90</td>
<td>8</td>
<td>93</td>
</tr>
<tr>
<td>Ba$_2$Ti$<em>5$O$</em>{12}$</td>
<td>Ammm</td>
<td>orthorhombic</td>
<td>0.99</td>
<td>1.14</td>
<td>2.35</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>10</td>
<td>94,95</td>
</tr>
</tbody>
</table>

plane in Ba$_6$Ti$_{17}$O$_{40}$ is $\approx 1.3^\circ$. The compositions of other Ti-rich barium titanates can be derived by analogy to the layers in Ba$_6$Ti$_{17}$O$_{40}$ and Ba$_4$Ti$_{13}$O$_{30}$ as was shown by Roth et al. for the phases Ba$_6$Ti$_{14}$Nb$_2$O$_{39}$, Ba$_{14}$Ti$_{40}$Nb$_2$O$_{99}$ and Ba$_{18}$Ti$_{54}$Nb$_2$O$_{132}$. Recently, a topotaxial orientation relationship between BaTiO$_3$ and Ba$_6$Ti$_{17}$O$_{40}$ as well as between BaTiO$_3$ and Ba$_4$Ti$_{13}$O$_{30}$ has been established. Despite the different procedure of sample preparation (solid state reaction of BaCO$_3$ and TiO$_2$ at high temperatures in air or chemical reaction of SiO$_2$ film with BaTiO$_3$ single crystals), the Ti-rich phases (TRP) grow in all cases according to the following orientation relationship:

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

(2.23)

Thus, the close-packed planes of Ba$_6$Ti$_{17}$O$_{40}$ and Ba$_4$Ti$_{13}$O$_{30}$ lie parallel to the close-packed planes of BaTiO$_3$. Crystalllographically, Kraševljev et al. explained the orientation relationship between Ba$_6$Ti$_{17}$O$_{40}$ and BaTiO$_3$ phases by the similarity of the stacking sequence of (111) planes of BaTiO$_3$ and (001) planes of Ba$_6$Ti$_{17}$O$_{40}$, if the larger unit cell of the monoclinic Ba$_6$Ti$_{17}$O$_{40}$ phase was appropriately cut. On the base of the above relationship a model of a topotactic boundary between Ba$_6$Ti$_{17}$O$_{40}$ and BaTiO$_3$ phases was constructed.

2.3 The system SrO-TiO$_2$

In the bulk phase diagram of the system SrO-TiO$_2$ (Fig. 2.10), several compounds are known such as Sr$_2$TiO$_4$, Sr$_3$Ti$_2$O$_7$ and SrTiO$_3$. There is an eutectic at 1440 °C between SrTiO$_3$ and TiO$_2$.

Sr$_2$TiO$_4$ has a tetragonal structure with a=b= 0.388 nm and c= 1.26 nm (space group I4/mmm) while Sr$_3$Ti$_2$O$_7$ has also a tetragonal structure with a=b= 0.39 nm and c= 2.038 nm (space group I4/mmm).
2.4 The system CaO-TiO₂

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):

$$\text{SrCO}_3 + \text{TiO}_2 \rightarrow \text{SrTiO}_3 + \text{CO}_2 \uparrow.$$  \hspace{1cm} (2.24)

No intermediate products were observed during SrTiO₃ synthesis by Tagawa and Igarashi¹⁰² as well as by Chang and Liu¹⁰³ However, recent results suggested that the above reaction occurred via an intermediate Sr₂TiO₄ compound.¹⁰⁴

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-Tc 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
2.5 The system MgO-TiO$_2$

In the system MgO-TiO$_2$, several compounds are known such as MgTi$_2$O$_5$, Mg$_2$TiO$_4$ and MgTiO$_3$ (Fig. 2.12). MgTi$_2$O$_5$ (armalcolite) has a pseudobrookite structure with $a=0.97$ nm, $b=1$ nm and $c=0.37$ nm (space group Bbmm), while Mg$_2$TiO$_4$ (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 P4$_1$22, spinel) at 500 °C. MgTiO$_3$ (geikielite) has a rhombohedral...
2.5 The system MgO-TiO$_2$

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-TiO$_2$ (Fig. 4336 in Ref. $^{101}$), see also Fig. A.5 in the appendix (magnified version of the diagram).](image)

Mg$_2$TiO$_4$ has attracted attention because of its optical properties to be used in integrated optics and as a dielectric material. Epitaxial layers of Mg$_2$TiO$_4$ grown by solid-state reaction between (001) MgO single crystals and TiO$_2$ have been used as buffer layers for growing high temperature superconducting thin films.$^{118-120}$ On the other hand, MgTiO$_3$ is known as a dielectric material which has good dielectric properties at high frequencies as well as a high thermal stability. Bulk MgTiO$_3$ is used for microwave ceramic capacitors and resonators.$^{121-124}$ MgTiO$_3$ has a refractive index of 1.95 which lies between that of LiNbO$_3$ (2.2) and Al$_2$O$_3$ (1.7).$^{125}$ Thus, MgTiO$_3$ thin films can be used as a cladding layer. Mostly, MgTiO$_3$ has been produced and studied in bulk ceramic form. However, there have been some reports on fabrication and properties of MgTiO$_3$ thin films.$^{126,127}$

Spinel-forming topotaxial solid state reactions like:

$$2AO + BO_2 \rightarrow A_2BO_4 \text{ or } AO + B_2O_3 \rightarrow AB_2O_4$$

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 Mg$_2$TiO$_4$, Mg$_2$SnO$_4$, MgIn$_2$O$_4$, MgAl$_2$O$_4$, MgCr$_2$O$_4$ and MgFe$_2$O$_4$, 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.