Materials Science Forum Vols. 294-296 (1999) pp. 597-600

Topotaxial Reaction Fronts in Complex Ba-Ti-Si Oxide Systems Studied by Transmission Electron Microscopy

D. Hesse, A. Graff, S. Senz and N.D. Zakharov

Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, D-06120 Halle/Saale, Germany

Keywords: Interfaces, Solid State Reactions, Titanates, High-Resolution TEM, Reaction Mechanisms

Abstract

Processes and interface structures occurring during $BaTiO_3$ sintering in the presence of the sintering aid SiO_2 are studied by model experiments. The formation of fresnoite $Ba_2TiSi_2O_8$ and different Ti-rich barium titanates by solid state reactions proceeding at the $(001)BaTiO_3/SiO_2$ interface is followed by XRD and TEM. High resolution transmission electron microscopy (HRTEM) permits the structure to be studied of the various solid-solid reaction fronts involved. The observations indicate, e.g., a certain topotaxial reaction mechanism at the $Ba_4Ti_{13}O_{30}/BaTiO_3(001)$ and $Ba_6Ti_{17}O_{40}/BaTiO_3(001)$ reaction fronts, which comprises the outdiffusion of barium, the indiffusion of titanium and oxygen, and a restacking of the $BaTiO_3\{111\}$planes.

1. Introduction

Complex reactions between $BaTiO_3$ and SiO_2 generally occur during the sintering processes of $BaTiO_3$ ceramics, if the sintering aid SiO_2 is applied [1-3]. Phases forming and processes or structures occurring during these complex reactions, have, however, not been studied in detail. Recently, spinel oxide reactions of medium complexity have successfully been evaluated, and certain topotaxial reaction mechanisms have been derived, after investigating the structure of the involved reaction fronts by high resolution cross-sectional electron microscopy. Interrelations between the structure of the reaction front, the mechanism of the interfacial reaction, and the overall kinetics were established [4-7]. In view of this rather successful approach investigations of more complex reactions in the $BaTiO_3$-SiO_2 system are now under way. After describing details of phase formation and orientation relationships in Refs. 8 and 9, we now report on recent results concerning the structure of the involved reaction fronts.

2. Experimental

Thin amorphous SiO_2 films of 100 nm thickness were electron-beam deposited onto polished $BaTiO_3(001)$ single-crystal surfaces ($10x10x1mm^3$) in high vacuum, maintaining an oxygen pressure of 10^{-2} Pa and a substrate temperature of 500 °C. After deposition, the samples were annealed in air in a laboratory furnace for 2 h and 8 h, respectively, at temperatures between 700 and 1300 °C. Thin-film X-ray diffraction (θ-2θ scans and pole figures) was performed in a Philips X'Pert MRD equipped with a Cu tube and an open Eulerian cradle. Specimens for TEM were prepared by mechanical and ion beam thinning following standard procedures. TEM/SAED and EDX investigations were performed in a Philips CM20T, whereas a JEOL 4000 EX was applied for HRTEM.

3. Results

3.1. Phase formation and crystallographic orientation

Starting at a reaction temperature of 700 °C, solid state reactions between the SiO_2 film and the $BaTiO_3$ substrate were observed to occur. At 700 and 800 °C, $Ba_2TiSi_2O_8$ (fresnoite) islands originate at the $BaTiO_3/SiO_2$ interface and grow through the SiO_2 film to the surface of the latter, where they continue to grow in lateral direction (Fig. 1). This reaction obviously follows the overall scheme

$$2\,BaTiO_3 + 2\,SiO_2 \rightarrow Ba_2TiSi_2O_8\ \text{(fresnoite)} + TiO_2. \tag{1}$$

From XRD, SAED and HRTEM the orientation relation

$$(120)_F \text{ or } (210)_F \parallel (001)_{BT};\ [001]_F \parallel [100]_{BT} \text{ or } [010]_{BT} \tag{2}$$

was deduced („F“- fresnoite; „BT“ - $BaTiO_3$) [8]. After about 2 h at 800 °C, large fresnoite grains have formed, with small amorphous regions remaining. At higher temperatures, fresnoite loses its orientation (2) and turns polycrystalline assuming a fiber texture [9]. A marker experiment [9], with platinum islands steadily marking the position of the initial $BaTiO_3/SiO_2$ interface, showed that during the fresnoite formation both in- and out-diffusion processes occur. Reactions of the released TiO_2 (*cf.* Eq. 1) with the $BaTiO_3$ substrate result in the formation of Ti-rich phases. For example, $Ba_4Ti_{13}O_{30}$ and $Ba_6Ti_{17}O_{40}$ form at temperatures above 1000 °C according to the overall reactions

$$4\,BaTiO_3 + 9\,TiO_2 \rightarrow Ba_4Ti_{13}O_{30}, \tag{3}$$

$$6\,BaTiO_3 + 11\,TiO_2 \rightarrow Ba_6Ti_{17}O_{40}. \tag{4}$$

The Ti-rich phases form grains of a distinct crystallographic habit. They are located between the fresnoite grains, but they are in contact with the $BaTiO_3$ substrate (Fig. 2). The Ti-rich phases („TRP“) proved [8,9] to grow according to the orientation relation (*cf.* [10])

$$(001)_{TRP} \parallel (111)_{BT};\ [010]_{TRP} \parallel [110]_{BT}. \tag{5}$$

Other Ti-rich phases also grow, the lattice parameters of which, however, do not correspond to either of the Ti-rich Ba-Ti-O phases known from the JCPDS files [11]. The characterization of these phases by SAED and PEELS is in progress. In terms of the present paper they will be named „new titania-rich“ („NTR“) phases. Structurally, these NTR phases are very similar to $Ba_4Ti_{13}O_{30}$ and $Ba_6Ti_{17}O_{40}$. For example, they are characterized by stacked planes and typical stacking faults (*cf.* Fig. 3) parallel to the $BaTiO_3\{111\}$ planes, on the very analogy of the (001) planes of $Ba_4Ti_{13}O_{30}$ and $Ba_6Ti_{17}O_{40}$. Their crystallographic orientation follows a relation most similar to Eq. 5.

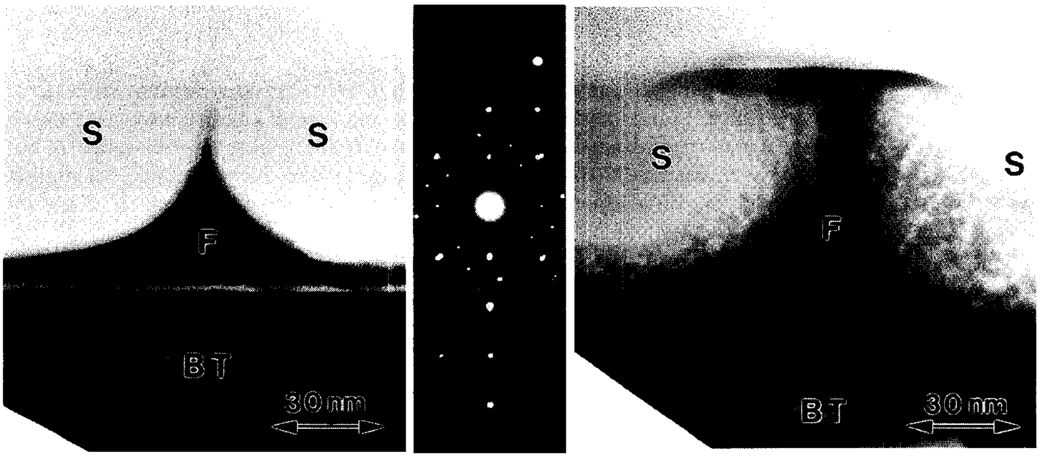

Fig. 1 Cross section TEM images demonstrating two growth stages of fresnoite islands (F) grown into the SiO_2 film (S) on the $BaTiO_3$ substrate (BT). The inset shows a fresnoite diffraction pattern together with some $BaTiO_3$ substrate reflections. Beam direction is $[100]_{BT} = [001]_F$.

3.2. Grain morphology

In TEM cross-sectional micrographs the TRP grains (including the NTR grains) are easy to recognize, because most of them have an elongated, distinctly plate-like shape (Figs. 2 and 3). The plate surfaces („PS"), seen edge-on in the figures, are formed by the $(001)_{TRP}$ planes. In accordance with Eq.5, the latter are parallel to the $\{111\}_{BT}$ planes of the substrate thus forming an angle of 54.7° (or 125.3°, resp.) with the $BaTiO_3(001)$ substrate surface. As Fig.3 also shows, the TRP grains contain stacking faults, most of which are parallel to the $(001)_{TRP}$ planes.

3.3. Reaction fronts

Figure 4 shows a cross section HRTEM image of a typical TRP/$BaTiO_3$ reaction front located under a TRP grain. Clearly visible are the plate surface („PS") and the $(001)_{TRP}$ planes, both making an angle of 125.3° with the „actual" $BaTiO_3(001)$ substrate surface („ASS"). Due to the reaction, the actual substrate surface most probably moved down from the initial position of the $BaTiO_3$ substrate surface. The proper reaction front is formed by the end faces of broad stacks of (001) planes separated by ledges („L"). The stacks, in turn, consist of bundles of individual (001) planes, which clearly suggest to have moved into the $BaTiO_3$ substrate. Taking into account that the formation of the TRP (NTR) phase *within* the $BaTiO_3$ substrate obviously proceeds in a stress-free manner, the following reaction mechanism has been derived: The grains of the Ti-rich phases, i.e. $Ba_4Ti_{13}O_{30}$, $Ba_6Ti_{17}O_{40}$, or one of the NTR phases, grow into the $BaTiO_3$ substrate along the $(111)_{BT}$ planes. Along the latter, Ba ions are outdiffusing and Ti and oxygen ions are indiffusing, whereas at the reaction front the $(111)_{BT}$ planes are rearranged into $(001)_{TRP}$ planes by corresponding atomic-scale steps. The nature of the latter may be deduced from a detailed evaluation of the structures. The lattice of $BaTiO_3$ consists of regularly stacked BaO_3 and Ti layers parallel to the $\{111\}$ plane. If Ba ions are removed from two neighbouring BaO_3 planes, and a Ti ion is allowed to occupy a corresponding site in the Ti layer in between, a Ti-rich lattice may form out of the $BaTiO_3$ lattice. Details are under investigation.

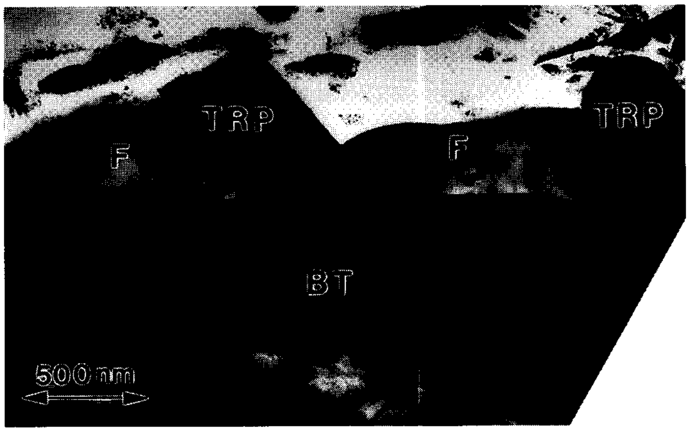

Fig. 2 Cross section TEM image showing two grains of Ti-rich phases (TRP) grown in between the fresnoite grains (F) on the $BaTiO_3$ substrate (BT). Beam direction is $[1\bar{1}0]_{BT} = [010]_{TRP}$.

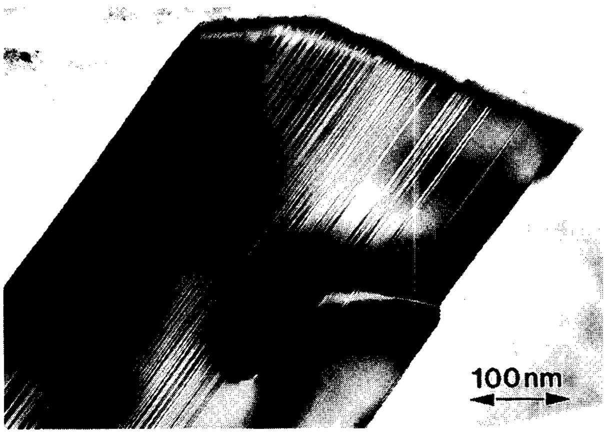

Fig.3 Cross section TEM image of a Ti-rich grain with a large number of stacking faults on the $(001)_{TRP}$ planes. Beam direction is $[010]_{TRP}$.

Fig.4 HRTEM cross section image of the reaction front under a Ti-rich grain. Beam direction is $[1\bar{1}0]_{BT} = [010]_{TRP}$.

4. Conclusions

Sintering processes of $BaTiO_3$ ceramics with SiO_2 as the sintering aid have been modeled by single-crystal investigations. At temperatures above 700 °C and 1000 °C, respectively, fresnoite $Ba_2TiSi_2O_8$ and various Ti-rich phases ($Ba_4Ti_{13}O_{30}$, $Ba_6Ti_{17}O_{40}$ and other new phases) form by solid state reactions. Fresnoite forms by the diffusion of Ba and Ti out of the $BaTiO_3$ substrate, and of Si into it. At low temperatures (700 and 800 °C), fresnoite obviously nucleates at the $BaTiO_3$ surface and grows topotaxially in a near-coincidence site lattice orientation, whereas at higher temperatures the nuclei are more or less randomly oriented. The Ti-rich phases (TRP) always grow well oriented. They are formed by a topotaxial reaction involving the barium outdiffusion and the titanium and oxygen indiffusion along the $(001)_{TRP}$ planes as well as a well-ordered restructuring of the $\{111\}_{BT}$ planes into the $(001)_{TRP}$ planes at the reaction front.

Acknowledgement

The authors are grateful to Professor H.-P.Abicht for numerous fruitful discussions and helpful comments, as well as to Professor U.Gösele for his continuous support.

References

[1] H.-P.Abicht, H.T.Langhammer, and K.-H.Felgner, J.Mater.Sci. **26** (1991) p.2337.
[2] K.H.Felgner, U.Nilius, H.T.Langhammer, and H.-P.Abicht, J.Mater.Chem. **2** (1992) p.575.
[3] H.F.Cheng, T.F.Lin, C.T.Hu, and I.N.Lin, J.Am.Ceram.Soc. **76** (1993) p.827.
[4] D.Hesse, Solid State Ionics **95** (1997) p.1.
[5] H.Sieber, D.Hesse and P.Werner, Phil. Mag. A **75** (1997) p.889.
[6] H.Sieber, P.Werner and D.Hesse, Phil. Mag. A **75** (1997) p.909.
[7] A.Graff, S.Senz, N.D.Zakharov and D.Hesse, *accepted by* Z.Phys.Chem. (1998).
[8] S.Senz, A.Graff, W.Blum, D.Hesse and H.-P.Abicht, *accepted by* J.Am.Ceram.Soc. (1998).
[9] S.Senz, A.Graff, W.Blum, H.-P.Abicht, and D.Hesse, *submitted to* Proc. 9th World Ceramic Congress & Forum on New Materials CIMTEC'98, Florence/Italy, June 14-19, 1998.
[10] V.Krasevec, M.Drofenik, and D.Kolar, J.Am.Ceram.Soc. **70** (1987) p.C-193.
[11] JCPDS data base on CD-ROM, Int. Centre for Diffraction Data, Newton Square, PA (1995).