Surface modification of barium titanate powder particles

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Abstract

The surfaces of n-doped barium titanate (BaTiO₃) powder particles were modified by milling in a Ca(NO₃)₂ solution both at room temperature and under hydrothermal conditions before they were analyzed by electron energy loss spectroscopy and transmission electron microscopy down to the nanometer range.

The room temperature treated powders showed BaTiO₃ particles covered with a CaO/BaO layer. Heating these particles caused a shell of (Ca,Ba)TiO₃ solid solution. Under hydrothermal conditions rectangular CaTiO₃ crystallites precipitated on the surface of the BaTiO₃ grains, which during heating transformed into a series of (Ba_{1-x}Ca_x)TiO₃ particles. These modifications of the shell structure change the sintering behavior and thus the microstructure as well as the electrical properties of the final ceramics. Especially the room temperature resistance and the voltage withstanding of the ceramic increased compared to that of conventionally prepared materials of identical composition. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

The influence of distilled water as the milling liquid on the surface properties of barium titanate (BaTiO₃) powders was described in detail [1,2]. At room temperature BaTiO₃ is thermodynamically unstable in water having a pH value lower than 12 [3–5]. Under the influence of water and by mechanical activation during ball-milling Ba²⁺ ions are dissolved superficially from the BaTiO₃ particles according to Eq. (1).

For these materials, an amorphous TiO_x layer ($x \approx 2$) of 3–5 nm in thickness was detected on the periphery of the BaTiO₃ grains [2]. This TiO_x region acts as a protecting layer against further attack. Furthermore, the pH value and the Ba²⁺ concentration in the solution, increasing with the dissolution progress (Eq. (1)), prevent the immediate and complete dissolution of the BaTiO₃ grains. The dissolution

of the BaTiO₃ grains takes place by the diffusion of Ba²⁺ ions through the amorphous TiO_x layer until there is an equilibrium between BaTiO₃ (s), Ba²⁺ (aq.) and TiO₂ (s) under strong alkaline conditions. Following the amorphous TiO_x layer inwards, a crystalline defect-perovskite layer with a Ba/Ti molar ratio increasing from about 0 (outside) to 1 (inside) was found. This layer depleted in barium has a thickness of about 10 nm.

Under hydrothermal leaching conditions ($T = 180^\circ\text{C}$) the mechanism of dissolution of BaTiO₃ changes in the following way [6]. Both lattice constituents (BaO, TiO₂) dissolve superficially at the same rate. There were no Ba/Ti gradients in the remaining BaTiO₃ grains. Barium enters into the aqueous phase as Ba²⁺ ions, titanium dissolves as Ti(OH)₄ (solubility 10⁻⁸ mol/dm³ [4]). The dissolved Ti-species polycondensate and precipitate as crystalline TiO₂ on the surface of the BaTiO₃ grains under the conditions described above.

The stability fields of BaTiO₃ and CaTiO₃ were investigated by Lencka and Riman [6]. They found that CaTiO₃ crystallizes under hydrothermal conditions ($T = 160\text{--}200^\circ\text{C}$), and they measured a Ca²⁺ concentration of 10⁻⁴ mol/dm³ at pH values higher than 8. The stability region of BaTiO₃ under comparable conditions is shifted to higher pH values by one unit.

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The aim of the investigations presented here was to change the destructive modification of the BaTiO₃ surface caused by milling in water into a substituting one by milling in a Ca²⁺ containing medium. The basic idea is as follows. Starting with BaTiO₃ particles in a neutral aqueous environment BaTiO₃ dissolves superficially according to Eq. (1), and the pH value increases. If Ca²⁺ ions are present, CaTiO₃ should form as the thermodynamically more stable phase as indicated by Eq. (2).

In the literature, the influence of calcium substitutions in n-doped BaTiO₃ ceramics is discussed in two different aspects: if Ca²⁺ ions are substituting Ba-sites in the BaTiO₃ structure the microstructure of the final ceramic is homogenized [7]. Under certain conditions the Ca²⁺-ions occupy Ti-sites forming acceptor defects Ca_{Ti}'', and thus increasing the voltage withstanding and the electrical resistance of the ceramic [8–10].

2. Experimental

There were two procedures to modify the surfaces of the BaTiO₃ powder particles (and thus the grain boundaries of the processed ceramics) by Ca²⁺ ions:

1. The BaTiO₃ starting powder of the composition La_{0.002}Ba_{0.998}TiO₃ was prepared by the mixed oxide technique (calcination: 4 h at 1100°C). The powder was ball milled for 24 h at room temperature using an aqueous 0.0235 M Ca(NO₃)₂ solution as the milling liquid.
2. The starting powder was crushed, and 20 g of this powder was stirred in 80 ml of an aqueous Ca(NO₃)₂ solution (0.044 M) in a laboratory autoclave (Berghof HR 200) under autogeneous pressure at 180°C for 24 h.

After powder treatment both suspensions were separated. The liquid phase was analyzed by atomic absorption flame spectroscopy (Varian, Spectr AA 20 instrument). To simulate the reaction process in the surface layers during the sintering procedure of the ceramic bodies both powders were heated up to 1000°C and 1300°C, respectively. The phase composition of the powders was studied by X-ray diffraction (Siemens D5000, Cu K_α radiation, monochromator, continuous scan mode, scan width 0.02°, Si as the inner standard). The interesting peculiarities concerning the microstructure and nanochemistry of the boundary layers or interfaces were investigated by high resolution and high-voltage electron microscopy (HREM, HVEM) and electron energy-loss spectroscopy (EELS), especially on near-edge fine structures (ELNES). EELS was performed with an energy resolution of 0.8–1 eV using the Gatan imaging filter (GIF 200) attached to the transmission (TEM)/scan-

ning transmission electron microscope (STEM) Philips CM 20 FEG operated at 200 keV. Either point analyses were made in the nanoprobe mode, or series of EEL spectra along a line were recorded in the STEM mode, with the electron probe of about 1–2 nm in diameter digitally scanned by the Gatan Digiscan model 688. For image and spectrum processing the software packages Digital Micrograph and EL/P of Gatan were used.

For TEM investigations, the specimens were prepared by dispersing a small amount of the powder in pure alcohol, mixing it in an ultrasonic generator, and pipetting a drop of this dispersion on a copper mesh covered with a holey Formvar film. To minimize contamination effects during the analyses, which are generally strong for small electron probes of some nanometers, the specimen grid was kept at liquid nitrogen temperature via a cooling specimen holder (Gatan model 668). To fabricate ceramic bodies the powders were mixed with 5 wt% poly(vinyl alcohol) solution as a pressing aid for 24 h, then pressed into pellets (12 mm in diameter, 2 mm thick) of 3.1 g/cm³ in density, and sintered in air (1350°C, 1400°C, 1 h annealing time). For testing the electrical resistance the sintered pellets were first polished and then connected to gallium–indium eutectic to provide an ohmic contact. The electrical resistance at room temperature was determined by measuring the current *I* at a voltage of *U* = 0.1 V. The voltage withstanding was ascertained as the voltage value for minimum *I* in the *I/U* plot. This voltage value was correlated to the thickness of the pellet.

For electron probe microanalysis (CAMEBAX, Cameca) the samples were coated with carbon.

3. Results and discussion

3.1. Procedure 1

After 24 h of milling at room temperature, the Ba content was 0.54 mol% (compared to the amount of barium in the starting powder) in the milling liquid. On the other hand, the Ca content in the milling liquid decreased to 20 mol% (referring to the initial amount of Ca), i.e. 0.45 mol% Ca (referring to the amount of barium in the starting powder) was fixed in the BaTiO₃ powder. That means 80% of the dissolved Ba ions were replaced by Ca ions. The pH value of the solution after milling was 11.

The microstructure and composition of this powder as revealed by the electron microscope techniques are summarized in Fig. 1: the TEM bright-field image (cf. Fig. 1(a)) shows a BaTiO₃ powder particle, whereas Fig. 1(b) presents a series of EEL spectra recorded in the energy range between about 300 and 800 eV along the line drawn in Fig. 1(a). Ca is clearly detected by its L₂₃ edge in an outer zone extending up to 20–30 nm from the surface into the particle. Surprisingly, there is a surface-near zone of less than 10 nm in extension containing no, or only a small

Fig. 1. EELS analysis of BaTiO₃ particles after milling in Ca(NO₃)₂ solution at room temperature for 24 h: (a) TEM bright-field image of an individual particle, and (b) series of EEL spectra along the line marked in (a).

amount of, Ti. Since Ti is completely missing or partly depleted, the presence of a mixed Ba/Ca oxide is assumed. Moreover, the O–K energy loss near edge structure (ELNES) measured in the outer part of the surface layer exhibits only a broad maximum without distinct fine structures which is typical of titanates. These results are interpreted by the help of the complex equation (3), using the Kröger–Vink–Notation [11]:

Milling in an aqueous Ca(NO₃)₂ solution causes the Ba ions to be dissolved from the BaTiO₃ surface, as described in [1,2]. The resulting lattice defects V_{Ba}'' are electronically compensated by protons from the solution diffusing into the lattice, adhering to oxygen ions and thus forming positively charged $\text{OH}_{\text{O}}^\bullet$ defects. As a result the pH value of the solution increases, and Ca(OH)₂ preferentially precipitates because the solubility product K_{L} of Ca(OH)₂ is three orders of magnitude smaller than that of Ba(OH)₂ ($\text{p}K_{\text{L-Ca}(\text{OH})_2} = 4.78$, $\text{p}K_{\text{L-Ba}(\text{OH})_2} = 1.5$) [12]. After the separa-

Fig. 2. EELS analysis of BaTiO₃ particles after milling in Ca(NO₃)₂ solution at room temperature for 24 h and subsequent heating at 1000°C: (a) STEM bright-field image of single particles investigated, and (b) series of EEL spectra along the line marked in (a).

tion of the powder from the liquid and after annealing at 500°C, Ca(OH)₂, precipitated at the particle surface, is transformed into CaO and the $\text{OH}_{\text{O}}^\bullet$ defects are removed according to

Heating the powder for 2 h at 1000°C changes the nanochemistry as follows. Ba and Ca ions diffuse into

the inner region. The former depletion in Ti near the particle surface is not detectable as Fig. 2(b) shows. However, focusing on the O–K edge reveals that in the direction to the core of the particle this zone is followed by another one exhibiting different ELNES features. A detailed analysis of particularly the Ti–L₂₃ and O–K edges was made to differentiate these regions (Fig. 3). For this purpose, the corresponding edges were taken from the series in Fig. 2(b) and presented in Fig. 3 with respect to their edge onset and shape. The O–K ELNES recorded at a depth of about 80 nm

Fig. 3. ELNES details (onset and shape) of the Ti-L₂₃ and O-K edges depending on the lateral position of the electron probe taken from the series of EEL spectra shown in Fig. 2(b).

(measuring point P₀) is in good agreement with that known of BaTiO₃ [13]. Unlike that, the fine structure of the O-K-edge measured in the surface region (P₅) is quite different, particularly the first peak at about 531 eV is missing. Moreover, the corresponding Ti-L₂₃ edge is shifted to lower energies by about 2 eV. Approaching the more central regions there is a gradual transition of the O-K ELNES to that of titanates (cf. P₃, P₁).

Hence, it is assumed that the surface-near zone represents a mixture of Ba-, Ca-, and Ti-oxides. Although the formation of orthotitanates (Ba₂TiO₄ or BaCaTiO₄) as well as Ruddlesden–Popper-phases [14] has been taken into account, there were no distinct hints of their existence. The adjoining inner region represents a mixed Ba/Ca titanate showing an almost undisturbed perovskite structure.

3.2. Procedure 2

After hydrothermal modification of the BaTiO₃ powder, the analysis of the mother liquid yielded a Ba content of 5.1 mol% dissolved from the powder into the liquid, and a Ca content of 3.9 mol% incorporated from the liquid into the solid (both referring to the amount of barium in the starting powder). After milling the pH value was about 10. The Ba content dissolved using distilled water as leaching liquid under the same conditions was found to be 0.68 mol%. Consequently, there is a synergy factor of 7.5

Fig. 4. Typical morphology of BaTiO₃ powder hydrothermally treated in Ca(NO₃)₂ solution: (a) TEM bright-field image of a BaTiO₃ grain surrounded by rectangular CaTiO₃ crystallites, and (b) EEL spectra of the BaTiO₃ grain (upper spectrum) and the CaTiO₃ surrounding particles (lower spectrum).

(dissolved Ba content in a Ca(NO₃)₂ solution/dissolved Ba content in a Ca²⁺-free solution). This effect is contributed to additional equilibria appearing in the presence of Ca ions, e.g. the ion exchange in the perovskite structure.

The TEM micrograph of Fig. 4(a) clearly shows a coverage of the large grains with smaller rectangular crystallites. The EEL spectra of the respective particles, shown in Fig. 4(b), unambiguously identify the large particles as BaTiO₃ (upper spectrum) and the smaller rectangular ones as CaTiO₃ (lower spectrum). In particular, no radial element distribution gradients were detected in both kinds of crystallites. The phases were identified unambiguously (Fig. 4(b)) by the EELS fingerprint method. Heating the powders at 1300°C for 2 h completely changes the structure and composition of the particles covering the BaTiO₃ crystals: as the TEM image of Fig. 5(a) shows, a large crystal is surrounded now by small irregularly shaped particles. The corresponding EEL spectra (cf. Fig. 5(b)) reveal that the large grain is again of BaTiO₃ (upper spectrum), but the smaller adhering

Fig. 5. Typical morphology of BaTiO_3 powder hydrothermally treated in $\text{Ca}(\text{NO}_3)_2$ solution and subsequently heated at 1300°C : (a) TEM bright-field image of a BaTiO_3 grain surrounded by irregularly shaped $(\text{Ba}_{1-x}\text{Ca}_x)\text{TiO}_3$ crystallites, and (b) EEL spectra of the BaTiO_3 grain (upper spectrum) and the $(\text{Ba}_{1-x}\text{Ca}_x)\text{TiO}_3$ surrounding particles (lower spectrum).

particles are composed of barium titanate containing a small amount (5 vol%) of Ca (lower spectrum). Probably, this is the result of a high-temperature diffusion between BaTiO_3 and the adhering CaTiO_3 crystals leading to the formation of $(\text{Ba}_{1-x}\text{Ca}_x)\text{TiO}_3$. Surprising, however, is the observation that Ca is not so much uniformly distributed in the large BaTiO_3 grains after heating, but rather aggregated in small $(\text{Ba}_{1-x}\text{Ca}_x)\text{TiO}_3$ particles around them.

X-ray diffraction studies confirmed these TEM/EELS findings, and moreover, they were also extended to other temperatures (Fig. 6(a)). After hydrothermal modification, besides BaTiO_3 , CaTiO_3 and also $\text{Ba}_4\text{Ti}_{13}\text{O}_{30}$ were identified as additional crystalline phases. These phases are stable up to 1000°C . Below this temperature, no $(\text{Ba,Ca})\text{TiO}_3$ mixed-crystal formation was detected. At higher temperatures, solid state diffusion proceeds resulting in a series of different $(\text{Ba}_{1-x}\text{Ca}_x)\text{TiO}_3$ solid solutions with $x \leq 0.25$ [15]. At 1200°C , CaTiO_3 has not yet been detected (Fig. 6(a)), however, the XRD graph (Fig. 6(b)) proves a change in the line profile of the (0 0 2) and (2 0 0) peaks of BaTiO_3 . With

Fig. 6. XRD investigations of BaTiO_3 powder hydrothermally treated in $\text{Ca}(\text{NO}_3)_2$ solution and annealed at different temperatures: (a) presenting minor phases, and (b) presenting the (0 0 2) and (2 0 0) peaks of BaTiO_3 .

increasing incorporation of the Ca ions into the BaTiO_3 structure, the unit cell parameters decrease resulting in a shift of the peak position to higher 2θ values. The XRD graph of the powder tempered at 1200°C clearly displays the changes in the high- 2θ flank of the peaks. In the powder tempered at 1300°C , these effects are still more pronounced and the intensity of the original, unmodified (2 0 0) peak at $2\theta = 45.36^\circ$ decreases considerably. At temperatures higher than 1320°C , a eutectic forms in the TiO_2 rich region of the BaO-TiO_2 system between BaTiO_3 and $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$. This eutectic mediates the recrystallization of the BaTiO_3 matrix, thus homogenizing the element distribution and resulting in a sharpening of the peaks. The (2 0 0) peak is located at $2\theta = 45.46^\circ$ indicating a substitution of about 4 mol% Ca on the Ba sites.

3.3. Electrical properties

The effect of the hydrothermal Ca modification (Procedure 2) of the BaTiO_3 powder (powder A) on the electrical

Table 1

Specific resistance ρ_{20} and voltage withstanding $E_{\max}$ of ceramics of comparable composition $\text{La}_{0.002}\text{Ba}_{0.958}\text{Ca}_{0.04}\text{TiO}_3$ prepared (A) by the hydrothermal modification of $\text{La}_{0.002}\text{Ba}_{0.998}\text{TiO}_3$ in $\text{Ca}(\text{NO}_3)_2$ -solution, (B) by the conventional mixed oxide method using $\text{La}_{0.002}\text{Ba}_{0.998}\text{TiO}_3$ and $(\text{CaCO}_3+\text{TiO}_2)$ as starting materials, and (C) by the conventional mixed oxide method using $\text{BaCO}_3+\text{CaCO}_3+\text{TiO}_2+\text{La}_2(\text{C}_2\text{O}_4)_3\cdot 9\text{H}_2\text{O}$ as starting materials calcined for 2 h at 1100°C

Sintering temperature	A	B	C
1350°C			
ρ_{20} ($\Omega\text{ cm}$)	174	68.5	19.3
$E_{\max}$ (V/mm)	58.5	50.7	11.3
1400°C			
ρ_{20} ($\Omega\text{ cm}$)	46.8	68.4	23.5
$E_{\max}$ (V/mm)	61.5	42.5	12.7

properties of the resulting ceramic was analyzed in comparison with ceramics prepared by conventional powders of comparable composition (powders B and C), for details, see [1]. Powder B was prepared using $\text{La}_{0.002}\text{Ba}_{0.998}\text{TiO}_3$ and $(\text{CaCO}_3+\text{TiO}_2)$, powder C, by using $\text{BaCO}_3+\text{CaCO}_3+\text{TiO}_2+\text{La}_2(\text{C}_2\text{O}_4)_3\cdot 9\text{H}_2\text{O}$ as starting materials, both milled in water and calcined at 1100°C for 2 h. The specific resistance at room temperature and the voltage withstanding of the corresponding ceramics sintered at 1350°C and 1400°C were measured. The results are summarized in Table 1. It is clearly shown that

1. after the BaTiO_3 powder has formed (powders A and B) the addition of Ca-containing additives increases not only the voltage withstanding, but also the specific resistance of the ceramic compared to the material produced with powder C;
2. the distribution of CaTiO_3 crystallites on the surface of the BaTiO_3 matrix powder produced by hydrothermal modification in $\text{Ca}(\text{NO}_3)_2$ -solution (powder A) further increases the voltage withstanding of the resulting ceramic compared to that produced by the conventionally prepared powder B.

The increase in the voltage withstanding is mainly attributed to the homogenization and the reduction of the grain size in the final ceramic. The mean diameter of the grains in the ceramic sintered at 1350°C was determined to be 8.3, 11.1 and $45\text{ }\mu\text{m}$ for ceramics A, B and C, respectively. The correlation of the voltage withstanding and the resistance of the ceramic to the number of grains per unit length showed similar values for ceramics A, B and C, i.e. the properties of the grain boundaries after recrystallization are the same for the three types of ceramics.

It is assumed that the reduction in the grain size of the ceramics derived from powder A is due to the change in nucleation as CaTiO_3 crystallites act as seed grains. Electron probe microanalysis showed the existence of Ca-rich cores in grains of ceramics sintered at 1350°C .

4. Summary

The surface of n-doped BaTiO_3 powders was modified by being milled in a $\text{Ca}(\text{NO}_3)_2$ solution, first at room temperature, and second under hydrothermal conditions. The effects of these modifications were studied on a nanometer scale using TEM and EELS methods. In the first procedure, these investigations proved the existence of a thin CaO/BaO shell on the BaTiO_3 grains. By heating these powders a shell of $(\text{Ba/Ca})\text{TiO}_3$ is formed. In the second procedure, i.e. under hydrothermal conditions the leaching of the BaTiO_3 powder in a $\text{Ca}(\text{NO}_3)_2$ solution leads to the crystallization of rectangular CaTiO_3 crystallites on the surface of the BaTiO_3 particles. At temperatures higher than 1000°C solid state diffusion produces a series of $(\text{Ba}_{1-x}\text{Ca}_x)\text{TiO}_3$ solid solutions with the large BaTiO_3 grains remaining Ca-free, but the small original CaTiO_3 particles transforming to $(\text{Ba,Ca})\text{-TiO}_3$ mixed crystals.

These shell modifications of BaTiO_3 powders influence the microstructure and the electrical properties of the final ceramic. The average grain size decreases, and consequently the voltage withstanding and the electrical resistance of the ceramics increase compared to that of conventionally prepared ceramics of identical composition. The reduction in grain size is attributed to changes in nucleation, with the original CaTiO_3 particles acting as seeds. Electron probe microanalysis showed the existence of Ca-rich cores within the grain of a ceramic sintered at 1350°C .

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