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Preparation of $BaTiO_3$ single crystals using the modified SiO_2-exaggerated grain growth method

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Abstract

$BaTiO_3$ single crystals were prepared by a modified exaggerated grain growth method with SiO_2 additions using commercially available $BaTiO_3$ powder ($BaO/TiO_2 = 0.987$) in place of high purity ($BaO/TiO_2 = 0.999$) expensive $BaTiO_3$ powders. The modification also involves dropping of a eutectic composition of SiO_2 and $BaTiO_3$ in place of pure SiO_2 on the green sample of $BaTiO_3$. Doing this, a complex system involving the two eutectics-one between $BaTiO_3$ and SiO_2 at 1260 °C and another between $BaTiO_3$ and TiO_2 at 1320 °C was identified. Controlling the sintering and grain growth procedure on heat rate, temperature and time to avoid the effect of the second eutectic at 1320 °C on the system, produces highly dense 5 mm size single crystals in a really easy experimental procedure. Presence of the phase $BaTiSiO_5$ is important for the exaggerated grain growth by forming a liquid phase at 1260 °C (eutectic temperature between $BaTiO_3$ and SiO_2) during heat treatment. This phase moves through the bulk and defines four different zones of grain growth. A detailed description of the method and the grain growth mechanism are presented. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: $BaTiO_3$; Eutectic reaction; Abnormal grain growth; Grain growth; Secondary phase

1. Introduction

The interest in the preparation of $BaTiO_3$ single crystals by exaggerated grain growth method arises, as it is inexpensive, simple and reproducible. The abnormal grain growth of $BaTiO_3$ is very sensitive to Ba/Ti ratio and takes place in $BaTiO_3$[1] with small Ti-excess. There are several theories on the abnormal grain growth. One is based on liquid phase sintering, the abnormal grain growth is associated with the eutectic liquid phase,[2] which forms between $Ba_6Ti_{17}O_{40}$ and $BaTiO_3$ and the governing growth mechanism is Oswald ripening.[1] The resulting microstructure consists mainly of exaggerated growth globular crystals and fine-grained matrix. On the other hand, Schmelz et al.[3] showed that abnormal grain growth takes place even in the first shrink stages of sintering process at temperatures 100 °C below the eutectic temperature, in the absence of a liquid phase. The proposed grain growth mechanism was the formation of twin lamellae in a defined crystallographic direction, resulting in abnormally grown crystals with lamellae forms. Both above-mentioned mechanisms are typical for commercial powders of $BaTiO_3$, which contain a small excess of TiO_2. Equivalent mechanisms of grain growth can be activated in the $BaTiO_3 + SiO_2$ binary system.[4]

Following the work of Kim et al. on the exaggerated grain growth method,[5] SiO_2 doping has been shown to be a very effective approach for the production of relatively high-density $BaTiO_3$ single crystals by conventional sintering in air. This method is very suitable for the preparation of single crystals having sizes of the order of centimeters, as it only involves pressureless sintering in air at temperatures around 1400 °C. However, in experiments of Kim et al.,[5] an expensive high purity $BaTiO_3$ powder was used ($BaO/TiO_2 = 0.999$). The experimental procedure was designed to activate a eutectic reaction between $BaTiO_3$ and SiO_2 locally in the contact area between the SiO_2-drop and compact green sample. The added SiO_2 was less than the 1 mol%, and the temperatures needed to activate the exaggerated grain growth were higher than 1320 °C.

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In the present modified method of exaggerated grain growth, for the preparation of single crystals, we replaced high purity expensive $BaTiO_3$ powder by inexpensive commercial $BaTiO_3$ powder.[6] Another important modification was the substitution of the SiO_2-drop placed on the green sample for a $BaTiO_3+SiO_2$ (eutectic composition). These imply a complete modification of the Kim's sintering procedure due to the effect of two eutectic reactions between $BaTiO_3$ and SiO_2 at 1260 °C and between $BaTiO_3$ and TiO_2 at 1320 °C coming into play because of the three components namely $BaTiO_3$, local added SiO_2 and the usual excess of TiO_2 in the used commercial powders. The method basically avoids the activation of the second eutectic ($BaTiO_3$-solid solution + $Ba_6Ti_{17}O_{40}$), which affects the whole specimen, since TiO_2 excess is homogeneously distributed. Responsible for the anomalous grain growth is a liquid phase due to the local effect of SiO_2-additions.

2. Experimental

The $BaTiO_3$ single crystals were prepared from the commercially available barium titanate powder, TICON HPB-Lot 790 (TAM Ceramics Inc., Niagara Falls, USA). The particle size of the powder was measured using a MasterSizer (Malvern Instruments, UK). Powder (150 g) was first homogenized by attrition milling for 5 h, using 1200 g ZrO_2 balls (diameter: 5 and 1 mm) and ethanol as the grinding media. The dried and sieved powders were then consolidated uniaxially at 100 MPa and by cold isostatically pressing at 700 MPa into compacts of 10×5×4 mm. A suspension of the eutectic composition between $BaTiO_3$ and SiO_2 (99.5%, Alfa GmbH), namely $BaTiO_3$ + 29 mol% SiO_2 with 50 vol.% of solids in ethanol was prepared. As for the original method a drop of the suspension was placed on the top of the $BaTiO_3$ green sample controlling the diameter of the drop to be less than 1 mm. This procedure provides a limited eutectic $BaTiO_3+SiO_2$-doped area. The compact was then dried for 24 h at room temperature in order to eliminate the excess ethanol. The sintering procedures were carried out in a chamber furnace (Naber Industrieofenbau GmbH).

A group of samples was sintered at different temperatures (from 1240 to 1400 °C with 20 °C increment), with a fix holding time of 5 and 20 h in order to find the optimum parameters for the formation of seeds and exaggerated grain growth during sintering. Additional variations of 1 °C were made for identification of the better temperature for maximal grain growth and highest density. Furthermore some of the samples were sintered under different times between 1 and 80 h. Microstructures were observed using optical microscopy (OM, Leitz Aristomet, Germany), scanning electron microscopy (SEM, Gemini 982 Leo, UK) and scanning force microscopy (SFM, Digital Instruments Dimension 3000, USA) on samples polished (diamond suspension, 9, 6, 3 and 1 μm) and chemically etched during polishing using a commercial colloidal silica suspension MASTERMET 2 (Buehler, USA). The average grain size ($\bar{D}$) was determined by measuring the average intercept length $\bar{l}$ and $\bar{D} = 1.5\times\ \bar{l}$. The density of the sintered samples was measured according to Archimedes principle. During grain growth, the phases were characterized by XRD and image analysis in SFM. The XRD characterization consisted of the analysis of different layers of the sample, which were cut, with a saw blade machine (EXAKT Accutom), parallel to the sample surface in contact with the SiO_2 drop. The localization of the secondary phase ($BaTiO_3+SiO_2$, no ferroelectric) were performed using SFM images containing ferroelectric information of the sample surface using the voltage modulated SFM method (piezoelectric force microscopy).[8] The orientation of the single crystals was determined by electron backscattered diffraction analysis (EBSD) performed in SEM using the software package OPAL (Oxford Instruments).

3. Results and discussion

When polycrystalline bodies are made from fine powder, the extent of secondary recrystallization depends on the particle size of the starting material.[1] Coarse starting material reduces the relative speed in grain growth.[1] Both used commercial powders are agglomerated and have an starting average particle size of 1.6 μm with maximum of 2 μm ($BaTiO_3$) and 5 μm with maximum of 15 μm for SiO_2. After attrition milling experiments, where milling time and size ratio of ZrO_2 balls were characterized, the best results were obtained for 5 h and a 1:1 size ratio of ZrO_2 milling balls, which gives an average particle size of 300 nm with maximum of 0.8 μm for $BaTiO_3$ and the correspondent values 0.5/1.8 μm for the used $BaTiO_3+SiO_2$ eutectic mixture.

3.1. Densification curve and grain size development

Dropping the eutectic composition between SiO_2 and $BaTiO_3$ on the $BaTiO_3$ green sample forces the system to form locally a liquid phase at temperatures between 1260 and 1320 °C. At this temperature there is no significant effect of TiO_2 excess on abnormal grain growth, compared with the effect of SiO_2 additions.

Fig. 1 shows the influence of temperature (between 1240 and 1400 °C) on densification and grain growth for a fixed holding time of 5 and 20 h for the SiO_2-doped and undoped systems, which are represented with symbols ▽, ▼ and ◆ (maximum grain size) respectively. Densification results, in percentage of the theoretical density (6.017 g/cm^3) are represented with circles. At

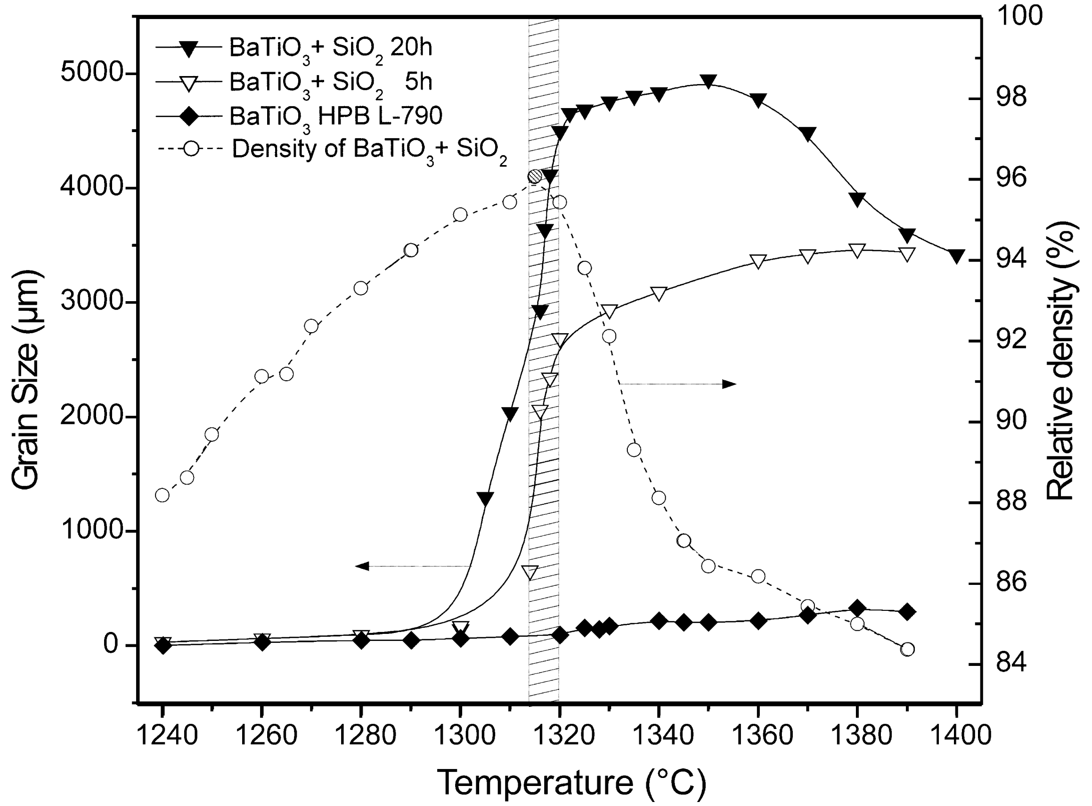


Fig. 1. Influence of temperature on grain growth and densification for fixed holding time (5 and 20 h); ◆ samples prepared with $BaTiO_3$ commercial powders [HBP L-790], and ▽, ▼ samples prepared with $BaTiO_3$ commercial powder and locally doped with SiO_2 [$(BaTiO_3 + TiO_2) + SiO_2$] 5 and 20 h, respectively. Density of SiO_2 doped $BaTiO_3$ is also showed (○). Dashed area shows the best temperature range for exaggerated grain growth without density decrease.

1320 °C, which corresponds to the eutectic temperature of the system $BaTiO_3 + TiO_2$ exaggerated grain growth was observed in both the SiO_2-doped and the undoped systems. However, the effect of the local addition of less than 1 mol% SiO_2 to the system of $BaTiO_3 + TiO_2$ increases the grain size up to 10 times when compared to the system without SiO_2 addition. It is also observed that above 1320 °C the density decreases abruptly (more than 10% of the theoretical density) for both systems, namely $BaTiO_3$ commercial powders (already reported elsewhere[7,8]) and $BaTiO_3$ commercial powders with additions of SiO_2, which is still a problem for the method. The highest densification results (96% of theoretical density) together with the maximum exaggerated grain growth (see dashed area in Fig. 1) can be reached at 1318 ± 2 °C.

The temperature for maximum grain growth should be selected considering the abrupt decrease of the density. High densification is important since this directly affects the quality of the single crystal. An aggregate of fine-grained crystals increases in average grain size when heated at elevated temperatures. As the average grain size increases some grains must shrink and disappear.

These results served to design the heat treatment for the modification of the exaggerated grain growth method when using commercial powders, which is discussed in the next section. The purpose was to find the correct matching of fixed holding time and temperature to take advantage of both possible eutectic reactions. To activate the correct eutectic reaction in the fixed holding time, it was necessary to design a sintering procedure to have the mutual action of both grain growth mechanisms, namely twinning and Ostwald ripening at 1260 and 1318 °C respectively.

3.2. Modification of the exaggerated grain growth method

Based on the results of Fig. 1, it is proposed that the modified method of exaggerated grain growth proceeds by a two step mechanism involving the formation of a seed crystal (by activation of the twinning grain growth between $BaTiO_3$ and SiO_2), during a pre-sintering step at 1240 °C for 10 h followed by grain growth during the second sintering step at 1318 ± 2 °C for 20 h. At this temperature the Ostwald ripening mechanism of grain growth should be activated by the local presence of a liquid phase near to the area of SiO_2 additions. The proposition is supported by microscopic observations.

The temperatures at both steps were fixed for 10 and 20 h respectively since the constant holding temperature of 5 h used in the previous characterization was observed to be too short for the complete anomalous grain growth in each step.

A scanning force microscopy (SFM) micrograph is presented in the Fig. 2b and shows an idiomorphic grain of barium titanate, grown during the first step of the above-described procedure. This microstructure is typical for the activation of the twinning grain growth mechanism between $BaTiO_3$ and the locally added SiO_2. According to the combination of time-temperature shown in Fig. 2a, the maximum dimensions of a typical exaggerated-grown grain are 6 µm width and 18 µm long. The best thermal treatment for seed formation was a sub-eutectic treatment at 1240 °C for 10 h, where grains grow into lamellae- (simple twinning) or hexagonal form (double twinning). These grown grains correspond to the seeds for the next step of exaggerated grain growth. A typical micrograph (optical microscope) showing the very first stages of exaggerated grain growth due to the presence of a liquid phase is presented in Fig. 2c. Clearly, the lamellae and hexagonal geometry of seeds (typical during solid state grain growth) are lost at this sintering temperature. On the other hand, grain size increases from 18 µm to a maximum of 200 µm. The usual temperatures used for the activation of the twinning and the Ostwald ripening grain growth mechanisms in the systems, ($BaTiO_3 + TiO_2$) and ($BaTiO_3 +$ SiO_2) are represented in Fig. 2a.

Fig. 3a shows a typical microstructure obtained during the heat treatment shown in Fig. 2 at 1318 °C/1 h after seed formation. This is the desired development of microstructure to successfully prepare single crystals using this method. A description of the configuration of this microstructure is as follows.

Fig. 3b shows a scheme for several typical zones of grain growth to be defined during heat treatment. These zones will be denoted in order of depth with letters E, G, S and A. Zone E is used to denote the area of excess of SiO_2; zone G is for the area, where single crystals will grow; zone S is for the area of suppression of grain growth and finally, zone A is for the area of typical abnormal growth in commercial powder of $BaTiO_3$ with a small excess of TiO_2. The condition of local effect of SiO_2 for grain growth was not present in this zone.

Single crystals usually grow from the zone G, wherein seeds are formed at the very first stages of sintering (Fig. 3a). Fig. 4 shows a micrograph of a typical abnormally grown grain of some millimeters in size, observed from the transverse cut of the sample. This grain was grown abnormally by secondary recrystallization in a polycrystalline sample, which was sintered as shown in the heat treatment of Fig. 2. The matrix around the giant grain is formed mainly of uniformly sized micrometric grains.

Due to secondary recrystallization, particularly for the case of Fig. 4, grain growth was inhibited by the presence of two other exaggeratedly grown neighboring grains (as well as by the presence of defects). These three giant grains have reached the point, at which the diameter of the exaggerated grain is much larger than the matrix diameter, $\bar{D}_G \gg \bar{D}_M$. Therefore, the growth rate of a unique single crystal is constant as long as the grain size of the matrix remains unchanged. This phenomenon

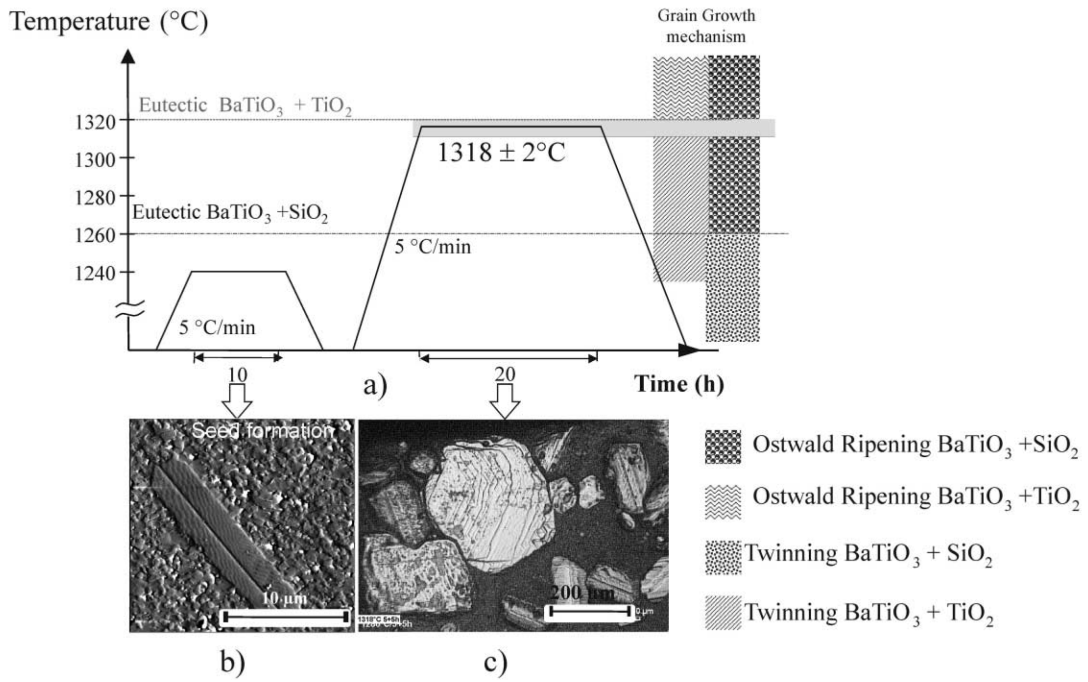


Fig. 2. Modified method of exaggerated grain growth for the commercial $BaTiO_3$ powder + locally added SiO_2 system, (a) proposed sintering process, (b) idiomorphic grain of $BaTiO_3$ in a fine-grained matrix as a result of the seed-formation step and (c) large grains of barium titanate grown by secondary recrystallization (exaggerated grain growth step).

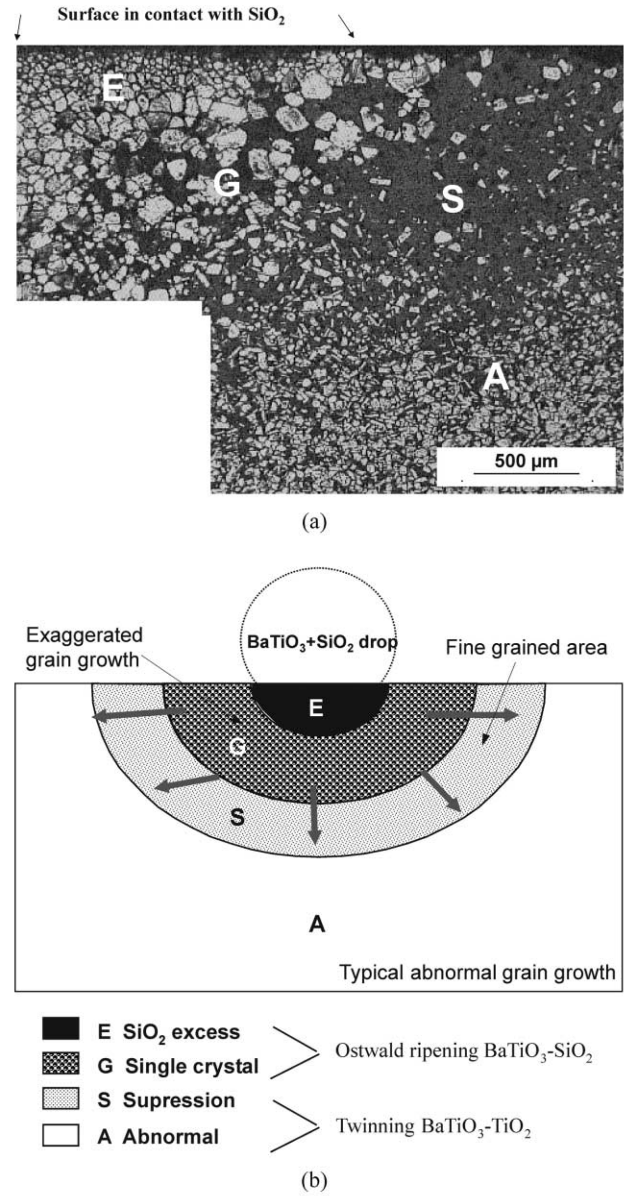


Fig. 3. Zones of grain growth in a transverse section of the sample sintered at 1260 °C/10 h + 1320 °C/5 min, polished and etched; (a) microstructure and (b) schematic of the grain growth zones.

arises because a broad area of the polycrystalline was in contact with the SiO_2 drop. Addition of SiO_2 seems to be one of the most important and delicate parameters to get a local effect for single crystal preparation with this method. However, highly dense (~96% of the theoretical density) and large-grained (~5 mm) $BaTiO_3$ single crystals (see Fig. 4) can be typically sintered by this modification of the exaggerated grain growth method.

Fig. 5 shows a typical EBSD result for the crystal orientation of the giant grain of Fig. 4. According to the results from EBSD, the orientation of the prepared single crystal is defined by a small deviation of the crystallographic plane (001). Fig. 5 consists of Kikuchi lines (a) and a scheme for the EBSP (pattern) with the respective stereographic representation (b). The small deviation of the crystal orientation from the (001) crystallographic plane was probably obtained during the grinding and polishing step. However, for the crystals prepared with this method, the <100> growth-direction was frequently found either on the sample surface in contact with the drop of the eutectic mixture or on their cross direction. Such crystal has been successfully used for further AFM characterization on the configuration of ferroelectric domains and for fracture mechanical tests to activate domain wall movement.[10]

3.3. Characterization of the $BaTiSiO_5$ phase

The dominant mechanism for the exaggerated grain growth in the present system of $BaTiO_3$ + excess of TiO_2 + a small addition of SiO_2 is the Ostwald ripening mechanism between $BaTiO_3$ and SiO_2 additions. This occurs locally in the presence of a secondary phase (zone with excess of SiO_2). The phase diagram of the $BaTiO_3$ + SiO2 system[4] and further microstructural characterization of the present work show that this secondary phase corresponds to $BaTiSiO_5$, which was present locally in the zone in contact between $BaTiO_3$ and SiO_2. At temperatures up to 1260 °C there are two phases, namely $BaTiO_3$ solid solution and a liquid phase rich in SiO_2 (≈28 mol%); this last phase corresponds to less than 1% of the complete system. The exaggerated grain growth is enhanced due to these conditions through Oswald ripening. During cooling, under 1260 °C the liquid phase (eutectic composition) transforms into $BaTiO_3$ solid solution (60%) and $BaTiSiO_5$ phase (40%). The presence of $BaTiSiO_5$ shows the participation of a liquid phase at temperatures up to 1318 °C. Resuming, the grain growth enhancement was only due to the effect of SiO_2 additions and not because the excess of TiO_2 in our commercial powders, where a liquid phase appears at temperatures above 1320 °C. We can conclude that (as shown in Fig. 2) the major grain growth mechanism participating in the anomalous grain growth is either in solid state grain growth the twining mechanism or at the presence of a liquid phase the Oswald ripening, always between $BaTiO_3$ and SiO_2 additions.

For this specific composition of commercial $BaTiO_3$ powders (with TiO2 excess) the sintering of the samples at temperatures above 1320 °C should not be allowed (like in Kim's or alternative methods[5,9]) due to the phenomena of abrupt decrease in density. As already mentioned the reason for this dedensification is clearly due to the formation of a liquid phase rich in TiO_2 in the entire bulk sample and specially in the zone in contact with SiO_2, where the $BaTiSiO_5$ liquid phase is at this temperature present. Additionally it seems to be a strong dependence of the TiO_2 content in the commercial $BaTiO_3$ powders on the manifestation of the critical temperature for exaggerated grain growth. In previous

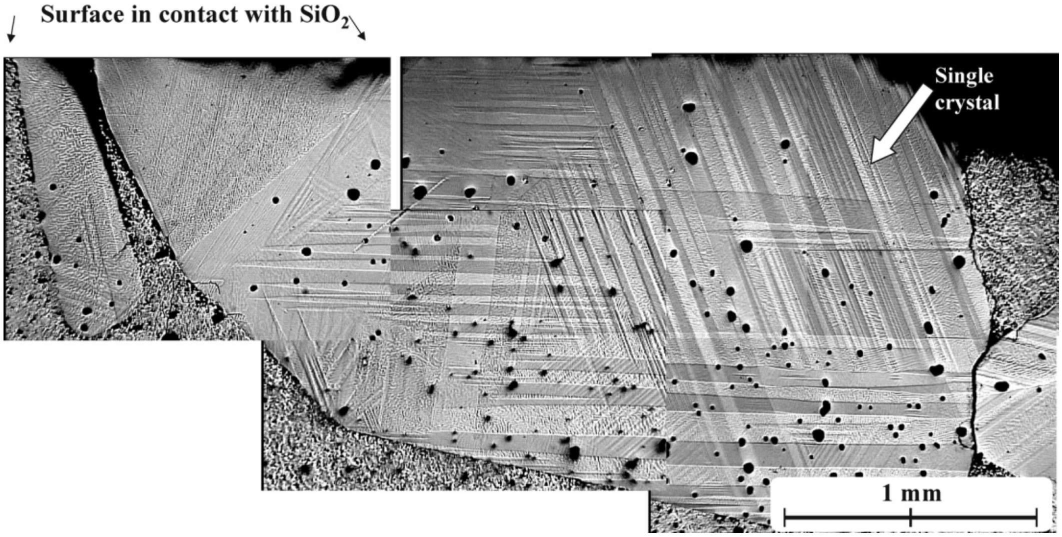
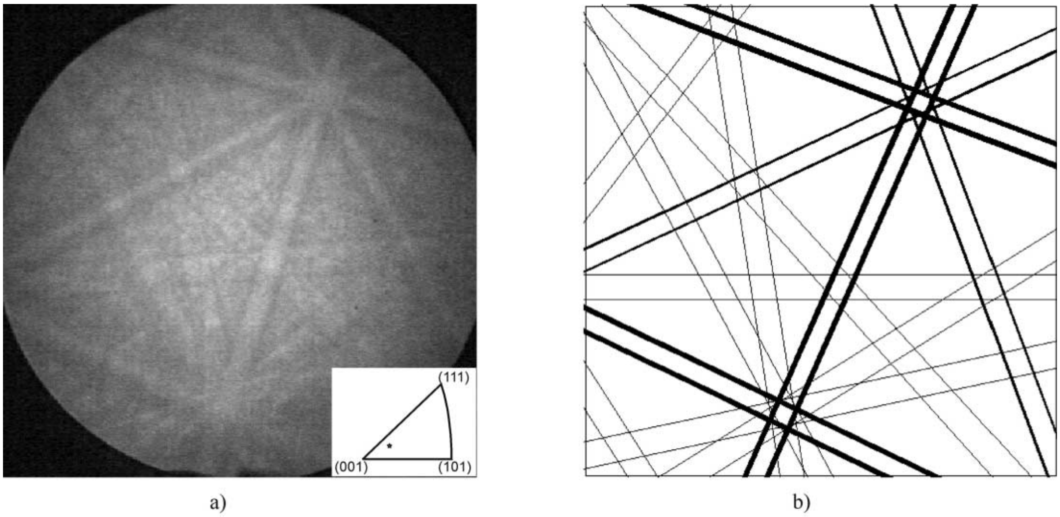


Fig. 4. A typical final microstructure of a transverse section of a sample prepared with the modified SiO_2-exaggerated grain growth method. Arrow shows the single crystal embedded into a matrix of uniformly fine sized grains.



a) b)

Fig. 5. Electron backscattering pattern (EBSP) from a $BaTiO_3$ single crystal. (a) Kikuchi lines, (b) schematic of the EBSP with the respective stereographic representation.

reports the found temperature for grain growth in $BaTiO_3$ powder with Ba/Ti = 0.999 is around 1350–1370 °C[5] and between 1355 and 1360 °C for a powder with Ba/Ti = 0.994.[9] For the powder used in this work (Ba/Ti = 0.987) the temperature was above 1318 °C.

Finally after exaggerated grain growth in the sample the secondary phase was identified by XRD and image analysis of SFM micrographs. The XRD results as shown in Fig. 6 are from the sample area in contact with the drop of SiO_2 (zone E) and clearly indicate the formation of $BaTiSiO_5$ in samples heated at 1318 °C. On the other hand, the SFM analysis of the sample was useful in locating the position of this phase. The analysis done in the boundary between an exaggeratedly grown crystal and the matrix revealed the presence of $BaTiSiO_5$. Again we emphasize the criteria to identify this phase, which does not have ferroelectric behavior because domain structure neither in topography nor in the piezoelectric response images of etched sample surface could be identified. The results corresponding to the topography and the z-component of the polarization vector[11] are shown in Fig. 7.

Exaggerated grain growth is enhanced by the presence of a SiO_2-rich ($BaTiSiO_5$) liquid phase at heat treatment temperatures. This grain growth enhancement has already been reported, as a gettering effect, in which already present grain growth inhibitors are rendered less effective by, for example, the formation of a compound to remove a component from solution or by coalescence of an already widely dispersed phase.

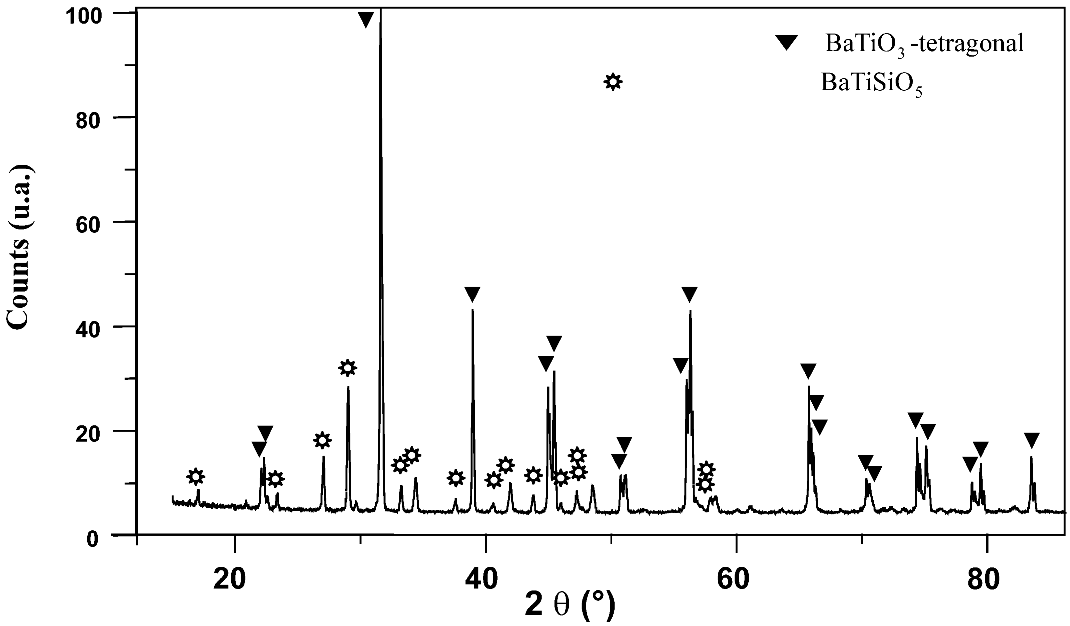
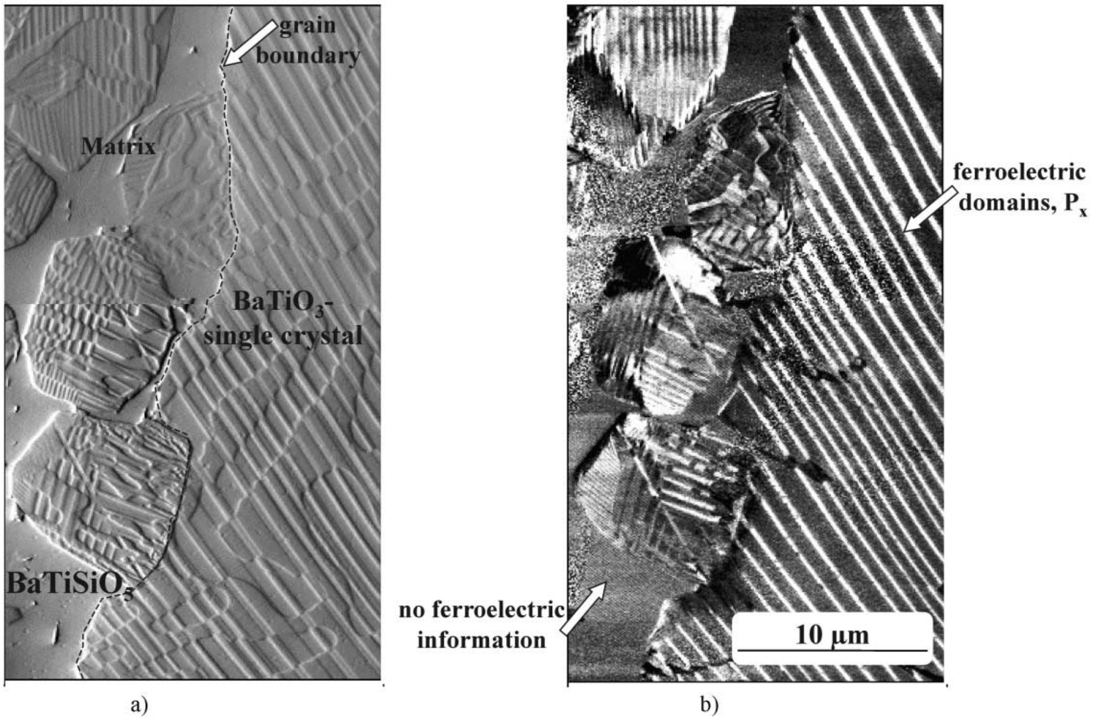


Fig. 6. XRD-results of the SiO_2-excess layer of a typical sample (zone E) after exaggerated grain growth.



a) b)

Fig. 7. SFM-images of the boundary between $BaTiO_3$ single crystal and the fine-grained matrix; (a) topography, (b) piezoresponse SFM-image. $BaTiSiO_5$ phase is observed through the boundary in the topography as a rounded polished area as well as in the piezoresponse image containing no ferroelectric information.

4. Conclusions

The experimental result supports the proposition that the critical event leading to exaggerated grain growth is the formation of intergranular SiO_2-rich liquid phase at temperatures between 1260 and 1320 °C. This liquid phase transforms during cooling into $BaTiSiO_5$ through an eutectic reaction. At temperatures above 1320 °C the samples prepared with this SiO_2-doped system show an abrupt decrease in density. Using the presented modification of the exaggerated grain growth method, highly dense (~96% of the theoretical density) and large-grained (~5 mm) $BaTiO_3$ single-crystals most with known orientation in <100> direction, could be prepared.

Acknowledgements

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