Grain growth kinetics of textured-BaTiO₃ ceramics

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Abstract. Textured BaTiO₃ (BT) ceramics were fabricated by templated grain growth method. Effects of sintering conditions on the grain growth process of textured-BT ceramics were investigated. Orientation degree increased initially and then decreased with increasing soaking time. The ceramics were composed of equiaxed matrix grains and brick-like template particles. The brick-like particles aligned parallel to the casting direction by observing from SEM images. A (*h*00)-preferred orientation was confirmed by SAED and XRD patterns. Mechanism of grain growth in textured-BT ceramics was studied. Both consumption of matrix by templates and grain growth of templates determined the orientation degree of ceramics. The kinetic mechanism for grain orientation was also discussed by the simplified phenomenological kinetic equation. The average activation energies were 364 kJ/mol for matrix grain and 918 kJ/mol for template particle, respectively. Finally, a dense ceramic with 85% grain orientation was obtained after sintering at 1400 °C for 2 h.

Keywords. Textured-BT ceramics; tape casting; grain growth; phenomenological kinetic.

1. Introduction

Lead-free ceramics are environmental friendly materials but hard to substitute lead-based material, because of their inferior electrical properties. Generally, there are two approaches to improve electrical properties of lead-free ceramics. One is compositional design by ways of element doping or composite such as BaTiO₃–(Bi_{0.5}Na_{0.5})TiO₃ (Cernea *et al* 2010), BiYbO₃–PbTiO₃–BaTiO₃ (Wu *et al* 2012), (Bi_{0.5}Na_{0.5})TiO₃–(Bi_{0.5}K_{0.5})TiO₃–BaTiO₃ (Dai *et al* 2010). The other is microstructure modification techniques, such as grain refinement or grain orientation. Grain orientation is one of the important microstructure modification methods to enhance the piezoelectric properties of lead-free ceramics. Element doping and composite often lead to the shift of Curie temperature, *T*_c, due to the formation of solid solution (Du *et al* 2008; Lei and Ye 2008; Lin and Kwak 2012; Ye 2012). Grain orientation, however, rarely affects *T*_c because of the unchanged composition of desired samples. Meanwhile, it also possesses other advantages, such as compositional flexibility and low production cost compared with single crystals (Takao *et al* 2006; Gao *et al* 2007; Zhang *et al* 2008).

Presently, various methods such as hot pressing, hot forging, magnetic orientation and templated grain growth (TGG) method, are employed to fabricate textured ceramics (Kimura *et al* 2004; Chen *et al* 2007a,b; Fu *et al*

2009). TGG is one of the most convenient methods to prepare textured ceramics by sintering a green compact with matrix and template particles. Template often considered being the key of TGG method, which usually chose anisotropic powders or small single crystals. BT-textured ceramics can also be fabricated by TGG method. However, most researchers focused on the enhanced properties of textured-BT ceramics (Sugawara *et al* 2003; Rehrig *et al* 1999; Takahashi *et al* 2006; Wada *et al* 2007; Sabolsky *et al* 2010), but not the grain growth mechanism. In recent years, three kinds of grain growth mechanisms have been concluded for grain orientation evolution based on studies of Na_{0.5}Bi_{0.5}TiO₃–BaTiO₃ textured ceramics (Fukuchi *et al* 2002; Fuse and Kimura 2006; Kimura and Yoshida 2006; Shoji *et al* 2008, 2009; Gao *et al* 2010). First one is the growth of template particles at the expense of matrix grains, second one is the formation of single-crystal layers with matrix phase on the surface of template grains and third one is the morphological change of matrix grains on the surface of template grains. Na_{0.5}Bi_{0.5}TiO₃-based matrix presents a cubic morphology, whereas BT ceramics was fabricated with round morphology matrix. The morphology of matrix grain is confirmed to play an important role on grain growth mechanism; hence, it is necessary to investigate the grain growth mechanism of BT-textured ceramics, which is properly different from Na_{0.5}Bi_{0.5}TiO₃-based ceramics.

(*h*00)-oriented BT ceramics were fabricated based on (*h*00)-oriented BT plate-like particles prepared by our

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Figure 1. Information of template (a) XRD pattern, (b) SEM image, (c) TEM image and (d) SAED pattern.

research team. Effects of ball-like matrix grains on orientation degree and microstructure of ceramics were investigated in detail. Mechanisms of matrix and template grain growth were also discussed by the phenomenological kinetic grain-growth equation.

2. Experimental

Plate-like BT template particles were prepared by molten salt method (Ding *et al* 2009). In order to observe the template grain growth, up to 50 wt% template content was added. The mixture of BT templates and equiaxed BT powders (with particle size of 100 nm, produced by Shandong Guoteng Function Materials Co. Ltd.) was milled for 12 h in solvent of toluene and ethanol by roller mill. Then the LS model binder (Lingguang Electric Chemical Materials Technology Corporation in Zhaoqing City, China) was added and milled for 3 h to stabilize the slurry. The stable slurry was used to produce the green sheet through a conventional tape casting equipment. The gap under doctor blade was 100 μm . The green sheet was cut and laminated to about $10 \times 10 \times 1$ mm and then pressed at 20 MPa for 5 min at 50 $^{\circ}\text{C}$. Subsequently, the green compact was heated to 550 $^{\circ}\text{C}$ for 4 h to remove the organic substance and then sintered at 1230–1350 $^{\circ}\text{C}$ for 0–20 h.

Phase structure of the annealed compact was examined by X-ray diffraction (XRD, Bruker D8 Advanced, Made in Germany) with $\text{CuK}\alpha$ radiation. Degree of grain orientation was represented by Lotgering's factor, which is calculated by the formula below (Lotgering 1959)

$$F = (P - P_0)/(1 - P_0), \quad (1)$$

where P is the sum $I(h00)/\text{sum } I(hkl)$, P_0 the sum $I_0(h00)/\text{sum } I_0(hkl)$. Sum I is the summation of the peak intensities of XRD pattern of sintered specimen. Sum I_0 is the summation of XRD peak intensities of the equiaxed reference powder. Microstructures of BT ceramics were investigated by scanning electron microscopy (SEM, JSM EMP-800, made in Japan).

3. Results and discussion

3.1 Grain growth of textured ceramics

Figure 1 shows XRD pattern, micrograph and corresponding selected area electron diffraction (SAED) pattern of BT plate-like particles. A sharp thickness of about 1 μm and width of 2–10 μm were observed for BT particles, whose size were adapted for using as template. The direction of plate-like particles can be proved to be $(h00)$ direction by SAED pattern.

Figure 2. Microstructure of BT-textured ceramics sintered at (a) 1220, (b) 1250, (c) 1280 and (d) 1330 °C.

Figure 2 shows microstructures of BT-textured ceramics with different sintering temperatures. The observed plane is parallel to the tape casting direction. All samples were composed of large brick-like template particles and small equiaxed matrix grains. Templates arranged parallel to the casting direction and their thicknesses were increased with increasing sintering temperature. Sizes of matrix grains increased rapidly after annealing above 1250 °C. The thermodynamic driving force for grain growth is supposed to be the different interfacial energy between large and small grains. Small matrix grains usually possess higher activity because of their large surface energy. Thus, they are easily absorbed by large matrix grains or templates in order to reduce the surface energy. Obviously, the growth velocity of both grains decreases above 1250 °C, as shown in figures 2(b–d). This could be attributed to the decreased driving force, which is caused by the reduced magnitude between large and small grains. Grain growth of matrix particles and formation of neck between templates and matrix grains at 1250 °C indicated the initial sintering stage. So this temperature is chosen to further discuss the whole grain growth process of BT-textured ceramics.

Figure 3 shows SEM images of BT-textured ceramics sintered at 1250 °C with different soaking times. The growth process can be divided into three stages according

to this figure. The first stage is the growth of template particles and large matrix grains at the expense of small matrix grains, as shown in figures 3(a) and (b). Driving force in this stage is the different interfacial energy between small matrix grains and large templates. Template particles grow large enough to contact with each other and begin to combine after 2 h sintering, as shown in figures 3(c and d). Both the growth of templates at the expense of small grains and combination of thick templates co-exist in this second stage. The driving forces in this stage are not only different interfacial energy but also reduction of grain boundary. In the last stage, all matrix grains are absorbed by template particles. The ceramics only compose of brick-like particles, as shown in figures 3(e and f). The dominated driving force changes to the reduction of grain boundary.

Figures 4(a–f) shows extended images of BT-textured ceramics sintered at 1250 °C with different soaking times. At first, brick-like templates are connected via several round matrix grains. The boundary between them is marked as ‘A’ in figure 4(a). Template particles grow thicker at the expense of matrix grains with prolonged soaking time. They continually grow to diminish the distance between them and finally contact with each other to form a flat boundary, as shown in area B, figure 4(d). The flat grain boundary can be clearly observed and the

Figure 3. SEM images of BT-textured ceramics sintered at 1250 °C for (a) 0 h, (b) 1 h, (c) 2 h, (d) 5 h, (e) 10 h and (f) 20 h.

matrix grains almost disappeared in this stage. In final stage, ceramics are only composed of large templates. They arranged along same direction and formed flat grain boundary marked with C in figure 4(e and f). Large templates grow to a bulk compact with the diminishment of grain boundary and pores. None of the single-crystal layers or terrace are observed on template grains during whole sintering process. This result is different from the conclusions of NBT-based ceramics (Kimura and Yoshida 2006; Shoji *et al* 2009), which properly attributed to the round matrix grain morphology of BT particles.

Figure 5(a–f) shows XRD patterns of BT-textured ceramics sintered at 1250 °C for different soaking times. In the first stage, the intensity of (110) peak is the strongest one, which coincides with the pattern of equiaxed powders. This indicates that the diffraction peaks of equiaxed matrix grains dominate the XRD pattern in this stage. The intensity of (*h*00) peaks becomes stronger than that of (110) peak with increasing soaking time. A preferential

growth happens in this second stage. Large amounts of matrix grains are absorbed by templates, which consequently leads to the preferential growth. Matrix grains almost depleted in final stage, hence the thermal energy is almost provided to the growth of templates. Growth of templates assumed to be anisotropic as reported by Fuse *et al* (2006), not only along perpendicular but also parallel to *c*-direction. As a result, XRD pattern becomes similar with the standard BT pattern. Therefore, the intensity of (110) peak becomes the strongest once again, as shown in figure 5(e and f). Two contrary types of grain growth formats co-exist in textured process based on our analysis: one is the absorption of matrix grains by template which benefits for grain orientation and another is the growth of templates which decreases the orientation degree. Both types seem to happen in second stage at 1250 °C, which result in the declined orientation degree. Thus, grain growth of templates should be prevented by controlling the sintering conditions in order to obtain

Figure 4. Extended images of BT-textured ceramics sintered at 1250 °C for (a) 0 h, (b) 1 h, (c) 2 h, (d) 5 h, (e) 10 h and (f) 20 h.

higher orientation degree. The optimum orientation degree appears at the junction of the finishing point of matrix grain growth and starting point of template growth.

XRD patterns of the ceramics sintered at 1250, 1280, 1300, 1330 and 1350 °C are shown in figure 6. The ceramics annealed at 1300 °C shows (*h*00)-preferred orientation and keeps a stable value at about 50% below 1350 °C. However, the samples sintered at 1350 °C for different times show continuous decrease in orientation degree, as shown in figure 7. Combined with SEM images of ceramics sintered for 0, 0.5 and 1 h, as shown in figure 8(a–c), this trend is properly induced by the fast process of matrix absorption at this sintering temperature. In other words, the absorption of matrix by templates is too fast to be observed, which makes the growth of templates dominate the grain growth process. This anisotropic templates growth results in the decrease of orientation degree. Ceramics sintered at 1300 °C for different times are chosen to optimize the orientation

degree. A higher orientation value of 71% is obtained for the ceramics sintered for 30 min as shown in figure 9.

3.2 Mechanism of crystallographic texture process

Crystallization of ceramics commonly comprises of the nucleation and crystal-growth process. The crystal-growth process is controlled by the grain-boundary curvature mechanism, lattice diffusion mechanism, grain-boundary diffusion mechanism, interface diffusion, solution–precipitation mechanism, evaporation–agglomeration mechanism, viscous flow mechanism, etc. Grain growth kinetics is usually determined by using the simplified phenomenological kinetic after Burke and Turnbull (1952) using parabolic law to describe grain growth characteristics of metallic materials. A general grain growth equation is developed as follows

$$D_t^n - D_0^n = A t \exp(-E_a/RT), \quad (2)$$

where D_t and D_0 are average grain size at time t and original grain size, n the grain growth exponent, t the sintering time, E_a the grain growth activation energy, A the pre-exponential constant and R the general gas constant. By logarithmizing the two sides, (2) can be plotted in the form

$$\ln D_t = \frac{1}{n} \left(\ln t + \ln A - \frac{E_a}{RT} \right). \quad (3)$$

Figure 5. XRD patterns of BT-textured ceramics sintered at 1250 °C for (a) 0 h, (b) 1 h, (c) 2 h, (d) 5 h, (e) 10 h and (f) 20 h.

Figure 6. XRD patterns of BT-textured ceramics sintered at different temperatures.

The grain-growth kinetic exponent can be determined from the slope of the $\ln D_t$ vs $\ln t$ curve. BT textured ceramics are composed by the matrix grains and template particles, as observed in figure 3. The matrix diminishes with prolonging soaking time to 10 h, so we simulate the grain-growth kinetic of matrix by the grain size of 1, 2 and 5 h. Otherwise, the template particles is hard to distinguish after 10 h sintering. 45 grains are selected from three SEM images (only one image shown in figure 3) to estimate the average grain size of the matrix and template particles. The values are listed in table 1. The average grain size increases with increasing sintering time, as expected from (3). Figure 10 shows functions of $\ln D_t$ vs $\ln t$ of the matrix grains and templates, respectively. It is obvious that both data of the matrix and templates show linear relationships and the n values are equal to 3.45 for matrix grains and 9.71 for templates, respectively. The exponents lie mostly between $n = 2$ and 6, but in some cases even up to $n = 10$ (Malow and Koch 1997; Rodewald et al 1997; Zhang et al 2002). Many reasons were put forward to explain deviations from the theoretically expected parabolic law, e.g. that impurities or pores affect the grain growth kinetics. Generally, if the grain growth is inhibited, the n value is large. Growth of template is smaller than matrix which resulted in bigger n value for templates. Grain growth of ceramics starts from the ion diffusion on the interface. Matrix grains preferentially adhere on the defects of template particles to reduce the surface energy. Once the nucleation has formed on the templates, the crystal will grow along the interface, which is shown in figures 4(b–d), and finally a brick-like morphology is obtained.

Equation (2) can also be expressed as

$$\ln \frac{D_t^n}{t} = \ln A - \frac{E_a}{RT}. \quad (4)$$

If x - and y -axes are set to be $1/T$ and $\ln(D_t^n/t)$, a linear relationship is established, in which $-E_a/R$ and $\ln A$

Figure 7. Grain orientation of samples sintered at 1350 °C for different times.

Table 1. Average grain size of matrix grain and strip-like grain in textured-BT ceramics at different soaking times.

Soaking time (min)	60	120	300	600	1200
Matrix grain size (nm)	833	1056	1333	—	—
Template length (nm)	3611	3889	4160	3655	3528
Template thickness (nm)	1864	2030	2424	3045	3515

Table 2. Average grain size of matrix grain and strip-like grain in textured-BT ceramics at different temperatures.

Sintering temperature (K)	1493	1523	1553	1603
Matrix grain size (nm)	556	667	778	1000
Template length (nm)	2552	2279	2134	2067
Template thickness (nm)	1121	1394	1546	1924

Figure 8. SEM images of BT-textured ceramics sintered at 1350 °C for (a) 0 h, (b) 0.5 h and (c) 1 h.

correspond to the slope ratio and interceptive space, respectively. The values of temperature and corresponding grain size are listed in table 2. These plots are constructed for BT-textured ceramics, as shown in figure 11. The average activation energy for the grain growth can be calculated from the slope. The values are 364 kJ/mol for matrix grains and 918 kJ/mol for template particles, respectively. The average activation energy of the matrix particles is lower than that of template grains, which indicates that the matrix grains are easier to grow. In the sintering stage, the matrix grains are much smaller than the templates and distribute randomly, then it possess high-energy grain boundary. It can be easily expanded by the templates to decrease the high-active grain boundary.

Whereas, the brick-like particles have large grain sizes and orderly arranged parallel to (*h*00) planes to form low-energy grain boundary. Therefore, the templates cannot be consumed.

3.3 Preparation of compact ceramics with high grain orientation

The ceramics prepared with 50 wt% templates show a loose microstructure and low grain orientation degree evenly sintered for 20 h. The large space between anisotropy templates is hard to remove to obtain a dense ceramics. The addition of templates should be decreased to

increase the density of ceramics because the small matrix particles would fill in the space between templates and reduce the porosity. Besides, too much templates make

them difficult to align parallel to the tape casting plane. Some templates are not parallel to the direction of tape casting plane as shown in figure 3. Therefore, the amount

Figure 9. XRD patterns of BT-textured ceramics sintered at 1300 °C for different times.

Figure 10. Plots of $\ln G_t$ vs $\ln t$ for BT-textured ceramics.

Figure 11. Plots of $1/T$ vs $\ln(D_t^n/t)$ for BT-textured ceramics.

Figure 12. XRD patterns of BT ceramics with different template contents.

Figure 13. Surface and cross-section microstructure of BT textured ceramics.

of templates should add in a certain amount to ensure the textured structure. The optimized content of templates is 10% according to our studies as shown in figure 12. A ceramic with high orientation degree of 85% is obtained. The orientation degree of the ceramics decreases with increasing amount of templates, which confirms our assumption. The grain orientation is almost diminished, when the amount of templates reaches to 40%. Analysis in §3.1 concludes two processes of grain growth in textured-BT ceramics. The key procedure is the absorption of matrix grains by the templates. In the ceramic with 10% templates, the amount of matrix is much more than templates which limit the absorption process of matrix. The temperature is designed to 1400 °C to accelerate the absorption process. However, the pores tend to lock in compact at this high temperature. As a result, a dense ceramic is obtained with 10 wt% template particles and sintered at 1300 °C for 10 h to eliminate the pores and finally it increases rapidly to 1400 °C to obtain high grain orientation degree. The surface and cross-section microstructure of this textured-BT ceramics are shown in figure 13.

4. Conclusions

Textured-BT ceramics were fabricated by TGG method. The results showed that the ceramics were composed with equiaxed matrix grains and brick-like template particles. BT specimens had a microstructure with brick-like particles aligned parallel to the casting direction and exhibited a (*h*00) preferred orientation. Competition of matrix absorption process and grain growth of templates determined the grain orientation degree. Round morphology of BT matrix resulted in the absence of terrace. The activation energy of matrix grains and templates were calculated. The value was 364 kJ/mol for matrix grains and 918 kJ/mol for templates. Grain growth exponent of templates was higher than matrix which indicated a slow growth rate of templates. A dense ceramic with 85% grain orientation was obtained with 10 wt% template particles after sintering at 1400 °C for 2 h.

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