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Solid state crystal growth of $BiScO_3$-$Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$

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Abstract Single crystals $0.26BiScO_3$-$0.25Pb(Mg_{1/3}Nb_{2/3})O_3$-$0.49PbTiO_3$ [BSPMNT] have been grown for the first time by the solid-state crystal growth (SSCG) method. A <110> oriented $Ba(Zr,Ti)O_3$ crystal seed was embedded in a matrix of BSPMNT compact which was annealed at high temperatures to induce the single crystal growth. Various fluxes, including Bi_2O_3, $LiBiO_2$, $PbO/LiBiO_2$, and PbO/Bi_2O_3, were used and their effects on the microstructure of the annealed compacts and the single crystal growth behavior were investigated. In the annealed samples with PbO/Bi_2O_3 flux, a considerable single crystal growth occurred at 1050 °C (with thickness on the order of 500–1000 μm), without the formation of abnormally large grains in the matrix. The results were explained in terms of the effect of various fluxes, based on the grain growth theory.

Keywords Interface · Grain growth · Single crystal

1 Introduction

Single crystals of $Pb(Mg,Nb)O_3$-$PbTiO_3$ (PMN-PT) and $Pb(Zn,Nb)O_3$-$PbTiO_3$ (PZN-PT) have been reported to exhibit superior properties near their respective morphotropic phase boundaries (MPB), compared to polycrystalline forms of the same compositions [1–3]. Since the discovery of those single crystals in the binary systems, it has been expected that their usage will provide a breakthrough in various piezoelectric applications such as medical transducers, actuators, and sensors. However, PMN-PT and PZN-PT single crystals have low phase transition temperatures, rhombohedral to tetragonal transition temperature (T_{rt}) of 60 °C–90 °C and Curie temperature (T_c) of 140 °C–175 °C, with coercive field (E_c) being on the order of 2–3 kV/cm [1–3]. Thus, new piezoelectric materials with high Curie temperatures and good piezoelectric properties are essential to applications. Instead of PMN-PT and PZN-PT single crystals, several compositions, based on relaxor-PT, such as $Pb(Yb,Nb)O_3$-$PbTiO_3$, $Pb(In,Nb)O_3$-$PbTiO_3$, and $BiScO_3$-$PbTiO_3$, with T_c higher than 250 °C have been explored [4–6]. These single crystals were grown by the flux method and their piezoelectric properties were characterized [4–6]. However, it is difficult to grow these single crystal systems due to the poor perovskite stability [7]. Alternative approach to increase T_c as well as the phase stability of relaxor-PT crystals, several compositions in ternary systems, such as $Pb(Mg,Nb)O_3$-$PbTiO_3$-$PbZrO_3$ and $Pb(In,Nb)O_3$-$PbTiO_3$, have been studied [8, 9].

Recently, Stringer et al. investigated relaxor ferroelectric $BiScO_3$-$Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ ternary system in polycrystalline ceramics [10–12]. In this ternary system, dielectric permittivity was reported to be >2000 at room temperature with a variety of electrical properties, while the T_{max} was relatively high, being on the order of ~300 °C. According to our preliminary experiments of this system, it was found that the value of T_c was relatively high about ~370 °C with large piezoelectric coefficient (d_{33}~385 pC/N). The above excellent properties of polycrystalline BSPMNT ceramics demonstrated

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that the $BiScO_3$-$Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ single crystals are promising candidates for next-generation electromechanical devices operated at elevated temperature.

In this work, $BiScO_3$-$Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ composition on rhombohedral side at proximity of MPB was selected based on our previous study, the $BiScO_3$-$Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ single crystals were grown for the first time by the solid-state single crystal growth (SSCG) method.

2 Experimental procedure

Conventional mixed oxide processing was used to prepare the $0.26BiScO_3$-$0.25Pb(Mg_{1/3}Nb_{2/3})O_3$-$0.49PbTiO_3$ (BSPMNT). Samples were fabricated with high-purity oxide powders: Bi_2O_3 (99.99 %, MCP Inc., Fairfield), Sc_2O_3 (99.9 %, PIDC), Pb_3O_4 (99.9 %, Alfa Aesar), $MgNb_2O_6$ (in-house-prepared precursor powders), TiO_2 (99.5 %, Ishihara Co.). The raw powders were stoichiometrically weighed and mixed for 24 h using ball milling in an anhydrous ethanol solution with stabilized zirconia media. These mixtures were then dried at 80 °C and calcined at 780 °C for 3 h to form the desired perovskite phase. For the growth of BSPMNT single crystals, four kinds of fluxes were used: Bi_2O_3, $LiBiO_2$ (in-house-prepared powders), and mixtures of ($PbO/LiBiO_2$ and PbO/Bi_2O_3). The calcined powders with 8 mol% of different fluxes were mixed again by vibratory milling and dried prior to sintering.

Powder compacts without a seed crystal were prepared as a function of various fluxes by pressing in a stainless steel die of 20 mm diameter, followed by cold isostatic pressing (CIP) at 300 MPa at room temperature. Samples were annealed at 1050 °C for 100 h in closed double alumina crucibles, with source powder of the same composition to minimize the loss of PbO/Bi_2O_3 during the sintering.

BSPMNT single crystals were grown by the solid state crystal growth(SSCG) process. A $Ba(Zr,Ti)O_3$ (BZT) seed crystal (Ceracomp Co., Ltd., Chungnam, Korea) oriented in the <110> direction was used and embedded in the prepared powders, followed by CIP at 300 MPa. The seed-embedded compacts were annealed at the same temperature of 1050 °C to affect the SSCG process.

The phase purity of the calcined powders was examined by X-ray powder diffraction (XRD; PAD V diffractometer, Scintag Inc., Cupertino, CA), showing the single rhombohedral perovskite phase. For the analysis, all seed-embedded samples were vertically diced with a low-speed diamond wheel saw and polished. In addition, microstructures of the annealed samples were studied using scanning electron microscopy (SEM; S-3500N, Hitachi).

3 Results and discussion

3.1 Effect of various fluxes on the microstructures of polycrystalline BSPMNT

Interface structures, dopants, annealing atmosphere, and annealing temperature have been identified as key variables that influence the grain growth [13, 14]. Among them, the type of solid/liquid interface or grain boundary, either faceted or rough, has been suggested to control the grain growth behavior in polycrystalline materials [15–25]. Two types of grain growth have been documented during sintering and annealing of powder compacts: normal grain growth (NGG) and abnormal grain growth (AGG). In NGG, the average grain size increases continuously with little changes in grain size distribution. In AGG, a few large grains grows rapidly at the expense of small matrix grains. Furthermore, the AGG prevails when the interface or boundaries are faceted [15–21, 26], while NGG occurs in systems with rounded or atomically rough interfaces or boundaries [22, 24, 27]. In SSCG, crystal acts as a large grain to initiate AGG into the matrix to form a single crystal while consuming the fine grains. In this case, the AGG should take place from the seed crystal only because large grains in the matrix impede the single crystal growth from the seed.

The variations in microstructure and grain size of annealed samples are illustrated as a function of different fluxes in Fig. 1. When $LiBiO_2$ flux was used, as shown in Fig. 1(a), the microstructure was porous with pores of different sizes and the average grain size was very big, being about 40 μm. With Bi_2O_3 flux in Fig. 1(b), the densification was not completed during the annealing and a number of cracks with large pores were developed in the matrix. In addition, the grain size was found to be small, being approximately 4 μm (see Fig. 1(b)). In the case of $PbO/LiBiO_2$ flux mixture in Fig. 1(c), the microstructure was similar to the $LiBiO_2$ case, but its grain size was significantly decreased, suggesting that the rate-controlling mechanism of grain growth in BSPMNT changed from phase-boundary reaction to diffusion through the liquid phase during the liquid-phase sintering stage [25]. In contrast, the PbO/Bi_2O_3-added BSPMNT ceramics revealed a relatively dense microstructure with small pores uniformly distributed in the whole matrix, as shown in Fig. 1(d). The grains were angular in shape and relatively uniform in size, being about 4 μm on average (see the inset of Fig. 1(d)).

As mentioned earlier, for successful single crystal growth by SSCG, the occurrence of AGGs in the matrix must be suppressed because large grains in the matrix would cause the driving force for SSCG to decrease and inhibit the growth of single crystal from the surface of the BZT seed. Thus, the grain size during the annealing should be controlled. When the $LiBiO_2$ flux was used, as shown in Fig. 1(a), the grain size was too large to grow single crystal from the BZT seed. For the

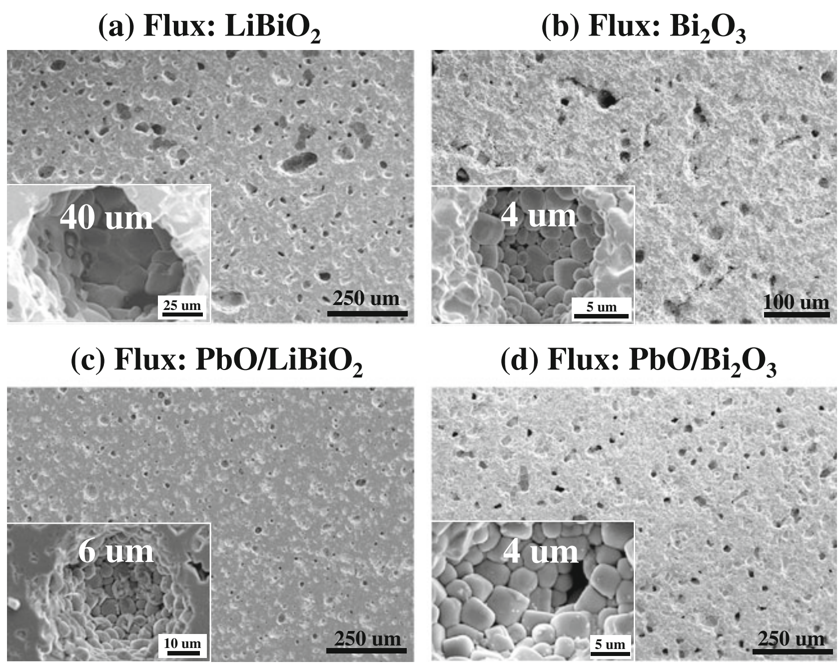

Fig. 1 Effect of fluxes on microstructures in polycrystalline BSPMNT

case of Bi_2O_3 or PbO/$LiBiO_2$ addition (see Fig. 1(b,c)), while the grain size was small, the porous microstructures would again limit the crystal growth. With PbO/Bi_2O_3 flux mixture, small grains with high uniformity were formed during the annealing process, as shown in Fig. 1(d), which will benefit the single crystal growth.

Grain shape control is very important to develop the AGG only at the surface of a seed crystal. Based on the single crystal growth theory, the growth mechanism depends on the atomic structure of the interface and the equilibrium shape of the growing grain, which is determined by the anisotropy of the interface energy [28–30]. As schematically shown in Fig. 2, for spherical grains having an atomically rough interface structure, there would be no energy barrier for atomic attachment at the interface. In the case, the grain coarsening rate is controlled by the diffusion through the liquid phase and resultant grain growth behavior follows the straight-dotted line shown in Fig. 2 [27]. On the other hand, faceted or angular grains reveal the presence of a few crystallographic planes with low interface energy [31], the attachment of atoms to the grain is energetically unfavorable and can only occur though the existence of a ledge formed by two-dimensional nucleation (2DN) [15, 27], screw dislocations [26, 32], or re-entrant edges (twins) [17, 33]. In case of 2DN controlled grain growth, the nuclei are thermodynamically unstable and the low driving force results in a low growth rate which , however, rapidly increases when the driving force exceeds a critical value, following the red line in Fig. 2 [34]. In the presence of screw dislocations, grain growth could start even at very low driving forces. The grain growth rate would follow a parabolic behavior initially, but changes to a linear behavior at certain critical driving forces (see the blue broken line in Fig. 2). The result is a less degree of AGG with abnormal grains. As shown in Fig. 1 (a)–(c), most grains were found to be spherical and/or/with rounded corners, which indicate that the grain growth is controlled by diffusion of atoms through the liquid phase. The growth rate in this case is linearly proportional to the driving force for grain growth, resulting in the normal grain growth. In contrast, the grain growth behavior for the sample with PbO/Bi_2O_3 mixed fluxes which exhibits an angular grain shape follows the 2DN or screw dislocation controlled growth described above.

3.2 Flux effect on the growth of BSPMNT single crystal

The flux for single crystal growth is usually required to have a low melting temperature, be stable at the melting

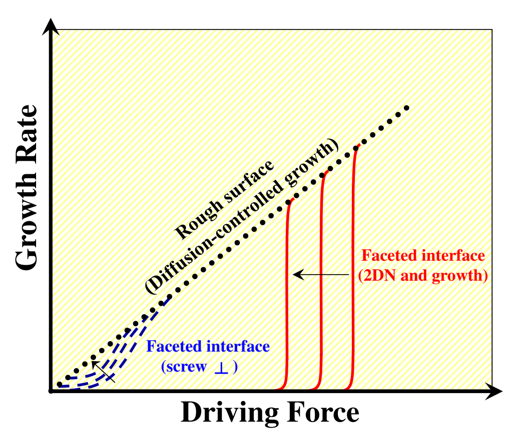

Fig. 2 Scheme of the growth rate against driving force for different types of solid/liquid interface [27]

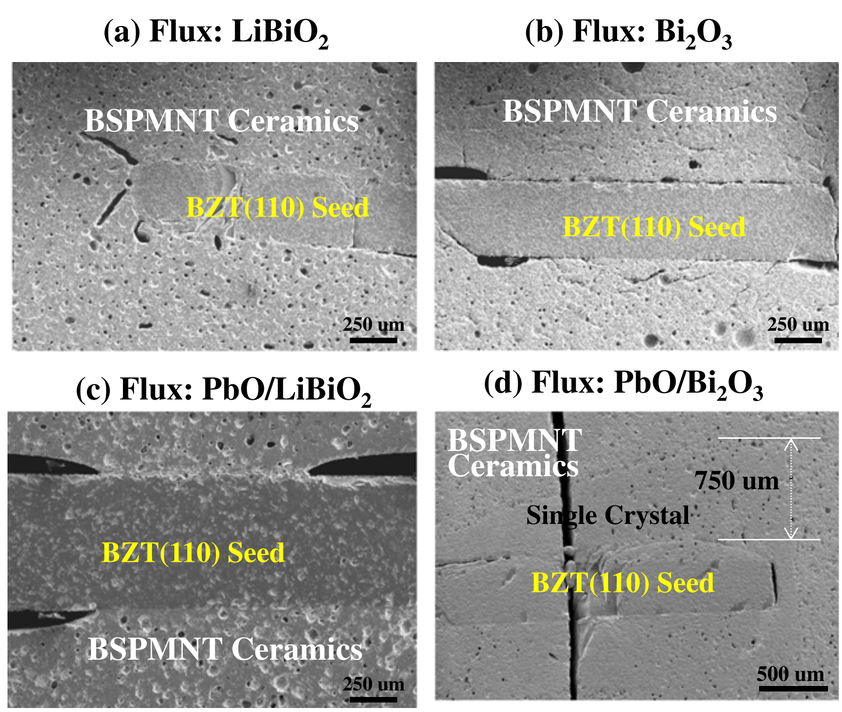

Fig. 3 Effect of fluxes on the growth of BSPMNT single crystal

temperature in various atmospheres, be a good solvent, form no compounds with the growing component, and have no solubility in the crystals being grown [35]. Excess PbO is commonly used to promote abnormal grain growth, yet few other dopants have been examined [13, 36]. Both PbO and Bi_2O_3 are used to compensate the loss of PbO and Bi_2O_3 and to enhance the material transfer by forming liquid phase during sintering, while Li_2O was added with the intention of suppressing abnormal grain growth in the matrix [37]. Figure 3 shows the effect of fluxes on the growth of BSPMNT single crystal by SSCG method. The <110> oriented BZT crystal seed was used and embedded in matrix, which was diffused to a polycrystalline body and grows by consuming fine matrix grains to become a large single crystal after long time annealing. The amount of fluxes in each composition was fixed at 8 mol%. As shown in Fig. 3 (a)–(c), the growth of BSPMNT single crystals were not observed at the surface of the BZT seed crystal, indicating that all fluxes were not contributed to the single crystal growth of BSPMNT. However, the single crystal of BSPMNT was found to grow from the embedded BZT seed, being on the order of ~750 μm, when the mixture of PbO/Bi_2O_3 was added, as shown in Fig. 3(d). In contrast to other fluxes in Fig. 3(a)–(c), it was found that the mixture of PbO/Bi_2O_3 flux is very effective to grow a single crystal of BSPMNT, as shown in Fig. 3(d), which is consistent with the result of microstructures in polycrystalline BSPMNT. Furthermore, the BZT seed crystal was not delaminated from the matrix and the interface between the seed crystal and matrix was distinct, which indicated that the BZT seed crystal in matrix is chemically stable against the flux. To confirm and clarify the stability of BZT seed in BSPMNT crystal, the energy-dispersive X-ray spectroscopy (EDS) point analysis was carried out to measure the composition of the BSPMNT crystal and the BZT seed in the above sample, as shown in Fig. 4. The point analysis exhibited that the as-grown single crystal and the seed single crystal have totally different compositions, indicating that there was no migration of Ba and Zr from the seed into the grown single crystal. Therefore, it can be confirmed that the BZT seed crystal is chemically stable in the matrix with the flux of PbO/Bi_2O_3 and good for growing the BSMNT single crystals. For the grown single crystals, however, a large amount of pores were trapped inside and consequently the

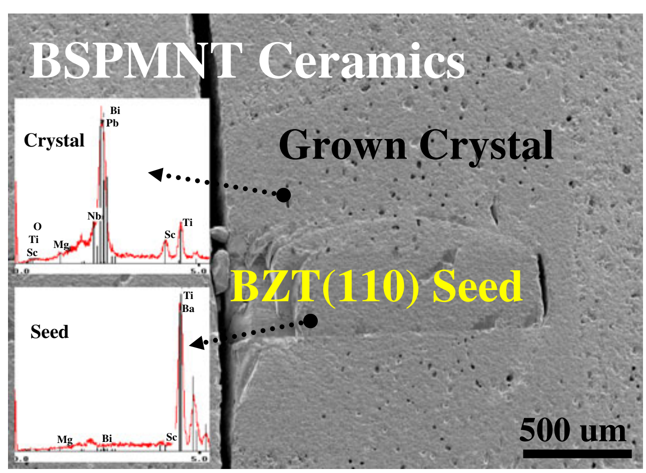

Fig. 4 EDS analysis for BSPMNT single crystal with a BZT seed crystal

grown crystal becomes porous during the growth. Such residual pores in the grown crystals are not desirable for use in piezoelectric applications. Since the pores have detrimental effects on the physical properties of the grown single crystals, it is necessary to remove pores in the precursor matrix before the crystal growth step, such as hot pressing treatment.

4 Conclusions

The BSPMNT single crystals were grown by solid-state crystal growth (SSCG) method. Four different kinds of fluxes were used and the effects on the microstructure and grain growth have been investigated for the single crystal growth of BSPMNT. During the SSCG process, small grain size in matrix is desirable, in order to grow single crystals from the surface of the seed. The grain shape can be controlled by the addition of dopants, because the equilibrium grain shape of a crystal is affected by the anisotropy of the interface energy. In addition, the growth rate is governed by the driving force through the difference in size between seed and the matrix grains. Considering the growth of high quality single crystal, optimum annealing conditions with the critical temperature for abnormal grain growth to get fully dense and fine-grained BSPMNT are required, to improve the reproducibility and increase growth rate. The preliminary results indicated that BSPMNT single crystals with size being on the order of 500–1000 μm were obtained, using PbO/Bi_2O_3 as flux and annealing at 1050 °C for 100 h, with a <110> oriented BZT crystal seed embedding in the BSPMNT ceramic matrix.

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