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The effect of $Bi_4Ti_3O_{12}$ particles addition in lead-free $Bi_{0.5}(Na_{0.75}K_{0.25})_{0.5}TiO_3$ ceramics

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Abstract We studied the effect of $Bi_4Ti_3O_{12}$ (BiT) platelet addition in $Bi_{0.5}(Na_{0.75}K_{0.25})_{0.5}TiO_3$ (BNKT) ceramics by preparing two kinds of BNKT ceramics. One type of BNKT ceramic was fabricated by a conventional solid state reaction method (normal sample), while the other by addition of 15 wt% BiT platelets to BNKT powders (BiT-added sample). In the case of BiT-added BNKT ceramics, plate like grains were formed by the reaction of BiT platelets with Na_2CO_3, K_2CO_3, and TiO_2 during the sintering process. The grain size of BiT-added BNKT ceramics was 10 times larger than that of normal BNKT ceramic. The piezoelectric strain and d_{33} values of BiT-added BNKT ceramics were 0.135% and 225 pm/V, respectively. These values were 35% higher than those of normal BNKT ceramics. The piezoelectric properties of BiT-added BNKT ceramics were enhanced by the higher domain activity due to a decrease in domain density at larger grain sizes.

Keywords Bismuth sodium potassium titanate · Piezoelectric · Grain size · Strain

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1 Introduction

The most widely used piezoelectric ceramics are lead oxide based ferroelectrics, especially $Pb(Zr,Ti)O_3$ (PZT). PZT exhibits high piezoelectric properties close to the morphotropic phase boundary (MPB) between rhombohedral and tetragonal phases. Nevertheless, the most used PZT ceramics contain 60 wt.% lead. Due to the high toxicity of lead, there is a significant interest in developing lead-free piezoelectric ceramics with a particular interest in developing lead-free solid solution systems exhibiting MPB range [1–10].

Bismuth sodium titanate, $Bi_{0.5}Na_{0.5}TiO_3$ (BNT)-based solid solution is considered to be an excellent candidate for lead-free piezoelectric materials because BNT is a strongly ferroelectric material with a high Curie temperature, T_c= 320°C, and a high remanent polarization, P_r=38 μC/cm^2 [1, 2]. However, BNT has the drawback of a high coercive field, E_c=73 kV/cm and high conductivity, which causes problems in the poling process. Therefore, some researchers have investigated BNT based ceramics that can be poled easily [1–7]. Among these investigations, bismuth potassium titanate, $Bi_{0.5}K_{0.5}TiO_3$ (BKT), is a well-known lead-free piezoelectric material with a tetragonal phase. The binary system of $(1-x)$BNT$-x$BKT piezoelectric ceramics was reported by Sasaki et al. [4]. These systems revealed relatively high piezoelectric and dielectric properties near the morphotropic phase boundary (MPB). Recently, Tani et al. prepared grain-oriented ceramics with perovskite structure by the reactive templated grain growth (RTGG) method [10–15], using plate like $Bi_4Ti_3O_{12}$ particles. The plate like $Bi_4Ti_3O_{12}$ particles were aligned parallel to the tape casting direction to act as templates for the oriented growth of BNKT grains. The grain oriented BNKT ceramics enhanced the electrical properties like planar coupling coefficient due to the increased crystallographic orientation [13–15]. In addition, the textured BNKT ceramics fabricated by RTGG with plate like $Bi_4Ti_3O_{12}$ particle not only increase the degree of the grain orientation but also the grain size. In this work, we have fabricated $Bi_{0.5}(Na_{0.75}K_{0.25})_{0.5}TiO_3$ (BNKT) ceramics by addition of 15 wt.% $Bi_4Ti_3O_{12}$ (BiT) particles and examined the effect of BiT crystal particles (platelets) in the BNKT ceramics by measuring piezoelectric properties.

2 Experimental procedure

To study the effect of BiT platelets addition in BNKT ceramics, we prepared two kinds of BNKT ceramics. One type of BNKT ceramics was fabricated by a conventional solid state reaction method (normal BNKT sample). The oxide powders Bi_2O_3, Na_2CO_3, K_2CO_3, and TiO_2 of above 99.9% purity were used as raw materials. These raw powders were ball-milled in methyl alcohol with zirconia balls for 10 h. The milled solids were dried and then heated in a covered alumina crucible at 800°C for 2 h. The calcined mixtures were compacted into disk samples with a pressure of 50 MPa, and sintered at 1150°C for 2 h in air ambient. The other type of BNKT ceramics contain BiT platelets (BiT-added sample). Plate like BiT particles were prepared from Bi_2O_3 and TiO_2 using molten-salt synthesis. Bi_2O_3 and TiO_2 were mixed in the molar ratio of 2:3 and ball-milled as described above. After drying, the ball-milled oxides were mixed with an equimolar mixture of NaCl and KCl (weight ratio of oxides to salt=1:1) and heated in a covered alumina crucible at 1050°C for 2 h in air atmosphere. After heat treatment, NaCl and KCl were removed by washing with distilled water. BiT platelets with an average diameter of 5~10 μm and a thickness of 0.5 μm were obtained. The BiT platelets were mixed with raw materials of BNKT powders. The amount of BiT platelets was 15 wt.% of BNKT powders. Additional amounts of Na_2CO_3, K_2CO_3, and TiO_2 to the stoichiometry were included in the mixing batch to react with the BiT by following reactions.

$$Bi_4Ti_3O_{12} + 1.5Na_2CO_3 + 0.5K_2CO_3 + 5TiO_2 \rightarrow 8Bi_{0.5}(Na_{0.75}K_{0.25})_{0.5}TiO_3 + 2CO_2 \quad (1)$$

The mixtures were compacted into disk samples with a pressure of 50 MPa, and sintered at 1150°C for 10 h in air ambient. The composition and microstructure of the sintered ceramics were measured using electron probe micro analysis (EPMA) and scanning electron microscopy (SEM) on the thermal etched surface. For electrical measurements, the specimens were cut into small pieces and silver electrodes were deposited on both sides of the specimens using dc sputtering. For piezoelectric measurement, the specimens were poled in silicon oil at 50°C with a dc field of 5 kV/mm for 30 min. The strain versus electric field was measured by linear variable differential transducer (LVDT). The piezoelectric coefficients (d_{33}) for the sample were estimated from the ratio of the maximum strain to the maximum field, S_{max}/E_{max}, in the unipolar strain–field curves.

3 Results and discussion

Figure 1 shows the XRD patterns of normal and BiT-added BNKT ceramics. The diffraction peaks of all specimens are consisted of only perovskite phase without secondary phase [4, 13]. Not only the normal BNKT ceramics, but also the BiT-added BNKT ceramics are randomly oriented without any crystalline orientation.

Figure 2 shows the microstructures of normal and BiT-added BNKT ceramics. The normal BNKT ceramics are composed of a rectangular solid type, and the grain size was smaller than 1 μm as shown in Fig. 2(a). However, the BiT-added ceramics are composed of two types of BNKT grains. One type of grain is a rectangular solid type (similar to that of normal BNKT ceramics), while the other type of grain is plate like. In the case of BiT-added BNKT ceramics, plate like BNKT ceramics are formed by the reaction of BiT platelets with Na_2CO_3, K_2CO_3 and TiO_2 during the sintering process as given in equation (1). The size of plate like BNKT grain was 5~10 μm in the edge length and 1~2 μm in thickness. So, the average grain size of BiT-added BNKT ceramics is about ten times larger than those of normal BNKT ceramics.

Figure 3 shows the unipolar electric field induced strain of normal and BiT-added BNKT ceramics. Electric field as high as 60 kV/cm was applied using a triangular wave form at 0.1 Hz. The longitudinal converse piezoelectric coefficient, d_{33}, was calculated from the ratio of maximum strain

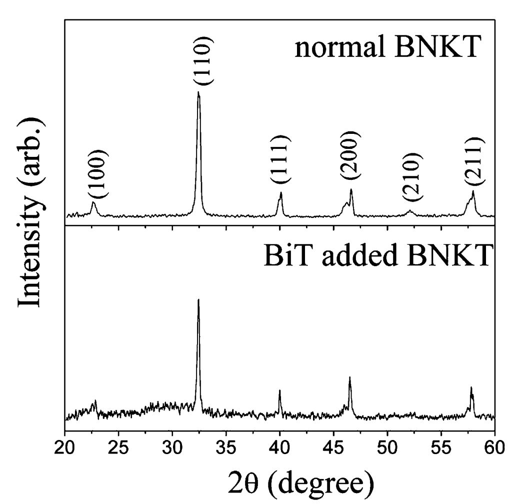

Fig. 1 XRD patterns of normal and BiT-added BNKT ceramics

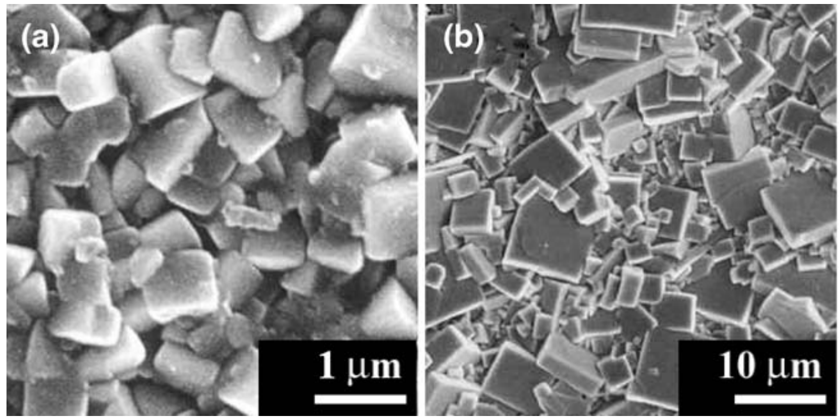

Fig. 2 SEM images of (**a**) normal and (**b**) BiT-added BNKT ceramics

to maximum field in the cycle, S_{max}/E_{max}. As expected, the BiT-added BNKT ceramics show superior piezoelectric properties. The strain and d_{33} values of normal BNKT ceramics were 0.1% and 165 pm/V, respectively. The BiT-added BNKT ceramics have higher strain values than those of normal BNKT ceramics. The strain and d_{33} values of BiT-added BNKT ceramics were 0.135% and 225 pm/V, respectively. These are the highest values among those of randomly oriented $(Bi_{0.5}Na_{0.5})TiO_3$-based ceramics reported by other researchers [11–15]. Moreover, the d_{33} value of BiT-added BNKT ceramics is similar to that of pure $Pb(Zr_{0.52}Ti_{0.48})O_3$ ceramics [16].

Figure 4 shows the bipolar electric field induced strain (butterfly loops) of normal and BiT-added BNKT ceramics with applied electric field of ±60 kV/cm. All curves show typical butterfly loops. The strain of the BiT-added BNKT ceramics was larger than that of normal samples. The rising of the curve near the coercive field in the BiT-added BNKT ceramics was more pronounced than normal BNKT ceramics. The coercive field of the BiT-added BNKT ceramics was lower than that of normal BNKT ceramics. Moreover, the hysteresis in unipolar electric filed induced strain of the BiT-added BNKT ceramics was lower than that of normal BNKT ceramics as shown in Fig. 3. The high d_{33} values, low coercive field and low hysteresis in the piezoelectric strain are the characteristic of the BiT-added BNKT ceramics related to higher domain activity. W. Cao and C. A. Randall et al. studied the effect of the grain size on piezoelectric and ferroelectric properties [17, 18]. According to their report, the piezoelectric coefficients, dielectric constant and remanent polarization were increased with increasing grain size up to 3 μm in the PZT ceramics. This trend was also consistent with $BaTiO_3$ and PZT thin films, as reported by Arlt [19] and Warren et al. [20]. They explained this effect by the change of the grain boundary conditions. The clamping of domain walls at the grain boundaries from their neighbors caused a relative increase in domain density at a smaller grain size [21, 22].

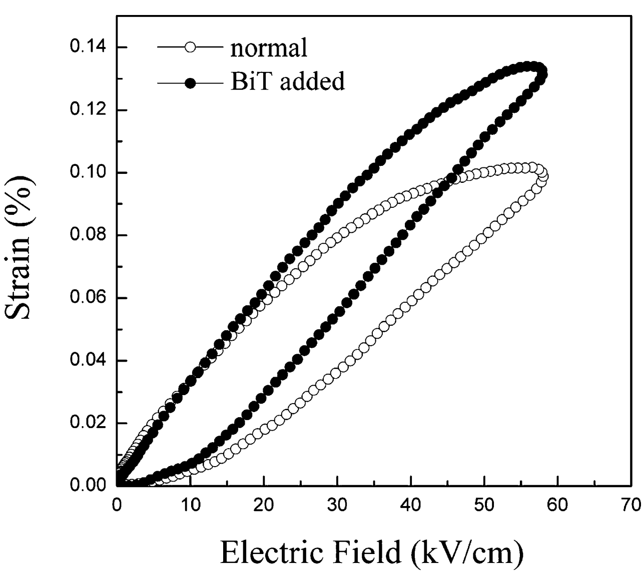

Fig. 3 Unipolar electric field induced strain of normal and BiT-added BNKT ceramics

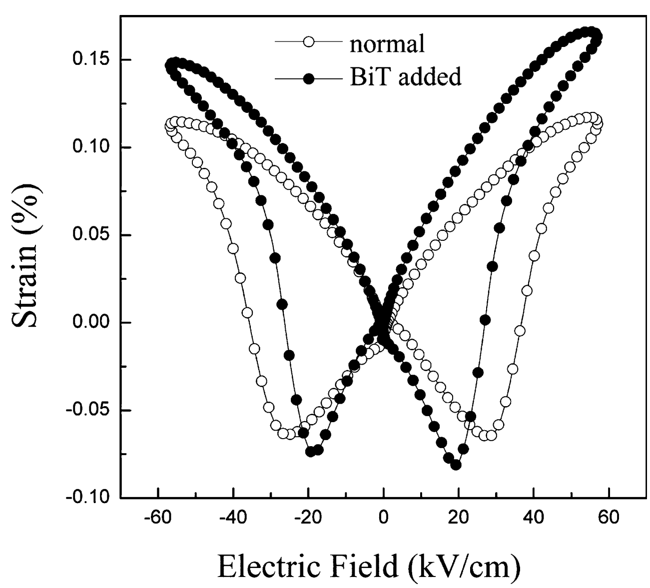

Fig. 4 Bipolar electric field induced strain of normal and BiT-added BNKT ceramics

For the submicrometer grain size, the strong coupling between the grain boundaries and the domain walls make the domain reorientation more difficult and severe to constrain the domain wall motion. This phenomenon reduced the piezoelectric coefficient, dielectric constant and remanent polarization.

In this work, the average grain size of the normal BNKT ceramics was smaller than 1 μm. However, the grain size of BiT-added BNKT ceramics was about ten times larger than those of normal BNKT ceramics as shown in Fig. 2. So, the values of the electric field induced strain and d_{33} of BiT-added BNKT ceramics were higher than those of normal BNKT ceramics. This effect was caused by higher domain activity due to decrease of domain density at larger grain sizes.

4 Conclusions

The effect of $Bi_4Ti_3O_{12}$ particle addition in $Bi_{0.5}(Na_{0.75}K_{0.25})_{0.5}TiO_3$ ceramics was investigated for lead-free piezoelectric ceramic actuators. In the case of the BiT-added sample, during the sintering process, BiT platelets combined with Na_2CO_3, K_2CO_3, and TiO_2 to form plate like BNKT ten times larger than those of normal BNKT ceramics. The strain and d_{33} values of BiT-added BNKT ceramics were 0.135% and 225 pm/V, respectively. This value is 35% higher than those of the normal BNKT ceramics. This effect was caused by a higher domain activity due to the decrease in domain density at larger grain sizes. So, increase in grain size by using the crystal particles will be a key in the development of lead-free ceramics with high piezoelectric performance.

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