The Dielectric and Piezoelectric Properties of K\(\text{NbO}_3\) / Ba\(\text{TiO}_3\) Composites With A Wide Ba\(\text{TiO}_3\) Size Distribution

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K\(\text{NbO}_3\) (KN) / Ba\(\text{TiO}_3\) (BT) composites with heteroepitaxial interfaces were solvothermally synthesized using the barium titanate powder with a wide particle size distribution. Compared with the composites prepared with a narrow particle size distributions, the relative density increased to 68 - 80 %. The dielectric constant was increased to 300 – 450, while an obvious increase in the electric-field-induced strain was not observed. The dielectric and piezoelectric properties were maximized at the K\(\text{NbO}_3\)/Ba\(\text{TiO}_3\) molar ratio of 0.5.

Key words: barium titanate, potassium niobate, solvothermal synthesis.

1. INTRODUCTION
Lead-free piezoelectric materials have been studied due to environmental concern. However, the piezoelectric properties were often lower than those of lead-based piezoelectrics. One of the methods to increase the piezoelectric properties is to make a system with a morphotropic phase boundary (MPB). Therefore, researches on making solid-solutions of end-members with different crystal structures have been conducted to increase the piezoelectric properties. MPB materials have been studied in recent years, and some new MPB materials such as rare-earth doped BiFeO\(_3\) [1], BiCoO\(_3\)-BiFeO\(_3\) [2], and (Na\(_{0.5}\)K\(_{0.5}\))NbO\(_3\)-BaZrO\(_3\)-(Bi\(_{0.5}\)K\(_{0.5}\))TiO\(_3\) [3] were found. However, the number of MPB materials is small, and thus a new method to create high performance piezoelectric materials is desired.

An alternative method to increase the piezoelectric properties is the use of an artificial superlattices’ structure. It was reported that Ba\(\text{TiO}_3\) (BT) / Sr\(\text{TiO}_3\) (ST) superlattices showed large dielectric properties [4] and these were attributed to the rotated polarizations near the BT / ST interfaces [5, 6]. Recently, this structure has been applied to solvothermally synthesized K\(\text{NbO}_3\) (KN) / BT composites and a large piezoelectric response was demonstrated [7-10]. The composites have heteroepitaxial interfaces between KN layers and BT particles, and the crystal structure near the interface was gradually changed [10]. Since an orthorhombic KN phase has the spontaneous polarization with \(<110>\) directions while a tetragonal BT phase has the spontaneous polarization with \(<100>\) directions at room temperature, the spontaneous polarization could have rotated near the interfaces.

There is a problem in preparing dense KN/BT composites; the relative density was as low as 64 – 70 % [9]. An approach to increasing the density is the use of BT powders of several different particle sizes. In previous study, BT powder of the average diameter of 0.3 \(\mu\)m with a narrow particle size distribution was used as the BT source for the Nb\(_2\)O\(_5\)-BT compacts which would be synthesized to KN/BT composites. If the particle size distribution of the BT powder is wide, smaller BT particles can fill the tetrahedral or octahedral interstices of a close-packed structure of large BT particles so that a dense composite could be expected. Mathematically, for a close-packed structure of \(n\) particles with the diameter \(r\), \(n\) particles with the diameter 0.414\(r\) can fill the octahedral interstices and 2\(n\) particles with the diameter 0.225\(r\) can fill the tetrahedral interstices. In this study, BT powders with the diameters of 0.5 \(\mu\)m, 0.3 \(\mu\)m, and 0.1 \(\mu\)m were used as the BT source of KN/BT composites (the mathematical relation of the diameters was slightly relaxed), with the ratio of the number of the particles with the diameters of 0.5 \(\mu\)m, 0.3 \(\mu\)m, and 0.1 \(\mu\)m being 1:1:2, and the density, microstructure, crystal structure, and dielectric and piezoelectric properties were investigated.

2. EXPERIMENTAL PROCEDURE
KN/BT composites with KN/BT molar ratios (\(x\)) of 0.2 – 1.0 were prepared by a solvothermal synthesis. The starting materials were BT powders with the average diameters of 0.5 \(\mu\)m (BT05, Sakai Chemical Industry), 0.3 \(\mu\)m (BT03, Sakai Chemical Industry), and 0.1 \(\mu\)m (synthesized from barium titanyl oxalate, Nippon Chemical Industrial [11]) and Nb\(_2\)O\(_5\) powder (99.9%, the particle diameter: approximately 1 \(\mu\)m, Rare Metal). The ratio of the number of the BT particles with the average diameters of 0.5 \(\mu\)m, 0.3 \(\mu\)m, and 0.1 \(\mu\)m was 1:1:2 and the mixed BT powders are referred to as BT05mix hereafter. They were ball-milled with ethanol and zirconia balls for 17 h. After 2 wt % polyvinyl butyral was added, the ethanol was dried at 80 \(^\circ\)C for 3 h. The mixture was ground, screened through a 250 mesh, and then pressed into green compacts using a uniaxial press at 250 MPa. After binder burnout at 600 \(^\circ\)C, the density of the compacts was measured by an
Archimedes method with ethanol. In an autoclave, the Nb\textsubscript{2}O\textsubscript{5}-BT compacts were heated at 230˚C for 20 h with KOH (UGR grade, Kanto Chemical), K\textsubscript{2}CO\textsubscript{3} (UGR grade, Kanto Chemical), and ethanol (EL grade, Kanto Chemical), with a ratio of 20 l of ethanol, 2 mol of KOH, and 9 mol of K\textsubscript{2}CO\textsubscript{3} per 1 mol of Nb\textsubscript{2}O\textsubscript{5} of the compact.

After the solvothermal reaction, the KN/BT composites were washed with ethanol and dried at 200 ˚C for 5 h. The density was remeasured. For the crystal structure analysis, the composites were crushed to powder and the crystal structure of the powder was investigated by laboratory X-ray diffraction (XRD, RINT2000, Rigaku) with Cu K\textsubscript{α} radiation and synchrotron radiation (SR) powder diffraction with the energy of 18.5 keV (the wavelength: 0.66861Å) at BL02B2 in SPring-8[10]. For selected composites, the microstructure was observed by high-resolution transmission electron microscopy (TEM) and the elemental mapping was performed with energy dispersive X-ray spectroscopy (EDS). For electric measurements, the composites were polished and sawed to a size of 2 x 2 x 0.4 mm\textsuperscript{3}. Au electrodes were sputtered on the top and bottom surfaces with an area of 2 x 2 mm\textsuperscript{2}. The room temperature dielectric properties were measured at 1 MHz using an impedance analyzer (HP4294A, Agilent). The polarization – electric field (P-E) loops were measured using a ferroelectric characteristic evaluation system (FCE-3, Toyo Corporation). The strain – electric field (S-E) curves were measured using a strain measuring system (Model JP005-SE, Kitamoto Denshi) with a displacement meter (Millitron 1202 IC, Mahr).

3. RESULTS AND DISCUSSION

The relative density of the Nb\textsubscript{2}O\textsubscript{5}-BT compacts and KN/BT composites prepared using either BT05mix (this study) or BT03 powder [9] is shown in Fig. 1. The relative density of the BT05mix compacts was approximately 65 %. After the reaction, the density of the BT05mix composites increased to 68 – 80 %. These densities of the BT05mix compacts and composites were larger than those of the BT03 compacts and composites. Thus, the use of BT powders with multiple particle size distributions was effective to increase the density of the KN/BT composites. Note that the density of the BT05mix composites increased with x simply because of the increase in KN content.

The XRD measurements indicated no Nb\textsubscript{2}O\textsubscript{5} peaks and only perovskite peaks for the BT05mix composites (not shown). The SR diffraction patterns near the tetragonal (200) and (002) peaks of the BT05 powder and the composites with x=0.2, 0.6, and 1.0 are shown in Fig. 2. It was observed that the intensity between the (200) and (002) peaks increased with increasing x. Such an increase in XRD intensity was also reported for the BT03 composites [10] and nano-sized BT particles [12]. In the reports, it was shown that the increase was attributed to gradually distorted crystal structures near the KN/BT interfaces and the surfaces of the BT nanoparticles. Thus, the increase in the XRD intensity of the BT05mix composites suggests the existence of the KN/BT interface region with gradually distorted crystal structures.

The TEM-EDS studies were performed for x=0.3, 0.5, and 0.8. They showed that BT particles were well separated from KN layers and there was no obvious diffusion. An example of x=0.3 is shown in Fig. 3. Here, the data show the chemical composition mapping images of Ba, Ti, O, K, and Nb atoms with the high-angle annular dark-field (HAADF) image. The thickness of the KN layers was measured from the TEM images. The measured KN thickness increased with increasing x, that is, 33±8, 56±5, and 58±11 nm for
The microstructures of the interface region of x=0.3, 0.5, and 0.8 were studied using high-resolution TEM. Typical images observed are shown in Fig. 4. The epitaxial interfaces between BT particles and KN layers were observed. It was found that all the three samples had dislocations (which appeared in white) in KN layers. This was probably associated with the KN layer thickness. In previous study, dislocations were not observed for the BT03 composites with KN layer thickness thinner than 22 nm; otherwise, they were observed. It is believed that the thicker samples have the dislocations to relax the strain generated due to the heteroepitaxy. The KN layer thickness of the BT05mix composite studied for the TEM observation was thicker than 33±8 nm. The thicker thickness is a possible reason for the dislocation. It is interesting to note that the dislocations were observed in the [001] direction, while they were not observed in the [01-1] direction.

Figure 5 shows the dielectric constant of the composites prepared using the BT05mix powder. The data of the BT03 powder composites are also presented for comparison [9]. It was found that the dielectric constant of the BT05mix composites was larger than that of the BT03 composites. This was attributed to the increased density of the BT05mix composites. In addition, the dielectric constant of the BT05mix composites was maximized at x=0.5, which was consistent with the result of the BT03 composites. A possible origin of the KN/BT ratio dependence was shown by Rietveld analyses of the SR diffraction patterns of the BT03 composites [10]. This pointed out that the dielectric property was a function of the volume of the KN/BT interface region of the gradually distorted crystal structures. The analysis of the BT05mix composites would be the future work for understanding this. Note that the dielectric loss (tanδ) of the BT05mix composites was about 0.03 throughout x, and that of the BT03 composites was reportedly lower.
than 0.05. There was no strong x dependence of tan δ.

Figs. 6 (a) - (c) show the bipolar S-E and P-E behaviors and the unipolar S-E curves of the composites, respectively. The bipolar S-E responses were ferroelectric butterfly-type curves, although they did not show a saturation behavior at the electric field amplitude. The P-E loops were slimer and less hysteretic. Similar to the dielectric constant data, the electric-field-induced strain and polarization were maximized at x=0.5. One can directly see this on Fig. 7, where the apparent piezoelectric coefficient calculated from the unipolar S-E curve was plotted as a function of x. The figure also shows the piezoelectric response of the BT03 composites [13]. The piezoelectric response of the BT03 composites was maximized at x=0.8, which was different from this study. Further studies are needed to understand the discrepancy. Compared with the BT03 composites, an obvious increase in the piezoelectric response was not observed for the BT05mix composites. It is believed that the density needs to increase for increasing the piezoelectric properties. A possible way to do this is to have BT particles partially connected by annealing BT compacts at a lower temperature. To this end, a process to deposit KN layers on the BT connected particles needs to be developed.

4. SUMMARY
The BT05mix composites with heteroepitaxial interfaces were prepared by a solvothermal synthesis. Compared to the BT03 composites, the relative density of the composites increased. Because of this, the larger dielectric constant of 300 – 450 was observed. On the other hand, an obvious increase in the piezoelectric response was not observed. The dielectric constant and the electric-field-induced strain and polarization were maximized at the KN/BT ratio of 0.5. A clear understanding for this needs further study.

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6. REFERENCES


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