Preparation of barium titanate–potassium niobate ceramics using interface engineering and their piezoelectric properties

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Barium titanate (BaTiO$_3$, BT)–potassium niobate (KNbO$_3$, KN) solid solution system (0.5BT–0.5KN) ceramics with various microstructures were prepared by two-step sintering method, and their piezoelectric properties were investigated. For 0.5BT–0.5KN ceramics, two phases, ferroelectric tetragonal and ferroelectric orthorhombic, coexisted in different grains at room temperature, owing to the limited solid solution system. The volume fraction of interface region between BT-rich tetragonal and KN-rich orthorhombic grains was controlled by sintering temperatures, and increased with decreasing sintering temperatures. Apparent piezoelectric constant $d_{33}{}^*$ was measured using slope of strain vs. electric field curves. As the results, the $d_{33}{}^*$ increased with decreasing sintering temperatures, which revealed that interface region between tetragonal and orthorhombic grains could contribute to enhancement of piezoelectric properties.

1. Introduction

Recently, lead-free ferroelectrics have become highly attractive materials from the viewpoint of providing a solution to the environmental problems associated with conventional ferroelectrics such as Pb(Zr,Ti)O$_3$ (PZT) ceramics.[1] However, compared with PZT ceramics,[2] their ferroelectric related properties are very poor, and therefore, it is difficult to use them to replace PZT ceramics. Many researchers have attempted to improve the piezoelectric properties of lead-free ferroelectrics such as bismuth layer-structure ferroelectrics, barium titanate (BaTiO$_3$, BT), and potassium niobate (KNbO$_3$, KN) by chemical modification; however, no significant improvements have been achieved.[1]–[4] Recently, however, chemically modified KN and sodium niobate (NaNbO$_3$) solid solution ceramics have been reported as new lead-free piezoelectrics with a new morphotropic phase boundary (MPB), which there are two ferroelectric phases coexistence, and piezoelectric properties similar to those of PZT ceramics.[5],[6] Thus, there are still some possibilities to obtain high performance lead-free piezoelectrics by introduction of new MPB system. Therefore, many researchers studied new complex oxide materials with new MPB systems.

Schonau et al. reported about an origin of monoclinic phase of PZT ceramics with MPB composition using transmittance electron microscopy (TEM) and synchrotron XRD measurement.[7] As the results, TEM observation revealed that there were very fine nano-ordered structures assigned to three phases in one grain, i.e., tetragonal, rhombohedral and interface between tetragonal and rhombohedral phases while synchrotron XRD measurement indicated that the crystal structure of MPB composition was assigned to monoclinic phase, which suggested

that the origin of monoclinic phase in PZT ceramics with MPB composition was a distorted interface region between tetragonal and rhombohedral phases. Thus, enhancement of piezoelectricity for the PZT ceramics might be related to this distorted interface region between tetragonal and rhombohedral phases. Ishibashi and Iwata reported that in the MPB region with tetragonal and rhombohedral phases, there are no energy barrier between two phases, and it is easy to induce field-induced phase transition.[8] Moreover, on the basis of first principle calculation, Fu and Cohen reported that ultrahigh electromechanical response can be originated from polarization rotation mechanism between tetragonal and rhombohedral phases by an external field.[9] The above discussion suggested that the distorted interface between two different ferroelectric phases can contribute to piezoelectric enhancement by polarization rotation mechanism. Therefore, for the piezoceramics with MPB composition, a control of interface volume fraction can lead to piezoelectric enhancement.[10]

Recently, it was reported that a unique ceramics system with "wide-band MPB region" between tetragonal and orthorhombic ferroelectric phases was reported for KN–BT system.[11] Moreover, for this ceramics system, detail microstructure investigation using TEM revealed that two different phases existed in different grains, and these grain boundary was distorted interface between Ba-rich tetragonal and KN-rich orthorhombic grains because of limited solid solution system between BT and KN.[12] Moreover, it was also reported that the dielectric and piezoelectric maximum were clearly observed at 0.5BT–0.5KN ceramics at room temperature. These results indicated that 0.5BT–0.5KN ceramics had maximum volume fraction of distorted interface region between tetragonal and orthorhombic grains. Therefore, for the BT–KN ceramics, it is very important to clarify a relationship between volume fraction of distorted interface region and enhancement of piezoelectric property.

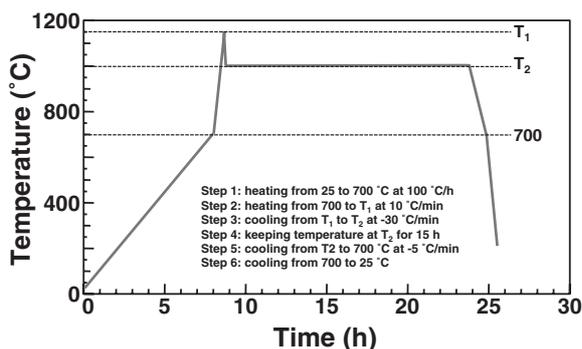[†] Corresponding author: S. Wada; E-mail: swada@yamanashi.ac.jp

Fig. 1.   A schematic two-step sintering program for the 0.5BT–0.5KN ceramics.

Fig. 2.   A SEM Micrograph of the 0.5BT–0.5KN ceramics prepared at 1115°C.

In this study, to clarify a roll of MPB region on piezo-electricity, a relationship between volume fraction of distorted interface region and piezoelectric property was investigated using the 0.5BT–0.5KN ceramics. For the objective, the 0.5BT–0.5KN ceramics with various volume fractions of interface region were prepared by a two-step sintering method, and these micro-structures were investigated by a scanning electron microscopy (SEM). Moreover, apparent piezoelectric constant $d_{33}{}^*$ was measured using slope of strain vs. electric field curves for these ceramics. Finally, the relationship between microstructure and piezoelectricity was discussed for the 0.5BT–0.5KN ceramics.

2.   Experimental procedure

To prepare fine-grained and dense ceramics, the 0.5BT–0.5KN ceramics were prepared by using a two-step sintering method reported for BT ceramics by Karaki et al.[13] As raw materials, KN nanopowders (Nippon Chemical Industrial, 100 nm) and BT nanopowders (Sakai Chemical Industry, 100 nm) were used. These powders were weighed at 0.5BT0.5KN, and then mixed well using ball milling with zirconia balls and ethanol for 17 h, then mixed with polyvinyl butyral (PVB, 2 wt %) as a binder, and dried at 130°C. The powders were meshed and then pressed into green pellets using a uniaxial press at room temperature. After the binder was burned out at 700°C for 10 h, the pellets were sintered by the two-step sintering methods with various temper-ature programs (temperature at the 1st step (T_1) from 1100 to 1150°C for 0 h and temperature at the 2nd step (T_2) from 995 to 1095°C for 15 h in a closed alumina crucible. The detailed sintering program is shown in **Fig. 1**. On the other hand, as a reference sample, some pellets were sintered at 1115°C for 10 h by a normal sintering process.

As in the first characterization, the absolute density of the sintered ceramics was measured by Archimedes method. The relative density was calculated using a theoretical density estimated from lattice parameters using a laboratory X-ray diffraction (XRD) method (Rigaku, RINT2000, Cu Kα, 50 kV, 30 mA). The crystal structure of the ceramics was measured using XRD. The microstructure was observed using SEM. Ceramics with relative densities of over 92% were polished with diamond slurry, and cut using a crystal cutter to sizes of $4.0 \times 1.5 \times 0.4\,mm^3$. Silver electrodes were printed on the top and bottom surfaces with an area of $4.0 \times 1.5\,mm^2$. The dielectric properties of the ceramics were measured at 300 Hz at room temperature using a d_{33} piezometer. Furthermore, both polarization–electric field (P–E) and strain–electric field (S–E) behaviors were measured at room temperature and 0.1 Hz using a ferroelectric character evaluation system. A slope of the S–E curve from 0 to 30 kV/cm was regarded as an apparent $d_{33}{}^*$ value.
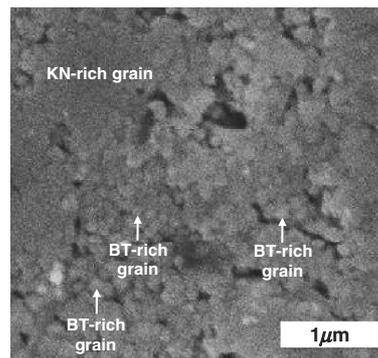
3.   Results and discussion

3.1   Preparation of 0.5BT–0.5KN system ceramics by conventional sintering method

0.5BT–0.5KN system ceramics with high density were prepared by conventional sintering method at 1115°C for 10 h. A color of the sintered ceramics was light yellow while a linear shrinkage ratio and relative density was around 17% and 96%, respectively. The XRD measurement revealed that there were only perovskite phases at room temperature. **Figure 2** shows microstructure of the ceramics observed using SEM. From Fig. 2, two kinds of microstructures were clearly observed, i.e., aggregation of BT-rich nanograins with a size of about 100 nm and fused large KN-rich grains with a size over 1 μm. As the chemical composition analysis, in the BT-rich grains, it was confirmed that there was small amount of KN, while in the KN-rich grains, there was small amount of BT.[12] The Dielectric constant was measured at 300 Hz and room temperature. As the result, dielectric constant was 913 and loss tangent was 1.1%. **Figure 3** shows P–E hysteresis loop and S–E curve for 0.5BT–0.5KN ceramics measured at 0.1 Hz and room temperature. From Fig. 3, apparent piezoelectric constant $d_{33}{}^*$ was estimated at around 15 pC/N. Through this study, the results obtained for 0.5BT–0.5KN ceramics prepared by normal sintering method was regarded as reference data.

3.2   Preparation of 0.5BT–0.5KN system ceramics by two-step sintering method

Next, 0.5BT–0.5KN system ceramics with high density and smaller grain sizes were prepared by two-step sintering method with different programs. First, the sintering temperature at the 1st step (T_1) was optimized, and finally, the T_1 was determined at 1120°C. Next, using various sintering temperatures at the 2nd step (T_2) from 995 to 1095°C, the 0.5BT–0.5KN system ceramics with various microstructures were prepared. A color of the sintered ceramics was almost white while relative density was always over 92%. The XRD measurement revealed that for all of samples, there were only perovskite phases at room temperature. **Figure 4** shows SEM micrograph of the 0.5BT–0.5KN ceramics prepared at T_2 of 995°C. From Fig. 4, many fine pores with sizes below 100 nm were clearly observed in the ceramics, and moreover, this ceramics was composed of fine grains with sizes below 1 μm. On the other hand, **Fig. 5** shows SEM micrograph of the 0.5BT–0.5KN ceramics prepared at T_2 of 1095°C. From Fig. 5, small pores disappeared and small amount of large pores with sizes over 100 nm were observed. Moreover, contrast between two kinds of regions became clear, and each grain sizes increased over 1 μm. The above results suggested that micro-
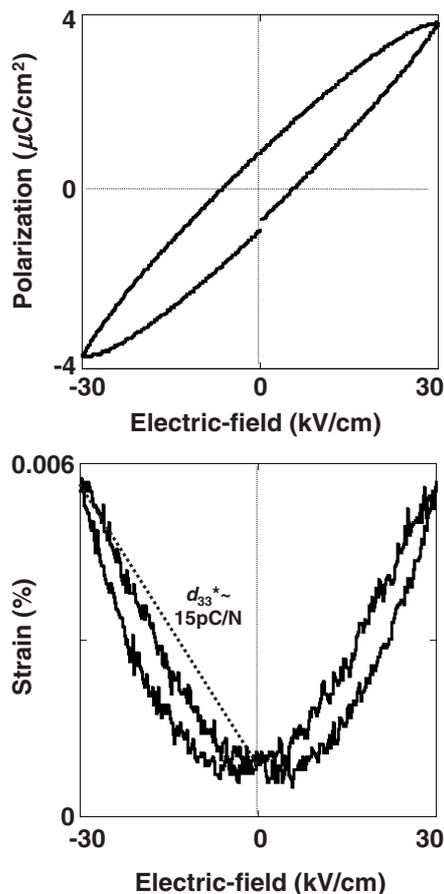
Fig. 3. P–E hysteresis loop and S–E curve for the 0.5BT–0.5KN ceramics measured at 0.1 Hz and room temperature.
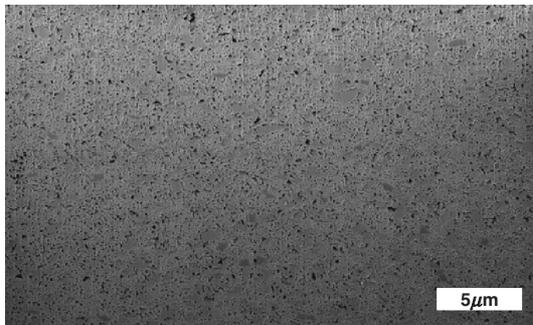

Fig. 4. A SEM micrograph of the 0.5BT–0.5KN ceramics prepared at T_2 of 995°C.

Fig. 5. A SEM micrograph of the 0.5BT–0.5KN ceramics prepared at T_2 of 1095°C.

structure of the 0.5BT–0.5KN ceramics can be controlled by T_2. Thus, more detailed microstructures of a series of the ceramics were investigated.

Figure 6 shows SEM micrographs of the 0.5BT–0.5KN ceramics prepared at T_2 of (a) 995, (b) 1020, (c) 1045, (d) 1070, and (e) 1095°C. First, for the 0.5BT–0.5KN ceramics prepared at T_2 of 995°C (Fig. 6(a)), it was confirmed that its microstructure was composed of two kinds of nanograins with sizes of around 100 nm. On the other hand, for the 0.5BT–0.5KN ceramics prepared at T_2 of 1095°C (Fig. 6(e)), it was confirmed that its microstructure was composed of two kinds of grains, i.e., BT-rich nanograins with a size of around 100 nm and larger fused KN-rich grains surrounding BT-rich nanograins. On the basis of SEM observations as shown in Fig. 6, it was considered that during two-step sintering process, BT-rich nanograins had no grain growth despite temperatures, while KN-rich nanograins became liquid at higher temperatures over 1045°C and composite structure such as larger KN-rich grains including BT-rich nanograins were formed.

Figure 7 shows S–E curves for the 0.5BT–0.5KN ceramics prepared at various T_2 from 995 to 1070°C. The obtained S–E curves were asymmetric shape, but this time, the reason could not be explained. It might be related to asymmetric space charge distribution originated from potassium volatilization. From Fig. 7, slope of S–E curves increased drastically with decreasing T_2, which revealed that electric strain became larger with change of microstructures from coarse to fine for two kinds of grains. Moreover, on the basis of these slopes of S–E curves, the apparent d_{33}^* was estimated. **Figure 8** shows the T_2 dependence of apparent d_{33}^* for the 0.5BT–0.5KN system ceramics. From Fig. 8, with decreasing T_2, apparent d_{33}^* increased drastically from 15 to 100 pC/N. It should be noted that for these ceramics, total chemical composition was always constant at 0.5BT–0.5KN. Therefore, it was considered that the increase of apparent d_{33}^* could be originated from different microstructures.

Karaki et al. reported similar piezoelectric enhancement for fine-grained BT ceramics, and for BT ceramics with sizes over 1.6 μm, the d_{33} increased with decreasing grain sizes.[13] It is known that domain sizes have a proportional relationship with grain sizes.[14],[15] Thus, this increase of piezoelectric constant might be strongly related to decrease of domain sizes. On the basis of this viewpoint, in this study, grain sizes were investigated as a function of T_2 for the 0.5BT–0.5KN ceramics. **Figure 9** shows the T_2 dependence of grain sizes of two kinds of grains for the 0.5BT–0.5KN ceramics. From Fig. 9, sizes of BT-rich grains were almost constant at around 100 nm despite various T_2, while sizes of KN-rich grains increased from 100 to 900 nm with increasing T_2. This is because sintering temperature of BT-rich grain with high melting point over 1500°C was too low for grain growth while that of KN-rich grains with low melting point of 1050°C was suitable for grain growth.

For BT ceramics with sizes below 1 μm, Arlt et al. reported that dielectric properties decreased with decreasing grain sizes despite domain wall contribution.[16] Thus, for BT ceramics with sizes below 1 μm, piezoelectric constant might decrease with decreasing grain sizes. In this study, both grain sizes of BT-rich and KN-rich grains were smaller than 1 μm, and thus, it is difficult to expect enhancement of piezoelectricity due to domain wall contribution because of smaller grain sizes below 1 μm.

Another origin of piezoelectric enhancement for the 0.5BT–0.5KN ceramics can be considered as distorted interface region between BT-rich tetragonal and KN-rich orthorhombic grains. As mentioned previously, PZT ceramics with MPB composition
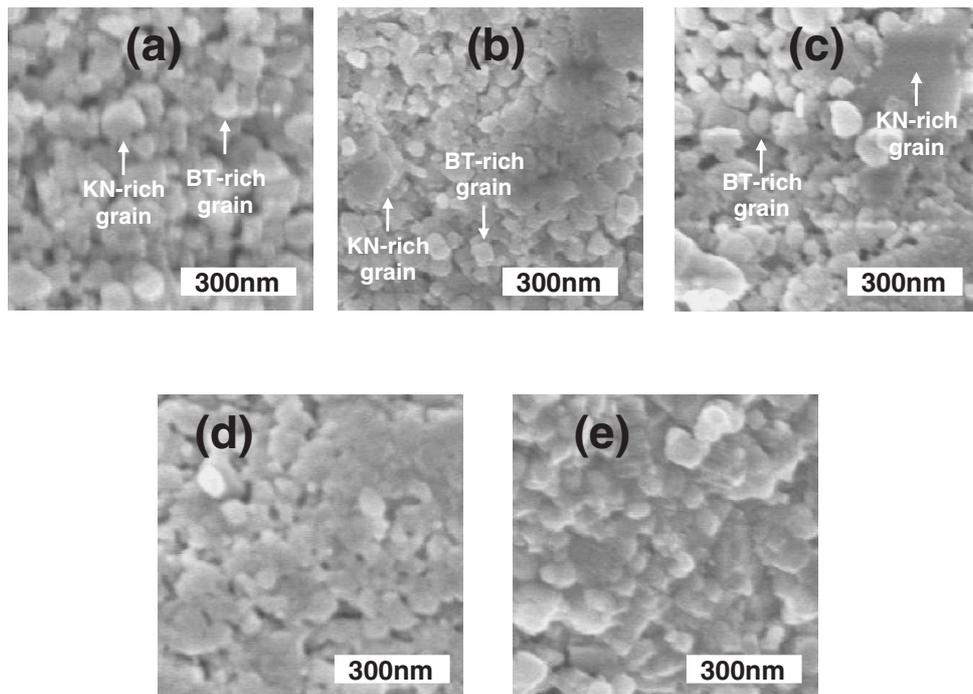
Fig. 6. SEM micrographs of the 0.5BT–0.5KN ceramics prepared at T_2 of (a) 995, (b) 1020, (c) 1045, (d) 1070, and (e) 1095°C.
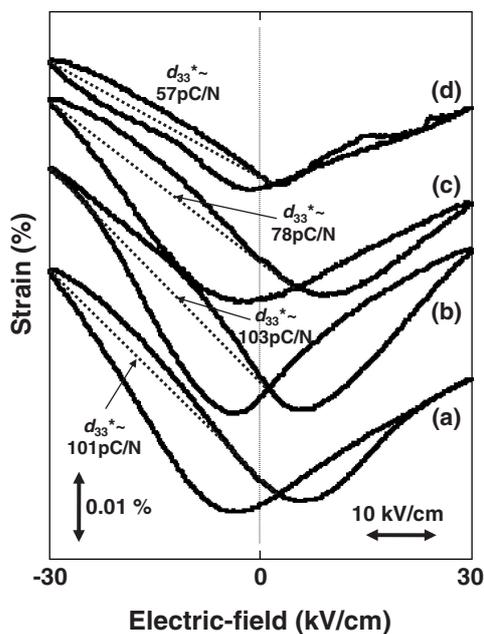

Fig. 7. S–E curves for the 0.5BT–0.5KN ceramics prepared at various T_2 of (a) 995, (b) 1020, (c) 1045, and (d) 1070°C.

Fig. 8. T_2 dependence of apparent piezoelectric constant d_{33}^* for the 0.5BT–0.5KN system ceramics.

exhibited nanotwinning structure between tetragonal and rhombohedral phases.[7),17)] Thus, this means that for piezoelectric enhancement using MPB region, even if size of each phase region becomes to nano-order, piezoelectric property can increase with increasing interface volume fraction. In this study, the BT–KN system ceramics with grain sizes below 1 μm were prepared, and with increasing interface volume fraction between BT-rich and KN-rich grains, the d_{33}^* increased. Thus, for piezoelectric ceramics with MPB composition, the increase of volume fraction of distorted interface region between two phases
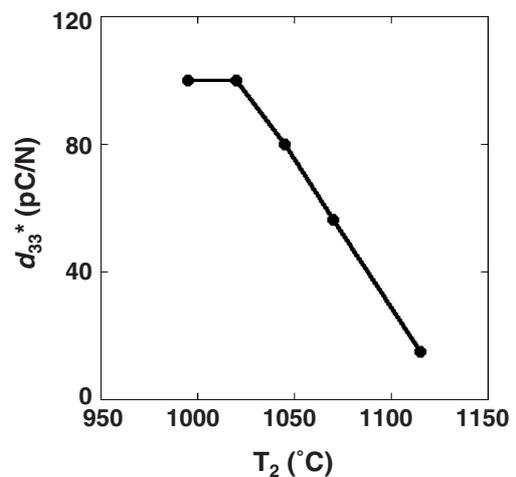
can lead to enhancement of piezoelectric constants. This piezoelectric enhancement mechanism can be called as "interface engineering". This concept should be universal for all of piezoelectric ceramics with MPB region, and it can be expected to enhance piezoelectric properties by interface engineering.

4. Summary

In this study, 0.5BT–0.5KN ceramics with various microstructures were prepared by two-step sintering method. For the ceramics, volume fractions of interface between tetragonal and orthorhombic grains were controlled by sintering temperatures at the 2nd step, and with decreasing T_2, this volume fraction increased. Apparent piezoelectric constant d_{33}^* was measured using slope of strain vs. electric field curves, and it was confirmed that the d_{33}^* increased with decreasing T_2, which
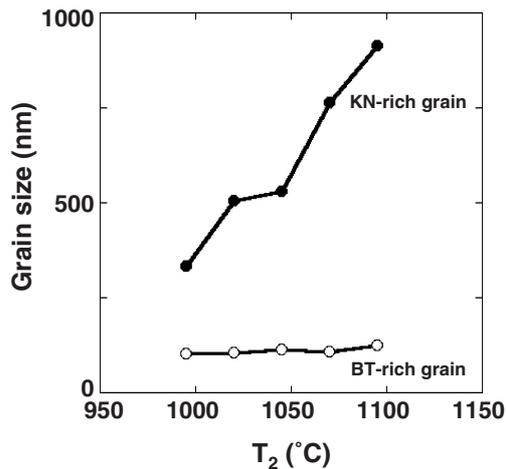
Fig. 9. T_2 dependence of grain sizes of two kinds of grains for the 0.5BT–0.5KN ceramics.

suggested that the distorted interface region between tetragonal and orthorhombic grains could contribute to enhancement of piezoelectric properties. This idea can be similar to piezoelectric enhancement by MPB region of PZT ceramics, which suggested that it was considered interface between tetragonal and orthorhombic grains for the BT–KN ceramics as "pseudo-MPB region".

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