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Piezoelectric enhancement of new ceramics with artificial MPB engineering

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ABSTRACT

Barium titanate ($BaTiO_3$, BT)–potassium niobate ($KNbO_3$, KN) (BT–KN) nanocomplex ceramics with various KN/BT molar ratios were prepared by a solvothermal method. From a transmittance electron microscopy (TEM) observation, it was confirmed that KN layer thickness of the BT–KN nanocomplex ceramics was controlled from 0 to 44 nm by controlling KN/BT molar ratios. Their apparent piezoelectric constants d^*_{33} were measured at 20 °C and 0.1 Hz, and the maximum d^*_{33} of around 167 pC/N was measured for the BT–KN nanocomplex ceramics with a KN thickness of 33 nm. The result suggested that the strained heteroepitaxial interface could be responsible to the enhanced piezoelectric properties.

1. Introduction

Lead-free piezoelectric materials have been important regarding the environmental problems associated with conventional piezoelectrics of $Pb(Zr,Ti)O_3$ (PZT) ceramics [1]. However, the piezoelectric properties are lower than those of the PZT ceramics [2–4], and therefore it is difficult to replace them. Why do the PZT ceramics always show a high piezoelectric performance as compared to the lead-free ones? The high performance can be originated from a morphotropic phase boundary (MPB) structure. A transmission electron microscopy (TEM) observation of a MPB composition of the PZT ceramics revealed very fine nano-ordered structures of three phases in one grain, i.e., the tetragonal phase, the rhombohedral phase, and the interface, while a synchrotron X-ray diffraction (XRD) measurement revealed the crystal structure of the MPB composition assigned to the monoclinic phase, which suggested that the origin of the monoclinic phase was a distorted interface region [5]. Moreover, the phenomenological approach [6] and the first principle calculation [7] proposed that the ultrahigh electromechanical response could be attributed to a polarization rotation mechanism (PRM) at the distorted interface region. Therefore, the MPB structure is the most important key to enhance the piezoelectric properties. For example, chemically modified KN and sodium niobate ($NaNbO_3$, NN) (KNN) ceramics have been reported as promising lead-free piezoelectrics with a new MPB, and their piezoelectric properties are similar to those of PZT ceramics [8,9]. However, it is not a universal microstructure, and systems with a MPB structure were limited. What can we do to create a MPB system? An artificial superlattice structure with a distorted interface region is one solution for this [10–12].

The MPB is, in definition, an epitaxial boundary between two thermodynamically stable ferroelectric phases in a phase diagram with temperature and chemical composition axes. In this study, MPB was extended to include an epitaxial boundary between two different ferroelectric materials that may create a solid solution if heated, e.g., the distorted interface of the artificial superlattice films, which was re-defined as an artificial MPB. For the artificial superlattice films, single crystal plates were used as substrates for an epitaxial film growth. If a single-crystal particle compact is used as a substrate for the epitaxial crystal growth, we can prepare complex nano-structured ceramics with the distorted interface region between the grown-crystal and the substrate particle compact, as shown in Fig. 1. Thus, if the distorted epitaxial interface region is created in the ceramics with a high density, we can design a variety of artificial MPB structures for piezoceramics.

Recently, barium titanate ($BaTiO_3$, BT) and potassium niobate ($KNbO_3$, KN) (BT–KN) nanocomplex ceramics was prepared by solvothermal method [13], and it was reported that the ceramics exhibited good ferroelectric property [14]. This is because BT has a tetragonal symmetry with a polar direction along [1 0 0], while KN

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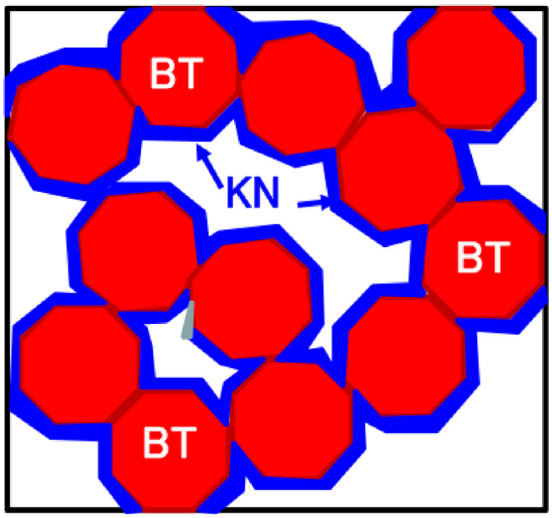

Fig. 1. Schematic image of the BT–KN nanocomplex ceramics with the artificial MPB structure and porosity of approximately 30%.

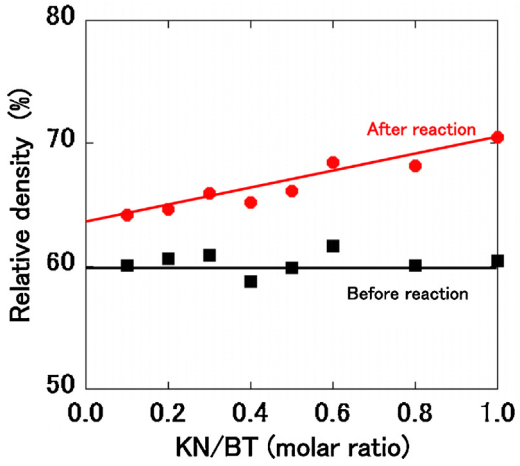

Fig. 2. KN/BT molar ratio dependence of relative density for the BT–KN nanocomplex ceramics before and after reaction.

has a monoclinic symmetry with a polar direction along [1 1 0], and their lattice mismatch is as small as 0.5% on the assumption that the system is a cubic cell [2,3]. Moreover, BT–KN system ceramics were reported as a unique ceramics system with the coexistence of the tetragonal and orthorhombic phases, and their dielectric and piezoelectric maxima were clearly observed in 0.5BT–0.5KN ceramics [15–19]. These results suggested that for BT–KN nanocomplex ceramics, the control of their microstructure, such as KN layer thickness, KN/BT interface density and connection between BT particles, could lead to enhancement of ferroelectric properties.

Thus, in this study, the BT–KN nanocomplex ceramics with various KN layer thickness were prepared by solvothermal method, and their piezoelectric properties were measured. Finally, a relationship between KN layer thickness and piezoelectric properties was discussed.

2. Experimental procedure

In this study, BT–KN nanocomplex ceramics were prepared by the solvothermal method with ethanol [13]. Ethanol (EL grade, Kanto Chemical) was used as the solvent, while KOH (UGR grade, Kanto Chemical), K_2CO_3 (UGR grade, Kanto Chemical), Nb_2O_5 (99.9%, Kanto Chemical), and BT single-crystal particles (BT03, particle size of approximately 300 nm, Sakai Chemical Industry) were used as the starting materials. The mixture of BT03 and Nb_2O_5 powders with various KN/BT molar ratios from 0 to 1.0 were mixed with poly(vinyl butyral) (PVB, 2 wt%) as a binder in ethanol, dried at 130 °C, sieved, and then pressed into a green compact using a uniaxial press at room temperature. The binder was burned out at 600 °C for 10 h. Before the reaction, the density of the compact was measured by the Archimedes method with ethanol, and the crystal structure of the compact was investigated by conventional X-ray diffraction (XRD) analysis (Rigaku RINT2000, Cu Kα, 50 kV, 30 mA). The BT03 and Nb_2O_5 compact was placed in the Teflon-coated autoclave container with ethanol, KOH and K_2CO_3, heated up to temperatures below 230 °C, and soaked for 20 h without stirring. After the reaction, the compact was washed with ethanol and dried at 200 °C for 5 h. The density of the compact was measured by the Archimedes method with ethanol, and the crystal structure of the compact was investigated by XRD analysis. The microstructure was observed using scanning electron microscopy (SEM) and transmittance electron microscopy (TEM). For electric measurements, the ceramics were polished and cut into a size of 2 mm × 2 mm × 0.5 mm. Gold electrodes were sputtered on the top and bottom surfaces with an area of 2 mm × 2 mm. The strain vs. electric-field (*S*–*E*) and polarization vs. *E* (*P*–*E*) curves were measured at 20 °C and 0.1 Hz using a ferroelectric character evaluation system, and a slope of the *S*–*E* curve was regarded as an apparent piezoelectric constant (d^*_{33}).

3. Results and discussion

3.1. Preparation of BT–KN nanocomplex ceramics with various KN/BT molar ratios

Using various KN/BT molar ratios from 0.1 to 1.0, BT–KN nanocomplex ceramics were prepared by solvothermal method. Fig. 2 shows the KN/BT molar ratio dependence of relative density for the BT–KN nanocomplex ceramics before and after reaction. Relative densities of the compact before reaction were almost constant at around 60%, while after reaction, the density of the BT–KN nanocomplex ceramics increased with increasing KN/BT molar ratios, and finally the maximum density of around 71% was obtained for the BT–KN nanocomplex ceramics with KN/BT molar ratio of 1.0. XRD measurement results revealed that after the reaction, XRD peaks associated with Nb_2O_5 almost disappeared and the formation of a large bridge structure between the tetragonal (0 0 2) and (2 0 0) BT peaks was clearly observed [13,14]. A similar "bridge structure" was reported for ferroelectric BT nanoparticles with three phases of a surface cubic phase, a bulk tetragonal phase, and the distorted interface region between the surface and the bulk [20], BT fine-grained ceramics with a high density of 90° domain walls [21], and layered ST nanocubes epitaxially coated by BT [22]. The authors concluded that the "bridge structure" between the tetragonal (0 0 2) and (2 0 0) peaks could be originated from the distorted interface regions [14,20–22]. Thus, we believe that the observed "bridge structure" in this study can be attributed to distorted epitaxial KN growth layers on the BT particles. Moreover, a cross-sectional SEM observation of the reacted compact revealed that the KN crystal growth on BT surfaces resulted in a formation of strong connections between the BT particles with KN [14].

Fig. 3 shows chemical composition distribution of Ba, Ti, O, K and Nb atoms for BT–KN nanocomplex ceramics with KN/BT molar ratio of 0.5. The distributions of Ba and Ti atoms were limited into the center of the complex particles, and their average diameter was estimated to around 300 nm, which almost consisted with the diameter of BT03 particles. On the other hand, the distributions of