Dielectric and Piezoelectric Properties of Barium Titanate – Potassium Niobate Nano-structured Ceramics with Artificial MPB Structure

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Barium titanate (BaTiO_3 , BT) - potassium niobate (KNbO_3 , KN) nano-structured ceramics with artificial morphotropic phase boundary (MPB) structure, were successfully prepared by solvothermal method at temperatures below 230 °C. Various characterizations suggested that the BT-KN nano-structured ceramics exhibited a porosity of around 30 % and heteroepitaxial interface between BT and KN. Their dielectric and piezoelectric properties were measured at room temperature, and the dielectric constant and apparent piezoelectric constant estimated from slope of strain and electric field curve was 370 and 136 pC/N, respectively.

Key words: barium titanate, potassium niobate, heteroepitaxial interface, artificial MPB structure, piezoelectric property

1. INTRODUCTION

Lead-free piezoelectric materials have become highly attractive materials from the viewpoint of providing a solution to the environmental problems associated with conventional ferroelectrics such as $\text{Pb}(\text{Zr,Ti})\text{O}_3$ (PZT) ceramics [1]. However, compared with PZT ceramics, their piezoelectric properties are very poor [2-4]. Why do PZT ceramics always show high piezoelectric performance as compared to the lead-free ones? This high performance can be originated from morphotropic phase boundary (MPB) structure. Schönau et al. reported about MPB structure of PZT ceramics, that transmittance electron microscopy (TEM) observation revealed that there were very fine nano-ordered structures assigned to three phases in one grain, i.e., tetragonal, rhombohedral and their interface, while synchrotron X-ray diffraction (XRD) measurement revealed 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 [5]. Thus, enhancement of piezoelectricity for the PZT ceramics might be related to this distorted interface region. Moreover, phenomenological approach [6] and first principle calculation [7] proposed that ultrahigh electromechanical response could be originated from polarization rotation mechanism (PRM) between tetragonal and rhombohedral phases by an external field. Therefore, the MPB structure was the most important key to enhance piezoelectric properties, but was not universal microstructure and very limited into small amount of material systems. So, what can we do to induce new MPB system? The artificial superlattice structure with the distorted interface region is one solution to create new artificial MPB structure. For the artificial superlattice films, single crystal plates are used as substrates for epitaxial film growth. If the single-crystal particle compact is used as substrate for the epitaxial film growth, we can prepare complex

Fig. 1. Schematic procedure for new preparation method of BT-KN nano-structured ceramics with heteroepitaxial interface region between BT and KN by using liquid state reaction.

nano-structured ceramics with the distorted interface region between film and substrate particle, as shown in Fig. 1. Thus, if the artificial superlattice structure is induced into ceramics, we can design wide variation of artificial MPB structure for piezoceramics. Recently, it was reported that barium titanate (BaTiO_3 , BT) - potassium niobate (KNbO_3 , KN) (BT-KN) nano-structured ceramics were successfully prepared by solvothermal method, and various characterizations revealed that the BT-KN ceramics exhibited a porosity of 35 % and with the distorted heteroepitaxial interface between BT and KN [8]. In this study, therefore, their dielectric and piezoelectric properties were investigated.

2. EXPERIMENTAL PROCEDURE

For the preparation of the BT-KN nano-structured ceramics with the distorted interface region, KN films were deposited on compact of BT single-crystal particles (BT03, particle size of around 300 nm, Sakai Chemical Industry Co., Ltd.) by solvothermal method with KOH, K_2CO_3 and Nb_2O_5 in ethanol [8]. BT03 and Nb_2O_5 powders were mixed at $\text{Nb}_2\text{O}_5/\text{BT}$ molar ratio of 0.5 with polyvinyl butyral (PVB, 2 wt%) as a binder in ethanol, dried at 130 °C, meshed and then pressed into green compact using a uniaxial press. The binder was burned out at 700 °C for 10 h, and the BT03 and Nb_2O_5

(BT03-Nb₂O₅) mixture compact was used as single-crystal substrate and raw materials of KN. Before reaction, the density of the compact was measured by Archimedes method with ethanol, and the crystal structure of the compact was investigated by XRD. The BT03-Nb₂O₅ compact was placed in the Teflon-coated autoclave container with ethanol, KOH, K₂CO₃, and Nb₂O₅, heated up to 230 °C, and soaked for 20 h without stirring. After reaction, the compact was washed by ethanol, and dried at 300 °C. The density of the compact was measured by Archimedes method with ethanol, and the crystal structure of the compact was investigated by XRD. The microstructure was observed using a scanning electron microscopy (SEM). For the electric measurements, the ceramics were polished and cut into sizes of 2x2x0.5 mm³. Gold electrodes were sputtered on the top and bottom surfaces with an area of 2x2 mm². The dielectric properties were measured at various frequencies from 0.1 to 10 MHz from 20 to 480 °C using an impedance analyzer (Agilent, HP4294A). The strain vs. electric-field (S-E) curves were measured at room temperature and 0.1 Hz using a ferroelectric character evaluation system, and this slope of the S-E curve was regarded as an apparent piezoelectric constant (d_{33}^*).

3. RESULTS AND DISCUSSIONS

First, the BT03- Nb₂O₅ compact was prepared with Nb₂O₅/BT molar ratio of 0.5, and used for the KN formation under the condition (K/Nb atomic ratio of 10, Nb concentration of 0.10 mol/L, KOH/K₂CO₃ molar ratio of 0.22). After reaction, it should be noted that XRD pattern assigned to Nb₂O₅ almost disappeared, which revealed that the Nb₂O₅ particles in the compact changed into KN through a reaction with KOH, and a KN/BT molar ratio in the ceramics could be almost 1. Figure 2 shows XRD peaks of (200) planes (assumed as cubic symmetry) for the crashed powders of the compacts before and after reactions at 230 °C for 20 h. Before reaction, clear splitting of (002) and (200) planes was observed owing to tetragonal BT symmetry. After reaction, on the other hand, a large formation of the bridge structure between tetragonal (002) and (200) peaks was clearly observed. The observation of the similar bridge structure for BT was reported for

Fig. 2. XRD peaks of (200) planes for the crashed powders of the compacts before and after reactions at 230 °C, K/Nb atomic ratio of 10, Nb concentration of 0.10 mol/L, and KOH/K₂CO₃ molar ratio of 0.22 for 20 h.

Fig. 3. SEM micrograph of a cross section of the compact after reactions at 230 °C, K/Nb atomic ratio of 10, Nb concentration of 0.10 mol/L, and KOH/K₂CO₃ molar ratio of 0.22 for 20 h.

Fig. 4. Temperature dependence of dielectric constant and loss tangent of the BT-KN nano-structured ceramics with the artificial MPB structure.

ferroelectric BT nanoparticles with three phases such as surface cubic phase, bulk tetragonal phase, and the distorted interface region between surface and bulk [9], BT fine-grained ceramics with high density of 90° domain walls [10] and layered ST nanocubes epitaxially coated by BT [11]. They concluded that the bridge structure between tetragonal (002) and (200) peaks was assigned to the distorted interface regions [9-11]. Thus, we believe that the observed bridge structure in this study can be assigned to distorted epitaxial KN growth layer on the BT particles. The density before reaction was 3.530 g/cm³ (relative density: 61.90%), while that after reaction was 4.013 g/cm³ (relative density: 70.36%), which confirms that there is clear increase of 8.46% caused by summation of two phenomena between (1) dissolution of Nb₂O₅ particles and (2) KN formation on the BT surface. Moreover, a cross section of the compact after reaction was observed by using SEM, as shown in Fig. 3. It was considered that KN crystal growth on the BT surface resulted in formation of the compact after reaction with strong connection between the BT particles. In this study, the BT-KN nano-structured ceramics with a relative density of around 70% was successfully prepared at 230 °C by solvothermal method. XRD measurement suggested the possibility, that the ceramics had the distorted interface region between BT and KN, owing to epitaxial KN growth on the BT surfaces.

The dielectric properties of the ceramics were measured at room temperature as a function of frequency from 40 Hz to 10 MHz. With increasing frequency, the both dielectric constant (ϵ_r) and loss tangent ($\tan \delta$) decreased gradually, and over 1 MHz, the ϵ_r and $\tan \delta$ became almost constant value of 370 and 0.10, respectively. It should be noted that this ceramics exhibited a porosity of 30 %. For KN porous ceramics with a porosity of around 30 %, the ϵ_r was reported as around 50 [12], while for the BT03 particle compact with a porosity of around 30 %, the ϵ_r was reported as around 62 [13]. As compared to the ϵ_r of 50 and 62 for each component, the ϵ_r of 370 was very high for the BT-KN nano-structured ceramics, which suggested that the interface region between BT and KN might contribute to the dielectric enhancement. In this study, the BT-KN nano-structured ceramics could be composed of BT, KN and their interface region, and if its dielectric properties are measured as a function of temperature, each phase transition should be observed. To confirm the possibility, temperature dependence of the dielectric properties were measured, as shown in Fig. 4. With increasing temperature, the ϵ_r decreased gradually, and two kinds of phase transition peaks were clearly observed, i.e., (1) sharp dielectric peak at around 130 °C (Curie temperature T_C of BT), and (2) broad dielectric peak at around 330 °C (phase transition temperature related to KN). KN had three kinds of phase transition temperatures at -50 °C (between orthorhombic and rhombohedral), 230 °C (between tetragonal and orthorhombic), and 430 °C (between cubic and tetragonal) [2,3]. At present, the broad dielectric peak at 330 °C cannot be assigned to the phase transition either between tetragonal and orthorhombic or between cubic and tetragonal. Previously, we reported that temperature dependence of dielectric constants for the BT-KN limited solid solution system ceramics with various KN contents [14,15]. Among various BT-KN ceramics, the dielectric constant vs. temperature curve of the 0.5BT-0.5KN ceramics was most similar to that in Fig. 4, which suggested that BT/KN molar ratio of the BT-KN nano-structured ceramics in this study could be close to 1, and this result was consistent with the KN/BT molar ratio expected from the starting materials.

Finally, S-E curve for the BT-KN nano-structured ceramics with the distorted interface region was measured at room temperature and 0.1Hz, as shown in Fig. 5. This S-E curve shows typical ferroelectric butterfly-curve behavior, and the apparent piezoelectric constant d_{33}^* estimated from a slope of the curve was 136 pC/N. Previously, for 0.5BT-0.5KN dense ceramics with both tetragonal and orthorhombic phases, it was reported that its apparent d_{33}^* was about 40 pC/N [14]. Thus, the d_{33}^* value obtained in this study was three times larger value than that of the 0.5BT-0.5KN dense ceramics [14]. It should be noted that the BT-KN nano-structured ceramics exhibited a porosity of 30 %. Thus, if the dense BT-KN nano-structured ceramics are prepared, it is possible that much higher d_{33}^* values can be obtained. At present, the origin of the above piezoelectric enhancement may be caused by the distorted interface region between BT and KN.

Fig. 5. Strain vs. electric-field behavior of the BT-KN nano-structured ceramics with the artificial MPB structure measured at room temperature and 0.1 Hz.

4. References

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