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Dielectric and piezoelectric properties of $(1-x)(Bi,Na)TiO_3$–$x(Bi,K)TiO_3$ lead-free ceramics for piezoelectric energy harvesters

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Abstract

The piezoelectric and dielectric properties of the $(1-x)(Bi,Na)TiO_3$–$x(Bi,K)TiO_3$ ($x=0.12$, 0.14, 0.18, 0.20 and 0.30) lead-free ceramics were investigated. Specimens were prepared by the conventional mixed oxide method and sintered at 1170 °C in air. Scanning electron microscopy indicated that increasing x from 0.12 to 0.30 causes a decrease in the grain size. The $(1-x)(Bi,Na)TiO_3$–$x(Bi,K)TiO_3$ ceramics shows a homogeneous microstructure and excellent dielectric and piezoelectric properties. Specimens with optimum composition showed a piezoelectric charge constant d_{33} of 166 pC/N, an electromechanical coupling factor k_p of 0.5, a dielectric constant ε_r of 1591.32 at 1 kHz and generated power output of 37.49 nW/cm^2.

Keywords: Piezoelectric ceramics; $(1-x)(Bi,Na)TiO_3$–$x(Bi,K)TiO_3$ ceramics; Energy harvester

1. Introduction

Recently, harvesting energy from renewable sources has been intensively studied in view of finding replacements for fossil fuels. Energy harvesting involves extracting energy that is usually wasted in the environment. Solar energy, thermoelectric energy, and mechanical vibration energy can represent extracting energy. It can involve the transformation of their energy to electrical energy, which can be used to power remotely placed wireless devices and sensors [1]. The behavior and the efficiency of energy harvesting devices depend on environmental conditions. For example, the efficiency of solar energy depends on cloudiness, thermoelectric energy depends on temperature. However, piezoelectric energy harvesters remain unaffected by environmental factors as long as ambient vibration exists. Therefore, much research has been directed toward piezoelectric energy harvesting.

Lead-based piezoelectric ceramics with their excellent piezoelectric properties are most widely used for harvesting piezoelectric energy. However, lead oxide in lead-based piezoelectric ceramics is harmful to humans and cause serious environmental problems. Furthermore, European Union (EU) legislations, such as waste from electrical and electronic equipment (WEEE), restriction of hazardous substances (RoHS), and end-of life vehicles (ELV), have suggested the prevention of use of lead based materials [2]. Therefore, lead-free piezoelectric ceramics have attracted attention in a bid to replace lead-based piezoelectric ceramics. Lead-free piezoelectric ceramics that have been investigated widely on account of their excellent piezoelectric and dielectric properties include $BaTiO_3$ (BT) [3], (K, Na)$KNbO_3$ (KNN) [4], $(Bi,Na)TiO_3$ (BNT) [5], and $(Bi,K)TiO_3$ (BKT) [6].

Perovskite structured BNT ceramics have been considered as a good candidate for lead-free piezoelectric material. Because BNT ceramics have a strong remanent polarization ($P_r=38$ μC/cm^2) and high coercive field ($E_c=73$ kV/cm) at room temperature [7]. However, there are some drawbacks in poling BNT ceramics because of its high coercive field and relatively high conductivity. Also, BNT ceramics show a relatively high reverse piezoelectric coefficient (498 pm/V) at high electric fields [8]. The high inverse piezoelectric effects can cause very large strain values [8]. However, this relatively large strain can only be observed at high

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electric fields because of the large coercive electric field. Therefore, many attempts have been made to improve the properties of BNT. For example, to overcome the poling problem and improve the piezoelectric properties, many solid solutions of BNT, such as BNT–$BaTiO_3$ [9], BNT–$(Ba,Sr)TiO_3$ [10], BNT–$NaNbO_3$ [11], BNT–$(Bi,K)TiO_3$ [12], BNT–$Ba(Cu,W)O_3$ [13], and BNT–$Ba(Ti,Zr)O_3$ [14] have been investigated.

Among them, BNT–$(Bi,K)TiO_3$ (BNT–BKT) material has excellent piezoelectric properties nearby the rhombohedral–tetragonal morphotropic phase boundary (MPB), similar to PZT-based ceramics [15]. The MPB of the $(1-x)(Bi,Na)TiO_3$–$x(Bi,K)TiO_3$ ceramics ($(1-x)$BNT–xBKT)) are in the compositional range of $0.18 \leq x \leq 0.20$, which can improve piezoelectric properties. Therefore, in this study, dielectric and piezoelectric properties of $(1-x)$ BNT–xBKT ceramics in various compositions ($x=0.12$, 0.14, 0.18, 0.2 and 0.3) will be investigated. In addition, BNT-based ceramics with BKT dopants could reduce the coercive electric field E_c ($E_c=4$ kV/mm) owing to BKT has a lower E_c [15]. In this study, we will investigate $(1-x)$BNT–xBKT ceramics, focusing on the influence of the various composition ($x=0.12$, 0.14, 0.18, 0.20 and 0.30) on their piezoelectric properties.

2. Experimental

The $(1-x)$BNT–xBKT ceramics ($x=0.12$, 0.14, 0.18, 0.20 and 0.30) were fabricated using the conventional mixed oxide method. The raw materials, i.e., bismuth oxide (Bi_2O_3, 99.9%), sodium carbonate (Na_2CO_3, 99.0%), potassium carbonate (K_2CO_3, 99.5%), and titanium oxide (TiO_2, 99.9%) powders, were weighed in stoichiometric quantities and ball-milled with zirconium balls (10 mm in diameter) for 24 h. After drying, the mixture was calcined at 850 °C for 2 h. The calcined powders were mixed with a binder (polyvinyl alcohol) and pressed using a pressure of 2 metric tons into discs 12 mm in diameter and about 1 mm in thickness. The discs were sintered at 1170 °C for 2 h and cooled to room temperature in air. The upper and lower faces of the sintered samples were attached to electrodes with silver paste. The samples were poled at 80 °C in silicone oil by applying a direct current (DC) electric field of 4 kV/mm for 30 min.

The crystalline properties of the $(1-x)$BNT–xBKT ceramics were analyzed by X-ray diffraction (XRD, Bruker-AXS; New D8-Advance). The microstructure of the $(1-x)$BNT–xBKT ceramics was observed by field emission scanning electron microscopy (FE-SEM, Carl Zeiss; SIGMA). The piezoelectric charge constant (d_{33}) was measured by Berlin-court quasi-static meter and capacitance versus frequency (C–f) was obtained employing an impedance analyzer (Agilent; 4294 A) to obtain the dielectric constant (ε_r) and the electromechanical coupling factor (k_p).

3. Results and discussion

The XRD patterns obtained from $(1-x)$BNT–xBKT ceramics ($0.12 \leq x \leq 0.30$) with Cu-Kα radiation are shown in Fig. 1. Fig. 1 shows the XRD patterns with 2θ ranging from 20–70°. Each of the ceramics exhibited a single perovskite phase and any secondary phase was not observed. In the case of samples with $x > 0.12$, XRD peaks slightly shifted to lower angles compared with the 0.80BNT–0.20BKT pattern, indicating an increase in the lattice parameters. As is known, the A-site cation of the perovskite structure is occupied by K^+ and Na^+ [16]. By increasing the concentration of BKT, Na^+ ions are substituted by K^+ ions. In addition, the theoretical coordination number of the A-site cations is 12 [17] and the ionic radius of K^+ (1.78 Å) is larger than that of Na^+ (1.39 Å). Therefore, due to the differences in the ionic radii of K^+ and Na^+, the lattice parameters were increased with increase in the BKT compositions.

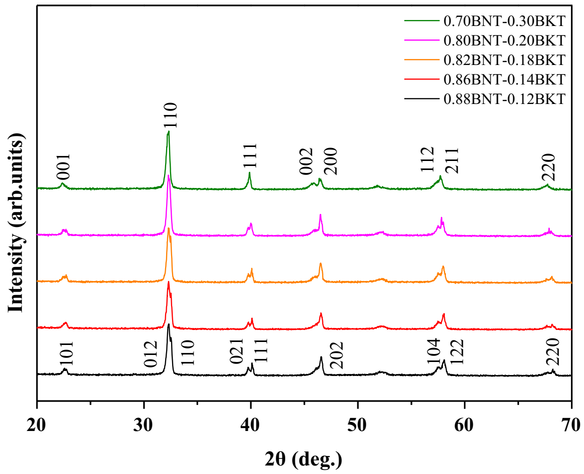

Fig. 1. The X-ray diffraction (XRD) patterns of the $(1-x)(Bi,Na)TiO_3$–$x(Bi,K)TiO_3$ ceramics in various composition ($x=0.12$, 0.14, 0.18, 0.20, 0.30).

At room temperature, the pure BNT ceramics show a rhombohedral structure, while pure BKT ceramics show a tetragonal structure [18]. The rhombohedral structure of pure BNT can be characterized by the splitting of the (021) and (111) peaks around 39° and (202) single peak near 46.5°. However, the tetragonal structure of BKT is characterized by (111) single peak near 46.5° and (002) and (200) peaks splitting around 46.5° [18]. When x ranged from 0.12 to 0.20, the splitting of the (021) and (111) peaks were observed around $2\theta=39°$. On the other hand, when $x=0.18$, 0.20, and 0.30, the splitting of the (002) and (200) peaks were observed at $2\theta=46.5°$. Therefore, when $x=0.18$ and 0.20, the ceramic consists of both tetragonal and rhombohedral phases. And, tetragonal phase was observed in $x=0.30$. So, the ceramic samples show phase transformation from rhombohedral to tetragonal with increase in x.

Fig. 2 shows peak ratio at (200) and full width at half-maximum (FWHM) of $(1-x)$BNT–xBKT ceramics ($x=0.21$, 0.14, 0.18, 0.20 and 0.30). The peak ratio of (200) calculated by following equation [19]:

$$\text{Peak ratio}(200) = [\text{Peak intensity}(200)]/\left[\sum \text{Peak intensity}(hkl)\right] \qquad (1)$$

Peak ratio (200) means relative peak intensities of (200) orientation, the higher peak ratio represents highly oriented crystalline properties. The peak ratio (200) was increased in the compositional range of 0.12–0.18. It means that crystallites grown for (200) orientation was improved by increasing BKT composition. However, $x=0.30$, the $(1-x)$BNT–xBKT ceramics