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The effects of the phase structure of the polymorphic phase boundary on the piezoelectric properties of (K,Na)NbO_3-based ceramics

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ABSTRACT

We report the effects of the phase, i.e., the rhombohedral (R), orthorhombic (O) and tetragonal (T) phase, within a polymorphic phase boundary on the piezoelectric properties of (K,Na)NbO_3 ceramics doped with Bi(Na,K,Li)ZrO_3 and (Bi,Na)TiO_3. For the R-O-T phase boundary, the formation of an R-T phase boundary by O phase shrinkage is clearly beneficial to enhance the piezoelectric performance, whereas the enrichment of the T phase in the R-T phase boundary negatively affects the piezoelectric activity. Electrical poling in relation to the piezoelectric property strongly depends on the nature of the phase boundary, requiring the optimization of temperatures corresponding to the R-T phase boundary without the O phase.

1. Introduction

(K,Na)NbO_3 (KNN)-based ceramics have become the most overwhelmingly investigated lead-free piezoelectric material system in the past ten years owing to a large piezoelectric coefficient d_{33} comparable to that of PZT and a higher Curie temperature T_C than PZT [1–7]. From the expectations of superior piezoelectric properties owing to the formation of a phase boundary, a great amount of attention has been directed toward the construction of a polymorphic phase boundary (PPB) of the KNN system near the working temperature, usually room temperature [3–5,8]. It is known that pure KNN undergoes a series of structural phase transitions, as the temperature increases. These are the rhombohedral-orthorhombic (R-O) transition at $-123\,^{\circ}C$ ($T_{R\text{-}O}$), the orthorhombic-tetragonal (O-T) transition at $210\,^{\circ}C$ ($T_{O\text{-}T}$), and the tetragonal-cubic (T-C) transition at $410\,^{\circ}C$ (T_C) [1]. Such PPBs do not form in the vertical direction with regard to compositions, instead showing strong temperature-dependence, clearly different from a traditional morphotropic phase boundary (MPB) that is only dependent on the composition. However, the underlying physical origins of the enhanced piezoelectricity observed at both boundaries are considered to be identical.

In KNN-based ceramics, two different PPBs are considered as the intrinsic characteristics, i.e., R-O and O-T, and their electrical properties are very sensitive to not only the compositions but also the temperatures. The most popular research strategy involves constructing the R-O or O-T phase boundary around room temperature, particularly by shifting the intrinsic $T_{R\text{-}O}$ and/or $T_{O\text{-}T}$ values close to room temperature by chemically modifying the relevant components [2,3,6,7,9–15]. Various additives, including Sb^{5+}, Ta^{5+}, $AZrO_3$ ($A = Ba^{2+}, Sr^{2+}, Ca^{2+}$), and $BiScO_3$, have been used to increase $T_{R\text{-}O}$, but rather poor piezoelectricity is common for the R-O phase boundary [9,10]. Great progress with regard to d_{33} has been made through the formation of the O-T phase boundary via the ion substitution of Li^{+}, Sb^{5+}, and Ta^{5+}, and the addition of ABO_3 multicomponents [2,11–13]. More recently, it was demonstrated that a new phase boundary consisting of R and T is more effective to promote the piezoelectric activity of KNN-based ceramics with respect to others [3,6,7,14,15], further increasing research interest in KNN-based piezoelectrics. However, such studies have mainly focused on the relationship between the type of phase boundary and the piezoelectric activity, while there are few studies [13,14] which attempt to clarify the respective roles of the R, O, and T phases formed in the associated phase boundaries on the piezoelectric properties.

In this study, we explore the influence of each phase within the phase boundary on the ferroelectric and piezoelectric properties of

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KNN-based ceramics through compositional engineering. To design the ceramics with the coexistence of the R, O and T phases or a phase boundary around room temperature, we introduced an ABO_3-type additive, i.e., Bi(Na,K,Li)ZrO_3 (BNKLZ), which is the most commonly investigated perovskite material to increase the $T_{R\text{-}O}$ value and decrease the $T_{O\text{-}T}$ value of KNN simultaneously [7,16–18]. For further modification of the phase boundary, we also added (Bi,Na)TiO_3 (BNT) as a third component. Finally, the (0.97-x) $[(K_{0.5}Na_{0.5})NbO_3]$-0.03$[Bi_{0.5}(Na_{0.7}K_{0.2}Li_{0.1})_{0.5}ZrO_3]$-x$[(Bi_{0.5}Na_{0.5})TiO_3]$ ternary composition (x = 0–0.02) was investigated in a case study in this work. In addition, because electrical poling is crucial for enhancing d_{33} without greatly sacrificing T_C, the phase-dependent poling behaviors in relation to the piezoelectric properties were investigated at different temperatures.

2. Experiment

The (0.97-x)KNN-0.03BNKLZ-xBNT ceramics with x = 0–0.02 were prepared using a conventional solid-state method with the starting materials of K_2CO_3 (≥99.0%, Sigma–Aldrich), Na_2CO_3 (≥99.5%, Sigma–Aldrich), Nb_2O_5 (99.9%, Sigma–Aldrich), Bi_2O_3 (99.9%, Sigma–Aldrich), Li_2CO_3 (99.997%, Sigma–Aldrich), ZrO_2 (99.0%, Sigma–Aldrich), and TiO_2 (≥99.9%, Sigma–Aldrich). The weighed powders were ball-milled in ethanol for 24 h and then calcined at 850 °C for 6 h. The calcined powders were pressed into disks with diameters of 10 mm using PVA as a binder. After burning off the PVA at 650 °C, the pellets were sintered at 1100 °C for 3 h. The investigated ceramics with different BNT concentrations had similar densities of 4.25–4.32 g/cm^3 (greater than 95% of the theoretical density) as well as similar grain sizes between 1.17 and 1.43 μm. The sintered ceramics were ground down until their thicknesses were 500 μm.

X-ray diffraction (XRD, D/Max-2500; Rigaku, Tokyo, Japan) was used with CuKα radiation at 40 kV and 30 mA. Temperature-dependent XRD investigations were also carried out in a temperature range between −150 °C and 450 °C. To investigate the phase structure, the peaks in the 2θ range at 21°–24° and 44°–47° were fitted and analyzed by using the origin Pro 8.5 software and the Joint Committee on Powder Diffraction Standards card Nos. 01-071-0946 (Orthorhombic, *A*mm2), 01-071-0947 (Rhombohedral, *R*3m), and 01-071-0948 (Tetragonal, *P*4mm).

For the electrical measurements, silver paste was coated onto two main surfaces of the ceramics, after which they were fired at 650 °C for 10 min. The prepared samples were poled in silicon oil at set temperatures ranging from 27 °C to 160 °C. It was found through pre-test of poling that the poling time from 10 s to 60 min did not largely affect the value of d_{33}, whereas an electric field significantly affected the value of d_{33}. The value of d_{33} sharply increased with increasing electric field to 60 kV/cm, then dropped with a further increase in electric field to 100 kV/cm, and finally the ceramic sample is electrically broken at electric field larger than 100 kV/cm. Therefore, the poling field and poling time were set to 60 kV/cm and 10 min, respectively. The dielectric properties were measured at a frequency of 100 kHz in the temperature range of 30 °C–500 °C using a Solartron 1260 Impedance Analyzer. Polarization versus electric field (*P*–*E*) hysteresis loops and electric-field-induced unipolar strain curves were determined at a probing frequency of 10 Hz using a commercial aixPES setup (aixACCT Systems GmbH, Germany), i.e., a computer-based measurement tool which characterizes ferroelectric ceramics. The converse piezoelectric coefficient (d^*_{33}) was determined from the ratio of the maximum strain to the peak electric field, $d^*_{33} = S_{max}/E_{max}$ using the obtained unipolar strain curves. The piezoelectric coefficient (d_{33}) was measured using a piezo-d_{33} m (ZJ-6B, China).

3. Results and discussion

Fig. 1(a) shows the XRD patterns of (0.97-x)KNN-0.03BNKLZ-xBNT ceramics measured at room temperature as a function of the BNT concentration (x). A pure perovskite structure without secondary phases was obtained in all of the samples, indicating the growth of a stable solid solution among the KNN, BNKLZ and BNT. The evolution of the phase structure of the ceramics with the BNT concentration is shown in Fig. 1(b). The concentration-dependence of the phase structure is clearly visible. The simulated data reveal that the ceramics with 0 ≤ x ≤ 0.01 show the coexistence of rhombohedral (R), orthorhombic (O), and tetragonal (T) phases, with their relative phase compositions changing with the BNT concentration: the O phase gradually decreases, while the T phase increases. At x ≥ 0.015, the O phase completely disappears and finally only the R and T phases remain. It is clear that an addition of BNT induces the shrinkage of the O phase.

To explore the temperature-dependence of the phase structure of the ceramics with different BNT concentrations, XRD experiments were carried out in a temperature range of −150 °C and 450 °C for ceramics with the selected BNT concentrations. As shown in Fig. 2, for the ceramics with 0 ≤ x ≤ 0.01, a common trend was noted in that the R-O, R-O-T, R-T, T, and C phases are formed in sequence with an increase in the temperature. The only notable difference is a gradual shift of the phase-transition temperature in each case as well as a shift in the ferroelectric Curie temperature (T_C) to a lower level with an increase in the amount of BNT. It should be noted that for the ceramics with the R-O-T phase boundary around room temperature, the R-T phase boundary is formed by the shrinkage of the O phase prior to the formation of the T phase region; for the ceramics with x = 0.015, the R-T phase boundary is formed near room temperature. Interestingly, a triphasic R-O-T at 0 ≤ x ≤ 0.01 and a diphasic R-T at 0.015 ≤ x ≤ 0.02 appear as the

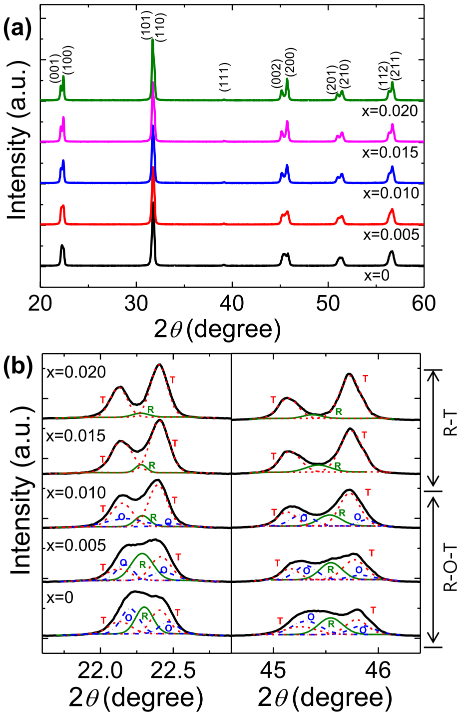

Fig. 1. (a) XRD patterns of (0.97-x)KNN-0.03BNKLZ-xBNT ceramics with x = 0–0.02 measured at room temperature and (b) the simulated patterns in the 2θ range of 21°–24° and 44°–47°. The terms "R", "O" and "T" indicate the rhombohedral, orthorhombic and tetragonal phases, respectively.