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Role of $BiScO_3$ in phase structure and electrical properties of potassium sodium niobate ternary materials

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ABSTRACT

In this work, we mainly studied the effects of $BiScO_3$ contents on the phase structure and electrical properties of lead-free (K,Na)NbO_3-based ternary ceramics, and the material system of $(0.97\text{-}x)K_{0.40}Na_{0.60}NbO_3\text{-}xBiScO_3\ \text{-}0.03Bi_{0.5}(Na_{0.6}K_{0.3}Li_{0.1})_{0.5}HfO_3$ was prepared by the normal sintering method. The rhombohedral-tetragonal (R-T) phase boundary could be tuned in the ceramics by controlling $BiScO_3$ contents. When the compositions approach the R-T phase boundary, the ceramics possess the enhancement of dielectric, ferroelectric and piezoelectric properties. The ceramics with $x = 1.2\%$ exhibited an excellent electrical behavior of $d_{33} = 362$ pC/N, k_p~0.42, P_r~19.9 μC/cm^2, ε_r~1671, and tan δ~0.02, which is assigned to the involvement of R-T phase boundary. Moreover, a high Curie temperature (T_C) of ~315 °C can be maintained even if the $BiScO_3$ contents increase because of the addition of both $BiScO_3$ and Li. As a result, the ceramics with $x = 1.2\%$ had both a large d_{33} and a high T_C, showing that such a lead-free piezoelectric ternary system is suitable to the high-temperature applications.

1. Introduction

Lead-based [Pb(Zr,Ti)O_3, PZT] ceramics are widely in some piezoelectric electronic devices due to their unique properties and a high Curie temperature (T_C), the applications including actuators, sensors, transducers and surface acoustic wave devices [1]. In contrast, the Pb toxicity will result in the prohibition of this kind of lead-based materials during their preparation and process. Seeking viable substitutes for the lead-based materials is very important for their wide applications in sensors and actuators in high temperature. In particular, some laws or regulations about prohibiting the lead-based materials have been legislated in some countries. Therefore, it is necessary to substitute the lead-based piezoelectric materials by developing high-performance lead-free ones [2–41].

Among these promising lead-free piezoelectric candidates, the (K,Na)NbO_3 (KNN) ceramics have been given to extensive attention because of the good properties [5–41]. As far as the lead-free piezoelectrics were concerned, the chemical composition becomes an effective method to enhance their electrical properties [3,6–9,33,34,39]. Especially, it was found that the electrical properties of KNN can be dramatically enhanced by the construction of phase boundaries using the composition modifications [6–10,21]. For example, the ion substitutions (Li, Ta and Sb) induced high piezoelectric constant (d_{33}) of ~416 pC/N in the textured KNN ceramics [5], which is due to the composition-induced orthorhombic-tetragonal (O-T) phase boundary [29,31]. In addition, the addition of ABO_3 additives can be well used to modify the structure and properties of KNN-based ceramics [7,10,21], and rhombohedral-tetragonal (R-T) phase boundary can be constructed [7,10,16,21,22,27,28,30,36]. Especially, the advances in physical mechanism for enhanced piezoelectricity in KNN-based ceramics have been achieved [27–29,31,36]. Although the d_{33} can be effectively improved in the KNN-based ceramics, their Curie temperature (T_C) was greatly dropped because of the effects of chemical compositions [7,10,21]. Therefore, we expected to attain both large d_{33} and high T_C in KNN-based ceramics for the high-temperature applications.

In this work, we studied the influences of $BiScO_3$ contents on the phase structure and electrical properties of $(0.97\text{-}x)K_{0.40}Na_{0.60}NbO_3\text{-}xBiScO_3\text{-}0.03Bi_{0.5}(Na_{0.6}K_{0.3}Li_{0.1})_{0.5}HfO_3$ ceramics prepared by the solid-state reaction methods. Previously, it was thought that the addition of $BiScO_3$ can improve the piezoelectric properties of KNN-based ceramics by forming the phase boundaries [22,23], and therefore the R-T phase boundary should be

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assigned to the involvement of $BiScO_3$. The ceramics with $x = 1.2\%$ possessed both a large d_{33} of 362 pC/N and a high T_C of 315 °C, showing that such a lead-free piezoelectric ternary system is suitable to the high-temperature applications. In addition, the evolutions of their phase structure and electrical properties with $BiScO_3$ contents were importantly emphasized, and the underlying physical mechanisms were also discussed.

2. Experimental procedure

Lead-free $(0.97\text{-}x)K_{0.40}Na_{0.60}NbO_3\text{-}xBiScO_3\text{-}0.03Bi_{0.5}(Na_{0.6}K_{0.3}Li_{0.1})_{0.5}HfO_3$ $(0 \le x \le 1.4\%)$ ceramics were prepared by the normal sintering method. Raw materials included K_2CO_3 (99%), Li_2CO_3 (99.0%), Na_2CO_3 (99.8%), Bi_2O_3 (99%), HfO_2 (99%), Nb_2O_5 (99.9%), and Sc_2O_3 (99.9%). All raw materials are purchased from Sinopharm chemical reagent co. LTD. All the raw materials of this work were ball milled for 8 hour (h) using alcohol, and then dried and calcined at 800 °C for 5 h in air. Recent studies on the reactivity of the sodium potassium niobate nanoparticles reveal that the perovskite structure can be formed at temperatures near 700 °C [32]. However, a higher calcined temperature may be suitable to obtain the ceramics with large piezoelectric constant [6,10]. These sintered powders were mixed again with a binder of 8 wt% polyvinyl alcohol (PVA) and then pressed into the green pellets with ~10 mm diameter and ~1.5 mm thickness under 15 MPa. After burning off the PVA, the green pellets with $x = 0\%$, 0.25%, 0.8%, 1.0%, 1.2%, and 1.4% were respectively sintered under 1080 °C, 1090 °C, 1100 °C, 1110 °C, 1120 °C, and 1150 °C for 5 h in air, and a direct current (*dc*) electric field of 2.0–3.0 kV/mm was employed to pole the samples in a silicone oil bath.

X-ray diffraction (XRD) was used to analyze the phase structure of all the samples. The surface morphology of the ceramics was measured using scanning electron microscopy (SEM) (Philips, XL30). The composition dependence of dielectric properties against the temperatures was conducted by an *LCR* analyzer, and their piezoelectric properties can be measured by a quasi-static d_{33} meter (ZJ-3A, Institute of Acoustics, Chinese Academy of Sciences, China). Their *P–E* hysteresis loops can be carried out by a Radiant Precision Workstation (USA) with a frequency of 10 Hz.

3. Results and discussions

Here, the XRD has been employed to characterize the phase structure of the ceramics. Fig. 1 shows the XRD patterns of the ceramics with different BS values, characterized at room temperature. As shown in Fig. 1, a pure phase can be found in the samples except for $x = 1.4\%$. The secondary phases can be considered as $K_3Li_2Nb_5O_{15}$ or $K_3LiNb_6O_{17}$ [29,40,41], indicating that the addition of excessive BS negatively affects the Li solubility of KNN. Moreover, it was also found from Fig. 1 that the XRD peaks at 43-47° will be changed with the variations of the compositions, indicating the change of phase structure. The corresponding phase structure will be confirmed by the temperature dependence of dielectric properties as well as the refinement results on XRD pattern [Figs. 2–5].

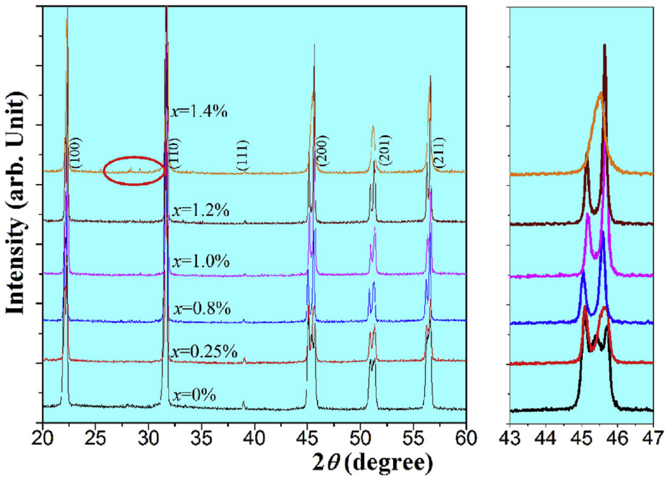

Fig. 1. XRD patterns of the ceramics with different *x* contents.

To further show the phase evolutions, we measured the temperature dependence of dielectric constant in all the samples, as shown in Fig. 2. It was found that their phase transition temperatures gradually moved with increasing *x* values, that is, their $T_{R\text{-}O}$ and $T_{O\text{-}T}$ gradually converged together. Finally, new phase boundary can be driven by optimizing the chemical compositions. In this work, the addition of BS and BNKLH is responsible for the shift of $T_{R\text{-}O}$ and $T_{O\text{-}T}$ [22,27,28,33]. According to the data of XRD patterns and temperature-dependent dielectric constant [7,10,26–28], the phase structure can be defined below: O-T for $x \le 0.8\%$, R-T for $0.8\% < x < 1.4\%$, and R for $x = 1.4\%$.

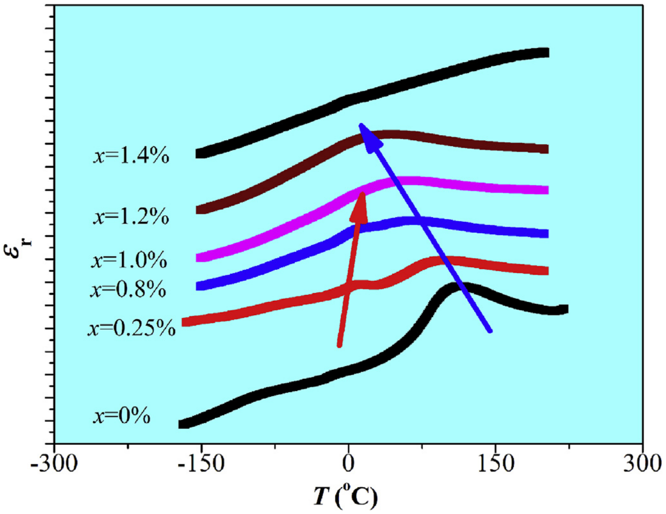

Fig. 2. Temperature dependence of dielectric constant of the ceramics, measured at −150–200 °C.

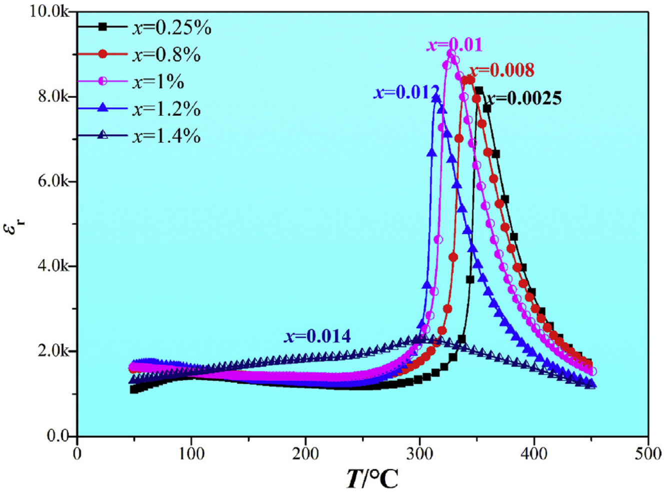

Fig. 3. Temperature (50–450 °C)-dependent dielectric constant in all the samples.