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Development of the electrical properties of KNN-based lead-free piezoceramics based on the phase boundary building and ternary composition designing

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ABSTRACT

Two kinds of ternary KNN-based lead-free piezoceramics: (0.985-*x*)$K_{0.5}Na_{0.5}NbO_3$-0.015$Bi_{0.5}Na_{0.5}TiO_3$-*x*$BiScO_3$ and (0.985-*y*)$K_{0.5}Na_{0.5}NbO_3$-0.015$Bi_{0.5}Na_{0.5}TiO_3$-*y*$BiFeO_3$ have been prepared by a conventional solid-state sintering. For these KNN-based ceramics, the increasing doping of $BiScO_3$ or $BiFeO_3$ changed the phase structure from orthorhombic symmetry to tetragonal symmetry and then to pseudocubic symmetry, while a typical bimodal grain size distribution was observed in their rectangular grains at x = 0– 0.015 or y = 0.06–0.012. With increasing *x* or *y*, $T_{O\text{-}T}$ gradually decreases to room temperature, and an orthorhombic-tetragonal (O-T) morphotropic phase boundary was formed at $0.009 \le x \le 0.015$ or $0.009 \le y \le 0.012$. Around the phase boundary, both a good piezoelectric activity and a high Curie temperature were obtained, such as d_{33}–320pC/N, k_p–0.45, $T_C = 327\,^{\circ}C$ at $x = 0.015$, and d_{33}–304pC/N, k_p–0.42, $T_C = 350\,^{\circ}C$ at $y = 0.012$. In addition, the test for the piezoelectric constant following the annealing temperature indicate that these two compositions also have a good thermal stability.

1. Introduction

Lead-based piezoelectric ceramics have been widely used in various devices due to their excellent piezoelectric properties, such as sensors, transducers and actuators [1–6]. However, the high toxicity of lead element makes them unfriendly to the natural environment and human health, thus the development of lead-free piezoelectric materials was put ahead of material researchers [3–7]. After Saito et al. found a group of lead-free ceramics with high piezoelectric ability, alkali niobate ceramics [5], $(K_{0.5}Na_{0.5})NbO_3$ (KNN) have received much attention and been considered as one of most promising materials to replace the lead-based ones.

However, pure KNN ceramics are poorly piezoelectric due to a single orthorhombic phase structure actually [2]. For perovskite-type compounds, it is well known that the phase boundary always plays an important role in the enhancement of piezoelectric and dielectric properties due to the instability of polarization state, which makes the polarization direction be rotated easily when materials are subjected to an external electric field [2]. So, a high piezoelectric property is always located around the morphotropic ferro-ferroelectric phase boundary for KNN-based ceramics. In fact, $(K_{0.5}Na_{0.5})NbO_3$ undergo three ferroelectric phases and one paraelectric phase transformation with the variation of surrounding temperature, as following rhombohedral → orthorhombic → tetragonal → cubic [2]. Therefore, both increasing the rhombohedral-orthorhombic phase transition temperature ($T_{R\text{-}O}$) and decreasing the orthorhombic-tetragonal phase transition temperature ($T_{O\text{-}T}$) are the effective method to obtain a morphotropic ferro-ferroelectric phase boundary, so that many materials systems with high piezoelectric property have been achieved by this method [6–10].

In order to obtain the phase boundary in KNN-based lead-free piezoceramics, Sb is usually used to replace Nb for decreasing $T_{O\text{-}T}$ or increasing $T_{R\text{-}O}$ [6]. However, Sb-doping tends to significantly decrease the Curie temperature (T_c) of system, as a result, the working temperature of material is largely limited. Thus it is always difficult to obtain both a large piezoelectric constant and a high Curie temperature in piezoelectric ceramics, especially in lead-free ones [11]. In this work, we try to develop a new composition system with both a large d_{33} and a high T_c in KNN-based ceramics. For this intention, it needs a special additive which has only a slight effect on T_C to decrease the $T_{O\text{-}T}$. $Bi_{0.5}Na_{0.5}TiO_3$

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(BNT), $BiScO_3$ (BS) and $BiFeO_3$ (BF) have been identified as a series of perovskite lead-free piezoelectric materials with high spontaneous polarization. According to some previous reports. BNT-doping could decrease $T_{O\text{-}T}$ significantly and decrease T_C slightly for KNN-based ceramics [12], while BS and BF doping could improve the piezoelectric properties significantly and have a slight effect on $T_{O\text{-}T}$ and T_C [13,14]. In addition, some researches have confirmed that the hybridization between the Pb 6p and O 2p orbits was responsible for the high piezoelectric response in Pb-based piezoelectric materials [15–17]. Considering the same electron configuration between Bi^{3+} and Pb^{2+}, BNT, BS and BF may be the good dopants for KNN. Their co-doping are expected to help KNN to gain both a large d_{33} and a high T_C.

In this work, two ternary systems of KNN-BNT-BS and KNN-BNT-BF were designed to achieve high piezoelectric properties without sacrificing T_C greatly. Such KNN-based ceramics were prepared by a conventional solid-state sintering method, as well as the effect of $BiScO_3$ and $BiFeO_3$ contents on the phase structure, grain morphology and electrical properties of ceramics were investigated. This research could help us to further understand the regulating mechanism for the electrical properties of KNN-based piezoceramics based on the phase boundary building.

2. Experimental procedure

According to two designed component formulation of KNN-based ceramics, $(0.985\text{-}x)K_{0.5}Na_{0.5}NbO_3\text{-}0.015Bi_{0.5}Na_{0.5}TiO_3\text{-}xBiScO_3$ ((0.985-x)KNN-0.015BNT-xBS, here $x = 0$, 0.003, 0.006, 0.009, 0.012, 0.015, 0.018) and $(0.985\text{-}y)K_{0.5}Na_{0.5}NbO_3\text{-}0.015Bi_{0.5}Na_{0.5}TiO_3\text{-}yBiFeO_3$ ((0.985-y)KNN-0.015BNT-yBF, here $y = 0.003$, 0.006, 0.009, 0.012, 0.015, 0.018), K_2CO_3 (99%), Na_2CO_3 (99.8%), Nb_2O_5 (99.5%), TiO_2 (99%), Bi_2O_3 (99%), Sc2O3 (99.999%) and Fe_2O_3 (99%) as raw materials were weighed and milled in nylon jar with zirconia ball and anhydrous ethanol for 12 h using planetary, then dried and calcined at 850 °C for 6 h in air. These dried powders were mixed with poly vinyl alcohol (PVA, 8 wt.%) binder solution and pressed into discs with a diameter of 10 mm and thickness of 1 mm under 10 MPa pressure. After burning off PVA, the pellets were sintered at a temperature range of 1040–1120 °C for 3 h in air. Sliver paste electrodes were coated on both sides of these sintered samples and fired at 600 °C for 10 min. These ceramics were poled in silicon oil under a DC electric field of 3 kV/mm for 15 min at room temperature, all the electrical properties of samples were measured after they have been laid in the natural enviroment for 24 h.

The crystal structures were determined by X-ray diffraction (X' Pert Pro MPD, Philips, Japan). Surface morphologies were characterized by Scanning electron microscopy (JSM-5900LV, JEOL, Japan). The curves of dielectric constant (ε_r) versus temperatures were measured using an LCR analyzer (HP 4980, Agilent, U.S.A.). Polarization verse electric field (P-E) hysteresis loops were conducted at room temperature and a frequency of 10 Hz using a Ferroelectric analyzer (TF2000, aixACCT, Germany). d_{33} and k_p were characterized by a Belincourt meter (ZJ-6A, Institute of Acoustics,

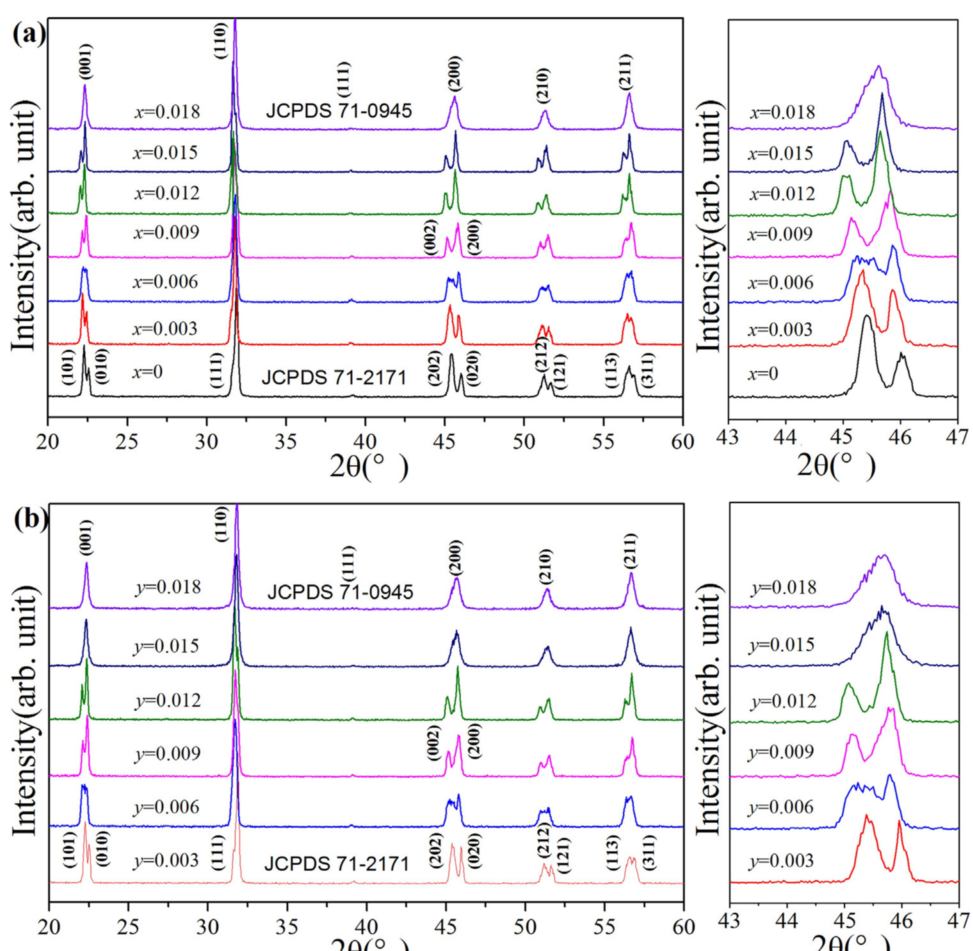

Fig. 1. XRD patterns of KNN-based ceramics, (a) (0.985-x)KNN-0.015BNT-xBS; (b) (0.985-y)KNN-0.015BNT-yBF.