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Phase structure and electrical properties of barium-modified potassium–sodium niobate-based lead-free ceramics

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ABSTRACT

In this work, effects of barium content on phase structure, microstructure, and electrical properties of $0.96K_{0.45}Na_{0.55}Nb_{0.96}Sb_{0.04}O_3$–$0.04Ba_x(Bi_{0.5}Na_{0.5})_{1-x}ZrO_3$ ceramics have been investigated. Their grain sizes climb up and then decline with increasing Ba^{2+} content, and Ba^{2+} is homogenously distributed in the matrix. With adding Ba^{2+} to replace both Bi^{3+} and Na^{+}, it slightly influences the T_C. A rhombohedral–tetragonal (R–T) phase boundary appears in the ceramics with the compositional range of $x = 0$–0.20, drastically enhancing both dielectric and piezoelectric properties of the ceramics. In addition, the ceramic with $x = 0.15$ has the largest d_{33} ~ 360 pC/N, together with a good temperature stability of ferroelectricity and an enhanced thermal stability of piezoelectricity. Therefore, it is proved that such a ceramic system is a promising candidate for piezoelectric devices.

1. Introduction

In recent years, the lead-based piezoelectric ceramics have been widely used in sensors, actuators, and other electronic devices due to their high electromechanical properties, good piezoelectricity, and a high Curie temperature [1,2]. Unfortunately, the Pb of lead-based materials is volatilized in the air during their preparation and processing, which is harmful to human and surrounding environment. So there are many countries calling on replacing the lead-based piezoceramics by using lead-free ones. Therefore, it is urgent to focus on developing lead-free piezoceramics with high performance. At present, most scholars focus on studying these perovskite material systems with a high piezoelectric constant (d_{33}), mainly including $Bi_{0.5}Na_{0.5}TiO_3$, $K_{0.5}Na_{0.5}NbO_3$ (KNN), and $BaTiO_3$.

KNN-based ceramic is one of the most promising materials to replace the lead-based ones owing to its good piezoelectric activity and a high Curie temperature (T_C), but its relatively low piezoelectricity limits the practical applications as compared with Pb(Zr, Ti)O_3 [3]. So we have to modify it for improving the electrical properties by different ways, such as construction of phase boundaries [4–27], advanced preparation method, and so on. Among those, it is an effective way to enhance the piezoelectric property by building the phase boundary using various ABO_3 compounds, such as KNN–$LiNbO_3$ [4], KNN–$BaZrO_3$ [7], KNN–$(Bi_{0.5}Na_{0.5})TiO_3$ [16] and KNN–$BaTiO_3$ [17]. Three kinds of phase boundaries (e.g., rhombohedral to orthorhombic (R–O), and orthorhombic to tetragonal (O–T) or rhombohedral to tetragonal (R–T) phase transition) have been mainly constructed [4–27]. Among those ABO_3 type additives, the $BaZrO_3$ with a paraelectric phase can stabilize the rhombohedral phase of KNN [7], and both Ba^{2+} and Zr^{4+} respectively replacing Na^{+} and K^{+} at A-site as well as Nb^{5+} at B-site can stabilize the R phase and form $A^{2+}B^{4+}O_3$-type perovskite ferroelectric, which possesses a negative physical pressure favoring the low-temperature phase [7]. Moreover, Zuo et al. has increased the T_{R-O} near room temperature by substituting Sb^{5+} for Nb^{5+} in KNN, but its T_{O-T} is still far above room temperature within the solubility limit of Sb^{5+} in the lattice [15]. From recent studies, both Sb^{5+} and $Bi_{0.5}Na_{0.5}ZrO_3$ can induce an R–T phase boundary of KNN-based ceramics, but a low d_{33} ~ 257 pC/N has been attained [12]. It is well known that the radius of doped ions in KNN is very important to those phase transition temperatures. For example, a smaller ion substituting a lager one can induce a positive physical pressure, favoring the formation of low temperature phases [16]. So in this work, we plan to dope the small ion $(Ba_{0.5}Na_{0.5})^{2+}$ and Sb^{5+} to respectively the material system of

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$0.96K_{0.45}Na_{0.55}Nb_{0.96}Sb_{0.04}O_3$–$0.04Ba_x(Bi_{0.5}Na_{0.5})_{1-x}ZrO_3$ (KNNS–B_xBNZ) to further improve their piezoelectric properties by form an R–T phase boundary, effects of the variation of Ba^{2+} content on the phase structure, microstructure, and electrical properties of KNNS–B_xBNZ ceramics have been importantly studied, and the underlying physical mechanisms have been clearly illuminated.

2. Experimental procedure

All $0.96K_{0.45}Na_{0.55}Nb_{0.96}Sb_{0.04}$–$0.04Ba_x(Bi_{0.5}Na_{0.5})_{1-x}ZrO_3$ ($x = 0$, 0.05, 0.10, 0.15, 0.20, 0.40, 0.60, and 1.0) ceramics were prepared by the conventional solid-state method, and the raw materials in this work were K_2CO_3 (99%), Na_2CO_3 (99.8%), $BaCO_3$ (99%), ZrO_2 (99%), Nb_2O_5 (99.5%), Bi_2O_3 (99.999%), and Sb_2O_3 (99.99%). First, we mixed the weighed powders covered with alcohol in a nylon jar, ball-milling 24 h, then dried and calcined at 850 °C for 6 h. The calcined powders were ground and mixed with PVA, and pressed in some disked samples with a diameter of ~1.0 cm and a thickness of ~1.0 mm. All of the samples were sintered at temperature range of 1100–1120 °C for 3 h by the sealed sintering, which is due to reduce the loss of the volatile elements during the sintering process [14]. Silver paste electrodes were coated on both sides of these sintered samples and fired at 700 °C for 10 min. After that, all samples were poled at room temperature in a silicone oil bath under a *dc* electric field of 2–4 kV/mm for 20 min, and then measured their electrical properties after 24 h.

The phase structure of the sintered ceramics was analyzed by the X-ray diffraction (XRD) using Cu *K*a radiation (DX-2700, Dandong, China). Their surface microstructure and element mapping were measured by a field emission-scanning electron microscope (FE-SEM) (JSM-7500, Japan). The dielectric properties of the poled samples were measured at different frequencies at room temperature by HP4294A. The temperature dependence of the dielectric properties of these ceramics was examined using an *LCR* meter (TH2816A, P. R. China and HP 4980, Agilent, U.S.A.) with the temperature ranged of −150 °C to 200 °C and room temperature ~450 °C. Their ferroelectric hysteresis loop was characterized by a ferroelectric tester (Radiant Technologies, Inc. Albuquerque, NM, USA) with a frequency of 10 Hz. The piezoelectric constant d_{33} of the poled samples was measured by a commercial Berlincourt-type d_{33} meter with a frequency of 100 Hz (ZJ-3A, China) and the planar electromechanical coupling factor (k_p) was determined by a resonance–antiresonance method with an impedance analyzer (Impedance Analyzer, PV70A, Beijing, China).

3. Results and discussion

Fig. 1(a) shows the room temperature XRD patterns of KNNS–BB_xNZ ceramics. All of the ceramics show a pure perovskite phase with increasing the content of Ba^{2+}. Fig. 1(b) shows the expanded XRD patterns in $2\theta = 43$–47°. It has been reported that Sb^{5+} and BNZ can increase T_{R-O} and lower T_{O-T} of KNN [15]. With increasing Ba^{2+}, the diffraction peaks located at 43–47° of the ceramics with $x \leq 0.20$ slightly shift to a lower angle because Ba^{2+} has a large radius (R_{Ba2+} ~ 1.61 Å) than those of both Bi^{3+}(1.36 Å) and Na^{+}(1.39 Å), leading to a lattice expansion [28]. And when x keeps increasing, the peaks then shift to a higher angle until $x = 1.0$ because the volume of the lattice has slight shrinkage caused by excessive Ba^{2+}, entering into the grain boundaries [16]. Fig. 2(a)–(h) shows the temperature dependence of the capacitance of KNNS–BB_xNZ ceramics in the measurement temperature from −150 °C to 200 °C. It is obvious that there is only one peak in the temperature range of −150 °C to 200 °C. We can know that their T_{R-O} increases from the subzero temperature to room temperature, and T_{O-T} also goes down to room temperature because of the comprehensive effects of Sb^{5+} [15], Ba^{2+}[7], and BNZ [12]. In order to clearly show the evolution of phase structures, we plot the phase diagram of this material system derived from Figs. 2 and 3, as shown in Fig. 2(i). Therefore, there appeared an R–T phase transition for the ceramics with $0 \leq x \leq 0.20$. With further increasing Ba^{2+}, the T_{R-T} was separated into both T_{R-O} and T_{O-T}, and then both T_{R-O} and T_{O-T} gradually shift a high temperature. As a result, the phase structure endures continuous transitions from R–T to O–T phases, finally an O phase. The O–T phase boundary could be observed in the ceramics with $0.20 < x < 0.60$, and the ceramics with $0.60 \leq x \leq 1.00$ possess an O phase.

Fig. 3 shows temperature dependence of the dielectric constant of KNNS–BB_xNZ ceramics in the temperature range of room temperature ~450 °C, measured at 100 kHz. It is obvious that the content of Ba^{2+} slightly affects their T_C, and T_C of all the ceramics is

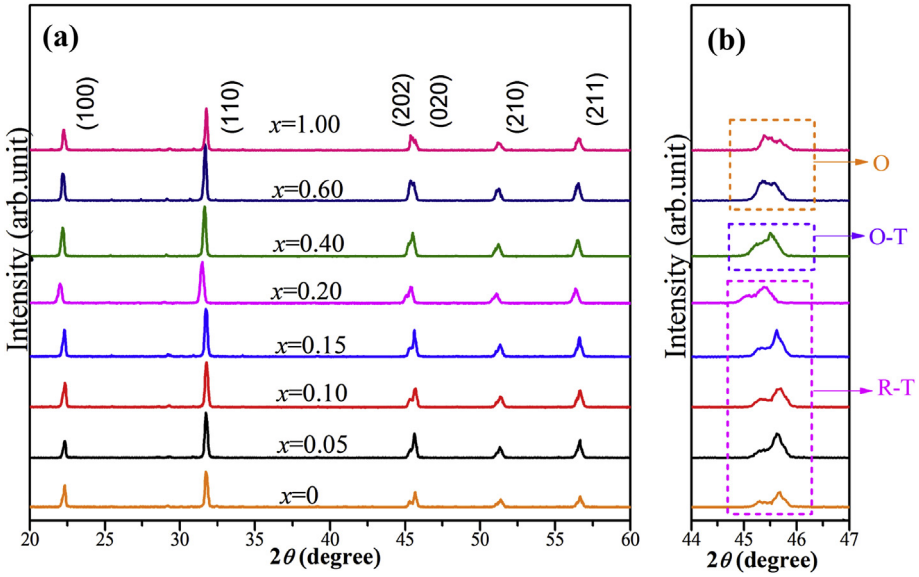

Fig. 1. XRD patterns of KNNS–BB_xNZ ceramics in the 2θ range of (a) 20–60° and (b) 43–47°.