Original Article

Study of the relationships among the crystal structure, phase transition behavior and macroscopic properties of modified (K,Na)NbO$_3$-based lead-free piezoceramics

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ABSTRACT

Although phase boundary engineering has made notable progress in improving the electrical properties of (K,Na)NbO$_3$-based piezoceramics, lattice distortion and spontaneous polarization of multiphase coexisting systems are a few of the remaining concerns. Here, new research employing XRD Rietveld refinement was performed to explore crystal structures, phase fractions and atomic parameters of Fe$_2$O$_3$-added (0.995-x)K$_{0.48}$Na$_{0.52}$NbO$_3$-xBi$_{0.5}$Na$_{0.5}$ZrO$_3$-0.005BiScO$_3$ ceramics. The distortion of the oxygen octahedron and the spontaneous polarization were presented. Central cation displacement provides a much larger contribution to polarization and the electric dipole moment in orthorhombic phase is much larger than that in tetragonal phase. Benefiting from tetragonal-orthorhombic phase coexistence and lattice distortion, optimized ferroelectric and piezoelectric properties ($d_{33} \sim 381$ pC/N, $P_r \sim 20.47$ μC/cm^2) were obtained. The ceramic still holds a large d_{33} (313 pC/N) after up to 300 °C of thermal annealing. A series of material constants was also calculated and compared to lead-based ones.

1. Introduction

Perovskite potassium-sodium niobate lead-free piezoelectric ceramics have been the subject of numerous studies because of their environmentally friendly features, superior piezoelectric activity and high Curie temperature (T_C) compared to other materials, especially when the composition is close to the polymorphic phase transitions (PPT) [1–4]. Resembling the morphotropic phase boundary (MPB) in lead zirconate titanate, phase boundary engineering in KNN-based ceramics has recently shown remarkable achievements in improving the piezoelectric properties [1,3–11]. Previous studies demonstrated that (K,Na)NbO$_3$ with ion substituting into the *A* or *B* sites [e.g., (K$_{0.455}$Li$_{0.045}$Na$_{0.5}$)(Nb$_{0.9}$Ta$_{0.1}$)O$_3$ [6], (K$_{0.5}$Na$_{0.5}$)$_{0.97}$Bi$_{0.01}$(Nb$_{1-x}$Zr$_x$)O$_3$ [7], etc.] or containing multi-compounding [e.g., K$_{0.5}$Na$_{0.5}$NbO$_3$-Bi$_{1/2}$Na$_{1/2}$TiO$_3$ [8], (Na$_{0.5}$K$_{0.5}$)NbO$_3$-(Bi$_{0.5}$Li$_{0.5}$)TiO$_3$-BaZrO$_3$ [9], etc.] could form new ceramic systems with new phase boundaries by tuning the tetragonal-orthorhombic (T-O) or orthorhombic-rhombohedral (O-R) phase transition temperature to room temperature. For example, in 2004, a groundbreaking piezoelectric coefficient ($d_{33} \sim 416$ pC/N) was reported by Saito et al. [10], who presented Li$^+$, Ta^{5+}, and Sb^{5+} co-doped textured KNN-based ceramics with a T-O phase boundary by

using the reactive template grain growth (RTGG) method. In 2016, Kai Xu et al. [11] also obtained superior piezoelectric properties ($d_{33} > 500$ pC/N) in the multi-phase coexistence in the KNNS-BZ-BKH ternary system. Although a breakthrough in piezoelectricity has been achieved, many important aspects remain elusive, such as the relationship among the electrical properties, phase structure, and lattice distortion, the contradiction between d_{33} and T_C, and the thermal stability.

The piezoelectric and dielectric properties originate from both extrinsic and intrinsic contributions. The piezoelectric properties are mainly ascribed to irreversible movement and domain switching, whereas the dielectric properties are primarily attributed to local atomic displacements within the unit-cell, which is closely linked to the spontaneous polarization (P_s) generated by linear lattice distortion [12–14]. On the one hand, benefiting from multiphase coexistence, domain movement and switching are easy to implement because of the plural phases with negligible differences in free energy as well as the more spontaneous polarization directions at the polymorphic phase boundary (PPB) zone [15]. The PPB zones where the electrical response would apparently be improved from domain rotation and polarization extension [13] are described by the following formula:
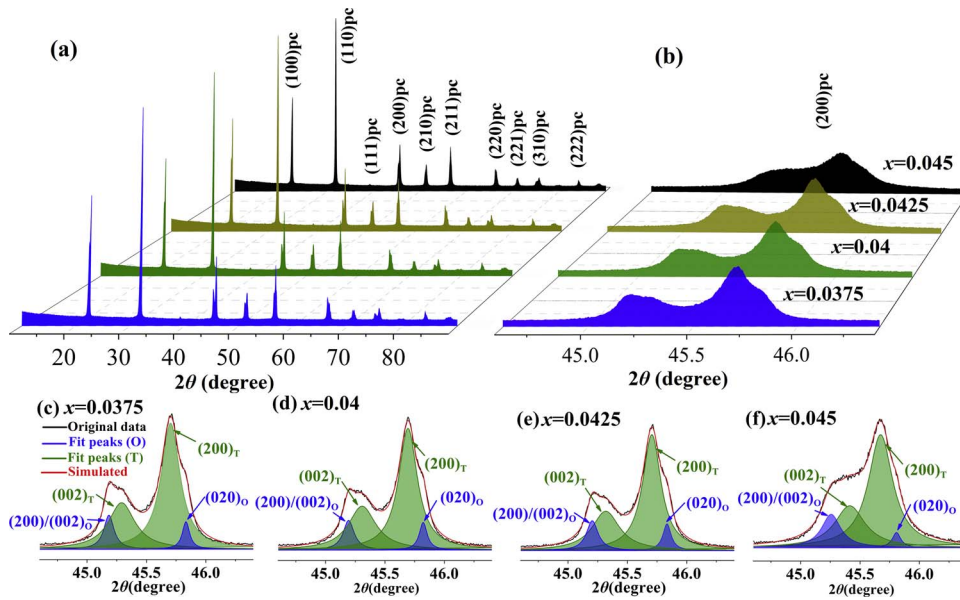
Fig. 1. (a) and (b) XRD patterns of Fe-KNNB*x* ceramics at $2\theta = 10°–90°$ and $44.5°–46.5°$ and (c)–(f) amplified XRD patterns simulated by Lorentz curve fitting.

$$d_{33} = 2Q_{11}\varepsilon_{33}P_3 \tag{1}$$

where Q_{11} is the electrostrictive parameter of the paraelectric phase and assumes a values between 0.05 and 0.1 $m^4 C^{-2}$; P_3 is the polarization along the polar axis and is approximately equal to the remnant polarization (P_r). Therefore, for KNN ceramics with a given component, attempting to increase P_r is a useful way to enhance piezoelectricity. On the other hand, the linear lattice distortion in each ceramic phase is different due to the differences in the cell structures. Therefore, the direction and magnitude of thr spontaneous polarization vary in different phase structures [14,16]. For a multi-phase coexisting system, the following fundamental question was raised: what is the contributor of spontaneous polarization? Until now, there is no detailed report regarding the influences of the added components on the lattice distortion and spontaneous polarization. Additionally, high piezoelectric activity in KNN ceramics is usually accompanied by a sacrifice in the T_C and unavoidable thermally unstable electromechanical properties because of the existence of the tilted PPB [17,18], which is different from the nearly vertical MPB in the well-known PZT system. For instance, the Curie temperatures of the systems reported by Saito et al. [10] and Kai Xu et al. [11] are 253 °C and 190 °C, respectively, which are far below that (421 °C) of the pure KNN ceramics and has restricted their further applications [19]. Therefore, the development of KNN-based ceramics with excellent electrical properties and a high T_C requires further study.

From this perspective, the most concerning subject in phase boundary engineering is to provide materials with the highest possible comprehensive performance and to discuss the underlying mechanisms. Here, new Fe$_2$O$_3$-added (0.995-*x*)K$_{0.48}$Na$_{0.52}$NbO$_3$-*x*Bi$_{0.5}$Na$_{0.5}$ZrO$_3$-0.005BiScO$_3$ (abbreviated as Fe-KNNB*x*) ternary system was designed to improve the piezoelectricity by composition modulation. Due to its high T_C and rhombohedral structure, using BiScO$_3$ as a component can effectively reduce the T_{T-O} without a large sacrifice to the T_C [18,20,21]. Bi$_{0.5}$Na$_{0.5}$ZrO$_3$ was introduced because of its excellent ability to modify and stabilize the PPT of KNN system [5,20]. As sintering additive, Fe$_2$O$_3$ is helpful for reducing the sintering temperature [20,22]. As a result, the stable ceramics with thermally stable piezoelectric properties were formed, in which both enhanced piezoelectricity ($d_{33} \sim 381$ pC/N) and high T_C (317 °C) were simultaneously observed. XRD Rietveld refinement was performed to systematically explore the phase structure, crystal parameters, and atomic parameters [23]. The visualized crystal structures were drawn, and P_s was calculated [14,24]. Then, the relationships among the macroscopic properties, crystal structure, and phase transition behavior were discussed. A

series of material constants, compared to lead-based ones, was also calculated from the impedance spectrum [25]. We believe this work can provide deeper insight into future theoretical analysis and practical applications.

2. Experimental procedure

Using conventional solid-state techniques, 0.3 mol% Fe$_2$O$_3$ added (0.995-*x*)K$_{0.48}$Na$_{0.52}$NbO$_3$-*x*Bi$_{0.5}$Na$_{0.5}$ZrO$_3$-0.005BiScO$_3$ lead-free piezoceramic was synthesized via Bi$_2$O$_3$ (99%), Na$_2$CO$_3$ (99.8%), K$_2$CO$_3$ (99.0%), Nb$_2$O$_5$ (99.5%), Sc$_2$O$_3$ (99%), and ZrO$_2$ (99.0%) raw materials, which were dried in an oven at 120 °C for 24 h before weighing. The dried stoichiometric raw materials were ball milled in ethanol for 12 h and then calcined at 860 °C for 6 h. The obtained powders were pressed into disks with a diameter of 10 mm and a thickness of 1 mm in a PVA binder using a uniaxial press under a pressure of 10 MPa. After burning off the binder, all the specimens were sintered in air for 3 h over a temperature range of 1040–1090 °C. Silver electrodes were plated on both sides of the pellets. A poling process was then conducted under a *d*c field of 3–4 kV/mm in a silicone oil bath 30 min.

X-ray diffraction (XRD, X' Pert Pro MPD, DY120 Panalytical, Netherlands) was carried out to identify the phase structure using a small scan step size (0.006°) and a long sampling time (16 s per step). The Materials Analysis using Diffraction (MAUD) program [26,27] were used to refine the XRD data to analyze the crystal structure parameters by selecting KNbO$_3$ (tetragonal *P4mm*: ICSD-9532 and orthorhombic *Amm*2: ICSD-9533) as the initial model. The surface topography was determined by the field emission scanning electron microscopy (FE-SEM) (JSM-7500, Japan). The material permittivities and dielectric loss for different measurement temperatures were measured by an LCR meter (HP 4980, Agilent, USA). The polarization-electric field (*P-E*) hysteresis loops were characterized by a ferroelectric measuring system (Precision LC, Radiant Technologies Inc., Albuquerque, NM). The piezoelectric constant d_{33} was characterized by a Belincourt-type d_{33} meter (ZJ-3A, Institute of Acoustics, Sinica, China), and the impedance spectrum was characterized by an impedance analyzer (Agilent 4294 A) in accordance with the IEEE standards.

3. Results and discussion

The X-ray diffraction (XRD) patterns from the Fe-KNNB*x* ceramics are shown in Fig. 1(a), which describes all the compositions as solid solutions with a typical perovskite structure. No trace of any secondary