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Microstructure and electrical properties of relaxor $(1-x)[(K_{0.5}Na_{0.5})_{0.95}Li_{0.05}](Nb_{0.95}Sb_{0.05})O_3$–$xBaTiO_3$ piezoelectric ceramics

Wenjuan Wu, Dingquan Xiao *, Jiagang Wu, Jing Li, Jianguo Zhu, Bin Zhang

Department of Materials Science, Sichuan University, Chengdu 610064, PR China

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Abstract

In order to solve the low temperature stability of electrical properties in KNN-based ceramics, $(1-x)[(K_{0.5}Na_{0.5})_{0.95}Li_{0.05}](Nb_{0.95}Sb_{0.05})O_3$–$xBaTiO_3$ [$(1-x)$KNLNS–xBT] lead-free piezoelectric ceramics were prepared by the conventional solid-state sintering method. The introduction of BT stabilizes the tetragonal phase of KNLNS ceramics at room temperature, results in a typical ferroelectric relaxor behavior, and shifts the polymorphic phase transition to below room temperature. Moreover, there is a strong $BaTiO_3$ concentration dependence of relaxor behavior and electrical properties, and the ceramic with $x = 0.005$ exhibits optimum electrical properties and typical relaxor behavior ($d_{33} = 269$ pC/N, $k_p = 0.50$, $\varepsilon_r = 1371$, $\tan\delta = 0.03$, $T_C \sim 349$ °C and $\gamma = 1.88024$). These results indicate that the BT is an effective way to improve the temperature stability as well as the electrical properties of KNN-based ceramics.

Keywords: C. Electrical properties; $(K_{0.5}Na_{0.5})NbO_3$; $BaTiO_3$; Lead-free piezoelectric ceramics; Ferroelectric relaxor

1. Introduction

Considerable attention for lead-free piezoelectric ceramics has been recently given to $(K_{0.50}Na_{0.50})NbO_3$ (KNN)-based ceramics, due to their excellent electrical properties, a high Curie temperature, and environmental friendliness [1–16]. These experimental results show that KNN-based lead-free ceramics exhibit arguable, comparable piezoelectric properties to conventional $Pb(Zr,Ti)O_3$ ceramics because of an orthorhombic to tetragonal (O–T) polymorphic phase transition (PPT) occurring near room temperature [2–5,11]. In contrast, this phase transition also correspondingly results in a strong temperature dependence of dielectric and piezoelectric properties, thus limiting the practical application of the KNN-based piezoelectric ceramics [3–5,11]. Recently, some attempts have been conducted on KNN-based solid solutions with $CaTiO_3$ (CT) for improving the temperature stability by decreasing the PPT, but their piezoelectric properties are not still ideal [3–5,11]. Therefore, the improvement in the temperature stability and piezoelectric properties of KNN-based ceramics currently becomes a tough issue for the practical application in the field of piezoelectric materials.

In the present work, we choose $BaTiO_3$ (BT) to dope KNN-based ceramics in order to decrease the O–T PPT to below room temperature. On introducing BT to KNN-based ceramics, there exists a valence mismatch both in the perovskite A-site and B-site, and the O–T polymorphic phase transition toward room temperature which seem to have a firm relation with the perovskite B-site ions [17,18]. The BT is suitable for the development of temperature stability. As our previous research reports [19], the lead-free ferroelectrics with a composition of 0.995KNLNS–$0.005BaTiO_3$ ceramic exhibits a typical ferroelectric relaxor behavior, that is, the dielectric peaks become increasingly broader, and the temperature of the maximum dielectric constant is shifted to a higher temperature with increasing frequencies. The dielectric relaxor behavior follows the modified Curie–Weiss law [19]. However, the investigations on the effect of BT content on the electric and relaxor properties of KNN-based were not detailed and exhaustive. Therefore, $(1-x)[(K_{0.5}Na_{0.5})_{0.95}Li_{0.05}](Nb_{0.95}Sb_{0.05})O_3$–$xBaTiO_3$

* Corresponding author.
E-mail address: nic0402@scu.edu.cn (D. Xiao).

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[(1 − x)KNLNS–xBT] lead-free ceramics were prepared. The effect of the BT addition on the microstructure, relaxor behavior, and electrical properties of (1 − x)KNLNS–xBT ceramics were systematically studied, and the underlying physical mechanisms were investigated.

2. Experimental

$(1-x)[(K_{0.5}Na_{0.5})_{0.95}Li_{0.05}](Nb_{0.95}Sb_{0.05})O_3$–$xBaTiO_3$ [(1 − x)KNLNS–xBT] (x = 0.0025, 0.005, 0.01, 0.015, 0.02 and 0.03, respectively) ceramics were prepared by the conventional solid state reaction fabrication technique. K_2CO_3 (99%), Na_2CO_3 (99.8%), Li_2CO_3 (99.99%), Nb_2O_5 (99.5%), Sb_2O_3 (98%), $BaCO_3$ (99%), and TiO_2 (99.99%) were used as starting raw materials. Stoichiometric powders were mixed by the ball milling for 24 h with the zirconia balls media in anhydrous ethanol and then dried, and these dried powders were calcined at 850 °C for 6 h. These calcined powders were pressed into disks at 20 MPa using polyvinyl alcohol (PVA) as a binder with diameters of ∼15 mm and thicknesses of ∼1.1–1.3 mm. After burning off PVA, these ceramic disks were sintered in the temperature range of 1090–1150 °C for 2–3 h in air. These specimens were poled in a silicon oil bath at 30 °C by applying a dc electric field of 3–4 kV/mm for 30 min. All electrical measurements were conducted on aged specimens (24 h after poling).

The phase structure of these specimens was examined by the X-ray diffraction (XRD) using Cu Kα radiation (λ = 1.54178 Å) in the θ–2θ scan mode (DX1000, Dandong, China). Surface morphologies of sintered specimens were observed by a scanning electron microscope (SEM) (JSM-5900, Japan). The density of sintered samples was determined by the Archimedes method. Silver paste was sintered on both sides of the specimens at 700 °C for 10 min to form electrodes for the dielectric and piezoelectric measurements. Their piezoelectric constant (d_{33}) was measured using a piezo-d_{33} meter (ZJ-3A, China). The dielectric constant as a function of temperature of these ceramics was obtained by using an *LCR* meter (HP 4980, Agilent, U.S.A.).

3. Results and discussion

Fig. 1(a) shows the XRD patterns of (1 − x)KNLNS–xBT ceramics as a function of x (x = 0.0025, 0.005, 0.01, 0.015, 0.02 and 0.03, respectively). (1 − x)KNLNS–xBT ceramics with $x \leq 0.015$ are of a single-phase perovskite structure, and no secondary phases were observed in the range detected. For these (1 − x)KNLNS–xBT ceramics with $x > 0.015$, a small amount of the secondary phase ($Ba_6Ti_2Nb_8O_{30}$) were formed due to too high sintering temperature, and these secondary phases are related to the volatilization of Na_2O at a high sintering temperature [20]. Therefore, a small amount of BT can easily enter into the KNLNS lattice to form a stable (1 − x)KNLNS–xBT solid solution. Fig. 1(b) plots the enlarged XRD patterns of (1 − x)KNLNS–xBT ceramics in the range of 2θ from 42° to 48°. It can be observed that the room-temperature phase structure of all (1 − x)KNLNS–xBT ceramics belongs to a tetragonal phase, whereas the temperature dependence of the dielectric constant (Fig. 5) also confirms that there is no coexistence of two phases at a room temperature. Moreover, it is of interest to note that the diffraction peaks slightly shift toward a higher diffraction angle as x increases. Fig. 2 shows the variation in lattice parameters as a function of x. The tetragonality (c/a ratio) of (1 − x)KNLNS–xBT ceramics decreases with the increase of x. It could be concluded that the BT addition results in the lattice distortion of (1 − x)KNLNS–xBT ceramics which is well in agreement with the peak shifts in Fig. 1.

Surface morphologies of (1 − x)KNLNS–xBT ceramics with x = 0.0025, 0.005, 0.01, 0.015, 0.02 and 0.03 are shown in

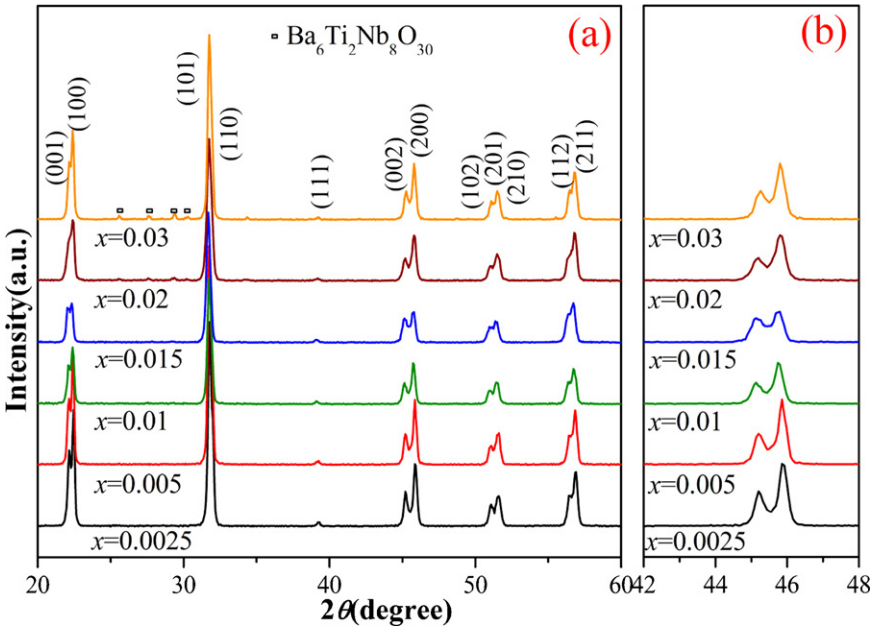

Fig. 1. (a) XRD patterns of (1 − x)KNLNS–xBT ceramics. (b) Enlarged XRD patterns of (1 − x)KNLNS–xBT ceramics in the range of 2θ from 42° to 48°.