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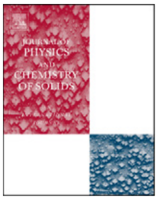

Structure, dielectric and piezoelectric properties of $K_{0.5}Na_{0.5}NbO_3$–$Bi_{0.5}(Na_{0.7}K_{0.2}Li_{0.1})_{0.5}TiO_3$ ceramics

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ABSTRACT

$(1-x)K_{0.5}Na_{0.5}NbO_3-xBi_{0.5}(Na_{0.7}K_{0.2}Li_{0.1})_{0.5}TiO_3+1$ mol% MnO_2 lead-free ceramics were prepared by an ordinary sintering method and their structure, dielectric and piezoelectric properties were investigated. A $K_{0.5}Na_{0.5}NbO_3$-based solid solution with perovskite structure is formed after the addition of $Bi_{0.5}(Na_{0.7}K_{0.2}Li_{0.1})_{0.5}TiO_3$ to $K_{0.5}Na_{0.5}NbO_3$. A small amount of $Bi_{0.5}(Na_{0.7}K_{0.2}Li_{0.1})_{0.5}TiO_3$ retards the grain growth, induces a diffuse phase transition at T_C, decreases Curie temperature and weakens the ferroelectricity of the ceramics. The ferroelectric orthorhombic-ferroelectric tetragonal phase at T_{O-T} is shifted to low temperature after the addition of $(Na_{0.7}K_{0.2}Li_{0.1})_{0.5}TiO_3$, leading to the formation of the coexistence of orthorhombic and tetragonal phases near room temperature at $0.015 < x < 0.035$. Because of the more possible polarization states resulting from the coexistence of the two phases, enhanced piezoelectric properties are obtained in the ceramics situated near the coexistence zone of two phases. The ceramic with $x=0.030$ possesses the relatively high T_C of 372 °C and large d_{33} of 183 pC/N.

1. Introduction

Lead-based perovskite ceramics of $Pb(Zr,Ti)O_3$ and $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ have been widely used for piezoelectric actuators, sensors, filters and transducers due to their superior piezoelectric and ferroelectric properties near morphotropic phase boundary (MPB). However, the use of these lead-based ceramics has caused serious environmental problems because of the high toxicity of lead oxide. Therefore, many investigations have been extensively carried out to develop lead-free piezoelectric ceramics with good electrical properties.

As a solid solution of antiferroelectric $NaNbO_3$ with ferroelectric $KNbO_3$, alkali niobate $K_{0.5}Na_{0.5}NbO_3$ (KNN) has been considered as one of the most promising alternatives to lead-based piezoelectric ceramics because of its high Curie temperature T_C of 420 °C [1]. However, a pure air-fired KNN ceramic usually exhibits poor piezoelectric properties ($d_{33}=80$ pC/N, $k_p=36\%$) [1]. In order to improve the piezoelectric properties of KNN ceramics, many ABO_3-type compounds (e.g., $LiSbO_3$ [2], $BaTiO_3$ [3], $LiNbO_3$ [4], $LiTaO_3$ [5], $AgNbO_3$ [6], $BiScO_3$ [7], $CaTiO_3$ [8], $AgSbO_3$ [9], etc) have been introduced into KNN to form lead-free KNN-based solid solutions with improved piezoelectricity. On the other hand, our previous study has shown that $Bi_{0.5}(Na_{0.7}K_{0.2}Li_{0.1})_{0.5}TiO_3$ is a strong ferroelectric with perovskite structure, exhibiting a large remanent polarization ($P_r=37\ \mu C/cm^2$) and a high d_{33} (231 pC/N) [10]. However, it has a low depolarization temperature (125 °C) which limits its application at high temperature. In the present work, a new lead-free solid solution of $(1-x)K_{0.5}Na_{0.5}NbO_3-xBi_{0.5}(Na_{0.7}K_{0.2}Li_{0.1})_{0.5}TiO_3+1$ mol% MnO_2 ($x=0.000$, 0.005, 0.010, 0.015, 0.020, 0.025, 0.030, 0.035, 0.040, 0.045, 0.050) was prepared by an ordinary solid-state sintering technique and its structure, dielectric and piezoelectric properties were studied. On the basis of our previous work [11], MnO_2 is an effective sintering aid and added in order to improve densification of the ceramics.

2. Experimental procedure

The $(1-x)K_{0.5}Na_{0.5}NbO_3-xBi_{0.5}(Na_{0.7}K_{0.2}Li_{0.1})_{0.5}TiO_3+1$ mol% MnO_2 ceramics ($x=0.000$, 0.005, 0.010, 0.015, 0.020, 0.025, 0.030, 0.035, 0.040, 0.045, 0.050) were prepared by a conventional mixed oxide route using metal oxides and carbonate powders: Na_2CO_3 (99.8%, Sinopharm Chemical Reagent Co., Ltd, China), K_2CO_3 (99%, Sinopharm Chemical Reagent Co., Ltd, China), Li_2CO_3 (99%, Sinopharm Chemical Reagent Co., Ltd, China), Nb_2O_5 (99.99%, Sinopharm Chemical Reagent Co., Ltd, China), TiO_2 (98%, Sinopharm Chemical Reagent Co., Ltd, China) and MnO_2 (97.5%, Sinopharm Chemical Reagent Co., Ltd, China). The powders in the stoichiometric ratio of $(1-x)K_{0.5}Na_{0.5}NbO_3-xBi_{0.5}(Na_{0.7}K_{0.2}Li_{0.1})_{0.5}TiO_3$ were first mixed

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thoroughly in ethanol using zirconia balls for 10 h. After the calcination at 850 °C for 4 h, 1 mol% MnO_2 powders was added. The mixture was ball-milled again for 10 h, mixed thoroughly with a poly(vinyl alcohol) binder solution and then pressed into disk samples. After removal of the binder, the disk samples were sintered at 1040–1100 °C for 2 h in air. Silver electrodes were fired on the top and bottom surfaces of the samples at 810 °C for 30 min. The ceramics were poled under a dc field of 3–4 kV/mm at 140 °C in a silicone oil bath for 40 min.

The crystallite structure of the sintered samples was examined using X-ray diffraction (XRD) analysis with CuKα radiation (DX1000, China). The relative permittivity ε_r and loss tangent tan δ were measured using a LCR meter (Agilent E4980A, Agilent Technologies Inc., Palo Alto, CA, USA). The polarization hysteresis (P–E) loops were measured using a ferroelectric measuring system (Premier II, Radiant Technologies, Inc. Albuquerque, NM, USA). The planar electromechanical coupling factor k_p was determined by the resonance method according to Ref. [12] using an impedance analyzer (Agilent 4294A, Santa Clara, CA, USA) [12]. The piezoelectric constant d_{33} was measured using a piezo-d33 meter (ZJ-6A, Institute of Acoustics, Chinese Academy of Sciences, Beijing, China).

3. Results and discussion

The XRD patterns of the $(1-x)K_{0.5}Na_{0.5}NbO_3-xBi_{0.5}(Na_{0.7}K_{0.2}Li_{0.1})_{0.5}TiO_3+1$ mol% MnO_2 ceramics are shown in Fig. 1. It can be seen that all the ceramics possess a pure perovskite structure, indicating that $Bi_{0.5}(Na_{0.7}K_{0.2}Li_{0.1})_{0.5}TiO_3$ has diffused into the KNN lattices, with the partial substitutions of $(Bi_{0.5}(Na_{0.7}K_{0.2}Li_{0.1})_{0.5})^{2+}$ for $(Na_{0.5}K_{0.5})^+$ and Ti^{4+} for Nb^{5+}, to form a homogeneous solid solution. As shown in Fig. 1, the doping level of $Bi_{0.5}(Na_{0.7}K_{0.2}Li_{0.1})_{0.5}TiO_3$ has an important influence on the crystal structure of the ceramics. Similar to KNN, the ceramics with $x \leq 0.015$ have an orthorhombic structure (the corresponding XRD patterns can be indexed by JCPDS card 71-2171). As x increases, a tetragonal phase appears and increases continuously. When $x \geq 0.035$, the ceramics are changed to tetragonal symmetry (the XRD patterns can be indexed by JCPDS card 71-0945). It can be clearly seen that orthorhombic and tetragonal phases coexist in the ceramics with $0.015 < x < 0.035$ at room temperature.

Fig. 2 shows the SEM micrographs of the $(1-x)K_{0.5}Na_{0.5}NbO_3-xBi_{0.5}(Na_{0.7}K_{0.2}Li_{0.1})_{0.5}TiO_3+1$ mol% MnO_2 ceramics with $x=0.000$, 0.015, 0.025 and 0.040. It can be seen that the addition of $Bi_{0.5}(Na_{0.7}K_{0.2}Li_{0.1})_{0.5}TiO_3$ decreases significantly the grain size of the ceramics. The ceramic with $x=0.000$ is well crystallized and has large grain size of about 4 μm. However, as x increases, the grain size of the ceramics decreases significantly. The grain sizes of the ceramics with $x=0.015$, 0.025 and 0.040 are about 1 μm, 0.8 μm and 0.5 μm, respectively. Previous studies on KNN–$BiScO_3$ ceramics [7] have shown that the addition of Bi-containing perovskites can retard the grain growth of the ceramics. This inhibition of grain growth in the KNN-based ceramics with the doping of Bi-containing perovskites may be attributed to the vacancies of metal ions induced by the partial substitution of Bi^{3+} for A-site ions (e.g., Na^+, K) of the KNN material. For the $(1-x)K_{0.5}Na_{0.5}NbO_3-xBi_{0.5}(Na_{0.7}K_{0.2}Li_{0.1})_{0.5}TiO_3+1$ mol% MnO_2 ceramics, A-site vacancies of metal ions created by the partial substitution of Bi^{3+} for A-site ions of KNN are supposed to be bound to the ions with high valance (e.g., Bi^{3+}) and consequently the mass transportation is weakened. As a result, the coefficient of the lattice diffusion of vacancies from pores to grain boundaries is decreased and thus the grain growth is inhibited [13–15]. Similar effect of the doping of high valance ions has been observed in La^{3+}- and Nb^{5+}-doped Pb(Ti,Zr)O_3 ceramics [13–15].

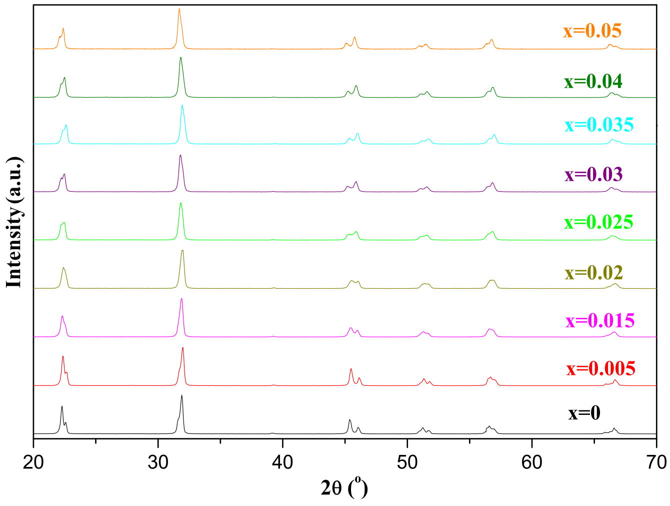

Fig. 1. XRD patterns of the $(1-x)K_{0.5}Na_{0.5}NbO_3-xBi_{0.5}(Na_{0.7}K_{0.2}Li_{0.1})_{0.5}TiO_3+1$ mol% MnO_2 ceramics.

Fig. 3 shows the temperature dependences of the ε_r for the $(1-x)K_{0.5}Na_{0.5}NbO_3-xBi_{0.5}(Na_{0.7}K_{0.2}Li_{0.1})_{0.5}TiO_3+1$ mol% MnO_2 ceramics. For the ceramic with $x=0.000$, two phase transition peaks are observed: one is associated with the paraelectric cubic-ferroelectric tetragonal phase transition at 422 °C (T_C) and the other is the ferroelectric tetragonal-ferroelectric orthorhombic phase transition at 201 °C (T_{O-T}). The addition of $Bi_{0.5}(Na_{0.7}K_{0.2}Li_{0.1})_{0.5}TiO_3$ shifts these two phase transition to low temperature. It can be seen that the ceramic with $x=0.030$ exhibit similar temperature dependences of ε_r, but with decreased T_C (372 °C) and T_{O-T} (45 °C, the inset of Fig. 3). As x further increases to 0.050, the cubic-tetragonal phase transition temperature decreases to 333 °C, while the tetragonal-orthorhombic phase transition cannot be observed. As shown in the inset of Fig. 3, the observed T_{O-T} (45 °C) for the ceramic with $x=0.030$ is very close to room temperature, implying that the coexistence of orthorhombic and tetragonal phases is formed near room temperature. These results are consistent with the measurement of XRD (Fig. 1).

From Fig. 3, the ceramic with $x=0$ exhibits a sharp phase transition peak at T_C, suggesting that the ceramic is a normal ferroelectric. As x increases, the transition peak at T_C becomes gradually broad. This shows that the addition of $Bi_{0.5}(Na_{0.7}K_{0.2}Li_{0.1})_{0.5}TiO_3$ causes a diffuse phase transition. The temperature corresponding to the maximum value of relative permittivity for the normal ferroelectric-paraelectric transition is denoted as Curie temperature (T_C, the ceramic with $x=0.000$), while the T_m is the temperature at which the relative permittivity ε_r reaches maximum for the diffusive ferroelectric-paraelectric transition (the ceramic with $x=0.030$ and 0.050) [16]. Similar compositional dependences of phase transition at $T_C(T_m)$ have been observed in KNN–$BiScO_3$ [7] and KNN–$BiAlO_3$ [17] ceramics. In order to determine the diffuseness of a phase transition, the modified Curie–Weiss law has been proposed: $1/\varepsilon_r - 1/\varepsilon_m = C^{-1}(T-T_m)^\gamma$ [18,19], where ε_m is the maximum value of relative permittivity at the phase transition temperature T_m (T_C), γ is the degree of diffuseness and C is the Curie-like constant. For a normal ferroelectric, the γ value should be 1, while an ideal relaxor ferroelectric possesses the γ value of 2. The graphs of $\ln(1/\varepsilon_r - 1/\varepsilon_m)$ vs. $\ln(T-T_m)$ for the ceramics with $x=0.000$, 0.030 and 0.050 were plotted and the results are shown in Fig. 4. A linear relationship is observed for all the ceramics. By least-squared fitting the experimental data to the modified Curie–Weiss law, the γ (i.e., the slope of the fitting curves) was determined. The calculated γ of the ceramic with $x=0.000$ is 1.01, showing that the ceramic with $x=0$ is a normal ferroelectric. When $x=0.030$ and 0.050, the