Phase transitional behavior and electrical properties of $(1 - x)(K_{0.475}Na_{0.48}Li_{0.05})Nb_{0.95}Sb_{0.05}O_3 - xCaZrO_3$ lead-free ceramics

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ABSTRACT

Lead-free piezoelectric ceramics $(1 - x)(K_{0.475}Na_{0.48}Li_{0.05})Nb_{0.95}Sb_{0.05}O_3 - xCaZrO_3$ with perovskite structure were prepared by conventional ceramic sintering technique, and the effects of the $CaZrO_3$ content on the phase transitions, dielectric and piezoelectric properties of the ceramics were investigated. With the increase of $CaZrO_3$, the crystal structure of the ceramics transformed from the orthorhombic–tetragonal phase coexistence to the coexistence of rhombohedral and orthorhombic phases at $x = 0.01$. Furthermore, both the rhombohedral–orthorhombic and orthorhombic–tetragonal phase transitions of the ceramics were found adjusted to be near room temperature with $x = 0.005$, which results in a significantly enhanced piezoelectric activity.

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1. Introduction

Lead zirconate titanate (PZT) piezoelectric ceramics are extensively applied in actuators, sensors, transducers, and other electronic devices because of their excellent dielectric and piezoelectric properties [1,2]. However, the PZT-based ceramics which contain up to 60 wt% PbO seriously damage both the environment and human health during production, usage, and waste treatment process, due to the toxicity of lead oxide and its high vapor pressure. Therefore, it is an urgent task to develop alternative lead-free piezoelectric materials. The $(K,Na)NbO_3$ (KNN) ceramics have been recently considered as one of the most promising lead-free piezoelectric ceramic systems owing to their high piezoelectric properties and Curie temperature (T_C) [3–29].

As well known, the phase boundary is generally associated with a two-phase coexistence zone over a narrow range of composition and temperature in functional materials [30], and forming a phase boundary is an effective way to improve the piezoelectric properties of piezoelectric ceramics, due to the easy polarization rotation [1]. Therefore, most researches on KNN-based ceramics have been carried out by modifying the orthorhombic–tetragonal (O–T) phase boundary that is also known as polymorphic phase boundary (PPB) down to around room temperature [4,6–10,13]. However, the piezoelectric properties obtained are still inferior in comparison with the PZT system. Recently,

some attempts have been performed to shift the rhombohedral–orthorhombic (R–O) phase boundary upward to near room temperature, but an even lower piezoelectric activity was acquired [11, 12,15,16]. Very recently, the constructing of the rhombohedral–tetragonal (R–T) phase boundary was paid more and more attentions [17–19,21,24,26,28], especially after successful construction of morphotropic phase boundary (MPB) between rhombohedral and tetragonal phases in $BaTiO_3$-based ceramics [31], and the role of the rhombohedral–tetragonal phase coexistence in enhancement of the piezoelectric properties was also revealed by F. Rubio-Marcos et al. [28].

In order to obtain the R–T phase boundary in KNN-based lead-free piezoelectric ceramics, both the R–O and O–T phase transition temperatures ($T_{R–O}$ and $T_{O–T}$) of the ceramics should be simultaneously adjusted to around room temperature. Many additives have been used to increase the $T_{R–O}$ value of KNN, including Sb^{5+}, Ta^{5+}, $AZrO_3$ (A = Ba^{2+}, Sr^{2+}, Ca^{2+}), $BiScO_3$, etc. [32]. As to the O–T phase boundary, it is the most hotly contested goal of research in KNN-based materials, and the methods of constructing it include ion substitutions, solid solutions with other ABO_3-type perovskites or ABO_3 multicomponents, variation of the K/Na ratio, new preparation techniques, etc. [32].

In the present work, the $(1 - x)(K_{0.475}Na_{0.48}Li_{0.05})Nb_{0.95}Sb_{0.05}$ $O_3 - xCaZrO_3$ [$(1 - x)$KNLNS–xCZ] system were designed and prepared by conventional ceramic solid-state method. In this system, the Li^+ and Sb^{5+} were selected to decrease the $T_{O–T}$ to around room temperature, and the $CaZrO_3$ was added to shift the $T_{R–O}$ to higher temperature. Furthermore, the small amount of excess sodium was introduced to compensate the volatilization during

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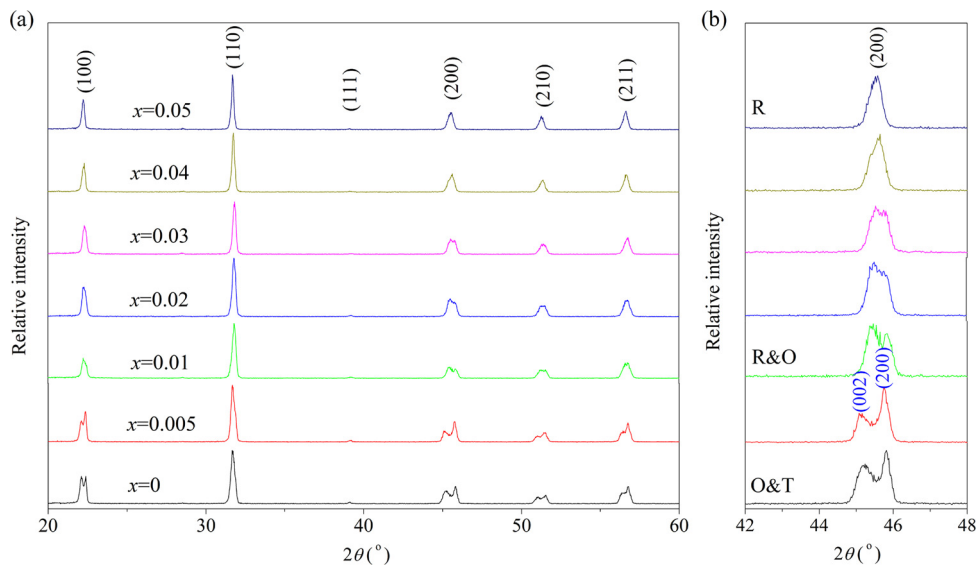 *E-mail address:* mrchenyi@swu.edu.cn (Y. Chen).

Fig. 1. XRD patterns of the $(1 - x)$KNLNS–xCZ ceramics in the 2θ range of (a) 20–60° and (b) 42–48°.

the high temperature treatment processes. The effects of the CZ content on the phase transitions, dielectric and piezoelectric properties of the ceramics were investigated. An enhanced piezoelectric behavior was obtained for the ceramics with the compositions near $x = 0.005$ that possesses both the R–O and O–T phase boundaries at near room temperature.

2. Experimental procedure

The $(1 - x)$KNLNS–xCZ ($x = 0$, 0.005, 0.01, 0.02, 0.03, 0.04, and 0.05) ceramics were prepared by traditional mixed oxide ceramic processing. The raw materials used in this study were K_2CO_3 (99.0%), Na_2CO_3 (99.8%), Li_2CO_3 (98.0%), Nb_2O_5 (99.5%), Sb_2O_3 (99.0%), $CaCO_3$ (99.0%), and ZrO_2 (99.0%) powders. The oxides powders were ball-milled in ethanol with agate media for 24 hours, dried, and then calcined at 850 °C for 4 hours in an alumina crucible. These calcined powders were milled and dried again. To improve the green strength of compacts, an addition of 3–5 wt% of poly(vinyl alcohol) was thoroughly mixed with these powders. These powders were granulated and pressed into pellets of 10 mm in diameter and 1 mm in thickness under 10 MPa uniaxial pressure. Following a removal of binder at 500 °C for 2 hours, pellets were sintered in sealed crucibles at temperature 1070–1120 °C for 2 hours.

Phase determination for sintered pellets was made using X-ray diffraction (XRD) (XRD-7000 diffractometer, Shimadzu). For electrical characterization, the sintered samples were polished, coated using a post-fire silver paste, and then fired at 700 °C for 10 min. Temperature-dependent dielectric measurements were carried out in the temperature range from room temperature to 550 °C using a computer controlled precision LCR meter (E4980A, Keysight Technologies) with a specially designed four-sample furnace. Specimens were poled in an oil bath under an electric field of 40–60 kV/cm at 120 °C for 20–30 min. After aging for 24 hours, the piezoelectric measurements were made using both a Berlincourt-type quasi-static d_{33} meter (YE2730A, Wuxi Yutian) and an impedance analyzer (E4990A, Keysight Technologies) using a resonance–antiresonance method.

3. Results and discussion

Fig. 1(a) shows the XRD patterns of the $(1 - x)$KNLNS–xCZ ceramics measured at room temperature. All the ceramics have only

phases with perovskite structure, indicating the formation of a stable solid solution between KNLNS and CZ. Fig. 1(b) exhibits the expanded XRD patterns in the 2θ range of 42–48°. The O–T phase coexistence was identified with $x \leq 0.005$, which can be confirmed by the T_{O-T} of near room temperature, based on the dielectric constant-temperature curves shown in Fig. 2. As the CZ content increases, the phase structure changes to a sole rhombohedral symmetry with $x = 0.05$, in which the split diffraction peaks at about 45° merge into one peak. Therefore, the R–O phase coexistence should exist in the composition range of $0.01 \leq x \leq 0.04$ in the system, and this can be verified by the following researches on the temperature dependence of the dielectric properties. However, no R–T phase coexistence has been gained in this piezoelectric ceramic system.

The temperature dependence of the dielectric constant (ε_r) and loss (tan δ) for the unpoled $(1 - x)$KNLNS–xCZ samples is shown in Fig. 2. For $x = 0$, two dielectric constant peaks are observed at 361 and 65 °C, corresponding to the phase transitions of tetragonal–cubic (T–C) and O–T, respectively, which is similar to the earlier report [10]. The two peaks of ε_r can also be spied with $x = 0.005$, although the positions of them are changed to 348.1 and 66.1 °C. For $x = 0.01$, the high temperature peak can be detected, but the low temperature peak turns to be a step-like dielectric anomaly, the ε_r of which increases in a wide temperature range. Besides, a small dielectric anomaly can be found below the step-like dielectric anomaly with $x = 0.01$. The appearance of the step-like dielectric anomaly is generally accompanied with the raising of T_{R-O} in KNN-based ceramics [17,24], such as in BaZrO$_3$ [11], or Sb^{5+} [15] modified KNN-based ceramics. Therefore, the small dielectric anomaly should be related to the R–O phase transition, and it changes to a clear peak at 64.9 °C for $x = 0.03$. These results together with the XRD analysis suggest that the rhombohedral and orthorhombic phases coexist in the composition range of $0.01 \leq x \leq 0.04$ at room temperature, as revealed in Fig. 1. Additionally, it can be concluded from the T_{R-O} of slightly above room temperature with $x = 0.01$ that the T_{R-O} of the ceramic should be at near room temperature with the composition of $x = 0.005$, which is increased by the addition of CZ [32]. This means that the sample with $x = 0.005$ has both R–O and O–T phase transitions at around room temperature. Furthermore, one can observe the apparition of a third peak at about 430 °C for $x = 0–0.005$, which might be caused by the possibility of Sb-lacked area existed in the ceramics [14]. The third peak may exist in $x \geq 0.01$, but it is