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# Effects of $CaAl_2O_4$ on the electrical properties and temperature stability of $(Na_{0.53}K_{0.404}Li_{0.066})Nb_{0.92}Sb_{0.08}O_3$ ceramics

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Lead-free $(1-x)(Na_{0.53}K_{0.404}Li_{0.066})Nb_{0.92}Sb_{0.08}O_3 + xCaAl_2O_4$ (NKLNS–*x*CA) ceramics were prepared by the conventional mixed oxide method. The effects of the addition of $CaAl_2O_4$ on the phase transitions and electrical properties of the KNN-based ceramics were studied and the temperature stability of their piezoelectric and electromechanical properties was also discussed. It is found that 1.5 mol% $CaAl_2O_4$ doped NKLNS ceramic exhibits stable piezoelectric and electromechanical properties in −40 to 60 °C due to the extended polymorphic phase transition region induced by the *B*-site composition fluctuation. The piezoelectric constant $d_{33}$, dielectric loss tan$\delta$, and electromechanical coupling factor $k_p$ of the NKLNS–0.0150CA ceramic are found to be 254 pC/N, 3.5%, and 45%, respectively, demonstrating that the NKLNS–0.0150CA ceramic is a very promising lead-free piezoelectric material for practical applications.

## 1. Introduction

Lead-based piezoelectric ceramics, $Pb(Zr_{1-x}Ti_x)O_3$ (PZT), have dominated the commercial market of the electronic industry, with applications in piezoelectric transducers, sensors, actuators and other electromechanical devices due to their excellent properties [1,2]. However, many lead-based ferroelectrics contain over 50 wt.% lead, which pollutes the environment and is harmful to human body [3]. Therefore, disposable, biocompatible and environmental friendly lead-free materials have been searched to substitute for the widely used PZT in high performance applications.

Up to now, great improvement has been obtained for lead-free piezoelectric ceramics, such as $BaTiO_3$ (BT), (K, Na)$NbO_3$ (KNN) and $Bi_{0.5}Na_{0.5}TiO_3$ (BNT)-based solid solutions [4–7]. Among them, KNN-based piezoelectric ceramics, particularly for Li and Sb-modified KNN compositions, are believed to be the most promising candidates to replace PZT ceramics due to their excellent piezoelectric and electromechanical properties [8–13]. The enhancement in piezoelectric properties of the Li, Sb-modified KNN-based ceramics is attributed to the existence of the polymorphic phases transition (PPT) between orthorhombic and tetragonal phases in the vicinity of room temperature [14]. The ceramics with the coexistence of two phases possess more possible polarization states which contribute to the high piezoelectric activities [15,16]. However, it has been found that Li, Sb-modified KNN-based ceramics exhibit low temperature stabilities, limiting their usefulness in today's applications [17,18]. To solve the problem, many experiments have been done by shifting the orthorhombic–tetragonal phase transition temperature ($T_{O-T}$) away from room temperature range [19–21]. Nevertheless, these methods also result in an obvious decrease of the piezoelectric properties. Therefore, in order to obtain KNN-based ceramics with high piezoelectric response along with temperature stable behavior, it is necessary to improve the temperature stability of PPT around room temperature [22]. Zhao et al. [23] prepared $Bi(Mg_{2/3}Nb_{1/3})O_3$-modified $(K_{0.5}Na_{0.5})NbO_3$ lead-free piezoelectric ceramics by introducing diffusion phase transition behaviors. A high $d_{33}$ (130 pC/N) associated with a significant enhancement in temperature stability were obtained for the $0.99(K_{0.5}Na_{0.5})NbO_3–0.01Bi(Mg_{2/3}Nb_{1/3})O_3$ composition. Based on the previous researches, in this work, $CaAl_2O_4$ (CA) was added into the $(Na_{0.53}K_{0.404}Li_{0.066})Nb_{0.92}Sb_{0.08}O_3$ (NKLNS) ceramics to obtain high piezoelectric coefficient, good temperature stability and other properties by introducing diffusion mechanisms. The effects of $CaAl_2O_4$ on the phase transitions, electrical properties and temperature stability of the NKLNS ceramics were mainly studied.

## 2. Experimental

Ceramics of stoichiometric compositions, $(1-x)(Na_{0.53}K_{0.404}Li_{0.066})Nb_{0.92}Sb_{0.08}O_3 + xCaAl_2O_4$ ($x = 0.0000, 0.0075, 0.0150, 0.0225$) (NKLNS–*x*CA), were prepared by a conventional ceramic fabrication technique using analytical-grade metal oxides or carbonate powders: $Li_2CO_3$, $Sb_2O_5$ of 99.9% purity, $Na_2CO_3$ of 99.8% purity, $K_2CO_3$, $Nb_2O_5$ of 99.5% purity, $Al_2O_3$ of 98.6% purity, and $CaCO_3$ of 99.0% purity. Before weighing, the powders were dried in an oven at 105 °C for 4 h. The powders were weighed according to the stoichiometric formula and milled

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for 12 h in polyethylene bottle with $ZrO_2$ balls using ethanol as a medium. After calcination at 885 °C for 4.5 h, the calcined powders were milled again for 12 h, and pressed into disks of 15 mm in diameter and 1.5 mm in thickness under 200 MPa pressure using poly vinyl alcohol (PVA) as a binder. The disk samples were fired at 650 °C for 1 h to burn off the PVA, and subsequently sintered in air at 1090 °C for 3.5 h. To minimize the loss of highly volatile elements such as Na and K, the disks were embedded in powders of the same composition.

The crystal structures of the ceramics were characterized by X-ray diffraction (XRD) analysis. Mass densities were measured by Archimede's technique. Silver electrodes were fired on the top and bottom surfaces of the samples at 570 °C for 20 min to form electrodes for the electrical measurements. The samples were poled in silicon oil by applying a dc field of 4 kV/mm for 20 min at room temperature. The piezoelectric constant $d_{33}$ was recorded using a Berlincourt-type quasi-static meter. The temperature dependences of the dielectric properties of the ceramics were examined using an Agilent 4294A impedance analyzer in the temperature range from 0 to 400 °C. Piezoelectric temperature stability was evaluated in an Espec SU-261 chamber. The electromechanical coupling coefficients were determined by a resonance and antiresonance method performed on the basis of IEEE standards using an impedance analyzer (Agilent 4294).

## 3. Results and discussion

Fig. 1 gives the XRD profiles of the NKLNS ceramics with different CA contents. As can be seen, pure perovskite structure is formed in the entire composition range of $x = 0.0000$–$0.0225$. No diffraction peaks corresponding to secondary impurity phases could be observed in the XRD profiles, suggesting that CA has completely diffused into the NKLNS lattice to form a new solid solution, with $Ca^{2+}$ (0.099 nm) entering the *A*-site and $Al^{3+}$ (0.051 nm) occupying the *B*-site of the $ABO_3$ perovskite structure. For the ceramics with $x \leqslant 0.0075$, the (002)/(200) peaks at about 45° are split, which are the characteristic of tetragonal structure. By increasing *x* to 0.0150, the split of diffraction peaks at about 45° becomes less evident, merging into one main peak with a weak shoulder locating at the lower angle side. The intensity of (200) peak decreases remarkably and the peak position of (002) also changes, which indicates that phase transformation occurs. Such XRD patterns are consistent with the reported tetragonal–orthorhombic phase transition in other KNN-based piezoelectric ceramics [24]. Therefore, the phase structure of the NKLNS–0.0150CA ceramic is the coexistence of tetragonal and orthorhombic phases. Further increasing *x* to 0.0225, only one peak can be observed, indicating the ceramic is of pseudo cubic phase.

Fig. 2 shows the temperature dependence of dielectric constant and loss measured at 1 k, 10 k, 100 k and 1 MHz for NKLNS–*x*CA ceramics. As shown in Fig. 2(a), the dielectric curves of NKLNS ceramic exhibit two dielectric anomalies, one at around 18 °C and the other at around 310 °C within the measuring temperature range, corresponding to the phase transitions from orthorhombic to tetragonal (at $T_{T-O}$) and from tetragonal to cubic (at $T_C$), respectively, so the ceramic is of tetragonal phase at room temperature. As the doping content increases, the $T_{O-T}$ shifts slightly to the higher temperature side. For the ceramic with $x = 0.0150$, the $T_{O-T}$ is about 55 °C, which is near room temperature, so the ceramic shows mixed phases. This is in good agreement with our room-temperature XRD results. However, for the ceramic with $x = 0.0075$, the $T_{O-T}$ result obtained through the dielectric measurement is inconsistent with the one acquired from the XRD analysis. While the dielectric measurement shows that the ceramic should be of orthorhombic–tetragonal coexistence phase, the actual crystalline structure is of tetragonal symmetry. The inconsistency is due to the thermal hysteresis since dielectric permittivity is measured during a heating process. When temperature increases, a proper time is required for the adjustment of domain structure inside the grains. Therefore, the dielectric measurement can only indirectly reflect the crystal structure [25,26]. As also seen in Fig. 2(b–d), the width of the $T_{O-T}$ peak becomes broadened with increasing CA content. Meanwhile, the maxima dielectric permittivity ($\varepsilon_m$) of NKLNS–*x*CA ceramics decreases with increasing frequency, whereas the transition temperature increases with increasing frequency, which is a typical characteristic of the relaxor ferroelectric materials. In addition, dielectric losses of all samples are minimum values at their Curie points, and the abrupt increase of $\tan\delta$ above $T_C$ is probably due to the conductive nature of the ceramics.

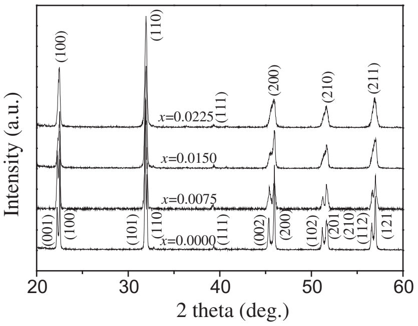

**Fig. 1.** X-ray diffraction patterns of the ceramics with different CA contents.

Fig. 3 shows the inverse dielectric permittivity measured at 100 kHz as a function of temperature. The deviation degree from the Curie–Weiss law can be defined by the following equation for $\Delta T_m$.

$$\Delta T_m = T_{dev} - T_m$$

in which $T_{dev}$ is the temperature at which the dielectric permittivity starts to deviate from the Curie–Weiss law. It is found that the calculated $\Delta T_m$ increases linearly from 17 to 91 °C as *x* increases from 0.0000 to 0.0225, indicating that the degree of diffuseness of the phase transition increases with increasing CA content. Uchino and Nomura [27] proposed a modified Curie–Weiss law to describe the diffuseness of a phase transition as:

$$\frac{1}{\varepsilon} - \frac{1}{\varepsilon_m} = \frac{(T - T_m)^{\gamma}}{C}$$

where $\gamma$ and *C* are assumed to be constant, and $\gamma$ is the indicator of the diffuseness degree, ranging between one corresponding to normal ferroelectric behavior and two representing the so-called complete diffuse phase transition. The insets of Fig. 3 show the plots of $\log(1/\varepsilon - 1/\varepsilon_m)$ as a function of $\log(T - T_m)$ at 100 kHz. The $\gamma$ value can be determined from the slope of the fitted lines. It is found that the obtained $\gamma$ values vary from 1.379 to 1.96, indicating that the NKLNS–*x*CA solid solutions are more relaxor ferroelectric characteristic with increase of *x*. The relaxor-like behavior in NKLNS–*x*CA ceramics should be attributed to the cationic disorder and compositional fluctuation induced by the random occupation of the *B*-site $Nb^{5+}$, $Sb^{5+}$ and $Al^{3+}$.

The electrical properties of the NKLNS–*x*CA ceramics at room temperature are shown in Table 1. It is found that the piezoelectric properties have only modest changes when adding a small amount of CA. However, further increasing *x* above 0.0150 makes the electrical properties deteriorate markedly due to the fact that the ceramic at $x = 0.0225$ has a pseudo cubic phase structure and poor density at room temperature.

In order to measure the temperature dependent $d_{33}$, the measuring probe of the $d_{33}$ meter is put in an environmental test chamber. The sample is raised to the designed testing temperature and maintained for 15 min in the chamber, and then its piezoelectric constant is recorded. Fig. 4 shows the piezoelectric constant $d_{33}$ as a function of temperature in the common usage temperature interval between −40 and 60 °C [28]. As can be seen, the properties are strongly temperature dependent for the NKLNS ceramic. Compared with the undoped ceramic, the CA-added NKLNS ceramics