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Phase transition behavior and temperature-stable piezoelectric properties of new quaternary (K, Na)NbO_3 based ceramics

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Abstract

(K, Na)NbO_3-based lead free materials have been found to exhibit good piezoelectric properties due to the orthorhombic–tetragonal polymorphic phase transition (PPT) temperature compositionally shifted downward to near room temperature. However, this transition correspondingly results in a strong temperature dependence of the dielectric and piezoelectric properties. In this work, new quaternary $(1-x)$ $(K_{0.4425}Na_{0.52}Li_{0.0375})(Nb_{0.8925}Sb_{0.07}Ta_{0.0375})O_3$ (KNLNST)–$x$$SrTiO_3$ (ST) lead-free piezoelectric ceramics were fabricated by a conventional ceramic technique and their structure and piezoelectric properties were also studied. The results of X-ray diffraction reveal that $SrTiO_3$ diffuses into the KNLNST lattices to form a new solid solution with a perovskite structure. After the addition of $SrTiO_3$, tetragonal–orthorhombic phase transition shifts to lower temperatures. The good piezoelectric properties of 0.995 KNLNST–0.005 ST material were found to be $d_{33}\sim 295$ pC/N, $k_p\sim 42\%$, and $\varepsilon_r\sim 1902$, with greatly improved temperature stability over the temperature range of 0–100 °C, demonstrating practical potential for actuator and ultrasonic transducer applications.
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Keywords: C. Electrical properties; Ceramics; Phase transformation

1. Introduction

Perovskite $Pb(Zr_xTi_{1-x})O_3$-based ceramics are conventional piezoelectric materials widely used in sensor and actuator. However, these ceramics with lead element cause crucial environmental pollution. Therefore, it is important to develop lead free ceramics with good piezoelectric properties.

Recently, lead-free (K, Na)NbO_3 (KNN) based ceramics have attracted special attention because of the breakthrough made by Saito et al. [1], who obtained high d_{33} (~ 300 pC/N) in the ternary KNN–$LiTaO_3$–$LiSbO_3$ (abbreviated as (K, Na, Li)(Nb, Sb, Ta)O_3) ceramics by a conventional ceramic technique. However, one of the critical issues of the KNN–$LiTaO_3$–$LiSbO_3$ system arises from potassium niobate composition. In the phase diagram of Nb_2O_5–K_2CO_3, there are several phases present besides the $KNbO_3$ (KN) perovskite phase. During the heat treatment, there is a chance to form non-stoichiometric phases with hygroscopic nature which is the root cause of instability in KN and hence, the KNN–$LiTaO_3$–$LiSbO_3$ system. Besides humidity issue, there is also a need for reliable processing route with high degree of reproducibility. In addition, the enhanced piezoelectric properties in (K, Na)NbO_3 based ceramics are found to be always accompanied by the occurrence of polymorphic phase transitions around room temperature [1–16]. In connection with it, strong piezoelectric temperature dependence is usually observed [5,6,9,10,12,15], which is often very undesirable for practical applications. For example, the temperature of piezoelectric materials could elevate several tens of degree, when the piezoceramics are used as actuators, especially at high frequency and alternating current field.

The addition of $CaTiO_3$ into KNN was found to shift T_{O-T} good below room temperature [15]. Considering that $SrTiO_3$ (ST) is similar to $CaTiO_3$ in phase structure, moreover the substitution of $SrTiO_3$ into $BaTiO_3$ can also lower T_{O-T} [17], it is expected that the addition of $SrTiO_3$

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into KNN based ceramics could be able to shift $T_{O–T}$ good down. Furthermore, doping $SrTiO_3$ into KNN based ceramics could prevent KNN based ceramics from deliquescence [18]. Therefore, it is reasonable to anticipate that addition of $SrTiO_3$ could settle the above two problems of deliquescence and piezoelectric instability around room temperature for ternary KNN based piezoceramics.

2. Experimental

K_2CO_3 (99%), Na_2CO_3 (99.8%), Li_2CO_3 (98%), Nb_2O_5 (99.5%), Ta_2O_5 (99.99%), Sb_2O_3 (99.5%), $SrCO_3$ (99%), and TiO_2 (99.9%) were used as raw materials to prepare $(1-x)(K_{0.4425}Na_{0.52}Li_{0.0375})(Nb_{0.8925}Sb_{0.07}Ta_{0.0375})O_3-xSrTiO_3$ ($x=0.004$, 0.005, 0.006, and 0.007) ceramics by the conventional mixed-oxide method. The stoichiometric powders were mixed by ball-milling in ethanol for 5 h, then dried and calcined at 900 °C for 5 h. The calcined powders were mixed with 3 wt% polyvinyl alcohol (PVA) solution, and then uniaxially pressed into pellets with a diameter of 1.5 cm under 300 MPa pressure. After burning out PVA, the green disks were sintered in air at selected temperatures for 3 h, depending on their x, in the range between 1100 and 1140 °C. For comparison, the KNLNST ceramic samples were also sintered by the conventional solid-state method at 1120 °C.

The microstructure was observed by a scanning electron microscope (SEM, JSM−5610LV/Noran-Vantage). Powder XRD (D8 Advance) was utilized to identify the crystal structures and the phases. For the measurement of dielectric and piezoelectric properties, silver paste electrodes were formed at the two circular surfaces of the disk-shaped specimens after firing at 700 °C for 10 min. The piezoelectric constant d_{33} was measured using a quasistatic piezoelectric constant testing meter (ZJ-3A, Institute of Acoustics, Chinese Academy of Science, Beijing, China). Dielectric property as a function of temperature and frequency was measured by an impedance analyzer (HP4294A). Polarization versus electric field hysteresis loops was measured using a ferroelectric tester (TF Analyzer 2000). The measurement of piezoelectric and electromechanical properties was carried out only 24 h after a poling process.

3. Results and discussion

Fig. 1 shows the XRD patterns of the ceramics with different $SrTiO_3$ contents. All the ceramics have a single perovskite phase and no second phase can be detected, which indicate that $SrTiO_3$ seems to have diffused into the perovskite lattice to form a solid solution. Fig. 1(b) is the magnification of Fig. 1(a) in the range from 44° to 47°. Besides, it can be seen from the figure that the ceramics are orthorhombic syngony at $x=0$. With increasing x from 0 to 0.004, the structure changes from orthorhombic to tetragonal phases. Further increasing x to 0.006 leads the structure to change from tetragonal to pseudocubic phases. It suggests that two phase boundaries, corresponding to the orthorhombic to tetragonal and tetragonal to pseudocubic phases exist at $0<x<0.007$.

The temperature dependence of dielectric constant of KNLNST ceramics is shown in Fig. 2(a) and the temperature dependence of dielectric permittivity for $(1-x)$ KNLNST–xST ceramics with $x=0.004$, 0.005, 0.006 and 0.007 are shown in Fig. 2(b). The KNLNST samples undergo two phase transitions, corresponding to the transition temperatures of orthorhombic to tetragonal and tetragonal to cubic, T_{O-T} (48 °C) and T_C (267 °C), respectively. It can be observed that T_C of the ceramics slightly decreases as increases from 0.004 to 0.007 for the addition of the paraelectric $SrTiO_3$ from Fig. 2(b). By increasing x, $T_{O–T}$ shifts towards

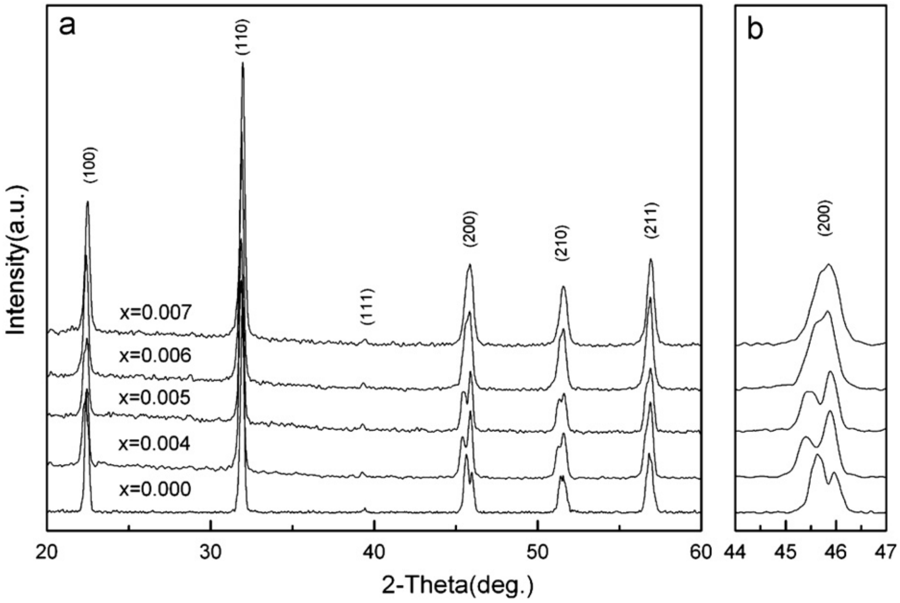

Fig. 1. XRD patterns of $(1-x)$KNLNST–xST ceramics with different ST contents.

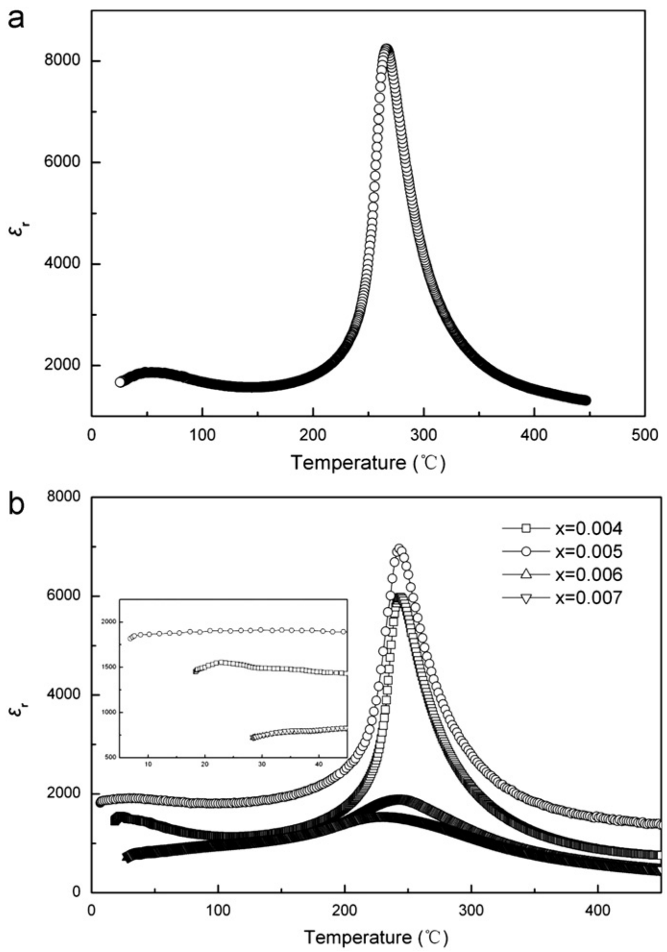

Fig. 2. Temperature dependence of ε_r for $(1-x)$KNLNST–xST ceramics: (a) $x=0$ and (b) $0.004<x<0.007$.

lower-temperature regions. The first phase transition disappears at $x>0.005$ from Fig. 2(b), which is very beneficial for practical devices applications. Sr^{2+} (0.113 nm) ions substitute the ions (Na^+ (0.095 nm), K^+ (0.113 nm), Li^+ (0.068 nm)) in A site, and Ti^{4+} (0.068 nm) ions substitute the ions (Nb^{5+} (0.070 nm), Sb^{5+} (0.062 nm)) in B site. The doped ions are different from the host ones not only in radius but also in valence. Therefore, the substitution of Sr^{2+} and Ti^{4+} will lead to a lattice distortion of the KNN-based ceramics. The phase transition energy needed by the distorted lattice may be less than the one needed by undistorted lattice. That is, the phase transition of the distorted lattice will take place in a lower temperature. This may be the reason for T_C and $T_{O\text{–}T}$ of $SrTiO_3$-doped KNN based ceramics shifting to much lower temperature than the undoped one. Furthermore, some broadening of the tetragonal–cubic transition peak can also be observed at $x>0.005$ from Fig. 2(b), which may imply a relaxation phase transition.

A modified empirical expression is proposed by Uchino and Nomura [19] to describe the diffuseness of the ferroelectric phase transition,

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

where ε_m is the peak value of the dielectric constant and T_m is the temperature at which the ε value reaches the maximum. r and C are assumed to be constants and the r value is between 1 and 2. The limiting value $r=1$ makes the equation fit the conventional Curie–Weiss law valid for the normal ferroelectric, and $r=2$ makes the equation fit the quadratic valid for an ideal relaxor ferroelectric. When r is between 1 and 2, it indicates a so-called incomplete diffuse phase transition. Based on the temperature plots of ε_r, the graph of log $(1/\varepsilon-1/\varepsilon_m)$ versus log $(T-T_m)$ for the ceramics is plotted and the results are shown in Fig. 3(a)–(d). The slope of the fitting curves is used to determine the r values. The r values are 1.12, 1.15, 1.91 and 1.95 at $x=0.004$, $x=0.005$, $x=0.006$ and 0.007, respectively, which indicates that the ceramics with $x\geq0.006$ show almost an ideal relaxer behavior due to both the A-site cation mixtures and B-site cation mixtures.

Fig. 4 shows the dielectric constant as a function of the temperature for $(1-x)$KNLNST–xST ($x=0.007$) ceramics under different measuring frequencies. The dielectric constant decreases with increasing the measuring frequency. The slight frequency dispersion of ε_r values exists between 1 kHz and 1 MHz, which present T_m at 226, 227, 229, and 230 °C. However, the frequency dispersion is a typical characteristic of relaxer behavior which results from compositional fluctuation. It has been known that for the A- and B-site complex $(A_1A_2)(B_1B_2)O_3$ perovskite ferroelectrics, a small difference in ionic radii of the A- and B-site cations is favorable for the formation of a disordered structure [18]. The solid solution of $SrTiO_3$ in KNLNST increases the A- and B-site disordered degree and hence the local compositional fluctuation. As a result, the ceramics become more relaxor.

As seen from Figs.1 and 2, T_C decreases with increasing ST content. $T_{O\text{–}T}$ shifts from 48 °C for pure KNLNST ceramics to 23 °C for $(1-x)$KNLNST–xST ($x=0.004$). In terms of previous studies [19–22], several essential characteristics of the piezoelectric ceramics with morphotropic phase boundary (MPB) should possess can be recapitulated as follows. Firstly, two different compounds with almost the same type of structure could form a complete solid solution and in the MPB region it has the characteristic of compositional homogeneity in the MPB region. Secondly, a MPB region is nearly independent of temperature in a proper region. Finally, although a MPB was initially defined as a boundary with equal amounts of two separated phases, in fact, the exact composition location of the MPB was hardly defined. Therefore, in fact, the MPB represents a narrow composition region with the coexistence of two different phases (or a transitional phase with lower symmetry such as monoclinic). Because the phase transition of orthorhombic to tetragonal is dependent of temperature, this result confirms that the phase transition of orthorhombic to tetragonal is owing to the decrease which the polymorphic phase transition temperature (from the orthorhombic to tetragonal phase) changes from 48 °C for pure KNLNST ceramics to 23 °C for

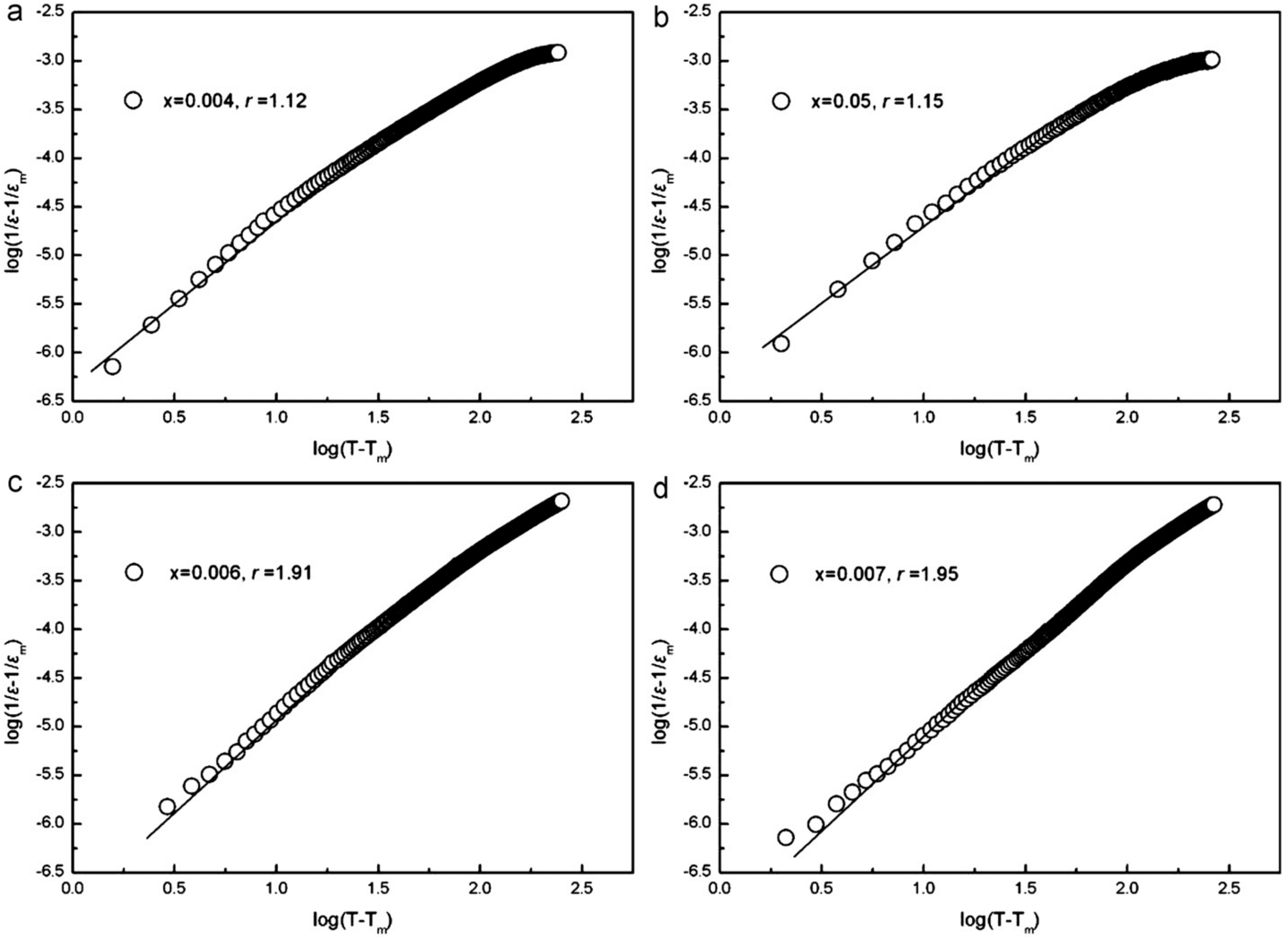

Fig. 3. log $(1/\varepsilon-1/\varepsilon_m)$ as a function of log $(T-T_\mathrm{m})$ for $(1-x)$KNLNST–xST ceramics.

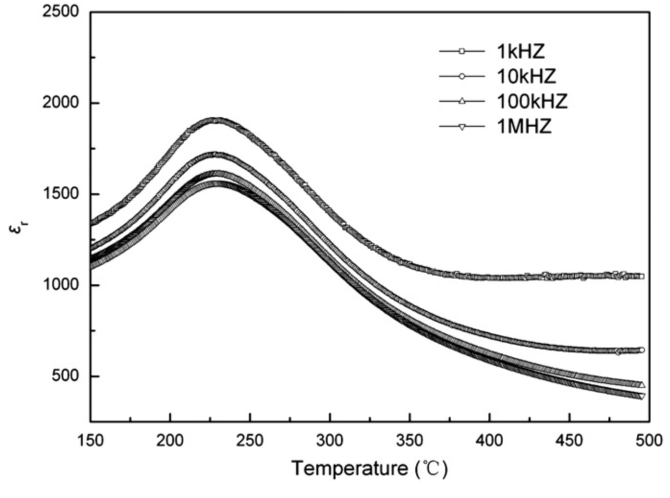

Fig. 4. The dielectric constant as a function of the temperature for $(1-x)$KNLNST–xST ceramic with $x=0.007$.

$(1-x)$KNLNST–xST ($x=0.004$) ceramics. There are two possible reasons resulting in the coexistence of O and T phases in the composition near 0.4 mol% ST. One is the diffusion of the phase transformation between the tetragonal to orthorhombic phase. The other may be attributed to the composition inhomogeneity which is inevitable in ceramics. But the morphotropic phase boundary corresponding to tetragonal to pseudocubic phase exists at $0.005<x<0.006$. With the increase of ST, the change of T_C is negligible which is above 230 °C as shown in Fig. 2(b). So the pseudocubic phase of $(1-x)$KNLNST–xST ($x\geq 0.006$) does not result from the change of T_C at room temperature from Fig. 1. The addition of ST results in morphotropic phase boundary since phase structure of ST is cubic. On the other hand, the phase transition of tetragonal to pseudocubic phase is independent of temperature. Therefore, it is a typical morphotropic phase boundary at $0.005<x<0.006$. In a word, the polymorphic phase transition and morphotropic phase boundary, corresponding to the orthorhombic to tetragonal and tetragonal to pseudocubic phase respectively, exist at $0<x<0.007$ at room temperature.

The result indicates that the properties of $(1-x)$KNLNST–xST ($x=0.005$) ceramics are stable with changing temperature from Fig. 2(b). As shown in Table 1, the dielectric

Table 1
Dielectric and piezoelectric properties of KNN-based ceramics at room temperature.

Samples	d_{33} (pC/N)	k_p (%)	ε_r	tan δ	References
0.995 KNLNST–0.005 ST	295	42	1902	2.7	In this work
KNLNST	300	48	1900	4	In this work
0.995 KNN–0.005 ST	96	32.5	412	4	[18]

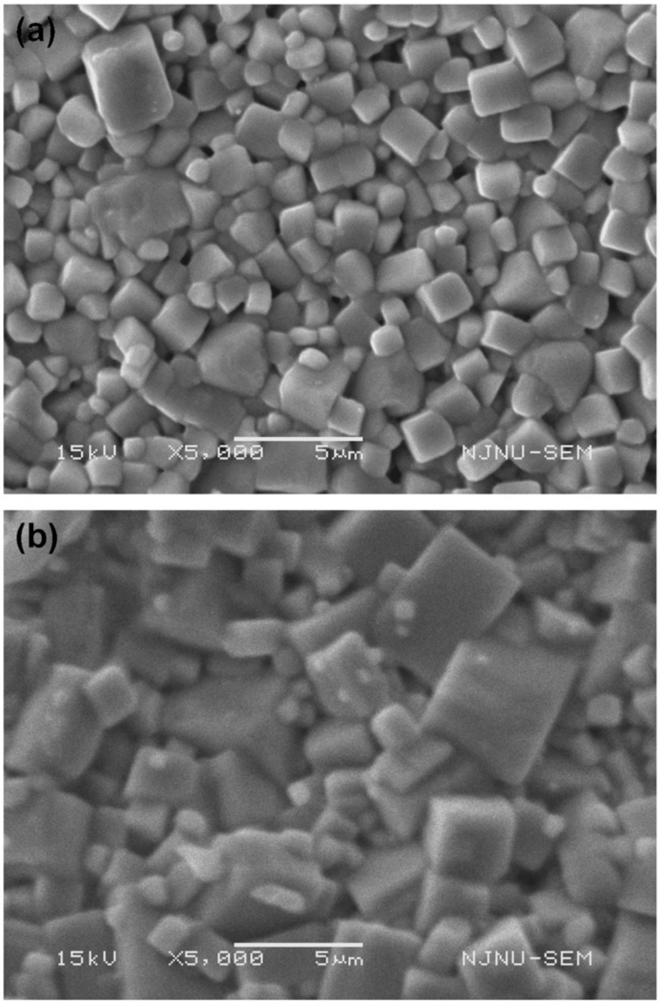

Fig. 5. SEM images of the $(1-x)$KNLNST–xST ceramics as a function of x: (a) $x=0$ and (b) $x=0.005$.

constant (ε), the piezoelectric coefficient (d_{33}), the electromechanical coupling (k_p) and mechanical quality factor (tan δ) of $(1-x)$KNLNST–xST ceramics with $x=0.005$, after sintering at 1120 °C for 3 h, are 1902, 295 pC/N, 0.42, and 2.7%, respectively. The electromechanical coupling slightly decreases and the mechanical quality factor is improved comparing with KNLNST ceramics. Therefore, the excellent piezoelectric properties of 0.995 KNLNST–0.005 ST ceramics surpass the 0.995 KNN–0.005 ST ceramics which are still comparable to KNLNST ceramics.

Fig. 5 shows the SEM images of the $(1-x)$KNLNST–xST ceramics with $x=0$ (a) and $x=0.005$ (b). All ceramics exhibit regular shaped grains with clear grain boundaries. It is clearly observed that the grains grow much larger and the microstructure becomes denser with increasing ST. Therefore it suggests that the $SrTiO_3$ can promote the densification of the KNN-based ceramics.

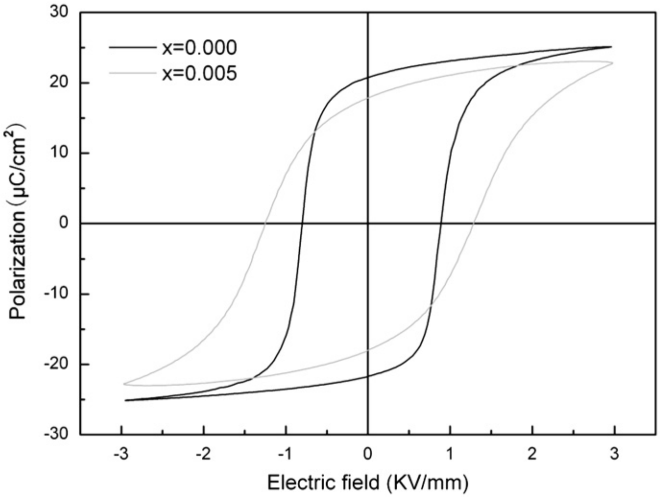

Fig. 6. P–E hysteresis loops of the $(1-x)$KNLNST–xST ceramics as a function of x.

Fig. 6 shows the P–E loops of $(1-x)$KNLNST–xST ceramics, which were measured at 3 kV and 30 HZ. The remnant polarization (P_r) is 20.79 μC/cm^2 for pure KNLNST ceramics, which is larger than that of 0.995 KNLNST–0.005 ST ceramics ($P_r=17.89$ μC/cm^2), as shown in Fig. 6. The coercive field (E_C) of the $(1-x)$KNLNST–xST ceramics increases with the increase of ST. The origin for the elevation of the coercive field may be due to the addition of ST, and ST decreases the rate of switching electrical field with applied electric field.

The temperature dependence of the planar mode electromechanical coupling factor k_p for $x=0$, and 0.005 compositions with temperature range from 0 °C to 90 °C are shown in Fig. 7. For the ceramics with $x=0$, k_p is found to be 0.34 at 0 °C, increasing to 0.48 at 40 °C and then gradually decreasing to 0.29 when the temperature reaches 90 °C, showing a sharp change around room temperature. For the ceramics with $x=0.005$, k_p is found to be 0.42 at 0 °C, reaching 0.38 at 40 °C, and then decreasing to a value of 0.3 at 90 °C. The inflection point corresponding to the phase transition between tetragonal and orthorhombic structure is not observed for the $SrTiO_3$ modified compositions over the range 0–40 °C, showing temperature-stable behavior of piezoelectric properties around room temperature.

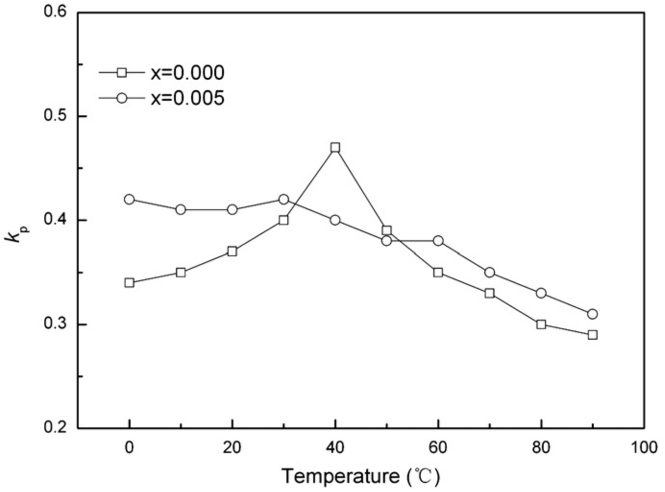

Fig. 7. Planar mode electromechanical coupling factor as a function of temperature for $(1-x)$KNLNST–xST.

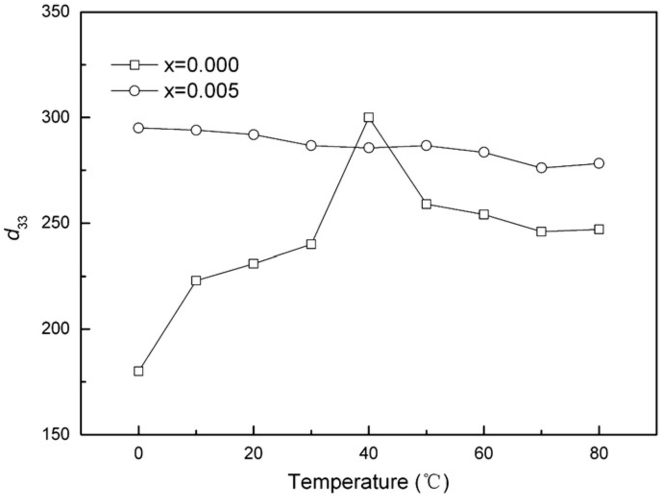

Fig. 8. Piezoelectric coefficient as a function of temperature for $(1-x)$KNLNST–xST.

Fig. 8 demonstrates the piezoelectric temperature dependence of the KNLNST and 0.995 KNLNST–0.005 ST ceramics in terms of d_{33}. As shown in Fig. 8, the 0.995 KNLNST–0.005 ST ceramic shows less change in d_{33} within the measured temperature range from 0 to 80 °C. Similar to the dielectric temperature behavior, a peak value of the piezoelectric coefficient as a function of temperature is observed for KNLNST materials owing to the polymorphic phase transition near room temperature. The change of the piezoelectric coefficient in the temperature range of 0–80 °C is on the order of 40%, while the change of the ST modified materials is found to be less than 6%, exhibiting a flat temperature dependence behavior.

4. Conclusions

$(1-x)$ $(K_{0.4425}Na_{0.52}Li_{0.0375})(Nb_{0.8925}Sb_{0.07}Ta_{0.0375})O_3$–$x$$SrTiO_3$ lead-free piezoelectric ceramics were fabricated by a conventional solid-state method and their structure and piezoelectric properties were studied. The polymorphic phase transition and morphotropic phase boundary, corresponding to the orthorhombic to tetragonal and tetragonal to pseudocubic phases respectively, exist at $0<x<0.007$ at room temperature. ST was used to shift the orthorhombic–tetragonal PPT in a modified KNN-based piezoelectric material to below room temperature. XRD patterns revealed a pure tetragonal phase for ST modified KNLNST. The KNLNST material exhibited strong temperature dependent properties due to the coexistence of orthorhombic and tetragonal phases at room temperature. The ST modified KNLNST materials exhibited good reliability. Together with its relatively good piezoelectric properties and wide temperature usage range, it demonstrates that ST modified KNLNST materials are potentially good candidates for applications in actuators and transducers, which require lead free piezoelectrics.

Acknowledgments

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