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Phase structure and electrical properties of (Li,Ta)-doped $(K,Na)NbO_3$ lead-free piezoceramics in the vicinity of Na/K = 50/50

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Abstract The phase structure and electrical properties of $(K,Na)NbO_3$ (KNN)-based lead-free piezoelectric ceramics with nominal composition $Li_{0.03}$ $(Na_xK_{1-x})_{0.97}Nb_{0.8}Ta_{0.2}O_3$ (LKNNT, $x = 0.50-0.55$) were investigated with an emphasis on the influence of Na/K ratio. By XRD and Raman measurements, it was revealed that the phase transition from the co-existence of O_1 and T_1 to the co-existence of O_2 and T_2 occurs when $x = 0.52$. At this Na/K ratio, a peak of dielectric constants was obtained, which also corresponds to a morphotropic phase boundary between T_1 and T_2 besides that between O_1 and O_2 in LKNNT ceramics. All the $Li_{0.03}$ $(Na_xK_{1-x})_{0.97}Nb_{0.8}Ta_{0.2}O_3$ ceramics with $x = 0.50 - 0.55$ show excellent piezoelectric performance, and the piezoelectric coefficient d^*_{33} can reach as high as 335 pm/V. The room-temperature piezoelectric properties in the present LKNNT ceramics are not sensitive to the change of Na/K ratio, indicating that the orthorhombic to tetragonal phase co-existence dominates the enhancement of piezoelectric properties. However, the results on the piezoelectricity measurement at elevated temperature showed possible to further enhance piezoelectric properties by adjusting Na/K ratio in the tetragonal LKNNT ceramics.

Introduction

Lead-based piezoelectric ceramics such as $Pb(Zr, Ti)O_3$ (PZT) have been widely used in sensors, transducers, actuators, and other important devices for decades. Because of the toxicity of lead, lead-free piezoceramics have received increasing attention from the view point of environment in recent years. Potassium sodium niobate (KNN)-based ceramics are considered as one of the promising lead-free candidates for its high-piezoelectric properties comparable to PZT-based ceramics [1–3]. However, pure KNN ceramics have very poor dielectric and piezoelectric properties, whose representative d_{33} data is ~80 pC/N for the normally sintered KNN ceramics [4], and ~148 pC/N even for its counterpart prepared by spark plasma sintering with high density [5]. Many studies to date revealed that Li, Sb, and Ta are effective elements for enhancing the piezoelectric properties of KNN ceramics [6–12], and the mechanism has also been gradually clarified in recent years. Doping Li, Sb, and Ta elements into KNN ceramics can significantly shift the tetragonal to orthorhombic transition point (T_{T-O}) from above 200 °C to room temperature, so the resultant materials show enhanced piezoelectric responses due to the effect of two-phase co-existence. Such a piezoelectricity enhancement in KNN system basically benefits from the polymorphism phase transition (PPT) effect, which is different from morphotropic phase boundary (MPB) effect in PZT system [13]. As a consequence, the KNN-based ceramics with enhanced piezoelectricity due to the PPT effect are lack of temperature stability of electrical properties. As one approach to resolve this problem, it is thought necessary to develop the KNN-based ceramics with MPB-like phase structures which can endow piezoelectric materials with enhanced and temperature-insensitive piezoelectric properties.

So far, Zhang et al. [14] investigated the compositional dependence of ferroelectric and piezoelectric properties of a series of nondoped KNN ceramics with different Na/K ratios in a wide range, and found that a phase boundary like MPB exists in KNN system and piezoelectric and dielectric

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constants show their peaks at the composition close to the boundary. Later, Dai et al. [15] revealed that a typical MPB exists at $x = 0.52$–0.525, separating the monoclinic and orthorhombic phases in $K_{1-x}Na_xNbO_3$ ceramics. They found that piezoelectric constant and electromechanical coupling coefficient show peaks at the composition near $x = 0.52$. Those studies suggested the possibility of enhancing the piezoelectric properties in KNN ceramics by the MPB effect through adjusting Na/K ratio as done in the PZT system by controlling the Zr/Ti ratio. Therefore, detailed investigations are meaningful to clarify if there is an optimal value of Na/K in (Li,Ta)-doped KNN-based ceramics, whose ferroelectric and piezoelectric properties are much better than nondoped KNN ceramics. Under such a motivation, this study was conducted by finely varying the Na/K ratio for a (Li,Ta)-doped KNN ceramics with fixed Li and Ta contents.

Experimental

KNN-based ceramics with nominal composition $Li_{0.03}(Na_x K_{1-x})_{0.97}Nb_{0.8}Ta_{0.2}O_3$ (abbreviated as LKNNT, $x = 0.50 - 0.55$, at internals of 0.01 or 0.005) were prepared by a conventional method. The raw materials in this experiment were lithium carbonate (Li_2CO_3, 97 wt%), potassium carbonate (K_2CO_3, 99 wt%), sodium carbonate (Na_2CO_3, 99.8 wt%), niobium oxide (Nb_2O_5, 99.95 wt%), and tantalum oxide (Ta_2O_5, 99 wt%). The raw materials after being weighed were milled for 24 h in ethanol, and then the slurry was dried and calcined at 850 °C for 5 h. The synthesized powder were ball milled again for 24 h also in ethanol and dried, after that the powders were pressed into small disks of 10 mm in diameter, followed by cold isostatic pressing under 200 MPa. Finally, these pellets were sintered in air at 1120 °C for 2 h. After being painted with sliver electrodes, the samples were poled at 120 °C for 20 min under an electric field of 4 kV/mm in silicone oil.

X-ray diffraction (XRD) characterization was conducted by using CuKα radiation (Rigaku, D/Max2500, Tokyo, Japan). The cross-sectional microstructures of the ceramics were observed by scanning electron microscopy (SEM, JSM6460, Tokyo, Japan). The Raman spectrum was measured by the LabRAM HR800 (France). The dielectric properties at room temperature were measured using an Agilent 4194A precision impedance analyzer (Hewlett-Packard, Palo Alto, CA) at 1 kHz. The ferroelectric properties and electric-field-induced strains were measured on the TF ANALYZER 1000 (aixACCT Systems GmbH, Germany). A d_{33} meter (ZJ-3A, Institute of Acoustics, Chinese Academy of Science, Beijing, China) was also used to measure room-temperature quasistatic piezoelectric constant. The temperature dependence of dielectric constants was measured in a temperature-regulated chamber which was connected with Agilent 4294(Hewlett-Packard, Palo Alto, CA) at 1 kHz.

Results and discussion

Figure 1 shows the SEM images of the cross sections of the $Li_{0.03}(Na_xK_{1-x})_{0.97}Nb_{0.8}Ta_{0.2}O_3$ ceramics with different x values. All samples have high density, ranging from 4.64 to 4.71 g/cm^3. The grains have uniform shape and rectangle facet. The change of Na/K ratio has tiny influence on the grain size. The average grain size of the LKNNT ceramics is less than 2 µm which is close to the reported results with similar compositions [9, 16].

Figure 2a shows the XRD patterns of the LKN-NT ceramics with different x values (Na/K ratios), and the enlarged patterns in the range of 2θ from 82.5° to 86.5° are shown in Fig. 2b. It appears that the XRD patterns have less change even comparing the enlarged peaks. KNN-based ceramics usually show orthorhombic and/or tetragonal symmetry at room temperature, which can be distinguished by focusing on the peaks around $2\theta = 45^{o}$. For an orthorhombic symmetry with $a = c > b$, its $I_{(200)}/I_{(020)}$ equals 2 and the (200) line has a smaller Bragg angle. But the $I_{(002)}/I_{(200)}$ equals 0.5 and the (002) line is located at a smaller Bragg angle for tetragonal symmetry $a = b < c$. Considering that the two peaks around $2\theta = 45^{o}$ shown in Fig. 2a almost have the same intensity, it can be speculated that both tetragonal and orthorhombic phases co-exist in the present LKNNT ceramics. To further confirm if there is any difference in phase structure caused by the change of Na/K ratios, more detailed XRD analysis was conducted by comparing the peaks at higher diffraction angles as shown in Fig. 2b. The broad peaks shown in Fig. 2b are similar to that reported by Wang and Li [17] for $0.94(K_{0.5}Na_{0.5})NbO_3-0.06LiNbO_3$ composition containing tetragonal and orthorhombic phase, again confirm the co-existence of two phases in the present LKNNT ceramics. As shown in Fig. 2b, the peak location and its half width change slightly as the Na/K ratio is varied, which may indicate there are very small changes in phase structure with various Na/K ratios. However, it seems difficult to distinguish them only by XRD.

Two phases co-existence in the present LKNNT ceramics result from the fact that T_{T-O} is shifted down to around the room temperature. It is presumed that the tetragonal and orthorhombic phase structures of the present LKNNT ceramics might be affected by changing Na/K ratios, as in the case of pure KNN ceramics reported by Dai et al. [15]. However, because the co-existence of tetragonal and orthorhombic phases make the phase analysis extremely difficult, the following experiments were conducted

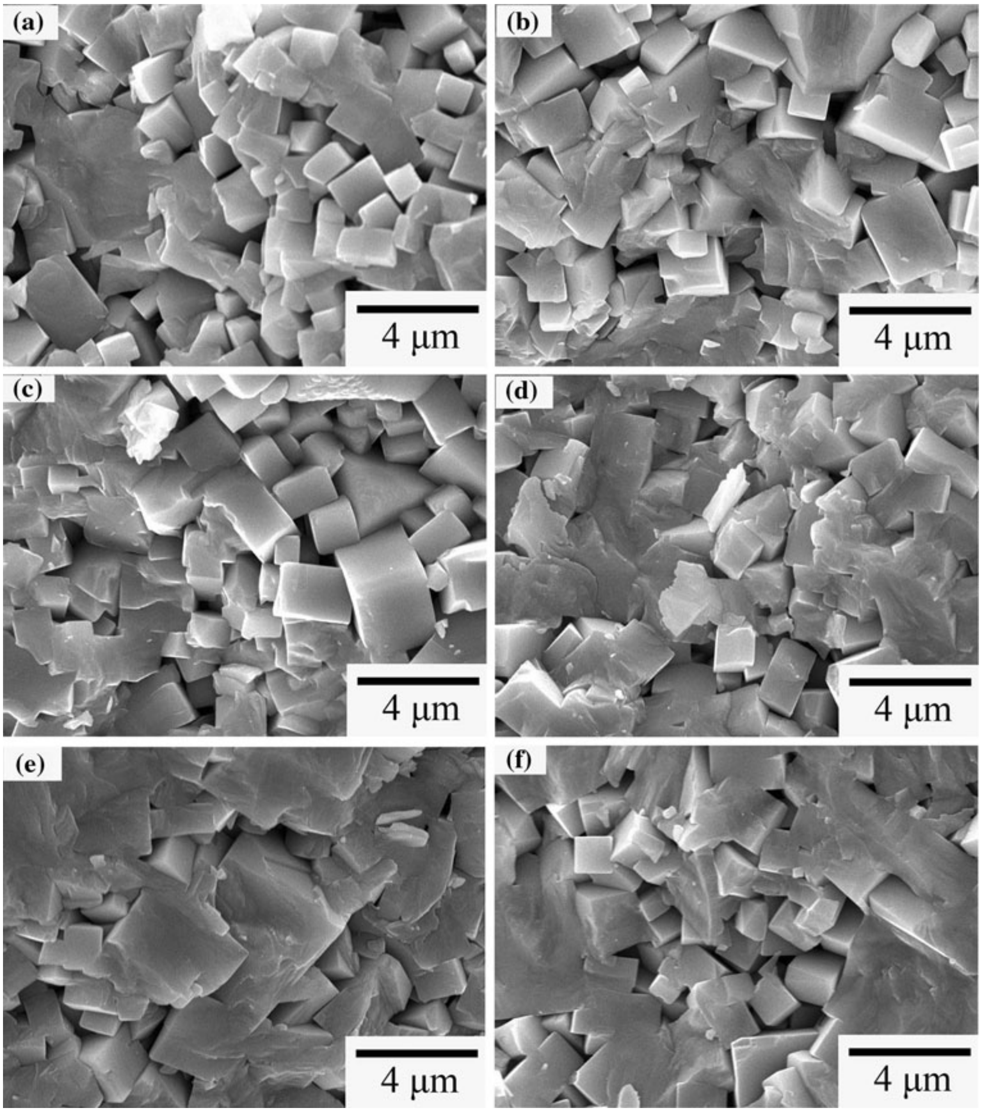

Fig. 1 SEM images of the $Li_{0.03}(Na_xK_{1-x})_{0.97}Nb_{0.8}Ta_{0.2}O_3$ ceramics with different x values, **a** $x = 0.50$, **b** $x = 0.51$, **c** $x = 0.52$, **d** $x = 0.53$, **e** $x = 0.54$, **f** $x = 0.55$

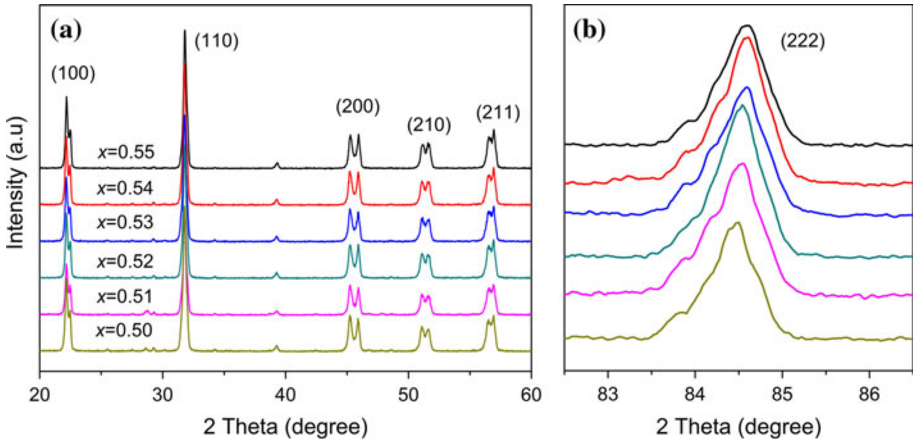

Fig. 2 XRD patterns of $Li_{0.03}(Na_xK_{1-x})_{0.97}Nb_{0.8}Ta_{0.2}O_3$ ceramics with different x values

at elevated (120 °C) and reduced (−50 °C) temperatures where only tetragonal or orthorhombic phase exist by using Raman spectroscopy that was suggested as a powerful tool to study the structural changes in the KNN-based ceramics [13, 18, 19]. Figure 3 shows a representative Raman spectrum of LKNNT ceramics in which the part between 450 and 700 cm^{-1} can be fitted using a sum of Gussian lines. The fitted line corresponds well to the original data with $R^2 > 0.99$ [18]. It was reported that the locations of peak 1 and peak 2 are sensitive to the change of phase structure [13, 18]. As shown in Fig. 4a, the wavenumber corresponding to peak 1 and peak 2 increases gradually and shows a peak at $x = 0.52$, when the Raman experiment was conducted at −50 °C. A similar trend was observed at 120 °C, although the wavenumber turned to further increase when $x > 0.53$. When the sample is cooled down to −50 °C (far below its T_{T-O}), it should be of orthorhombic phase. As reported by Dai et al. [15], there is a phase boundary separating two orthorhombic phase (O_1 to O_2) at $x = 0.52$ as indicated in the KNN phase diagram [20]. On the other hand, at 120 °C, well above T_{T-O}, only tetragonal phase should exist in these tested samples. Therefore, the results shown in Fig. 4b indicate that the tetragonal phases may have tiny difference when the Na/K ratio changes across $x = 0.52$. By referring the KNN phase diagram [20], it can be speculated that there also exists a phase boundary in the tetragonal region, which separates two kinds of tetragonal phases (T_1 to T_2) in KNN system. However, more studies are needed to clarify their difference in detail, but such experiments are challenging because their lattice parameters are extremely close.

Figure 5 demonstrates the dielectric constant versus the temperature at $x = 0.51, 0.52, 0.53, 0.54$, and 0.55, and the inset shows the dielectric constants measured at 1 kHz with different x values at room temperature. After the lowering of T_{T-O} by adding Li and Ta, the dielectric constant will reach maximum when the temperature is around room temperature, because of the effect of two-phase co-existence. The T_{T-O} is independent of Na/K ratio and estimated about 40 °C from this figure (actually lower than this temperature because of thermal hysteresis). In addition, when $x = 0.52$, the dielectric constant reaches the maximum and has better thermal stability than any other composition.

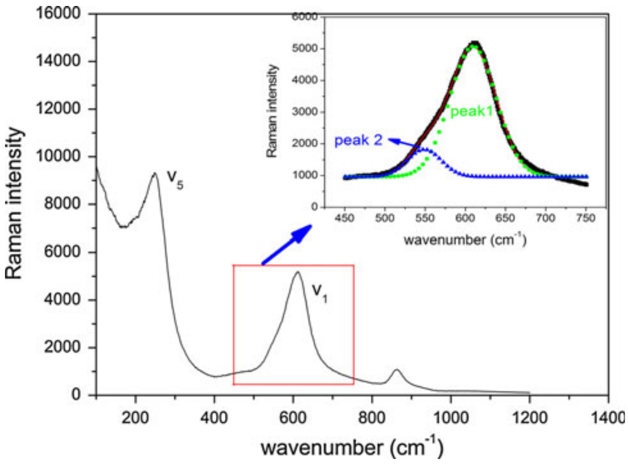

Fig. 3 Raman spectrum of $\mathrm{Li}_{0.03}(\mathrm{Na}_x\mathrm{K}_{1-x})_{0.97}\mathrm{Nb}_{0.8}\mathrm{Ta}_{0.2}\mathrm{O}_3$ ceramics with $x = 0.54$ at 120 °C and the *inset* shows fitted Raman spectrum between 450 and 700 cm^{-1}

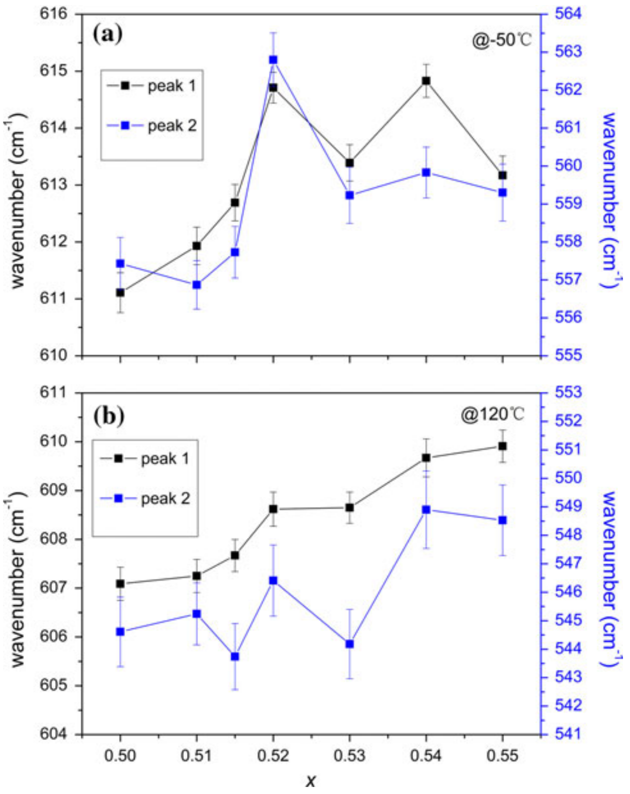

Fig. 4 Positions of fitted Raman peaks of the $\mathrm{Li}_{0.03}(\mathrm{Na}_x\mathrm{K}_{1-x})_{0.97}\mathrm{Nb}_{0.8}\mathrm{Ta}_{0.2}\mathrm{O}_3$ ceramics with different x values at −50 and 120 °C

The typical P-E loops of the ceramics with different x values are shown in Fig. 6. The loops change little with the variety of x; also do the remnant polarization P_r and the coercive field E_c. The P_r ranges from 13 to 15 $\mu\mathrm{C/cm}^2$, while the E_c ranges from 14 to 16 kV/cm. When $x = 0.53$, the P_r reaches the largest 15.06 $\mu\mathrm{C/cm}^2$, with a corresponding E_c value of 14.8 kV/cm. Figure 7 shows the piezoelectric constant d_{33} and planar electromechanical coefficient k_p of the $\mathrm{Li}_{0.03}(\mathrm{Na}_x\mathrm{K}_{1-x})_{0.97}\mathrm{Nb}_{0.8}\mathrm{Ta}_{0.2}\mathrm{O}_3$ ceramics with different x values at room temperature, also including the piezoelectric constant d^*_{33} of several representative compositions at room and elevated temperature. The d^*_{33} were determined by measuring the strain induced by applying electrical field, whose corresponding curves of strain versus electric field at two temperatures are shown in Fig. 8. The piezoelectric constant d_{33} values match well

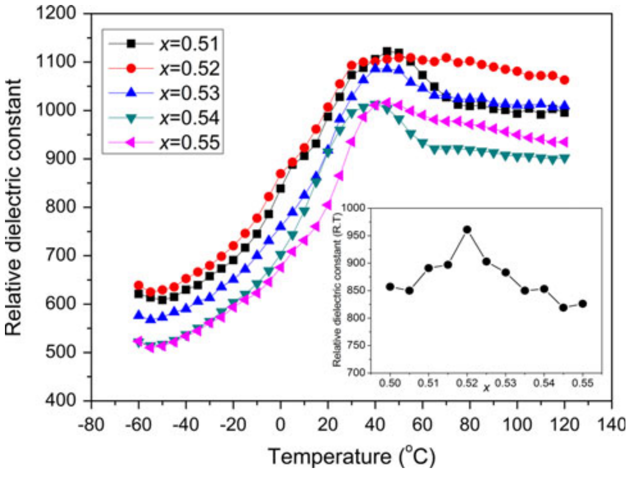

Fig. 5 Relative dielectric constant as a function of temperature for $Li_{0.03}(Na_xK_{1-x})_{0.97}Nb_{0.8}Ta_{0.2}O_3$ ceramics with different x values. Measurements were performed at 1 kHz during the heating process. The *inset* shows the relative dielectric constants measured at 1 kHz with different x values at room temperature

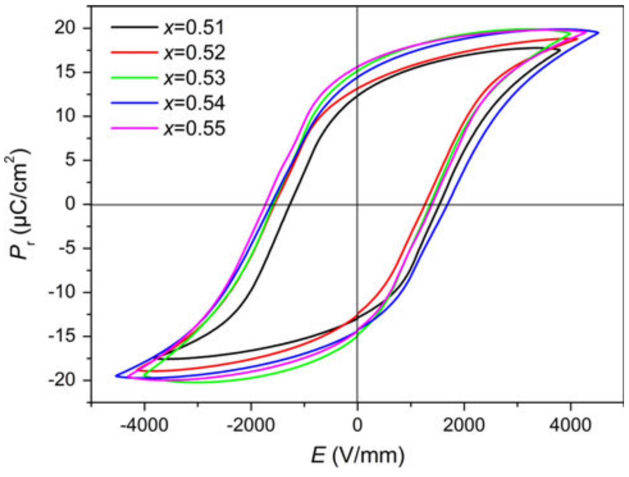

Fig. 6 P-E loops of the $Li_{0.03}(Na_xK_{1-x})_{0.97}Nb_{0.8}Ta_{0.2}O_3$ ceramics with different x values measured at 10 Hz at room temperature

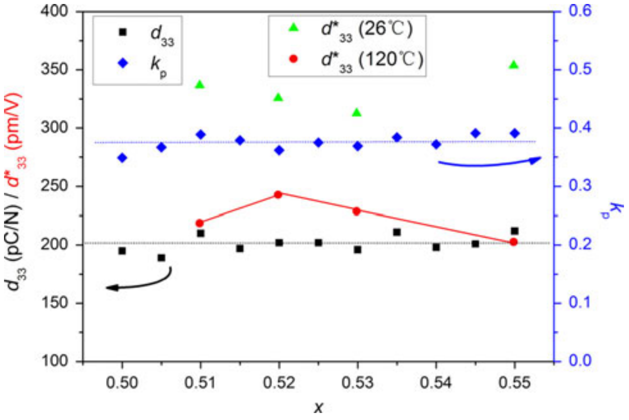

Fig. 7 Piezoelectric constant d_{33} and planar electromechanical coefficient k_p at room temperature, as well as converse piezoelectric constant d^*_{33} at room and elevated temperatures for the $Li_{0.03}(Na_xK_{1-x})_{0.97}Nb_{0.8}Ta_{0.2}O_3$ ceramics with different x values

with the results which were described previously [2, 7, 16]. The electromechanical coupling coefficient k_p is slightly lower than reported [7]. The d_{33} and k_p also change surprisingly little when x changes in the range between 0.50 and 0.55, where the most recognized MPB region exists in pure KNN ceramics [15, 20]. However, the inset of Fig. 5 demonstrates that the dielectric constant reaches a maximum when $x = 0.52$. Two phases (orthorhombic and tetragonal) exist in the sample at room temperature because its T_{T-O} is about 40 °C. Then the sample will experience two different phase transitions from the co-existence of O_1 and T_1 to the co-existence of O_2 and T_2 when the value of x crosses 0.52. These transitions lead to the peak of dielectric constant, but have little effect on piezoelectric and ferroelectric properties. The reasons are clear, but it is considered that the difference between two tetragonal (T_1 and T_2) and orthorhombic(O_1 and O_2) phases may not be so pronounced to further affect the piezoelectric and ferroelectric properties, which have been already enhanced to a high level due to the PPT effect in the present LKNNT ceramics.

Figure 8 displays the curves of electric-field-induced strains at 26 and 120 °C for the samples with different x values. The hysteresis in the strain versus E-field behavior conducted at 26 °C is a result of domain wall movement. It should be noted that the present LKNNT ceramics should be of tetragonal phase at 120 °C (much higher than T_{T-O}). The piezoelectric constant d_{33} changes with various Na/K ratios more significantly at 120 than at 26 °C. At 120 °C, the sample of $x = 0.52$ has the highest d^*_{33} value of 242 pm/V which is similar to that value of PZT-8, also shows the highest dielectric constant (see Fig. 5). This Na/K ratio should corresponds to the T_1 and T_2 phase boundary according to the KNN phase diagram [20]. This result suggests the possibility to enhance the piezoelectric properties for (Li,Ta)-doped KNN-based ceramics with tetragonal phase by adjusting the Na/K ratio, being similar to the case of un-doped KNN ceramics with orthorhombic phase structure as revealed by previous studies [14, 15].

Conclusions

Lead-free $Li_{0.03}$ $(Na_xK_{1-x})_{0.97}Nb_{0.8}Ta_{0.2}O_3$ piezoelectric ceramics with finely varied Na/K ratio in the vicinity of equal value were synthesized by the conventional method. All the compositions are composed of orthorhombic and tetragonal phases, and showed good piezoelectric and ferroelectric properties due to the polymorphism phase transition (PPT) effect. When the Na/K ratio is changed across

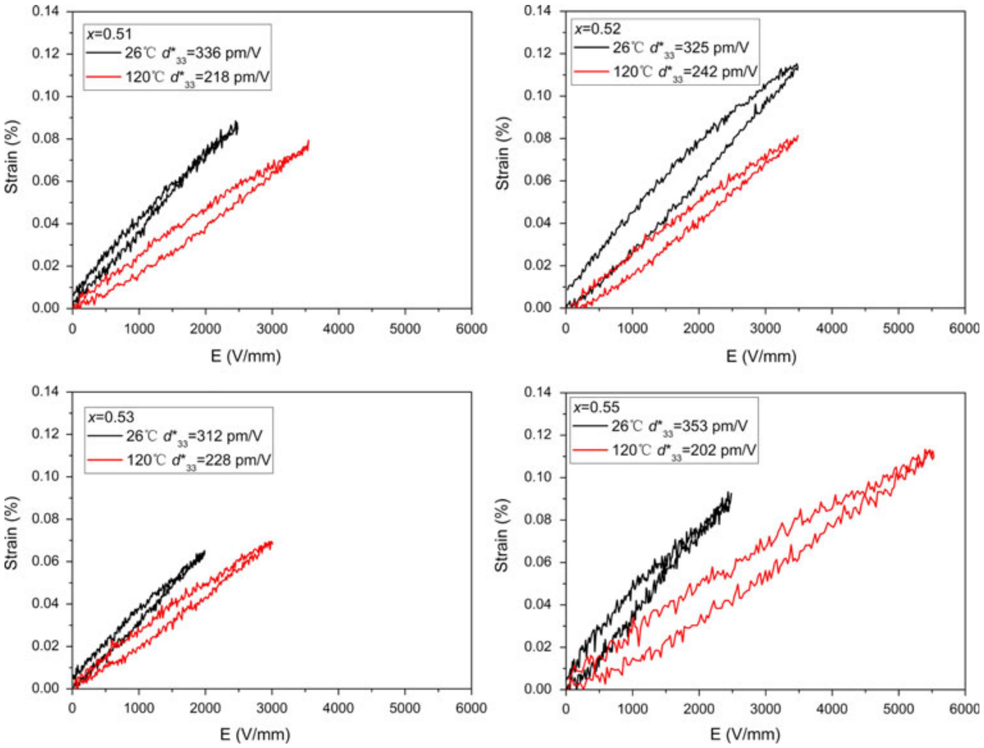

Fig. 8 The curves of strain versus electric field measured at 26 and 120 °C for the $Li_{0.03}(Na_xK_{1-x})_{0.97}Nb_{0.8}Ta_{0.2}O_3$ ceramics with different x values

$x = 0.52$, it seems that there is a phase transition both for orthorhombic and tetragonal phases. However, when orthorhombic and tetragonal phases co-exist, the change of Na/K ratio made a little difference on the piezoelectric properties of the ceramics because of the predominant PPT effect on the piezoelectric properties. Nevertheless, the transition from the co-existence of O_1 and T_1 to the co-existence of O_2 and T_2 leads to a dielectric peak during the variety of Na/K ratio. The authors confirm that a phase transition occurs in tetragonal LKNNT ceramics when the Na/K ratio crosses 52/48, which can lead to the peak of electrical properties.

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