Effects of A-site non-stoichiometry on the structural and electrical properties of $0.96K_{0.5}Na_{0.5}NbO_3$–$0.04LiSbO_3$ lead-free piezoelectric ceramics*

Zhao Jing-Bo(赵静波)[a)b)], Du Hong-Liang(杜红亮)[a)b)], Qu Shao-Bo(屈绍波)[a)c)†], Zhang Hong-Mei(张红梅)[a)], and Xu Zhuo(徐 卓)[c)]

[a)] *The College of Science, Air Force Engineering University, Xi'an* 710051, *China*

[b)] *State Key Laboratory of Electrical Insulation and Power Equipment, Xi'an Jiaotong University, Xi'an* 710049, *China*

[c)] *Electronic Materials Research Laboratory (Key Laboratory of the Ministry of Education), Xi'an Jiaotong University, Xi'an* 710049, *China*

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Effects of A-site non-stoichiometry on the structural and electrical properties of $0.96K_{0.5+x}Na_{0.5+x}NbO_3$–$0.04LiSbO_3$ lead-free piezoelectric ceramics were examined for $0 \leq x \leq 0.02$. The piezoelectric coefficients exhibited a maximum, $d_{33} = 187$ pC/N at $x = 0.0075$, coinciding with the maximum of the grain size and the apparent density at $x = 0.0075$. The apparent density and the piezoelectric coefficients decreased with increasing x at higher x which was likely due to the crystal geometrical distortion of $0.96K_{0.5+x}Na_{0.5+x}NbO_3$–$0.04LiSbO_3$. In addition, super-large grains were found and this may be due to liquid phase sintering. Excess (K^++Na^+) attracted a sum of space charges to keep the charge neutral, resulting in charge leakage during the course of ceramic polarization, influencing the piezoelectric and ferroelectric properties. These findings are of importance for guiding the design of $K_{0.5}Na_{0.5}NbO_3$-based lead-free ceramics with enhanced electrical properties.

Keywords: lead-free ceramics, piezoelectric, non-stoichiometry, $K_{0.5}Na_{0.5}NbO_3$

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1. Introduction

In the last few years, much attention has been focused on $(K_{0.5}Na_{0.5})NbO_3$ (KNN)-based lead-free ceramics[1−10] because of their high piezoelectric properties, which are comparable to those of conventional $Pb(Zr,Ti)O_3$ ceramics. The enhanced dielectric and piezoelectric properties in these systems had initially been attributed to the effects of the MPB separating the orthorhombic and tetragonal phases. It was later found that the enhanced properties were in fact caused by PPT (polymorphic phase transition).[11−14]

However, there is a drawback of KNN-based ceramics in that Na and K are volatile during the sintering process. This makes it difficult to control the sintering process and stoichiometry of KNN-based ceramics.[15] Studies have shown that the sintering behaviour, crystal structure, microstructure and electrical properties can be affected considerably by a small deviation from stoichiometry in the ceramics.[16,17] Several reports recently confirmed the importance of adjusting the K/Na ratio and the amount of excess A-site alkali to attain enhanced dielectric and piezoelectric properties.[18,19] In contrast, little attention has been paid to KNN-based ceramics with A-site non-stoichiometry. Therefore, it is necessary to understand the effects of A-site non-stoichiometry on the densification, structural and electrical properties of KNN-based ceramics.

In this paper, the dielectric, piezoelectric and ferroelectric properties of $0.96K_{0.5+x}Na_{0.5+x}NbO_3$–$0.04LiSbO_3$ ($0 \leq x \leq 0.02$) ceramics are studied. The results show that A-site non-stoichiometry has a remarkable influence on the structural and electrical properties of KNN-based ceramics. These findings are of importance for guiding the design of KNN-based lead-free ceramics.

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†Corresponding author. E-mail: qushaobo@126.com

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2. Model and method

$0.96(K_{0.5+x}Na_{0.5+x})NbO_3$–$0.04LiSbO_3$ (x = 0, 0.0025, 0.005, 0.0075, 0.01, 0.0125, 0.015, and 0.02) ceramics were prepared using the conventional solid-state sintering method. Reagent-grade oxide and carbonate powders of K_2CO_3 (99.0%), Na_2CO_3 (99.8%), Nb_2O_5 (99.99%), Li_2CO_3 (98%), and Sb_2O_3 (99%) were used as the starting materials. Before weighing them, these powders were separately dried in an oven at 120 °C for 5 h, milled for 24 h using a planetary milling with zirconia ball media and ethanol, and calcined at 860 °C for 5 h. Then, these powders were ball-milled again for 12 h, dried and pressed into discs with diameters of 12 mm and thickness of 1 mm under 300 MPa using 5 wt% polyvinyl alcohol (PVA) as the binder. After the PVA was burned off, the pellets were sintered at 1140 °C for 2 h in sealed Al_2O_3 crucibles. The obtained samples were polished. Silver paste was fired on both sides of the samples at 810 °C for 20 min as the electrodes for the sake of measurements. The microstructural evolution was observed using a scanning electron microscope (SEM) (model JSM-6360, JEOL, Tokyo, Japan). The dielectric spectrum measurements were performed using the LCR meter (TH2816, Tonghui Electronics, Chang Zhou, China) at a heat rate of 2 °C/min in the temperature range of 25 °C–500 °C and the frequency range of 1 kHz–100 kHz. The samples were painted with silver pastes and poled in silicone oil at 3 kV/mm for 15 min at 25 °C. The piezoelectric constant was measured using a piezoelectric d_{33}-meter (ZJ-3A). The polarization versus electric field (P–E) hysteresis loop was observed using the TF2000 test equipment.

3. Results and discussion

Figure 1 shows the X-ray diffraction (XRD) patterns of $0.96(K_{0.5+x}Na_{0.5+x})NbO_3$–$0.04LiSbO_3$ (x = 0, 0.0025, 0.005, 0.0075, 0.01, 0.0125, 0.015, and 0.02) ceramics at room temperature. It is clear that a pure perovskite structure is obtained in the $0.96(K_{0.5+x}Na_{0.5+x})NbO_3$–$0.04LiSbO_3$ ceramics with different K and Na contents. To further analyse the effect of K and Na addition on the phase structure of $0.95K_xNN$–0.05LS ceramics, XRD analysis was performed in the range of 2θ from 40° to 50°. Figure 1(b) shows the corresponding expanded XRD patterns of $0.96(K_{0.5+x}Na_{0.5+x})NbO_3$–$0.04LiSbO_3$ ceramics in the range of 2θ from 40° to 50°. As shown in Fig. 1(b), the positions of the diffraction peaks of the $0.96(K_{0.5+x}Na_{0.5+x})NbO_3$–$0.04LiSbO_3$ ceramics shift to lower angles with the increase of x. This may be because the diameter of $K^+$and Na^+ is much larger than that of Li^+ and the geometrical distortion of the $0.96(K_{0.5+x}Na_{0.5+x})NbO_3$–$0.04LiSbO_3$ was induced by the substitution of a part of K and Na for Li.

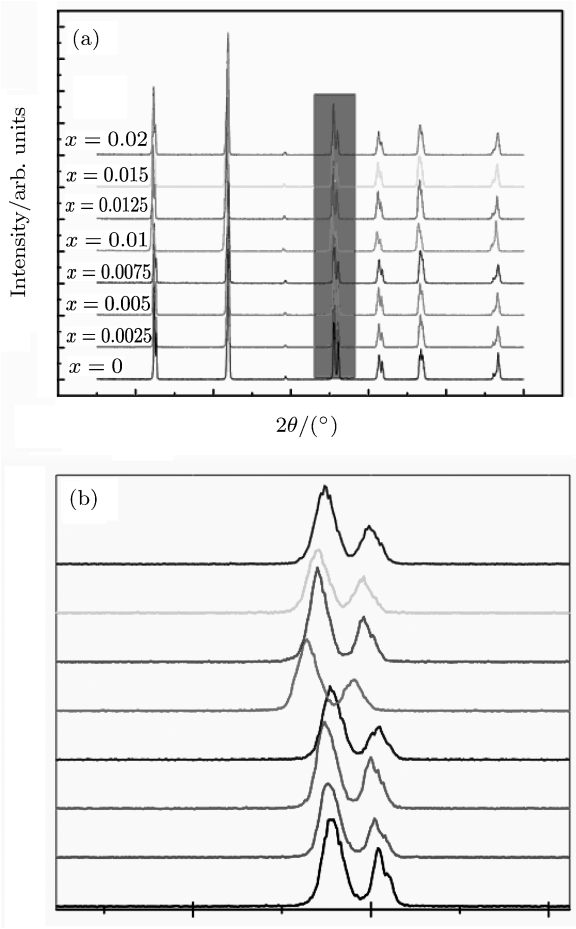
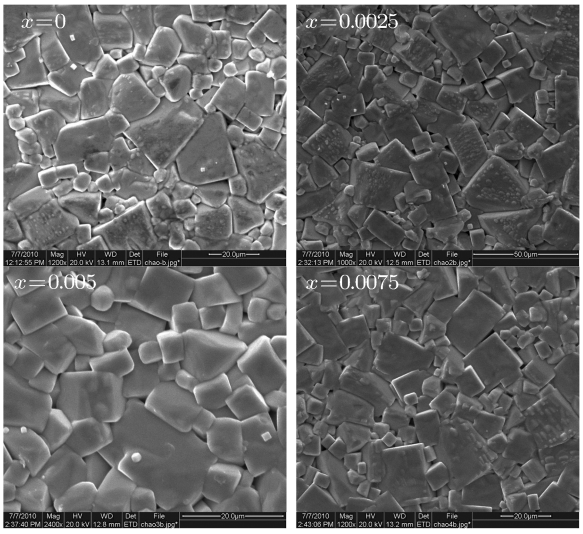


Fig. 1. The X-ray powder diffraction pattern for the $0.96(K_{0.5+x}Na_{0.5+x})NbO_3$–$0.04LiSbO_3$ (x = 0, 0.0025, 0.005, 0.0075, 0.01, 0.0125, 0.015, and 0.02) ceramics at 25 °C.

Figure 2 shows the scanning electron microscope images of $0.96\,(K_{0.5+x}Na_{0.5+x})\,NbO_3$–$0.04LiSbO_3$ (x = 0, 0.0025, 0.005, 0.0075, 0.01, 0.0125, 0.015, and 0.02) ceramics sintered at 1140 °C for 2 h. It can be seen that the $0.96(K_{0.5+x}Na_{0.5+x})NbO_3$–$0.04LiSbO_3$ ceramic is dense. When $x < 0.0125$, the grain size in $0.96(K_{0.5+x}Na_{0.5+x})NbO_3$–$0.04LiSbO_3$ ceramics increases with increasing excess of (K^++Na^+), accompanied by the appearance of abnormal grains. It is believed that the liquid phase related to the excess of (K^++Na^+) is responsible for the abnormal grain growth. When x = 0.0125, the ceramics produced a

mass of liquid phase. When $0.02 > x > 0.0125$, the grain size is more homogeneous and dense, and no liquid phase is observed. This implies that the excess of (K^++Na^+) suppresses the formation of the liquid phase. When $x = 0.02$, it can be seen that some substance is separated out, demonstrating that an excess of (K^++Na^+) cannot be dissolved in the crystal.



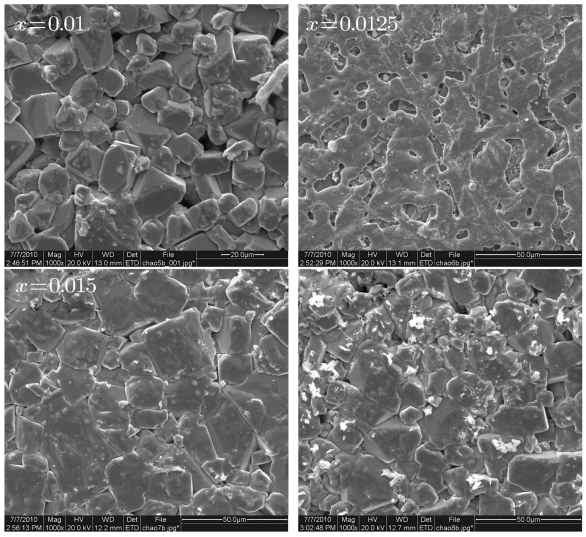


Fig. 2. The SEM images of $0.96(K_{0.5+x}Na_{0.5+x})NbO_3$–$0.04LiSbO_3$ (x = 0, 0.0025, 0.005, 0.0075, 0.01, 0.0125, 0.015, and 0.02) ceramics sintered at 1140 °C for 2 h.

Figure 3 shows the apparent density of $0.96(K_{0.5+x}Na_{0.5+x})NbO_3$–$0.04LiSbO_3$ ceramics, as can be seen that when $x < 0.0075$, the density increases with increasing content of (K^++Na^+); this may be because appropriate excessive (K^++Na^+) can cause liquid phase sintering, improving the density. When $x = 0.0075$, the apparent density reaches the maximum (4.31 g/cm^3); when $x > 0.0075$, the apparent density decreases with increasing content of (K^++Na^+); this may be due to the excessive (K^++Na^+) that cannot be dissolved in crystal and volatilization deteriorates the density.

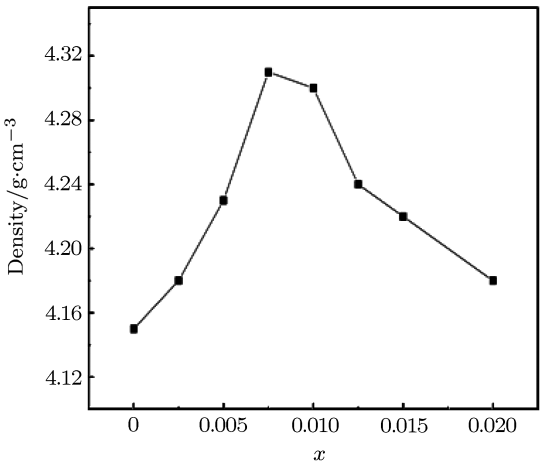


Fig. 3. The apparent density of $0.96(K_{0.5+x}Na_{0.5+x})NbO_3$–$0.04LiSbO_3$ (x = 0, 0.0025, 0.005, 0.0075, 0.01, 0.0125, 0.015, and 0.02) ceramics sintered at 1140 °C for 2 h.

Figure 4 shows the dielectric permittivity and loss of the $0.96(K_{0.5+x}Na_{0.5+x})NbO_3$–$0.04LiSbO_3$ ceramics as a function of the temperature. For all of the $0.96(K_{0.5+x}Na_{0.5+x})NbO_3$–$0.04LiSbO_3$ ceramics, two phase-transition temperatures corresponding to cubic–tetragonal (T_c) and orthorhombic–tetragonal (T_{O-T}) are observed. It is clear that the T_c of the $0.96(K_{0.5+x}Na_{0.5+x})NbO_3$–$0.04LiSbO_3$ ceramics shifts continuously to a lower temperature with an increasing content of (K^++ Na^+); however, the T_{O-T} of the $0.96(K_{0.5+x}Na_{0.5+x})NbO_3$–$0.04LiSbO_3$ ceramics shifts to a higher temperature. The loss of the $0.96(K_{0.5+x}Na_{0.5+x})NbO_3$–$0.04LiSbO_3$ ceramics as a function of the temperature can be seen in Fig. 4(b), and it is clear that dielectric loss is below 6% in the range of 20 °C–370 °C for all of the $0.96(K_{0.5+x}Na_{0.5+x})NbO_3$–$0.04LiSbO_3$ ceramics, and the dielectric loss is below 5% in the range of 20 °C–400 °C for $x = 0.0025$, which demonstrates that the $0.96(K_{0.5+x}Na_{0.5+x})NbO_3$–$0.04LiSbO_3$ ceramics has important engineering application values. The low loss of the $0.96(K_{0.5+x}Na_{0.5+x})NbO_3$–$0.04LiSbO_3$ ceramics should be mainly attributed to the high density of the $0.96(K_{0.5+x}Na_{0.5+x})NbO_3$–$0.04LiSbO_3$ ceramics, as can be seen in Fig. 2.

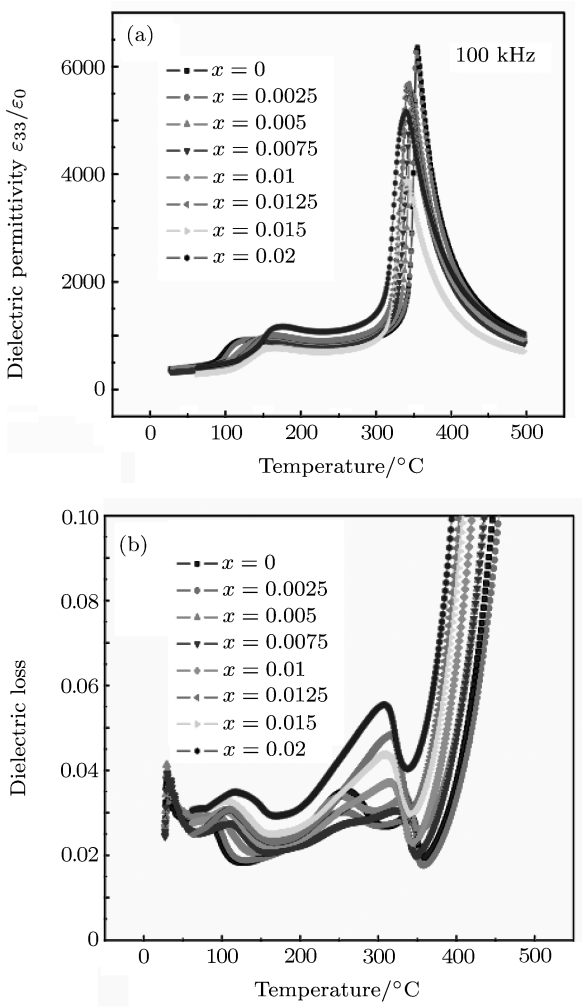


Fig. 4. The dielectric permittivity and the loss of the $0.96(K_{0.5+x}Na_{0.5+x})NbO_3$–$0.04LiSbO_3$ ceramics as functions of temperature.

Figure 5 illustrates the piezoelectric property of $0.96(K_{0.5+x}Na_{0.5+x})NbO_3$–$0.04LiSbO_3$ ceramics as a function of composition. It is evident that when $x < 0.0075$, the piezoelectric constant d_{33} increases with increasing (K^++Na^+); when $x > 0.0075$, the piezoelectric constant d_{33} decreases rapidly with increasing (K^++Na^+); when $x = 0.0075$, the piezoelectric constant d_{33} reaches the maximum (187 pC/N). This may be because the diameter of K^+ and Na^+ is much larger than that of Li^+ and the geometrical distortion of the $0.96(K_{0.5+x}Na_{0.5+x})NbO_3$–$0.04LiSbO_3$ is induced by the substitution of a part of K and Na for Li, as can be seen in Fig. 1. Otherwise, it also comes from the fact that the melting point of Na is higher than that of K and the diameter of Na^+ is much smaller than that of K^+, the geometrical distortion of the $0.96(K_{0.5+x}Na_{0.5+x})NbO_3$–$0.04LiSbO_3$ was induced by the substitution of a part of Na for K.

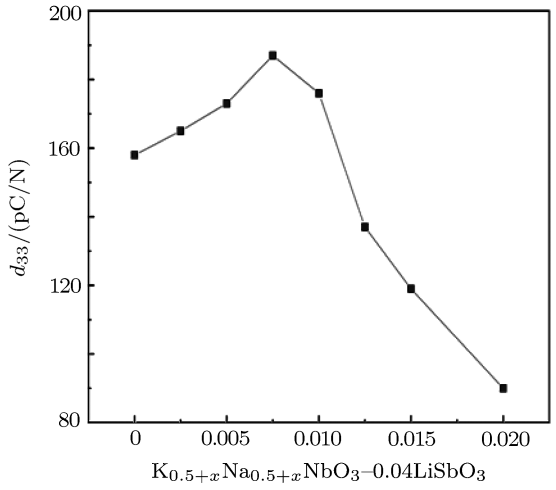


Fig. 5. The piezoelectric properties of the ceramics $0.96(K_{0.5+x}Na_{0.5+x})NbO_3$–$0.04LiSbO_3$ as a function of composition.

Figure 6 shows the typical P–E hysteresis loops (at 1 Hz) of $0.96(K_{0.5+x}Na_{0.5+x})NbO_3$–$0.04LiSbO_3$ ceramics measured at room temperature. When $x = 0$, the remnant polarization $P_r \approx 41$ μC/cm^2; when $x > 0$, the hysteresis loops is irregular. This may be attributed to space charge related to the excess (K^++Na^+). A sum of space charges was attracted to keep the charge neutral, which resulted in charge leakage during the course of ceramics polarization, influencing the piezoelectric and ferroelectric properties.

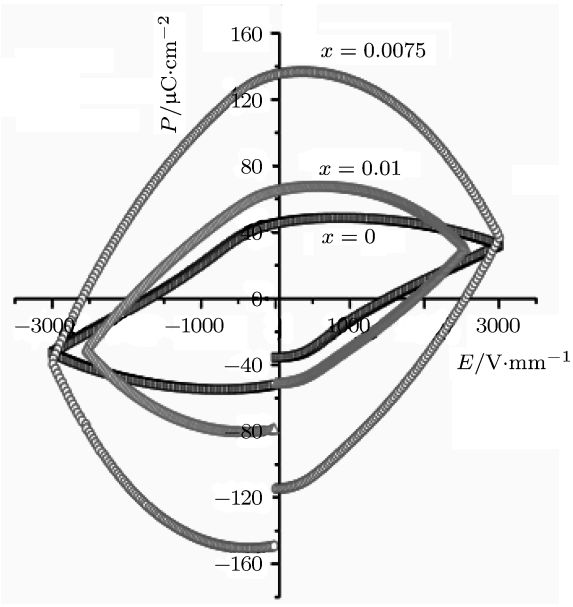


Fig. 6. The typical P–E hysteresis loops (at 1 Hz) of the $0.96(K_{0.5+x}Na_{0.5+x})NbO_3$–$0.04LiSbO_3$ ceramics measured at room temperature.

4. Conclusions

(i) A-site non-stoichiometry has an important influence on the dielectric, piezoelectric and ferroelectric properties of the 0.96KNN–0.04$LiSbO_3$ ceramics.

(ii) When $x = 0.0075$, the piezoelectric constant d_{33} reaches the maximum (187 pC/N). This should be attributed to the geometrical distortion of the 0.96($K_{0.5+x}Na_{0.5+x}$)NbO_3–0.04$LiSbO_3$ which was induced by the substitution of a part of K and Na for Li.

(iii) Excess of (K^++Na^+) attracted a sum of space charges to keep the charge neutral, which resulted in charge leakage during the course of ceramic polarization, influencing the piezoelectric and ferroelectric properties.

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