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Sintering and electrical properties of La-modified $(Na_{0.52}K_{0.45}Li_{0.03})_{1-3x}La_x(Nb_{0.88}Sb_{0.09}Ta_{0.03})O_3$ lead-free ceramics

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Abstract

$(Na_{0.52}K_{0.45}Li_{0.03})_{1-3x}La_x(Nb_{0.88}Sb_{0.09}Ta_{0.03})O_3$ (NKLL$_x$NST) lead-free ceramics were prepared by normal sintering and their dielectric and piezoelectric properties were investigated. The X-ray methods indicate that the NKLL$_x$NST ceramics with $x \leq 0.003$ present a pure perovskite phase at room temperature. The bulk density of NKLL$_x$NST ceramics increases with proper amount of La_2O_3 contents, and reaches its highest value of 4.544 g/cm^3 with the addition of 0.3 mol% La_2O_3. At $x=0.003$, remnant polarization P_r, piezoelectric constant d_{33} and planar mode electromechanical coupling factor k_p of NKLL$_x$NST ceramics reach the highest values of 37.80 μC/cm^2, 346 pC/N and 40%, respectively, exhibiting excellent "soft" piezoelectric characteristics, demonstrating a tremendous potential of the compositions studied for device applications.

Keywords: A. Sintering; B. X-ray methods; C. Piezoelectric properties; Lead-free; Ceramics

1. Introduction

Lead oxide based materials such as lead zirconate titanate (PZT) possess excellent piezoelectric properties and hence have been widely used in actuators, sensors and transducers. Nevertheless, due to the toxicity of lead, considerable attention has been directed toward lead-free alternatives. Lead-free (K, Na)NbO_3 (KNN) piezoelectric ceramics have been widely investigated during the last years owing to their relatively high Curie temperature (T_C) and moderate piezoelectric response [1–3]. The volatility of alkali elements at high temperatures [4] and the hygroscopic nature of reactant powders [5] lead to non-stoichiometry and inhomogeneous compositions, which prevent wide scale industrial use of KNN ceramics. In order to address these problems, various consolidation techniques have been considered such as hot pressing and spark plasma sintering processes [6–8]. Also, numerous compositional engineering approaches have been explored to optimize the piezoelectric properties of KNN materials like adding $BaTiO_3$ [9], $SrTiO_3$ [10], $LiNbO_3$ [11], $LiTaO_3$ [12], and $LiSbO_3$ [13] to form new solid solutions. Among these KNN-based systems, (K, Na, Li)(Nb, Ta, Sb)O_3 is more focused [14,15].

Zuo et al. reported that the $(Na_{0.52}K_{0.45}Li_{0.03})(Nb_{0.88}Sb_{0.09}Ta_{0.03})O_3$ ceramic had the peak values of the piezoelectric constant d_{33} of 400 pC/N and the planar electromechanical coupling coefficient k_p of 54% [16]. On the other hand, recent research showed that La doped $(Na_{0.52}K_{0.44}Li_{0.04})Nb_{0.8}Ta_{0.2}O_3$ ceramics exhibited high density ($\rho \sim 95\%$) and outstanding piezoelectric performances ($d_{33} \geq 200$ pC/N, $k_p \geq 40\%$) [17]. In order to promote piezoelectric properties to compete with lead-based piezoelectric materials, the system $(Na_{0.52}K_{0.45}Li_{0.03})_{1-3x}La_x(Nb_{0.88}Sb_{0.09}Ta_{0.03})O_3$ (NKLL$_x$NST) ($x=0.000$, 0.003, 0.006 and 0.009) was fabricated in this work. The crystal phases and electrical properties of the NKLL$_x$NST ceramics with different La^{3+} contents were investigated. The effect of the sintering temperature on the densification behavior of this material was also reported.

2. Experimental

The reagent grade powders of K_2CO_3, Na_2CO_3, Li_2CO_3, Nb_2O_5, Ta_2O_5, Sb_2O_3 and La_2O_3 were utilized as the starting materials. The preparation processes adopted in this study were

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the same as those used in previous studies [18]. Calcination and sintering were carried out at 860 °C for 4.5 h and 1070–1110 °C for 3 h, respectively. Silver paste was painted on both surfaces of the sintered disks as the electrodes for piezoelectric measurements. The samples were poled in silicon oil by applying a dc field of 4 kV/mm for 30 min at room temperature. The phase structure of the specimens was examined by X-ray diffraction (XRD). The bulk density was measured by the Archimede′s technique. The piezoelectric constant d_{33} was recorded using a Berlincourt-type quasi-static meter. The planar electromechanical coupling factor k_p was determined by the resonance-antiresonance method on the basis of IEEE standards using the Agilent 4294A impedance analyzer.

3. Results and discussion

Fig. 1 (a) (2θ=20–60°) and (b) (2θ=45.1–46.4°) show the X-ray diffraction patterns of the NKLL$_x$NST samples sintered at each of their optimum sintering temperatures. It can be seen that the NKLL$_x$NST ceramics with $x \leq 0.003$ present a pure perovskite phase at room temperature and no secondary phase can be detected. A trace amount of $SbTaO_4$ and $K_{0.5}La_{0.5}Nb_2O_6$ second phases indicated by the asterisk and hash can be detected with further increase in x value. The radius of the doped La^{3+} (0.106 nm) is close to those of the host Na^+ (0.102 nm), K^+ (0.138 nm) and Li (0.076 nm), therefore, La^{3+} occupies the A-site of the ABO_3 perovskite structure. As a result, geometrical distortion of the ceramics is induced by the substitution of La^{3+} for NKLNST lattice. When $x \leq 0.003$, more than two peaks exist between 45.1° and 46.4°, revealing the coexistence of both orthorhombic and tetragonal phases [19]. When $x \geq 0.006$, the split peaks around 45.1–46.4° are gradually combined into one single peak for pseudo-cubic structure. Previous research showed that the NKLL$_{0.000}$NST ceramic exhibited coexisted orthorhombic and tetragonal phases at room temperature [16], which is consistent with our results.

Fig. 2 shows the influence of sintering temperature on piezoelectric constant d_{33} and bulk density ρ of the NKLL$_x$NST ceramics. Both d_{33} and ρ increase with the increase of sintering temperature, and then decrease due to the evaporation of potassium oxide at high temperature. The maximum d_{33} of 346 pC/N for NKLL$_{0.003}$NST sample can be reached when sintered at 1090 °C. Zuo et al. reported that the piezoelectric constant d_{33} of the NKLL$_{0.000}$NST ceramic was 400 pC/N [16]. However, in our study, d_{33} of NKLL$_{0.000}$NST reaches its maximum value when sintered at 1090 °C, being 331 pC/N. The disparity in results could be ascribed to different powder precursors and different processing procedure [20]. The tendency for the loss of alkali metals during sintering can also result in some variability in properties between different research groups.

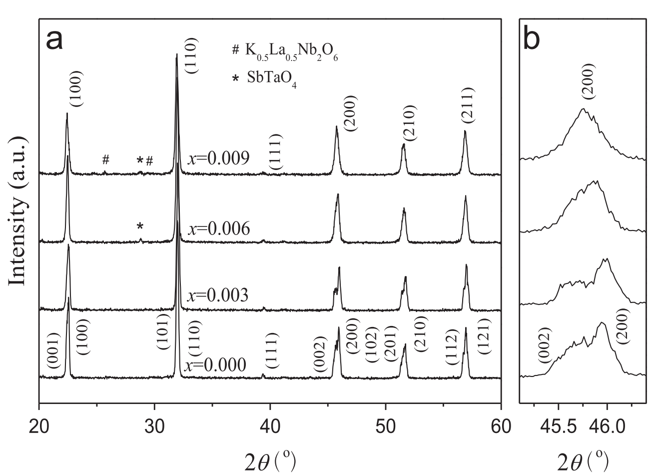

Fig. 1. XRD patterns for (a) 2θ=20–60° and (b) 2θ=45.1–46.4° of the NKLL$_x$NST ceramics.

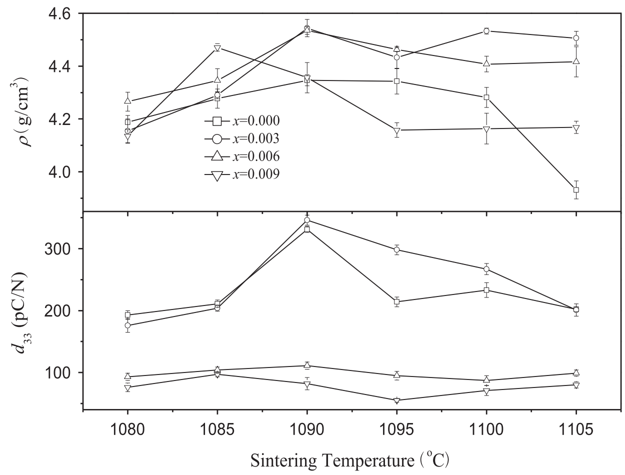

Fig. 2. Effect of sintering temperature on piezoelectric constant d_{33} and bulk density ρ of NKLL$_x$NST ceramics.

Fig. 3 indicates the SEM patterns of the sintered surfaces of NKLL$_x$NS piezoelectric ceramics sintered at different temperatures. It is seen that the sintering temperature strongly affects the microstructure of NKLL$_x$NST ceramics. For the ceramics with x=0.000 and 0.003, low sintering temperature of 1070 °C leads to inhomogeneous microstructure, while the proper sintering temperature of 1090 °C induces more uniform grains and high density. However, when the sintering temperature increases further to 1110 °C, the microstructure becomes fine. The variations of the d_{33} with sintering temperature are closely related with the microstructure. At 1090 °C, the enhancement of the compact degree and the relatively uniform microstructure help to improve the piezoelectric properties of NKLL$_x$NST samples. In addition, it is seen from Fig. 3 (c), (f) and (i) that the doping of 0.06 mol% La suppresses the grain growth of the ceramics.

Fig. 4 shows the ferroelectric P–E hysteresis loops of NKLL$_x$NS ceramics measured at 10 Hz, while the inset of Fig. 4 gives the remanent polarization P_r and the coercive field E_C as functions of x for the NKLL$_x$NST ceramics. The ceramics with x=0.000 and 0.003 exhibit well developed P–E hysteresis loops. The P–E loops become slanted and constricted as x increases to 0.006. The P_r first increases due to the increase of the bulk density which enhances the polarization in process, and then decreases linearly with further increasing x. Increasing amount of La^{3+} leads to more defects in the NKLNST lattice, which hinder the switching of the domains and cause poor P_r. The E_C decreases gradually with increasing La^{3+} content. The decrease of E_C values may be

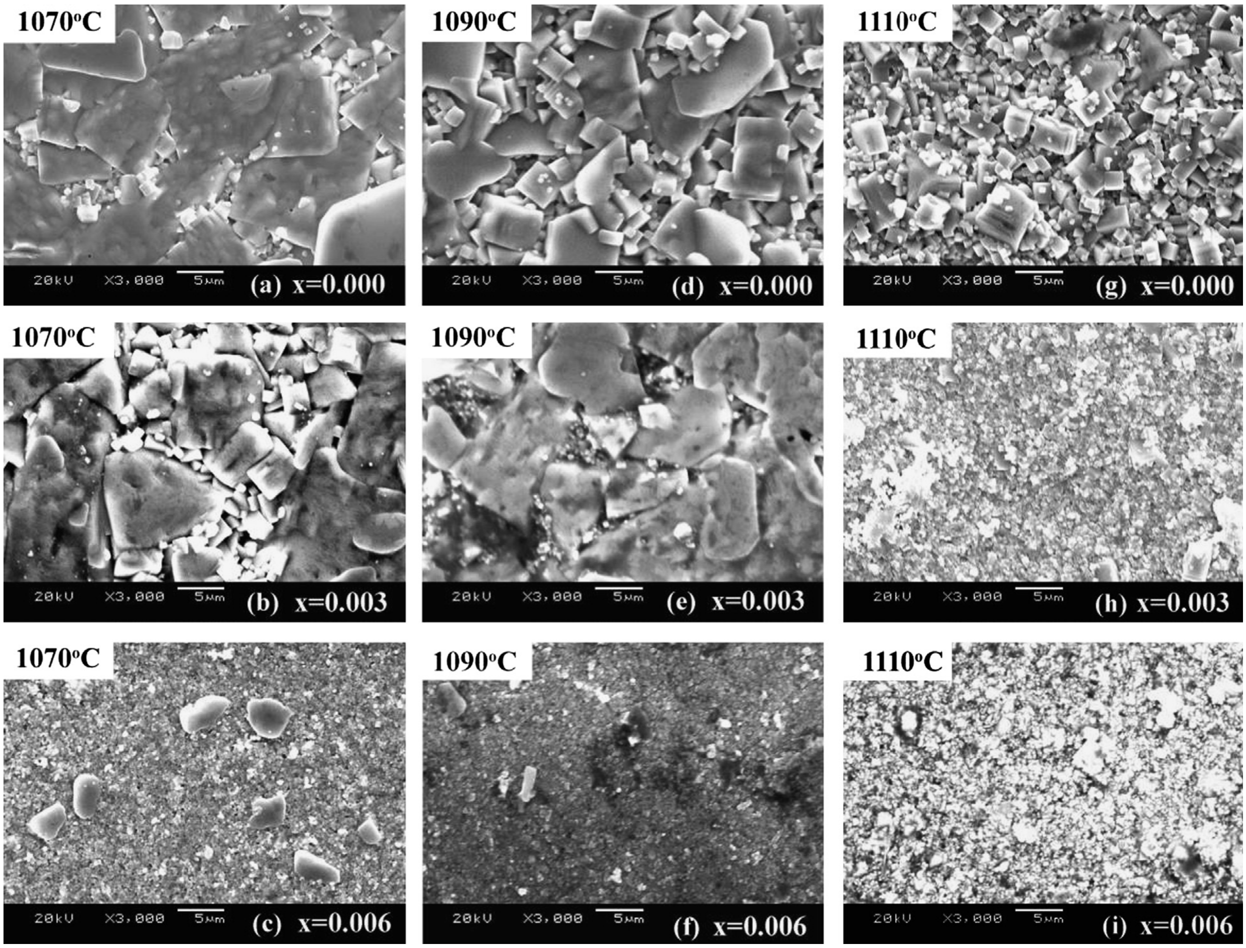

Fig. 3. SEM morphology of NKLL$_x$NST ceramics with $x=0.000$, 0.003 and 0.006 sintered at different temperatures: (a)–(c) 1070 °C; (d)–(f) 1090 °C; and (g)–(i) 1110 °C.

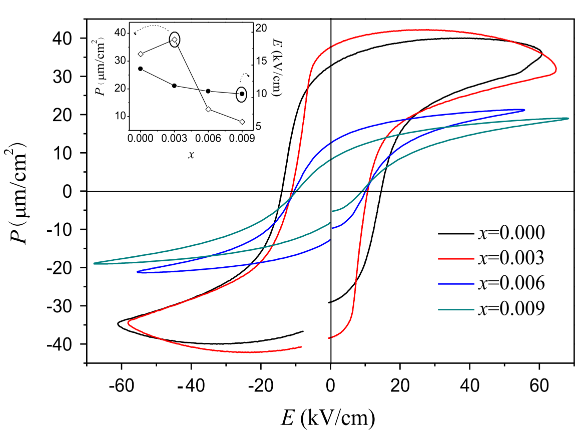

Fig. 4. Ferroelectric P–E hysteresis loops of NKLL$_x$NST ceramics. (Inset: the remanent polarization P_r and coercive field E_C as functions of x.)

due to the "soft" effect of La^{3+}, which reduces oxygen vacancies to maintain the charge neutrality and facilitates the poling process of the ceramics. The $x=0.003$ ceramic presents P_r of 37.80 μC/cm^2 and E_C of 11.30 kV/cm, showing excellent ferroelectric properties.

Fig. 5 shows the variations of k_p, k_{33}, ε_r and tanδ with x for NKLL$_x$NST ceramics measured at 100 kHz. The optimum sintering temperature for each composition and the corresponding bulk density ρ are also given in Fig. 5. The k_p values of NKLL$_x$NST ceramics increase with increasing La_2O_3 content, reach a maximum value of 40% at $x=0.003$, and then decrease with further increasing La_2O_3. Similar to the change of k_p, k_{33} also reaches a maximum value of 49% at $x=0.003$. The variation of tanδ with the amount of La_2O_3 is opposite to those of k_p and k_{33}. When the content of La_2O_3 is 0.3 mol%, tanδ reaches its minimum of 4.1%. Dielectric constant ε_r increases up to 1814 and then decreases. This variation can be considered due to the results appeared in the variation of ρ. The ε_r increases again at $x=0.009$, which could be associated with the chemical inhomogeneities [21].

It is seen that addition of small amounts of La_2O_3 yields to larger electrical properties. The promotion may be attributed to three reasons. Firstly, the phase structure of NKLL$_{0.003}$NST ceramics at room temperature is the coexistence of orthorhombic and tetragonal phases. There are a large number of thermodynamically stable polarizations which allow a high degree of domain alignment, contributing to enhanced piezoelectric properties [22]. Secondly, the La_2O_3 modification in NKLNST softens the materials. So the NKLL$_{0.003}$NST ceramic is thought to have more extrinsic contribution in the piezoelectric coefficient when compared with pure NKLL$_{0.000}$NST. Finally, the optimum La_2O_3 addition and the optimum sintering temperature can improve the density of the ceramics,

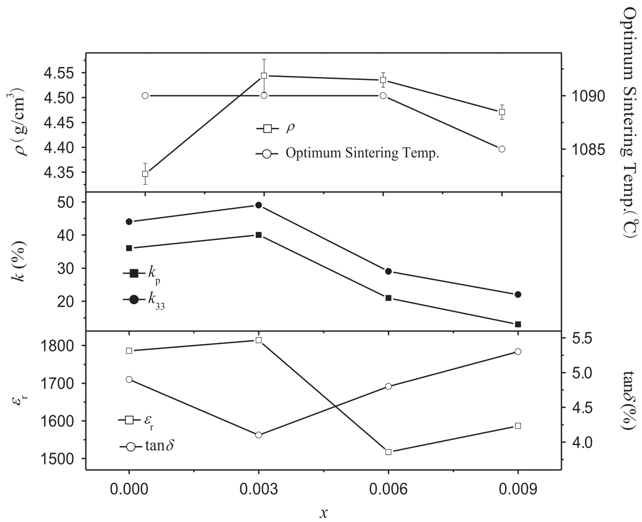

Fig. 5. Electrical properties of NKLL$_x$NST ceramics.

which has positive effects on the electrical properties. However, excess La_2O_3 addition results in decrease of the bulk density, leading to poorer piezoelectric properties.

4. Conclusions

$(Na_{0.52}K_{0.45}Li_{0.03})_{1-3x}La_x(Nb_{0.88}Sb_{0.09}Ta_{0.03})O_3$ (NKLL$_x$NST) ($x=0.000$, 0.003, 0.006 and 0.009) lead-free piezoelectric ceramics with good piezoelectric properties have been developed by the conventional solid state method. XRD data shows that the orthorhombic and tetragonal phases coexist in the composition range of $x \leq 0.003$ at room temperature. By adding La_2O_3, the densification of the NKLL$_x$NST ceramics is improved. The ferroelectric and piezoelectric properties of the NKLL$_x$NST ceramics have been enhanced with the addition of appropriate La_2O_3. The NKLL$_x$NST ceramics at $x=0.003$ have the highest piezoelectric constant ($d_{33}=346$ pC/N), the highest remnant polarization ($P_r=37.80$ μC/cm^2), the highest planar coupling factor ($k_p=40\%$), and the lowest dielectric loss ($\tan\delta=4.1\%$) at room temperature. The NKLL$_x$NST ceramics developed in this study are expected to be suitable substitutes for PZT ceramics.

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