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Piezoelectric properties of lead-free (1-x)$(Na_{0.5}K_{0.5})NbO_3$-x$Li(Sb_{0.17}Ta_{0.83})O_3$ ceramics

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The (1-x)$(Na_{0.44}K_{0.52})Nb_{0.84}O_3$-x$Li_{0.04}(Sb_{0.06}Ta_{0.1})O_3$ ($0.01 \le x \le 0.05$) lead free ceramics were prepared using a conventional mixed oxide method. Adding various contents of $Li(Sb,Ta)O_3$ to $(Na,K)NbO_3$ makes it easy to conduct the sintering processes of pure $(Na,K)NbO_3$ which is difficult to sinter. It was found that the piezoelectric properties of (1-x)NKN-xLST(x = 0.02) ceramic sintered at 1080 °C for 2 h has a piezoelectric constant and a planar electromechanical coupling coefficient of 159 pC/N and 38% respectively. It is found that the addition of LST can improve poling procedures of the ceramics because of substitution. These solid solution ceramics look attractive candidates for lead-free piezoelectric applications.

Key words: Lead-free, NKN-LST, Piezoelectric constant, Dielectric constant.

Introduction

The morphotropic phase boundary (MPB) in lead-based materials such as $Pb(Zr_{1-x}Ti_x)O_3$(PZT), (1-x)$Pb(Mg_{1/3}Nb_{2/3})O_3$-x$PbTiO_3$(PMN-PT) and (1-x)$Pb(Zn_{1/3}Nb_{2/3})O_3$-x$PbTiO_3$ (PZN-PT), plays a special role [1-3]. It is believed that a sample with its composition around the MPB shows excellent piezoelectric and dielectric properties. However, lead-based materials are dominated by containing more than 60 wt% lead [4]. The lead evaporation during the sintering process of PZT and discarded PZT components pollute the environment and are harmful to health [5-6]. Therefore, it is an urgent task that environment-friendly piezoelectric materials are developed to replace lead-based materials [7]. Among them, $(Na,K)NbO_3$ (hereafter NKN) exhibits an MPB at around 50% Na and 50% K separating two orthorhombic phases and as for PZT, an increase in piezoelectric and dielectric properties for compositions close to the MPB [9-13]. Hot-pressed NKN ceramics have been reported to possess a high Curie temperature (T_c~420 °C), a large piezoelectric longitudinal response (d_{33}~160ρC/N) and a high planar coupling coefficient (k_p~45%) [14-15]. However, for NKN ceramics there is the need for special processing of the starting materials, a sensitivity of properties to nonstoichiometry and a complex densification process [16-17]. Sintering under ordinary conditions shows lower properties (d_{33}~80ρC/N) due to a poor density. Thus, adding other perovskite compounds to form solid solutions with NKN has been performed to obtain lead-free materials comparable with lead-based materials [18]. The goal of this paper is to obtain a system of NKN-based piezoelectric materials with enhanced piezoelectric, dielectric properties by adding different amounts of $Li(Sb,Ta)O_3$ (hereafter LST).

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Experimental

The chemical molecular formulae used in this experiment for the perovskite ceramics with (Na, K, Li) complex A-sites and (Nb, Sb, Ta) complex B-sites is (1-x)NKN-xLST ceramics (0.01×0.05). For specimens prepared by the conventional mixed oxide method from Na_2CO_3, K_2CO_3, Nb_2O_5, Li_2CO_3, Sb_2O_5, Ta_2O_5 as the staring materials, these powders were separately dried in an oven at 100 °C for 4 h. They were ball-milled for 24 h using ZrO_2 balls in alcohol. After drying at 110 °C for 24 h, the powders were calcined at 850 °C for 5 h. The calcined powders were pressed into disk samples of φ 12 mm. The samples were sintered at 1080 °C for 2 h. After the samples were polished to 1.0 mm thickness, silver paste was screen-printed on the surfaces as electrodes and then fired at 400 °C for 10 minutes. We used X-ray diffraction (XRD) to analyze the crystallinity and microstructures. The dielectric properties were measured using an LCR meter (PM6306, Pluke). Hysteresis loops of the samples were measured by a Sawyer-Tower circuit. The samples were poled under a DC field of 4 kV/mm for 20 minutes. The piezoelectric strain constant d_{33} was measured by a d_{33} meter (Channel Product DT-3300). The electromechanical coupling factor k_p was calculated by measuring the anti-resonance and resonance frequencies. The relative density of the sintered samples was measured by the Archimedes method.

Results and Discussion

Fig. 1 shows the X-ray diffraction patterns of (1-x)

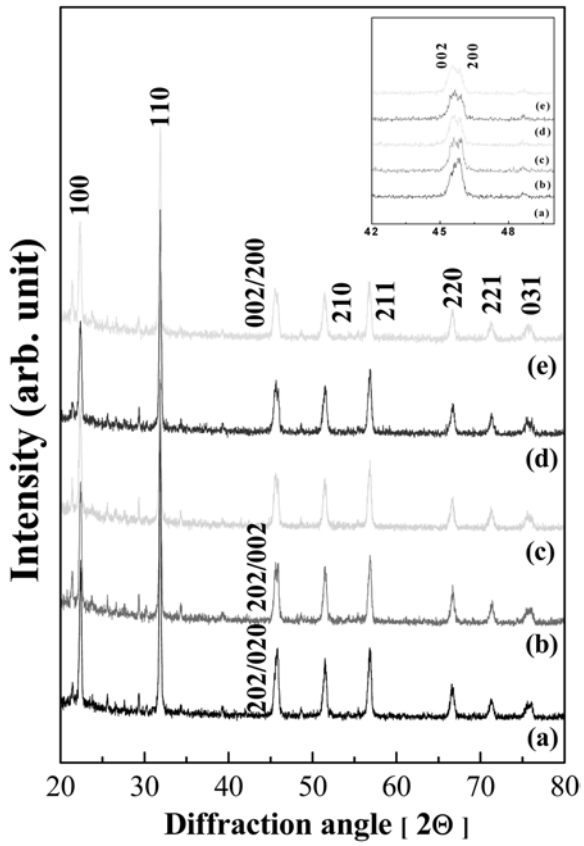

Fig. 1. XRD patterns of the (1-x)NKN-xLST (x mol%) ceramics (a) 0.01 mol%, (b) 0.02 mol% (c) 0.03 mol% (d) 0.04 mol% (e) 0.05 mol%.

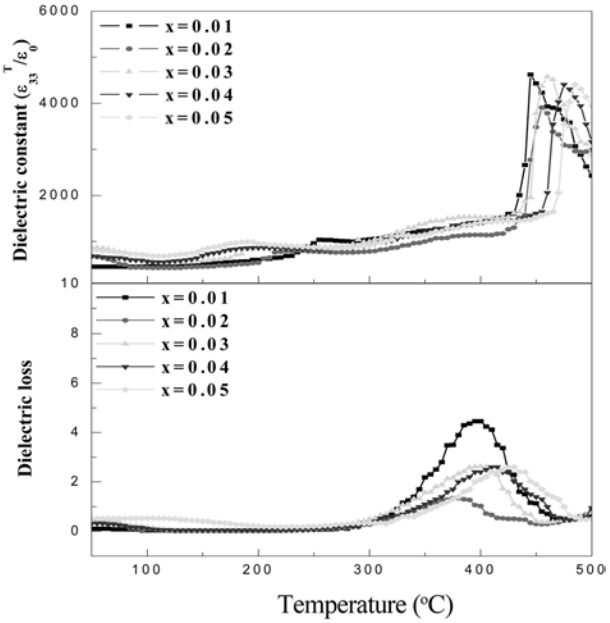

Fig. 2. The dielectric constant and loss of the (1-x)NKN-xLST (x mol%) ceramics at frequency of 1 kHz.

$(Na_{0.44}K_{0.52})Nb_{0.84}O_3$-x$Li_{0.04}(Sb_{0.06}Ta_{0.1})O_3$ $(0.01 \le x \le 0.05)$ ceramics sintered at 1080 °C for 2 h. The pure NKN ceramics are usually sintered at 1150 °C. For (1-x)NKN-xLST ceramics not only is suppressed the sintering temperature lowered but also volatilization the of Na^+, K^+. As seen from these patterns, all samples show a pure perovskite phase, and no secondary phase could be identified. This indicates that LST has diffused into the NKN lattice and formed solid solutions. In this case, Li^+ ion diffuses to the Na^+, K^+ sites of NKN, while Sb^{5+}, Ta^{5+} occupies the Nb^{5+} sites of NKN. The inset of Fig. 1 exhibits the variation of peak transitions of (1-x)NKN-xLST ceramics near $2\theta = 45°$. The orthorhombic phase is characterized by (202)/(020) peak splitting at about 45° Also, the tetragonal phase is characterized by (002)/(200) peak splitting at about 45° Therefore, at room temperature, it can be concluded that (1-x)NKN-xLST ceramics have orthorhombic symmetry at $x < 0.02$, has a tetragonal structure at $x > 0.03$ and has a coexistence of orthorhombic and tetragonal phases at $x = 0.02, 0.03$. As a result of these phenomena, we expect before further experiments, that there is a composition of the so-called MPB in (1-x)NKN-xLST ceramics at $x = 0.02, 0.03$.

The dielectric properties versus temperature measurements of unpoled (1-x)NKN-xLST $(0.1 \le x \le 0.5)$ ceramics at 1 kHz are shown in Fig. 2. For the pure NKN ceramic, two phase transition temperatures are reported at approximately 450 °C and 250 °C, conforming to the phase transition of tetragonal-cubic (T_c) and orthorhombic-tetragonal (T_{O-T}) respectively. The samples with $x = 0.01$, show similar behavior to the pure NKN ceramics with respect to NKN, the T_{O-T} is shifted to a lower temperature as the LST content x is increased. It can be inferred that the lithium and antimony additions stabilize the tetragonal structure. However, the T_c shifts to a higher temperature with an increase in the LST content from 0.01 to 0.05. In the case of the lithium and tantalum dominantly substituted (1-x)NKN-xLST ceramics, T_c is increased by increased substitution.

Fig. 3 shows the polarization versus electric field (P-E) hysteresis loops for the (1-x)NKN-xLST sintered 1080 °C for 2 h. As shown in the figures, the polarization loops grow wider with an increase in the LST content. The remnant polarization of the 0.98NKN-0.02LST is about 11.3 μC/cm^2, which increased with the content of LST, exhibiting a maximum value of 14.2 μC/cm^2 When the LST content was 0.05. The increase in P_r could be related to an increase in the bulk density. Therefore, it is considered that because the radius of Li^+(0.68 Å), Ta^{5+}(0.70 Å), Sb^{5+} (0.62 Å) ions are similar to that of Nb^{5+}(0.70 Å), Li^+, Ta^{5+} and Sb^{5+}ion these entered the Nb^{5+} sites of the (1-x)NKN-xLST ceramics, and might behave as a hardener.

The compositional dependence of poled piezoelectric properties and relative density were measured for the NKN-LST system, as shown in Fig. 4. Similar to PZT, it is well known that the electrical properties rapidly increase at the MPB. For (1-x)NKN-xLST ceramics, the electromechanical coupling factor *k*p varied in the range of 24%-38%

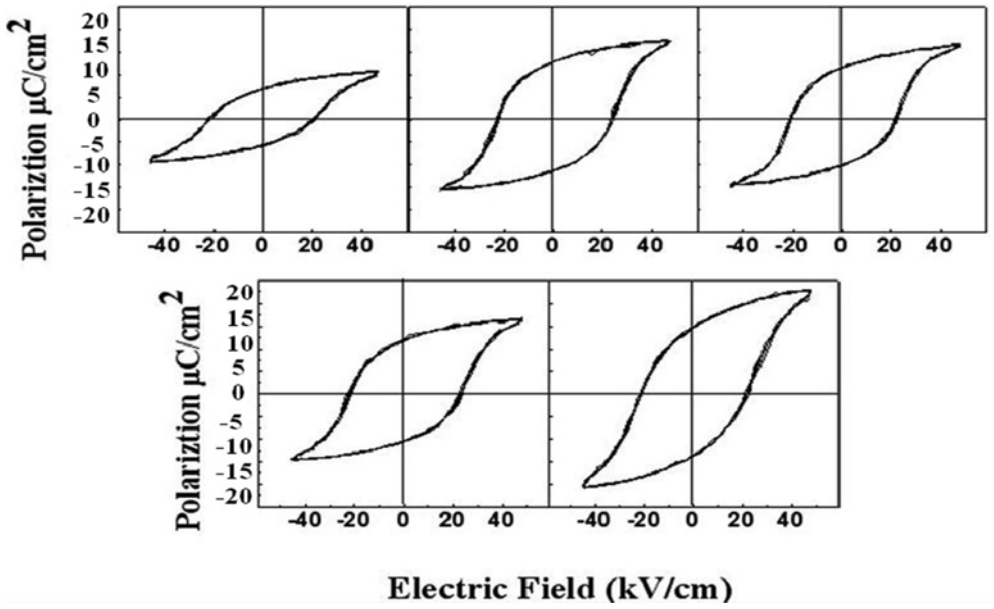

Fig. 3. Hysteresis loops of the (1-x)NKN-xLST (x mol%) ceramics (a) 0.01 mol%, (b) 0.02 mol% (c) 0.03 mol% (d) 0.04 mol% (e) 0.05 mol%.

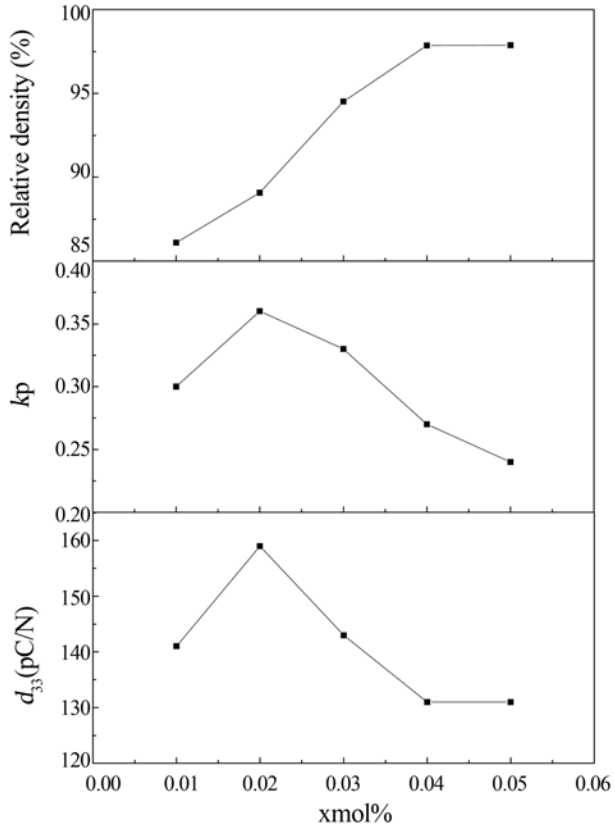

Fig. 4 Piezoelectric properties and relative density of the (1-x)NKN-xLST (x mol%) ceramics.

and the piezoelectric constant d_{33} was in the range of 131ρC/N-159ρC/N, which had enhanced values as compared with the pure NKN ceramic. Poled samples show the highest values of the electromechanical coupling coefficient kp = 38% and piezoelectric coefficients d_{33} = 159 ρC/N for 0.98NKN-0.02LST ceramics. The improvement of piezoelectric properties could be explained by an increase in the bulk density. With an increase in the LST content the piezoelectric properties increased. However, for LST contents in excess of 0.02, the piezoelectric properties decreased due to a transformation of the microstructure. It is significant that the MPB plays the most important factor in improving piezoelectric properties of NKN-LST ceramics. Also, Fig. 4 shows the effect of the substitutional content. All samples reached a density of more than 85% of the theoretical density at a sintering temperature of 1080 °C. The relative density increased with the LST content. However, with an increase in the LST content above 0.02 mol%, the piezoelectric properties of (1-x)NKN-xLST ceramics were decreased due to the excessive substitution by LST.

Conclusion

(1-x)($Na_{0.44}K_{0.52}$)$Nb_{0.84}O_3$-x$Li_{0.04}$($Sb_{0.06}Ta_{0.1}$)O_3 ($0.01 \le x \le 0.05$) lead free ceramics were prepared using a conventional mixed oxide method. From the X-ray diffraction analysis, we found that (1-x)NKN-xLST ceramics were crystallized and showed a MPB (orthorhombic and tetragonal structures) at x = 0.02, 0.03. The P-E hysteresis loops for the 0.98NKN-0.02LST ceramics sintered at 1080 °C shows a high remnant polarization of 1 μC/cm^2. Also, we found that 0.98NKN-0.02LST ceramics sintered at 1080 have a relatively high piezoelectric coefficient (d_{33}) of 159 ρC/N and electromechanical coupling coefficient kp = 38%. These excellent piezoelectric properties mean that this lead-free 0.98NKN-0.02LST piezoelectric ceramic can be a promising lead-free piezoelectric material.

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