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Effect of monovalent ions on the piezoelectric properties of $(Na_{0.5}K_{0.5})NbO_3$–$(M)TaO_3$ ceramics

Young Seok Lee, Young Ho Kim, Dong Heon Kang *

Department of Electronic Materials Engineering, The University of Suwon, TIC, Suwon 445-743, Republic of Korea

Abstract

Sodium potassium niobate (NKN) ceramics modified by lithium or silver tantalates were prepared in order to compare the effect of monovalent additives and then their crystal structure, sinterability, and dielectric and piezoelectric properties were investigated with varying the amount of additives. It was clearly seen for the silver tantalate added NKN ceramics that dielectric constant, k_p and d_{33} were dependent on the density and microstructure. While NKN ceramics added with lithium tantalate exhibited strong dependence on the existence of morphotrophic phase boundary and second phase formation rather than the density. These results were explained in terms of the phase formed and microstructure and sinterability.

Keywords: A. Grain growth; C. Piezoelectric properties; Sodium potassium niobate; Dopant

1. Introduction

$Pb(Zr,Ti)O_3$ (PZT) is a well-known piezoelectric ceramics widely used in sensor and actuator applications [1]. However, the toxicity of lead and its high vapor pressure during the manufacturing process have led to demand for alternative lead-free piezoelectric materials. The search for alternative piezoelectric materials is now focused on alkali niobate-modified bismuth titanates and compositions in which a morphotropic phase boundary (MPB) occurs [2]. Among them, $(Na_{0.5}K_{0.5})NbO_3$ (NKN) has been considered as a good candidate for lead-free piezoelectric ceramics because of its strong piezoelectricity, ferroelectricity and high Curie temperature [3–5]. However, NKN ceramics heat-treated in the ordinary sintering process show relatively inferior electrical properties due to difficulty in the processing for denser ceramics [4]. Thus various techniques, such as hot pressing [4], cold-isostatic pressing [6] and spark plasma sintering [7], have been utilized to improve the electrical properties of NKN ceramics. At the same time, for industry applications, many studies have been conducted in order to prepare NKN based ceramics by the conventional solid state sintering method based on different compositions rather than nonconventional treatment. Some related results have shown that increased piezoelectric properties with the addition of Li, Sb, Ag, Ba and Ta are ascribed mainly due to the presence of MPB between orthorhombic and tetragonal ferroelectric phases [8–11]. However, there have been discrepancies in the experimental results when different compounds or ions with the same valence or structure were added. Subsequently, the effects of incorporation of various dopants on the electrical properties of NKN ceramic should be addressed in detail. There have been few studies on the piezoelectric properties of NKN regarding the incorporation of different monovalent ions. In this study, NKN ceramics were modified by different monovalent ions, silver(1+) and lithium(1+) containing tantalate and their piezoelectric properties were investigated in terms of crystal structure, microstructure and sinterability.

2. Experimental

$(1-x)(K_{0.5}Na_{0.5})NbO_3$–$(x)AgTaO_3$ and $(1-x)(K_{0.5}Na_{0.5})NbO_3$–$(x)LiTaO_3$ ceramics (abbreviated as NKANT(x), NKLNT(x), respectively, with x ranging from 0 to 0.1) were prepared by a conventional mixed-oxide technique using commercially available metal oxides or carbonate powders with high purity above 99.9%; Na_2CO_3, K_2CO_3, Ag_2O, Li_2CO_3, Nb_2O_5 and Ta_2O_5. The powders were weighed and mixed well in

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* Corresponding author. Tel.: +82 31 220 2498; fax: +82 31 220 2665.
E-mail address: dhkang@suwon.ac.kr (D.H. Kang).

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ethanol with YSZ balls by ball-milling for 12 h. After drying them, the calcination was conducted at 850 °C for 4 h. The calcined mixture was ball-milled in ethanol again for 10 h. The dried powders were mixed thoroughly with a PVA binder solution. After sieving treatment, they were uniaxially pressed into disk specimen with a diameter of 10 mm and a thickness of 2 mm. The pressed pellets were then sintered at temperature ranges from 1050 °C to 1120 °C for 2 h in air in order to obtain optimum sinterability for each composition. The optimum sintering temperatures were found to be 1120 °C for pure NKN ceramics, 1100 °C for NKANT(x) series and 0.03 mol $LiTaO_3$ (LiT) added NKN ceramics, 1080 °C for 0.075 and 0.1 mol LiT added NKN ceramics, respectively. In this study, all the results were obtained from the measurements using the specimens sintered under the optimal conditions. The crystalline structures of the calcined and sintered specimens were examined using an X-ray diffractometer (290621A, Rigaku). The apparent density of the ceramics was measured by the Archimedes method. The surface morphology was examined by a scanning electron microscopy (JSM 5610, Jeol). After poling at 3.5 kV for 30 min, dielectric properties of the specimens were examined using an impedance analyzer (4194A, Hewlett Packard) and a precision pro (Radiant Tech.). The piezo-d_{33} meter (APC International) was applied to measure the piezoelectric properties of the specimens.

3. Results and discussion

Fig. 1 shows XRD patterns of NKANT(x) and NKLNT(x) specimens sintered at optimum temperatures. The NKANT(x) series developed the perovskite NKN structures without secondary phases even though the amount of $AgTaO_3$ (AgT) increased up to $x = 0.1$. These results indicate that the AgT have completely diffused into the NKN lattices. In case of the NKLNT(x) series, the typical orthorhombic symmetry was observed for the specimens with $x = 0$ and 0.03 at room temperature, and the peak splitting was detected for the specimen with $x = 0.075$. Further increasing the $LiTaO_3$ (LiT) up to $x = 0.1$, secondary phase was detected near $2\theta = 29°$ of XRD patterns. It is considered that the secondary phase of $K_3Li_2Nb_5O_{15}$ with tetragonal tungsten bronze structure was formed since compared to Ag^+ (1.15 Å), the ionic radius of Li^+ (0.76 Å) is very different to that of $(Na_{0.5}K_{0.5})^+$ (1.2 Å) of NKN. Relatively lower solubility of LiT in the perovskite

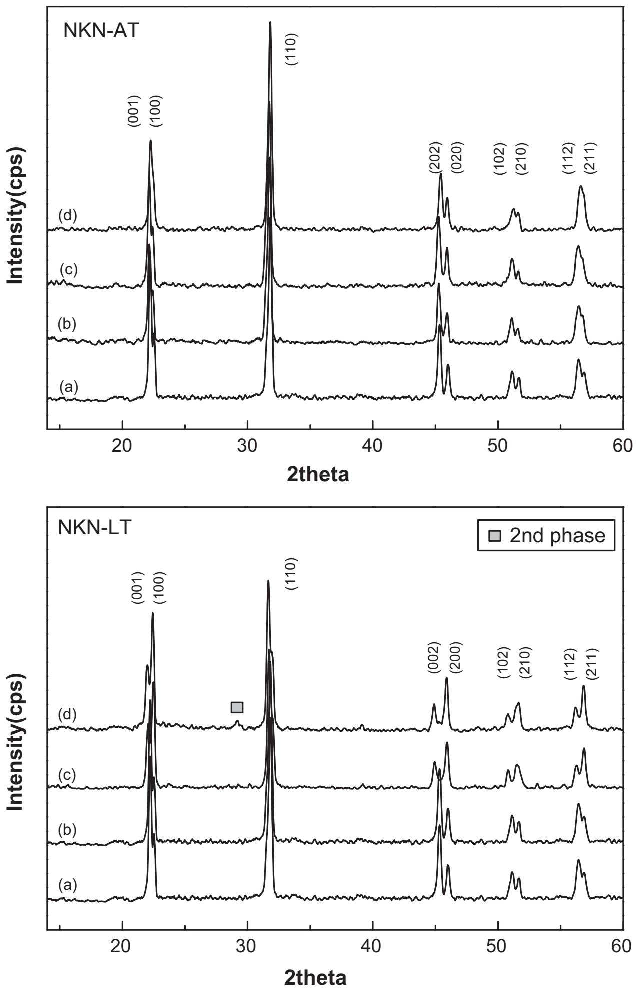

Fig. 1. XRD patterns of the sintered NKN–(x)AgT and NKN–(x)LiT specimens: (a) $x = 0$, (b) $x = 0.03$, (c) $x = 0.075$ and (d) $x = 0.1$.

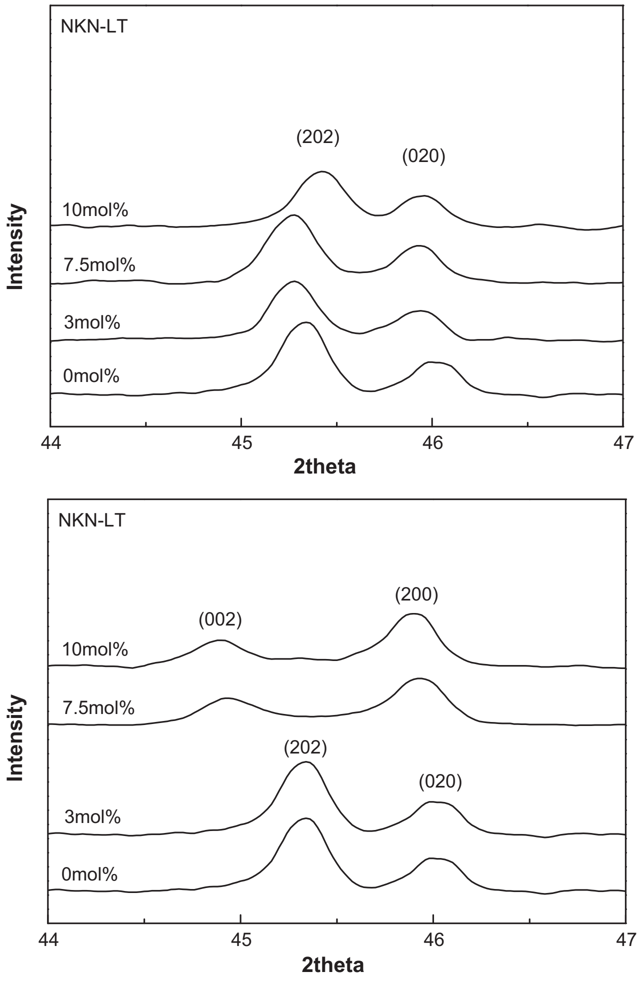

Fig. 2. XRD patterns of the NKN–(x)AgT and NKN–(x)LiT specimens in the 2θ range of 44–47°.

structure has been reported by Guo et al. [11]. The XRD patterns of NKANT(x) and NKLNT(x) specimens with enlarged angles are shown in Fig. 2. Compared to the addition of AgT, it can be seen that with adding the LiT above 0.075 mol, the phase structure of specimens transforms from orthorhombic to tetragonal, which was confirmed by the splitting of (2 0 2) and (0 2 0) peaks to the splitting of (0 0 2) and (2 0 0) peaks. Because the tetragonal phase is characterized by (0 0 2)/(2 0 0), the presence of MPB from orthorhombic to tetragonal phases was confirmed near $x(\mathrm{LT}) = 0.075$ composition. This result is similar to previous reports for Li doped NKN ceramics [11,12]. While, in the case of Ag doped NKN ceramic, the change of crystalline structure was rarely reported [5], and only for the $0.95[(K,Na)Li]NbO_3$–$0.05AgSbO_3$ ceramic containing 0.055 mol Li, its phase change into tetragonal phase has been occurred [13]. The result implies that the monovalent ions with different ionic radii, i.e. Ag of 1.15 Å and Li of 0.76 Å [14], affect the crystallization of NKN ceramics in a different way. Fig. 3 shows the SEM photographs of the LiT and AgT doped NKN ceramics sintered at the optimum sintering temperature. For the LiT doped NKN, the grain growth occurred with increasing the LiT. However, for $x = 0.1$, the specimen included the pores accompanied with the grain growth (Fig. 3(d)). This phenomenon can be similarly seen in the microstructures of $LiNbO_3$ doped NKN ceramics [8]. The lowering of sintering temperature and the distribution of grains and pores may be resulted from the effect of lithium addition on lowering melting point. Compared to the LiT addition, the grain growth is more clearly seen for the AgT added NKN as shown in Fig. 3(e) and (f), where the grain size of ∼5 μm was measured for the specimen with $x = 01$. It was revealed that the addition of $AgSbO_3$ or $(Ag,K)NbO_3$ led to the grain growth in NKN ceramics [5,13,15]. The grain growth due to silver addition has been reported in $BiZnNbO_7$ ceramics as well, which was occurred by liquid phase sintering [16]. The apparent density with AgT and LiT addition is shown in Fig. 4. The increasing tendency of density with additives can be expected from the observation of microstructures as shown in Fig. 3. The measured relative density approaches to 95–96% compared to that of the theoretical density of NKN. The highest density could be obtained for 0.1 mol AgT added NKN ceramics, probably due to larger grains and higher density value of AgT itself [17]. The decreased density of the 0.1 mol LiT–NKN ceramics possibly can be attributed to its inferior microstructure and the presence of the secondary phase exhibiting lower density of ∼4.37 g/cm^3 as indicated in Figs. 1 and 3 [13]. Fig. 5

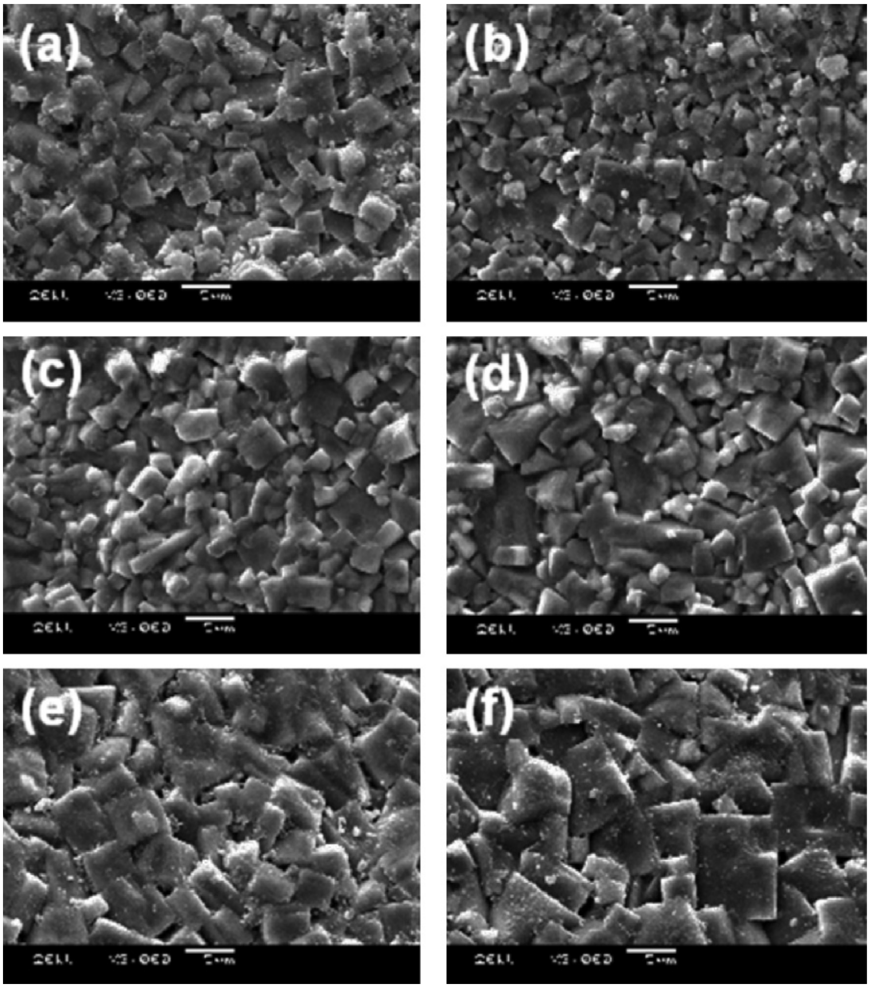

Fig. 3. SEM images of the NKN–(x)MT specimens: (a) $x = 0$, (b) $x = 0.03$ (M = Li), (c) $x = 0.075$(Li), (d) $x = 0.1$(Li), (e) $x = 0.075$(Ag) and (f) $x = 0.1$(Ag).

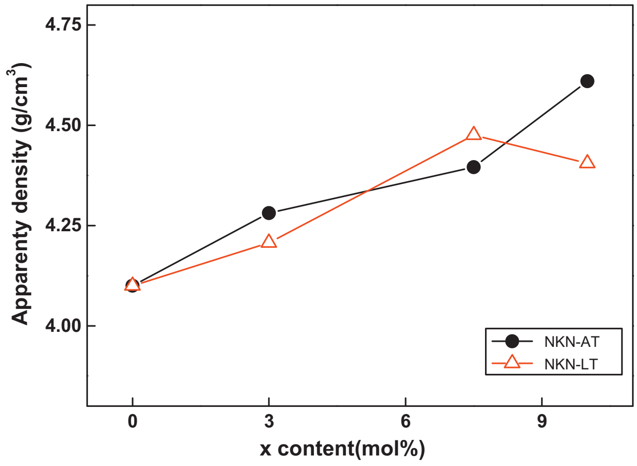

Fig. 4. Apparent densities of NKN–(*x*)AT and NKN–(*x*)LT specimens as a function of *x*.

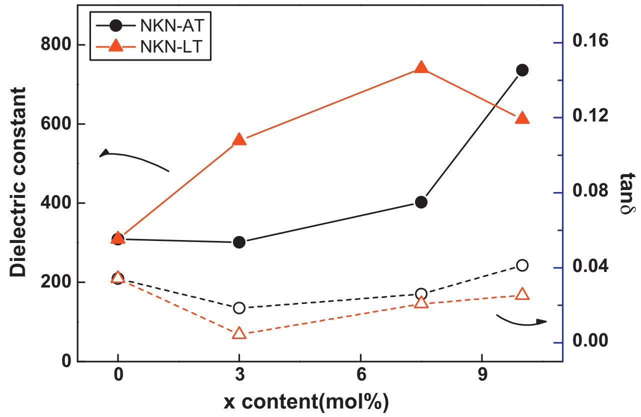

Fig. 5. Dielectric constant and loss of NKN–(*x*)AgT and NKN–(*x*)LiT specimens as a function of *x*.

shows room temperature dielectric constant and tan δ as a function of AgT and LiT content. The dielectric constant gradually increases up to 0.075 mol LiT addition and then decreases. The apparent variation can be considered due to the existence of morphotropic phase boundary, corresponding to the results appeared in the variations of density and XRD pattern. On the other hand, for the AgT doped NKN, the dielectric constant increases with the increase of AgT content, highly depending on the changes in density and microstructure. The correlation between the density and dielectric constant can be found in other literature [16,18].

Piezoelectric properties of NKANT(x) and NKLNT(x) ceramics including d_{33}, k_p and Q_m are shown in Fig. 6. The improved piezoelectric properties up to 20–30% are observed by the addition of tantalum compared to those of NKN ceramics doped with silver or lithium single elements. Some researchers have reported that by substituting tantalum or antimony for niobium in NKN system, it becomes more covalent than ionic due to the higher electronegativities of this B site dopant in perovskite structure and then the resultant hybridization of covalency over the ionic bond leads to further improvement in piezoelectric properties [3,19,20]. For NKANT(x) ceramics, electromechanical coupling factor, k_p approaches to more than 0.4 with the increase of AgT amount, exhibiting the maximum k_p of 0.46 at $x = 0.1$, and piezoelectric constant, d_{33} gradually increases. For NKLNT(x) ceramics, k_p is maximized at $x = 0.075$ and then slightly decreases with further increasing the amount of LiT. The overall piezoelectric constants of NKLNT(x) ceramics are higher than those of NKANT(x) ones and the maximum d_{33} is 215 pC/N. This tendency is similar to the variation of density as shown in Fig. 4. However, the variation of Q_m is opposite to those of the k_p and d_{33}. Relatively lower Q_m values below $x = 0.075$ for the NKLNT(x) ceramics can be probably attributed to the presence of MPB composition, where inner stress resulted from domain orientation decreases and domain walls move more easily [21]. In case of the NKANT ceramic showing unclear MPB, the variation of Q_m exhibits similar tendency to those of both the d_{33} and the k_p, as in the same result obtained from the Sb-doped NKN ceramics [22].

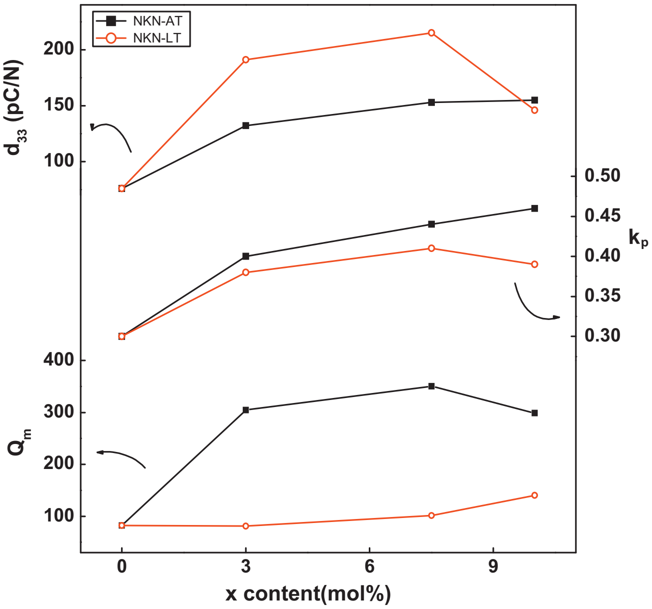

Fig. 6. Piezoelectric properties (d_{33}, k_p, Q_m) of NKN–(*x*)AgT and NKN–(*x*)LiT specimens as a function of *x*.

4. Conclusions

NKN ceramics modified by silver or lithium tantalates were successfully prepared at lower temperatures by 20–60 °C compared to the pure ones. For the NKANT(x), dielectric and piezoelectric properties increased with increasing AgT content showing $k_p \sim 0.46$ and $d_{33} \sim 155$ at $x = 0.1$, similar to the variations of microstructure and density. For the NKLNT(x), those properties were improved with the increase of LiT content, showing the maximum values of $k_p \sim 0.41$ and $d_{33} \sim 215$ at $x = 0.075$ and then slightly decreased at $x = 0.1$. This result can be explained by the phase transition from orthorhombic to tetragonal due to the substitution of lithium and also the precipitation of the second phase ($K_3Li_2Nb_5O_{15}$) showed a strong influence on the piezoelectric properties of

NKLNT(x). The NKANT(x) compositions sensitive to the variation of density exhibited the maximum Q_m of 320, higher than that of the NKLNT(x) one on MPB.

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