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Temperature dependence on the piezoelectric property of $(1-x)(Na_{0.5}K_{0.5})NbO_3$–$x$$LiNbO_3$ ceramics

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Abstract

Lead-free $(1-x)(Na_{0.5}K_{0.5})NbO_3$–$x$$LiNbO_3$ ($(1-x)$NKN−xLN) piezoelectric ceramics have been synthesized by solid state sintering between $x=0.040$ and 0.080. The effects of temperature on the dielectric, ferroelectric and piezoelectric properties were investigated. For all the samples measured, the remanent polarization (P_r) and coercive field (E_c) showed a tendency of reduction with increasing temperature, but a planer-mode electromechanical coupling coefficient (k_p) and frequency constant (N_p) varied in non-linearity as a function of temperature. The temperature dependence of the piezoelectric properties of $(1-x)$NKN–xLN ceramics was strongly affected by the lithium content, too. The k_p values enhanced at the tetragonal–orthorhombic phase transition temperature for all the specimens with different Li contents due to the MPB effects. Especially for the $x=0.055$ and 0.060 sample, the variation of elastic compliance also affected their piezoelectric property.

Keywords: Dielectric properties; Ferroelectric properties; Piezoelectric properties; Temperature dependence

1. Introduction

Lithium potassium sodium niobate $(1-x)(Na_{0.5}K_{0.5})$-NbO_3–$x$$LiNbO_3$ (abbreviated as $(1-x)$NKN–xLN) is considered as one of the most important lead-free piezoelectric ceramics.[1–4] The piezoelectric property is maximized at around the composition of 0.94NKN–0.06LN, and shows the piezoelectric constant d_{33} reaching 200–235 pC/N and planner (k_p) and thickness (k_t) mode electromechanical coupling coefficients reaching 0.38–0.44 and 0.44–0.48, respectively.[1] This seems to be due to the existence of morphotropic phase boundary (MPB) between orthorhombic ($x<0.060$) and tetragonal ($x>0.060$) perovskite phase transition at the vicinity of room temperature. Furthermore, it was reported that the solid solution was formed until $x=0.070$ and the $K_3Li_2Nb_5O_{15}$ phase with a tetragonal tungsten–bronze structure was appeared at $x>0.07$ in $(1-x)$NKN–xLN ceramics.

It is fact that the 0.94NKN–0.06LN ceramics demonstrate the highest piezoelectric property in this series at room temperature due to the existence of MPB, but their temperature dependence has not been well known. Furthermore, the relationship between phase transition and piezoelectric property has not been clarified yet in the $(1-x)$NKN–xLN ceramics.

In this study, therefore, we measured the temperature variations of dielectric and piezoelectric property for the $(1-x)$NKN–xLN with $x=0.040$, 0.055, 0.060 and 0.080. The effect of their phase transition and temperature on the piezoelectric property of $(1-x)$NKN–xLN ceramics was discussed.

2. Experimental

K_2CO_3 (99.9%), Na_2CO_3 (99.9%), Nb_2O_5 (99.9%) and Li_2CO_3 (99.0%) were used as the raw materials. These powders were weighed according to the formula of $(1-x)(Na_{0.5}K_{0.5})NbO_3$–$x$$LiNbO_3$ (with $x=0.040$, 0.055, 0.060 and 0.080). The weighed powders were mixed in a polyethylene pot and milled with ZrO_2 balls for 24 h using ethanol as a medium. After calcination at 850 °C for 10 h, the calcined powders were again ball-milled for 24 h. The granulated powders using polyvinyl alcohol as a binder were sieved through a 150-mesh screen and pressed into disks of 12 mm in diameter. The disks were cold-isostatic-pressed under 200 MPa and sintered in air at selected temperatures, depending on their x value, in the range between 1088 and 1076 °C to obtain dense ceramics. The calcinations and sintering treatments were carried out under K_2O-riched atmosphere in a closed crucible.

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The density of sintered ceramics was measured by the Archimedes method. Silver paste was painted on the lapped surfaces of the specimens as the electrodes for dielectric and piezoelectric measurements. The dielectric constant was measured using a LCR meter (NF ZM2355) at 1 kHz in an environmental chamber in the temperature range from 150 to −40 °C. *P–E* hysteresis loops were recorded at 1 Hz using an aixACT TF2000FE-HV ferroelectric test unit with a high-voltage power supply (Trek 610D). Specimens for the piezoelectric measurements were poled in silicon oil at 150 °C by applying a dc electric field of 3 kV/mm for 30 min. The piezoelectric constant d_{33} was measured using quasi-static method by a d_{33} meter. The electromechanical coupling coefficients were determined from the resonance–anti-resonance method performed on the basis of IEEE standards using an impedance analyzer (Agilent 4294A). These ferroelectric and piezoelectric measurements were carried out in the temperature range from room temperature to 150 °C and 150 to −30 °C, respectively.

3. Results and discussion

The measured density of $x = 0.040$, 0.055, 0.060 and 0.080 specimens reached 4.42, 4.32, 4.28 and 4.28 g/cm^3, respectively. All the specimens showed dense microstructures.

The temperature dependence of the dielectric constant (ε_r) for the unpoled $(1-x)$NKN–xLN samples at 1 kHz are shown in Fig. 1. While tetragonal–orthorhombic phase transition temperature ($T_{t\text{–}o}$) was confirmed at 200 °C for pure NKN specimen,[5,6] $T_{t\text{–}o}$ of $(1-x)$NKN–xLN samples is shifted to lower temperature as x is increased. It is estimated that $T_{t\text{–}o}$ for $x = 0.040$, 0.055, 0.060 and 0.080 are approximately 75, 55, 15 and −26 °C, respectively. Of all the samples, the $x = 0.060$ sample shows the highest ε_r at room temperature because of the MPB composition. The dielectric loss of all samples was confirmed 6% or less at temperature ranging from 150 to −40 °C.

The remanent polarization (P_r) and coercive field (E_c) evaluated from the saturated ferroelectric hysteresis loop (see Fig. 2(c)) are shown in Fig. 2. P_r significantly decreases in the temperature range from room temperature to around 100 °C, and remains almost constant over the 100 °C. E_c also decreases with increasing temperature.

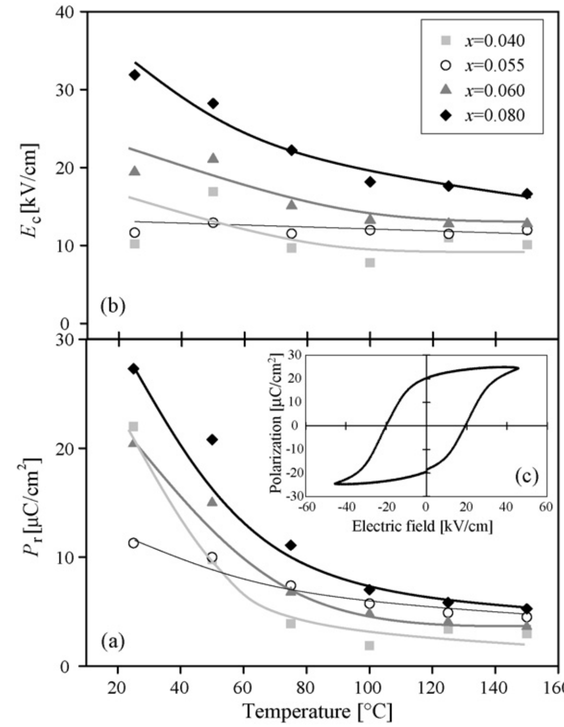

Fig. 2. Temperature dependence of the (a) remanent polarization (P_r), (b) coercive field (E_c) and (c) *P–E* hysteresis loop of $(1-x)$NKN–xLN with $x = 0.060$ at room temperature.

Fig. 3 shows the planner mode electromechanical coupling factor (k_p) as a function of temperature. k_p shows the maximum values of 0.33 ($x = 0.040$), 0.41 ($x = 0.055$), 0.43 ($x = 0.060$) and 0.37 ($x = 0.080$) at temperature closed to each $T_{t\text{–}o}$. This is due to the MPB effects. Compared with other samples, temperature dependence of k_p for $x = 0.080$ sample is different in the manner as a function of temperature. Its k_p decreased almost linearly with increasing temperature. This may have been resulted from the fact that the $x = 0.080$ specimen is not a perovskite single phase

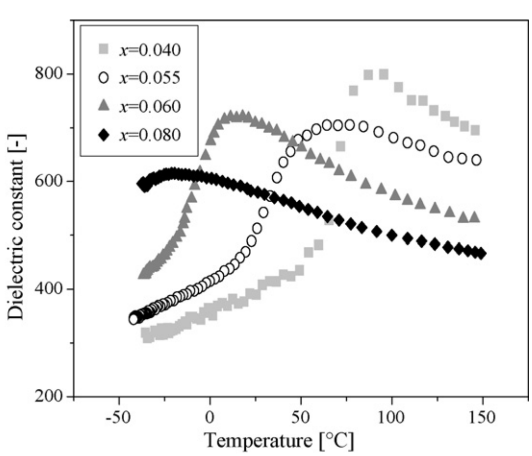

Fig. 1. Temperature dependence on dielectric constant of the $(1-x)$NKN–xLN ceramics at 1 kHz.

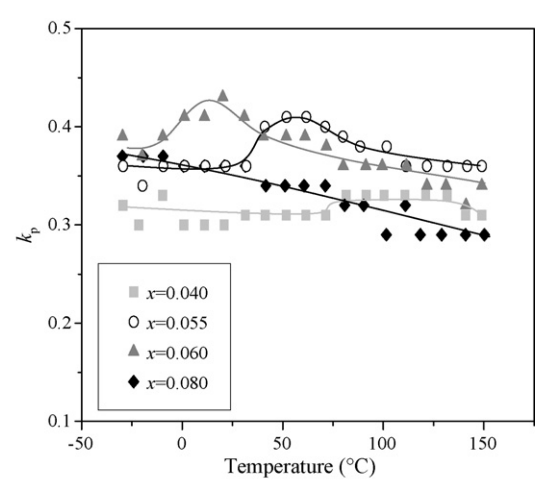

Fig. 3. Temperature dependence of the k_p for $(1-x)$NKN–xLN ceramics with $x = 0.040$, 0.055, 0.060 and 0.080.

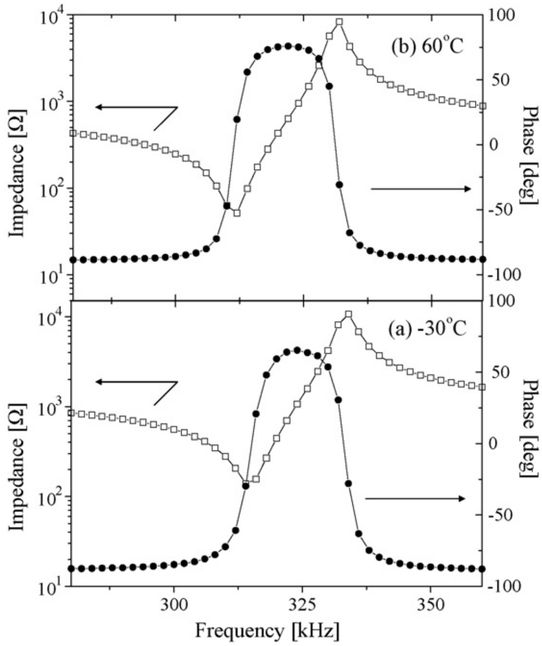

Fig. 4. Frequency dependence of impedance and phase for the $x = 0.060$ specimens poled at 150 °C for 30 min under the dc bias of 3 kV/mm, (a) measured at −30 °C and (b) measured at 60 °C.

but includes a secondary $K_3Li_2Nb_5O_{15}$ phase with a tetragonal tungsten–bronze structure.[1,7] On the other hand, k_p in NKN system remains almost constant in the temperature range from room temperature to $T_{t–o}$, and then dramatically decreases from 37 to 15% with increasing temperature until the curie point.[8]

Fig. 4 shows the resonant (f_r) and anti-resonant (f_a) frequency in the impedance measurement for the $x = 0.060$ sample at different temperatures of −30 and 60 °C for example. Clear resonance peaks were confirmed in the measured temperature. The phase shift of the sample at −30 and 60 °C reaches 65.4° and 75.9° in the inductive region, respectively. It is clear that the f_r changes from 314 to 312 kHz with increasing temperature from −30 to 60 °C. Such f_r change can be discussed with the data of the frequency constant (N_p), as follows.

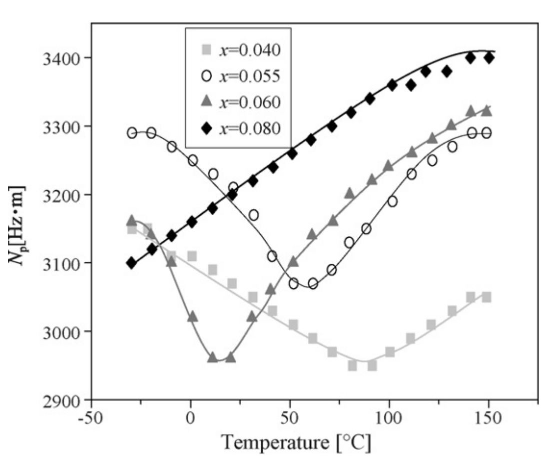

Fig. 5. Temperature dependence of the frequency planner constant (N_p) for $(1 - x)$NKN–xLN ceramics with $x = 0.040$, 0.055, 0.060 and 0.080.

Fig. 5 shows the variation of N_p as a function of temperature. N_p was calculated using the equation:

$$N_p = f_r \times L, \quad (1)$$

where L is diameter of sample. As a result, N_p reaches to the minimum values of 2950 ($x = 0.040$), 3070 ($x = 0.055$) and 2960 ($x = 0.060$) at the temperatures corresponding to each $T_{t–o}$. On the other hand, the minimum peak of N_p does not appear for the $x = 0.080$ sample. It is known that N_p is related closely with elastic compliance. The relational expression described by

$$s^E = \frac{1}{4{N_p}^2\rho} \quad (2)$$

where s^E is elastic compliance and ρ is the density. Therefore, the decrease of N_p means the increase of elastic compliance. The reason why elastic compliance was maximized and N_p was minimized at phase transition temperature seems to be because the mechanical hardness of samples and/or the bonding strength of ionic constituents in NbO_6 octahedral are changed due to the phase transition. According to the previous report by Raman spectroscopic analysis that bonding distance and its symmetry in the NbO_6 octahedral which is the main cause for ferroelectricity for $(1 - x)$NKN–xLN were gradually changed by the increase of Li doping ratio.[7]

4. Summary

The temperature dependence on the piezoelectric property of $(1 - x)$NKN–xLN has been investigated. The k_p showed the maximum values at temperatures closed to the phase transition. This is due to the change of dielectric constant and elastic compliance. While the variations of k_p for $x = 0.040$ was relatively stable in the measurement temperature range, those for $x = 0.050$ and 0.060 showed the enhanced properties at the temperature range. It may be caused by the variation in Li content.

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