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# Temperature dependence of elastic and piezoelectric properties of lead-free $(Li,Na,K)NbO_3$ ceramics

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**Abstract**

Temperature dependence of both elastic and electric properties for tetragonal $(Li_{0.06}Na_{0.47}K_{0.47})NbO_3$ (LNKN-6) ceramics was investigated. The sample was prepared using a conventional solid-state reaction method. The elastic and piezoelectric properties were characterized using the resonance method as a function of temperature ranging from −50 to 50 °C. Elastic compliance $S_{31}^{E}$ and $S_{33}^{E}$ showed the maximum values at specific temperatures of 0 and −5 °C, respectively, while dielectric constant $\varepsilon_{11}^{T}$ and $\varepsilon_{33}^{T}$ showed anomalies at 20 and 7 °C, respectively. Such anisotropic properties were also observed in the measurement of the temperature dependence of the piezoelectric properties. Anisotropic temperature dependence of both the elastic and electric properties in LNKN-6 ceramics was evaluated.


*Keywords:* C. Dielectric properties; C. Piezoelectric properties; D. Niobates; E. Actuators

## 1. Introduction

Lead-free piezoelectric $(Li,Na,K)NbO_3$ (abbreviated as LNKN) ceramic system has attracted much interest because of its high $T_c$ and good piezoelectric property [1–4]. The piezoelectric property is maximized at around the composition of $(Li_{0.06}Na_{0.47}K_{0.47})NbO_3$ (LNKN-6), and LNKN-6 ceramics shows the piezoelectric constant $d_{33}$ reaching 235 pC/N and planner ($k_p$) mode electromechanical coupling coefficient reaching 0.43 at room temperature [1]. LNKN-6 forms a tetragonal phase at room temperature, and maintains its structure even at higher temperature up to approximately 465 °C, corresponding to the Curie temperature ($T_c$).

In our previous study [5], it was found that a planer-mode electromechanical coupling coefficient ($k_p$) and frequency constant ($N_p$) varied in non-linearity as a function of temperature. Simultaneously, the remanent polarization ($P_r$) and coercive field ($E_c$) showed a tendency of reduction above room temperature. Other related works also reported that the alkaline niobate-based piezoelectric materials exhibit maximum piezoelectric properties value at $T_{O\text{–}T}$ [6–10]. However, we have as yet very little information in the temperature range lower than room temperature, despite LNKN-6 shows another phase transition from tetragonal to orthorhombic system below room temperature. In this work, therefore, we measured the temperature dependence of elastic and piezoelectric properties for LNKN-6 ceramics in the temperature range from 50 to −50 °C with the temperature decrease sequence using resonance methods.

## 2. Experimental

$(Li_{0.06}Na_{0.47}K_{0.47})NbO_3$ (LNKN-6) ceramics were prepared by the mixed oxide method using $K_2CO_3$ (99.9% purity), $Na_2CO_3$ (99.9% purity), $Nb_2O_5$ (99.9% purity) and $Li_2CO_3$ (99.0% purity) powders as starting materials. These powders were weighed and mixed in a polyethylene pot and milled with $ZrO_2$ balls for 24 h using ethanol as a medium. The dried mixture was calcined at 850 °C for 10 h. By addition of polyvinyl butyral (PVB) as a binder, the granulated powders were sieved through a 150-mesh screen and pressed uniaxially into disk of 12 mm in diameter. The disks were cold-isostatic-pressed under 200 MPa, and then sintered in air at 1082 °C for 2 h.

The sintered samples were cut and polished to satisfy the five sample resonance geometries in radial mode (diameter: 10.00 mm, thickness: 0.65 mm), thickness mode (diameter:

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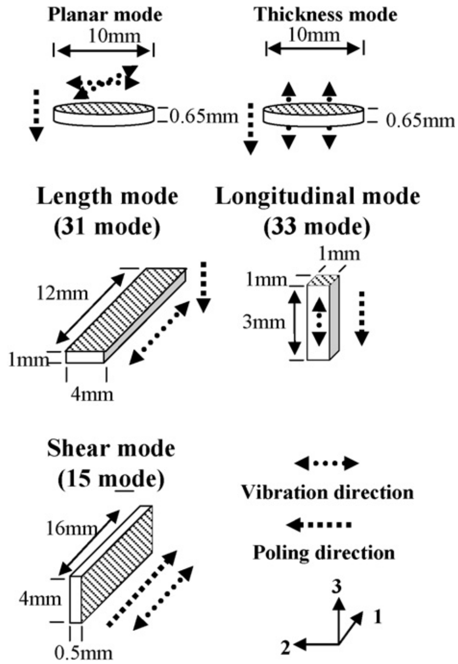


Fig. 1. The five types of sample geometries and poling and vibration directions.

10.00 mm, thickness: 0.65 mm), length extensional mode (12 mm × 4 mm × 1 mm), length thickness extensional mode (3 mm × 1 mm × 1 mm), and shear mode (16 mm × 4 mm × 0.4 mm). These sample dimensions are schematically shown in Fig. 1. Silver paste was painted on the lapped surface of the above specimens as the electrodes for the electrical measurement (see hatchings in Fig. 1). The specimens were then subjected to the polling treatment by applying a dc electric field of 5 kV/mm for 30 min in silicon oil bath kept at 150 °C. The polling direction for each sample is also indicated as dotted arrows in Fig. 1. The dielectric constant was measured using a LCR meter (NF ZM2355) at 1 kHz. The electromechanical coupling coefficients were determined from the resonance–antiresonance method on the basis of IEEE standards using an impedance analyzer (Agilent 4294A). These measurements were performed as a function of temperature using an environmental chamber in the temperature range from 50 to −50 °C with the temperature decrease sequence.

## 3. Results and discussion

Fig. 2 shows the temperature dependence of $\varepsilon_{11}^{T}$ and $\varepsilon_{33}^{T}$ in comparison to $\varepsilon_r$. Dielectric anomaly appears at 20 and 7 °C for $\varepsilon_{11}^{T}$ and $\varepsilon_{33}^{T}$, respectively, whereas $\varepsilon_r$ shows it at their intermediate temperature of around 15 °C. Upon cooling from 50 to −50 °C, the tetragonal LNKN-6 shows small temperature dependence in the dielectric permittivity, but the orthorhombic LNKN-6 demonstrates a substantially higher decrease. The difference in the observed dielectric anomaly between the poled and unpoled specimens are probably due to the different distribution of polarization against the direction of the applied electrical field, since the dielectric properties are generally

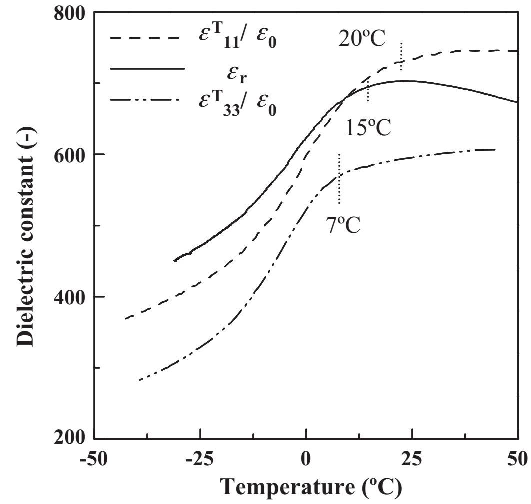


Fig. 2. Temperature dependence of dielectric constant $\varepsilon_{33}^{T}/\varepsilon_0$, $\varepsilon_r$ and $\varepsilon_{11}^{T}/\varepsilon_0$ for poled. LNKN06.

affected by the contribution of both 180° and non-180° domain walls [11,12].

The temperature dependence of the elastic compliance coefficients $S_{11}^{E}$ and $S_{33}^{E}$ compares in Fig. 3. As decreasing the temperature, a broad peak can be observed around 0 and −5 °C in the plots of $S_{11}^{E}$ and $S_{33}^{E}$, respectively. Because these broad peaks are originated from the activation of the domain wall motion, these broad peaks may correspond to the start and finish temperature faithfully during the phase transition from tetragonal to orthorhombic system. The overall temperature variations in $S_{11}^{E}$ and $S_{33}^{E}$ also show almost symmetrical shapes in the centre of the broad peaks, and they are quite different from those observed in the dielectric constants (Fig. 2).

Fig. 4 plots the electromechanical coupling coefficients ($k_{31}$, $k_{33}$, $k_{15}$, $k_p$ and $k_t$) as a function of temperature. In order to show maximal points clearly for comparison, the extension graphs in

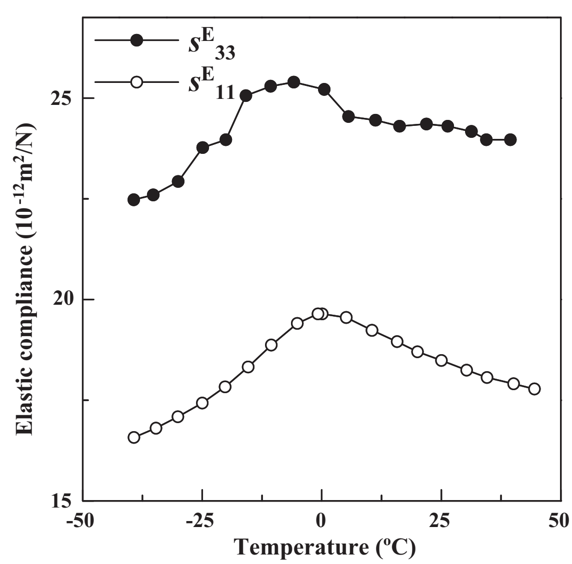


Fig. 3. Temperature dependence of elastic compliance $S_{33}^{E}$ and $S_{11}^{E}$ for poled LNKN-6.

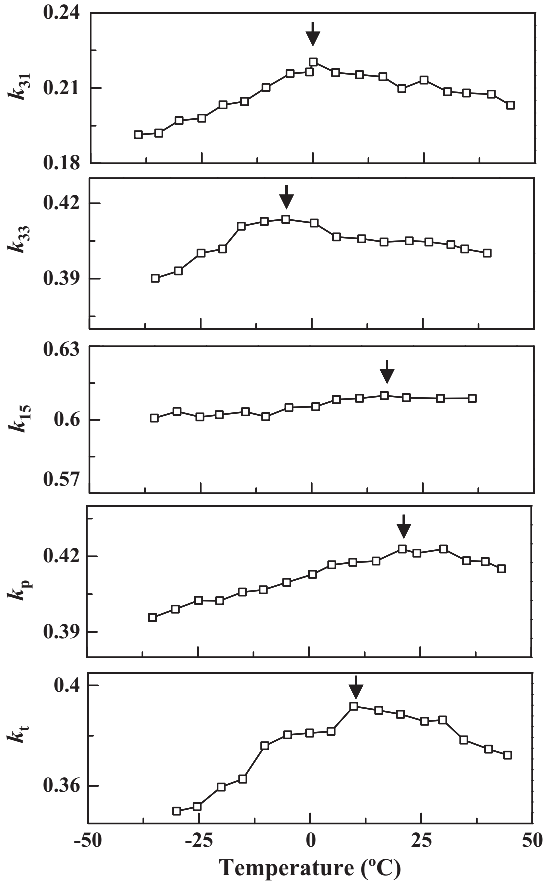


Fig. 4. Temperature dependence of electromechanical coupling coefficient ($k_{31}$, $k_{33}$, $k_{15}$, $k_p$, and $k_t$) for LNKN-6.

the vertical scale were adopted. In fact, the temperature variations in the measured electromechanical coupling factors were much smaller than those of dielectric constant. $k_{31}$ slightly increased with decreasing temperature, and a broad peak can be observed around 0 °C. Then $k_{31}$ decreased with the temperature cooling gradually. Similar to the behavior of $k_{31}$, $k_{33}$ reached maximal value at −5 °C, then decreased at lower temperature. In contrast, $k_{15}$ showed higher peak temperature of 16 °C. On the other hand, $k_p$ and $k_t$ reached their maximal values near room temperature. $k_p$ was found to be 0.41 at 40 °C, slightly increasing to 0.42 at 20 °C, and then gradually decreasing to 0.39 with the temperature reaching at −40 °C. $k_t$ was found to be 0.37 at 40 °C, reaching 0.39 at 9 °C and then decreasing to value of 0.34 at −40 °C.

It is again listed that a broad peak can be observed around 0 °C in the $k_{31}$ plot, −5 °C in the $k_{33}$ plot, 16 °C in the $k_{15}$ plot, 21 °C in the $k_p$ plot, and 9 °C in the $k_t$ plot. The electromechanical coupling coefficients are not the first-principle material constants, because they use elastic, dielectric and piezoelectric constants for calculation. However, it is useful to know the fact that the maximal point temperatures of $k_{33}$ and $k_t$ are lower than those of $k_{31}$ and $k_p$, respectively. The former vibration modes are extended parallel to the poling direction, and the latter ones are stretched normal to the poling direction.

The temperature dependence of their frequency constants $N_{31}$, $N_{33}$, $N_{15}$, $N_p$ and $N_t$ was also measured, $N_{31}$, $N_{33}$ and $N_{15}$ showed the minimal values of 1930, 2171 and 1400 at 0, −5.0 and 16 °C, respectively. $N_p$ reached to the minimal values of 2920 at 20 °C, while $N_t$ showed the minimal values of 2466 at 9 °C. These results are directly related to those obtained in the measurement of the electromechanical coupling factors. Fig. 5 plots the temperatures showing the minimal values versus the calculated $N$ constants. Except for $N_{15}$, a good linear relationship can be obtained for the other $N$ constants. This unique relation cannot be readily explained, but it will be solved near in future by examining other LNKN series ceramics showing different phase transition temperatures.

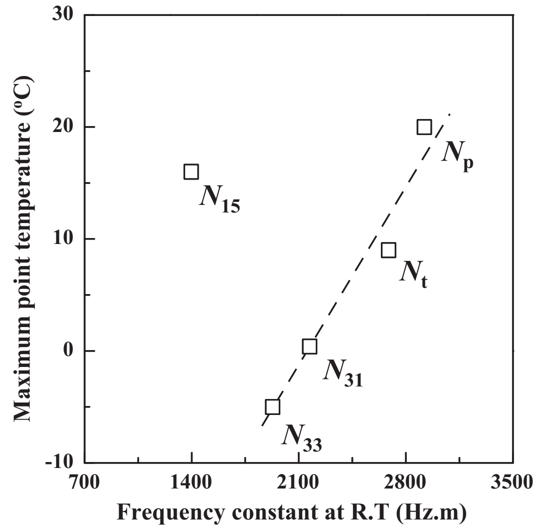


Fig. 5. Plots the temperatures showing the minimal values versus the calculated frequency constants.

## 4. Conclusions

The temperature dependence on the piezoelectric, dielectric and elastic properties of poled tetragonal LNKN-6 ceramics has been investigated. All the material coefficients exhibit nonlinearity with decreasing temperature. Dielectric constant $\varepsilon_{11}^T$ and $\varepsilon_{33}^T$ showed anomalies at 20 and 7 °C, respectively. On the other hand, the elastic compliance coefficients $S_{11}^E$ and $S_{33}^E$ showed broad peak around 0 and −5 °C, respectively. As a result, the anisotropic properties were recognized in the temperature dependence of elastic and electric properties. The temperature dependence of their frequency constants $k_{31}$, $k_{33}$, $k_{15,}$ $k_p$ and $k_t$ showed maximum values at 0, −5, 16, 21 and 9 °C, respectively. There was a correlative relationship between the temperature dependence and sample resonance geometries in LNKN ceramics.

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