Temperature Stability of Lead-Free Niobate Piezoceramics with Engineered Morphotropic Phase Boundary

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The temperature dependence of piezoelectric properties (direct piezoelectric coefficient $d_{33}$, strain $S$ and electromechanical coupling coefficient $k_p$) for two niobate-based lead-free piezoceramics have been contrasted. $0.92\text{(Na}_{0.5}\text{K}_{0.5})\text{NbO}_3-0.02\text{(Bi}_{1/2}\text{Li}_{1/2})\text{TiO}_3-0.06\text{BaZrO}_3\ (6\text{BZ/2BLT/92NKN})$ has a morphotropic phase boundary (MPB) between rhombohedral and tetragonal at room temperature and $0.92\text{(Na}_{0.5}\text{K}_{0.5})\text{NbO}_3-0.03\text{(Bi}_{1/2}\text{Li}_{1/2})\text{TiO}_3-0.05\text{BaZrO}_3\ (5\text{BZ/3BLT/92NKN})$ features an MPB engineered to be located below room temperature. At $30°C$, $d_{33}$, $d_{33}(E=0)$, $S$ (at 2 kV/mm), and $k_p$ are 252 pC/N, 230 pm/V, 0.069%, 0.51 for 5BZ/3BLT/92NKN; and 348 pC/N, 380 pm/V, 0.106%, 0.57 for 6BZ/2BLT/92NKN, respectively. With increasing temperature, the piezoelectric properties decrease. At $200°C$, $d_{33}(E=0)$, $S$ (at 2 kV/mm), and $k_p$ are 170 pC/N, 160 pm/V, 0.059%, 0.36 for 5BZ/3BLT/92NKN; and 181 pC/N, 190 pm/V, 0.06% for 6BZ/2BLT/92NKN. It is found that the electromechanical coupling coefficient has a better temperature stability than the piezoelectric coefficient in the studied system due to a large temperature-dependent compliance change. The results demonstrate that engineering an MPB is highly effective in tailoring temperature stability of piezoceramics.

I. Introduction

Piezoelectric materials, which are capable of both sensing and actuating displacements, have found applications in medical imaging devices, acoustic sensors, transducers, actuators, etc. Presently, lead-based piezoceramics, such as lead zirconate titanate Pb(Zr,Ti)O$_3$ (PZT), are the most widely used in commercial applications. PZT possesses the perovskite crystal structure and exhibits not only excellent piezoelectricity, but also good temporal and thermal stability (high Curie point). However, demand for materials that are benign to the environment and human health is growing throughout the world, which has intensified interest in environmentally friendly lead-free piezoceramics. Lead-free piezoceramics with potential to replace PZT should possess comparable piezoelectric and ferroelectric properties, in addition to a high Curie point. Thus, sodium potassium niobate [Na$_x$K$_{1-x}$NbO$_3$], which is a solid solution of ferroelectric potassium niobate (KNbO$_3$) and antiferroelectric sodium niobate (NaNbO$_3$), has been considered a promising base-material for lead-free piezoceramics and has attracted much attention in recent years, in part due to a Curie point of approximately 400°C. The piezoelectric properties of niobate piezoceramics can be enhanced by forming either a polymorphic phase boundary (PPB), a transition involving temperature change; or a morphotropic phase boundary (MPB), a transition with changes in composition only and independent of temperature. For practical applications, not only excellent piezoelectric properties at room temperature but also good temperature stability are required. For niobate piezoceramics exhibiting a PPB, the temperature dependence of piezoelectric properties, including large signal properties (e.g., strain under high electric field), small signal properties, and electromechanical coupling coefficient $k_p$, measured by in situ methods, have been reported. Small signal measurements reveal that the temperature dependence of piezoelectric coefficient $d_{33}$ is relatively strong as expected due to the temperature dependence of the PPB. The addition of 1–2 mol% CaTiO$_3$ into (Na$_x$K$_{1-x}$Li)$_2$(Nb,Sb)O$_3$ was found to greatly enhance the temperature stability over the temperature range −50°C–200°C, due to downward shifting of the polymorphic phase transition temperature $T_{P-T}$ from room temperature to −50°C. CaZrO$_3$ modification improved the temperature stability of the large signal properties (at 4 kV/mm) with a variation of less than 10% from room temperature up to 175°C, better than PZT5H ceramics. This had been attributed to large reduction in remanent polarization which balanced a smaller reduction in maximum polarization.

The origin of the very high piezoelectricity in PZT around the MPB have been extensively studied. First principles calculations have found that, in terms of conventional piezoelectric response, the excellent piezoelectric properties of a tetragonal Pb(Zr$_{1-x}$Ti$_x$)O$_3$ could not be described. It is found that the estimated $d_{33}$ value is about three times smaller than the experimental data, indicating that extrinsic contributions play an important role. Guo et al. carried out high resolution X-ray powder diffraction measurements on poled PZT ceramic samples close to the MPB. They found that the piezoelectric elongation of the unit cell does not occur along the polar directions but along those directions associated with the monoclinic distortion. This further confirmed that the piezoelectric response for
The goal of this study is to investigate the temperature stability of the piezoelectric properties, including small and large signal properties as well as the electromechanical coupling coefficient, for niobate piezoceramics. This temperature stability is, for example, found in the (33) for a non-MPB composition in BaTiO₃-based piezoceramics. The evaluation of the piezoelectric properties of lead-free niobate piezoceramics as a function of temperature in situ is highly pertinent for practical applications as well as establishing the strategy for material tailoring.

The goal of this study is to investigate the temperature stability of the piezoelectric properties, including small and large signal properties as well as the electromechanical coupling coefficient, for niobate piezoceramics with compositions in the vicinity of the MPB using in situ measurement methods. Through comparison of the results of niobate piezoceramics exhibiting PPB and to PZT, the features of niobate piezoceramics around the MPB can be better understood.

Table 1. The Curie Point and R–T Phase Transition Temperature as well as the Electromechanical Coupling Coefficient, Relative Permittivity, and Loss Tangent of 5BZ/3BLT/92NKN and 6BZ/2BLT/92NKN at Room Temperature

<table>
<thead>
<tr>
<th>Material</th>
<th>Tc (°C)</th>
<th>Tp–T (°C)</th>
<th>kp (k₃₃)</th>
<th>εr</th>
<th>tanδ</th>
</tr>
</thead>
<tbody>
<tr>
<td>5BZ/3BLT/92NKN</td>
<td>256</td>
<td>-25</td>
<td>0.50 (0.25)</td>
<td>1580</td>
<td>0.025</td>
</tr>
<tr>
<td>6BZ/2BLT/92NKN</td>
<td>243</td>
<td>45</td>
<td>0.58 (0.34)</td>
<td>2000</td>
<td>0.020</td>
</tr>
<tr>
<td>PZT5A</td>
<td>365</td>
<td>-</td>
<td>0.60 (0.36)</td>
<td>1700</td>
<td>-</td>
</tr>
</tbody>
</table>
temperature lower than room temperature [separate measurement with PPMS (Quantum Design, San Diego, CA)].

In Table 1, the Curie point \( T_C \), rhombohedral–tetragonal phase transition temperature \( T_{RT} \), permittivity \( \varepsilon \) and dielectric loss \( \tan \delta \) at 1 kHz, and planar electromechanical coupling coefficient \( k_p \) at room temperature for the two samples are listed. \( k_p \) is widely used in the community as an indicator for the electromechanical coupling factor; however, it lacks any physical meaning. Hence, we utilized \( k_p^2 \) which is the ratio of electrical energy converted into mechanical energy and vice versa, for the mechanism study. For a comparison, those properties of PZT5A are listed as well. Both samples exhibit high performance at room temperature and are competitive to that of PZT5A.

(1) Large Signal Strain Behavior
Figures 2(a) and (b) depict the large strain results at 30°C and 200°C for both samples, measured under a unipolar electric field \( (E) \) with \( E_{max} = 2 \) kV/mm. The strain \( (S) \) of 5BZ/3BLT/92NKN provides linear variation with electric field, whereas that of 6BZ/2BLT/92NKN depends on \( E \) nonlinearly. The strain hysteresis, which is the area within the strain–electric field curve and reflects the motion of domain walls, is less for 5BZ/3BLT/92NKN than for 6BZ/2BLT/92NKN at both temperatures. Especially in the case of soft piezoceramics, the nonlinear \( S(E) \) behavior and strain hysteresis originate from non-180° domain wall motion.\(^{30}\) This indicates that the domain wall motion is more significant in 6BZ/2BLT/92NKN than in 5BZ/3BLT/92NKN, which contributes to the larger strain response. The measured strain values at 2 kV/mm were 0.069% (30°C) and 0.059% (200°C) for 5BZ/3BLT/92NKN and 0.106% (30°C) and 0.061% (200°C) for 6BZ/2BLT/92NKN. Correspondingly, the \( d_{33} \) values were found to be 345 pm/V (30°C) and 295 pm/V (200°C) for 5BZ/3BLT/92NKN; and 530 pm/V (30°C) and 305 pm/V (200°C) for 6BZ/2BLT/92NKN.

Figure 2(c) contrasts the temperature dependence of the maximum unipolar strain at 2 kV/mm for both compositions as a function of temperature \( \varepsilon \).

(2) Field Dependence of Small Signal Properties
Figure 3 displays the field-dependent response of the small signal parameters \( d_{33}(E), \varepsilon(E), \) and \( \tan \delta(E) \) at 30°C and 200°C. At 30°C, both samples feature a well-defined \( d_{33}(E) \) curve. The coercive field \( E_c \), which is the field corresponding to \( d_{33} = 0 \), is 1.4 kV/mm for 5BZ/3BLT/92NKN and 1.0 kV/mm for 6BZ/2BLT/92NKN. With increasing temperature, \( E_c \) decreases rapidly. At 200°C, \( E_c \) is 0.5 kV/mm for 5BZ/3BLT/92NKN and 0.3 kV/mm for 6BZ/2BLT/92NKN. The
values of $d_{33}$ at $E = 0$ [hereafter referred as $d_{33}(E = 0)$] are, respectively, 230 pm/V (30°C) and 160 pm/V (200°C) for 5BZ/3BLT/92NKN, and 380 pm/V (30°C) and 190 pm/V (200°C) for 6BZ/2BLT/92NKN.

The shape of $d_{33}(E)$ varies between the two compositions. $d_{33}(E)$ of 6BZ/2BLT/92NKN, marked by a dotted line in Fig. 3(d), increases noticeably as the electric field is decreased from the maximum field, whereas that of 5BZ/3BLT/92NKN remains practically constant [Fig. 3(a)]. This implies that in the case of 6BZ/2BLT/92NKN, the domain walls are so mobile that its density increases significantly with decreasing electric field, whereas in the case of 5BZ/3BLT/92NKN, the domain wall density is not susceptible to the field strength. This nonlinearity, however, was found to almost vanish at 200°C [Fig. 3(d)], implying that the contribution of domain wall motions is negligible because the $c/a$ ratio is close to unity. Similar to soft PZT and PLZT, a maximum in $d_{33}(E)$ is observed in 6BZ/2BLT/92NKN. In contrast, no prominent peak of $d_{33}(E)$ is observed for 5BZ/3BLT/92NKN, the behavior of which is very similar to that has been seen, for example, in a 2 mol% Bi(Zn$_{1/2}$Ti$_{1/2}$)O$_3$-doped (Bi$_{1/2}$Na$_{1/2}$)$_2$TiO$_3$ ceramics.

$e_{33}(E)$ and tan $\delta(E)$ are provided in Fig. 3. Around the coercive field, both $e_{33}(E)$ and tan $\delta(E)$ display a distinct maximum, which is typical for a normal ferroelectric. In addition, a shallow local minimum is observed for $e_{33}(E)$ for both compositions at electric fields right above the coercive value for 30°C (insets). A similar observation has been made in PZT and PLZT and has been proposed to correspond to the coercive field for 180° domains. Compared to 5BZ/3BLT/92NKN, 6BZ/2BLT/92NKN provides a larger $d_{33}(E = 0)$ and a smaller $E_c$ at both temperatures, consistent with the fact that 6BZ/2BLT/92NKN is an MPB composition.

The temperature dependence of $d_{33}(E = 0)$ is depicted in Fig. 3(g). With increasing temperature from 30°C to 200°C, $d_{33}(E = 0)$ for 6BZ/2BLT/92NKN decreases monotonically by -49%, whereas that for 5BZ/3BLT/92NKN displays an initial decrease followed by a saturation above 150°C, totaling ~29%.

(3) Temperature-Dependent Direct Piezoelectric Coefficient

The results are provided in Fig. 4. At room temperature, the value of $d_{33}$ was found to be 348 pC/N for 6BZ/2BLT/92NKN and 252 pC/N for 5BZ/3BLT/92NKN, consistent with the previous converse piezoelectric coefficients determined at zero electric field (Fig. 3). With increasing temperature, $d_{33}$ monotonically decreases for both compositions; about 28% (5BZ/3BLT/92NKN) and 35% (6BZ/2BLT/92NKN) decrement was observed from 30°C to 100°C. Above approximately 100°C for 5BZ/3BLT/92NKN and 150°C for 6BZ/2BLT/92NKN, this effect saturated for temperatures up to ~210°C. At temperatures beyond ~210°C, there is an apparent local maximum in the piezoelectric coefficient below $T_c$, followed by a sharp decrease and a succeeding tail that persists until 300°C and 280°C for 5BZ/3BLT/92NKN and 6BZ/2BLT/92NKN, respectively. Similar temperature-dependent $d_{33}$ behavior has been previously observed in PZT and BaTiO$_3$. This behavior is due to the interplay between permittivity $e_{33}$, which increases significantly at $T_c$, and polarization $P_z$, which decreases at $T_c$, through the following equation:

$$d_{33} = 2Q_{11}P_z e_{33}$$

where $Q_{11}$ is the electrostriction coefficient. Based on thermodynamic analysis, electrostriction coefficients are temperature independent. From the experimental aspect, temperature-independent electrostriction has also been observed in typical ferroelectrics such as BaTiO$_3$, KNbO$_3$, PZT, and Bi$_{1/2}$ (Na$_{0.82}$K$_{0.18}$)$_{1/2}$TiO$_3$.

Piezoelectric properties are usually maximized in the vicinity of a phase transition, with decreasing values on the low- and high-temperature side. This continuous decrease generally extends above this phase transition temperature until another phase transition temperature is reached. As mentioned in the previous section, the rhombohedral–tetragonal phase transition is located slightly above room temperature for 6BZ/2BLT/92NKN and below room temperature for 5BZ/3BLT/92NKN, meaning that the crystal symmetry for both compositions is dominantly tetragonal. It is well-known that, piezoelectric properties can be divided into intrinsic parts and extrinsic parts. The intrinsic parts are closely related to the change in $c/a$ ratio. And the extrinsic parts are related to the dynamics of domain wall motions. As the extrinsic parts such as both reversible and irreversible domain wall motions contributes to the increase of $d_{33}$ as temperature increases, it is considered that the overall decrease in $d_{33}$ with increasing temperature from room temperature results from the decrease in the $c/a$ ratio, as known in typical ferroelectrics such as BaTiO$_3$.

(4) Temperature-Dependent Electromechanical Coupling Coefficient

Temperature dependence of resonance frequency $f_r$, antiresonance frequency $f_a$, and $k_p$ for both samples are displayed in Fig. 5. For 5BZ3BLT/92NKN, both $f_r$ and $f_a$ increase monotonically with increasing temperature, whereas $k_p$ increase linearly from 0.51 (30°C) to 0.36 (200°C). The average

![Fig. 4](image-url)  
Fig. 4. Temperature dependence of the direct piezoelectric coefficient for 5BZ/3BLT/92NKN and 6BZ/2BLT/92NKN.

![Fig. 5](image-url)  
Fig. 5. Temperature dependence of the resonance frequency $f_r$ and the antiresonance frequency $f_a$ for (a) 5BZ/3BLT/92NKN and (b) 6BZ/2BLT/92NKN; $k_p$ for (c) 5BZ/3BLT/92NKN and (d) 6BZ/2BLT/92NKN. The inset of (d) shows the $k_p^2$ of 6BZ/2BLT/92NKN as a function of temperature. The presence of an MPB near room temperature is indicated by the broad peak at ~50°C.
temperature coefficient $T_k(x)$ for the parameter $x$, which is defined as

$$T_k(x) = \frac{1}{200^\circ C - 30^\circ C} \times \frac{x(200^\circ C) - x(30^\circ C)}{x(30^\circ C)} \times 10^6 \text{ (ppm/}^\circ C)$$

is $T_k(f_d) \sim 460 \text{ ppm/}^\circ C$, $T_k(f_a) \sim 100 \text{ ppm/}^\circ C$, and $T_k(k_p) \sim -1680 \text{ ppm/}^\circ C$. For 6BZ/2BLT/92NKN, both $\kappa_f$ and $\kappa_a$ also increase with increasing temperature with a larger slope than for 5BZ/3BLT/92NKN, implying that the changes in the temperature-dependent piezoelectric properties are larger. It is noted that $f_d$ is almost temperature-independent up to $-50^\circ C$, where the local maximum in $k_p^2$ was observed [inset, Fig. 5(d)]. This unusual change results in a slight increase in $k_p$ from 0.569 (30°C) to 0.573 (50°C), and then a subsequent decrease to 0.39 (200°C). The average temperature coefficients are $T_k(f_d) \sim 800 \text{ ppm/}^\circ C$, $T_k(f_a) \sim 280 \text{ ppm/}^\circ C$, and $T_k(k_p) \sim -1800 \text{ ppm/}^\circ C$. Note that $k_p$ was very stable during thermal treatment. One thing to be noted is that the temperature coefficient of $f_d$ in both compositions is significantly larger than that of $f_a$, implying that mechanical capacitance, that is, compliance, is more susceptible to temperature change than the electrical capacitance, that is, dielectric permittivity, in the studied system.

After annealing at 100°C for 2 h, $k_p$ at 30°C remained almost unchanged from its initial value (97% for 6BZ/2BLT/92NKN and 99.4% for 5BZ/3BLT/92NKN). The resistance to depoling is better than that of $k_p$ in 3–6 at.% Li-modified niobate ceramics exhibiting PPB,\textsuperscript{18} and attractive for practical applications.

### (5) Comparison and Discussion

In Figs. 6(a) and (b), the temperature dependence of the direct $d_{33}$, the converse $d_{33}(E = 0)$, and the large signal $d_{33} = S_{max}/E_{max}$ are compared for the two compositions. For both samples, $d_{33}$ and $d_{33}(E = 0)$ are almost identical over the entire temperature range, whereas $d_{33}(E = 0)$ is larger.

The direct piezoelectric coefficient is determined by applying a small cyclic mechanical load and measuring the change in polarization, whereas the converse piezoelectric coefficient was determined by applying a small cyclic electrical signal and measuring the strain signal. As expected, $d_{33}$ and $d_{33}(E = 0)$ are almost the same. The large signal measurement, however, applies large electric fields ($E_{max} = 2 \text{ kV/mm}$) above the coercive electric field of both samples which leads to hysteretic processes due to domain wall motion that result in $d_{33} > d_{33}(E = 0)$ for both samples.

In Figs. 6(b) and (d), the temperature-dependent $d_{33}$, $d_{33}(E = 0)$, $d_{33}(E = 0)$, and $k_p$ values are normalized to the corresponding values at 30°C and compared for both compositions. Interestingly, the normalized $d_{33}$, $d_{33}(E = 0)$ and $d_{33}(E = 0)$ merge into one curve for 6BZ/2BLT/92NKN, whereas for 5BZ/3BLT/92NKN the normalized $d_{33}$ values are larger throughout the whole temperature range and exhibit better temperature stability.

As mentioned in the foregoing part, piezoelectric properties can be divided into intrinsic and extrinsic parts. The intrinsic part decreases with increasing temperature, and results in a decrease of $d_{33}$, $d_{33}(E = 0)$, $d_{33}(E = 0)$, and $k_p$. Based on the experimental data presented in this study, it is considered that the difference for the two samples is closely related the extrinsic parts (dynamics of domain wall motions). From Fig. 2, we concluded that domain wall motion in 6BZ/2BLT/92NKN is facilitated as compared to 5BZ/3BLT/92NKN. We suggest that domain wall motion off the MPB requires a higher activation energy than at the MPB and therefore its contribution to strain becomes more pertinent at higher temperature. Hence, the temperature-dependent change in $d_{33}$ in 5BZ/3BLT/92NKN is expected to be better than $d_{33}(E = 0)$ due to increasing domain wall contribution with increasing temperature.

In addition, for both samples, normalized $k_p$ is less temperature-sensitive than the normalized $d_{33}$, $d_{33}(E = 0)$, and $d_{33}$. Similar behavior has been observed in PZT5A\textsuperscript{40} and BiFeO\textsubscript{3}-K\textsubscript{1/2}Bi\textsubscript{1/2}TiO\textsubscript{3}-PbTiO\textsubscript{3} ceramics,\textsuperscript{41} where $k_p$ is found to be relatively stable as compared to the transverse piezoelectric coefficient $d_{31}$. For piezoceramics, the piezoelectric
coefficient $d$ and the electromechanical coupling coefficient $k$ obey the following relationship:

$$d = k \sqrt{\varepsilon_0 SE}$$  \hspace{1cm} (3)

here $\varepsilon$ is dielectric permittivity and $S$ the elastic compliance. Figure 7 displays $k^2(T)$, $d_33^2(T)$, and computed $S_{33}(T)$ according to Eq. (3) of 6BZ/2BLT/92NKN, which clearly show that the different temperature dependence of $k^2$, $d_33$, and $S_{33}$ is mainly due to a highly temperature-sensitive $S_{33}$. It is well-known that the slope of the MPB has an impact on the temperature stability of piezoelectric properties. To improve the temperature stability of niobate piezoceramics, a vertical MPB like that in PZT is necessary. Recently, Karaki et al. reported that the slope of the MPB in niobate lead-free piezoceramics is adjustable. By increasing the $(\text{Bi}_{2/3}\text{Na}_{1/3}\text{Ti})O_3$ content, the MPB slope of a BaZrO$_3$-(Na,K,Li)NbO$_3$ binary system was adjusted from negative to positive. The results imply that, by further composition tailoring, the simultaneous realization of a high piezoelectricity and a good temperature stability is highly possible in our lead-free niobate piezoceramics with an engineered MPB.

### IV. Conclusions

We have measured the temperature dependence of a set of piezoelectric properties ($d_{33}$, $d_{33}(E = 0)$, $d_{33}$, and $k_{33}$) for niobate piezoceramics exhibiting an MPB. Similar to lead-based piezoceramics, the piezoelectric properties provide stronger temperature dependence for the MPB composition (6BZ/2BLT/92NKN) than for the non-MPB composition (5BZ/3BLT/92NKN). This material system is very attractive for applications as $d_{33}$ and $d_{33}$ remain above 200 pm/V and $300$ pm/V up to $200{^\circ}$C, respectively.

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### References