High thermal stability of piezoelectric properties in (Na0.5Bi0.5TiO3)x–(BaTiO3)y–(Na0.5K0.5NbO3)1xy ceramics

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High thermal stability of piezoelectric properties in $(Na_{0.5}Bi_{0.5}TiO_3)_x$–$(BaTiO_3)_y$–$(Na_{0.5}K_{0.5}NbO_3)_{1-x-y}$ ceramics

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We report the piezoelectric and ferroelectric properties of $(Na_{0.5}Bi_{0.5}TiO_3)_x$–$(BaTiO_3)_y$–$(Na_{0.5}K_{0.5}NbO_3)_{1-x-y}$ ceramics for $Na_{0.5}K_{0.5}NbO_3$ rich end of composition (x, y $\leq$ 0.04 mol. %). These compositions were found to exhibit significantly improved thermal stability of piezoresponse. Variation of dielectric constant as a function of temperature revealed that orthorhombic–tetragonal (T_{o-t}) and tetragonal–cubic (T_c) transition temperatures for these compositions were in the vicinity of $0\,°C$ and $330\,°C$, respectively. Dynamic scaling and temperature dependent X-ray diffraction analysis were conducted. Results are discussed in terms of intrinsic and extrinsic contributions to the piezoelectric response explaining the temperature dependent behavior. © *2013 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4773983]

High Curie temperature (T_c) piezoelectric materials are highly desired for applications in actuators and transducers. In past few decades, $PbZr_xTi_{(1-x)}O_3$ (PZT) based compositions have dominated these applications because of its excellent piezoelectric properties and high $T_c = 390\,°C$.[1] One of the limitation of soft PZT as high temperature piezoelectric material is the thermal degradation of its electromechanical properties above $150\,°C$.[1,2] In addition, toxic nature of lead-based compositions is also a concern.

Sodium potassium niobate $K_{0.5}Na_{0.5}NbO_3$ (KNN) having orthorhombic crystal structure at room temperature (RT) is a possible alternative for high temperature applications having T_c close to $420\,°C$.[1] However, the presence of the orthorhombic to tetragonal transition at $200\,°C$ deteriorates the thermal stability of piezoelectric properties between RT and Curie point. In addition, the piezoresponse of KNN is much inferior to that of PZT and other lead-based compositions. In last decade, doping of different A-site (Ca, Ba, Li, etc.) and B-site (Ta, Nb, Ti, etc.) elements has been reported to reduce the orthorhombic–tetragonal transition temperature (T_{o-t}) close to room temperature, resulting in an improved room temperature piezoresponse.[2–4] But at the same time, the presence of T_{o-t} at room temperature results in a poor thermal behavior and the problem of reproducibility in piezoelectric properties.[5] By further lowering the T_{o-t}, it is possible to achieve the broad existence of tetragonal region from RT to T_c, which could impart good thermal stability of the piezoelectric properties. Very few studies have addressed the temperature variation of piezoelectric properties in this system and hence thermal stability of KNN based compositions is not well understood. A study worth mentioning here is that by Zhang *et al.*, which showed that small amount of $CaTiO_3$ incorporated into KNNLS ($K_{0.5}Na_{0.5}NbO_3$–$LiSbO_3$) resulted in better thermal stability of the piezoelectric properties in the temperature ranging from $-60\,°C$ to $200\,°C$.[2]

In this study, we report the temperature dependent piezoelectric properties of ternary $(Na_{0.5}Bi_{0.5}TiO_3)_x$–$(BaTiO_3)_y$–

$(Na_{0.5}K_{0.5}NbO_3)_{1-x-y}$ (xNBT-yBT-(1−x−y)KNN) compositions. Role of 90° domains and tetragonality was investigated to explain the observed stability of piezoelectric response. Since one of the components of xNBT-yBT-(1-x-y)KNN compositions (BT, calcination temperature $1350\,°C$) has higher calcination temperature than the melting point of other (KNN, melting temperature $1200\,°C$),[1] mixed perovskite method was preferred to synthesize these ceramics. The compositions xNBT-yBT-(1-x-y)KNN with x = 0.035 y = 0.01 (S1), x = 0.03 y = 0.015 (S2), x = 0.035 y = 0.015 (S3), x = 0.04 y = 0.015 (S4), and x = 0.0375 y = 0.0125 (S5) were synthesized in two steps. In the first step, KNN and NBT ceramics were synthesized by mixed-oxide method. For KNN precursors, K_2CO_3, Na_2CO_3, and Nb_2O_5, while for NBT precursors Na_2CO_3, Bi_2O_3 and TiO_2 (Alfa Aesar, purity > 99%) were calcined at temperatures $850\,°C$ and $900\,°C$, respectively. In the second step, appropriate amounts of these two components along with commercially available $BaTiO_3$ were ball milled and calcined at $850\,°C$ to achieve the desired KNN-NBT-BT stoichiometry. Samples of different sizes were compacted and subjected to cold isostatic pressure of 20 kPa before muffled sintering at $1080\,°C$. To perform the electrical measurements, silver nanoparticles based conductive paste was painted on these samples followed by firing at $650\,°C$.
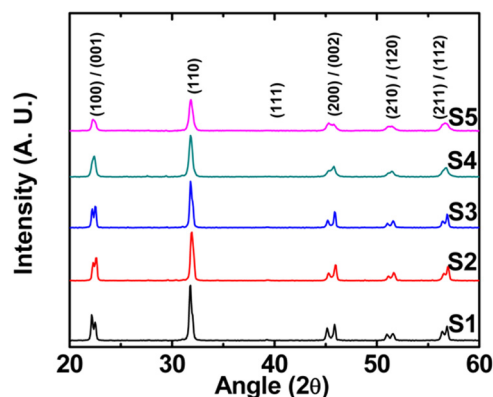

FIG. 1. X-ray diffraction patterns of KNN-NBT-BT samples showing the presence of perovskite phase with tetragonal symmetry.

TABLE I. Dielectric, ferroelectric and piezoelectric properties of KNN-NBT-BT ceramic compositions.

Sample	S1	S2	S3	S4	S5
Composition (x, y)	0.035, 0.01	0.03, 0.015	0.035, 0.015	0.04, 0.015	0.0375, 0.0125
Tetragonality ($c/a - 1$)	0.0147	0.0133	0.0143	0.0103	0.0105
K (100 kHz)	531	644	583	398	440
Loss (100 kHz)	0.038	0.041	0.036	0.06	0.051
T_{o-t} (°C)	0	11	−5	8	0
T_c (°C)	329	333	327	339	333
P_r ($\mu C/cm^2$)	18.3	12	11.6	13.5	13.7
d_{33} (pC/N)	210	148	182	145	150
$-d_{31}$ (pC/N)	63	…	…	48	…
d_h (pC/N)	84	…	…	49	…
k_p	0.32	0.3	0.3	0.29	0.29
k_{31}	0.21	…	…	0.17	…
Δd_{31} (%)	24	…	…	25	…
Δk_p (%)	31	…	…	4	…
Δk_{31} (%)	19	…	…	0.5	…

Figure 1 shows the X-ray diffraction (XRD) patterns of all the ceramic samples with 2θ values between 20° and 60°. All the samples crystallized in the perovskite phase with splitting of $(200)_{pc}$ peaks suggesting crystallization in tetragonal symmetry. Minor peaks existing in the 2θ range of 25°–30° for S2 and S4 compositions could be attributed to the tetragonal tungsten bronze phase which is common to appear during synthesis of alkali niobates.[6] Tetragonality of these compositions was determined using the peak positions of (200)/(002) reflections as listed in Table I. Samples S1 and S4 were found to exhibit largest and smallest values of tetragonality ($c/a - 1$) having values of 0.0147 and 0.0103, respectively.

For piezoelectric characterization, samples were poled at the electric field of 4 kV/mm in the silicone oil bath for 45 min. Values of low field longitudinal piezoelectric coefficients (d_{33}) and other parameters of interest for different compositions are listed in Table I. Longitudinal piezoelectric coefficients (d_{33}) of these compositions exhibited similar trend as that of tetragonality. The composition S1 had highest value of tetragonality and was also found to exhibit the highest piezoresponse with d_{33} value of 210 pC/N. Room temperature dielectric measurements conducted at 100 Hz also suggested the high dielectric constant values for compositions S1, S2, and S3 with high tetragonality. Planar electromechanical coupling coefficients determined using resonance–anti-resonance technique were found to have values in the narrow range of 0.29–0.32. The composition S1 was found to have hydrostatic piezoelectric coefficient (d_h) value of 84 pC/N, which is comparable to the values obtained for lead-based piezoelectric compositions such as APC841 and APC855 (APC International Ltd.). Figure 2(a) shows the P-E loops for all the compositions. Electric field and frequency were kept same for all the samples having values of 70 kV/cm and 200 Hz, respectively. Saturated ferroelectric loops confirm the high resistive nature of these samples, with sample S1 having highest remanent polarization value of 18.3 $\mu C/cm^2$.

To reveal the phase transition behavior, temperature dependent dielectric measurements were performed in the range of −60 °C to 500 °C. As can be seen in Fig. 2(b), all the samples were found to have orthorhombic–tetragonal (T_{o-t}) and
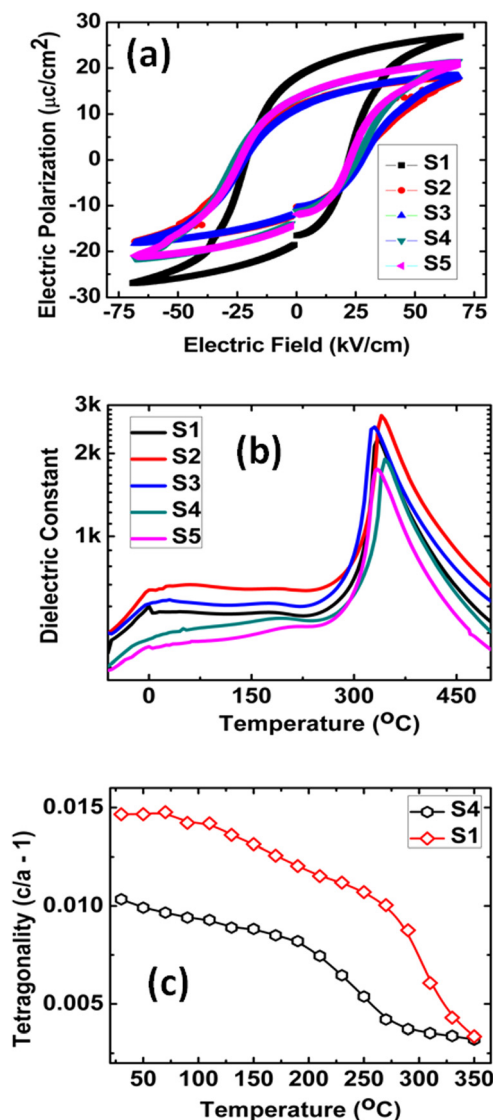

FIG. 2. (a) P-E loops, (b) dielectric constant vs. temperature plots obtained for KNN-NBT-BT samples, (c) variation in tetragonality with temperature for compositions S1 and S4.
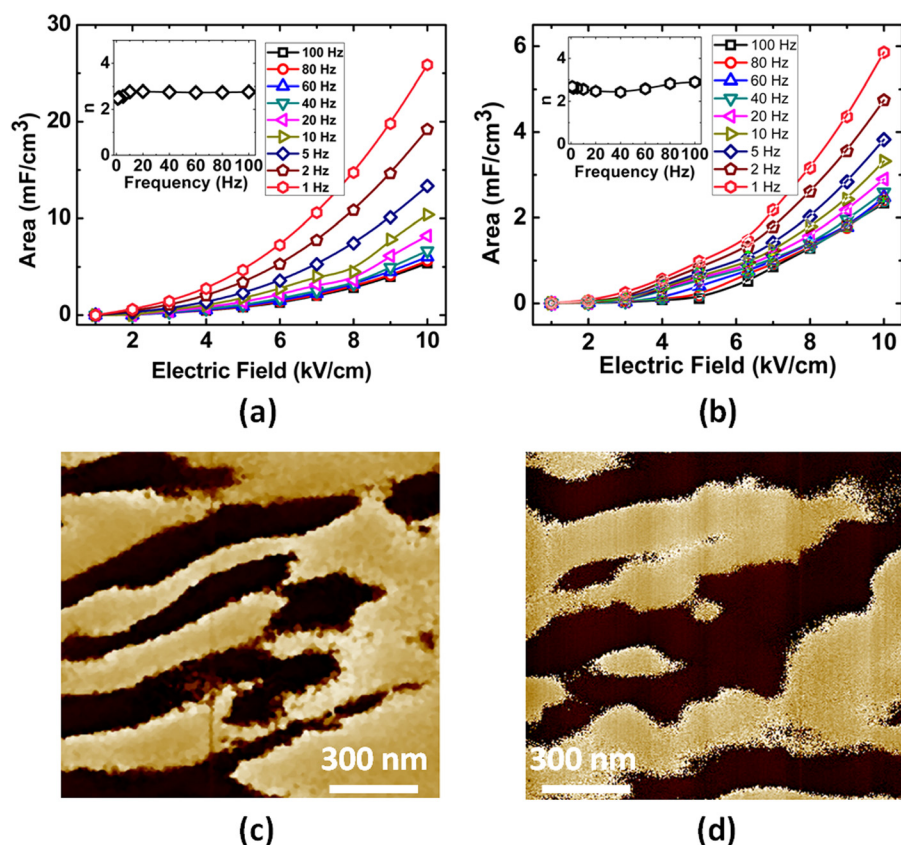
FIG. 3. (a) and (b) Variation of area under ferroelectric loops vs. electric field at different frequencies for S1 and S4. Insets of figures show the values of parameter n at different frequencies for two compositions, (d) and (e) PFM phase images of samples S1 and S4, respectively.

tetragonal–cubic phase transition temperatures close to $0\,°C$ and $330\,°C$, respectively. It is interesting to note that compositional modifications to KNN shift the T_{o-t} by about $200\,°C$ in contrast to shift in T_c by only about $90\,°C$, giving a broad temperature span of about $330\,°C$ without any phase transformation. This kind of behavior is quite unique for KNN-based compositions. Except for few lithium incorporated compositions like KNNLS ($K_{0.5}Na_{0.5}NbO_3$–$LiSbO_3$) and KNLN ($K_{0.5}Na_{0.5}NbO_3$–$LiNbO_3$), most of the other compositions reported in literature maintain the temperature span of $200\,°C$ or lower between T_{o-t} and T_c.[7]

Careful observation of dielectric constant profiles in tetragonal regime reveals that the compositions having high tetragonality at room temperature (S1, S2, and S3) show better stability as compared to those with lower tetragonality (S4 and S5). To exemplify, the compositions S1 and S4 having tetragonality values of 0.0147 and 0.0103 showed 0.76% and 18% variation in dielectric constant in the temperature range of $0\,°C$–$200\,°C$. Dielectric constant of a polar perovskite composition can be given as the sum of intrinsic and extrinsic contributions.[8] Intrinsic contribution comes from the relative displacements of ions within unit cell, while on the other hand extrinsic contribution results from the domain wall motion under electric field. The extrinsic contribution increases with temperature due to higher mobility of domain walls at higher temperature. On the other hand, intrinsic contribution to dielectric constant decreases with temperature due to decrease in tetragonality.[8] Experimental as well as theoretical results obtained for hard and soft PZTs suggest that the extrinsic contribution to dielectric properties is about 67%–70% of total response at room temperature.[8,9] Since extrinsic contribution dominates at room temperature and

increases sharply with temperature in contrast to intrinsic contribution, the dielectric constant shows a net increase with temperature.[8,9]

To understand the temperature dependent dielectric of behavior of KNN-NBT-BT ceramics, temperature dependent XRD analysis was conducted on two samples with extreme tetragonality values (S1 and S4). Figure 2(c) shows the variation of tetragonality of these samples in the temperature range of $30\,°C$–$350\,°C$, calculated using peak positions of (200)/(002) reflections. It can be seen that S1 having high tetragonality at room temperature maintains the dominance over low tetragonality sample S4 in the entire temperature range. Thus, stability of dielectric constant in high tetragonality compositions could be explained if the decrease in intrinsic contribution with temperature is quantitatively comparable to increase in extrinsic contribution in the temperature span of $0\,°C$–$200\,°C$.

Let us analyze the role of domain contribution in dielectric behavior of tetragonal compositions. Previous studies suggest that 180° domains cannot respond to low fields at which dielectric measurements were performed.[8] Theoretical calculations conducted for tetragonal compositions suggest that the domain wall energy for 180° domains is about 10 ergs/cm^2 in contrast to 3 ergs/cm^2 for 90° domains.[10] It has been found in the case of $BaTiO_3$ that 180° domains started responding to electric field only when the applied field magnitude was comparable to that of coercive field.[10] Thus, low extrinsic contribution to dielectric constant indicates only the inability of 90° domains in responding to the changes in external electric field. Since only 90° domains can contribute to the piezoelectric properties, this hypothesis is consistent with comparatively low values of piezoelectric
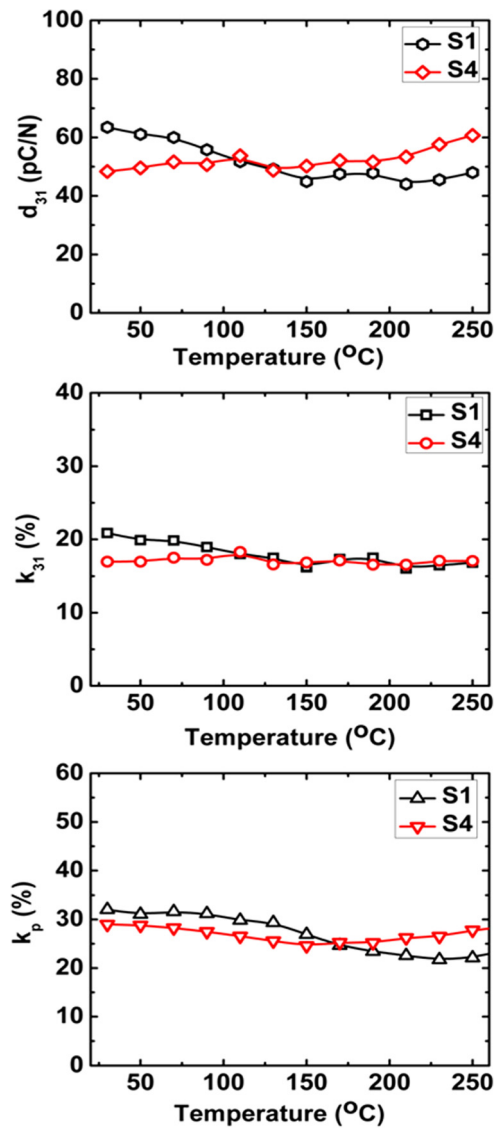
FIG. 4. (a) Variation of piezoelectric coefficients (a) d_{31}, (b) k_{31}, and (c) k_p with temperature.

coefficients (d_{33}, d_{31}, k_p and k_{31}) in KNN-NBT-BT ceramics as compared to other KNN modified compositions having PPB close to RT.[2,3]

Contribution of domain wall motion to piezoelectric properties depends on their width as well as their dynamics under electric field.[11,12] For example, theoretical calculations conducted for 90° domains in two dimensional (2D) BaTiO$_3$ single crystal using time dependent Ginzburg–Landau (TDGL) model suggest about threefold increase in low field longitudinal piezoresponse (d_{33}) by decreasing the domain size from 22.6 nm to 4.5 nm. Altering piezoelectric coefficients by controlling the domain wall mobility is a well-established procedure for lead-based piezoelectrics.[1] To understand the 90° domain dynamics in KNN-NBT-BT ceramics, scaling analysis was conducted on samples S1 and S4. In this analysis, area under the ferroelectric loops is related to frequency (f) and electric field amplitude (E) according to Eq. (1). This concept was first developed for magnetic materials but holds good for ferroelectrics as well[12–14]

$$\langle A \rangle \propto f^m E^n. \tag{1}$$

The exponent m in this relation is a measure of switching time of domains, while n represents the ability of domains to respond to changes in electric field direction. Theoretical calculations suggest the values of these parameters to be −1 and 2, respectively, for magnetic materials.[15] Though very few ferroelectric materials follow these values,[16] dynamic scaling remains an effective tool to study the domain response. Since we are interested in understanding the ability of 90° domains in responding to the applied electric field, present analysis focuses on determining the value of parameter n only. Also, this analysis was conducted at low fields ($E < E_c/2$), as 180° domain walls do not respond at low electric fields and thus the ferroelectric response would be mainly from 90° domains.[10]

Ferroelectric loops were measured for S1 and S4 for various possible combinations of electric field values ranging from 1 kV/cm to 10 kV/cm and frequencies in the span of 1 Hz–100 Hz. Area under these loops was calculated and its variation with electric field at different frequencies can be seen in Figs. 3(a) and 3(b) for these two compositions. All these curves were fitted to the equation $\langle A \rangle \propto E^n$ providing the values of n ranging from 2.5 to 2.8 for two compositions at different frequencies, suggesting the similar dynamic behavior of domains. Analysis conducted on tetragonal ferroelectric BaTiO$_3$ ceramic and single crystal at sub-coercive field gives the values of parameter n to be 3.64 and 4.16, respectively.[13,16] These values are clearly higher as compared to the values obtained for KNN-NBT-BT compositions and hence it can be concluded that 90° domains in KNN-NBT-BT ceramics exhibit slower switching, consistent with our hypothesis. To ensure the role of any size difference of domains in determining the piezoresponse of two compositions S1 and S4, piezoresponse force microscopy (PFM) was conducted. Phase contrast images obtained for S1 and S4 are shown in Figs. 3(c) and 3(d), respectively, showing the presence of stripe-like domains for both the compositions having width of about 200 nm and extending through the grains with dimensions of 1–2 μm. Hence, similar to the dynamic behavior given by magnitude of parameter "n", size of ferroelectric domains is not expected to play preferred role in determining the piezoelectric properties in any of these two compositions. In this scenario, these two compositions are expected to exhibit similar extrinsic contribution to piezoresponse. Thus, the superior piezoresponse of high tetragonality composition can be attributed to its higher intrinsic contribution. This hypothesis can be further understood by noticing the phenomenological expression given by Eq. (2), suggesting that intrinsic contribution to longitudinal piezoelectric coefficient varies with tetragonality and dielectric constant.[10,17]

$$d_{33} = 2\varepsilon_o \varepsilon_{33} [Q(c/a - 1)]^{1/2}, \tag{2}$$

where Q is the electrostriction coefficient, and ε_o and ε_{33} represent the permittivity of free space and piezoelectric composition, respectively.

Figure 4 shows the variation of piezoelectric coefficient (d_{31}) and electromechanical coupling coefficients (k_{31}, k_p) with temperature for compositions having highest and lowest values of tetragonality. For most of the tetragonal piezoelectric compositions reported in literature, an increase in piezoelectric properties was observed with temperature due to dominance of extrinsic contribution which increases due to enhanced domain wall mobility at higher temperatures.[18,19] But, in the present case, composition S1 having prominence of intrinsic contribution shows small drop in all three parameters with temperature, suggesting a decrease in tetragonality with temperature leading to poorer intrinsic contribution. On the other hand, composition S4 having low tetragonality and hence more balanced intrinsic and extrinsic contributions shows almost no variation in the electromechanical coupling coefficient k_{31} and k_p, and small increase in d_{31}. Both of these observations are consistent with our hypothesis about the role of intrinsic and extrinsic contributions to piezoelectric properties. Table I lists the percent variation of three electromechanical parameters for two compositions. If we compare the variation of piezoelectric parameters with various lead-based compositions used in devices for high temperature applications, our compositions definitely exhibit better thermal stability.[18,19] For example, both soft and hard PZT ceramics show about 50% change in d_{31} values in contrast to about 24% variation in KNN-NBT-BT ceramics for the same temperature range.[18]

In summary, KNN-NBT-BT ceramics were characterized for the thermal stability of piezoelectric parameters in the broad tetragonal region. Slow dynamics of 90° domains in these compositions leads to moderate values of piezoelectric coefficients at room temperature but at the same time provides higher thermal stability. This work provides significant insight towards the temperature dependent behavior of piezoelectric coefficients along with the role of intrinsic and extrinsic contributions in tetragonal compositions of KNN-based perovskites. It can be concluded that by controlling the mobility of 90° domains in tetragonal compositions, piezoelectric compositions with good thermal stability of piezoresponse can be designed.

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