

Technical note

Phase transition behavior and electrical properties of lead-free $(1-x)(0.98\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3-0.02\text{LiTaO}_3)-x(0.96\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3-0.04\text{BaTiO}_3)$ piezoelectric ceramics

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Abstract

Lead-free piezoelectric ceramics $(1-x)(0.98\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3-0.02\text{LiTaO}_3)-x(0.96\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3-0.04\text{BaTiO}_3)$ (KNN-LT-BNT-BT) with $x=0-0.10$ have been synthesized by a conventional sintering technique. All samples possess pure perovskite structure, showing room temperature symmetries of orthorhombic at $x < 0.02$, and tetragonal at $0.05 \leq x \leq 0.10$. A coexistence of orthorhombic and tetragonal phases in the composition range of $0.02 \leq x < 0.05$ in this system is caused by the temperature of the polymorphic phase transition (PPT) decreasing to around room temperature but not the behavior of the morphotropic phase boundary (MPB). The samples near the coexistence region exhibit improved properties, which are as follows: piezoelectric constant $d_{33} = 155$ pC/N, remnant polarization $P_r = 24.2$ $\mu\text{C}/\text{cm}^2$, and coercive electric field $E_c = 2$ kV/mm. The results indicate that although this kind of ceramics displays good properties, further study is needed to promote the stabilities of the ceramics in order to utilize them in varying temperature environments.

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Keywords: Dielectric properties; Ferroelectric properties; Piezoelectric properties; Perovskites; Lead-free ceramics

1. Introduction

Lead oxide-based ceramics with perovskite structure have been the mainstay for high performance actuators, transducers and other applications, owing to their superior dielectric, piezoelectric, and electromechanical coupling coefficients but can only operate over a limited temperature range typically -50 to 150 °C.¹ However, in recent years many fields have expressed the need for actuation and sensing which can be used at higher temperatures (>400 °C) than currently available, such as automotive, aerospace, and related industrial applications. On the other hand, their evaporation of harmful lead oxide during the preparation of lead-containing ceramics has resulted in an increasing demand for environmentally benign alternative materials. Therefore, research on high temperature and high performance lead-free piezoelectric ceramics has become more

and more concentrated in the past few years. $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ (NBT)-based and $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ (KNN)-based materials are two main material systems with perovskite structure, which have been studied for lead-free piezoelectric applications.²

It is believed that in lead-based systems the high piezoelectric response is related to the morphotropic phase boundary (MPB) which separates the rhombohedral (pseudocubic) state from the tetragonal state. The existence of these thermodynamically equivalent phases permits almost continuous rotation of the polarization vector under the external electric field, exhibiting enhanced dielectric, piezoelectric, and electromechanical responses.^{3,4}

Sodium bismuth titanate, $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$, is a kind of lead-free material with perovskite structure discovered by Smolenskii et al.⁵ Because of its large coercive field and relatively large conductivity, pure $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ is difficult to polarize and its piezoelectric properties are not desirable. In addition, it reveals an anomaly of dielectric properties as a result of a low temperature phase transition from the ferroelectric to the anti-ferroelectric phase at about 200 °C which can be called the

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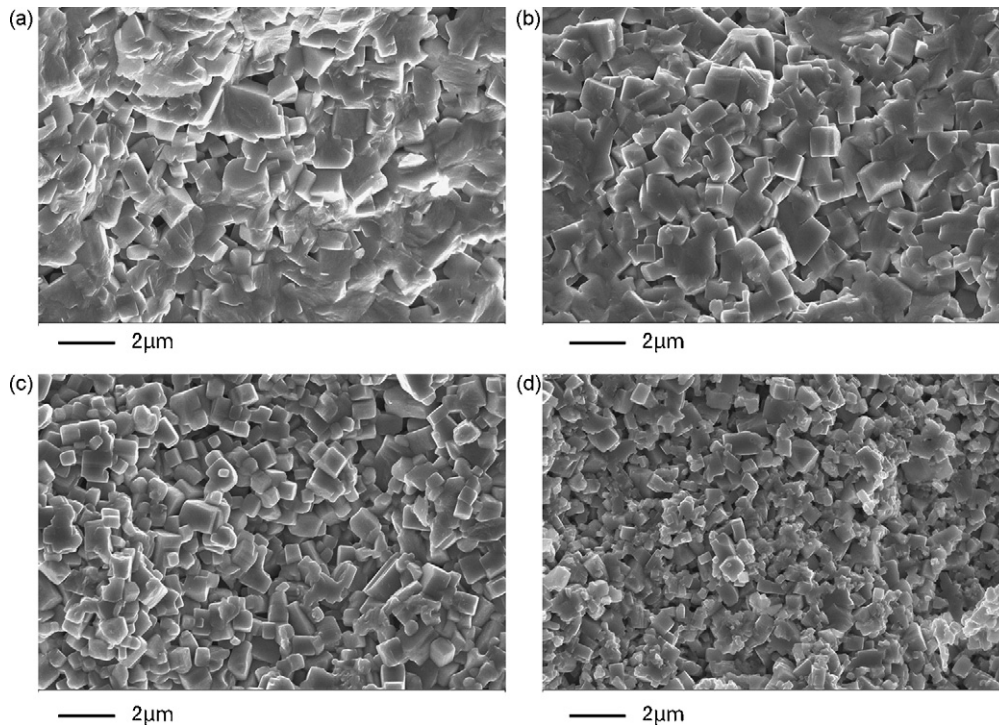


Fig. 1. SEM micrographs of fracture surface for KNNLT–BNTBT ceramics ((a) $x=0.005$, (b) $x=0.02$, (c) $x=0.05$, and (d) $x=0.10$).

depolarization temperature (T_d).⁶ Therefore, $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ -based materials were studied to improve their piezoelectric properties.^{6–10} $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ – BaTiO_3 (BNT–BT) shows better dielectric, ferroelectric, piezoelectric, and electromechanical properties than pure BNT ceramics, this system having a rhombohedral–tetragonal MPB.

On the other hand, $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ (KNN) ceramics have begun to attract much attention because Li and Ta substitution for a K, Na or Nb site improved the dielectric and piezoelectric properties of the KNN ceramics.^{11–16} However, it is difficult to prepare well-sintered KNN ceramics under the atmospheric conditions because of the evaporation of alkaline metal elements at high temperatures, but the density of KNN was enhanced by using the hot-pressing technique. The more general system, $(\text{K}, \text{Na}, \text{Li})(\text{Nb}, \text{Ta}, \text{Sb})\text{O}_3$, seems to be a big breakthrough and was made by Saito et al.,¹⁷ who obtained high d_{33} (416 pC/N) in textured KNN-based ceramics, suggesting promising candidates for lead-free piezoelectric ceramics. However, as shown by our previous work, for most published papers of KNN systems the improved properties are caused by the PPT temperature between tetragonal and orthorhombic decreasing to around room temperature due to the Li and Ta doping, and not by constituting a region of real MPB.¹⁸ Since the phase boundary between tetragonal and orthorhombic has strong temperature dependence, the use of KNN-based ceramics in varying temperature environments should be considered carefully.

To develop a new lead-free piezoelectric material, we tried to design a new solid solution between 0.96BNT–0.04BT and 0.98KNN–0.02LT, possessing rhombohedral and orthorhombic phases, respectively. In this work, solid solution ceramics between these two typical lead-free perovskite materials,

0.96BNT–0.04BT and 0.98KNN–0.02LT, were investigated for their phase transition behavior and electrical properties.

2. Experimental procedure

$(1-x)(0.98\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3-0.02\text{LiTaO}_3)-x(0.96\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3-0.04\text{BaTiO}_3)$ ($(1-x)\text{KNNLT}-x\text{BNTBT}$) ceramics ($x=0.005, 0.01, 0.02, 0.03, 0.05, 0.07, 0.10$ mol%) were prepared by conventional ceramic processing. The raw materials used in this work were K_2CO_3 , Na_2CO_3 , Nb_2O_5 , Ta_2O_5 , BaCO_3 , TiO_2 , and Li_2CO_3 . Firstly, after weighing according to the designed chemical formulae and milling in

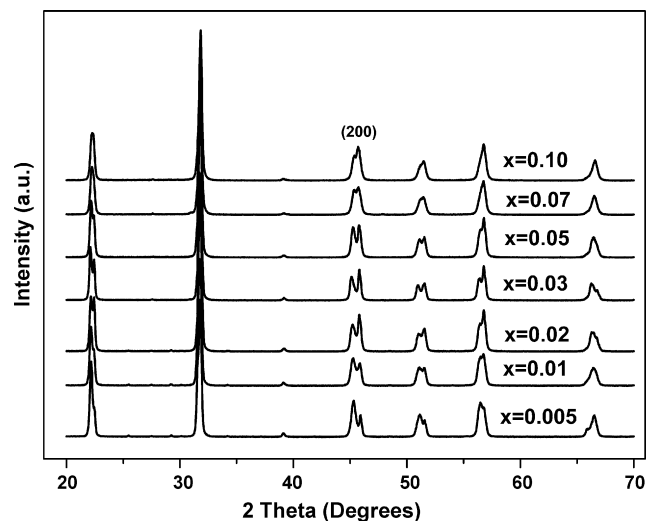


Fig. 2. XRD patterns of $(1-x)\text{KNNLT}-x\text{BNTBT}$ ceramics.

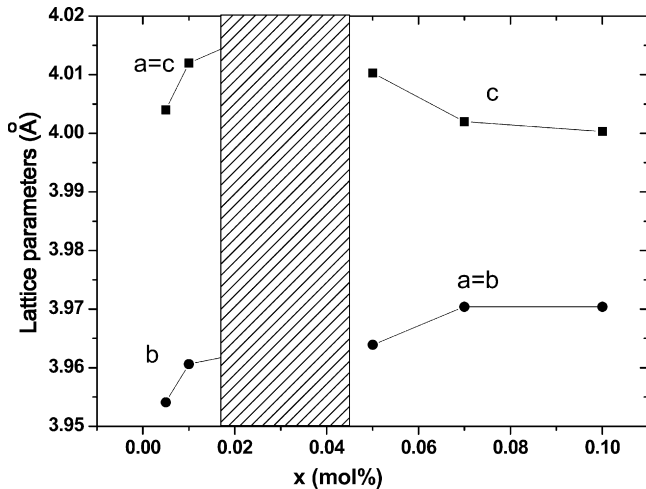


Fig. 3. Lattice parameters of $(1-x)\text{KNNLT}-x\text{BNTBT}$ ceramics.

a polyethylene jar with ZrO_2 balls for 20 h using ethanol as the liquid medium, $0.98\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3-0.02\text{LiTaO}_3$ and $0.96\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3-0.04\text{BaTiO}_3$ were synthesized at 850°C for 5 and 2 h, respectively. After calcination, the two synthesized powders were mixed with different values of x , milled once again, sieved (200 mesh), dried, and granulated by adding polyvinyl butyral (PVB) as a binder. The granulated powders were pressed into disks of 12 mm diameter and 1 mm thickness and then pressed using a cold isostatic pressing (CIP) technique under 200 MPa. These disks were sintered in air at $1090-1130^\circ\text{C}$.

The grain morphology of the samples was observed by means of scanning electron microscopy (SEM, LEO-1530, Germany). The crystal structures of sintered ceramics were determined by an X-ray diffraction technique (XRD) (Rigaku, D/Max3B, Tokyo, Japan). For electrical characterization, samples were polished and painted with silver paste on the sample surfaces. Dielectric behaviors were measured by an HP4192A Precision LCR meter in the temperature range of -40 to 500°C . The frequency used in measurement was 1 kHz. For piezoelectric

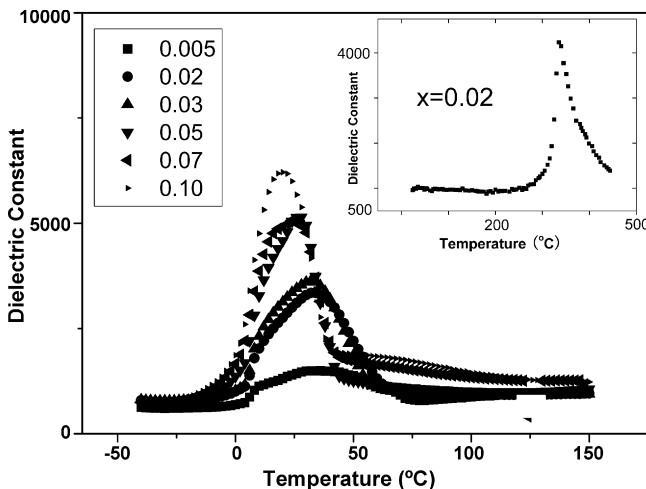


Fig. 4. Dielectric constants at 1 kHz as a function of temperature for $(1-x)\text{KNNLT}-x\text{BNTBT}$ ceramics.

measurements, samples were immersed in silicon oil and polarized in a $2-4\text{-kV/mm}$ field. The electric field was applied at a temperature of 120°C for 30 min. The piezoelectric constant d_{33} was measured using a quasi-static piezoelectric constant testing meter (ZJ-3A, Institute of Acoustics, Chinese Academy of Sciences, Beijing, China). $P-E$ hysteresis loops were observed by a ferroelectric tester (RT6000HVA, Radiant Technologies Inc., Albuquerque, NM). During measurement, the samples were submerged in silicon oil to prevent arcing. Raman spectrum experiments were performed by using a Microscopic Confocal Raman Spectrometer (RM2000, Renishaw, England) equipped with a nitrogen-cooled detector. The excitation source was 633 nm radiation from an argon ion laser.

3. Results and discussion

Fig. 1 shows the SEM photomicrographs of $(1-x)\text{KNNLT}-x\text{BNTBT}$ ceramics. From these figures, we can see that all samples have relatively high density with the average grain size decreasing significantly with the increasing BNTBT composition. The grain size changes from 1 to $2\ \mu\text{m}$ for

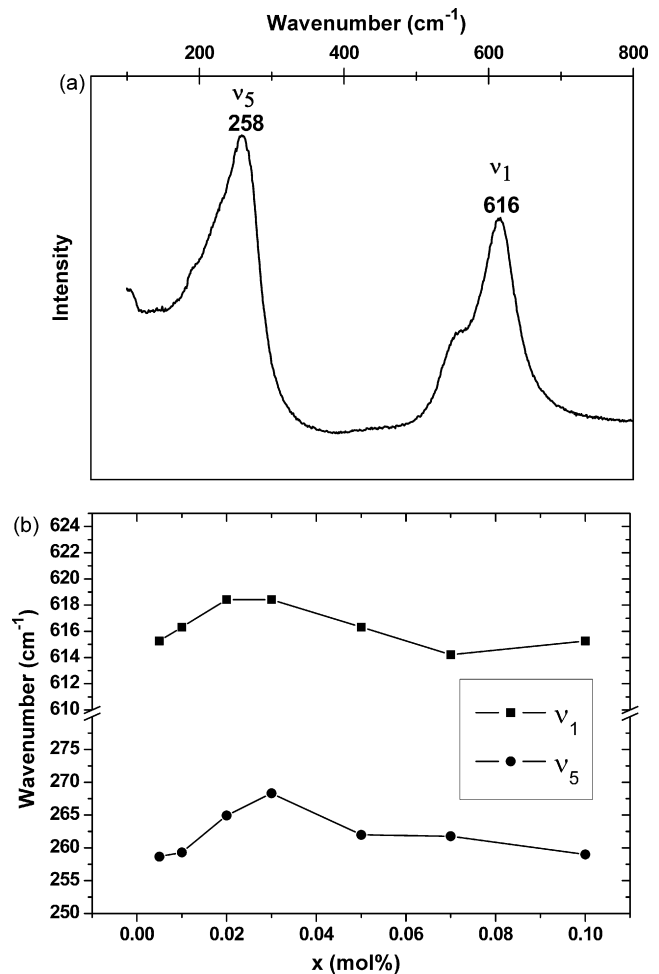


Fig. 5. (a) Raman spectrum of $0.995\text{KNNLT}-0.005\text{BNTBT}$ ceramics for wavenumber with ν_1 and ν_5 modes of the NbO_6 unit between 100 and 800 cm^{-1} . (b) Composition dependence of ν_1 and ν_5 bands of the Raman spectra of $(1-x)\text{KNNLT}-x\text{BNTBT}$ ceramics.

0.995KNNLT–0.005BNTBT samples to about $0.5\ \mu\text{m}$ for 0.90KNNLT–0.10BNTBT samples. We tried different sintering temperatures and sintering times to increase the grain size, but the grain size did not change very much under different sintering conditions. In this range of composition, it seems the addition of BNTBT into the system helps to improve the sintering behavior of KNN ceramics.

Fig. 2 shows the X-ray diffraction patterns of $(1-x)\text{KNNLT}-x\text{BNTBT}$ ceramics. It is clear that a series of continuous solid solutions between KNNLT and BNTBT was formed. At room temperature, crystal structures of all samples are pure perovskite, with no traces of other phases being detected. An orthorhombic symmetry is observed at room temperature when $x \leq 0.01$ and a tetragonal phase appears when $x \geq 0.05$. The (200) peak split into (002) and (200) peaks and the intensities of the two peaks change with the increase of tetragonality. The orthorhombic–tetragonal coexistence is observed in the composition around $0.02 \leq x < 0.05$. The lattice constants of this system as a function of the BNT–BT content are shown in Fig. 3. Because KNNLT solid solutions exhibit orthorhombic structure and BNT–BT solid solutions exhibit rhombohedral structure at room temperature, this coexistence region could not be identified as a typical MPB for $(1-x)\text{KNNLT}-x\text{BNTBT}$ system. According to the concept of MPB, the MPB should separate orthorhombic from rhombohedral (the structure type of 96BNT–4BT) but not

from tetragonal.¹⁸ Therefore, the orthorhombic–tetragonal coexistence is not a real morphotropic phase boundary but a thermodynamics phase transition identified as polymorphism behavior, which is caused by the temperature of the polymorphic phase transition decreasing to around low temperatures. The dielectric constants at the frequency of 1 kHz as a function of temperature for unpolarized samples are shown in Fig. 4. It is well known for pure KNN that two sharp phase transitions are reported at 420 and 200 °C, corresponding to the phase transitions of cubic–tetragonal ($T_{\text{C-T}}$) and tetragonal–orthorhombic ($T_{\text{T-O}}$), respectively.¹⁹ There are two peaks appearing in the graphs, the one at the higher temperature indicating the Curie temperature, which means a phase transition from tetragonal to cubic phase. As shown in Fig. 4, it shows that when $x=0.02$ the Curie temperature is about 340 °C which is lower than that of pure KNN. Another peak, which appears around room temperature, is associated with the T–O phase transition. In addition, we can see that the temperature of T–O phase transition shifts to lower temperature with the increase of BNT–BT content, which is consistent with the XRD results shown in Fig. 2.

Recently, Raman spectrum experiments on KNN-based systems have indicated the vibrations of NbO_6 octahedra to be sensitive to the occurrence of phase transitions.²⁰ In our study, ν_1 represents a double-degenerate symmetric O–Nb–O stretching vibration and ν_5 represents a triply degenerate sym-

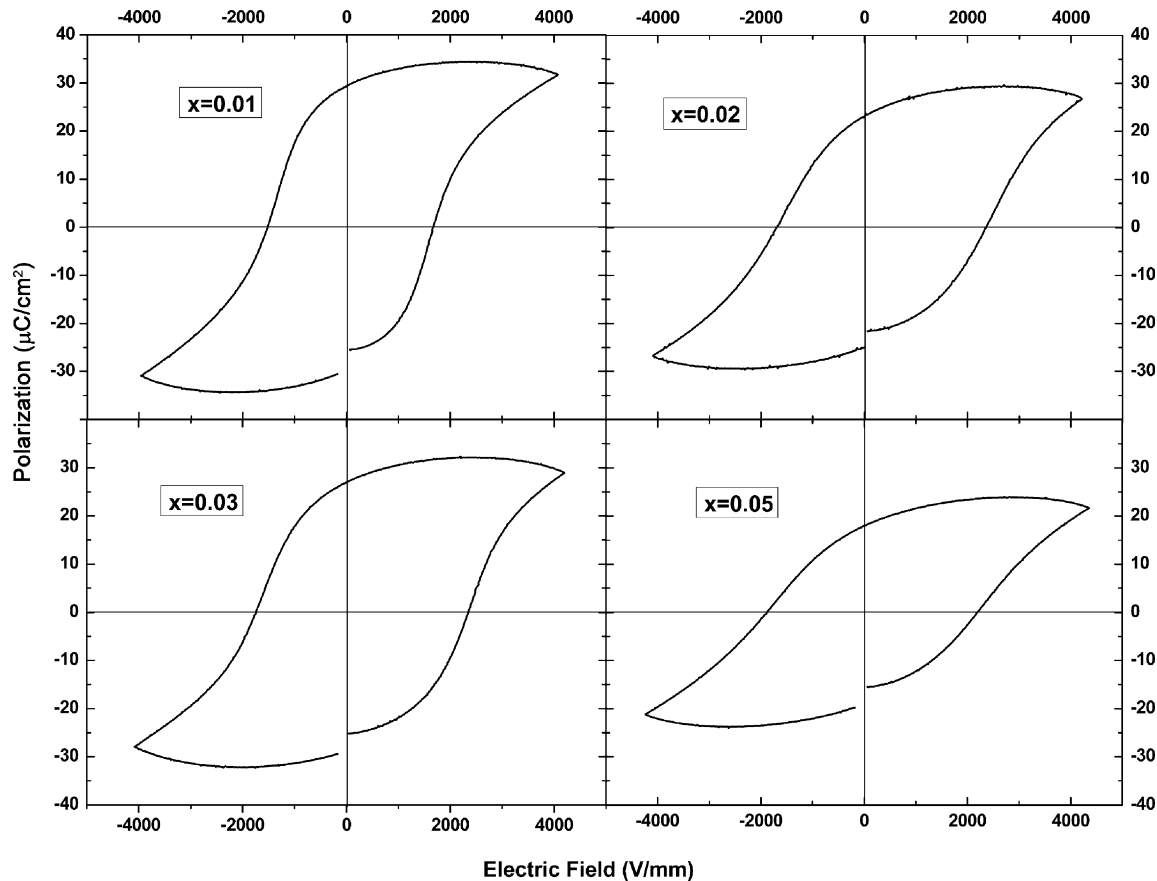


Fig. 6. P – E loops of $(1-x)\text{KNNLT}-x\text{BNTBT}$ ceramics measured at room temperature.

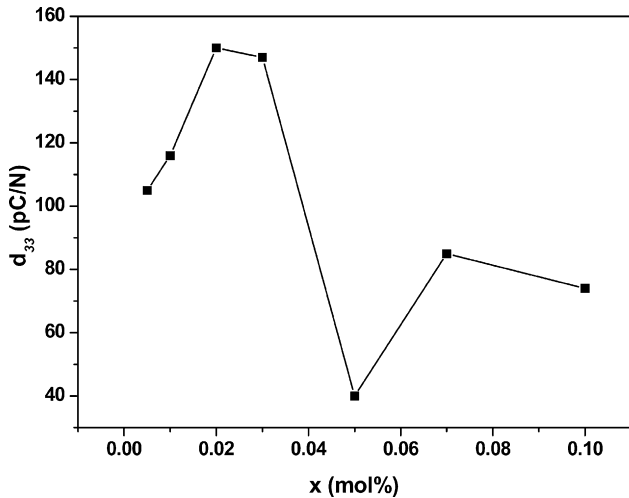


Fig. 7. Piezoelectric constants of $(1-x)$ KNNLT- x BNTBT ceramics as a function of the BNTBT content x .

metric O–Nb–O bending vibration.²¹ In addition, a typical Raman spectrum of a 0.995KNNLT–0.005BNTBT ceramic with orthorhombic symmetry is shown in Fig. 5(a). Fig. 5(b) shows the shift of ν_1 and ν_5 bands of the Raman spectra of $(1-x)$ KNNLT- x BNTBT ceramics with the increase of BNTBT content. When the BNTBT content increases to 3 mol%, the wave number shows a turning point and begins to decrease. The results demonstrate that there are phase transitions happening associated with the increasing BNTBT content. It is further evidence of the existence of PPT around room temperature which has also been proved by XRD and dielectric constant measurements.

Ferroelectric measurements were carried out at a maximum electric field of 4 kV/mm. It can be seen that $(1-x)$ KNNLT- x BNTBT shows a typical ferroelectric polarization hysteresis loop. For $x=2$ mol% ceramics, remnant polarization $P_r \sim 24.2 \mu\text{C}/\text{cm}^2$ and coercive electric field $E_c \sim 2$ kV/mm are observed in Fig. 6, which means that excellent ferroelectricity can be obtained in certain compositions of this system.

Fig. 7 shows the piezoelectric properties of polarized $(1-x)$ KNNLT- x BNTBT ceramics. The best properties of the system exist in the coexistence region with $x=0.02$ and 0.03 . It can be seen that the property exhibits a compositional dependence. Although apparently similar to MPB, it is not surprising that the PPT in other systems also could contribute to high dielectric constant and piezoelectric property.^{2,15}

4. Conclusions

In conclusion, KNN–LT–BNT–BT ceramics were investigated to determine phase transition behavior and electrical properties. The addition of BNTBT to KNNLT shifts the phase transition of T_{C-T} and T_{O-T} to lower temperatures, which contributes to the coexistence of orthorhombic and tetragonal phases at $x=2$ and 3 mol%. The electrical properties exhibit a compositional dependence. The samples showing the coexistence region of polymorphic phase transition (PPT), but not

the behavior of morphotropic phase boundary (MPB), exhibit improved properties, which are as follows: piezoelectric constant $d_{33} = 155$ pC/N, remnant polarization $P_r = 24.2 \mu\text{C}/\text{cm}^2$ and coercive electric field $E_c = 2$ kV/mm. The results indicate that although this kind of ceramics displays good properties, further study is needed to improve their stabilities of the ceramics in order to utilize them in varying temperature environments.

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References

- Jaff, B., Cook, W. R. and Jaffe, H., *Piezoelectric Ceramics*. Academic Press, New York, 1971, pp. 115–181.
- Shrout, T. R. and Zhang, S. J., Lead-free piezoelectric ceramics: alternatives for PZT? *J. Electroceram.*, 2007, **19**, 111–124.
- Fu, H. and Cohen, R. E., Polarization rotation mechanism for ultrahigh electromechanical response in single-crystal piezoelectrics. *Nature*, 2000, **403**, 281–283.
- Guo, Y., Luo, H., Ling, D., Xu, H., He, T. and Yin, Z., The phase transition sequence and the location of the morphotropic phase boundary region in $(1-x)[\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3]-x\text{PbTiO}_3$ single crystal. *J. Phys.: Condens. Matter*, 2003, **15**, L77–L82.
- Smolenskii, G. A., Isupov, V. A., Afranovskaya, A. I. and Krainik, N. N., New ferroelectrics of complex composition. *J. Sov. Phys. Sol. Stat.*, 1960, **2**, 2651–2654.
- Takenaka, T., Maruyama, K. and Sakata, K., $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ – BaTiO_3 system for lead free piezoelectric ceramics. *Jpn. J. Appl. Phys.*, 1991, **30**(9B), 2236–2239.
- Sasaki, A., Chiba, T., Mamiya, Y. and Otsuki, E., Dielectric and piezoelectric properties of $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ – $(\text{Bi}_{0.5}\text{K}_{0.5})\text{TiO}_3$ systems. *Jpn. J. Appl. Phys.*, 1999, **38**, 5564–5567.
- Nagata, H., Yoshida, M., Makiuchi, Y. and Takenana, T., Large piezoelectric constant and high curie temperature of lead-free piezoelectric ceramic ternary system based on bismuth sodium titanate–bismuth potassium titanate barium titanate near the morphotropic phase boundary. *Jpn. J. Appl. Phys.*, 2003, **42**, 7401–7403.
- Xiao, D. Q., Lin, D. M., Zhu, J. G. and Yu, P., Investigation on the design and synthesis of new systems of BNT-based lead-free piezoelectric ceramics. *J. Electroceram.*, 2006, **16**, 71–75.
- Dai, Y. J., Pan, J. S. and Zhang, X. W., Composition range of morphotropic phase boundary and electrical properties of NBT–BT system. *Key Eng. Mater.*, 2007, **336–338**, 206–209.
- Guo, Y. P., Kakimoto, K. and Ohsato, H., Phase transitional behavior and piezoelectric properties of $(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3$ – LiNbO_3 ceramics. *Appl. Phys. Lett.*, 2004, **85**, 4141–4143.
- Matsubara, M., Kikuta, K. and Hirano, S., Piezoelectric properties of $(\text{K}_{0.5}\text{Na}_{0.5})(\text{Nb}_{1-x}\text{Ta}_x)\text{O}_3$ – $\text{K}_{5.4}\text{CuTa}_{10}\text{O}_{29}$ ceramics. *J. Appl. Phys.*, 2005, **97**, 114105.
- Guo, Y. P., Kakimoto, K. and Ohsato, H., $(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3$ – LiNbO_3 lead-free piezoelectric ceramics. *Mater. Lett.*, 2005, **59**, 241–244.
- Matsubara, M., Yamaguchi, T., Sakamoto, W., Kikuta, K., Yogo, T. and Hirano, S. I., Processing and piezoelectric properties of lead-free $(\text{K},\text{Na})(\text{Nb},\text{Ta})\text{O}_3$ ceramics. *J. Am. Ceram. Soc.*, 2005, **88**, 1190–1196.
- Zhang, S. J., Xia, R., Shrout, T. R., Zang, G. Z. and Wang, J. F., Piezoelectric properties in perovskite $0.948\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ – 0.052LiSbO_3 lead-free ceramics. *J. Appl. Phys.*, 2006, **100**, 104108.
- Hollenstein, E., Davis, M., Damjanovic, D. and Setter, N., Piezoelectric properties of Li- and Ta-modified $(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3$ ceramics. *Appl. Phys. Lett.*, 2005, **87**, 3182905.

17. Saito, Y., Takao, H., Tani, T., Nonoyama, T., Takatori, K., Homma, T. *et al.*, Lead-free piezoceramics. *Nature*, 2004, **432**, 84–87.
18. Dai, Y. J., Zhang, X. W. and Zhou, G. Y., Phase transitional behavior in $K_{0.5}Na_{0.5}NbO_3$ – $LiTaO_3$ ceramics. *Appl. Phys. Lett.*, 2007, **90**, 362903.
19. Jaeger, R. E. and Egerton, L., Hot pressing of potassium–sodium niobates. *J. Am. Ceram. Soc.*, 1962, **45**, 209–213.
20. Lima, R. J. C., Paraguassu, W., Freire, P. T. C., Sasaki, J. M., Melo, F. E. A., Mendes Filho, J. *et al.*, Temperature-dependent Raman spectra of $K_{0.2}Na_{0.8}NbO_3$. *J. Raman Spectrosc.*, 2005, **36**, 28–32.
21. Xia, H. R., Chen, H. C., Yu, H., Wang, K. X. and Zhao, B. Y., Vibrational spectra of a $K_{0.30}Na_{0.10}Sr_{0.48}Ba_{0.32}Nb_2O_6$ single crystal studied by Raman and infrared reflectivity spectroscopy. *Phys. Stat. Sol. (b)*, 1998, **210**, 47–59.