Ya-Ting Zhang, Ying Yang*, Yi-Ping Wang and Jing Chen

Properties of $0.96(Bi_{0.5}Na_{0.5})TiO_3$-(0.04-x) $BaTiO_3$-x$LiNbO_3$ Lead-Free Piezoceramics Near Morphotropic Phase Boundary

Abstract: The structure, dielectric and piezoelectric properties of $0.96(Bi_{0.5}Na_{0.5})TiO_3$-$(0.04\text{-}x)BaTiO_3$-$xLiNbO_3$ ($x =$ 0, 0.01, 0.02, 0.03, 0.04) ceramics were investigated by a conventional solid-state reaction method. All compositions show a single perovskite structure without any second phases. It was ascertained that the morphotropic phase boundary (MPB) of ferroelectric rhombohedral and relaxor tetragonal lies in the range of $0.02 \leq x \leq 0.04$ at room temperature. As a result, the MPB compositions show improved properties; the saturated polarization, remnant polarization and coercive field are 43.7 μC/cm^2, 38.7 μC/cm^2 and 48.7 kV/cm for $x = 0.02$ and 43 μC/cm^2, 37.9 μC/cm^2 and 47 kV/cm for $x = 0.03$, respectively. The maximum of piezoelectric constant d_{33} (124pC/N) was obtained for the ceramic with $x = 0.03$, which was located at the MPB region. Our results do not only supplement for BNT-based lead-free piezoelectric ceramics but also provide a way to develop new high-performance Pb-free piezoceramics.

Keywords: piezoelectric properties, morphotropic phase boundary, BNT, lead free

DOI 10.1515/ehs-2014-0057

Introduction

At present, lead zirconate titanate (PZT)-based ceramics are the most widely applied piezoelectric materials due to their excellent piezoelectric properties. However, the evaporation of toxic lead during the fabrication of the ceramics would cause environmental problem. Therefore, there is an increasing interest to develop lead-free piezoelectric materials to replace PZT-based ceramics.

$(Bi_{0.5}Na_{0.5})TiO_3$ (abbreviated as BNT) is considered to be a promising candidate of lead-free piezoelectric ceramics because of its large remnant polarization (P_r = 38μC/cm^2) at room temperature and relatively high Curie temperature (T_c = 320°) (Hagiyev, Ismailzade, and Abiyev 1984; Suchanicz et al. 1988). However, it is difficult to pole for its large coercive field (E_c = 73 kV/cm), which makes its piezoelectric properties much lower than PZT based ceramics. Recently, a number of studies have been carried out to improve the properties of BNT ceramics by introduction other perovskite oxides, such as $BaTiO_3$ (Chu et al. 2002; Qu, Shan, and Song 2005), $(Bi_{1/2}K_{1/2})TiO_3$ (KBT) (Sasaki et al. 1999; Jiang et al. 2006; Yang et al. 2008), $(K_{0.5}Na_{0.5})NbO_3$ (KNN) (Kounga et al. 2008; Zhang et al. 2008), $NaNbO_3$ (Li et al. 2004), $SrTiO_3$ (Zhou, Liu, and Meng 2007) and so on. It has been proved that these modifications on BNT show much better piezoelectric properties and it is easier to handle their poling process compared with pure BNT ceramics.

It is well known that the MPB plays a very important role in PZT-based ceramics because the piezoelectric and dielectric properties show a maximum over a specific compositional range around the MPB. Among BNT-based solid states, the BNT-BT system has rhombohedral–tetragonal MPB in the range of 0.06–0.07 mol BT and reveals relatively high piezoelectric and ferroelectric properties at the composition near the MPB (Takenaka, Maruyama, and Sakata 1991). However, Ba^{2+} entering into A-site of BNT lattice will induce the T_c shifting to lower temperature, which suggested that the materials were not suitable for high-temperature applications. Nevertheless, by doping lithium niobate ($LiNbO_3$) with super high T_c at about 1,210°C(Jaffe, Cook, and Jaffe

---

***Corresponding author: Ying Yang,** State Key Laboratory of Mechanics and Control of Mechanical Structures, Nanjing University of Aeronautics and Astronautics, China, E-mail: yingyang@nuaa.edu.cn
Ya-Ting Zhang, College of Materials Science and Technology, Nanjing University of Aeronautics and Astronautics, China; State Key Laboratory of Mechanics and Control of Mechanical Structures, Nanjing University of Aeronautics and Astronautics, China
Yi-Ping Wang, State Key Laboratory of Mechanics and Control of Mechanical Structures, Nanjing University of Aeronautics and Astronautics, China
Jing Chen, College of Materials Science and Technology, Nanjing University of Aeronautics and Astronautics, China; State Key Laboratory of Mechanics and Control of Mechanical Structures, Nanjing University of Aeronautics and Astronautics, China

1971), the T_c of BNT-BT ceramics will be increased correspondingly. Furthermore, $LiNbO_3$ as one of the ABO_3-type ferroelectrics has been widely used to modify the BNT-based materials (Kim et al. 2011; Kim et al. 2012; Hao et al. 2013). Jin et al. (Kim et al. 2011) reported that the BNT-LN ceramics at the BNT-rich have rhombohedral–tetragonal MPB in the range of 0.03–0.05 mol LN. This work suggests that the MPB will be existed in BNT-BT-LN ceramics at the BNT rich. Usually, the multicomponent system of piezoelectric materials will be effective to improve the piezoelectric properties. Until now, there has been no report about the work on BNT-BT-LN system. In this study, the crystal structures and electric properties of ternary ceramics $0.96(Bi_{0.5}Na_{0.5})TiO_3$-(0.04-$x$)$BaTiO_3$-$x$$LiNbO_3$ system is to be investigated.

Experimental

The $0.96(Bi_{0.5}Na_{0.5})TiO_3$-(0.04-$x$)$BaTiO_3$-$x$$LiNbO_3$ (abbreviated as 0.96BNT-(0.04-x)BT-xLN, with x varying from 0 to 0.04) ceramics were prepared by solid state reaction using Bi_2O_3 (99.99%, Alfa Aesar), Na_2CO_3 (99.5%, Alfa Aesar), Li_2CO_3 (99.0, Alfa Aesar), Nb_2O_5 (99.5%, Alfa Aesar), $BaCO_3$ (99.95%, Alfa Aesar) and TiO_2 (99.9%, Alfa Aesar) as starting raw materials. For each composition, the starting materials were first put in the oven at 120° C for 2 h to dry, then weighed according to the stoichiometric formula and ball-milled for 20 h in ethanol with zirconia balls. The dried slurries were calcined at 800°C for 2 h, and then ball-milled again for 20 h. The powders were subsequently pulverized, mixed with polyvinyl alcohol (PVA) as a binder for granulation, and pressed into green disks with diameters of 13 mm under a pressure of 150 MPa. Sintering was performed at 1,000–1,060°C in covered alumina crucibles for 2 h. To minimize the evaporation of Bi, Na and Li, the samples were embedded in atmospheric powder of the same composition.

Phase structures of the sintered ceramics were characterized by using X-ray diffraction (D8 Advance, Bruker, Germany). Electrical property measurements were done on ground disk-shaped specimens with a thin layer of silver paste as an electrode, fired at 700°C for 10 min. Dielectric permittivity and loss of the poled specimens were measured using an impedance analyzer (Agilent Technologies Japan, Ltd). The dependence of the polarization P on an external electric field E was measured using a ferroelectric test system (Radiant Technologies, INC, Model P-PMF). The piezoelectric constant d_{33} at zero field was determined by using a quasi-static d_{33} meter (Institute of Acoustics, Chinese Academy of Sciences, ZJ-3A) after poling the samples with an electric field of 6 kV/mm for 20 min at room temperature.

Results and Discussion

Crystal Structures

Figure 1(a) shows the XRD patterns of 0.96BNT-(0.04-x)BT-xLN ($0 \leq x \leq 0.04$) piezoceramics in the 2θ range of 20°–60°. All ceramics are crystallized into a pure perovskite phase without any second impurity phases. The X-ray diffraction patterns of these ceramics suggest a phase transition from rhombohedral to tetragonal with increasing x. The rhombohedral symmetry of 0.96BNT-0.04BT at room temperature was characterized by (003)/(021) peaks splitting at around 2θ of 40° and a single peak of (202) at around 2θ of 46.5°, as shown in Figure 1(b) and (c). However, a distinct splitting of the (002)/(200) peaks at around 2θ of 46.5° could be seen when $x \geq 0.02$, corresponding to a tetragonal symmetry. The (003)/(021) peak splitting is obvious until $x = 0.03$, then became weak. It is demonstrated that the MPB of 0.96BNT-(0.04-x)BT-xLN system exists in the composition range of $0.02 \leq x \leq 0.04$ at room temperature, where the rhombohedral and tetragonal phases coexist. In comparison with binary BNT-BT system (Takenaka, Maruyama, and Sakata 1991), the MPB of ternary BNT-BT-LN would move to lower BT amount when the LN content is increasing.

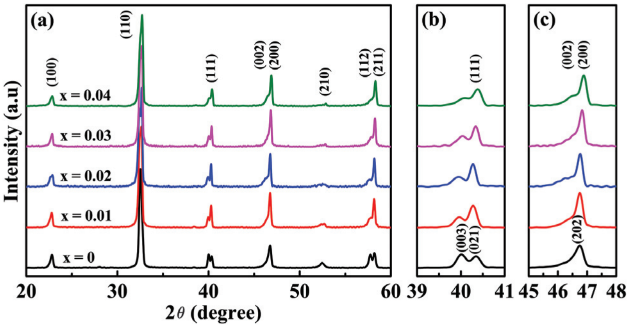

Figure 1: X-ray diffraction (XRD) patterns of 0.96BNT-(0.04-x)-xLN ceramics ($x = 0$–0.04) in the 2θ ranges from (a) 20–60°, (b) 39–41° and (c) 45–48°.

Electric Properties

Figure 2 presents the ferroelectric characteristics of 0.96BNT-(0.04-x)BT-xLN ceramics. It can be seen that the polarization P_s, P_r and coercive field E_c reached the maximum values of 43.7 μC/cm^2, 38.7 μC/cm^2 and 48.7

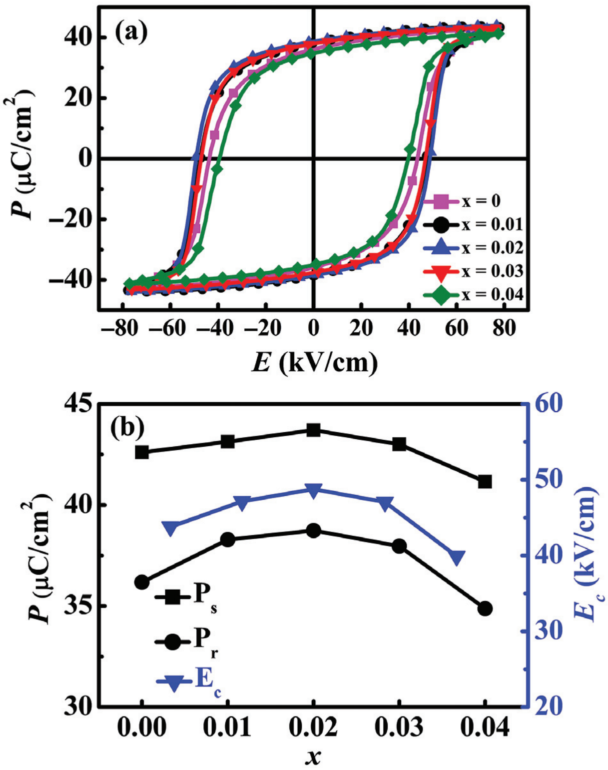

Figure 2: (a) P-E hysteresis loops of 0.96BNT-(0.04-x)BT-xLN system ($x = 0$–0.04) and (b) composition-dependent P_s, P_r, and E_c.

kV/cm at $x = 0.02$, respectively. The saturated polarization P_s, remnant polarization P_r and coercive field E_c vary a lot, and the pronounced difference is near the MPB composition range. For $x \leq 0.02$, the polarization and coercive field increased with the increasing concentration of x. When $x \geq 0.03$, however, the polarization and coercive field decreased rapidly. It is demonstrated that the enhanced ferroelectric properties were obtained near the morphotropic phase boundary (MPB). Although we are known that the coercive field E_c will be decreased near MPB due to the increased number of degrees of freedom of domain orientation (Kounga et al. 2008), the opposite trend occurred. It is because that Bi_2O_3, Na_2CO_3 and Li_2CO_3, which have relatively low melting point, are volatiles at high temperature during the sintering process. Oxygen vacancies would be formed to maintain charge neutrality in the lattice, and they are known to be mobile to pin domain walls (Park and Chadi 1998; Zhang and Whatmore 2003), causing difficulties for domains to be aligned during poling. As a result, coercive field E_c increased in the vicinity of the MPB.

The corresponding piezoelectric constant d_{33} of 0.96BNT-(0.04-x)BT-xLN ceramics was described in Figure 3. The piezoelectric properties of the specimens show strong compositional dependence close to MPB. It is observed that the optimal piezoelectric properties can be obtained at the composition of $x = 0.03$, which exhibits a d_{33} of 124 pC/N, indicating the existence of MPB. Away from this boundary, the properties decrease rapidly as a function of LN content. Although the composition of $x = 0.02$ and 0.04 are located in the area of MPB, the piezoelectric d_{33} of $x = 0.03$ is higher than $x = 0.02$ and 0.04. It is proposed that high remnant polarization and low coercive field are responsible for high piezoelectric properties (Wang, Tang, and Chan 2004), and decreasing coercive field was usually regarded as an important method to modify poling process and improve piezoelectric properties. For $x = 0.03$, the relatively high remnant polarization and lower coercive field were identified as the critical reasons for higher piezoelectric properties than $x = 0.02$ and 0.04. It is noted that the piezoelectric constant d_{33} increased near MPB. However, we have discussed that oxygen vacancies would be formed, and it would cause d_{33} decrease due to the difficulties for domains to be aligned (Sung et al. 2010). This suggests that although E_c could be influenced by oxygen vacancies in the vicinity of MPB, the domain would reorient when the electric field exceeded E_c. In other words, oxygen vacancies induced by chemical inhomogeneity could be overcome as the polarization field is 6 kV/mm, which is larger than E_c (about 4 kV/mm).

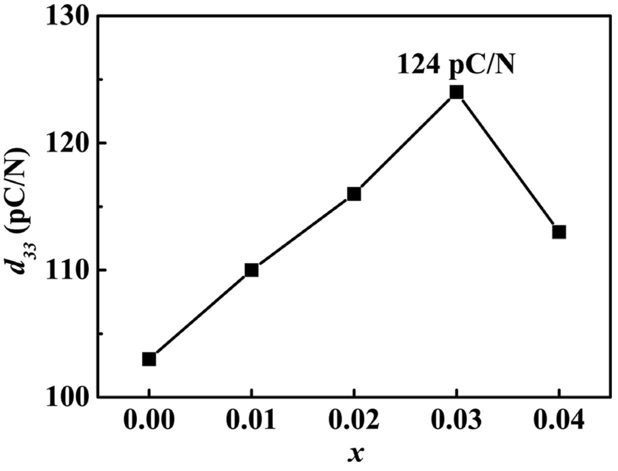

Figure 3: Dependence of piezoelectric constant d_{33} on the composition of 0.96BNT-(0.04-x)BT-xLN ceramics.

Figure 4 shows the relative dielectric constant ε_r and dielectric loss tanδ of the 0.96BNT-(0.04-x)BT-xLN ceramics with $x = 0$–0.04 at room temperature. It can be clearly seen that ε_r increases with increasing LN (x) and reaches the maximum of 674 at $x = 0.03$. Actually, the corresponding increase in ε_r values from $x = 0$ (rhombohedral structure) to $x = 0.03$ (rhombohedral + tetragonal structures) may be mainly due to the presence of

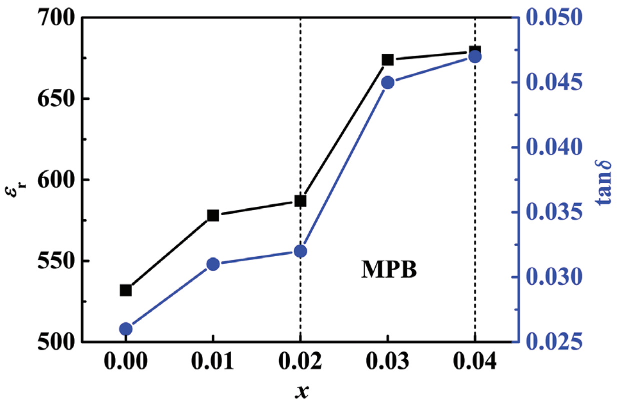

Figure 4: Dependence of dielectric constant ε_r and dielectric loss tanδ on the composition of 0.96BNT-(0.04-x)BT-xLN ceramics.

phase coexistence in the MPB compositions. The similar tendency of the dielectric loss tanδ was also found to increase up to $x = 0.03$, above which it increases slightly with increasing LN content.

Figure 5 provides the temperature dependence of dielectric constant and loss tangent measured for poled 0.96BNT-(0.04-x)BT-xLN samples with x from 0 to 0.04 under 100 Hz to 100 kHz. Two dielectric anomalies are observed for all of the compositions. One is permittivity maximum temperature T_m. The other is located at low temperature defined as ferroelectric to relaxor temperature ($T_{F\text{-}R}$). It is evident that the phase structure has been transferred from ferroelectric rhombohedral to relaxor tetragonal. Although $T_{F\text{-}R}$ had been referred to as depolarization temperature T_d (Hiruma, Nagata, and Takenaka 2009), recent studies by Anton et al. (2011) stated that T_d is determined by thermally stimulated depolarization current (TSDC). When the temperature is beyond $T_{F\text{-}R}$, obvious frequency dispersion remained, which exhibits that external poling field could not set up the long-range-order rhombohedral, and the macrodomains of tetragonal were formed. Apart from T_m and T_d, another characteristic temperature where the frequency dispersion vanished was also found, which is defined as T_{DV} (Wang et al. 2012). However, the permittivity kept rising beyond the Curie temperature for the samples with $x = 0.01$, 0.03 and 0.04 at low frequencies. As known, such permittivity

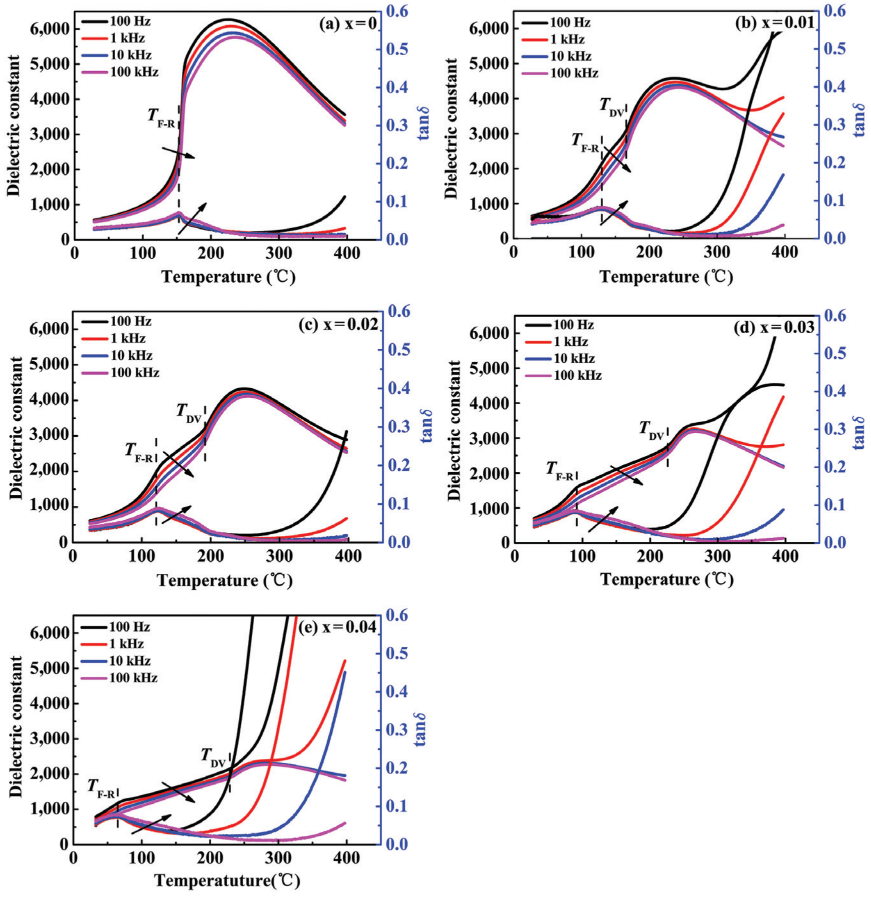

Figure 5: Frequency, composition and temperature dependence of the dielectric properties in poled 0.96BNT-(0.04-x)BT-xLN samples: (a) $x = 0$, (b) $x = 0.01$, (c) $x = 0.02$, (d) $x = 0.03$ and (e) $x = 0.04$.

anomaly is usually attributed to space charges. This kind of space charges existed in many BNT-based ceramics (Zuo et al. 2008; Cernea et al. 2010; Lin and Kwok 2010), which is also severed as charged vacancies. It has been proved that the space charges are produced by A-site deficiency (Zuo et al. 2008). And it could also be existed in the stoichiometric composition as A-site cations volatilize at high temperature. Although the specimens were embedded in atmospheric powder of the same composition, and 0.5% mol Bi was excessed, the evaporated A-site elements happened inevitably.

Based on the above electric data and structure analysis, a schematic phase diagram was provided for poled 0.96BNT-(0.04-x)BT-xLN system shown in Figure 6. It is noted that the transition temperature from ferroelectric rhombohedral to relaxor tetragonal phase ($T_{\text{F-R}}$) decreased with increasing LN content. However, the inverse regulation was observed for frequency dispersion vanished temperature T_{DV}. It is obvious that an MPB was existed near the composition of $x = 0.02$–0.04. Furthermore, the Curie temperature rising up from 228°C to 266°C when the LN content increased from 0 to 0.04. This suggests that this system would be of great interest for high-temperature applications.

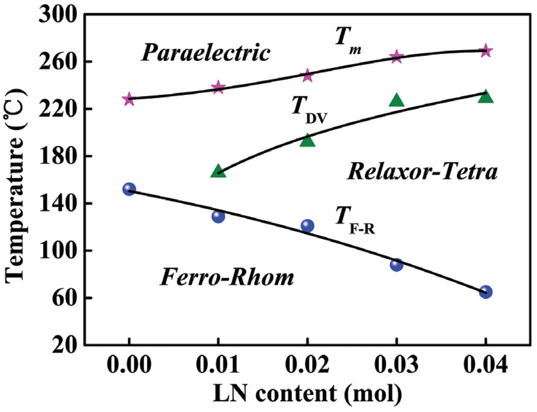

Figure 6: A schematic phase diagram of poled 0.96BNT-(0.04-x)BT-xLN system.

Conclusion

In conclusion, the crystal structure, ferroelectric, piezoelectric and dielectric properties of the ternary $0.96(Bi_{0.5}Na_{0.5})TiO_3$-$(0.04$-$x)BaTiO_3$-$xLiNbO_3$ were investigated and a schematic diagram was constructed. Phase transition from ferroelectric rhombohedral to relaxor tetragonal was observed with increasing LN fraction in the range from 0 to 0.04 mol%, and the MPB lies where the LN amount is near 0.02–0.04. The maximum value of piezoelectric constant d_{33} (124 pC/N) was obtained for the composition of $x = 0.03$ near the MPB region. The saturated polarization, remnant polarization and coercive field are 43 μC/cm^2, 37.9 μC/cm^2 and 47 kV/cm for $x = 0.03$. Dielectric measurement indicates typical relaxation process due to A- and B-site cation mixture.

Acknowledgments: This work was supported by the National Key Project for Basic Research of China (2012CB619406), the 111 project (Grant no. B12021) and NUAA research funding (no. NJ20120012).

References

Anton, E.-M., W. Jo, D. Damjanovic, and J. Rödel. 2011. "Determination of Depolarization Temperature of $(Bi_{1/2}Na_{1/2})TiO_3$-Based Lead-Free Piezoceramics." *Journal of Applied Physics* 110: 094108.

Cernea, M., E. Andronescu, R. Radu, et al. 2010. "Sol-Gel Synthesis and Characterization of $BaTiO_3$-Doped $(Bi_{0.5}Na_{0.5})TiO_3$ Piezoelectric Ceramics." *Journal of Alloys and Compounds* 490: 690–94.

Chu, B.-J., D.-R. Chen, G.-R. Li, et al. 2002. "Electrical Properties of $Na_{1/2}Bi_{1/2}TiO_3$-$BaTiO_3$ Ceramics." *Journal of the European Ceramic Society* 22: 2115–21.

Hagiyev, M., I. Ismailzade, and A. Abiyev. 1984. "Pyroelectric Properties of $(Na_{1/2}bi_{1/2})TiO_3$ Ceramics." *Ferroelectrics* 56: 215–17.

Hao, J., W. Bai, W. Li, et al. 2013. "Phase Transitions, Relaxor Behavior, and Large Strain Response in $LiNbO_3$-Modified $Bi_{0.5}(Na_{0.80}K_{0.20})_{0.5}$ TiO_3 Lead-Free Piezoceramics." *Journal of Applied Physics* 114: 044103.

Hiruma, Y., H. Nagata, and T. Takenaka. 2009. "Thermal Depoling Process and Piezoelectric Properties of Bismuth Sodium Titanate Ceramics." *Journal of Applied Physics* 105: 084112.

Jaffe, B., W. Cook, and H. Jaffe. 1971. *Piezoelectric Ceramics [M]*, 271–80. London: Academic Press.

Jiang, X., L. Li, M. Zeng, et al. 2006. "Dielectric Properties of Mn-Doped $(Na_{0.8}K_{0.2})_{0.5}Bi_{0.5}TiO_3$ Ceramics." *Materials Letters* 60: 1786–90.

Kim, J. S., C. H. Chung, H. S. Lee, et al. 2011. "Dielectric and Ferroelectric Properties of $LiNbO_3$ Doped Lead-Free $Bi_{0.5}Na_{0.5}TiO_3$ (BNT) Ceramics." *Journal of the Korean Physical Society* 58: 659–62.

Kim, J. S., A. Hussain, M. H. Kim, et al. 2012. "Dielectric and Conduction Behaviors of Lead-Free $LiNbO_3$-Modified $Bi_{0.5}Na_{0.5}TiO_3$ Ceramics." *Journal of the Korean Physical Society* 61: 951–5.

Kounga, A. B., S. -T. Zhang, W. Jo, et al. 2008. "Morphotropic Phase Boundary in $(1$-$x)Bi_{0.5}Na_{0.5}TiO_3$-$xK_{0.5}Na_{0.5}NbO_3$ Lead-Free Piezoceramics." *Applied Physics Letters* 92: 222902.

Li, Y. M., W. Chen, J. Zhou, et al. 2004. "Dielectric and Piezoelecrtic Properties of Lead-Free $(Na_{0.5}Bi_{0.5})TiO_3$-$NaNbO_3$ Ceramics." *Materials Science and Engineering B-Solid State Materials for Advanced Technology* 112: 5–9.

Lin, D., and K. Kwok. 2010. "Structure and Electrical Properties of $Bi_{0.5}Na_{0.5}TiO_3$-$Y_{0.5}Na_{0.5}TiO_3$-$BaTiO_3$ Lead-Free Piezoelectric

Ceramics." *Journal of Materials Science: Materials in Electronics* 21: 291–7.

Park, C., and D. Chadi. 1998. "Microscopic Study of Oxygen-Vacancy Defects in Ferroelectric Perovskites." *Physical Review B* 57: R13961.

Qu, Y., D. Shan, and J. Song. 2005. "Effect of A-Site Substitution on Crystal Component and Dielectric Properties in $Bi_{0.5}Na_{0.5}TiO_3$ Ceramics." *Materials Science and Engineering B* 121: 148–51.

Sasaki, A., T. Chiba, Y. Mamiya, et al. 1999. "Dielectric and Piezoelectric Properties of $(Bi_{0.5}Na_{0.5})TiO_3$-$(Bi_{0.5}K_{0.5})TiO_3$ Systems." *Japanese Journal of Applied Physics* 38: 5564.

Suchanicz, J., K. Roleder, A. Kania, et al. 1988. "Electrostrictive Strain and Pyroeffect in the Region of Phase Coexistence in $Na_{0.5}Bi_{0.5}TiO_3$." *Ferroelectrics* 77: 107–10.

Sung, Y., J. Kim, J. Cho, et al. 2010. "Effects of Na Nonstoichiometry in $(Bi_{0.5}Na_{0.5+x})TiO_3$ Ceramics." *Applied Physics Letters* 96: 022901–3.

Takenaka, T., K. -I. Maruyama, and K. Sakata. 1991. "$(Bi_{1/2}Na_{1/2})TiO_3$-$BaTiO_3$ System for Lead-Free Piezoelectric Ceramics." *Japanese Journal of Applied Physics* 30: 2236.

Wang, X., X. Tang, and H. Chan. 2004. "Electromechanical and Ferroelectric Properties of $(Bi_{1/2}Na_{1/2})TiO_3$-$(Bi_{1/2}K_{1/2})TiO_3$-$BaTiO_3$ Lead-Free Piezoelectric Ceramics." *Applied Physics Letters* 85: 91–3.

Wang, F., M. Xu, Y. Tang, et al. 2012. "Large Strain Response in the Ternary $Bi_{0.5}Na_{0.5}TiO_3$-$BaTiO_3$-$SrTiO_3$ Solid Solutions." *Journal of the American Ceramic Society* 95: 1955–9.

Yang, Z. P., B. Liu, L. L. Wei, et al. 2008. "Structure and Electrical Properties of (1-x)$Bi_{0.5}Na_{0.5}TiO_3$-$x$$Bi_{0.5}K_{0.5}TiO_3$ Ceramics Near Morphotropic Phase Boundary." *Materials Research Bulletin* 43: 81–9.

Zhang, S. -T., A. B. Kounga, E. Aulbach, et al. 2008. "Lead-Free Piezoceramics with Giant Strain in the System $Bi_{0.5}Na_{0.5}TiO_3$-$BaTiO_3$-$K_{0.5}Na_{0.5}NbO_3$. I. Structure and Room Temperature Properties." *Journal of Applied Physics* 103: 034107.

Zhang, Q., and R. Whatmore. 2003. "Improved Ferroelectric and Pyroelectric Properties in Mn-Doped Lead Zirconate Titanate Thin Films." *Journal of Applied Physics* 94: 5228–33.

Zhou, R. C., Y. X. Liu, and X. M. Meng. 2007. "Dielectric and Piezoelectric Properties of La_2O_3 Doped $(Bi_{0.5}Na_{0.5})_{0.92}(Ba_{0.8}sr_{0.2})_{0.08}TiO_3$ Lead-Free Piezoelectric Ceramics." *Journal of Electroceramics* 18: 9–12.

Zuo, R., S. Su, Y. Wu, et al. 2008. "Influence of A-Site Nonstoichiometry on Sintering, Microstructure and Electrical Properties of $(Bi_{0.5}Na_{0.5})TiO_3$ Ceramics." *Materials Chemistry and Physics* 110: 311–15.