Phase diagram of $(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3\text{-(Bi}_{0.5}\text{Na}_{0.5})\text{ZrO}_3$ solid solution

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Received 31 January 2016; Revised 18 April 2016; Accepted 19 April 2016; Published 13 June 2016

Phase diagram of $(1-x)\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3\text{-}x(\text{Bi}_{0.5}\text{Na}_{0.5})\text{ZrO}_3$ solid solution has been established from dielectric constant measurements and structure analyses. It is found that with increasing x , the $C\text{-}T$ phase transition temperature T_{C-T} and the $T\text{-}O$ phase transition temperature T_{T-O} decrease, while the $O\text{-}R$ phase transition temperature T_{O-R} increases. T_{T-O} of $\text{NKN-}x\text{BNZ}$ is much different from that of $\text{NKN-}x\text{BZ}$ solid solution. The result could be mainly elucidated by the hybridization between the A-site ion and oxygen.

Keywords: Lead-free; piezoelectric; niobate; phase transition.

1. Introduction

$\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3$ is well known to be a promising base-material for lead-free piezoelectrics and has attracted much attention recent years.¹⁻⁸ The piezoelectric properties of $\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3$ -based piezoelectric solid solutions can be enhanced by controlling the phase transitions to form 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, at room temperature.^{9,10} Thus, to understand how the ion doping (substituting) affects the phase transition temperatures is very important for enhancing the piezoelectric properties of $\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3$ -based piezoelectric solid solutions.

$\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3$ shows orthorhombic structure at room temperature. With changing temperature from high temperature to low temperature, $\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3$ undergoes successive phase transitions: cubic to tetragonal ($C\text{-}T$) at ~ 690 K, tetragonal to orthorhombic ($T\text{-}O$) at ~ 480 K, and orthorhombic to rhombohedral ($O\text{-}R$) at ~ 150 K. Our pervious study shows that, in solid solution $(1-x)(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3\text{-}x\text{SrTiO}_3$, with increasing the SrTiO_3 content x , the $C\text{-}T$ phase transition temperature T_{C-T} , the $T\text{-}O$ phase transition temperature T_{T-O} , and the $O\text{-}R$ phase transition temperature T_{O-R} all shift to lower temperature side.³ And the tetragonal structure could become stable at room temperature. While in solid solution $(1-x)(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3\text{-}y\text{BaZrO}_3$, with increasing the BaZrO_3 content y , T_{C-T} , and T_{T-O} shift to lower temperature side, while T_{O-R} shifts to higher temperature side. That is, by introducing BaZrO_3 to $(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3$, the rhombohedral structure could be tuned to above

room temperature.¹¹ Therefore, the crystal structure of $(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3$ could be tailored by introducing perovskite titanate and/or zirconate into it.

Our further study reveals that in $(1-x)(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3\text{-}x\text{M}_A\text{M}_B\text{O}_3$ solid solution when the B-site ion (M_B) of dopants ($\text{M}_A\text{M}_B\text{O}_3$) is fixed to Ti^{4+} and changes the A-site ion (M_A) of dopants from Ba^{2+} to Sr^{2+} , Ca^{2+} , and $\text{Bi}_{0.5}\text{Li}_{0.5}$, T_{C-T} , T_{T-O} , and T_{O-R} all shift to lower temperature side and the phase diagram is very similar.⁴ And when the M_B is fixed to Zr^{4+} and changes M_A from Ba^{2+} to Sr^{2+} and Ca^{2+} , T_{C-T} , T_{T-O} shift to lower temperature side and T_{O-R} shifts to higher temperature side and the phase diagram is very similar too.¹² It is thus obvious that, the phase diagrams of $(1-x)(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3\text{-}x\text{M}_A\text{M}_B\text{O}_3$ solid solution mainly depend on the B-site ion of the dopant ($\text{M}_A\text{M}_B\text{O}_3$).

Though the increase or decrease of the phase transition temperatures mainly depend on the B-site ions of the dopants, the value of the phase transition temperatures to a great extent is affected by the A-site ions of the dopants. For example, at the same doping level, $(1-x)(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3\text{-}x(\text{Bi}_{0.5}\text{Na}_{0.5})\text{-TiO}_3$ and $(1-x)(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3\text{-}x(\text{Bi}_{0.5}\text{K}_{0.5})\text{-TiO}_3$ solid solutions show higher T_{C-T} and lower T_{T-O} than $(1-x)(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3\text{-}x\text{ATiO}_3$ ($A = \text{Ba}, \text{Sr}, \text{and Ca}$) solid solutions.^{13,14}

In the present study, we try to fix M_B to Zr^{4+} and choose M_A as $\text{Bi}_{0.5}\text{Na}_{0.5}$ to investigate the effects of A-site ion of dopants on the successive phase transition temperatures as well as the dielectric properties by studying the structure and dielectric properties of $(1-x)\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3\text{-}x(\text{Bi}_{0.5}\text{Na}_{0.5})\text{-ZrO}_3$ solid solution.

2. Experimental Procedure

The powder of $(1-x)\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3-x(\text{Bi}_{0.5}\text{Na}_{0.5})\text{ZrO}_3$ (NKN- x BNZ) ($0 \leq x \leq 0.20$) solid solution was made via the conventional solid-state reaction method. Raw materials K_2CO_3 (99.9%), Na_2CO_3 (99.9%), Nb_2O_5 (99.99%), Bi_2O_3 (99.9%), and ZrO_2 (99.9%) were mixed in stoichiometric proportions by a planet ball-miller (P-7, Fritsch) and then calcined at 1000°C until a uniform solid solution has been completely formed. The resultant powder was mixed with PVA binder and then pressed into pellets under uniaxial pressure. The sintering temperature for the pellets changes with x and is in the range of 1100 – 1300°C .

The crystal structure of the sintered samples was identified by powder X-Ray diffraction (XRD, Philips X'Pert X-ray diffractometer) at room temperature. For dielectric measurements, the sintered pellets were ground to a thickness of about 1 mm and then gold was sputtered onto the surfaces to serve as electrode. The temperature-dependent dielectric constant was measured using an LCR meter (Agilent, 4263B) in the temperature range of 300 – 770 K by a custom-made apparatus and an impedance analyzer (Agilent, HP4294A) in the temperature range of 10 – 300 K by PPMS (Quantum Design).

3. Results and Discussion

XRD patterns of the solid solution (Fig. 1) show that all the samples exhibit pure perovskite phase. The diffraction peaks located at 44 – 46.5° , which correspond to the pseudocubic (200) reflection, are magnified in Fig. 1(b). For $x = 0$ sample, two distinct peaks are observed and reveal that the structure is an orthorhombic. With increasing x , the splitting of the peaks decreases and at last for $x \geq 0.08$ samples, the two peaks merge into one symmetric peak, showing that the structure changes to a rhombohedral symmetry.

Figures 2 and 3 show the temperature dependence of dielectric constant (ϵ) at frequency $f = 10$ kHz at temperatures

Fig. 1. (a) X-ray diffraction patterns at room temperature. (b) Pseudocubic (200) reflection peaks for NKN- x BNZ solid solution.

Fig. 2. Dielectric constant versus temperature at frequency $f = 10$ kHz from 300 to 700 K.

above room temperature and below room temperature, respectively. For the NKN-0.03BNZ sample, the peaks corresponding to C-T and T-O phase transitions are sharp and well defined. Contrary to the $x = 0.03$ sample, for samples with $x \geq 0.06$, the peaks are rounding and become broader and broader, a behavior often observed in solid solutions.^{11–17} During forming solid solutions, ionic substitution occurs. In the present study, ionic substitution ($(\text{Bi}_{0.5}\text{Na}_{0.5})^{2+}$ for $(\text{Na}_{0.5}\text{K}_{0.5})^{+}$; Zr^{4+} for Nb^{5+}) introduces size mismatch ($r_{(\text{Na}_{0.5}\text{K}_{0.5})^{+}}(\text{VIII}) = 1.345 \text{ \AA}$ versus $r_{(\text{Bi}_{0.5}\text{Na}_{0.5})^{2+}}(\text{VIII}) = 1.175 \text{ \AA}$; $r_{\text{Nb}^{5+}}(\text{VI}) = 0.64 \text{ \AA}$ versus $r_{\text{Zr}^{4+}}(\text{VI}) = 0.72 \text{ \AA}$) and valence mismatch (Na^{+} , K^{+} , Bi^{3+} in A-site and Nb^{5+} , Zr^{4+} in B-site) among both the A-site ions and B-site ions. Size mismatch could setup random strains and valence mismatch could setup local electric fields, similar to that occurred in

Fig. 3. Dielectric constant versus temperature at frequency $f = 10$ kHz from 10 to 300 K for samples with (a) $x = 0$, (b) $x = 0.03$, and (c) $x = 0.06$.

relaxors.^{18–20} The relaxor state is believed to form because of defects/substituents-induced quenched random fields.^{21,22} For normal ferroelectric phase transition, ionic substitution-induced random fields are not sufficient enough to breakdown the long-range ferroelectric phase transition, but could flatten the sharpness of the transitions.^{23,24} We think the same situation occurs in the present study and the rounding of the C–T phase transition could be attributed to the random electric (elastic) fields introduced by $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{ZrO}_3$ doping.

With increasing x , $T_{\text{C-T}}$, and $T_{\text{T-O}}$ shift to lower temperature side (Fig. 2), while $T_{\text{O-R}}$ shifts to higher temperature side (Fig. 3). The results are in consistent with the crystal structure analysis (Fig. 1).

Phase diagram summarized from dielectric constant measurements and structure analyses is plotted in Fig. 4. For comparison, phase diagram for $(1-x)\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3-x\text{BaZrO}_3$ (NKN- $x\text{BZ}$) solid solution is also plotted (dotted lines). It is evident that the phase diagram for the two solid solutions is rather similar: with increasing x , $T_{\text{C-T}}$, and $T_{\text{T-O}}$ shift to lower temperature side, while $T_{\text{O-R}}$ shifts to higher temperature side. Among the three phase transition temperatures, $T_{\text{O-R}}$ shows little A-site ion dependence, $T_{\text{C-T}}$ shows a moderate A-site ion dependence, while $T_{\text{T-O}}$ shows a much stronger A-site ion dependence.

For the same x , the ferroelectric phase transition temperature $T_{\text{C-T}}$ (Curie temperature) of NKN- $x\text{BNZ}$ is higher than that of NKN- $x\text{BZ}$. BZ is a paraelectric, while BNZ is a ferroelectric with Curie temperature ~ 593 K.¹¹ Therefore, the higher $T_{\text{C-T}}$ of NKN- $x\text{BNZ}$ than that of NKN- $x\text{BZ}$ could be understood according to Vegard's rule.

In the NKN- $x\text{BNZ}$ solid solution, the larger size A-site cation $(\text{Na}_{0.5}\text{K}_{0.5})^+$, $(r_{(\text{Na}_{0.5}\text{K}_{0.5})^+}(\text{VIII}) = 1.345 \text{ \AA})$ is substituted by the smaller size A-site cation $(\text{Bi}_{0.5}\text{Na}_{0.5})^{2+}$ ($r_{(\text{Bi}_{0.5}\text{Na}_{0.5})^{2+}}(\text{VIII}) = 1.175 \text{ \AA}$); and the smaller size B-site

Table 1. The interatomic distances (A–O1, A–O2, B–O1, B–O2), lattice parameters (a, b, c), and the volume of the primitive cell for perovskite (V_p) calculated by the Rietveld refinement (space group: $\text{Amm}2(\text{O})$).

	NKN-3BZ	NKN-3BNZ
A–O1	2.702	2.701
A–O2	2.819	2.810
B–O1	1.874	1.876
B–O2	2.236	2.211
a (Å)	3.966	3.953
b (Å)	5.645	5.629
c (Å)	5.663	5.639
V_p (Å ³)	63.39	62.80

cation Nb^{5+} ($r_{\text{Nb}^{5+}}(\text{VI}) = 0.64 \text{ \AA}$) is substituted by the larger size B-site cation Zr^{4+} ($r_{\text{Zr}^{4+}}(\text{VI}) = 0.72 \text{ \AA}$). That is the average A-site ionic radius decreases and the average B-site ionic radius increases. When x is small, the effects of A-site substitution seems dominate and result in the decrease of the interatomic distances, lattice parameters, and the volume of the primitive cell for perovskite (V_p) (Table 1). For example, V_p is $62.80 \text{ \AA}^3$ for NKN-3BNZ, and $63.11 \text{ \AA}^3$ for pure NKN, respectively. However, in the NKN- $x\text{BZ}$ solid solution, V_p increases with increasing x .¹¹

Previous results for BaTiO_3 ²⁵ and SrTiO_3 ²⁶ show that for the $\text{A}^{2+}\text{B}^{4+}\text{O}_3$ -type perovskite ferroelectrics, a negative physical pressure favors a low-temperature phase. In increasing the volume of the unit cell, introducing BZ to NKN acts in a similar way as negative physical pressure,^{15,16} and the increase of $T_{\text{O-R}}$ could be understood. However, in the NKN- $x\text{BNZ}$ solid solution, V_p decreases, a behavior not in consistent with that under a negative physical pressure, $T_{\text{O-R}}$ increases as well. Combining this result with those for $(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3-x\text{AZrO}_3$ ($\text{A} = \text{Sr}, \text{Ca}$),¹² it seems that the increase or decrease of the $T_{\text{O-R}}$ in $(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3-x\text{AZrO}_3$ ($\text{A} = \text{Ba}, \text{Sr}, \text{Ca}$, and $\text{Bi}_{0.5}\text{Na}_{0.5}$) solid solution mainly depends on the B-site cations and has little relation with the A-site cations.

It is interesting to notice that $T_{\text{T-O}}$ shows strong A-site ion dependence. $T_{\text{T-O}}$ is 386 K for NKN-0.03BNZ and 453 K for NKN-0.03BZ, respectively. The difference is about 90 K.

The solid solutions $(1-x)\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3-x\text{BaZrO}_3$ and $(1-x)\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3-x(\text{Bi}_{0.5}\text{Na}_{0.5})\text{ZrO}_3$ have the same B-site ions. The difference between them is only in A-site, that is Ba^{2+} in $(1-x)\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3-x\text{BaZrO}_3$ is replaced by $(\text{Bi}_{0.5}\text{Na}_{0.5})^{2+}$ in $(1-x)\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3-x(\text{Bi}_{0.5}\text{Na}_{0.5})\text{ZrO}_3$. Thus, the different phase transition temperature for the two solid solutions is closely related to the difference between Ba^{2+} and $(\text{Bi}_{0.5}\text{Na}_{0.5})^{2+}$. In Table 2, the differences between Ba^{2+} and $(\text{Bi}_{0.5}\text{Na}_{0.5})^{2+}$ are listed. Compared to Ba^{2+} which is a single ion, $(\text{Bi}_{0.5}\text{Na}_{0.5})^{2+}$ is a combination of Bi^{3+} and Na^+ , and possesses both valence mismatch (Bi^{3+} , Na^+) and size mismatch ($r_{\text{Bi}^{3+}}(\text{VIII}) = 1.17 \text{ \AA}$; $r_{\text{Na}^+}(\text{VIII}) = 1.18 \text{ \AA}$). Furthermore, Bi^{3+} ion is characterized by the electronic

Fig. 4. Phase diagram of NKN- $x\text{BNZ}$ solid solution (solid lines). For comparison, the phase transition temperatures of NKN- $x\text{BZ}$ (dotted lines) are plotted too.

Table 2. comparison of NKN-xBNZ and NKN-xBZ solid solutions.

	(Bi _{0.5} Na _{0.5}) ²⁺	Ba ²⁺
Valence mismatch	Yes	No
Size mismatch	Yes	No
Electronic configuration	Lone pair (Bi ³⁺ :[Xe]4f ¹⁴ 5d ¹⁰ 6s ²)	No lone pair (Ba ²⁺ :[Xe])

configuration [Xe]4f¹⁴5d¹⁰6s² and 6s lone pair electrons; while the electronic configuration of Ba²⁺ is [Xe] and no lone pair electrons exist. Thus, valence mismatch, size mismatch, and/or the lone pair electrons could be all responsible for the difference of T_{T-O} .

Ferroelectricity are very sensitive to chemistry. PbTiO₃ and BaTiO₃ are ferroelectrics with similar perovskite structure, same B-site ions, but different A-site ions. And they play very different ferroelectric behavior. The ground state is tetragonal for PbTiO₃ and rhombohedral for BaTiO₃, respectively. Besides, the Curie temperature of PbTiO₃ (~763 K) is much higher than that of BaTiO₃ (~400 K). The first principles calculations revealed that the hybridization between the Ti(3d) states and O(2p) states is the origin of the ferroelectric instability for both PbTiO₃ and BaTiO₃.^{27,28} Whereas, because of the existence of the Pb(6s) lone pair electrons, the interaction between Pb(6s) states and O(2p) states is covalent and that between Ba and O is almost ionic for BaTiO₃.²⁹ Cohen pointed out that the different ferroelectric phase behavior of PbTiO₃ and BaTiO₃ rest on the interaction of perovskite A-site ion and oxygen: in PbTiO₃, the lead and oxygen states hybridize, leading to a large strain that stabilizes the tetragonal phase, whereas in BaTiO₃ the interaction between barium and oxygen is completely ionic, favoring a rhombohedral structure.²⁸ The result means that the tetragonal phase of PbTiO₃ is closely related to the Pb(6s) lone pair electrons.

In the present study, T_{T-O} NKN-xBNZ is much lower than that in NKN-xBZ solid solution. That is the tetragonal phase is more stable in NKN-xBNZ than that in NKN-xBZ solid solution. Considering that there are 6s lone pair electrons in NKN-xBNZ and there are not lone pair electrons in NKN-xBZ, we believe that the hybridization of Bi(6s) and O(2p) is responsible for the more stable tetragonal phase in NKN-xBNZ than that in NKN-xBZ.

4. Summary

$(1-x)\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3-x(\text{Bi}_{0.5}\text{Na}_{0.5})\text{ZrO}_3$ solid solution has been prepared using the solid station reaction method. Dielectric constant measurements and powder X-ray diffraction measurement found that with adding BNZ, the C-T phase transition temperature T_{C-T} , the T-O phase transition temperature T_{T-O} shift to lower temperature side, and the O-R phase transition temperature T_{O-R} shifts to higher

temperature side, further confirming that the room temperature structure of $(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3-\text{M}_A\text{M}_B\text{O}_3$ solid solution depends on the B-site cations.

It is considered that the hybridization of Bi(6s) and O(2p) makes the tetragonal phase in NKN-xBNZ more stable than that in NKN-xBZ, thus T_{T-O} in NKN-xBNZ decreases much faster than that in NKN-xBZ solid solution. However, the roles of size mismatch and valence mismatch are still open question and need further research.

Acknowledgments

This work is partially supported by Collaborative Research Project of Materials and Structures Laboratory, Tokyo Institute of Technology.

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