



Orthorhombic to tetragonal structural phase transition in $\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3$ -based ceramics

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ARTICLE INFO

Article history:

Received 12 June 2011

Accepted 30 October 2011

Available online 6 November 2011

Keywords:

Ceramics

Crystal structure

Phase transformation

Piezoelectric materials

X-ray techniques

ABSTRACT

We report the temperature-dependent x-ray powder diffraction of the $\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3$ (NKN)-based piezoelectric ceramics in the range between 320 and 700 K. In the case of NKN we have detected the structural phase transition region from the orthorhombic phase to the tetragonal phase over a broad temperature range from 496 to 458 K. The region is enlarged and shifted to lower temperature by introducing trace impurity or second component. It is considered that the coexistence of orthorhombic and tetragonal phases in NKN-based ceramics observed near room temperature are essentially due to the shift and enlargement of the phase coexistence region induced by lattice chemical pressure.

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1. Introduction

$(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3$ (NKN)-based ceramics have been extensively studied as potential candidates for lead-free piezoelectric materials because of their high piezoelectric properties [1,2]. It is believed that morphotropic phase boundary (MPB), which is nearly vertical in the temperature-composition phase diagram [3,4], plays a very important role because piezoelectric property shows a maximum near the MPB. However, the “MPB” in NKN-based ceramics is very different from that in lead-based ceramics. It is actually an orthorhombic-tetragonal (O–T) polymorphic phase transition (PPT) and shows strong temperature dependence [5–7].

The large number of thermodynamically equivalent states allows a high degree of alignment of ferroelectric dipoles near the PPT, which results in a dramatic enhancement in the electrical properties of NKN-based ceramics [8]. Since the PPT is temperature dependent, many studies concern about designing different composites to turn the O–T phase transition from about 200 °C to room temperature. [9–15] However, the intrinsic drive of the shift of the phase transition region is not clear.

In this letter, we present the results of a temperature dependent X-ray powder diffraction study on the structural phase transition from orthorhombic to tetragonal in NKN-based ceramics. A coexistence of O–T has been found in NKN-based ceramics in the temperature range

from 460 K to 500 K by XRD. The essential reason related to the coexistence of O–T can be interpreted based on lattice chemical pressure.

2. Material and methods

Carbonates and oxides Na_2CO_3 , $\text{K}_2\text{CO}_3 \cdot 1.5\text{H}_2\text{O}$, Nb_2O_5 , Bi_2O_3 , and TiO_2 were used as starting materials. The powders in the stoichiometric ratio of the compositions were mixed thoroughly in ethanol using high-energy ball-milling for 2, 8 and 20 h. After calcined at 850 °C for 2.5 h, the resulting powder was uniaxially pressed into discs of 10 mm in diameter and 2 mm in thickness under 300 MPa and then pressed under 650 MPa with cool isostatic pressing method. These discs were sintered at 1070 °C for 2 h in a sealed alumina crucible in air.

High resolution x-ray diffraction measurements were performed on a highly accurate two-axis diffractometer in a Bragg-Brentano geometry with $\text{Cu-K}\alpha$ wavelength issued from an 18 kW rotating anode generator with diffraction angle precision better than 0.002° (2 θ). The data were collected in a furnace from 320 to 700 K. Selected regions of the diffractogram, containing the (002), (022), and (222) pseudo-cubic reflections, were recorded. Because of complicated peak shapes, a very careful peak-fitting analysis was realized using TOPAS software to find the position of peaks. Electrical characterization was carried out on ceramic discs on which Ag electrodes had been painted. The phase transition temperature was also measured with a Hewlett-Packard 4192A impedance analyzer. Temperature was varied in 2 K intervals between 370 and 800 K along a heating/cooling cycle. The samples were poled in silicon oil at room temperature for 20 min

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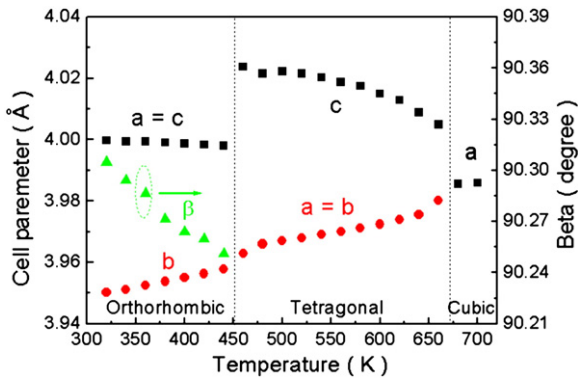


Fig. 1. Temperature dependence of unit cell parameter of NKN powder.

under a dc field of 2.0 kV/mm. The piezoelectric coefficient d_{33} were measured using a quasi-static piezoelectric constant testing meter (ZJ-4A) at 50 Hz. The planar electromechanical coupling coefficients k_p and the mechanical quality factor Q_m were determined by a resonance and antiresonance method according to IEEE standards.

3. Results and discussion

The unit cell parameters of NKN milled 8 h are calculated based on Bragg formula, shown in Fig. 1. The b axis continues to elongate with the increase of temperature. Two skips appear clearly at ~ 450 K and 670 K, corresponding to the phase transitions of orthorhombic-tetragonal and tetragonal-cubic, respectively.

X-ray-diffraction patterns of the pseudocubic Bragg peaks (002), (022) and (222) for NKN milled 8 h at 500 K, 460 K and 400 K, respectively, are shown in Fig. 2. The characteristic Bragg peaks belonging to

tetragonal phase are obtained at 500 K. Similarly, the orthorhombic characteristic Bragg peaks present at 400 K. However, the coexistence of tetragonal and orthorhombic is observed clearly at 460 K. These Bragg peaks are composed of both tetragonal peaks and orthorhombic peaks. This is a powerful proof that the coexistence of tetragonal and orthorhombic can be obtained in a given temperature in pure NKN.

In order to research the range of the narrow coexistence region, the temperature interval 5 K is chosen for NKN milled 8 h from 400 K to 520 K. The positions of Bragg peaks (002) and (022) are shown in Fig. 3a. The orthorhombic Bragg peak (200) disappears at ~ 500 K during heating even though the strong tetragonal Bragg peak (002) presents at ~ 460 K. Similarly, the orthorhombic Bragg peak (200) disappears at ~ 500 K. The temperature range of the coexistence of O-T is about 38 K.

Ahart, et al. [16] found that a phase boundary region can present in a pure material under pressure at low temperature and consequently the polarization can easily rotate between different symmetries. In order to obtain a compression in lattice constant, they applied chemical pressure by substituting a smaller atom with similar polarizability for Pb in the A site in PbTiO_3 . We found this mechanism is also suitable for NKN system. Trace impurities (tungsten and cobalt) were introduced into NKN by prolonging the milling time. The ionic radiuses of tungsten and cobalt are smaller than that of niobium, which leads to the decrease of lattice constant and also makes phase transition temperature shift to low temperature. Fig. 4 shows the cell volume and the temperature of phase transition of orthorhombic to tetragonal (T_{O-T}) dependence of milling time for NKN. Both the cell volume and T_{O-T} of NKN decrease monotonously with the increase in milling time. The $(1-x)\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3-x\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ (NKN-xBNT) solid solution was prepared in order to observe the effect of second component on the O-T phase transition. The phase

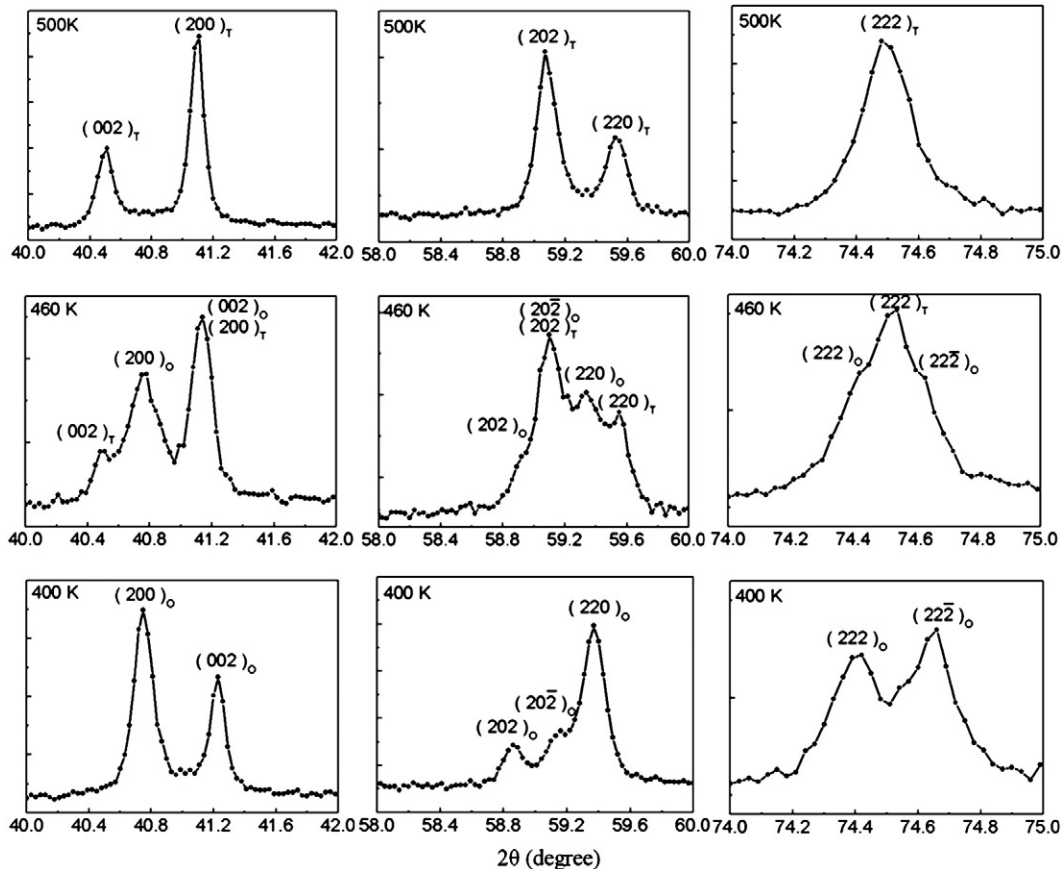


Fig. 2. X-ray-diffraction patterns of the pseudocubic Bragg peaks (002), (022) and (222) for NKN milled 8 h at 500 K, 460 K and 400 K, respectively.

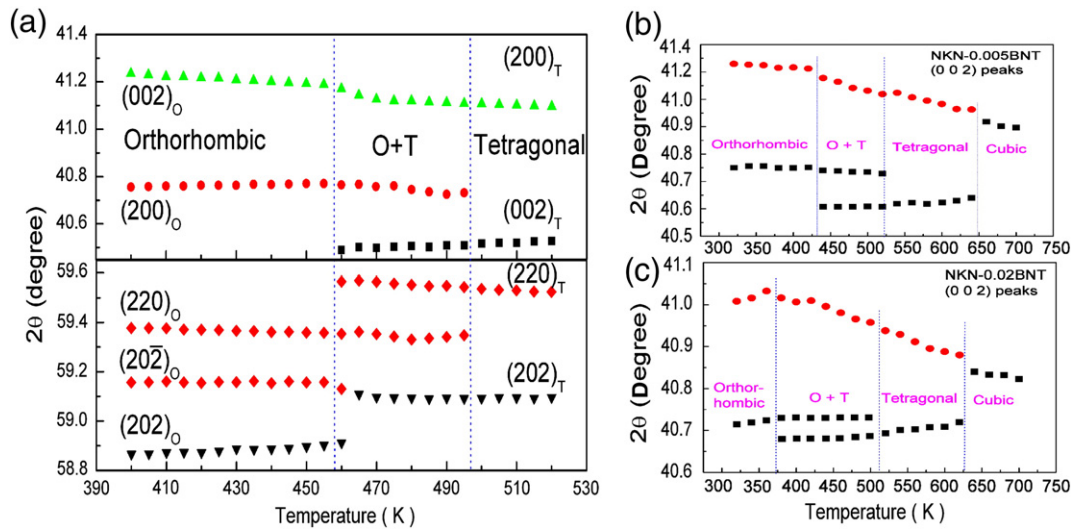


Fig. 3. (a) positions of the pseudocubic Bragg peaks (002) and (022) for NKN milled 8 h near the coexistence of orthorhombic and tetragonal region; (b) positions of the pseudocubic Bragg peaks (002) for NKN-0.005BNT; (c) positions of the pseudocubic Bragg peaks (002) for NKN-0.02BNT.

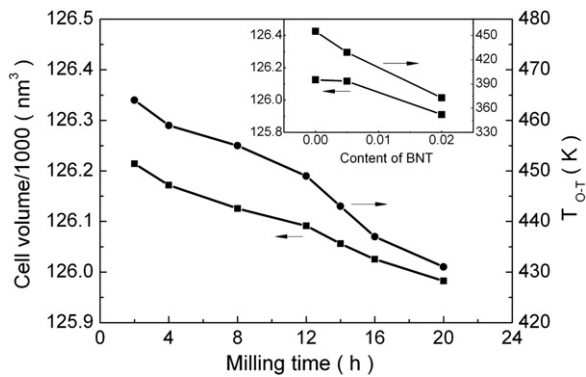


Fig. 4. Cell volume and the temperature of phase transition of orthorhombic to tetragonal (T_{O-T}) dependence of milling time for NKN. Insert, cell volume and T_{O-T} dependence of BNT content for NKN-xBNT.

coexistence regions of NKN-0.005BNT and NKN-0.02BNT can be seen from Figs. 3b and c, respectively. Fig. 4 insert shows the cell volume and T_{O-T} dependence of BNT content for NKN-xBNT solid solution. The similar phenomenon appears in NKN-xBNT, that is to say, the T_{O-T} shifts quickly to lower temperature with the increase of amount of BNT. In addition, the piezoelectric properties of NKN are enhanced by prolonged milling time or introduction of BNT. The piezoelectric coefficients, d_{33} , are 66 pC/N, 72 pC/N, 70 pC/N, 78 pC/N for NKN milled 2 h, NKN milled 8 h, NKN-0.005BNT and NKN-0.02BNT, respectively, while the planar electromechanical coupling coefficients, k_p , were calculated to be 0.29, 0.33, 0.31 and 0.36, respectively. Therefore, the “MPB” of NKN-based ceramics [9–15] should be the phase coexistence region shifting to room temperature. Furthermore, the intrinsic drive of the shift of coexistence of $O-T$ is the lattice chemical pressure.

4. Conclusions

In summary, a phase coexistence of orthorhombic and tetragonal was found in NKN and its solid solution. The coexistence region enlarged and shifted to lower temperature as the second component or smaller ions were introduced. The lattice chemical pressure was responsible for the phase transition characteristic of NKN solid solution.

Acknowledgements

This work was financially supported by the Natural Science Foundation of China (Grant Nos. 51002036, 21061004 and 50962004), and by the Natural Science Foundation of Guangxi (Grant No. C013002) and the Projects of Department of Science and Technology of Guangxi (Grant Nos.0842003 and 09-007-02).

References

- [1] Wang K, Li J. *Adv Funct Mater* 2010;20(12):1924–9.
- [2] Matsubara M, Kikuta K, Hirano S. *J Appl Phys* 2005;97:114105.
- [3] Guo R, Cross LE, Park SE, Noheda B, Cox DE, Shirane G. *Phys Rev Lett* 2000;84:5423–6.
- [4] Noheda B, Gonzalo JA, Cross LE, Guo R, Park SE, Cox DE, et al. *Phys Rev B* 2000;61:8687–95.
- [5] Shrout TR, Zhang SJ. *J Electroceram* 2007;19:111–24.
- [6] Dai Y, Zhang X, Zhou G. *Appl Phys Lett* 2007;90:262903.
- [7] Du HL, Zhou W, Luo F, Zhu D, Qu S, Pei Z. *Appl Phys Lett* 2007;91:202907.
- [8] Wang C, Hou Y, Ge H, Zhu M, Yan H. *J Eur Ceram Soc* 2009;29(12):2589–94.
- [9] Guo Y, Kakimoto K, Ohsato H. *Solid State Comm* 2004;129:279.
- [10] Guo Y, Kakimoto K, Ohsato H. *Jpn J Appl Phys* 2004;43:6662–6.
- [11] Zuo R, Fang X, Ye C. *Appl Phys Lett* 2007;90:092904.
- [12] Zuo R, Fang X, Ye C, Li L. *J Am Ceram Soc* 2007;90:2424.
- [13] Zhang S, Xia R, Shrout TR, Zang G, Wang J. *J Appl Phys* 2006;100:104108.
- [14] Guo YP, Kakimoto K, Ohsato H. *Appl Phys Lett* 2004;85:4121.
- [15] Hollenstein E, Davis M, Damjanovic D, Setter N. *Appl Phys Lett* 2005;87:182905.
- [16] Ahart M, Somayazulu M, Cohen RE, Ganesh P, Dera P, Mao H, et al. *Nature* 2008;451:545 (London).