

Structural phase transitions in KNbO_3 and $\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3$

T Sakakura¹, J Wang¹, N Ishizawa^{1,3}, Y Inagaki² & K Kakimoto²

¹ Ceramics Research Laboratory, Nagoya Institute of Technology, Asahigaoka, Tajimi 507-0071, Japan

² Department of Materials Science and Engineering, Graduate School of Engineering, Nagoya Institute of Technology, Gokiso-Cho, Showa-Ku, Nagoya 466-8555, Japan

E-mail: ishizawa@nitech.ac.jp

Abstract. The *in-situ* high-temperature single-crystal X-ray diffraction experiments on KNbO_3 (KN) and $\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3$ (NKN) revealed a series of structural evolution associated with two transitions among orthorhombic, tetragonal and cubic forms. Upon heating, the pseudocubic unit cell volume collapsed discontinuously at these transition points, whereas the reverse took place upon cooling, indicating that both transitions were of the first-order. The coordination numbers of Nb showed a decreasing tendency with decreasing temperature, i.e., 6 in cubic, 5+1 in tetragonal, and 4+2 in orthorhombic. The difference in ionic size between Na and K gave the Na atom an attribute of rattling in the cavity surrounded by corner-sharing NbO_6 octahedra in NKN. The small Na not only vibrated with large amplitude, but also shifted further from the centre of the cavity than K. The coordination number of Na was always small compared with K at all temperatures, and showed an decreasing tendency upon cooling, i.e., 8+4 in tetragonal and cubic, and 7+5 in orthorhombic. The structural phase transition of KN occurred in a similar way as NKN, though the transition temperatures were shifted slightly toward the high temperature side.

1. Introduction

Potassium niobate, KNbO_3 (KN), and sodium potassium niobate, $\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3$ (NKN), and associated compounds containing various additional elements as dopants, are potential candidates for piezoelectric and ferroelectric applications, not only because of their high performance, but also their lead-free nature [1]. The orthorhombic (O) crystal of KN undergoes a phase transition into a tetragonal (T) form at *ca.* 493K, and becomes paraelectric in a cubic (C) form at *ca.* 707 K [2]. The twinning problem due to ferroelectric domains had left the *in-situ* single-crystal X-ray diffraction study unchallenged for many years. The authors found that departures from cubicity in ferroelectric forms were less significant in NKN than KN, enabling the pseudomerohedral twin analysis at elevated temperatures [3]. The present study was thus undertaken to elucidate the structural phase transitions of NKN for the first time. However, we found that the presence of both Na and K in NKN caused a structural complexity even in the cubic form, which then led us to investigate the twin-free cubic structure of pure KN, paying a special attention to the anharmonic vibration of constituent atoms.

³ To whom any correspondence should be addressed.

2. Experimental

Crystals were grown by the flux method [3, 4]. Single-crystal diffraction experiments were carried out on a CCD diffractometer (Smart Apex II, Mo $K\alpha$, Bruker AXS) with a heating apparatus [5]. A mono-capillary collimator of 300 μm in diameter was used to enhance the diffracted intensities. A preliminary analysis at room temperature indicated that ferroelectric domains were present even in a tiny crystal *ca.* 30 μm in size, because many diffraction spots were faintly split or slightly extended in reciprocal space. The splitting in the NKN crystal was rather incomplete compared with the orthorhombic KN, owing to a small departure from cubicity. This was favorable for the single-crystal analysis assuming the pseudomerohedral twin. Regarding the cell choice of the O form, the present paper follows the one given by Katz & Megaw [6], in which $Bmm2$ is assumed with the polar axis being parallel to c .

An NKN crystal shaped in a sphere of 80 μm in diameter was heated by hot nitrogen gas flowing at the rate of 5 L/min. Diffraction data were first taken at 10, 11 and 7 different temperatures in the O, T and C forms, respectively, during heating the crystal from room temperature to 739 K. Then, further diffraction data were taken at 7, 14 and 6 different temperatures in the C, T, and O forms, respectively, during cooling. Refinements were undertaken, taking into consideration a domain structure composed of coexistent 90° and 180° domains. In all forms, the positional and isotropic atomic displacement parameters of the Na and K atoms were refined independently.

Diffraction data of KN were also taken in a similar way, paying a special attention to the thermal behavior in the cubic form. The least-squares refinement was carried out for the 792 K dataset, utilizing the Gram-Charlier expansion to the 6th order term for thermal motions of constituent atoms. The probability density functions and the effective one-particle potentials of K, Nb and O at 792 K were then calculated from the coefficients of the expansion series.

3. Results and discussion

Typical structures of the O (at 295 K), T (at 474 K) and C structures (at 674 K) on cooling are drawn in figure 1. The polar axis c of the O form is tuned by 45° about b with respect to those in T and C. In the O form, the z coordinates of O1 and O2 show that the oxygen sublattice shifted along the $-c_0$ direction with respect to Nb, which provided a net polarization along $+c_0$. The z coordinates of Na and K show that the Na sublattice shifted along $+c_0$ with respect to the oxygen sublattice further than the Nb sublattice did, whereas the K sublattice shifted the least. The same was true for the T form. These phenomena could be understood as follows: the Na cation in 12-fold coordination has an ionic radius of 1.39 \AA , which is much smaller than the 1.64 \AA radius of the K cation [7]. This discrepancy gave the Na atoms an attribute of rattling in

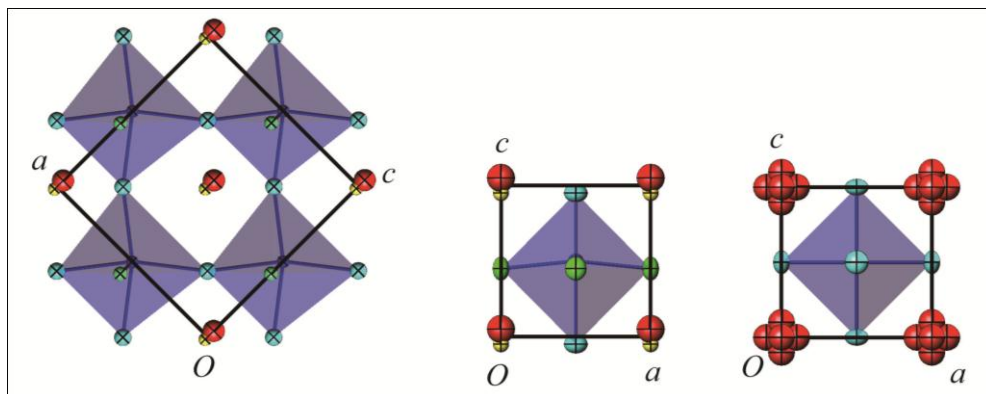


Figure 1. The orthorhombic (left), tetragonal (middle) and cubic (right) NKN structures with Na (red), K (yellow), Nb (dark blue), O (green and pale blue). The ADP ellipsoids are drawn at 75% probability level. Any atom shifts from their ideal positions are exaggerated.

the cavity surrounded by the corner-sharing NbO_6 octahedra. The small Na not only vibrated with large amplitude but also shifted further from the centre of the cavity than K, resulting in a larger contribution to the total polarization in the ferroelectric O and T forms.

In the C form, diffuse scattering was slightly observed running along the three $\langle 100 \rangle^*$ directions of reciprocal space, as shown in figure 2. Difference Fourier synthesis showed a relatively large compilation of residual electrons around the origin which the Na and K atoms were first assumed to occupy randomly as in the ideal perovskite model. A final model was eventually adopted, in which the Na atom was assumed to statistically occupy the Wyckoff 6c positions of the space group $Pm-3m$, whereas the K atom resided at the origin, $1a$.

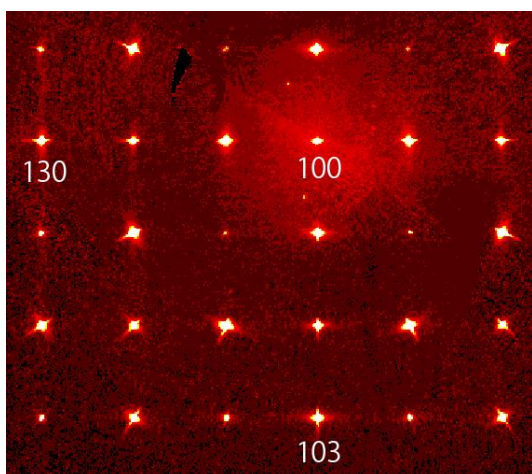


Figure 2. The $(1kl)^*$ reciprocal section of cubic NKN at 792 K, showing diffuse streaks running parallel to $[010]^*$ and $[001]^*$.

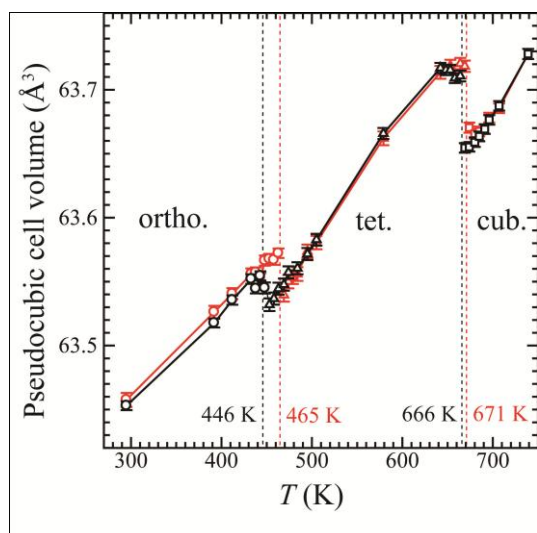


Figure 3. Changes in the pseudocubic cell volume of NKN as a function of temperature. The data points measured upon heating and cooling procedures are connected by red and black lines, respectively. The inset is an enlargement near the O-T/T-O transition.

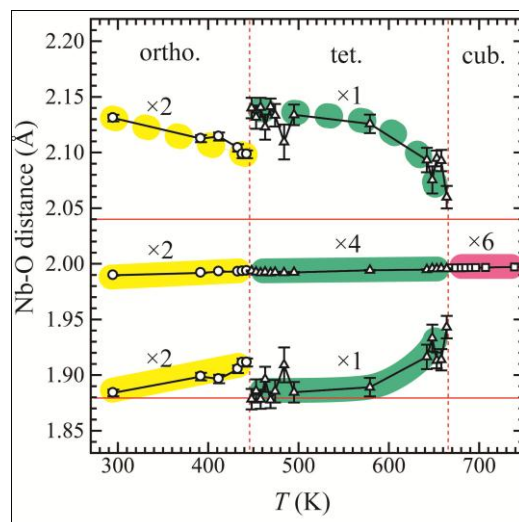


Figure 4. Changes in Nb-O distances in NKN upon cooling as a function of temperature. The upper and lower horizontal lines (red) indicate the sum of ionic radii, $^{VI}\text{Nb}^{5+} + \text{O}^{2-}$ and $^{IV}\text{Nb}^{5+} + \text{O}^{2-}$, respectively. Number of equivalent distances is also indicated.

Changes in the unit cell volume of the O, T, and C forms induced by temperature are shown in figure 3, where the orthorhombic unit cell was reduced into the pseudocubic representation for comparison. The O-T and T-C transitions upon heating were detected at 465 K and 671 K from volumetric discontinuities, respectively. The C-T and T-O transitions upon cooling were detected at 666 K and 446 K, respectively. Disagreement between transition points upon heating and those upon cooling suggested that both transitions were of the first order.

The temperature dependence of the Nb-O interatomic distance is shown in figure 4. Considering the sum of ionic radii, ${}^{\text{VI}}\text{Nb}^{5+} + \text{O}^{2-}$ ($=2.04 \text{ \AA}$), the C-T-O transitions upon cooling could be considered as a series of reductions in the coordination number of Nb (i.e., 6 in cubic, 5 in tetragonal and 4 in orthorhombic, or at the least 5+1 in tetragonal and 4+2 in orthorhombic). If we further speculate the rhombohedral structure at lower temperatures, the coordination number would be 3, or 3+3 at the least. The stepwise change in coordination number for an Nb also reflects the nature of the first order phase transition.

The difference in ionic sizes between Na and K gave the Na atom an attribute of rattling in the cavity surrounded by the corner-sharing NbO_6 octahedra in NKN. In all forms, Na and K occupied different positions with different atomic displacement parameters, resulting in different interatomic distances for Na and K. At all temperatures investigated in three forms, the twelve K-O interatomic distances were less than the sum of ionic radii, $\text{K}^+ + \text{O}^{2-}$ ($=3.04 \text{ \AA}$). On the other hand, the coordination number of Na was always small compared with K in O, T, and C forms, and it had an increasing tendency upon heating, i.e., 7+5 in orthorhombic to 8+4 in T and C. Since the O-T/T-O transition was accompanied by changes in coordination number of both Nb and Na, its transition mechanism was supposedly more complicated than the T-C/C-T transition. In another point of view, this would allow room for tuning the O-T/T-O transition behaviours in practical applications by appropriate doping at the alkaline sites as well as the niobium sites.

The structural phase transition of KN occurred in a similar way as NKN, though the transition temperatures were shifted slightly toward the high temperature side. A strong anharmonic vibrational behaviour of O atoms was observed in cubic KN. The probability density function around O atom at 792 K consisted of central peak at the ideal position accompanied by sub-peaks at both sides along the Nb-O-Nb linear bond, showing a sign of the C-T phase transition. The X-ray diffuse scattering running parallel to the principal axes of the C form, as shown in figure 2, could be ascribed to the one-dimensional instability of the -O-Nb-O-Nb- linear chain with a dynamical perturbation in O atom positions along the chain direction. Further examination is in progress.

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