Local structure analysis of NaNbO$_3$

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Abstract. NaNbO$_3$ has an antiferroelectric structure at room temperature and finds important technological applications. It exhibits an unusual complex sequence of temperature- and pressure-driven structural phase transitions. NaNbO$_3$ shows unambiguous evidence for the presence of the ferroelectric $R3c$ phase coexisting with an antiferroelectric phase ($Pbcm$) over a wide range of temperatures. We have carried out atomic pair-distribution function (PDF) analysis on NaNbO$_3$ to understand the phase transitions. High-energy X-ray PDF using powder samples were carried out at the SPring-8, which is provided to become rhombohedral structure if $A$-site atoms did order and to become orthorhombic structure if $A$-site atoms did disorder.

1. Introduction

Many of antiferroelectric (AFE) crystal has orthorhombic structure. Although the AFE crystal does not show a novel characteristic, it sometimes shows a excellent characteristic by the combination with ferroelectric crystals, like Pb(Zr,Ti)O$_3$ (PZT). PZT, Bi(Mg$_{0.5}$Ti$_{0.5}$)O$_3$ (BMT), and (Li,Na)NbO$_3$ (LNN) have the orthorhombic structure, but the details are not understood still well. The local structure of PZT has been revealed by the neutron pair-distribution function (PDF) analysis [1]. However, the local structure has not been reproduced by any average structure model [2, 3, 4]. NaNbO$_3$ is a well known AFE material with orthorhombic $Pbcm$ structure, but there have been few reports on double hysteresis in this material [5, 6]. There have still a lot of uncertain points of these materials with AFE structure.

Among them, we are specially paying attention to NaNbO$_3$. NaNbO$_3$ shows various ferroelectric properties depending on Li substitution [7]. The structure of NaNbO$_3$ changed to a rhombohedral $R3c$ with increasing the Li substitution for Na. Li$_{0.12}$Na$_{0.88}$NbO$_3$ becomes ferroelectric material and has a large electromechanical coupling [8]. This situation is very similar to LaMnO$_3$. LaMnO$_3$ is a magnetic materials and it shows various magnetic properties depending on oxygen stoichiometry. The stoichiometric LaMnO$_3$ is an antiferromagnetic (AFM) insulator with no local lattice distortion. With increased oxygen deficiency, the local atomic structure becomes distorted and deviates from the average crystallographic structure and shows ferromagnetic (FM) ordering. PDF analysis for the perovskite LaMnO$_3$ clarified the local Jahn-Teller distortion, playing a major role in the magnetic and transport transitions [9, 10].

In this study, the local structure of NaNbO$_3$ crystal was analyzed by the PDF analysis [11] obtained by high-energy synchrotron X-ray powder diffraction. The local structure analysis should be needed in such orthorhombic perovskite system.
2. Experimental

NaNbO₃ ceramics was prepared by a conventional powder processing technique. The starting materials were prepared by mixing high-purity Na₂CO₃ (99.99%), and Nb₂O₅ (99.99%) in appropriate ratios. The powders were mixed and calcined at 1173 K, and then sintered at 1353 - 1523 K in O₂ atmosphere. The phase purity of the ceramics was confirmed by laboratory powder X-ray diffraction, and no impurity phase appeared.

High-energy X-ray powder diffraction data were collected over a wide temperature range by using a closed-cycle helium refrigerator and an electric furnace with 60-keV X-rays at BL04B2 and BL14B1 in SPring-8. The incident X-ray beam was focused on the samples by using a bent crystal [12, 13, 14]. Samples of approximately 0.2 g were sealed between Kapton foils for the low-temperature data correction and were sealed in a quartz tube for the high-temperature data correction. Scattered radiation was collected with an intrinsic germanium detector. Both short- and long-range structural parameters were refined by the PDF method with the program pdffit [15] and by Rietveld refinement with the program RIETAN-FP [16]. The crystal structure was drawn using the program VESTA [17].

3. Results and discussion

Pure NaNbO₃ has an AFE structure at room temperature and exhibits an unusual complex sequence of temperature driven structural phase transitions. Above 913 K, NaNbO₃ has a paraelectric cubic structure with the space group of Pm₃m. At 848 K, tetragonal P4/mmb structure appeared, then, AFE phase with the orthorhombic Pbcm structure appeared at 633 K, and finally, ferroelectric phase with rhombohedral R3c structure appeared at 173 K. We obtained the X-ray diffraction profiles of the cubic, tetragonal, orthorhombic, and rhombohedral phases as shown in Fig. 1. The diffraction data of four phases can be indexed unambiguously and sufficiently satisfactory fits were obtained in all phases. The temperature dependence of the refined lattice parameters are shown in Fig. 2.

![Figure 1](image-url)

Figure 1. (Color online) Result of Rietveld refinement of NaNbO₃ in (a) cubic phase at 1023 K, (b) tetragonal phase at 723 K, (c) orthorhombic phase at 300 K, and (d) rhombohedral phase at 5 K.
Figure 2. (Color online) Temperature dependence of lattice parameters refined by Rietveld analysis.

Figure 3. (Color online) Temperature evolution of Bragg reflections of NaNbO$_3$.

Figure 3 shows the evolution of powder X-ray diffraction profiles of NaNbO$_3$ with temperature in the range of 5 – 1023 K. The AFE phase consists of two or more sublattice polarizations of antiparallel nature, which give rise to superlattice reflections in the diffraction patterns. We have observed such reflection in the AFE phase, which appeared at 4.75°, as shown by arrows in Fig. 3. From the knowledge of the Miller indexes of the superlattice reflections and lattice type of the structure, as revealed by the splitting of main Bragg peaks, one can find a signature of the presence of structural phase transition. Additionally, an anomalous peak broadening was observed when the rhombohedral – orthorhombic phase transition occurred at 200 K. Below 100 K, the width of Bragg peaks were sharper than those observed above 200 K. Although all the diffraction data were collected with the same resolution, the width of Bragg peaks broadened drastically at 200 K. The crystal structure not only changed, but coherent size also changed owing to its disordered feature. In such cases, the conventional structure analysis with assuming a periodic structure is difficult to clarify the disordered structure. Unlike the conventional crystallographic analysis, lattice periodicity is not assumed in the PDF analysis. Hence it is possible to detect nonuniform atomic displacements those are not directly observed by standard crystallographic techniques. In system with which rhombohedral structure and orthorhombic structure compete, PDF analysis is effective similar to LaMnO$_3$. We performed PDF analysis on NaNbO$_3$ to clarify the phase transition mechanism.

Temperature evolution of the PDF for NaNbO$_3$ is shown in Fig. 4(a). The PDF peak lying at 2 Å seems to be singlet shape at 300 K. The doublet feature appeared at 200 K, and finally clear split peaks observed down to 5 K. A clear evidence of an order – disorder type phase transition was found in the local structure. We attempted to reproduce the experimental PDF by introducing the local displacement of Nb atoms. The calculated PDF is good agreement with the experimental PDF, as shown in Fig. 4(b). We refined the observed PDF obtained at all the temperature and could reproduce the order-disorder phase transition. Since the rattling space of NbO$_6$ octahedra of NaNbO$_3$ is too small to extract from the average structure analysis, the change of the atomic coordination in the rhombohedral and the orthorhombic phases is small, as shown in Fig. 5. In the low temperature ordered phase, the Nb atoms shifted from the average atomic coordination, and the local shift of Nb atoms caused the change of the rattling space, and thus, the order – disorder phase transition occurred at 200 K.
Figure 4. (Color online) (a) Temperature evolution of experimental PDF of NaNbO$_3$. (b) Result of PDF refinement of NaNbO$_3$ in rhombohedral phase at 5 K.

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Figure 5. (Color online) Crystal structures of rhombohedral (below 200 K) and orthorhombic (above 200 K) phases in NaNbO$_3$. Rhombohedral and orthorhombic unit cells are also drawn. Atomic coordination of these phases are similar.