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Featured Letter

Monoclinic ferroelectric NaNbO₃ at room temperature: Crystal structure solved by using super high resolution neutron powder diffraction

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ABSTRACT

The crystal structure of NaNbO₃ at ambient temperature was solved using time-off-flight neutron data obtained from Super High Resolution Neutron Powder Diffractometer in J-PARC. The solved structure was a novel monoclinic type with the space group Pm and lattice parameters of $a = 5.50453(1)$, $b = 15.52975(3)$, $c = 5.56779(1)$ Å, and $\beta = 90.0645(2)°$. Bond valence calculation indicates that the solved structure is chemically valid. This solved structure corresponds with the observed ferroelectric behaviors ($P_s = 11$–$25\ \mu C/cm^2$, $S = 0.03$–0.04%). The calculated P_s ($\sim 21\ \mu C/cm^2$) using the refined atomic parameters for one-quarter unit cell conform well to the observed value. Cooperative NbO₆ octahedral tilting accompanied by the phase transition from the parent structure $Pcmb$ to the Pm mainly contributes to the spontaneous polarization.

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1. Introduction

Although NaNbO₃ has been studied for several decades, both the crystal structure and electric properties are not completely understood [1–3]. This material has attracted considerable interest because it provides not only a matrix phase for various lead-free piezoelectric materials, such as (Ag, Na, K)NbO₃ [4] and (Li, Na)(Nb, Ta)O₃ [5], but also has potential applications in piezoelectric nanodevices [6]. The actual structure of NaNbO₃ has been a long standing issue because its observed electric properties do not conform to the generally known orthorhombic structure. Previous studies reported contradictory results on the electric properties at room temperature: antiferroelectricity [7], ferroelectricictiy [8,9], and field-induced ferroelectricity [10].

The crystal structure of NaNbO₃ at room temperature (RT) is generally believed to be an orthorhombic with the space group $Pbma$ ($a \approx 5.56$, $b \approx 15.3$ and $c \approx 5.50$ Å) [11], which is nominally known as an antiferroelectric phase. As discussed in our previous report [12], from a crystallographic point of view, this $Pbma$ structure belongs to the centrosymmetric crystal class, mmm. This crystal class can be neither antiferroelectric nor ferroelectric due

to the presence of inversion center, i.e., the antiparallel dipole moments produced by the ion displacement are completely canceled out within the unit cell. According to the definition of antiferroelectricity by Kittel [13], two sublattices polarize in opposite directions form a centrosymmetric structure. However, none of the antiferroelectric crystals satisfy Kittel's criterion of centric symmetry. For example, well-known antiferroelectrics, PbZrO₃, (Bi, Na)TiO₃, AgNbO₃, and PbHfO₃, have been determined to be non-centrosymmetric [14,15]. Therefore, it is quite interesting that NaNbO₃ with the centrosymmetric structure $Pbma$ has been reported to be antiferroelectric or ferroelectric.

Interestingly, a few recent studies reported that the actual crystal structure could have lower symmetry than the centrosymmetric $Pbma$ at RT [16–18]. For example, Yuzyuk et al. [16] performed an extensive Raman study on a single crystal NaNbO₃. They suggested that the $Pbma$ region at the temperature range of 250–633 K actually consisted of three phase regions: monoclinic (250–410 K), incommensurate (INC, 410–460 K), and nominally known $Pbma$ (460–633 K). The formation of the INC and monoclinic phases was attributed to the further rotation of the NbO₆ octahedra from $Pbma$. Johnston et al. [3] recently reported that the NaNbO₃ prepared using sol–gel method was comprised of a mixture of two different polymorphs, i.e., the well-known orthorhombic phase ($Pbma$) and the polar orthorhombic phase $P2_1ma$.

This polar structure $P2_1ma$ had also been observed in NaNbO₃ prepared under a few special conditions, such as Li-doping [12], a single crystal under an applied electric field [19], and submicron-sized powder synthesis [2].

Li-doping in NaNbO₃ expedited the phase transition to the polar orthorhombic phase ($P2_1ma$) and enhanced ferroelectric properties at $0.04 \leq x \leq 0.10$ [12]. Very interestingly, this $P2_1ma$ phase underwent an extensive phase transition to rhombohedral ($R3c$) with applying external mechanical stress. Moreover, it showed the reverse phase transition to the $P2_1ma$ from the $R3c$ by thermal annealing at as low as 300 °C. This peculiar behavior of NaNbO₃ was considered to originate from the unusually smaller ion size of Na⁺ compared to the Na–O polyhedral cage and that the Na⁺ off-centering could have multiple energy-minimum positions including equilibrium and meta-stable states [12].

To understand why the reported electric properties of NaNbO₃ is contradictory to its nominally known crystal structure, we carried out precise structural analysis work by using time-off-flight (TOF) neutron data obtained from Super High Resolution Powder Diffractometer (SuperHRPD) with its best resolution $\Delta d/d = 3.5 \times 10^{-4}$ in J-PARC (Japan Proton Accelerator Research Complex). The high resolution and large accessible range of d-spacings in a TOF diffractometer allow for a structural determination with both high precision (i.e. small e.s.d.'s) and high accuracy (i.e., agreement with the physically correct structure) because it provides for greater peak separation; hence, greater accuracy in determining the intensities of the overlapped peaks [20].

Since external stress may induce structural modification to the NaNbO₃ the sample for structural analysis was prepared in two ways: sintered-pellet and its powdered form obtained by grinding in a mortar. The crystal structure could be determined unambiguously to be monoclinic with the space group Pm ($a \approx 5.5045$, $b \approx 15.5297$, $c \approx 5.5678$ Å, and $\beta \approx 90.065°$). This model Pm could be deduced after assessing various potential structural models including the well-known $Pbma$, the structural subgroups of the $Pbma$, and the structure symmetry generated by applying group-theoretical methods by Stokes et al. [21] To prove feasibility of this solved structure bond valence calculation, P(S)-E loop measurement, and the calculation of spontaneous polarization using the atomic displacements of the Pm from the parent structure $Pcmb$ have been carried out in this study.

2. Experimental details

For the neutron measurement the stoichiometric NaNbO₃ (Na/Nb=1.0) was prepared using a solid state reaction method. The mixture of Na₂CO₃ (99.99%) and Nb₂O₅ (99.99%) was calcined at 1173 K for 4 h in air. The calcined powder was ground and pressed into pellets, 9 mm in diameter and 10 mm in height. The pressed pellets were sintered at 1573 K for 2 h in an alumina crucible covered with a lid. The crucible was filled with an atmosphere powder with the same composition to inhibit Na-evaporation. The neutron data was collected from both the sintered pellet and its powder-form sample obtained by pulverizing it. For the P–E (polarization–electric field) and S–E (electric field–induced strain) loop measurements, stoichiometric (Na/Nb=1.0) and Na-excess (Na/Nb=1.01) samples were prepared. The calcined powders were cold pressed isostatically into disks, 9 mm in diameter and 1.5 mm in thickness. The pressed pellets were embedded in the NaNbO₃ atmosphere powder inside an alumina crucible with a lid and sintered at temperatures of 1603–1623 K for 3 h in air. The P–E and S–E loops were measured simultaneously at RT using a Precision LC Ferroelectric Tester equipped with a MTI2100 photonic sensor and a high voltage source of 10 kV.

The neutron powder diffraction data was collected at RT from the SuperHRPD installed on the pulsed spallation neutron source of J-PARC. The data was collected by detectors of the back scattering bank to achieve a higher resolution. The back scattering bank covers a 2θ range, 150–175°, corresponding to d-spacing range, 0.3–4.0 Å. The best resolution of $\Delta d/d = 3.5 \times 10^{-4}$ was achieved at 2θ=172°. In this study, all the signals of the bank were focused on 172° using the time focusing method. Data was collected twice using the same sample to check the reproducibility. The diffraction data was analyzed by the Rietveld refinement using the Z-Rietveld program in a software suit, Z-Code [22,23]. The XRD data was also collected using a general purpose X-ray diffractometer and analyzed by the Rietveld refinement using Rietan 2000, and the electron density map was calculated by the maximum entropy method (MEM) implanted in the software suit, VENUS.
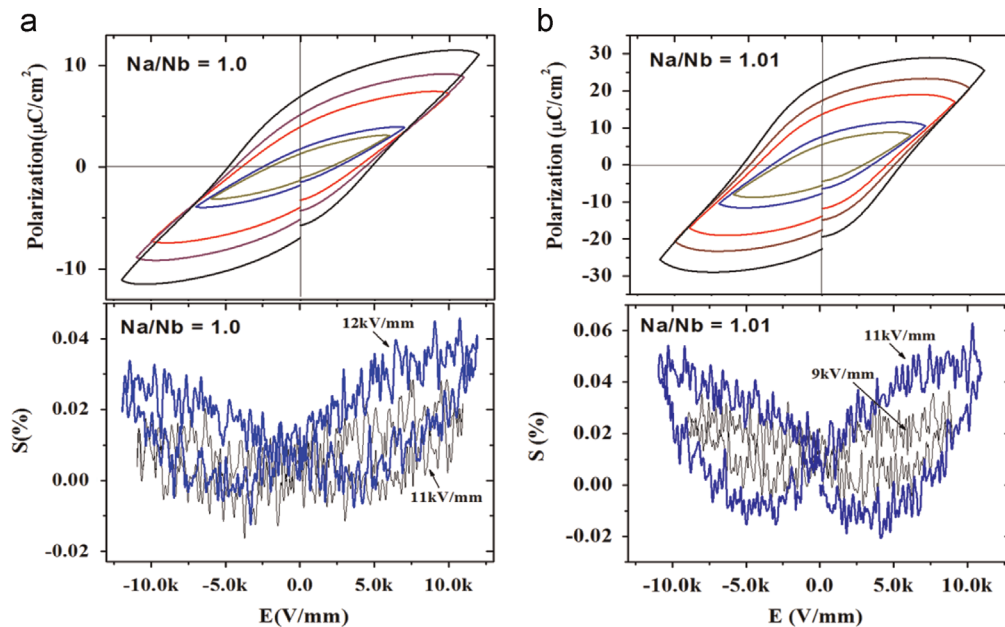

Fig. 1. P–E and S–E hysteresis loops for the Na/Nb=1.0 (a) and 1.01 (b) samples.