Effect of Bi non-stoichiometry on the crystallographic structure of $Na_{1/2}Bi_{1/2}TiO_3$

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Recently, there has been considerable interest in developing high energy density solid-state energy storage systems, where $Na_{1/2}Bi_{1/2}TiO_3$-based materials have also received significant interest for the exceptional large-field electromechanical response. In addition, nonstoichiometric NBT has been reported to be an excellent oxygen-ion conductor. As such, NBT has gained significant interest as the potential new materials for solid-oxide fuel cells and oxygen separation membranes. In this contribution, the effect of Bi non-stoichiometry on the crystal structure has been investigated. Bi non-stoichiometric $Na_{0.5}Bi_xTiO_{3-y}$ ceramics with x = 0.485–0.51 were prepared by a conventional solid-state reaction method. The chemical analysis of the 4 sintered samples were performed using ICP-OES. The effects of Bi non-stoichiometry on structural transition and ferroelectric stability of NBT ceramics were systematically investigated by the Neutron diffraction at room temperature (RT), *in situ* high-temperature X-ray diffraction (HTK-XRD up to 560 °C, see Fig. 1), dielectric analyses, and electromechanical measurements. For all compositions, the room temperature structure was found to be rhombohedral $R3c$ without secondary phases. Whereas at 250 °C and 500 °C, tetragonal $P4bm$ phase and cubic $Pm\bar{3}m$ were observed, respectively. These results are consistent with previous reports. [1-3] In this study, the temperature-dependent phase transition of nonstoichiometric NBT is presented. The changes in the tilt angle (ω) and octahedral strain (ξ) were calculated from distortion parameters after Megaw and Darlington [4]. An in-depth analysis of the temperature-dependent data shows that the Bi-nonstoichiometry does not alter the average crystallographic structure and phase transition temperatures of the investigated compositions.

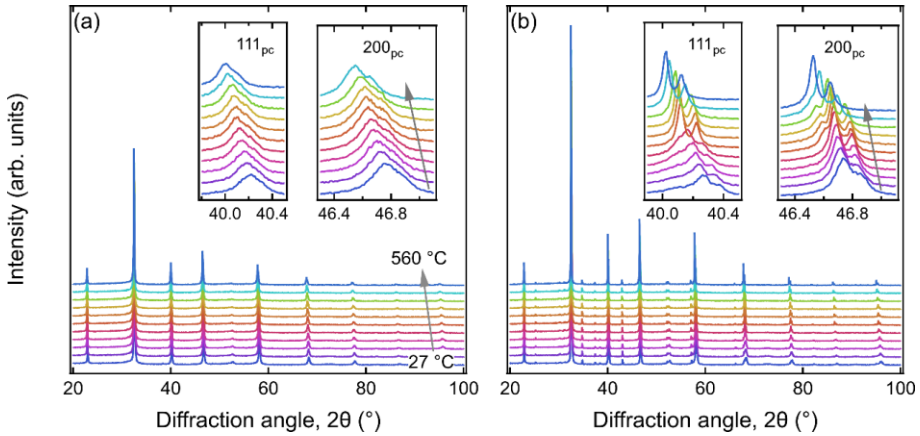

Figure 1. Temperature-dependent XRD data of (a) powder and (b) bulk $NB_{0.51}T$ from 27 °C (lowest data set) to 560 °C (top data set).

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Keywords: Ferroelectrics; $Na_{0.5}Bi_{0.5}TiO_3$; *in situ* HTK-XRD; Perovskite.