Nanoscopic look at the lead-free $(Bi_{1/2}Na_{1/2})TiO_3$-$BaTiO_3$ piezoelectric ceramics

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Abstract. The (1-x)$(Na_{0.5}Bi_{0.5})TiO_3$–x$BaTiO_3$ system (BNBT100x) is intensively studied as a candidate for lead-free ferroelectrics. BNBT6 ceramics, obtained by the self-combustion sol-gel method, hot pressing and recrystallization, were studied by synchrotron radiation and electron microscope techniques. Rietveld analysis of the XRD patterns provided the parameters of the coexisting crystalline structures as (globally) Pm3m and rhombohedral R3c phases for unpoled and poled samples. Both symmetries have been observed at the HRTEM as well. Permanent polarization of the cell structures for powder and ceramic samples has been confirmed by X-ray absorption near edge structure.

Key words: Synchrotron radiation techniques, High-resolution transmision electron microscopy, Lead-free piezoelectric ceramics.

Currently, the (1-x)$(Na_{0.5}Bi_{0.5})TiO_3$–x$BaTiO_3$ system (BNBT100x), is considered one of the best candidates for lead-free ferroelectrics in actuator applications and it is intensively studied. In these ceramics, the Ti-cation off-centering is the result of the hybridized chemical bond between the titanium d and the octahedral oxygen 2p orbitals. This effect is superposed to the stereochemical activity of the Bi3+ cations. The resulting effect is the observed asymmetric coordination environment with the oxygen 2p orbitals, leading to ferroelectricity.

In our work BNBT6 ceramics were obtained by the self-combustion sol-gel method, hot pressing at 800 ° C + recrystallization at 1000 - 1050 ° C. X-ray experiments have been performed at the Stanford Synchrotron Radiation Lightsource (SSRL, USA): High resolution XRD allowed the determination of crystalline symmetry in the BNBT6 cells (beamline 2-1); moreover, X-ray absorption near edge structure (XANES) was employed to evaluate the Ti cation displacement from centrosymmetry (beamline 4-3). Ab initio methods were used to calculate the electric dipole of the model crystal, employed to interpret XANES spectra. On the other hand, we have used high-resolution transmission electron microscopy (HRTEM, JEOL model JEM 2200FS, with a CCD camera MSC 2048 × 2048 GATAN and EDS) to study the coexistence of the various symmetries in these ceramics.

The Rietveld analysis of the XRD patterns (Figure 1) of these samples provided the parameters of the coexisting crystalline structures as (globally) Pm3m and rhombohedral R3c phases, atomic positions and the predominance of one or the other phase for unpoled and poled samples. Two images of the poled ceramic, observed at the HRTEM for different magnifications are presented in Figure 2. The pre-edge features obtained in the XANES spectra of the powder, unpoled and poled ceramic samples allowed to estimate that the titanium cation displacement is of the same order for all the three structures, suggesting that their crystal cells have the same permanent polarization.

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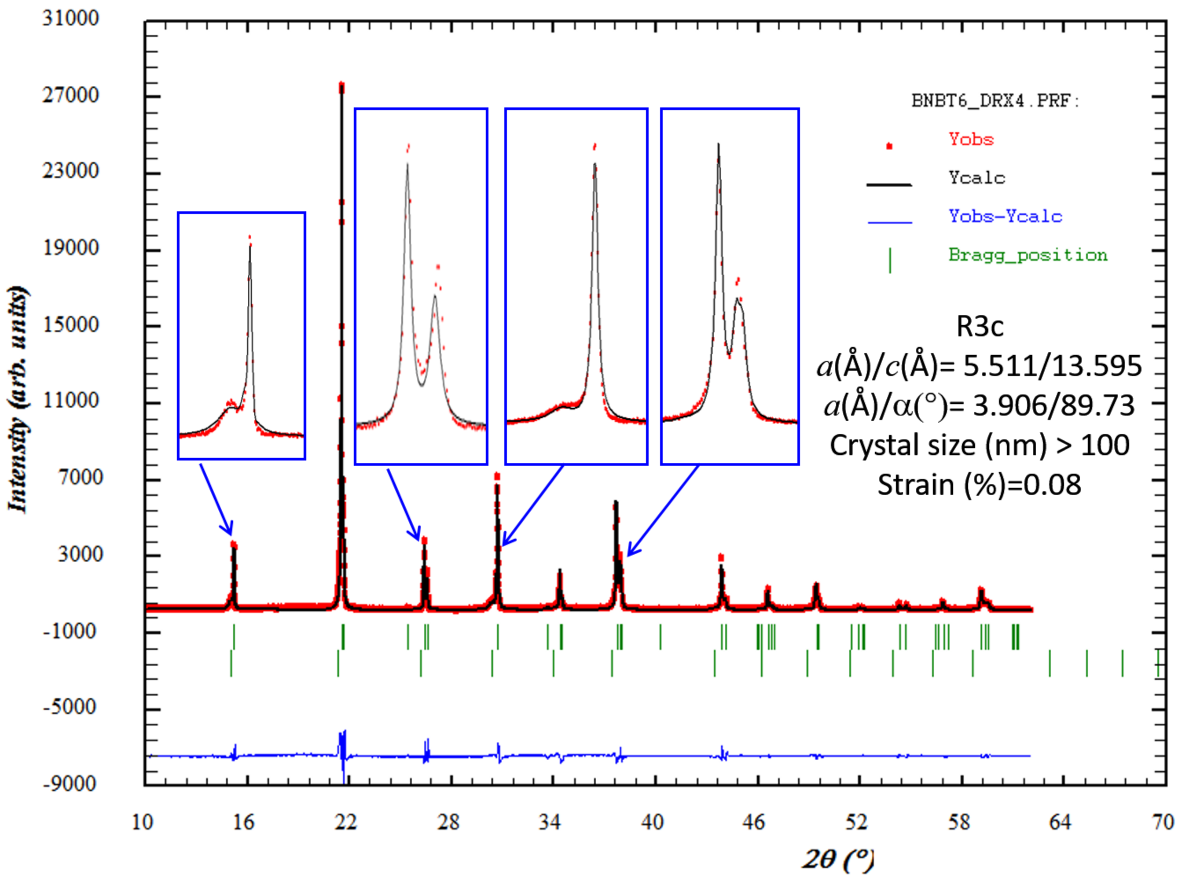

Figure 1. Rietveld refinement of the high-resolution XRD pattern from the poled sample BNBT6. The insets show details of some representative peak groups. Parameters of the R3c structures are presented as well. The contributions of the two phases considered in the sample model are visible.

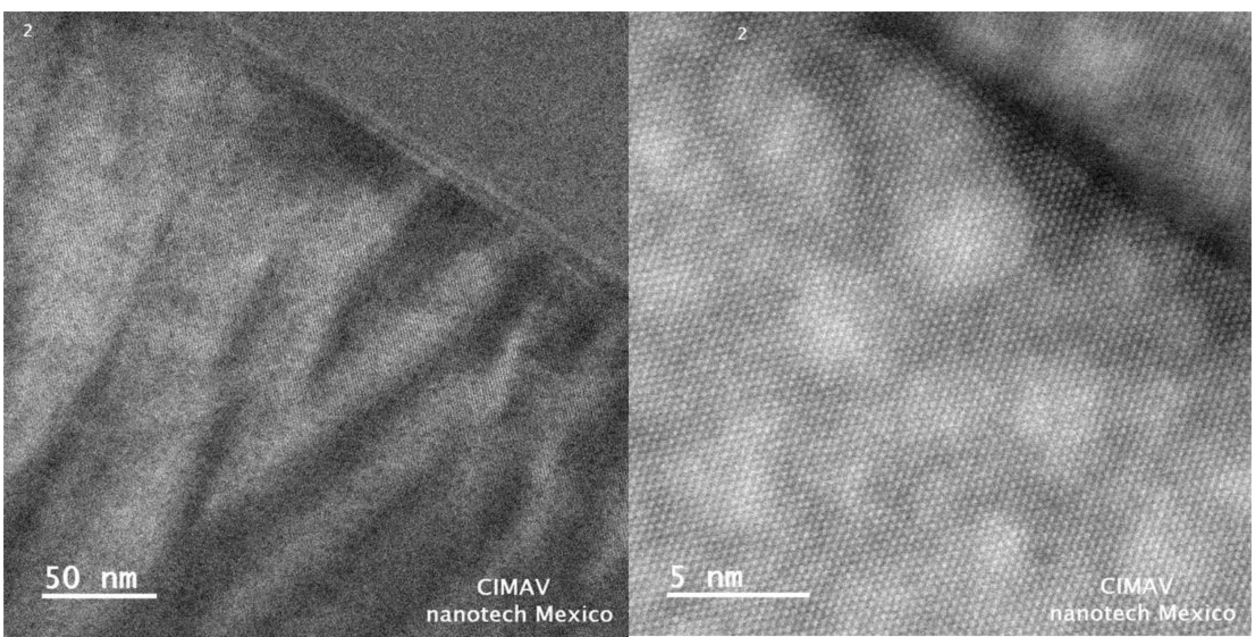

Figure 2. HRTEM images of the poled BNBT6 ceramic. At left, strips oriented domains ~ 30 nm wide are observed. At right, Z contrast image shows the average of zones enriched in bismuth cations.