Exploring Local Order/Disorder in Relaxor Ferroelectric Materials via TEM and STEM Methods

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Background incl. aims
Perovskite relaxor ferroelectric materials are very interesting for a variety of applications due to their extraordinary piezoelectric properties. However, understanding the complicated local order/disorder phenomena within these materials is crucial for optimizing their performance. Transmission Electron Microscopy (TEM) and Scanning Transmission Electron Microscopy (STEM) techniques were employed to study the local order/disorder phenomena in (1-x)$Na_{1/2}Bi_{1/2}TiO_3$-x$BaTiO_3$ (NBT-BT) compositions with varying $BaTiO_3$ concentration (x = 2.5, 7.5, and 15 mol%).

Methods
The samples with mol fractions of 0.025, 0.075, and 0.15 were prepared using conventional synthesis methods for mixed oxides. High-purity powders of Bi_2O_3, Ti_2O, Na_2CO_3, $BaCO_3$, and K_2CO_3 were combined in stoichiometric ratios and then milled in a planetary mill at 250 RPM for 2 hours. After drying, the mixture was calcined three times at 920°C for 5 hours to ensure the formation and purity of the perovskite-type phase. The resulting powder was ground again and passed through a 100 µm sieve. Afterward, the powders were compacted uniaxially and isostatically at 180 Mpa pressure into discs, then sintered at 1080°C for 10 hours in a powder bed of the same composition to minimize element volatilization. Cross-sectional samples were prepared using the ThermoFischer Scios 2 DualBeam in the Scientific and Technical Resources Service of the Universitat Rovira i Virgili.

Our research was aimed at understanding the chemical composition, domain configurations, and structural evolution of these materials. The crystalline structure was analyzed by selected area diffraction (SAED); local changes in lattice parameters were monitored using HAADF-STEM and the presence of polar nanodomains (PNRs) was assessed by iDPC imaging techniques. The samples were observed in a ThermoFisher SPECTRA (S)TEM 300 at 300 kV (ALBA synchrotron), in a JEOL 2010F TEM, and in a JEOL 2100 TEM, both working at 200 kV (Scientific and Technological Centers of the Universitat de Barcelona).

Results
Our findings showed the presence of various phases within the samples. For lower x value, R3c symmetry coexisted with Pm-3m, but higher BaTiO3 ratios resulted in a transition from Pm-3m to P4bm symmetry. For the sample with x=0.15 mol, only P4bm symmetry was observed. Conversely, for x=0.025 mol, R3c and Pm-3m symmetries were detected, and for x=0.075 mol, all three symmetries were observed in distinct grains. The analysis of the lattice parameters through HAADF and iDPC images also showed the transition from a rhombohedral phase for x=0.025, to a cubic phase for x=0.075, and to the tetragonal phase for x=0.15 mol. Polarization maps from iDPC technique will highlight the presence of PNRs. Electron Energy Loss Spectroscopy (EELS) also exhibited particular features in the spectra when increasing the $BaTiO_3$ ratio. Low-loss energy loss spectroscopy was also conducted to observe variations in the optical response and to compare them with Density Functional

Theory (DFT) simulated data of $BaTiO_3$, $BiTiO_3$, and $NaTiO_3$ using the Vienna Ab initio Simulation Package (VASP).

Conclusion

This study explores the general panorama of domain configurations and structural complexities in these materials, as well as the spectroscopic properties observed, including the dielectric function and ELF, as the $BaTiO_3$ ratio is incrementally increased.

Graphic:

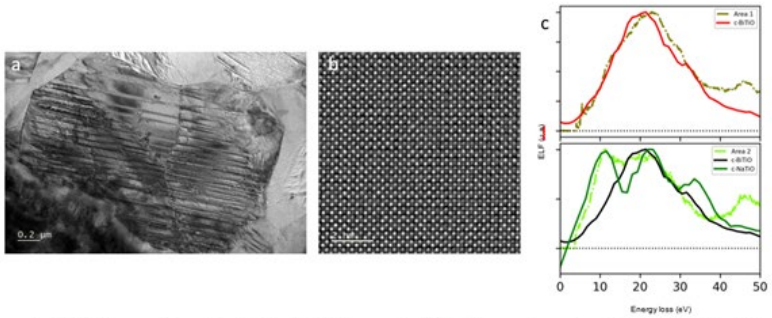

Figure 1: a) BF-TEM image of sample x=0.15mol in [310] zone axis. b) iDPC image of sample x=0.075 mol in [001]. c) ELF of experimental data obtained from Kramers-Kronig calculation and simulated data obtained from DFT simulation. The experimental data are from two different areas of sample x=0.025 mol, while the simulations data was obtained from the cubic structure of $BiTiO_3$ and $NaTiO_3$.

Keywords:

Relaxor-ferroelectrics, TEM, STEM, NBT-BT

Reference:

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