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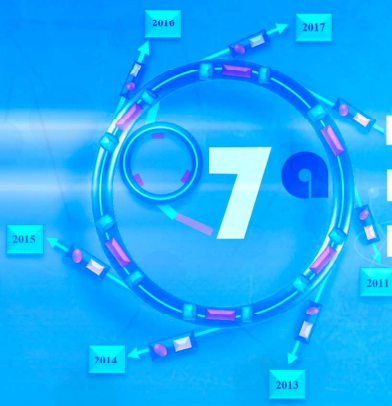

REUNIÓN DE USUARIOS DE LUZ SINCROTRÓN

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Interpretation of X-ray Absorption Spectra of $0.94(Na_{0.5}Bi_{0.5})TiO_3–0.6BaTiO_3$ Titanium Using *Ab Initio* Modeling

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Abstract

We performed X-ray absorption spectroscopy measurements on Ti K-edge of the ceramic $0.94(Na_{0.5}Bi_{0.5})TiO_3–0.6BaTiO_3$. X-ray near edge structure (XANES) spectra were compared with theoretical calculations. For the calculation of XANES spectra, we used a Rhombohedral structure (R3m) and primitive structure (P1) of $Na_{0.5}Bi_{0.5}TiO_3$. On the other hand, the density of states (DOS) allows to determine the contributions of the different atomic orbitals to the valence and conduction bands; at the same time, the band gap is the parameter from which it is known if this material can be used as ferroelectric. DOS calculations are performed from purely ab initio calculations and from XANES analysis. The results from DFT method shows the value of the band gap, which is around 3 eV; so it is unlikely to present a leakage current, fulfilling one of the factors necessary to be applied in the transducers. Other interesting theoretical and experimental results, from the comparison with the optimal simulated cell, are the computation of the polarization of the cell in R3c and the analysis of the variation of XANES spectra from low to high polarization.

Introduction and Aims

Materials with ferroelectric and piezoelectric properties are required globally, due to their wide variety of applications, such as transducer, actuators, and sensors [1]. Ferroelectric crystals and ceramic are also piezoelectric. Applied materials science faces today the challenge of finding lead-free ferroelectric materials with high ferro-piezoelectric properties [2]. The $(1-x)(Na_{0.5}Bi_{0.5})TiO_3–xBaTiO_3$ $(0 \leq x \leq 12)$ disordered solution,

commonly denoted as BNBT100x, is considered one of the best candidates for lead-free ferroelectrics. Their Ti-cation off-centering is the result of the hybridized chemical bond between the titanium d and the octahedral oxygen 2p orbitals. This effect, together with the stereochemical activity of the Bi^{3+} cations, results in the observed overall asymmetric environment, leading to ferroelectricity. The deformation of the crystalline cell is detectable by the X-ray absorption fine structure, near the absorption edge (XANES), through transitions that intensify below the Ti K-edge. These transitions have been verified experimentally and reported for BNBT4 and BNBT6.

Methods

XANES spectra of BNBT6 powders and ceramics (unpoled and fully poled) at room temperature were measured. Ti K absorption edge (about 4966 eV) spectra were obtained at SSRL beamline 4-3, with a Si(220) double crystal monochromator, using ion chamber transmission detectors and a silicon diode as fluorescence detector. Raw data were processed with Athena GUI for the IFEFFIT package [3].

For the calculation of XANES spectra of $Na_{0.5}Bi_{0.5}TiO_3$ (BNT), we used a Rhombohedral structure (R3m) and primitive structure (P1). All the simulations associated with XANES spectra were calculated with the code FEFF9.0 [4]. DFT Calculations to the $Na_{0.5}Bi_{0.5}TiO_3$ structure was modeled with a 10 atoms unit cell, using PBE pseudopotentials implemented in Quantum Espresso software.

Results

The experimental absorption spectrum of BNBT6 is presented in Figure 1a. The spectrum in the pre-edge region shows three main features: the labeled as A, corresponding to a dipole-forbidden transition of a 1s electron into the t_{2g} states for octahedrally coordinated Ti [5,6]. The feature labeled as B corresponding to a dipole-allowed transition of a 1s electron into hybridized 3d-4p states with eg symmetry. The feature labeled as C, corresponds to the transition of a 1s electron into the unoccupied 3d states of neighboring Ti cations [5]. The spectrum in the near edge region shows fourth main features: the hybridization of Ti 4p

states with the bonding states of nearest and next-nearest neighboring atoms [7] *i.e* Bi 6p/Na 3p (labeled D).

The white line peak (labeled as E), corresponding to transitions from Ti 1s to empty 4p states, a small peak about 8 eV above the white line (feature F), and a peak about 18 eV above the white line peak (feature G). In the figure 5(b) we showed the spectrum calculated, it clear that calculation reproduces the qualitative features B, D, E, F and G.
In Figure 2 we present the lDOS of BNT Rhombohedra structure (Figure 2a) and primitive structure (Figure 2b). In both, Primitive and Rhombohedral crystal structure, we observed that the lDOS are similar to the lDOS calculated with DFT for the relaxed structure of $Na_{0.5}Bi_{0.5}TiO_3$ (Figure 3).

Future perspective

Our results show that the DFT calculations are useful for understanding the underlying mechanism behind $Na_{0.5}Bi_{0.5}TiO_3$ ferroelectricity and, on the other hand, FEFF calculations show how it behaves under X-ray radiation.

Acknowledgements

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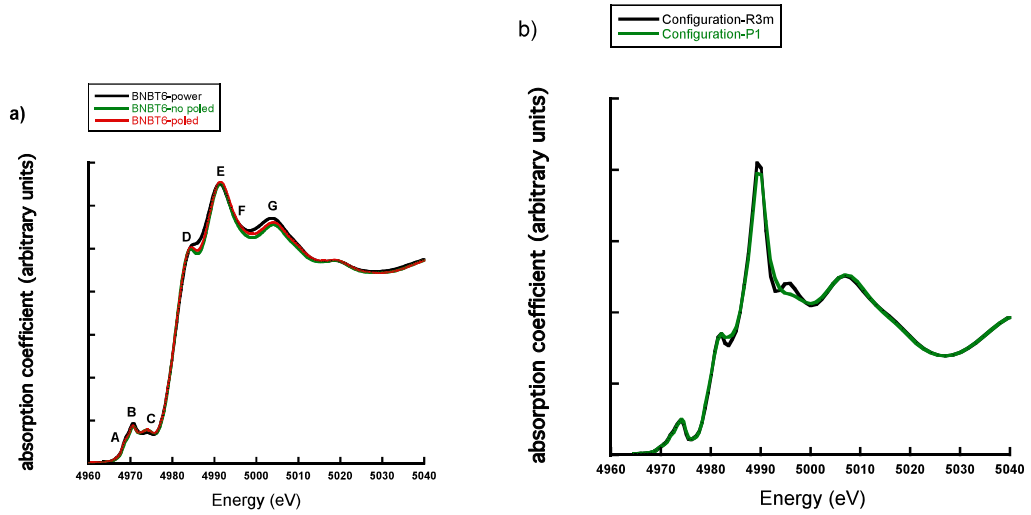

Figure 1.- a) experimental data and b) calculated XANES spectrum.

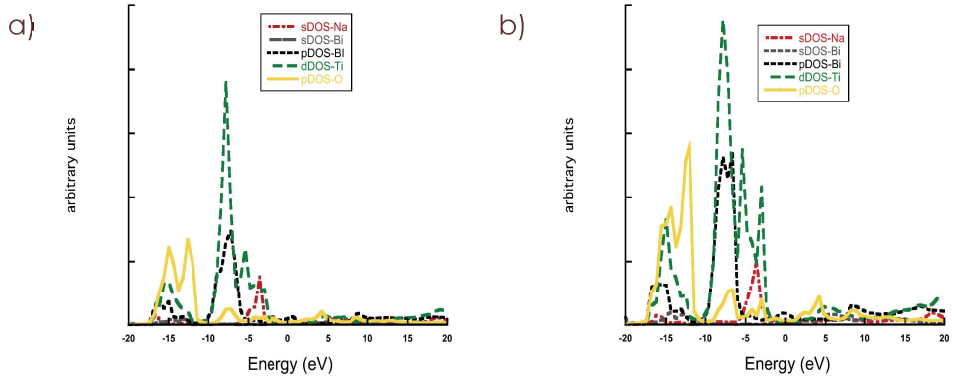

Figure 2.- lDOS of BNT a) Rhombohedral structure (R3m) and Primitive structure (P1).

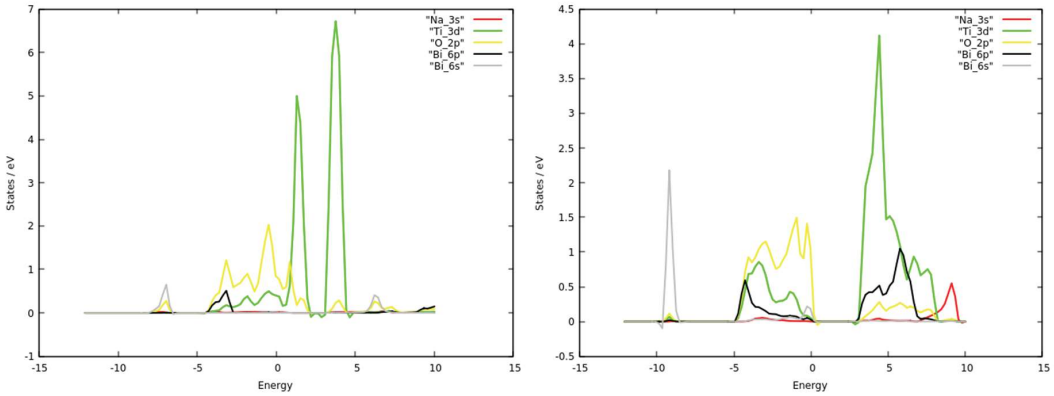

Figure 3.- At left: DOS results of the centro-symmetric structure. At right: DOS results of the relaxed structure.