

Structural evolution in lead free perovskite electro-ceramics based on $Ba_{1-x}Ca_xTi_{0.9}Zr_{0.1}O_3$ by micro-XANES.

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Abstract

The lead free electro-ceramics based on $Ba_{1-x}Ca_xTi_{0.9}Zr_{0.1}O_3$ (denoted as BCZT), have interesting non-centrosymmetric perovskite structures that exhibit a piezo/ferro-response. These compositions stay around the morphotropic phase boundary and their piezo-response values are close to the commercial electro-ceramic that contains Pb. The purpose of this work is to monitor significant structural variations (better diffraction peaks separation and the intensity variations) as the Ca concentration increases by high resolution X-ray diffraction (HR-XRD, $\lambda = 0.95 \text{ \AA}$ and FWHM = 0.016-0.040°). On the other hand, by the micro-X-ray absorption near edge spectroscopy (μ -XANES) is possible to determine structural features associated with short-range order. Additionally, this technique is applied to investigate local departures from centro-symmetry of Ti cation position in the structure of BCZT. The samples were doped at different concentration (x) of Ca (with x = 0.1, 0.15, 0.175 and 0.2) and prepared by the modified Pechini method. They were sintered in a range of temperatures between 1200 up to 1400 °C at 5 h. The experiments took place simultaneously in the 7.1 MCX and the 10.1L X-ray fluorescence beamlines (with a photon energy resolution of 0.5 eV) at the Elettra Sincrotrone Trieste under proposals No. 20165097 and No. 20165205, respectively. The HR-XRD patterns showed a perovskite structure with a single tetragonal phase (P4mm space group). In the present investigation, the (400) peak was measured with high counting statistics to elucidate the splitting associated to the tetragonal phase and then to monitor their evolution when Ca concentration changes. With increasing the Ca content, preferred crystal orientation was also observed. The experimental results were refined to refine the lattice parameters. The Rietveld method was applied to analyze the experimental diffraction patterns using the

Fullprof software. In the experimental absorption spectra of BCZT (Ti K-edge), we observed three main features in the pre-edge region (4965-4985 eV). The feature localized around 4969 eV, corresponds to a dipole-forbidden transition of a 1s electron into the t_{2g} states for octahedrally coordinated Ti. The feature localized around 4972 eV corresponds to a dipole-allowed transition of a 1s electron into hybridized 3d-4p states with e_g symmetry. The feature localized around 4976 eV, corresponds to the transition of a 1s electron into the unoccupied 3d states of neighboring Ti cations, these ones are followed by the white line region corresponds to transitions from Ti 1s to empty 4p states. The intensity of features labeled in 4969 eV, 4972 eV and 4976 eV decreased in this region, when Ca concentration was increasing. An ab initio approximation using the FEEF software version 9.6 was used to model the XANES for Ti K-edge. The obtained refined lattice parameters were used as input for this calculation. HR-XRD experiments performed in the BCZT compounds were important to elucidate the crystal structure with fine peak splitting. The shape, intensity and position of peaks in the pre-edge region of XANES (Ti K-edge) were different in the BCZT compounds. The intensity of pre-edge transitions was important to observe the distortion of the transition metal in the oxygen octahedron.