doi:10.1017/S1431927616010382
Microsc. Microanal. 22 (Suppl 3), 2016

Low loss Electron Energy Spectroscopy Characterization of Electronic Structure and Piezo-response of $Ba_{0.9}Ca_{0.1}Ti_{0.9}Zr_{0.1}O_3$ Nanocrystals.

G. Herrera-Pérez[1], D. Morales C.[2], F. Paraguay-Delgado[2], A. Hurtado-Macias[2], R. Borja Urby[3], G. Tapia-Padilla[1], A. Reyes-Rojas[2], L. E. Fuentes-Cobas[2].

[1.] CONACYT Research Fellow. Centro de Investigación en Materiales Avanzados Miguel de Cervantes 120, Chihuahua 31109, Chihuahua, Mexico.
[2.] Physics of Materials Department. Centro de Investigación en Materiales Avanzados (CIMAV), Miguel de Cervantes 120, Chihuahua 31109, Chihuahua, Mexico.
[3.] Instituto Politécnico Nacional. Centro de Nanociencias Micro y Nanotecnologías, C. P. 07300, México, DF, Mexico.

Perovskite-type oxides have been the subjects of extensive investigations because of their wide variety of physical properties such as piezoelectricity and ferroelectricity. Barium titanate doped with Ca and Zr (BCZT) [1] can be considered a pseudo cubic perovskite-type oxide (PDF card # 31-0174). This compound was prepared by using a modified Pechini method [2]. Rietveld refinements (Fig. 1-a) for the X-ray diffraction results suggest that the material crystallize in the tetragonal symmetry for the sample obtained at 700 ^{o}C for 1 h. Fig. 1-b and 1-c show TEM bright field micrograph for the powders heated at 700 ^{o}C and the corresponding histogram to determine the particle size distribution center at approximately 30 nm. This work shows the structural, chemical and the local piezoelectric characterization for BCZT nanoparticles by X-ray diffraction (XRD), UV-Vis spectroscopy, low loss region (0 - 40 eV) electron energy spectroscopy (EELS) based on scanning transmission electron microscopy (STEM) and piezo-response force microscopy (PFM).

The diffuse reflectance spectrum (Fig. 2-a) were translated into the absorption spectra by the Kubelka-Munk method (Fig. 2-b). Through extrapolation of the $(\alpha h\nu)^{1/2}$ data, the band gap energy of BCZT powders can be obtained to be about 3.13 eV. Fig. 2-c shows valence excitation spectra of BCZT in an energy range from 0 to 40 eV. Energy resolution were 0.5 eV. Onset energy of this spectrum intensity is 3.13 eV (Fig. 2-d). The onset energy correspond to excitation energy of electrons from the top of the valence band to the bottom of the conduction band, i.e., the band gap energy of BCZT. The energy obtained by EELS agrees well with our previous Uv-Vis experiment. This band gap energy in both cases may be related to the presence of intermediary energy levels within a band gap, which is associated to the degree of structure order–disorder on the lattice.

On the other hand, figure 3-a and 3-b show the switching domains respect before and after make the hysteresis loop in the region marked with a red circle. The green regions indicate the positive domains (polarization pointing towards bottom electrode). The purple regions depict the negative domains (polarization pointing towards top electrode). From the curve in Figure 3-c, the value of local piezoelectric coefficient d_{33} for BCZT sample was determined around 8.25 pm V^{-1} (Fig. 3-d).

In summary, the low loss region of EELS analysis are in good agreement with Ultraviolet-Visible measurements supporting the argument associated to the degree of structure order–disorder on the lattice. The local piezo-response determined by PFM on the sample annealing at 700 ^{o}C suggest that the global pseudo-cubic structure is not compatible with these electrical response. In fact, this response suggest that could be arrangement of local tetragonal configurations.

References:

[1] A Reyes-Montero *et al*, J. Alloys Compd. **584** (2014), p. 28-33.
[2] G Herrera-Pérez *et al*, Encuentro de Química Inorgánica (EQI-2015) Proceedings (2015) p. 749-754
[3] The authors acknowledge funding from Cátedras-CONACyT-Mexico, Grant Number 2563.

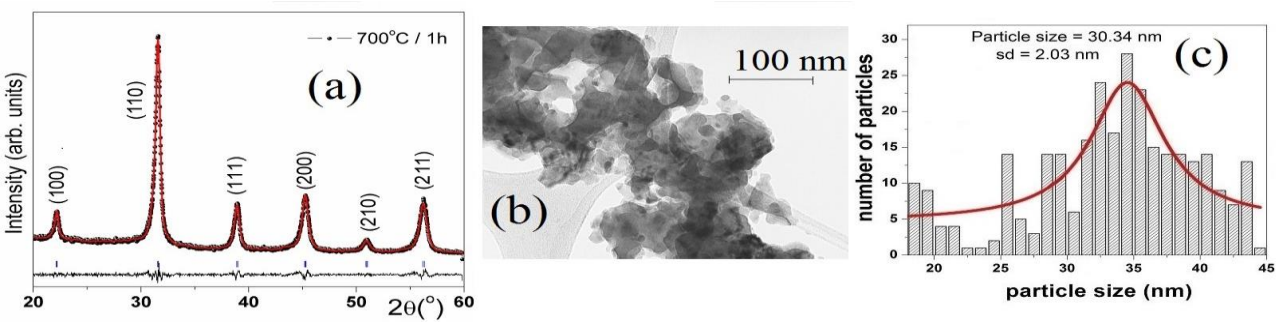

Figure 1. (a) Rietveld Refinement for X-ray diffraction pattern of BCZT. (b) TEM micrograph for powders heated at 700 °C for 1 h. (c) Analysis of the particle size distribution for micrograph in (b).

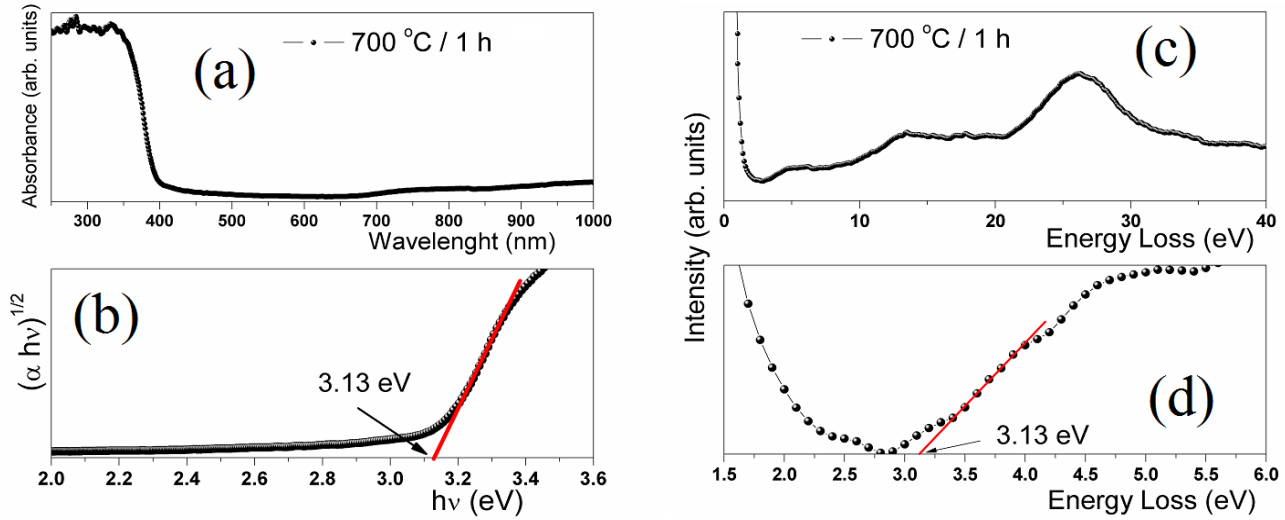

Figure 2. (a) UV-Vis absorption spectrum. (b) Band gap energy determination for BCZT. Valence electron excitation spectra of BCZT nanocrystals. (c) 0-40 eV. (d) 1-7 eV.

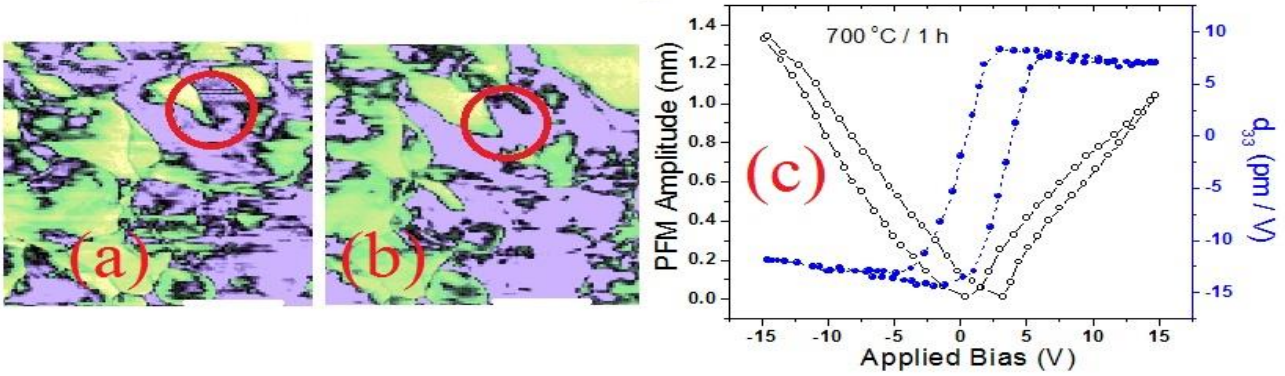

Figure 3. (a) and (b) PFM signal phase before and after measurements the hysteresis loops in the zone of red circle marked. (c) Amplitude-voltage butterfly loop and piezo-response (d_{33}) versus AC Applied bias voltage of BCZT ceramics.