# MICROSTRUCTURE AND CHEMICAL COMPOSITION EVOLUTION IN $Ba_{0.9}Ca_{0.1}Ti_{0.9}Zr_{0.1}O_3$ COMPOUND PREPARED BY PECHINI METHOD

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The development of lead free materials such as $Ba_{0.9}Ca_{0.1}Ti_{0.9}Zr_{0.1}O_3$, (BCZT) to preserve the environmental protection is a scientific challenge [1]. Technological aspects are also interesting when an appropriate selection of their stoichiometry is chosen; this material could be to stay near to called morphotropic boundary phase [2]. This phase is important due to BCZT shows a high piezoelectric coefficient [3]. The aim of this work is to prepare the perovskite BCZT by Pechini polymeric precursor method, monitoring the microstructure and chemical composition evolution. Two important process were considered in the synthesis; the chelation process where cations were chelated with ethylenediaminetetraacetic acid and citric acid; and the polymerization process where ethylene-glycol was incorporated to the solution. A gel was obtained and dried at 60 ºC during 12 h. The resulting material was analyzed by X-ray diffraction (XRD) and the amorphous phase was confirmed (Fig. 1a). This precursor was heated at 700 ºC during 1h in order to stabilize the tetragonal crystal phase (PDF 05-0626) with P4mm symmetry. The XRD pattern was refined by Rietveld method using Fullprof software (Fig. 1b) in order to elucidate the crystal parameters. The atomic force microscopy (AFM, MFP-3D Infinity) image (Fig. 1c) shows a homogeneity of particles size. These particles also shows a homogeneous round shape distribution. The surface has a root-mean-square roughness of 5.2 nm. Figure 2a shows the particle morphology of BCZT powders heat-treated at 700 ºC obtained by transmission electron microscopy (TEM-Philips CM 200) during 1h. The analysis shows large pieces of agglomerated particles with average diameter of 18.3 ± 1.4 nm. One can observe also homogeneous polygon-shape particles. The elemental analysis in TEM-electron energy loss spectroscopy (EELS) mode were performed through the Zr $M_{2,3}$-edge, Ca $L_{2,3}$-edge, Ti $L_{2,3}$ edge, O K-edge and Ba $M_{4,5}$-edge (Fig. 2b). In order to study the possibility of a lowered oxidation state for Ti ions atomic multiplet theory including the crystal field was employed. The calculation shows the presence of only one oxidation state $Ti^{4+}$ $L_{2,3}$ in Oh symmetry with a crystal-field splitting about 2.15 eV. The Field Emission Scanning Electron Microscopy (FESEM, JSM-7401F) image of the heat-treated sample is shown in Fig. 3a, which indicates well-developed grains in the compound. The average grain size was determined with the help of image J and it found to be 58.7 ± 2.8 nm. The chemical composition as revealed by energy dispersive X-ray analyzer (EDAX, Hitachi SU3500) shown in Fig 3b is found to be near to stoichiometric ratio of the compound.

## REFERENCES

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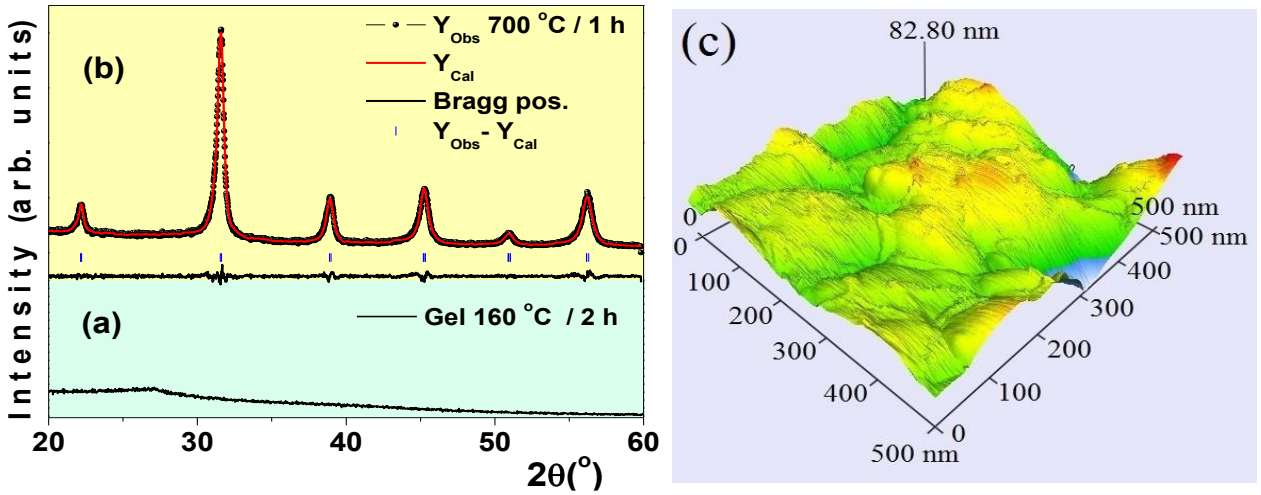


Fig. 1. (a) XRD pattern for amorphous Ba-Ca-Zr-Ti-O precursor. (b) XRD pattern and Rietveld refinement for 50BCZT compound. (c) Tridimensional AFM micrographs obtained in tapping mode for BCZT powders heated at 700 ºC during 1h.

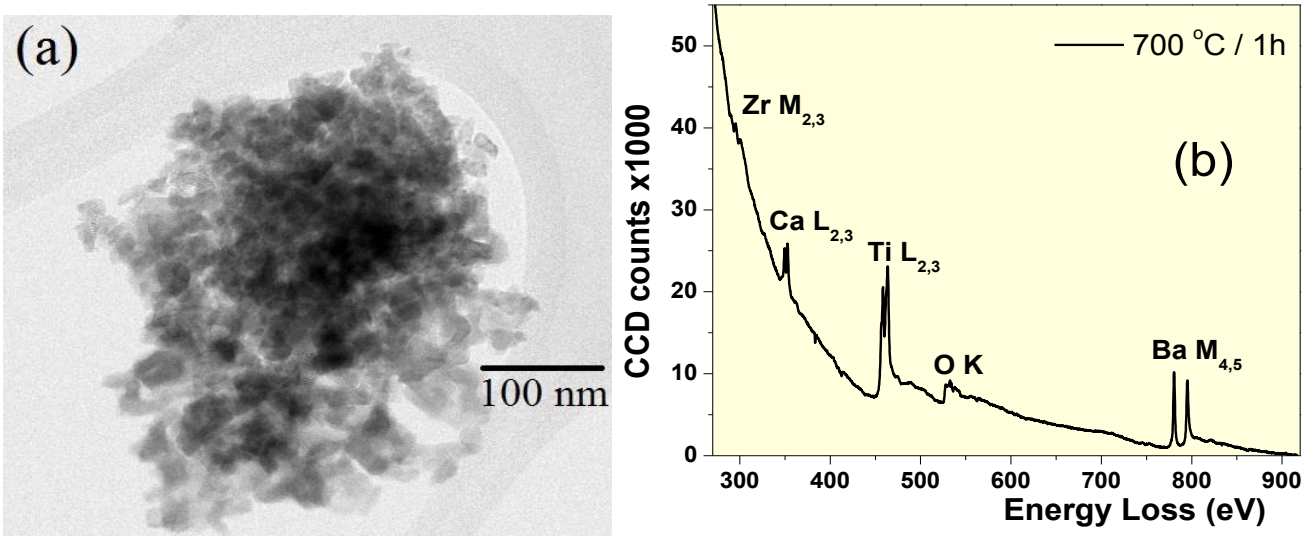


Fig. 2. (a) TEM micrograph for BCZT compound. (b) EEL spectrum performed with an energy resolution of 0.8 eV using the Gatan imaging filter (GIF 200) for BCZT powders heated at 700 ºC during 1h.

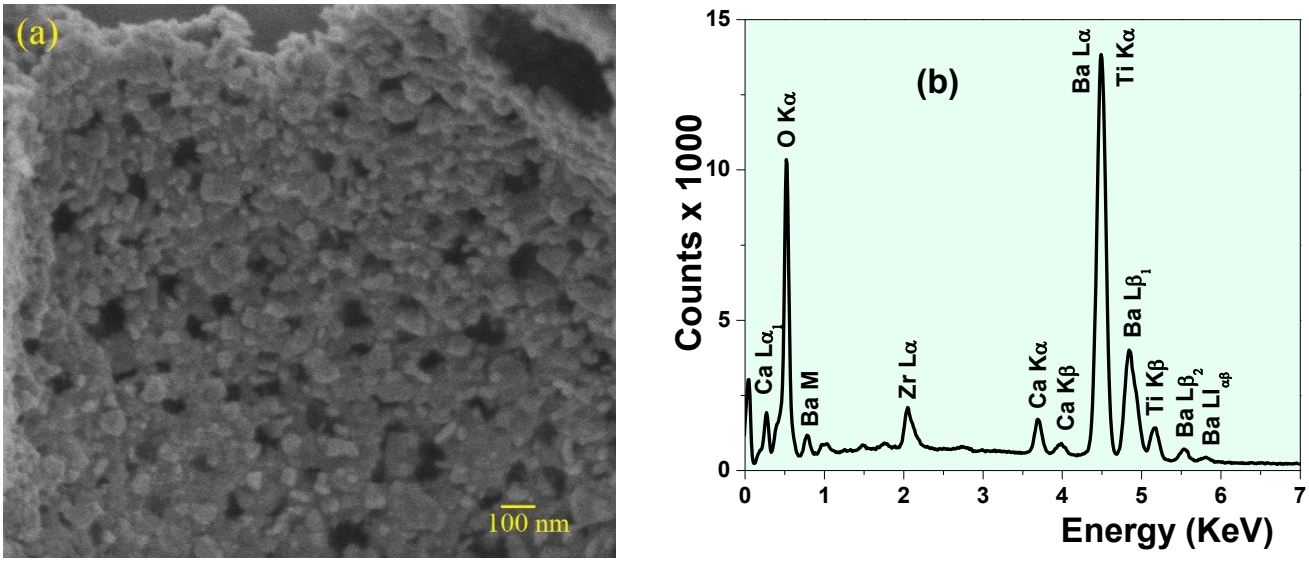


Fig. 3. (a) SEM micrograph obtained with an electron beam accelerating voltage = 5kV for BCZT heated at 700 ºC during 1 h. (b) EDAX analysis with X-ray counting live time = 100 s for BCZT powders heated at 700 ºC during 1h.