Electronic Characterization of $BaTiO_3$:Pb by EELS and ab-initio Calculations

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The ferroelectric ceramics oxides, whose prototype is $BaTiO_3$, have seen an increased attention because the demands for smaller and speedy electronic devices. There are several processing methods of ceramics and, among them, the mechanical alloyed method (also known as Mechanical Activation) is a novel method used in the late years at laboratory level and industrial scale. This involves a combination of chemistry reactions and milling [Zhang et al] for the materials processing. The Mechanical Activation method is highly effective and economic compared with others methods that also promote the dopant diffusion in solid state reactions. The dopant atoms (Sr or Pb) in the perovskite structure, is used to improve the physical properties of the materials for diverse applications. Certainly, the chemistry bond nature is of crucial importance on these materials and therefore the valence electrons could be considered as responsible for the ferroelectric properties [Andrezj et al].

In this work we performed ab-initio calculations of the electronic structure and optical properties of $Ba_{1-x}Pb_xTiO_3$ (BPTO) perovskite by DFT method (Density Functional Theory) with the interchange and correlation potential GGA within the Wien2k code. As main experimental tool we used Electron Energy Loss Spectroscopy (EELS) technique. EELS spectra were acquired in diffraction mode with 0.1 eV/channel dispersion, an aperture of 3 mm and a collection semi-angle of 2.7 mrad. The spectrum resolution was determinate by measuring the full width at half maximum (FWHM) of the elastic peak and this was close to 1.5 eV. The analyzed BPTO samples were obtained as a result of $BaTiO_3$ and PbO reaction powders for 1h milling using a high energy mill Spex 8000. The milled powders were analyzed to estimate the Pb contents qualitatively and quantitatively by Plasma Emission Spectroscopy.

Figure 1 show the X-ray diffraction peaks results. The analysis reveals the presence of only one phase for different Pb concentrations (0, 0.125 and 0.25 % at). The distortion of the BPTO crystalline structure with Pb concentration is evident because the diffractions peak are displaced to the right as the dopant contents is increased, caused by changes in lattice parameters (increasing a and decreasing c).

Figs. 2(a), (b), and (c) show the numerical calculations (dashed line) and the experimental results (continuous line) for the energy loss function $Im(-1/\varepsilon)$ and the real and imaginary part of dielectric function (ε_1 and ε_2) respectively, for $Ba_{0.875}Pb_{0.125}TiO_3$ (BPTO12). An acceptable similarity is observed for both, numerical calculations and experimental results, allowing the interpretation of the features in the spectrum. The small differences observable in the plasmon position (Fig. 2(a) are due to changes in the energy gap (Piskunov et al). Figs. 3(a) (b), and (c) shows, for $Ba_{0.75}Pb_{0.25}TiO_3$ (BPTO25), that plasmon position presents a small displacement towards the left, compared with that of $BaTiO_3$ (27.6 eV). These shifts are due to the difference in size between the Ba ions (r = 1.35A°) and Pb ion. Our calculations are in good agreement with the experimental data, in both the peak shape and energy position. Numerical calculations are then of great help for EELS spectra interpretation.

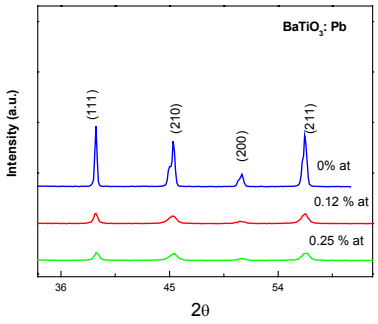

Figure 1. X- ray analysis of $Ba_{1-x}Pb_xTiO_3$ with different dopant concentration

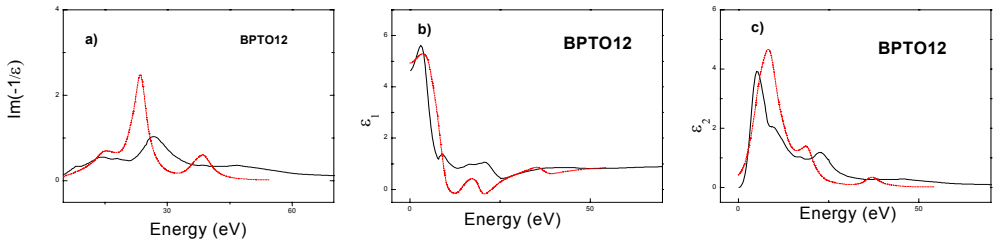

Figure 2. EELS Spectra of $Ba_{0.875}Pb_{0.125}TiO_3$ (BPTO12), experimental results (continuos line) and Wien2k calculated (dashed line) (a) Im(-1/ε), Energy loss Function, (b) ε_1, (c) ε_2,

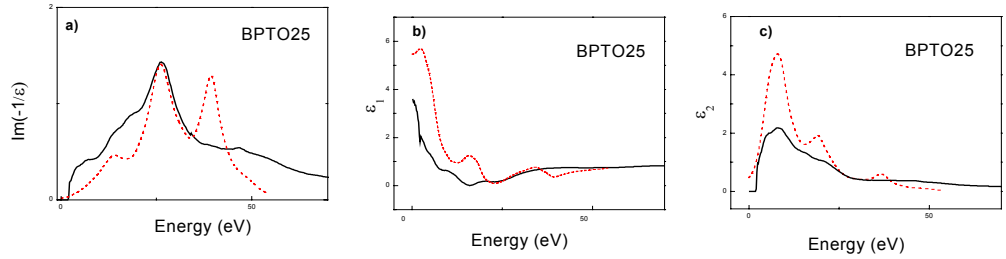

Figure 3. EELS Spectrum of $Ba_{0.75}Pb_{0.25}TiO_3$ (BPTO25), experimental results (continuous line) and Wien2k calculations (dashed line). (a) Im(-1/ε), (b) ε_1, (c) ε_2,