

Complex Dielectric Function and Optical Properties for the Perovskite BCZT via VEELS–STEM.

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Valence electron energy-loss spectroscopy scanning transmission electron microscopy (VEELS–STEM) is an alternative option to elucidate the electronic structure of materials in the region between 0 to 50 eV [1]. The analysis of this region using the Kramers-Kronig (K–K) relations allows determining the complex dielectric function, $\epsilon^* = \epsilon_1 + i\epsilon_2$ [1]. The monitoring of optical properties such as absorption coefficient (μ), refractive index (n) and the extinction coefficient (k) of materials is determined via the dielectric function. There are no reports in the literature that exhibits the K–K analysis of VEELS for the perovskite Ba_{0.8}Ca_{0.2}Ti_{0.9}Zr_{0.1}O₃ (BCZT) compound. This compound is a good lead-free ferro-piezoelectric material that exhibits a tetragonal phase [2]. The motivation of this work is to present the dielectric function and the optical properties for perovskite BCZT via VEELS–STEM analysis using the K–K relations.

BCZT was prepared by the modified Pechini method, the experimental details were reported elsewhere [3]. EELS spectra were obtained with an electron energy loss spectrometer (EELS GAT–777 STEMPack) attached to a JEM-2200FS (200 kV), which offers an energy resolution of 1.0 eV. The electron probe size was below 1 nm. The spectra were acquired using a dispersion of 0.05 eV/channel to record spectra up to 1000 eV. The convergence semi-angle was $\alpha = 9.0$ mrad for a 2.5 mm spectrometer entrance aperture and 40 mm camera length, and the corresponding collection semi-angle was $\beta = 17.3$ mrad [2]. The deconvolution of the zero-loss peak (ZLP) from the VEELS region, the Fourier-log method to remove plural scattering and K–K analysis were carried out using the Gatan Suite software [4].

Figure 1a shows the VEELS–STEM region where the ZLP is identified and elemental analysis is performed for the perovskite BCZT. Panel b shows the ZLP that was extracted from the VEELS region considering in the fit the extrapolation of a logarithmic function [4]. The dominant broad peak located at 27.1 eV is attributed to the bulk plasmon and the peak located at 13.6 eV is related to the surface plasmon. The inelastic contribution spectrum was corrected for multiple scattering events using the Fourier-log method [4] obtaining the single scattering distribution (SSD). A polynomial fit up to the x-axis suggests bandgap energy, E_g of 3.2 eV (panel c) which agrees with the value reported in the literature. Figure 2a exhibits the complex dielectric function, where ϵ_1 and ϵ_2 are, respectively, the real and imaginary parts of ϵ [1]; and the imaginary part of $\{\epsilon-1\}$ also known as the energy loss function (ELF). These curves were obtained through the K–K analysis [4]. Refractive index (n) and k behavior in the range of 0–50 eV are displayed in panel b. Optical absorption coefficient as calculated from ϵ_1 , ϵ_2 (panel c). Panel d shows an optical region expanded.

VEELS–STEM technique combined with K–K analysis is a very useful technique to monitor (a) the elemental composition and locate the plasmon contributions in the valence region; (b) the complex dielectric function, and (c) to determine the bandgap energy, refractive index, extinction and absorption coefficient in particular for ferro–piezoelectric materials such as BCZT.

G. H-P thanks to CONACyT-SEP Basic Research Project No. 253605 and catedras-CONACYT program No. 580.

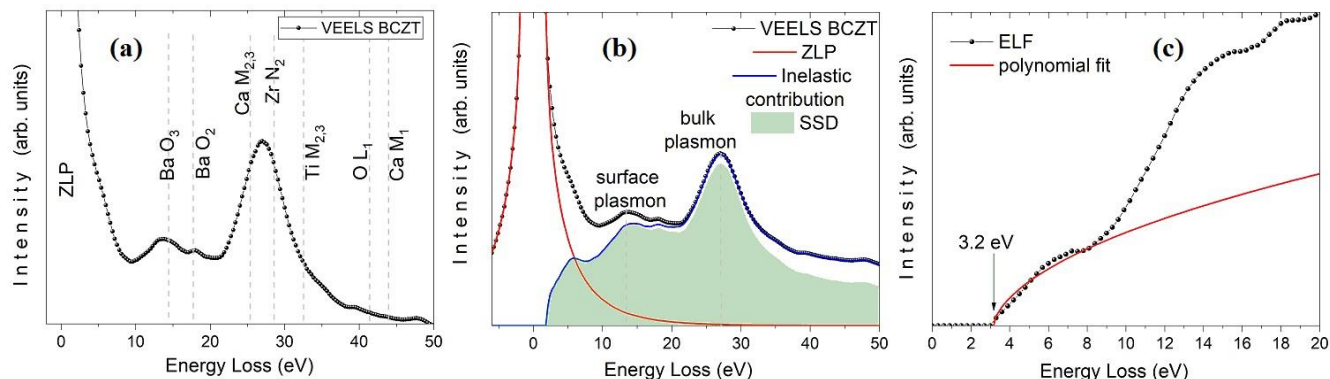


Figure 1. (a) Elemental analysis in the VEELS region. (b) ZLP deconvolution, inelastic contribution, bulk plasmon and SSD. (c) Bandgap determination using a polynomial fit in the ELF for perovskite BCZT.

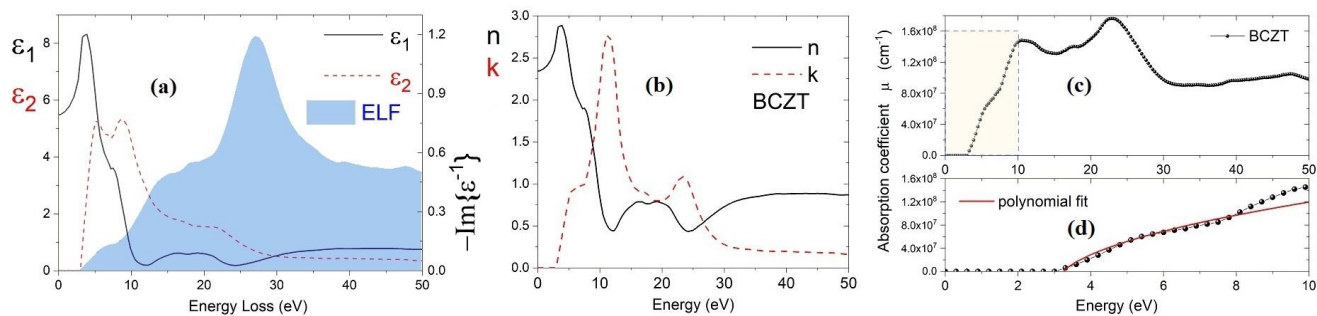


Figure 2. (a) Dielectric function and ELF. (b) Refractive index, n and extinction coefficient, k . (c) The optical absorption coefficient, μ . (d) Optical region expanded for ferro-piezoelectric BCZT.

References

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