

Multiplet Structure for the Perovskite Vanadium-doped BCZT using EELS

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Few reports have been monitored the vanadium oxidation state effects on the optical and electrical properties in perovskite BCZT [1]. In this context, no reports considering the electronic structure using electron energy loss spectra (EELS) have been published. Here, the motivation of this work is to elucidate, the multiplet structure through the vanadium $V L_{2,3}$ -edge for the perovskite $Ba_{0.9}Ca_{0.1}Ti_{0.85}Zr_{0.1}V_{0.05}O_3$ (denoted in this work as $BCZTV$) and to determine how it influences the electronic structure of other edges such as the $Ti L_{2,3}$ -edge. Because one expects that the V ions substitute the B sites occupied by the Ti cations in the perovskite formula ABO_3 . To perform this task, we collected EELS in the valence region (0-50 eV) and also in the core region (50-1000 eV). The multiplet calculation was performed using the CTM4XAS software [2].

The $BCZTV$ was prepared by the modified Pechini method. Previous to acquiring the EELS for this material; x-ray diffraction analysis confirmed the perovskite structure in the tetragonal phase. The EEL spectra were acquired by a Gatan imaging filter spectrometer (GIF Quantum 956ER) attached to a JEOL JEM ARM200CF microscope with cold FEG emission working at 200 kV in the TEM mode. To analyze the acquired core loss EELS spectrum, the background subtraction using the power-law algorithm, plural scattering correction using the Fourier-ratio deconvolution and, the three window method were performed through Gatan microscopy suite version 3.5 and Origin software version 2018.

Figure 1(a) shows the low-loss EELS region, identifying the three principal components. The pronounced peak at 0 eV is labeled as the zero-loss peak. Some peaks observed in this area correspond to interband transitions. The energy range of ~10-30 eV is dominated by the plasmon peaks. More structures could be observed above 30 eV, and they are attributed to the elemental composition (three vertical dashed lines) [3]. Panel (b) reveals the core loss EELS structure, identifying also the elemental analysis. First, we investigate the multiplet structure of $Ca L_{2,3}$ -edge shown in Figures 2(a) and (b). In the calculation we considering Ca^{2+} in octahedral symmetry (O_h) with $10Dq = 1.2$ eV [4]. Figure 2(c) and (d) show the $Ti L_{2,3}$ -edge spectrum and calculated spectrum, respectively. In the calculated spectrum, we take into account mixed-valence states (Ti^{3+} and Ti^{4+}) in O_h with $10Dq = 1.5$ eV and 1.7 eV, respectively [5]. Next, we magnify the $V L_{2,3}$ -edge in Figure 2(e), which exhibits a similar electronic structure reported previously [6]. For the multiplet structure through the $V L_{2,3}$ -edge, we proposed the V^{3+} oxidation state in O_h symmetry with $10Dq = 1.0$ eV [6]. Our theoretical vanadium spectrum shown in Figure 2(f) agrees well with the experimental results. Thus, the substitution of V^{3+} ions on Ti sites provokes changes in the electronic structure of $Ti L_{2,3}$ -edge [7].

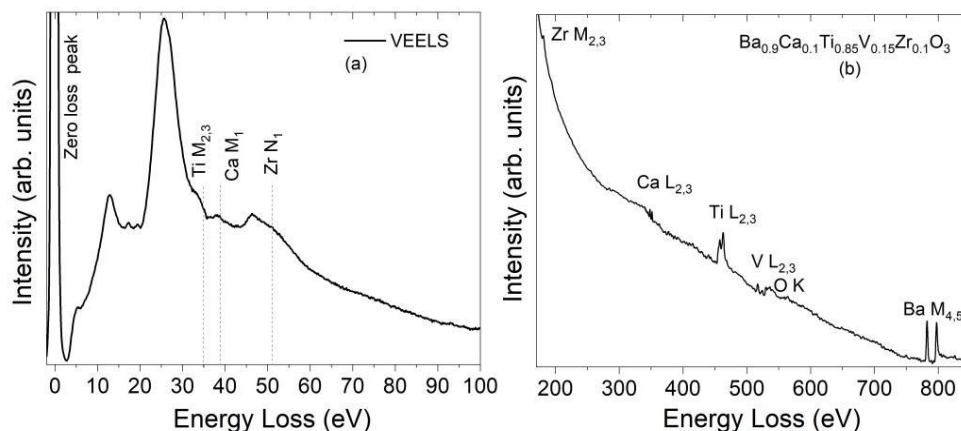


Figure 1. (a) Low-loss EELS spectral shape showing the zero-loss peak, the volume plasmon and, the elemental analysis. (b) Core loss EELS spectrum showing the elemental analysis for *BCZTV*.

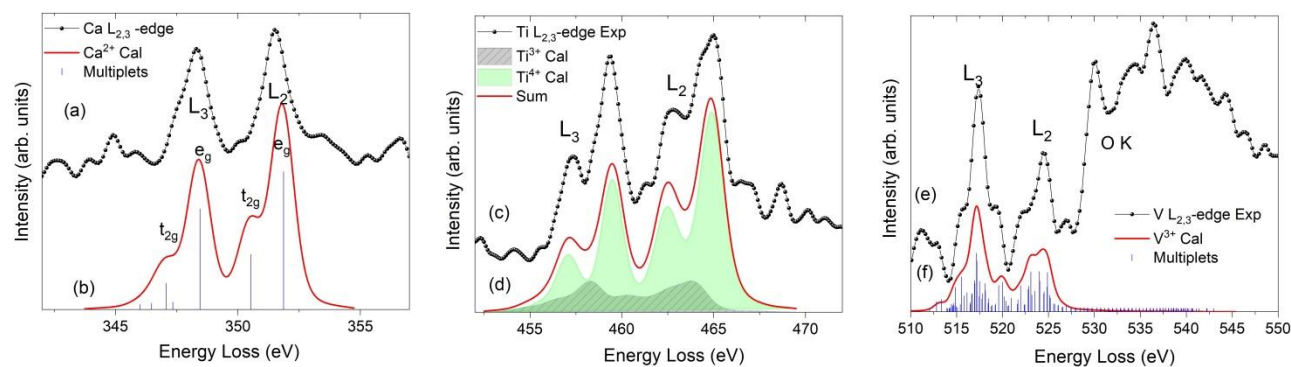


Figure 2. Core-loss edges (a) *Ca* L_{2,3}-edge. (b) Multiplet calculation (MC) in *O_h* symmetry. (c) *Ti* L_{2,3}-edge. (d) MC considering *Ti*⁴⁺ and *Ti*³⁺ (green and blue sparse filled area under the curve) in *O_h* symmetry. (e) *V* L_{2,3}-edge and *O* *K*-edge. (f) MC for vanadium region in *O_h* symmetry.

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