

Charge transfer contribution in Rutile-TiO₂, perovskite- Ba_{0.9}Ca_{0.1}Ti_{0.9}Zr_{0.1}O₃ and monazite-LaVO₄ by X-ray absorption and X-ray emission spectroscopies.

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Abstract

Core-hole spectroscopies such as X-ray absorption (XAS), X-ray emission (XES) and electron energy loss (EELS) spectroscopies are important techniques to monitor the charge transfer effects in the electronic structure of metal transition compounds. XAS in total electron-yield (TEY) and XES were collected at beamline 8.0.1 of the Advanced Light Source in the Lawrence Berkeley National Laboratory in the Ti L_{2,3}-edge and V L_{2,3}-edge of TiO₂ and LaVO₄ compounds. The EELS in transmission electron microscopy in scanning mode (STEM) was performed to collect the Ti L_{2,3}-edge for the Ba_{0.85}Ca_{0.15}Ti_{0.9}Zr_{0.1}O₃ (BCZT). The interpretation of XAS-TEY and EELS-STEM profiles was performed by the multiplet calculation using CTM4XAS software. The structural interpretation for these compounds was performed using the Rietveld refinement method (FullProf software) for the X-ray diffraction (XRD) patterns. The XRD interpretation confirms a single phase for: rutile-type TiO₂ with tetragonal phase and P4₂/mnm (No. 136) space group, for the BCZT a perovskite-type with tetragonal phase and P4mm (No. 99) space group; and the LaVO₄ that

shown a monazite-type with monoclinic phase and $P2_1/n$ (14) space group. The Fourier electron density contour maps were obtained by the GFourier software in order to investigate the chemical bonding behavior for these compounds. The electron density plots shown an important interaction of contours between Ti and O atoms for TiO_2 and BCZT compounds; as well as, for V and O atoms for $LaVO_4$. These results indicated a different degree of covalent character. The purpose of this work is to monitor the covalent degree by the interpretation of the electronic structure through the Ti $L_{2,3}$ -edge for TiO_2 and the BCZT. This procedure was also implemented to the V $L_{2,3}$ -edge for $LaVO_4$. The calculation takes into account the crystal field parameters in tetragonal D_{4h} symmetry (D_q , D_t and D_s) and the charge transfer parameters such as the charge transfer energy Δ , the core hole potential U_{pd} and the d-d repulsion U_{dd} . The results lead to a weight of the d^0 and $d^1\bar{L}$ configurations in these spectra with 50 and 50 % for TiO_2 and BCZT; and the 67 and 33 % were determined for $LaVO_4$. These results indicate that the hybridized nature between Ti 3d states with O 2p states is more important in the Ti compounds. The evolution of the XES results as we scanned the incoming photon energy across the $L_{2,3}$ absorption edge was analyzed. In order to monitor the evolution of the scattering process and to identify the charge transfer state, a complementary analysis was performed in the energy position of the emission as a function of the excitation energy (the energy dispersion plots). In summary, the multiplet calculation that consider the charge transfer, is an important tool to analyze XAS-TEY and EELS-STEM spectra. Moreover, it is important for the quantification of the covalent character in ceramics that contain Ti and V atoms. We consider that the results presented in this work may provide a helpful reference for core-hole spectroscopies.