Characterization Of A Novel Mixed Conductor –CeO_2-Sm_2O_3-ZrO_2 Solid Solution

M. Croft, W. Huang, P. Shuk, M. Greenblatt, F. Chen, and M. Liu (Rutgers U.)

Abstract No. Crof7080
Beamline(s): **X19A**

Solid electrolytes (like those based on CeO_2) are key components of solid-state electrochemical devices, which are increasingly important for applications in energy conversion, chemical processing, sensing and combustion control. Motivated by our recent ceria based work on ionic conductivity, we have investigated $(Ce_{0.83}Sm_{0.17})_{1-x}Zr_xO_{2-\delta}$ solid solutions. These materials were synthesized, for the first time, by the hydrothermal method and the cubic fluorite structure stabilized to x= 0.50 after calcination at 1500°C.

The WL ("white line") features at the $L_{2,3}$ edges of 4d transition metal compounds involve 4d final states, and can yield direct information on the occupancy/energy-distribution of these states. The Zr-environment in the cubic fluorite structure leads to the four-fold degenerate e_g orbitals lying at an energy Δ below the six-fold t_{2g} orbitals. The Zr-$L_{2,3}$ spectra for $(Ce_{0.83}Sm_{0.17})_{0.5}Zr_{0.5}O_{2-\delta}$ (below) manifest a clearly bimodal structure with the A-feature (C-feature) involving the e_g (t_{2g}) final states. The magnitude of the crystal field splitting (about Δ = 2.3 eV from this A-C feature splitting) is consistent with electronic structure calculations [1]. The Zr-$L_{2,3}$ spectra for tetragonally-distorted $ZrO_{2-\delta}$ manifest a similar two peak A-C structure, however an additional unresolved intermediate B-feature (or features) is also clearly present. The lowering of the cubic-O_h symmetry to the tetragonal-D_{4h} splits the energies of the $[(x^2-y^2)]$ and $[(z^2)]$ states of the e_g orbitals and the [(xz), (yz)] and [xy] states of the t_{2g} orbitals. Thus, the intermediate energy states, of the B-feature in the Zr-$L_{2,3}$ spectra of $ZrO_{2-\delta}$, are consistent with these lower symmetry splittings. Again electronic structure calculations for tetragonal- $ZrO_{2-\delta}$, [1] manifests a similar filling-in of intermediate energy states in the e_g–t_{2g} gap.

References[1] R. Orlando, C. Pisani, C. Roetti, and E. Stefanovich , *Phys. Rev.*, **B45**, 592 (1992).

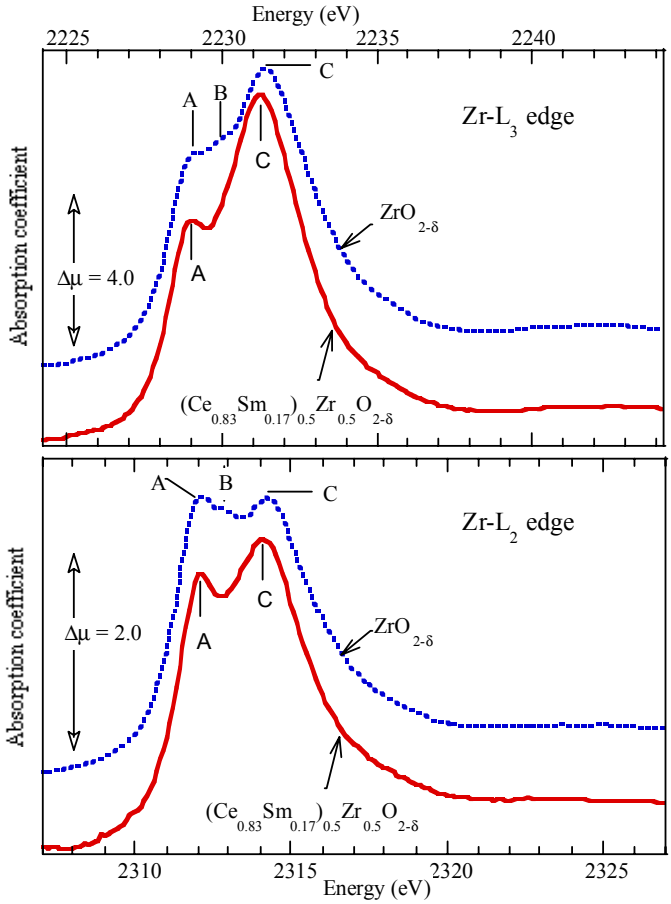

Figure. The Zr-L_3 (top) and L_2 (bottom) spectra for the cubic $(Ce_{0.83}Sm_{0.17})_{0.5}Zr_{0.5}O_{2-\delta}$ and for the tetragonally distorted ZrO_2. Note the A and C features of the cubic material that are associated with the 4-fold e_g and 6-folds t_{2g} orbitals, respectively with the CEF splitting, Δ being 2.3 eV.