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# Probing Bonding Environments in Osmium-Based Double Perovskites Using Monochromated Dual Electron-Energy Loss Spectroscopy

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The ability to use the spin of the electron (±½) for read/write capabilities in solid-state devices has the potential to double capacity and increase speed without altering weight. The key to "spintronics" is to find functional materials that deliver the required properties [1]. Double perovskite (DP) crystals have the generic formula, $A_2BB'O_6$, where A, B, and B' are transition metal atoms. DPs, especially half-metallic ones, have been shown to exhibit high spin polarization and Curie temperatures above room temperature [2, 3]. To fully realize the potential of DPs as spin injectors, high quality, ordered and epitaxial thin films must be grown. This has proved challenging. The B and B' atoms occupy the same type of sites in the crystal and the properties are sensitive to the relative spatial pattern of these atoms. Our goal is to develop experimental methods that allow us to probe this arrangement with sub-nanometer spatial spectro-microscopy methods in order to directly probe on the atomic scale the relationship between structure, chemistry and properties in these complex oxides.

We have investigated osmium-based DP (B'=Os) powders using monochromated dual electron-energy loss spectroscopy (EELS) in the scanning transmission electron microscope (STEM). The range of B site atoms studied were Cr, Fe, and Co. Powders with each B site atom were made with Sr or Ca, separately, on the A site. The B and B' atoms occupy octahedral sites in the crystal with six oxygen atoms at the apices of the octahedron. By varying the valance state of the A and B site atoms, the oxygen octahedra can tilt away from the orthogonal axes of the unit cell, which has an effect on the overlap of the bonding between the oxygen and the metal species. Ultimately, this can affect the magnetic properties of interest by altering the J-couplings within the material. STEM-EELS studies allow us to probe the unoccupied electron energy levels on the oxygen sites via the oxygen K-edge transition. By systematically varying the chemistry of the DPs, a reference set of oxygen K-edge spectra were obtained for comparison with thin film DPs grown for device applications, as seen in Figure 1.

In order to fully explain the EELS, and where possible, X-ray absorption near-edge structure (XANES) data, density functional theory (DFT) was employed to calculate the density of states (DOS) around the Fermi energy. This, in turn, can help to distinguish different features within the experimental EELS data to better define the electronic configuration of each system. As an example, in Figure 2 it can be seen that the EELS and XANES data are in very good agreement for $Ca_2CoOsO_6$, with the calculated O-*p* states below the two spectra. The features in the calculated O-*p* states above the Fermi energy can be identified by looking at the hybridization between oxygen and the other elements in the full DOS calculation (not shown). In understanding the electronic states above the Fermi energy and the ways in which they manifest themselves in EELS spectra, one can track changes in those states around defects, interfaces, or in thin films. In studying the calculated electronic states along with the experimental data for a set of systematically altered materials, a much clearer understanding of the electronic and magnetic

phenomena can be gained. This can help to guide future materials selection for materials of interest with applications in spintronics.

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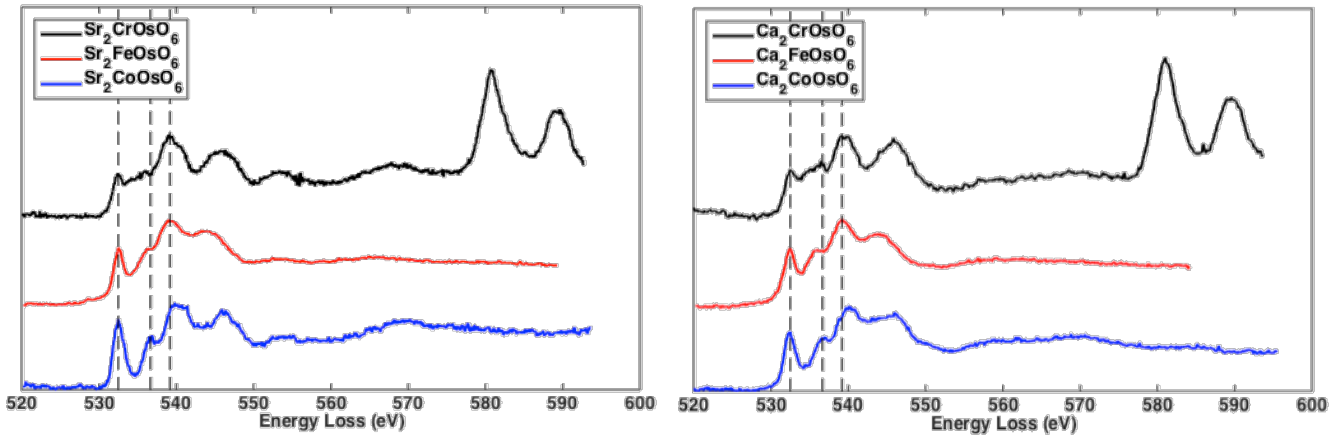


**Figure 1.** Sr- and Ca-based Osmate DP EELS spectra show changes in the density of states correlated with changes in valence state

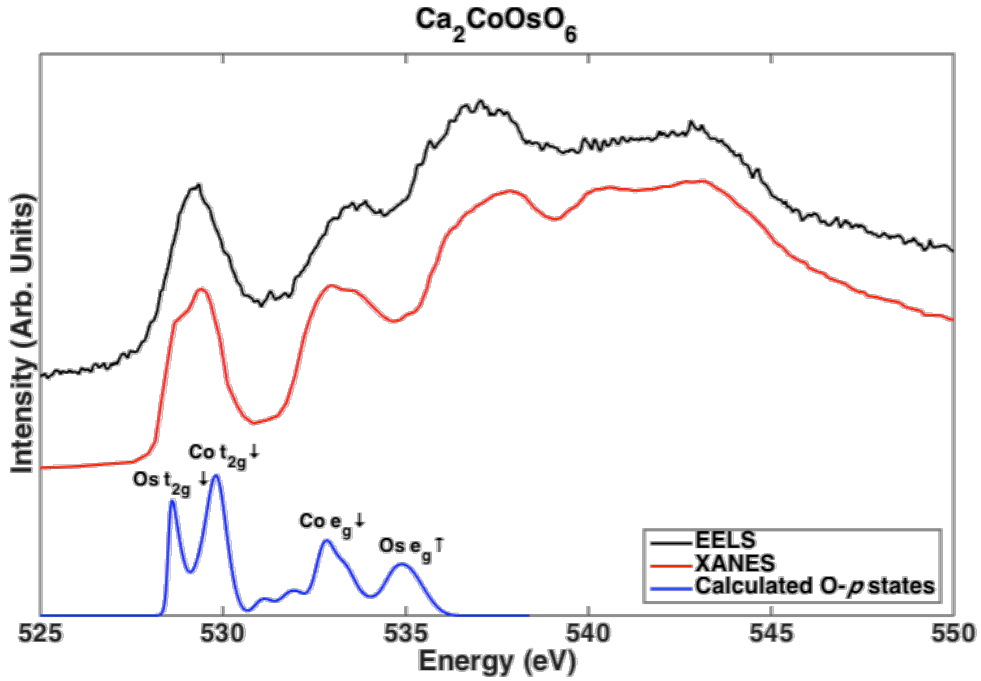


**Figure 2**. Comparison of EELS, XANES, and Calculated O-*p* states from DFT results for $Ca_2CoOsO_6$

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