**CHEMICAL EFFECTS OF LANTHANIDES AND ACTINIDES IN
GLASSES DETERMINED WITH ELECTRON ENERGY LOSS
SPECTROSCOPY**

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CHEMICAL EFFECTS OF LANTHANIDES AND ACTINIDES IN GLASSES DETERMINED WITH ELECTRON ENERGY LOSS SPECTROSCOPY

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The chemical and structural environments of *f*-electron elements in glasses are the origin of many of the important optical, electronic, and magnetic properties of materials incorporating these elements. Thus, the oxidation state and chemical coordination of lanthanides and actinides in host materials is an important design consideration in optically active glasses, magnetic materials, perovskite superconductors, and nuclear waste materials.

The energy loss spectra of the lanthanides are characterized by sharp $3d_{3/2} \rightarrow 4f_{5/2}$ (M_4) and $3d_{5/2} \rightarrow 4f_{7/2}$ (M_5) lines, the relative intensities of which are determined by the *4f*-shell occupancy of the excited ion. For the light lanthanides, the dependence of these relative peak heights on *4f*-shell occupancy is quite pronounced. In particular, the ratio of the M_4 to M_5 peak areas in the second derivative spectra is extremely sensitive to the formal valence of the multivalent elements Ce and Pr. In figure 1, the EELS spectra are presented for Ce(III) and Ce(IV) in well-characterized reference materials. The ratio of the M_4/M_5 lines calculated by various methods is plotted against *f*-shell occupancy in figure 2. The present second derivative data are plotted along with those of Manoubi *et al.* [1], who fit their experimental peaks from lanthanide oxides with Lorentzian functions, and also the theoretical multiplet calculations of Thole *et al.* [2] ($A_{3/2}$ and $A_{5/2}$ used instead of M_4 and M_5 , respectively). The systematic divergence of the second derivative data from the Lorentzian fits and theoretical peak areas occurs because the M_4 line is broader than the M_5 line, which reduces its relative intensity in the second derivative accordingly.

We have made use of the characteristic line shapes of cerium to determine its oxidation state in alkali borosilicate glasses that are being developed for immobilization of plutonium. Cerium, it should be noted, is often used as a "surrogate" element for plutonium in materials design because of its similar ionic size (for Pu in the +3 and +4 states) and preferred chemical coordination. The solubility of the plutonium (or cerium) in a waste glass will likely be determined by its redox state in the glass. By examining several prototype glass compositions with EELS (figure 3), it was found that the redox state of cerium doped to 7 wt % could be varied by suitable choice of alkali elements in the glass formula.

By analogy with the lanthanides, the intensity ratio of the N_4 and N_5 lines in actinide elements, which correspond to $4d_{3/2} \rightarrow 5f_{5/2}$ and $4d_{5/2} \rightarrow 5f_{7/2}$ transitions, respectively, might be expected to decrease as occupancy of the *5f* orbitals increases. For example, by this argument, the uranyl ion should display a N_4/N_5 ratio close to 1.0; instead, the ratio is smaller. In actinides, the relativistic contraction leads to strong hybridization of *5f* orbits with the *6d* and *7s* orbitals. This relativistic contraction is around 2% for the lanthanides but at least 30% for the actinides. Excitation will occur to these *6d* and *7s* levels and will complicate the edge shape. Thus, we cannot assume that the same correlation of N_4/N_5 intensity ratios with *f*-orbital occupancy that is seen for the lanthanides will be observed in the actinides. Instead, it is probable that crystal field effects will determine the spectral shape for the actinides. In glasses, however, the flexible local structure may lead to coupling between the oxidation state and crystal field effects, allowing a straightforward interpretation. Preliminary EELS results on a plutonium-doped glass appear in figure 4, illustrating the small actinide N_4/N_5 ratio. This figure also shows that the Pu- $N_{4,5}$ white line cross section is comparable to that of gadolinium $M_{4,5}$ [3].

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Figure 1. Second derivative EELS spectra of cerium (IV) oxide and cerium(III) orthophosphate. Note the dramatic change in the ratio of the M_4 (903 eV) to M_5 (886 eV) lines.

Figure 3. Second derivative EELS spectra of cerium $M_{4,5}$ edges in prototype glasses designed for plutonium disposition. The formal valence of the cerium varies from 3.4 ("7-1") to 4 ("9-2") as a function of the relative proportions of K and Li in the glasses.

Figure 2. Dependence of the M_4/M_5 spin-orbit group ratio on the occupancy of the 4f level for the light lanthanides.

Figure 4. Plutonium N-edges in a glass doped to 7 wt % Pu. Gadolinium is a neutron poison present in a 1:1 ratio with the plutonium, providing a relative measure of the plutonium N-edge cross sections.

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