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SPECTROSCOPIC INVESTIGATIONS OF ACTINIDES IN THE SOLID STATE

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We have continued spectroscopic investigations of f-species in selected solid matrices. In one focus area we are performing systematic investigations of excited-state interactions between An/Ln and/or An/An species in host matrices. Numerous reports exist in lanthanide/lanthanide systems, but interactions leading to energy-transfer in either actinide/lanthanide or actinide/actinide donor/acceptor pairs are very limited. We have focused on actinide/lanthanide pairs chosen primarily for spectral overlap within donor/acceptor electronic transitions.

In the Am/Tb pair, for example, a proper energy match-up exist between the $^5D_{2'}$ and $^5L_{6'}$ levels of americium and the $^5D_4$ level of terbium. Exclusive excitation of Am(III) provides a sensitized emission from Tb(III), indicating that energy-transfer occurs between the two species. The direction of the energy transfer process was established with an excitation profile analysis and found to proceed from the donor americium to the acceptor terbium. We are continuing our effort on other actinide/lanthanide pairs which have the proper energy match-up and are expected to display efficient energy-transfer processes.

Information regarding the effects of radiation on the spectroscopy and oxidation state of the progeny species have also been pursued with Es^{3+} and Bk^{3+} containing glasses. A blue self-luminescence band at 455 nm is believed to originate from oxygen defect centers within the Si-O-Si network that are produced by radiation. Other luminescence bands originating from non-bonding oxygen hole centers (NBOHC), and Si-micro cluster sites have also been observed. We are planning for additional collaborative XANES studies (with LBNL) on such systems to complement our spectroscopic investigations.

Another area that we are actively pursuing involves the investigation of energy up-conversion processes in actinide systems. While numerous studies have been conducted on anti-Stokes luminescence of rare-earth doped materials, similar data for the transuranium elements are very limited. Among the transuranium elements, so far only halides of Cm^{3+} and Cf^{3+} in the solid phase have been reported to display this phenomenon. In addition, we have recently discovered anti-Stokes luminescence in Am^{3+}. Our future effort in this area will be two fold. First, due to the limited information currently available on anti-Stokes luminescence from actinides, we will continue with the search for other systems that might display the behavior. For example, it is not known whether halide samples of Am^{3+}, like their Cm^{3+} and Cf^{3+} counterparts, will display this phenomenon. The possibility of energy up-conversion in Bk and/or Es materials will also be explored. Second, we are planning to examine the effects of pressure on up-conversion and energy transfer processes in multi-doped systems. One of the effects of pressure involves a shift in the energy of certain orbitals with respect to others. The consequences of these changes on the efficiency of energy transfer processes will be monitored spectroscopically. An added advantage of this procedure is that we will also be able to collect vibrational Raman data under high pressure and complement the group's effort in high pressure diffraction work. For example, our plan to investigate the correlation between Raman peak width and degree of disorder in actinide pyrochlores, and the initiation of pressure-induced phase transition studies are aimed at complementing the group's high pressure expertise.

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