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**Fundamental Aspects of Actinide-Zirconium Pyrochlore Oxides:
Systematic Comparison of the Pu, Am, Cm, Bk and Cf Systems***

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Abstract

Zirconium- and hafnium-based oxide materials have gained attraction for various nuclear applications. These materials have features in common with one of the early, well-publicized inorganic ceramics for immobilizing nuclear waste has been Synrock, which is a multi-phased titanate system. There have been extensive efforts to establish the materials science and technological application of these materials with the goal of resolving important issues of the nuclear community. As a result, many of these efforts have concentrated on specific f-elements.

Several fundamental science issues are encountered when pursuing the application of these materials, and there have been a number of sophisticated studies performed on them. Our efforts on these materials concentrated on exploring systematically the fundamental solid state chemistry of selected types of these f-element, zirconium- or hafnium-based oxides. We have synthesized and studied polycrystalline pyrochlore oxides of the general formula, $A_nM_2O_7$ and solid solutions of $(An,M)O_2$, where An is considered trivalent Pu, Am, Cm, Bk and Cf and M is tetravalent Zr or Hf).

Our interests have addressed the fundamental structural and chemical properties of these oxide systems. We pursued both the crystal chemical constraints of the oxide matrices, as well as the importance of the chemistry of the f-elements. By incorporating five actinide elements in our studies, we were able to compare systematically the materials science of these materials with the fundamental chemistry and electronic configurations of these actinides employed. It is expected that this basic information will be useful technologically in the realm of tailored made materials for different applications.

The polycrystalline pyrochlore oxides discussed here have the general formula of $A_2M_2O_7$; more precisely, $A_2B_2O_6O^*X$, where the one oxygen is in a special site (general position) and the X is an oxygen vacancy. The structure can be visualized as a fluorite-type cell with a double unit cell and an ordered deficiency of oxygen atoms. If the oxygen vacancy is filled fully (e.g., the trivalent actinide ion is oxidized fully), a solid solution of the dioxides may be generated. Formation of this pyrochlore structure is possible only if A^{3+} is larger than B^{4+} , and the ratio $r_{A^{3+}}/r_{B^{4+}}$ is between 1.46 and 1.80.

Using accepted values for An^{3+} radii, this suggests such pyrochlore oxides would form for the actinides through Es in the series.

From a structural standpoint, the special oxygen site (located in **48f**, space group Fd3m, no. 227) has one unknown structural parameter, x . Generally, such parameters are obtained from diffraction experiments but given the difficulty with radioactive materials and the limited quantities of these higher actinides, we explored a calculation approach based on valence-bond relationships, where priori assumptions about the nature of the chemical bonds or knowledge of the radii are not required. From the experimental cell parameter, it is then possible to deduce the structural parameter, x . We have used this approach to estimate this parameter for these actinide pyrochlores and several lanthanide pyrochlores.

One observes an excellent correlation between the ionic radii of the trivalent metal ions of actinides and lanthanides and the lattice parameters of the pyrochlores. This relationship is useful in conceiving and/or forming custom pyrochlore ceramics for various technological applications. This relationship also provides predictability of crystal lattice parameters and/or the degree of reduction of the f element for pure or mixed f-element pyrochlore oxides.

For f-elements that can exhibit both a trivalent and a tetravalent oxidation state, a solid solution of the f-element and the transition metal dioxides may be generated via oxidation of the pyrochlore oxides; the stoichiometry required for the pyrochlore fixes the mole ratio of the metal ions at ~50 mol %. Thus, for some of the f-elements, an oxidation/reduction cycle can be established, that appears as a form of a Born-Haber cycle. This cycle for these pyrochlore oxides involves: (1) the reduced pyrochlore oxide; (2) an oxygen-rich pyrochlore oxide; (3) an oxygen deficient dioxide solid -solution; and (4) a solid solution of the dioxides. The five transneptunium elements discussed here are all known to form dioxides but the extent to which this cycle is observed for each element depends on the pseudo-oxidation potential of the f-element and the stabilization afforded by the two crystal forms.

The presentation will present the structural data obtained for the different actinide materials and compare them with known data for the lanthanide elements. Important structural aspects of the pyrochlore oxides, the actinide oxide phase behavior and the pseudo-oxidation potentials of the actinide elements will be discussed in the context of formation and stability of these pyrochlore materials. In addition, comments concerning the physicochemical nature of these materials with regard to their technological applications will be mentioned.

