

Thermodynamic Complexities in Fluorite Derivative Materials

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The fluorite structure is the parent, or aristotype structure, for a large family of ordered and partially ordered derivatives, especially in oxide systems. Cation order-disorder and vacancy creation and ordering on the anion sublattice are unique and bring structural and thermodynamic complexity that must be considered in thermodynamic modeling. Structural and spectroscopic studies, including methods sensitive to the oxygen sublattice (e.g. neutron scattering and NMR), provide detailed information on complex order-disorder phenomena. There are a number of first principles computational studies in this area.

High-temperature oxide melt solution calorimetry offers unique insights, especially when combined with DSC and *in situ* high-temperature structural studies. This presentation reviews the thermodynamic and structural evolution of three classes of fluorite-derived systems: the energetic relations among amorphous, defect fluorite, and pyrochlore structures at $A_2B_2O_7$ stoichiometry, the behavior of lanthanide-doped zirconia, hafnia, ceria and actinide oxides, and high-temperature phase transitions in binary rare earth oxides. In all cases, ordering at different length and time scales plays a dominant role.

These systems pose three major challenges to the computational community: describing order-disorder on different length scales, distinguishing equilibrium from metastable behavior, and describing the enthalpy and entropy of mixing in a fundamentally realistic way. Applications of fluorite-related materials include nuclear fuels, nuclear waste containment, solid electrolytes, thermal barrier coatings, sensors, and optical and electronic materials, so accurate descriptions of their thermodynamics as a function of composition, temperature, and grain size is essential to a variety of technologies.