Experimental Modeling of Complex Rare Earth Element Phosphate Solid Solutions

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Natural ore deposits of rare earth elements (REEs) are typically carbonate minerals (bastnäsites) or phosphates (monazites or xenotimes) where a solid solution of all REEs can be found. The proclivity for light-REEs (La to Gd) for forming monazite while heavy-REEs (Gd to Lu) form xenotime in the phosphate minerals is an example of naturally occurring fractionation between them. Monazite and the hydrated light-REE phosphate, rhabdophane, have been found with heavy-REEs incorporated in the structure despite the tendency for the endmembers to crystalize as xenotime. $REEPO_4$ endmember behaviors have been explored extensively. However, since natural REE minerals occur as solid solutions, thermodynamic modeling to capture the mixing behavior of two or more REE and actinides in these solid matrices is required. In this work, multiple examples of trinary solid solution rhabdophanes/monazites with mixed LREE and HREE have been studied for elucidation on mixing thermodynamics based on similar average ionic radii of the solution series. Local structure of these multicomponent REE phosphates were examined by in situ high temperature synchrotron X-ray diffraction and PDF. We obtained structural evolutions of these REE-mixed phases, including step-wise dehydration and phase transitions, which provide valuable insight to the behavior of the elements in natural ore systems. Solid phase thermodynamics including hydration energetics and enthalpies of formation and mixing were determined by differential scanning calorimetry and drop solution calorimetry. This will establish some framework for solution phase thermodynamics as well, and ultimately lead to a better understanding of the formation of REE deposits.