

Probing the Formation and Alteration of Lanthanide Phosphates

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Monazite, xenotime and rhabdophane are widely available in the Earth's crust and represent abundant sources of lanthanide in nature. Phosphate-based compounds have wide applications, particularly as solid nuclear waste matrices for immobilizing heavy radionuclides, due to their high chemical durability, radiation resistance, structural flexibility and thermal stability.^{1,2} Its hydrated forms (rhabdophane), REEPO₄·nH₂O, are usually used as low-temperature precursors for synthesizing monazite ceramics and occur as possible alternation products (neoformed phases) in a geological repository for nuclear waste disposal. Knowledge of the formation mechanism of phosphates and their thermal alteration has significance in evaluating the fate of such materials. Thus, we performed *in situ* synchrotron X-ray diffraction experiments under hydrothermal conditions to investigate the crystallization processes of YPO₄ and LaPO₄ from aqueous solutions. *In situ* heating X-ray scattering experiments were performed on rhabdophanes up to 300 °C to reveal their multiple dehydration processes. These measurements coupled with Rietveld analysis enable us to obtain the temperature-dependent local and long-range structural information (*e.g.* unit-cell parameters, atomic positions, and atomic displacement parameters) of various phosphate phases. In addition, the water structure of rhabdophanes was determined by low-T inelastic neutron scattering. The obtained structural landscape as a function of temperature can enhance our understanding of the thermal behavior of phosphates, such as encountered in geological repositories, etc. ¹Terra, et al. *New J Chem* **2003**, *27*, 957. ²Dacheux, et al. *Am. Mineral.* **2013**, *98*, 833.