Thermodynamic properties of CaTh(PO₄)₂ synthetic cheralite

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ABSTRACT

The mineral cheralite [CaTh(PO₄)₂] allows for the incorporation of tetravalent actinides in monazite-based crystalline phases. Experimental determination of its thermodynamic properties is crucial for defining its stability and subsequent long-term ability to immobilize radionuclides. Low-temperature heat capacity from 0.5 to 300 K, enthalpy increments from 485 to 1565 K, and the enthalpy of formation of cheralite from the oxides were measured and reported on for the first time. At 298.15 K, \( S^\circ = (201.6 \pm 2.6) \text{ J/(K}\cdot\text{mol)} \), which includes the configurational entropy of Ca and Th mixing, \( \Delta H^\circ = -(506.4 \pm 9.5) \text{ kJ/mol} \), \( \Delta G^\circ = -(501.6 \pm 9.6) \text{ kJ/mol} \), and \( \Delta G^\circ = -(3635.5 \pm 10.2) \text{ kJ/mol} \).

In aqueous environments, cheralite is able to form from whitlockite or apatite and thorianite. Under anhydrous conditions, cheralite can form by solid-state reaction only if the resultant product includes very stable Ca salts instead of CaO.

Keywords: Cheralite, actinide phosphates, thermodynamic properties, nuclear waste

INTRODUCTION

Since the middle of the last century, the concept of immobilization and long-term disposal of nuclear waste in mineral forms has been investigated. Several ceramics based on the mineral structures of brannerite, zircon, zirconolite, pyrochlore, or monazite have been proposed as candidates for the conditioning of actinides (Lutze and Ewing 1988; Brookins 1984). The mineral monazite, LnPO₄, where Ln³⁺ could be Ce³⁺, La³⁺, Nd³⁺, Sm³⁺, or Pr³⁺ has great potential as a nuclear waste host because of its specific structure and because of its remarkable ability to retain significant amounts of tetravalent actinides, particularly U⁴⁺ and Th⁴⁺ (McCarthy et al. 1978; Beall et al. 1981; Sales et al. 1983; Lutze and Ewing 1989; Meldrum et al. 1996). The crystal structure of monazite (\( P_2_1/n \)) is composed of one-dimensional chains of alternating PO₄ tetrahedra and REO₆ polyhedra extending along the c-direction (Ni et al. 1995). Low symmetry constraints on the irregular ninefold coordination environment around the lanthanide, with eight RE-O distances averaging ~2.5 Å, and one longer ~2.8 Å distance, allow substitution of La³⁺ by Th⁴⁺ or other large ions.

In natural systems, charge balance for Ln³⁺-Th⁴⁺ substitution is maintained by two major mechanisms ( Förster 1998; Montel et al. 2002; Seydoux-Guillaume et al. 2002; Montel et al. 2006). In the substitution of the huttonite (ThSiO₄) component, incorporation of Th⁴⁺ is charge balanced by substitution on tetrahedral sites, Ln³⁺ + P⁴⁺ = Th⁴⁺ + Si³⁺. In the cheralite substitution, 2Ln³⁺ = Th⁴⁺ + Ca³⁺, exchange takes place only in the large cation position (Hughes et al. 1995; Linthout 2007).

Several studies have been made of the synthesis of monazite-based ceramics incorporating actinides. Of these, the cheralite substitution has been studied extensively (Montel et al. 2002, 2006; Hikichi et al. 1978; Podor and Cuney 1997; Tabuteau et al. 1987; Deschanels et al. 2006; Terra et al. 2006). Continuous solid solutions of the composition CePO₄-Ca₀.₅Th₀.₅PO₄ (Montel et al. 2006) and LaPO₄-Ca₀.₅Th₀.₅PO₄ (Podor and Cuney 1997) have been obtained experimentally. A simple procedure for LaPO₄-Ca₀.₅Th₀.₅PO₄ synthesis, suitable for highly radioactive environments, was developed, and could be employed for the synthesis of Pu-bearing phases (Seydoux-Guillaume et al. 2002; Montel et al. 2006). Leaching tests in aggressive aqueous media for Ca₀.₃Th₀.₇U₀.₃PO₄ and La₀.₃Ca₀.₇U₀.₃PO₄ solid solutions show it to be chemically resistant to alteration compared to UO₂ (Terra et al. 2006). CaNp(PO₄)₂ and the solid solution CaNp₁₋ₓPuₓ(PO₄)₂ have also been obtained (Tabuteau et al. 1988). The limited solubility of Pu (\( x < 0.4 \)) has been explained by the instability of Pu⁴⁺ relative to Pu³⁺ at higher x. Recently, the Pu mixed valent compound Puₓ⁺⁺³P₀.₅Ca₀.₅PO₄ has been obtained and characterized (Bregiroux et al. 2007).

For the further assessment and modeling of the ability and limitations of monazite and monazite-cheralite mixed phases to incorporate actinides, thermodynamic information is essential. Recently, the heat capacities of lanthanide and actinide orthophosphates were explored for LnPO₄ (Ln = La, Ce, Nd, Sm, Eu, Gd) at 0.5–1570 K (Thiriet et al. 2004, 2005a, 2005c; Popa et al. 2006a, 2006b, 2006c), (La₀.₃Ln₀.₇)PO₄ solid solutions (Ln = Nd, Nd, Eu, Sm, Gd), and CePO₄ using the DTA and calorimetric methods. The enthalpy of formation of CePO₄ was obtained and characterized (Popa et al. 2006b, 2006c).