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Synthesis and microstructure of fluorapatite-type $Ca_{10-2x}Sm_xNa_x(PO_4)_6F_2$ solid solutions for immobilization of trivalent minor actinide

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ABSTRACT

$Ca_{10-2x}Sm_xNa_x(PO_4)_6F_2$ (x = 0.8–1.2) solid solutions were successfully synthesized by the solid state reaction method using samarium (Sm) as the surrogate for trivalent minor actinide neptunium (Np). The influences of calcining temperature, holding time and Sm doping content on the phase composition and microstructure of $Ca_{10-2x}Sm_xNa_x(PO_4)_6F_2$ were investigated. The results indicated that the optimized calcining temperature and holding time for preparing $Ca_{10-2x}Sm_xNa_x(PO_4)_6F_2$ were 1000 °C and 2 h. $Ca_{10-2x}Sm_xNa_x(PO_4)_6F_2$ were confirmed to be the discontinuous solid solutions and solid solubility limit of Sm in the $Ca_{10-2x}Sm_xNa_x(PO_4)_6F_2$ was 1.2 formula units. The rod-like grains of $Ca_{10-2x}Sm_xNa_x(PO_4)_6F_2$ had typical hexagonal characteristics with a diameter of 3–5 μm and a length of 10–20 μm. No significant changes on the microstructures of $Ca_{10-2x}Sm_xNa_x(PO_4)_6F_2$ were observed with the increase of Sm doping content. The Ca, Sm, Na, P, O and F elements were nearly distributed uniformly in the $Ca_8Sm_1Na_1(PO_4)_6F_2$ solid solution.

1. Introduction

Minor actinides [neptunium (Np), americium (Am) and curium (Cm)], which are mainly produced by reprocessing spent nuclear fuel [1]. Although the amount of minor actinides is less than 1 wt%, these actinides are primarily responsible for the high toxicity and long-term radioactivity of the high level waste (HLW) [2]. In particular, the isotope ^{237}Np of the minor actinide neptunium can have significantly hazardous influence on the biosphere owing to its quite long half-life (2.1×10^6 years) [3]. In order to avoid or much delay their release to the environment, these minor actinides must be incorporated into the extremely durable host phases [4].

Fluorapatite with the chemical formula $[Ca_{10}(PO_4)_6F_2]$ is one of the most abundant and stable naturally occurring apatite mineral [5,6], which has been considered as a potential host matrix for immobilization of actinide-rich nuclear waste [7–10]. Firstly, a substantial amount of phosphates (up to 15 wt% P_2O_5) of HLW can be utilized as the phosphorus source for preparing the fluorapatite, owing to the use of bismuth phosphate or tributyl phosphate during the reprocessing of spent nuclear fuel [11]. Furthermore, fluorapatite has a stable hexagonal structure (space group $P6_3/m$) and possesses the capability to accommodate mono-, di-, tri-, and tetravalent cations due to its considerable flexibility of the crystal structure and composition [12,13]. Especially, the fluorapatite retaining significant ^{235}U enrichment and high concentration fission products has been found to be geologically stable for nearly two billion years in the Oklo natural nuclear reactor of Gabon [14,15]. In addition, the fluorapatite not only has a very low solubility ($K_{sp} = 3.19 \times 10^{-61}$) [16], but also exhibits the retrograde solubility [17], which enables it to become more and more stable at elevated temperature. In particular, the structure of fluorapatite has relatively high resistance to self-radiation [18,19].

The fluorapatite compounds which incorporated with minor actinides, other actinides and long-lived radionuclides were synthesized in the literature [20–22]. Weber reported that 1.2 wt%

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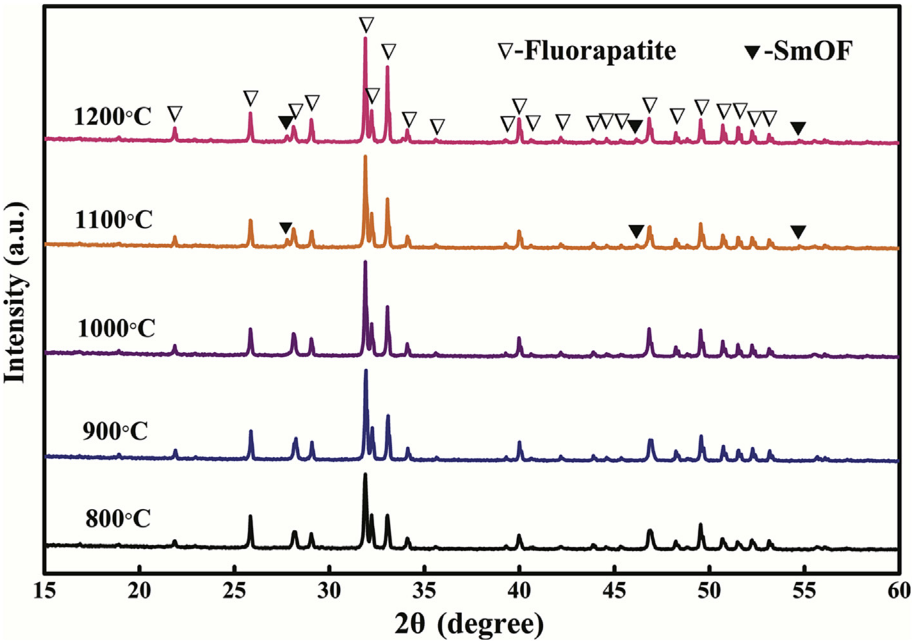

Fig. 1. XRD spectra of $Ca_8Sm_1Na_1(PO_4)_6F_2$ calcined at different temperatures for 2 h.

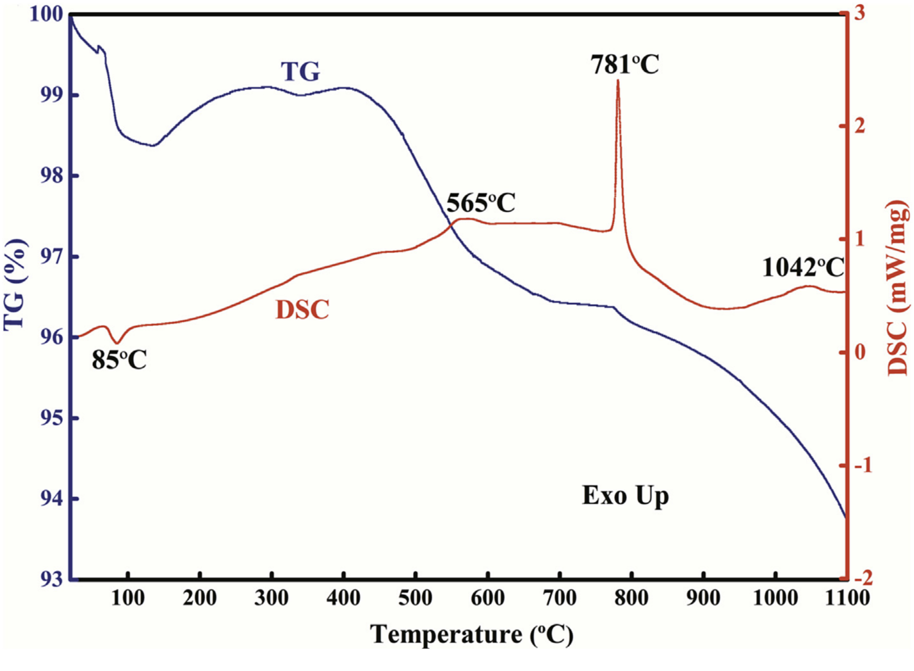

Fig. 2. TG-DSC curves of a $Ca_2P_2O_7$-CaF_2-Sm_2O_3-Na_2CO_3 mixture for synthesizing $Ca_8Sm_1Na_1(PO_4)_6F_2$ solid solution.

^{244}Cm was doped into the polycrystalline $Ca_2Nd_8(SiO_4)_6O_2$ with the apatite structure [20]. Vance et al. reported that Pu^{3+} and Pu^{4+} were incorporated into the Ca site of fluorapatite using Na^+ as the charge compensator through the sol-gel method [23]. Indeed, Na^+ was released relatively easily compared to other ions in solution during the dissolution/leaching process [24], which could reduce the chemical durability of the immobilization materials. However, similar to the fluorapatite-type host matrix, sodium zirconium phosphate [$NaZr_2(PO_4)_3$, NZP] was proposed as a promising Na-bearing phosphate nuclear waste form [25,26]. The normalized leaching rate of Na in the NZP was on the order of 10^{-2} g m^{-2} d^{-1} [27], which was comparable to those of borosilicate glasses [28] and Synroc specimens [29]. Zyryanov et al. reported the Na-bearing NZP-based nuclear waste ceramic possessed the chemical durability within an order of magnitude of that for the titanate-based waste form Synroc-C [30]. In addition, Pu, U, and Hf had been immobilized in the silicate apatite to form $Ca_2Pu_8(SiO_4)_6O_2$ and $Ca_2Gd_7(U/Hf)$ $(SiO_4)_6O_2$ [31]. Rakovan et al. reported that the powder sample of U-rich fluorapatite $Ca_{9.9}U_{0.1}(PO_4)_6F_{1.8}$ was synthesized at 1380 °C for 1–2 days by the solid state reaction process [32]. Luo et al. prepared the single crystals of U- and Th-doped fluorapatite from phosphate-halide-rich melts using the modified