

Thermodynamic studies on charge-coupled substituted synthetic monazite

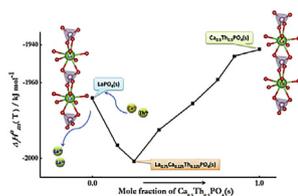


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GRAPHICAL ABSTRACT



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ABSTRACT

Phosphate-based monazite ceramic is considered worldwide as a potential crystalline host matrix for immobilization of long-lived tri- and tetra-valent actinides present in high-level nuclear waste. Monazite is chemically stable with respect to the leaching processes and has high radiation stability. The present paper describes the influence of charged coupled (Ca^{2+} , Th^{4+}) substitution in place of La^{3+} on thermodynamic stability of synthetic monazite ceramics. XRD-analysis of Ca, Th substituted LaPO_4 viz., $\text{La}_{1-x}\text{Ca}_x/2\text{Th}_{x/2}\text{PO}_4$ ($0 \leq x \leq 1$) points to the formation of ideal solid-solution in the entire range of composition. However, thermodynamic analysis indicates deviation from ideal solid-solution with a minima at $x = 0.25$. The substituted $\text{La}_{1-x}\text{Ca}_x/2\text{Th}_{x/2}\text{PO}_4$ system is found to be iso-entropic and stabilized mainly by enthalpy. Enthalpies of formation as a function of Ca^{2+} , Th^{4+} substitution were analysed to provide insights into the development of thermodynamically stable nuclear waste matrix.

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1. Introduction

Immobilization of long-lived high level radio nuclides with half-lives in the range of 10^3 – 10^5 years is a serious challenge. Various ceramic matrices with mineral structures of monazite, zircon, thorite, britholite, pyrochlore, perovskite or zirconolite have been proposed for the immobilization of long lived radio isotopes such as minor actinides [1,2]. Among these, phosphate-based ceramics like monazites are the most prominent host matrix for immobilization

of trivalent and tetravalent actinides. A detailed description on crystal chemistry of monazite has been given by Clavier et al. [3]. Dacheux et al. explained the high-structural flexibility and chemical durability of monazite [4]. Schlenz et al. [5] reviewed monazite and their solid solutions to corroborate the suitability of this matrix as a potential waste form. Monazite has high chemically stable with respect to leaching [6,7], has high radiation resistant property [8,9] and ability to incorporate large amounts of U, Th and other actinides [10,11]. The incorporation of tetravalent ions (Th^{4+} and U^{4+}) in monazite minerals can be explained by Cheralite (or Brabantite) and Huttonite-type substitution reactions. In Cheralite-type substitution, the trivalent lanthanide (Ln^{3+}) sites are substituted by tetravalent actinide An^{4+} along with divalent alkaline earth metal

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ions (M^{2+}) for charge compensation, The Cheralite-type substitution reaction can be expressed as: $2Ln^{3+} \leftrightarrow An^{4+} + M^{2+}$, whereas in Huttonite-type substitution reaction: trivalent lanthanide (Ln^{3+}) and pentavalent P^{5+} sites are substituted by tetravalent An^{4+} and Si^{4+} ions expressed as: $Ln^{3+} + P^{5+} \leftrightarrow An^{4+} + Si^{4+}$. Recent studies on monazite minerals indicate that the Cheralite-type is the predominant substitution mechanism for actinides [12–14]. Experimental observations indicate the formation of an ideal solid solution between the two end-members i.e. monazite ($M^{3+}PO_4$) and cheralite ($M^{2+}M^{4+}(PO_4)_2$), with the formation of a complex phosphate having general formula $M^{3+}_{1-x}M^{2+}_x/2M^{4+}_{x/2}PO_4$. Terra et al. [15] reported synthesis and characterization of single phase (Th,U)-brabantites ($Ca_{0.5}Th_{0.5-y}U_yPO_4$) and (Th,U)-monazite/brabantite solid solutions with general formula $Ln_{1-2x}Ca_xTh_{x-y}U_yPO_4$ (with $0.1 \leq x \leq 0.4$ and $y = x/5$). Montel et al. [16] and Podor and Cuney [17] have reported the complete solid solution between $LaPO_4$ – $Ca_{0.5}Th_{0.5}PO_4$ systems. The formation of solid solution between $LaPO_4$ – $CaU(PO_4)_2$ pseudo-binary systems was reported by Podor et al. [18]. Konings et al. [19] have carried out the drop calorimetry measurements on $LaPO_4$ – $Ca_{0.5}Th_{0.5}PO_4$ and $CePO_4$ – $Ca_{0.5}Th_{0.5}PO_4$ solid solutions at 1005 K to determine the excess thermodynamic properties. Popa et al. [20] determined the low-temperature heat capacity from 0.5 to 300 K, enthalpy increments from 485 to 1565 K, and the enthalpy of formation of cheralite; $Ca_{0.5}Th_{0.5}PO_4$, from the oxides. To the best of our knowledge, there are no previous reports on thermodynamic properties of pseudo binary $LaPO_4$ – $Ca_{0.5}Th_{0.5}PO_4$ solid solution system.

In the present work, we report synthesis, characterization and thermodynamic properties of Ca^{2+} , Th^{4+} substituted $LaPO_4$ solid solutions measured employing calorimetric techniques. High temperature calorimetry has been used to determine the standard molar enthalpy of formation of $La_{1-x}Ca_{x/2}Th_{x/2}PO_4(s)$ ($x = 0, 0.15, 0.25, 0.40, 0.60, 0.75, 0.85, 1$) compositions. The isobaric heat capacities of the compounds have been measured by differential scanning calorimetric technique. Based on the experimental data obtained from these studies and the available thermodynamic data for the component oxides, thermodynamic functions for $La_{1-x}Ca_{x/2}Th_{x/2}PO_4(s)$ ($x = 0, 0.15, 0.25, 0.40, 0.60, 0.75, 0.85, 1$) have been generated.

2. Experimental

2.1. Material synthesis and characterization

$La_{1-x}Ca_{x/2}Th_{x/2}PO_4(s)$ ($x = 0, 0.15, 0.25, 0.40, 0.60, 0.75, 0.85, 1$) solid solutions were synthesized by solid state synthesis route in the lines of the procedure given in the literature [21]. Homogeneous mixtures of La_2O_3 (Sigma Aldrich), $CaCO_3$ (Sigma Aldrich), ThO_2 (Nuclear Grade) and ammonium dihydrogen phosphate $NH_4H_2PO_4$ (Alfa, 99.99%) in appropriate molar ratios were heated at a rate $3 K \cdot min^{-1}$ up to 1073 K and equilibrated for 8 h. The products were again homogenized, pelletized and further heated at 1473 K for 10 h. The sintered products were characterized by a STOE X-ray diffractometer employing $Cu K\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). X-ray scans were recorded in the 2θ range of 10° to 70° with a step width 0.02° . Structural analysis of the samples were done using Fullprof-2000 Rietveld refinement program. In the starting step the background parameters were adjusted with sixth order polynomial and appropriate scale factor. The observed diffraction peak profile was fitted with Pseudo-Voigt profile function and U, V, W parameters were refined. No absorption and displacement parameter were considered during the refinement. The purity of the samples and the starting materials were determined by chemical analysis method using ICP-AES technique and is given in Table 1.

2.2. Heat capacity measurements

Heat capacity $C_{p,m}(T)$ of $La_{1-x}Ca_{x/2}Th_{x/2}PO_4(s)$ ($x = 0, 0.15, 0.25, 0.40, 0.60, 0.75, 0.85, 1$) samples were measured employing a Mettler Toledo Differential Scanning Calorimeter (DSC 1). The temperature and heat flow calibration of the DSC were performed by melting high purity In and Zn standards. Heat capacity measurements were carried out in the temperature range of 300–825 K. High purity argon gas was passed at a flow rate $0.02 \text{ dm}^3 \text{ min}^{-1}$ over the samples. For measurement of $C_{p,m}(T)$, classical three-step method [22] was used for blank, sapphire and sample runs in a step heating mode. The first step of each run was an isothermal run for fifteen minutes at an initial temperature; the second step was a dynamic one with a heating rate of 5 K min^{-1} and the final step was another isothermal run for fifteen minutes at the final temperature. 80 mg of each sample of $La_{1-x}Ca_{x/2}Th_{x/2}PO_4(s)$ ($x = 0, 0.15, 0.25, 0.40, 0.60, 0.75, 0.85, 1$) was pelletized and loaded in sealed 40 μl Al pan for the heat capacity measurements. The specific heat capacity was calculated from following relation:

$$C_{p,m}^o(T)_{\text{sample}} = \left(\frac{HF_{\text{sample}} - HF_{\text{blank}}}{HF_{\text{ref.}} - HF_{\text{blank}}} \right) \left(\frac{M_{\text{ref.}}}{M_{\text{sample}}} \right) \cdot C_{p,m}^o(T)_{\text{ref.}} \quad (1)$$

where, HF_{blank} , $HF_{\text{ref.}}$ and HF_{sample} represent heat flow during blank, sapphire and sample runs, respectively. $C_{p,m}(T)_{\text{sample}}$ and $C_{p,m}(T)_{\text{ref.}}$ are the specific heat capacity, and M_{sample} and $M_{\text{ref.}}$ are the molar masses of sample and sapphire, respectively. The heat capacity measurement was standardized by properly adjusting the sample size, heating rate and carrier gas flow conditions.

2.3. High temperature calorimetry

The standard molar enthalpies of formation of $La_{1-x}Ca_{x/2}Th_{x/2}PO_4(s)$ ($x = 0, 0.15, 0.25, 0.40, 0.60, 0.75, 0.85, 1$) samples were determined from the heat of dissolution data of each composition in liquid $PbO + B_2O_3$ (2:1 molar ratio) solvent at 1089 K employing a high temperature Calvet calorimeter (Setaram, Model HT-1000). The molar enthalpies of dissolution of the binary constituents such as $La_2O_3(s)$, $CaO(s)$ and $ThO_2(s)$ were also determined following similar procedure.

The solvent was prepared by heating 2:1 molar mixture of perfectly dried $Pb(NO_3)_2$ (BDH, reagent grade) and boric acid (BDH, reagent grade) in an ALLOY-690 container at 933 K. $Pb(NO_3)_2$ and boric acid decomposed to PbO and B_2O_3 , forming a eutectic mixture. The melt was maintained at 933 K for 3 h for homogenization. The entire mass was removed from the ALLOY-690 container and grinded again to make uniform powder. The solvent powder was characterized by chemical analysis and XRD techniques. The atom percent of Pb, B and O obtained from the chemical analysis of the solvent were found to be 22.21 ± 0.04 , 22.23 ± 0.05 and 55.54 ± 0.08 , respectively. No other chemical impurity was observed from elemental analysis of the solvent mixture. Powder ($PbO + B_2O_3$, 2:1 molar ratio) from the same lot was used as solvent in all reaction enthalpy measurements.

6 g of $PbO + B_2O_3$ solvent was taken in each of the two identical platinum tubes which act as a protective lining and having outer diameter matching exactly with the alumina reaction cell for proper thermal contact. The reaction cell assembly was slowly lowered into the calorimeter and it was programmed up to 1089 K at a heating rate of 0.5 K min^{-1} and maintained at $1089 \pm 0.05 \text{ K}$ during each drop experiment. The reaction tubes were equilibrated inside the chamber for 12 h to attain a steady base line for heat flux signal. The slope of the base line of the

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