STUDIES ON THORIUM BEARING MONAZITE-BRABBANTITE SOLID SOLUTIONS: AN ACTINIDE STORAGE MATRIX

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INTRODUCTION

India has an active research program on thorium fuel cycle due to lack of uranium resources and significant thorium reserves and it was excluded from international uranium markets between 1974 to 2008. Thorium can be used as a fuel for light water reactors, heavy water reactors, sodium-cooled fast reactors, sub-critical accelerator driven reactors and molten salt reactors. The $^{232}$Th-$^{233}$U fuel cycle involved in these reactor types are attractive for lower levels of long lived minor actinides (Np, Am, Cm) for at least first few cycles. However, it is probable that the back end of thorium fuel cycle containing long-lived $^{210}$Pa, $^{228}$Th, $^{230}$Th and low level of minor actinides would still require high level waste (HLW) management for the geological repositories. 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, zirconlote, pyrochlore and monazites have been proposed as candidates for the storage of actinides. The natural monazites mineral exist for billions of years with appreciable amounts of thorium and uranium has suggested that analogs of these minerals would be ideal hosts for the immobilization of HLW. The LnPO$_4$ (Ln = La-Gd) with monazite-type structure incorporates a remarkably wide range of cations because of presence of low symmetry LnO$_6$ coordination polyhedron in it. In natural monazite system, charge balance for Ln-Th substitution is maintained by two major mechanisms: brabantite and huttonite substitutions. In the brabantite substitution $2$Ln$^{3+}$ ↔ An$^{3+}$ + Ca$^{2+}$, exchange takes place in the large cation position and in huttonite-type substitution: Th$^{4+}$ is charge balanced by substitution takes place on tetrahedral sites, Ln$^{3+}$ + P$^{5+}$ ↔ An$^{4+}$ + Si$^{4+}$. The brabantite CaTh(PO$_4$)$_2$; belong monazite type in which two trivalent Ln$^{3+}$ ions are randomly substituted by Ca$^{2+}$ and Th$^{4+}$ leaving the total charge balanced. The monocarbonate-brabantite solid solution with general formula $\text{M}_{1-x-y}$-$\text{Ca}_{x}$-$\text{Th}_{y}$$(\text{PO}_4)_2$(s) could appear as a suitable matrix for the incorporation of minor actinides in the trivalent and tetravalent oxidation states. The studies on LaPO$_4$–CaU(PO$_4$)$_2$ and CePO$_4$–CaU(PO$_4$)$_2$ systems have been reported in the literature [1,2]. However, specific heat capacities of these solid solutions have not been reported in the literature. In order to prevent heat up of actinide storage matrix due to decay heat of the actinides, the material with high specific heat is desirable. Hence, the goal of this study is to synthesize and characterized $\text{La}_{2-x}$-$\text{Ca}_{x}$-$\text{Th}_{y}$($\text{PO}_4$)$_2$(s) ($x = 0, 0.25, 0.5, 0.75, 1$) solid solutions and measured their heat capacities using differential scanning calorimeter.

EXPERIMENTAL

Synthesis and characterization of $\text{La}_{2-x}$-$\text{Ca}_{x}$-$\text{Th}_{y}$($\text{PO}_4$)$_2$(s) ($x = 0, 0.25, 0.5, 0.75, 1$) $\text{La}_{2-x}$-$\text{Ca}_{x}$-$\text{Th}_{y}$($\text{PO}_4$)$_2$(s) ($x = 0, 0.25, 0.5, 0.75, 1$) solid solutions were synthesized by the solution chemistry route using co-precipitation method. In this method, reagents, $\text{La(NO}_3$)$_3$; $7$H$_2$O (Sigma-Aldrich, 99.999%), Ca(NO$_3$)$_2$; $4$H$_2$O (Fisher, 99%) and Th(NO$_3$)$_3$; $5$H$_2$O (NFC, Hyderabad, 99.999%), were mixed in required stoichiometry and dissolved in deionized water with constantly stirring to ensure homogeneity. Addition of an aqueous solution of ammonium dihydrogen phosphate NH$_4$H$_2$PO$_4$ (Alfa, 99.99%) to this homogeneous solution resulted in the formation of precipitate which was washed with distilled water and dried using infra-red lamp. The dried products were heated at 550 K for 4 h, then pelletized and heated at 1100 K for 4 h and finally heated pellet was reground and re-pelletized for further heating at 1473 K for 6 h. $\text{La}_{2-x}$-$\text{Ca}_{x}$-$\text{Th}_{y}$($\text{PO}_4$)$_2$(s) ($x = 0, 0.25, 0.5, 0.75, 1$) were characterized using a STOE theta–theta X-ray diffractometer using a graphite monochromatic Cu $K\alpha$ radiation ($\lambda = 1.5406$ Å). The 20 positions obtained for $\text{La}_{2-x}$-$\text{Ca}_{x}$-$\text{Th}_{y}$($\text{PO}_4$)$_2$(s) ($x = 0, 0.25, 0.5, 0.75, 1$) are shown in Fig. 1. The XRD pattern of pure LaPO$_4$(s) and CaTh(PO$_4$)$_2$ matched well with the reported patterns [1,2].

Heat capacity measurements

The Heat capacity measurements of $\text{La}_{2-x}$-$\text{Ca}_{x}$-$\text{Th}_{y}$($\text{PO}_4$)$_2$(s) ($x = 0, 0.25, 0.5, 0.75, 1$) were carried out using a heat flux-type differential scanning calorimeter (DSC 823/700 of M/s. Mettler Toledo GmbH, Switzerland explained in our previous study [3]. Heat capacity measurements were carried out using classical three-step (blank, sapphire and sample runs) method in a continuous heating mode in the temperature range of 298–873 K with heating rate of 5 K min$^{-1}$ under high pure oxygen gas flow rate of 0.05 dm$^3$ min$^{-1}$ over the sample. Each run has an initial isothermal section of fifteen minutes; middle section was a dynamic one with a heating rate of 5 K min$^{-1}$ and the final section at the final temperature was another isothermal run for fifteen minutes. A thin disc of sapphire was used as a heat
RESULTS AND DISCUSSION

Indexing cell parameters of \( \text{La}_{x} \text{Ca}_{3-x} \text{Th}_{x} \text{(PO}_4)_2(s) \)

The Fig. 1 shows that \( \text{La}_{x} \text{Ca}_{3-x} \text{Th}_{x} \text{(PO}_4)_2(s) \) (\( x = 0, 0.25, 0.5, 0.75, 1 \)) solid solutions are crystalline and indexed in the monoclinic system. The room temperature lattice parameters of \( \text{La}_{x} \text{Ca}_{3-x} \text{Th}_{x} \text{(PO}_4)_2(s) \) (\( x = 0, 0.25, 0.5, 0.75, 1 \)) solid solutions with equal amount of Ca and Th substitution at the site of La were refined using least squares method. The calculated lattice parameters of these solid solutions were found to deviate smoothly from the Vegard’s law. However, the unit cell volume of monoclinic \( \text{LaPO}_4(s) \) and \( \text{CaTh(PO}_4)_2(s) \) are in good agreement with that reported in the literature.

Heat capacity

Heat capacities for \( \text{La}_{x} \text{Ca}_{3-x} \text{Th}_{x} \text{(PO}_4)_2(s) \) (\( x = 0, 0.25, 0.5, 0.75, 1 \)) solid solutions were measured in the temperature range 290–873 K and is given in Fig. 2 and fitted into least square expression as a function of temperature and are given in Table 1.

Table 1: Coefficients of heat capacity of \( \text{La}_{x} \text{Ca}_{3-x} \text{Th}_{x} \text{(PO}_4)_2(s) \)

<table>
<thead>
<tr>
<th>Solid solutions</th>
<th>( C_p^\infty(T) = A + BT + CT^2 )</th>
<th>( J \text{ mol}^{-1} \text{ K}^{-1} \text{ (298-873 K)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( x )</td>
<td>( A )</td>
<td>( B )</td>
</tr>
<tr>
<td>0</td>
<td>114.97</td>
<td>0.0366</td>
</tr>
<tr>
<td>0.25</td>
<td>234.79</td>
<td>0.0691</td>
</tr>
<tr>
<td>0.50</td>
<td>239.25</td>
<td>0.0652</td>
</tr>
<tr>
<td>0.75</td>
<td>243.40</td>
<td>0.0615</td>
</tr>
<tr>
<td>1</td>
<td>265.85</td>
<td>0.0479</td>
</tr>
</tbody>
</table>

The specific heat capacity values for \( \text{La}_{x} \text{Ca}_{3-x} \text{Th}_{x} \text{(PO}_4)_2(s) \) (\( x = 0.25, 0.5, 0.75 \)) solid solutions are not reported in the literature to compare. However, values for heat capacities of \( \text{LaPO}_4(s) \) and \( \text{CaTh(PO}_4)_2(s) \) measured in this study show reasonable agreement between that reported by Popa et al. [2]. It was also observed from Fig. 2 that specific heat of \( \text{La}_{x} \text{Ca}_{3-x} \text{Th}_{x} \text{(PO}_4)_2(s) \) (\( x = 0.25, 0.5, 0.75 \)) increase with increase in the concentration of Ca and Th in the solid solutions.

CONCLUSION

\( \text{La}_{x} \text{Ca}_{3-x} \text{Th}_{x} \text{(PO}_4)_2(s) \) (\( x = 0, 0.25, 0.5, 0.75, 1 \)) solid-solutions were synthesized by solution chemistry route and characterized by XRD. A single phase solid solution was found for \( \text{La}_{x} \text{Ca}_{3-x} \text{Th}_{x} \text{(PO}_4)_2(s) \) (\( x = 0, 0.25, 0.5, 0.75, 1 \)), however, the lattice parameters of these solid solutions were found to deviate (negative) from Vegard’s law. It might be due to lattice strains resulting from the substitution of ions of different sizes on the cation sites. The specific heat capacity data of \( \text{La}_{x} \text{Ca}_{3-x} \text{Th}_{x} \text{(PO}_4)_2(s) \) (\( x = 0.25, 0.5, 0.75 \)) solid solutions were measured for the first time and were found to increase with increasing concentration of \( \text{CaTh(PO}_4)_2(s) \).

REFERENCES