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Investigations on the charge compensation on Ca and U substitution in $CePO_4$ by using XPS, XRD and Raman spectroscopy

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Abstract

This article discusses the charge compensation mechanism in Ca and U - substituted monazite ($CePO_4$). The monazite compositions $Ce_{0.6}Ca_{0.2}U_{0.2}PO_4$, $Ce_{0.8}Ca_{0.2}PO_4$ and $CePO_4$ were prepared by solution chemistry route. XRD and μ-Raman studies confirm that the compounds are single phase materials. XPS studies on $Ce_{0.8}Ca_{0.2}PO_4$ shows the presence of Ce^{4+} in addition to Ce^{3+} whereas in $Ce_{0.6}Ca_{0.2}U_{0.2}PO_4$ cerium is in +3 state with uranium in +4 valence state. Partial substitution of Ca in $CePO_4$ (i.e. $Ce_{0.8}Ca_{0.2}PO_4$), leads to the generation of Ce^{4+} which subsequently reverts to Ce^{3+} in $Ce_{0.6}Ca_{0.2}U_{0.2}PO_4$ upon U substitution. The $Ce^{3+} \rightleftharpoons Ce^{4+}$ intrinsic charge compensation existing in monazite, essential for the incorporation of higher valence cations, is demonstrated. This mechanism assists the incorporation of $M^{2+/4+}$ in the monazite lattice without requiring coupled substitution.

Keywords: Cerium orthophosphate; Ca and U substitution; Thermal analysis; Laser Raman and XPS studies; Nuclear materials

1. Introduction

Immobilization of high level radioactive wastes (HLW) has become a thrust area in nuclear technology. Presently, borosilicate glass is used for the waste immobilization. However, the devitrification of the glass due to decay heat leads to the potential risk of leaching of the radioactive elements from the glass waste form. Hence there is a need for the search for alternate matrices with greater radiation, chemical and thermal stability. Monazite, one of the sources for the actinides, thorium and uranium, is a mixed rare-earth orthophosphate, a natural crystalline mineral known to exist for billions of years [1]. The idea that this natural mineral contains appreciable amounts of alpha active thorium and uranium has led researchers across the globe to explore its potential as a host for the immobilization of radioactive waste[2]. Its excellent chemical and radiation stability[3] augments its candidature to be an alternative crystalline host for the high-level radioactive waste (HLW). Besides, monazites have survived geological upheavals such as earthquakes and intrusion of igneous melts. The advantage of monazite as the ceramic host is that it is single-phase and accommodates almost all the elements of the HLW as solid solution in its crystal structure. Monazite also has excellent thermal stability with a melting point above 2000 °C, and does not decompose until it melts[3].

The crystal structure of monazite is monoclinic[4] ($P2_1/n$, No.14) and Fig. 1(a) shows the crystal structure of typical monazite, $CePO_4$. The lattice parameters of $CePO_4$ (PDF # 32-0199)[5] are $a=6.800$ Å, $b=7.023$ Å, $c=6.471$ Å and $\beta=103.46^\circ$ with the cell volume $V=300.60$ Å^3 and number of formula units $Z=4$. In this structure all the atoms occupy the general site (Wyckoff symbol 4e) and therefore can move around in cohesion without disturbing the crystal symmetry during atomic substitutions. It is probably this property or flexibility of monazite crystal structure that makes it unique to accommodate chemically diverse cations of the HLW into its crystal lattice. The structure of $CePO_4$ is composed

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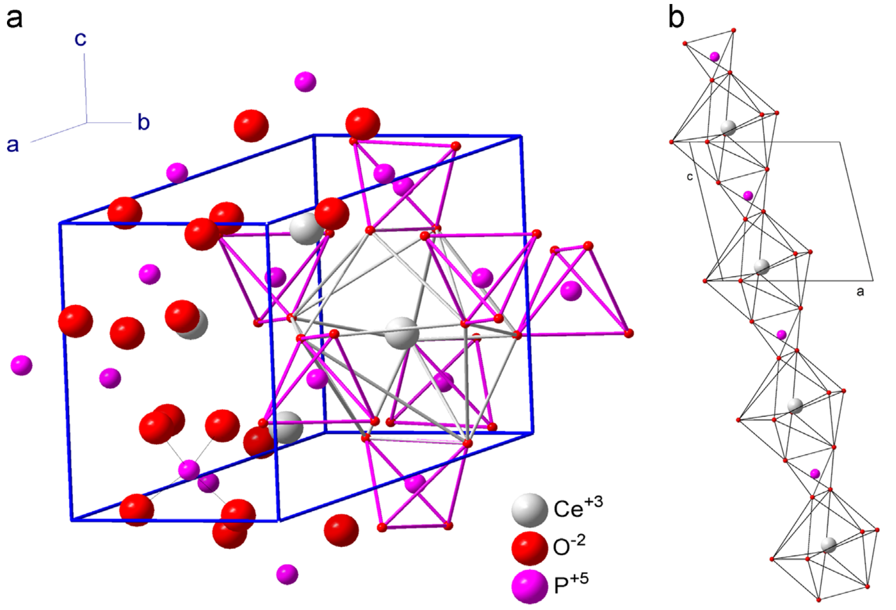

Fig. 1. (a) Crystal structure of monazite, $CePO_4$, (b) Inter-linked chain-like strands of PO_4 and CeO_9 polyhedra along the c-axis.

of nine-coordinated Ce atoms linked together by distorted phosphate tetrahedra. The edge shared PO_4 tetrahedra and the CeO_9 polyhedra form inter-linked chain-like strands along the c-axis[6] as shown in Fig. 1(b).

The objective of the research is to identify a single matrix which can accommodate high level radioactive waste comprising of elements with oxidation states varying from +1 (for example, Cs) to +6 (for example Mo) with an average valence state more than +3. The HLW contains such diverse elements. The rare earth monazite ($LnPO_4$, $Ln=RE^{3+}$) cannot accommodate cations with valence other than three, without coupled substitution[7,8]; for example $Ln^{3+}_{1-2x}M^{2+}_xR^{4+}_xPO_4$ in $Ln^{3+}PO_4$. In other words, incorporation of a tetravalent ion in $LnPO_4$ needs an equal amount of a divalent cation substitution. This problem can be avoided if we develop a general monazite composition which can offer variable valences for charge compensation.

$CePO_4$, with cerium offering variable valences (+3 and +4) stands as a promising base monazite which prompted us to explore the internal charge balance offered by cerium in $CePO_4$. The average oxidation state of HLW being greater than three, a divalent substituted matrix ($Ce_{0.8}Ca_{0.2}PO_4$) is worked out as a base to satisfy the charge balance during HLW immobilization, and the valence states of cerium in this material is investigated[9]. Partial substitution of calcium in $CePO_4$ leads to a partial oxidation of Ce^{3+} to Ce^{4+}. If this is the case, substitution of a higher valence cation in $Ce_{0.8}Ca_{0.2}PO_4$ should force the reduction of Ce^{4+} to Ce^{3+} in proportion. The objective is to establish the flexibility of this intrinsic charge compensation mechanism which provides unique features in accommodating elements with different valence by using the case study of $Ce_{0.8}Ca_{0.2}U_{0.2}PO_4$. The Ce and U have multiple valences and their valence states in this compound are determined by using XPS. The valence balancing in this compound is revealed by comparing it with that in Ca doped $CePO_4$ without U ($Ce_{0.8}Ca_{0.2}PO_4$, i.e., $Ce^{3+}_{0.6}Ce^{4+}_{0.2}Ca^{2+}_{0.2}PO_4$).

Table 1
Mole ratios of the starting materials taken for the preparation.

Compound	$CePO_4$	$Ce_{0.8}Ca_{0.2}PO_4$	$Ce_{0.6}Ca_{0.2}U_{0.2}PO_4$
$Ce(NH_4)_2(NO_3)_6$	1.0	0.80	0.600
$Ca(NO_3)_2 \cdot 4H_2O$	–	0.20	0.200
U_3O_8	–	–	0.067
$NH_4H_2PO_4$ (ADP)	1.0	1.00	1.000

2. Experimental

2.1. Sample preparation

Samples of the nominal composition of $Ce_{0.6}Ca_{0.2}U_{0.2}PO_4$, $Ce_{0.8}Ca_{0.2}PO_4$ and $CePO_4$ were prepared by a wet chemical route as reported elsewhere[9]. Analytical reagent grade ceric ammonium nitrate ($Ce(NH_4)_2(NO_3)_6$), calcium nitrate tetrahydrate ($Ca(NO_3)_2 \cdot 4H_2O$), uranium oxide (U_3O_8) and ammonium dihydrogen phosphate (ADP, $NH_4H_2PO_4$) were used and the mole ratios taken for the preparation are given in Table 1. ADP solution was added to a mixture of the other solutions under constant stirring. A yellowish precipitate was formed in the case of $Ce_{0.6}Ca_{0.2}U_{0.2}PO_4$ whereas a gelatinous white precipitate was formed in the case of $Ce_{0.8}Ca_{0.2}PO_4$ and $CePO_4$. The products were dried on a hot plate kept at around 70 °C. The as-dried precipitate was ground and heated at 300 °C for 2 h in air. During the drying process, ammonium nitrate decomposes at about 270 °C resulting in the formation of very reactive nanocrystalline precursor powders. The calcined powders were ground, pelletized and sintered at 1000 °C in air.