



Synthesis and leachability study of a new cesium immobilized langbeinite phosphate: $\text{KCsFeZrP}_3\text{O}_{12}$



Sathasivam Pratheep Kumar*, Buvanewari Gopal

Materials Chemistry Division, School of Advanced Sciences, VIT University, Vellore 632 014, Tamil Nadu, India

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ABSTRACT

A potassium cesium iron zirconium phosphate, $\text{KCsFeZrP}_3\text{O}_{12}$, was synthesized by simple solution method for the first time. Powder X-ray diffraction analysis confirmed that the compound crystallizes in cubic langbeinite structure (space group: $P2_13$) with the cell parameters of $a = 10.103$ (2) Å and $V = 1031$ Å³. Fourier transform infrared spectrum showed the stretching and bending vibrational bands of phosphate tetrahedra. Energy dispersive X-ray analysis proved the presence of elements. Leachability of a powder specimen was studied by MCC-5 test for a period of one month. Inductive coupled plasma and atomic absorption spectroscopic results revealed the negligible leaching of cesium. The normalized mass loss of potassium, iron, zirconium and phosphorous were found to be in the order of 10^{-4} – 10^{-3} g/m², 10^{-6} – 10^{-4} g/m², 10^{-5} – 10^{-3} g/m² and 10^{-4} – 10^{-3} g/m² respectively. For comparison, a cesium zirconium phosphate ($\text{CsZr}_2\text{P}_3\text{O}_{12}$) with the sodium zirconium phosphate structure was synthesized, and its leach rates of zirconium and phosphorous were comparable to those of the langbeinite phase. The cesium leach rate was negligible for both compounds.

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1. Introduction

Since the discovery of a mineral $\text{K}_2\text{Mg}_2(\text{SO}_4)_3$, compounds of langbeinite structure with the general formula $\text{M}_2^+\text{M}_2^{2+}(\text{XO}_4)_3$ where M^+ : K, Na; M^{2+} : alkaline earth metals; X: S, P, V have been widely investigated in various fields. This class of compounds is impressive as they exhibit interesting properties such as magnetic, luminescence and phase transitions [1–4]. The crystal structure of langbeinite is closely related to the structure of Nasicon ($\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$), Garnet ($\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$) and $\text{Sc}_2(\text{WO}_4)_3$ [5]. The basic unit of these family of compounds is $[\text{M}_2(\text{XO}_4)_3]$ which is formed by the corner sharing MO_6 octahedra and XO_4 tetrahedra. Sodium zirconium phosphate (NZP) and langbeinite structures have the similar framework but different spatial packing. The three dimensional framework of langbeinite structure consists of MO_6 octahedra and XO_4 tetrahedra interlinked via vertexes [6]. This leads to the formation of interstitial holes which are large enough to accommodate a bigger mono and divalent cations.

A wide range of high temperature synthetic compounds belongs to langbeinite structure are known with a variety of ionic substitutions. The crystal structures of zirconium based phosphates such as

$\text{K}_2\text{FeZr}(\text{PO}_4)_3$, $\text{K}_2\text{LnZr}(\text{PO}_4)_3$ (Ln = Ce–Yb, Y), $\text{Rb}_2\text{FeZr}(\text{PO}_4)_3$, $\text{Cs}_{1+x}\text{Ln}_x\text{Zr}_{2-x}(\text{PO}_4)_3$ (Ln = Sm–Lu) and $\text{K}_2\text{LuZr}(\text{PO}_4)_3$ were reported [6–10]. Shpanchenko et al. have studied the structure and magnetic susceptibility of lead vanadium langbeinite phosphate [11]. Furthermore, $\text{Na}_2\text{MTi}(\text{PO}_4)_3$ (M = Fe, Cr), $\text{K}_2\text{MTi}(\text{PO}_4)_3$ (M = Er, Yb or Y), $\text{K}_2\text{AlTi}(\text{PO}_4)_3$, $\text{NaBaFe}_2(\text{PO}_4)_3$, $\text{Ba}_{1.5}\text{Fe}_2(\text{PO}_4)_3$, $\text{K}_2\text{YHf}(\text{PO}_4)_3$, $\text{Rb}_2\text{YbTi}(\text{PO}_4)_3$, $\text{Rb}_2\text{Ti}_{1.01}\text{Er}_{0.99}(\text{PO}_4)_3$, $\text{Cs}_2\text{Ni}_2(\text{MoO}_4)_3$, and $\text{K}_2\text{Sn}_x(\text{PO}_4)_3$ ($x = \text{Fe, Yb}$) were established [12–21]. Recently, the crystal structure of strontium substituted iron phosphate with langbeinite framework was developed by Hidouri et al. [22].

High Level Nuclear Waste (HLW) produced during the reprocessing of spent nuclear fuel contains long half-life fission products such as cesium, strontium and transuranic elements. For the safe disposal of HLW, immobilization of these radioactive elements into different matrices such as borosilicate glasses [23], synroc [24], phosphate ceramics and their crystal chemistry have been investigated by several researchers [25–27]. Among the phosphate ceramics, sodium zirconium phosphate (NZP) has been extensively studied as host lattice for the HLW disposal due to its structural flexibility towards the ionic substitutions [27,28]. Similarly, a recent review by Orlova et al. emphasized that langbeinite could be a possible candidate to accommodate various radioactive elements present in the high level nuclear waste [29]. Zaripov et al. proved that cesium can be introduced into the cavity of langbeinite structure [30].

* Corresponding author. Present address: National Institute for Materials Science, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan. Tel.: +81 29 859 2000x3795; fax: +81 29 859 2401.

E-mail address: pratheepvit@gmail.com (S.P. Kumar).

Isotope of cesium (^{137}Cs) is considered as one of the most important radioactive elements present in the HLW due to its higher half-life period ($t_{1/2}$: 30 years), volatility at higher temperatures, capability to form water soluble phases and radiation effects to the human tissues [31,32]. Therefore, ^{137}Cs has to be immobilized in an inert matrix for the safe disposal. In this regard, immobilization of cesium into borosilicate glass [33], synroc [34], sodium zirconium phosphate [35] and apatite [36] structures has been investigated in the literature. However, cesium incorporation into the langbeinite structure is limited. The crystal chemistry of langbeinite structure indicates that the closed cavity present in the framework can accommodate a bigger cesium ion and effectively restrict its leachability from the lattice. Hence, in the present work a novel single phasic cesium containing langbeinite phosphate was synthesized by simple solution method. In order to compare the leachability of cesium and zirconium ions from langbeinite structure, a known sodium zirconium phosphate (NZP) family member $\text{CsZr}_2(\text{PO}_4)_3$ has been synthesized and analyzed.

2. Experimental

2.1. Materials

$(\text{COOK})_2\cdot\text{H}_2\text{O}$ (99.5%, CDH, India), CsNO_3 (99.5%, Sigma Aldrich, India), $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$ (98%, Qualigens), $\text{ZrOCl}_2\cdot 8\text{H}_2\text{O}$ (Loba Chemie, India) and H_3PO_4 (88%, S.D. Fine) were used as starting materials.

2.2. Synthesis of $\text{KCsFeZrP}_3\text{O}_{12}$ (KCFZ) and $\text{CsZr}_2\text{P}_3\text{O}_{12}$ (CZP)

Stoichiometric amounts of potassium oxalate, cesium nitrate, zirconyl chloride and phosphoric acid were dissolved separately in minimum quantity of deionized water. Initially, the clear solutions of cesium nitrate, zirconyl chloride and potassium oxalate were mixed together. To the homogeneous metal solutions, phosphoric acid solution was added drop wise with constant stirring. The resultant mixture was further stirred for 20 min at room temperature and dried at 80°C for 24 h. The dried precursor was calcined at $600^\circ\text{C}/8\text{ h}$ and $800^\circ\text{C}/24\text{ h}$. In the case of cesium zirconium phosphate (CZP) preparation, the precursor was calcined at 300, 600, 900 and $1200^\circ\text{C}/24\text{ h}$ to obtain the product.

2.3. Leachability analysis

Leachability of the powder samples KCFZ and CZP were analyzed by Soxhlet test (MCC-5) under dynamic condition. The detailed experimental conditions were given in our previous study [36]. The experiment involves continuous exposure of the sample to fresh leachant (deionized water) in a Soxhlet apparatus. 1.0 g of the sieved powder sample was introduced into the sample holder of the Soxhlet extractor into which 500 ml of deionized water was taken as a leachant. The leachant was heated to boil, vaporized and condensed through the condenser. The condensed vapors were allowed to fall on the sample as droplets. The flow of fresh leachant was maintained at the rate of 1.0 L/day. After each 24 h interval, 20 ml of the leachate was collected for elemental analysis and the same volume of the leachant was replaced by a fresh deionized water to maintain the constant volume. BET surface area of powder samples KCFZ and CZP was found to be 2.4102 and $1.2005\text{ m}^2/\text{g}$ respectively by nitrogen adsorption method.

2.4. Characterization

Phase formation of the synthesized compounds was analyzed by Powder X-ray diffraction (XRD) method (Cu $K\alpha$, Bruker, D8 Advanced) at room temperature. The unit cell parameters and cell volume were calculated by least square refinement method. Fourier Transform Infrared Spectrum (FTIR) was recorded on JASCO, FTIR/4100 spectrometer using KBr pellet technique in the frequency range of $400\text{--}4000\text{ cm}^{-1}$. FEI Quanta FEG 200 attached with EDS Scanning Electron Microscope (SEM) was used to observe the morphology of samples. Surface area for the powder sample was measured using BET technique on Micromeritics, ASAP 2020 V3.00H. Elemental analysis was obtained by Inductively Coupled Plasma Optical Emission Spectroscopic (ICP-OES) technique using Perkin Elmer, Optima 5300 DV ICP-OES. Cesium concentration was also performed using Atomic Absorption Spectrometer (Varian AA240).

3. Results and discussion

3.1. Powder XRD, FTIR and SEM analysis

Powder XRD pattern of KCFZ indexed based on $\text{K}_2\text{FeZrP}_3\text{O}_{12}$ (ICDD No: 056-0313) was compared with $\text{K}_2\text{FeZrP}_3\text{O}_{12}$ and given in Fig. 1. Analysis of the data reveals that the compound is phase pure and crystallizes in cubic langbeinite structure. The unit cell parameter was calculated by least square refinement method and compared with $\text{K}_2\text{FeZrP}_3\text{O}_{12}$ (Table 1). An increase in the cell parameter and cell volume of KCFZ was noticed with replacement of potassium ion by cesium ion. This is due the difference between ionic radii of 'Cs' and 'K'. Partial replacement of smaller potassium ion K^+ (1.38 Å) by bigger cesium ion Cs^+ (1.67 Å) lead to the expansion of the lattice and increased the 'a' parameter and cell volume. The powder XRD pattern of $\text{CsZr}_2\text{P}_3\text{O}_{12}$ indexed based on ICDD No: 34-0196 showed the formation of pure phase.

FTIR spectrum of KCFZ is shown in Fig. 2b. For comparison the FTIR spectrum of parent $\text{K}_2\text{FeZrP}_3\text{O}_{12}$ is given in Fig. 2a. The vibrational modes of P–O in the spectrum are comparable to that of $\text{K}_2\text{FeZrP}_3\text{O}_{12}$ [6]. The stretching and bending vibrational modes of PO_4^{3-} tetrahedra were noticed in the region between $1000\text{--}1100\text{ cm}^{-1}$ and $400\text{--}550\text{ cm}^{-1}$ respectively. The broad asymmetric stretching and bending absorption bands of P–O were observed at 1097 cm^{-1} , 1051 cm^{-1} and 1005 cm^{-1} . Broadness of the bands indicates that the tetrahedral symmetry of phosphate group is distorted due to the introduction of bigger cesium ion in the octahedral site of langbeinite structure. Symmetric stretching and bending vibrational modes of P–O were noticed at 626 cm^{-1} , 588 cm^{-1} and 545 cm^{-1} , 443 cm^{-1} . The scanning electron micrograph and EDX spectrum of the compound are shown in Fig. 3a and b. Morphology of the compound indicates that the particles are highly agglomerated. EDX results confirmed the presence of all elements in the compound.

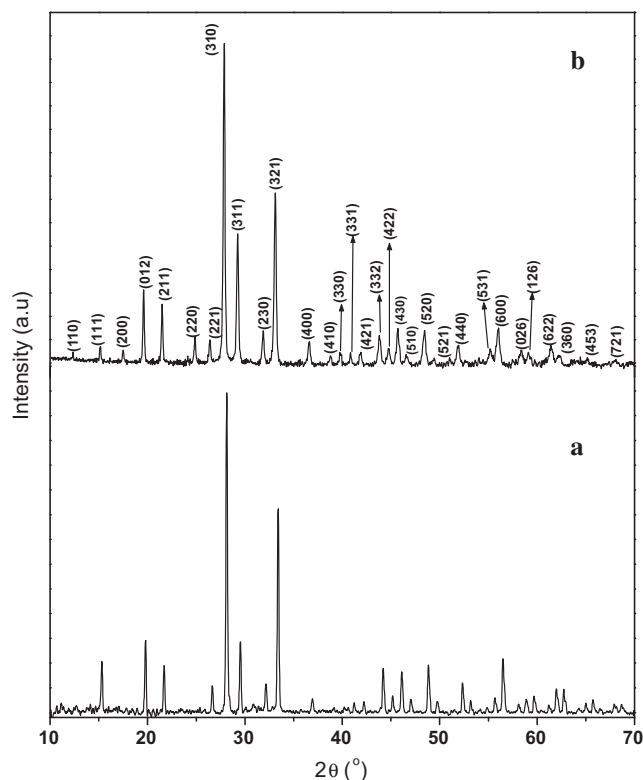


Fig. 1. Powder XRD patterns of (a) $\text{K}_2\text{FeZrP}_3\text{O}_{12}$ and (b) $\text{KCsFeZrP}_3\text{O}_{12}$.

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