



The study of the crystalline phosphates of kosnarite type structure containing different alkali metals

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ABSTRACT

The incorporation possibilities of different alkali elements into crystalline phosphates $A_{1-x}A'_x\text{Hf}_2(\text{PO}_4)_3$ ($A=\text{Li, Na, K, Rb, Cs}$) were studied, the formation regions of kosnarite solid solutions were determined. $\text{Na}_{0.5}\text{K}_{0.5}\text{Hf}_2(\text{PO}_4)_3$ crystal structure was studied by powder X-ray diffraction, and the distribution of alkali metals in kosnarite structure was found out. The phosphate crystallizes in the space group $R\bar{3}c$, with $a=8.7295(1)\text{ \AA}$, $c=23.2023(4)\text{ \AA}$, $V=1531.24(4)\text{ \AA}^3$, $Z=6$; $R_{wp}=6.15$, $R_p=4.43$. The concentration region knowledge of the kosnarite phase existence and peculiarities of their phase formation in the $A_{1-x}A'_xM_2(\text{PO}_4)_3$ ($M=\text{Ti, Zr, Hf}$) systems allow us to choose phosphate matrix compositions suitable for solidification of reprocessing wastes of spent U–Pu nuclear fuels.

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1. Introduction

The crystalline compounds of mineral kosnarite $\text{KZr}_2(\text{PO}_4)_3$ (synthetic analog is $\text{NaZr}_2(\text{PO}_4)_3$, known as NZP/NASICON) type structure are of interest as constructional and functional ceramics due to their stability to the extreme environmental conditions (high temperature and pressure, aggressive media, radiation), near-zero thermal expansion, low thermal conductivity, superionic conductivity, etc. [1]. Their high stability and ability to incorporate wide variety of different cations in the crystal structure are the reasons of which these substances are proposed as the hosts for immobilizing radioactive wastes [2]. The important advantage of such matrices compared to other candidate mineral-like matrices is ability to immobilize alkali metals in the insoluble phase.

The alkali metal immobilization problem is topical in the pyrochemical reprocessing of spent nuclear fuels using high temperature melts of alkali metal salts (for example, NaCl-KCl melts [3]). After several cycle reusing, the spent melt containing impurities of radioactive elements needs to be immobilized. The blend melt precipitation in the phosphate forms is very convenient for solving this problem. Since there are different alkali metals in nuclear wastes, it is necessary to examine the ability of the kosnarite framework to accommodate different alkali metals simultaneously.

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It is known [4] that the compounds $ML_2(\text{PO}_4)_3$ ($M=\text{Li, Na, K, Rb, Cs}$; $L=\text{Ti, Zr, Hf}$) crystallize in the rhombohedral kosnarite structure, some of them also have other polymorphs. Their kosnarite structure basis is three-dimensional framework $\{[L_2(\text{PO}_4)_3]^{p-}\}_{3\infty}$ (L is octahedrally coordinated cation), alkali metal cations occupy framework cavities. In [5] we studied possibilities of isovalent isomorphism in the cavities of the structure of $M_{1-x}M'_xL_2(\text{PO}_4)_3$ phosphates ($L=\text{Ti and Zr}$), determined the regions of the kosnarite solid solution stability. A phase transition in $\text{LiL}_2(\text{PO}_4)_3$ between a low-temperature triclinic phase and a high-temperature rhombohedral phase was reported (for $L=\text{Zr, Hf}$) approximately at room temperature. The low-temperature triclinic phase appears as a distortion of the classical kosnarite skeleton $L_2(\text{PO}_4)_3$ into which the Li atoms are differently distributed [6–9].

In this study, we examined the conditions of crystalline phosphate $M_{1-x}M'_x\text{Hf}_2(\text{PO}_4)_3$ ($M=\text{Li, Na, K, Rb, Cs}$) formation and determined the regions of solid solution existence in these systems. In order to find out the alkali metal distribution in the kosnarite structure, the study of $\text{Na}_{0.5}\text{K}_{0.5}\text{Hf}_2(\text{PO}_4)_3$ crystal structure by powder X-ray diffraction is undertaken.

2. Experimental

The crystalline phosphates $M_{1-x}M'_x\text{Hf}_2(\text{PO}_4)_3$ with pairs of different alkali metals M and M' were synthesized by solid-state reactions. The following reagent grade reactants were used:

Li_2CO_3 , MCl ($M=\text{Na, K, Rb, Cs}$), HfO_2 and $\text{NH}_4\text{H}_2\text{PO}_4$. All used chemicals were provided by REACHEM, their purity was not less than 99.5%. A fine mixture of the stoichiometric amounts of the reactants was dried at 200°C for 10–16 h, then thermally processed in unconfirmed air access at 600 and 800–1200 $^\circ\text{C}$ with a step interval of 100 $^\circ\text{C}$ for at least 24 h at each stage. To avoid the formation of by-products (unreacted HfO_2 and HfP_2O_7) the low heating rates (0.5–1 K min^{-1}), intermediate regrinding, and appropriated final temperatures, which depend upon the M metal, were used.

The obtained samples were white polycrystalline powders. Their chemical composition and homogeneity were checked with the aid of a CamScan MV-2300 microprobe with a Link INCA ENERGY 200C energy-dispersion detector. The uncertainty of the chemical composition determination was within 2.5% mass.

Phase purity was established by powder X-ray diffraction (XRD) at ARL X'TRA powder diffractometer (Thermo Electron Corporation) equipped with a Peltier detector ($\text{CuK}\alpha$ radiation). Unit cell parameters of the compounds were determined at room temperature from the corresponding diffraction patterns indexed within 2θ range 10–60 $^\circ$. Data for the structure refinement were collected between 2θ 5 $^\circ$ and 100 $^\circ$ with a step interval of 0.02 $^\circ$. Structure refinements were performed by the Rietveld method [10] with JANA2000 program [11].

Functional composition of the samples was confirmed by IR spectroscopy on an IR Fourier spectrometer FSM 1201 (OOO NPF "Spectralnitpribor") within range 1400–400 cm^{-1} .

3. Results and discussion

Complex phase formation character was observed in the phosphate systems. XRD patterns of the reaction mixtures treated at 600 $^\circ\text{C}$ contained $\text{Hf}_2\text{P}_2\text{O}_7$ reflections and amorphous phases, which reacted at higher temperatures. The crystalline kosnarite type products in the systems $M_{1-x}M'_x\text{Hf}_2(\text{PO}_4)_3$ were obtained at temperatures 900–1100 $^\circ\text{C}$ (Li-containing samples crystallized at

lower temperatures, and Cs-containing—at higher ones) and thermally stable not less than up to 1300 $^\circ\text{C}$.

The prepared samples form a series of kosnarite-like structural analogs or kosnarite phase mixtures. The powder XRD data of the single-phase samples showed a similar distribution of Bragg reflections in the patterns of $M_{1-x}M'_x\text{Hf}_2(\text{PO}_4)_3$ with smooth changing in their relative intensities and 2θ values over the entire composition range studied (Fig. 1a). The results of their electron microprobe analysis confirmed the homogeneity of the samples and indicated that their compositions were close to the theoretical values calculated for the general formulae.

The IR spectra of the synthesized single-phase samples (Fig. 2) are typical of orthophosphates crystallizing in the kosnarite structure with rhombohedral symmetry. The spectra showed the characteristic PO_4 vibrations of the NZP framework (the broad absorption bands at 1240–1000 cm^{-1} , ν_3 and ν_1 ; 650–530 cm^{-1} , ν_4 ; 450–400 cm^{-1} , ν_2). Shift and intensity redistribution of absorption bands was observed in the spectral patterns with the changing composition of phosphates.

So, XRD and IR spectroscopy data are in good agreement and show the existence of solid solutions in some of the studied systems (Table 1). To confirm the data and make clear the distribution of alkali metals in the crystallographic positions of the kosnarite structure, the crystal structure of $\text{Na}_{0.5}\text{K}_{0.5}\text{Hf}_2(\text{PO}_4)_3$ ($x=0.5$) was refined by the Rietveld method.

For the initial fractional coordinates for the Rietveld analysis of $\text{Na}_{0.5}\text{K}_{0.5}\text{Hf}_2(\text{PO}_4)_3$, we used those of $\text{NaZr}_2(\text{PO}_4)_3$ (space group $R\bar{3}c$) [10]. In the kosnarite structure, alkali metal cations may be distributed between the $M1$ (6b) and $M2$ (18e) sites in the cavities of the framework, but usually the $M1$ site is occupied at first. It was shown that Na^+ and K^+ cations are statistically distributed in the $M1$ sites. The $M2$ site occupancy (g) variation showed that $g=0$ in them, so the sites remain vacant. The Hf^{4+} cations occupy the framework L (12c) sites.

The experimental and refinement conditions, unit cell parameters and R factors are presented in Table 2. The observed,

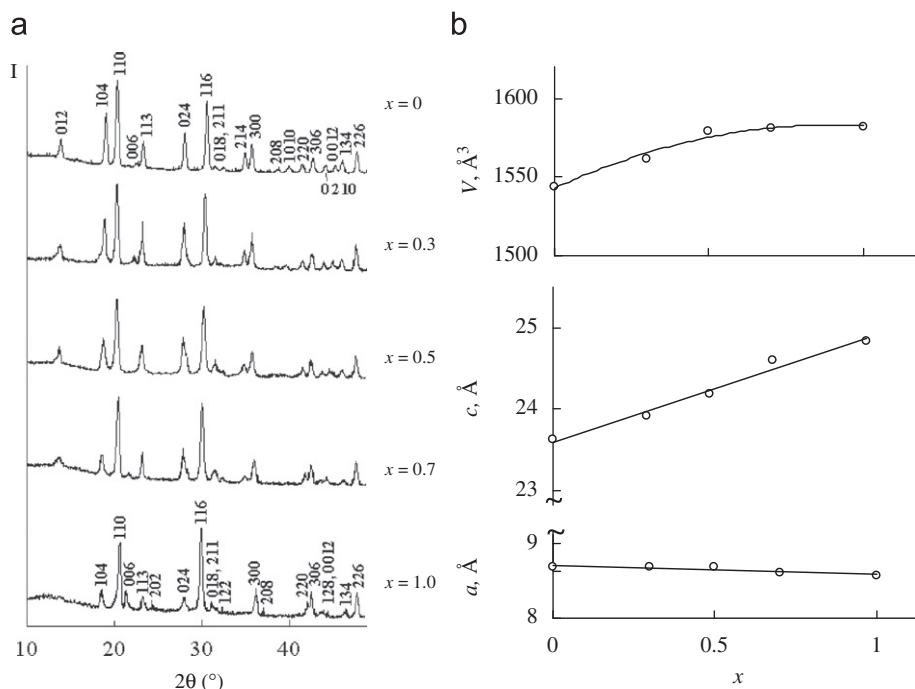


Fig. 1. X-ray diffraction patterns (a) and unit cell parameters (b) of the solid solutions $\text{K}_{1-x}\text{Cs}_x\text{Hf}_2(\text{PO}_4)_3$ (space group $R\bar{3}c$, $Z=6$).

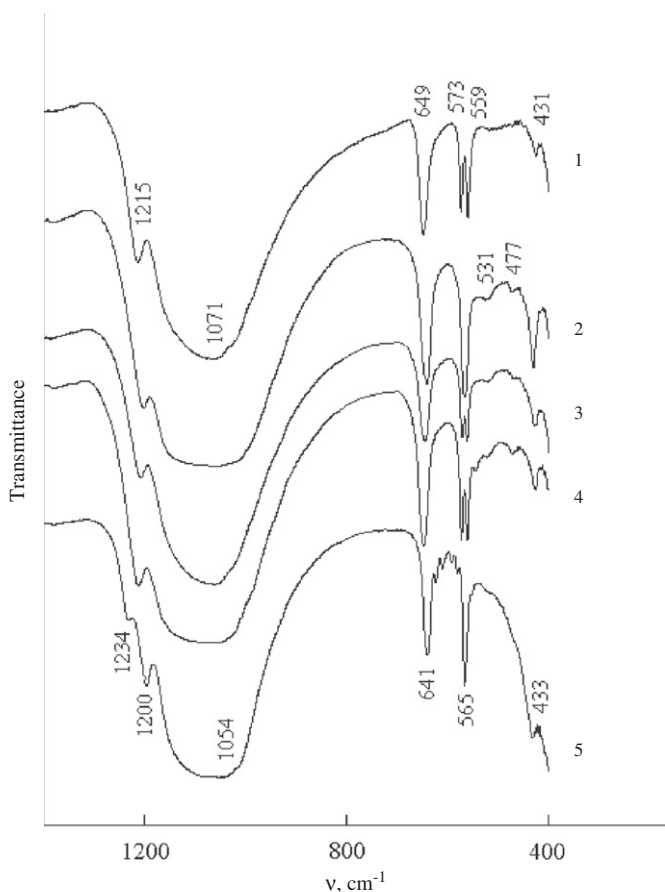


Fig. 2. IR spectra of phosphates crystallizing in the $K_{1-x}Cs_xHf_2(PO_4)_3$ system: 1. $x=0$; 2. $x=0.3$; 3. $x=0.5$; 4. $x=0.7$; and 5. $x=1.0$.

Table 1

Concentration regions of kosnarite-type solid solutions in the $M_{1-x}M'_xL_2(PO_4)_3$ systems.

<i>M</i>	<i>M'</i>	<i>L</i>		
		Ti	Zr	Hf
Li	Na	$0 \leq x \leq 1$	$0 \leq x \leq 1$	$0 \leq x \leq 1$
Na	K	$0 \leq x \leq 1$	$0 \leq x \leq 1$	$0 \leq x \leq 1$
	Rb	$0 \leq x \leq 0.3$, $0.7 \leq x \leq 1$	$0 \leq x \leq 1$	$0 \leq x \leq 1$
K	Cs	$0 \leq x \leq 0.2$	$0 \leq x \leq 0.3$, $0.7 \leq x \leq 1$	$0 \leq x \leq 0.3$, $0.7 \leq x \leq 1$
	Rb	$0 \leq x \leq 1$	$0 \leq x \leq 1$	$0 \leq x \leq 1$
	Cs	$0 \leq x \leq 0.3$	$0 \leq x \leq 1$	$0 \leq x \leq 1$

calculated and difference XRD patterns are shown in Fig. 3. It is seen that the observed and calculated profiles are in good agreement. The final fractional coordinates and isotropic atomic displacement parameters are listed in Table 3. In the chosen model all *B* parameters are positive and reasonable. The bond lengths and angles in structure-forming polyhedra (Table 4) agree with the corresponding data for other kosnarite phosphates [6,9,12].

The fragment of the structure of $Na_{0.5}K_{0.5}Hf_2(PO_4)_3$ is shown in Fig. 4. The basis of the structure is the framework built up of corner-sharing HfO_6 -octahedra and PO_4 -tetrahedra. Alkali metal cations are distributed in the *M1* cavities situated in the ribbons of octahedra and tetrahedra, parallel to the *c*-axis. Thus, the statistical Na/K distribution is observed in the studied solid

Table 2

Conditions of XRD experiment and part of refinement results for $Na_{0.5}K_{0.5}Hf_2(PO_4)_3$.

Space group	$R\bar{3}c$ (no. 167)
2θ range (deg)	5–100
2θ step width (deg)	0.02
I_{max} (counts)	75,966
Unit cell parameters	
<i>a</i> (Å)	8.7295(1)
<i>c</i> (Å)	23.2023(4)
<i>V</i> (Å ³)	1531.24(4)
<i>Z</i>	6
Number of reflections	214
Variables	
Structural	13
Other	22
Reliable factors (%)	
R_{wp} ; R_p	6.15; 4.43

solution systems. With regard to the Li^+ cations, the large number of different sites in the kosnarite structure and little Li^+ ionic radius may lead to another distribution of the cations in related phases (as for instance, in $LiHf_2(PO_4)_3$ [8,9]).

The XRD patterns of all triple phosphates of the $M_{1-x}M'_xHf_2(PO_4)_3$ systems were indexed in space group $R\bar{3}c$ (Table 5). As an example, the unit cell parameters of the series $K_{1-x}Cs_xHf_2(PO_4)_3$ are shown in Fig. 1b. The incorporation of a larger Cs^+ cation instead of K^+ into the *M1* position leads to the *c* parameter increasing. Bridging PO_4 tetrahedron stretching in the *c* direction and contraction in the *a* direction lead to simultaneous *a* parameter decreasing [1].

Basing on the results of this study and literature data, we compared the concentration regions of kosnarite-type phase existence in the $M_{1-x}M'_xL_2(PO_4)_3$ (*M*=Ti, Zr, Hf) systems (Table 1). The continuous kosnarite-type solid solutions are formed in the Li–Na, Na–K, K–Rb systems with *L*=Ti, Zr, Hf; Na–Rb, K–Cs systems with *L*=Zr, Hf and Li–K system with *L*=Hf. On the whole, the concentration limits of kosnarite solid solution existence *x* are characterized by the least values in the case of titanium containing phosphates. In $Li_{1-x}K_xHf_2(PO_4)_3$ system continuous solid solutions are formed while in Ti- and Zr-systems solid solution formations are not found. The reason of different behavior of Zr and Hf-phosphates (in spite of close ionic radii of framework cations) may be wider region of temperature stability of kosnarite modification in the case of $LiHf_2(PO_4)_3$ [8] compared with zirconium analog [6].

Kosnarite-like frameworks of zirconium and hafnium containing phosphates ($r_{Zr^{4+}}=0.72$ Å, $r_{Hf^{4+}}=0.71$ Å) may incorporate wide variations of cations in their cavities to form series of continuous solid solutions. Lower concentration limits of the kosnarite structure in titanium phosphates may be explained by the small ionic radius of the framework forming cation Ti^{4+} ($r_{Ti^{4+}}=0.61$ Å) and the difficulty of the incorporation of large cations Cs^+ in the cavities of the kosnarite-type $[Ti_2(PO_4)_3]^-$ framework. As it was shown in [7], $CsTi_2(PO_4)_3$ phosphate crystallizes in $CsTi_2(AsO_4)_3$ structure with another spatial connection of framework-forming polyhedra. So the radius of the cavities cation has influence on the stability of the given framework type.

Concentration limits of the kosnarite structure existence in Ti-containing systems may be widened and stabilized by the portion isomorphous replacement of some amount of Ti by Zr or Hf (as it was shown in [13,14]) and the corresponding gradual varying of the average L^{4+} radius.

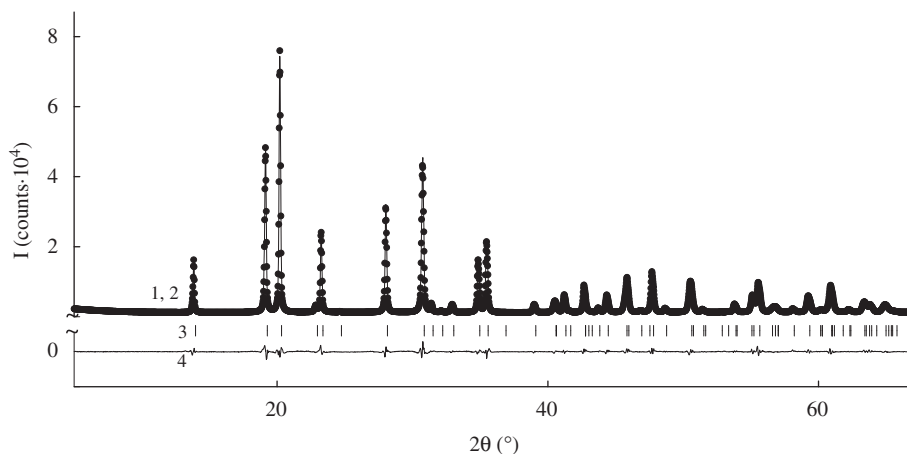


Fig. 3. Portions of the Rietveld refinement profiles for $\text{Na}_{0.5}\text{K}_{0.5}\text{Hf}_2(\text{PO}_4)_3$: 1. observed; 2. calculated; 3. Bragg reflections; and 4. difference XRD patterns. The calculated pattern is shifted from the observed pattern.

Table 3

Fractional coordinates and isotropic atomic displacement parameters for $\text{Na}_{0.5}\text{K}_{0.5}\text{Hf}_2(\text{PO}_4)_3$.

Atom	Site	g	x	y	z	$B (\text{Å}^2)$
Na/K	6b	0.5	0	0	0	3.6(3)
Hf	12c	1	0	0	0.1475(3)	0.57(2)
P	18e	1	0.7098(4)	0	0.25	0.7(1)
O1	36f	1	0.7873(6)	-0.0334(6)	0.1966(2)	0.4(1)
O2	36f	1	0.5278(5)	-0.1632(6)	0.2577(2)	0.4(1)

Table 4

Bond lengths (Å) and angles (deg) in $\text{Na}_{0.5}\text{K}_{0.5}\text{Hf}_2(\text{PO}_4)_3$.

Bonds (Å)	Angles (deg)	
(Na/K)–O2 (× 6)	2.651(4)	O1–P–O1' 113.9(2)
Hf–O1 (× 3)	2.072(5)	O1–P–O2 (× 2) 105.9(2)
Hf–O2 (× 3)	2.069(5)	O1–P–O2 (× 2) 110.7(2)
P–O1 (× 2)	1.508(6)	O2–P–O2' 109.8(2)
P–O2 (× 2)	1.524(4)	O1–Hf–O1' (× 3) 92.6(1)
		O1–Hf–O2 (× 3) 90.4(2)
		O1–Hf–O2 (× 3) 92.5(1)
		O1–Hf–O2 (× 3) 173.9(2)
		O2–Hf–O2' (× 3) 84.2(2)

Table 5

The unit cell parameters of the solid solutions $A_{1-x}A'_x\text{Hf}_2(\text{PO}_4)_3$ (space group $R\bar{3}c$, $Z=6$).

Composition			Unit cell parameters		
A	A'	x	a (Å)	c (Å)	V (Å ³)
Li	Na	0	8.837(4)	22.08(2)	1493
		0.3	8.820(4)	22.25(2)	1499
		0.5	8.807(4)	22.37(2)	1503
		0.7	8.797(5)	22.47(3)	1506
Na	K	1.0	8.780(5)	22.62(3)	1510
		0.3	8.752(4)	22.92(2)	1520
		0.5	8.7295(1)	23.2023(4)	1531.24
		0.7	8.714(4)	23.35(2)	1536
K	Rb	1.0	8.686(4)	23.63(3)	1544
		0.3	8.737(5)	23.13(3)	1529
		0.5	8.708(5)	23.48(3)	1542
		0.7	8.679(5)	23.82(3)	1554
K	Cs	1.0	8.635(4)	24.33(2)	1571
		0.3	8.671(4)	23.84(2)	1552
		0.5	8.661(4)	23.98(2)	1558
		0.7	8.650(4)	24.12(2)	1563
K	Cs	0.3	8.683(4)	23.91(3)	1561
		0.5	8.682(4)	24.18(3)	1579
		0.7	8.615(4)	24.60(3)	1581
		1.0	8.574(4)	24.83(3)	1582

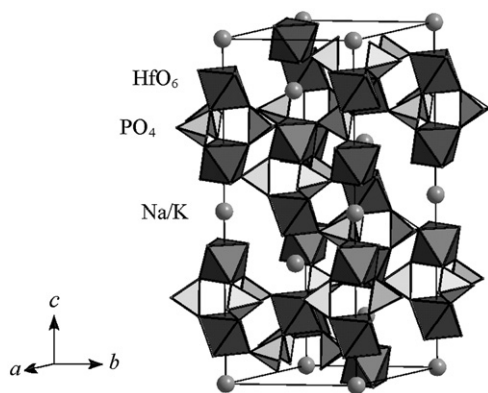


Fig. 4. Fragment of the structure of $\text{Na}_{0.5}\text{K}_{0.5}\text{Hf}_2(\text{PO}_4)_3$.

4. Conclusions

It is known [1], that kosnarite ceramics show high stability to the aggressive media action, radiation damage and thermal-shock resistance. The removal of some multivalent radionuclide and stable ions (Cs, Mg, Sr, Ba, Zr, Cr, Mo, Mn, Re, Fe, Ru, Ni, Cd, Bi, Te, lanthanides) from molten alkali salt wastes arising from pyrochemical reprocessing of spent U–Pu nuclear fuels by a phosphate precipitation technique was investigated in [2]. This study demonstrates the potential possibility of single-phase environmentally stable kosnarite materials to the immobilization of significant concentrations of different alkali metals from the melts. The incorporation of hafnium in the composition of waste forms is important considering its applying as neutron absorber. The knowledge of concentration regions of the kosnarite type phases existence and peculiarities of their phase formation allows us to choose the compositions of phosphate matrices depending on waste compositions. Understanding the basic chemistry and

crystal chemistry of the kosnatite compounds of variable compositions is a key factor for developing safe and effective reprocessing technologies.

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