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Formation of complex phosphates $K_2M^{III}Sn(PO_4)_3$ from solutions in melts under crystallization conditions

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This article studies the regularities of formation of isostructural to langbeinite phosphates from solutions in melts under crystallization conditions for K_2O–P_2O_5–$M^{III}{}_2O_3$–SnO_2 (M^{III} — Fe, Cr) and K_2O–P_2O_5–LnF_3–SnO_2 (Ln — Y, REE) systems. Based on X-ray powder diffraction method the phase composition of synthesized samples and lattice parameters have been determined for a number of new compounds with common composition $K_2M^{III}Sn(PO_4)_3$. Analysis of obtained results shows that the crystallochemical criterion for formation of langbeinite-type framework on the basis of different multivalent metals is the difference in their ionic radii up to 35 %.
Keywords: complex phosphates, langbeinite, flux crystallization, XRD.

Исследованы закономерности формирования изоструктурных лангбейниту фосфатов в условиях кристаллизации из растворов в расплавах для систем K_2O–P_2O_5–$M^{III}{}_2O_3$–SnO_2 (M^{III} — Fe, Cr) и K_2O–P_2O_5–LnF_3–SnO_2 (Ln — Y, REE). Методами порошковой рентгенографии установлен фазовый состав синтезированных образцов и проведен расчет параметров кристаллических решеток для ряда новых соединений общего состава $K_2M^{III}Sn(PO_4)_3$. Анализ полученных результатов показал, что кристаллохимическим критерием формирования лангбейнитоподобного каркаса на основе различных поливалентных металлов является разность в их ионных радиусах до 35 %.

Формування складних фосфатів $K_2M^{III}Sn(PO_4)_3$ в умовах кристалізації із розчинів у розплавах. *І.В.Затовський, М.С.Слободяник, Т.І.Ущапівська, В.Хань.*

Досліджено закономірності формування ізоструктурних лангбейніту фосфатів в умовах кристалізації із розчинів у розплавах для систем K_2O–P_2O_5–$M^{III}{}_2O_3$–SnO_2 (M^{III} — Fe, Cr) та K_2O–P_2O_5–LnF_3–SnO_2 (Ln — Y, REE). Методами порошкової рентгенографії встановлено фазовий склад синтезованих зразків і проведено розрахунок параметрів кристалічних граток для низки нових сполук загального складу $K_2M^{III}Sn(PO_4)_3$. Аналіз отриманих результатів виявив, що кристалохімічним критерієм формування лангбейнітоподібних каркасів на основі різних полівалентних металів є різниця в їх іонних радіусах до 35 %.

1. Introduction

Disposal of radioactive wastes of spent fuel is one of the top priorities in modern nuclear industry. This problem can be solved now by incorporation of highly radioactive isotopes into composition of chemically and thermodynamically stable crystalline or glasses oxide matrices with the purpose of their subsequent long-term storage. Specifically, over the last thirty years borosilicate and Fe–Pb-phosphate glasses [1] as well as aluminosilicates, perovskite structure compounds, compounds based on titanium or zirconium dioxides, and etc., all within SYNROC concept, have been proposed for use as matrices for immobilization of highly active radionuclides [2–4]. Radioactive wastes are multi-component. Consequently, the crystalline immobilization matrix should have high chemical stability and ensure wide range of substitutions in anion and cation sites. Isostructural to langbeinite phosphates, which regarded as novel prospective material for immobilization of highly radioactive isotopes, fully meet the mentioned above criteria [3, 5]. It should be also noted that this class of compounds has potential to be used as base matrix for new luminophores with wide spectral range [6–8].

In general, crystallochemical formula of langbeinites can be described as follows: $(A1)(A2)[(M1)(M2)(TO_4)_3]$, where A1 and A2 — positions of cations of monovalent, divalent and trivalent metals with CN 12 and 9, respectively (can remain partially vacant); M1 and M2 — framework-forming positions of di-, tri-, tetra- and pentavalent metals; TO_4 — anionic tetrahedrons with charges from −2 to −4. The flexibility of this structure with regard to iso- and heterovalent substitutions in nearly all positions of metals should be also noted [3]. This matrix can also contribute to realization of anion substitution [5, 9]. It allows to cover a very wide spectrum of elements with charges from +1 to +6 and combine them within one immobilization matrix. At the same time, the crystallochemical criteria for formation of complex oxide compounds with langbeinite structure have not been elucidated in full.

This article presents results on the study of formation of isostructural to langbeinite phosphates with common composition $K_2M^{III}Sn(PO_4)_3$ (MIII — Cr, Fe, Y, REE) from solutions in melts under crystallization conditions. The crystallochemical criteria for formation of the said type of compounds have been analyzed on the basis of X-ray powder diffraction method data.

2. Experimental

The maximum solubility of stannic oxide in $K_2O–P_2O_5$ melts with baseline K/P ratios ranging from 1.0 to 1.5 at 1100–1150°C is reached at the level of 7–9 wt. %. Further increases in the temperature may lead to sublimation of potassium as well as gradual changes in pre-set elements ratio within the system. Therefore, the quantity of stannic oxide was set at the level of 5–7 % wt. %. and the mole ratios M^{III}/Sn^{IV} varied from 0.5 to 2.0 in order to obtain homogeneous melts of $K_2O–P_2O_5–LnF_3–SnO_2$ (M^{III} — Fe, Cr). KPO_3, $K_4P_2O_7$, SnO_2, Fe_2O_3 or Cr_2O_3 of at least analytical grade have been used as initial reagents. Calculated weighed quantities of starter components were thoroughly grinded, placed in platinum crucibles, heated to 1150°C and hold at this temperature for 7–10 h. Thereafter, obtained homogeneous melts were cooled with the rate 30–50°/h to temperature of 820–780°C. Then the melt underwent decanting from obtained crystalline phases and was washed free from melt residues with hot water.

Interaction of lanthanide oxides with alkali metals phosphate melts is accompanied by formation of high-melting orthophosphates $LnPO_4$ on their surface, which inhibits further dissolution of oxide and conversion into homogeneous state. This process can be prevented by the use of lanthanide fluoride instead of oxide as a starting reagent, which is demonstrated in our previous works [10, 11]. Specifically, stannic oxide 6 wt. % was first dissolved in $K_2O–P_2O_5$ melts at 1150°C, then the temperature was lowered to 1050°C and the required quantity of LnF_3 (Ln^{III}/Sn^{IV} ratio = 1.0) was transferred during mixing. This procedure resulted in formation of homogeneous melts $K_2O–P_2O_5–LnF_3–SnO_2$ (Ln — La, Pr, Nd, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y) already in 10–15 min, which were cooled to 820°C at the rate of 50°/h. Prior to decantation of melts, they were kept under isothermal conditions for 2 h to reach the steady state. Obtained crystalline phases were washed with hot distilled water according to the procedure stated above.

Phase composition of obtained samples was determined on the basis of X-ray powder diffraction data using Shimadzu XRD-6000 X-ray diffractometer (Cu Kα emission, $\lambda = 1.54178$ Å, curved graphite monochro-

Table 1. Conditions of synthesis and phase composition of phosphates obtained from solutions in melts under crystallization conditions in $K_2O–P_2O_5–M^{III}{}_2O_3–SnO_2$ (M^{III} – Fe, Cr) and $K_2O–P_2O_5–LnF_3–SnO_2$ (Ln – Nd, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y) systems

Starting ratios in homogeneous solution-melt	Crystallization interval, °C	Phase composition of obtained samples, wt. %
K/P = 1.1; Cr:Sn = 1:1; Sn = 9 wt. %	1050 → 820	$K_2CrSn(PO_4)_3$ — 50, $KCrP_2O_7$ — 35, $KSn_2(PO_4)_3$ — 15
K/P = 1.1; Fe:Sn = 3:2; Sn = 9 wt. %	1100 → 760	$K_2FeSn(PO_4)_3$ — 100
K/P = 1.0; Fe:Sn = 1:1; Sn = 9 wt. %	1100 → 800	$K_2FeSn(PO_4)_3$ — 85, $KSn_2(PO_4)_3$ — 15
K/P = 1.0; Y:Sn = 1:1; Sn = 9 wt. %	1000 → 820	$K_2YSn(PO_4)_3$ — 80, $KSn_2(PO_4)_3$ — 20
K/P = 1.0; Lu:Sn = 1:1; Sn = 9 wt. %	1000 → 800	$K_2LuSn(PO_4)_3$ — 95, $KSn_2(PO_4)_3$ — 5
K/P = 1.0; Yb:Sn = 1:1; Sn = 9 wt. %	1000 → 800	$K_2YbSn(PO_4)_3$ — 85, $KSn_2(PO_4)_3$ — 15
K/P = 1.0; Tm:Sn = 1:1; Sn = 9 wt. %	1000 → 820	$K_2TmSn(PO_4)_3$ — 70, $KSn_2(PO_4)_3$ — 30
K/P = 1.0; Er:Sn = 1:1; Sn = 9 wt. %	1000 → 820	$K_2ErSn(PO_4)_3$ — 70, $KSn_2(PO_4)_3$ — 30
K/P = 1.0; Ho:Sn = 1:1; Sn = 9 wt. %	1000 → 820	$K2HoSn(PO_4)_3$ — 60, $KSn_2(PO_4)_3$ — 40
K/P = 1.0; Dy:Sn = 1:1; Sn = 9 wt. %	1000 → 800	$KSn_2(PO_4)_3$ ~ 100, $K_2DySn(PO_4)_3$ — traces
K/P = 1.0; Tb:Sn = 1:1; Sn = 9 wt. %	1000 → 800	$KSn_2(PO_4)_3$ ~ 100, $K_2TbSn(PO_4)_3$ — traces
K/P = 1.0; Gd:Sn = 1:1; Sn = 9 wt. %	1000 → 800	$KSn_2(PO_4)_3$ — 100

mator, method of continuous scanning with the rate of 0.5 deg/min within angular range 2θ 5.0–70.0°). Infrared (IR) absorption spectra have been recorded using FTIR Perkin Elmer Spectrum BX infrared spectrometer within the frequency range of 400–4000 cm^{-1} (samples were prepared by pressing in discs with extra pure grade KBr). The chemical composition of crystallization products has been determined using X-ray fluorescence analysis (energy dispersive spectrometer SEDX-01 "Elvax Light") and inductively coupled atomic emission analysis (AES-ICP, Spectroflame Modula ICP "Spectro").

3. Results and discussiion

Monophasic isostructural to langbeinite phosphate $K_2FeSn(PO_4)_3$ has been obtained for studied systems only in case of crystallization from $K_2O–P_2O_5–Fe_2O_3–SnO_2$ solution-melts (Table 1). This compound in pure form is crystallized within the temperature range of 1100–760°C with cooling of melts with following baseline ratios: K/P = 1.1 and Fe/Sn = 1.0–1.5. KPO_3 melt also gives rise predominantly to this triple phosphate, however along with $KSn_2(PO_4)_3$ (up to 15 % wt. according to results XRD). The same regularity is observed in chrome systems. At the same time, nucleation of both $K_2CrSn(PO_4)_3$ and $KCrP_2O_7$ fist occurs at the point with K/P ratio = 1.1 during cooling, and the lower temperatures lead to appearance of $KSn_2(PO_4)_3$ phase (Table 1). $KCrP_2O_7$ nucleating and subsequent growth is attributable to the high melting temperature of this double diphosphate. This results in quick depletion of the melt by chrome and establishment of unfavorable conditions for further formation of $K_2CrSn(PO_4)_3$.

In the case of lanthanide-containing systems of Lu–Ho series and yttrium, isostructural to langbeinite phosphates $K_2M^{III}Sn(PO_4)_3$ form in the melts with baseline K/P ratios = 1.0–1.2 simultaneously with $KSn_2(PO_4)_3$. The maximum yield of langbeinite-type phases is realized under cooling to 820°C in KPO_3 melt with starting values of M^{III}/Sn = 1.0. According to XRD (Table 1), the amount of $KSn_2(PO_4)_3$ in the composition of obtained mixtures gradually increases with transition from lutecium to holmium (Fig. 1). In particular, the content of $KSn_2(PO_4)_3$ in the synthesized $K_2LuSn(PO_4)_3$ sample is less than 5 wt. %, while in the case of $K_2HoSn(PO_4)_3$ it reaches nearly 40 wt. %. With dysprosium- and terbium-containing systems, only isolated tetrahedral crystals with faceting specific to langbeinite-type phases were registered in crystallization products obtained by light-microscopical method, and according to XRD, the crystallization product was $KSn_2(PO_4)_3$ double orthophosphate. $K_2Sn(PO_4)_3$ compound was also obtained in case of Gd-containing systems with baseline K/P ratios in melts = 1.0–1.2 (Fig. 1), and with increase in base-

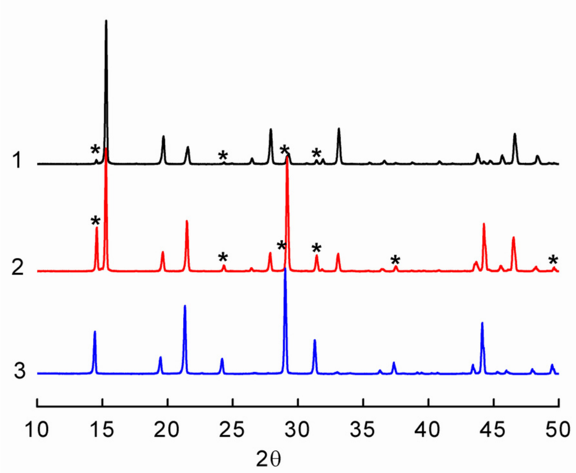

Fig. 1. Sample X-ray patterns of crystalline phases obtained under crystallization of K_2O–P_2O_5–LnF_3–SnO_2 solution-melts: 1) $K_2LuSn(PO_4)_3$ (95 wt. %) + $KSn_2(PO_4)_3$ (5 wt. %); 2) $K_2HoSn(PO_4)_3$ (60 wt. %) + $KSn_2(PO_4)_3$ (40 wt. %); 3) $KSn_2(PO_4)_3$, synthesized in K_2O–P_2O_5–GdF_3–SnO_2 system. Asterisks refer to $KSn_2(PO_4)_3$ reflections, which do not overlap reflections of $K_2M^{III}Sn(PO_4)_3$\ phase.

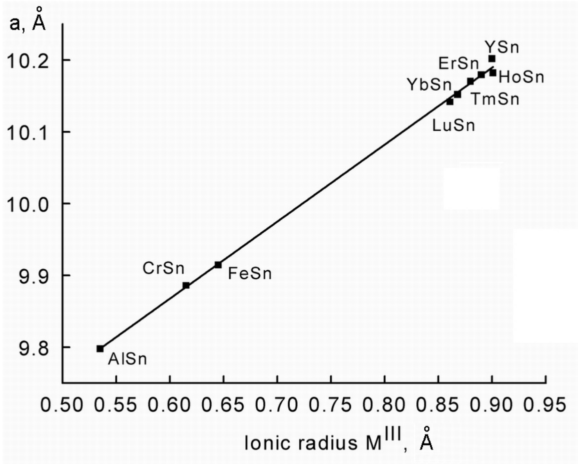

Fig. 2. Changes in crystal lattice parameters for complex phosphates $K_2M^{III}Sn(PO_4)_3$ according to the ionic radius of three-valence metal.

line values of K/P = 1.3 crystallization of $KSnOPO_4$ was observed. Formation of $K_2Sn(PO_4)_3$ or $KSnOPO_4$ occurred simultaneously with $LnPO_4$-type monazites under respective ratios of La-, Pr- and Nd-containing systems.

Infrared spectra of obtained compounds and mixtures contain the very wide absorption lines within a frequency range of 850–1200 cm^{-1} pertaining to stretch vibrations of P–O links in isolated phosphate tetrahedrons, which is very typical to framework orthophosphates. Respective absorption lines of P–O links bending have been seen within a frequency interval of 540–650 cm^{-1}.

It should be noted that structural studies for $K_2M^{III}Sn(PO_4)_3$-type compounds are limited to only three compounds, namely: $K_2FeSn(PO_4)_3$ [12, 13], $K_2YbSn(PO_4)_3$ [12] and $K_2AlSn(PO_4)_3$ [14]. They belong to cubic system, space group $P2_13$. Calculated crystal unit cell parameters for isostructural to langbeinite phosphates obtained in this work are listed in Table 2. They change in proportion to the changes of ionic radius of three-valence metal, which is demonstrated in Fig. 2. On this basis, the principle of obtained compounds formation can be formally considered as solid solutions. Table 2 presents the ratios between iodic radii M^{III}/Sn^{IV}. This ratio is about 35 % with formation of isostructural to langbeinite phosphates. Despite the fact that $K_2DySn(PO_4)_3$

Table 2. Unit cell parameters of synthesized isostructural to langbeinite triple phosphates $K_2M^{III}Sn(PO_4)_3$ and their formation criteria (ionic radii of metals for CN 6 as per [15])

Composition	*a*, Å	M^{III}/Sn^{IV} value
$K_2AlSn(PO_4)_3$*	9.7980(8)	0.775
$K_2CrSn(PO_4)_3$	9.8861(9)	0.891
$K_2FeSn(PO_4)_3$	9.91473(7)	0.935
$K_2LuSn(PO_4)_3$	10.1419(7)	1.248
$K_2YbSn(PO_4)_3$	10.1521(6)	1.260
$K_2TmSn(PO_4)_3$	10.1702(7)	1.275
$K_2ErSn(PO_4)_3$	10.1795(6)	1.290
$K_2YSn(PO_4)_3$	10.2022(6)	1.304
$K_2HoSn(PO_4)_3$	10.1822(7)	1.306
$K_2DySn(PO_4)_3$	—	1.322
$K_2TbSn(PO_4)_3$	—	1.334
$K_2GdSn(PO_4)_3$	—	1.359

* — as per data of work [14].

and $K_2TbSn(PO_4)_3$ compounds have not been derived, as noted above, their isolated crystals determined in crystallization products indicate the potential for synthesis using other methods.

Literature data analysis for other couples of metals forming the basis of anionic langbeinite sublattice also support the crystallographic criterion in the maximum ionic radii difference about 35 %. In particular, neodymium and zirconium ionic radii difference for $K_{1.822}Nd_{0.822}Zr_{1.178}(PO_4)_3$ solid solution [11] obtained using crystallization from solution in melt technique is about 37 %, however in this case zirconium is a priority component in phosphate composition. Maximum ionic radii difference of framework-forming metals for this type of compounds was seen with $K_2BiZr(PO_4)_3$ [8] (amounts to 43 %). At the same time, the studies of crystalline structure revealed in the latter case the significant intensity of anionic sublattice, which led to the changes in coordination environment of potassium atoms. Accordingly, the difference in ionic radii of various polyvalent metals up to 35 % should be considered as crystallochemical criterion for formation of langbeinite-type framework.

It is notable that decrease in target yield of isostructural to langbeinite phases along with increase in ionic radius of lanthanide for the studied systems, in our view, should be primarily attributed to steady state of various coordination forms of lanthanide in the melt (CN 6 and 8).

4. Conclusions

The regularities of formation of isostructural to langbeinite phosphates from solutions in melts under crystallization conditions for $K_2O–P_2O_5–M^{III}{}_2O_3–SnO_2$ (M^{III} — Fe, Cr) and $K_2O–P_2O_5–LnF_3–SnO_2$ (Ln — Y, lanthanide) systems have been identified. Obtained crystalline phases have been characterized using IR-spectroscopy and X-ray powder diffraction techniques. Analysis of obtained results shows that the crystallochemical criterion for formation of langbeinite-type framework on the basis of different multivalent metals is the difference in their ionic radii up to 35 %. The summaries can be used for tailor-made synthesis of phosphate matrices designed for immobilization of the highly-radioactive isotopes and of base matrices for the new luminophores with langbeinite-type lattices.

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