

Orlova A.I., Trubach I.G., Orlova V.A. Complex mineral-like zirconium orthophosphates as perspective material for immobilization of radionuclides into ceramics

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One of the most perspective method of decrease of toxicity of highly nuclear wastes is their inclusion into the ceramic mineral-like matrixes, which can serve as an additional barrier for the immobilization of radionuclides. In the last years, complex zirconium orthophosphates with the kosnarite $\text{KZr}_2(\text{PO}_4)_3$ structure (a synthetic analog is sodium-zirconium phosphate $\text{NaZr}_2(\text{PO}_4)_3$, i.e. NZP, NASICON) were studied as a basis of such matrixes.

The kosnarite structure is described by crystal formula $(\text{M1})(\text{M2})_3\text{L}_2(\text{PO}_4)_3$. The basis of this structure is a three-dimensional network $[\text{Zr}_2(\text{PO}_4)_3]^{n-}_{3\infty}$, composed of the ZrO_6 octahedrons and PO_4 tetrahedrons, connected by oxygen atoms and containing cavities of two types: M1 (occupied by potassium) and M2 (vacant). Along with zirconium, other cations can participate in the network formation. In dependence on the network charge, the cavities can be partially or completely occupied, or be vacant as well.

In the present study, we suggest for production of the crystalline matrixes complex zirconium orthophosphates with the network structure, composed of the groups $[\text{TT}'(\text{PO}_4)_3]^{3-}_{\infty}$ including TT' – 1-, 2-, and 3-valent elements and zirconium. High stability of these materials with respect to some aggressive environments characterizes these compounds as perspective matrixes, which are able to accommodate different cations.

Complex orthophosphates $\text{Na}(\text{K})_{m-x}\text{A}'_x\text{Zr}_{2-(m-1)/4}(\text{PO}_4)_3$ ($\text{A}' = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}$) (I), $\text{Na}(\text{K})_{m-2x}\text{B}_x\text{Zr}_{2-(m-1)/4}(\text{PO}_4)_3$ ($\text{B} = \text{Mg}, \text{Ca}, \text{Sr}, \text{Ba}$) (II), and $\text{Na}(\text{K})_{m-3x}\text{R}_x\text{Zr}_{2-(m-1)/4}(\text{PO}_4)_3$ ($\text{R} = \text{Al}, \text{Ga}, \text{Fe}, \text{Pr}$) (III) ($m = 1, 3, 5$ is the network charge) were studied by XRD and IR spectroscopy. These compounds differ in anion network and cation sub-lattice. The fields of stability of monophase products and their structural types should be identified.

Analysis of the obtained data allowed detection of the following phase formation specifics in the each structural type.

A formation of wide spectrum of crystalline phosphates with the kosnarite ($\text{KZr}_2(\text{PO}_4)_3$, space group $\text{R}\bar{3}\text{c}$) structure is observed in the sequence I. Crystallization of binary monoclinic lithium and zirconium phosphates ($m = 1, 3$) of the scandium tungstenate (SW) structure ($\text{Sc}_2(\text{WO}_4)_3$, space group $\text{P}2_1/\text{n}$).

In the sequence II, the kosnarite structure is characteristic for sodium compounds. In potassium compounds, the role of this structure decreases. Phosphate $\text{K}_2\text{Mg}_{0.5}\text{Zr}_{1.5}(\text{PO}_4)_3$ is firstly produced. It belongs to the langbeinite structural type ($\text{K}_2\text{Mg}_2(\text{SO}_4)_3$, space group $\text{P}2_13$). The eulite structural type ($\text{Bi}_4(\text{SiO}_4)_3$, space group $\text{I}\bar{4}3\text{d}$) is found in binary zirconium-strontium and zirconium-barium phosphates of type $\text{B}_{2.5}\text{Zr}(\text{PO}_4)_3$. All compounds $\text{Mg}_{0.5+2x}\text{Zr}_{2-x}(\text{PO}_4)_3$ ($0 \leq x \leq 1$) form the SW structure.

Most of compounds in the sequence III form the kosnarite structure. However, some of them form the langbeinite and SW structures.

The concentration boundaries for the above structures and influence of cation composition are identified for the studied systems. On the basis of both the above data and the published data, we are able to describe a general scheme of phase formation in complex phosphates of zirconium, alkalis (sodium, potassium) and 1, 2, 3-valent elements.

Most of the above phosphates are mineral-like compounds. A formation of a monophase product depends on a possibility of joint occupation by cations of crystallographically non-equivalent sites, as well as by the conditions of the synthesis. Structure of phosphates depends both on composition of the anionic network, and the cation sub-lattice. To greater extend, structure of phosphates depends on relation of ionic radiuses of network-forming cations and compensators.

The most extensive fields of iso- and heterovalent substitutions both in the network and in the cavities are observed for the kosnarite-structured phosphates. It can be explained by ability of the rigid three-dimensional network to be stable at diverse substitutions, as well as by the presence of numerous cavities. Therefore, the kosnarite structure is more isomorphically capable.

The langbeinite structure forms in sulfates and phosphates with small network-forming cations (T, Mg, Fe, Zn, Mn, Cd, Co) and large compensators (Na, K, Ba, Tl).

The eulite structure forms in compounds of a general formula $\text{M}_4(\text{XO}_4)_3$, containing large cations (Ca, Sr, Ba, Bi, Pb, REE), whose total amount per one formula unit is 4. That corresponds to the complete occupation of all available cavities.

The monoclinic structure (the SW structural type) forms in compounds with diverse networks, where small cations (Li, Mg, Fe, Ga) serve as compensators. The tetrahedral coordination in the cavities is preferential for these cations.

The above study can be a basis for the directed synthesis of the complex ceramic materials and an adaptation of the phosphate zirconium matrixes for the real nuclear wastes.

As a model, we took nuclear wastes forming during the pyroelectrochemical treatment of the worked-out fuel of the BOR-60 reactor. The complex ceramics based on the zirconium orthophosphates were produced. It includes 18 % of alkalis (sodium and potassium) ($\text{K}_{1.5}\text{Na}_{1.5}\text{Al}_{0.67}(\text{PO}_4)_3$). Also it imitates a composition of real wastes and containing (Na+K) mass 17 %, Al mass 3.7 %, Fe mass 0.6 %, Nd mass 1.5 %, Ca mass 0.1 %, and Sr 0.27 mass. %. The samples were tested in hydrothermal conditions in water at $T = 90^\circ\text{C}$ (a dynamic regime). The XRD analysis was performed before and after the hydrothermal treatment. A leaching of potassium and sodium from the above ceramics is studied.

The phase composition of the initial samples has not changed after the treatment. Minimal rates of leaching of alkalis for two days are $6 \cdot 10^{-4} \text{ g/cm}^2 \cdot \text{day}$ for Na and $6 \cdot 10^{-5} \text{ g/cm}^2 \cdot \text{day}$ for K. Zirconium phosphate ceramics with high alkali content, which were not destroyed after water treatment and preserved the phase composition, were produced for a first time.

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