Volkov Yu.F., Kitaev D.B.[2], Lizin A.A., Lukinykh A.N., Orlova A.I.[2] New mineral-like ceramics for immobilization of plutonium (structures of monazite and kosnarite)

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The most reliable method of fixation of long-life radionucleides, the wastes of nuclear circle, is their substitution into hardly soluble mineral-like materials [1]. Mineral-like matrixes are based on monazite, zircon, eulytite, garnet, pyrochlore, etc. [2, 3]. The most developed branch of investigations is an substitution of radionucleides into hardly soluble phosphate compounds [4].

Among the phosphate compounds, the most interesting are complex orthophosphates with structures of $NaZr_2(PO_4)_3$ and $CePO_4$ [5-7]. A general quality of these structures is an ability to accumulate different cations without changes in the structural type.

In the present study, ceramic phosphate NZP and monazite-like compounds containing uranium and plutonium were synthesized. Compositions of common titanate ceramics of the pyrochlore structure, utilized for the immobilization of plutonium, were taken into account [2]. These data could be useful for subsequent comparison of properties of titanate and phosphate ceramics of similar cation composition.

Four phosphate compounds (samples 1-4) containing Ca^{2+}, Cd^{2+}, Gd^{3+}, Hf^{4+}, Ti^{4+}, Ce^{4+}, U^{4+}, and Pu^{4+} were synthesized. Peculiarities of phase formation and x-ray characteristics of the compounds of different cation composition were investigated.

For the phosphates with the expected NZP structure, the following compositions were suggested: (Ca, Gd, Hf, Ti, Ce, U) $(PO_4)_3$ (sample 1) and (Ca, Gd, Hf, Ti, U, ^{239}Pu) $(PO_4)_3$ (sample 2). For the monazite analogs, the following compositions were suggested: (Ca, Cd, Gd, Ce, U) $(PO_4)_3$ (sample 3) and (Ca, Cd, Gd, U, Ce, ^{239}Pu) $(PO_4)_3$ (sample 4). Cerium (IV) was used as an imitator of plutonium in the samples 1 and 3.

All starting materials were of an analytical purity. Oxides were used for the synthesis of orthophosphates (samples 1 and 2) [2]. Other starting materials were used in the synthesis of the samples 3 and 4. Mass fractions of uranium and plutonium in the samples 2 and 4 were similar.

The synthesis was performed by reactions of oxides with phosphoric acid with the subsequent addition of calcium into the intermediate products, their pressing and high-temperature annealing.

An optimal temperature of the annealing was 1250-1300^{O}C and time of 2 hours. A bulk composition is shown on the basis of stoicheometry. Table 1 shows suggested mole fractions of elements in the products. The products were identified by XRD in the Debye-Schairer chamber using Cu radiation.

According to XRD, the phase of the NZP type is dominating in the sample 1. Intensities (I) and interplanar distances (d) of this phase are close to the NZP-like phase $Ca_{0.5}Ti_2(PO_4)_3$ [8]. The phase of the monazite type prevails in the sample 2 [9]. Samples 3 and 4 were uni-phase. I and d parameters were close to that of monazite. Table 2 shows unit-cell parameters of the samples 3, 4, and dominating phases in the samples 1 and 2.

The unit-cell parameters (a, c, and V) of the NZP-like phase of the sample 1 are slightly larger than the corresponding values of $Ca_{0.5}Ti_2(PO_4)_3$. It can be explained by the enter of large cations Hf^{4+} (r = 0.82 Å), Ce^{4+} (r = 0.88 Å), Gd^{3+} (r = 0.94 Å), and U^{4+} (r = 0.89 Å) along with Ti^{4+} (r = 0.64 Å). Unit-call values of the monazite-like phases are comparable or slightly lower than of $CePO_4$. It corresponds to the substitution of ions which are smaller than Ce^{3+} = 1.02 Å).

An average radius of cations in the samples 1 and 2 recalculated for one PO_4^{3-} group is 0.71 Å, whereas for the samples 3 and 4, this value is 0.95 Å. This assists to the formation of the monazite-structured phase in the samples 3 and 4 with larger coordination number of cations (CN = 9) in comparison to the phases of the NZP type, where CN = 6. Taking the appropriate conditions for the number of cations of the samples 1 and 2, the equilibrium can be shifted to one or another phase. However, since both structural types are technically, thermally, and nuclear stable, a presence of one type along with another does not lower the characteristics of the ceramics.

Table 1. Mole fractions of components in the produced orthophosphate phases.

Sample	Ca^{2+}	Gd^{3+}	Cd^{2+}	Hf^{4+}	Ti^{4+}	U^{4+}	Ce^{4+}	Pu^{4+}	$(PO_4)^3$
1	0.525	0.130	-	0.150	1.329	0.273	0.138	-	3
2	0.525	0.130	-	0.150	1.329	0.273	-	0.138	3
3	0.304	0.044	0.174	-	-	0.116	0.362	-	1
4	0.304	0.044	0.174	-	-	0.116	0.304	0.058	1

Table 2. Unit-cell parameters of dominating phosphate phases.

Sample	a, E	b, E	c, E	β, grad.	V, E^3
1	8.427±0.003	-	22.20± 0.01	-	1365.6

2	6.667± 0.005	6.828± 0.004	6.347± 0.004	103.64± 0.05	280.8
3	6.775± 0.008	7.031± 0.008	6.46± 0.01	103.6± 0.1	299.2
4	6.72± 0.01	6.965± 0.007	6.42± 0.01	103.5± 0.1	292.3

References:

1. Baluev A.V., Galkin B. Ya., Mityakhina V.S. et al. // Radiokhimiya. 2000. V. 42. no. 4. pp. 295-307.
2. Volkov Y. F., Lukinykh A.N., Spiryakov V.I. et al. // In: Excess Weapons Plutonium Immobilization in Russia. Proc. Meet. Coord. Review of Work Held in St. Petersburg. Ed.: Jardin L.J., Borisov G.B., Russia, St. Petersburg. 1999. pp. 229-246.
3. Volkov Yu.F. // Sbornik GNTS RF NIIAR. Dmitrovograd. 2000. Issue 3. pp. 3-17.
4. Orlova A.I., Volkov Yu. F., Skiba O.V., Bychkov A.V. // Proc. Second Russian Conference on Radiochemistry. Dmitrovograd. 1997. pp. 155-156.
5. Orlova A.I., Petkov V.I., Skiba O.V. et al. // Proc. Int. Conf. “Future of Nuclear Systems” Global 97. Japan. Yokogama. 1997. pp. 1555-156.
6. Hirose Y., Suruoki A., Fukasawa T. et al. // Proc. Int. Conf. “Future of Nuclear Systems” Global 97. Japan. Yokogama. 1997. pp. 1181-1186.
7. Donald I.W., Metcalee B.L., Taylor R.N. // J. Mat. Sci. 1997. V. 32. pp. 5851-5887.
8. Senbhagaraman S., Guru Row T.N., Umarji A.M. // J. Mat. Chem. 1993. V. 3. pp. 309-314.
9. Ni Y-X., Hughes J.M., Mariano A.N. // Am. Mineral. 1995. V. 80. pp. 21-26.