Mineralogy of conserving mineral-like matrixes of high-level waste with garnet structure

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Perspective crystalline matrixes on a ferrite garnet basis for HLW lanthanide and actinide fractions immobilization and with high content of corrosion products aimed at their long-term safe storage and further geological isolation are considered in the article. Their synthesis parameters are optimized, the content of actinides (Th), lanthanides (La, Gd, Ce) and zirconium is determined. This content exceeds considerably all currently known natural garnet values. Implementation of further researches is necessary in order to specify optimum matrix composites as to radiation and chemical durability of taken samples.

In recent years there has been demonstrated influence of new up-to-date demands as to the development of nuclear energetic and opinions on its perspective, methods of spent fuel treatment with the purpose to avoid environmental distribution of radioactive materials [1, 8].

From the standpoint of waste radiation-equivalent disposal and creation of energetic on fast reactors with plutonium (or thorium), a new long-term strategy concerning underground storage [5, 9] is being under development. This strategy is based on two new technologies that fully change the general strategy of underground storage. The first of the above mentioned is the technology on fractionation of all the kinds of liquid HLW, by which radionuclide (RN) fractions are separated selectively from the general mass of waste. The radionuclides differentiate in lifetime, toxicity, specific radioactivity and volumes. The foundation of technology is extraction-sorption-precipitating method of liquid HLW separation into actinoid, cesium-strontium, rare earth and palladium fractions. The comprehension of given technology make it possible to decide particularly the problem on safety localisation provision of fractions.

The second of mentioned technology under development is a technology of synthesis of high resistance mineral matrixes (immobilisators) in order to incorporate the most dangerous long-lived radioisotopes into crystal grating on a basis of izomorphous substitution mechanism. A choice of optimum materials is one of the currently central moments for HLW derived from nuclear fuel cycle safety management to be assured. This choice can be improved with the information at hand about natural minerals-concentrators of radioactive elements. Garnets are the most perspective mineral matrixes for RN immobilisation of rare earth and HLW actinoid fraction [12, 14].

Mineral-geochemical aspects concerning a choice of mineral-like matrixes with garnet structure for immo-

bilisation of high-level waste are considered in the article. Brief review of such matrix working-outs is given and new results of author's own studies are brought.

Garnets are originated at different geological conditions, under various temperature and pressure intervals. They are resistant to leaching [7].

Minerals and synthetic compounds of garnet structure, which can be described by general formulae $X_3Y_2(ZO_4)_3$, are crystallised in cubic crystal system (s.g.Ia3d). Grating is a body centred cell. X cations are in dodecahedron environment of oxygen atoms (c.n. 8), Y - in octahedron (c.n. 6), Z - in tetrahedron (c.n. 4). The isolated tetrahedrons and oxygen octahedrons constitute the base of structure (Fig. 1).
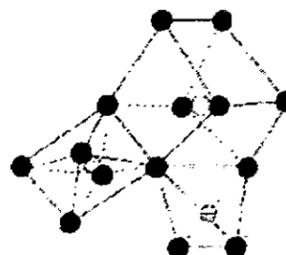

Fig. 1. Combination of structural polyhedrons within the garnet structure

When refining the garnet structure it appeared that polyhedrons were deformed. The availability of three structural positions, namely: X-, Y- and Z- positions with corresponding co-ordination numbers 8, 6 and 4, creates large opportunities for cations of different charge and size (including those composing radwaste) to be entered the garnet structure, also for multicomponent hard solutions to be formed. Divalent (Ca, Mn, Mg, Fe, Co, Cd) and trivalent (Y, REE) cations usually occupy X-position. Trivalent (Fe, Al, Ga, Cr, Mn, In, Sc, V) - and quadrivalent (Zr, Ti, Sn) ions fill in Y-position. Trivalent (Al, Ga, Fe), quadrivalent (Ge, Si, probably Ti), or quinquivalent (V, As) cations occupy Z-

position [18]. Non-compactly packed up oxygen frame, which is a foundation of garnet structure imposes certain geometrical conditions, namely restrictions for cations' sizes and their interrelation in all crystallographic positions, which are within wide borders: $0.080 \leq r^{VIII} \leq 0.150$ nm, $0.050 \leq r^{VI} \leq 0.115$ nm and $0.026 \leq r^{IV} \leq 0.049$ nm (for silicate garnets Z - Si) [20]; $0.096 \leq r^{VIII} \leq 0.126$ nm, $0.054 \leq r^{VI} \leq 0.091$ nm, and $0.039 \leq r^{IV} \leq 0.049$ nm (for ferrogarnets Z - Fe) (r^{VIII}, r^{VI}, r^{IV} - cation radiuses according to dodecahedron, octahedron and tetrahedron co-ordination on evidence [21]) [11].

With this the garnet crystal-grating parameter (a) varies from 1.1459 to 1.3648 nm. The widest zones of formation will have hard solutions with garnet structure, if displacement in all the crystal positions takes place simultaneously and leads to synchronous variation of all three correspondences of ion radiuses. That is, at bringing ions of large radiuses in dodecahedron positions it is essential (with the purpose to hold the structure) simultaneous entering of ions of larger radiuses into octahedron and advisable into tetrahedron positions, and vice versa. In particular, enlargement of ion radius in Z-position in series $Si^{4+} > Al^{3+} > Ga3+ > Fe^{3+}$ leads to a shift of correspondent garnet durability field into the region of large sizes of cations in X- and Y-positions [11].It follows that formation of REE compositions and those with trivalent actinoides with garnet structure will be the most advantageous for ferrite and gallates.

Natural garnets are represented mainly by silicates and their compositions can be varied within wide limits at the expense of different iso- and hetero-valent displacements. The most high content of rare earth is characteristic for spessartines (up to 3.05% REE_2O_3) [7]. Existence of yttrium (till 2 %) in spessartines that is less prevalent in greatly magnesial garnets is characteristic too. Andradites enclose from 0.75 to 2.65 % of yttrium. The next schemes of isomorphous exchange: $3Ca^{2+}$ = $=2REE^{3+}$ + vacancy; $Ca^{2+} + Si^{4+} = REE^{3+} + Fe^{3+}$ and $Fe^{3+} + Si^{4+}$ = = $Zr^{4+} + Fe^{3+}$ can be realised in REE-enclosing andradite grating. Lantanoides enter Ca^{2+} positions with Si^{4+} displacement for Fe^{3+} and Al^{3+}.

Almandines also differ in high content of rare earth (up to 2.64 % REE_2O_3) [7]. Uranium content in garnet varies within $10^{-6} - 10^{-5}$ g/g limits by data of track fragments of uranium spontaneous and constrained fission. Its more high concentrations are charasteristic for considerable calcium garnets, confined to alkaline rocks [4]. The same garnets have titanium and zirconium of higher concentrations as well. Content of yttrium - an element which crystal chemical feature is comparatively

close to uranium doesn't correlate with uranium content. Some kinds of natural garnets have high content of zirconium (kimceit) and titanium (schorlomite). Content of ZrO_2 in kimceit reaches 29.9 %, and silicon quantity can falls one atom for formulae unit below the meaning at the expence of Al^{3+} and Fe^{3+} displacement. ZrO_2 in quantity of 13.11 % is brought out in schorlomite [7].

As it was mentioned above uranium and thorium content in natural garnets does not exceed some parts in per cent, and REE - some first per cent. That is why the studying of natural garnets does not allow to assess isomorphous content of actinoids and lantanoides, their radiation endurance and to make a choice of optimum among them by composition, the most appropriate as a matrix for immobilization of lantanoid - and actinoid-enclosing HLW. Just only experimental data with crystal chemical features of garnet structure taken into account can give such an information.

REE ions also trivalent and quadrivalent actinoids occupy predominatingly dodecahedron positions in the garnet structure owing to their sizes. The structural factor influence upon chemical content of compositions for REE garnets has been investigated in the work [10]. Study of systems $Ln_2O_3 - Al_2O_3$, $Ln_2O_3 - Ga_2O_3$ and $Ln_2O_3 - Fe_2O_3$ (Ln = =Lu..... Pr) has shown the fact that oxides of aluminium, gallium and ferrum together with REE oxides at ratio 3:5 form compositions of aluminate, gallate and ferrite content $(REE_3Y_2Z_3O_{12})$, $Y = Z = Al^{3+}$, Ga^{3+} or Fe^{3+} with garnet structure.

It has been found that REE garnets are formed in aluminate system from Lu^{3+} to Dy^{3+} with radiuses from 0.098 to 0.103 nm. The structure of garnet type for gallates is resistant up to Nd^{3+} (0.111 nm). An existence of composition with Pr (0.113 nm) should be expected for ferrites as well. If ion radius is outside the geometric criteria of garnet structure existence, then compositions with other structure can be created instead of garnet (oxides with perovskite and fluorite structure, as a rule). Reasoning from the ion radius close meanings and electronic structure of trivalent actinoids - Am^{3+} and Cm^{3+}, from the one hand, and Gd^{3+} i Nd^{3+} - from the other one, a similar behaviour of these elements is possible at synthesis of garnet matrixes.

Experimental getting into some zyrconium-enclosing garnets from quadrivalent lantanoides and actinoides was verified for thorium and cerium [19]. Monophase samples with garnet structure were resulting from the mixture of $Ca_4ThZrFe_3O_{12}$,$Ca_{2.5}Th_{0.5}Zr_2Fe_3O_{12}$ and $Ca_{2.5}Ce_4+0.5Zr_2Fe_3O_{12}$ content. The garnet samples and insignificant additions of thorium dioxide are the resultants from the mixes of $Ca_4ThZrFeFe_3O_{12}$ content at 1200 °C for 3 hours of hold time.

Introduced studies were not directed for studying of garnet features as probable matrix material for lantanoid- and actinoid-enclosing waste immobilisation. Within the last years the special researches were carried out with the purpose to solve this problem.

Rare earth alumo-gallate garnet with general formulae $(Y,Gd,...)_3(Al,Ga,...)_5O_{12}$ was taken as a basis for the works [14, 15]. Resulting mixtures with garnet stoichiometry was prepared with the next powder oxides in use: Y_2O_3, Al_2O_3, Ga_2O_3, SnO_2, CeO_2, Gd_2O_3, CaO, UO_2. Oxides of cerium and uranium or their compound mixture modeling waste from plutonium production, served as HLW imitators. Synthesis of ceramic samples was fulfilled by melting in the open air at temperatures from 1300 °C up to 2000 °C. It was found that resulting products were polyphase ceramics, mainly with phases of garnet- and perovskite-type and insignificant additions of hibonite and also of zirconium and aluminium. The influence of chemical composition for phase content of samples was determined: perovskite dominates in Gd_2O_3 - Al_2O_3 system, and garnet becomes the main phase in Gd_2O_3 - Ga_2O_3 system. The garnet phase included till 6 % of Ce and till 0.3 % of U, which correlated with increasing of Ga content and decreasing of Al content. It was found that perovskite grating ability to enclose Ce and U is higher then garnet grating possibility and it reaches approximately 8 and 7 %, correspondingly. Thus, these experimental studies pointed to the fact that rare earth Al-Ga garnets have low ability for uranium and cerium incorporation and, probably, cannot be recommended for the purpose of immobilization of HLW with high content of actinoids and lantanoides.

Ferrite garnets in comparison with alumogallate present oneselves as more perspective from the angle on structural-chemical criteria of their durability [11, 23].

Taking into account this fact and also previous experimental data as concerning synthesis of some zirconium-enclosing ferrites with garnet structure [12] an experimental study of the resulting phases in CaO - Fe_2O_3 - ZrO_2 - $Gd(La)_2O_3$ - ThO_2 - CeO_2 system was carried out, Ca-Zr-Fe garnets, which comprise radwaste elements-imitators - thorium, cerium, lantanium and gadolinium were received and their content was determined (Table 1).

Zr and Fe are incorporated into garnet content aimed at maximum using of HLW solution macrocomponent composition. The latter one is formed at disollution of covering of nuclear fuel waste heat-generating assemblies and apparatus corrosion. The structural positions X in studied garnets are filled with Ca (r = 0.011nm), REE (r =

=0.105 - 0.116 nm), Th (r = 0.105 nm) and Ce^{4+}(r = 0.097 nm); Y positions - Fe^{3+}(r = 0.055 nm) and Zr (0.072 nm); Z positions - Fe^{3+} (r = 0.049 nm). The cation sizes in X, Y and Z positions are put into the above mentioned ranges of structural durability for ferrite garnets [11].

Resulting polycrystalline samples, which answered the garnet stoichiometry content, have been received by the method of joint concentration of nitrate saline mixtures by evaporation (JES). Nitrates of c.p. grade were used as resultant salts. Water solutions of specific concentrations were mixed in necessary ratio. Obtained mixture was evaporated at constant intermixing till salt crystallization and their partial dissolution. Removal of main bulk of nitrogen oxides was executed by the process of preliminary heating at 800 °C during 1-1,5 hours. Then the samples were subjected to grinding, pressing for tabloid form under 200-400 MPa, next they were subjected to sintering at 1200-1250 °C with a space of 2 - 4 hours in the open air, and they came into cooling till indoor temperature.

Separate samples of $Ca_{1.5}GdCe_{0.5}ZrFe_4O_{12}$ content taken for comparison were received by sintering method applied for the jointly deposited components (JDC). Sintering was fulfilled in the ammoniacal-carbonate buffer. The pH value of such kind of buffer solution was ~9. The mixture of nitrate salt solutions was poured in the buffer while mixing. After sedimentation the solution (together with precipitate) was heated up till boiling temperature, then went cooling up till indoor temperature, filtration and drying up. The pH value after sedimentation and boiling reached 8.6- 8.7. Under such conditions Ca, Fe, REE and Zr are sedimentated quantitatively.

At temperature of sintering equal 800 °C the powder looked like grains of 0.05-0.1 µm size. Further rising of temperature leads to grain coagulation, probably for account of powder particle surface energy alteration. After sintering at 1100-1250 °C the powder particles look like complex conglomerate comprising a mixture of interlinked grains of different dispersity with specific size of 100-200 µm.

Obtained samples were studied by roentgenography analysis method (method of powder on the DRON-3.0 device, $Cu_{Kα}$ with Ni filter, interior standard of KCl or Si.), IR-spectroscopy (spectrometer UR-10 within range of 400-1500 cm^{-1} in tablets KBr), Mossbauer spectroscopy (spectrometer NGRS-4M at indoor temperature with $^{57}Co(Cr)$ sources).

The majority of studied samples appeared to be monophase, i.e. they contained 90-100 % of garnet.The

Table 1.

Characterization of garnet ceramics samples

Sample	Calculated formula	Sintered tablets				Phase composition	Parametrs of garnet cell
		Sintered temperature and duration, hours	Diametric shrinkage, %	Average density, g/cc			
				Experiment	Theoretic		
1H	$Ca_2LaZr_2Fe_3O_{12}$	1200°C, 2	14,3	4,77	4,817	Gr	1.2803 (3)
2H	$Ca_2ThZrFe_4O_{12}$	1200°C, 2	13,8	5,407	5,344	Gr >> Per	1,2672 (3)
3H	$Ca_{2.5}Th_{0.5}Zr_2Fe_3O_{12}$	1200°C, 2	14,0	4,80	4,873	Gr	1,2737 (2)
1H-Th	$Ca_{1.5}GdTh_{0.5}ZrFe_4O_{12}$	1250°C, 3	14,9	5,31	5,516	Gr >> x+	1,2646 (1)
4H	$Ca_{2.5}Ce_{0.5}Zr_2Fe_3O_{12}$	1200°C, 2	14,5	4,61	4,588	Gr	1,2727 (1)
1H-Ce	$Ca_{1.5}GdCe_{0.5}ZrFe_4O_{12}$	1250°C, 3	14,1	5,15	5,249	Gr >> x+	1,2618 (2)
1H-Ce1	$Ca_{1.5}GdCe_{0.5}ZrFe_4O_{12}$	1100°C, 3	15,3	5,29	5,423	Gr >> Per	1,2482 (3)
5H	$Ca_{1.5}Sr_{0.5}LaZr_2Fe_3O_{12}$	1200°C, 2	14,3	4,81	4,892	Gr >>> Per	1,2868 (1)
6H	$Ca_2Th_{0.5}Ce_{0.5}ZrFe_4O_{12}$	1200°C, 2	14,0	5,18	5,106	Gr >> Per	1,2620 (3)
7H	$Ca_{1.5}Sr_{0.5}Th_{0.5}Ce_{0.5}ZrFe_4O_{12}$	1200°C, 2	14,2	5,19	5,158	Gr >> Per	1,2705 (3)
10H	$Ca_2GdZr_2Fe_3O_{12}$	1200°C, 2	13,9	5,03	5,049	Gr	1,2704 (4)
12H	$Ca_{1.5}SrTh_{0.5}Zr_2Fe_3O_{12}$	1200°C, 2	14,2	5,10	5,081	Gr	1,2818 (3)
17H	$La_{0.16}Nd_{0.49}Sm_{0.18}Gd_{0.17}Ca_2Zr_2Fe_3O_{12}$	1200°C, 2	13,8	4,82	4,911	Gr	1,2763 (1)

Note. Gr – garnet, Per – perovskite, x+ – non-identified phase, 1H-Ce1 – sample received by JDC method

samples were revealed, which comprised together with garnet some other phases – Ca-Zr oxide with perovskite structure also non-identified Ca and Fe oxide in the samples 1H-Th and 1H-Ce (Table 1). For the most the information of garnet composition aren't based on direct definition by application of local methods, but they were obtained owing to supposition of correspondence between received garnet stoichiology and resulting mixture content. The lack of other crystal phases (or their negligible amount) among the synthesis products, except of garnet, served for the basis. The conclusion was made of the fact that interrelation between the components in the resulting mixture characterizes the end-product content. This is also proved out by the data obtained from roentgenography analysis executed on separate samples, by which the composition of samples received doesn't differ practically from the set composition (Table 2).

The tablets produced under pressure 200–400 MPa from polycrystalline powder sintered before at 800 °C had stabilized density that formed 90–93 % from theoretical meaning (Table 1) and satisfactory form (absence of chips, fractures, form deformation). Distinctive microstructure of polished specimen of sintered tablets, which is defined by homogeneity and very fine porosity distributed evenly over the area of polished specimen, is shown in Fig. 3.

Hardness of tablets (1050÷1250 kg/mm²) being determined on PMT-3 (P=100g) device is close to analogous meanings of almandine (1228÷1290 kg/mm² [6]).

According to microstructure features the garnet ceramics (sintered from produced mixture received by
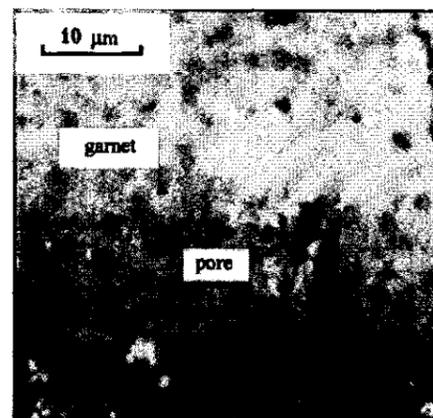

Fig. 3. CEM-picture of sample of the garnet ceramic (sample 1H, Table 1).

JES and JDC methods) of similar chemical composition are contiguous in between (Table 1, samples 1H-Ce and 1H-Ce*). We ought to mark that a rise in the sintering temperature till 1250 °C for powders received by JDC method leads to their melting.

Analytical studies carried out had shown that synthesized ferrite garnets can include a considerable amount of La, Gd and Zr (till 18.25; 20.17; 34.60 wt. %, correspondingly). Maximum content of Th and Ce reaches 28.34 and 9.83 wt.% in Ca–Zr–Fe garnets of $\{Ca_2Th\}[Zr, Fe](Fe_3)O_{12}$ and $\{Ca_{2.5}Ce_{0.5}\}[Zr_2](Fe_3)O_{12}$, compositions correspondingly (Table 1). It is well to mark for comparison that uranium content in synthetic Si garnets composes 0.6-0.8 wt.% [14]. Decreasing of actinoid concentration, probably, is brought about due to size decreasing of all structural positions at Fe^{3+} ion exchange in tetrahedron for smaller Si^{4+} cations, that is a compression of structur-

Table 2.

**Averaged composition
and chemical formulas of garnets***

Oxides/	Sample 12H			Theoretical
ions	P–12/3	P–6	P–12/4	content
ZrO_2	26,5	30,1	29,1	30,58
ThO_2	16,6	16,8	16,1	16,39
Fe_2O_3	30,2	30,0	29,4	29,73
CaO	8,4	10,8	9,4	10,44
SrO	17,3	12,3	12,5	12,86
Formulas calculated for 12 oxygen atoms				
Zr^{4+}	1,79	2,00	1,98	2,0
Th^{4+}	0,52	0,51	0,51	0,5
Fe^{3+}	3,15	2,99	3,08	3,0
Ca^{2+}	1,25	1,53	1,40	1,5
Sr^{2+}	1,39	0,95	1,01	1,0
Total	8,1	7,98	7,98	8,0

*by evidence of roentgenospectral analysis, microanalyzer
IXA-5, analyst A.Bondarenko, IGMOF NAS of Ukraine

al polyhedrons impedes actinoid ions (large by size) to enter the garnet cell. Recently executed experimental studies concerning U and Pu entry the aluminate and ferrite garnets [23] affirmed these conclusions.

As it was exhibited by analysis of studied Mossbauer spectra, the cations displacement in dodecahedron and octahedron positions of ferrite garnet structure effects for spectrum parameters. So, quadrupole disintegration in tetrahedrons is considerably more than in octahedrons. This indicates that deformation of tetrahedrons is more than that of octahedrons. This is stipulated by the fact that tetrahedrons "are connected" with dodecahedron by vertexes, while octahedrons have common edges, that is they are connected considerably stronger. Chemical shift of $\delta_{tr} < \delta_{oct}$ (for ^{9}Fe nucleuses in tetrahedrons and octahedrons). It means increasing of $Fe^{3+}_{tr} - O^{2-}$ covalent bond in comparison with such one for $Fe^{3+}_{oct} - O^{2-}$ [12, 13].

Radiation and chemical durability together with isomorphous capacity and mechanical characteristics are the most important characteristics of garnets as a matrix material. Natural silicate garnets have very low content of REE and actinides such as Th and U. Thus, there is impossible to calculate radiation durability of the by the results of metamict mineral study. Radiation durability of garnet structure consisted of REE and actinides and its transformation into amorphous state was investigated while ago in the work [22]. The experiments were carried out on synthetic silicate and alumoferrite garnets by ion bombing 1.0 MeV Kr. Critical temperatures (Tc) of transformation into amorphous state were defined as 777 and 857 °C – for silicate garnets; 827, 617 – for alumoferrite; and 757 – for andradite. It is ascertained that garnet Tc increases with

increasing of average atomic mass and size of elemental cell. We ought to contemplate that T_c will have close or higher meanings at the expense of larger mass and size of elemental cell for ferrite garnets synthesized by us.

It is known that within the period of about 500 years radiation fields from the HLW side as well as from the NFW side will be consisted mainly from β- and γ-radiation and then – from α-radiation [3]. Under radiation research the tablets of Ce-containing ceramics were irradiated by retarding irradiation that is received on the liner electron accelerator [2]. Cerium being used as actinoid imitator was generated during irradiation process according to ^{140}Ce (n, γ) > ^{141}Ce reaction (half-life period $T_{1/2}$ = 31.2 days). Irradiation was carried out till the absorbed dose meaning of 2.3 · 10^7 Gy, period of dose collecting formed 60 days. Realization of like conditions is of interest for garnet radiation durability assessment in conditions of HLW disposal. Absorbed dose meaning (generally they are 10^3 – 10^6 Gy) corresponds completely to conditions under research carried out by different authors with the purpose to determine radiation durability of immobilizing matrixes. At g-quantum irradiation of samples to dose of 10^7 Gy, there are no considerable changes in volume, density and color; integrity is kept, joints are absent.

The method of x-ray investigation was used for the purpose of garnet matrix crystalline structure study before and after research. X-ray analysis of output and γ-irradiated ferrite garnet samples (maximum absorbed dose formed 2.3 x 10^7 Gy) has shown that radiograms obtained were not practically subjected to changes. That is to say, there were no observed processes of radiation amorphization in worked-out ceramic materials under these radiation load. At the same time it is not inconceivable that radiation-physical and radiation – chemical processes originate in the samples under the effect of ionizing radiation owing to radiation defects (of different kinds) negligible quantity arising. Special methods of studies must be applied for their assessment.

The fact that homogenous systems with garnet structure are stable to acid action (HCl, HNO_3, H_2SO_4 etc) has to be taken into consideration at determination of garnet matrix chemical durability. In case of other phases addition these phases can be easy transformed into solution under heating of sample with HCl (1:1). Exceptions are those samples composing of complex oxides with perovskite structure, which are not also dissolved by acids. Isothermal testing of matrixes contacted with distilled water has been carried out (sample 10H, Table 1). Testing on interaction with water was under execution within the autoclave with Teflon bushing (disposed samples were in opened platinum containers) dur-

ing the period of 10 hours at 180 °C. Samples were not changed in their appearance and phase composition. Special studies have been started now concerning garnet matrix chemical durability. The first received results by rate of actinoid imitators leaching – Gd and Ce (<10⁻⁷ g/m²·day) have shown their correspondence to demands came upon the proved HLW forms [16], and affinity to analogous meanings for other mineral-like matrixes – zirconolite, perovskite and etc. [17].

Thus perspective ceramic materials were elaborated on the base of ferrite garnets for immobilization of HLW lantanoid and actinoid fractions with the purpose of their long-term safe storage and further geological isolation. Synthesized ceramic materials are a crystalline matrix that comprises garnet crystals with negligible addition of perovskite and metal oxides. The parameters of their synthesis with model nitrate solutions of HLW lantanoid and actinoid fractions are optimized. It is ascertained that isomorphous displacement

of calcium for Th, Ce, La and Gd in ferrite garnets occurs within the limits 11 – 32 % in conversion for the oxide quantity. Zr content reaches to 35 wt/ %. Entry of lantanoid ions (Lu..... Pr) and actinoid ions (U⁴⁺, Th⁴⁺, Np⁴⁺, Pu⁴⁺) into garnet is promoted by filling of octahedron and tetrahedron positions with large low-valent cations – Fe³⁺. The γ-quantum irradiation of garnet samples till ~2.3 x 10⁷ Gy doses have shown that radiation amorphization processes in the elaborated ceramic materials at such kinds of radiation loads don't occur. It is ascertained that microstructure of ceramic materials is not subjected to changes after γ- irradiation as well. Previous researches as to study of chemical durability demonstrated that rate of actinoid imitators leaching is close to analogous meaning for other the most stable mineral-like matrixes.

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В статті викладено результати досліджень перспективних кристалічних матриць на основі феритових гранатів для іммобілізації лантаноїдної і актиноїдної фракцій ВАВ з високим вмістом продуктів корозії з метою їх тривалого безпечного зберігання і подальшого захоронення в геологічних формаціях. Оптимізовано параметри їх синтезу, визначено вміст в них актиноїдів (Th), лантаноїдів (La, Gd, Ce) і цирконію, які значно перевищують відомі дотепер дані для природних гранатів. Для визначення оптимальних матричних композитів необхідна постановка подальших досліджень щодо радіаційної і хімічної стійкості отриманих зразків.

В статье изложены результаты изучения перспективных кристаллических матриц на основе ферритных гранатов для иммобилизации лантаноидной и актиноидной фракций ВАО с высоким содержанием продуктов коррозии с целью их долгосрочного безопасного хранения и дальнейшего захоронения в геологических формациях. Оптимизированы параметры их синтеза, определено содержание в них актиноидов (Th), лантаноидов (La, Gd, Ce) и циркония, которое значительно превышает известные к настоящему времени значения для природных гранатов. Для определения оптимальных матричных композитов необходима постановка дальнейших исследований радиационной и химической стойкости полученных образцов.