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Experimental study of modifying component agency on devitrification of $Na_2O–Al_2O_3–P_2O_5$ glasses under elevated temperatures

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The immobilization of radio nuclides containing in a high level liquid radioactive waste (HLW) into aluminophosphate glasses is the basic solidification technology of the most dangerous to the nature and human person nuclear fuel cycle waste in our country. Behavior of glasses as metastable phase under the influence of various factors represents direct practical interest for the radiochemical industry. One of processes which considerably changes properties of glass matrixes is their crystallization. Influence of the elevated temperature, as crystallization (devitrification) factor on glasses and dependence of this process on presence in glasses Si and Fe is investigated in the present study.

Samples for research and experimental procedure

It is a little exemplary of transparent modeling glasses having a smooth surface and conchoidal fracture prepared by CZL FGUP PO "Mayak" have been selected for experiments. Chemical compounds of glasses have been studied by electron microprobe analysis (EMPA) on a scanning electron microscope (SEM) Tescan Vega II XMU combining with X-ray energy dispersive spectrometer INCAx-sight. Glasses differ on color (fig. 1) depending on presence of impurity (tab.1). Base glass (C-0) has no impurity and on figurative compound coincides with average procedural compound of glassing HLW by FGUP PO "Mayak" (fig.2). Other glasses have additives of various components and there compounds are richer with aluminum. Slices of glasses in weight 0.2 g subjected to heating on air at temperatures 420ºC (44 hours), 470ºC (39 hours), 530ºC (12 hours), 640ºC (4 hours) and 690ºC (4 hours).

Table 1. Average procedural compound of glassed HLW by FGUP PO "Mayak" and compounds of samples by EMPA results in mol.%. Symbols of phases correspond to the same on fig. 2

Sample, phase	Characteristic	Na_2O	Al_2O_3	SiO_2	P_2O_5	CaO	Fe_2O_3	NiO
Glassed HLW by FGUP PO "Mayak"		40(5)	17(4)	-	38(2)	3(2)	1(1)	1(1)
C-0, glass (■)	Starting	43.2(6)	17.7(3)	-	39.1(4)	-	-	-
C-0, NAP+ glass (□)	530ºC (12 hours)	42(1)	18(2)	-	40(2)	-	-	-
C-3, glass (▲)	Starting	38.1(2)	20.5(1)	1.3(2)	37.3(4)	1.0(2)	1.8(2)	-
C-3, glass (Δ^1)	530ºC (12 hours)	38.7(5)	19(1)	1.7(3)	36.5(7)	2(1)	2.2(5)	-
C-3, NAP (Δ^2)	530ºC (12 hours)	36(2)	22(1)	2.4(8)	38(1)	0.6(3)	1.0(4)	-
C-4, glass (♦)	Starting	34.1(3)	20.2(4)	9.1(2)	34.8(4)	-	0.8(1)	0.9(3)
C-4, glass (◊)	530ºC (12 hours)	32.9(7)	20.4(5)	9.3(2)	35.6(5)	-	0.8(1)	1.0(1)
C-5, glass (●)	Starting	41.0(4)	20.6(2)	-	34.7(6)	-	3.6(2)	-
C-5, glass (○^{1})	640ºC (4 hours)	40(1)	20.7(2)	-	33.5(4)	-	6.0(8)	-
C-5, NAP (○^{2})	640ºC (4 hours)	40.7(6)	19.7(3)	-	38(1)	-	1.9(5)	-
C-5, NFP (○^{3})	640ºC (4 hours)	32(1)	-	-	35.3(8)	-	33(1)	-

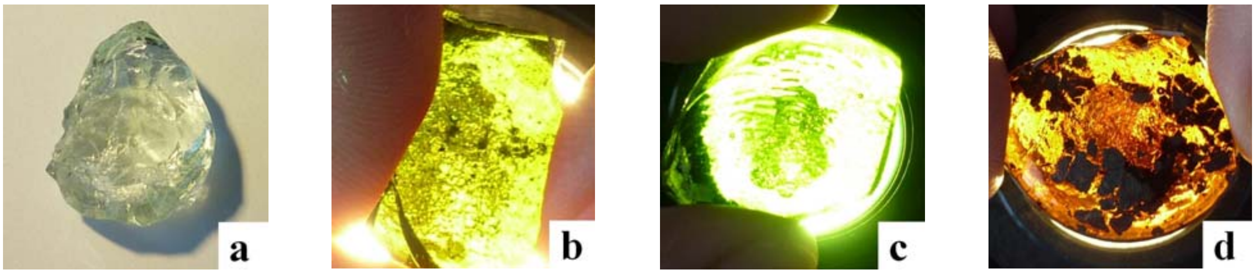

Fig.1. Photos of starting glasses: a – C-0, b – C-3, c – C-4, d – C-5

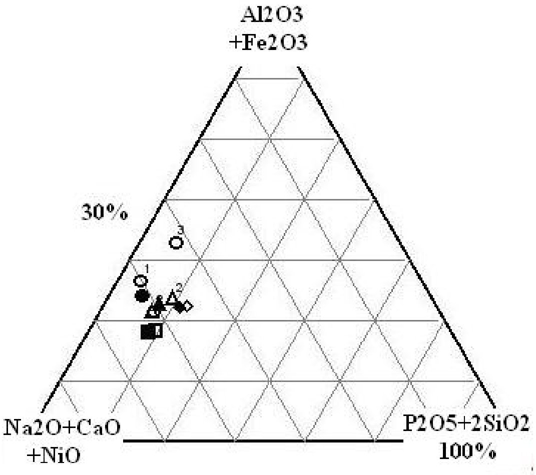

Fig.2. Chemical compounds of samples by EMPA results in mol.%. Symbols see table 1

Experimental results

On visual supervision over products of experiments melting and crystallization processes occurred differently depending on compound of glasses. Glass C-4 containing SiO_2, melted at 530ºC, but didn't crystallize. In samples C-0 (base compound) and C-3 (the small containing of impurity) crystallization occurred from melt, formed at 470ºC. In glass C-5 enriched with iron, at first there was a crystallization in a solid condition, and partial melting occurred at the further rise in temperature to 690ºC.

After heat treatment the glasses have been investigated by X-ray powder diffraction (XRPD) method, EMPA and infrared (IR) spectroscopy.

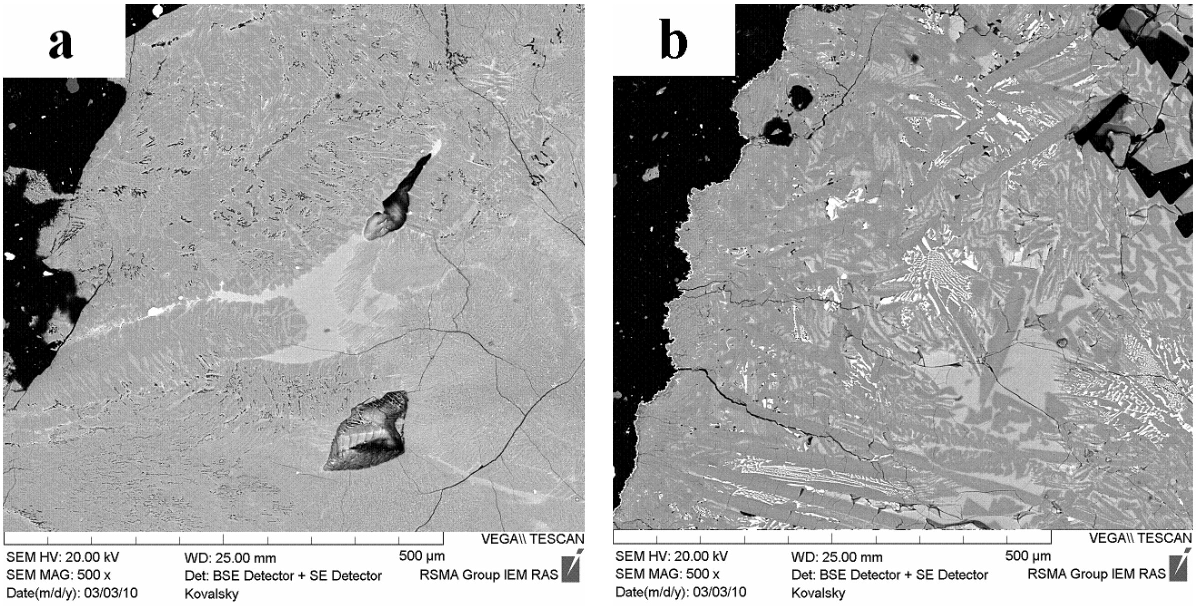

Fig.3. The polished cuts of samples C-3 (a) and C-5 (b) after heat treatment. Images are received on SEM backscattered electron detector.

XRPD pattern of sample C-4 after heat treatment (fig.4c) has confirmed the assumption about absence of crystallization. Also it is not revealed some heterogeneity of phase and chemical compound of this sample by EPMA (tab.1). Other picture was observed after heat treatment of glasses C-0 and C-3 (fig.4a,b). On both XRPD patterns there are reflections of the phase identified as sodium aluminophosphate (NAP) having compound $Na_3Al_2(PO_4)_3$ (database PCPDFWIN v.2.02, card 31-1265). For sample C-0 compound of this phase coincides with the glass one, that doesn't allow to observe phase heterogeneity by SEM backscattered electron detector. We have another matter for sample C-3 (fig.3a) in which microimpurity are distributed irregularly between glass (light) and a crystal phase (dark) (tab.1), and structure of the sample generated at devitrification is reveal. The most expressed effect of phase compound change is found out in sample C-5, in which after heat treatment without melting two crystal phases (fig.4d) were formed: Fe-NAP–$Na_{3.3}Al_{1.6}Fe_{0.1}P_{3.1}O_{12}$ (dark gray on fig.3b) and NFP–$Na_{2.6}Fe_{2.4}P_{3.1}O_{12}$ (white), and the glass (light gray) has remained also. All phases had contrast compounds (табл.1).

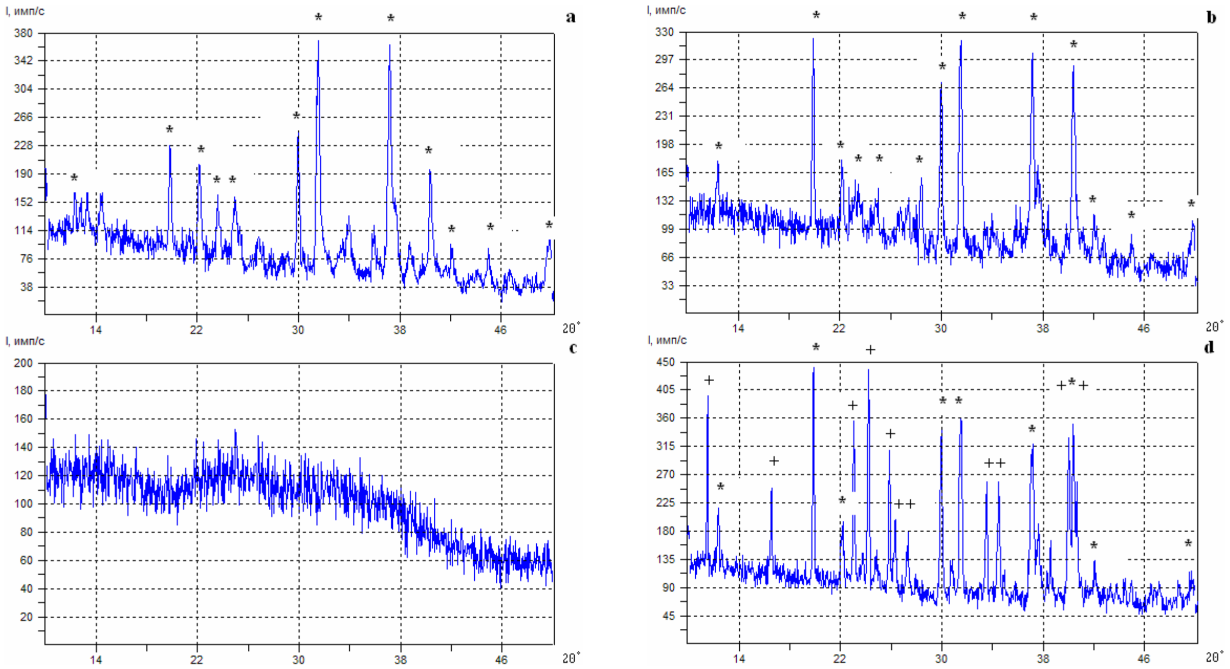

Fig.4. XRPD patterns of the samples C-0 (a), C-3 (b), C-4 (c) and C-5 (d) after heat treatment: * - NAP, + - NFP. Dron-7 diffractometer, $CoK\alpha_1$ radiation (λ = 1.78892 Å), Fe-filter.

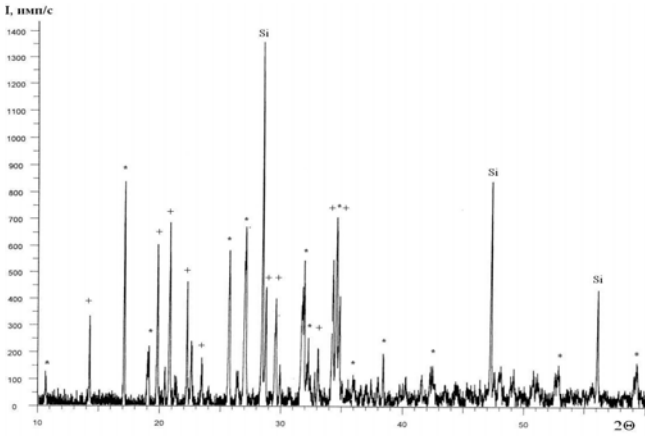

Fig.5. XRPD pattern of sample C-5 after heat treatment: * - Fe-NAP, + - NFP, Si - spectral pure 4305 Å. $CuK\alpha_1$ radiation (λ = 1.5406 Å)

XRPD pattern of the polyphase sample C-5 has been removed at 25°C on Bruker D8 ADVANCE X-ray diffractometer, using $CuK\alpha_1$ radiation (λ = 1.5406 Å) with step of 0.010°2Θ for specification of crystal phases structures (fig.5). Angular positions of reflections were corrected by the internal standard (spectral pure Si, a = 5.4305 Å). CRYSFIRE 2004 (THEOR90 procedure) and CHEKCELL computer programs have been used for definition of reflection indexes and calculation of unit cell parameters. 14 reflections for Fe-NAP and 12 ones for NFP in the angular interval of 10–60°2Θ have been involved for calculations. The decision for unit cell parameters of Fe-NAP has been found in terms of the tetragonal system: a = 9.303(1) Å, c = 18.733(2) Å, V = 1621.3(6) Å^3, body centered lattice is possible. The orthorhombic crystal system, PBAM space group has been offered for NFP: a = 18.114(3) Å, b = 9.251(2) Å, c = 8.533(2) Å, V = 1430.0(8) Å^3.

IR spectra of samples have been recorded at room temperature on Specord M80 spectrophotometer with the instrumental resolution of 4 sm^{-1} (fig. 6). Samples were dispersed in melted NaCl matrix. The quantity of the sample in a matrix made 1.5 wt.%. The IR spectra of initial glasses in the region of 1200–1050 cm^{-1} shows the intense strongly overlapping absorption bands assigned to stretching vibrations ν_{as} and ν_s of different phosphate groups (PO_4). The bands of medium intensity in the region 1050–900 cm^{-1} are correspond to the antisymmetric vibrations of the bridging groups ν_{as} P–O–P and P–O–Al. Very weak bands exhibits in the spectral range 750–640 cm^{-1} due to stretching vibrations (AlO_4) tetrahedra. The weak bands in the region 600–400 cm^{-1} are indicative of bending vibrations of the bridging groups (T-O-T), where T = P or Al.

The IR spectra of C-0, C-3 and C-5 glasses after heat treatment are demonstrated not only the best resolution of the absorption bands of ν(PO4) and bridging groups (P–O–P) and (P–O–Al), but also increase their intensity, which is probably associated with greater ordering of the high-temperature phase. The spectrum of melted glass C-4 differs slightly from the parent spectrum, and shows only a decrease of the intensity of deformation vibrations δ(T–O–T) at low frequencies. Thus, the original glasses undergone some structurisation already in the course of storage at room temperature, and for devitrificated samples these changes far more radical as they are connected with the formation of crystalline phases.

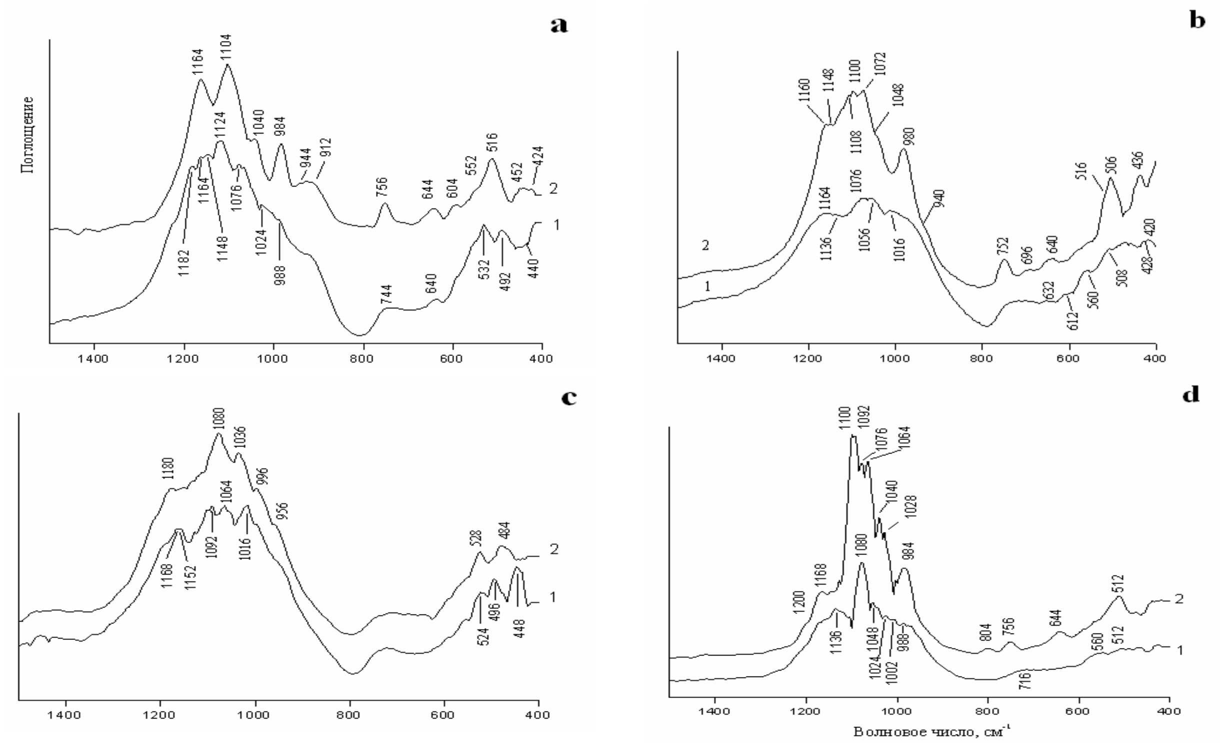

Рис.6. ИК-спектры образцов С-0 (a), С-3 (b), С-4 (c) и С-5 (d) до (1) и после (2) термообработки

Discussion of results and conclusions

On radiochemical manufacture all glasses after pouring in containers cool down long enough. Our experiments simulate processes which can occur at slow cooling glassed radioactive waste. It is shown that elements-modifiers can both to brake process of glass devitrification (Si), and to make active it (Fe). Anyway all laboratory tests on mechanical and chemical stability of glasses are correct for spending not with the quenched metastable glass, and with the material after heat treatment.

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