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PHASE COMPOSITION AND STRUCTURE OF GLASSY MATERIALS ON SODIUM ALUMINOPHOSPHATE BASIS CONTAINING RARE EARTH OXIDES

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Phase composition of sodium-aluminum-phosphate glasses containing rare earth (RE = lanthanum, cerium, europium, and gadolinium) oxides produced by melt quenching and slow cooling, their structure and hydrolytic stability were determined. It was demonstrated that incorporation of up to ~5 wt.% lanthanide oxides does not cause their devitrification during quenching (with the exception of La-containing glass) and has no significant effect on their structure and hydrolytic stability. After annealing, the sodium-aluminophosphate based glasses were subject to devitrification with segregation of sodium-aluminophosphate, RE- (monazite) and sodium RE-phosphate phases.

Keywords: *leaching, hydrolytic stability, infrared spectroscopy, sodium-aluminophosphate glass, rare earth elements, X-ray diffraction analysis.*

Introduction

Rare earth elements (REE — lanthanum, lanthanides, yttrium) are used as components of IR-transparent, UV-absorbing, radiation-optical, acid- and heat-resistant glasses [1]. REE in the range from La to Gd are uranium fission products and are present in spent nuclear fuel (SNF) in quantities of about 11 kg per 1 t of SNF. In process of SNF reprocessing with extraction of uranium and plutonium, REE are transferred to high-level waste (HLW) (which also accumulates ^{90}Y and ^{90}Zr due to ^{90}Sr β-decay) and their total content in HLW produced in SNF reprocessing may reach up to ~50% mass. and up to 10% mass for vitrified HLW [2]. It is considered that RE^{3+} ions act as grid modifiers located in its cavities, but may also be incorporated in the grid. In higher concentrations REE oxides form crystalline phases. RE^{4+} ions, mainly Ce^{4+}, have low solubility and are also found in crystal phases.

The current paper presents systematic study of REE oxides behaviour for La, Ce, Eu and Gd (Ce and Gd are considered as simulants of Pu, Am and Cm) in sodium-aluminophosphate glass corresponding to the type used for HLW vitrification at PA “Mayak” [3].

Experimental part

REE element oxides effect on the structure of SAP glass with the composition (mol %) 40 Na_2O, 20 Al_2O_3, 40 P_2O_5 was studied (1). 1 g of Ce_2O_3 (2), 1 g of La_2O_3 + 4 g Ce_2O_3 (3) and 5 g each of CeO_2 (4), Eu_2O_3 (5), EuO (6) and Gd_2O_3 (7) (Table 1) were introduced into glass (1) on top of 100% mass. The glass was synthesized from $NaPO_3$ and Al, Fe(III) and REE oxides in quartz crucibles of a resistance furnace in a mode typical for phosphate glass production [4] with maximum temperature of 1300 °C and curing time of 30 minutes.

The translation is done by V. I. Shpinkov

Table 1. Calculated composition of SAP glasses (mass %)

Sample	Na_2O	Al_2O_3	P_2O_5	RE_2O_3	REO_n
1	24.3	20.0	55.7	-	-
2	24.1	19.8	55.1	1.0 (La)	
3	23.2	19.0	55.1	1.0 (La)+3.8(Ce)	-
4	23.2	19.0	53.0		4.8 (CeO_2)
5	23.2	19.0	53.0	4.8 (Eu)	-
6	23.2	19.0	53.0		4.8 (EuO)
7	23.2	19.0	53.0	4.8 (Gd)	-

Part of each melt was poured on top of a metal plate, and the rest was cooled in the inactive furnace in accordance with the mode corresponding to glass cooling in the centre of 200 l canister at the HLW vitrification facility of PA "Mayak" [5].

The obtained samples were studied by X-ray diffraction analysis using EMPYREAN diffractometer (CuK α-radiation with nickel filter) and Fourier Transform Infrared Spectrometry (FTIS) using spectrophotometer Shimadzu IR Prestige 21 (powdered glass was pressed into KBr pellets). Hydrolitical stability of the glass was determined using RST-A/MSS-3 method [6]: glass samples were ground, powder fraction with particle sizes 0.071-0.125 mm was separated, placed into teflon vessels and covered by bidistilled water and maintained at temperature (90±2) °C for 7 days. Element composition of the solutions after leaching was determined by inductively coupled plasma emission spectrometry using ICAP 6500 spectrometer. Normalized release of NR element (g/l) was calculated out of [7]:

$$NR_i = C_i/F_i,$$

where C_i — mass of element "*i*" in the solution (g/l), F_i — fraction of element "*i*" in the glass (g_i/g_{glass}).

Results and discussion

All specimen obtained in melt quenching were X-ray amorphous. Following annealing, the SAP glass samples were partly crystallized with release of phosphotridimite phase. Specimen 1, which did not contain REE oxides, demonstrated traces of the phase with parameters roughly equivalent to the compound β-$Na_6Al_3(P_2O_7)_3$ [8], specimen 3, 4, and 5, showed admixture of a phase with monazite structure (Fig. 1 and Table 2).

IR spectra of the glasses consisted of bands 3200—3600 cm^{-1} and 1630—1660 cm^{-1}, corresponding to stretching and deformation oscillations in the molecules of structurally bound and absorbed water, and wide intense bands in the ranges 800—1400 cm^{-1} and below 600 cm^{-1}, a low intensity band at 700—800 cm^{-1}, and a leg at 600 cm^{-1}, corresponding to stretching and deformation oscillations in aluminophosphorousoxygen glass grid.

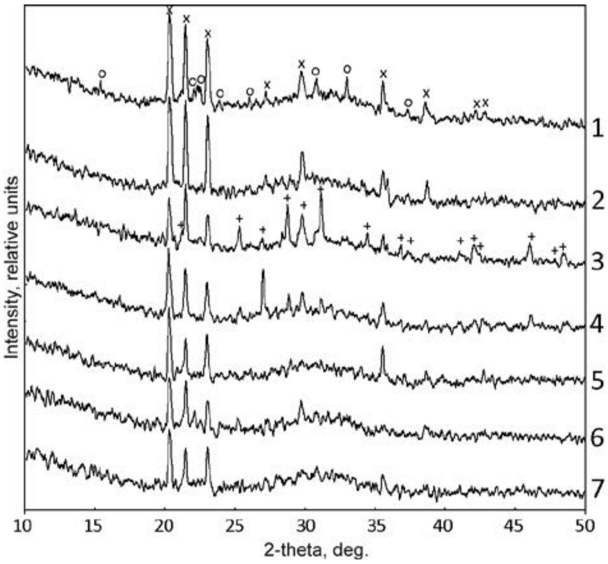

Fig. 1. X-ray diffraction patterns for products obtained in slow cooling (annealing) of the melts
× — phosphotridimite, o — β-$Na_6Al_7(P_2O_7)_3$, + — monazite

Table 2. Phases released in annealing of the studied glasses

Sample	RE^{n+}*	Phases
1	–	$AlPO_4$ (PT) > glass (G) > β-$Na_6Al_3(P_2O_7)_3$ (NAP)
2	Ce^{3+}	$AlPO_4$ (PT) > glass (G)
3	La^{3+}, Ce^{3+}	$AlPO_4$ (PT) > $(La,Ce)PO_4$ ≈ glass (G)
4	Ce^{4+}	$AlPO_4$ (PT) > $(Ce)PO_4$ ≈ glass (G)
5	Eu^{3+}	$AlPO_4$ (PT) > $EuPO_4$ ≈ glass (G)
6	Eu^{2+}	$AlPO_4$ (PT) ≈ glass (G)
7	Gd^{3+}	$AlPO_4$ (PT) ≈ glass (G)

*assumed charge of ions introduced into respective compounds.

The most intense band 800—1400 cm^{-1} was a superposition of several bands (Fig. 2) both asymmetric (ν_{as}) and symmetric (ν_s 1000—1100 cm^{-1}) of stretching oscillations in bonds O–P–O in pyrophosphate $P_2O_7^{4-}$ (1150—1200 and 1000—1100 cm^{-1}) and orthophosphate PO_4^{3-} (1000—1100 and 950—1000 cm^{-1}) groups and bridge P–O–Al. Bands 900—950 cm^{-1} and 700—750 cm^{-1} correspond to ν_s and ν_{as} oscillations of bridge bonds P–O–P in pyrophosphate groups [9,10].

The band 700—750 cm^{-1} included O–Al–O bonds oscillations in aluminooxygen tetrahedrons AlO_4, and the leg at 600 cm^{-1} may be attributed to bond oscillations in AlO_5 pyramids (Fig. 2) [11]. Deformation oscillations in phosphorus-oxygen groups and bond oscillations in octahedrons AlO_6 were localized below 600 cm^{-1} [10, 11].

Introduction of REE oxides to the glass lead to minor changes of the spectra form (Fig.2), and, therefore, minor glass structure changes. These changes included a certain reduction of intensity of band 900—950 cm^{-1} and a less noticeable intensity

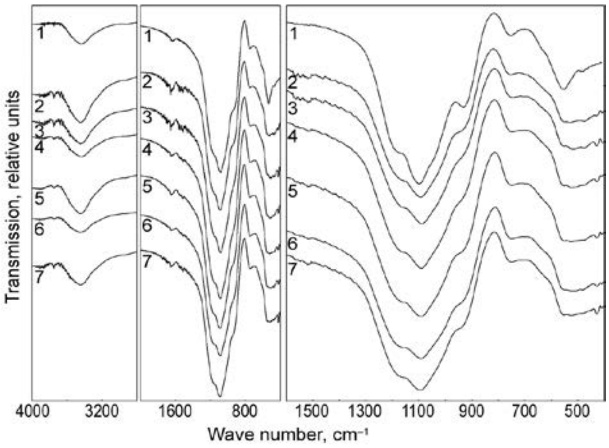

Fig. 2. IR spectra of aluminophosphate glasses with REE (1–7 – see text)

reduction for band 700—750 cm^{-1}, redistribution of intensities in bands 1000—1100 and 1150—1200 cm^{-1} with increase of the intensity of the first one, and increase of absorption in the range 400—500 cm^{-1} (Fig. 2).

The listed changes were most noticeable for spectra of glasses containing La/Ce (3) and Ce (4), and they could be explained by depolymerization effect of REE ions on the structural grid of phosphate glass, therefore increasing the fraction of isolated orthogroups of PO$_4$ in the glass structure and decreasing the number of pyrogroups. Respectively, the intensity of P–O–P bridge bond bands also reduced. Also the fraction of aluminum in octohedral oxygen surrounding increases with respect to other alumino-oxygen groups.

Normalized elementary release (Table 3) and element leaching rate (Fig. 3) measurements using RST method for glasses obtained by melt quenching showed that SAP glasses have close values with respect to Na, P and REE with account for measurement errors (Table 3). Normalized Na releases and leaching rates remained the highest for all glasses, whilst they were the lowest for Gd, which was considered as a simulant for Am(III) and Cm(III) (Table 3 and Fig. 3).

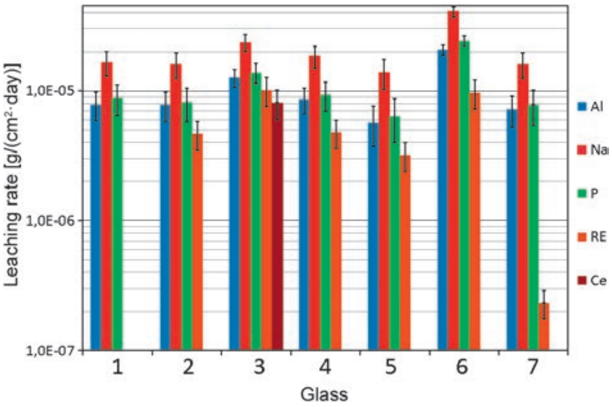

Fig. 3. Element leaching rates for SAP glasses with REE additives obtained by melt quenching

Table 3. Normalized releases (g/l) of elements according to RST method from SAP glasses produced by melt annealing on a metal plate

Glass	Number	Al	Na	P	REE
SAP	1	0.59	2.11	1.51	-
	2	0.57	2.02	1.40	0.03 (La)
	3	0.90	2.88	2.27	0.23 (La); 0.05 (Ce)
	4	0.61	2.23	1.51	0.13 (Ce)
	5	0.40	1.66	1.04	0.09 (Eu)
	6	1.47	4.91	3.95	0.29 (Eu)
	7	0.51	1.93	1.27	0.01 (Gd)
Hanford MS26AZ102 LAW[1] [12]	LRF[3]	0.47–0.50	1.35–1.60	0.69–0.74	Not identified
	CJHM[4]	0,44–0,74	1,28–1,94	0.63–1.05	-«-
	IMCC[5]	0.54–0.71	1.39–1.70	0.60–0.84	-«-
LABS[2]	EA [7]	-	13.78	4.04 (Si)	Not regulated

[1] vitrified waste simulant at Hanford site;
[2] Lithium-alumo-ferrous-borosilicate glass;
[3] laboratory resistance furnace, quartz crucibles;
[4] ceramic Joule heater melter (electric pool furnace);
[5] induction melter – cold crucible.

Normalized release of Na (1.14-4.91 g/l) was 4—6 times below the thresholds of US Environmental Protection Agency (13.78 g/l [7]). There are no threshold values for P and Al, but they could be compared with values for Si (4.04 g/l) and B (18.11 g/l) as the main and additional glass-forming elements in borosilicate glasses. They were lower by 1.3—4 times (0.70—3.95 g/l) and 12—45 times (0.40—1.47 g/l) than the threshold values for Si and B [7]. Normalized releases of macrocomponents from SAP glasses were approximately the same as for SAP glasses used in vitrified waste at Hanford site (USA) [12].

Conclusions

1. Addition of up to ~5% mass of REE oxides (La, Ce, Eu, Gd) to sodium-aluminophosphate (SAP) glass does not cause its crystallization in quenching, but promotes its partial crystallization in slow cooling (annealing) with release of phosphotridimite and monazite admixtures in SAP glasses.
2. IR spectrometry data demonstrated that minor addition of REE oxides did not affect significantly the anionic glass grid.
3. La, Ce, Eu and Gd were present in sodium-aluminophosphate glasses in three-valence form, and, similar to the basic glass components (Na, Al, P), had low leaching rates — 10^{-7}—10^{-6} g/(cm^2·day), thus indicating that such glasses can become promising materials for immobilization of REE and minor actinides-containing HLW.

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