



# The phase composition, structure, and hydrolytic durability of sodium-aluminum-(iron)-phosphate glassy materials doped with lanthanum, cerium, europium, and gadolinium oxides

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## ABSTRACT

Sodium-aluminum-(iron)-phosphate glasses containing lanthanum, cerium, europium, and gadolinium (*Ln*) oxides were examined by X-ray diffraction, infrared spectroscopy, and X-ray photoelectron spectroscopy. Phase composition of the quenched and annealed materials was determined. It has been shown that introduction of up to ~5 wt% *Ln* oxides to sodium-aluminum-phosphate (SAP) and sodium-aluminum-iron-phosphate (SAIP) baseline compositions did not cause their devitrification at quenching (except the La-bearing glass) and did not offer significant impact on their structure and hydrolytic durability. All the *Lns* studied are present in a trivalent form. After annealing the SAP-based glasses were partly devitrified with segregation of aluminophosphate, sodium-aluminophosphate, *Ln*- (monazite) and Na/*Ln* phosphate phases while in the *Ln*-bearing SAIP glasses sodium-iron orthophosphate and monazite were found. Devitrification at annealing reduced hydrolytic durability of glasses by factors of 5 to 10 as compared to the quenched samples (glasses).

## 1. Introduction

Rare earth elements including lanthanides (La, *Ln*, Y) enter the compositions of colored, luminescent, infra-red transparent, ultra-violet absorbing, high-refraction, radiation optically resistant, acid-resistant, and ovenproof glasses [1]. Some of them (La...Gd, Y) are uranium fission products and present in spent nuclear fuel (SNF) in amount of about 11 kg per 1 metric ton of SNF. During extraction reprocessing of SNF after recovery of U and Pu the *Lns* are concentrated in high-level nuclear waste (HLW). Their total content in HLW may reach ~50 wt% or up to ~10 wt% in glass produced from this waste [2]. In the case of realization of HLW partitioning concept with separation of *Ln*-, *Ln*-actinide or *Ln*-*TM* (*TM* – transition metal) fractions the *Ln* concentrations in glasses may be even higher [3]. A special case is the lanthanide borosilicate glass to immobilize excess weapons-grade plutonium in which composition up to 35 wt% *Ln*<sub>2</sub>O<sub>3</sub> is especially introduced to increase PuO<sub>2</sub> solubility [4].

There are rather broad glass forming ranges in binary *Ln*-phosphate glasses (up to 30 mol% or ~50 wt% *Ln*<sub>2</sub>O<sub>3</sub>) [5]. In ternary alkali

aluminophosphate systems the solubility of *Ln* oxides depends strongly on composition, atomic number (mass) of the element, its oxidation state, and glass melting temperature [6–17]. The solubility is reduced in the row: ultraphosphate > metaphosphate > pyrophosphate compositional areas. The latter corresponds to formulations of HLW glasses [7]. So, the solubility of *Ln*<sub>2</sub>O<sub>3</sub> in SAP glasses with composition (wt%) 22–26 Na<sub>2</sub>O, 15–24 Al<sub>2</sub>O<sub>3</sub>, 49–56 P<sub>2</sub>O<sub>5</sub> increases at the increase of the *Ln* atomic number from 1.5–1.7 wt% for La<sub>2</sub>O<sub>3</sub> to 3.7–3.8 wt% for Sm<sub>2</sub>O<sub>3</sub> and melting temperature (from 900 to 1200 °C by ~6 times) but decreases at the increase of oxidation state (2.0–2.3 wt% for Ce<sub>2</sub>O<sub>3</sub> and < 2.0 wt% for CeO<sub>2</sub>) [6–8]. The solubility of a mixture of *Ln* oxides obeys the rule of additivity [6–8]. The solubility of Gd, Ce, and La oxides in iron phosphate glass was found to be higher [12–14]. No data on solubility of *Ln* oxides in SAIP glasses have been found.

While there is a number of works on the study of the structure of *Ln*-phosphate glasses [9–17] information on the effect of *Lns* on the structure of the glasses on aluminum- and aluminum-iron phosphate basis is very limited. *Ln*<sup>3+</sup> ions are mainly believed to be the network-modifiers located in network voids and weakly bonded with the

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**Table 1**  
Target compositions of SAP and SAIP glasses (wt%).

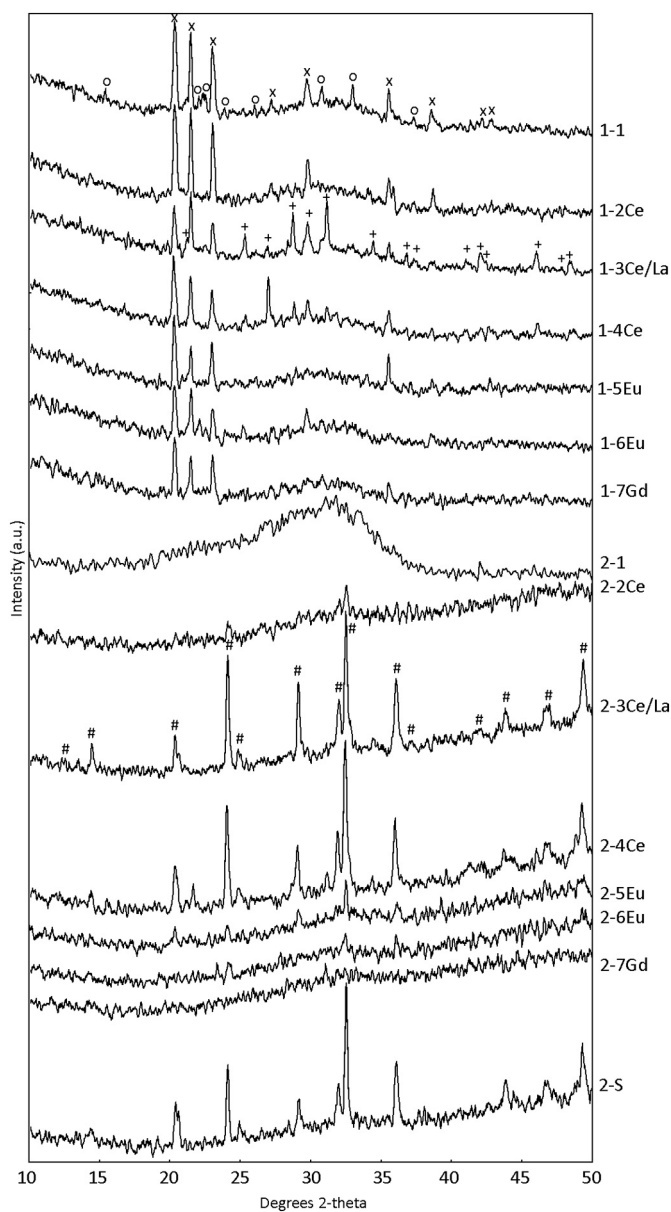
Glass	Sample	Na <sub>2</sub> O	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	RE <sub>2</sub> O <sub>3</sub>	REO <sub>n</sub>
SAP	1-1	24.3	20.0	–	55.7	–	–
	1-2Ce	24.1	19.8	–	55.1	1.0 (Ce)	–
	1-3La/Ce	23.1	19.0	–	53.1	1.0 (La) + 3.8 (Ce)	–
	1-4Ce	23.1	19.0	–	53.1	–	4.8 (CeO <sub>2</sub> )
	1-5Eu	23.1	19.0	–	53.1	4.8 (Eu)	–
	1-6Eu	23.1	19.0	–	53.1	–	4.8 (EuO)
	1-7Gd	23.1	19.0	–	53.1	4.8 (Gd)	–
SAIP	2-1	23.0	9.5	14.8	52.7	–	–
	2-2Ce	22.8	9.4	14.7	52.2	0.9 (Ce)	–
	2-3La/Ce	21.9	9.0	14.1	50.2	1.0 (La) + 3.8 (Ce)	–
	2-4Ce	21.9	9.0	14.1	50.2	–	4.8 (CeO <sub>2</sub> )
	2-5Eu	21.9	9.0	14.1	50.2	4.8 (Eu)	–
	2-6Eu	21.9	9.0	14.1	50.2	–	4.8 (EuO)
	2-7Gd	21.9	9.0	14.1	50.2	4.8 (Gd)	–

**Table 2**  
Crystalline phases segregated in annealed samples of glasses.

Glass	Sample	RE <sup>n+</sup> + <sup>a</sup>	Phases
SAP	1-1	–	AlPO <sub>4</sub> (PT) <sup>b</sup> > glass (G) > β-Na <sub>6</sub> Al <sub>3</sub> (P <sub>2</sub> O <sub>7</sub> ) <sub>3</sub> (NAP)
	1-2Ce	Ce <sup>3+</sup>	AlPO <sub>4</sub> (PT) > glass (G)
	1-3La/Ce	La <sup>3+</sup> , Ce <sup>3+</sup>	AlPO <sub>4</sub> (PT) > (La,Ce)PO <sub>4</sub> ≈ glass (G)
	1-4Ce	Ce <sup>4+</sup>	AlPO <sub>4</sub> (PT) > CePO <sub>4</sub> ≈ glass (G)
	1-5Eu	Eu <sup>3+</sup>	AlPO <sub>4</sub> (PT) > glass (G)
	1-6Eu	Eu <sup>2+</sup>	AlPO <sub>4</sub> (PT) ≈ glass (G)
	1-7Gd	Gd <sup>3+</sup>	AlPO <sub>4</sub> (PT) ≈ glass (G)
SAIP	2-1	–	Amorphous (glass)
	2-2Ce	Ce <sup>3+</sup>	Glass ≫ Na <sub>3</sub> (Fe,Al) <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub>
	2-3La/Ce	La <sup>3+</sup> , Ce <sup>3+</sup>	Na <sub>3</sub> (Fe,Al) <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub> ≥ glass
	2-4Ce	Ce <sup>4+</sup>	Na <sub>3</sub> (Fe,Al) <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub> ≥ glass
	2-5Eu	Eu <sup>3+</sup>	Glass ≫ Na <sub>3</sub> (Fe,Al) <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub> (trace)
	2-6Eu	Eu <sup>2+</sup>	Amorphous (glass)
	2-7Gd	Gd <sup>3+</sup>	Amorphous (glass)
2-S (second phase)	–	Na <sub>3</sub> (Fe,Al) <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub>	

<sup>a</sup> Suggested charges of ions incorporated in glasses.

<sup>b</sup> PT - phosphotridymite.



**Fig. 1.** XRD patterns of the annealed samples.

x - Phosphotridymite, o - β-Na<sub>6</sub>Al<sub>3</sub>(P<sub>2</sub>O<sub>7</sub>)<sub>3</sub>, + - monazite, # - Na<sub>3</sub>(Al,Fe)<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>.

network itself but are able to be embedded in it under some conditions. At high concentrations these Ln oxides form crystalline phases. Ln<sup>4+</sup> ions, mainly Ce<sup>4+</sup>, have low solubility and produce crystalline phases [6–8].

In the present work we conducted a first systematic study of Ln-bearing SAIP compositions and behavior of some Lns in SAP and SAIP glasses with two formulations positioned on a ternary diagram between the ortho- and pyrophosphate lines and actually or potentially suitable for vitrification of some types of HLW. Chemical composition of the SAP glass is an approximate baseline composition of the glass produced at vitrification of high-Na and high-Na/Al HLW at the EP-500 Joule-heated ceramic melter operated at PA Mayak, Chelyabinsk reg., Russia [7]. In the composition of the SAIP glass 50 wt% Fe<sub>2</sub>O<sub>3</sub> was substituted for Al<sub>2</sub>O<sub>3</sub> and this glass was proposed as a baseline composition to vitrify high-Al/Fe legacy HLW [18].

## 2. Experimental

Glasses with compositions (mol%) 40 Na<sub>2</sub>O, 20 Al<sub>2</sub>O<sub>3</sub>, 40 P<sub>2</sub>O<sub>5</sub> (SAP) and 40 Na<sub>2</sub>O, 10 Al<sub>2</sub>O<sub>3</sub>, 10 Fe<sub>2</sub>O<sub>3</sub>, 40 P<sub>2</sub>O<sub>5</sub> (SAIP) have been previously selected as the most chemically durable and resistant to devitrification [18,19]. Ln oxides were added in amount of 1 to 5 wt% (over 100%). Target compositions of glasses are given in Table 1. Glasses were synthesized from reagent-grade chemicals using a procedure typical of phosphate glasses [7]. Mixtures of reagent-grade sodium metaphosphate (NaPO<sub>3</sub>), aluminum (Al<sub>2</sub>O<sub>3</sub>) or/and iron (Fe<sub>2</sub>O<sub>3</sub>), lanthanum (Ln<sub>2</sub>O<sub>3</sub>), cerium (Ce<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>), europium (EuO, Eu<sub>2</sub>O<sub>3</sub>), gadolinium (Gd<sub>2</sub>O<sub>3</sub>) oxides were fed in fused quartz crucibles, heated in a resistive furnace for 4–6 h to a melting temperature of either 1000 °C (SAP) or 1200 °C (SAIP) and kept at these temperatures for 1 h. Portion of each melt was poured onto a stainless steel plate (quenching), the remainder was slowly-cooled (annealed) in furnace by a regime corresponding to the Canister Centerline Cooling in the center of 200 L canister with vitrified HLW at PA Mayak (Russia) [19].

The samples obtained were examined with X-ray fluorescent (XRF) spectroscopy using a PW-2400 spectrometer (Philips Analytical B.V., The Netherlands) with a Philips Super Quantitative & IQ Software 2001, X-ray diffraction using an EMPYREAN diffractometer (CuK<sub>α</sub> radiation with Ni filter), Fourier-Transform infrared (FTIR) spectroscopy using a Shimadzu IR Prestige 21 spectrophotometer (compaction of glass powders in pellets with KBr). Microstructure and composition of co-existing phases were determined using a JSM-5610LV scanning electron microscope equipped with a JED-2300 energy dispersive X-ray spectrometer (SEM/EDX).

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