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The effect of electron irradiation on the structure and iron speciation in sodium aluminum (iron) phosphate glasses

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ABSTRACT

The effect of 8 MeV electron irradiation on the structure of glasses in the series 40 Na_2O, (20-x) Al_2O_3, x Fe_2O_3, 40 P_2O_5 (mol.%) and on the iron speciation in these samples was studied by FTIR and Mössbauer spectroscopic techniques. Irradiation up to a dose of 1.0 MGy has no appreciable effects on the character of the bonds within anionic motif of the glass network. Electron irradiation increases the fraction of aluminum in octahedral coordination. Iron in both unirradiated and irradiated glasses is present mainly as Fe(III) (60–75% of the total amount) in the glasses and partly as Fe(II) and the ratio of two forms remains constant up to a dose of 1.0 MGy.

1. Introduction

Sodium aluminum phosphate (SAP) and sodium aluminum iron-phosphate (SAIP) glasses are considered as promising nuclear waste forms [1–8]. Study of their structure is also of interest due to the simultaneous occurrence of aluminum and iron in various coordination positions and presence of iron in two valence states, Fe(II) and Fe(III). Along with that, both aluminum and iron ions can be network-formers and network-modifiers. Complex crystal chemical behavior of Al and Fe determines wide variety of glass properties including chemical durability in aqueous conditions that is one of the key characteristic of nuclear waste forms.

Formation of glass and its structure in ternary systems Na_2O-Al_2O_3-P_2O_5 and Na_2O-Fe_2O_3-P_2O_5 were well-studied (see, for example, [6–31]), but these were limited-studied in a number of works, including our previous papers, on the structure and properties of the glasses in four-component Na_2O-Al_2O_3-Fe_2O_3-P_2O_5 (actually five-component Na_2O-Al_2O_3-FeO-Fe_2O_3-P_2O_5) system [1–7,25,26].

Aluminum and iron coordination, as well as and iron oxidation state in the glass depend on glass composition and conditions of the synthesis (redox conditions, heating and cooling rates, melting temperatures). In glasses with composition positioned between ortho- and pyrophosphate lines synthesized at temperatures up to 1300 °C, iron mainly exists as Fe(III) in a distorted octahedral environment and a minor part of iron is present as Fe(II) primarily in the octahedral environment of coordinated oxygen atoms [8,25,32–34]. In the SAP [14,16,18,20,22] and SAIP glasses, Al(III) is located in both octahedral and tetrahedral oxygen environment, and the latter is predominant [32–34].

The SAP and SAIP glasses have high chemical durability in aqueous conditions [1,6,7,32,34] similarly to that of borosilicate glasses with high Fe and Al contents [35,36]. Radiation stability is another important suitability criterion of the matrices for immobilization of the high level wastes (HLW). The nature of radiation defects in glass, particularly under exposure to radiation with various linear energy transfer (γ-rays, accelerated electrons, α-particles, α-recoil, accelerated ions, fission fragments, etc.), mechanisms and kinetics of their formation and recombination are of a specific interest as well. There is a number of studies concerning the effect of γ-irradiation and accelerated electrons on the structure and properties of sodium-bearing and other aluminophosphate glasses [8,24,37–43]. Gamma and electron irradiation up to a dose of ~10^8 Gy produces electron, hole paramagnetic and other color centers that are not connected to cracks in the glass network. Higher doses of electron and ion-irradiation in these types of glass [44–48] lead to charge accumulation [36,39] and formation of gas bubbles [43–46], similarly to the processes in

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silicate and borosilicate glasses [47], and nano-sized crystals [44,48]. Oxygen gas bubbles are probably produced through the stage of O_2^- и O_3^- ion-radicals formation [46]. Conditions of irradiation have significant influence on chemical durability of the glass. Under oxidizing conditions an increase of absorption dose of γ-irradiation resulted in an increase of the depth of destruction of the surface layer of the glass submerged in water and an increase of Na leaching rate while such effects were not observed under in-vacuum irradiation. No changes in density and microhardness of the SAP glass samples were found at β-γ-irradiation doses up to 10^8 Gy and α-doses up to ~10^{24} m^{-3} [8].

In the present paper the effect of electron irradiation on the structure of anionic motif of the SAP and SAIP glasses was studied using Fourier transform infrared spectroscopy (FTIR) and the change of iron oxidation state and coordination environment in the structure of the SAIP glasses after irradiation was analyzed by Mössbauer spectroscopy.

2. Experimental

Glasses in the series (mol.%) 40 Na_2O, (20-x) Al_2O_3, x Fe_2O_3, 40 P_2O_5 were synthesized as described in Ref. [34]. Melts were poured onto a metal plate. Actual chemical composition of the obtained samples was determined by X-ray fluorescent spectroscopy using Philips PW-2400 spectrometer.

The milled samples (particle size of ~200 ± 50 μm) were irradiated with 8 MeV electrons using a UELV-10-10-C70 linear accelerator up to doses of 0.1, 0.5, and 1.0 MGy (pulse duration – 6 μs, pulse repeating frequency – 300 Hz, beam current – 200–800 μA, vertical scan beam frequency – 1 Hz, scan width – 245 mm). The range of 8 MeV electrons in the glass samples was calculated to be ~17 mm [49].

Amorphous state of both unirradiated and irradiated samples was checked by X-ray diffraction (XRD) using an EMPYREAN diffractometer (Cu K_α radiation, Ni filter). FTIR spectra were recorded using Shimadzu IR Prestige 21 spectrophotometer (pellets compacted with KBr powder). FTIR spectra were deconvoluted using the Origin 9.1 software package with a method based on the procedure described in Ref. [50].

The ^{57}Fe Mössbauer spectra for Fe-bearing glass samples were recorded with a MS-1104Em constant acceleration spectrometer. The spectrometer was calibrated at 300 K against a standard α-Fe absorber using a ^{57}Co(Rh) source. The spectra were processed by model fitting and simulation of partial spectra hyperfine parameter distribution using a SpectrRelax software [51]. The ^{57}Fe chemical shifts in the spectra of the samples are referenced to α-Fe at room temperature.

3. Results

Chemical compositions of the obtained glass samples were close to the target ones. Concentration of SiO_2 did not exceed 0.5 wt%. All pristine and irradiated samples were found to be X-ray amorphous.

3.1. FTIR spectra

FTIR spectra of pristine (unirradiated) glass samples were described in details in Refs. [33,34]. The distinct bands can be observed within the ranges of 400–700 cm^{-1}, 700–800 cm^{-1}, 800–1400 cm^{-1}, 1600–1700 cm^{-1}, and 3600–4000 cm^{-1} (Fig. 1). The bands lower than 700 cm^{-1} are attributed to bending modes in phosphorus-aluminum-(iron)-oxygen network and stretching modes of Al-O and Fe-O bonds in AlO_n and FeO_n polyhedra. The bands of 700–800 cm^{-1} and 850–950 cm^{-1} are related to symmetric (ν_s) and asymmetric (ν_{as}) stretching modes of P–O–P and P–O–Al bridging bonds. The bands within the range of 950–1250 cm^{-1} are due to superposition of the bands due to O–P–O stretching modes in PO_4 tetrahedra and PO_3 end-units [52,53]. This multicomponent band may be interpreted as a superposition of the bands due to three-fold degenerated ν_{as} (F_2) stretching modes of P–O bonds in PO_4 units with T_d symmetry and ν_{as} (E) modes of P–O bonds in PO_3 units with C_{3v} symmetry. Lowering the symmetry of PO_4 units to C_{3v} or C_{2v} increases the number of bands within this range to 6 or 9, respectively. Positions of maxima in the aforementioned bands at 740–760, 870–895, 915–930, 985–1000, 1030–1050, 1100–1120, and 1170–1175 cm^{-1} (Fig. 2 and Table 1) obtained by deconvolution correspond to vibrations ν_s P–O–P, ν_s P–O–Al, ν_{as} P–O–P, ν_s P–O in PO_4 and PO_3 units, ν_{as} P–O in PO_4 units, ν_{as} P–O–Al + ν'_s P–O in PO_3, and ν_{as} + ν'_{as} P–O in PO_3 units, respectively [53]. Deconvolution of the broad band within the range of 800–1400 cm^{-1} do not exhibit occurrence of clear additional bands due to de-degeneration of stretching modes in PO_4 units (Fig. 1) so it may be concluded that PO_4 units experience only minor degree of distortion.

Deconvolution of the bands located below 700 cm^{-1} is more difficult and the results are ambiguous because of superposition of a large bands number due to bonds vibrations in various phosphorus-oxygen (mainly bending modes), aluminum-, and iron-oxygen (stretching modes) fragments of the glass network.

Thus, the structural network is built of ortho- and pyrophosphate units, AlO_n and FeO_n polyhedra linked by P–O–Al(Fe) bonds. Vibrations due to of P–O–Fe bridging bonds are overlapped with those due to vibrations in PO_4 and PO_3 units and cannot be resolved correctly. Weak band at 1300–1400 cm^{-1} is attributed to the vibration of P=O bond (see also [53]). The bands at 1600–1700 cm^{-1} and 3400–3700 cm^{-1} are referred to bending and stretching modes in structurally-bonded and absorbed water molecules. On the whole, Fe_2O_3 substitution for Al_2O_3 in glass samples of the series (mol.%) 40 Na_2O, (20-x) Al_2O_3, x Fe_2O_3, 40 P_2O_5 did not result in significant changes in the structure of anionic motif of the glass network [33,34].

Comparison of FTIR spectra of pristine and irradiated glasses (Figs. 1 and 2) demonstrates changes in position and intensity of absorption bands mainly within the ranges of 3200–4000 cm^{-1}, 1600–1700 cm^{-1}, and below 700 cm^{-1}. Within the first range an increase of the irradiation dose leads to enhancing intensity and splitting of the bands into three bands: broad one with the maximum at 3440 cm^{-1} and two narrower at 3700–3750 cm^{-1} and 3800–3900 cm^{-1}, which can be attributed to vibrations in hydroxyl-containing species. Similar changes are observed within the second range referred to bending modes in hydroxyl-containing species (Fig. 1).

As can be seen from Fig. 1 and results of the spectra deconvolution (Fig. 2), stronger absorption intensity below 700 cm^{-1} is observable for glasses with low iron content (x = 0 and x = 5). At x = 10 absorption intensity slightly grows at a dose of 0.1 MGy and remains the same at a dose of 0.5 MGy. After irradiation to a dose of 1 MGy absorption intensity has returned to an initial level. There are no changes observable in FTIR spectra of glasses with x = 15 and x = 20 (Figs. 1 and 2) after increasing the dose of irradiation. Thus, this effect is caused by changes in Al rather than Fe environment in the glass structure. Absence of changes in the structure of glasses with high iron content points to their high radiation stability.

Fitting the bands in the range below 700 cm^{-1} is complicated due to the high level of noise that is growing with the increase of irradiation dose. However, some general features can be tracked. Position of a maximum within the ~400–600 cm^{-1} FTIR spectrum in the glasses is nearly independent from irradiation dose (Fig. 2). In the spectra of Fe-free (x = 0) and low-Fe (x = 5) glasses after irradiation to a dose of 0.1 MGy, clear band with maximum at