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Iron oxidation state and coordination, and hydrolytic durability of sodium-aluminum iron phosphate glasses

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ABSTRACT

The structure of anionic motif, oxidation state and coordination of iron in the series of glasses (mol.%): 40 Na_2O, (20-x) Al_2O_3, x Fe_2O_3, 40 P_2O_5 considered as matrices for immobilization of high Fe/Al legacy high level waste were determined by FTIR, Raman and Mössbauer study. The glass network is built from ortho- and pyrophosphate units linked by aluminum-oxygen and iron-oxygen polyhedra. Iron in all the glasses was present as primarily octahedrally coordinated Fe(III) and Fe(II). Fe(III) content in the glasses increased with the increase of the x value and reached ~74% of total Fe in the glass with $x = 15$ while reduced to ~67% of total Fe at $x = 20$. At the same time the lowest values of cumulative release from glasses into a deionized water for all the elements were found at $x = 5$. Thus no correlation between the Fe(III)/Fe(II) ratio and cumulative elemental release values was found and iron speciation seems to be not a key factor determining their chemical durability.

1. Introduction

The structure of double phosphate including sodium phosphate glasses is studied in details. With the increase of Na_2O to P_2O_5 ratio the units with three (Q^3), two (Q^2), and one (Q^1) bridging oxygens are predominant. Such glasses are soluble in water but their hydrolytic and acidic durability may be significantly improved by addition of oxides of multivalent elements capable to form MeO_4 and MeO_6 polyhedra embedded in the chains of PO_4 tetrahedra thus increasing total glass network connectedness (Van Wazer, 1958; Brow, 2000).

The effect of improvement of chemical durability at incorporation of Al_2O_3 in sodium phosphate glasses was discovered in 1940s (Van Wazer, 1958) and is of very practical importance, in particular, in nuclear waste management (Brezhneva et al., 1979). Sodium aluminophosphate based glass was developed for immobilization of high level waste (HLW) from reprocessing of spent nuclear fuel (SNF) with Al cladding from transport nuclear reactors and successful application of this glass allowed to use it for HLW from different types of SNF for more than 20 yrs (Remizov et al., 2014).

Iron in a trivalent state exhibits behavior similar to that of trivalent aluminum forming $Fe^{3+}O_4$ tetrahedra capable to be embedded in the phosphorus-oxygen chains similarly to AlO_4 tetrahedra. However, crystal chemical of iron is markedly influenced by its valence state and coordination because iron in glasses may be present as Fe(III) and Fe(II) in both tetrahedral and octahedral oxygen environments. Moreover, these ions exhibit a tendency to form crystalline phases (hematite, magnetite-type spinel, Fe and mixed Fe phosphates) resulting in partial or full devitrification (Russo et al., 2008; Gonzales Oliver et al., 2010; Stefanovsky et al., 2014).

The glasses on aluminophosphate and iron-phosphate basis are considered as promising nuclear waste forms especially for high/Al-Fe wastes (Brezhneva et al., 1979; Russo et al., 2008; Gonzales Oliver et al., 2010; Stefanovsky et al., 2014). While iron-phosphate glasses are under study now and not implemented yet elsewhere, sodium aluminophosphate glass is used for EP-500 J-heated ceramic melter at Production Association “Mayak” to incorporate HLW generated at SNF reprocessing (Remizov et al., 2014). In the new melter (planned to be put in operation in 2017) HLW from both SNF of commercial reactors and former defense programs will be vitrified (Remizov et al., 2014). The latter contains iron as well as

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other transition metals (Cr, Mn, Co, Ni). So, the main goal of this work is to estimate Fe speciation and its effect on the structure and hydrolytic durability of glasses at equimolar Al_2O_3 substitution for Fe_2O_3 in the series 40 Na_2O, (20-x) Al_2O_3, x Fe_2O_3, 40 P_2O_5.

2. Experimental

Formulation of the baseline glass (mol.%) 40 Na_2O, 20 Al_2O_3, 40 P_2O_5 or (wt.%) 24,3 Na_2O, 20,0 Al_2O_3, 55,7 P_2O_5 corresponds to composition within the glass forming region in the Na_2O–Al_2O_3–P_2O_5 system determined by Brezhneva et al. (1979). Fe_2O_3 substitution for Al_2O_3 simulates increasing of Fe_2O_3 content in final glass waste form.

Glasses were prepared from reagent-grade chemicals $NaPO_3$, Al_2O_3 and Fe_2O_3 in 20 cm^3 fused silica crucibles. Mixtures were heated to temperatures from 1100 to 1300 °C (depending on Fe_2O_3/Al_2O_3 ratio), melts were kept at the final temperature for 30 min and poured onto a metal plate.

The actual chemical composition of the products was determined by X-ray fluorescent spectroscopy using a Philips PW-2400 spectrometer. The products were characterized by X-ray diffraction using an EMPYREAN diffractometer (CuK_α radiation, Ni-filter), Fourier Transform Infrared (FTIR) spectroscopy using a Shimadzu IR Prestige 21 spectrophotometer (compaction of powdered samples in pellets with KBr), and Raman spectroscopy using a Jobin Yvon U1000 spectrophotometer operated at an excitation wavelength of 532 nm.

Fe speciation was determined by ^{57}Fe Mössbauer spectroscopy using 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 ^{57}Fe chemical shifts in the spectra of the samples are referenced to α-Fe at room temperature. The spectra were processed by model fitting and simulation of partial spectra hyperfine parameter distribution using a SpectrRelax software (Matsnev and Rusakov, 2012).

Hydrolytic durability was determined using a PCT-A procedure (Standard Test Methods…, 1994). 100–200 mesh powdered sample were leached in 100 ml distilled water in a sealed Teflon container at 90 °C for 7 days.

3. Results and discussion

Comparison of target and analyzed chemical compositions of the samples produced demonstrates their good agreement. Trace of SiO_2 (≤1.5 wt%), MgO (≤0.1 wt%) and CaO (≤0.1 wt%) in the samples is due to impurities in crucible materials and chemicals.

As follows from XRD data all the samples in the series were fully amorphous and homogeneous. FTIR spectra within the range of 4000–400 cm^{-1} (Fig. 1a) demonstrate the bands at 3800-3200 cm^{-1} and 1700-1400 cm^{-1} due to stretching and bending modes in molecules of water (Nakamoto, 2009) both structurally-bound and absorbed on the surface of glass powders. Position and intensity of these bands remain approximately the same in the

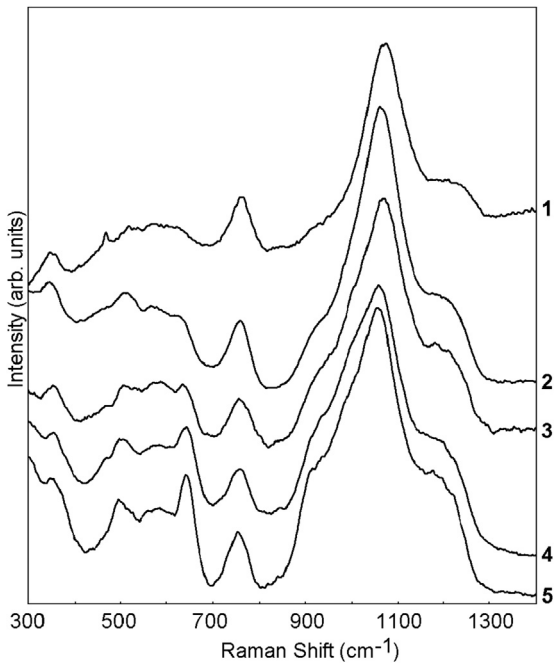

Fig. 2. Raman spectra of glasses in the series, mol.%, 40 Na_2O, (20-x) Al_2O_3, x Fe_2O_3, 40 P_2O_5 at x = 0 (1), 5 (2), 10 (3), 15 (4), and 20 (5).

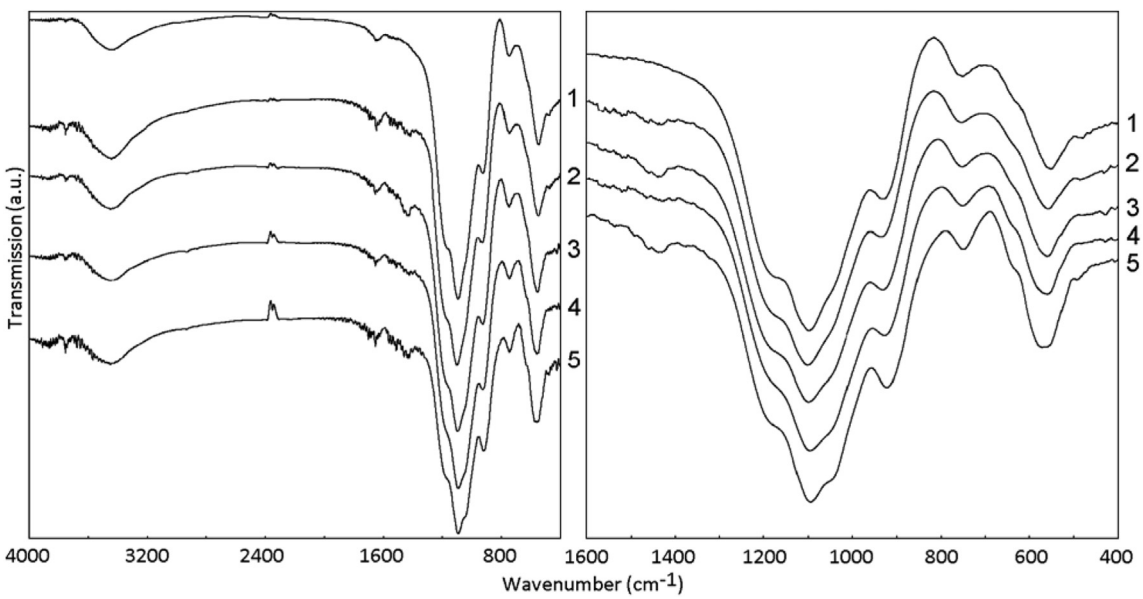

Fig. 1. FTIR spectra of glasses in the series, mol.%, 40 Na_2O, (20-x) Al_2O_3, x Fe_2O_3, 40 P_2O_5 at x = 0 (1), 5 (2), 10 (3), 15 (4), and 20 (5). Right spectrum is a fragment of the left one.

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