Oxidation State and Coordination Surrounding of Iron and Uranium in Sodium Aluminum Iron Phosphate Glasses

S. V. Stefanovsky^{*a}, A. A. Shiryaev^{a,b}, Yu. A. Teterin^{b,c}, S. N. Kalmykov^{a,b}, and Ya. S. Glazkova^b

^a Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Leninskii pr. 31, korp. 4, Moscow, 119071 Russia

^b Radiochemistry Chair, Moscow State University, Moscow, Russia

^c National Research Centre Kurchatov Institute, pl. Akad. Kurchatova 1, Moscow, 123182 Russia

*e-mail: serge.stefanovsky@yandex.ru

Received February 15, 2017

Abstract—The oxidation state of Fe and U and the coordination surrounding of Fe in uranium-containing sodium aluminum iron phosphate glasses were determined by analysis of the FeK and UL₃ X-ray absorption nearedge structure (XANES), X-ray photoelectron spectroscopy (XPS), and Mössbauer spectroscopy on ⁵⁷Fe nuclei. Uranium is present in the glasses in the form of U(V) and U(VI), and iron, in the form of Fe(III) and Fe(II), mainly in the distorted octahedral surrounding. The fraction of U in various oxidation states depends on the form of untroducing uranium (UO₂ or UO₃) and on the oxide concentration. With an increase in the UO₃ concentration in glasses, the fraction of U(VI) increases and the fraction Fe(III) relative to Fe(II) decreases.

Keywords: iron, uranium, sodium aluminum iron phosphate glasses, XANES method, X-ray photoelectron spectroscopy, Mössbauer spectroscopy

DOI: 10.1134/S1066362217060030

The oxidation state and structural position of U in glasses depend on the temperature and redox conditions of glass melting, in particular, on the presence of other polyvalent elements, e.g., Fe [1–7]. In glasses on both silicate and phosphate base, prepared under oxidizing conditions (in air), the prevalent uranium species is U(VI) in the form of uranyl ions, UO_2^{2+} , but in the presence of iron ions the fraction of uranium in lower oxidation states, U(V) and U(IV), increases [4–7]. We assumed previously [7] that, in sodium aluminum iron phosphate glasses, like in borosilicate glasses [5, 6], an increase in the fraction of U in oxidation states lower than U(VI) is due to the reduction of U(VI) with Fe(II) ions. This study was aimed at checking this assumption.

EXPERIMENTAL

The glass samples (Table 1) were synthesized as described in [7]. Into the base glass formulation (mol %: 40 Na₂O, 10 Al₂O₃, 10 Fe₂O₃, 40 P₂O₅), we introduced UO₂ or UO₃ (using uranyl nitrate as the initial form).

X-ray absorption spectra of the glasses were measured on the Structural Materials Science Station of the Kurchatov synchrotron radiation source (National Research Center Kurchatov Institute, Moscow) [8] in the near-threshold (XANES) range at FeK and UL_3 absorption edges in the transmission and fluorescence geometries simultaneously using two ionization chambers filled with air-argon mixtures to reach the optimum absorption in the chambers arranged before and after the sample. An avalanche photodiode (FMB Oxford) was used. The incident radiation was monochromated using a "butterfly" crystal with Si(220) cut. As Fe references we used Fe metal, wüstite $Fe_{0.95}O$, α -Fe₂O₃, γ -Fe₂O₃, magnetite Fe₃O₄, enstatite ^{VI}(Mg,Fe)₂Si₂O₆, and staurolite ^{IV}Fe²⁺Al₄[SiO₄]₂O₂(OH)₂, and as U references, UO₂ and UO₃. The references were measured under identical conditions.

The X-ray photoelectron spectra of uranium-free and uranium-containing glasses were taken with a Kratos Axis Ultra DLD spectrometer using monochromated Al K_{α} radiation (E = 1486.6 eV) under the following conditions: X-ray tube power 150 W, pressure 1.3×10^{-7} Pa, room temperature. The binding energies

	-		-	-					
Sample	U oxide	Na ₂ O	Al_2O_3	Fe ₂ O ₃	P_2O_5	UO ₂	UO_3	SiO ₂	Total
2-1	-	23.0/23.3	9.5/8.9	14.8/14.8	52.7/50.8	_	—	-/2.0	100.0/99.8
2-2	UO ₂	22.7/20.9	9.4/9.0	14.7/15.1	52.2/52.1	1.0/1.1	_	-/2.1	100.0/100.3
2-3		21.9/19.6	9.0/8.4	14.1/14.5	50.2/50.3	4.8/5.0	-	-/2.3	100.0/100.1
2-4	UO ₃	21.9/20.8	9.0/8.5	14.1/14.2	50.2/49.2	-	4.8/5.2	-/2.1	100.0/100.0
2-5		20.9/19.5	8.6/7.8	13.5/13.6	47.9/47.6	_	9.1/9.9	-/1.7	100.0/100.1
2-6		15.3/14.2	6.3/5.4	9.9/10.2	35.1/33.7	_	33.4/34.2	-/2.6	100.0/100.3
2-7		13.1/13.0	5.4/5.6	8.5/8.6	30.1/30.3	_	42.9/41.7	-/0.9	100.0/100.1
2-8		11.4/11.1	4.8/5.1	7.4/7.6	26.4/26.0	—	50.0/49.2	-/0.9	100.0/99.9

Table 1. Content of components (wt %) in the glass samples studied (calculated/found)

 $(E_{\rm b})$ were measured relative to $E_{\rm b}$ of C1s electrons of hydrocarbons adsorbed on the sample surface (assumed equal to 285.0 eV). The line full widths at half-maximum (ΔE , eV) are given relative to that of the C1s electron line of hydrocarbons on the sample surface (assumed equal to 1.3 eV). The error in determination of the binding energy and line width did not exceed ± 0.05 eV, and the uncertainties in the determination of the relative peak intensity did not exceed $\pm 5\%$. Quantitative elemental analysis of sample layers (depth of several nanometers) was based on the fact that the spectral intensity is proportional to the amount of the corresponding atoms in the sample. We used the following relationship: $n_i/n_i = (S_i/S_i)(k_i/k_i)$, where n_i/n_i is the relative concentration of the atoms studied, S_i/S_i is the relative intensity of the spectrum, and k_i/k_i is the relative experimental sensitivity coefficient. The following coefficients relative to C1s were used: 1.00 (C1s), 2.81 (O1s), 0.69 (Al2p), 1.75 (P2p), 6.06 (Na1s), 7.09 (Fe2 $p_{3/2}$), 36.0 (U4 $f_{7/2}$) [9].

The ⁵⁷Fe Mössbauer spectra were measured with an MS-1104Em spectrometer operating in the constant

acceleration mode. The spectrometer was calibrated at 300 K using standard α -Fe absorber and a 57 Co(Rh) source. Samples were prepared in the form of chips of glass pieces and were placed on an adhesive tape. Chipping was performed in air immediately before introducing the sample into the spectrometer. The spectra were processed using methods of simulation and restoration of the distributions of hyperfine parameters of the partial spectra, implemented in the SpectrRelax program [10]. The chemical shifts in the Mössbauer spectra of the 57 Fe nuclei in the samples are given relative to α -Fe at room temperature.

The results obtained were compared to the published data [4, 11-14] and to the data that we obtained previously [15-17].

RESULTS

XANES

The XANES spectra of the FeK absorption edge and their first derivatives with respect to energy (Fig. 1) show that iron is present in the form of Fe(III)



Fig. 1. (a) FeK XANES spectra of the glasses studied and (b) their first derivatives.

Sample	XANES				Mössbauer		XPS			
	Fe(III)	Fe(II)	U(VI)	U(V) + U(IV)	Fe(III)	Fe(II)	Fe(III)	Fe(II)	U(VI)	U(V)
2-1	70(1)	30(1)	-	—	66(1)	34(1)	87(2)	13(2)	_	-
2-2	80(2)	20(1)	25(2)	75(3)	76(1)	24(1)	81(2)	19(2)	27(1)	73(2)
2-3	75(1)	25(1)	50(2)	50(2)	83(1)	17(1)	91(2)	9(1)	60(2)	40(2)
2-4	90(2)	10(1)	55(2)	45(2)	85(1)	15(1)	89(1)	11(1)	53(2)	47(2)
2-5	85(2)	15(1)	60(2)	40(2)	88(1)	12(1)	89(1)	11(1)	58(2)	42(2)
2-6	90(2)	10(1)	80(2)	20(2)	83(1)	17(1)	82(1)	18(1)	64(2)	16(1)
2-7	85(2)	15(1)	90(2)	10(1)	80(1)	20(1)				
2-8	80(2)	20(1)	95(2)	5(1)	70(1)	30(1)				

Table 2. Relative content of Fe and U in different oxidation states, according to data of different spectroscopic methods

and Fe(II), but the prevalent iron state in all the glasses is Fe(III) in the octahedral oxygen surrounding, in agreement with the XPS and Mössbauer data that we obtained previously [15, 16].

The Fe(III) to Fe(II) ratio can be estimated by analysis of the near-edge peak caused by the $1s \rightarrow 3d$ transition [11–14]. As seen from Fig. 2, the peak is asymmetrical because of the overlap of several peaks corresponding to different oxidation states and different coordination surroundings of iron ions in the glasses. According to [11, 14], the difference in the position of the maximum of this peak for Fe(II) and Fe(III) is ~2 eV, and its intensity increases in going from regular octahedral to distorted octahedral and then to tetrahedral oxygen coordination of iron.

In the FeK XANES spectra of all the synthesized glasses, the intensity of the near-edge peak is virtually equal (Figs. 1 and 2), and the spectrum shape and the position of the maximum, 7113.9 ± 0.5 eV, are typical of Fe(III) in the distorted octahedral surrounding, although the presence of slight energy variations sug-



Fig. 2. Fragments of the FeK XANES spectra of the glasses studied in the region of the near-edge peak.

gests certain contribution of Fe(II) and possible variability of the Fe coordination surrounding. At the UO₃ concentration in the glass of \sim 33–34 wt % and higher, when it significantly exceeds the concentration of iron oxides (samples 2-5, 2-6, 2-7, and 2-8), the prevalent iron form is Fe(III).

The uranium L_3 XANES spectra were presented and discussed in our previous paper [16]. It is difficult to determine the contribution of each of the three uranium oxidation states from the XANES spectra. Only the U(VI) fraction (approximately 25%) can be determined sufficiently reliably (Table 2). The remainder corresponds to U(V) and U(IV). As judged from the line shape, the relative content of U(V) exceeds that of U(IV). As the concentration of uranium introduced both as UO₂ and as uranyl nitrate is increased, the fraction of U(VI) increases, and that of lower valence states decreases (Table 2).

Mössbauer Effect

The Mössbauer spectra can be presented as superposition of two line systems (distributions) corresponding to iron cations of different charges. Restoration of the distributions $p(\delta)$ and $p(\Delta)$ (Fig. 3) allowed us to determine the mean values of the corresponding hyperfine parameters ($\langle \delta_i \rangle$ and $\langle \Delta_i \rangle$) for the Fe(1) and Fe(2) quadrupole doublets and the partial contributions (I_i) of each of them to the total experimental spectrum (Table 2). The mean values of the first partial spectrum (1), $\langle \delta_1 \rangle \approx 0.42$ mm s⁻¹ and $\langle \Delta_1 \rangle \approx$ 0.71 mm s⁻¹ (Table 2), correspond to high-spin cations of iron with the formal oxidation state Fe(III) in a distorted octahedral oxygen surrounding. The second doublet (2) with the higher shift, $\langle \delta_2 \rangle \approx 1.15 \text{ mm s}^{-1}$, corresponds to high-spin Fe²⁺ cations. Analysis of the dependences of $\langle \delta_i \rangle$ and $\langle \varepsilon_i \rangle$ for each partial spectrum, of the relative contributions (I_1/I_2) of differently



Fig. 3. ⁵⁷Fe Mössbauer spectra of glasses and distribution functions of hyperfine parameters, chemical shift (δ) and quadrupole splitting (Δ), for Fe(III) and Fe(II).

RADIOCHEMISTRY Vol. 59 No. 6 2017

Sample	Partial spectrum	$\langle \delta \rangle$, mm s ⁻¹	$\langle \Delta \rangle$, mm s ⁻¹	$D_{\delta}, ({ m mm \ s}^{-1})^2$	$D_{\Delta}, ({ m mm \ s}^{-1})^2$	<i>I</i> , %	$d\delta/d\Delta$
2-1	Fe ³⁺	0.42(1)	0.70(2)	~0	0.040(2)	66(1)	
	Fe ²⁺	1.18(2)	2.16(4)	~0	0.06(1)	34(1)	
2-2	Fe ³⁺	0.42(1)	0.71(2)	$3(2) \times 10^{-4}$	0.044(2)	76(1)	-0.055(17)
	Fe^{2+}	1.16(3)	2.19(5)	$1(5) \times 10^{-4}$	0.074(14)	24(1)	0.030(50)
2-3	Fe ³⁺	0.43(1)	0.70(2)	$1(1) \times 10^{-4}$	0.044(2)	83(1)	-0.036(13)
	Fe^{2+}	1.10(5)	2.25(10)	3(9)×10 ⁻⁴	0.064(22)	17(1)	0.046(80)
2-4	Fe ³⁺	0.42(1)	0.70(2)	$4(5) \times 10^{-5}$	0.043(3)	85(1)	-0.022(13)
	Fe ²⁺	1.11(4)	2.30(10)	$1(6) \times 10^{-4}$	0.064(28)	15(1)	0.024(110)
2-5	Fe ³⁺	0.43(3)	0.71(1)	6(4)×10 ⁻⁵	0.042(2)	88(1)	-0.026(8)
	Fe^{2+}	1.05(2)	2.30(5)	26(19)×10 ⁻⁴	0.068(16)	12(1)	0.139(60)
2-6	Fe ³⁺	0.41(1)	0.76(1)	$4(6) \times 10^{-5}$	0.051(2)	83(1)	-0.021(13)
	Fe^{2+}	1.04(2)	2.34(4)	$40(17) \times 10^{-4}$	0.060(12)	17(1)	0.184(40)
2-8	Fe ³⁺	0.40(1)	0.87(1)	$13(7) \times 10^{-5}$	0.063(1)	70(1)	0.032(8)
	Fe ²⁺	0.96(1)	2.23(3)	85(9)×10 ⁻⁵	0.224(10)	30(1)	-0.044(1)

Table 3. Hyperfine parameters of the partial Mössbauer spectra at T = 300 K

566

charged Fe cations, and of the distribution variances $D_i(\delta)$ and $D_i(\Delta)$, performed for different samples of this series, shows that the fraction of Fe(III) relative to Fe(II) increases as the U concentration is increased from 1 to 5 wt % UO_2 (samples 2-2 and 2-3), the relative content of Fe(III) and Fe(II) (83-85 and 15-17%, respectively) in the glasses prepared with addition of equivalent amounts of UO₂ and uranyl nitrate (~5 wt % in terms of U_3O_8) is approximately equal, and the Fe(III) fraction decreases to ~70% as the content of uranium (introduced in the form of uranyl nitrate) is increased to ~50 wt % (Table 3). This fact suggests minor role of redox reactions between uranium and iron oxides, especially when the concentration of uranium oxides exceeds that of iron oxides, compared to the equilibria in the iron-oxygen system, i.e., the major cause of a decrease in the Fe(III) content is its reduction to Fe(II).

XPS

The published binding energies of $Fe2p_{3/2}$ {~712 eV for Fe(II) and ~714 eV for Fe(III) [18]} and U4 $f_{7/2}$ electrons {380.0–380.4 eV for U(IV), 380.8–381.0 eV for U(V), and 381.6–381.9 eV for U(VI) [19–21]} are in good agreement with the values obtained in this study (Figs. 4, 5).

According to the XPS data, addition of 1% UO₂ to glass 2-1 leads to a certain decrease in the Fe(III)/ Fe(II) ratio. As the amount of uranium introduced in the form of UO₂ (samples 2-2 and 2-3) is increased from 1 to \sim 5 wt %, the relative content of Fe(III)

increases from ~81 to ~91% of the total Fe content, although the U(VI) content also increases from 27 to 60% relative to the U(VI) + U(V) sum (Table 2). Comparison of the data for glass samples 2-3 and 2-4 containing 5 wt % UO₂ and UO₃, respectively, shows that the percent ratio of U(V) and U(VI) in them is approximately equal and remains equal at the UO₃ concentration increased to 10 wt % (sample 2-5), whereas the fraction of U(VI) in sample 2-4, into which U was introduced in the form of uranyl nitrate, is somewhat lower than in sample 2-3 (53 and 60% of the total U content, respectively) into which U was introduced in the form of UO₂ (Table 2).

As the concentration of U introduced in the form of uranyl nitrate is increased (Table 1), the fraction of Fe(III) relative to Fe(II) gradually decreases, probably because of reduction of Fe(III) to Fe(II), and the fraction of U(VI) relative to U(V) increases (Table 2; Figs. 4 and 5).

DISCUSSION

Whereas the XANES and Mössbauer data furnish information on the averaged oxidation states and coordination surroundings of elements in the bulk of the samples, the XPS data mainly characterize the surface layer of the samples, contacting with air, and the fraction of higher oxidation states of Fe and U in this layer is higher than in deep layers (Table 2). Nevertheless, the XPS, Mössbauer, and XANES data well agree with each other within the margin of error (Table 2).

Because at low uranium concentrations, even when

 $U4f_{7/2}$

U(V)

 $U4f_{5/2}$





Fig. 4. X-ray photoelectron spectra of uranium in glasses and their computer deconvolution.

it is introduced in the form of UO_2 , a part of uranium is oxidized from U(IV) to higher valence states, irrespective of the presence of iron in the glasses, the decisive role is played by reactions with atmospheric oxygen, whereas the role of redox reactions U(IV) + Fe(III) =U(V) + Fe(II) and U(V) + Fe(III) = U(VI) + Fe(II) is considerably lower.

The results obtained correlate well with the data given in our previous papers [7, 15-17], with the results of studying the mutual effect of iron and uranium ions in borosilicate glasses [5, 6], and with the data of other authors [3, 4, 13, 23]. In ferrophosphate glasses, the addition of UO₂ decreases the fraction of Fe(II) in the total content of iron oxides [4]. When the glasses

RADIOCHEMISTRY Vol. 59 No. 6 2017



Fig. 5. X-ray photoelectron spectra of iron in glasses and their computer deconvolution

contain iron oxides, uranium, usually present in the U(VI) state in the form of uranyl ions UO_2^{2+} , can undergo partial or complete reduction to the less oxidized forms, up to the coexistence of U(IV) and Fe(III), as determined in [4]. In borosilicate glasses, U(IV) can be stable in the presence of Fe(III) [23]. As we found in our previous study [15], at up to ~10 wt % content of

uranium oxides in sodium aluminum iron phosphate glasses, uranium mainly occurs in the form of U(V), presumably owing to the occurrence of the reaction $U^{6+} + Fe^{2+} = U^{5+} + Fe^{3+}$, and only at higher UO₃ concentrations, significantly exceeding the concentration of iron oxides (Table 1), under oxidizing conditions of glass melting, both uranium and iron can remain in Thus, the redox reactions U(IV) + Fe(III) = U(V) + Fe(II) and U(V) + Fe(III) = U(VI) + Fe(II) play a noticeable role at relatively low concentrations of uranium oxides in sodium aluminum iron phosphate glasses (≤ 10 wt %, or 5 mol %). At higher UO₃ concentrations (~30–50 wt %), when the UO₃ concentration considerably exceeds the concentration of iron oxides, the role of these reactions becomes insignificant. At low concentrations of uranium oxides, it is present mainly in the form of U(V), and with increasing UO₃ concentration the fraction of U(VI) increases, and it becomes the prevalent form at the UO₃ content of ~30 wt % and higher. The prevalent form of iron is Fe(III) in a distorted tetrahedral oxygen surrounding.

ACKNOWLEDGMENTS

The study was financially supported by the Russian Science Foundation (project no. 14-13-00615). The authors are grateful to A.L. Trigub (National Research Center Kurchatov Institute) for the assistance in recording XANES spectra.

REFERENCES

- Veal, B.W., Mundy, J.N., and Lam, D.J., in *Handbook* on the Physics and Chemistry of the Actinides, Freeman, A.J. and Lander, G.H., Eds., Elsevier Science, 1987, pp. 271–309.
- Farges, F., Ponader, C.W., Calas, G., and Brown, G.E., Jr., *Geochim. Cosmochim. Acta.*, 1992, vol. 56, pp. 4205–4220.
- Aloy, A.S., Trofimenko, A.V., Iskhakova, O.A., and Jardine, L.J., *Mater. Res. Soc. Symp. Proc.*, 2004, vol. 824, pp. 345–350.
- Karabulut, M., Marasinghe, G.K., Ray, C.S., et al., J. Mater. Res., 2000, vol. 15, no. 9, pp. 1972–1984.
- 5. Stefanovsky, S.V., Marra, J.C., Shiryaev, A.A., and Zubavichus, Y.V., *Glass Technol.: Eur. J. Glass Sci. Technol. A*, 2009, vol. 50, no. 1, pp. 47–52.
- Stefanovsky, S.V., Shiryaev, A.A., Zubavichus, J.V., et al., *Glass Phys. Chem.*, 2009, vol. 35, no. 2, pp. 141– 148.

- Stefanovsky, S.V., Stefanovskaya, O.I., Murzin, V.Yu., et al., *Dokl. Phys. Chem.*, 2016, vol. 468, part 1, pp. 76– 79.
- Chernyshov, A.A., Veligzhanin, A.A., and Zubavichus, Y.V., *Nucl. Instr. Meth. Phys. Res. A*, 2009, vol. 603, pp. 95–98.
- 9. Brow, R.K., Arens, C.M., Yu, X., and Day, D.E., *Phys. Chem. Glasses*, 1994, vol. 35, no. 3, p. 132.
- Matsnev, M.E. and Rusakov, V.S., *AIP Conf. Proc.*, 2012, vol. 1489, pp. 178–185.
- Brown, G.E., Jr., Waychunas, G.A., Ponader, C.W., et al., *J. Phys. Coll.*, 1986, vol. 47, no. C8, pp. C8-661– C8-668.
- Binsted, N., Greaves, G.N., and Henderson, C.M.B., J. Phys. Coll., 1986, vol. 47, no. C8, pp. C8-837– C8-840.
- 13. Karabulut, M., Marasinghe, G.K., Ray, C.S., et al., *J. Non-Cryst. Solids*, 2002, vol. 306, pp. 182–192.
- 14. Berry, A.J., O'Neill, H.St.C., Jayasuriya, K.D., et al., *Am. Miner.*, 2003, vol. 88, pp. 967–977.
- Stefanovsky, S.V., Shiryaev, A.A., Zubavichus, Y.V., et al., *Mater. Res. Soc. Symp. Proc.*, 2013, vol. 1518, pp. 59–64.
- 16. Glazkova, Ya.S., Kalmykov, S.N., Presniakov, I.A., et al., *Dokl. Phys. Chem.*, 2015, vol. 463, part 1, pp. 145–149.
- 17. Stefanovsky, S.V., Stefanovsky, O.I., Kadyko, M.I., et al., *J. Non-Cryst. Solids*, 2015, vol. 425, pp. 138–145.
- Yu, X., Day, D.E., Long, G.R., and Brow, R.K., J. Non-Cryst. Solids, 1977, vol. 215, pp. 21–31.
- 19. Yamashita, T. and Hayes, P., *Appl. Surf. Sci.*, 2008, vol. 254, pp. 2441–2449.
- Teterin, Yu.A., Kulakov, V.M., Baev, A.S., et al., *Phys. Chem. Miner.*, 1981, vol. 7, pp. 151–158.
- Bera, S., Sali, S.K., Sampath, S., et al., J. Nucl. Mater., 1998, vol. 255, pp. 26–33.
- Schindler, M., Hawthorne, F.C., Freund, M.S., and Burns, P.C., *Geochim. Cosmochim. Acta*, 2009, vol. 73, pp. 2471–2487.
- Schreiber, H.D., Minnix, L.M., Carpenter, B.E., and Solberg, T.N., *Phys. Chem. Glasses*, 1983, vol. 24, pp. 155–160.

Translated by G. Sidorenko