

CHARACTERIZATION OF U-CONTAINING BOROSILICATE GLASS GP-91 WITH X-RAY PHOTOELECTRON SPECTROSCOPY

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ABSTRACT

Vitreous materials, such as borosilicate and alumophosphate glasses, are the only type of matrices currently employed for high level waste immobilization. Thus, research of structural and compositional features of the glass-composed radioactive waste forms has a great importance for their properties estimation. Conventional methods of XRD and TEM research are not suitable for the vitreous materials characterization. In the present work we have studied peculiarities of U-bearing borosilicate glass GP-91 using X-ray photoelectron spectroscopy (XPS). The samples were prepared by inductive melting in a cold crucible in air at T 1200°C followed by quick quenching the melt. Fourteen samples containing 0, 15, and 30% uranium dissolved were examined. The results obtained give rise to the conclusions:

- surface of the specimens (up to depth of 500Å) is greatly differed relatively their volume both a composition and structure. This is due to elements redistribution during additional energy accumulation in the course of the samples grinding.
- uranium in the glasses was present as U(IV) and U(VI) oxidation states only; Ratio between their amounts is equal to 4:1 in favour of the tetravalent state.
- increasing uranium content in the glasses results in distinctive changes of their structure; At the uranium content 15 wt% and higher rearrangement of the glass network was observed resulting in formation of U-O domains structure not visible by SEM/EDS; when uranium content reached 30 wt% a grains of uranium dioxide were found with SEM/EDS method pointed to oversaturation of the melt with uranium.

INTRODUCTION

The structural features of matrices for high-level wastes (HLW) determine their durability and, eventually, the safe burial in the Earth's interior. Nowadays, the solidification of liquid HLW at radiochemical plants in the United States and West Europe is carried out with the use of borosilicate glasses. The traditional methods of optical and X-ray powder diffraction analysis and also transmission electron microscopy provide little information in the structural study of vitreous composites. In this paper, we demonstrated the possibilities of X-ray photoelectron

spectroscopy for the investigation of uranium-containing borosilicate glasses prepared using induction melter with a cold crucible (CCIM).

EXPERIMENTAL

The glass samples were obtained at the Bochvar All-Russia Research Institute of Inorganic Materials (SSC RF VNIINM) by progressive saturation of glass melt of composition (wt %) 19.4 Na₂O, 3.0 K₂O, 3.4 CaO, 3.4 Fe₂O₃, 5.7 Al₂O₃, 13.4 B₂O₃, 51.7 SiO₂ with uranium oxide up to a calculated level of 35 - 40 wt %. The procedure of preparing samples and the data obtained in investigation of their chemical and phase compositions by a JSM-5300 scanning electron microscope (Japan) with a LINK ISIS energy-dispersive spectrometer (Oxford, UK) were reported previously in [1 - 3].

Electron Microscopic Study of Glasses

In our earlier works, it was revealed that samples containing up to 20 wt % uranium are structurally homogeneous and involve the sole vitreous phase. The crystalline phase inclusions located predominantly in the bottom part of a glass block were found only in the sample with the highest uranium content. The electron microscopic investigation showed that the top and middle parts of a glass block are formed from a glass with a homogeneous composition (Table 1, Fig. 1a).

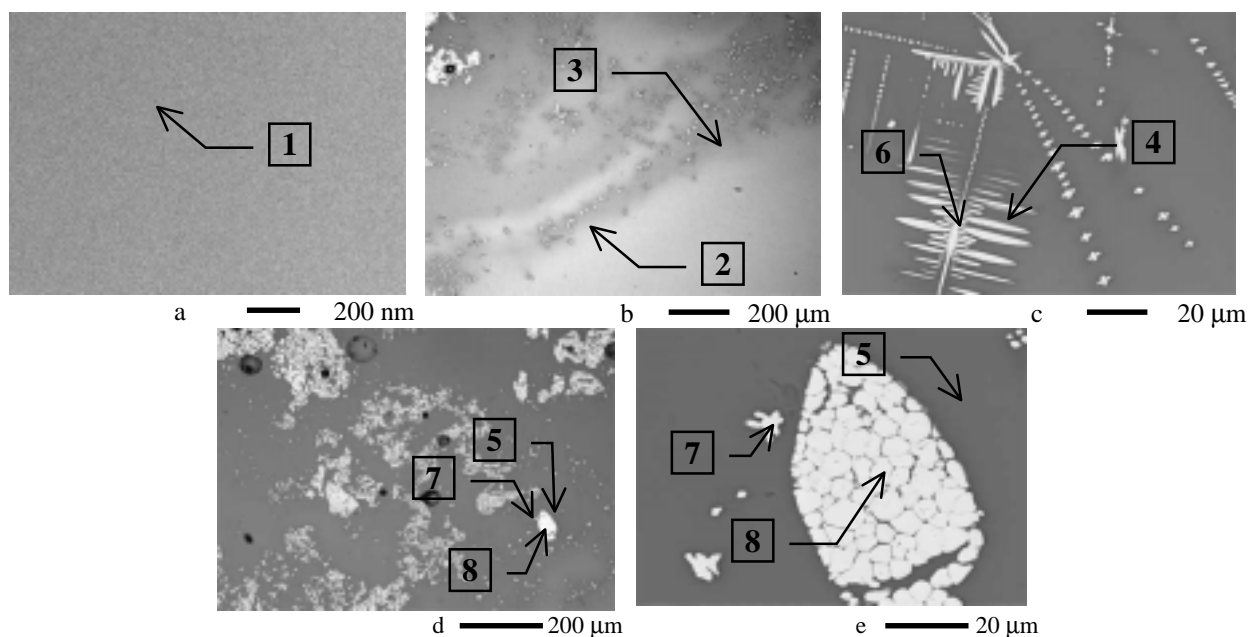


Fig. 1. SEM micrographs of samples.

No any phases other than the vitreous phase were observed even at a maximum magnification of 3500. The phase inhomogeneity is characteristic only of the sample taken from the bottom part of a block (Figs. 1b - 1e), which contains particles of crystalline phase of two morphological types.

The first type is characterized by crystals that depending on the direction of a section can be rosette-like or elongated raylike in shape (Figs. 1b, 1c).

In composition, these crystals correspond to uranium oxide with an impurity of additional components (Table 1, point no. 6). Among these components, calcium entering into the composition of crystals as a structural impurity is prevailing. In regions containing aggregates of these particles and on the particle boundaries, the surrounding glass is depleted in uranium. This follows from both the change in the glass color (Fig. 1b) in these regions in back scattered electron micrographs (the darker the color of a material, the smaller its mean atomic weight with due regard for all elements) and the direct determination of glass composition in these points (Table 1, point no. 4).

Table 1. Compositions of glass and crystalline phases in the studied samples

Point of analysis	Material composition, wt %							
	Na ₂ O	Al ₂ O ₃	SiO ₂	CaO	Fe ₂ O ₃	UO ₂	K ₂ O*	B ₂ O ₃ *
1	11.0	5.0	44.2	2.0	2.7	23.9	2.8	9.2
2	10.5	3.7	37.5	1.1	2.3	33.3	2.9	8.7
3	11.7	3.6	41.2	0.9	2.6	28.1	2.9	8.8
4	12.7	4.8	41.2	1.3	3.0	25.4	3.0	8.8
5	11.3	3.5	41.2	1.0	2.5	30.1	3.0	7.8
6	0.3	<0.2	1.0	4.9	0.2	93.1	0.1	0.4
7	2.9	1.0	0.5	<0.2	0.2	91.4	0.9	3.0
8	0.9	0.4	0.3	4.6	0.2	91.7	0.5	1.5

Contents of potassium and boron in the studied samples are evaluated from the data of chemical analysis (atomic absorption spectroscopy after the chemical dissolution of samples). Positions of point of analysis are shown in Fig. 1.

These changes in the uranium concentration in the glass near particles and also their shape and character of distribution allow one to assume that particles are formed by crystallization of a melt. The skeleton-like shape of crystals is associated with the fact that such a shape is most energetically favorable upon supersaturated melt characterized by a slow diffusion of components. In this case, the growth rate is highest at the sites with a maximum specific surface area, i.e., at vertices and edges of crystals.

Isometric and elongated inclusions of sizes as much as 150 - 200 microns across (Figs. 1d, 1e) are characteristic of the crystalline phase of the second type. A detailed examination demonstrated that these inclusions consist of a large number of tiny rounded particles with diameter varying from 1 - 3 to 5 - 7 and, rarely, to 15 microns. These particles are close in composition to skeleton crystals of the first type (Table 1). Most likely, the particles are the undissolved (in a melt) relicts of uranium oxide particles introduced into the composition of initial glass frit. The number of particles considerably increases in the bottom part of a block, which is apparently connected with their sedimentation under gravity in the course of experiment. Unlike crystals of the first type, the uranium content in the glass near these crystals does not decrease (Table 1, point no. 5).

It is known that cubic uranium oxide with the fluorite-type structure is the only stable phase in the U-O system under the conditions of synthesis in CCIM [4]. On this basis, the unit cell parameter of crystalline phase of uranium oxide was calculated from X-ray powder diffraction pattern. It was found that this parameter is equal to $\sim 5.4 \text{ \AA}$, which corresponds to uranium oxide of chemical composition $\text{UO}_{2.25}$.

X-ray Photoelectron Spectroscopic Investigation of Glasses.

The reported data indicate that uranium in glasses can occur in several oxidation states [5-12]. Different uranium ions exhibit different solubility in a melt [6], which indicates that they occupy particular positions in the glass structure. This can affect the chemical durability of a matrix and capability of fixing waste components including actinides. The uranium valence in samples and character of changes in the glass structure with an increase in uranium content were determined by X-ray photoelectron spectroscopy. This technique was previously used for explorations of uranium oxidation states in natural and synthetic uranium oxides [13, 14] and also uranium sorption on the surface of minerals [15].

The X-ray photoelectron spectra of glasses were recorded on an EC-2401 instrument at the Institute of Geology of Ore Deposits, Russian Academy of Sciences. Photoelectrons were excited with the Mg $K\alpha_{1,2}$ radiation with a pass energy of a 50 eV. Vacuum in a working chamber was no worse than 10^{-8} torr. The spectra were calibrated against the C 1s line (binding energy, 285.0 eV). The locations of line maxima were determined accurate to ± 0.1 eV. The spectra were obtained for freshly ground powders that were pressed into indium substrates. With the aim of comparing the states of elements at the surface of glass particles and in their bulk, samples were etched with argon ions to a depth of 1500 \AA with a step of 500 \AA . We studied uranium-free initial glass and 13 samples that contained 5, 15, and 30 wt % U and were drawn from the surface and bottom part of a block. The B 1s, O 1s, Na 1s, Na 2s, Al 2s, Si 2s, Al 2p, Si 2p, K 2p, Ca 2p, U 4f, U 5p_{3/2}, and U 5d spectra and also the spectrum of uranium valence band were measured.

The obtained data (Tables 2 - 6) reflect a high variability of structural-chemical properties of the studied glasses. First and foremost, one can note the differences between concentrations and charges of ions of elements at the surface and in the bulk of the same sample. At the glass surface, the contents of sodium, potassium, and boron increases, whereas the uranium content decreases (Table 3). An increase in sodium content is accompanied by a decrease in a fraction of the Si-O-Si silicon-oxygen bridging bonds with the formation of a two-dimensional chain structure instead of a three-dimensional structural network. The initial tetrahedral coordination of a part of boron atoms changes to trigonal with the escape of boron from the three-dimensional silicate network and formation of individual borate groups. On the whole, the reactivity of particle surface is higher than that of deep regions. This is likely explained by redistribution of elements due to accumulation of surface energy in the course of sample grinding. These features are equally characteristic of both uranium-containing and uranium-free samples.

The introduction of uranium into the system leads to the rearrangement of the structural glass network. The addition of 5 wt % U results in a narrowing of the Si, Al, and B spectral lines (Tables 4, 5). In the general case, the line narrowing is associated with an increase in equivalence of atomic positions in the structure. For glasses, this attests that the nearest environment of

atomic positions becomes more regular, which reflects the process of glass structurization. An increase in the uranium concentration up to 15 wt % and, then, to 30 wt % is attended by a line broadening. This indicates that glass matrix is heterogenized and the electron density of oxygen is redistributed in favor of uranium atoms with respect to other elements. After the formation of uranium oxide particles, the width of spectral lines decreases again, which reflects an increase in homogeneity of a glass owing to its structural relaxation upon the exsolution of surplus uranium.

The valence state of uranium in glasses was evaluated taking into account the shape and location of lines of elements in the spectra after their decomposition into individual components within the Gauss-Lorentz approximation. The binding energies of the 4f_{7/2} electrons for tetravalent and hexavalent uranium in UO₂ and UO₂(OH)₂ oxides are equal to 380.1 and 381.9 (±0.1) eV, respectively [15]. Since these energies are close to each other, the U 4f_{7/2} spectrum consists of a broad asymmetric line rather than of individual components characterizing different oxidation states of uranium. The mathematical processing of the spectra makes it possible to assume that uranium in glasses exhibits only two valence states: 4+ and 6+. It is unlikely that uranium occur in the form of U⁵⁺, because the total width of the U 4f line is no more than 2.5 eV (Table 5), whereas in the presence of pentavalent uranium it should be no less than 2.8 eV [14].

Table 2. Location of lines of elements in silicate matrix, eV

Line	Na 2s	Al 2p	Si 2p	Al 2s	Si 2s	B 1s	K 2p	Ca 2p	O 1s	Na 1s
1	62.8	73.7	101.8	118.8	152.8	191.6	291.2	347.0	532.1	1072.9
1a	63.4	74.4	102.3	119.4	153.3	192.0	291.4	347.2	532.5	1073.2
2	62.9	73.9	102.0	119.2	153.0	191.7	291.2	347.2	532.0	1072.8
2a	63.2	74.1	102.2	118.9	153.2	192.0	291.2	347.2	532.3	1073.1
3	62.8	73.7	101.8	118.8	152.8	191.6	291.2	347.1	532.0	1072.9
3a	63.0	74.2	102.4	119.3	153.4	192.2	291.3	347.2	532.5	1073.2
4	62.7	73.7	101.8	118.7	152.8	191.5	291.2	347.0	532.1	1072.8
4a	63.2	74.5	102.3	119.5	153.3	192.2	291.3	347.2	532.5	1073.1
4b	63.2	74.4	102.2	119.5	153.2	192.2	292.2	347.2	532.4	1073.1
4c	63.4	74.5	102.3	119.5	153.3	192.2	291.3	347.2	532.5	1073.1
5	62.9	73.7	101.8	118.7	152.8	191.7	291.2	347.0	532.1	1072.9
5a	63.0	73.9	102.0	119.0	153.0	191.9	291.2	347.1	532.3	1073.0
5b	63.4	74.4	102.3	119.4	153.3	192.2	291.3	347.2	532.5	1073.2
5c	63.4	74.5	102.4	119.5	153.5	192.2	291.3	347.2	532.5	1073.2

Note: Uranium-free glass: 1 - at the surface, 1a - at a depth of 500 Å. Glass with 5% UO₂: 2 - at the surface, 2a - at a depth of 500 Å. Glass with 15% UO₂: 3 - at the surface, 3a - at a depth of 500 Å. Homogeneous glass with 30% UO₂: 4 - at the surface, 4a - at a depth of 500 Å, 4b - at a depth of 1000 Å, 4c - at a depth of 1500 Å. The same glass with uranium phase: 5 - at the surface, 5a - at a depth of 500 Å, 5b - at a depth of 1000 Å, 5c - at a depth of 1500 Å.

Table 3. Relative concentrations of elements at the surface and in the bulk of glasses as calculated from the ratio between intensities of the corresponding line and Si 2s line

Sample	Na 2s	Al 2p	B 1s	K 2p	Ca 2p	U 5p	U 4f
1	0.38	0.13	0.21	0.23	0.25	-	-
1a	0.16	0.12	0.14	0.16	0.17	-	-
2	0.42	0.13	0.20	0.16	0.20	0.04	0.32
2a	0.18	0.13	0.15	0.17	0.18	0.09	0.78
3	0.45	0.13	0.18	0.27	0.16	0.11	1.06
3a	0.14	0.14	0.15	0.15	0.17	0.23	2.08
4	0.42	0.14	0.23	0.22	0.17	0.49	4.45
4a	0.25	0.13	0.14	0.19	0.16	0.72	6.52
4b	0.25	0.13	0.15	0.20	0.16	1.08	9.77
4c	0.20	0.13	0.14	0.18	0.17	1.03	9.61
5	0.38	0.10	0.20	0.25	0.15	0.28	2.46
5a	0.23	0.12	0.14	0.17	0.16	0.54	4.80
5b	0.25	0.13	0.16	0.17	0.17	0.77	6.95
5c	0.20	0.15	0.15	0.16	0.17	1.06	9.61

Sample designation is the same as in Table 2.

Table 4. Widths of spectral lines of different elements, eV

Sample	Si 2p	Si 2s	B 1s	Al 2p	Na 2s	U 4f7/2	U 4f5/2
1	1.65	2.16	1.61	1.75	1.90	-	-
2a	1.60	2.04	1.55	1.71	1.82	2.2	2.5
3a	1.75	2.19	1.66	1.75	1.87	2.1	2.2
4*	1.79±0.04	2.12±0.05	1.73±0.04	1.77±0.03	1.85±0.05	1.95±0.05	2.1±0.1
5*	1.63±0.02	2.04±0.03	1.55±0.02	1.62±0.03	1.66±0.03	1.95±0.05	2.1±0.1

* - The mean for three etching steps (at depths of 500, 1000, and 1500 Å from the surface).

Table 5. Parameters of X-ray photoelectron spectra of uranium atoms

Sample	U 3d5/2		U 3d3/2		U 4f7/2		U 4f5/2		U 5f	I _{U5f} /I _{U4f7/2} rel. units
	E _{bind}	σ	E _{bind}	σ	E _{bind}	σ	E _{bind}	σ	E _{bind}	
2	97.9	2.3	106.4	3.5	381.6	2.1	392.5	2.3	-	-
2a	97.7	2.4	106.3	3.7	381.6	2.2	392.5	2.5	2.0	0.009
3	97.7	2.3	106.4	3.5	381.4	1.9	392.3	2.1	2.1	0.010
3a	97.6	2.4	106.2	3.6	381.3	2.1	392.2	2.2	2.0	0.014
4	97.9	2.5	106.5	3.6	381.5	2.1	392.4	2.3	2.1	0.011
4a	97.5	2.3	106.3	3.5	381.1	2.0	392.0	2.2	2.0	0.015
4b	97.5	2.2	106.2	3.5	381.0	1.9	391.9	2.0	2.0	0.017
4c	97.4	2.3	106.2	3.6	381.0	1.9	391.9	2.1	1.9	0.019
5	97.7	2.4	106.4	3.5	381.7	2.1	392.6	2.4	2.0	0.008
5a	97.7	2.5	106.4	3.5	381.3	2.0	392.2	2.2	2.0	0.014
5b	97.5	2.5	106.2	3.6	381.1	1.9	392.0	2.1	1.9	0.017
5c	97.4	2.5	106.3	3.6	381.0	1.9	391.9	2.0	1.9	0.020

E_{bind} is the binding energy, σ is the half-width of spectral line, eV, and I is the intensity of spectral line.

Sample designation is the same as in Table 2.

A change in location and shape of spectral lines suggests the difference in ratio between contents of uranium in different valence states at the surface of glass particles and in their bulk. Except for a very thin near-surface layer ($< 500 \text{ \AA}$), the content of tetravalent form varies from ~ 60 to 80% (Table 6) and is 1.5 - 4 times higher than that of hexavalent uranium. At the surface, the U^{4+} content decreases, and the U^{4+}/U^{6+} ratio becomes less than 1. Earlier, it was demonstrated that the Na concentration also increases in this region. Likely, this is responsible for a rise in the oxidation state of uranium, because an increase in alkali activity brings about an increase in the fraction of uranium in the highest oxidation state, all other factors being the same [16]. One more explanation of change in the valence of uranium at the surface of glass particles is its oxidation by air oxygen.

As a whole, the data on the valence state of uranium in the studied samples differs from those obtained for other types of vitreous materials [5-7]. In particular, the presence of U^{5+} that takes a notable part in other vitreous composites is unlikely in the samples studied in this work. Moreover, hexavalent form of uranium is prevailing in aluminosilicate and aluminophosphate glasses prepared at the same temperatures and under the same redox conditions. The tetravalent uranium is predominant in the studied borosilicate matrix. This distinction is likely caused by the difference in compositions and structure of glasses and also induction heating of melt in a cold crucible.

Table 6. Evaluations of relative content and ratio of differently charged uranium ions in the samples (total amount of different oxidation states of uranium is 1)

Sample	(U^{4+}) $U_{4f7/2}$	(U^{4+}) $U_{4f5/2}$	(U^{6+}) $U_{4f7/2}$	(U^{6+}) $U_{4f5/2}$	U^{4+}/U^{6+} $U_{4f7/2}$	U^{4+}/U^{6+} $U_{4f5/2}$
2	0.32	0.29	0.68	0.71	0.47	0.41
2a	0.55	0.54	0.45	0.46	1.22	1.17
3	0.62	0.59	0.38	0.41	1.63	1.44
3a	0.70	0.71	0.30	0.29	2.33	2.45
4	0.63	0.61	0.37	0.39	1.70	1.56
4a	0.75	0.73	0.25	0.27	3.00	2.70
4b	0.77	0.77	0.23	0.23	3.35	3.35
4c	0.82	0.81	0.18	0.19	4.55	4.26
5	0.31	0.30	0.69	0.70	0.45	0.43
5a	0.62	0.61	0.38	0.39	1.63	1.56
5b	0.76	0.77	0.24	0.23	3.17	3.35
5c	0.85	0.83	0.15	0.17	5.67	4.88

Sample designation is the same as in Table 2.

CONCLUSIONS

The near-surface region (to a depth of $1000 - 1500 \text{ \AA}$) of glass particles differs in composition and structural features from their bulk. This difference manifests itself as an increase in the alkali and silica contents, a decrease in concentration of uranium with simultaneous increase in its oxidation state, and the transformation of a three-dimensional glass structure to a two-

dimensional chain-type structure. A likely cause of these changes is the accumulation of energy at the particle surface upon mechanical comminution of glasses.

In samples, uranium occurs in two oxidation states; in this case, the content of U^{4+} is considerably higher than that of U^{6+} . No intermediate pentavalent state of uranium was observed in the studied glasses, which disagrees with the available literature data and calls for a further verification with other experimental techniques. Possible cause is the participation of currents generated by a high-frequency inductor in the reduction of uranium. In order to verify this assumption, the uranium valence is currently investigated in glasses that have the same composition and are prepared under the same T- P_{O_2} conditions in an electric resistance furnace.

An increase in the uranium concentration leads to a change in the glass structure. Only for the sample containing 5 wt % UO_2 , it can be believed that uranium is uniformly dissolved over the glass. As the UO_2 content increases up to 15 wt %, the chemical bonds of oxygen atoms are redistributed in favor of uranium with respect to other elements. This implies the appearance of small regions with uranium-oxygen composition, which likely are the crystallization nuclei of individual oxide phase. According to the SEM data, the sample exhibits a homogeneous distribution of uranium. Therefore, the size of the above regions does not exceed several hundreds of angstroms. At the same time, this indicates that glasses prepared by the CCIM method and containing 15 wt % U and more are uranium-supersaturated and prone to crystallization with the precipitation of uranium dioxide phase. With a further increase in the uranium content up to 30 wt %, uranium oxide precipitates in the form of skeleton crystals.

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