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STRUCTURAL FEATURES AND PROPERTIES OF SODIUM-RUBIDIUM ALUMINOBOROSILICATE GLASSES WITH ZIRCONIUM

V. E. Eremyashev,[1] G. G. Korinevskaya,[1] D. E. Zhivulin,[2] and V. N. Bocharov[3]

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By means of vibrational spectroscopy, the study examines the structure of matrix materials synthesized through the quenching of sodium-rubidium aluminoborosilicate melts with the addition of zirconium. Zirconium was found to have a significant effect on the ratio of the main structural units and the distribution of modifier cations among them in the glass structure. The obtained results were used to explain changes in the glass-melt transition temperature and synthesized material density; they can be useful in adjusting the composition and synthesis parameters of matrix materials for the immobilization of high-level radioactive waste containing significant amounts of zirconium.

Keywords: aluminoborosilicate glass, spectroscopy, structure, thermal properties, radioactive waste, vitrification, zirconium.

INTRODUCTION

In the immobilization of high-level waste (HLW) via vitrification [1 – 4], the composition of waste is shown to have a significant effect on the physicochemical properties of the resulting melt and synthesized matrix materials.

Zirconium is a common and major component of high-level radioactive reactor waste [3]. In the process of vitrification of zirconium-containing HLW, the dissolution of zirconium in the initial melt leads to uneven distribution of zirconium across the glass structure and crystalline phases [5, 6], which significantly affects the viscosity and homogeneity of the melt and synthesized materials.

In order to predict and provide a detailed structural interpretation of this effect, we conducted a spectroscopic study of the structure and properties of two series of model sodium-rubidium glasses synthesized with the addition of different amounts of zirconium in the form of ZrO_2. The effect of zirconium dissolution in the melt on the structural features of glasses obtained via quenching was studied using infrared (IR) and Raman spectroscopy. The spectroscopic data of synthesized materials were compared with those of their thermal analysis and density determination, as well as with the results of studying other similar zirconium-containing systems [7 – 10].

EXPERIMENT

The study used two series of model sodium-rubidium aluminoborosilicate matrix materials of the system Na_2O–Rb_2O–B_2O_3–SiO_2–Al_2O_3–ZrO_2 with different Na_2O-to-Rb_2O content ratios (NRZ-5 and NRZ-10 series of samples) and different ZrO_2 content. These samples were previously synthesized via melt quenching in order to establish the maximum solubility of zirconium in aluminoborosilicate matrix materials of various compositions [5, 6]. The chemical composition of the samples presented in Table 1 was determined via x-ray spectroscopy using the sections of glass samples without crystalline phases.

The IR spectra of the samples were recorded by means of a Shimadzu IRAffinity-1S FTIR spectrometer within the range of 400 – 4000 cm^{-1} via KBr pellet formation. The Raman spectra were obtained from the polished surface of the samples in the backscattering geometry within the range of 200 – 2000 cm^{-1} using a Horiba Labram HR800 high-resolution spectrometer equipped with an Olympus BX41 mi-

[1] South Urals Federal Research Center of Mineralogy and Geoecology of the Urals Branch of the Russian Academy of Sciences, Miass, Chelyabinsk Oblast, Russia (e-mail: vee-zlat@mineralogy.ru).
[2] South Ural State University (National Research University), Chelyabinsk, Russia.
[3] St. Petersburg University, St. Petersburg, Russia.

The observed structural changes can be attributed to the increased polymerization of the anionic glass network, which helps to explains the significant increase in the T_g value.

With a higher amount of zirconium added (10 – 15 mol.% ZrO_2), only partial incorporation of zirconium into the glass structure and emergence of zirconium-containing crystalline phases are observed. This factor reduces the effect of added zirconium on the glass structure; this also explains the further less pronounced increase in the T_g value against the background of a significant increase in the density of the samples [9, 10].

CONCLUSIONS

The ZrO_2 content in the initial aluminoborosilicate melt has a significant effect on the ratio of basic units in the anionic structure of glass formed as a result of its cooling. These changes can be attributed to the competition between the main network cations (silicon, aluminum, boron, and zirconium) for sodium cations as a compensator for the electrical charge of structural units. Since rubidium cations practically do not participate in the formation of zirconium-containing structural units, only the sodium content in glass affects the Zr solubility in glass.

The vitrification of HLW with high zirconium content requires conditions for the complete charge compensation in zirconium-containing structural units, taking into account the content and ratio of all modifying and network cations in the glass composition. The incorporation of zirconium into the structure of aluminoborosilicate glass increases the polymerization of the glass network, the melt-glass transition temperature (softening/vitrification temperature, T_g), and the glass density.

The obtained study results should be taken into account when adjusting the composition and synthesis parameters of matrix materials in the process of vitrification of high-level radioactive waste containing significant amounts of zirconium as per [21].

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