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INFLUENCE OF RADIATION AND MULTIVALENT CATION ADDITIONS ON PHASE SEPARATION AND CRYSTALLIZATION OF GLASS

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RESEARCH OBJECTIVES

The major objectives of this proposed investigation are as follows:

(1) To investigate the influence of multivalent cations on the thermodynamics and kinetics of phase separation and crystallization in simple model glasses. (2) To study the influence of α and β particle, heavy ion bombardment and γ irradiation on phase separation and crystallization in simple model glasses. (3) To examine the structural changes produced by radiation just prior to the onset of phase separation and/or crystallization. (4) To develop models to explain the observed effects of multivalent cations and radiation on phase separation and crystallization. (5) To utilize the results of these experimental and modeling studies to provide guidelines for the allowed range of composition choices and processing conditions in order to avoid the formation of unwanted phases in nuclear waste disposal glasses.

RESEARCH PROGRESS AND IMPLICATIONS

We have been pursuing research activities in three areas: (1) assessment of the influence of γ radiation on phase transformation behavior, (2) measurement of valence state ratios of iron in glass, and 3) study of the effect of iron redox ratio on phase separation behavior in a glass.

For topic (1), we have selected glasses in three composition families ($\text{Na}_2\text{O-SiO}_2$, $\text{Li}_2\text{O-SiO}_2$, and $\text{K}_2\text{O-SiO}_2$, called NS, LS, and KS) for investigation, and glasses of all of these compositions have been prepared and have been cut into one cm. cubes and have been insertion into the gamma ray pit at PNNL. The KS glass is believed to have an incipient phase separation. Calculations have indicated that this glass composition should undergo phase separation, but since the predicted critical temperature is quite low kinetic factors might prevent its observation. We postulated that an irradiated KS glass might show signs of phase separation when heated. However, our studies did not confirm this

hypothesis. The second system which is being investigated is the NS system. NS glasses show a region of immiscibility from about 0 - 20 mol % NS, and while NS₂ only exhibits surface crystallization, compositions in the vicinity of NS show both internal and surface crystallization. It is believed that radiation bombardment could qualitatively change the crystallization behavior of these glasses. In particular, we are studying the crystal growth rates in a particular NS composition. We plan to compare the growth behavior of the irradiated glasses with those which do not receive radiation treatment.

Redox ratios have been determined using a colorimetric method, Mossbauer analysis, and optical absorption. The experimental procedures were described in our previous report. We found that these three methods gave excellent agreement for the values of the $\text{Fe}^{++}/\text{Fe}^{+++}$ (redox ratio) in the glasses. Also, using the results of the colorimetric analysis we were able to find the extinction coefficients for the 18.56% NS and the 13% NS glasses.

We are utilizing the optical absorption data that was taken for purposes of determining redox ratios to provide glass structural information. In particular, it has been suggested that the band centered near $14,500\text{ cm}^{-1}$ is indicative of $\text{Fe}^{2+} - \text{O}^{2-} - \text{Fe}^{3+}$ formation. In addition, the relative band intensities at $10,000\text{ cm}^{-1}$ and $4,800\text{ cm}^{-1}$ could give us information as to the environment around the Fe^{2+} responsible for the $4,800\text{ cm}^{-1}$ band. The Mossbauer data will provide supporting structural information. For example, the relative number of clustered and free ferric ions can be computed from the ratio of areas under the doublet and sextet in the liquid He spectra. Also, the change in shift parameter with redox ratio will provide an indication of whether there is an increase or decrease in tetrahedral site symmetry about both ferrous and ferric ions. Finally, the quadropole splitting parameter provides information regarding the site symmetries about the Fe^{++} and Fe^{+++} . Currently, we are analyzing our spectral data for these purposes. We plan to write a manuscript describing our results within the next couple of weeks.

The thermodynamics of phase separation has been studied as a function of $\text{Fe}^{++}/\text{Fe}^{+++}$ (redox ratio) in the glasses. Binodal temperature measurements have been made for two compositions (18.56% NS and 13% NS) that contain identical total iron concentrations but different redox ratios. For both compositions it was found that the addition of iron suppresses the immiscibility temperature. However, we observed that the value of the redox ratio had only a small effect upon the immiscibility temperature. The decline in binodal temperature with iron additions was explained using a model proposed by Tomozawa. However, an adequate explanation for the insensitivity of the immiscibility temperature to oxidation state could not be found. We plan to write a separate manuscript discussing the results of the phase separation studies.

PLANNED ACTIVITIES

The end date of this contract is 9/00. Hence, in the next year the only planned activity is the completion of the crystal growth study. A renewal proposal has been submitted, and the goals of that study are described therein.

INFORMATION ACCESS

L.L. Burgner and M.C. Weinberg, "Crystal Nucleation Rates in a $\text{Na}_2\text{O-SiO}_2$ Glass", J. Non-Crystalline Solids 261, 163 (2000)

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