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The Influence of Radiation and Multivalent Cation Additions on Phase Separation and Crystallization of Glass

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Research Objective

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 separationand crystallization in simple model glasses.
(2) To study the influence of a and b particle, heavy ion bombardment and g 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.

At the fundamental level, the effects of radiation, of transition metal ion additions, and of melting history in the case of multi-valent cations, on phase separation and crystallization behavior will be evaluated for simple glasses whose baseline behavior is characterized and understood. At the practical level, the program will determine the magnitude of the risk associated with the effects of radiation in inducing phase separation and crystallization. It will also provide approaches to ameliorating such effects through controlled complementary dopants and control of melting/processing conditions.

Research Progress and Implications

As of six months into the award we have begun work in two areas: (1) influence of g radiation on phase transformation behavior, (2) effect of valence state of multivalent ion on upon crystallization kinetics and mechanisms. For topic (1), after careful consideration, we have selected glasses in three composition families(Na_2O-SiO_2, Li_2O-SiO_2, and K_2O-SiO_2, called NS, LS, and KS) for investigation. NS glasses show a region of immiscibility from about 0 - 20 mol % N, and while NS2 only exhibits surface crystallization, compositions in the vicinity of NS show both internal and surface crystallization. KS glasses do not phase separate , but there is a region of “incipient” phase separation at compositions near 9 mol % K. LS2 glass appears to nucleate homogeneously, but the process may be complicated by metastable phase formation. It is believed that radiation bombardment could qualitatively change the phase separation behavior of these glasses. Glasses of all of these compositions have been prepared and have been cut into one cm. cubes for insertion into the gamma (Co^{-60}) irradiation facility at PNNL in May 1998. Sample holders have been designed and will be constructed in the near future. In order to study the influence of valence state on crystallization behavior we have chosen to examine the Iron-Soda-Silica (FeNS) system first. We have prepared a $5Na_2O$-Fe_2O_3-$8SiO_2$(5-1-8) glass under conditions where the iron is predominantly in the Fe^{3+} oxidation state. The crystallization behavior of this composition was investigated using two stage heat treatments. Nucleation temperatures of TN

= 450°C, 500°C were selected and a development temperatures of TD = 685°C was used. Analysis of the heated glasses only showed the development of surface crystallization. Internal nucleation could not be evoked. Needle-like crystals grew from the surface with a growth rate of approximately 50 µm/ s. A second glass batch of 5-1-8 composition was melted using iron oxalate as a source and with a mixture of H_2/N_2 gas flowing through the furnace in order to produce a glass containing predominantly Fe^{2+}. However, liquidus measurements of the two glasses indicated that very little of the reduced species was produced. As expected, the second glass did not exhibit internal nucleation either.

Planned Activities

In the next year the following activities are planned: (1) Prepare a reduced version of the 5-1-8 glass and measure its total Fe content as well as the % Fe^{2+}. (2) Examine the crystallization behavior of the reduced glass. (3) Perform structural studies and additional characterizations of the "unperturbed" glass compositions inserted into the gamma pit (to serve as baseline). (4) Melt NS glasses with small Fe concentrations and examine their crystallization behavior as a function of Fe content and oxidation state.