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Project Title: **The Influence of Radiation and Multivalent Cation Additions on Phase Separation and Crystallization of Glass**

Lead Principal Investigator:

Dr. Michael C. Weinberg
Department of Materials Science and Engineering
University of Arizona
Building 12
Tucson, Arizona 85721
Telephone: 520-621-6909
e-mail: MCW@U.arizona.edu

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

Michael C. Weinberg, University of Arizona

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 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.

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(Na_2O-SiO_2, Li_2O-SiO_2, and K2O-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 first glass system which is being investigated is the NS system. NS glasses show a region of immiscibility from about 0 - 20 mol % NS, and while NS_2 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 phase separation and crystallization behavior of these glasses. While a portion of the glasses have been undergoing radiation, the crystallization behavior of other NS glasses (which did not receive radiation) has been studied. We have determined the steady-state crystal nucleation rates of several NS compositions, and we have currently initiated an investigation of transient nucleation in one NS composition. We plan to compare the crystallization 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. Our work utilizing these methods is described below.

A UV/Vis Colorimetric method for determining Fe^{2+} as well as total iron was obtained from PNNL (Procedure number APSL-02). We have modified the PNNL procedure slightly. For the determination of total iron, the PNNL procedure suggests diluting a small amount of the Fe^{2+} sample by 100, then reducing the Fe^{3+} to Fe^{2+} by hydroquinone. This dilution step was suggested as the operating procedure was designed forrock or mineral samples that had a large amount of total iron, with a large amount of the iron in the ferric state. Diluting the samples was required in order to get the concentration of the iron ions to be low enough to obtain a solution that could be used in the spectrometer. For the glasses that we are using, the iron concentration is low enough that no dilution is necessary. We also have some glasses with very high Fe^{2+} concentrations, so dilution is an unnecessary step. We now take the Fe^{2+} solutions, and add hydroquinone directly (without dilution) to determine the total iron level. This non-dilution technique has resulted in analyses which are much more reproducible and accurate, as any small errors in dilution has a large effect on the calculated redox ratio. This technique has been used successfully for 18.56 NS with up to 4 mol % FeO, 13 NS with up to 2 mol % FeO, and the 518 composition (5 Na2O, 1 Fe2O3, 8 SiO2)

Mossbauer analysis of 2 samples of the 518 glass with different oxidation levels and 2 samples of the 18.56 NS glass with two different oxidation levels has been completed at PNNL. The redox results are consistent with the modified UV/Vis Colorimetric procedure. We have prepared a number of thin glass samples for use in the UV/Vis/NIR Spectrometer for the determination of redox level. Initial results indicate that the absorption around 1120 nm is dependent on the iron redox ratio. We will be using the full range of glass compositions and oxidation states available to us to verify this technique for the determination of iron redox level. One other potential advantage to this technique is that the amount of water in the glass can be determined concurrently from the spectra.

The thermodynamics of phase separation in iron doped NS glasses has been studied as a function of Fe^{++}/Fe^{+++} (redox ratio) in the glasses. Binodal temperature measurements have been made for two compositions (18.56% N and 13% N) within the binodal which contain identical total iron concentrations but different redox ratios. For both compositions it is found that the addition of iron suppresses the immiscibility temperature. However, we observed that to within experimental error the immiscibility temperature is independent of redox ratio. This is a rather surprising result since arguments based on ionic field strength of cations would indicate a strong dependence of the binodal to the value of the redox ratio. Currently, we are seeking explanations for this unusual behavior.

PLANNED ACTIVITIES

In the next year the following activities are planned:
(1) Prepare a manuscript describing our results on the influence of Fe^{++}/Fe^{+++} on the immiscibility temperature of glasses in the NS system. (2) Examine the crystallization behavior of the NS glasses which received γ irradiation. (3) Perform structural studies and additional characterizations of the "unperturbed" glass compositions inserted into the gamma pit (to serve as baseline). (4) Complete our studies and prepare a manuscript on a comparison of experimental methods for obtaining iron redox ratio values in glass.
(5) Examine the phase separation behavior of glasses in the KS and NS systems which have and have not been irradiated. (6) Examine metastable crystal phase formation in irradiated LS_2 glasses.

INFORMATION ACCESS

L.L. Burgner and M.C. Weinberg, "Crystal Nucleation Rates in a Na_2O-SiO_2 Glass", J. Non-Crystalline Solids (submitted)
J.S. Jeoung, W.H. Poisl, M.C. Weinberg, G.L. Smith, and H. Li, "Effect of Iron Oxidation State on Immiscibility Temperature in Sodium Silicate Glass" Amer. Ceram. Soc. Bull. 78, #4 p. 205 (1999)