FINAL REPORT

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

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ABSTRACT

This report presents results of: (1) measurement of valence state ratios of iron in glass, and (2) a study of the effect of iron redox ratio on phase separation behavior in a glass. The redox ratio of iron in two sodium silicate (NS) glasses has been determined using a colorimetric method, Mossbauer analysis, and optical absorption. The experimental procedures were described in a previous report. We found that these three methods gave excellent agreement for the values of the $\text{Fe}^{2+}/\text{Fe}^{3+}$ (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 have utilized 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

quadrupole splitting parameter provides information regarding the site symmetries about the Fe^{++} and Fe^{+++} . Currently, we are analyzing the spectral data for these purposes. The Mossbauer work was done in conjunction with colleagues at PNNL, and a manuscript is currently in preparation.

The effect of oxidation state of iron on the phase separation of $x\text{Na}_2\text{O} \cdot (100-x)\text{SiO}_2$ glasses, $x = 18.56$ and 13 , containing 0.5 mole % iron oxide was studied. The oxidation state of iron in the glasses was varied by changing the melting conditions such as melting temperature and melting atmosphere. The oxidation states of the iron ion were determined by the colorimetric method and by the UV-VIS NIR spectrophotometric method, and a comparison was made between the results obtained using these two techniques. Immiscibility temperatures of the glasses were determined by opalescence and clearing methods. The immiscibility temperature of the sodium silicate binary glasses decreased approximately 25°C with the addition of 0.5 mole % Fe_2O_3 . The immiscibility temperature of the doped glasses increased slightly with increasing concentration of Fe^{2+} ion in the glass.

The liquidus temperature of the 18.56 NS_2 glass was determined using an X-ray diffraction technique. Approximately 3 grams of glass powder were heated for 4 hours in the temperature region near the liquidus temperature. XRD patterns were obtained from the samples to determine if any crystalline material was present. The heat-treatment temperatures were incremented in 2°C intervals, and the liquidus temperature was taken as the minimum heat-treatment temperature where the crystalline XRD peaks disappeared in the XRD pattern. From this analysis it was determined that the liquidus temperature decreased about 26°C by the addition of 0.5 mole % Fe_2O_3 .

The prediction of immiscibility tendency upon the addition of a minor amount of third component was made using models proposed by Tomozawa and Obara and Nakagawa and Izumitani. Tomozawa and Obara's model showed good agreement with the measured immiscibility values.

Report

I. RESEARCH OBJECTIVES

The major objectives of the proposed investigation were 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 alpha and beta particles, heavy ion bombardment and gamma 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.

II. RESEARCH PROGRESS -- Effect of oxidation state of iron on phase separation in sodium silicate glasses

Introduction

It has been recognized that liquid-liquid immiscibility and crystallization processes have significant potential to alter the storage behavior¹ in glasses used for nuclear waste disposal. In order to mitigate the chance for deleterious phase separation during storage of nuclear-waste-loaded glasses it is necessary to examine the influence of multivalent cations on the thermodynamics and kinetics of the phase transformation process. In general, transition metal ions can exist in multivalent states depending upon the base glass composition, temperature of melting, duration of heat treatment, and partial pressure of oxygen above the glass melt.² A number of multivalent elements can be present in high level nuclear waste that is to be immobilized within a glass matrix. Among such multivalent elements, prime attention should be paid to iron since high level radioactive wastes inevitably contain iron oxide. Under normal conditions, iron can be present in silicate glasses only as Fe^{2+} and Fe^{3+} .

The oxidation state of a glass is expected to influence the immiscibility tendency since Fe^{2+} and Fe^{3+} have different ionic field strengths and different coordination numbers in the glass. In this study, the effect of the oxidation state of iron on phase separation was investigated using two different compositions of sodium silicate binary glasses.

Experimental

(1) Glass preparation

Sodium silicate base glasses were prepared with the composition of $x\text{Na}_2\text{O} \cdot (100-x)\text{SiO}_2$, $x = 13$ and 18.56. The 13 mole % glass was melted using reagent grade Na_2CO_3 and silica powder (SiO_2) at 1600 °C for 8 hours in a platinum crucible in an electric furnace. The glass melt was poured on a brass plate and cooled to room temperature. Homogenization of glass was achieved by crushing and re-melting two times. The 18.56 mole % glass had been previously prepared at Owens-Illinois.³ Sodium silicate glasses doped with 0.5 mole % Fe_2O_3 were prepared in 150 gram batches by melting the crushed base glass powder and reagent grade Fe_2O_3 . It should be noted that both base composition glasses used in this study were from the same initial melt, so no variation in base glass composition occurred for the different melts.

Most batches of the iron containing glasses were melted at 1300-1600 °C in a platinum crucible for 1.5-8 hrs then poured into a brass mold of approximately 4 by 4 by 2 cm, then annealed at 500 °C for 2 hrs and furnace cooled. In order to vary the oxidation state of iron in the glass, different melting temperatures, melting times and atmosphere were used. In order to obtain highly reduced glasses, a CO/CO_2 gas mixture was bubbled into the glass melt while the glass was molten. The gas mixture was introduced into the melt through a platinum tube. Before the glass was removed from the furnace, the tube was withdrawn from the melt and gas was allowed to flow over the surface of the melt for a period of 30 minutes. This procedure allowed bubbles to be removed from the melt while still maintaining the reduced atmosphere over the glass. The melting conditions used in this study are shown in Table I.

(2) Measurement of $\text{Fe}^{2+}/(\text{Fe ratio})$

To measure the ratio of $\text{Fe}^{2+}/(\text{Fe in the glasses})$ two different techniques, colorimetric^{4,6} and UV-VIS NIR spectrophotometric methods,^{7,8} were used. In the colorimetric method, ferrous ions react with 1,10-phenanthroline and forms the orange-red complex $((\text{C}_{12}\text{H}_8\text{N}_2)_3\text{Fe}^{2+})$ in solution over a pH range of 2-9. Optical absorbance of this complex at 510 nm follows Lambert-Beer's law. Therefore, optical absorbance of the solution containing that complex can be converted to a concentration of Fe^{2+} in the solution. Calibration curves for converting measured absorbance to concentration of Fe^{2+} were established at 510 nm using an atomic absorption iron standard solution.

For the analysis of ferrous ion concentration, glass samples were ground to a fine powder using an alumina mortar and pestle. About 20-30 mg of the glass powder sample was weighed into a 100 ml plastic beaker. An indicating solution of 25 ml of 4 % boric acid, 7 ml of 10 % potassium hydrogen phthalate, 6 ml of 0.25 % 1,10-phenanthroline solution, and 2 ml of concentrated ammonium hydroxide was prepared in a second 100 ml plastic beaker. The glass powder was then digested by the addition of 0.5 ml of concentrated H_2SO_4 and 1.5 ml of concentrated HF into the sample beaker. Immediately after dissolution of the glass (within 15 seconds of the addition of the acids to the glass powder), the indicating solution described above was added and the pH of the mixed solution was adjusted to 3.3-3.5 using diluted ammonium hydroxide and/or diluted H_2SO_4 . This solution was transferred to 100 ml volumetric flask and diluted to 100 ml by adding iron free deionized water. Visible spectrophotometric absorbance measurement

of the sample solution was made with a Milton Roy Spectronic 2101 digital UV-VIS Spectrophotometer using a matched polystyrene cell.

For the analysis of total iron, 20 ml of the above sample solution was transferred to 100 ml plastic bottle and hydroquinone (25 (5 mg) was added to the solution to reduce all the ferric ions to ferrous ions. The absorbance of this solution was measured after full color development of the orange-red complex. The measured absorbances were converted to concentration of Fe^{2+} and total iron present in the solution. This allowed the ratio of Fe^{2+}/Fe to be calculated from the measured absorbance values.

UV-VIS NIR spectroscopy was also used to determine the Fe^{2+}/Fe ratio in these glasses. This method provides a direct evaluation of the Fe^{2+} content in glass without having to carry out chemical dissolution. However, knowledge of the extinction coefficient of the Fe^{2+} ion in the given glass composition is required. The ferrous ion in a glass has a maximum absorption peak around 1100 nm in the optical spectra. The position and intensity of this peak varies with the base glass composition. There is a linear relationship between the optical absorbance at this peak position and the Fe^{2+} ion concentration for a glass of constant composition. Therefore, the amount of ferrous iron in the glass can be found by the spectrophotometric method. Each of the bulk glasses, annealed at 500 °C for 2 hours, was cut into pieces of dimensions 10 (10 mm with four different thicknesses (1.5, 2.0, 2.5 and 3.0 mm) using a low speed diamond saw. After cutting, all glass samples were ground using flat alumina grinding media and then polished using 1(m CeO_2 to achieve uniform thickness and parallel and polished surfaces.

Spectrophotometric absorbances of glasses were measured by a Varian 500 Scan Spectrophotometer with a double beam mode. Since the extinction coefficient for our glasses were not known, we calculated the extinction coefficient using the Lambert-Beer equation. The Lambert-Beer equation is given by $A = (\epsilon c t)$, where A = absorbance (dimensionless), ϵ = extinction coefficient (mm^{-1}), c = concentration of ferrous ion (Fe^{2+}/Fe), and t = sample thickness (mm). A plot of absorbance near 1100 nm versus thickness gives a linear relation, and the slope of this plot is ϵc . To find the extinction coefficient, the concentration of ferrous ion (Fe^{2+}/Fe) obtained from the colorimetric method was used. Then, the ratio of Fe^{2+}/Fe for each of the glasses was determined using the calculated extinction coefficient and the slope of the absorbance vs. thickness plot.

(3) Determination of immiscibility temperature

The immiscibility temperatures of glasses were determined by both opalescence and clearing methods.^{9,10} In the opalescence method, glass samples of approximately 10(10(5 mm were held at temperatures near the expected binodal temperature for various times depending upon the glass composition and heat-treatment temperature. The heat-treated samples were then evaluated to determine if phase separation had occurred.

In the clearing method one determines the minimum heat-treatment temperature at which a previously phase separated glass clears. The detection of opalescence and clearing by the naked eye can be aided by the use of a concentrated beam of light, such as a laser beam, or by placing the sample in an index matching solution and viewing against a black background. If the samples showed any evidence of surface

crystallization, then the crystalline material was removed before seeking signs of the presence of phase separation. The accuracy of these techniques is determined by the temperature interval between the heat-treatment temperatures and the number of samples used.

(4) Liquidus temperature measurement

X-ray diffraction¹¹ was used to determine liquidus temperatures of the 18.56Na₂O·81.44 SiO₂ base glass and the 0.5 mole % Fe₂O₃ doped glass. To measure liquidus temperature approximately 3 grams of glass powder was heated in the temperature range of 1130 - 1180 °C for 4 hrs. X-ray diffraction patterns were obtained after each heat-treatment to determine if crystalline material was present. In order to find a precise value of the liquidus temperature successive heat-treatment experiments, with 2 °C intervals, were performed at the temperatures close to the anticipated liquidus temperature as determined from the initial measurements. The liquidus temperature was taken as the minimum heat treatment temperature where all of the crystalline peaks disappeared in the XRD pattern. XRD measurements were performed using a step scan with a 0.02 degree step with an integration time of 2 seconds at each step.

Results and Discussion

(1) Oxidation state of iron by the colorimetric method

The results of measurements of oxidation states by the colorimetric method are shown in Table II. As one expects from the redox equilibrium of iron, the concentration of ferrous ion in the glass increases with increasing melting temperature and with increasing the ratio of CO/CO₂ bubbling gases for a given melting temperature. Column 2 of this table shows the measured percentage of iron in the Fe²⁺ state. The error in these values, shown in the third column, was computed from data obtained by repeated evaluations of the same glass. The fourth column contains the measured total amount of iron. The last column gives the anticipated amount of iron in the glass if one assumes that there is no batch loss due to volatility. One observes that there is generally good agreement between the measured and expected values of the total iron content.

The possible sources of errors for oxidation ratio of iron by this method are the oxidation of ferrous ion during decomposition of glass, and the formation of precipitate after mixing the indicating solution into the decomposed glass solution. The potential for the oxidation of the ferrous iron ion was significantly reduced by using very finely ground glass powder to reduce the time for complete dissolution of the glass to less than 15 seconds, and by introducing the indicating solution immediately after dissolution. Precipitation could be avoided by adjusting the pH of the solution quickly after introducing the indicating solution into the digested glass solution.

(2) *UV-VIS NIR spectroscopic method*

The UV-VIS NIR absorbance spectra of the 13NS-series glasses are shown Figure 1. One can clearly see that the absorbance near 1100 nm, due to the Fe^{2+} ion, increases with increasing Fe^{2+} ion concentration in the glass. The results of linear regression analysis of absorbance near 1100 nm versus thickness for each of the 13NS-series and 18NS-series glasses are shown in Figures 2 and 3. All linear regression lines showed an excellent fit to the data, with correlation coefficients close to 1. From these plots we confirmed that the absorbance of the Fe^{2+} ion in these glasses followed Lambert-Beer's law. The slopes of the lines in the figures gives the product of the Fe^{2+} concentration and the extinction coefficient. We used the results of the $\text{Fe}^{2+}/(\text{Fe})$ concentrations determined by the colorimetric method and the slope of the line from the figures to determine an extinction coefficient for each individual glass sample (Table III). An average extinction coefficient for each base glass composition with 0.5 mole % Fe_2O_3 addition was then calculated from the individual results. Using the calculated average extinction coefficients, concentrations of $\text{Fe}^{2+}/(\text{Fe})$ for each of the glasses were then determined from the experimental absorbance measurements. These results are shown in Table IV.

In the UV-VIS NIR spectrophotometric method, the main causes of error are small bubbles in the specimen, lack of uniformity of thickness, and poor specimen homogeneity, all of which can affect the absorbance, and hence the calculation of the extinction coefficient. In order to enhance the accuracy of measurement, care is required during the specimen preparation processes.

(3) *Comparison of colorimetric and UV-VIS NIR spectroscopic methods*

The colorimetric method is relatively accurate and can be used to analyze concentrations of Fe^{2+} , Fe^{3+} and total Fe in one glass digestion, but it is tedious and time consuming and cannot be applied in an in-line analysis. The spectrophotometric method is very simple and quick, but one must depend on wet chemical methods to obtain the extinction coefficient. However, once the glass is well characterized by a wet chemical method, one can apply the spectrophotometric method to in-line analysis of the oxidation state of iron in a glass factory for rapid determination of the oxidation state.

The results of the two methods in the present study can be compared in a couple of ways. First, in Fig. 4(a, b) we compare the results for the 18NS and 13NS glasses, respectively, by plotting the % ferrous ion found by the spectrophotometric method versus the % ferrous ion found by the colorimetric method. One observes excellent agreement between the methods for all oxidation state ratios, save the most reduced glass. Although the reason for the discrepancy in this composition is not known, it could be related to the quality of this glass and its somewhat inhomogeneous nature. The former comparison procedure is somewhat tainted in that the results of the colorimetric experiments were used to obtain the extinction coefficient employed in the spectrophotometric technique. Hence, we chose to use a second method of comparison using concentration ratios so that prior knowledge of the extinction coefficient is not required. If one assumes that the extinction coefficient is independent of concentration (which is an excellent assumption in the low concentration regime), then the ratio of slopes in Figures 2 and 3 should give the concentration ratios. These ratios are shown in Table V in the columns labeled "Slope Ratio". The concentration ratios found from the

colorimetric technique are given in the columns called "Concentration Ratio". Once again one observes excellent agreement between the results of the two methods, with the exception of glass 13NS-50/50.

The molar extinction coefficients determined in this study have been compared to published values of molar extinction coefficients found in the literature for glasses of similar composition. These extinction coefficients are shown in Table VI. One can see that the extinction coefficients determined in the present study are similar to those found in the literature.

(4) Immiscibility temperatures of glasses

Binodal (i.e. immiscibility) temperatures were found by using both the opalescence (clouding) and clearing methods. In order to evaluate the accuracy of these two techniques, the binodal temperature of the 18NS base glass (not doped with Fe) was determined. When this glass was heated for 8 hours anywhere in the temperature range 600 °C – 630 °C, phase separation occurred. However, long time heat treatments (up to 48 hours) of the glass above this temperature did not produce phase separation. Clearing of these phase separated glasses occurred near 660 °C. Since the immiscibility temperature determined by opalescent and clearing should be fairly close, we felt that the opalescent technique was in error. We surmised that the source of the difficulty was the lack of ability of the glass to nucleate in the higher temperature regime. In order to overcome this problem we used two-stage heat treatments. The glasses were given a 24 hour heat treatment, the 18NS glass at 530 °C and the 13 NS glass at 580 °C, prior to the heat treatment at the clouding temperature. Using two-stage heating, the differences in binodal temperatures found by clearing and clouding methods were reduced to 5 °C. However, comparison of the results of these methods with FE-SEM (see Figs. 5, 6) indicated that the clearing technique was more accurate. Also, due to the simplicity of the latter method, it was decided to rely solely upon this technique for subsequent investigations. All immiscibility temperatures reported here were obtained from clearing experiments. Oxidation ratio measurements were made in several cases upon completion of immiscibility determinations in order to ensure that the iron oxidation ratio did not change as a result of the heat treatment.

The results of the immiscibility temperature for the 18NS and 13NS series glasses as a function of oxidation state of iron are shown in Figure 7 and Table VII. One can observe from the figure that the addition of 0.5 mole % Fe₂O₃ to both the 13NS and 18NS base glass causes a decrease in the binodal temperature. This decrease is relatively constant for all oxidation states, on average approximately 25 °C, though there is a slight increase in binodal temperature as the Fe²⁺ concentration increases.

The effects of addition of third components on the immiscibility tendency of binary glass systems have been studied by Nakagawa and Izumitani¹⁶ and Tomozawa and Obara.¹⁷ Nakagawa and Izumitani¹⁶ suggested a simple criterion to predict the tendency of immiscibility of binary glass with addition of a third component by applying Prigogine's theory¹⁸ to ternary glasses.

Prigogine's theory¹⁸ is based on the use of a regular solution model, and the underlying idea of the method is to ascertain if the addition of a third component will

lower or raise the critical temperature, T_c , of the binary mixture. The variation of T_c with concentration of third component is expressible in terms of three parameters, α_{AB} , α_{AC} , α_{BC} , where $\alpha_{IJ} = Z\{W_{IJ} - 1/2[W_{II} + W_{JJ}]\}$, Z is the coordination number and W is a bond energy. If C refers to the minor component and $\alpha_{AB} > (\alpha_{AC} - \alpha_{BC})$, then the tendency towards phase separation decreases. However, if the latter inequality is reversed, then the tendency towards immiscibility increases. We have employed this model assuming that all the iron is in the Fe^{2+} state or all is in the Fe^{3+} state. In both cases the model predicts a decrease in immiscibility tendency (as observed).

Tomozawa and Obara¹⁷ proposed a simple method for estimating the effect of a minor third component on the metastable immiscibility temperature of binary glasses. According to their model, the change in immiscibility temperature caused by the addition of a third component is approximately equal to the change in the liquidus temperature when the entropy change is small.

Although the decrease of immiscibility temperature with addition of Fe_2O_3 is easy to rationalize, the variation of binodal temperature with redox state is much more puzzling. The reason for the insensitivity of the immiscibility temperature to the iron oxidation state ratio (especially in the 18NS composition) is not clear. In the 13NS composition there is a more apparent, but small, rise in immiscibility content as the Fe^{2+} concentration increases. This result is difficult to understand since on the basis of ionic field strength arguments one would expect a decrease in binodal temperature.

Tomozawa *et. al.*¹⁹ have examined the influence of iron oxidation state upon immiscibility in a borosilicate glass. They observed that as the Fe^{2+} concentration increases the binodal temperature first decreases and then increases. They explained the rise in immiscibility temperature in terms of $Fe^{2+} - Fe^{3+}$ and $Fe^{3+} - Fe^{3+}$ clustering. It is possible that similar effects come into play for our system, but structural studies would be needed to confirm this hypothesis.

In order to apply Tomozawa and Obara's¹⁷ ideas to the present system we performed liquidus measurements on the 18NS glasses. The liquidus determinations were made using XRD intensities as function of temperature. Figure 8 shows the diffraction patterns of the $18.56Na_2O \cdot 81.44SiO_2$ base glass and the glass doped with 0.5 mole % Fe_2O_3 , both below and at the liquidus temperature. Tridymite was the predominant crystalline phase for both glasses when the ground glasses were heat-treated. The three most intense diffraction peaks for tridymite occurs near 2θ of 20.6° , 21.7° , and 23.3° . The liquidus temperature of the $18.56Na_2O \cdot 81.44SiO_2$ base glass determined by this procedure was $1184 \pm 2^\circ C$. This result shows good agreement with the established Na_2O-SiO_2 phase-diagram information for this composition.²⁰ The liquidus temperature of this glass doped with 0.5 mole % Fe_2O_3 was found to be $1158 \pm 2^\circ C$. The addition of 0.5 mole % Fe_2O_3 to the 18NS base glass resulted in a decrease in liquidus temperature of about $26^\circ C$. As the change in immiscibility temperature was on average about $25^\circ C$, our results are in good accord with the Tomozawa and Obara model.

Conclusions

The oxidation states of iron in sodium silicate glasses were determined by means of two different methods, colorimetric and spectrophotometric, and the results given by these two methods were in good agreement.

The liquidus temperature of $18.56\text{Na}_2\text{O}\cdot 81.44\text{SiO}_2$ glass decreased about 26°C by the addition of 0.5 mole % Fe_2O_3 . The immiscibility temperatures of 18NS-series and 13NS-series glasses decreased about 25°C by adding 0.5 mole % Fe_2O_3 , and were almost independent of oxidation state of iron in the glass. The decrease in binodal temperatures were found to be in good agreement with a model proposed by Tomozawa and Obara.

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Table I. Composition and melting conditions of glasses

Glass	Composition (Mole %)	Melting condition Temp.(°C)/Time(hr)/Atmosphere
18NS	18.56Na ₂ O•81.44SiO ₂	1565/74/Air
18NS-1300	18.56Na ₂ O•81.44SiO ₂ + 0.5 mole % Fe ₂ O ₃	1300/8/Air
18NS-1400		1400/8/Air
18NS-1500		1500/8/Air
18NS-1600		1600/8/Air
18NS-12/88		1500/1.5/Gas bubbling (CO/CO ₂ =12/88)
18NS-24/76		1500/1.5/Gas bubbling (CO/CO ₂ =24/76)
18NS-36/64		1500/1.5/Gas bubbling (CO/CO ₂ =36/64)
18NS-50/50		1500/1.5/Gas bubbling (CO/CO ₂ =50/50)
13NS	13Na ₂ O•87SiO ₂	1600/20/Air
13NS-1400	13Na ₂ O•87SiO ₂ + 0.5 mole % Fe ₂ O ₃	1400/8/Air
13NS-1500		1500/8/Air
13NS-1600		1600/8/Air
13NS-12/88		1600/1.5/Gas bubbling (CO/CO ₂ =12/88)
13NS-24/76		1600/1.5/Gas bubbling (CO/CO ₂ =24/76)
13NS-36/64		1600/1.5/Gas bubbling (CO/CO ₂ =36/64)
13NS-50/50		1600/1.5/Gas bubbling (CO/CO ₂ =50/50)

**Table II. Oxidation states of iron in glasses by the
colorimetric method**

Glass	Fe ²⁺ /ΣFe (%)	Error (%)	Total Fe (g Fe/100g Glass)	Batch Total Fe (g Fe/100g Glass)
18NS-1300	6.22	3.5	0.866	0.92
18NS-1400	9.55	2.9	0.845	0.92
18NS-1500	14.37	3	0.850	0.92
18NS-1600	17.33	1.3	0.850	0.92
18NS-12/88	36.05	0.8	0.875	0.92
18NS-24/76	51.54	1.2	0.889	0.92
18NS-36/64	61.22	1	0.880	0.92
18NS-50/50	90.78	0.4	0.992	0.92
13NS-1400	9.32	3.7	0.929	0.925
13NS-1500	13.90	4	0.927	0.925
13NS-1600	17.69	4	0.931	0.925
13NS-12/88	52.62	1.4	0.939	0.925
13NS-24/76	49.55	1.3	0.958	0.925
13NS-36/64	60.09	1.2	0.943	0.925
13NS-50/50	73.61	1.2	0.926	0.925

Table III. Extinction coefficient of glasses calculated from Figures 2 and 3

Glass	Extinction coefficient ε (mm ⁻¹)	Mean ε (mm ⁻¹)	Glass	Extinction coefficient ε (mm ⁻¹)	Mean ε (mm ⁻¹)
18NS-1300	1.330	1.294	13NS-1400	1.235	1.20
18NS-1400	1.370		13NS-1500	1.211	
18NS-1500	1.330		13NS-1600	1.257	
18NS-1600	1.210		13NS-12/88	1.215	
18NS-12/88	1.282		13NS-50/50	1.064	
18NS-24/76	1.283				
18NS-36/64	1.260				
18NS-50/50	1.290				

Table IV. Oxidation states of iron in glasses by the spectrophotometric method

Glass	$\text{Fe}^{2+}/\Sigma\text{Fe}$ (%) (Average $\varepsilon = 1.294$)	Glass	$\text{Fe}^{2+}/\Sigma\text{Fe}$ (%) (Average $\varepsilon = 1.20$)
18NS-1300	5.76	13NS-1400	9.74
18NS-1400	9.42	13NS-1500	15.24
18NS-1500	13.90	13NS-1600	18.82
18NS-1600	22.58	13NS-12/88	54.10
18NS-12/88	34.02	13NS-50/50	66.27
18NS-24/76	49.38		
18NS-36/64	59.69		
18NS-50/50	88.76		

Table V. Comparison of slope ratios and concentration ratios of glasses

Glass	Slope	Slope Ratio (M/M ₁₃₀₀)	Concentration Ratio (C/C ₁₃₀₀)	Glass	Slope	Slope Ratio (M/M ₁₄₀₀)	Concentration Ratio (C/C ₁₄₀₀)
18NS-1300	0.0831	1	1	13NS-1400	0.1151	1	1
18NS-1400	0.1308	1.57	1.54	13NS-1500	0.1618	1.41	1.49
18NS-1500	0.1919	2.31	2.31	13NS-1600	0.2224	1.93	1.90
18NS-1600	0.209	2.52	2.79	13NS-12/88	0.6395	5.56	5.64
18NS-12/88	0.462	5.56	5.80	13NS-50/50	0.7833	6.81	7.90
18NS-24/76	0.6614	7.96	8.29				
18NS-36/64	0.7736	9.31	9.84				
18NS-50/50	1.175	14.14	14.60				

Table VI. Molar extinction coefficient of ferrous iron in silicate glasses

Glass Composition (Mole %)	Molar Extinction Coefficient ($l \text{ mole}^{-1} \text{ cm}^{-1}$)	Peak Wavelength (nm)	Ref.
18.56Na ₂ O·81.44SiO ₂	31.4	1140	Present
13Na ₂ O·87SiO ₂	30.33	1170	Present
30Na ₂ O·70SiO ₂	28.91	1050	[12]
30Na ₂ O·70SiO ₂	27.9	1100	[13]
30Na ₂ O·70SiO ₂	26.69	1100	[14]
Commercial Soda- lime and Amber Glass	27.4	1100	[15]

**Table VII. Immiscibility temperatures of 18NS-series
and 13NS-series glasses**

Glass	Immiscibility Temperature (°C)	Glass	Immiscibility Temperature (°C)
18NS	660 ± 2.5	13NS	767 ± 2.5
18NS-1300	631 ± 2.5	13NS-1400	735 ± 2.5
18NS-1400	631 ± 2.5	13NS-1500	737 ± 2.5
18NS-1500	634 ± 2.5	13NS-1600	739 ± 2.5
18NS-1600	636 ± 2.5	13NS-12/88	744 ± 2.5
18NS-12/88	636 ± 2.5	13NS-24/76	744 ± 2.5
18NS-24/76	636 ± 2.5	13NS-36/64	748 ± 3.0
18NS-36/64	638 ± 3.0	13NS-50/50	750 ± 3.0
18NS-50/50	640 ± 3.0

Figure 1. UV-VIS NIR spectra of 13NS-series glasses.

Figure 2. A plot of UV-VIS NIR absorbance versus thickness for 13NS-series glasses doped with 0.5 mole % Fe_2O_3 .

Figure 3. A plot of UV-VIS NIR absorbance versus thickness for 18NS-series glasses doped with 0.5 mole % Fe_2O_3 .

Figure 4. Comparison of the two different methods of iron oxidation state analysis: (a) for 18NS-series and (b) for 13NS-series glasses. The solid line indicates a 1:1 correlation between the two techniques.

(a)

(b)

Figure 5 SEM micrographs of 18NS base glass heat treated at (a) 655 °C for 8 hrs, (b) 660 °C, for 8 hrs.

(a) 18NS-1300 glass, heat treated at 596 °C for 8hrs

(b) 18NS-1400 glass, heat treated at 598 °C for 8 hrs

Figure 6 FE-SEM micrographs of phase separated glasses

Figure 7. Effect of oxidation state of iron on the binodal temperature:
 (a) 18.56Na₂O·84.44SiO₂ glasses doped with 0.5 mole % Fe₂O₃.
 (b) 13Na₂O·87SiO₂ glasses doped with 0.5 mole % Fe₂O₃.
 * The solid line is the binodal temperature of the base glass

Figure 8. X-ray patterns of $18.56\text{Na}_2\text{O}\cdot 81.44\text{SiO}_2$ heated glass: (a) base glass, and (b) glass doped with 0.5 mole % Fe_2O_3 .

III. PUBLICATIONS UNDER THIS GRANT

The work summarized here resulted in a Master's Thesis being submitted by Mr. Jun-Sik Jeoung in the Department of Materials Science and Engineering at the University of Arizona, as well as a manuscript published in the Journal of the American Ceramic Society. The reference for the manuscript is given below:

J.S. Jeoung, W.H. Poisl, M.C. Weinberg, G.L. Smith, and H. Li, "Effect of Oxidation State of Iron on Phase Separation in Sodium Silicate Glasses", Journal of the American Ceramic Society, **84** [8] 1859-64 (2001).