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Effect of Iron and Sodium Inclusion on Some Properties of Silicate Glass

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Abstract: Sodium silicate glasses with a fixed molar percentage of iron and varying percentages of sodium alkali have been synthesized by the method of melt quenching in air. The variation of glass transition temperatures T_g in this series can be correlated to the relative fractions of Fe^{2+} and Fe^{3+} as well as Na^+ ions present in these glasses. UV-Visible spectra showed a trend of optical band gap with Na concentration which is related to the fraction of non-bridging oxygen atoms present in each glass. Magnetization studies showed these glasses to be purely paramagnetic at room temperature but at a temperature of 5K, to have some ferromagnetic character with a ten-fold enhanced magnetization.

INTRODUCTION

Iron is one of the most abundant naturally occurring elements and finds itself as a component in silicate glasses found in nature. The role of iron in the structures of silicate glasses has been the subject of much scientific study. Iron when introduced in a glass possesses dual redox states irrespective of its initial oxidation state. Iron in the trivalent state, Fe^{3+}, is reported to be a network former while Fe^{2+} has a network modifying role [1].

Weigel et al. (2008) and A.C. Wright et al. (2014) have examined soda lime silicate glasses containing iron. The detailed study on these samples show that the property of such glasses are highly dependent on the ratio of Fe^{2+} to Fe^{3+}. The final average of these redox states would have a major effect on the mechanical, structural and spectroscopic properties of these glasses [4-6].

The majority of studies have been made on silicates with variable concentrations of iron in the glass. Few if any authors have examined the properties of these glasses when the iron has been kept constant with variable concentrations of silicate and an alkali ion such as sodium. Presented here are thermal, spectroscopic and magnetic properties of sodium silicate glass with iron kept at a fixed level.

EXPERIMENTAL

Compositions and Preparation

The constituent oxide powders used for the preparation of each glass sample were mixed together in the required relative amounts to yield the desired composition. These initial molar percentages are listed in Table 1. Sodium oxide was derived from sodium carbonate - being a stable salt of sodium - which releases carbon dioxide during the heating process. The samples are coded as Na1, Na2, Na3 and Na4, where Na1 is the glass without iron.

All the samples were synthesized by the melt quench method using a platinum crucibles in batches of 15 g in a 1600 C Carbolite furnace. The mixtures were initially heated to 900 C and held at this temperature for 1 hour for the decomposition of sodium carbonate to sodium oxide. The crucible were held at 1400 C for 15 minutes before removal to an ambient air temperature and cooling within the crucible. The samples were then transferred to a pre-heated (350 C) muffle furnace and cooled overnight to room temperature.

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TABLE 1. Compositions in mole% of the glass under study

Sample	SiO_2(99.9%,Sigma Aldrich)	Na_2O(99.8%, Thomas Baker)	Fe_3O_4(99.8%, Thomas Baker)
Na1	80	20	0
Na2	80	12	8
Na3	76	16	8
Na4	72	20	8

Characterization

Use of the X-ray powder diffraction method found all samples to be vitreous by the absence of any sharp Bragg reflection peaks and the presence of broad oscillations in Q space beyond the first diffraction maximum (data not shown). The differential thermal analyses for the glass transition temperature were performed in the range of 30 C to 1000C using the Shimadzu DTG60 (air environment) at a heating rate of 10 C/min. The oxidation states and optical band gaps were estimated using the Shimadzu UV-2401 PC in reflection mode in the range of 200-800 nm. The Quantum Design, USA PPMS vibrating sample magnetometer at 9 Tesla was used for magnetization studies of the samples in the temperature range of 5K to 300K.

Results and discussion

Differential Thermal Analysis

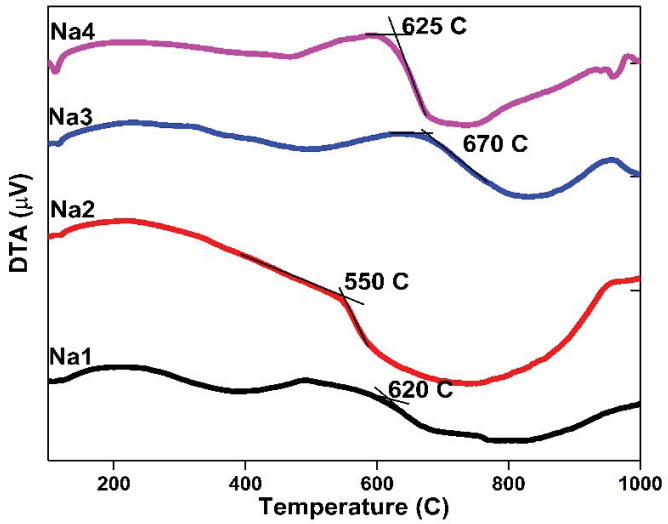

FIGURE 1. . Differential thermal analysis of glasses with and without iron

The Differential Thermal Analysis data of the glass samples are shown in Fig. 1. The sample without iron (Na1) shows a glass transition temperature Tg of 620 C which drops to 550 C with the introduction of iron at the lowest Na concentration of this series. In this glass the low sodium content may have caused the viscosity of the melt to have reduced and led to a lower transition temperature. The role of iron in as a network modifier or former is linked [7] to the presence of Fe^{2+} and Fe^{3+} ions in the melt near Tg. However, with increase in sodium content i.e Na3 and Na4 the glass transition temperature increases to 670 C and then decreases to 625 C. In order to understand the reason for the shift of Tg with Na content, it is necessary to consider the action of both Na and Fe taken together in their roles as network modifier and former ions of the silica.

Spectroscopic Studies using UV-Vis Spectroscopy

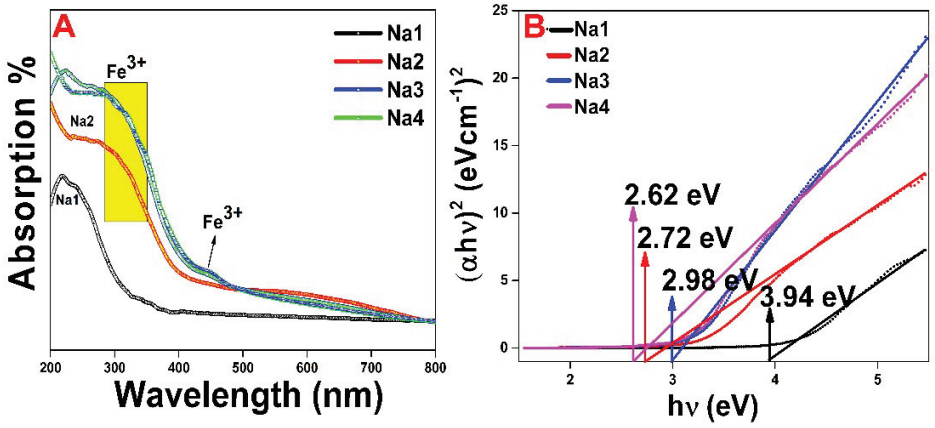

FIGURE 2. (A) Ultra-Violet absorption spectra (B) Tauc's Plot for samples with and without iron.

The absorption spectra in Fig. 2(A), clearly shows the shoulder due to Fe^{3+} at ~ 300-350nm. The absorption is high in the iron containing samples compared to the Na1 on account of its dense dark brown (blackish) color, which makes these glasses opaque. Tauc's plot obtained from the absorption spectra shown in Fig. 2(B) represents the optical band gap energies of each of the samples. The sample without iron (Na1), shows a high band gap energy of 3.94 eV which decreases to ~2.9 – 2.6 eV with the introduction of iron. It is known that in the case of bridging oxygen's the binding is stronger compared to the non-bridging oxygen atoms [8]. Fe^{2+}ions in the iron containing samples, which is known to play the role of network modifier, would promote a larger fraction of non-bridging oxygen ions in the glass structure causing increase in the ionicity of the oxygen ions and leading to a decrease in the optical band gap.

Magnetization study using V S M

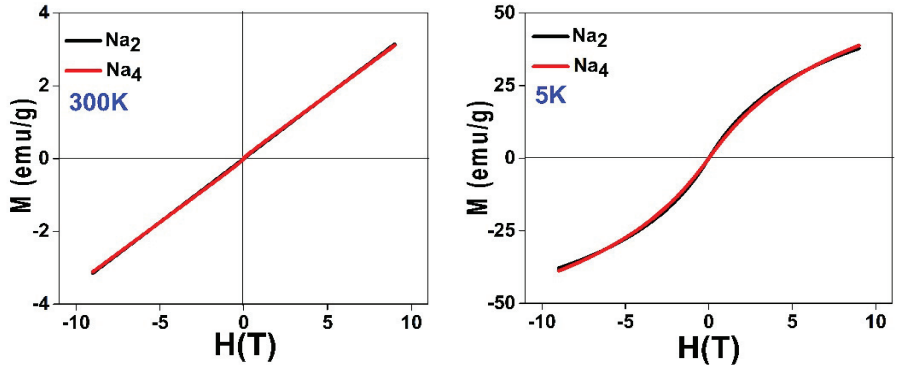

FIGURE 3. M vs H curve of iron containing samples at 300K and 5K.

Figure 3 depicts the room temperature and low temperature magnetic hysteresis (M–H) loops for the iron containing samples. The samples at room temperature are purely paramagnetic, however at 5K a slight tendency to saturation can be observed. At room temperature the maximum value of magnetization at an applied field of 9T is 3 emu/g while at 5K it is 38 emu/g. This large difference in magnetization may be ascribed to the independent

contributions of Fe^{3+} and Fe^{2+}ions in the samples [7]. It may be noted that for the Na2 and Na4 samples, magnetization curves are almost coincident even though their sodium concentrations are substantially different. Hence, it may be said that in these sodium silicate glasses, the magnetization depends on the concentration of iron rather than on the concentrations of sodium ions.

CONCLUSION

The effect of introducing iron and alkali (sodium) into a silica network causes the glass transition temperature to increases or decrease, depending on the relative fractions of these two ion types. This variation of Tg is related to the joint action of the network former or modifier properties of Fe^{2+} and Fe^{3+} as well as that of the Na^{+} ions. UV-Visible absorption spectra show the presence of ferric ions in the glass samples. The optical band gaps were found to decrease with an increase in Na concentration and may be due to the increase of non-bridging oxygen atoms in the iron containing glasses. Magnetization measurements of the samples show them to be paramagnetic at room temperature. The magnetization increases by about an order of magnitude with decrease of temperature. This can be attributed to the contribution to the total magnetic moment by the ferric and ferrous ions individually in a magnetically dilute system like glass.

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