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Effect of manganese oxide on redox iron in sodium silicate glasses

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In this study, Effect of increasing amount of manganese oxide on ultraviolet-visible spectrum in sodium silicate glasses containing iron oxide has been investigated. Iron oxide is existed as ferric and ferrous ions in glasses that presence of manganese oxide leads to iron attend as ferric ions. In this state, glasses absorption ultraviolet light and can be used as a filter of ultraviolet light. In this study, the effect of increasing amount of manganese oxide by ultraviolet-visible spectroscopy has been investigated and changing of ferrous and ferric ions has been measured by wet chemical analysis.

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1. Introduction

Color in glasses is due to attraction and emission of electronic clouds of formed ions. Adding element like Fe, Mn, Ni, Cu, Co… in glasses gives the simplest types of colorful glasses[1]. Presence of these element in glass, leads to resonance in electronic clouds under the radiation of Wight light. When multivalent ions of different elements are brought together interaction take place between them. Resulted valence balance for each element is different from that state that these elements existed by themselves[2-4]. The nature of this interaction is so that one of these elements is oxidized and the other as a complementary of reaction is reduced. This phenomenon has been proved by Khol, Ruddow and Weyl on the basis of interpretation of optical attraction spectra in glasses contain dual compounds of these elements. These spectra are differ from spectra of these element individually and forms of them indicate that increasing relative concentration of high valency of one element take place in the expense of reduction of relative concentration of low valency of other element[3-6]. Iron in glasses exists in two different oxidation states, ferric and ferrous ions. Changing in iron oxidation state in glass along with other transient multivalent elements depend on iron in chemical potential series. Table (1) shows chemical potential series of transient elements that usually are used in changing of reduction-oxidation state. Elements that are over iron in this series if existing in glass contain iron result in more iron oxidation and increasing of Fe^{3+}. Also, presence of tin in glass mixture that has lower chemical potential than iron leads to reduction of iron and increase amount of Fe^{3+}. Also gases like SO_3 are used in kiln atmosphere during melting of glass contain iron for iron oxide and increasing ferric iron. Tin [7] or carbon [3, 6] can be used for reduction of iron in glasses. Manganese, besides being a colouring agent, also played an important role as decolouriser because it oxidises the iron (II). It also by its own colour compensates for the green shade, which the iron produces in glass. Manganese can be present in the glasses as divalent or trivalent ions. In this study, ultraviolet-visible spectrum of sodium silicate glasses contains iron oxide and manganese oxide has been taken by spectroscopy and amount of ferric and ferrous ions has been measured.

Table .1. chemical potential series of some transient elements.

metals	Coupled ionic multivalent
Chromium	Cr^{3+}/ Cr^{6+}
Cerium	Ce^{3+}/ Ce^{4+}
Manganese	Mn^{2+}/ Mn^{3+}
Vanadium	V^{3+}/ V^{5+}
Copper	Cu^{+}/ Cu^{2+}
Arsenic	As^{3+}/ As^{5+}
Antimony	Sb^{3+}/ Sb^{5+}
Iron	Fe^{2+}/ Fe^{3+}
Tin	Sn^{2+}/ Sn^{4+}

2. Experimental

The glass compositions in the mol% are given in Table 2. The glass batches were prepared from reagent grade powders: quartz (SiO_2, 99.9%), sodium carbonate (Na_2CO_3, 99.98%), iron oxide (Fe_2O_3, 99.9%) and manganese oxide (MnO_2, 99.98%).

Table 2. Nominal glass compositions (mol%).

SiO_2	Na_2O	Fe_2O_3	MnO_2
66.5	33.0	0.5	0.0
66.37	32.93	0.5	0.2
66.17	32.83	0.5	0.5
65.84	32.66	0.5	1.0
65.5	32.50	0.5	1.5

The amounts of oxides were weighed by using digital electronic balance. The chemical were then mixed in a pestle mortal. The mixed powder of these samples were placed in recrystallized alumina crucible and melted in an electrically heated furnace. The powder of the samples were initially kept at 1000˚C for 1 hour for calcination to occur and release of water from the starting materials then they were reheated at 1450˚C and kept at this temperature for half an hour in order to achieve the homogeneity. These temperatures should not be higher because it causes a substantial volatilization of reagents. After an entire batch was pre-melted and sintered in the crucible, the temperature was increased stepwise to the melting temperature(1450˚C). The glasses melt were quickly cast at the same temperature in a preheated (T=450˚C) stainless steel mold with dimensions of 2cm×2cm×2.2mm to avoid temperature-caused inhomogeneity. It was then cooled in a preheated furnace to ambient temperature using a cooling rate of $30K.h^{-1}$. After grinding and polishing, the absorption spectra of the glass samples were recorded by a Camspec Double (Beam UV-VIS 350m) spectrophotometer in an optical range from 200 to 1100 nm. Wet chemical analysis was performed according to the Jeoung method [12]. For conducting wet chemical analysis, samples were powdered in mill. Indictor solution was produced in order to ferrous color change be created. For preparing indicator solution, 25 mL of 4% boric acid and 7 mL of 10% potassium hydrogen phthalate and 6 mL of 0.25 % (1,10- phenanthroline) and 2 mL concentrated ammonium was added to beaker. Enough amount of this solution (approximately 2 liters) was prepared for conducting all stage of wet chemical analysis. For changing amount of absorption in 510 nm into ferrous ions, indicator solution is required for drawing calibration schema. Therefore, (0.025, 0.01, 0.05, 0.1, 0.5, 1.5, 2) amount of iron sulfate (II) was added to indicator solution mentioned above and absorption in 510 nm wavelength for all amount of iron sulfate were measured. 30 mg of these powders were dissolved in solution with concentration of 0.4 mL and 1.2 mL HF acid. PH of solutions was reached to 3.3-3.5 by adding ammonium or sulfuric acid. Indicator solution was added to these solutions and volume of them reached to 50 cc. Absorption of these solutions in 510 nm was measured by UV-Vis spectroscopy. After measuring amount of ferrous ions in samples, this amount is subtracted as iron oxide form total added iron and finally amount of ferric iron that is presented in glass obtained.

3. Results and discussion

Fig. 1 shows ultraviolet-visible spectrum of sodium silicate glasses containing iron oxide.

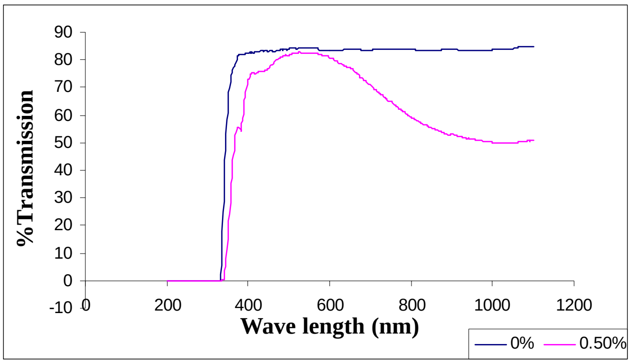

Fig.1 . Ultraviolet-visible spectrum of sodium silicate glasses containing iron oxide.

In spectrum of sodium silicate glass free of additive is not observed absorption peak. Increasing amount of iron oxide leads to absorption peaks appears. The absorbance for Fe^{3+} produces peaks at about 380nm, 420nm and 435 nm on the UV absorption edge, while Fe^{2+} indicates a broad band peak at around 1050 nm. Figure. 2 shows ultraviolet-visible spectrum of sodium silicate-iron containing manganese oxide glasses.

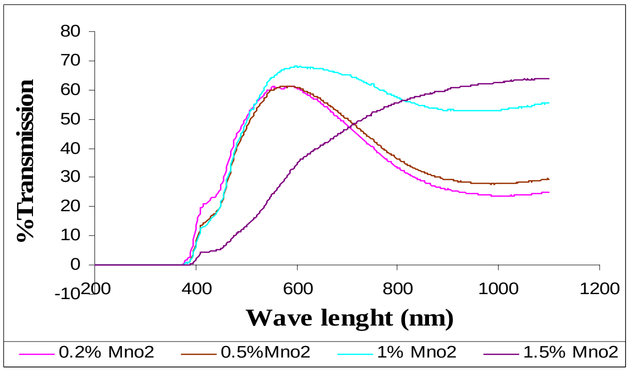

Fig. 2. ultraviolet-visible spectrum of sodium silicate-iron glasses containing manganese oxide.

The concentration of Fe^{3+} increased and that of Fe^{2+} decreased with the addition of more manganese, as indicated by the increase or decrease in their respective absorbances. Thus, manganese, as expected, operated as an oxidizing agent with respect to iron in the glass. As shown in the figure, with increasing manganese oxide, absorption peaks in 380-420 nm and 435 nm have been increased. This phenomenon shows that with increasing amount of manganese oxide, more ferric ions have been formed and absorption peaks have been increased. Absorption peak in 1050 nm has been reduced very much. It can be seen that, glass contain iron oxide without manganese oxide has 60% transmission at ultraviolet region and due to increase of manganese oxide up to 1.0%mol ultraviolet transmission is near zero. Results of wet chemical analysis shows amount of ferrous and ferric ions in the glasses (Table 3).

Table 3. Results of wet chemical analysis due to increasing of manganese oxide.

Fe^{2+}/ Fe^{3+}	Fe^{3+}Wt%±0.01	Fe^{2+}Wt%±0.01	Samples
0.14	0.88	0.12	0.0% mol MnO_2
0.1	0.91	0.09	0.2% mol MnO_2
0.09	0.92	0.08	0.5% mol MnO_2
0.07	0.93	0.07	1.0% mol MnO_2
0	1	0	1.5% mol MnO_2

As shown in the table, increasing of manganese oxide up to 1.5% mol prevent from forming ferrous ions and all of iron attend as ferric ions in glass network. Manganese oxide locates over iron in chemical potential series and reduces iron oxide. Therefore ferrous ions are reduced and existed iron in glass change to ferric iron. Figure 3 shows changing of reduction-oxidation ratio of iron with increasing manganese oxide.

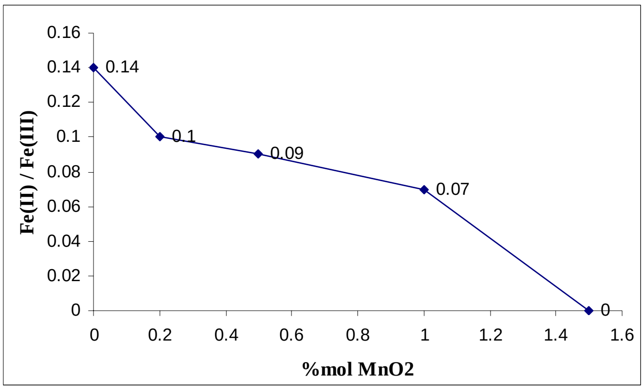

Fig.. 3. Reduction-oxidation of iron in glasses with increasing manganese oxide.

4. Discussion

Based upon the series of reduction potentials (Table 1), manganese should be the most effective oxidizing agent for iron. In glasses containing 0.5%mol Fe, increasing manganese oxide in samples has a different effective oxidizing agent. Iron and manganese in this glass exists as an equilibrium between iron and manganese ions, as represented by (Eq):

$$Mn^{2+} + Fe^{3+} \leftarrow\rightarrow Mn^{3+} + Fe^{2+}$$

It is shown, that the redox reaction is shifted to the left during cooling. This change in the reduction potential of manganese may be the result of a Mn–Fe complex that forms within the melt. This complex removes Mn^{3+} from the melt, making the percent of manganese available as a potential oxidizer much less than expected. This complex may register in the visible spectrum as a weak peak around 420 nm, shown in figure .2 shows that the peak attributed to this complex is sensitive to the presence of both iron and manganese; alternatively, the Mn–Fe complex may enhance the weak Fe^{3+} absorption in this spectral region. The amount of the Mn–Fe complex formed is a function of the concentration of manganese oxide. Changing the amount of manganese in the glass had the greatest effect on the formation of the Mn–Fe complex, as is evidenced by the reduction in effectiveness of Mn^{3+} as an oxidizing agent. In all glasses increasing manganese oxide in glasses was more effective at oxidizing Fe^{2+} (reducing intensity of 1050 nm peak) [13-14]. Ferric iron in glass develop brownish- yellow color and ferrous develop blue color. Color of glass contain iron is combination of these two colors. Therefore it is bluish-green. Increasing of manganese oxide and consequently ferric ions color of glass is more yellow and in more manganese oxide is brownish-yellow.

5. Conclusion

Sodium silicate glasses containing iron and manganese oxide as additives were prepared by melting at 1450˚C temperatures. The redox state of iron in the glass was measured by optical absorption spectroscopy and wet chemical analysis. The oxidation-reduction of ferric and ferrous ions was controlled by manganese oxide. The results of wet chemical analysis also showed that increasing of manganese oxide cause forming more ferrous ions.

Increasing manganese oxide in sodium silicate glasses contain iron oxide lead to increases ferric ions and reduced ferrous ions in glass.

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