



Optical spectroscopy of sodium silicate glasses prepared with nano- and micro-sized iron oxide particles

Behzad Mehdikhani^{1,2,*}, Gholam Hossein Borhani²

¹Standard Research Institute, Building and Construction Department, Karaj, Iran

²Malek-e-ashtar University of Technology, Department of Materials Engineering, Isfahan, Iran

Received 4 June 2013; received in revised form 27 July 2013; received in revised form 4 September 2013; accepted 7 September 2013

Abstract

Wet chemical analysis and UV-VIS spectroscopy methods were used to determine the oxidation state of iron in Na₂O-2SiO₂ glasses, containing 0.3 mol% of Fe₂O₃. The oxidation state of iron in the sodium silicate glasses was varied by changing the size of iron oxide particles used for preparation of glass batches and the melting temperature. In sodium silicate glasses iron commonly exists as an equilibrium mixture of ferrous ions, Fe²⁺, and ferric ions Fe³⁺. The increase of the melting temperature led to the transformation of ferric ions to ferrous ions. It was also shown that in the glasses prepared from nano-sized iron oxide particles the Fe²⁺/Fe³⁺ equilibrium ratio is lower (i.e. smaller amount of ferrous ions were formed) comparing to that in the glasses prepared from micro-sized iron oxide particles.

Keywords: sodium silicate glass, iron oxide, UV-VIS spectroscopy, wet chemical analysis

I. Introduction

Iron in glasses exists as equilibrium between the yellow ferric ion, Fe³⁺, and the blue ferrous ion, Fe²⁺. However, the absorbance of Fe²⁺ in the near-infrared is so strong that even a small amount, less than 4% of the total iron present in the glass, will give the glass an undesirable green hue. In addition, the concentration of Fe³⁺ in the glass has to be relatively high in order to induce sufficient yellow colour. However, glasses with relatively high concentrations of iron are becoming more common commercially. The majority of commercial green glass contains iron oxide [1–7] because it is made with raw materials with low purity. Iron absorption peaks in the visible region lead to the development of green colouring [2]. The control of the iron oxidation state in commercial glasses with a special application is very important [4], and the effects of iron on the optical properties of glass have been studied widely by many researchers [5–9]. Because iron has two redox states, Fe²⁺ and Fe³⁺, and these states have different colours, control of the redox condition during melting is impor-

tant in adjusting the transmittance of glass in the wavelength regions of UV, visible light and IR [6]. The presence of absorption peaks of ligand field of ferric iron in obtained spectra from silicate glasses is distinguishable at 380 nm, 420 nm and 435 nm wavelengths [10], and broad absorption peak at wavelength of 1050 nm is due to ferrous iron [3]. It has been already shown [10,11] that change in melting point results in different amount of ferrous and ferric ions in sodium silicate glasses containing iron oxide. Thus, increasing the melting point leads to an increase of the absorption at wavelength of 1050 nm, i.e. increase of ferrous iron concentration in glasses (Fig. 1) [10].

In our previous paper [11], the influence of melting temperature on the redox state of iron in sodium silicate glasses prepared with nano-sized iron oxide particles (0.5 mol%) was investigated. In this study, sodium silicate glass batches containing 0.3 mol% of nano-sized and micro-sized iron oxide particles were prepared and melted at various temperatures. The prepared glasses were analysed by UV-VIS spectroscopy and wet chemical analysis, and the influence of iron oxide particle size and melting temperature on the Fe²⁺/Fe³⁺ equilibrium ratio was discussed.

* Corresponding author: tel: +98 91 264 17 516
fax: +98 24 132 30 496, e-mail: mehdikhani@standard.ac.ir

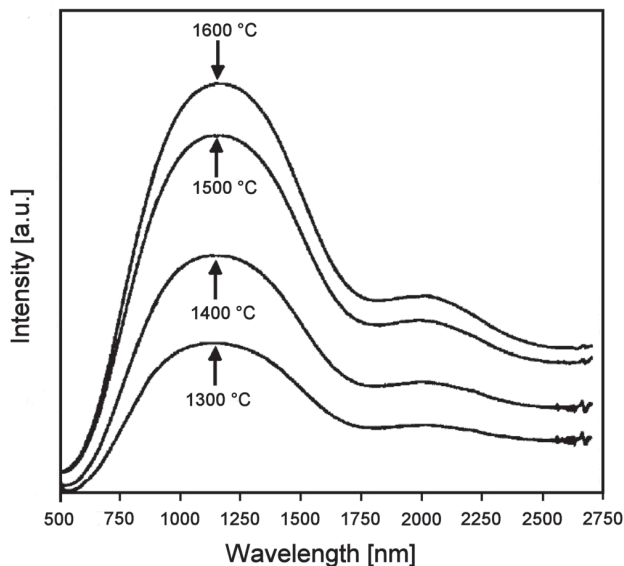


Figure 1. UV-VIS-NIR spectra: temperature effects on 1050 nm band intensities for glasses melted between 1300 and 1600 °C in air [10]

II. Experimental procedure

2.1. Glass preparation

The batches were prepared by mixing of reagent grade raw materials, quartz (SiO_2 , 99%) and sodium carbonate (Na_2CO_3 , 99.9%), in $\text{SiO}_2/\text{Na}_2\text{O}$ molar ratio 2 : 1 and addition of 0.3 mol% of iron oxide. Two types of iron oxide were used: i) nano-sized powder with the average grain size of 6 nm (GmbH Plasma Chem Company, 99.9%) and ii) micro-sized powder (Merck, 99.8%). Glass batches were melted in an alumina crucible positioned in Vecstar kiln. Heating rate of 5 °C/min and air atmosphere were used. The batches were heated at temperatures between 900 °C and 950 °C. These conditions were used for pre-melting as higher temperature 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, which was

varied from 1350 °C to 1650 °C with the holding time of 2 to 2½ hours. In the next step, the formed glass melt was quickly cast in a preheated ($T = 450$ °C) stainless steel mold with dimensions of 20×20×2.2 mm to avoid temperature-caused inhomogeneity. It was then cooled in a preheated furnace to ambient temperature using a cooling rate of 30 °C/h. After 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.

2.2. Wet chemical analysis

Wet chemical analysis was performed according to the Jeoung method [12] for the analysis of Fe^{2+} 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 NH_4OH was prepared in the 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 to the sample beaker. Immediately after dissolution of the glass (within 15 s 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 NH_4OH and/or diluted H_2SO_4 . This solution was transferred to a 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 using a digital UV-VIS spectrophotometer.

III. Results and discussion

Figure 2 shows the UV-VIS spectra (in the wavelength interval 350–500 nm) of sodium silicate glasses prepared from the micro-sized iron oxide powder at 1350–1650 °C. Peaks at about 380 nm, 420 nm and 435

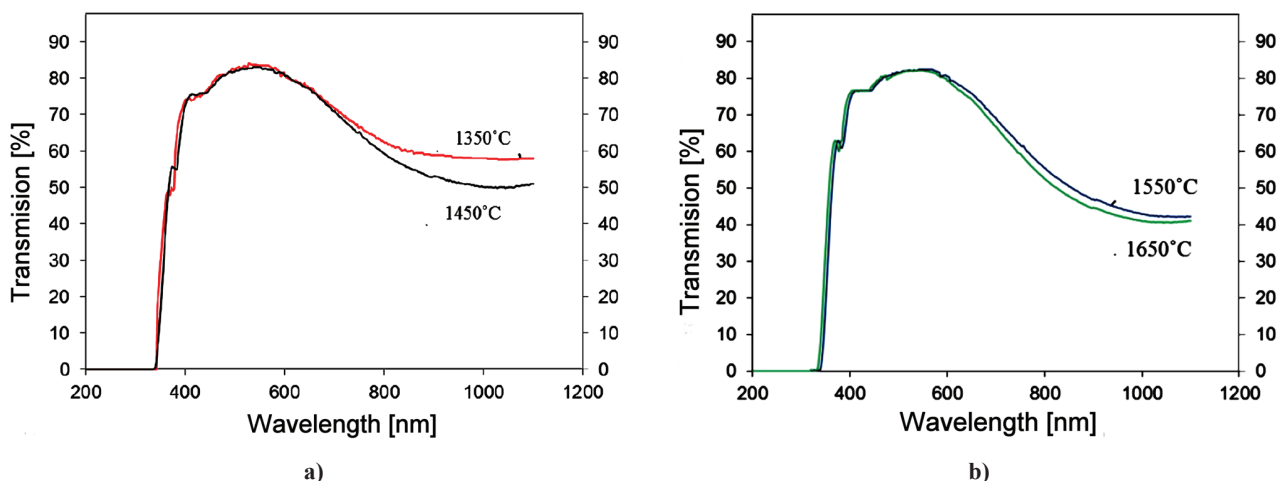


Figure 2. UV-VIS spectra of glasses prepared with micro-sized iron oxide powder and melted at: a) 1350 °C and 1450 °C, b) 1550 °C and 1650 °C

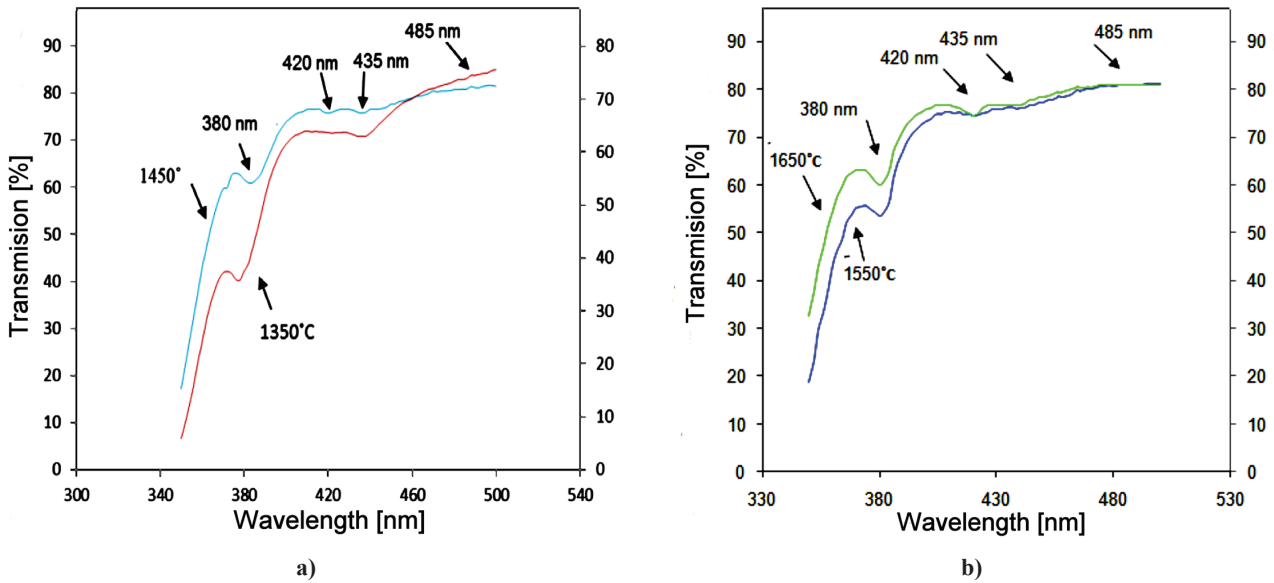


Figure 3. UV-VIS spectra of glasses prepared with micro-sized iron oxide powder and melted at: a) 1350 °C and 1450 °C, b) 1550 °C and 1650 °C

Table 1. Amount of Fe³⁺ and Fe²⁺ ions obtained by wet chemical analysis in glasses prepared with micro-sized iron oxide powder

Melting temperature [°C]	Fe ³⁺ concentration [wt.%]	Fe ²⁺ concentration [wt.%]	Fe ²⁺ /Fe ³⁺ ratio
1350	0.92	0.08	0.08
1450	0.88	0.12	0.13
1550	0.82	0.18	0.22
1650	0.81	0.19	0.23

nm are due to the presence of Fe³⁺. The characteristic peaks can be seen in all glass samples (Fig. 2). However, the intensity of absorbance peaks decreases with the increase of the melting temperature, indicating that the amount of ferric ions decrease.

Figure 3 shows the UV-VIS spectra in broader wavelength interval, from 350 nm to 1100 nm, where the characteristic broad absorption band at around 1050 nm (due to presence of Fe²⁺) can be seen. It is obvious that the intensity of the absorption peak at 1050 nm, and

thus the amount of ferrous ions, increases with the increase of the melting temperature (Fig. 3).

The amount of ferric and ferrous ions in the glass samples prepared with the micro-sized iron oxide particles and melted at different temperatures was determined by wet chemical analysis, and the results are shown in Table 1 and Fig. 4. The obtained results confirmed the trends observed by UV-VIS spectroscopy, i.e. the increase of ferrous and decrease of ferric ions with the increase of the melting temperature.

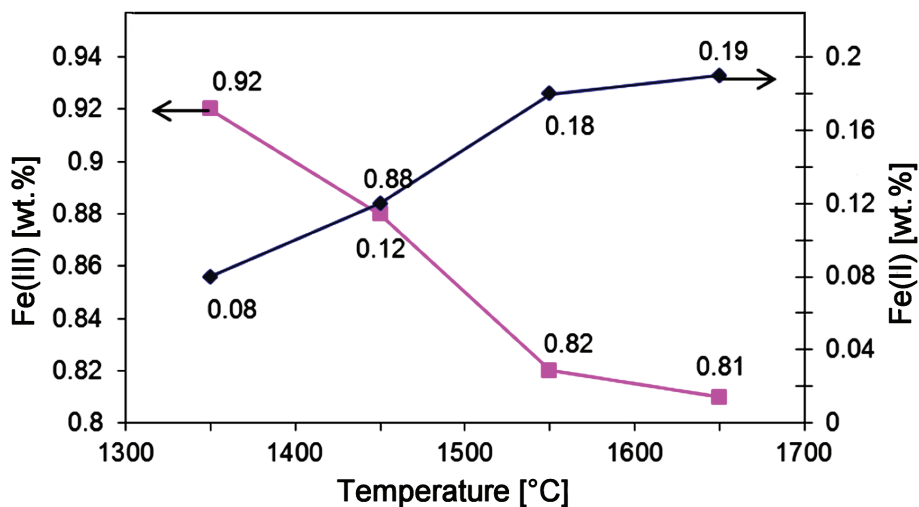


Figure 4. Amount of Fe³⁺ and Fe²⁺ ions (obtained by wet chemical analysis) in glasses prepared with micro-sized iron oxide powder versus melting temperature

Table 2. Amount of Fe³⁺ and Fe²⁺ ions obtained by wet chemical analysis in glasses prepared with nano-sized iron oxide powder

Melting temperature [°C]	Fe ³⁺ concentration [wt.%]	Fe ²⁺ concentration [wt.%]	Fe ²⁺ /Fe ³⁺ ratio
1350	0.92	0.08	0.08
1450	0.91	0.09	0.10
1550	0.87	0.13	0.15
1650	0.85	0.15	0.17

The concentration of ferric and ferrous ions in the glass samples prepared with the nano-sized iron oxide particles and melted at different temperatures was also determined by wet chemical analysis and the results are shown in Table 2 and Fig. 5. It is obvious that addition of the nano-sized iron oxide particles in glass batches have similar influence on the concentration of Fe³⁺ and Fe²⁺ ions like addition of the micro-sized iron oxide particles, only the change of the ions concentration is less pronounced.

As it was already mentioned [11], at low temperatures (before a melt formation) reaction between oxygen in the atmosphere and species in the raw material occurs easily, and this can have influence on the redox state of the species and the oxygen activity in the melt. During the melting, oxygen can be produced at elevated temperature if the material contains Fe³⁺ as a result of a reaction with O²⁻ [6]:



The equilibrium of the reaction shifts to the right at higher temperatures, which cause an increase in oxygen concentration in the glass melt. Such phenomena are well known not only in glass [6] but also in melt containing redox species by oxygen equilibrium pressure [13] or voltammetry [14]. Thus, if a glass batch is prepared with the micro-sized iron oxide particles the concentration of Fe²⁺ ions and Fe²⁺/Fe³⁺ equilibrium ratio will increase with increasing the melting temperature,

completely confirmed by our results (Fig. 4). On the other hand, the addition of iron oxide nanoparticles in a Na₂O·2SiO₂ batch cause the formation of the melt layers at lower temperature. With the increase of temperature, more oxygen is generated by the reduction of ferric ions; thus, more ferrous ions will be formed [6]. However, the release of oxygen from the batch containing the melt layers to the atmosphere is prevented due to the low diffusion coefficient of oxygen in the melt. Under such conditions, the reaction (1) is suppressed due to the high oxygen activity, and the concentration of Fe²⁺ in the melt is kept low. Thus, in the Na₂O·2SiO₂ glasses prepared with the nano-sized iron oxide particles an increase of temperature leads also to the transformation of ferric ions to ferrous ions, but the concentration of Fe²⁺ ions in the melt is kept lower than in the glasses prepared with the micro-sized iron oxide powder.

The results obtained in this paper, on the effect of the melting temperature increase on the Fe²⁺/Fe³⁺ equilibrium ratio, is compared with already published results (Fig. 6) [1, 15]. The slope variation in Fig. 6 can be correlated to different characteristics of batches used for preparation of sodium silicate glasses, i.e. mostly due to different size of iron oxide particles. It is obvious that the lowest slope has sample prepared from the glass batch containing the nano-sized iron oxide particles. This can be explained with the fact that the concentrations of oxygen, Fe²⁺ and Fe³⁺ ions in the melts are controlled by the

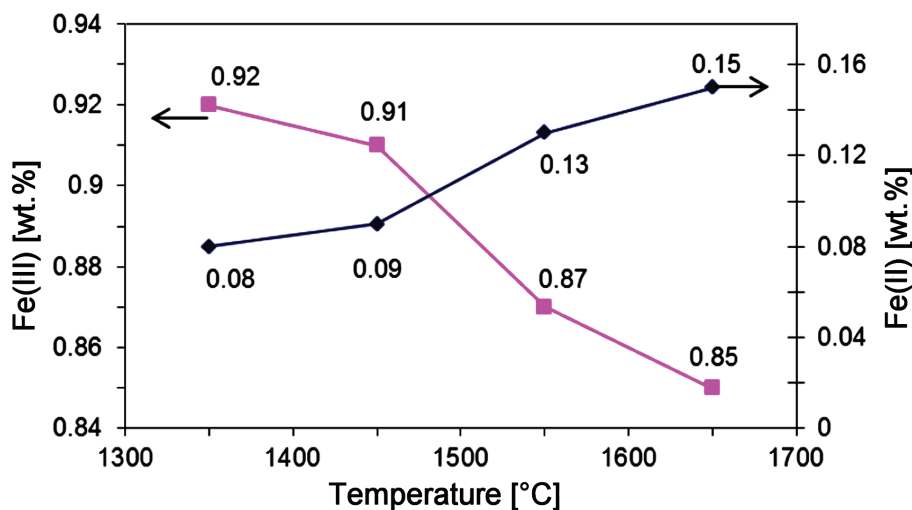


Figure 5. Amount of Fe³⁺ and Fe²⁺ ions (obtained by wet chemical analysis) in glass prepared with nano-sized iron oxide powder versus melting temperature

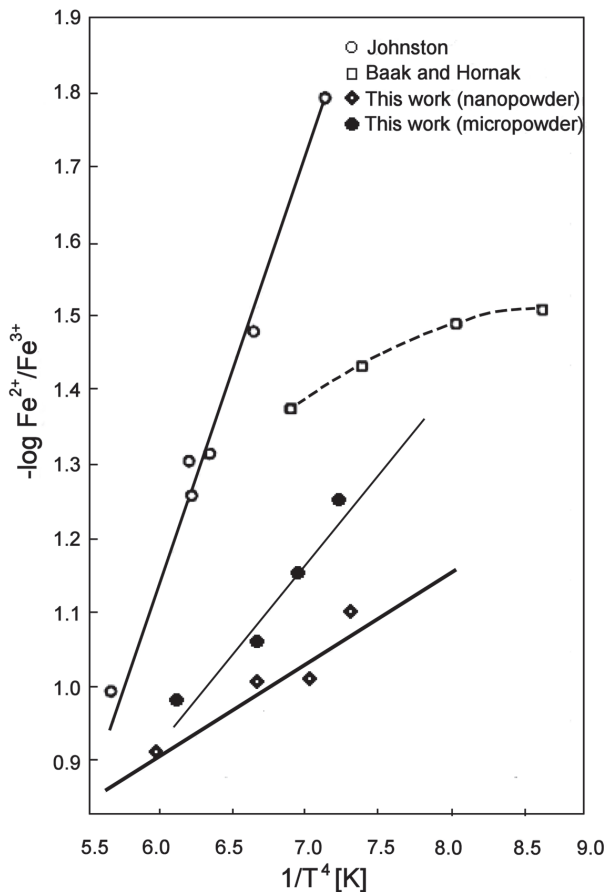


Figure 6. Effect of melting temperature on $\text{Fe}^{2+}/\text{Fe}^{3+}$ equilibrium ratio in iron-sodium silicate glasses

reaction (1) and the equilibrium of the reaction is strongly influenced by the formation of the molten layers especially at lower melting temperatures.

IV. Conclusions

Sodium silicate glasses with 0.3 mol% iron oxide were prepared at different melting temperatures. The oxidation state of iron in the $\text{Na}_2\text{O}\cdot 2\text{SiO}_2$ glasses was controlled by changing the particle size of iron oxide powder used for preparation of glass batches and the melting temperature. The redox state of iron in the glass was measured by optical absorption spectroscopy and wet chemical analysis. The increase of melting temperature led to the reduction of ferric ions to ferrous ions. The introduction of iron oxide nanoparticles into the glass batches caused fewer ferrous ions to be formed and lower $\text{Fe}^{2+}/\text{Fe}^{3+}$ equilibrium ratio compared with micro-sized iron oxide powder.

Acknowledgements: The authors are indebted to the ceramic laboratory of the Standard Research Institute, which supplied the raw materials for the development of this re-

search and to the Building and Construction Department of Standard Research Institute for its financial support.

References

1. W.D. Johnston, "Oxidation-reduction equilibria in iron-containing glass", *J. Am. Ceram. Soc.*, **47** [4] (1963) 198–201.
2. W. Vogel, *Properties of Colored Glasses, Vol. 1*, pp. 138–200, Chemistry of Glass, New York, 1925.
3. C.R. Bamford, *Glass Science and Technology, Color Generation and Control in Glass*, Elsevier Scientific, New York, 1977.
4. F.V. Tolly, *Foundation of Glass Industry*; Vol. 3, pp. 1316–1318, Qazvin glass Co, Qazvin, 1991.
5. K.R. Kukadapu, G.L. Li, H. Smith, "Moossbauer and optical spectroscopic study of temperature and redox effects on iron local environments in a Fe-doped (0.5 mol% Fe_2O_3) $18\text{Na}_2\text{O}\cdot 72\text{SiO}_2$ glass", *J. Non-Cryst. Solids*, **317** [3] (2003) 301–318.
6. M. Yamashita, T. Akai, R. Sawa, "Effect of preparation procedure on redox states of iron in soda-lime silicate glass", *J. Non-Cryst. Solids*, **354** [40–41] (2008) 4534–4538.
7. K. Sakaguchi, T. Uchino, "Compositional dependence of infrared absorption of iron-doped silicate glasses", *J. Non-Cryst. Solids*, **353** [52–54] (2007) 4753–4761.
8. S.B. Donald, A.M. Swink, H.D. Schreiber, "High-iron ferric glass", *J. Non-Cryst. Solids*, **352** [6–7] (2006) 539–543.
9. C. Weigel, L. Cormier, G. Calas, L. Galois, D.T. Bowron, "Nature and distribution of iron sites in a sodium silicate glass investigated by neutron diffraction and EPSR simulation", *J. Non-Cryst. Solids*, **354** (2008) 5378–5385.
10. W.A. Weyl, *Coloured Glasses*; Vol. 1, pp. 60–89, Dawson's of Pall Mall, London, UK, 1959.
11. B. Mirhadi, B. Mehdikhani, "Effect of batch melting temperature and raw material on iron redox state in sodium silicate glasses", *J. Korean Ceram. Soc.*, **48** [2] (2011) 117–120.
12. J.S. Jeoung, W. Hoard, "Effect of oxidation state of iron on phase separation in sodium silicate glasses", *J. Am. Ceram. Soc.*, **84** [8] (2001) 1859–1864.
13. T. Tran, M.P. Brungs, "Applications of oxygen electrodes in glass melts: II, Oxygen probes for the measurement of oxygen potential in sodium disilicate glass", *J. Physics Chem. Glasses*, **21** (1980) 178–183.
14. K.D. Kim, S.K. Kwon, "Redox equilibrium of $\text{Fe}^{3+}/\text{Fe}^{2+}$ and diffusivity of iron in alkali-alkaline earth-silicate glass melts", *J. Ceram. Process. Res.*, **11** (2010) 460–464.
15. J.E. Fenstermacher, "Optical absorption due to tetrahedral and octahedral ferric iron in silicate glasses", *J. Non-Cryst. Solids*, **38** [1] (1980) 239–244.

