SPECTROSCOPIC ANALYSIS OF IRON DOPED GLASSES WITH COMPOSITION CLOSE TO THE E-GLASS: A PRELIMINARY STUDY

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The iron doped glasses with composition close to the commercially produced E-glass, approximated by a five component system MgO–CaO–B_2O_3–Al_2O_3–SiO_2, were studied by UV VIS NIR spectroscopy. The calibration of the absorbance with respect to Fe^{2+} concentration allowed to determine the extinction coefficient for Fe^{2+} species for this type of glasses; at 10000 cm^{-1} was found to be 15.99 ± 0.09 $dm^3.mol^{-1}.cm^{-1}$. The iron redox ratio, $Fe^{2+}/\Sigma Fe$, was determined from the spectra. It was found that redox ratio increases with the increasing amount of alkaline-earth oxides in the glass. Principal component analysis of the set of studied spectra (in the range form 6700 cm^{-1} to 18000 cm^{-1}) resulted in two to three independent spectral components. Deconvolution of the spectral bands centred at about 5000 cm^{-1} and 10000 cm^{-1} showed that Fe^{2+} ions in studied glasses are predominantly in octahedral coordination.

INTRODUCTION

The behaviour of iron species in glass continues to be studied for several reasons. Iron is a key colorant in glasses used for optical applications, and it can be present in many glasses either as a deliberate addition or as an impurity arising from raw materials or furnace refractories. Iron may occur in a number of oxidation states, however in silicate glasses it is usually present as Fe(II) and Fe(III). Iron in these oxidation states may occur predominantly in tetrahedral and octahedral coordination. The contribution of each of these redox states to the transmission spectrum is notably different. The redox ratio and coordination polyhedra of iron and the chemistry of glass matrix in which it is present are closely interrelated and can substantially influence the resulting optical properties. In this respect, many systems, especially of iron doped three or four component oxide systems, have been studied [1-7].

In the present paper, we report a preliminary spectroscopic study of iron doped glasses with composition close the commercially produced E-glass (Table 1), which was approximated by a five component system MgO–CaO–B_2O_3–Al_2O_3–SiO_2. The effect of alkaline-earth oxides on $Fe^{2+}/\Sigma Fe$ ratio is discussed in more details.

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EXPERIMENTAL

Glass batches were prepared using fine powdered analytical grade purity Al_2O_3, $CaCO_3$, MgO, H_3BO_3, SiO_2 and Fe_2O_3. Batches to produce 200 g or 400 g of glass were mixed thoroughly in a homogenizer (plastic container was used) for 24 h and melted in a superkanthal furnace at 1500°C for 3 h in ambient atmosphere. The furnace was equipped with motorized Pt-10%Rh stirrer to assure the homogeneity of glass melts. Molten glasses were poured into preheated stainless steel mould, allowed to cool slightly, and the glass blocks were then placed in an electric muffle furnace and annealed at temperature of approximately 600°C. Samples were held at this temperature for 1 h to release internal stress, and were then slowly (~1°C/min) cooled down to room temperature.

Density of prepared iron doped glasses at room temperature was measured by the Archimedes method using distilled water as the suspension medium.

Wet chemical analysis of the $Fe^{2+}/\Sigma Fe$ ratio was conducted by spectrophotometry, after complexation of Fe^{2+} ions by 1,10-phenathroline, using a technique described in ICG/TC2 report compiled by O. Corumluoglu et al. [8].

Samples for optical spectroscopy were prepared in the form of polished glass plates with typical specimen dimensions of 20×20 mm and thickness between

1-2 mm. UV-VIS-NIR spectra were recorded in the wavelength range of (300-2200) nm using a UV-VIS-NIR spectrometer Varian Cary 2380. The spectra of the iron containing samples were recorded versus air as reference, corrected for reflectance and normalised to the 1 cm thickness of glass specimen. The spectra were deconvoluted using the software PeakFit® (ver. 4.12, Seasolve Inc.).

RESULTS AND DISCUSSION

Table 1. Composition of iron doped glasses in molar %.

Glass	SiO_2	B_2O_3	Al_2O_3	CaO	MgO	Fe_2O_3
Center (0.5)	57.02	4.59	8.96	26.49	2.44	0.50
Center (0.25)	57.27	4.59	8.96	26.49	2.44	0.25
Center (0.1)	57.42	4.59	8.96	26.49	2.44	0.10
MgO^- (0.25)	58.71	4.70	9.18	27.15	0.00	0.25
MgO^+ (0.25)	55.90	4.48	8.75	25.86	4.76	0.25
CaO^- (0.25)	59.05	4.73	9.24	24.22	2.52	0.25
CaO^+ (0.25)	55.59	4.46	8.70	28.63	2.37	0.25

The optical spectra of the studied iron doped glasses are shown on Figure 1. Several typical spectral features due to the transitions originating from both Fe^{2+} and Fe^{3+} oxidation states of iron are clearly seen. The main absorptivities of Fe^{2+} occur at wavenumbers of around 5000 cm^{-1} and 10000 cm^{-1}, those of Fe^{3+} are usually observed at (20000, 22500, 24000 and 26000) cm^{-1} [3,4]. Additionally, an oxygen-metal charge-transfer band (OMCT) due to both Fe^{2+} and Fe^{3+} occurs at wavenumbers >27000 cm^{-1}. The absorption at ~5000 cm^{-1} and 10000 cm^{-1} can be attributed to the spin-allowed transitions corresponding to the $^5T_2(D) \rightarrow {}^5E(D)$ transition for octahedrally and $^5E(D) \rightarrow {}^5T_2(D)$ for tetrahedrally-coordinated Fe^{2+} sites, respectively [1,5]. Fe^{3+} produces a more complicated set of absorptions than Fe^{2+}. Since Fe^{3+} is a d^5 ion, all d-d transitions are spin-forbidden and approximately 10-100 less intense than spin-allowed transitions. The majority of Fe^{3+} d-d bands are observed at energies greater than ~20000 cm^{-1} (see Figure 1), although some Fe^{3+} bands are observed at energies as low as ~14000 cm^{-1} [1,3-5]. Unfortunately, the absorption band centered at about 26300 cm^{-1} (380 nm), typical for Fe^{3+} species and used for redox ratio determination, was not resolved; this band is obscured by strong charge transfer absorption. This fact disables to determine either precise position of this absorption band or its intensity.

In order to estimate the iron redox ratio from optical spectra, the scaling of the absorption band at 10000 cm^{-1} with respect to concentration of Fe^{2+} ions was needed due to the lack of the experimental data for studied glasses. The spectral absorbance at 10000 cm^{-1} of the peak, which has been widely attributed to Fe^{2+} cations occupying a range of distorted octahedral sites, has been obtained for each sample by optical absorption spectroscopy. Calibration is provided using measured peak absorbances for three glass samples (samples denoted as "Centre"), similar in composition to others studied glass samples, with different total iron concentration (as Fe_2O_3 in the batch). The concentration of Fe^{2+} ions, Fe_{total}, and iron redox ratio ($Fe^{2+}/\Sigma Fe$) were determined by wet chemical analysis. The results of wet chemical analysis are summarized in Table 2. Using the measured absorbance of the peak at 10000 cm^{-1} for three samples and determined concentration of Fe^{2+} ions (or $Fe^{2+}/\Sigma Fe$) by wet chemical analysis, a calibration graph has been obtained. The extinction coefficient for 10000 cm^{-1} was found to be (15.99 ± 0.09) $dm^3.mol^{-1}.cm^{-1}$. This allows quantification of the optically-detected $Fe^{2+}/\Sigma Fe$ ratio; iron redox ratio was estimated from absorption of Fe^{2+} at 1000 nm and total iron concentration. The mentioned method makes the following assumptions: (i) all Fe contents fall within the limits of applicability of Lambert-Beer´s law; (ii) iron ions are found in separate octahedral and tetrahedral sites not in clusters; (iii) the

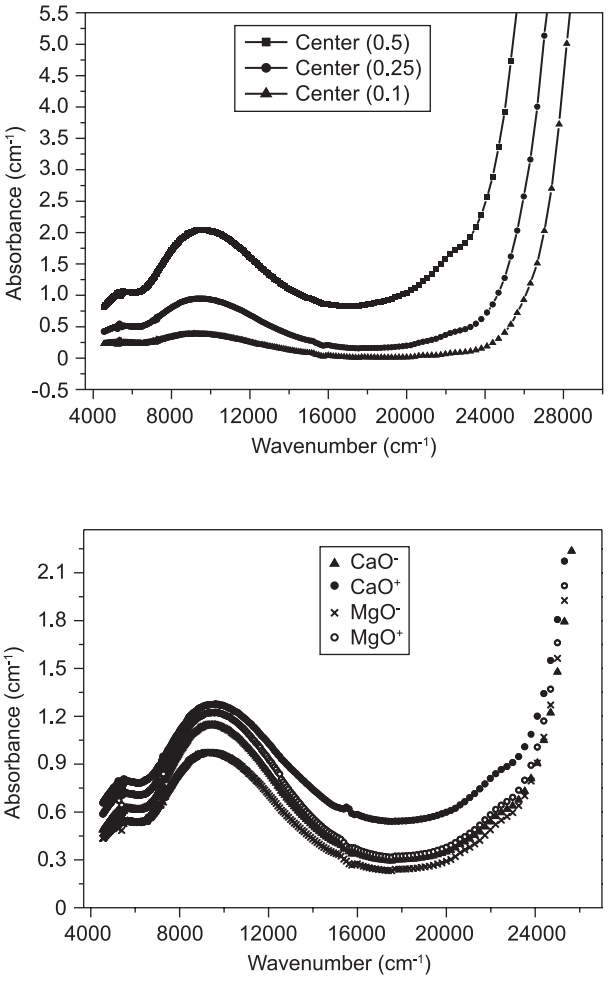

Figure 1. Experimental UV-VIS-NIR spectra of studied glasses doped with Fe_2O_3.

only contribution to the peak at 10000 cm^{-1} arises from Fe^{2+}; (iv) Fe^{2+} extinction coefficients remain unchanged; and (v) the fraction of Fe^{2+} cations that are octahedrally coordinated remains constant for all samples and calibration glasses.

The results of the estimated iron redox ratios, $Fe^{2+}/\Sigma Fe$, for the studied glasses are presented in Figure 2. For the samples denoted as "Center", the redox ratio increases with increasing amount of Fe_{total}. For the pairs of glass samples MgO^+ and MgO^-, and CaO^+ and CaO^-, the lower redox ratio values were found for the glasses MgO^- and CaO^-. Thus, increasing amount of alkaline-earth oxides increases the iron redox ratio. This effect is more pronounced for MgO^+ and MgO^- glass samples (see Figure 2). This behaviour can be rationalized in terms of equilibrium between Fe^{3+} ions in tetrahedral coordination and Fe^{2+} ions in octahedral coordination as described by the following reaction:

$$2^{[6]}Fe^{2+} + 1/2\ O_2 = 2^{[4]}Fe^{3+} + O^{2-} \qquad (1)$$

where $^{[4]}Fe$ and $^{[6]}Fe$ denotes 4-fold and 6-fold coordination of iron. Many authors [1-5, 9] showed that Fe^{3+} ions in glasses should be 4- or 6-fold coordinated, preferably 4-fold coordinated in silicate glasses. Fe^{2+} ions preferably should be 6-fold coordinated. In terms of reaction (1), increasing amount of alkali earth oxides thus leads to the increasing concentration of Fe^{2+} ions in glasses and vice versa.

Table 2. Ferrous, ferric and total iron concentration (mol/dm^3) and redox ratio as determined by wet chemical analysis.

	Glass		
	Center (0.5)	Center (0.25)	Center (0.1)
Fe_2O_3(wt.%)	1.363 ±0.003	0.712 ±0.001	0.3052 ±0.0001
Fe^{2+}	0.129 ±0.002	0.061 ±0.005	0.0249 ±0.0004
Fe^{3+}	0.332 ±0.001	0.180 ±0.004	0.0782 ±0.0004
Fe_{total}	0.4605 ±0.0008	0.2408 ±0.0005	0.10312 ±0.00004
Fe^{2+}/Fe_{total}	0.279 ±0.004	0.25 ±0.02	0.241 ±0.004

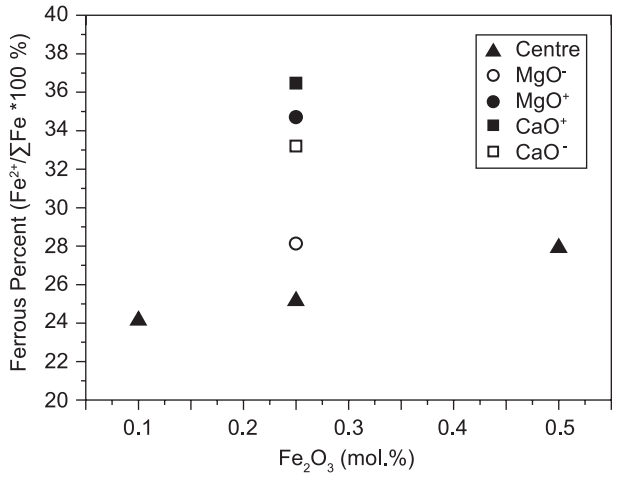

Figure 2. Redox ratios determined from UV-VIS-NIR spectra for studied glasses.

Deconvolution of the spectral bands centred at about 5000 cm^{-1} and 10000 cm^{-1} showed that Fe^{2+} ions in studied glasses are predominantly in octahedral coordination. The spectral band centred at about 5000 cm^{-1} was simulated by one band, and band centred at about 10000 cm^{-1} was decomposed into 3 bands, two of higher intensity and one of low intensity (Figure 3).

Using the Matlab® Factor analysis Toolbox (www.chemometrics.com) the dimension of the linear space spanned by the full set of measured spectra was determined by the principal component analysis (PCA) method [10-12]. Only the spectral data ranging from 6700 cm^{-1} to 18000 cm^{-1} were taken into account in the PCA treatment. The obtained results can be summarized as indicating three independent spectral components. First two components were identified with Fe^{2+} spectra, and the third component (~14000 cm^{-1}) is a minor significance. The origin of this band seems to be unclear, some authors assume that it is due to the both Fe^{2+} and Fe^{3+} [2,13].

CONCLUSIONS

The iron doped glasses from five component system $MgO–CaO–B_2O_3–Al_2O_3–SiO_2$ have been studied by optical absorption spectroscopy. Several typical spectral features due to the transitions originating from both Fe^{2+} and Fe^{3+} ions have been observed in the spectra. Absorption band at about 380 nm, typical for Fe^{3+} ions, was not resolved due to the strong charge-transfer absorption. This fact disables to determine the iron redox ratio from absorptions of Fe^{2+} and Fe^{3+} at 1000 nm and 380 nm. The iron redox ratio was therefore estimated from absorption of Fe^{2+} at 1000 nm (10000 cm^{-1}) and total iron concentration. It has been found, that iron redox

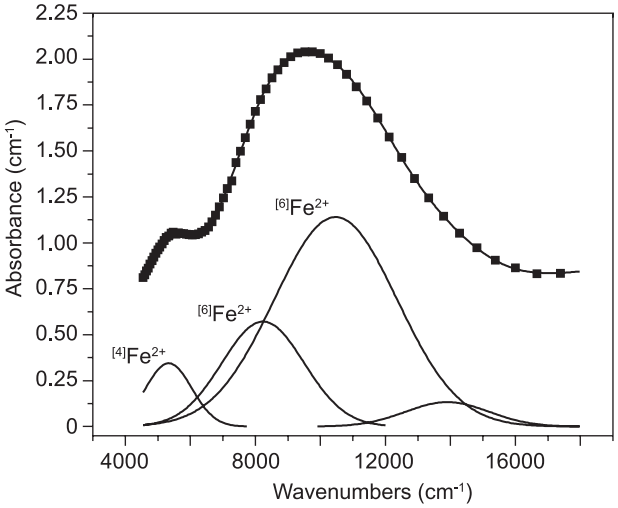

Figure 3. Deconvolution of spectral bands centred at about 5000 (into one band) and 10000 cm^{-1} (into three bands). Upper spectrum: ■ experimental data points, ━ fitted spectrum.

ratio increases with increasing total iron concentration. Increasing amount of alkaline-earth oxides increases iron redox ratio. This can be rationalized in terms of structural model for the incorporation of Fe^{2+} and Fe^{3+} ions into glass. Deconvolution of the spectral bands centred at about 5000 cm^{-1} and 10000 cm^{-1} showed that Fe^{2+} ions in studied glasses are predominantly in octahedral coordination.

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