Ferric-ferrous equilibrium in low-iron sodium-silicate glasses

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Abstract: Mössbauer and Electron paramagnetic resonance measurements have been performed on iron-containing sodium-silicate glasses with Na_2O/SiO_2 ratio equal to 19/81 and Fe_2O_3 content up to 7 wt. %.. The influence of total iron content on local environment of ferric and ferrous ions and ferric/ferrous ratio were investigated by the combination of both spectroscopic methods. Fe^{2+} behaves as a network modifier occupying predominantly octahedral sites while Fe^{3+} is a network former occupying tetrahedral sites. It was also observed "isolated" Fe^{3+} (broad hyperfine magnetic splitting) in low-iron samples by Mössbauer spectroscopy. Ferrous/ ferric ration decreases with increasing total iron content.

Key words: silicate glass melt, RedOx ratio, EPR, Mössbauer spectroscopy

1. Introduction

Transition metal ions can exist in multivalent states which are defined by several points: the base-glass composition, temperature of melting, duration of heat treatment, and partial pressure of oxygen above the glass melt. One of the serious problem concerning to the thermodynamic modeling of equilibrium composition is insufficiency of experimental data about quantity of Fe^{2+} and Fe^{3+} at various conditions. In many cases the available data are scattering and contradictory. The reliability of data may be increased by using of two or even more methods of chemical analysis.

The aim of this work was to test the convergence of the results of Electron-paramagnetic resonance (EPR) and Mössbauer spectroscopy as a nondestructive methods of iron glasses analysis. Another purpose is to obtain some information about the structure of low-iron glass. This data are necessary for the thermodynamic model clarification.

2. Experimental

2.1 Sample preparation

The glasses studied were based on 19 mol% Na_2O, 81 mol% SiO_2 with Fe_2O_3 content varying from 0.05 to 7 wt% (Table 1).

Table 1. Initial content of iron oxide in mixtures with fixed molar ratio of sodium and silica oxides

Sample number	1	2	3	4	5	6	7	8
Fe_2O_3, wt%	13	7	4.5	2.5*	0.55*	0.25*	0.1*	0.05*

* Fe2O3 was reached by 50% of $57Fe_2O_3$.

Batches were from analytically pure materials. The raw materials were sodium carbonate (Na_2CO_3), pure powdered quartz (SiO_2) and iron oxide (Fe_2O_3). The mixtures were fused at 1400°C in an electric furnace. All experiments were carried out in 90Pt/10Rh crucibles in air at 1400°C. Temperature was measured with a Pt-Pt/10 Rd thermocouple and was accurate to ±0.1°C. 4 hours fuse of 1500 mg sample is enough to make them homogeneous and equilibrated. The glasses were quenched with distilled water. The chemical composition of the samples were determined by inductively coupled plasma (ICP) mass spectrometry.

2.2 Mössbauer spectroscopy

Transmission ^{57}Fe Mössbauer spectra were recorded using a conventional Mössbauer spectrometer operating in constant acceleration mode with a ^{57}Co source embedded in Rh kept at room temperature using a multi-channel analyzer with 1024 channels. All spectra were collected on a large velocity scale (-12 and +12 mm/s) because lower velocity measurements (-4 and +4 mm/s) showed an indication of magnetic interaction (hyperfine magnetic structure). Data collection times varied from 2 days to 2 weeks, according to used iron concentrations. Isomer shift values refer to α-Fe at 293 K. We assumed that the recoil-free fractions of Fe^{2+} and Fe^{3+} were equal, thus the relative areas of the Fe^{2+} doublet and the Fe^{3+} doublet and sextet peaks are proportional to the relative abundances of each redox state.

2.3 EPR spectroscopy

The CW-EPR spectra were collected using Bruker Elexsys-E680X spectrometer in X-band (9.8 GHz) with field modulation at 100 kHz. Measurements were made at room temperature with fine powdered samples. The magnetic field was scanned from 0 to 600 mT and the microwave power used was 5 mW. Each ground specimen of approximately 60 mg mass was inserted in a fused quartz tube for EPR measurements.

3. Results and Discussion

ICP MS

The chemical analysis of the samples (Table 1) was made by the inductively coupled plasma (ICP) mass spectrometry. ICP analysis showed that more than 98.5% of mass sample were sodium, silicum, iron and oxygen. The main impurities were aluminum, potassium and chlorine. Molar ratio Si/Na varies from 4.3 to 4.4 and agrees with initial oxide contents used in fuse process. Such result proves that easy fugitive oxide Na_2O doesn’t vaporise during synthesis procedure. Total iron content obtained by ICP analysis in each sample was less than initial one. The function of total iron change according to initial content is presented in Fig. 1. All furthers total iron content values will be presented with ICP MS analysis correction.

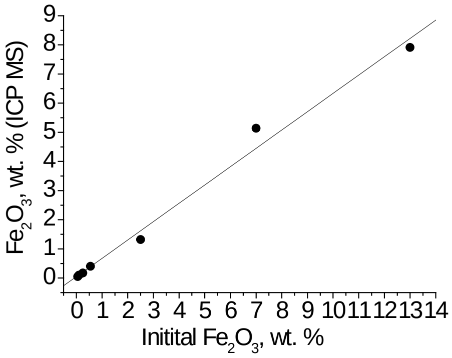


Fig. 1. Linear correlation of total iron content obtained by ICP MS analysis and initial iron content in oxide mixture

The main goal of the work is to investigate the influence of total iron content on RedOx ratio and the trend of Fe^{2+}/Fe^{3+} ratio changing with temperature, matrix composition etc, that is why the proportional decreasing of total iron content during the fuse process doesn't prevent the investigation. Decreasing of iron might be explained by Pt-Fe solid solutions under experimental conditions [1], but it was not found Pt traces in glass samples thus some iron could diffuse into Platinum crucible.

Both chosen spectroscopic methods (Mössbauer and EPR spectroscopy) give opportunity to investigate local iron environment and to make some conclusion about structure of glasses necessary to the thermodynamic modeling.

Using both spectroscopic methods estimation of RedOx ratio is possible only by Mössbauer spectroscopy because it can detect ferric and ferrous ions simultaneously. In crystalline fields the usual high-spin state is common for Fe^{2+} ions ($3d^6$) $t_{2g}^4 e_g^2$ according to Mössbauer data where IS of Fe^{2+} varies from 2.0 to 2.2 [2]. Spin state of Fe^{3+} is not so easy to detect by Mössbauer spectroscopy, isomer shift values of Fe^{3+} ($3d^5$) varies from 0.2 to 0.5 mm/s.

EPR spectroscopy is sensitive only to unpaired electrons, in practice there are high-spin Fe^{3+} ions ($t_{2g}^3 e_g^2$) and high-spin Fe^{2+} ions. However, conventional EPR of high-spin Fe^{2+} can either be impossible ('EPR silent' system). That is why EPR spectroscopy gives information only about Fe^{3+} ions environment. So Mössbauer and EPR spectroscopy are mutually supportive methods.

Mössbauer spectra

The Mössbauer spectra were evaluated with a standard computer software. The evolution of Mössbauer spectra shape with the decreasing of total iron content is illustrated in Fig. 2

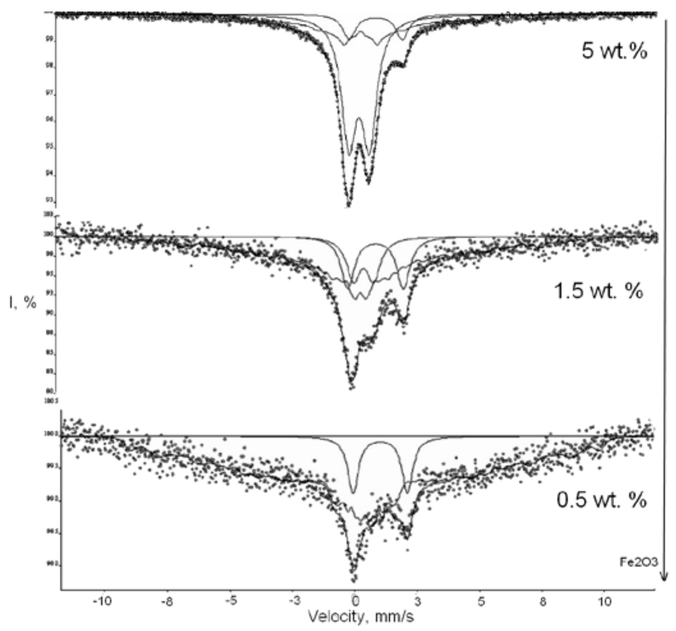
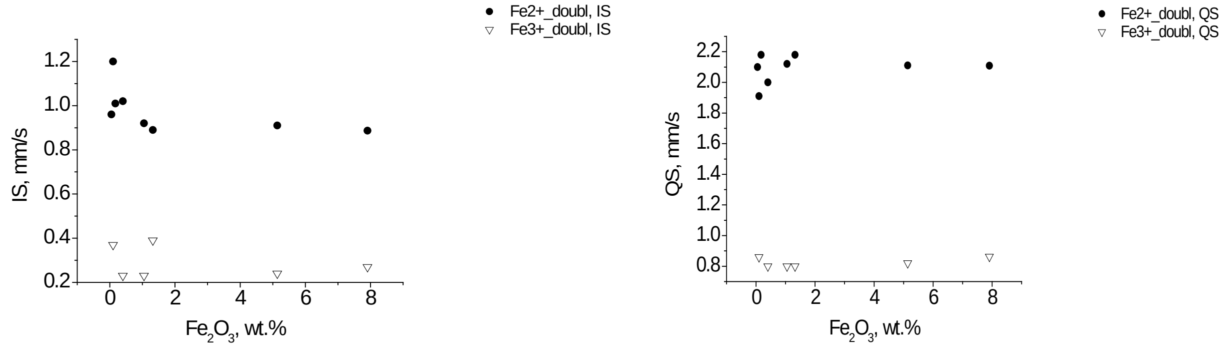


Fig. 2. ^{57}**Fe Mössbauer spectra of glass samples containing different content of** Fe_2O_3 **(iron content was obtained by ICP MS analysis)**

Each spectrum shows the presence of Fe^{2+} -and Fe^{3+} -doublets. The curved baseline (Fig. 2) indicated the presence of broad hyperfine splitting (hfs) which is explained by "isolated" Fe^{3+} sites. Measured parameters of Mössbauer spectra are shown in Fig. 3

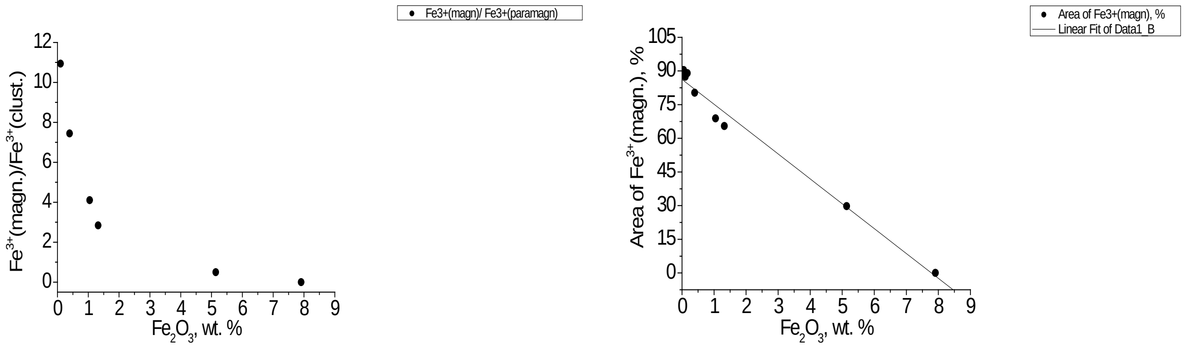


(a) **(b)**

Fig. 3. Variation of (a) the ^{57}**Fe isomer shift (IS) and (b) the** ^{57}**Fe quadrupole splitting (QS) of** Fe^{2+} **(•) and** Fe^{3+} **(∇) with** Fe_2O_3 **concentration**

The isomer shift values of Fe^{3+} in glass may be compared with isomer shift values in crystalline iron silicates in order to estimate the most probable coordination number of ferric ions in silicate glass. For Fe^{3+}, isomer shifts near 0.3 mm/s and below (at 298 K) are typical for Fe^{3+} in 4-fold coordination with oxygen, at the same time IS values above 0.4 mm/s are typical for Fe^{3+} in 6-fold coordination with oxygen [3, 4]. Such data allow us to assume that Fe^{3+} in tetrahedral coordination is the most probable structure in all samples except low-iron ($x < 0.55$ wt%) where the IS of broad HFS (Fe^{3+}) shifts to 0.5 mm/s.

Analysis of Mössbauer parameters shows that for the samples with total iron content more that 2.5 wt% doublets of Fe^{2+} is characterized by IS from 0.85 to 0.9. Such parameters are generally taken to represent delocalization of electrons between adjacent Fe^{3+} and Fe^{2+} resulting in an averaged value of IS that can be assigned to $Fe^{2..5+}$ or Fe^{2+} in 5-coordination [4]. However authors [3] moves this poorly defined region to the interval (0.9;1) mm/s and referring [2] suggested that IS near 0.9 mm/s or less of Fe^{2+}-silicates was observed when Fe^{2+} is 4-fold coordination. IS values above 1 mm/s are found when Fe^{2+} is in 6-coordination with oxygen.



(a) (b)

Fig. 4. (a) Dependence of ratio Fe^{3+}(magn)/Fe^{3+}(clust.) and (b) HFS area of Fe^{3+} on total iron content from Mössbauer spectra.

In low-iron glasses (< 0.25 wt%) paramagnetic doublet of Fe^{3+} vanished and all Fe^{3+} ions moved to broad magnetic hyperfine structure (HFS) which is explained by “isolated” Fe^{3+} sites.. HFS is caused by spin-spin relaxation that occurs on a timescale slower than that of the Mössbauer effect ($\sim 10^{-8}$s). Several authors [5-9] showed that magnetic part extremely increased with decreasing of total iron content. The same behavior was found in the present investigation. Fe^{3+} doublet refers to the exchange-coupled or clustered ions. [9] Hence Mössbauer spectra give opportunity to estimate the percentages of isolated and clustered Fe^{3+} ions present, and results are reported in Fig.4 (a). It was also demonstrated that HFS area linearly decreased with increasing of total iron content and finally vanished for the sample containing 7 wt% of Fe_2O_3 (Fig. 4 (b)).

The redox state Fe^{2+}/Fe^{3+} may be estimated from the area under Fe^{3+} (doublet and HFS) and Fe^{2+} (doublet) signals.

$$\mathrm{Fe}^{2+}/\mathrm{Fe}^{3+} = \frac{\mathrm{Area}(\mathrm{Fe}^{2+}\_\mathrm{doublet})}{\mathrm{Area}(\mathrm{Fe}^{3+}\_\mathrm{doublet}) + \mathrm{Area}(\mathrm{Fe}^{3+}\_\mathrm{HFS})}.$$

The calculated ratios Fe^{2+}/Fe^{3+} as a function of iron concentration obtained by analysis of Mössbauer spectroscopy is presented in Fig. 5.

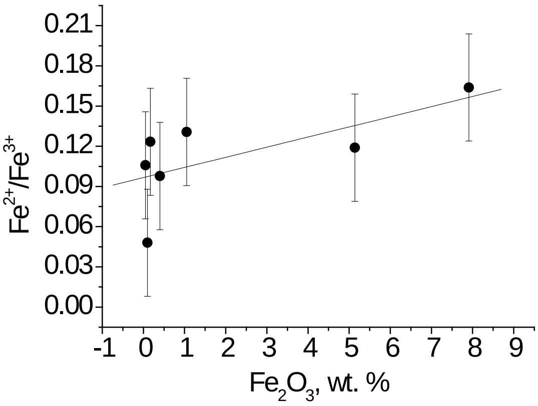


Fig. 5 Variation of Fe^{2+}/Fe^{3+} ratio with iron concentration obtained by Mössbauer spectroscopy

It is seen the moderate decreasing of Fe^{2+}/Fe^{3+} ratio with decreasing iron content. Within the experimental error it is not possible to say that Fe^{2+}/Fe^{3+} ratio is independent of total iron content. Similar behavior was found in several investigations [6, 9, 10] and it is necessary to have additional data in order to prove or rebut such behavior which disagrees with FactSage calculations [11]. According to the cited work the Fe^{2+}/Fe^{3+} ratio is inversely proportional to total iron content.

EPR spectra

The EPR absorption spectra were obtained for all samples. The main lines from the EPR spectra of iron doped samples (Fig. 4) are characterized by an intense sharp resonance signal at $g \approx 4.3$, a moderately intense signal at $g \approx 2.1$ and a shoulder in the region of $g \approx 7.20$. It is shown the direct influence of total iron content on the EPR spectra structure.

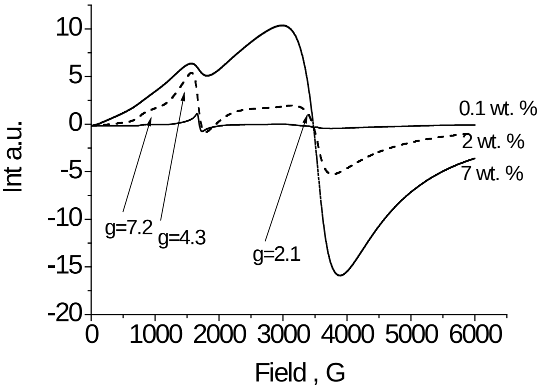
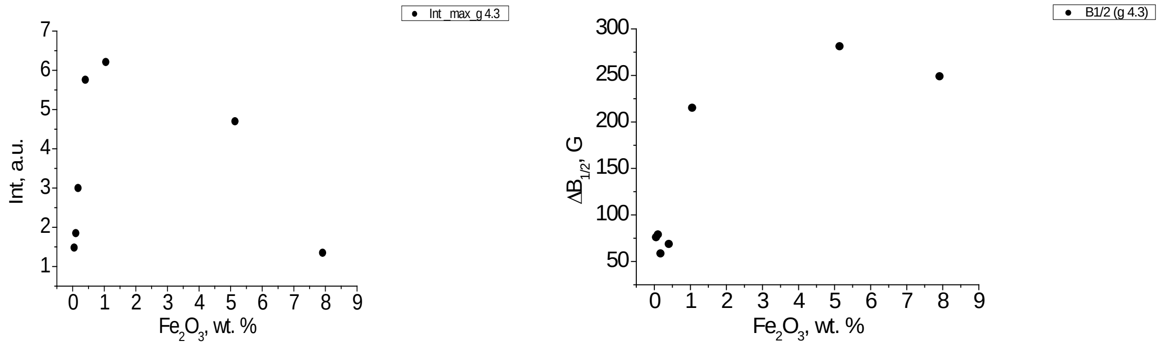


Fig. 6. The effect of total iron content on the structure of EPR spectra. The highest iron content corresponds to numb 1, the lowest to number 6

The evolution of the resonance line with increasing of total iron content is followed in the dependence of EPR parameters. They are the line integral (I) and the peak to peak linewidth ($\Delta B_{1/2}$).

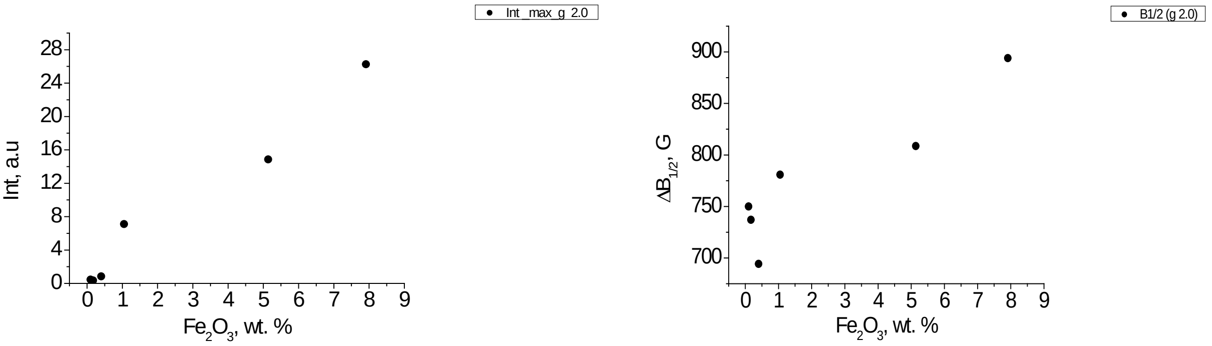
The origins of the three main Fe^{3+} resonances at g = 4.3, g = 7.2 (“shoulder” resonance) and g = 2 have been intensively debated [12- 15]. Some have attributed them to Fe^{3+} ions occupying tetrahedral and octahedral coordination sites, respectively. Last publications agree in views that the g = 4.3 resonance can be produced by “isolated” Fe^{3+} ions occupying either tetrahedral or octahedral sites with low-symmetry rhombic distortions [14- 16] and g ≈ 2.0 resonance is associated with both axially distorted sites and spin-spin interactions.

As can be seen from Fig.7-8 total iron content effects differently on intensities and peak-to-peak line-widths of resonance absorptions. Such investigations illustrate the different nature of the resonances with g ≈ 4.3 and g ≈ 2.0.



(a) **(b)**

Fig. 7.Composition dependences of the line integral (a) and line-width (b) of resonance absorptions at g ≈ 4.3



(a) **(b)**

Fig. 8. Composition dependences of the line integral (a) and line-width (b) of resonance absorptions at g≈2.0

The intensity of the resonance absorption and line-width depends on Fe_2O_3 concentration (Fig. 7,8). The similar results are published recently [15], however in B_2O_3 matrix [12] it was not found total iron content influence on line-width of absorption peaks, perhaps matrix composition is also quite important.

Intensity from g ≈ 2.1 increases in the whole region, especially for x> 5wt%. On the contrary intensity from g ≈ 4.3 decreases in the same concentration interval of iron, in high-iron glasses (more than 5wt %) Fe^{3+} ions start participating in dipole-dipole or super-exchange interactions. Fig. 7 (b) shows $\Delta B = f(x)$ dependence. Authors [14] suggest that it reflects the competition between the broadening mechanisms as the dipole-dipole interactions, the increased disordering of the matrix structure and the superexchange interactions within the pairs of iron ions.

According to Fig 7 (a) the intensity of the absorption line centered at $g \approx 4.3$ increases up to $x \approx 1$ wt% and after that starts decreasing. It might be explained by destruction of the configuration from the iron ions vicinities which give opportunity for magnetic isolation. Essential increasing of iron content from 0.05 wt% to 5 wt% destroys the local ordering of the Fe^{3+} ion vicinities.

There are anomalies in ΔB behaviour in low-iron region ($x < 0.2$wt%), it is observed a deviation from linearity (Fig.7(b), 8(b)). Investigation of such low-iron samples was not found that is why the explanation of it needs additional experiments.

4. Conclusions

Glasses of the system $19Na_2O$-$81SiO_2$-xFe_2O_3 were obtained over the $0.05<x<7$ wt% concentration region.

Local iron environment of ferric and ferrous ions were systematically studied using Mössbauer (at room temperature) and EPR (at room temperature) spectroscopic methods.

Combination of EPR and Mössbauer spectroscopy give opportunity to assume that Fe^{2+} exists in 5-fold coordination in high-iron glasses (x>2 wt.%) but not as an ion $Fe^{2..5+}$ because there were not any changes in EPR spectra for these samples. Mössbauer spectra of other samples showed that Fe^{3+} behave as a network-former (4-fold coordination) and Fe^{2+} was a network-modifier (6-fold coordination).

Fe^{2+}/Fe^{3+} ratio is inversely proportional to total iron content in glasses with the identical glass matrixes. Therefore we would conclude that it is observed the total iron effect on RedOx state of iron in glass.

Low-iron region (x<0.5 wt. %) is poorly investigated. Therefore obtained anomalies in EPR absorption spectra for low-iron samples also prove that it is necessary to continue complex investigation of glass matrix and low-iron content influence on iron ions behaviour in glasses.

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