

Influence of redox equilibrium on the properties of glasses with a high iron concentration

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In glasses of the system $\text{Na}_2\text{O}-\text{CaO}-\text{SiO}_2-\text{Fe}_2\text{O}_3$, Fe^{2+} and Fe^{3+} ions were found by Mössbauer spectroscopy. In samples melted in oxidizing atmosphere, both ions occurred in tetrahedral coordination, whereas they occurred in coordination number 6 in samples with high iron content and melted under reducing conditions. It is shown that a total iron concentration has a stronger influence on the glass properties than the redox state.

Differences in the properties of glasses melted in oxidizing and reducing atmosphere, respectively, were observed at lower temperatures, while at higher temperatures they are very small (however, the tendency is still maintained). Density, microhardness, transition temperature and thermal expansion coefficient of the glasses studied are affected by the changes in redox equilibrium. One can conclude that after reducing treatment iron ions present in the glass structure play a similar role as a network modifier. At higher temperatures, this kind of activity is very weak, according to viscosity and liquidus temperature measurements.

1. Introduction

The glassy state is particularly suitable for immobilization of hazardous substances and creating of new products from residues. The classical glass products contain up to 1 wt% Fe_2O_3 . Especially by the vitrification of wastes high iron concentrations (more than 10 %) occur. The redox state in such glasses has already been studied [1]. The influence of iron on the structural, chemical and physical properties is not well known and opinions about this subject are controversial [2 to 8]. This is because iron can appear in two valences (2+ and 3+) and in two coordination numbers (4 and 6) which are assumed for each ion form. This problem, actually, depends on the basicity and kind of glass, iron concentration and temperature.

There are many methods of structural iron determination in glass, which yield more or less realistic results. Selection of the measuring technique depends on the total iron content. In the case of small iron amounts following methods were used: electron paramagnetic resonance (EPR) [9 and 10], nuclear magnetic resonance (NMR) [11 and 12] and optical spectroscopy [13 and 8]. The Mössbauer spectroscopy seems to be the best method for determination of high iron concentration [14]. Glass samples in this work were analysed with the latter technique. It allows a precise determination of iron content and its position in the glass structure.

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Table 1. Chemical composition of studied glasses in wt%

| sample | SiO_2 | CaO | Na_2O | $[\text{Fe}_2\text{O}_3]_{\text{total}}$ |
|--------|----------------|-------|-----------------------|--|
| 0/S | 72.87 | 10.00 | 16.99 | 0.15 |
| 2 | 71.52 | 9.80 | 16.65 | 2.03 |
| 2R | 71.56 | 9.80 | 16.65 | 1.99 |
| 5 | 69.46 | 9.50 | 16.14 | 4.90 |
| 5R | 69.45 | 9.50 | 16.14 | 4.91 |
| 9 | 66.73 | 9.10 | 15.46 | 8.71 |
| 9R | 66.76 | 9.10 | 15.46 | 8.68 |

2. Experimental

As typical glass systems representing slags or residues the soda-lime-silica system ($\text{Na}_2\text{O}-\text{CaO}-\text{SiO}_2$) and the aluminosilicate system ($\text{Al}_2\text{O}_3-\text{CaO}-\text{SiO}_2$) with a relative small alkali content were chosen. The glass samples studied in this work consist of 17 Na_2O , 10 CaO, and 73 SiO_2 with addition of Fe_2O_3 up to 9 wt% respectively. Moreover, the amount of Fe^{2+} was changed through appropriate reducing or oxidizing treatment. Fe_2O_3 was added at the expense of all other glass components (see table 1). The melts with higher iron content were thin fluid during casting. Reducing atmosphere intensified this effect. Furthermore, the colour of the glasses changed from light green to dark blue green. For analyses of glass structure the Mössbauer effect was applied. It takes advantage of the interaction between γ -rays with particular atomic cores. This interaction depends on the environment so that as a result the information about valence and coordination number is obtained. Samples for

Table 2. Comparison of results from wet chemical analysis and Mössbauer spectroscopy for Fe²⁺/Fe³⁺ determination in wt% (alkali-alkaline earth silicate glasses)

| sample | Fe ²⁺ | Fe ³⁺ | Fe ²⁺ /Fe _{total} | Fe ²⁺ /Fe ³⁺ (analysis) | Fe ²⁺ /Fe ³⁺ (spectroscopy) |
|--------|------------------|------------------|---------------------------------------|--|--|
| 0/S | 0.04 | 0.11 | 0.27 | 0.32 | — |
| 2 | 0.25 | 0.78 | 0.12 | 0.14 | — |
| 2R | 1.37 | 0.62 | 0.69 | 2.23 | 2.69 |
| 5 | 0.58 | 3.51 | 0.14 | 0.14 | 0.15 |
| 5R | 3.00 | 1.91 | 0.61 | 1.56 | 1.7 |
| 9 | 1.18 | 7.53 | 0.14 | 0.16 | 0.18 |
| 9R | 5.68 | 3.00 | 0.65 | 1.86 | 1.86 |

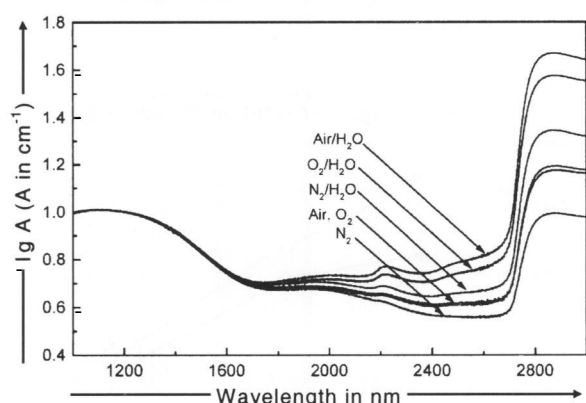


Figure 1. Logarithmic absorbance spectra showing the ferrous and free hydroxyl absorption bands [15].

the Mössbauer spectroscopy were finely ground (grain size < 25 μm). Following measurement conditions were performed: duration 88 h, air atmosphere, room temperature, source Co⁵⁷-Pt.

As a reference method a wet chemical analysis was chosen. In this procedure a fine glass powder was used (grain size < 63 μm) and the measurement of Fe²⁺ proceeded by the photometric analysis. The results of both analyses are given in table 2.

To investigate the changes in coordination number of Fe²⁺ optical absorption in a range of 200 to 2500 nm and its logarithm (lg *A* method) was employed.

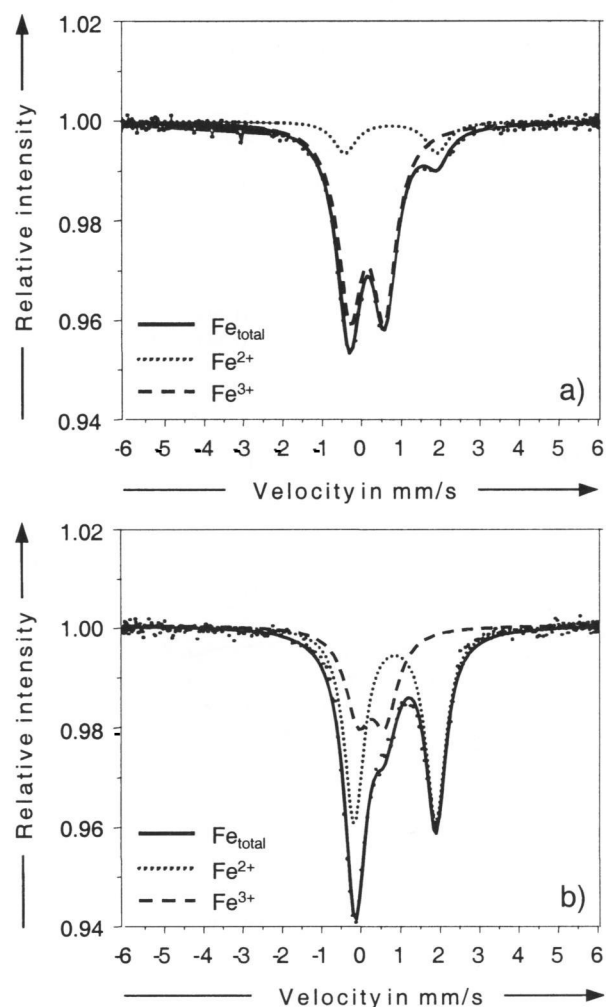
$$A = c \cdot l \cdot \varepsilon \quad (1)$$

where ε is the molar extinction coefficient ($l \text{ mol}^{-1} \cdot \text{cm}^{-1}$), *A* the absorbance, *c* the concentration of absorbing species ($\text{mol} \cdot \text{l}^{-1}$), and *l* the path length in cm.

$$\lg(A) = \lg(c) + \lg(l) + \lg(\varepsilon) \quad (2)$$

The logarithmic absorbance of the same substances but with different concentrations gives an identical spectral shape. The resulting curves are only shifted along the y-axis (figure 1 [15]). The smallest differences in the shape of the spectra become obvious with this method [16].

In order to establish an influence of iron on glass properties the following properties were measured: viscosity



Figures 2a and b. Mössbauer spectra of alkali-alkaline earth silicate glasses; a) oxidized glass, b) reduced glass.

(transition temperature and working point), density and coefficient of thermal expansion, microhardness and crystallization (liquidus temperature).

3. Results and discussion

3.1 Redox equilibrium and incorporation of iron in glass structure

Typical Mössbauer spectra for “oxidized” and “reduced” glasses are shown in figures 2a and b. The content of Fe²⁺ and Fe³⁺ was calculated in wt% from the area of a doublet. By Mössbauer spectroscopy it was found that in soda-lime-silica glasses with a high iron concentration and melted in oxidizing atmosphere Fe²⁺ is tetrahedrally coordinated. Only in samples with a small iron concentration Fe²⁺ is 6-fold coordinated. Reducing conditions favour octahedral oxygen arrangement around this species, which points out that the position of ions in the structure of the glasses studied has been changed. However, Fe³⁺ is incorporated in oxidized melts as four-fold coordinated (in reduced glasses only at an Fe₂O₃ content of 2 wt% (see table 3)). Figure 3 shows the absorption spectra of samples with different Fe²⁺ con-

Table 3. Isomer shifts and quadrupole splitting (I.S. and Q.S. in ± 0.02 mm/s), and coordination number (C.N.) (alkali-alkaline earth silicate glasses) [14]

| sample | Fe ²⁺ | | | Fe ³⁺ | | |
|--------|------------------|-------|------|------------------|-------|------|
| | I.S. | Q.S. | C.N. | I.S. | Q.S. | C.N. |
| 2R | 1.000 | 2.030 | 6 | 0.228 | 0.145 | 4 |
| 5 | 0.846 | 2.128 | 4 | 0.269 | 0.844 | 4 |
| 5R | 0.985 | 2.051 | 6 | 0.391 | 0.745 | 6 |
| 9 | 0.886 | 2.290 | 4 | 0.293 | 0.855 | 4 |
| 9R | 0.969 | 2.036 | 6 | 0.384 | 0.672 | 6 |

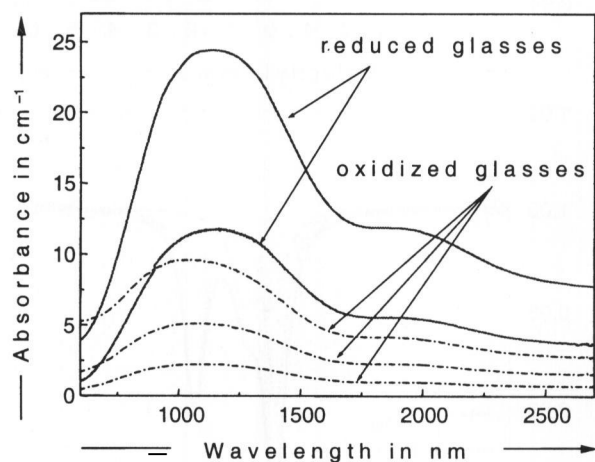


Figure 3. Absorption spectra of glasses with a different Fe²⁺ content.

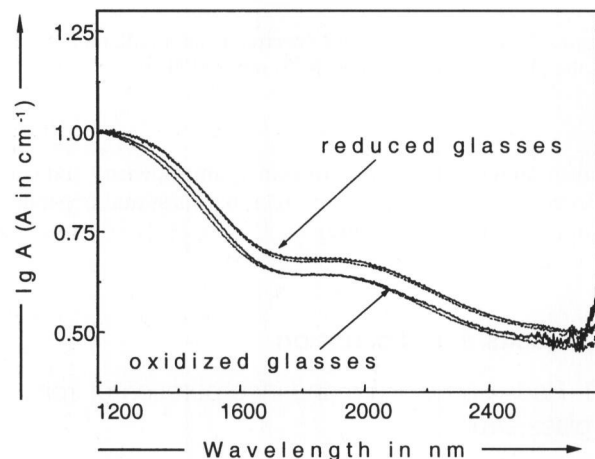


Figure 4. Logarithm of the absorption spectra.

concentrations. The absorption maxima of reduced samples, in comparison with the oxidized glasses, are shifted towards longer wavelengths. The explanation of Fe²⁺ incorporation in a structure was made through the lg A method. After finding the logarithm of absorption, spectra have been normalized to 1 at maximum absorption of the ferrous iron at 1100 nm. Figure 4 shows differences of spectral positions for corresponding glass samples. The spectra of glasses with the same redox ratio overlap independently of the Fe²⁺ concentration. These determinations confirm another posi-

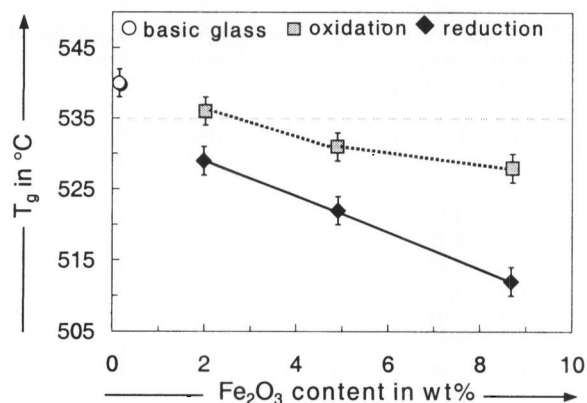


Figure 5. Transition temperature, T_g , as a function of Fe₂O₃ content and redox state.

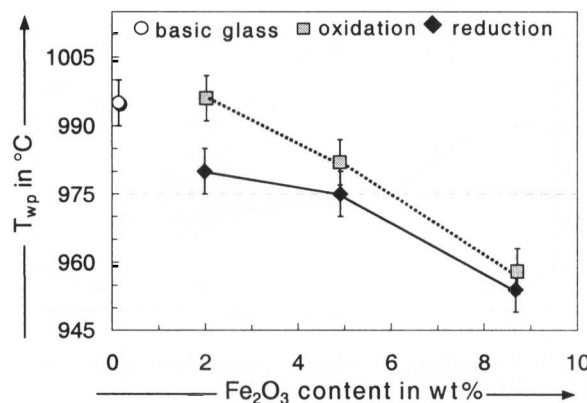


Figure 6. Working point temperature, T_{wp} , as a function of Fe₂O₃ content and redox state.

tioning of Fe²⁺ in the structure, i.e. change of a coordination number.

3.2 Properties of glasses with high iron content

It is well known that Fe₂O₃ considerably reduces the viscosity of glasses [1 and 17]. Changes in the redox equilibrium influence the viscosity in a lower temperature range (figure 5). The transition temperature ranges from 540 °C for oxidized to 512 °C for strongly reduced glasses. In this temperature interval Fe²⁺ causes a decrease in viscosity. As mentioned above, after the reducing treatment, the coordination number of Fe²⁺ changes from 4 to 6. Moreover, in this condition, the amount of ions which act as network modifiers increases. At high temperatures (working point) the viscosity decreases much stronger than in the low temperature range. The temperature differences amount to 50 K, whereby the differences between oxidized and reduced samples are very small; with an increase in total iron content these differences become even smaller (figure 6).

At lower temperatures in reduced glasses an oxygen deficiency is present. With Fe²⁺ ions only physically dissolved oxygen can react. The oxygen from the surrounding atmosphere can not participate because of a small diffusion coefficient. The higher the temperature the greater is the diffusion coefficient and oxygen can penetrate into glass [18].

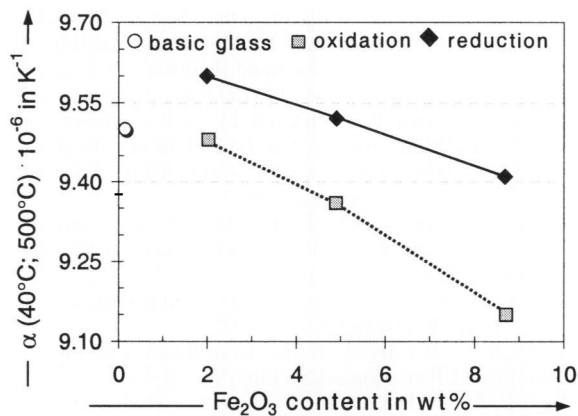


Figure 7. Thermal expansion coefficient, α , as a function of Fe_2O_3 content and redox state.

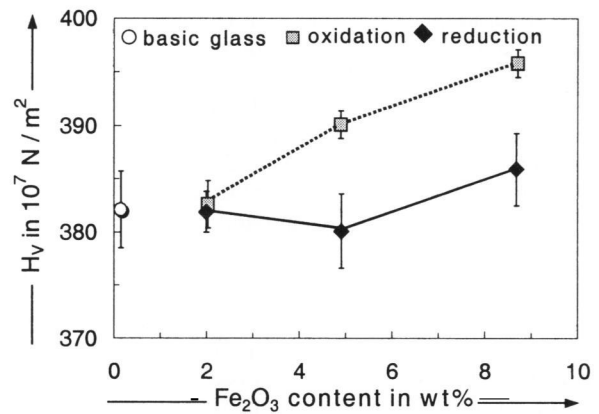


Figure 9. Microhardness, H_v , as a function of Fe_2O_3 content and redox state.

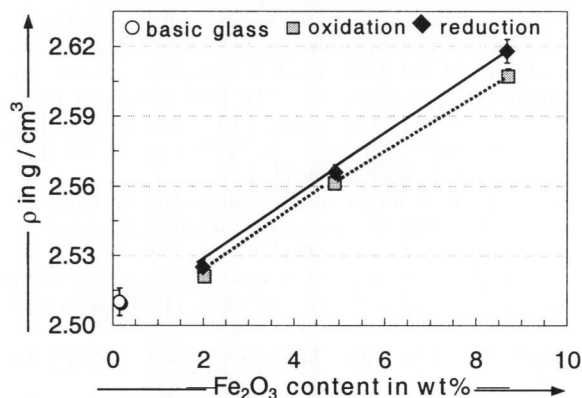


Figure 8. Density, ρ , as a function of Fe_2O_3 content and redox state.

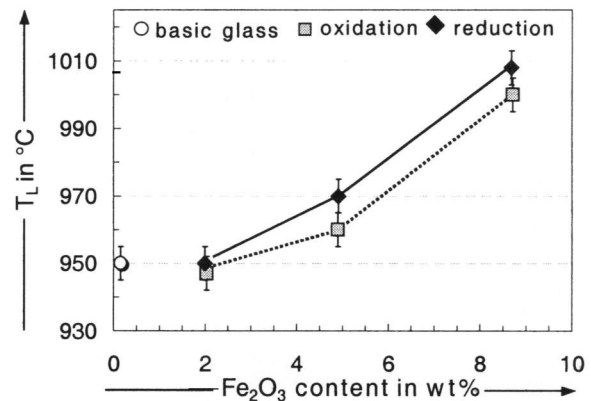


Figure 10. Liquidus temperature, T_L , as a function of Fe_2O_3 content and redox state.

Above 1000 °C according to thermodynamic equilibrium the oxygen which was first absorbed is being released. With increasing temperature the redox reaction rate rises [19]. That is why at this temperature range the differences in viscosity of both types of glasses are so small. Nevertheless, Fe^{3+} ions are incorporated into the oxidized silicate structure as four-fold coordinated, while in the reduced glasses they change their coordination number, as well as Fe^{2+} , from 4 to 6. In the glass specimens with 2 wt% Fe_2O_3 there is a sufficient oxygen amount causing a tetrahedral coordination of Fe^{3+} (see table 2). With an increase in total iron content the concentration of Fe^{3+} ions in reduced glasses rises proportionally.

The changes in the redox equilibrium have an impact on thermal expansion, microhardness and density. The thermal expansion coefficient ranges from $9.54 \cdot 10^{-6} \text{ K}$ for oxidized to $9.88 \cdot 10^{-6} \text{ K}$ for reduced glass (figure 7). Fe^{2+} causes, analogously to alkalis, an increase in the thermal expansion and density (figure 8). On the other hand, microhardness decreases (see figure 9) as the redox equilibrium shifts in the reduction direction. Only the total iron concentration has an influence on the crystallization – the greater the Fe_2O_3 concentration the higher the liquidus temperature. As is apparent from figure 10 reduction shifts the beginning of crystallization towards higher temperatures, whereas discrepancy between reduced and oxidized glasses lies in an error

range. However, a certain tendency in liquidus temperature for reduced glasses can be seen.

4. Conclusion

With the aid of Mössbauer spectroscopy it was established that in oxidized classical soda-lime-silica glasses and also in glasses with high iron concentrations both Fe^{2+} and Fe^{3+} occurred as four-fold coordinated. Under the reducing melting conditions both species appear in octahedral coordination, whereby Fe^{3+} seems to change its coordination number at a higher total iron concentration.

This phenomenon can be explained as follows: iron with its relatively weak bonding energy to oxygen fits the resources of oxygen in the matrix. This pursuit of creating a bond at an oxygen deficiency can be compensated only in a competition with other ions. However, because of the weak bonding energy only a faint connection in octahedral coordination can occur. Furthermore, the Fe^{3+} is favoured in the matrix and depending on the availability of oxygen it can earlier come into tetrahedral coordination. The structural incorporation is determined not only by the availability of oxygen but also by the oxygen demand, therefore the dependence on the iron concentration is expected.

The structural incorporation of iron affected by the oxygen resources changes the whole glass structure. In fact, the optical spectroscopy proved the distinct variations in extinction coefficient for oxidized and reduced glasses which can be related to the structural modifications (see figure 4). The current approach to the COD-COS (Chemical Oxygen Demand/Source) concept, in which the available oxygen in the glass melt is defined only by the amount of polyvalent material, should be enhanced because the oxygen-dependent structural changes of the melts are apparent, and this interconnection seems to extend the previous concepts.

The oxygen deficiency is a reason for a lower polymerization of the structure. The resulting changes of the macroscopic properties support this hypothesis: viscosity decrease, higher thermal extension coefficient, decreasing microhardness. Basically, increasing total iron content seems to act as glass modifier. It is apparent in increase of density with increasing iron content under reduction conditions (or lack of oxygen). The liquidus temperature also rises significantly with the degree of reduction and the total iron content (see figure 10).

This overview of the studied properties, which depend on the available amount of oxygen in the melt, can interpret the obtained experimental results with respect to the structural consideration.

5. References

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