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ESR STUDY OF THE STRUCTURE OF Fe (III) IN SILICATE GLASSES OF DIFFERENT BASICITIES

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Résumé: Des verres de silicate de Li, Na, K et Cs contenant diverses concentrations de Fe_2O_3 sont étudiés par la méthode RPE. La basicité des verres est également déterminée. Le comportement systématique des resonances $g=4,2$ et $g\approx 2$ du Fe^{3+} dans ces verres montre que la ligne $g=4,2$ représente bien le Fe^{3+} en position "tétraédrique" et la ligne $g\approx 2$ la position "octaédrique" du Fe^{3+} .

Abstract: Li, Na, K, Cs silicate glasses which contain various iron concentrations were investigated by ESR. The basicity of these glasses was also determined. The systematic behaviour of Fe^{3+} in these glasses shows clearly that the resonance $g=4,2$ represents Fe^{3+} in "tetrahedral" coordination and $g\approx 2$ Fe^{3+} in "octahedral" position.

1. Introduction

Transition elements occur in glass in various oxidation states and coordinations and are as colour elements very important for glass. The determination of their oxidation states and their coordinations is the primary aim of each structural investigation of these elements in glass. One of the most important of these elements, Iron, occurs always in the oxidation states Fe^{3+} and Fe^{2+} . Although it is very easy to determine the structure of Fe^{2+} (d^6 , D) with the optical spectroscopy - e.g. by using the band 1050 nm which is typical for sixfold coordinated Fe^{2+} - there are only a few methods for Fe^{3+} which have a high sensitivity for this ion. The ESR is today one of the most sensitive methods and the most used for the structural analysis of Fe^{3+} . In glass iron generally shows 2 ESR-lines at $g=4,2$ and $g\approx 2$. The ratio of the intensities of the two lines depends on the iron concentration and on the type of the glass¹⁾. Generally the following Hamiltonian H_S is used to describe the spectrum:

$$H_S = g \cdot \mu_B H_S + D \left[S_z^2 - \frac{1}{3} S(S+1) \right] + E (S_x^2 - S_y^2), \text{ with } S = 5/2. \quad (1)$$

The first theoretical analysis and structural interpretation of this H_S were given by Castner et al.²⁾. In order to achieve resonance $g=4,2$ they gave the condition: $D=0$ and $E \neq 0$ and characterized the Fe^{3+} which is responsible for this signal as a network former, with the coordination number 4 (Symetry: C_{2v}). But a very important result of the general theory^{2,3,4)} of the signal at $g=4,2$ is e.g. the knowledge that Fe^{3+} in tetrahedral and octahedral coordination may give this signal. This led some authors^{5,6)} to the conclusion that this signal in glass may not be used as characteristic for a fourfold coordinated Fe^{3+} . Because the theory for this resonance leaves such possibilities, it is of great importance to know the nature of the Fe^{3+} -lines in glass. Thus, it follows that further

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investigations must be done on appropriate glasses. Depending on the different iron concentrations we have studied the behaviour of the Fe^{3+} -ESR-Spectrum in Silicate, Borate and Phosphate glasses¹⁾. The present work continues this work and investigates the behaviour of the Fe^{3+} spectrum in Li-, Na-, K-, and Cs-Silicate glasses.

2. Experimental Section

2.1 The Investigated Glasses

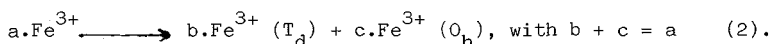
The composition of the glasses is (mol %): 69 SiO_2 , 25 Me_2O ($\text{Me} = \text{Li, Na, K, Cs}$) 6 CaO . 0,06, 0,2 resp. 1,6 Fe_2O_3 were added to the batch. The raw materials used were rock crystal and Me_2CO_3 ($\text{Me} = \text{Li, Na, K, Cs}$), CaCO_3 and Fe_2O_3 of p.a. quality. The glasses were melted in Al_2O_3 crucibles in an electrical furnace at 1400°C and under air atmosphere for 3 h. All 4 glasses (Li, Na, K, Cs) of the same iron concentration were melted together. Thus all have the same melting conditions. The glasses were crushed and sieved. To measure this, the sieved fractions of 0,6-1 mm in diameter were used. The same initial weight (100 mg) was used for all measurements, thus the spectra may be compared quantitatively.

2.2 ESR-Measurement

The spectra were recorded in x-Band (9,5 GHz), with the ESR Spectrometer 414 (Bruker Physik). The resonance field and frequency were recorded as²⁾.

3. Results and Discussions

The structure (coordination) of a d-element depends on the number of d-electrons Fe^{3+} with the configuration d^5 has the ground term 6S which under the influence of a tetrahedral, octahedral or every other ligand field changes into the ground state A_1 without splitting. This makes Fe^{3+} relatively insensitive to small changes in the environmental symmetry. Another property of the d^5 configuration which plays a role in the structural behaviour of Fe^{3+} is the fact, that the Crystal-Field Stabilization Energy (CFSE) for the tetrahedral coordination as well as for the octahedral, is equal and both are zero. Therefore, Fe^{3+} has no particular "site preference" for either of the two coordinations. Both coordinations may simultaneously occur in the glass melt and we can write for the structure of Fe^{3+} :



The ratio of b to c depends on the iron concentration and on the glass composition^{1,11)}. It was found¹⁾ that at low concentration the tendency to form the fourfold coordination is very pronounced, while for the sixfold coordination dominates at high iron concentration. This result was obtained by the analysis of the behaviour of $g=4,2$ and $g \approx 2$ in different glasses¹⁾, with the assumption, that $g=4,2$ represents the fourfold coordinated Fe^{3+} (network former) and $g \approx 2$ the sixfold coordinated Fe^{3+} (modifier). The present work is done with the aim of checking these assumptions. The direct comparison of Fe^{3+} in the Li-, Na-, K- and Cs-silicate glasses offers some interesting possibilities: 1) Because Fe^{3+} needs the neighbourhood of alkali ions for charge compensation for its different coordinations, these alkali metals directly participate in the structure of the Fe^{3+} and they may be used, with their specific properties, as a probe. 2) The exchange of one alkali ion with another does not change the point group of Fe^{3+} coordinations. Thus, all Fe^{3+} resonances, which represent a given coordination, do not change the g -values through changing from Li to Cs. A change may only occur if the coordination of the Fe^{3+} ion changes, due to the different sizes of the alkali ions (Li^+ : 0,70 Å; Na^+ : 1,00 Å; K^+ : 1,33 Å; Cs^+ : 1,70 Å). The corresponding Fe^{3+} resonances may be identified.

3.1 The Li-, Na-, K- and Cs Glasses

In 1940 Stegmaier and Dietzel⁹⁾ discussed the alkaline properties of glass melts and showed that the alkalinity of a Li-, Na-, and K-glass is comparable to the alkalinity of these metals in aqueous solutions. To characterize our glasses, the pH was measured according to the method of Oel¹⁰⁾. For the pH measurement glass grits were used.

Fig. 1 shows the results for the different alkali glasses. As it can be seen, the pH increases from Li to Cs, which exactly correspond to the behaviour of these metals in aqueous solutions. For glasses containing 1,6 % Fe_2O_3 , a chemical analysis of iron was made. The quantity of Fe^{3+} in the different alkali glasses is also shown in Fig. 1. As the pH, Fe^{3+} increases from Li to Cs. The Li-glass contains the lowest Fe^{3+} , K and Cs have the highest Fe^{3+} . These results are very important for the analysis of the ESR-spectra.

3.2 Structure of Fe^{3+} in Li-, Na-, K- and Cs-Silicate Glasses

It was shown¹⁾ that the structural behaviour of Fe^{3+} depends on the iron concentration. At low concentration the signal at $g=4,2$ predominates.

Therefore, this region must be first considered. Fig. 2 shows the behaviour of this resonance for glasses containing 0,06% Fe_2O_3 . As it can be seen, the intensity of Fe^{3+} decreases in the different glasses, in a very characteristic manner, from Li to Cs, Cs having the lowest intensity. Because the line shape of the resonance clearly is not changed, this intensity behaviour indicates that the Cs-glass has the lowest Fe^{3+} here. The missing Fe^{3+} in this position must occur at $g \approx 2$ (Fig. 3). As expected, the Cs-glass, here has the highest intensity and accordingly the highest Fe^{3+} . At this position the Li-glass possesses the lowest Fe^{3+} . These relationships were also investigated for other iron concentrations. Fig. 4 (a: first derivat. spectra, b: absorption spectra) shows the results for 1,6 % Fe_2O_3 . As Fig. 2, 3 and 4 obviously show there is a distribution of Fe^{3+} between the resonances $g=4,2$ and $g \approx 2$. The total Fe^{3+} of each glass being the sum of the quantity of iron at $g=4,2$ and $g \approx 2$, exactly as this is described through equation (2). As the chemical analysis of Fe^{3+} for the glasses containing 1,6 % Fe_2O_3 (Fig.1) has shown, and as it can be seen from Fig. 4, the intensity of Fe^{3+} at $g=4,2$ and at $g \approx 2$ is the lowest for the Li-glass. This shows, that the sum of the intensities of the two resonances exactly corresponds to the total Fe^{3+} in the interesting glass. For example, it can be seen (Fig. 4 a, b), that the sum of the intensities of the resonances at $g=4,2$ and $g \approx 2$ is the highest for the Cs-glass. These relationships clearly indicate, that the two resonances characterize two different structures (coordinations) of Fe^{3+} . The ratio of the two coordinations is different in the Li, Na, K and Cs-glasses. The Li-glass possesses the highest population of Fe^{3+} at the tetrahedral coordination, here the Cs-glass has the lowest. For the octahedral structure predominates the Cs-glass, while Li supports the tetrahedral

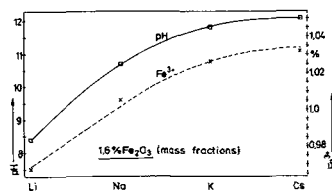


Fig. 1

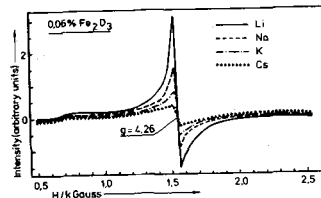


Fig. 2

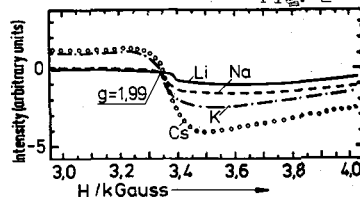


Fig. 3

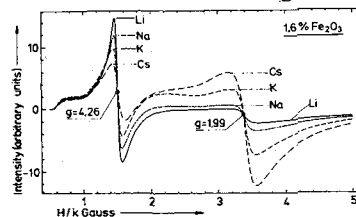


Fig. 4 a

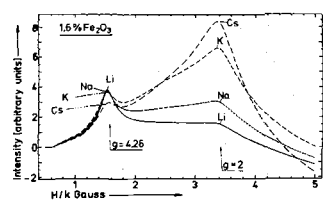


Fig. 4 b

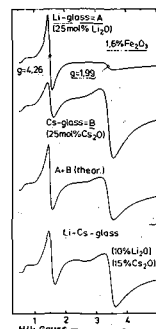


Fig. 5

coordination. The different roles of Li and Cs can be observed in a glass, which contains the two alkalis together, as this is shown in Fig. 5. Through the presence of Cs, the resonance at $g \approx 2$ is very marked. In order to generally characterize the distribution of the two structures of Fe^{3+} in the glasses investigated, the fraction of the tetrahedral coordination to the octahedral was established (Fig. 6). Fig. 7 shows the behaviour of N_4 for two iron concentrations. In a characteristic manner, it can be seen, that the tetrahedral coordination of Fe^{3+} decreases also following: $\text{Li} \rightarrow \text{Na} \rightarrow \text{K} \rightarrow \text{Cs}$. This means, that the possibility for Fe^{3+} to take tetrahedral coordination is very supported by the Li-ion. In the Cs-glass the octahedral coordination occurs easily. It is interesting to note that the observed coordination changes of the Fe^{3+} in the different alkali glasses proceed in the same direction as the coordination affinities of the alkali metals themselves⁸⁾. It is known, that very often Li realizes the coordination number 4. This coordination number occurs very rarely with K and Cs.

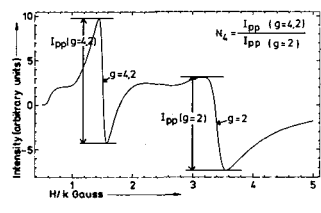


Fig. 6

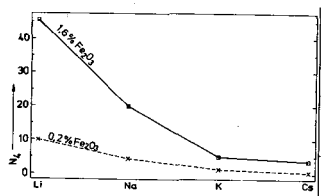


Fig. 7

4. Summary

The characteristic behaviour of the resonances at $g=4,2$ and $g \approx 2$ of Fe^{3+} in Li-, Na-, K- and Cs-silicate glasses clearly shows that the two resonances represent two different structures of Fe^{3+} . The resonance at $g=4,2$ corresponds to Fe^{3+} in tetrahedral coordination, the resonance $g \approx 2$ characterizes an octahedral coordinated Fe^{3+} . Both coordinations occur simultaneously in glass. The ratio of one structure to another depends on the iron concentration and on the glass composition.

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