Original Paper

ESR studies of iron-containing lithium, sodium and potassium silicate glasses before and after irradiation with γ- and X-rays[1])

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Lithium, sodium and potassium silicate glasses containing different Fe_2O_3 amounts were irradiated with γ- and X-rays and investigated by using ESR. The well-known iron resonances at $g = 4.2$ and $g = 1.99$ show a characteristic behaviour at the transition from lithium to potassium and by changing the Fe_2O_3 concentration. The resonance at $g = 4.2$ decreases from lithium to potassium, whereas the resonance at $g = 1.99$ increases. The concordance of the intensity course of the two resonances with the preference of the alkali metals to take tetrahedral or octahedral coordination is an interesting support for the attribution of $g = 4.2$ to 4-fold coordinated Fe^{3+} and $g = 1.99$ to 6-fold coordination of this ion.

γ- and X-rays induce the same defect centres (colour centres). These centres are characterized by a strong resonance at $g = 2.01$. All radiation defects have a strong dependence on the type of alkali metal – they increase from lithium to potassium – and on the Fe_2O_3 concentration of the glasses. In glasses which contain a very small quantity of Fe_2O_3 the irradiation induces more defects than in the corresponding iron-free glasses. With increasing Fe_2O_3 content the glasses become more resistant against irradiation and at a high concentration no more defects can be produced.

ESR-Untersuchungen an eisenhaltigen Lithium-, Natrium- und Kaliumsilicatgläsern vor und nach Bestrahlung mit γ- und Röntgenstrahlen

Lithium-, Natrium- und Kaliumsilicatgläser unterschiedlicher Fe_2O_3-Konzentrationen wurden mit γ- und Röntgenstrahlen bestrahlt und mit der ESR untersucht. Die bekannten Eisenresonanzen bei $g = 4{,}2$ und $g = 1{,}99$ zeigten ein charakteristisches Verhalten beim Übergang von Lithium zu Kalium und bei Änderung des Fe_2O_3-Gehaltes. Die Resonanz bei $g = 4{,}2$ nimmt von Lithium zu Kalium ab, die bei $g = 1{,}99$ dagegen zu. Die Übereinstimmung des Intensitätsverlaufs der beiden Resonanzen mit der Neigung der Alkalimetalle, tetraedrische oder oktaedrische Koordinationen zu bilden, stellt einen interessanten Beweis für die Zuordnung von $g = 4{,}2$ zum 4fach-koordinierten Fe^{3+}-Ion und von $g = 1{,}99$ zur 6er Koordination dar.

γ- und Röntgenstrahlen produzieren die gleichen Defektzentren (Farbzentren). Sie sind durch eine starke Resonanz bei $g = 2{,}01$ gekennzeichnet. Alle Defekte zeigen eine ausgeprägte Abhängigkeit von der Art der Alkalimetalle – sie nehmen von Lithium zu Kalium zu – und von der Fe_2O_3-Konzentration. In Gläsern mit niedrigem Fe_2O_3-Gehalt entstehen mehr Strahlungsdefekte als in den entsprechenden eisenfreien Gläsern. Mit zunehmendem Fe_2O_3-Gehalt werden die Gläser strahlungsresistenter, und bei hoher Konzentration treten keine Defekte mehr auf.

1. Introduction

Previous investigations [1 and 2] of X-ray irradiated sodium silicate glasses have shown that the Fe_2O_3 content has a large influence on the occurrence of radiation defects in glass and on the resulting glass colour. Particularly very important for the effects concerned are the quantity and structure of the Fe^{3+} ions present. It is also known that the coordination behaviour of the Fe^{3+} ions in alkali silicate glasses is largely influenced by the alkali metals (lithium, sodium, potassium, cesium) [3]. In the present work lithium, sodium and potassium silicate glasses of various Fe_2O_3 concentrations were irradiated with γ- and X-rays and studied by means of ESR. The aim was to compare directly the effect of the two radiations and to characterize the induced radiation defects as a function of the alkali metals.

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[1]) Presented in German at the 63rd Annual Meeting of the German Society of Glass Technology (DGG) on May 24, 1989, in Stuttgart (FRG).

2. Experimental

2.1. Investigated glasses

The investigated glasses had the following composition (in mol%): $69-x$ SiO_2, 25 Me_2O (Me = lithium, sodium, potassium), 6 CaO, x Fe_2O_3 ($x = 0$, 0.002, 0.004, 0.01, 0.02, 0.04, 0.1, 0.2, 0.5, 1, 2, 2.5).

Rock crystal and Me_2CO_3, $CaCO_3$ and Fe_2O_3 of reagent-grade quality were used as raw materials. After homogeneous mixing, the raw materials were

melted in platinum crucibles for 3 h in an electric furnace (Nabertherm GmbH + Co. KG, Lilienthal (FRG)) at 1400 °C in air atmosphere. The glasses were quenched on a metal plate. All Li_2O glasses investigated had a strong tendency to crystallize, if cooled slowly in air.

2.2. Sample preparation and irradiation

For all investigations, the glasses were crushed and sieved. Only fractions of 0.6 to 1 mm in diameter were used.

X-ray irradiation was carried out using a Siemens Dermopan (Siemens AG, Berlin und München (FRG)). The experimental parameters were 50 kV, 25 mA and 27 min exposure. γ-ray irradiation was achieved using the Buchler equipment OB29/4 (Buchler GmbH, Braunschweig (FRG)) with the experimental parameters 660 keV, ^{137}Cs as source.

To enable comparison of the lithium, sodium and potassium glasses, all samples containing no iron or having the same Fe_2O_3 content were melted in the same furnace at the same time and irradiated simultaneously. A more detailed description of the irradiation methods is given by Schels [4].

2.3. ESR measurements

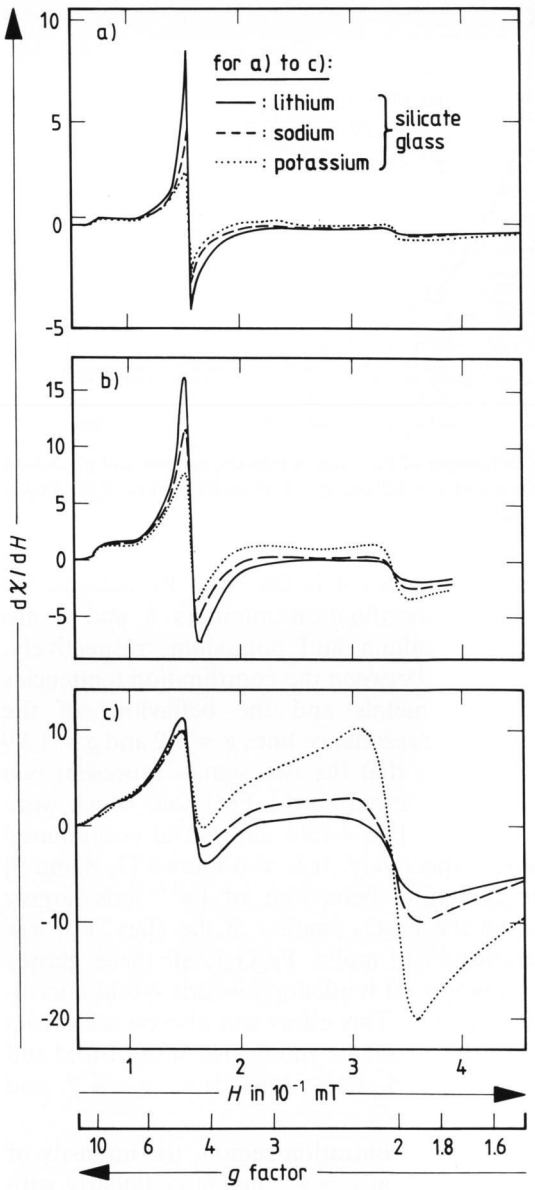
The ESR spectra were recorded at room temperature at X band (9.5 GHz) using a Bruker spectrometer B 414 (Bruker Physik AG, Rheinstetten-Forchheim (FRG)). 100 mg of glass powder (0.6 to 1.0 mm fraction) were used in each case. Thus, the filling factor was the same for each measurement. The spectra can be compared both, qualitatively and quantitatively.

3. Results and discussion

3.1. Fe^{3+} in lithium, sodium and potassium silicate glasses before irradiation

The Fe^{3+} ion is a very sensitive agent for ESR investigations of lithium, sodium and potassium silicate glasses both before and after irradiation. The coordination behaviour of Fe^{3+} ions in lithium, sodium, potassium and cesium silicate glasses was reported by Camara [3]. The present study is dealing with the same glasses after irradiation with γ- and X-rays. Figures 1a to c show the ESR spectra of lithium, sodium and potassium silicate glasses with three different Fe_2O_3 concentrations before irradiation.

One can see, particularly from the 0.1 and 0.5 mol% Fe_2O_3 spectra that the intensity of the Fe^{3+} resonance line at $g = 4.2$ decreases systematically in the series lithium, sodium, potassium. At the same time the intensity of the resonance line $g = 1.99$ increases in the reversed direction. This reversed behaviour of the two signals can easily be understood,



Figures 1a to c. ESR spectra show the structural behaviour of Fe^{3+} ion in lithium, sodium and potassium silicate glasses ($(69 - x)$ $SiO_2 \cdot 25\ Al_2O_3 \cdot 6\ CaO \cdot x\ Fe_2O_3$) for three Fe_2O_3 concentrations (in mol%) before irradiation, a) 0.1 Fe_2O_3, b) 0.5 Fe_2O_3, c) 2.0 Fe_2O_3.

if it is assumed that they represent two distinct Fe^{3+} structures, each having its own interaction with the alkali ions. Such an interaction may occur, e.g. if the Fe^{3+} and the alkali ions are both involved in a coordination polyhedron. In both, 4-fold and 6-fold coordinations, the Fe^{3+} ions can have alkali ions as "nearest neighbours" – to assure charge compensation – and can build tetrahedral or octahedral groups with them. Which of these arrangements really occurs, depends on which case the individual alkali metals prefer. Due to their different ionic radii (lithium: 0.06, sodium: 0.095, potassium: 0.133, cesium: 0.169 nm), the alkali metals have in fact different tendencies in an oxygen environment (O^{2-}: 0.140 nm). It is well known [5 and 6] that the

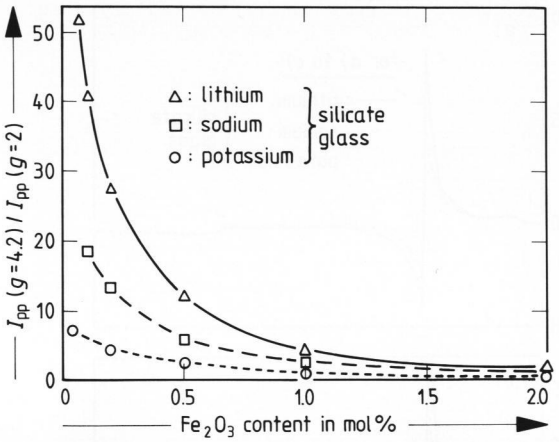
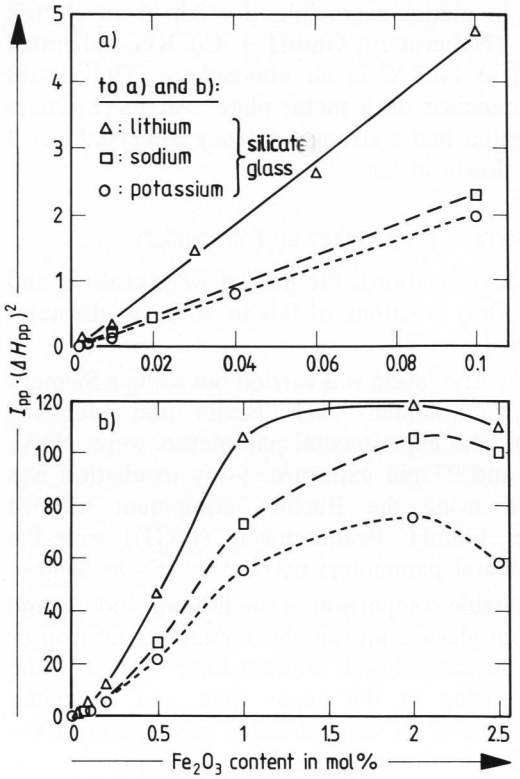


Figure 2. Behaviour of Fe^{3+} ion in lithium, sodium and potassium silicate glasses at $g = 4.2$ and $g = 1.99$ as a function of the Fe_2O_3 concentration.

coordination number 4 is favoured by lithium. By contrast, the coordination numbers 6 and 8 are preferred by sodium and potassium, respectively. This agreement between the coordination tendencies of the alkali metals and the behaviour of the intensities of the resonance lines $g = 4.2$ and $g = 1.99$ strongly suggests that the two signals represent two different coordinations of the Fe^{3+} ion, which were assigned [7 to 10] to 4-fold and 6-fold coordinated Fe^{3+} ions, respectively. It is also known [3, 8 and 9] that the structural behaviour of Fe^{3+} ions largely depends on the Fe_2O_3 content of the glass. For low concentrations (0.1 mol% Fe_2O_3), all three glasses show a pronounced tendency towards 4-fold coordination (figure 1a). This effect can also be seen from the ratio of the resonance intensities of the 4-fold and 6-fold coordinated Fe^{3+} ions (i.e. $g = 4.2$ and $g = 1.99$) in figure 2.

In the low-concentration region, the intensity of the resonance line at $g = 4.2$ increases linearly with



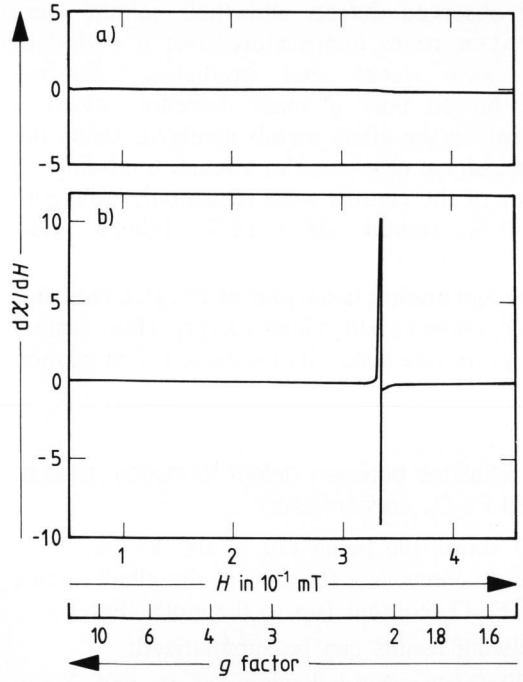
Figures 3a and b. Behaviour of Fe^{3+} ion in lithium, sodium and potassium silicate glasses at $g = 4.2$ as a function of the Fe_2O_3 content, a) low Fe_2O_3 contents, b) high Fe_2O_3 contents.

increasing Fe_2O_3 content for all three alkali metals (figure 3a). Increasing the Fe_2O_3 concentration alters the structural behaviour of the signal at $g = 4.2$ (figure 3b).

The following two effects can be summarized from figure 3b: The increase of the signal at $g = 4.2$ becomes slowly. At the same time, the intensity of the signal at $g = 1.99$ – not shown here – increases significantly. This means that the number of the

Table 1. Effects of X-ray irradiation on the colour behaviour of lithium, sodium and potassium silicate glasses

Fe_2O_3 in mol%	lithium glass		sodium glass		potassium glass	
	X-ray irradiation					
	before	after	before	after	before	after
trace	colourless	brownish	colourless	grey	colourless	bluish grey
0.002	–	–	–	–	colourless	bluish grey
0.003	colourless	brownish	colourless	grey	–	–
0.004	–	–	–	–	colourless	bluish grey
0.01	colourless	brownish	colourless	grey	colourless	bluish grey
0.02	–	–	–	–	colourless	bluish grey
0.03	colourless	brownish	colourless	grey	–	–
0.04	–	–	–	–	colourless	bluish grey
0.06	pale blue-green	brownish	–	–	–	–
0.1	pale blue-green	pale brown-green	pale green	light green	pale green	bluish grey
0.2	blue-greenish	blue-greenish	greenish	grey-greenish	greenish	greyish-green
0.5	yellow-green	yellow-green	greenish	greenish	greenish	greenish
1.0	dark green	dark green	olive green	olive green	yellow-green	yellow-green
2.0	dark green	dark green	dark olive green	dark olive green	brown-green	brown-green



Figures 4a and b. ESR spectra of an iron-free silicate glass (composition (in mol%): 69 SiO_2, 25 K_2O, 6 CaO) at the resonance line $g = 2.01$ before (figure a) and after (figure b) irradiation.

6-fold coordinated Fe^{3+} ion [8] increases much more. If the Fe_2O_3 content continues to increase, the intensity of the resonace line at $g = 4.2$ decreases significantly. In agreement with [8], this effect could be explained by the occurrence of phase separation and the formation of a Fe_2O_3-rich phase. All three alkali glasses exhibit this effect.

3.2. γ- and X-radiation effects

Both types of radiation were used simultaneously in order to obtain a direct comparison of their actions.

3.2.1. Effect on the colour of the glasses

Table 1 shows the effect of X-radiation on the colour behaviour of the lithium, sodium and potassium glasses before and after irradiation.

All the glasses containing very low or no iron were colourless before irradiation. After irradiation with either X- or γ-rays the following colours were observed:
lithium glass: brownish,
sodium glass: grey,
potassium glass: bluish.

X- und γ-rays induced the same shade. However, the intensity of the X-ray induced colour is mostly stronger than the effect caused by the γ-rays. This indicates that the X-rays produced more colour centres than the γ-irradiation does. The characteristic

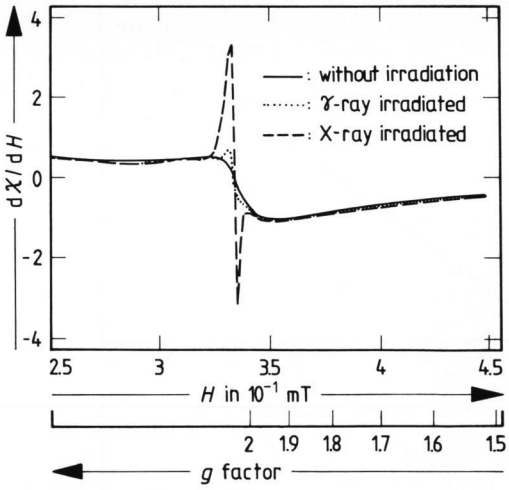


Figure 5. ESR spectra of an iron-containing (0.2 mol% Fe_2O_3) potassium silicate glass irradiated with γ- and X-rays in comparison to the non-irradiated glass.

"radiation colours" decrease with increasing iron concentration. For high iron concentrations (≥ 0.2 mol% Fe_2O_3) the glasses exhibit only the colour due to iron. In this case, the colour remains the same before and after irradiation.

3.2.2. Nature and lifetime of defect centres (colour centres)

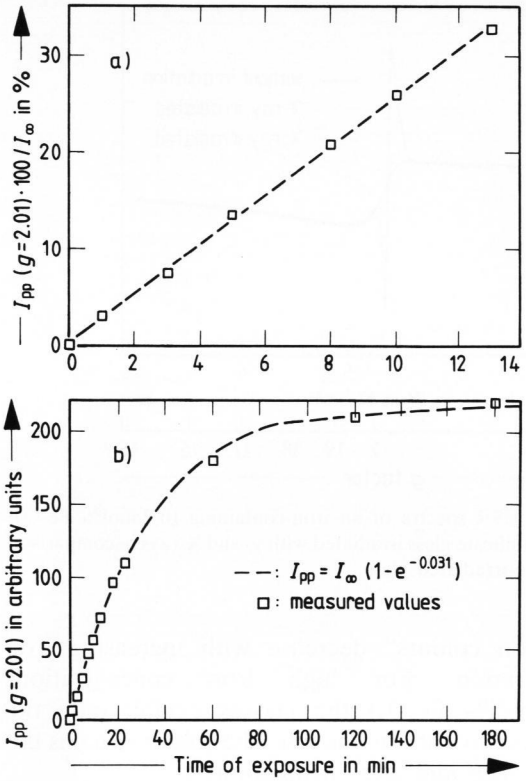
The defects produced by the X- and γ-rays are characterized by a strong resonance line at $g = 2.01$ (figures 4a and b).

This signal is used in the present study in order to characterize the defects depending on
the alkali metals (lithium, sodium, potassium, cesium),
the Fe_2O_3 concentration and
the kind of irradiation and exposure time.

Figure 5 shows the ESR spectra of one iron-containing (0.2 mol% Fe_2O_3) potassium glass, which was irradiated with γ- and X-rays. For both types of radiation the same resonance signal ($g = 2.01$) is obtained. This is an indication that the two radiations really induce the same defect centres, this being in good agreement with Stroud [11].

However, the intensity of the signal induced by X-ray irradiation is considerably higher than that caused by γ-rays (figure 5). This indicates once more that X-rays produce more defect centres. This result has soon been discussed in analyzing the colour behaviour of the irradiated glasses. The exposure time influences the formation of the radiation defects differently. Two periods can be distinguished:

a) For short periods of exposure (≤ 15 min) the defects increase linearly with time (figure 6a). The potassium glass shown contains 0.004 mol% Fe_2O_3 and was irradiated with X-rays. Qualitatively, γ-radiation produces the same results.



Figures 6a and b. Behaviour of defect formations in potassium silicate glass with 0.004 mol% Fe_2O_3 and irradiated with X-rays (30 keV) as a function of periods of exposure, a) $t \leq 15$ min, b) $t \geq 15$ min.

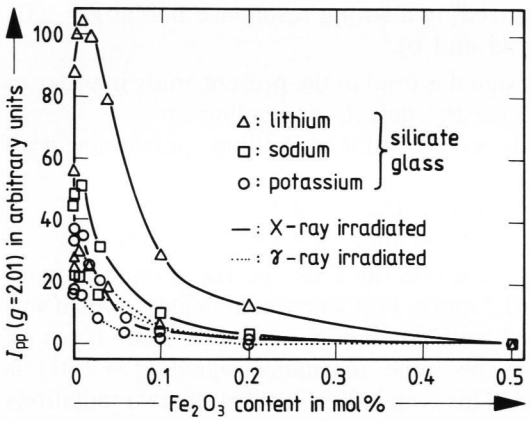


Figure 7. Behaviour of defects induced by X- and γ-ray radiation as a function of the Fe_2O_3 concentration up to 0.5 mol% Fe_2O_3 and with the alkali metals in silicate glass as parameter.

b) For long periods (> 15 min) the behaviour of the defect formation is different as shown in figure 6b.

These results can be described by the equation

$$I_{pp} = I_\infty (1 - e^{-at}) , \quad (1)$$

where I_{pp} = peak-to-peak height of $g = 2.01$, I_∞ = saturation value, t = time of exposure, $a = 0.03$ (computer calculated for the potassium glass).

The observed defects and their colours were conserved at room temperature over a period of months. Five weeks after irradiation, iron-free glasses showed only a small decrease, which is dependent on the alkali metals involved. Using the resonance signal at $g = 2.0$ as a scale, the following decreases of the centres were registered: potassium glass: 10 %, sodium glass: 14 %, lithium glass: 24 %.

The regeneration behaviour of the glasses is also clearly dependent on the alkali ions [4]. Thus, lithium glasses regenerate faster than sodium and potassium glasses.

3.2.3. Relations between defect formation, type of alkali and Fe_2O_3 concentration

Figure 7 shows the behaviour of the X- and γ-ray irradiation defects as a function of the alkali metals and the Fe_2O_3 content (up to 0.5 mol% Fe_2O_3).

Following results can be summarized:

a) Qualitatively, the behaviour of γ- and X-ray induced defects is the same for all three alkali metals; this is also the case for their behaviour as a function of the Fe_2O_3 concentration.

b) The influence of iron on defect formation changes with Fe_2O_3 concentration in two ways:

– For low iron content more defects occur than in the corresponding iron-free glasses. For the glasses investigated, there is a maximum of occurrence at 0.01 mol% Fe_2O_3 (figure 7).

– For glasses containing more Fe_2O_3 than 0.01 mol% the irradiation defects decrease continually with increasing iron content. This effect has already been described by Camara and Oel [2]. The iron concentration at which no further defects are observed, depends on the alkali metals [4]. For lithium glass this is at 0.2 mol% Fe_2O_3, for potassium glass at 0.5 mol%. γ- and X-rays produce the same effect. The defect formation increases as follows: Li → Na → K → Cs. It is important to note that the ionization energies (bonding energies) of the alkali metals concerned decrease in the same direction. This indicates that a connection exists between alkali ions and the defects. It is assumed that these defects are localized between the non-bridging oxygen atoms and the alkali ions.

3.2.4. Behaviour of the Fe^{3+} ion at $g = 4.2$

The behaviour of the Fe^{3+} ion in X-ray irradiated sodium silicate glass has already been investigated by Kordas [1] and Camara and Oel [2]. The present study deals with the behaviour of the Fe^{3+} ion in lithium, sodium and potassium silicate glasses after irradiation with γ- and X-rays.

Figure 8 shows the behaviour of the resonance line of the Fe^{3+} ion at $g = 4.2$ after irradiation with γ-

and X-rays. The investigated glass is a potassium glass containing a small quantity of Fe_2O_3 (0.004 mol%). Both radiations cause a decrease of Fe^{3+} ions. However, the decrease caused by X-rays is significantly greater. Since X-ray irradiation produces more defects than γ-rays do (as discussed in section 3.2.1.), the large reduction of Fe^{3+} ions caused by the X-radiation indicates that an interaction must exist between the defects and Fe^{3+} ions.

The irradiation-induced decrease of Fe^{3+} ions is generally accepted to be [1, 2, and 10] a reduction of Fe^{3+} ions, which may be written as follows:

$$Fe^{3+} + e^- \longrightarrow Fe^{2+*} \qquad (2)$$

where * means radiation-induced oxidation state.

Together with the just described observations that Fe^{3+}ions and radiation defects decrease at the same time, equation (2) means that the defects concerned are electrons, not holes. This is in agreement with the generally accepted theory [12], that the most important X- and γ-ray irradiation effects are in nature electron processes. From the clearly observed dependence of these defect electrons on the alkali metals – periodic increase in the series $Li \rightarrow Na \rightarrow K \rightarrow Cs$ – it can be assumed that they belong to the alkali ions or are localized in their vicinity.

From the supposed reduction mechanism $Fe^{3+} + e^- \rightarrow Fe^{2+*}$ – this explains the decrease of Fe^{3+} ions as well as that of the defects – the Fe^{2+*} ion is formed. This Fe^{2+*} ion must have the same structure (coordination) as the Fe^{3+} ion at $g = 4.2$, because the irradiation can not cause any change in the coordination state of the Fe^{3+} ion. Thus, the determination of the coordination of the Fe^{2+*} ion is very important, if the interpretation of the resonance line at $g = 4.2$ is considered. The best method of determining the Fe^{2+} structure is, without doubt, the optical spectroscopy. The ligand field absorption (Δ) of Fe^{2+} in octahedral coordination (Δ_o) occurs in sodium silicate glass at 1050 nm (9523 cm^{-1}). The corresponding energy in tetrahedral coordination (Δ_t) in the same glass system can be calculated. From the well-known equation:

$$\Delta_t = -\frac{4}{9}\Delta_o \qquad (3)$$

($\Delta_o = 9523\ cm^{-1}$) one obtains 2360 nm (4232 cm^{-1}). Both Bishay [10] and Kordas [1] reported that sodium silicate glasses which were irradiated with γ-rays [10] and X-rays [1] showed an absorption of Fe^{2+} in this spectral region. The occurrence of radiation-induced Fe^{2+} around 2000 nm is a strong support for the assignment of the Fe^{3+} ion at $g = 4.2$ to tetrahedral coordination (network former) [8 to 10].

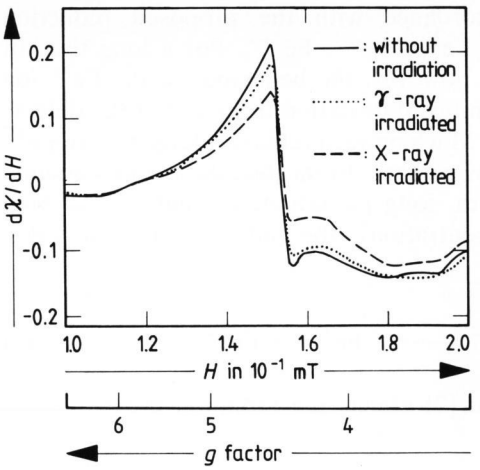
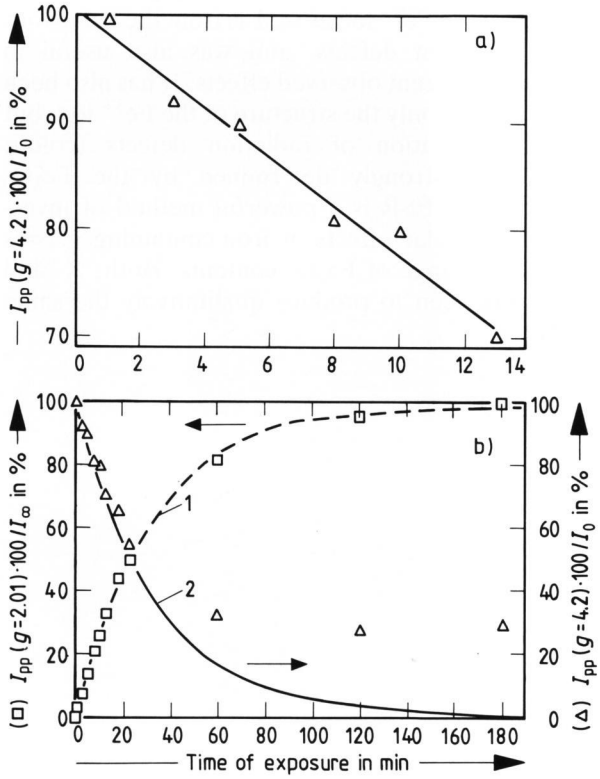


Figure 8. Behaviour of Fe^{3+} ion in a potassium silicate glass at $g = 4.2$ with 0.004 mol% Fe_2O_3.



Figures 9a and b. Behaviour of Fe^{3+} ion in X-ray irradiated (30 keV) potassium silicate glass with 0.004 mol% Fe_2O_3 as a function of time of exposure for a) $t \leq 15$ min, b) $t \geq 15$ min (curve 1: $I_{pp}\ (g = 2.01) = I_\infty\ (1 - e^{-0.031})$; curve 2: $I_{pp}\ (g = 4.2) = I_0\ e^{-0.031}$).

It was pointed out that the occurrence of defects was affected by the time of exposure. For this reason, the effect of various irradiation times on the behaviour of the Fe^{3+} ion at $g = 4.2$ was also investigated. The results are shown in figure 9a. The glass shown is a potassium glass containing 0.004 mol% Fe_2O_3. It can be seen that for short periods of irradiation the Fe^{3+} ion decreases linearly. The linear increase of the defects and the corresponding decrease of Fe^{3+} ions

are in accordance with the proposed reduction mechanism $Fe^{3+} + e^- \rightarrow Fe^{2+*}$. For a long time of irradiation, however, the behaviour of the Fe^{3+} ion shows a significant deviation from that of the defects (figure 9b). Much more, a relatively large part of Fe^{3+} ions remains present. From this, the authors assume that for both, long periods of irradiation and high Fe_2O_3 concentrations, the radiation-induced redox reaction

$$Fe^{2+} + Fe^{3+} \longrightarrow Fe^{3+*} + Fe^{2+*}, \qquad (4)$$

described in [2] affects the radiation process.

4. Conclusion

The periodicity of the alkali elements lithium, sodium, potassium and cesium emerged from the structure of the Fe^{3+} ion as well as from the behaviour of the radiation defects, and was also useful in explaining different observed effects. It has also been shown that not only the structure of the Fe^{3+} ion, but also the formation of radiation defects (colour centres) are strongly determined by the Fe_2O_3 concentration. ESR is a powerful method of investigating particular effects in iron-containing glasses over a wide range of Fe_2O_3 contents. Both, X- and γ-rays were seen to produce qualitatively the same results.

5. References

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