Microstructure and properties of transparent glass-ceramics

Part 3 *ESR studies of glass crystallization*

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Crystallization in glasses based on the $ZnO-Al_2O_3-SiO_2$ system nucleated with ZrO_2 have been studied by electron spin resonance. The glass crystallization has been monitored by observing the change in the coordination of Fe^{3+} ions present in the glasses as an impurity.

1. Introduction

Very few published reports deal with the ESR method in the investigation of the crystallization process in glasses [1–4].

Electron spin (or paramagnetic) resonance studies are particularly concerned with the structure and localization of paramagnetic centres produced either by high-energy radiation (X-rays, γ-rays, fast neutrons) or by the presence of paramagnetic impurities (e.g. 3d ions). At the same time, the centres act as a probe for their surroundings and so provide information about the glass structure.

Most of the work performed on glass in the past twenty years has been mainly concerned with looking at the effect of ionizing radiation on glass and the effect of transition metal ion impurities.

The role of Fe^{3+} ions in glasses has been extensively researched [5–11]. Similarly, work has been performed by ESR on the role of manganese in glasses [12, 13].

2. Experimental

Electron spin resonance spectra were run on a Decca spectrometer, at room temperature, operating in the X-band at a frequency of 9.270 GHz. Carbon (coke) was used as a g-marker, producing a sharp resonance at $g = 2.0023$.

The glass and glass-ceramic studied was that given in previous publications by the authors [14, 15] namely glass 3. The glass, given in Table I was heat-treated at 800° C for 4 h and 950° C for 1 to

TABLE I Composition of glass 3 in wt %

Material	SiO_2	Al_2O_3	ZnO	CaO	ZrO_2
Glass 3	63.6	17.3	5.5	4.5	9.1

6 h. Identical samples measuring 8 mm × 3 mm × 1 mm were used in all investigations.

3. Results

The spectra obtained of glass and glass-ceramic 3 (heat-treated at 800° C for 4 h and 950° C for 6 h) are shown in Fig. 1. Several interesting resonances are present; two asymmetric resonances at $g = 4.27 \pm 0.03$ and $g = 3.92 \pm 0.02$, and six small symmetric lines centred around $g = 2$ with $\Delta B = 83.0$ Gauss (0.00830 T). The untreated parent glass only shows the $g = 4.27$ resonance.

The six small resonances centred around $g = 2$ were identified as the hyperfine structure of Mn^{2+} ions present in the glass as an impurity [6, 10–13, 16–18].

The other two resonances at $g = 4.27$ and $g = 3.92$ were more difficult to interpret. It was thought that one or both of these could be due to iron, Fe^{3+}, again present as an impurity, because of previous work on the role of iron in glass systems. Castner *et al.* [19] identified unknown resonances at $g = 4.27$ and $g = 6$ determined by Sands [5], as being due to Fe^{3+} ions.

Kurjian and Sigety [9] investigated the ESR, optical and Mössbauer spectra of Fe^{3+} in silicate and phosphate glasses. They found that in silicate
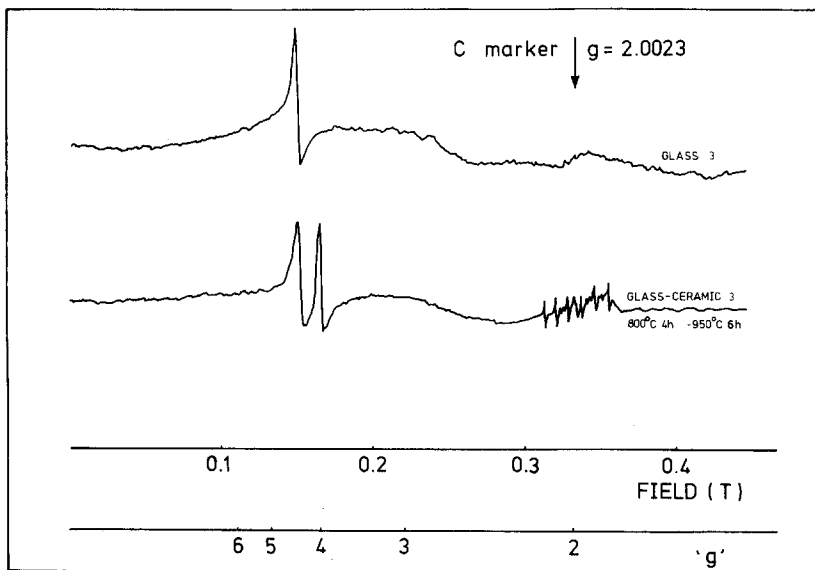
Figure 1 ESR spectra of glass and glass-ceramic 3.

glasses the Fe^{3+} was four-coordinated and in phosphate glasses it was six-coordinated. Two resonances were observed, one at $g = 4.3$ when a low concentration of Fe^{3+} was present, and $g = 2$ with a high concentration of Fe^{3+}.

Tucker [6] in this study of Fe^{3+} in sodium silicates, found that the $g = 2$ resonance indicated the Fe^{3+} to be in a network modifier position and that the $g = 4.28$ resonance showed the Fe^{3+} to be in a network former position. This was supported by Kurjian and Sigety [9] and Hirayama *et al.* [20] following ESR work on iron in alkaline earth phosphate glasses where they inferred the resonances at $g = 2$ and $g = 4.3$ to arise from Fe^{3+} in six- and four-fold coordination respectively.

Karapetyan *et al.* [7] studied Fe^{3+} in barium and lead silicates, and concluded that the resonance at $g = 4.3$ belonged to the Fe^{3+} ion in the role of a lattice former in tetrahedral coordination, and that the $g = 2$ resonance was due to six-fold coordinated iron.

Dickson and Srivastava [21] performed work on the Mössbauer hyperfine spectra of dilute Fe^{3+} in synthetic $Mg\,Al_2O_4$ spinel. Ferric ions introduced into spinel should be able to enter the octahedral (mainly Al) sites or tetrahedral (Mg) sites. In low concentrations, the iron has a strong preference to enter the tetrahedral site.

From the above survey, it was now thought that the two resonances at $g = 4.27$ and $g = 3.92$ were due to Fe^{3+} ions present as an impurity in the glass.
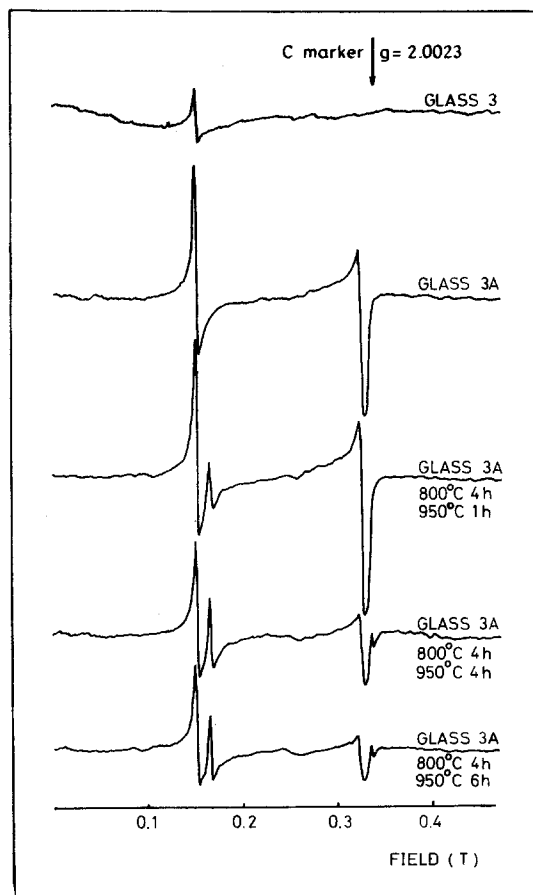
Atomic absorption measurements were ob-

Figure 2 ESR spectra of glass and glass-ceramic 3A.

tained on a powdered sample of glass 3. Emphasis was put on the amount of iron and manganese in the glass. The amount of iron was determined to

be 130 p.p.m. and of manganese to be 3.1 p.p.m. The ESR resonance of manganese observed was therefore real, but direct evidence was still required in order to prove that the two $g = 4$ peaks were due to iron. A glass (glass 3A) was prepared involving the addition of an excess of 0.08% Fe^{3+} (800 p.p.m.) in the form of ferric oxide Fe_2O_3 to glass 3 and melting the batch in the usual way.

Fig. 2 shows the resulting spectrum of this glass. There is a marked increase in the $g = 4.27$ resonance, and also present is an additional asymmetric resonance at $g = 2.075 \pm 0.002$ which could not be identified. Crystallization of this glass resulted in the appearance of the resonance at $g = 3.92$. Further heat treatment increased the peak-to-peak height of this resonance while at the same time decreasing the intensity of the $g = 2.075$ resonance and also of the $g = 4.27$ resonance.

Both the $g = 4.27$ and $g = 3.92$ resonances produced in glass and glass-ceramic 3A were of a greater intensity than those of glass and glass-ceramic 3, indicating that these resonances must be due to the presence of iron, Fe^{3+}. On this basis, glass 3 was analysed in more detail. Fig. 3 shows the spectra of glass and glass-ceramic 3 for varying crystallization heat treatments. It is clear that the resonance at $g = 3.92$ increases in intensity as the glass crystallizes. Nucleated glasses showed only the $g = 4.27$ resonance. Similarly, the Mn^{2+} peaks tend to increase in intensity, indicating some structural rearrangement as the heat treatment proceeds.

From the preceding results it was thought that the iron could possibly change its state of coordination as the glass crystallized, taking on a four-fold coordination in the glass as a network former, and changing to six-fold coordination during the growth of gahnite crystals.

Sugiura [22] and Drumheller et al. [23] studied the paramagnetic resonance of Fe^{3+} in $MgAl_2O_4$ and $Zn Al_2O_4$ spinel and assumed that in gahnite ($Zn Al_2O_4$) the Fe^{3+} ions occupy B-sites, i.e. either four-fold or six-fold coordination.

In the glass and glass-ceramic studied, it can therefore be assumed that the $g = 4.27$ resonance is due to Fe^{3+} ions in four-fold coordination, and that once the glass crystallizes, the Fe^{3+} ions in six-fold coordination in gahnite can be detected at the value of $g = 3.92$. The resonance observed by previous workers at $g = 2$ in other glass systems could have been shifted to a higher value, due to the crystal field splitting. The iron present in the
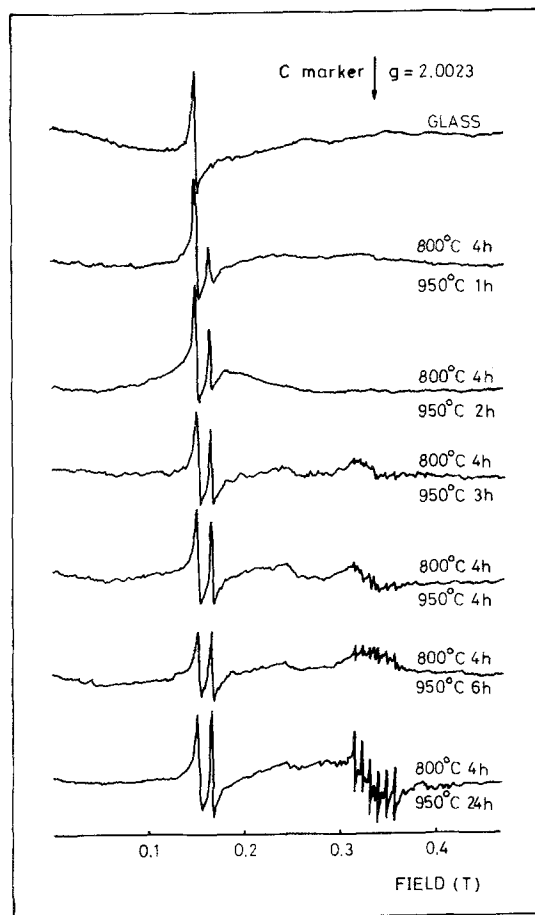

Figure 3 ESR spectra of glass 3 for various heat treatments.

glass and glass-ceramic could play a similar role to that of aluminium in that the aluminium in the glass can take up a four- or a six-fold coordination, whilst in gahnite the aluminium is in six-fold coordination and the zinc in four-fold coordination.

Since the resonance of glass 3, which in fact was annealed and showed signs of phase separation [14], produced an asymmetric feature, it could be established that the Fe^{3+} ions reside fairly closely to an asymmetric crystal field which in this case would be tetragonal zirconia or even zirconia-rich regions. Similarly, the appearance of the asymmetric six-fold coordinated Fe^{3+} ion resonance at $g = 3.92$ during heat treatment might indicate that the gahnite crystals grow very close to, or even around the tetragonal zirconia nuclei, since the gahnite itself is cubic and would lead to a symmetric resonance.

A plot of the ratio of intensities of the right hand ($g = 3.92$) peaks to the left hand ($g = 4.27$) peaks of the crystallization series, (to normalize
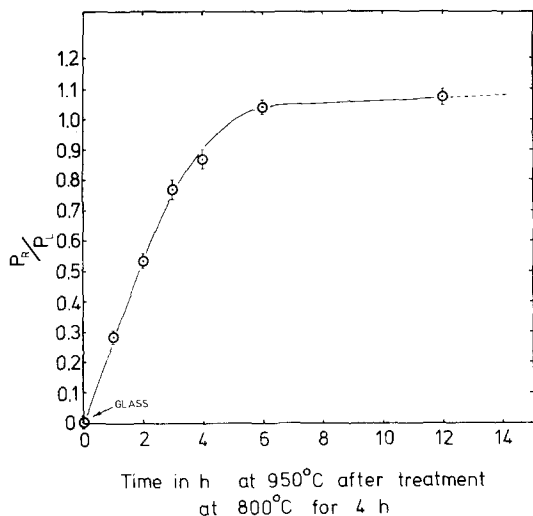
Figure 4 Variation in ratio of the intensities of the two Fe^{3+} peaks with heat treatment of glass-ceramic 3.

the height of the $g = 4.27$ peak) leads to a smooth curve, as seen in Fig. 4., tailing off after the five-hour heat treatment, presumably indicating that maximum crystallization has occurred, since no additional six-coordinated Fe^{3+} ions in gahnite are detected.

Spectra were run on all the glasses and glass-ceramics mentioned in previous publication by the authors [14], and all produced the same results, except that the $g = 3.92$ resonance is reduced in intensity. The $g = 3.92$ resonance even appeared in glass-ceramic 1 where a β-quartz s.s. was the dominant crystal phase. It is not known whether iron in β-quartz could take up a six-fold coordination.

4. Discussion

For the particular system under investigation, electron spin resonance proved invaluable in monitoring the heat treatment schedule, especially when impurities, such as iron or manganese are present. In the particular investigation, it was found that iron produced the much surveyed resonance at $g = 4.27$, indicating that Fe^{3+} ions take up a tetrahedral coordination as a network former. Crystallization led to introduction of Fe^{3+} ions into the gahnite crystal phase (and to a lesser extent β-quartz s.s.) which take up a six-fold coordination, giving the resonance at $g = 3.92$. The height of this resonance increased with increasing time at the crystallization temperature

and reached a maximum after 5 h, just as did the volume fraction, indicating that no more Fe^{3+} ions can be introduced in to six-fold coordination. This shows that the maximum volume fraction of gahnite crystals has been reached.

Acknowledgements

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