JOURNAL OF MATERIALS SCIENCE 15 (1980) 2081–2090

Spectroscopic behaviour and internal friction of glasses containing iron having different redox ratios

A. K. BANDYOPADHYAY, P. AURIC*, J. PHALIPPOU, J. ZARZYCKI
Laboratory of Materials Science and CNRS Glass Laboratory, University of Montpellier II, 34060 Montpellier-Cedex, France

The Mössbauer and ESR spectra and internal friction behaviour of Na_2O–$3SiO_2$ glasses having different redox ratios have been studied. As the redox ratio changes over a considerable range, there is a significant structural change associated with both the Fe^{3+} and Fe^{2+} ions, as evidenced from the analysis of the molar volume and Mössbauer data. The ESR data qualitatively supports the Mössbauer data on the Fe^{3+} ions. The change of internal friction behaviour of these glasses around 50% Fe^{3+} is described in terms of the structural changes associated with the Fe ions, which is thought to influence the oxygen structure of these glasses. The importance of this structural change on the electronic conductivity behaviour of these types of glasses is mentioned.

1. Introduction

The internal friction (I.F.) of glasses is associated with their anelastic behaviour and is a measure of the lag of strain behind a periodic stress. This process is described in terms of different relaxation processes occuring in the material. Internal friction measurements as a function of temperature show that for oxide glasses the spectra generally consist of two wide peaks below the transformation range emerging from a non-negligible continuous background. The first of these peaks is usually attributed to a stress-induced diffusion of the alkali ions present in the glasses. The cause of the second peak, which is at a higher temperature, is less clear. This high temperature peak was attributed by many authors to the stress-induced diffusion of the non-bridging oxygen ions [1]. Other authors thought that this peak which is dielectrically inactive would be due to the reorientation of the elastic dipoles composed of alkali ions and neighbouring protons [2]. In $NaPO_3$ glasses, the second peak emerges from the background when water content is about 0.0056 wt%; the intensity of this peak was shown to increase as the water content increased [3]. This implies participation of oxygen ions, when OH^- ions take part in mechanical relaxation.

The first two references are concerned with the work where Al_2O_3 was introduced in alkali–silicate glasses. It should be pointed out that in this case the infra-red absorption band at 2750 cm^{-1} (Si–OH) decreased when Al_2O_3 was added in these glasses and the decrease of this band which is ascribed to the bonded OH groups was associated with an increase of the band at 3600 cm^{-1} (free OH) [4]. By contrast, in metaphosphate glasses containing Al_2O_3, the second peak in the I.F. spectra was found to vary in relation with the water content rather than with the concentration of Al_2O_3. Some doubts exist for the interpretation of this second peak, because the same feature was not observed in alkali borate glasses which do not exhibit this peak at all [5]. However, we think that, for glasses with comparable water content, the second peak in the internal friction spectra will be influenced by the structure of oxygen ions in the glass.

The second peak was also found to be influenced by the redox ratio (Fe^{3+}/Fe_{total}) when iron is introduced in a soda–silica glass. Internal friction

---

*Present address: Laboratory of Hyperfine Interaction, Department of Fundamental Research, Centre of Nuclear Studies, 38 000 Grenoble-Cedex, France

0022–2461/80/082081–10$03.00/0

behaviour of some of these glasses was reported earlier [6] where it was found that the second peak goes down with decreasing Fe^{3+}/Fe_{total} ratio. It is known that Al^{3+} ions take tetrahedral positions in a soda–silica glass when their concentration increases and it was found that the second peak goes down with increasing concentration of Al^{3+} ions. This peak ultimately vanishes when the number of tetrahedral Al^{3+} ions is optimum at $Na/Al \sim 1.0$. It is also known that Fe^{3+} ions can take both tetrahedral and octahedral positions in glasses, particularly in silicate glasses [7]. If we look at the paper by Phalippou *et al.* [6], we find that, in a $Na_2O–3SiO_2$ glass at almost constant total Fe, the height of the second peak goes up when the concentration of Fe^{3+} increases. If the Fe^{3+} ions were taking tetrahedral positions (as do Al^{3+} ions), the second peak should go down, which was not observed. Therefore, it could be thought that the number of octahedral Fe^{3+} ions increases with increasing concentration of Fe^{3+}. It could be also thought that even if the Fe^{3+} ions were taking tetrahedral positions when their concentration increases (like Al^{3+} ions), their behaviour inside the glass structure might be different from Al^{3+} ions in terms of polarising oxygen ions around them, which has a significant influence in the behaviour of the second peak in the I.F. spectra.

To resolve this problem, it was thought appropriate to carry out Mössbauer and ESR spectroscopy on these glasses to throw some light on the structural behaviour of Fe^{2+} and Fe^{3+} ions. Molar volume data are also presented to see whether there is any effect of the change of redox ratio and configurational changes (if any) on the oxygen structure of these glasses.

It should be mentioned here that our interest in these glasses is also due to the fact that during the last decade or so there has been a considerable activity in the field of semiconducting oxide glasses containing transition metal (TM) ions (see, for example, Bandyopadhyay *et al.* [8], for references). TM ions can remain in two (or more) valence states in glasses, and the charge transfer is due to electron hopping from lower to higher valence states. For vanadium phosphate glasses a maximum in conductivity was observed at $V^{4+}/V_{total} = 0.1$ to 0.2, contrary to the expectation from the simple hopping theory, and many ideas were put forward to explain the results [9]. But for iron phosphate glasses, a maximum in conductivity was observed at $Fe^{2+}/Fe_{total} \sim 0.5$ bv Hansen [10] as expected from the theory, although Vaughan and Kinser [11] observed that the maximum in conductivity is shifted to a higher value of redox ratio with increasing concentration of iron ions. Compared to a huge amount of work done on semiconducting phosphate glasses, not much work has been done on borate glasses [8, 12, 13], or on silicate glasses [14]. Moreover, no systematic spectroscopic work has been undertaken to throw light on the valence states, or on the coordination and covalency of TM ions in glasses as a function of redox ratio, and consequently to correlate them with conductivity data, as no conductivity results are being presented. It is shown from spectroscopic data that there are structural changes associated with the Fe^{2+} and Fe^{3+} ions as the redox ratio changes, which could have a significant influence on the conductivity behaviour of these glasses.

2. Experimental procedure

The glasses were prepared with the base glass composition as $Na_2O–3SiO_2$ and then adding ferrous oxalate and also ferric oxide. The glasses were melted at different temperatures for different times, and also at different partial pressures of oxygen to obtain higher degree of reduction (e.g. for glasses 4, 5 and 6 in Table I). Although total iron was kept almost constant (about 5.6 wt% as determined by chemical analysis), the compositions of these glasses are expressed as FeO and Fe_2O_3 separately, following Vanghan and Kinser [11], since the redox ratio varies over a considerable range in the same composition (see Table I).

The details of internal friction (IF) measurements are given elsewhere [15]. Glasses were annealed for three hours at a temperature where internal friction kept a constant value of 10^{-2}. The IF spectra for glasses 1 to 4 have already been published [6]. The values of the height of the second peak (Q^{-1}_{max}) in the last reference were found to be 9.8, 8.5, 7.5 and 6.45×10^{-3} for glasses 1, 2, 3 and 4 respectively, but in this work the values of Q^{-1}_{max} are presented having been corrected for background according to the method of analysis of Mohyuddin and Douglas [16]. These values along with those for glasses 5 and 6 (also corrected for background) are given in Table I.

Mössbauer spectra were recorded at room temperature with a source ^{57}Co in Cu matrix. The 14.4 KeV γ-rays were detected by means of a proportional counter. The source was moved by conventional constant acceleration drive; the velocity

TABLE I Composition, density, molar volume, internal friction and resistivity data for the glasses

Glass No.	*Composition (mol%)		% Fe^{3+}	Density (gm cm^{-3})	Q^{-1}_{max} (× 10^3)	Apparent molar volume (cm^{-3})	Log ρ_{300k} †
	FeO	Fe_2O_3					
1	2.60	9.70	88.1	2.555	9.16	27.56	15.2
2	5.60	8.50	75.1	2.556	7.10	27.22	14.8
3	6.30	8.30	72.7	2.557	6.23	27.16	14.7
4	9.10	7.00	60.5	2.566	4.93	27.17	14.6
5	11.70	4.80	44.8	2.548	5.20	26.13	14.8
6	17.30	1.50	14.9	2.553	5.00	25.05	15.1

*The rest of the glass consists of Na_2O:SiO_2 in the molar ratio 1:3
†ρ is the resistivity in ohm-meter.

signal of the electromechanical transducer was a symmetrical triangle. The counts were stored in the time mode of a 400 channel analyser.

ESR spectra were recorded at room temperature in a Brüker spectrometer operated at X-band frequency (9.6 GHz). The modulation frequency employed was 18 KHz, and the magnetic field was calibrated linearly upto 6000 Gauss. All the spectra were recorded with the same sample weight (350 mg) under identical conditions: in terms of gain, modulation sensitivity, microwave power, time constant and recorder sensitivity to make the results of these glasses comparable with each other.

3. Results and discussion

3.1. Molar volume and internal friction

Densities of these glasses were measured by Archimedes principle, and the values are given in Table I. From the densities and compositions of the glasses, the molar volume was calculated (Table I), and when plotted against mol% Fe_2O_3 (not shown) showed a change of slope around 6 mol% Fe_2O_3 (i.e. after glass 4). Following Drake and Scanlan [17], who plotted apparent molar volume (AMV) of oxygen ions against mol% Cu and showed a structural change associated with the Cu ions, the AMV of these glasses were calculated assuming that oxygen ions make up the volume of the glass. This is plotted against mol% Fe_2O_3 in Fig. 1. It is seen from Fig. 1 that AMV data of oxygen can be fitted by two straight lines with a distinct change around 6 mol% Fe_2O_3. When the redox ratio changes in a glass, it makes a change in the oxygen structure. Fig. 1 shows that the oxygen structure, in terms of the number and distribution of the bridging and non-bridging oxygen ions, is different in the first four glasses than that of the last two. Since a significant change in the coordination of Fe^{2+} ions is not observed in silicate glasses [7], the behaviour in Fig. 1 can be mainly attributed to the change of coordination of the Fe^{3+} ions. However, the effect of the change of coordination of the Fe^{2+} ions could be appreciable for the last two glasses as shown by our Mössbauer results (see later).

In fact, it is found that the values of Q^{-1}_{max} for the first three glasses, where Q^{-1}_{max} is strongly dependent on the concentration of Fe^{3+} ions, are very different from those of the last three glasses, where the values of Q^{-1}_{max} are almost constant (see Table I). The ratio Fe^{3+}/Fe^{2+}, which represents the number of Fe^{3+} ions around one Fe^{2+} ions, plays a very important role in the internal friction behaviour of the glasses. With an increase in the ratio, the competition between the Fe^{3+} ions to polarize the oxygen ions around them increases and consequently this influences the mobility of the oxygen ions. If a comparison between internal friction spectra of these glasses and that of the base glass is made, it is found that the first peak due to the stress-induced diffusion of alkali ions decreases strongly. This peak is found to be shifted to a higher temperature in the same manner

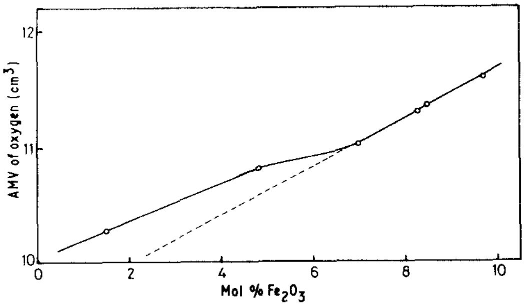

Figure 1 Apparent molar volume of oxygen against mol% Fe_2O_3.

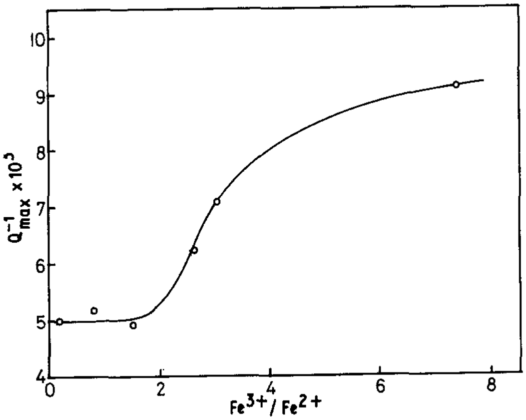

Figure 2 Q^{-1}_{max} against Fe^{3+}/Fe^{2+} ratio.

as in the mixed alkali effect. By measuring the infra-red spectra of these glasses, we observed no band at 2750 cm^{-1}, while there was a very little trace of the second band at 3600 cm^{-1} for only glass 1, so that the amount of water in this glass could be thought to be insignificant. Therefore, the effect of water content on the internal friction behaviour of these glasses can be neglected. This implies that the variation in the values of Q^{-1}_{max} in these glasses must be due to the variation of the polarization of oxygen ions with the change of Fe^{3+}/Fe^{2+} ratio.

The plots of Q^{-1}_{max} against Fe^{3+}/Fe^{2+} ratio and against AMV of oxygen are shown in Fig. 2 and 3. In Fig. 2, it is seen that Q^{-1}_{max} remains almost constant from glasses 6 to 4 and then it increases parabolically with Fe^{3+}/Fe^{2+} ratio up to glass 1. Similar behaviour is observed in Fig. 3, except that after glass 4 the Q^{-1}_{max} increases linearly with AMV of oxygen. As suggested earlier, the oxygen structure of the glass changes around this composition (glass 4) and influences the internal friction spectra, which is what we note in these two figures. It is noted from Fig. 1 that the AMV of oxygen follows a linear behaviour from glasses 1 to 4 and then it changes its slope quite significantly which is not so precisely reflected in the behaviour of Q^{-1}_{max} in Fig. 2 and 3. However, this behaviour can be attributed either to the change of concentration of the oxygen ions as Fe^{3+}/Fe^{2+} ratio increases (AMV of oxygen also increases), or to the change in the manner of distribution of the oxygen ions inside the glass structure. It is suggested that both these factors play an important role in the internal friction behaviour of these glasses. Even if the concentration of non-bridging oxygen ions increases from glasses 6 to 4, the values of Q^{-1}_{max} remain almost constant. This suggests that the distribution of the oxygen ions with respect to the iron ions is such that the mobility of these ions remains practically constant keeping the values of Q^{-1}_{max} constant. After glass 4 towards glass 1 with increasing Fe^{3+}/Fe^{2+} ratio (around 60% Fe^{3+}), the increasing number of oxygen ions along with a significant change of the distribution of these ions make the values of Q^{-1}_{max} increase. It is seen from Fig. 1 that the AMV of oxygen in the high Fe^{3+} concentration region increases linearly but with a higher slope

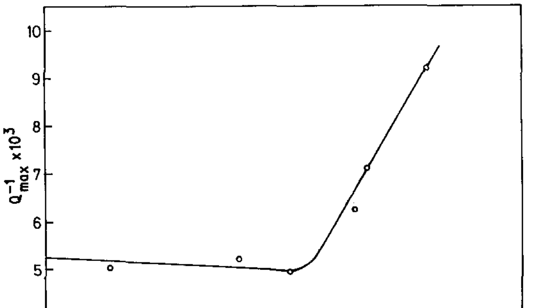

Figure 3 Q^{-1}_{max} against apparent molar volume of oxygen.

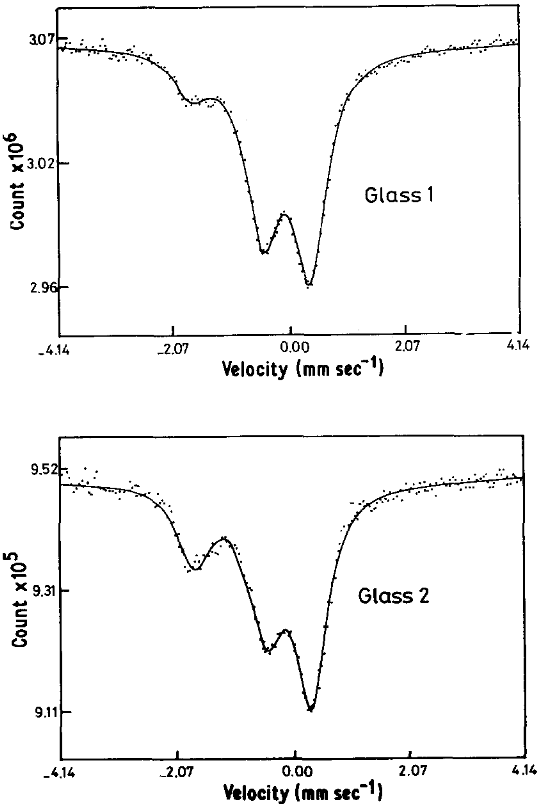

Figure 4 Mössbauer spectra of glasses 1 and 2.

TABLE II Mössbauer parameters and the concentrations of Fe^{3+} for the glasses

Glass No.	Fe^{2+}		Fe^{3+}		% Fe^{3+}
	($mm\,sec^{-1}$)	($mm\,sec^{-1}$)	($mm\,sec^{-1}$)	($mm\,sec^{-1}$)	
1	0.72 ± 0.07	2.15 ± 0.10	0.10 ± 0.01	0.84 ± 0.04	81.9 ± 0.5
2	0.72 ± 0.02	2.09 ± 0.03	0.12 ± 0.01	0.78 ± 0.02	65.0 ± 0.5
3	0.72 ± 0.02	2.15 ± 0.03	0.14 ± 0.01	0.74 ± 0.02	64.1 ± 0.5
4	0.72 ± 0.01	2.14 ± 0.02	0.15 ± 0.02	0.71 ± 0.02	54.0 ± 0.5
5	0.75 ± 0.04	2.08 ± 0.01	0.15 ± 0.02	0.68 ± 0.04	43.8 ± 0.5
6	0.78 ± 0.01	1.99 ± 0.02	0.18 ± 0.08	0.45 ± 0.14	11.5 ± 3.0

than that in the low Fe^{3+} concentration region. It is also noted that the oxygen structure is so sensitive to the Fe^{3+}/Fe^{2+} ratio that at a value of about 2 (i.e. 67% Fe^{3+} and 33% Fe^{2+}) the oxygen structure actually begins to change, which is significant for the internal friction behaviour of these glasses.

3.2. Mössbauer spectra

The Mössbauer spectra of the first two glasses are shown in Fig. 4. The spectra were computer-fitted by a least square procedure with the sum of four Lorentzian peaks, assuming the superposition of two doublets, the one from the Fe^{2+} and the other from the Fe^{3+} ions. It was not possible to fit the Fe^{3+} doublet into four Lorentzian peaks to separate the contribution of the octahedral and tetrahedral Fe^{3+} ions, as done by Levy *et al.* [7].

The calculated values of the quadrupole splitting (Δ) and isomer shift (δ) referred to Cu for both the Fe^{2+} and Fe^{3+} ions are given in Table II. From the ratio of the areas of the four Lorentzian peaks for these ions, their concentrations (in %) were determined assuming the same recoilles fraction for the two species. The concentration of Fe^{3+} ions is given in Table II. It is seen from Tables I and II that the concentration of Fe^{3+} ions determined by Mössbauer spectroscopy is lower (by an average of 6%) than that obtained by chemical analysis. This kind of anomaly is usual considering the different nature of the two experiments. This may be due to errors in both techniques. In the chemical analyses, the glasses are difficult to dissolve making it difficult to have all the Fe^{2+} ions in solution, i.e., oxidizing some of the Fe^{2+} ions to Fe^{3+}. In Mössbauer spectroscopy, however, the results are very much dependent on the fitting procedure. The spectra from glassy materials can not be very well fitted by a single Lorentzian function. It may be necessary to use a distribution of Lorentzian functions to get a better fit. However, it is worthwhile to note that an exactly opposite trend was observed by Levy *et al.* [7] on Na_2O–CaO–SiO_2 glasses, and by Gosselin *et al.* [18] as well as Belyustin *et al.* [19] on Na_2O–$3SiO_2$ glasses at higher concentration of Fe_2O_3 (> 6 mol%). The present work shows that no clear-cut trend can be predicted for the determination of the valence states of the iron cations, considering the difficulties mentioned above, as also emphasized by Kurkjian [20].

3.2.1. *Isomer shift and quadrupole splitting for Fe^{3+}*

Kurkjian and Sigety [21] measured Mössbauer spectra in silicates and phosphates in both glassy and crystalline forms, and compared their isomer shift values. They concluded that Fe^{3+} ions are in tetrahedral coordination in silicate glasses ($\delta < 0.10\,mm\,sec^{-1}$) and in octahedral coordination in phosphate glasses ($\delta > 0.15\,mm\,sec^{-1}$). Optical and ESR studies were used to substantiate these conclusions. Their isomer shift data agreed well with those of Mattern [22] and Hirayama *et al.* [23] for alkaline earth phosphates ($\delta = 0.22\,mm\,sec^{-1}$), and also with those of Gosselin *et al.* [18] and Belyustin *et al.* [19] for sodium silicates ($\delta = 0.07$ to $0.08\,mm\,sec^{-1}$). However, Levy *et al.* [7] observed for soda–lime–silica glasses that both octahedral and tetrahedral Fe^{3+} ions are present. Walker *et al.* [24] have calculated that the electron density at the tetrahedral site is greater than that at the octahedral site, which confirms all these results. The quadrupole splitting measures the departures from the cubic symmetry. Since the Fe^{3+} ion is spherically symmetric, it shows a more pronounced difference in the values of quadrupole splitting for tetrahedral and octahedral coordinations; the former having a higher value than that of the latter, because the tetrahedral site is characteristically less symmetric than the octahedral one. For many silicate glasses where the Fe^{3+} ions are generally tetrahedrally coordinated, the values of quadrupole splitting range from 0.70 to $1.00\,mm\,sec^{-1}$, while for the phosphate glasses where the Fe^{3+} ions are usually

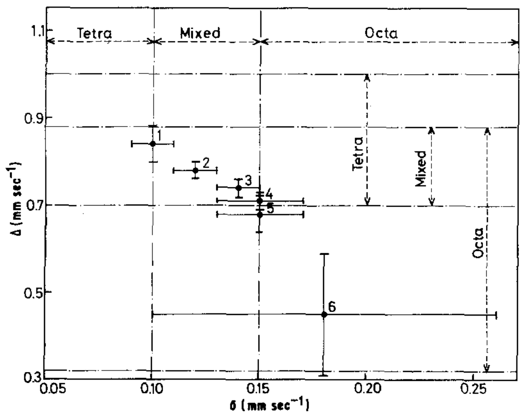

Figure 5 A Compendium of Δ against δ for the Fe^{3+} ions.

octahedrally coordinated the values show a wide range: 0.32 to 0.88 mm sec^{-1} [20].

A good insight can be obtained when both the values of δ and Δ are represented in a copendium [25]. This is shown in Fig. 5 where Δ is plotted against δ; the tetrahedral and the octahedral domains are shown by the dotted lines taking the data from the references [20, 21]. This shows that for glasses 1 to 4 the Fe^{3+} ions have mixed site occupancy, but for glass 5 the Fe^{3+} ions are mainly octahedrally coordinated from the consideration of the Δ value, while for glass 6 the Fe^{3+} ions are octahedrally coordinated.

Fig. 5 shows that the change of coordination of the Fe^{3+} ions from the octahedral to mixed site occupancy take place around 45% Fe^{3+} (see Tables I and II), which has also been reflected in the molar volume–composition plot, where the change of slope takes place around 50% Fe^{3+}. The work of Levy *et al.* [7] shows that the mixed site occupancy is possible in the high Fe^{3+} glasses, while our work shows that it is equally probable in the low Fe^{3+} glasses down to about 45% Fe^{3+}, although we have not been able to fit the Fe^{3+} spectra of glasses 1 to 4 (in particular) into four Lorentzian peaks. The occupancy of the Fe^{3+} ions in octahedral sites below 45% is not unexpected considering that most of the Mössbauer investigations have been carried out on silicate glasses containing a very high concentration of Fe^{3+} ions (> 90%). This shows that Fe^{3+} ions do not behave in the same way in all silicate glasses. This is particularly evident when silicate glasses are studied as a function of a wide range of Fe^{3+}/Fe^{2+} ratio, as in the present work.

As the concentration of Fe^{3+} increases (i.e. the Fe^{3+}/Fe^{2+} ratio increases), the isomer shift of Fe^{3+} decreases; this reflects an increase of the s-electron density of the ^{57}Fe nucleus. This could be considered to be either the result of an increase of the 4s contribution from the ligand ions or a greater delocalization of the 3d electrons of the Fe^{3+} ions due to an increase of the covalency of the Fe^{3+}–O bonding. This increase of covalency can be associated with the evolution from an octahedral to a predominantly tetrahedral site, as the concentration of Fe^{3+} increases.

3.2.2. Isomer shift and quadrupole splitting for Fe^{2+}

From the survey of the literature [20, 25], it is noted that a value of isomer shift < 0.72 mm sec^{-1} can be associated with the tetrahedral Fe^{2+} ions, while a value > 0.84 mm sec^{-1} corresponds to octahedral Fe^{2+} ions; there is a region around 0.78 mm sec^{-1} where the two ranges may overlap. There is very little Mössbauer work reported on Fe^{2+} ion in the literature. The values of quadrupole splitting range from 2.00 to 2.29 mm sec^{-1} [20].

As for the Fe^{3+} ions, the data for the Fe^{2+} ions are also represented in a compendium of Δ and δ in Fig. 6. The tetrahedral and octahedral domains are marked for the isomer shift values alone (dotted lines). This compendium shows that, for the first five glasses, the Fe^{2+} ions are mainly tetrahedrally coordinated, while for glass 6 there may be a mixed site occupancy for the Fe^{2+} ions. It is, however, noted that glass 5 could also have a significant number of octahedral Fe^{2+} ions, but the number will be obviously more in glass 6. Although the ranges of two different coordinations are not marked for the Δ values, it should be mentioned that a change of Δ from 2.15 mm sec^{-1} for glass 1 to 1.99 mm sec^{-1} for glass 6 could be quite

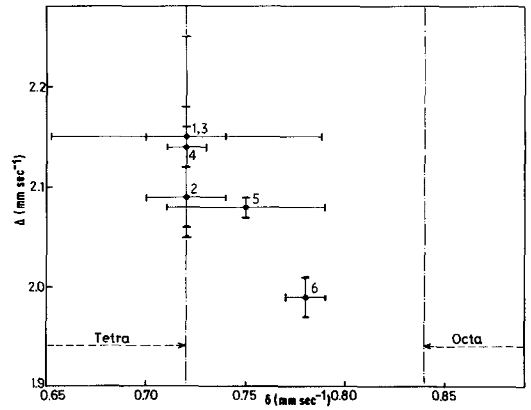

Figure 6 A Compendium of Δ against δ for the Fe^{2+} ions.

significant considering that these glasses contain almost the same concentration of total iron. According to the analysis of Kurkjian [20], the Fe^{2+} ions can be tetrahedrally coordinated in silicate glasses and octahedrally coordinated in phosphate glasses. However, in alkali silicate glasses there is a possibility of the mixed site occupancy for the Fe^{2+} ions at higher concentrations [25], which is what is also suggested for the glass 6 (and to some extent for the glass 5) where the concentration of Fe^{2+} is high.

The increase of isomer shift after glass 4 can again be interpreted on the basis that a structural change above 40% Fe^{2+} results in a decrease of the covalency of the Fe^{2+}–O bonding which decreases the s-electron density, therby increasing the isomer shift.

Finally, it can be said that in glasses containing higher than 45% Fe^{3+} (i.e. below 55% Fe^{2+}) the Fe^{3+} ions have a mixed site occupancy and the Fe^{2+} ions are mainly tetrahedrally coordinated, while in glasses containing lower than 45% Fe^{3+} (i.e. above 55% Fe^{2+}) the Fe^{3+} ions are octahedrally coordinated and the Fe^{2+} ions have a mixed site occupancy. Although it is very difficult to throw light on the precise nature of the interplay between the Fe^{2+} and Fe^{3+} ions, the structural change associated with both these ions evidently influences the oxygen structure of these glasses. It is suggested that the different structural behaviour of these two ions below and above 45% Fe^{3+} creates two different oxygen structures for these glasses, which are also reflected in the molar volume–composition plot around 50% Fe^{3+}; this might explain different internal friction behaviour of these glasses below and above 60% Fe^{3+}.

Moreover, it seems that the behaviour of the Fe^{3+} ions is quite similar to that of the Al^{3+} ions in soda–silicate glasses in that the concentration of the tetrahedral Fe^{3+} evidently increases with increasing concentration of the Fe^{3+} ions, because the Al^{3+} ions also take increasingly tetrahedral positions with the increase of their concentration in such glasses. But with increasing concentration of the Fe^{3+} ions, the nature of the competition among the Fe^{3+} ions to polarize the oxygen ions might be quite different from that of the Al^{3+}. This could explain why above a certain concentration of the Fe^{3+} ions (> 60%) the height of the second peak in the internal friction spectrum increases instead of decreasing, as expected from the behaviour of the Al^{3+} ions.

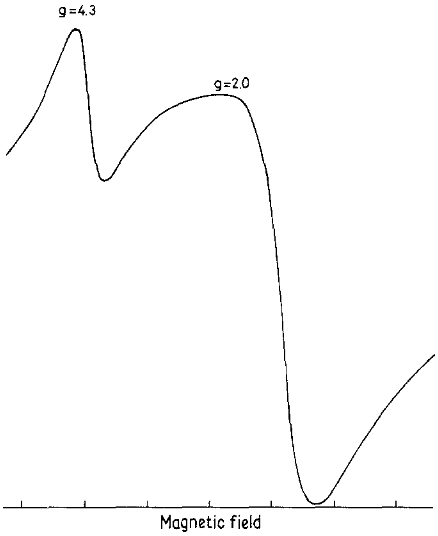

Figure 7 A typical ESR spectrum for the Fe^{3+} ions.

3.3. ESR spectra

An ESR spectrum for glass 1 is shown in Fig. 7, which is typical for all the other glasses. It is seen that there are two resonances: a resonance at $g = 4.3$ and another at $g = 2.0$. The resonance at $g = 4.3$ was often ascribed to the presence of Tetrahedral Fe^{3+}ions by Tucker [26] Hirayama *et al.* [23], Bishay and Makar [27], and Firsov *et al.* [28]. This was substantiated by other spectroscopic data such as Mössbauer [23], [28], and optical absorption [23, 27], and this was found to be consistent with the electrical conductivity data [27, 28]. The resonance at $g = 2.0$ was ascribed by the above authors to the presence of octahedral Fe^{3+} ions. These interpretations were not supported by Kurkjian and Sigety [21], who combined Mössbauer, optical and ESR measurements to show that the resonances at $g = 4.3$ and $g = 2.0$ can not be used as direct evidence of tetrahedral and octahedral coordinations respectively. The latter view was supported by Loveridge and Parke [29], who showed that rhombic (distortion) symmerty of Fe^{3+} ions could be associated with a $g = 4.3$ resonance. In the more recent literature (see Moon *et al.* [30] for references), the $g = 2.0$ resonance has been attributed to clusters of paramagnetic ions containing two or more ions coupled by exchange interaction, because the analysis of an interaction Hamiltonian would give rise to a g value close to 2.0.

Moon *et al.* [30] observed an increase of linewidth for the $g = 4.3$ resonance up to 3 mol%

Fe_2O_3 in a $BaO–4B_2O_3$ glass and then the line-width decreased and again changes its slope. This behaviour was ascribed to the presence of Fe^{3+} ions randomly distributed below 3% Fe_2O_3 and to the presence of Fe^{3+} ion-clusters above this composition. Since our results are very different than those of Moon *et al.* in that the line-widths of both the $g = 2.0$ and $g = 4.3$ resonances increase with increasing concentration of Fe^{3+} ions, we shall exclude the possiblity of cluster formation in our glasses. Asuming that these two resonances arise from the crystal field terms in the spin Hamilitonian for the ions with $S = 5/2$, it is noted from the survey of the literature that the $g = 4.3$ resonance could be associated with the lower symmetry elements compared to those given by the $g = 2.0$ resonance.

The intergrated intensity for the observed resonances was calculated as $I \times \Delta H^2$, where I is the peak to peak derivative intensity in some arbitraty units and ΔH is the peak to peak width in Gauss. Many authors [14, 30], have taken the integrated intensity of the $g = 4.3$ resonances equal to the concentration of the Fe^{3+} ions. In the present work we find that only 5 to 10% (between glasses 6 and 1) of the total Fe^{3+} ions contribute to the observed $g = 4.3$ resonance. From our Mössbauer results, it is noted that a considerable number of Fe^{3+} ions should be in tetrahedral coordination for the glasses 1 to 4, even for the glass 5. Therefore, it is difficult to ascertain whether the $g = 4.3$ resonance arises solely due to the tetrahedral Fe^{3+} ions. The intensity and the line-width are plotted against % Fe^{3+} for both the resonances in Fig. 8 and 9 respectively. It is seen from Fig. 8 that both the intensity and the line-width increase with increasing concentration of Fe^{3+} ions. Both the curves in Fig. 8 show changes of the slopes around 60% Fe^{3+}. This could be ascribed to a structural change associated with the Fe^{3+} ions having sites which give rise to the $g = 4.3$ resonance; this was also revealed by our Mössbauer data, but at a lower value of 45% Fe^{3+}. As pointed out earlier, a very little proportion of the contributing Fe^{3+} ions cast doubt whether this resonance could be associated with the tetrahedral Fe^{3+} ions. Even considering this resonance is only due to the tetrahedral Fe^{3+} ions, it could be suggested, following Kurkjian and Sigety [21], that there is spin–spin interaction at this site, because the concentration of the tetrahedral Fe^{3+} ions is high, particularly for the glasses 1 to 4. But the observed line-widths (94 to 230 Gauss between glasses 6 and 1) are comparable with those reported by Loveridge and Parke [29] on soda–silica glasses, where no mention was made about the spin–spin interaction. Firsov *et al.* [28] studied a variety of silicate, borate and phosphate glasses containing upto 15 mol% Fe_2O_3, but did not mention anything about the spin–spin interaction while comparing the intensities of the observed resonances. From the change of slope of the intensity plot, it can be, however, suggested that there are two types of sites with different rhombic distortions [19, 21] contributing to the $g = 4.3$ resonance above about 60% Fe^{3+}, and below this composition only one site contributes predominantly, which could be octahedral. There are a variety of sites responsible for the $g = 4.3$ resonance as emphasized by many authors [21, 29]. Therefore, the structural change, suggested for the Fe^{3+} ions from our Mössbauer data, seems to be reflected in the ESR data as well.

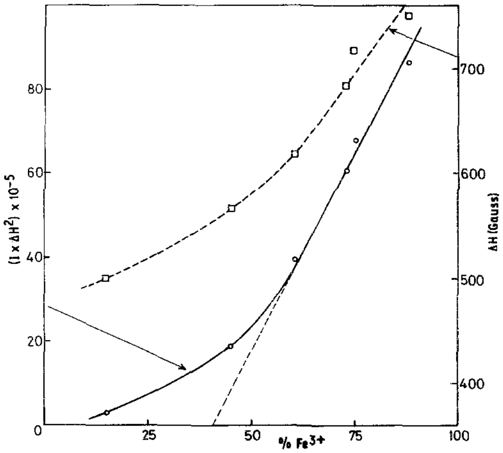

Figure 9 The integrated intensity and the line-width for the $g = 2.0$ resonance.

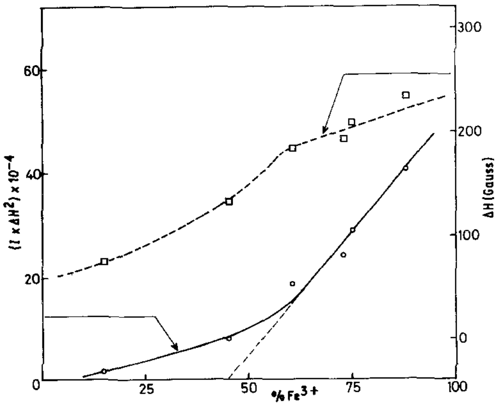

Figure 8 The integrated intensity and the line-width for the $g = 4.3$ resonance.

It is also noted, that the $g = 4.3$ resonance can not be uniquely assigned to the one site for Fe^{3+} ions for our glasses, as also noted in other silicate glasses. It should be mentioned that neither the intensity of any of the observed resonances nor the total intensity showed any meaningful correlation with the concentration of the Fe^{3+} ions. Therefore, no attempt is made here to calculate the concentration of the Fe^{3+} ions in different sites.

Friebele *et al.* [31] studied a 55% FeO–45% P_2O_5 (mol%) glass with three different redox ratios and showed that the line-width went through a maximum around 50% Fe^{3+}. They suggested an interaction between Fe^{2+} and Fe^{3+} ions. From the continuous increase of the line-width with increasing concentration of Fe^{3+} (Fig. 8), it can be suggested that the magnetic interaction if any is mainly between the Fe^{3+} ions. This shows that the magnetic interaction pattern between the Fe ions is different in silicate glasses than that in phosphate glasses. It is also suggested that the change of slope in the ΔH–% Fe^{3+} plot, which reflects a change in the interaction pattern of the Fe^{3+} ions, could be associated with a structural change.

Following Moon *et al.* [30], it is suggested that the contribution to the line-width from the usual spin–spin and spin–lattice relaxation times can be negligible. Therefore, the principal contributions to the increasing line-width with increasing Fe^{3+} arise from the distribution in environments in the glass, which is a concentration independent contribution (ΔH_{cf}), and the dipole–dipole interaction between Fe^{3+} ions ($\Delta H_{d\text{-}d}$). Thus the line-width can be expressed by equation [30].

$$\Delta H_{g=4.3} = \Delta H_{cf} + \Delta H_{d\text{-}d} = \Delta H_{cf} + (g\mu/a^3) \times X$$

where μ is the magnetic moment, a is some average lattice spacing and X is the concentration of Fe_2O_3 in mol%. A plot of the experimental line-width (ΔH) against mol% Fe_2O_3 was almost linear. This yielded a value of 70 Gauss for ΔH_{cf}, which compares well with that reported by Moon *et al.* for the barium borate glasses containing low Fe_2O_3. This also shows that the distribution of the Fe^{3+} ions is strictly random in our glasses.

It is seen from Fig. 9 that the behaviour of the intensity and the line-width for the $g = 2.0$ resonance is very similar to that of the $g = 4.3$ resonance. Following the discussion above, it can be suggested that above about 60% Fe^{3+} more than one site is contributing to this resonance, and below this composition, the octahedral Fe^{3+} ions predominantly contribute to the $g = 2.0$ resonance. However, the possibility of the spin–spin interaction can not be ruled out [21]. It is evident that the line-width for this resonance is about three times that for the $g = 4.3$ resonance. The increased line-width with increasing Fe^{3+} again shows that the magnetic interaction is between the Fe^{3+} ions and that the interaction at the sites which give rise to this resonance is relatively strong. From the changes of the slopes in both the intensity and the line-width plots, it is apparent that a considerable structural change of the Fe^{3+} ions takes place as the Fe^{3+}/Fe_{total} ratio is varied, as also revealed by our analysis of the Mössbauer data. This might again qualitatively explain why the IF behaviour of these glasses is different below and above 60% Fe^{3+}.

4. Conclusion

As the redox ratio changes over a considerable range, there is a significant structural change associated with the Fe ions. From the molar volume and Mössbauer data, it is concluded that there are both tetrahedral and octahedral Fe^{3+} ions above about 50% Fe^{3+} and below this composition only octahedral Fe^{3+} ions are present. In the former composition range (i.e. below about 50% Fe^{2+}), the Fe^{2+} ions are mainly tetrahedral, while in the latter range these ions may have a mixed site occupancy. The ESR data qualitatively supports our Mössbauer results on the Fe^{3+} ions. It is found that more than one site contributes to both the $g = 4.3$ and $g = 2.0$ resonances above about 60% Fe^{3+}, and below this composition these resonances arise mainly from one site, although there is a considerable spin–spin interaction contributing to the $g = 2.0$ line-width. The very different structural behaviour of the Fe^{2+} and Fe^{3+} ions below and above 50% Fe^{3+} creates two different oxygen structures for these groups of glasses. This might explain the qualitatively different IF behaviour of these two groups of glasses.

Finally, it is noted that the electronic resistivity, calculated theoretically by using the Austin and Mott [32] equation (see the last column in Table I), showed a minimum around $Fe^{3+}/Fe_{total} \sim 0.5$ as expected from the simple hopping theory. In this calculation, the hopping energy and 3d-electron localization coefficient were taken as 0.8 eV and 0.8 $Å^{-1}$ respectively for all the six glasses. The minimum was sharper than that observed by Hansen [10], where hopping energy varied slightly as a function of redox ratio. It is concluded that the different structural behaviour of the Fe^{2+} and Fe^{3+} ions, observed by our spectroscopic analysis, has a strong influence on the electronic conductivity behaviour of these types of glasses. This can possibly explain the departure of the experimental results from the theory as observed in many other semiconducting oxide glasses.

Acknowledgements

The authors would like to thank Dr F. Pernot for experimental assistance and Dr A. Collet for his help with ESR measurements.

References

1. D. E. DAY and G. E. RINDONE, *J. Amer. Ceram. Soc.* 45 (1962) 496.
2. D. E. DAY and J. M. STEVELS, *J. Non-Cryst. Solids* 11 (1973) 459.
3. D. E. DAY, *J. Amer. Ceram. Soc.* 57 (1974) 530.
4. H. SCHOLZE, Glass Industry, part 2 (1966) 622.
5. W. J. T. GEMERT, Ph.D. Thesis, Eindhoven, (1977).
6. J. PHALIPPOU, S. MASSON, F. PERNOT and J. ZARZYCKI, "Non-Crystalline Solids" edited by H. Frischat (Trans. Tech. Publication, Clausthal-Zellerfeld 1977), p. 554.
7. R. A. LEVY, C. M. P. LUPIS and P. A. FLINN, *Phys. Chem. Glasses* 17 (1976) 94.
8. A. K. BANDYOPADHYAY, J. O. ISARD and S. PARKE, *J. Phys. D* 11 (1978) 2559.
9. G. S. LINSLEY, A. E. OWEN and F. M. HAYATEE, *J. Non-Cryst. Solids* 4 (1970) 208.
10. K. W. HANSEN, *J. Electrochem. Soc.* 112 (1965) 994.
11. J. G. VAUGHAN and D. L. KINSER, *J. Amer. Ceram. Soc.* 58 (1975) 326.
12. A. K. BANDYOPADHYAY and J. O. ISARD, *J. Phys. D* 10 (1977) L99.
13. *Idem*, Proceedings of the Seventh International Conference on Amorphous and Liquid Semiconductors, Edited by W. E. Spear (C.I.C.L. Edinburgh, 1977) p. 683.
14. R. A. ANDERSON and R. K. MACCRONE, *J. Non-Cryst. Solids* 14 (1974) 112.
15. J. PHALIPPOU, S. MASSON, A. BOYER and J. ZARZYCKI, *ibid.* 14 (1974) 178.
16. I. MOHYUDDIN and R. W. DOUGLAS, *Phys. Chem. Glasses* 1 (1960) 71.
17. C. F. DRAKE and I. F. SCANLAN, *J. Non-Cryst. Solids* 4 (1970) 234.
18. J. P. GOSSELIN, U. SHIMONY, L. GRODZINS and A. R. COOPER, *Phys. Chem. Glasses* 8 (1967) 56.
19. A. D. BELYUSTIN, Y. M. OSTANEVICH, A. M. PISAREVSKII, S. B. TOMILOV, U. BAI-SHI and L. CHER *Sov. Phys. Solid State*, (1965) 1163.
20. C. R. KURKJIAN, *J. Non-Cryst. Solids* 3 (1970) 157.
21. C. R. KURKJIAN and E. A. SIGETY, *Phys. Chem. Glasses* 9 (1968) 73.
22. P. L. MATTERN, Ph. D. Thesis Cornell University (1966).
23. C. HIRAYAMA, J. G. CASTLE Jr. and M. KURIYAMA, *Phys. Chem. Glasses* 9 (1968) 109.
24. L. R. WALKER, G. K. WERTHEIM and V. JACCARINO, *Phys. Rev. Lett.* 6 (1961) 98.
25. J. M. D. COEY, *J. de Physique* C6 (1974) 89.
26. R. F. TUCKER in "Advance in Glass Technology" (Plenum Press, New York 1962) p. 103.
27. A. M. BISHAY and L. MAKAR, *J. Amer. Ceram. Soc.* 52 (1968) 605.
28. M. FIRSOV, V. M. FIRSOV, N. V. PETROVYKH and P. I. LITVINOV, Tenth International Congress on Glass, Kyoto (1974) p. 73.
29. D. LOVERIDGE and S. PARKE, *Phys. Chem. Glasses* 12 (1971) 19.
30. D. W. MOON, J. M. AITKEN, R. K. MACCRONE and G. S. CIELOSZYK, *Phys. Chem Glasses* 16 (1975) 91.
31. E. J. FRIEBELE, L. K. WILSON, A. W. DOZIER and D. L. KINSER, *Phys. Stat. Solidi (b)* 45 (1971) 323.
32. I. G. AUSTIN and N. F. MOTT, Adv. Phys. 18 (1969) 41.

Received 3 January and accepted 30 January 1980.