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EPR in a barium borosilicate glass containing titanium ions

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EPR spectra were studied in an equimolar barium borosilicate glass containing 0 to 12 mol % titanium ions. The valence concentration ratio, defined as the ratio of the concentration of the lower valence state transition metal ion Ti^{3+} to the total concentration of the transition metal ion $Ti^{3+} + Ti^{4+}$, was varied between 0.15 and 0.85 at each concentration. The spectra were studied as a function of temperature down to 15 K. A broad asymmetric absorption peak is observed with effective $g \sim 1.938$ at room temperature. This absorption is attributed to a tetragonally distorted octahedral ligand field around Ti^{3+} ion. The g value decreases as the temperature decreases, with a distinct transition between 60 and 100 K. Accompanied by this decrease in g is a distinct broadening of the curves with a transition in the same transition range. These and other observations are explained in terms of a lengthening of the spin-lattice relaxation time in this transition range and this transition is analogous to the NMR motional narrowing phenomena in solids. Many observations at low temperatures suggest a non-random distribution of titanium ions in these glasses.

1. Introduction

Titanium oxides are the most widely used nucleating agents in oxide glasses for enhanced rates of uniform crystalline nucleation [1]. Although extensive work has been done on the role of Ti oxides in glass ceramics, the mechanism of nucleation is uncertain [1]. Various structure sensitive properties have been investigated in an equimolar barium borosilicate glass containing low concentrations ($\leqslant 12$ mol%) of titanium ions [2] to enhance the understanding of the role of titanium oxides in this glass. Earlier a detailed analysis of electrical conductivity [3, 4] and optical absorption [5] was carried out and many observations could not be explained on the basis of a random distribution of titanium ions in these glasses. It was proposed [3–5] that in these glasses, the titanium ions are distributed in clusters. The coupling between the ions is through the oxygen ion by an exchange mechanism proposed by Mott [6] of the type $M^{+n}–O–M^{+(n+1)}$, where M is a transition metal ion.

The Ti^{4+} ion has the electronic structure of an argon (A) atom and therefore has no unpaired electrons; thus it is diamagnetic. On the other hand, Ti^{3+} has the electronic structure (A) $(3d^1)$ and this single unpaired electron makes Ti^{3+} paramagnetic. This has been shown to be experimentally true. Many authors [7–10] have investigated the EPR spectra in glasses containing Ti^{3+} ions but all investigations were concerned with very low concentrations (less than 1 mol%) of Ti^{3+} ions. No

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effort has been made to investigate the EPR spectra as a function of the valence concentration ratio (VCR) or the composition of Ti^{3+} ions. Studies of the temperature dependence of these spectra are minimal and only scattered data exist.

Assuming an isotropic value of the spectroscopic factor or the Lande factor g, the resonance condition is given by

$$h\nu = g\beta H \qquad (1)$$

where h is Planck's constant, ν is the resonant frequency, β is the Bohr magneton and H is the applied magnetic field. For free electrons, the g value is around 2 (actually 2.0023).

In the literature, for Ti^{3+} the g value departs markedly from the free electron value. This has been attributed to the tetragonally distorted octahedral ligand field around the Ti^{3+} ion due to the Jahn–Teller effect [7, 10, 11].

2. EPR spectra in glasses

2.1. Line shapes

Due to advantages in the design of experimental apparatus, most EPR experimental results are obtained as derivatives of the absorption spectra. In glasses, most spectra obtained are broad, and often asymmetric line shapes are obtained. The random nature of the glass structure has made the line shape analysis difficult but some effort has been made in recent years to investigate these and three approaches seem to have developed.

The first approach [12] compares the given transition in a glass to the one in a single crystal or a powder specimen and qualitatively describes 'the average site' in a glass specimen. The broad spectra obtained in glasses are explained as a consequence of the randomness of the glass structure. This has been seen earlier where the optical absorption in glasses due to Ti^{3+} was attributed to a distorted octahedron [5] and this latter information was obtained from the behavior of Ti^{3+} in hydrated Ti^{3+} or alums [13, 14]. The spectra obtained in glasses is, however, broader.

The second approach is due to Bray and co-workers [15, 16]. In this procedure, the broad spectra normally found in glasses are generated by convoluting a crystalline powder specimen with a 'smearing function'. The spectra obtained is of a powder specimen with reduced resolution and is found to explain certain general characteristics of the experimental spectra.

The third approach recently proposed by Peterson *et al.* [17, 18] is based upon probability theory and views the spectra as a probability density function in a magnetic field variable. As pointed out by Jellison *et al.* [19], the last two procedures are apparently equally good. Peterson *et al.* qualitatively derive the asymmetric EPR spectra of Ti^{3+} by considering a Gaussian distribution of the crystal field splitting δ, and show that the corresponding distribution of $g_\perp$, one of the principal g values, is highly asymmetric due to the non-linear transformation from δ to $g_\perp$. This feature has been experimentally observed by Griscom *et al.* [15] in their study of radiation induced boron hyperfine structure of lithium borate glasses.

We look at some of the parameters obtained from the derivative absorption spectra and the absorption spectra itself. These parameters facilitate the qualitative comparison of different spectra. Fig. 1a shows a typical derivative EPR spectra obtained for a glass specimen. H_0 is the value of the magnetic field H at the inflection point between the two peaks and the g value is calculated from Equation 1 using this effective value of H_0. Conventionally, ΔH_{pp}, the width between the two peaks is used to compare different spectra. Fig. 1b shows the absorption peak corresponding to Fig. 1a and $\Delta H_{1/2}$ defines the full width at half

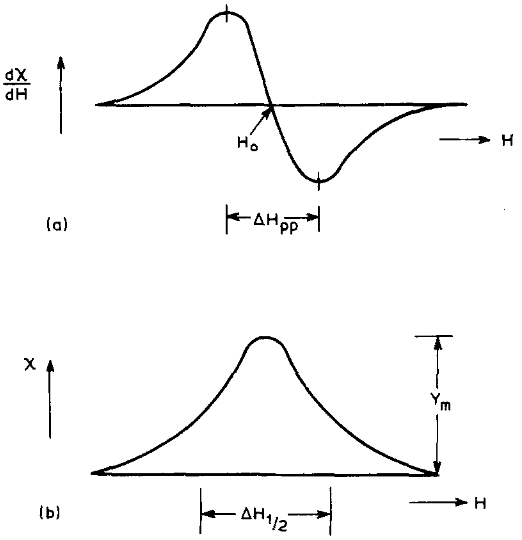

Figure 1 (a) Schematic diagram of an EPR derivative absorption spectra for a glass specimen. (b) Schematic diagram of an EPR absorption spectra for a glass specimen.

maximum. The two parameters, ΔH_{pp} and $\Delta H_{1/2}$, can be used to specify the nature of line shapes [20]. For Gaussian line shapes,

$$\frac{\Delta H_{1/2}}{\Delta H_{\mathrm{pp}}} = 1.178 \qquad (2)$$

whereas for Lorentzian line shapes,

$$\frac{\Delta H_{1/2}}{\Delta H_{\mathrm{pp}}} = \sqrt{3} = 1.732 \qquad (3)$$

Fig. 1b also shows y_{m}, the peak height, and the product $y_{\mathrm{m}} \times \Delta H_{1/2}$ gives a good approximation of the area under the absorption curve.

2.2. Temperature dependence of EPR spectra

Our experimental results of the temperature dependence of the EPR spectra of glasses containing Ti^{3+} show a behaviour analogous to the phenomena of motional narrowing observed extensively in nuclear magnetic resonance (NMR) studies of solids and liquids. The latter phenomenon is briefly summarized.

NMR line-broadening occurs in solids due to dipole–dipole interaction between nuclei. As the temperature increases, thermal activation of ions tends to decrease the dipole–dipole interaction between ions and NMR line widths narrow. This, referred to as motional narrowing, is accompanied by Lorentzian line shapes. The theory for this phenomena was put forward by Bloembergen *et al.* [21] for liquids and the theory can be extended to the study in solids. Let τ_{j} be the average time between jumps of an atom from one atomic site to another. Then ν_{j}, the jump frequency $(=\tau_{\mathrm{j}}^{-1})$ can be found from NMR line widths, w, from

$$\nu_{\mathrm{j}} = \alpha w \cot \frac{\pi}{2}\left[\frac{w}{A}\right]^2 \qquad (4)$$

where α is a constant, about unity and A is the low temperature line width. This equation was modified by Gutowsky and Pake [22] to the case where the transition takes place from the low temperature broad line width to a narrower line width, D,

$$\nu_{\mathrm{j}} = \alpha w \cot \frac{\pi}{2}\left[\frac{w^2 - D^2}{A^2 - D^2}\right] \qquad (5)$$

The jump frequency for a thermally activated process is also given by

$$\nu_{\mathrm{j}} = \nu_0 \exp\left(-Q/kT\right) \qquad (6)$$

where ν_0 is the atomic vibrational frequency, Q is the activation energy, k is the Boltzmann's constant and T is the absolute temperature.

In most experimental results, the jump frequencies are distributed and this gave the value of calculated activation energies too low. Hendrickson and Bray [23] developed a phenomenological relation to avoid this difficulty and this is

$$\ln\left[\frac{1}{w} - \frac{1}{A}\right] = -\frac{Q}{kT} - \ln\left[\frac{1}{B} - \frac{1}{A}\right] \qquad (7)$$

where B is the contribution to the line width due to the thermally activated ions. In this relation, D has been neglected.

In EPR, the corresponding effect is the exchange narrowing phenomena [6] between the ions of different valence states and the corresponding dispersion is at much lower temperatures.

3. Experimental

The details of glass sample melting along with the technique to determine the experimental VCR values of all samples investigated have been presented earlier [3]. The samples investigated for this study are listed in Table I.

TABLE I Composition of glasses and corresponding VCR values.

Sample	Total Ti Composition (mol %)	VCR experimental ($\mathrm{Ti}^{3+}/\mathrm{Ti}^{\mathrm{total}}$)
G0	0	–
G1	2	0.47
G2	4	0.46
G3	6	0.14
G4	6	0.30
G5	6	0.45
G6	6	0.60
G7	6	0.80
G8	8	0.2
G9	8	0.46
G10	8	0.70
G11	8	0.85
G12	10	0.15
G13	10	0.26
G14	10	0.36
G15	10	0.64
G16	10	0.85
G17	12	0.49

The EPR spectra of 320 mesh powder glass samples were obtained between 15 K and room temperature by the use of a Varian E–9 X-band spectrometer. The resonance frequency was 9.5 GHz with the modulation frequency of 100 kHz. 0.1500 g of each sample was introduced in the cavity resonator in 4 mm o.d., 2 mm i.d. Clear Fused Quartz TO8 tubes from Amersil, Inc.

In comparing the EPR spectra, the power level, the signal level and the modulation amplitude were kept constant. Only the spectrometer gain was changed to bring the spectra within scale. Hydrated copper sulphate single crystal in KCl was used as a standard. No signal was recorded when the powdered base glass, containing no titanium ions, was analysed indicating that the spectra obtained were from Ti^{3+} ions only.

4. Results and discussion

As reported by previous investigators [7–10], the EPR spectra reported below consist of one broad asymmetric line. No hyperfine structure was observed even though natural Ti contains 7% ^{47}Ti and 5% ^{49}Ti [10]. None of the previous investigators have made any systematic effort to analyse the shapes of the experimental spectra of glasses containing Ti^{3+}. Even though the parameters $\Delta H_{1/2}$, ΔH_{pp} and $\Delta H_{1/2}/\Delta H_{pp}$ were defined for symmetric spectra in Section 2.1, these parameters discussed below are used only for qualitative information; they help the comparison of different spectra. Extensive analysis of the line shapes of these spectra are being carried out and the general conclusions of the discussion below will be shown to be valid; this quantitative analysis will be presented elsewhere [24].

4.1. EPR spectra at room temperature

A typical derivative spectra obtained at room temperature for an 8 mol% glass is shown in Fig. 2. This curve is asymmetrical. From Equation 1 the effective g value is calculated to be 1.938 and this is in agreement with the values found in various previous investigations [7-10]. At room temperature this effective g value calculated for all specimens is independent of the composition and the VCR.

From the derivative absorption spectra similar to the one in Fig. 2, one can get ΔH_{pp}, the width between the two maxima. ΔH_{pp} is shown against VCR for 6, 8 and 10 mol% glasses in Fig. 3a. The values of the widths, ΔH_{pp}, are interpolated at VCR = 0.5 and are then plotted against total titanium concentration in Fig. 3b. Both figures show that ΔH_{pp} increases linearly with VCR and total titanium content.

The dashed zero line shown in Fig. 2 is somewhat arbitrary as at both ends of the spectra the curve goes to zero asymptotically. The curve is integrated, using a modified form of Simpson's rule, and the difference in the areas above and below the zero line is used to shift the baseline [20] so that the areas become equal. The integrated curves are now normalized for comparison. A typical normalized curve is shown in Fig. 4 for an 8% glass at room temperature. The curve appears to be near-Lorentzian in shape. This assertion will be further checked below. Fig. 5a

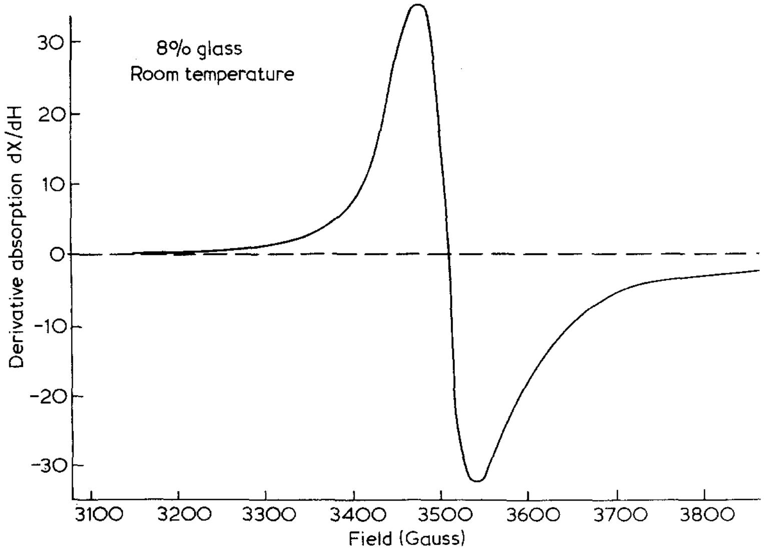

Figure 2 Experimental EPR derivative spectra at room temperature for an 8% glass.

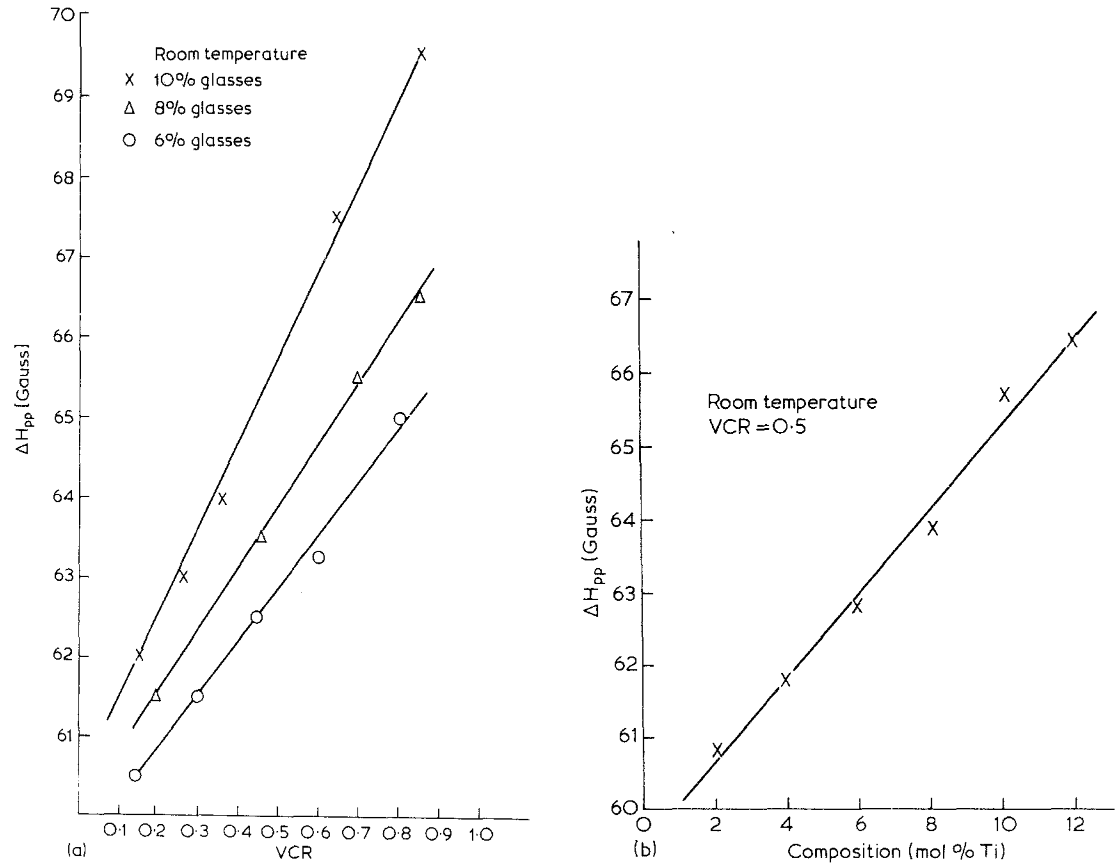

Figure 3 (a) ΔH_{pp} versus VCR for 8% glasses at room temperature. (b) ΔH_{pp} versus composition for VCR = 0.5 at room temperature.

shows $\Delta H_{1/2}$, the FWHM of the absorption curves, versus VCR for 8% glasses. The values of the widths interpolated for VCR = 0.5, from similar curves at other compositions, are then plotted against total titanium content in Fig. 5b. The width $\Delta H_{1/2}$ increases linearly with both VCR and total titanium content.

The line shape parameter [20], $\Delta H_{1/2}/\Delta H_{pp}$, can be calculated from Figs. 4 and 5 and other similar plots for various glasses investigated. This parameter turns out to be 1.89 ± 0.05 independent of the composition and the valence concentration ratio, a surprising result. A value of 1.89 for the line shape parameter shows that the earlier as-

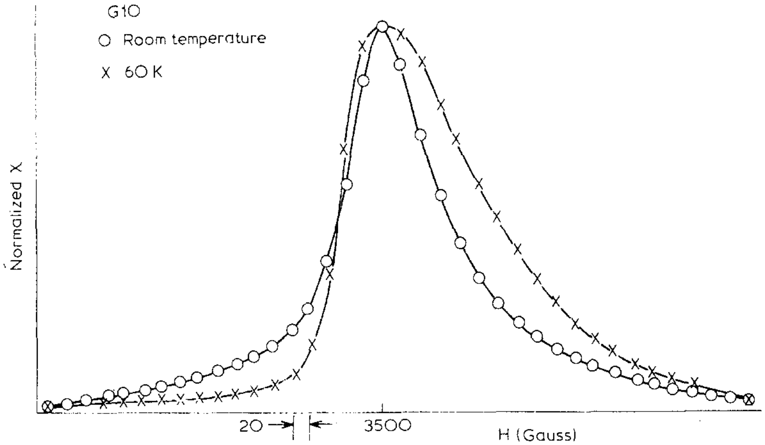

Figure 4 Normalized EPR absorption spectra at room temperature and at 60 K for an 8% glass.

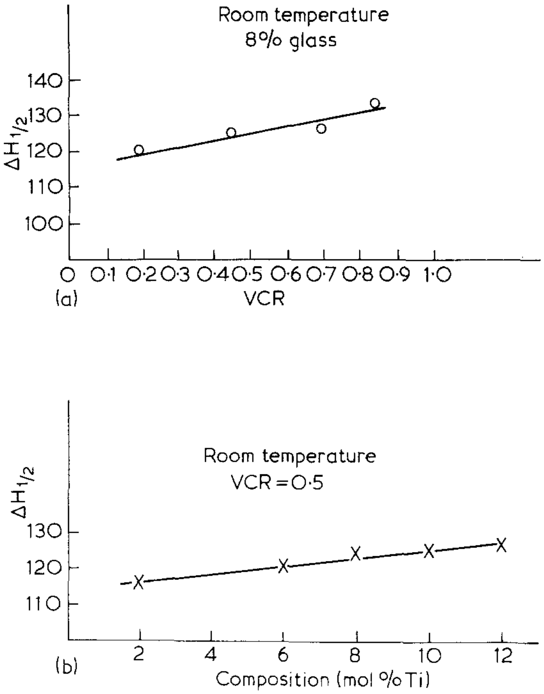

Figure 5 (a) $\Delta H_{1/2}$ versus VCR for 8% glasses at room temperature. (b) $\Delta H_{1/2}$ versus composition for VCR = 0.5 at room temperature.

sertion of the curves being near-Lorentzian in shape is correct. A constant value suggests that the overall shape of the curve does not change with increasing Ti concentration and VCR. Various authors have used either ΔH_{pp} or $\Delta H_{1/2}$ to compare different spectra; it is suggested that this parameter be used instead.

No change in the overall shapes of the spectra may suggest that there is no effect of the increasing concentration of Ti ions, thus no increasing interactions between ions, in contrast to the results of electronic conduction and optical absorption studies [3, 4] in these glasses. This apparent discrepancy can be resolved by investigating the low temperature EPR spectra. At room temperature, the spin-lattice relation time is short [10]. Only "small structural units" [3] containing a few Ti ions contribute to the EPR spectra. The exchange narrowing phenomenon between ions of different valence states characterized by near-Lorentzian line shapes [6, 12] is seen. This is further substantiated by comparing the spectra of the $CuSO_4$ standard with the Ti^{3+} spectra. Special care was exercised during this comparison and the procedure recommended by Bolton *et al.* [25] was followed, wherein the errors introduced due to sample shape and sample size were minimized. The double integration was carried out using a computer programme following a procedure of Wyard [26]. An estimate of the errors involved suggests that the calculated compositions of Ti^{3+} from the comparison of the standard and the experimental Ti^{3+} spectra may be off by at most 50%. The ratios of the Ti^{3+} concentrations determined by EPR to the experimentally determined Ti^{3+} concentrations by chemical analysis, expressed as a percentage, are listed as ratio at a particular temperature in Table II. As suggested by Table II, at room temperature the ratio is around 20% for all samples. This suggests that many Ti^{3+} ions do not contribute to the EPR spectra. This aspect will be discussed further below.

Fig. 6a shows the EPR peak heights from the absorption spectra as a function of VCR for 6, 8 and 10 mol% glasses, a typical result. The peak height values are interpolated for VCR = 0.5 and they are shown as a function of Ti ion composition in Fig. 6b. The peak heights increase linearly with the VCR and with the composition. The areas under the absorption spectra show a similar behaviour; they are not shown. Also, the results of the double integration of each of the derivative spectra by the computer, plotted as a function of Ti ion composition for VCR = 0.5, show a similar linear increase and thus are not shown.

4.2. Temperature dependence of EPR spectra

Now we consider the EPR spectra as a function of

TABLE II Ratios of Ti^{3+} concentrations from EPR spectra to Ti^{3+} concentrations from chemical analysis.

Sample	Ratio (%) (room temperature)	Ratio (%) (60 K)	Ratio (%) (15 K)
G1	18.4	79.2	84.8
G2	21.6	79.3	85.5
G3	19.2	79.1	84.9
G4	21.1	79.4	85.8
G5	20.8	79.4	86.1
G6	20.4	79.8	87.2
G7	19.6	80.0	88.0
G8	22.0	79.6	87.8
G9	18.4	80.6	89.2
G10	19.7	82.2	90.3
G11	20.0	82.5	91.8
G12	21.4	80.0	90.0
G13	20.8	80.5	90.8
G14	19.4	81.4	91.6
G15	18.9	83.0	93.3
G16	21.0	84.8	94.6
G17	22.0	84.0	96.0

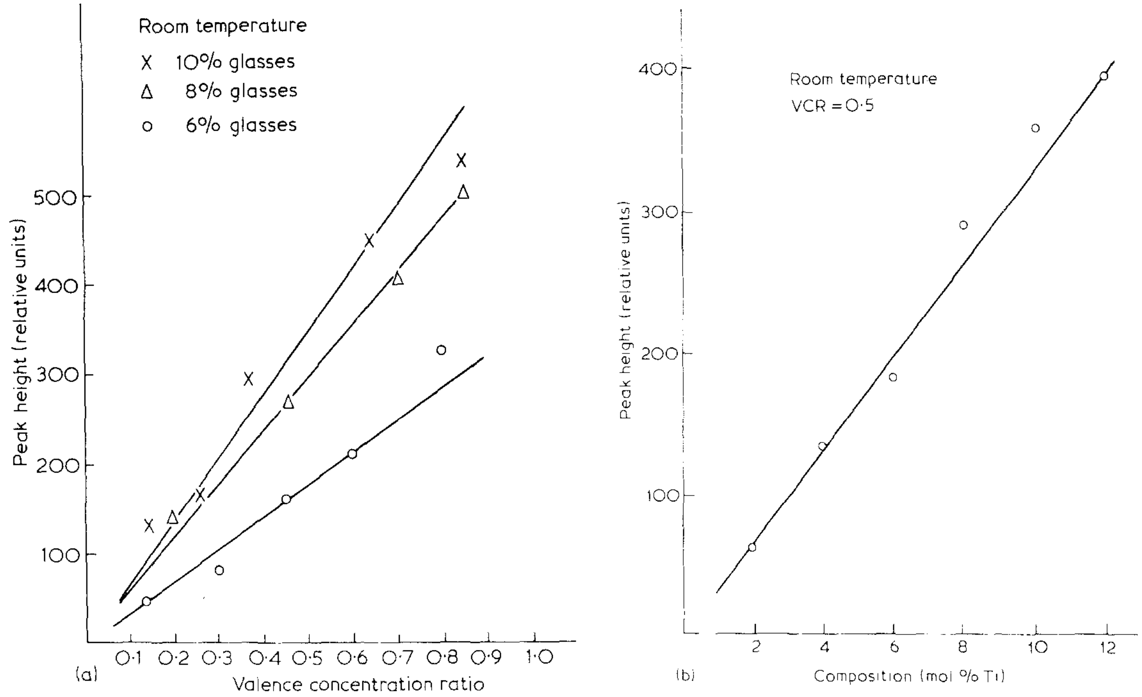

Figure 6 (a) Peak heights versus VCR for 8% glasses at room temperature. (b) Peak heights versus composition for VCR = 0.5 at room temperature.

temperature from room temperature down to 15 K. No new absorption peaks were recorded even at these low temperatures, however there were many new features. The absorption spectra of an 8% glass at 60 K is shown with the room temperature spectra shown earlier in Fig. 4. The curves have been normalized and they are shifted along the abscissa till the peak maxima coincide with each other. The comparison of the spectra shows that the curves are much broader at lower temperatures.

Fig. 7a shows ΔH_{pp} as a function of VCR at 15 K for 8% glasses and Fig. 7b shows ΔH_{pp} as a function of total titanium content at VCR = 0.5. These curves show that ΔH_{pp} values are much larger compared to the values at room temperature and they increase non-linearly both with the VCR and with the composition, in contrast to the linear increase at room temperature shown in Fig. 3. When ΔH_{pp} is plotted as a function of VCR, the total number of Ti ions is constant and a non-linear increase suggests increasing interaction between ions. Also shown in Figs. 7a and b are the effective g values calculated from Equation 1. The g values decrease non-linearly with VCR and with composition. This result is in contrast to a constant g value at room temperature. The g values at lower temperatures are significantly lower, indicative of an increasing octahedron distortion. This was further substantiated [24] by calculating the principal g values from the crystal field splittings obtained during quantitative analyses of line shapes.

The line shape parameters, $\Delta H_{1/2}/\Delta H_{pp}$, calculated at 15 K for all samples show that the values are significantly lower compared to the room temperature values and the values are no longer constant. These values are close to those suggested for Gaussian shaped curves. They are plotted as a function of VCR and are then interpolated at VCR = 0.5. Fig. 8 shows $\Delta H_{1/2}/\Delta H_{pp}$ as a function of total Ti composition for VCR = 0.5 at 15 K. The values decrease slowly at lower concentrations, but above 6% the rate of decrease increases. This critical composition is characteristic of many experimental results obtained in this system when the electrical [3] and optical properties [5] were investigated. At lower temperatures, the spin lattice relaxation time lengthens [10] to the extent that increasing number of Ti^{3+} ions begin to participate in the absorption. This is substantiated by comparing the experimental spectra with the standard spectra at that temperature using the approach mentioned earlier [25]. The

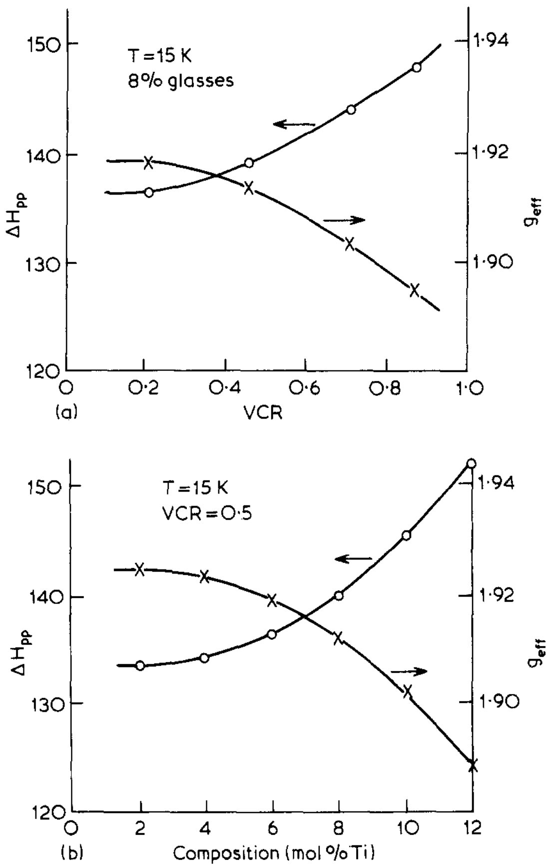

Figure 7 (a) ΔH_{pp} and effective g versus VCR for 8% glasses at 15 K. (b) ΔH_{pp} and effective g versus composition for VCR = 0.5 at 15 K.

Ti^{3+} concentration determined by this comparison increases as the temperature decreases, and the values are around 79 to 96% of the values determined by chemical analysis as the temperature decreases from 60 to 15 K respectively. The values expressed in terms of ratio at 60 and 15 K are listed in Table I and they support this conclusion. Considering the errors in the analysis, these values are within experimental errors of the actual Ti^{3+} concentrations. The agreement is better as the VCR and the concentration increase, especially at and above 6 mol%. This suggests that the increasing number of Ti^{3+} and Ti ions result in increasing interactions between ions, especially above the critical composition, a result in agreement with the results of other measurements [3–5]. This analysis also reveals that the common practice of determining ion concentrations by EPR at room temperature may result in erroneous conclusions. The Ti^{3+} concentrations were also estimated from magnetic susceptibility measurements, carried out as a function of temperature [24], and the agreement with the above conclusions is excellent. The peak heights from the absorption spectra are plotted as a function of VCR and they are then interpolated for VCR = 0.5 at 15 K. Fig. 9 shows the peak heights as a function of Ti ion concentration at VCR = 0.5. The peak heights increase with composition with a break around 6% above which the increase is very rapid. This break around 6% is once again characteristic of the various properties investigated in this glass system [3, 4] and supports the ideas presented in the last paragraph and elsewhere [3–5].

The insert in Fig. 10 shows the ΔH_{pp} values and the g values plotted as a function of temperature for an 8% glass. Both the ΔH_{pp} values and the g values, show a transition between 60 and 100 K as the temperature increases. Using an

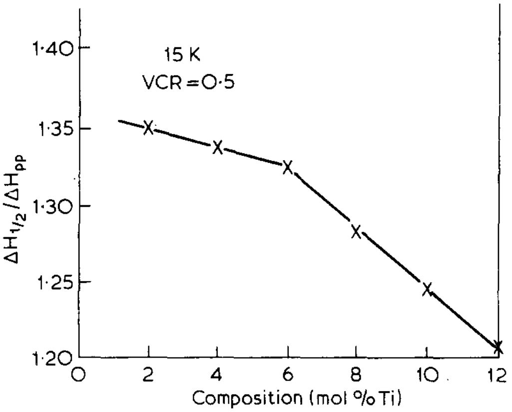

Figure 8 $\Delta H_{1/2}/\Delta H_{pp}$ versus composition for VCR = 0.5 at 15 K.

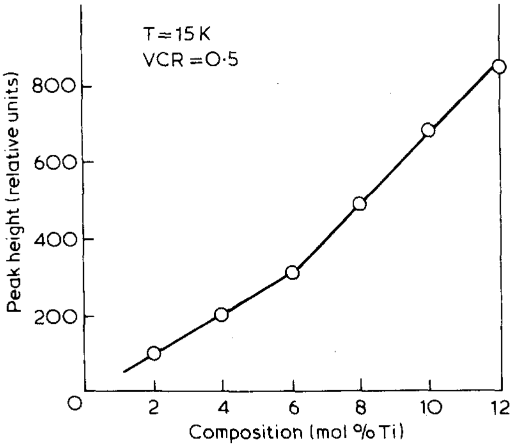

Figure 9 Peak heights versus composition for VCR = 0.5 at 15 K.

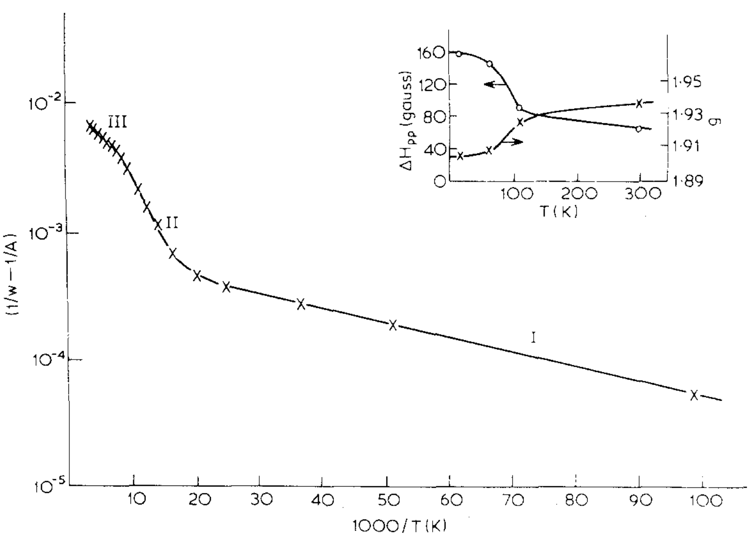

Figure 10 ΔH_{pp} and effective g values versus temperature for an 8% glass (insert). The ΔH_{pp} values plotted according to Equation 7, text, as a function of 1/T (K).

equation analogous to the phenomenological Equation 7 suggested by Hendrickson and Bray [23], with ΔH_{pp} as the width and the A value obtained by extrapolating ΔH_{pp} at $T = 0$ K, three regions I, II and III are obtained. These three regions are analogous to the regions observed by Hendrickson and Bray in their study of NMR motional narrowing in glasses [27]. These regions are shown in Fig. 10 and the corresponding activation energies are 0.0021 eV, 0.025 eV and 0.005 eV. The reasons for the applicability of Equation 7 and the detailed computer analysis will be presented elsewhere [24]. However, in brief, the activation energies of regions I and III are associated with the activation energies for the short range motion of the electrons in these glasses; these activation energies correspond to the disorder energy, W_D [3, 6]. This provides an alternative approach to obtain estimates of W_D, the other being by electrical conductivity measurements [3].

The reciprocal magnetic susceptibility measurements [3] plotted as a function of temperature, at low temperatures, suggest that the glasses exhibit antiferromagnetic interactions. This result cannot be explained on the basis of a random distribution of Ti ions. Above the transition region between 60 and 100 K, the glasses are paramagnetic [24]. The activation energy in region II is associated with this transition and will be dealt with in detail in the later publication [24]. As indicated earlier, it is below the transition region that there is good correspondence between the chemically determined Ti^{3+} concentrations and the Ti^{3+} concentration determined from the comparison of the experimental EPR spectra and standard spectra. This suggests that the spin lattice relaxation time changes over this region as well [10].

5. Conclusions

The study of EPR in an equimolar barium borosilicate glass containing Ti ions revealed new features. At low temperatures the non-linear increase of ΔH_{pp} as a function of VCR suggests an increasing interaction between ions. Also the line shape parameter $\Delta H_{1/2}/\Delta H_{pp}$, the Ti^{3+} concentrations determined from EPR spectra and the peak heights plotted as a function of composition show a characteristic break around 6 mol% Ti ion concentration at VCR = 0.5 suggesting once again that at and above this critical composition there are increasing interactions between ions. These observations coupled with the earlier results of electrical conductivity [3], optical absorption [5] and magnetic susceptibility measurements [3] suggest that clusters of Ti ions exist at and above this critical composition. The temperature dependence of EPR spectra was analogous to NMR motional narrowing phenomena in solids with a transition between 60 and 100 K. Below the transition range the magnetic susceptibility measurements show that the glasses exhibit antiferromagnetic interactions and above this transition range the glasses are paramagnetic.

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