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On the physical properties of $20Fe_2C_380$ $[3B_2O_3$ $(1-x)PbO$ x $GeO_2]$ glasses

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The results of X-ray, electron microscopy, magnetic measurements, Mössbauer effect, electron paramagnetic resonance and electrical resistivity studies on $20Fe_2O_380$ $[3B_2O_3(1-x)PbOxGeO_2]$ glasses are reported. Two sets of samples with $0 \leqslant x \leqslant 25$ mol% GeO_2 equilibrated at 1250° C and 1150° C, respectively, were investigated. All the samples were in the amorphous state. The number of ferrous ions in glasses equilibrated at 1250° C decreased by increasing the GeO_2 content. In the case of the samples melted at 1150° C no evidence of Fe^{2+} ions was shown by magnetic and Mössbauer effect measurements. The magnetic susceptibility for $T > 80$ K obeys a Curie–Weiss law and the effective moments of iron cations may be described by the free-ion values. The influence of the glass matrix composition and the equilibration temperatures on the intensities of $g = 2.00$ and $g = 4.20$ resonance lines is analysed. The EPR data suggest a clustering tendency of the iron ions in samples equilibrated at 1150° C. The resistivity measurements may be described by a mechanism involving electron hopping. The presence of two activation energies is shown. Finally, the experimental data are correlated in order to give a unitary description of the physical behaviour of the analysed glass system.

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1. Introduction

Study of the transition metal ions in amorphous matrix is one of the interesting research subjects both from theoretical and experimental points of view. Various physical methods are used to obtain information on this matter. Among these we mention the Mössbauer effect, paramagnetic resonance, magnetic and electrical resistivity measurements. The studies have in view the analysis of the structure and bonding in glasses, the magnetic properties of ions or crystalline precipitates and also the electrical conduction mechanisms.

Two standpoints are expressed concerning the localization of transition metal ions in glasses. Kurkjian [1] and Levy *et al.* [2] consider that the amphoteric cations, i.e. Fe^{3+} can occupy tetrahedral and octahedral sites in a lattice of oxygen anions. The Fe^{2+} cations occupy octahedral sites. Bukrey *et al.* [3] suggest that the linewidths of the doublets are broadened by a factor of 2 or 3 times than the natural width because of the site non-uniformity. The matter of the linewidth in glasses was also reviewed by Coey [4].

Previously, we analysed the magnetic behaviour of iron cations in $PbO \cdot 3B_2O_3$ glasses [5, 6]. The B_2O_3–PbO glass matrix is transparent in the composition range 10 to 80 mol% PbO [7, 8]. The introduction of PbO in B_2O_3 converts the boron atoms from three to four co-ordination. In the $PbO \cdot 3B_2O_3$ glass matrix, approximately 30% of the boron atoms are four co-ordinated [7, 9]. The NMR data on ^{207}Pb [7, 9] in $PbO–B_2O_3$ system are analysed considering two more intense resonances as the field is lowered. The data suggest two different co-ordinations for Pb^{2+} ions. It is assumed that the PbO configurations (discernible in both tetragonal or orthorombic PbO) appear in the glass network. However, this supposition does not exclude the presence of other lead–oxygen configurations.

Based on the structure of the $PbO \cdot 3B_2O_3$ glasses, we analysed the localization of the iron

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cations in $x\mathrm{Fe_2O_3}(1-x)[\mathrm{PbO}\cdot 3\mathrm{B_2O_3}]$ system, with $x \leqslant 50$ mol% Fe_2O_3 [6]. The ferric ions occupy tetrahedral and octahedral co-ordinations in the matrix. Two types of evironment have also been suggested for Fe^{2+} ions [6]. The ratio between the number of Fe^{2+} and Fe^{3+} ions is a function of the iron content.

Further to the above studies we analyse in this paper the influence of the matrix composition and the equilibration temperature on the physical properties of $20\mathrm{Fe_2O_3}80[3\mathrm{B_2O_3}(1-x)\mathrm{PbO}\ x\mathrm{GeO_2}]$ glasses with $0 \leqslant x \leqslant 25$ mol% GeO_2. In this case, even for the lowest PbO content transparent B_2O_3–PbO glasses are formed. We keep constant the Fe_2O_3 content, substituting gradually PbO by GeO_2. To demonstrate the influence of the equilibration temperature, two sets of samples were prepared at 1250 and 1150° C.

Several experimental techniques were used to study the physical properties of PbO–B_2O_3–GeO_2–Fe_2O_3 glass system. These include Mössbauer effect studies, magnetic measurements, X-rays and electron microscopy studies, electron paramagnetic resonance as well as resistivity measurements. Some preliminary Mössbauer effects have been already reported [10].

2. Preparation of the samples

The glasses were prepared by mixing H_3BO_3, PbO and GeO_2 in suitable proportions, and then this mixing was melted in a sintercorundum crucible. After cooling, the host glass was crushed and the resulting powder mixed with an appropriate Fe_2O_3 amount, before the final remelting of the samples. Two sets of glasses, having similar composition, were prepared. The melting temperature for set I was $(1250 \pm 5)^\circ$ C, and for set II, this was $(1150 \pm 5)^\circ$ C. After being kept at this temperature, for 2 h, the glasses were poured onto a steel plate.

The X-ray patterns show that the samples were in the amorphous state. Chemical analysis reveals no sensible deviations from the initial composition.

3. Experimental details

The electron diffraction measurements were made with a JEM-120 machine. The powdered samples were mixed with a collodium solution and then laid on a glass plate, under the form of thin films. The collodium films were then taken out and fixed on a grill. The acceleration voltage was 100 kV.

The magnetic data were obtained with a translation balance in the temperature range (78 to 500) K. The measurements were performed at the two values of the magnetic field. Preliminary studies were also made in the lower temperature range (4.2 to 78) K with "Oxford Instruments" equipment.

The Mössbauer effect measurements were performed using standard "Austin Science Associates" equipment for the first set of samples, and for the second one, "KFKI" Hungary equipment was used. The data were obtained at room temperature. A ^{57}Co source of 40 mCi in copper matrix was used. The spectra were fitted, using a FORTRAN program, assuming a Lorentzian shape of the lines. The program gives the integrated area under the absorption curves and consequently, the relative content of iron in various co-ordination or valence states.

The electron paramagnetic resonance studies were performed at 9.4 GHz (X-band), using standard JEOL equipment, in the temperature range (78 to 300) K. The weight of the samples was in all cases 0.1 g.

The electrical resistivity measurements were performed using the two electrode method [11, 12]. The thickness of the samples was 0.5 to 1.0 mm and their surface areas were 1.0 to 1.5 cm^2. To obtain a good contact between sample and electrode, the contact area was silvered. Control of the results was made using the current–voltage method: the I–V characteristics were linear and the samples did not have surface polarization. After the voltage was applied, no time dependence of the electrical resistivity was observed. The thermoelectric power shows that the current carriers are electrons.

4. Electron microscope studies

The selected-area diffraction studies were used to check the structure of the glasses. Generally, only the diffraction patterns, characteristic for amorphous structure were observed. Fig. 1 shows the diffraction images for some glasses equilibrated at 1250 and 1150° C, respectively.

In the samples with $x = 10$ and 25 mol% GeO_2, melted at $T_M = 1150^\circ$ C, we showed the presence of small B_2O_3 single-crystal particles. Because of very small quantities of a crystalline phase, this cannot be shown by X-ray measurements. Electron microscope studies show further evidence that the glasses are in the amorphous state.

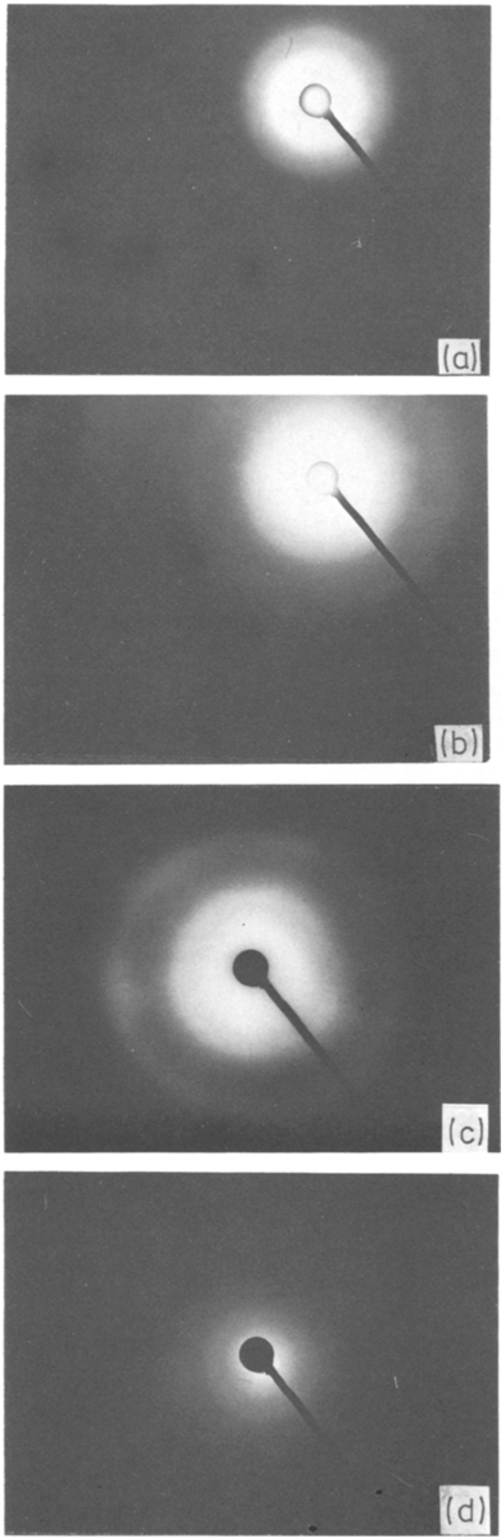

Figure 1 Electron diffraction patterns for the samples equilibrated at 1250° C: (a) $x = 10\,\text{mol}\%\ \text{GeO}_2$, (b) $x = 25\,\text{mol}\%\ \text{GeO}_2$; and at 1150° C: (c) $x = 10\,\text{mol}\%\ \text{GeO}_2$, (d) $x = 25\,\text{mol}\%\ \text{GeO}_2$.

5. Magnetic measurements

Figs. 2 and 3 show the thermal variation of reciprocal susceptibility for some glasses equilibrated at 1250 and 1150° C respectively. In the temperature range studied, a Curie–Weiss behaviour is shown:

$$\chi = \frac{C}{T-\theta}. \tag{1}$$

To determine accurately the values of the Curie

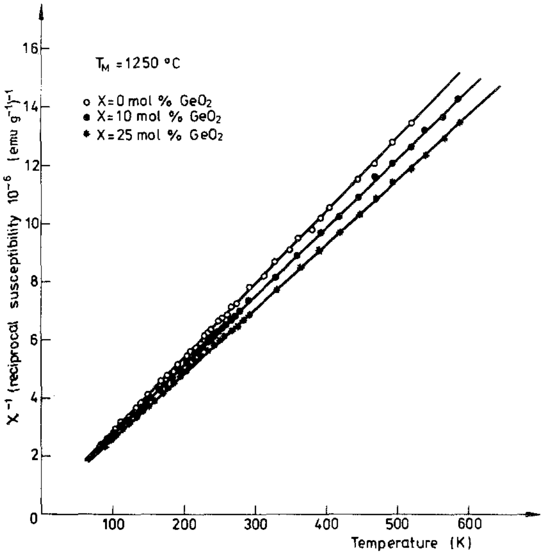

Figure 2 Thermal variation of reciprocal susceptibility for the glasses equilibrated at 1250° C with $x = 0$, 10 and 25 mol% GeO_2.

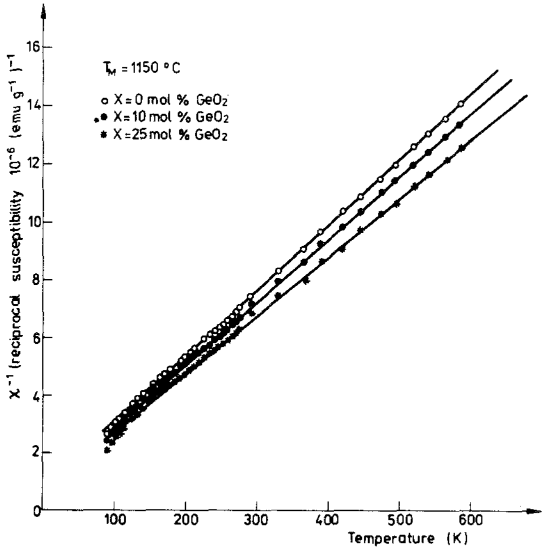

Figure 3 Thermal variation of reciprocal susceptibility for the glasses equilibrated at 1150° C with $x = 0$, 10 and 25 mol% GeO_2.

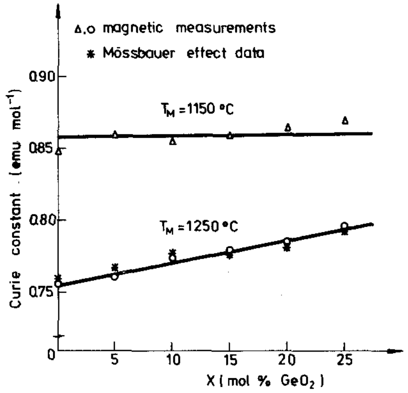

Figure 4 The composition dependence of the Curie constants.

constants C, corrections due to the diamagnetism of glass matrix and Fe_2O_3 core electrons were taken into account. The C values are plotted in Fig. 4 as function of GeO_2 content. In the case of the samples equilibrated at 1150° C, the Curie constants are not composition-dependenent. For glasses equilibrated at 1250° C, the C values increase with increasing GeO_2 content, being situated below the characteristic values for the second set of samples.

All the glasses were prepared with the same Fe_2O_3 content (20 mol%). On the other hand, chemical analysis showed no deviations from the initial composition. Thus, the variation of C values can be ascribed only to the change of the valence states of some iron ions. It is known that the effective moments are 5.92 μ_B in case of free ferric ions, and 4.90 μ_B for ferrous ions (e.g., [13]).

For the samples equilibrated at 1150° C, the experimentally determined effective moments are very close to the free-ion value (Table I). If Fe^{2+} ions are present, their number is smaller than 0.5%, from the total number of iron cations. For the glasses equilibrated at 1250° C, smaller C values are observed. This can be ascribed only to the presence of a quantity of ferrous ions in the sample. The increase in the Curie constants is probably due to the decrease of the ratio between the number of ferrous and ferric ions, as result of the changes in the glass matrix composition. We can expect, from the Curie constants, a fraction of ferrous ions to be present, even for the glass with 25 mol% GeO_2. The extrapolation to the C value characteristic of the effective moment of the ferric ion, gives a composition of about 80 mol% GeO_2.

The paramagnetic Curie temperatures, θ, are negative (Table I). These values are nearly constant for each set of samples. For the glasses equilibrated at 1250° C, $\theta = -13$ to ~ -15 K, while for the samples melted at 1150° C, they are between $\theta = -41$ and ~ -44 K. The negative θ values suggest that a predominant antiferromagnetic order appears at temperatures lower than 78 K. Preliminary measurements performed in this temperature range on the sample with $x = 0$ mol% GeO_2, show that the magnetic ordering of glasses may be described by the so-called sperromagnetism [4] or mictomagnetism [14]. In this case, the antiferromagnetic order is formed only in a short-range. Such a behaviour has also been observed in $BaO–B_2O_3–Fe_2O_3$ or $BaO–Na_2O–Fe_2O_3$ glasses [15, 16].

The increase in the absolute value of the paramagnetic Curie temperatures for the samples equilibrated at 1150° C is due to the increase of the magnetic interactions. This may be ascribed to the clustering tendency showed by the iron ions. We use the term "cluster", to describe the ions which are not completely isolated, interacting by a super exchange-type mechanism.

For the samples equilibrated at $T_M = 1150°$ C, the thermal variation of reciprocal susceptibility deviates from the linearity at temperatures around 100 K. This behaviour is ascribed to the onset of

TABLE I Magnetic characteristics of $20Fe_2O_3 80[3B_2O_3(1-x)PbO\,xGeO_2]$ glasses

x (mol% GeO_2)	Samples equilibrated at T_M = 1250° C		Samples equilibrated at T_M = 1150° C		
	Curie constant (emu mol^{-1})	Paramagnetic Curie temperature (K)	Curie constant (emu mol^{-1})	Paramagnetic Curie temperature (K)	Effective ion moment (μ_B)
0	0.755	−15	0.850	−44	5.87
5	0.760	−13	0.860	−45	5.91
10	0.773	−14	0.855	−42	5.90
15	0.780	−14	0.860	−43	5.91
20	0.785	−15	0.865	−41	5.93
25	0.795	−17	0.870	−42	5.95

magnetic order, involving a small number of iron ions in a cluster, where the exchange interactions are greater than a critical value. For the samples melted at 1250° C, the iron ions are more randomly distributed in the glass; for $T > 78$ K only a Curie–Weiss behaviour is observed.

6. Mössbauer effect measurements

The Mössbauer spectra for the samples with $x = 0, 10$ and 25 mol% GeO_2, equilibrated at 1250° C are shown in Fig. 5. We notice the presence of three absorption peaks, the third being well-separated from the two more intense ones. These are due to the presence of both ferric and ferrous cations. The relative intensities of the absorption lines are dependent on the glass matrix composition. The third peak (ascribed to the presence of Fe^{2+} ions) decreases in intensity by increasing the GeO_2 content. The Mössbauer spectra for the samples with $x = 0, 10$ and 25 mol% GeO_2, equilibrated at $T_M = 1150$° C are plotted in Fig. 6. In this case only the presence of the two absorption peaks due to ferric ions are observed.

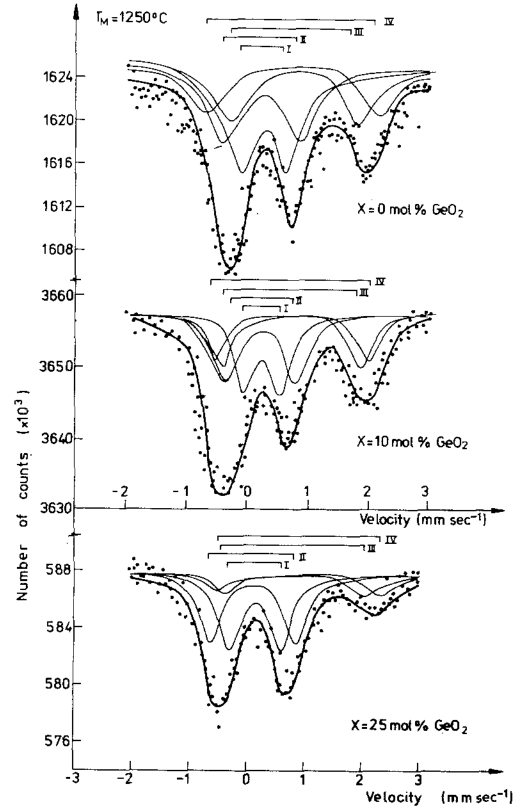

Figure 5 The Mössbauer spectra of the samples equilibrated at 1250° C with $x = 0, 10$ and 25 mol% GeO_2.

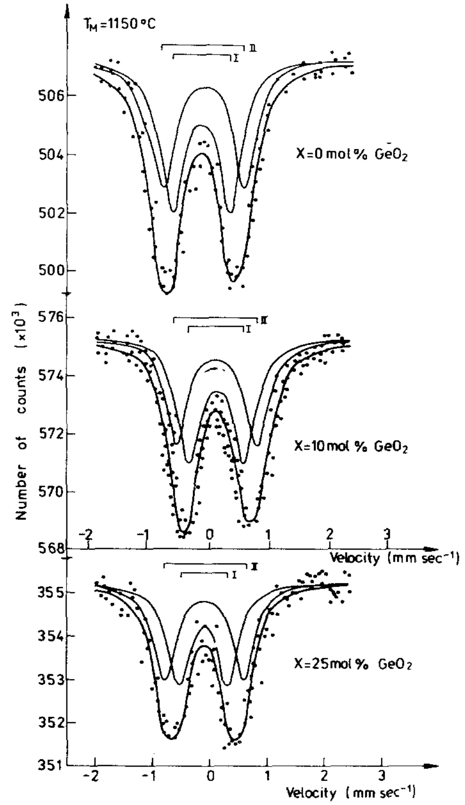

Figure 6 The Mössbauer spectra of the samples equilibrated at 1150° C with $x = 0, 10$ and 25 mol% GeO_2.

The spectra were analysed bearing in mind two assumptions:

(1) the ferrous and ferric cations, respectively, are non-uniformly distributed in the glass. Thus, the linewidth of the doublets is expected to be broadened comparative to the natural width due to non-uniformity of the sites [3]. This can explain the rather great linewidth, of the order of 0.70 to ~ 0.75 mm sec^{-1}, observed in all the studied glasses;

(2) the Fe^{2+} and Fe^{3+} ions occupy two types of co-ordinations. For glasses containing amphoteric cations as Fe^{3+} it is generally accepted that they are distributed among tetrahedral and octahedral sites [2]. The presence of two non-equivalent sites for the ferrous ions merits comment [6]. As previously noted, the NMR measurements [7, 9] suggest that Pb^{2+} ions have two different co-ordinations in B_2O_3–PbO glasses. Because the basic cations such as Fe^{2+} are network modifiers [17] it seems reasonable to assume similar distributions as for Pb^{2+} ions [9].

The fit of experimental spectra leads, in the above assumptions, to the same χ_f^2 values and

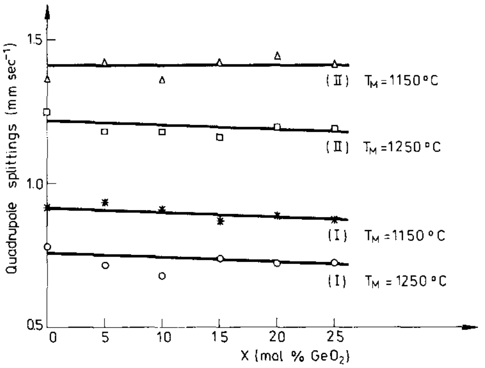

Figure 7 The composition dependence of the quadrupole splittings for Fe^{3+} ions.

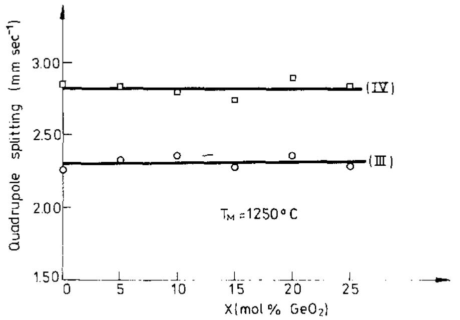

Figure 8 The composition dependence of the quadrupole splittings for Fe^{2+} ions.

consequently cannot supply information on this matter.

Next we shall analyse the spectra according to the latter supposition. A number of experimental data are in agreement with this type of decomposition. The linewidth of the doublets is of the order 0.42 to ~0.45 mm sec^{-1}. A detailed discussion concerning this type of analysis was previously given [6].

The composition dependence of the quadrupole splittings ΔQ, is presented in Fig. 7 for doublets I and II and in Fig. 8 for doublets III and IV. The ΔQ values obtained for doublets I and II are greater for the samples equilibrated at 1150° C, showing a more distorted environment. A slight decrease of the quadrupole splittings by increasing GeO_2 content can be observed.

The values of the quadrupole splittings and isomer shifts δ, can be used to infer the co-ordination and the valence states of iron ions in these materials. Larger quadrupole splittings are generally observed for the Fe^{2+} ions. This is the result of an axial or rhombic symmetry distortion, generated by the electrons outside the half-filled spherical cell. Doublets III and IV are attributed to the Fe^{2+} ions. The determined quadrupole splittings in SiO_2–Na_2O–CaO glasses [2] or other glass systems [4] are close to those observed for doublets III of our spectra; $\Delta Q = 2.28$ to ~2.40 mm sec^{-1}. The ΔQ values determined for doublet IV are between 2.74 and ~2.90 mm sec^{-1} showing a co-ordination with a lower symmetry than for the ferrous ions contributing to doublets III. Possible configurations for Fe^{2+} cations as suggested above may be those discernible in both tetragonal and orthorombic PbO. This does not exclude the presence of other co-ordinations [6]. Doublets I and II are due to the presence of Fe^{3+} ions.

Values of the isomer shift and quadrupole splittings of ferric cations were reported for crystalline and vitreous oxides [1, 18]. For the Fe^{3+} ions in tetrahedral co-ordination in crystalline materials, an isomer shift in the range 0.0 to ~0.19 mm sec^{-1} (relative to copper source) has been observed, while for octahedral co-ordination it is between 0.16 and ~0.29 mm sec^{-1} [2]. Because of the overlap of the ranges, this criterion seems to be somewhat doubtful to infer the types of co-ordinations. More reliable information can be obtained from the analysis of quadrupole splitting.

In the case of ferric ions, the 3d electrons are spherically symmetric and therefore will not contribute to the electric field gradient at nucleus. Thus, the quadrupole splittings supply information on the deviation of the environment from the cubic symmetry. The tetrahedral sites are characteristically less symmetric than the octahedral ones. In this case, a more pronounced difference in ΔQ values for the two types of sites in crystalline materials is observed. The splitting for the tetrahedral sites ranges from 1.4 to 1.8 mm sec^{-1}, while that for octahedral ones range from 0.56 to 0.64 mm sec^{-1} [2]. These values are very close to those determined for doublets I and II. Accordingly, doublet I can be attributed to the Fe^{3+} ions in octahedral environment, while doublet II to those tetrahedrally co-ordinated.

Coey [4] has plotted the values of the quadrupole splittings as function of the isomer shifts for the various glass systems. The tetrahedrally co-ordinated Fe^{3+} ions seem to have a lower isomer shift, comparative to those octahedrally co-ordinated. This is in agreement with the present data (Fig. 9). The isomer shifts for the octahedral

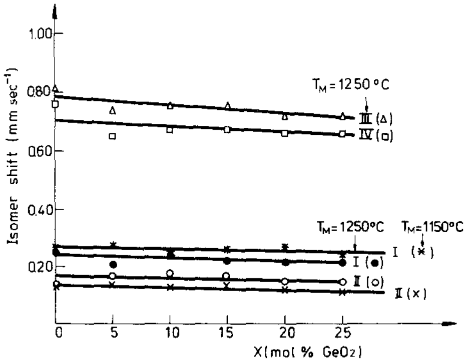

Figure 9 The composition dependence of the isomer shifts.

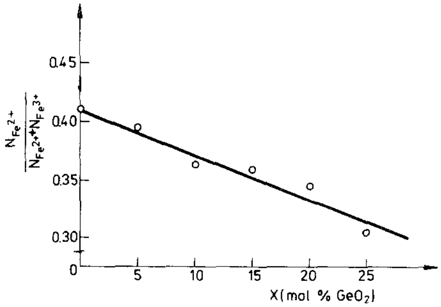

Figure 10 The ratio r between the number of ferrous ions and the total number of iron cations, as function of glass composition. The samples were equilibrated at $T_M = 1250°$ C.

sites, 0.21 to ~0.27 mm sec^{-1}, and for the tetrahedral ones, 0.11 to ~0.17 mm sec^{-1}, are in the range of characteristic values for corresponding crystalline systems. The isomer shifts decrease little with increase in the GeO_2 content showing an increase in the covalency degree [19].

To determine the number of iron ions in various co-ordinations and valence states, we have analysed the spectra according to the above assumptions. The computer analysis of the spectra shows that the integrated areas, under the absorption curves, are nearly the same if we consider one or two sites for Fe^{3+}, Fe^{2+} ions, respectively. Both analyses lead to the same results.

The areas S_i, under the absorption curves, are proportional to the product of the number of resonating iron ions and the fraction of resonating ions, f_i, which are recoil-free. As generally accepted [2] we assume that the ratios between the fractions of resonating ions in different co-ordinations and the valence states, f_i, which are recoil-free, do not differ much from unity, or are highly dependent on concentration. Taking this assumption into account, the ratio $r = N_{Fe^{2+}}/N_{Fe}$, between the number of ferrous ions and the total number of iron ions $N_{Fe} = N_{Fe^{2+}} + N_{Fe^{3+}}$ is given by the integrated areas under the absorption curves. The r ratios for the glasses equilibrated at 1250° C, as function of GeO_2 content are given in Fig. 10. These data show that by increasing the GeO_2 content, the number of Fe^{2+} ions decreases.

Starting from the number of Fe^{2+} and Fe^{3+} cations determined in Fig. 10, we have calculated the Curie constants C, supposing that the effective magnetic contributions are given by the free-ion values. The calculated C values are plotted in Fig. 3. These are very close to the Curie constants experimentally determined. The data obtained from magnetic measurements and by Mössbauer effect are consistent.

7. Electron paramagnetic resonance (EPR) measurements

Typical EPR spectra for the samples equilibrated at $T_M = 1250°$ C are given in Fig. 11, and those obtained in the case of the samples melted at $T_M = 1150°$ C are plotted in Fig. 12. Inspection

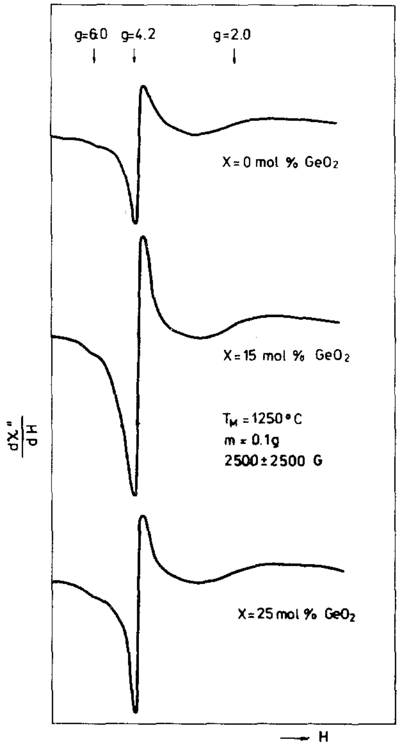

Figure 11 The room temperature EPR spectra of the glasses with $x = 0$, 15 and 25 mol% GeO_2, equilibrated at $T_M = 1250°$ C.

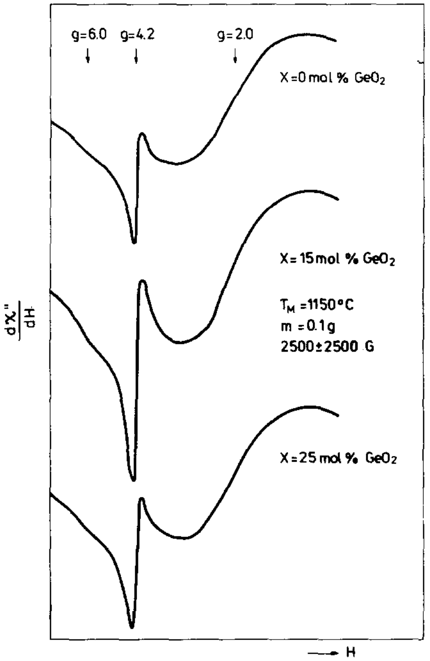

Figure 12 The room temperature EPR spectra of the glasses with $x = 0$, 15 and 25 mol% GeO_2, equilibrated at $T_M = 1150°$ C.

of the spectra show that they are characterized by the resonance absorption at $g = 6.0$, 4.2 and 2.0. The intensities of the resonance lines are dependent both on composition and equilibration temperature.

The resonance line at $g = 4.20$ is typical for isolated Fe^{3+} ions, situated predominantly in a rhombical distorted octahedral or tetrahedral oxygen environment [20–22]. Kurkjian and Sigety [18], on the basis of optical absorption studies on silicate and phosphate glasses, showed that both tetrahedral and octahedral co-ordinations of ferric ions give an EPR resonance at $g = 4.20$ in case of low iron content. The $g = 6.0$ resonance is due to the weak crystal field terms. The origin of the $g = 2.00$ resonance has been a matter of dispute. More recent data suggest that their predominant contribution may be assigned to the clusters of more than one iron ion [21–23]. In our discussion we do not analyse the $g = 6.00$ resonance line. The number of ions participating at this resonance is very small.

The resonance spectra for $g = 4.2$ and $g = 2.00$ were generally decomposed by computer analysis. The linewidth for $g = 4.2$ resonance was determined with an accuracy of ± 2%. In the case of $g = 2.00$ resonance, because of the very large linewidth, the errors are considerably greater, being of the order ± 10%.

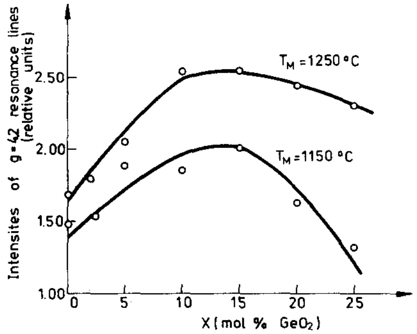

Figure 13 The composition dependence of the intensity of $g = 4.2$ resonance lines at $T = 293$ K.

To analyse the composition dependence of the number of spins participating in $g = 4.20$ and $g = 2.00$ resonance we calculated the area A_i under the absorption curves. In terms of the first derivative, we have $A_i \simeq I_i \Delta H_i^2$, where ΔH_i is the linewidth and I_i the peak-to-peak height of the first derivative of the spectra.

The composition dependence of the intensity of $g = 4.20$ resonance lines for the two sets of samples is plotted in Fig. 13. They have a similar composition dependence, the number of isolated Fe^{3+} ions, being greater in case of the samples melted at higher temperature. The effect of the equilibration temperature on the intensities of the resonance lines shows that the decrease in the T_M value increases the number of exchange-coupled Fe^{3+} ions, a clustering tendency. The number of isolated Fe^{3+} ions is also increased by replacing PbO by GeO_2 up to a concentration of 10 to 15 mol%, the quantity of these ions decreasing for higher concentrations.

The composition dependence of the intensity of $g = 2.00$ resonance is plotted in Fig. 14. The

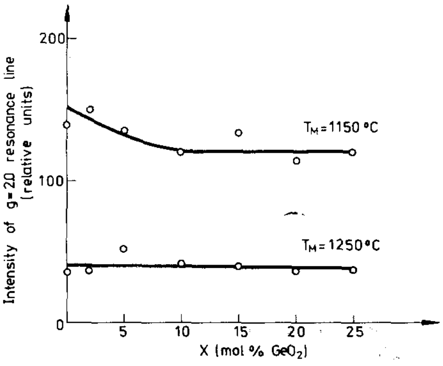

Figure 14 The composition dependence of the intensity of $g = 2.0$ resonance lines at $T = 293$ K.

number of ferric ions situated in a cluster for the samples equilibrated at lower temperatures is greater than in case of samples melted at 1250° C. This is due both to the increased number of Fe^{3+} cations as result of the lack of ferrous ions in sample, and to the smaller number of isolated Fe^{3+} ions.

For the samples equilibrated at 1150° C, the $A_{Fe^{3+}}$ values decrease slightly up to 10 mol % GeO_2 and after this are nearly constant. This may be correlated with an increase in the number of isolated Fe^{3+} ions, as shown in Fig. 13. For the samples melted at 1250° C, the number of Fe^{3+} cations participating at $g = 2.0$ resonance seems to be constant. This is due to two contradictory tendencies. One is the result of the increase of the number of ferric ions by increasing GeO_2 content and the other is due to the decrease of the number of ions in the cluster as a result of increasing the quantity of isolated Fe^{3+} ions.

Comparative analysis of the EPR data with those obtained by Mössbauer effect measurements suggest that both tetrahedrally and octahedrally co-ordinated Fe^{3+} cations contribute to a resonance line with the same g value, as previously assumed [22]. The presence of a greater number of ferric cations in the cluster, for the samples equilibrated at 1150° C, is in agreement with the results of magnetic measurements, revealing an increase in the exchange interactions in the system.

The composition dependence of the linewidth of $g = 4.2$ resonance is plotted in Fig. 15. The ΔH_i values obtained in the case of the samples equilibrated at 1150° C, though having the same dependency as those obtained at $T_M = 1250°$ C, are greater by ~ 25 G. This is due to the increased dipolar interactions as the result of a more distorted environment.

The two sets of ΔH_i values decrease with increasing GeO_2 content. The environment of the ferric ions is more symmetrical when increasing the GeO_2 content. The above conclusion is in agreement with the Mössbauer effect data which show a decrease of the quadrupole interactions, with increasing GeO_2 content.

8. Resistivity measurements

Figs. 16 and 17 show the temperature dependence of the electrical resistivity, ρ, for the samples with $x = 0, 10$ and 25 mol % GeO_2, equilibrated at 1250 and 1150° C, respectively. The $\log(\rho T^{-1})$ versus T^{-1} curves show a linear variation with a slope change at the characteristic temperature, T_t.

The temperature dependence of the resistivity is the same for all the glasses studied. The resistivity of the samples equilibrated at 1250° C increased with increasing GeO_2 content (Fig. 17). The ρ values for the samples melted at 1150° C are nearly identical and greater by two orders of magnitude than those for the first set of glasses. These data show that the resistivity is strongly dependent on the fraction of ferrous ions.

The 3d bandwidth is essentially zero in iron

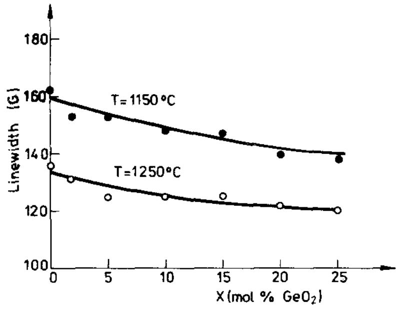

Figure 15 The composition dependence of the linewidths for $g = 4.2$ resonance ($T = 293$ K).

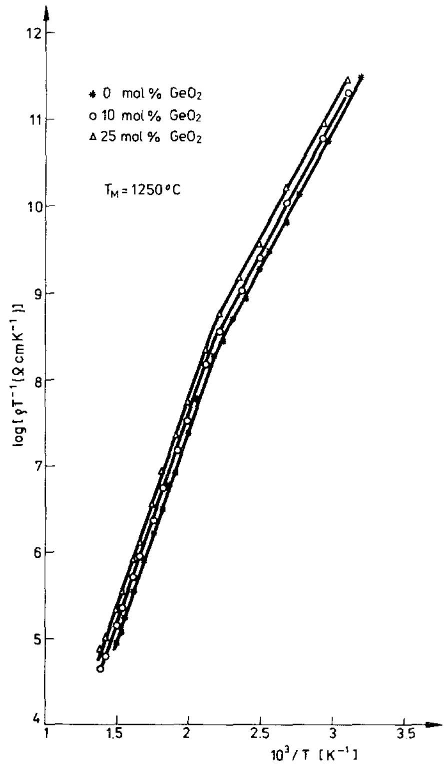

Figure 16 The dependence of $\log(\rho T^{-1})$ as function of T^{-1} for the glasses equilibrated at $T_M = 1250°$ C.

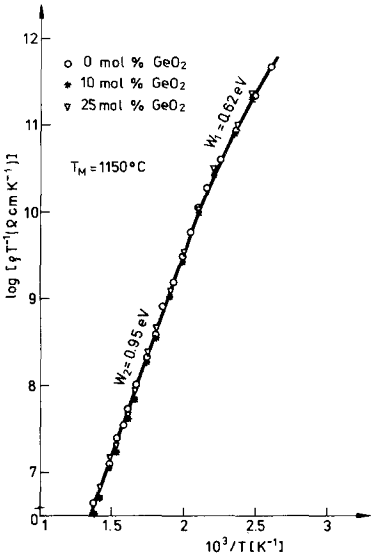

Figure 17 The dependence of log (ρT^{-1}) as function of T^{-1} for the glasses equilbrated at $T_M = 1150°$ C.

oxides and the electronic wave-functions are best thought of as being localized on a particular site. Thus, we cannot expect to observe an overlap between the iron cations and consequently the formation of the bands. This supposition is in agreement with previous studies made on oxide glasses [24]. The current carriers in this case are localized and the conduction mechanism may be described by the electron hopping [24–26]. The activation energy W, for this mechanism involves a disorder term W_D and a polaron term W_P.

Austin and Mott [27] discuss the conduction in a model involving a small polaron. The expression of the electrical conductivity, $\sigma = \rho^{-1}$ is given by:

$$\sigma = \frac{\nu n e^2 R}{k_B T}(1 - r)\exp(-2\alpha R)\exp(-W/k_B T). \tag{2}$$

The activation energy at high temperature is $W = \frac{1}{2}(W_P + W_D)$ for $T \geqslant \theta_D/2$ and $W = \frac{1}{2}W_P$ for $T \geqslant \theta_D$. At lower temperature, we have $W = W_D$, for $T \leqslant \theta_D/4$. In the intermediate temperature range, the activation energy is given by Schnakenberg [28].

Here θ_D is the Debye temperature, R the distance between the transition metal ions, $\exp(-\alpha R)$ the decay of the wave function with radius R, ν is the phonon frequencies, e the electron charge and n is the carrier concentration. The composition dependence of the ratio r is given in Fig. 10.

The similarities in the $\log(\rho T^{-1})$ versus T^{-1} curves suggest the same conduction mechanism in both sets of samples. The conduction mechanism involves the presence of ferric and ferrous cations. The Mössbauer effect studies and magnetic measurements show the presence of the iron cations in the two valence states for the glasses equilibrated at 1250° C. In case of the samples melted at 1150° C, within limit of experimental error, no evidence of ferrous cations was found. From the resistivity measurements, a small number of Fe^{2+} ions may be expected. A rough estimation of the ratio r from resistivity, using Equation 2 gives a quantity of ferrous ions for the second set of glasses, smaller than 0.2% of the total number of iron ions. This value is very small and cannot be demonstrated by magnetic and Mössbauer effect measurements.

From inspection of the $\log(\rho T^{-1})$ versus T^{-1} curves (Figs. 16 and 17) one notices a change in the slope at a temperature T_t, the two regions being characterized by different activation energies. The activation energy is $W_1 = 0.62 \pm 0.01$ eV for $T < T_t$, while for $T > T_t$, $W_2 = 0.97 \pm 0.02$ eV being composition independent (Table II). A similar change in slope was previously reported in iron phosphate glasses [24, 29], or for lead borate glasses [12]. The reason for this break is not completely understood. The presence of the activation energies can be justified by the predominant

TABLE II The activation energies W_1 and W_2, the carrier concentration, n, and the phonon frequency, ν

x (mol% GeO_2)	Samples equilibrated at $T_M = 1250°$ C			Samples equilibrated at $T_M = 1150°$ C
	$x = 0$	$x = 10$	$x = 25$	$x = 0; 10; 25$
$T < T_t$ W_1 (eV)	0.63	0.62	0.62	0.62
$T > T_t$ W_2 (eV)	0.98	0.99	0.97	0.95
n (cm^{-3})	8.82×10^{20}	7.48×10^{20}	6.21×10^{20}	
ν (sec^{-1})	2.70×10^{12}	2.30×10^{12}	2.10×10^{12}	

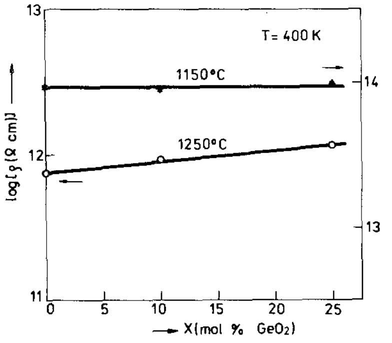

Figure 18 The composition dependence of the electrical resistivity at 400 K.

contribution of the charge transfer between Fe^{2+} and Fe^{3+} ions in similar environments at lower temperatures and between these ions in different environments at higher temperatures [26, 30]. The presence of iron cations in various oxygen environments was suggested by Mössbauer effect measurements, this supposition being in agreement with the structural information on these glasses.

From Equation 2 we estimate the phonon frequencies ν using the data obtained at 400 K (Fig. 18), the activation energies W_1 and the n values listed in Table II. We admit that $R \simeq 5.5$ Å [31, 32] and a $\alpha \cong 10^8\ cm^{-1}$ [26]. The calculated phonon frequencies are in the range 2.10 to ~ 2.70 $10^{12}\ sec^{-1}$, very close to the lattice vibrational fequency [25, 26].

In the case of phosphate glasses with transition metal ions, Sayer and Mansingh [33] show that the experimental results are better explained by using an adiabatic hopping process. In this case $(1-r)$ from Equation 2 is substituted by $(1-r)^{P+1}$, where P is the number of sites surrounding the polaron at which interactions occur. For $50Fe_2O_3$–$50P_2O_5$ glasses by using $P = 5, \nu = 8.4 \times 10^{12}\ sec^{-1}$ is obtained. According to this model, we determine $\nu \simeq 10^9\ sec^{-1}$, which is smaller by three orders of magnitude than the lattice vibrational frequency. To have ν of the order of $10^{12}\ sec^{-1}$, then, it is necessary that $P \simeq 21$, which has no physical significance. This suggests that the relation given by Mott and Austin describes better the present results.

From the relation

$$\sigma = ne\mu \qquad (3)$$

we calculated the current carriers mobility. For the first set of samples, the mobility at 400 K is of the order $10^{-14}\ cm^2\ V^{-1}\ sec^{-1}$. This value is in agreement with the data obtained from the studies of oxide glasses with transition metal ions [24–26].

The samples were prepared with the same Fe_2O_3 content. On the basis of density measurements, we conclude that the mean distances between iron ions are nearly the same. The parameter which changes with the glass matrix composition or equilibration temperature is the ratio r. This is in agreement with the prediction of Equation 2. The resistivity data is thus a convincing experimental evidence of the validity of polaron model for the conductivity of PbO–B_2O_3–GeO_2–Fe_2O_3 system.

9. Discussion

A careful examination of the glasses by X-ray and electron microscope showed that these were in the amorphous state. The samples did not crystallize at the temperature used for magnetic measurements, in agreement with Laville *et al.* [16]. These authors demonstrated that BaO–Na_2O–Fe_2O_3 glasses are in the amorphous state in the temperature range $T < 700$ K.

The equilibration temperature has a very important effect on the valence states of iron ions. For the samples melted at 1150° C, within the limit of experimental error, no presence of ferrous ions was observed. Estimation of the number of Fe^{2+} ions, from the resistivity measurements, suggests a value which is smaller than 0.2% of the total number of iron cations.

Levy [34] showed a linear increase in the fraction of Fe^{2+} cations in SiO–CaO–Fe_2O_3 glasses from an average value of 7.61% at 1315° C to 23.44% at 1569° C. The extrapolation of data gives a temperature $T_M \simeq 1170°$ C at which the number of ferrous ions is nil. This behaviour is explained considering the equilibrium reaction $2O^{2-} + 4Fe^{3+} \rightleftarrows 4Fe^{2+} + O_2$ that yields a concentration equilibrium constant, K, which displaces the redox reaction towards the reduced side with increasing temperature of the melt. Paul [35] showed that the distribution of cations into different states of oxidation in an oxide melt depended on time and temperature of melting, the melt decomposition and the furnace atmosphere. In a given set of conditions, after sufficient melting time, the melt reaches equilibrium with the partial pressure of oxygen in the ambient atmosphere and the relative concentration of oxidation states reach equilibrium values.

Probably in our case, the melts at the lower temperature (1150° C) did not reach equilibrium.

We can assume that Fe_2O_3 was incorporated into the glasses before decomposing into FeO, and the rate of diffusion of O_2 in the glass is so low at 1150° C that the number of Fe^{3+} ions did not change during the melting time (2 h).

Analysing the valence states of iron ions in samples melted at 1250° C, we notice that by increasing the GeO_2 content, the number of Fe^{2+} cations is decreased. Data obtained from Mössbauer effect and magnetic measurements are in good agreement. Levy *et al.* [2] showed that the ratio of ferrous to ferric cations increases with decreasing basicity, higher temperatures and gradual replacement of Na_2O and CaO. Our samples were equilibrated at the same temperature, also keeping constant the Fe_2O_3 content. Thus, the composition dependence of the ratio r may be due to the activity coefficients γFe_2O_3 and γFeO which change with the melt composition. Paul [35] has shown a logarithmic dependence of the ratio r in $(30-x)$ $A_2O\,x CaO\,70SiO_2$ glasses, as function of A_2O content (A = K, Na, Li). Levy and co-workers [2, 34] report a linear variation of the ratio r in SiO_2–Na_2O–CaO glasses, as function of CaO content.

The present data show a linear dependence of r as function of GeO_2 content. It is of interest to obtain further experimental data on various glass systems, in order to determine the validity of these relationships in connection with the glass matrix composition.

By decreasing the equilibration temperature, the Fe^{3+} ions tend to be situated in a cluster to a greater extent than is the case in samples melted at higher temperatures. This is reflected by the increase in the magnetic interactions in the system and consequently higher θ values, as well as by the increase in the intensity of the $g = 2.0$ resonance line.

The number of isolated Fe^{3+} ions, both in the glasses melted at $T_M = 1250$ and 1150° C increases up to 10 to 15 mol% GeO_2, and decreases for a higher GeO_2 content. The number of isolated ferric ions is greater in case of the samples equilibrated at 1250° C.

The electrical resistivity measurements show the presence of two activation energies for conduction. The predominant contribution at lower temperatures is due to the charge transfer between Fe^{2+} and Fe^{3+} ions in similar environments and between these ions in different environments at higher temperatures. An evident correlation between the values of the resistivity and the number of Fe^{2+} ions is found. The conduction mechanism is well described by a model involving electron hopping.

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