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Review

Electrical conductivity in iron-containing oxide glasses

LEON MURAWSKI
Institute of Physics, Technical University of Gdańsk, 80952 Gdańsk, Poland

The electrical properties of silicate, borate, phosphate and tellurite glasses containing iron are reviewed. The highest electrical conductivity has been observed in iron–tellurite glasses. The problem of the structure and influence of different glass modifiers on the electrical conduction of iron-containing glasses is discussed.

1. Introduction

A general condition for semiconducting behaviour is that the transition-metal ions should be capable of existing in more than one valence state so that conduction can take place by the transfer of electrons from the ion of low valence state to that of high valence state. Therefore, the ratio $M_{\text{reduced}}/M_{\text{total}}$, where M represents the transition-metal ion, becomes one of the factors determining electrical conductivity. Other important factors are the concentrations of transition-metal oxide, glass former and glass modifier and also the melting conditions. The transport of electrons in these glasses is usually termed "small polaron hopping". A general formula for the electrical conductivity of these glasses was proposed by Mott [1, 2] in which the conductivity, τ, is given by

$$\sigma = \frac{\nu_{\text{ph}} e^2 C(1-C)}{kTR} \exp(-2\alpha R) \exp(-W/kT), \tag{1}$$

where ν_{ph} is a phonon frequency, α is the rate of the wave function decay, C is the ratio of ion concentration in the low valency state to the total concentration of transition-metal ions, R is the average hopping distance, W is the activation energy, e is the electronic charge, k is Boltzmann's constant and T is the absolute temperature.

Equation 1 can be compared to the common Arrhenius equation

$$\sigma = \sigma_0 \exp(-W/kT), \tag{2}$$

where

$$W \cong W_{\text{H}} + \tfrac{1}{2} W_{\text{D}}, \tag{3}$$

W_{H} is the hopping energy and W_{D} is the disorder energy arising from the energy difference of neighbours between two hopping sites [1].

The semiconducting oxide glasses can contain V, W, Mo, Fe, Ti, Cu, Mn, Co and Ni ions [3]. The value of the ratio, C, should lie between 1 or 0. This type of behaviour is easy to obtain in V_2O_5-, Fe_2O_3- or FeO-containing glasses. Iron oxides can form stable glasses with different kinds of glass-former oxides such as SiO_2, P_2O_5, B_2O_3 and TeO_2. Our study concerns iron–phosphate systems. In this paper the electrical conductivities in different iron-containing oxide glasses will be compared and discussed.

2. Structure

Iron commonly exists in both the valence states, Fe^{2+} and Fe^{3+}. In view of the existence of the three crystalline oxides: FeO, Fe_3O_4, Fe_2O_3, with totally different structures, it is to be expected that a multiplicity of environments for both ions can exist in glasses. The co-ordination number of Fe ion can be determined from optical, electron spin resonance (ESR), magnetic susceptibility and Mössbauer spectroscopy studies.

These methods give good results in the case of low concentrations of Fe ions (< 2 mol % Fe_2O_3). When the concentration of Fe ions is high (> 5 mol % Fe_2O_3) overlap between ferrous and ferric bands occurs in optical studies and it is difficult to speculate on the structural environments of iron in the glass matrix [4]. The ESR method is also ineffective because in many cases magnetic

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interactions deform the ESR spectra [5]. It has been shown [6] that the effect of exchange interaction between Fe ions in different valency states involves broadening resonance lines. Mössbauer spectroscopy is probably the most useful technique in structural studies of iron in a glass matrix. The Mössbauer effect provides essentially local information the electric and magnetic field at a nuclear site Fe^{57}, and the mean square velocity. and displacement of the resonating nucleus. The isomer shift and quadrupole interaction are determined mainly by the immediate neighbours, so it should be possible to discover something of the bonding co-ordination number and local structure around the Fe ions using this technique. The author is aware of two review papers detailing the Mössbauer effect in glass solids: the review by Kurkijan of the oxide glasses [7] covers the earliest work and that by Coey [8] deals with the applications of the Mössbauer effect to amorphous solids.

The Mössbauer spectra [9–15] in phosphate systems indicate octahedral co-ordination for Fe^{3+} and Fe^{2+} ions. The detailed temperature study of Taragin *et al.* [12] confirmed the octahedral co-ordination of Fe ions in phosphare glasses. Taragin *et al.* have also found that the Debye tempetatures for Fe^{2+} and Fe^{3+} are different. This fact indicates a difference in the dynamic properties of the two ions and hence a difference in the way that the ions are incorporated in the glass structure.

The isomer shift for Fe^{3+} Mössbauer spectra in alkali silicate and alkali borate glasses is typical for tetrahedrally co-ordinated ferric ions in crystalline oxides and silicates [8]. Both co-ordinations of ferric ions have been found in alkaline-earth silicate and borate glasses [13, 16]. The co-ordination of Fe^{2+} is not as well defined as that of Fe^{3+} in glasses. The structural state of Fe^{2+} depends significantly on the chemical nature of the glass modifiers. Mössbauer spectra indicate that ferrous ions in silicate and borate glasses may have co-ordination numbers of either 4 or 6 [13].

The glass-formation region in iron–phosphate systems extends up to 80 mol% Fe_2O_3 when the glasses are melted in an oxidizing atmosphere. Glasses containing more than 60 mol% Fe_2O_3 were found to exhibit glass–glass phase separation [17, 18]. ESR studies [5] showed that most Fe ions in 55 mol% FeO–45 mol% P_2O_5 glasses are highly antiferromagnetically coupled in Fe^{3+}–Fe^{2+} ion pairs. The short-range antiferromagnetic ordering is also confirmed by a magnetic susceptibility study [5, 19, 20] in a series of ion–phosphate glasses. The first attempts to interpret these data were attempted through microcrystalline models [19]. The evidence for a microcrystalline interpretation was based on the fact that the general behaviour of the 56 mol% Fe_2O_3–44 mol% P_2O_5 glass was very different from CoO– and MnO–phosphate glasses. It has been found that the Néel temperature of Fe_2O_3–P_2O_5 glasses was independent of the Fe^{3+} ion concentration, whereas the CoO–P_2O_5 and MnO–P_2O_5 Néel temperature was found to be a function of the magnetic ion content. The detailed study of neutron magnetic scattering by Wedgwood and Wright [21] on the 56 mol% Fe_2O_3–44 mol% P_2O_5 glass showed that the microcrystalline model is not acceptable. They proposed a model in which not acceptable. They proposed a model in which the Fe–Fe nearest-neighbour distance and the co-ordination number of Fe ions are constant. In this model Fe ions tend to cluster so that the glass exists in two phases, the first containing alternate FeO_4 and PO_4 tetrahedra and the second containing only P_2O_5 which forms a pure glass. This type of arrangement is only possible with a trivalent magnetic ion and thus could not occur with CoO– and MnO–phosphate glasses. However, this model is not consistent with Mössbauer data which indicate that Fe^{3+} ions in phosphate glasses can exist only in octahedral co-ordination.

In iron–silicate and iron–borate glasses, the glass-formation regions are much narrower than in phosphate systems, generally containing less than 20 mol% Fe_2O_3 [13, 22, 30]. The maximum amount of iron oxide present depends on the kind of network modifiers and on the melting conditions. It was reported that in iron–lead borate glasses the maximum content of Fe_2O_3 is 50 mol% [31–33].

The structural study of iron–silicate and iron–borate glasses has showed that Fe ions are not randomly distributed [24, 25, 27, 34] and some magnetic inhomogeneities exist in these glasses. The model of Anderson and MacCrone [27] proposes that the great majority of Fe ions are situated in relatively well-ordered clusters containing various numbers of Fe ions. Most of the Fe ions exist in pairs (diads) or groups of three (triads) and are antiferromagnetically coupled within these groups. Within each structure the nearest-neighbour inter-ion distance and relative orientation is assumed to be very similar to that in the crystalline oxides (Fe_2O_3, Fe_3O_4, FeO). The average cluster sizes depend on the iron concentration and heat treatment. For example, in the dilute concentration regime (5 mol% Fe_2O_3) in B_2O_3–BaO–Fe_2O_3 glass it is expected that the average cluster size is less than 1.5 nm [27]. However, the magnetic studies of Ardelean *et al.* [31] on x Fe_2O_3 $(1-x)$ [PbO·3 B_2O_3] glasses suggest that the Fe ions are randomly distributed in the glass matrix even at high Fe_2O_3 contents.

A new class of semiconducting iron-oxide glasses can be prepared from a TeO_2 glass-former base. The glass-forming limits are from 2.3 to 20.0 mol% Fe_2O_3 in a binary system of TeO_2–Fe_2O_3 [35, 36]. A structural model has been proposed, based on neutron diffraction and Mössbauer data [37, 38]. In this model, tellurite glass is characterized by an "open" structure which is characterized by the change of Te(4) co-ordination and in a certain freedom of rotation of TeO_4 polyhedra. The Fe ions exist mainly in the Fe^{3+} state with an octahedral environment and are randomly distributed in the glass matrix.

3. Electrical conductivity

3.1. Iron–phosphate glasses

Representative data from studies of the present author of electrical conductivities for iron–phosphate systems are presented in Table IA and B. Iron–phosphate glasses show a good agreement with the Mott equation, Equation 1. The maximum conductivity occurs at a concentration ratio, $C = Fe^{2+}/Fe_{total} = 0.5$, as shown in Fig. 1. For high iron concentrations (> 55 mol% FeO) there is a marked movement of the maximum conductivity to the Fe^{2+} side [17]. However, glasses containing more than 55 mol% FeO are not homogeneous and it is possible that these glasses could have segregated some Fe^{2+} ions to isolated microstructural islands which do not enter into the conduction process. The activation energy for electrical conduction of homogeneous iron–phosphate glasses decreases with decreasing temperature (see Fig. 2). This is consistent with the "small polaron" theory [1, 2].

The values of activation energy, W, were found to depend on oxide modifiers. Table IB shows that the addition of different alkali-earth oxides

TABLE IA The electrical properties of binary iron–phosphate glasses [39, 40]

Composition (mol%)		C	σ* (Ω^{-1} cm^{-1})	W (eV)	R† (nm)
FeO	P_2O_5				
55	45	0.30	1.8×10^{-10}	0.58	0.47
50	50	0.33	5.6×10^{-11}	0.61	0.50
45	55	0.31	2.0×10^{-11}	0.62	0.52
40	60	0.31	7.8×10^{-12}	0.63	0.53

TABLE IB The electrical properties of iron–phosphate glasses of the form $(50-x)FeO-50P_2O_5-xMO$

MO	x (mol%)	C	σ* (Ω^{-1} cm^{-1})	W (eV)	R† (nm)
MgO	10	0.35	2.20×10^{-12}	0.64	0.55
	20	0.38	1.55×10^{-13}	0.68	0.60
	25	0.38	2.7×10^{-14}	0.69	0.66
	30	0.32	8.0×10^{-15}	0.73	0.69
	35	0.30	5.0×10^{-16}	0.76	0.75
CaO	10	0.28	4.2×10^{-12}	0.64	0.56
	20	0.25	6.6×10^{-13}	0.65	0.59
	25	0.22	2.0×10^{-13}	0.67	0.65
	30	0.24	3.3×10^{-14}	0.69	0.69
BaO	10	0.38	1.5×10^{-11}	0.59	0.57
	20	0.35	5.0×10^{-12}	0.61	0.62
	25	0.37	1.4×10^{-12}	0.61	0.66
	30	0.39	3.0×10^{-13}	0.62	0.69
	35	0.31	3.8×10^{-14}	0.63	0.79

*Conductivities measured at 20° C.

†Values of R, the mean distance between Fe ions, were calculated from the compositions (after chemical analyses) and densities, assuming Fe ions to be uniformly distributed.

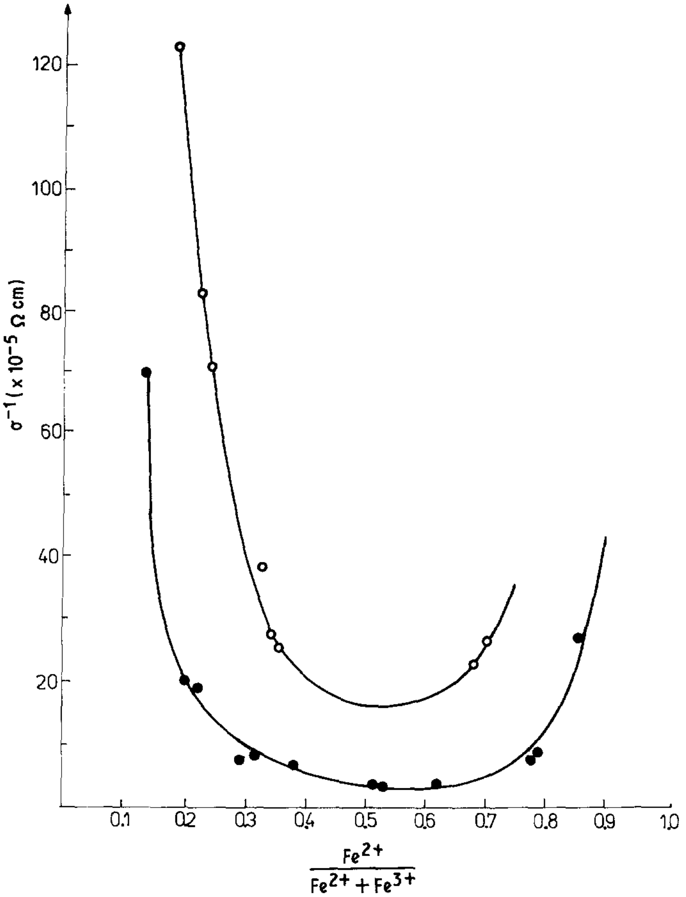

Figure 1 The effect of Fe^{2+}/Fe_{total} ratio, C, on resistivity, σ^{-1}, measured at 200° C for: ●, 45 mol% P_2O_5–55 mol% FeO [41]; and ○, 50 mol% P_2O_5–50 mol% FeO [42] glasses.

changes both the conductivities and activation energies of the glasses. The highest conductivity and the lowest activation energy are exhibited by iron–phosphate glasses with BaO as modifiers. An opposite effect has been observed for glasses with MgO as modifiers. One observes that with an increase in electric field strength of the cation modifiers, activation energy also increases. Hence, it is concluded that the deformation of the nearest environment of Fe ions will be largest for the introduction of MgO into the glass. Edwards *et al.* [43] came to identical conclusions from the results

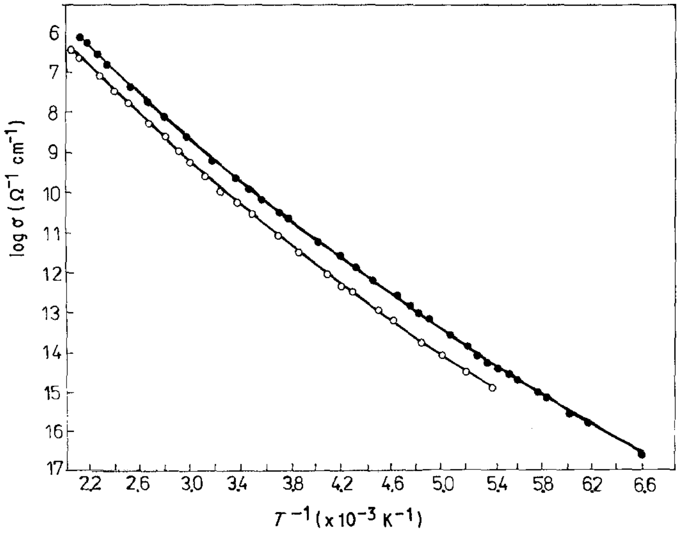

Figure 2 The temperature dependence of conductivity for: ○, 50 mol% P_2O_5–50 mol% FeO; and ●, 45 mol% P_2O_5–55 mol% FeO glasses.

of their optical investigations of P_2O_5–MO–FeO (Fe_2O_3) glasses, where M = Mg, Ca, Sr or Ba. They observed the shifts in the position of the absorption maxima for Fe^{2+} ions for different cation modifiers. This effect was maximal for MgO and progressively smaller for CaO, SrO and BaO, that is, the effect became progressively smaller as the field strength of the cation modifiers decreases. According to Edwards *et al.* [43] the shift in the position of the absorption maximum indicates that the change in the ligand field strength occurs with the different polarizing power of the cation modifiers.

The thermoelectric power of semiconducting glasses is of interest because of the information it yields on W_D term in the activation energy equation, Equation 3, and on the variation of carrier concentration with temperature. The Seebeck coefficient of iron–phosphate glasses is nearly independent of temperature in the high-temperature range (> 125° C) [41]. This implies that the carrier concentration is insensitive to the temperature. In the low-temperature range, the resistivity is too high for measurement of the Seebeck coefficient.

The thermoelectric power between 125° C and 400° C is very strongly dependent on the ratio, C. However, the change from p-type conduction to n-type conduction does not occur for a value $Fe^{3+}/Fe^{2+} = 1$ as predicted in the equation developed by Heikes [44, 45] for the hopping mechanism

$$S = \frac{k}{e}\left[\ln\left(\frac{C}{1-C}\right)\right]. \tag{4}$$

Mott [1] has suggested that in iron glasses there is a great variety of environments for Fe ions and a wide spread of energies for the sites occupied by the electrons. In this case the density of states would not necessarily be symmetrical. This point of view seems to be consistent with the Mössbauer data [12]. Mössbauer studies have confirmed that, despite the single type of coordination of Fe ions in phosphate glasses, there are differences in the ways in which the ions are incorporated in the glass network. These differences in iron sites may be caused by magnetic interactions between Fe ions. Detailed study of the activation energies in iron–phosphate glasses [39] has also shown the significant role of the W_D term. Iron–phosphate glasses show evidence of much larger W_D values in comparison with V_2O_5–, WO_3– and TiO_2–phosphate glasses [46].

Application of the Mott theory has indicated that the polaron term, W_H, lies between 0.3 and 0.35 eV. Since the total activation energies have values of 0.58 to 0.76 eV (see Table I) the derived W_D value is higher than the estimated theoretical disorder term (< 0.1 eV) for the randomly distributed impurities in a broad-band semiconductor [47, 48]. This implies that an additional term, ΔU, describing structure differences between Fe ions should appear in the activation energy expression [48] such that

$$W = W_H + \tfrac{1}{2}W_D + \Delta U. \tag{5}$$

Iron–phosphate glasses show a good agreement with Equation 1 for non-adiabatic transport of small polarons. This means that the tunnelling factor, $\exp(-2\alpha R)$, should be taken into consideration in Equation 1. A detailed discussion of this problem has been published elsewhere [39, 40, 45].

3.2. Iron-borate and iron-silicate glasses

In iron–borate and iron–silicate glasses the co-ordination of Fe ions need not be the same. It has been found that Fe^{3+} ions can exist with a co-ordination number of either 4 or 6 [13, 16, 49, 50]. It is very likely that four-fold co-ordination of tri-valent iron has a significant influence on the electrical conductivity. Kuznetzov and Tsekhomskii [26], in their study of semiconducting iron–silicate glasses, suggested that electron transport is possible only through 6-co-ordinated Fe^{3+}.

The [$Fe^{3+}O_4$] tetrahedron has at least one negative charge which hinders the approach of electrons. The glass must contain weakly-bonded oxygen atoms to allow iron to acquire 4-fold co-ordination.

The content of such atoms increases with decrease of the field of the modifying ion. This was confirmed in magnetic susceptibility studies and Mössbauer spectroscopy studies by Firsov *et al.* [13]. They found that the fraction of Fe ions at octahedral sites increases with increase in the ionic potential of the cation modifiers. The conductivity data (see Table IIA and B) [51, 52] show that calcium glasses have higher conductivity than barium glasses. Similar behaviour has been observed in iron–calcium silicate and iron–barium silicate glasses (see Table IIIA and B).

The interpretation of conductivity measure-

TABLE IIA The electrical properties of iron–borate glasses of the form $70B_2O_3$–$15FeO_x$–$15MO$ [13]

MO	σ^* (Ω^{-1} cm^{-1})
MgO	3.16×10^{-13}
CaO	5.0×10^{-14}
SrO	1.0×10^{-14}
BaO	3.16×10^{-16}

TABLE IIB The electrical properties of iron-borate glasses of the form $70B_2O_3$–$15Fe_2O_3$–$15MO$ [42]

MO	σ^* (Ω^{-1} cm^{-1})	C	W (eV)
CaO	3.3×10^{-12}	0.35	0.70
BaO	2.0×10^{-12}	0.3	0.69

*Conductivities measured at 20° C.

ments is different compared with those of iron–phosphate glasses. Anderson and MacCrone [27] have suggested that the relative spatial positions of the Fe ions are not random in the glass for which the Fe_2O_3 content is greater than 10 mol%. Most of the Fe ions are situated in some kind of clusters containing various numbers of Fe ions.

Charge transport takes place along the chains of clusters. It is possible that, in the case of small amounts of Fe_2O_3, direct current conductive paths do not connect all the clusters. In this case the change of conductivity with concentration of Fe ions should be very high, as has been observed in iron–borate and iron–silicate glasses.

3.3. Lead–silicate, lead–borate and lead–phosphate glasses containing iron

Lead glasses have some specific properties and it is possible to prepare glasses containing up to 90 wt% PbO. It is thought that some Pb^{2+} ions form links between two SiO_4 tetrahedra by bonding the corner oxygens and may therefore be considered as taking part in the formation of a network.

The easily polarizable lead ions exhibit the covalent characteristic of bonding with the oxygen. This covalency therefore accounts for the tendency of lead ions to participate in the glass-forming network [54].

Lead–borate glasses exhibit a similar behaviour. However, in lead–borate glasses the network units can form two different groups, BO_3 and BO_4, and the conversion from one group to the other depends on the concentration of lead in the glass matrix.

It was anticipated that the structure of lead glasses would have a great influence on the electrical conductivity of iron-containing lead–silicate and lead–borate glasses. Fig. 3 shows some conductivity data for lead glasses containing 10 mol% Fe_2O_3. It can be observed that, in borate systems, increase of the PbO/B_2O_3 ratio causes an appreciable increase in conductivity. However, an opposite tendency occurs in silicate systems for which the complexity of structure in lead–borate might be responsible. It is also very likely that the migration effect of lead ions has a significant influence at higher temperatures [55, 56].

The activation energy for lead–borate glasses is a little higher than for lead–silicate glasses. This indicates that in lead–borate glasses the migration effects are more intensive and that fact is reponsible for the increase in conductivity with PbO content. It is interesting that the conductivity of iron–silicate glasses agrees with the model of Kuznetsov and Tsekhomskii [26]. In this model, as the lead content increases, the proportion of

TABLE IIIA The electrical properties of iron–silicate glasses of the form SiO_2–Fe_2O_3–CaO [53]

SiO_2 (mol%)	CaO (mol%)	Fe_2O_3 (mol%)	σ^* (Ω^{-1} cm^{-1})	W (eV)
55.5	33.3	11.2	7.81×10^{-7}	0.65
51.4	34.3	14.3	2.46×10^{-5}	0.66
53.5	29.5	17.0	5.13×10^{-5}	0.59

TABLE IIIB The electrical properties of iron–silicate glasses of the form SiO_2–Fe_2O_3–BaO [26]

SiO_2 (mol%)	BaO (mol%)	Fe_2O_3 (mol%)	σ^* (Ω^{-1} cm^{-1})	W (eV)
59	39	2	6.6×10^{-11}	0.99
57.5	37.5	5	7.9×10^{-9}	0.83
55	35	10	2.5×10^{-7}	0.74
52.5	32.5	15	2×10^{-6}	0.67

*Conductivities measured at 300° C.

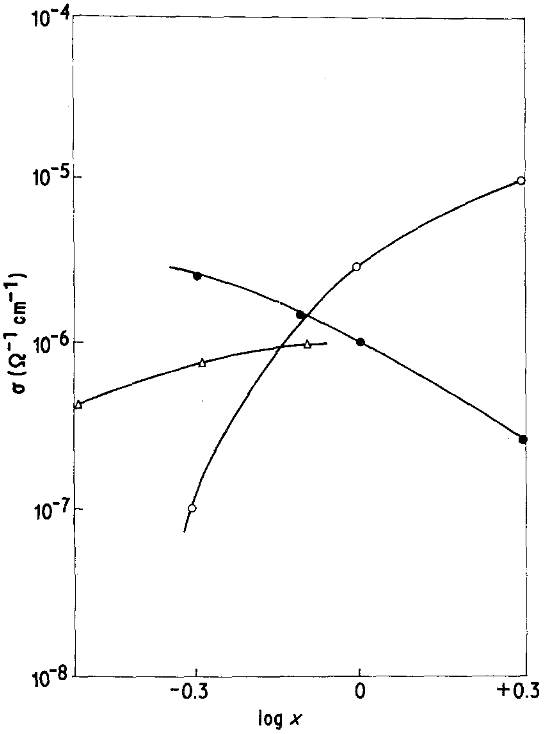

Figure 3 The effect of the ratio $x = [PbO/SiO_2]$; $[PbO/P_2O_5]$; $[PbO/B_2O_3]$ on the conductivities (measured at 300° C) of glasses containing 10 mol% Fe_2O_3: ●, Fe_2O_3–PbO–SiO [26]; ○, Fe_2O_3–PbO–B_2O_3 [22]; △, Fe_2O_3–PbO–P_2O_5 [53].

Fe^{3+} ions in tetrahedral co-ordination rises and these ions cannot take part in the conductivity process.

The conductivity in Fe_2O_3–PbO–P_2O_5 systems is similar to that of other iron–phosphate glasses. The influence of PbO on conductivity is the same as that of other modifiers such as MgO, CaO and BaO (see Table I) because Fe ions in phosphate glasses can exist in only one octahedral co-ordination [9–15].

3.4. Iron–tellurite glasses

The electrical properties of binary iron–tellurite glasses have been studied in the range from 5 mol% to 20 mol% Fe_2O_3 [42]. The electrical conductivity of these glasses is higher than that of similar iron glasses containing the same amount of iron oxides. The results of electrical conduction measurements at 100° C as a function of FeO content are shown in Fig. 4. The corresponding dependence for the iron–phosphate glasses is also included, for comparison. The conduction of iron–tellurite glasses is more than three orders of magnitude higher than that of similar iron–phosphate glasses. The same sort of effect can be observed by a comparison of glasses with the same R value, where R is the mean distance between Fe ions (see Tables I, IV and V). Analysis of the values of the activation energies (see Tables I and IV) reveals that the increase of conduction cannot arise from the lowering of the activation energy of the iron–tellurite glasses. Therefore, it is concluded that the great increase in conductivity arises from the pre-exponential factor, because the C value is very small for tellurite glasses. This suggests that the concentration of charge carrier in TeO_2–Fe_2O_3 glasses may be much greater than would be predicted by the Mott theory [1, 2] of electron hopping between ions of different valency states. (According to this theory $\sigma_0 \sim C(1-C)$.)

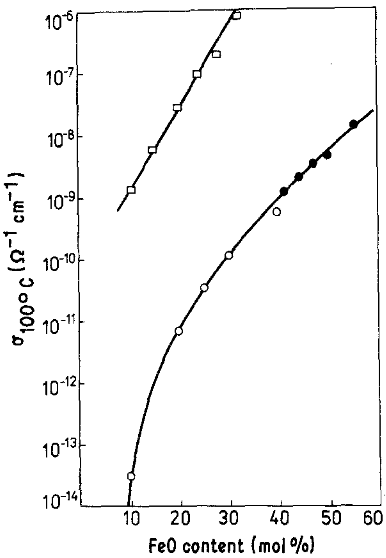

Figure 4 The dependence of electrical conductivity on FeO content (measured at 393 K) for: □, TeO_2–Fe_2O_3; ●, P_2O_5–FeO; and ○, P_2O_5–FeO–CaO (see Tables I and IV).

The very small concentration of Fe^{2+} ions, compared with other phosphate glasses (see Tables I and IV), seems to exclude the possibility of such a high conductivity resulting from electron hopping between Fe^{2+} and Fe^{3+}. Therefore, the TeO_2 network must play a decisive role.

The change in the co-ordination number of Te(IV) in the series of compounds Fe_2TeO_5, $Fe_2Te_3O_9$ and $Fe_2Te_4O_{11}$ produced by the surrounding oxygen atoms has been discussed and it has been indicated [57] that, in compounds of this system, the lone electron pair of tellurium atoms is stereo-chemically active. This means that the intro-

TABLE IV The electrical properties of TeO_2–Fe_2O_3 glasses [42]

Fe_2O_3 (mol%)	σ* (Ω^{-1} cm^{-1})	C	W (eV)	R† (nm)
5	6×10^{-12}	0.05	0.72	0.79
7.5	3×10^{-11}	0.09	0.66	0.71
10	1.75×10^{-10}	0.095	0.63	0.64
12.5	7.4×10^{-10}	0.075	0.62	0.59
15	2.0×10^{-9}	0.10	0.57	0.56
17.5	8.5×10^{-9}	0.06	0.53	0.53
20	3.2×10^{-7}	0.20	0.48	0.51

*Conductivities measured at 20° C.

†Values of R were calculated from the composition (after chemical analyses) and densities, assuming Fe ions to be uniformly distributed.

duction of Fe_2O_3 in the network of TeO_4 polyhedra leads to the formation of new bonds and defects. The number of non-bridging oxygen atoms is increased and microholes and new unshared electron pairs are created [38]. It may be suggested that the presence of unshared electron pairs probably influences the conductivity and the mechanism of conductivity through the tellurium ions.

4. Summary

The following conclusions can be formulated from the systematic studies of the electrical properties of iron-containing glasses:

(a) The electrical conductivity increases with concentration of iron oxides.

(b) The ratio, $C = Fe^{2+}/Fe_{tot}$, is one of the factors determining the electrical conductivity. The maximum conductivity for iron–phosphate glasses occurred at $C \simeq 0.5$. As far as the author is aware, no information has to date been published concerning other systems.

(c) The nature of the glass former has a minor influence on the electrical conduction (except in the case of TeO_2). In order to demonstrate this, SiO_2, B_2O_3, P_2O_5 and TeO_2 glasses containing 15 mol% Fe_2O_3 and 15 mol% BaO [42] have been produced. The results are presented in Table V. Iron–silicate, iron–borate and iron–phosphate glasses have similar values of room-temperature conductivity. The conductivities shown by iron tellurite glasses are three orders of magnitude higher than those of other glasses.

(d) In phosphate glasses the conductivity decreases (in the order BaO > SrO > CaO > MgO) with increase in the average electric field strength of the cation modifier. The converse behaviour has been observed in borate and silicate glasses. In phosphate glasses Fe ions exist in only one octahedral co-ordination while in borate and silicate glasses octahedral and tetrahedral co-ordinations are predicted. It is very likely that Fe ions in tetrahedral co-ordination do not take part in the conduction process.

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TABLE V The electrical properties of 70 mol% (SiO_2, B_2O_3, P_2O_5, TeO_2)–15 mol% Fe_2O_3–15 mol% BaO glasses [42]

Glass former	σ* (Ω^{-1} cm^{-1})	C	W (eV)	R† (nm)
TeO_2	1.8×10^{-9}	0.036	0.57	0.56
B_2O_3	1.84×10^{-12}	0.30	0.69	0.58
P_2O_5	1.2×10^{-12}	0.30	0.71	0.59
SiO_2	1.6×10^{-12}	0.16	0.76	0.54

*Conductivities measured at 20° C.

†Values of R were calculated from the compositions (after chemical analysis) and densities, assuming Fe ions to be uniformly distributed.

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