

## Study of structural, optical and transport properties of semiconducting Fe<sub>2</sub>O<sub>3</sub>-PbO-B<sub>2</sub>O<sub>3</sub> glasses

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Semiconducting oxide glasses of compositions  $x\text{Fe}_2\text{O}_3\cdot(40-x)\text{PbO}\cdot 60\text{B}_2\text{O}_3$  have been prepared by the standard melt-quenching technique over the range  $0 \leq x \leq 20$  ( $x$  is in mol%). The amorphous nature of the samples was ascertained using X-ray diffraction patterns. The structural changes in these glasses have been investigated by IR spectroscopy. The values of characteristic glass transition temperature ( $T_g$ ) have been found from differential scanning calorimetry (DSC) traces and corresponding specific heat capacity ( $C_p$ ) was also estimated. It is found that the density of these glasses decreases but glass transition temperature increases as Fe<sub>2</sub>O<sub>3</sub> content is increased. The change in both the density and molar volume was discussed in terms of the structural modifications that take place in the glass matrix upon replacing PbO by Fe<sub>2</sub>O<sub>3</sub>. The  $dc$  conductivity of these samples was measured in the temperature range 473-623 K. In this temperature range, the  $dc$  conductivity increases from  $10^{-9}$  to  $10^{-4}$  S/m with increasing Fe<sub>2</sub>O<sub>3</sub> content due to electron hopping from Fe(II) to Fe(III) ions. The values of the theoretical optical basicity of these glasses have also been determined.

**Keywords:** Semiconducting glasses, XRD, DSC, Density, IR,  $dc$  Conductivity

### 1 Introduction

Oxide glasses containing transition metal ions show interesting electrical properties arising from the fact that transition metal ion can exist in more than one valence states in glasses<sup>1</sup>. Some of the transition metals that fulfill this condition are Ti, V, Cr, Fe, Co, Ni and W. The conductivity, in general, is controlled with the hopping of small polarons or electrons between the localized states<sup>2</sup>. Lead oxide (PbO) is unique in its influence on the structure of glasses. When PbO is added to network forming oxide glasses<sup>3,4</sup>, it acts both as a network modifier and network former depending upon its concentration in the glass. Unconventional novel oxide glasses based on PbO have recently been attractive materials of research as heavy metal oxide glasses (HMO), nonlinear optical materials and as glass ceramic superconductor materials<sup>5-8</sup>. Such interesting properties of these glasses are mainly due to the high polarizability and the relatively low field strengths of Pb cations as compared to other conventional glass formers such as SiO<sub>2</sub> and GeO<sub>2</sub>. The broad infrared transmission is a consequence of the small field strengths and relatively large masses of the components of the glasses containing heavy metal oxide<sup>9,10</sup> such as PbO. B<sub>2</sub>O<sub>3</sub> is one of the most common glass former. According to Krogh-Moe<sup>11</sup>, the structure of vitreous B<sub>2</sub>O<sub>3</sub> consists of a random

network of boroxol rings and BO<sub>3</sub> triangles connected by B-O-B linkages. Mozzi and Warren<sup>12</sup> found that the addition of other oxides causes a progressive change of the boron atom of coordination number from 3 to 4 and results in the formation of various cyclic units like diborate, triborate or tetraborate groups. At low modifier content, the BO<sub>4</sub> units are grouped to form tetraborate units. By increasing the content of other oxides in borate glasses, the BO<sub>4</sub> units are predominantly associated with diborate groups. At higher concentration of the modifier, the formation of BO<sub>3</sub> units with non-bridging atoms is reported<sup>13</sup>. It was found in earlier studies that it acts as network modifier as well as a network former<sup>14,15</sup>. Glasses containing Fe<sup>3+</sup> ions are found to have a high electrical conductivity at room temperature and these glasses may find useful applications as a sensor in magneto resistance effect. In the conduction of these glasses, a valence change,  $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + e$  takes place between two Fe ions in the glass. Hence, it was expected that when the iron oxide glasses were melted with reducing materials like Pb, redox reaction in the glass melt produces glasses with relatively high content of Fe<sup>2+</sup> ion, which may have high conductivity if the activation energy of these glasses does not change. It has been reported that Fe<sup>2+</sup> ion can only be sixfold coordinated in glasses<sup>16</sup>, therefore, acting as a modifier, while Fe<sup>3+</sup> ion exists in both tetrahedral and

octahedral environments. Further, the valency of the Fe ions determines the covalency of the Fe-O bond and reflects the effect of the ionic radius of the Fe atom on the Fe-O bond length. Thus, both the coordination geometry and the valency of the Fe ion determine its structural role. On the other hand, the high polarizability of the  $\text{Pb}^{2+}$  ion has an essential effect on the glass forming ability of the Pb atom. It has been reported that in Pb-silicate glasses, PbO plays the role of glass modifier<sup>17</sup> when the PbO concentration is below 40%, while for higher PbO concentration it acts as a glass former. The conductivity of borate glasses containing sufficient amount of a transition metal oxide, such as  $\text{Fe}_2\text{O}_3$ , is mainly carried out by polarons<sup>18,19</sup>. During preparation of such glasses some  $\text{Fe}^{3+}$  ions are reduced to  $\text{Fe}^{2+}$  ones. The electron transfer could be ascribed as a small polaron hopping process from  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  ions. The electrical properties of these glasses show a semiconducting behaviour and depend greatly on the type and concentration of the transition metal oxide as well as on the type of the host glass matrix. The characteristics features of the polaronic hopping conduction in  $\text{Fe}_2\text{O}_3$ -PbO- $\text{B}_2\text{O}_3$  glasses, in which the formation of non-bridging oxygen ions is expected, have been studied. In the present work, lead borate glasses doped with  $\text{Fe}_2\text{O}_3$  have been prepared in order to study the effect of  $\text{Fe}_2\text{O}_3$  on the several physical properties such as glass transition temperature ( $T_g$ ), density and molar volume, IR spectra and the  $dc$  electrical conductivity mean spacing ( $R$ ) and polaron radius ( $r_p$ ).

## 2 Experimental Details

$x\text{Fe}_2\text{O}_3$ ·(40- $x$ )PbO·60 $\text{B}_2\text{O}_3$  ( $0 \leq x \leq 20$ ) glasses have been prepared from analytical reagent grade chemicals  $\text{Fe}_2\text{O}_3$ , PbO and  $\text{H}_3\text{BO}_3$ . The mixture of these chemicals was melted in porcelain crucibles by putting it in an electrical muffle furnace at about 1473 K in air for about 30 min. The melt was swirled frequently to assure homogeneity. The melt was then quickly poured onto a stainless steel plate and pressed with another stainless steel plate to get the coin shaped samples of 1-2 mm thickness. Thus, the glasses obtained were apparently homogeneous and partially transparent. X-ray diffraction (XRD) patterns of the glass samples were recorded using Rigaku X-ray diffractometer. Differential Scanning Calorimetry (DSC) of the samples was performed using a TA DSC-Q10 model with the heating rate of 10°C/min. The density of these glasses was measured at room temperature using Archimedes's principle with xylene

as the immersion liquid. The molar volume was estimated using the relation  $V_m=M/d$ , where  $d$  is the density and  $M$  is the molecular weight of the multicomponent system which is determined as:

$$M = X_{\text{Fe}_2\text{O}_3} Z_{\text{Fe}_2\text{O}_3} + X_{\text{PbO}} Z_{\text{PbO}} + X_{\text{B}_2\text{O}_3} Z_{\text{B}_2\text{O}_3}$$

where the  $X_{\text{Fe}_2\text{O}_3}$ ,  $X_{\text{PbO}}$  and  $X_{\text{B}_2\text{O}_3}$  are the mole fraction of constituent oxides i.e. the proportion of oxide atoms that contribute to the glass system and  $Z_{\text{Fe}_2\text{O}_3}$ ,  $Z_{\text{PbO}}$  and  $Z_{\text{B}_2\text{O}_3}$  are the molecular weights of the different oxides. The theoretical optical basicity ( $\Lambda_{\text{th}}$ ) of the given glasses has been calculated using the following relation:

$$\Lambda_{\text{th}} = X_{\text{Fe}_2\text{O}_3} \Lambda(\text{Fe}_2\text{O}_3) + X_{\text{PbO}} \Lambda(\text{PbO}) + X_{\text{B}_2\text{O}_3} \Lambda(\text{B}_2\text{O}_3)$$

where  $\Lambda(\text{Fe}_2\text{O}_3)$ ,  $\Lambda(\text{PbO})$  and  $\Lambda(\text{B}_2\text{O}_3)$  are the optical basicity values assigned to the constituents oxides. Here the values of  $\Lambda(\text{Fe}_2\text{O}_3) = 1.02$ ,  $\Lambda(\text{PbO}) = 1.18$  and  $\Lambda(\text{B}_2\text{O}_3) = 0.425$  have been taken from the literature. The IR transmission spectra of these glasses in KBr pellets were recorded using Perkin Elmer Spectrophotometer in the wave number range 600-1600  $\text{cm}^{-1}$ . The concentration of Fe ion,  $N$  ( $\text{cm}^{-3}$ ), was estimated<sup>20</sup> using the equation  $N = (dPN_A)/(A_W \cdot 100)$  where  $d$  is the density of the glass sample,  $P$  the weight percentage of atoms,  $N_A$  the Avogadro constant and  $A_W$  the atomic weight. The mean spacing ( $R$ ) between Fe ions was determined<sup>20</sup> using the relation  $R = (N4\pi/3)^{-1/3}$ . The polaron radius for a non-dispersive system<sup>20</sup> is calculated by the relation  $r_p = 1/2 (\pi/6)^{1/3} R$ . Further, the density of states at Fermi level  $N(E_F)$  is calculated in terms of activation energy ( $W$ ) as given<sup>20</sup> by the equation  $N(E_F) = 3/(4\pi R^3 W)$ . To measure the  $dc$  conductivity, samples in the form of slices of nearly 1mm uniform thickness were ground and polished to obtain parallel surfaces and these parallel surfaces of annealed samples were coated with colloidal silver paint as an electrode material were used to measure  $dc$  conductivity in the temperature range 473-623 K. Before measuring the  $dc$  conductivity, each sample was annealed at 473 K for 2 h. Further, a constant voltage of 50 V was applied across the sample and the circulating current was measured by using a Keithley 6485 picoammeter. To minimize the polarization effects, current was passed only for a short period (less than 30 s at a time).

### 3 Results and Discussion

#### 3.1 X-ray diffraction

XRD patterns are found to be similar for all the samples have been taken which are found to be similar and the typical XRD patterns for  $x = 0$  and  $x = 20$  are shown in Fig. 1. Perusal of Fig. 1 shows two broad humps only suggesting thereby the glassy nature of synthesized samples with no traces of crystalloid. The study indicates that all the added amount of  $\text{Fe}_2\text{O}_3$  (at least up to  $x = 20$ ) has entered the glass network.

#### 3.2 Differential scanning calorimetry (DSC)

DSC traces were taken for all the samples at a heating rate of  $10^\circ\text{C}/\text{min}$ . The glass transition temperature ( $T_g$ ) and specific heat ( $C_p$ ) of the present glasses were determined by these DSC traces. The softening of the glass structure occurs at glass transition temperature ( $T_g$ ). DSC helps to determine the glass characteristics temperature, such as glass transition temperature ( $T_g$ ), onset crystallization temperature ( $T_x$ ) and liquids temperature ( $T_l$ ). These

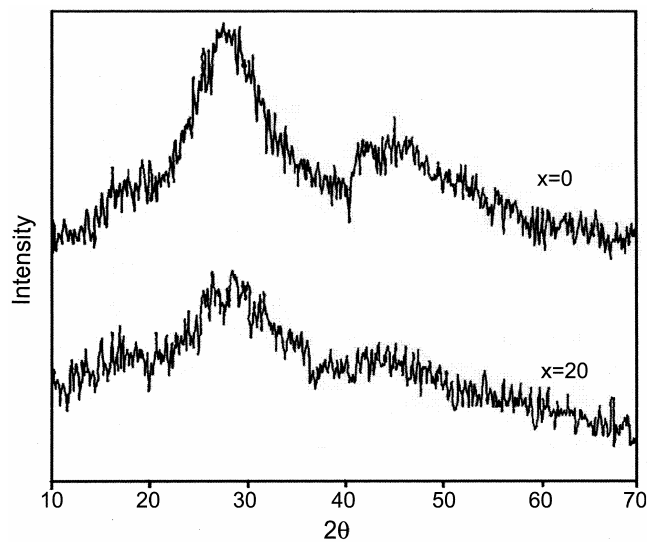


Fig. 1 — XRD patterns of two samples of the present glasses

thermal parameters are important for a qualitative estimation of the thermal stability and forming ability of glasses<sup>21</sup>. The observed values of  $T_g$  are presented in Table 1. The composition dependence of glass transition temperature of the present glasses is shown in Fig. 2. Both  $T_g$  as well as  $C_p$  increase with increase in  $\text{Fe}_2\text{O}_3$  content and this is consistent with network strengthening. It is known that addition of  $\text{Fe}_2\text{O}_3$  can also improve durability very markedly<sup>22,23</sup>. Because this oxide can act both as an intermediate and a glass modifying oxide and can be present in both the  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  states in the glass network. The replacing of B-O-B bonds by more durable B-O- $\text{Fe}^{2+}$  or B-O- $\text{Fe}^{3+}$  bonds with increasing  $\text{Fe}_2\text{O}_3$  content,  $\text{Fe}^{3+}$  ions provide the greatest durability and also increase in  $T_g$ .

#### 3.3 Density and molar volume

The measured values for all the samples are presented in Table 1 and the composition dependence of the density of these glasses is shown in Fig. 3. Fig. 3 shows that the glass density ( $d$ ) decreases with increase of  $\text{Fe}_2\text{O}_3$  concentration in the glass. This indicates that the glass structure becomes less tightly packed with increasing  $\text{Fe}_2\text{O}_3$  concentration.

The molar volume of the glass systems, changes with  $\text{Fe}_2\text{O}_3$  content in a specific manner as shown in

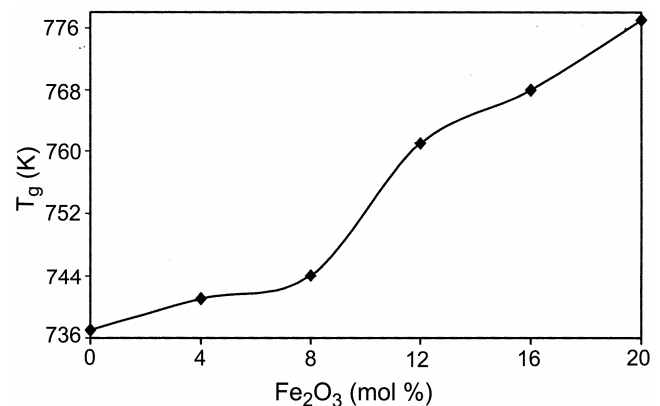


Fig. 2 — Variation of  $T_g$  with  $\text{Fe}_2\text{O}_3$  (mol%) content of the present glasses

Table 1 — Glass transition temperature ( $T_g$ ), specific heat ( $C_p$ ), density ( $d$ ), molar volume ( $V_M$ ), Fe-ion concentration ( $N$ ), mean spacing ( $R$ ) and polaron radius ( $r_p$ ) of  $x\text{Fe}_2\text{O}_3\cdot(40-x)\text{PbO}\cdot 60\text{B}_2\text{O}_3$  glasses

$X$ (mol %)	$T_g$ (K)	$C_p$ (J/g $^\circ\text{C}$ )	$d$ (g/cm $^3$ )	$V_M$ (cm $^3$ /mol)	$R$ ( $10^{-8}$ cm)	$N$ ( $10^{21}$ cm $^{-3}$ )	$r_p$ ( $10^{-8}$ cm)
0	737	0.638	4.98	26.32	0.0	0.0	0.0
4	741	0.652	4.45	28.88	5.6	2.14	2.26
8	744	0.879	4.26	29.57	4.4	3.74	1.77
12	761	0.904	4.17	29.60	3.8	5.52	1.53
16	768	0.934	4.04	29.92	3.3	7.32	1.33
20	777	1.129	3.94	30.03	3.1	9.07	1.25

Fig. 3. It increases with increasing  $\text{Fe}_2\text{O}_3$  content. The change in molar volume depends on the rate of change of both density as well as molecular weight. The density and molar volume values indicate that  $\text{Fe}_2\text{O}_3$  in these glasses is acting partly as network modifier and partly as network former.

### 3.4 Theoretical optical basicity

The theoretical optical basicity ( $\Lambda_{\text{th}}$ ) of the  $x\text{Fe}_2\text{O}_3 \cdot (40-x)\text{PbO} \cdot 60\text{B}_2\text{O}_3$  ( $0 \leq x \leq 20$ ) glasses has been calculated using the following relation<sup>24</sup>.

$$\Lambda_{\text{th}} = X_{\text{Fe}_2\text{O}_3} \Lambda(\text{Fe}_2\text{O}_3) + X_{\text{PbO}} \Lambda(\text{PbO}) + X_{\text{B}_2\text{O}_3} \Lambda(\text{B}_2\text{O}_3) \quad \dots(1)$$

here  $\Lambda(\text{Fe}_2\text{O}_3)$ ,  $\Lambda(\text{PbO})$  and  $\Lambda(\text{B}_2\text{O}_3)$  are the optical basicity values assigned to the constituents oxides and  $X_{\text{Fe}_2\text{O}_3}$ ,  $X_{\text{PbO}}$  and  $X_{\text{B}_2\text{O}_3}$ , respectively which are the equivalent fractions of the different oxides i.e. the proportion of oxide atoms that contributes to the glass system. Here the values of  $\Lambda(\text{Fe}_2\text{O}_3) = 1.02$ ,  $\Lambda(\text{PbO}) = 1.18$  and  $\Lambda(\text{B}_2\text{O}_3) = 0.425$  have been taken from the literature<sup>25</sup>. The calculated values of  $\Lambda_{\text{th}}$  of the given glasses are presented in Table 2. In general, the

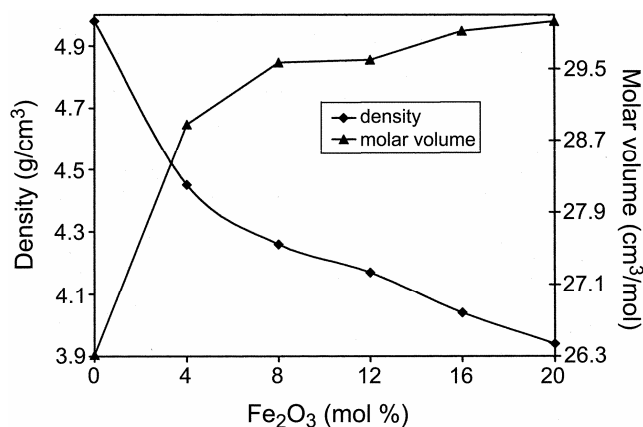


Fig. 3 — Variation of density and molar volume with  $\text{Fe}_2\text{O}_3$  (mol%) content of the present glasses

optical basicity is nothing but the basicity of a glass in terms of electron density carried by oxygen. Many physical and chemical properties of oxidic media in the molten state have been related to the basicity. From Table 2, it is found that the optical basicity increases with increase in  $\text{Fe}_2\text{O}_3$  content. This is explained more clearly according to the relation<sup>26</sup>:

$$\Lambda_{\text{th}} = 1.67[1 - (1/\alpha_0^{2-})] \quad \dots(2)$$

here  $\alpha_0^{2-}$  is the oxide ion polarizability. From Eq. (2), it is clear that the basicity increases with decrease in polarizability. Moreover,  $\text{B}_2\text{O}_3$  possesses a low oxide ion polarizability, high O1s binding energy and hence low optical basicity.

### 3.5 IR spectra

Figure 4 shows the IR spectra of lead-borate glasses containing iron as a function of  $\text{Fe}_2\text{O}_3$  compositions. The IR spectra of borate glasses occurs mainly in three regions: the absorption bands between  $1200\text{-}1600\text{ cm}^{-1}$  which arise from borate units in which boron is connected to three oxygen atoms (both bridging and non-bridging types), second bands are those which lies between  $800\text{-}1100\text{ cm}^{-1}$  which is due to boron in tetrahedral oxygen coordination and third absorption bands in the range  $650\text{-}750\text{ cm}^{-1}$  are due to the manifestation of B-O-B bending. Perusal of Fig. 4 shows that all glass samples show great similarity in general shape of their absorption spectra. In the present glass system, a broad band at  $800\text{-}1100\text{ cm}^{-1}$  is found in each glass, due to stretching vibration of  $\text{BO}_4$  tetrahedron<sup>27-30</sup>. Also another broadband in the range  $1200\text{-}1600\text{ cm}^{-1}$  is found in each glass which is due to the stretching vibration of B- $\Theta$  ( $\Theta$  represents non-bridging oxygen) bonds in borate triangular units. A broad band in the region  $650\text{-}750\text{ cm}^{-1}$  is also found in each sample due to the bending of B-O linkages.

Table 2 — dc conductivity ( $\sigma$ ) at two different temperatures,  $\log \sigma_0$ , activation energy ( $W$ ), density of states  $N(E_F)$  and theoretical optical basicity ( $\Lambda_{\text{th}}$ ) of  $x\text{Fe}_2\text{O}_3 \cdot (40-x) \cdot \text{PbO} \cdot 60\text{B}_2\text{O}_3$  glasses

$x$ (mol%)	$\log \sigma_0$ (S/m)	$\sigma_{\text{at}373}$ (S/m)	$\sigma_{\text{at}473}$ (S/m)	$W$ (eV)	$N(E_F)$ ( $10^{21} \text{ eV}^{-1} \text{ cm}^{-3}$ )	$\Lambda_{\text{th}}$
0	5.21	$1.92 \times 10^{-9}$	$1.30 \times 10^{-8}$	0.33	0.0	0.563
4	3.65	$5.67 \times 10^{-9}$	$7.47 \times 10^{-8}$	0.43	3.16	0.576
8	1.49	$1.41 \times 10^{-8}$	$4.20 \times 10^{-6}$	0.85	3.30	0.588
12	2.44	$3.17 \times 10^{-7}$	$4.52 \times 10^{-5}$	0.84	5.18	0.600
16	2.80	$7.82 \times 10^{-7}$	$1.11 \times 10^{-4}$	0.84	7.91	0.610
20	3.03	$9.83 \times 10^{-7}$	$1.52 \times 10^{-4}$	0.84	9.55	0.620

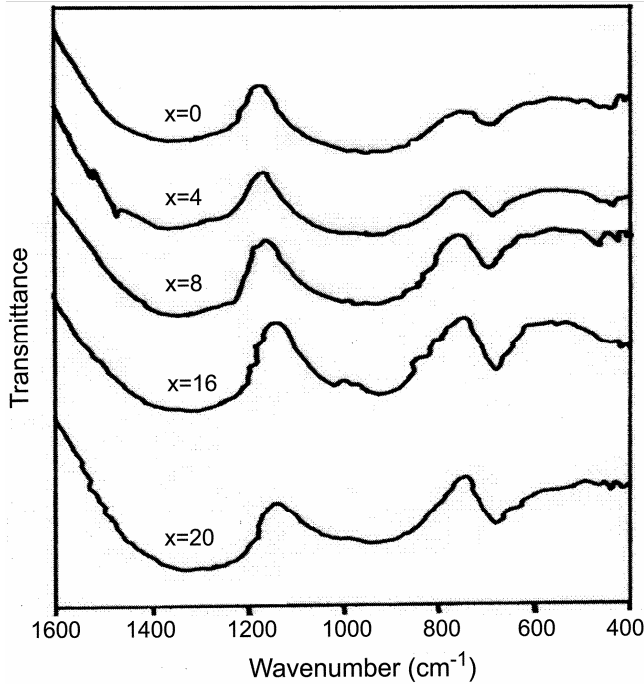


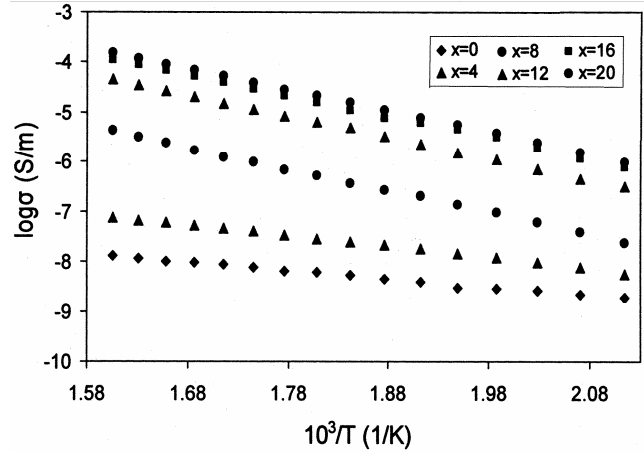
Fig. 4 — IR spectra of the present glasses

### 3.6 Electrical conductivity

Figure 5 shows the temperature dependence of  $dc$  conductivity of the  $x\text{Fe}_2\text{O}_3 \cdot (40-x)\text{PbO} \cdot 60\text{B}_2\text{O}_3$  glasses. The linear relationship between the logarithm of the  $dc$  conductivity ( $\log \sigma$ ,  $\sigma$  measured in S/m) and inverse of temperature ( $1000/T$ ,  $T$  measured in K) with a negative slope indicates that temperature dependence of the  $dc$  conductivity follows in the studied temperature range, the well-known Arrhenius law given by the following equation:

$$\sigma = \sigma_0 \exp(-W/kT) \quad \dots(3)$$

where  $\sigma_0$  is the pre-exponential factor,  $k$  the Boltzmann constant and  $W$  is the activation energy for conduction. The values of the  $dc$  conductivity at 473 and 623 K and the calculated values of  $W$  and  $\log \sigma_0$  are presented in Table 2. Perusal of the data presented in this Table 2 and Fig. 5, shows that  $dc$  conductivity increases with rise in temperature. Further, it is observed that  $dc$  conductivity increases with increase in  $\text{Fe}_2\text{O}_3$ :  $\text{PbO}$  ratio keeping  $\text{B}_2\text{O}_3$  constant for all compositions whereas the activation energy first increases from  $x=0$  to  $x=8$  and thereafter, becomes constant. The transport of electrons in the transition metal oxide glasses (TMO) is usually termed as small polaron hopping between Fe ions under different valence states. In the present glasses, it is expected that the  $dc$  conductivity may have contribution in the

Fig. 5 — Variation of  $\log \sigma$  versus  $10^3 T^{-1}$  of the present glasses

form of electronic conductivity due to electron hopping from the lower valence state to the higher valence state<sup>31</sup>. In  $\text{Fe}_2\text{O}_3$ - $\text{PbO}$ - $\text{B}_2\text{O}_3$  glasses, both  $\text{Fe}_2\text{O}_3$  [Ref. 32] and  $\text{PbO}$  [Refs 33, 34] enter the structure in two forms: as a network former and/or a network modifier. It is well known that  $\text{Fe}_2\text{O}_3$  acts as a glass modifier at low concentrations while at higher concentration it acts partially as a network former<sup>35</sup>. The average distance  $R$  between  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions is calculated from the relation:

$$R = (N4\pi/3)^{-1/3} \quad \dots(4)$$

where  $N$  is the concentration of iron ions per unit volume, which can be calculated from batch composition and the measured density. The calculated average distance  $R$  is shown in Table 1. It is obvious that increasing  $\text{Fe}_2\text{O}_3$  concentration causes a decrease in the distance between the iron ions. Next, using the average distance values  $R$ , as given in Table 1, the polaron radius  $r_p$  may be calculated using the formula<sup>36</sup>:

$$r_p = 1/2 (\pi/6)^{1/3} R \quad \dots(5)$$

where  $r_p$  was found to be between  $2.26 \times 10^{-8}$  cm and  $1.25 \times 10^{-8}$  cm and are presented in Table 1. Moreover,  $W$  is expressed in terms of density of states at Fermi level  $N(E_F)$  as follows<sup>37,38</sup>:

$$N(E_F) = 3/(4\pi R^3 W) \quad \dots(6)$$

The value of  $N(E_F)$  so obtained lies in the range  $3.16 \times 10^{-21}$ - $9.55 \times 10^{-21}$   $\text{eV}^{-1} \text{cm}^{-3}$  as presented in Table 1 with the estimated  $W$  and  $R$ -values. The values of  $N(E_F)$  are reasonable for localized states. The density of

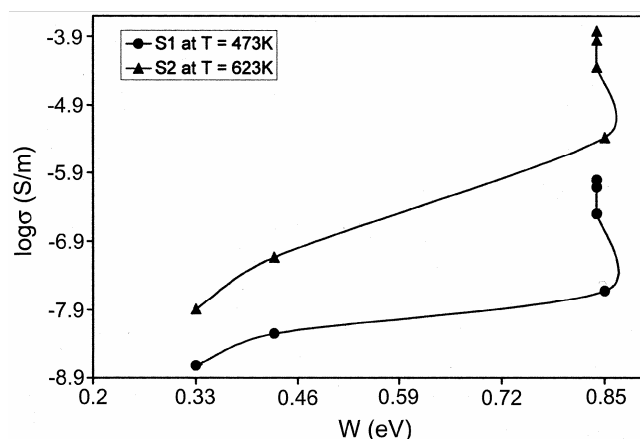


Fig. 6 — Variation of  $\log \sigma$  at two different temperatures versus  $W$  of the given glasses

states at Fermi level increases with increasing  $\text{Fe}_2\text{O}_3$  content. The nature of polaron hopping mechanisms (adiabatic or non-adiabatic) of these glasses could be estimated by various experimental aspects. If graph is plotted between logarithm of conductivity at a given experimental temperature and the activation energy and if it is linear, hopping is adiabatic<sup>39,40</sup>. If there is any deviation of linearity (non-linear), the hopping is supposed to be non-adiabatic<sup>41-43</sup>. Such plots of  $\log \sigma$  versus activation energy at a given experimental temperature are obtained for all these glasses as shown in Fig. 6. These plots deviate considerably from the straight-line pattern indicating a non-adiabatic hopping mechanism (Fig. 6).

#### 4 Conclusions

The semiconducting behaviour of the present glasses was understood by hopping of small polaron between Fe ions under different valence states. XRD pattern indicates that the given glasses are amorphous in nature. The characteristic glass transition temperature ( $T_g$ ) increases but density decreases with increasing  $\text{Fe}_2\text{O}_3$  content. The change in both the density and molar volume is correlated with the structural modifications that take place in the glass matrix upon replacing PbO by  $\text{Fe}_2\text{O}_3$ . The IR spectra exhibit the characteristic bands features corresponding to B-O-B and  $\text{BO}^-$  vibrations. The dc conductivity increases with increase in the ratio of  $\text{Fe}_2\text{O}_3$ :PbO whereas activation energy first increases up to  $x=8$  and thereafter, becomes constant in  $x\text{Fe}_2\text{O}_3$ .  $(40-x)\text{PbO}.60\text{B}_2\text{O}_3$  glasses, which is possible due to the increasing contribution of the electronic conductivity. The conduction of the present glasses was confirmed to be a non-adiabatic hopping of small

polaron between  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions in the glass network. The theoretical optical basicity increase with increasing in  $\text{Fe}_2\text{O}_3$  content.

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#### References

- Murawski L, Chung C H & Mackenzie J D, *J Non-Cryst Solids*, 32 (1979)91.
- Austin I G & Mott N F, *Adv Phys*, 18 (1969) 41.
- Rao B G, Sunder H G K & Rao K J, *J Chem Soc Faraday Trans*, 80 (1984) 3491.
- Rao K J, Rao B G & Elliot S R, *J Mater Sci*, 20 (1985) 1678.
- Miyaji F, Yoko T & Saka S, *J Non-Cryst Solids*, 126 (1990)170.
- Miyaji F, Fujimine S, Yoko T & Saka S, *J Non-Cryst Solids*, 150 (1992) 107.
- Hall D W, Newhouse M A, Borrelli N F, Dumbaugh W H & Widman D L, *Appl Phys Lett*, 54 (1989) L1293.
- Bahgat A A, Eissa S A & Salah S H, *J Mat Sci Lett*, 13 (1994) 826.
- Coleman D, Kackson S D, *et al.*, *J Opt Soc Am B*, 19 (2002) 1982.
- Heo J, Kim C G & Kim Y S, *J Am Ceram Soc*, 78(5) (1995) 1285.
- Krogh-Moe J, *J Phys Chem Glasses*, 3 (1962) 101.
- Mozzi R L & Warren B E, *J Appl Crystallogr*, 3 (1970) 251.
- Dwivedi B P, Rahman M H, Kumar Y & Khanna B N, *J Phys Chem Solids*, 54(5) (1993) 621.
- Rao B G, Sunder H G K & Rao K G, *J Chem Soc Faraday Trans*, 80 (1984) 3491.
- Rao K J, Rao B G & Elliot S R, *J Mater Sci*, 20 (1985) 1678.
- Vogel W, *Glass Chemistry*, Second edn, (Springer-Verlag, Berlin), 1994, p.251.
- Wang P W & Zhang L, *J Non-Cryst Solids*, 194 (1996) 129.
- Doweidar H, El-Damrawi G M & Moustafa Y M, *J Phys Condens Matter*, 6 (1994) 8829.
- Doweidar H, Moustafa Y M, Sultan A H & Al-afiez A A, *Phys Chem Glasses*, 38 (1997) 239.
- Al-Hajry A, Tashtoush N & El-Desoky M M, *J Physica B*, 368(2005)51.
- Yin Cheng, Hanning Xiao, Wenming Guo & Weiming Guo, *J Thermochemica Acta*, 444 (2006) 173.
- Yu X, Day D E, Long G J & Brow R K, *J Non-cryst Solids*, 215 (1997) 21.
- Marasinghe G K, Karabulut M, Ray C S, *et al.*, *J Non-cryst Solids*, 263 & 264 (2000) 146.
- Duffy J A, Kamitsos E I, *et al.*, *J Phys Chem Glasses*, 34 (1999) 153.
- Dimitrov V & Komatsu T, *J Ceram Soc Japan*, 107 (1999) 1012.
- Reddy R R, Ahammed Y, Azeem P A, Gopal K R & Rao T, *J Non-Cryst Solids*, 286 (2001) 169.
- Kamitsos E I, Patsis A P & Chryssikos G D, *J Non-cryst Solids*, 152 (1993) 246.

- 28 Kamistsos E I & Chryssikos G D, *J Mol Struct*, 247 (1991) 1.
- 29 Chryssikos G D, Kamistsos E I, Patsis A P, Bitsis M S & Karakassides M A, *J Non-cryst Solids*, 126 (1990) 42.
- 30 Varsamis C P, Kamistsos E I & Chryssikos G D, *Phys Rev B*, 60 (1990) 3885.
- 31 Hekmat-Shoar M H, Hogarth C A & Moridi G R, *J Matter Sci*, 20 (1985) 889.
- 32 Miller-Warmuth W & Eckert H, *Phys Rep*, 88 (1982) 91
- 33 Bray P J, Leventhal M & Hooper H O, *J Phys Chem Glasses*, 4 (1963) 3
- 34 Bray P J, *Magnetic Resonance*, (Plenum, New York), 1970.
- 35 Nishida T, Shiotsuki T & Takashima Y, *J Non-cryst Solids*, 43 (1981) 123.
- 36 Bogomolov V N, Kudinov E K & Firsov Yu, *Sov Phys Solid State*, 9 (1968) 2502.
- 37 Al-Hajry A, Tashtoush N & El-Desoky M M, *J Physica B*, 368 (2005) 51.
- 38 Mott N F & Davis E A, *Electronic processes in Non-cryst Mater* (Clarendon, Oxford), 1979.
- 39 Ramesh K V & Sastry D L, *J Physica B*, 387 (2007) 45.
- 40 Ghosh A & Chaudari B K, *J Non-cryst Solids*, 83 (1986) 151.
- 41 Mandal S & Ghosh A, *Phys Rev B*, 49 (1994) 3131.
- 42 Mandal S & Ghosh A, *Phys Condens Matter*, 8 (1996) 829.
- 43 Ghosh A, *Phys Rev B*, 42 (1990) 5665.