



Characterization and transport properties of semiconducting $\text{Fe}_2\text{O}_3\text{--Bi}_2\text{O}_3\text{--Na}_2\text{B}_4\text{O}_7$ glasses

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Abstract

Semiconducting oxide glasses of the system $\text{Fe}_2\text{O}_3\text{--Bi}_2\text{O}_3\text{--Na}_2\text{B}_4\text{O}_7$ were prepared by a press-quenching method. Their DC conductivity was measured in the temperature range of 300–473 K. In this temperature range, the DC conductivity increased from 10^{-9} to 10^{-5} Scm^{-1} with increasing Fe_2O_3 concentration. Bi_2O_3 acted as a reducing agent for redox reaction during glass synthesis and affected the conductivity. Mössbauer results revealed that the relative fraction of Fe^{2+} increases with an increasing Fe_2O_3 concentration. The conduction mechanism was found to obey the non-adiabatic small polaron hopping model, and was mainly due to hopping between Fe-ions in the glasses. The small polaron coupling γ_p was calculated and found to be in the range of 17.06–26.25. For varying glass compositions, hopping mobility and carrier density were calculated and their values were in the range of 3.66×10^{-8} – $8.17 \times 10^{-5} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and 1.29×10^{17} – $5.04 \times 10^{18} \text{ cm}^{-3}$ at 400 K, respectively.

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1. Introduction

During the last two decades, many binary and ternary transition metal oxide (TMO) glasses have been studied because of their interesting semiconducting properties. Semiconducting behavior in

these glasses is due to the hopping of ‘polarons’ from the higher to the lower valence states of the transition metal ions [1–4]. Strong electron–phonon interaction is considered to be responsible for the formation of small polarons in these glasses [5]. The data of the temperature dependence of conductivity in these TMO glassy systems, like $\text{NiO--V}_2\text{O}_5\text{--TeO}_2$ [6], $\text{BaO--CaO--Fe}_2\text{O}_3\text{--P}_2\text{O}_5$ [7], $\text{V}_2\text{O}_5\text{--P}_2\text{O}_5$ [8], $\text{V}_2\text{O}_5\text{--Bi}_2\text{O}_3\text{--BaTiO}_3$ [9], $\text{V}_2\text{O}_5\text{--MnO--TeO}_2$ [10], $\text{V}_2\text{O}_5\text{--SnO--TeO}_2$ [11], $\text{Fe}_2\text{O}_3\text{--V}_2\text{O}_5\text{--P}_2\text{O}_5$ [12], $\text{V}_2\text{O}_5\text{--Sb}_2\text{O}_3\text{--TeO}_2$ [13], etc., were

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explained by using the ‘small polaron’ hopping (SPH) model based on the strong electron–lattice interaction in the high temperature regime (above the Debye temperature) [14,15].

It was reported that it is possible to form a glass using Fe_2O_3 ions with a concentration ranging between 15 and 20 mol% [16]. Therefore, it sounds relatively difficult to prepare a glass using high concentration of Fe_2O_3 ions. In our endeavor to obtain Fe-ion-containing-glasses of high conductivity, we were interested in the Fe_2O_3 – Bi_2O_3 – $\text{Na}_2\text{B}_4\text{O}_7$ system. This is because its glass formation region and its maximum range of Fe_2O_3 concentration were expected to expand further, considering that B_2O_3 is a good glass network former and Bi_2O_3 -containing-glasses could be formed without other conventional network formers by rapid quenching [2,3,17].

In this study, Fe_2O_3 – Bi_2O_3 – $\text{Na}_2\text{B}_4\text{O}_7$ glasses were prepared by the press quenching technique, and the DC conductivity was measured to elucidate the conduction mechanism.

2. Experimental

Glass samples were prepared from the reagent grade chemicals Fe_2O_3 (99.9), Bi_2O_3 (99.9) and $\text{Na}_2\text{B}_4\text{O}_7$ (99%). The chemicals in appropriate properties (Table 1) were mixed uniformly. The mixture was melted in the temperature range of 1150–1220°C depending on the compositions for 1 h. The melt was press-quenched between two copper blocks. Glass samples of about 1 mm thick and with an area of 4 cm² were prepared. X-ray diffraction (XRD) of the samples were recorded using a XRD – 6000 Shimadzo. The thermal

behavior was investigated using a Shimadzu DSC-50 differential scanning calorimeter (DSC). The densities of the samples were estimated using Archimedes principle with acetone as an immersion liquid. The concentration of iron ion, $N(\text{cm}^{-3})$, was calculated using the formula: $N = dpN_A/(A_w \times 100)$, where d is the density of the sample, p the weight percentage of atoms, N_A the Avogadro’s constant and A_w the atomic weight. The $\text{Fe}^{2+}/(\text{Fe}^{2+} + \text{Fe}^{3+})$ ratio (C) was determined by Mössbauer spectral analysis at room temperature in a transition geometry employing ⁵⁷Co in a rhodium matrix as the radioactive source. The results obtained were analyzed using a computer program based on the Lorentzian distribution. Electrical measurements were carried out using a Keithly electrometer (Model 485). Silver paste electrodes were deposited on both faces of the polished samples. The absence of barrier layers at the contacts was confirmed by linear I – V characteristics. The DC conductivity of the as-quenched glasses was measured at temperatures between 300 and 473 K.

3. Results and discussion

3.1. Characterization

From the XRD studies it is observed that homogenous glasses were formed for Fe_2O_3 concentration between 5 and 20 mol%. The XRD patterns of present glasses, which is shown in Fig. 1, indicate a glassy behavior with a broad hump at about $2\theta = 30^\circ$. No peak corresponding to Fe_2O_3 is observed, which indicates that Fe_2O_3 has completely entered the glass matrix.

Table 1
Chemical composition and physical properties of Fe_2O_3 – Bi_2O_3 – $\text{Na}_2\text{B}_4\text{O}_7$ glasses

Glass no.	Composition (mol%)			W (eV)	d (gcm ⁻³)	R (nm)	T_g (K)	$\ln \sigma_{(400\text{K})}$ (Sm ⁻¹)
	Fe_2O_3	Bi_2O_3	$\text{Na}_2\text{B}_4\text{O}_7$					
1	5	20	75	0.89	3.757	0.394	677.2	-7.53
2	10	15	75	0.83	3.706	0.388	678.6	-6.94
3	15	10	75	0.78	3.638	0.382	680.5	-6.44
5	20	5	75	0.62	3.587	0.375	682.7	-5.77

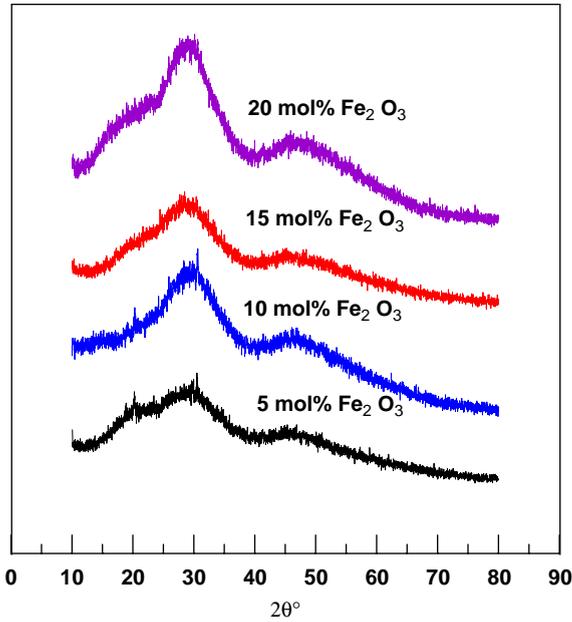


Fig. 1. XRD for different glass compositions.

The glass transition temperature (T_g) of the present glasses was determined by DSC with a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ (Table 1). A relatively small change of T_g (677.2–682.7 K) was observed due to an increase in Fe_2O_3 concentration in the Bi_2O_3 sites [16,18]. This indicates that when Fe_2O_3 is substituted for Bi_2O_3 , the Fe–O–Bi and Bi–O–Bi bonds are broken and new bonds such as the Fe–O–Fe bonds are probably formed. This leads to an increase of Fe_2O_3 concentration in the glasses, which causes an increase in their electrical conductivity and thermal stability [18].

Table 1 shows that the glass density (d) decreases with the increase of Fe_2O_3 concentration in the glass. This indicates that the glass structure becomes less tightly packed with increasing Fe_2O_3 concentration. These trends can be explained rather simply as the replacement of heavier cation (Bi) by lighter one (Fe) [18,19].

3.2. Electrical conductivity

Fig. 2 shows the variation of the logarithm of DC conductivity of $\text{Fe}_2\text{O}_3\text{–Bi}_2\text{O}_3\text{–Na}_2\text{B}_4\text{O}_7$ glasses

as a function of inverse temperature (T). As shown in Fig. 3, the conductivity of the glasses increases, while the activation energy decreases with increasing Fe_2O_3 concentration in the glass. This is consistent with the behavior of many other TMO glasses [3–8], where electrical conduction arises

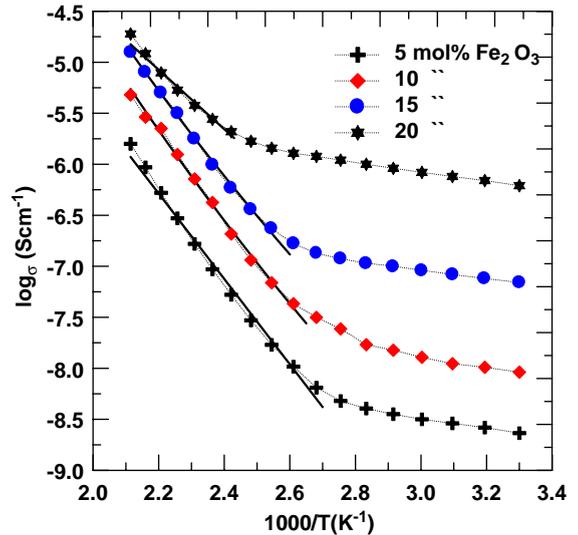


Fig. 2. Temperature dependence of DC conductivity, σ , for different glass compositions. The solid lines are calculated by using the least-squares technique.

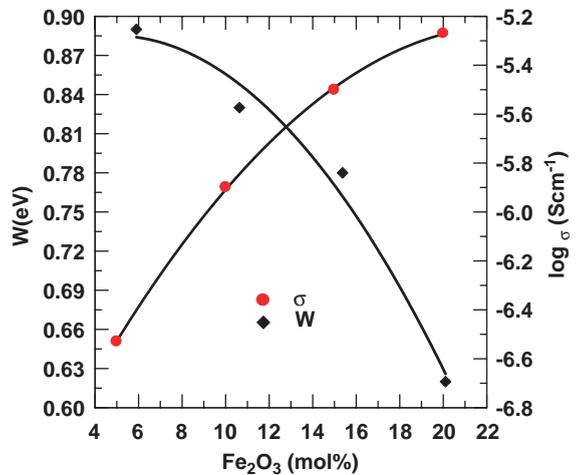


Fig. 3. Effect of Fe_2O_3 concentration on DC conductivity, σ , at $T = 443\text{ K}$ and activation energy W , for different glass compositions.

from the hopping of electrons or polarons between mixed valence states [17,19]. At high temperatures ($T > \theta_D/2$, where θ_D is the Debye temperature), the conductivity data of the present glasses can be interpreted in terms of the phonon-assisted hopping model given by Mott and Davis [20], namely

$$\sigma = (\sigma_o/T) \exp(-W/kT), \quad (1)$$

where $\sigma_o = v_o N e^2 R^2 C(1-C) \exp(-2\alpha R)/kT$, v_o is the longitudinal optical phonon frequency, R is the average distance between the transition metal ion (TMI), α is the inverse localization length of the s-like wave function assumed to describe the localized state at each site, $C (= \text{Fe}^{2+}/\Sigma\text{Fe})$ is the fraction sites occupied by an electron (or polaron) and therefore is the TMI concentration in the low valence state to the total TM ion concentration, and W is the activation energy of the hopping conduction. There is no exact formula to determine C for TMO glasses with transition metal ion. Therefore, used the value of C as shown in Table 1, which was estimated from the Mössbauer spectral. Those values have the same order of magnitude as compared with Fe_2O_3 doped Bi_2O_3 – B_2O_3 glasses [18]. The experimental data of conductivity, above a typical temperature $\theta_D/2$ (where non-linear behavior is observed as shown in Fig. 2), are fitted with Eq. (1) by the least-squared method. The best fit parameters are shown in Tables 1 and 2. The small polaron hopping model predicts an appreciable departure from the linear curve of $\log \sigma$ against $1/T$ at temperature $\theta_D/2$.

Assuming a strong electron-phonon interaction, Austin and Mott showed that [21]

$$\begin{aligned} W &= W_H + W_D/2 & \text{for } T > \theta_D/2, \\ &= W_D & \text{for } T < \theta_D/4, \end{aligned} \quad (2)$$

where W_H is the polaron hopping energy, and W_D is the disorder energy arising from the energy difference of the neighbors between two hopping sites.

The increase in DC conductivity with increasing Fe_2O_3 concentration, as indicated in Fig. 2, is attributed to the decrease in the average distance R between Fe^{2+} and Fe^{3+} ions. It has been previously reported [3,4,18] that in Fe_2O_3 -doped Bi_2O_3 – B_2O_3 the DC conductivity is electronic and strongly depends on the average distance R . The average distance R is calculated from

$$R = (1/N)^{1/3}, \quad (3)$$

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 Fe_2O_3 concentration cause a decrease in the distance between the iron ions. Assuming that the conductivity is due to electron hopping from Fe^{2+} to Fe^{3+} , then decreasing R from 0.394 to 0.375 nm, it is reasonable to expect an increase in DC conductivity. At the same time, the activation energy appears to increase with increasing distance between the iron ions. This result suggests that the DC conductivity is controlled by electron hopping, and depends on the distance R [2,3,6,7].

The values of the activation energy and the average distance R are illustrated in Table 1. In the range of measurements, W depends on the site-to-site distance R . This result shows that there is a prominent positive correlation between W and R of transition metal ions. This agrees with the results suggested by Sayer and Mansingh [22], Killias [23], Austin and Garbert [24], delineated

Table 2
Polaron hopping parameters of Fe_2O_3 – Bi_2O_3 – $\text{Na}_2\text{B}_4\text{O}_7$ glasses

Glass no.	θ_D (K)	v_o ($\times 10^{13} \text{ s}^{-1}$)	W_H (eV)	r_p (nm)	ϵ_p	$N(E_F)$ ($\times 10^{21} \text{ eV}^{-1} \text{ cm}^{-3}$)	γ_p
1	752	1.566	0.86	0.159	22.49	4.538	26.25
2	766	1.595	0.81	0.156	24.18	5.046	24.52
3	786	1.637	0.75	0.154	26.58	5.710	22.13
4	816	1.699	0.60	0.151	33.86	7.545	17.06

the dependence of W on the Fe–O–Fe site distance.

Fig. 4 shows the electrical conductivity, σ , and the fraction of reduced transition metal ion C , as a function of Fe_2O_3 concentration in the present glasses. Fig. 4 shows that the electrical conductivity, σ , for the present glasses, is within an order of magnitude of that of iron borate glasses [2,3,18]. Since the electrical conduction in iron borate glasses is assumed to be due to electron hopping from Fe^{2+} to Fe^{3+} sites [18]. Also, it is clear that C increases with increasing Fe_2O_3 concentration; a similar behavior is shown for the electrical conductivity results. This indicates that the mechanism of electrical conductivity of present glass samples were understood by SPH between iron ions under different valance states [6,7].

The optical phonon frequency ν_o , in Eq. (1), was estimated using the experimental data from Table 1, and according to the formula $k\theta_D = h\nu_o$ (where h is Plank's constant) [3,23]. To determine ν_o for all different compositions, the Debye temperature θ_D was estimated by $T > \theta_D/2$ (Eq. (2)). θ_D of the present glasses was obtained to be in the range of 752–816 K, which are nearly the same values as that of $\text{V}_2\text{O}_5\text{--P}_2\text{O}_5$ [25] and alkaline silicate glasses [26]. Thus, these estimated θ_D values are physically reasonable. The calculated values of θ_D and ν_o are summarized in Tables 1 and 2.

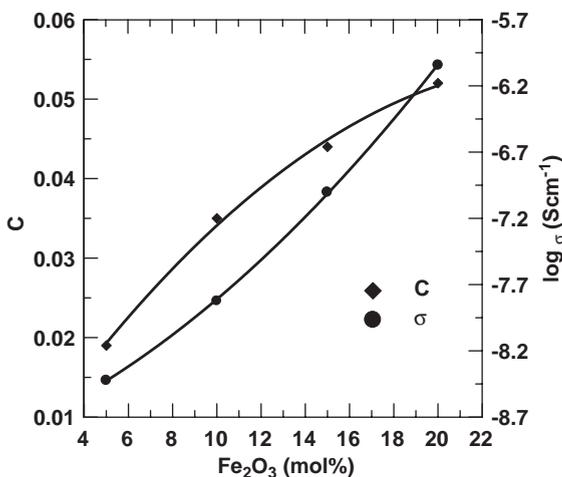


Fig. 4. The DC conductivity, σ , at 343 K and TM ion ratio, C , for different glass compositions.

Moreover, W is expressed in terms of the density of states at Fermi level $N(E_F)$ as follows [20]:

$$N(E_F) = 3/4\pi R^3 W \tag{4}$$

we obtained $N(E_F) = 4.538 \times 10^{21} - 7.545 \times 10^{21} \text{ eV}^{-1} \text{ cm}^{-3}$, as shown in Table 2 with the estimated W and R values (Table 1). The values of $N(E_F)$ are reasonable for a localized states.

The nature of polaron hopping mechanism (adiabatic or non-adiabatic), of all these glasses, can be estimated from a plot of logarithm of the conductivity against activation energy at fixed experimental temperature T [5,15]. It is expected that the hopping will be in the adiabatic regime if the temperature estimated T_c , from the slope of such a plot, is close to the experimental temperature T . Otherwise the hopping will be in the non-adiabatic regime. In this way, hopping at higher temperatures is inferred to be in the adiabatic regime for the vanadate glasses with conventional glass formers [6]. From the plot of $\log \sigma$ against W for the present glasses (Fig. 5), the estimated temperatures (shown within parenthesis) obtained from the slopes, are quite different from the experimental temperature (shown outside the parenthesis). Fig. 6 presents the effect of Fe_2O_3 concentration on the pre-exponential factors obtained from the least squares straight line fits

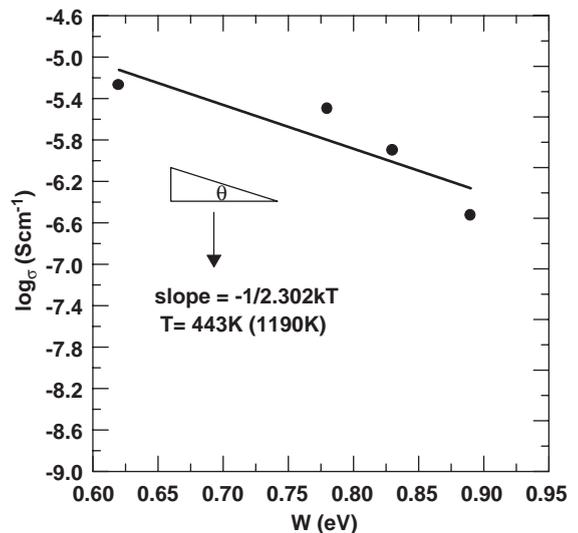


Fig. 5. Effect of activation energy W , on DC conductivity, σ , at $T = 443 \text{ K}$ for different glass compositions.

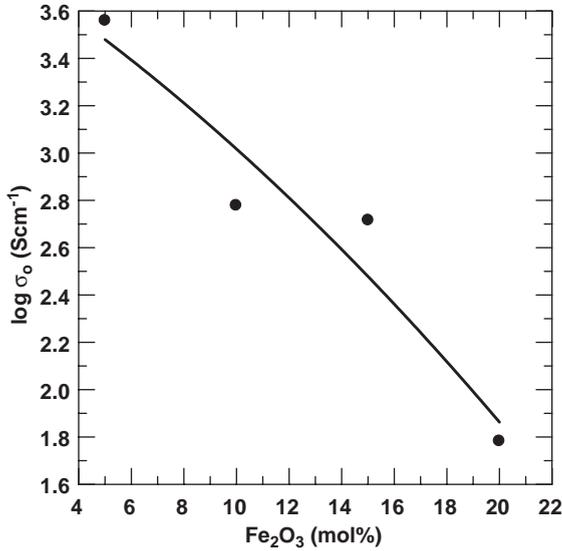


Fig. 6. Effect of Fe₂O₃ concentration on pre-exponential factor, σ_0 , for different glass compositions.

of the data σ_0 . The figure indicates a decrease in σ_0 with Fe₂O₃ concentration from 5 to 20 mol%. From the above results, we conclude that the conduction mechanism in the present glasses is due to non-adiabatic hopping of the polarons [5,15]. This non-adiabatic conduction mechanism is further confirmed from the calculation of the polaron bandwidth (J) from the following relation [27]:

$$J > \left(\frac{2kTW_H}{\pi} \right)^{1/4} \left(\frac{hv_0}{\pi} \right)^{1/2} \quad (\text{adiabatic})$$

and

$$J < \left(\frac{2kTW_H}{\pi} \right)^{1/4} \left(\frac{hv_0}{\pi} \right)^{1/2} \quad (\text{non-adiabatic}), \quad (5)$$

where J is the polaron bandwidth related to the electron wave function overlap on the adjacent sites. The $>$ and $<$ are for adiabatic and non-adiabatic hopping, respectively. The values of $(2kTW_H/\pi)^{1/4} (hv_0/\pi)^{1/2}$ varies from 0.0507 to .0533 eV at 400 K for all glassy compositions. The values of J , independently estimated from the relation; $J = e^3 [N(E_F) \epsilon_p^3]^{1/2}$, are found to be in the range of 0.022–0.035 eV depending on the concentration (Fe₂O₃ = 5–20 mol%). These values of J are much smaller than those estimated from the

right-hand side of Eq. (5) confirming non-adiabatic hopping conduction for these glasses.

Next, using the average distance values R , given in (Table 1), polaron radius r_p can be calculated using the formula [28]

$$r_p = \left(\frac{\pi}{6} \right)^{1/3} \frac{R}{2}, \quad (6)$$

where r_p was found to be between 0.151 and 0.159 nm (Table 2) for values of R ranging between 0.375 and 0.394 nm (Table 1). The polaron hopping energy given by $W_H = W_p/2$ is expressed by Sayer et al. [29]

$$W_H = W_p/2 = \left(\frac{e^2}{4\epsilon_p} \right) \left(\frac{1}{r_p} - \frac{1}{R} \right), \quad (7)$$

where $1/\epsilon_p = 1/\epsilon_\infty - 1/\epsilon_0$, and ϵ_0 and ϵ_∞ are the static and high-frequency dielectric constant of the glass respectively, and ϵ_p the effective dielectric constant. The values of r_p , ϵ_p and W_H are given in Table 2.

The values of small polaron coupling constant γ_p , which is a measure of electron–phonon interaction, is given by the formula $\gamma_p = 2W_H/hv_0$ were also evaluated for the present glasses [15]. The estimated value of γ_p is in the range of 17.06–26.25 (Table 2), which is larger than those for V₂O₅–Bi₂O₃ glasses doped with BaTiO₃ (7.05–7.60) [30,31]. Such large values give an indication of a strong electron phonon interaction of the present glasses [6,7,15].

Finally, the hopping carrier mobility μ is expressed for non-adiabatic hopping conduction as [15],

$$\mu = \left(\frac{eR^2}{kT} \right) \left(\frac{1}{\hbar} \right) \left(\frac{\pi}{4W_H kT} \right)^{1/2} J^2 \exp(-W/kT), \quad (8)$$

where μ values were calculated for $T = 400$ K with the data of W , R , J and W_H given in Tables 1 and 2. The hopping carrier concentration N_c , is then obtained using the well-known formula $\sigma = eN_c\mu$. Table 3 show these results, which indicate that μ values increase with increasing Fe₂O₃ concentration. μ values were evaluated to be between 8.17×10^{-5} and $3.66 \times 10^{-8} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and N_c values between 1.29×10^{17} and $5.04 \times 10^{18} \text{ cm}^{-3}$, being in the same order as those for NiO–V₂O₅–

Table 3

Hopping carrier mobility, μ , and carrier density, N_c , of $\text{Fe}_2\text{O}_3\text{-Bi}_2\text{O}_3\text{-Na}_2\text{B}_4\text{O}_7$ glasses

Glass no.	μ ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$) (400 K)	N_c (cm^{-3}) (400 K)
1	3.66×10^{-8}	5.04×10^{18}
2	1.99×10^{-7}	3.60×10^{18}
3	8.25×10^{-7}	2.74×10^{18}
4	8.17×10^{-5}	1.29×10^{17}

TeO_2 glasses [6]. Because the localization condition for hopping electrons was given by $\mu \ll 0.01 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ [15], these small μ values confirmed that hopping electrons in the present glasses are localized mainly at iron sites, corresponding to the strong electron–lattice interacting the large γ_P [6].

4. Conclusions

Glasses in the system $\text{Fe}_2\text{O}_3\text{-Bi}_2\text{O}_3\text{-Na}_2\text{B}_4\text{O}_7$ were prepared using the press-quenching technique from the glasses melts and the DC conductivity was investigated. The conduction of the present glasses was confirmed to be due to primarily non-adiabatic hopping between Fe^{2+} and Fe^{3+} ions in the glass network. The small polaron coupling γ_P was large (17.06–26.25). The estimated hopping mobility was in the range of 3.66×10^{-8} – $8.17 \times 10^{-5} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. The carrier density was estimated to be between 1.29×10^{17} and $5.04 \times 10^{18} \text{ cm}^{-3}$ at 400 K. The principal factor determining conductivity was the polaron hopping mobility in these glasses.

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