Polaron conduction mechanisms in (B₂O₃)-(TeO₂)-(MoO₃)-(Er₂O₃) glasses

M Amarkumar¹, T Sankarappa¹, J S Ashwajeet¹ and T Sujatha²

¹ Department of Physics, Gulbarba University, Kalaburagi, Karnataka, India.
² Government Higher Primary School, Kishan nagar, Gulbarga Dt, Karnataka, India

sankarappa@rediffmail.com, malgea@rediffmail.com

Abstract. A set of borotellurite glasses in the compositions, (B₂O₃)₀.₁₋₀.₅₋ₓ(TeO₂)₀.₅₋ₓ₋ₓ(MoO₃)₀.₄₋ₓ₋ₓ(Er₂O₃)ₓ₋ₓ; x = 0.01, 0.02, 0.03, 0.04, 0.05 have been synthesized and investigated for structure, density and dc conductivity as a function of temperature. Powder XRD patterns confirmed non-crystalline nature of glasses. Density and molar volume both varied arbitrarily with Er₂O₃ nano particle concentration revealing dynamic nature of the glass network. Some parameters associated with polarons have been determined. Semiconducting behavior of the glasses has been established by dc conductivity data. Mott’s small polaron hopping (SPH) model fit to the conductivity data enabled to determine Debye’s temperature and activation energy for conduction. Both Conductivity and activation energy decreased with Er₂O₃ nano particle concentration which infer that the structure of the glasses is changing in such a way that hindrance to the polaronic motion is developed in the increasing order with increase of Er₂O₃ concentration. The conductivity data deviated from SPH fit has been analyzed using Mott’s variable range hopping model and from it the density of states at Fermi level has been determined. For the first time, polaron conduction mechanisms have been probed in borotellurite glasses doped with MoO₃ and Er₂O₃.

Key words: Oxide glasses, polaron hopping, erbium oxide, density of states

1. Introduction

High mechanical strength, low melting point, high resistance to corrosive and excellent optical properties are the characteristics of tellurite glasses. In order to enhance their glass forming ability, durability towards moisture and thermal stability, boron like oxides are added. Addition of transition metal (TMI)/or alkali ions to borotellurite glass will give rise to polaronic or ionic conductivity as the case may be [1].

The TMI, MoO₃ can act as network modifier in the presence of glass formers such as TeO₂ and B₂O₃ and produce excellent electronic and optoelectronic properties [2]. Conductivity in MoO₃ glasses can arise from electronic hopping between Mo⁵⁺ and Mo⁶⁺ ions [3]. In TeO₂-MoO₃ glasses the basic structural units are fourfold coordinated TeO₄ tetrahedra, TeO₆, TeO₅, and six-fold coordinated single and paired MoO₆ octahedral [4]. There is always added interest towards rare earth ions (RE) doped glasses due to their practical importance in many fields such as color display, optical data storage, sensors, lasers, optical amplifiers etc [5].
Boro-tellurite glasses also have attracted attention due to their high conductivity. The dc conductivity and transport studies have been reported for the quaternary system, Ag2SO4–TeO2–B2O3 glasses [6] and electronic contributions to the total conductivity reported for Ag2O-B2O3-TeO2 [7]. Electrical conductivity has been investigated in rare earth doped glasses, Pr6O11-TeO2-B2O3 [8]. Electronic/ionic conductions and dielectric properties have been reported for several borotellurite glasses doped with transition metal/alkali ions [9-15]. Vanado tellurite glasses doped with La2O have been explored for electrical conductivity [16].

From the above mentioned literature survey, it is clear that there are no many conductivity studies reported for transition metal and rare earth ions doped borotellurite glasses. Therefore, density and conductivity studies have been carried out on a set of borotellurite glasses doped with MoO3 and nano particles of Er2O3. Data so obtained have been analyzed and presented in the present article. These glasses offer unique opportunity to understand polaronic conduction in the presence of rare earth ions in molybdo-boro-tellurite glasses.

2. Experimental
The desired glasses were produced by following melt quenching procedure. AR grade chemicals such as H3BO3, MoO3 (sd-fine), Er2O3 nano particles (Otto make) and TeO2 (Sigma Aldrich) have been used. The chemicals in the required ratio were taken in silicon crucibles, mixed thoroughly and melted at 1200K. The silica crucibles were used previously by other researchers for synthesizing borotellurite glasses [17]. The melt was left at that temperature for an hour to attain homogenization and suddenly quenched between two stainless steel plates. The detailed preparation of glasses is described in our previous paper [18]. In order to remove thermal strains, if any, developed in the samples during quenching, the prepared glasses have been annealed at 473K.

The composition of the present gasses are defined as (B2O3)0.1-(TeO2)0.5-x-(MoO3)0.4-(Er2O3)x (where x =0.01, 0.02, 0.03, 0.04, 0.05) and labeled as BTMEr1, BTMEr2, BTMEr3, BTMEr4 and BTMEr5 respectively.

For structural phase confirmation, powder XRD studies were carried out on the present samples in a Rigaku make diffractometer with Cu-Kα radiation in the Bragg’s angle range 10°-80°. By employing Archimedes principle, Density, D has been measured using Xylene as an immersion liquid. A piece from each sample has been shaped and it’s large bottom and top surfaces have been coated with silver paste. It was then investigated for dc conductivity by two probe method after confirming ohmic contact between the glass and electrodes. Conductivity has been measured in the temperature range 300K-640K. Details of dc conductivity experiment can be found in reference [19].

3 Results and discussion

3.1 XRD
The X-ray powder diffraction patterns of all the five samples showed single broad peak (figure 1). There are no sharp peaks in the patterns which is an indication for non-crystallinity of the samples. Similar XRD patterns were reported for Er3+ doped zinc boro-tellurite glasses [20] and zinc molybdenum borotellurite glasses containing different network modifier ions [21].

3.2 Density (D)
For the present glasses, the density D is measured to be in the range 5.181 g/cm³ - 6.034 g/cm³. Molar volume, \( V_m = (M/D) \) has been determined with M being molecular.
The M of each glass has been calculated as per the procedure mentioned in reference [22]. Density determined is in the range 25.55 cm³/mole - 30.62 cm³/mole. Variation of density and molar volume with erbium content can be seen from tabulated values in Table 1. Both D and V_m varied non-linearly with Erbium concentration, which can be taken as an evidence for drastic changes occurring in glass network. Increase of D and decrease of V_m with increase of Er₂O₃ content can be usually expected because of substitution of high densed Er₂O₃ (8.795 gm/cm³) to low densed TeO₂ (6.24 gm/cm³) in the glass composition. As against this understanding, D and V_m varied non-monotonously with Er₂O₃ which clearly hints at drastic network changes occurring in the glasses with Er₂O₃ incorporation. Similar changes in D and V_m with rare earth oxides concentration have been reported for borotellurite glasses [23].

The TMI density, N has been estimated as per relation [12]

\[ N = 2\left\{ \frac{D (m_{TeO_2} + m_{Er_2O_3})}{(M_{TeO_2} + M_{Er_2O_3})} \right\} N_A \]  

(1)

Where, m and M corresponds to mole fractions and molecular weights of the corresponding oxides. And N_A, the Avogadro number. Mean spacing R (= \(1/N\)^{1/3}) between TMI has been estimated like in reference [24]. Obtained N and R values are in the order of \(10^{21}\) per cm³ and fraction of a nanometer respectively and these are nearer to the valued reported in reference [25]. The small polaron radius (r_p) has also been determined. All the obtained polaron parameters are tabulated in table 1.

3.3 DC Conductivity

DC conductivity of the present glasses is found to vary in the range \(10^{-4} - 10^{-5}\) (Ωm)^{-1}. Increase of conductivity with increase of temperature has been noted and this is viewed as semiconductor behavior of the samples. Temperature variation of conductivity, \(\sigma\) has been considered for analysis under Mott’s
Table 1: Density, D, molar volume, Vm and some polaron related parameters estimated from density.

| Glass   | Mole fraction of Er₂O₃, x | Density, D (g/cm³) | Molar volume, Vm (cm³/mol) | N (cm⁻³ x10²¹) | R (nm) | r_p (nm) |
|---------|---------------------------|--------------------|----------------------------|----------------|--------|---------|
| BTMEr1  | 0.01                      | 5.757              | 26.39                      | 19.27          | 0.372  | 0.150   |
| BTMEr2  | 0.02                      | 6.034              | 25.55                      | 20.19          | 0.367  | 0.147   |
| BTMEr3  | 0.03                      | 5.357              | 29.20                      | 17.93          | 0.381  | 0.153   |
| BTMEr4  | 0.04                      | 5.181              | 30.62                      | 17.34          | 0.386  | 0.155   |
| BTMEr5  | 0.05                      | 5.974              | 26.93                      | 19.99          | 0.368  | 0.148   |

small polaron hopping (SPH) model. Mott’s SPH model gives conductivity in the non-adiabatic regime as [16],

\[
\sigma = \sigma_0 \exp \left(-\frac{W}{k_B T}\right) \tag{2}
\]

Where, \(\sigma_0\) being pre-exponential factor and \(W\) the activation energy. As per equation (2), Mott’s plots of \(\ln(\sigma T)\) versus \(1/T\) are sketched (figure 2). From the figure, it can be seen that \(\ln(\sigma T)\) is linear from high temperature down to \(T_p\). That is why the best linear fits are obtained for \(T > T_p\). Using slopes obtained from these linear fits, activation energy, \(W\) for individual glass has been determined. They were found to be between 0.275 eV and 0.494 eV and decreased with increase of mole fraction of Er₂O₃. The present values are nearer to the values quoted for silver ion conducting borotellurite glasses [26].

![Figure 2. The plots of ln(σT) versus (1/T) for present glasses. Linear fits at high temperature are shown as solid lines.](image)

DC conductivity, \(\sigma\) at 623K and activation energy, \(W\) as a function of mole fraction of Er₂O₃ are plotted and shown in figure 3. It can be observed that both conductivity and activation energy decreases nonlinear with \(x\). This decrement in \(\sigma\) and \(W\) values with increment of \(x\) informs that the structure of the glasses changes in such a way that hindrance to the polaronic motion is developed in the increasing order with increase of \(x\).
Figure 3. Plots of conductivity, at 623K and activation energy, W versus mole fractions of Er$_2$O$_3$.

The data deviated from Mott’s (SPH) fit has been considered under Mott’s variable range hopping model. As per this model, the conductivity is given by [12],

$$\sigma = A \exp \left( - \frac{B}{T^{1/4}} \right) \quad \text{or} \quad \ln(\sigma) = \ln A - \left( \frac{B}{T^{1/4}} \right)$$

(3)

Where, $A = \left[ \frac{e^2}{2(8\pi)^{3/2}} \right] v_0 \left[ N(E_F) / \alpha k_B T \right]^{1/2}$, $B = 4 \left[ 2 \alpha^3 / 9 \pi k_B N(E_F) \right]^{1/4}$ and $N(E_F)$ the density of states at Fermi level.

Figure 4. Mott’s VRH plots of ln($\sigma$) versus (T$^{-1/4}$) for BTMEr glasses. The solid lines are the least square linear fits to the data.

The plots of ln($\sigma$) vs (T$^{-1/4}$) are made and shown in figure 4. The linear lines were fit to the data. Using slope of the linear lines in B, the N(E$_F$) values have been determined. The N(E$_F$) values so obtained are found to be in the order between $10^{28}$ eV$^{-1}$m$^{-3}$ and $10^{31}$ eV$^{-1}$m$^{-3}$ (Table 2). These N(E$_F$) values are close to the values mentioned in reference [27]. Therefore, conductivity below $T_D$ can be considered to be explained by Mott’s (VRH) model.
Table 2. Mott’s (SPH) cut off temperature, \( T_D \), Debye’s temperature, \( \theta_D \), Conductivity at 623K, \( \sigma \), activation energy, \( W \) obtained from Mott’s (SPH) fit and \( N(E_f) \) values obtained from Mott’s VRH model for \( T < T_D \).

| Glass   | Mole fraction of Er\(_2\)O\(_3\), x | \( T_D \) (K) ±2K | \( \theta_D \) (K) ±2K | \( \sigma_{623K} \) (\( \Omega \)m\(^{-1}\)) x10\(^3\) | \( W \) (eV) | \( N(E_f) \) (eV\(^{-1}\)m\(^{-3}\)) |
|---------|-----------------------------------|------------------|------------------|---------------------------------|-----------|------------------|
| BTM Er1 | 0.01                              | 573              | 1146             | 2.426                           | 0.494     | 3.452x10\(^{28}\) |
| BTM Er2 | 0.02                              | 558              | 1116             | 1.837                           | 0.416     | 5.110x10\(^{29}\) |
| BTM Er3 | 0.03                              | 578              | 1156             | 1.176                           | 0.337     | 5.590x10\(^{29}\) |
| BTM Er4 | 0.04                              | 583              | 1166             | 0.932                           | 0.324     | 2.133x10\(^{30}\) |
| BTM Er5 | 0.05                              | 548              | 1096             | 0.944                           | 0.275     | 4.903x10\(^{31}\) |

4. Conclusions

Structure, density and dc conductivity have been investigated in rare earth doped borotellurite glasses, \((B_2O_3)_{0.1}-(TeO_2)_{0.5-x}-(MoO_3)_{0.4}-(Er_2O_3)_x\); \( x = 0.01 \) to \( 0.05 \). These studies lead to the following conclusions.

1. Non-crystallinity of the samples has been confirmed by XRD studies.
2. Density and molar volume are found to vary arbitrarily with \( Er_2O_3 \) content revealing drastic changes occurring in the glass network with \( Er_2O_3 \) incorporation.
3. Mott’s small polaron hopping model has been employed to analyze dc conductivity variation with temperature and from that activation energy has been determined. Both conductivity and activation energy decreased with \( Er_2O_3 \) concentration indicating increasing trend of hindrance to polaron motion developed in the glass network with increase of \( Er_2O_3 \) concentration.
4. Data deviated from Small polaron Hopping model fit has been analyzed using Mott’s variable range hopping model and the density of states at Fermi level have been determined. These density of states are found to be comparable with already reported values for various oxide glasses.

For the first time, polaronic conduction in the presence of rare earth ions in molybdo-boro-tellurite glasses has been investigated and analyzed.

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