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Structural and other physical properties of barium vanadate glasses

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Abstract

XRD, IR spectra, DTA, density, oxygen molar volume and dc conductivity of barium vanadate glasses of compositions xBaO–$(100-x)V_2O_5$, where $x = 30$, 35, 40, 45 and 50 mol%, are reported. The IR studies of the glasses suggest the glass network is built up of mainly VO_4 polyhedra. The glass transition temperatures are observed to increase with an increase of BaO content in the compositions. The cross-linking density decrease with increasing BaO content in the compositions. Introduction of BaO into the V_2O_5 matrix changes the 2D layer structure of the crystalline V_2O_5 into a more complicated 3D structure. Analysis of the electrical properties has been made in the light of small polaron hopping model. The parameters obtained from the fits of the experimental data to this model are reasonable and consistent with glass composition. The conduction is attributed to non-adiabatic hopping of small polaron.

Keywords: Vanadate glasses; XRD; IR spectra; DTA; Conductivity; SPH

1. Introduction

Extensive studies have been carried out on semiconducting oxide glasses containing transition metal oxides (TMO) owing to interests in their conduction mechanism and glass structure [1–7]. These glasses have been given considerable attention because of their technical application, namely optical and electrical memory switching, cathode materials, and so on [8,9]. The structures of vanadate semiconductor glasses play a significant role in the transport. One or more ions surrounding vanadium–oxygen polyhedra may lead to changes in the hopping of electron. The semiconducting nature of these glasses arises from the presence of two valance states of TMO. Glasses containing vanadium process both V^{4+} and V^{5+} ions and electrical conduction occurs due to the hopping of an unpaired $3d^1$ electron from a V^{4+} site to V^{5+} site. However, there exists a controversy over the nature of hopping mechanism in different temperature and composition regions [10,11]. There are also contradictory reports [12] on the effect of the network formers and modifiers on the hopping mechanism. Studies of the infrared (IR) properties of a number of vanadate glasses have been reported [13–15]. It has been observed that the structure of these glasses depends on the nature of the network formers as well as the network modifiers. In this paper, we have studied the glass formation and the composition dependence of the structure and electrical properties of the BaO–V_2O_5 glasses. Interestingly, we have recently shown [9] single phase amorphous materials with random structure in the BaO–V_2O_5 system can be obtained for a wide composition rang, where TMO V_2O_5 acts as a unique glass network former and BaO as a modifier. However, the polarizing power strength (ratio of valance charge of the cation divided by the square of its ionic radius) of barium cation is lower than that of other alkali and alkaline-earth such as strontium and sodium cation, respectively.

2. Experimental

Glass samples were prepared using analytical reagent grade chemicals according to the formula xBaO–$(100-x)$ V_2O_5, where $x = 30$, 35, 40, 45 and 50 mol%. Batches that produced 20 g of glass were prepared by mixing BaO and V_2O_5 dry crystalline powder that were melted in a platinum crucible in an electrical furnace for 1 h at temperatures

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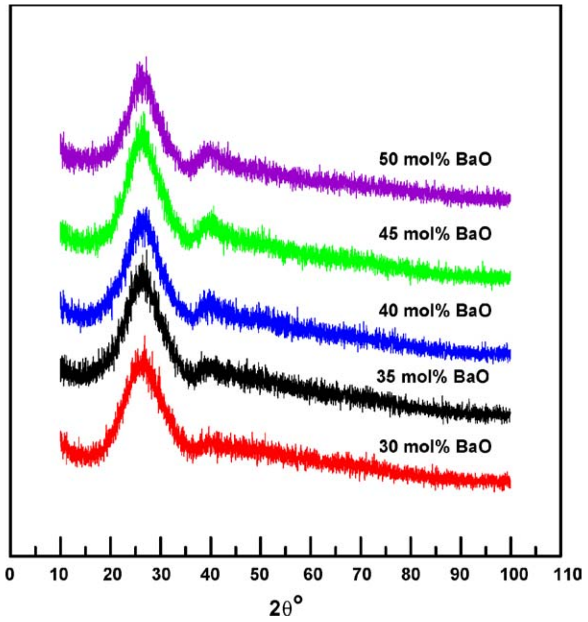

Fig. 1. XRD of BaO—V_2O_5 glasses.

ranging from 950 to 1100 °C, depending on the composition. It was observed that the melting temperature decreased with increasing the V_2O_5 content in the compositions. The melts were rapidly quenched between two brass plates to obtain glass samples of thickness ~1 mm. The amorphous nature of the glasses was examined using a Shimadzu X-ray diffractometer XRD-600. IR spectra of the glass samples were measured from 400 to 4000 cm^{-1} by a conventional KBr pellet method on a Fourier transform infrared (FT-IR) spectrometer (Perkin-Elmer 1760X). The density of the glasses was measured by the Archimedes method using toluene as the immersion liquid. Differential scanning calorimeter (DSC) of the samples was investigated using a Shimadzu DSC-50 with heating rate 30 °C min^{-1}. For the conductivity measurements, disk shaped samples of 8 mm diameter were cut and polished with very fine lapping papers. Silver paste electrodes were painted on both faces of the polished sample. The dc conductivity was measured under a constant dc voltage, employing the potential probe method. Before the measurements, the ohmic behavior (*I*–*V*) was ascertained from the linearity of the voltage current characteristic. The dc conductivity was also observed to be independent of time, which indicates no dc polarization due to ionic current.

3. Results and discussion

3.1. XRD

The XRD patterns of the present samples are shown in Fig. 1. These patterns show a broad main peak at $2\theta \approx 26.5°$, a second much smaller peak at $2\theta \approx 39.5°$. Beyond the second peak no further strong oscillations are observed. The second smaller peak differs in height as a function of BaO content in the specimens. It is very weak for the 30 mol% BaO sample, but it develops to a sharper peak as the BaO content increases, reaching a maximum at the 45 mol% BaO sample, then starts to decrease again in the 50 mol% BaO sample. Similar behavior is observed for the first main peak, although not as pronounced. The overall features of these XRD curves confirm the amorphous nature of the present samples. A more detailed structural study is underway, to elucidate the real space structure of these samples on an atomic scale.

3.2. IR spectra

In Fig. 2 we show the room temperature IR spectra in the range 400–1500 cm^{-1} for different glass compositions. The spectra show a strong band at about 1070–1090 cm^{-1} which has been assigned to the vibration of isolated V=O vanadyl groups in VO_5 trigonal bi-pyramids [16]. With the introduction of BaO, a new band is observed at 910–920 cm^{-1} with reduced intensity in the spectra. Dimitiev and coworkers [13] reported that in glasses containing V_2O_5 and MgO the band at 1020–1070 cm^{-1} exists along with formation of new bands in the range 920–915 cm^{-1}.

It is known that from pure V_2O_5 toward the orthovanadates [14,15] a trend is observed of an increase in the symmetry of the polyhedra, the length of the chemical bonds and a decrease in the coordination number of the vanadium with respect to the oxygen. We observe from IR studies (Fig. 2) that there is a pronounced effect of the introduction of BaO on the V=O bonds that are present in the VO_5 polyhedra in crystalline V_2O_5 [14,15]. According to the structural model reported earlier [16], BaO ions may either occupy positions in the vanadate chain itself or may be located between vana-

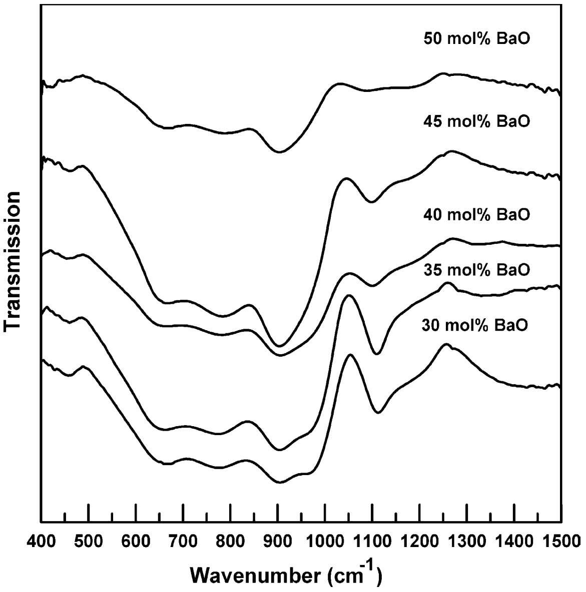

Fig. 2. Room temperature IR spectra of BaO—V_2O_5 glasses.

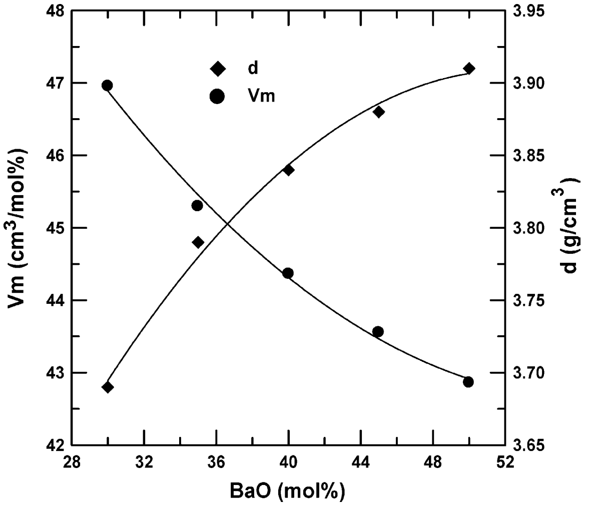

Fig. 3. Composition dependence of density, *d*, and oxygen molar volume, V_m, for BaO—V_2O_5 glasses.

date chains and layers. In the first case, Ba ions will break up some of V–O–V bands and form new V–O–Ba bridges. The influence of Ba ions on the V=O bonds in the glasses is restricted and it may have an indirect manifestation. On the other hand, in the second case Ba ions interact directly with the V=O bonds, as a result of which these bonds will be longer and the frequencies of the vibration should be shifted towards lower wave numbers. The shift of the bands for the glasses towards the lower wave numbers implies that Ba ions in these compositions are located between vanadate chains and layers and the glass structure consists of VO_4 polyhedra [14–16].

3.3. Density and molar volume

The composition dependence of the density of the present glass samples is shown in Fig. 3 and Table 1. It may be observed that density, *d*, increases gradually with the increase of the barium oxide content in the glass compositions. The relationship between density and composition of an oxide glass system can be expressed in terms of an apparent volume V_m occupied by 1 g atom of oxygen. The value of V_m has been calculated from the density and composition using the formula reported earlier [17] and its composition dependence is shown in Fig. 3 and Table 1. It is observed that V_m decreases monotonically with an increase of BaO content in the composition which indicates that the topology of the network does not significantly change with composition. On the other hand, these trends can be explained rather simply as due to the replacement of a lighter cation (V) by a heavier one (Ba) [14,15].

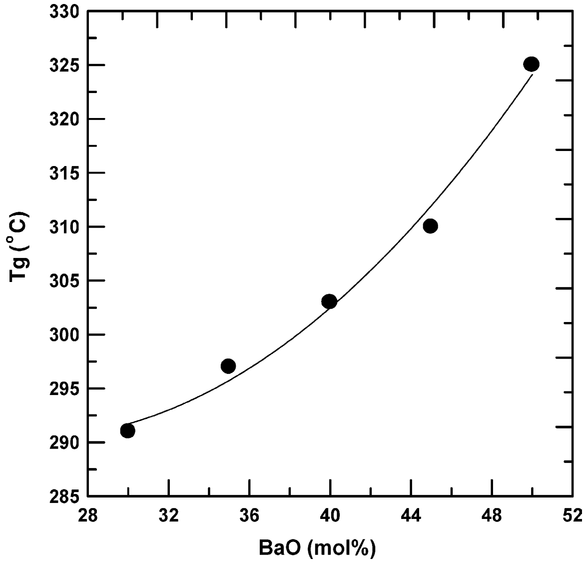

Fig. 4. Composition dependence of glass transition temperature, T_g, for BaO—V_2O_5 glasses.

3.4. DSC

The composition dependence of glass transition temperature (T_g) is shown in Fig. 4 and Table 1. It is observed that T_g gradually increases with decreasing V_2O_5 content in the composition. Previous studies of differential thermal analysis (DTA) of several glasses [14,15] have shown that T_g is strictly related to the coordination number of the network former, density of cross-linking, tightness of packing in the network, formation of non-bridging oxygen atoms, etc. The studies of T_g of some vanadate glasses [14,15] indicated that the increase of T_g with the increase of the network former (V_2O_5) arises mainly from the higher cross-linking density in the glasses than in the vitreous V_2O_5 itself. From the present barium vanadate glasses similar arguments are applicable. As the content of the network former V_2O_5 is decreased, there is a continuous change in the glassy matrix from 2D layer structure of the crystalline V_2O_5 to more complicated 3D

Table 1
Density (*d*), molar volume (V_m), concentration of vanadium ions (*N*) and average distance (*R*) for BaO—V_2O_5 glasses

Nominal composition (mol%)		*d* (g cm^{-3})	V_m (cm^3 mol%$^{-1}$)	*N* ($\times 10^{22}$ cm^{-3})	*R* (nm)
BaO	V_2O_5				
30	70	3.69	46.96	1.76	0.384
35	65	3.79	45.30	1.69	0.389
40	60	3.84	44.36	1.62	0.395
45	55	3.88	43.56	1.51	0.405
50	50	3.91	42.86	1.40	0.415

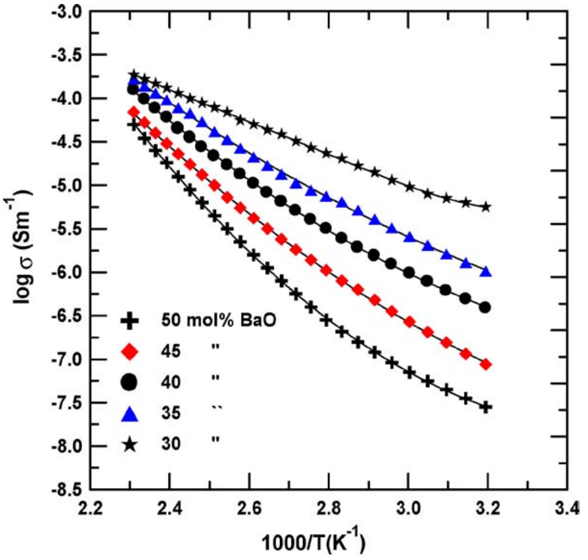

Fig. 5. Temperature dependence of dc conductivity as a function of reciprocal temperature for BaO—V_2O_5 glasses.

structure [14,15]. On the other hand, the increase of oxygen molar volume (see Fig. 4) with increase of V_2O_5 content in the composition supports this conclusion [14,15].

3.5. dc conductivity

The dc conductivity for different glass compositions is shown in Fig. 5 as a function of reciprocal temperature. All glass compositions show a smooth variation of the conductivity with reciprocal temperature, indicating temperature dependent activation energy. The high temperature activation energy was computed from the slopes of the curves at in the highest rang of temperature measured (see Table 2). The variation of the conductivity and the high temperature activation energy with the glass composition is shown in Fig. 6. It is clear from the figure that the conductivity increases while the activation energy decreases with the decrease of the BaO content in the glass. Such behavior is a feature of small polaron hopping (SPH) [1,2]. The high value of activation energy and low value of electrical conductivity are similar to those for MgO–V_2O_5 glasses [8]. This change in conductivity and activation energy may help to detect the structural changes as a consequence of increasing BaO and decreasing V_2O_5 content. Generally, it is known that addition of barium oxide to the glass increases the bridging oxygen ions [5]. This may decrease the open structure (i.e. the non-bridging oxygen ions), through which the charge carriers can move with lower mobility. On the other hand, this result provides an explanation to why the coulombic binding force of the barium ion is affected by the type of TMO which is located at a neighboring site. The change in the binding force may cause the change in the barium ion mobility, due to the large difference in ionic sizes of Ba, V leading to smaller values of mobility an increase in stability and a decrease in conductivity [4,8].

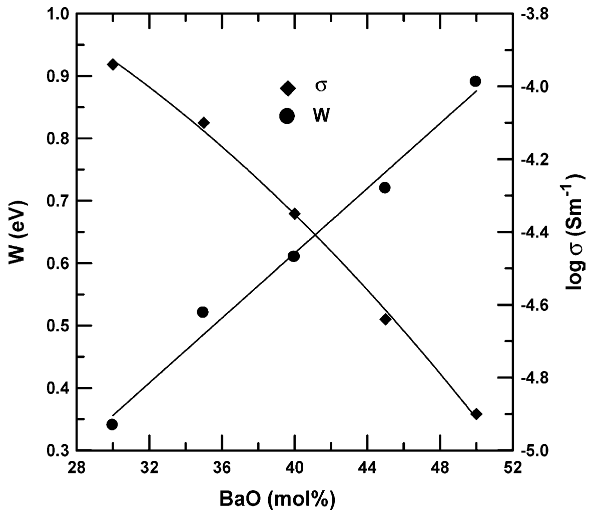

Fig. 6. Variation of the dc conductivity at 413 K and the high-temperature activation energy for BaO—V_2O_5 glasses.

Also, an increase in dc conductivity and decrease in activation energy for the present glass samples suggests some changes in conduction mechanisms. It has been previously reported [4,8] that in vanadate glasses the dc conductivity is electronic and depends strongly upon the average distance R, between the vanadium ions. The average distance R, was calculated for the present glasses (see Fig. 7) from the relation $R = (1/N)^{1/3}$, where N is the concentration of vanadium ions per unit volume, calculated from batch composition and the measured density. The density d, and the average distance, R, are given in Table 1. The addition of BaO obviously increases the distance between the vanadium ions. Assuming that the conductivity is due to electron hopping from V^{4+} to V^{5+} then with increasing R from $R = 0.384$ nm for 30BaO–70V_2O_5 (mol%) glass to $R = 0.415$ nm for 50BaO–50V_2O_5 (mol%) glass, it is reasonable to expect an decrease in dc conduc-

Table 2

Activation energy (W), glass transition temperature (T_g), polaron radius (r_p) and density of state $N(E_F)$ for BaO—V_2O_5 glasses

Nominal composition (mol%)		W (eV)	T_g (°C)	r_p (nm)	$N(E_F)$ ($\times 10^{21}$ eV^{-1} cm^{-3})
BaO	V_2O_5				
30	70	0.34	291	0.172	12.40
35	65	0.52	297	0.170	7.79
40	60	0.61	303	0.169	6.35
45	55	0.72	310	0.168	4.99
50	50	0.89	325	0.166	3.75

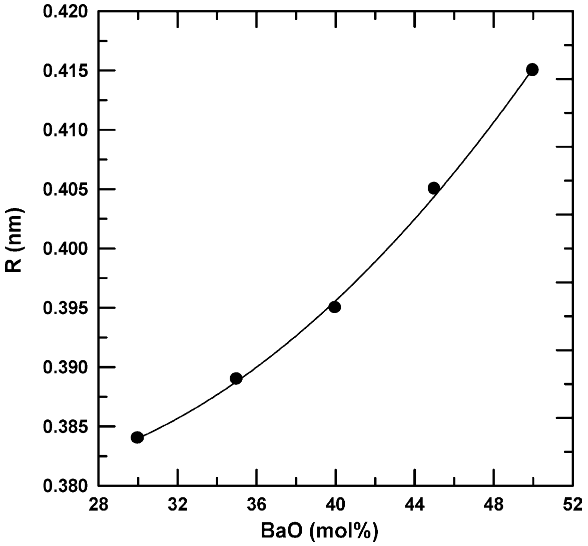

Fig. 7. Composition dependence of average distance, *R*, for BaO—V_2O_5 glasses.

tivity. At the same time, the activation energy appears to increase with increasing distance between the vanadium ions. Clearly, the small value of activation energy (0.34 eV) for the 30BaO–70V_2O_5 (mol%) glass suggests that the dc conductivity is controlled by electron hopping and depends upon the distance *R*, between the vanadium ions.

The relation between the average distance *R*, and activation energy *W*, is illustrated in Fig. 8. The activation energy clearly increased with an increase in the average distance similar to the other vanadate glasses [4,8]. A prominent positive correlation between *W* and *R* agrees with the results suggested by Sayer and Mansingh [2]. Austin and Garbet [18] explained the dependence of the V–O–V site distance for vanadate glasses on activation energy. This study indicted that the electronic conduction is due to electrons hopping from V^{4+} to V^{5+} on vanadium ions is probable.

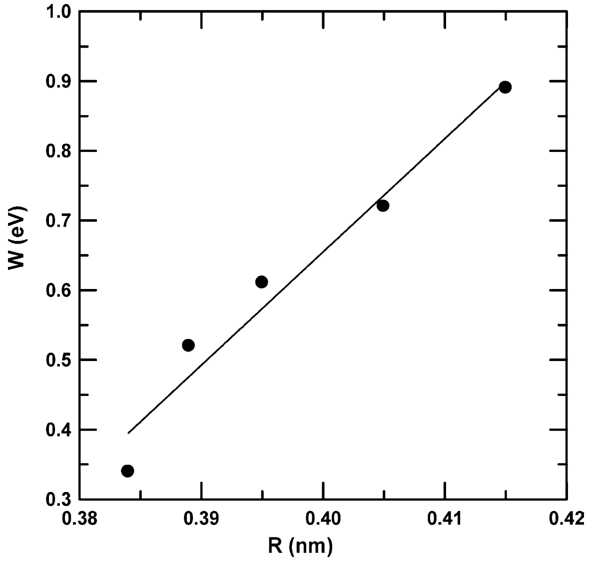

Fig. 8. Variation of average distance, *R*, and the high-temperature activation energy for BaO—V_2O_5 glasses.

We note in Fig. 5 that the magnitude of the conductivity tend to be highest for those compositions having the lowest activation energy. Such a behavior is a feature of SPH [1,2]. So we first discuss the thermal variation of conductivity assuming SPH model [1,2] based on a strong coupling of electron with the lattice by a single phonon. This model gives σ in the non-adiabatic regime for TMO glasses as follows:

$$\sigma = \frac{\nu_0 N e^2 R^2}{kT} C(1-C)\exp(-2aR)\exp\left(-\frac{W}{kT}\right) \tag{1}$$

The activation energy *W* can be written as

$$W = W_\mathrm{H} + \frac{W_\mathrm{D}}{2} \quad \left(\text{for } T > \frac{\theta_\mathrm{D}}{2}\right) \tag{2a}$$

$$W = W_\mathrm{D} \quad \left(\text{for } T < \frac{\theta_\mathrm{D}}{4}\right) \tag{2b}$$

The pre-exponential factor σ_0 in Eq. (1) is given by

$$\sigma_0 = \nu_0 N e^2 R^2 C(1-C)\,\exp\left(-\frac{2\alpha R}{kT}\right) \tag{3}$$

where ν_0 is the optical phonon frequency (generally $\nu_0 \simeq 10^{13}\,\mathrm{s}^{-1}$) [19], *C* the fraction of reduced transition metal ion ($C = V^{4+}/V_\mathrm{total}$), α the tunneling factor (the ratio of wave function decay), W_H the hopping energy and W_D is the disorder energy defined as the difference of electronic energies between two hopping sites [19].

In the adiabatic hopping regime, however, αR in Eq. (3) becomes negligible [1,2,19], then the conductivity σ, and the pre-exponential factor σ_0 in Eq. (1) is expressed by the following equations [1,2]:

$$\sigma = \frac{\nu_0 N e^2 R^2}{kT} C(1-C)\exp\left(-\frac{W}{kT}\right) \tag{4}$$

and

$$\sigma_0 = \frac{\nu_0 N e^2 R^2 C(1-C)}{kT} \tag{5}$$

For adiabatic hopping conduction the term of σ_0 in Eq. (4) does not depend on the BaO concentration, and hardly varying [1,2,4]. Therefore the dominant factor contributing to the conductivity should be *W* in adiabatic regime [1,2]. Fig. 9 presents the effect of BaO concentration on σ_0, indicating a decrease in σ_0 with BaO content from 30 to 70 mol%. From this result, we conclude that the conduction in the present glasses is to be due to non-adiabatic hopping of polarons [19].

In the framework of Mott's model [1,19], the nature of hopping mechanism in the high temperature range, where a nearly activated behavior of the conductivity was observed, can be ascertained from the plot of logarithmic conductivity versus activation energy at an arbitrarily chosen experimental

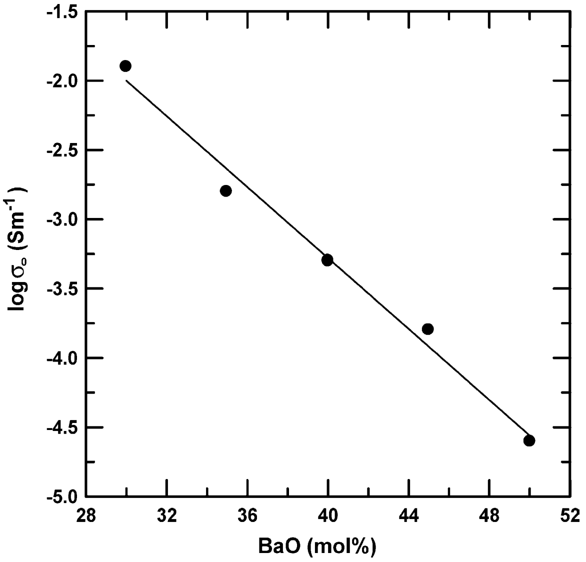

Fig. 9. Composition dependence of pre-exponential factor, σ_0, for BaO—V_2O_5 glasses.

temperature in this range. It has been suggested [1,19] that the hopping would be in the adiabatic regime if the temperature estimated from such a plot is close to the experimental temperature. Otherwise, the hopping would be in the non-adiabatic regime. In this way, the hopping of small polarons was inferred to be in the adiabatic regime for the TMO glasses formed with traditional glass formers [4,8]. A plot of $\log \sigma$ at 413 K versus W is shown in Fig. 10 for different compositions of the present barium vanadate glasses. A least squares straight line fit of the data yields a temperature of 2706 K, indicating non-adiabatic hopping in the present glasses in contrast to traditional vanadate glasses [8,9].

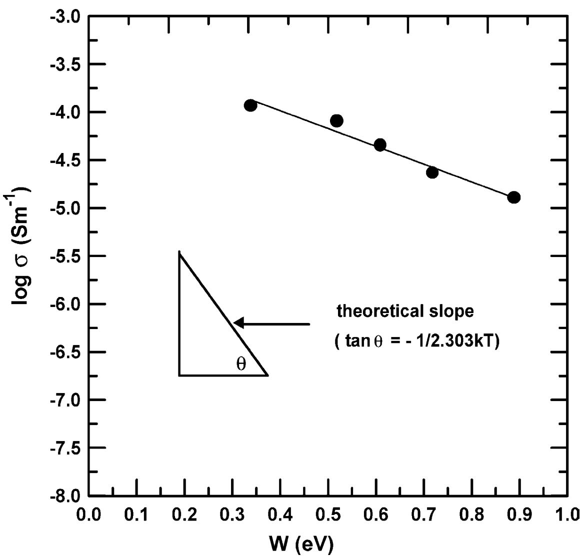

Fig. 10. Plots of $\log \sigma$ at 413 K vs. W for BaO—V_2O_5 glasses.

Holstein [20] has suggest a method for calculating the polaron hopping energy W_H

$$W_H = \frac{1}{4N} \Sigma_p [\gamma_p]^2 \hbar \omega_p \tag{6}$$

where $[\gamma_p]^2$ is the electron–phonon coupling constant and ω_q is the frequency of the optical phonons of wave number. Bogomolov et al. [21] have calculated the polaron radius r_p for a nondispersive system of frequency ν_0 for Eq. (6) as

$$r_p = \left(\frac{\pi}{6}\right)^{1/3} \frac{R}{2} \tag{7}$$

The values of the polaron radii r_p, calculated from Eq. (7), using R from Table 1 is shown in Table 1 for all compositions. Although the possible effect of disorder has been neglected in the above calculation, the small values of polaron radii suggest that the polarons are highly localized. These results are very similar to the magnesium vanadate glasses [8].

Besides, W is expressed in terms of the density of states at Fermi level $N(E_F)$ as follows [19]:

$$N(E_F) = \frac{4}{3\pi R^3 W} \tag{8}$$

we obtained $N(E_F) = 3.75 \times 10^{21}$ to 12.4×10^{21} eV^{-1} cm^{-3}, as shown in Table 2 with the estimated W and R data. The values of $N(E_F)$ are reasonable for localized states.

4. Conclusions

Several properties carried out on the barium vanadate glasses in the composition range of 30–50 mol% BaO, suggest that these glasses are single phase and homogeneous. The increase of the glass transition temperature with the increase of the BaO content indicates the formation of complicated network structure in the glassy matrix. The cross-linking density decreases with the increase of BaO content in the compositions. The infrared studies of the glasses suggest that the glass network is built up of mainly VO_4 polyhedra. The analysis of high-temperature dc conductivity for the present glasses is adequately explained by Mott's small polaron theory. The conduction in the high-temperature region can be explained by the non-adiabatic hopping of polarons. The average distance R, evaluated as 0.384–0.415 nm increased with increasing BaO content. The values of $N(E_F)$ are reasonable for the localized states.

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