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Characterization and electrical conductivity of Vanadium doped strontium bismuth borate glasses

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Glasses with composition *x*SrO (40-*x*) Bi_2O_3 60 B_2O_3, *x* = 0, 5, 10, 15 and 20 molar % containing 2 mol % of V_2O_5 were prepared. The effect of SrO in the present glass matrix was investigated by means of physical, FT-IR, UV-VIS and dc conductivity measurements. The conversion of three fold (BO_3) to four fold (BO_4) coordination of boron observed in the glass system under study results in the formation of Non-bridging oxygen's (NBO's). The formation of NBO's causes the decrease in band gap energy with increase in SrO content. The dc conductivity was found to increase with increase in temperature. A transition observed in the conductivity curve shows the conversion of electronic to ionic conductivity. This transition shifted to lower temperature region with increase in SrO content is due to decrease in band gap energy.

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1. Introduction

Study on heavy metal oxide based borate glasses have been considered more attention due to their wide applications in the field of glass ceramics, layers for optical and electronic devices, thermal and mechanical sensors, reflecting windows, etc. [1]. It has been reported that heavy metal oxide glasses containing bismuth are investigated for possible use in scintillation detectors for high-energy physics [2]. The large polarazibilty and smaller field strength of bismuth ions (Bi^{3+}) in these glasses makes them more suitable in fabrication of optical devices [3]. Basically, Bi_2O_3 is a non conventional glass former, however in the presence of B_2O_3 it may result in the formation of [BiOn] (n=3, 6) polyhedra [4]. The structural role played by Bi_2O_3 in these glasses is complicated and poorly understood. The problem is complex because the formation of pyramids which are highly distorted due to lone pair electrons. [4]. Due to wide applications of heavy metal oxide based glasses, we have planed to prepare these glasses with B_2O_3 as a glass former, because of the large glass forming tendency of B^{3+} ions in B_2O_3 as compared to Bi^{3+} ions in Bi_2O_3. Further, B_2O_3 glasses are insulating in nature and insensitive to the hopping process [5]. The addition of transition metal ions (TMIs) and alkaline earth ions in these glasses exhibit mixed (electronic and ionic) electrical conductivity and improved their optical and electrical properties [6]. Recently, various researchers [7-8], investigated the local structure of alkaline earth ions doped borate glasses containing transition metal ions. The aim of the present work is to study the effect of alkaline earth ions (SrO) on structural, physical, optical and electrical properties of vanadium doped bismuth borate glasses.

2. Experimental details

2.1 Sample Preparation

Vanadium doped strontium bismuth borate glasses were prepared from analytic regent grade powder of SrO, V_2O_5, Bi_2O_3 and H_3BO_3 which are thoroughly mixed in appropriate proportions. The batch materials were dry mixed and melted in porcelain crucibles placed in an electrically heated muffle furnace at 1250 K for about one hour, until a bubble free liquid was formed. The molten glass was equilibrated at the melting temperature until a clear and homogeneous melt was obtained. The glass melt was poured and subsequently pressed on a cooled carbon die held at room temperature. As prepared samples were then polished and cut into desired geometry. X-ray diffraction measurement on each glass sample was carried out to ensure the amorphous nature.

2.2 FTIR measurements

The glass powder was mixed with spectroscopically pure KBr. To obtain pellets, the mixed glass samples were pressed in a die by subjecting to a pressure of 5 tons/cm^2. The infrared (IR) transmission spectra of the glass pellets were measured at room temperature using Perkin-Elmer FTIR spectrometer in the range 500-3000 cm^{-1}.

2.3 Density and molar volume

The density *(d)* of the present glass system was determined at room temperature using Archimede's principle with Xylene as an inert immersion liquid. The molar volume *(V_M)* of each glass sample was calculated using the general formula [9].

$$V_M = \sum \frac{x_i M_i}{d} \tag{1}$$

where x_i is the molar fraction and M_i is the molecular weight of the *i*th component

2.4 Optical absorption measurements

The optical absorption spectra of the glasses under study were recorded at room temperature in the wave length range 350-600 nm using Perkain-Elmer UV-VIS spectrometer.

2.5 Conductivity measurements

The dc conductivity measurements were carried out by using Keithely electrometer (Model 617) in the temperature range 413-513 K. On both faces of the polished samples the silver paste electrodes were deposited. The absence of the barrier layers at the contacts was confirmed by linear *I - V* characteristics.

3. Results and discussion

The infrared spectra of vanadium doped *x* SrO (40- *x*) Bi_2O_3 $60B_2O_3$ glass system, are projected in Fig. 1. It has been reported that the IR spectra of the borate glasses can be divided into three main infrared regions [10-14]. The first group of bands which occur in the range 1200-1600 cm^{-1} is due to the asymmetric stretching relaxation of the B-O bond of trigonal BO_3 structural units. The second group of bands lies in between 800 -1200 cm^{-1} and is due to the B-O bond stretching of the tetrahedral BO_4 structural units and the third group of bands is observed around 700 cm^{-1} and is due to the bending of B-O-B linkage in the borate networks. In pure B_2O_3 glasses, the absorption band at 806 cm^{-1} is the characteristic of the boroxol ring. The absence of this band in the present IR spectra indicate that the formation of boroxol rings do not occur in the glass system under study. It has been reported that characteristic vibration of isolated vanadium oxygen (V-O) bonds lies in the region 900-1020 cm^{-1} [15]. The absorption band observed in the region 900-924 cm^{-1} in the present glass system (listed in Table 1) is due to the overlapping of vibrations of VO_2 groups of theVO_4 polyhedra as well as vibrations of tetrahedral BO_4 structural units [16]. The frequency bands which appear in the region 900-924 cm^{-1}, shifted to higher wave number and became broader on increasing SrO content indicate the conversion of BO_3 to BO_4 tetrahedral structural units.

It is well established that in the bismuth borate network, Bi_2O_3 appears as deformed [BiO_6] groups either [BiO_6] along with [BiO_3] polyhedra or only as [BiO_3] pyramidal units [17-19]. The existence of [BiO_3] pyramid in bismuth borate glasses must show its characteristics band at 830 cm^{-1} [17]. The absence of this band in the IR spectra of glasses under study indicate that the formation of [BiO_3] pyramid does not occur, which in turn suggest that [Bi_2O_3] enter in the borate network in the form of only [BiO_6] octahedra. However, the existence of [BiO_6], which has its characteristics frequency at 480 cm^{-1}, could not be confirmed due to present measurement range of the IR spectra.

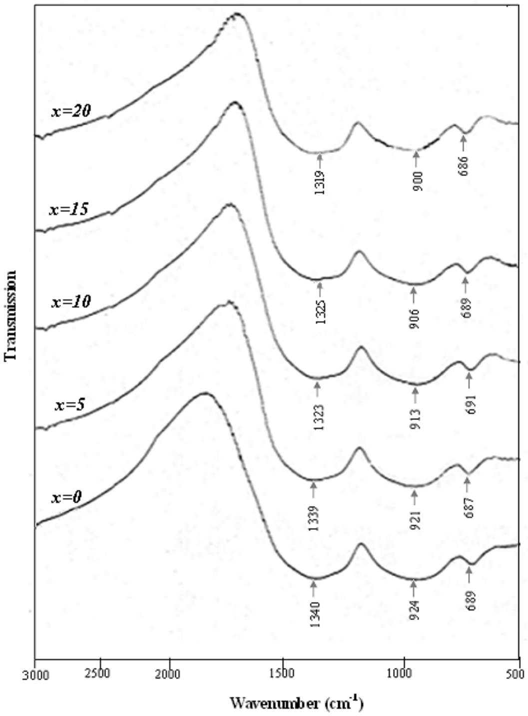

Fig. 1. FTIR spectra of Vanadium doped SrO- Bi_2O_3- B_2O_3 glasses.

Table 1. FTIR spectral analysis of Vanadium doped SrO- Bi_2O_3- B_2O_3 glasses

Peak position (cm^{-1})	Assignments
686, 687, 689, 691	B-O-B bending [19]
900, 906, 913, 921, 924	B-O stretching vibrations of tetrahedral BO4 units Symmetric stretching vibrations of the isolated VO_2 group in VO_4 polyhedra [15].
1319, 1325, 1323, 1339, 1340	Stretching vibration of B-O and B-O^- bonds in borate in borate triangular BO_3 structural units [17].

The high frequency bands which lie in the region 1319-1340 cm^{-1} can be attributed to the stretching vibration of B-O and B-O^- bonds in borate triangular BO_3 structural units [18]. A sharp dip observed in all the samples in the spectral range 686-691 cm^{-1} is assigned to the bending of B-O-B linkages in the borate network [20]. In the glasses under study, it is observed that on increasing of SrO content, the frequency bands shifts from higher to lower wave number, suggest the formation of non bridging oxygen (NBO's) i.e. conversion of BO_3 to BO_4 structural units. The formation of NBOs indicates that the addition of strontium oxide (SrO) in present glass system act as a modifier.

The density and molar volume of all the glass compositions were calculated and listed in Table 2. It is observed that density (d) and molar volume (V_M) decreases with increase in SrO content (Fig. 2). It has been reported that on introduction of one mole of strontium oxide into B_2O_3 matrix, converts two BO_3 units into two BO_4 units [21].

Table 2. Chemical composition and physical properties of vanadium doped SrO - Bi_2O_3-B_2O_3 glasses.

Glass ID (x)	Glass composition x SrO (40-x) Bi_2O_3-$60B_2O_3$ + 2 mol% V_2O_5				Density d (g/cm^3)	Molar Vol. V_M (cm^3/mol)
	SrO	Bi_2O_3	B_2O_3	V_2O_5		
0	0	40	60	2	4.97	46.63
5	5	35	60	2	4.83	44.23
10	10	30	60	2	4.61	42.41
15	15	25	60	2	4.47	39.69
20	20	20	60	2	4.30	37.04

Similar results are observed in IR spectra of the present glass system i.e. introduction of SrO converts the BO_3 into BO_4 structural units which increase the number of non-bridging oxygens. The increase in NBO's randomized the structure, cause in decrease of both density and molar volume. These results are found consistent with other borate glasses [22-24].

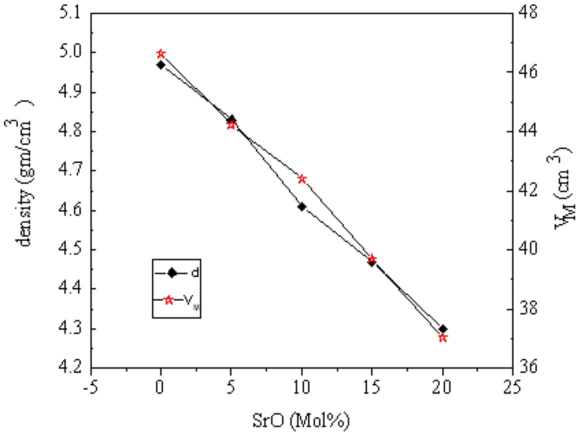

Fig. 2. Variation of density and molar volume of studied glasses with SrO (mol %)

The optical absorption spectra of all the samples recorded at room temperature are displayed in Fig. 3. The absorption co-efficient α (ν) near the edge of each curve was determined from the relation [25]

$$\alpha(\nu) = \left(\frac{1}{t}\right) In\left(\frac{I_i}{I_t}\right) \qquad (2)$$

where t is the thickness of the each sample, $ln(I_i/I_t)$ is the absorbance factor, I_i and I_t are the intensities of incident and transmitted beams respectively. It is observed (Fig. 3) that the optical absorption edge is not sharply defined which clearly indicates the amorphous nature of the glass system under study.

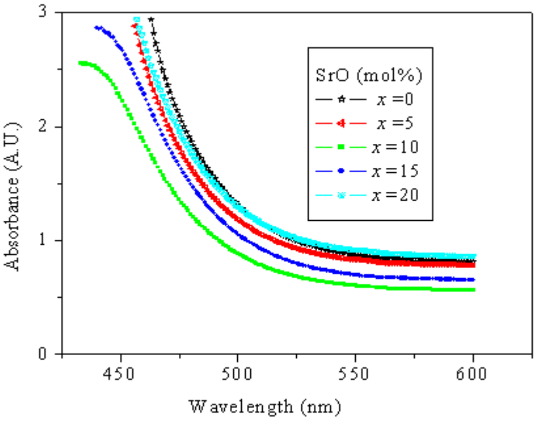

Fig. 3. Optical absorption as a function of wavelength for Vanadium doped SrO - Bi_2O_3- B_2O_3

For amorphous materials, the optical absorption at higher value of α (ν) (≥10^4 cm^{-1}) above the exponentional tail follows a power law given by Davis and Mott [25]

$$\alpha h\nu = B\left(h\nu - E_g\right)^r \qquad (3)$$

where r is the index which can have different values 2, 3, 1/2 & 1/3 corresponding to indirect allowed, indirect forbidden, direct allowed and direct forbidden transitions respectively. B is a constant called as band tailing parameter, $h\nu$ is the incident photon energy and E_g is the optical band gap energy. The values of optical band gap energy (E_g) listed in Table 3 were determined from the Tauc's plot $((\alpha h\nu)^{1/r}$ vs $h\nu)$ by extrapolating the linear portion of the curve to meet the $h\nu$ axis at $(\alpha h\nu)^{1/r} = 0$, for r = 2 & 3 (Fig. 4 & 5).

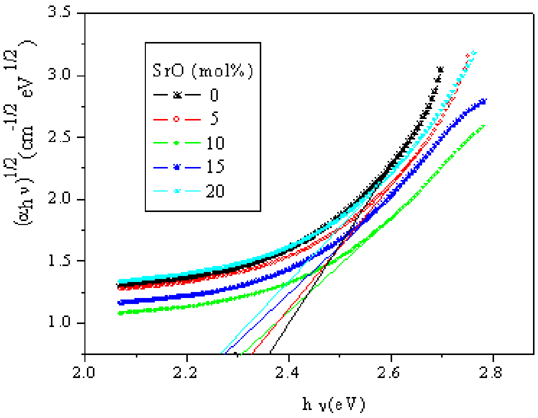

Fig. 4. Tauc's plot for Vanadium doped SrO-Bi_2O_3-B_2O_3 glasses for r = 2.

The values of band gap energy obtained from these two best fit for the two transitions lies between 2.35-2.25 eV and 2.22-2.17 eV, which is generally observed in semiconducting borate glasses. On the basis of theoretical fitting of experimental absorption coefficient, it is concluded that the present glass system behaves as an indirect band gap semiconductor.

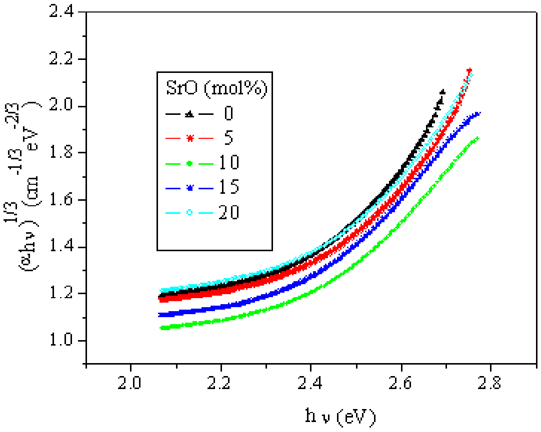

Fig. 5. Tauc's plot for Vanadium doped SrO-Bi_2O_3-B_2O_3 glasses for r = 3.

Table 3. Cutoff wavelength (λ_{cutoff}), Optical band gap (E_g), Tailing parameter (B) and Urbach energy (ΔE) for Vanadium doped SrO- Bi_2O_3- B_2O_3 glasses

x mol %	λ_{cutoff} (nm)	r = 2		r = 3		ΔE
		Eg (eV)	B (cm eV)$^{-1/2}$	Eg (eV)	B (cm$^{-1/3}$ V$^{2/3}$)	
0	450	2.35	3.94	2.22	2.35	0.25
5	452	2.33	4.74	2.21	2.24	0.25
10	456	2.31	4.00	2.20	1.93	0.28
15	457	2.27	3.66	2.18	2.00	0.29
20	462	2.25	4.23	2.17	2.38	0.29

Further it is observed (Fig. 6) that, on increasing SrO content the band gap energy *(E_g)* decreases which is attributed to the structural changes (conversion of BO_3 to BO_4 structural units i.e. increase in NBO's) occurred in the present glass system.

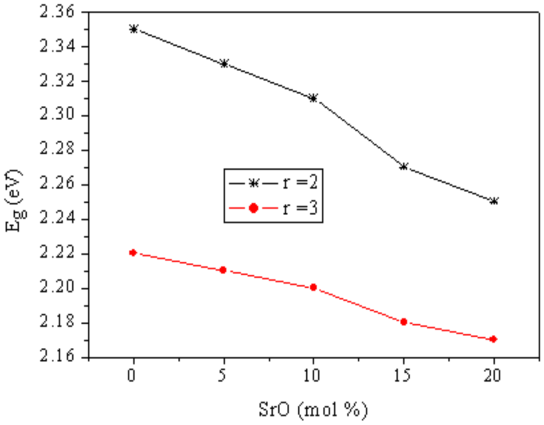

Fig. 6. Variation of band gap energy of studied glasses with SrO (mol %) for r = 2 & r = 3.

The values of band tailing parameter *(B)*, obtained from linear portion of the Tauc's plot for *r* = 2 and 3 are given in Table 3. These values are in accordance with the results reported earlier [21]. The values of Urbach energy *(ΔE)* are calculated (Table 3) from the reciprocal of the slopes of the linear portion of curves between $ln\ \alpha(\nu)$ and $h\nu$ (Fig. 7) using relation [26]

$$\alpha(\nu) = C \exp\left(\frac{h\nu}{\Delta E}\right) \tag{4}$$

where C is a constant.

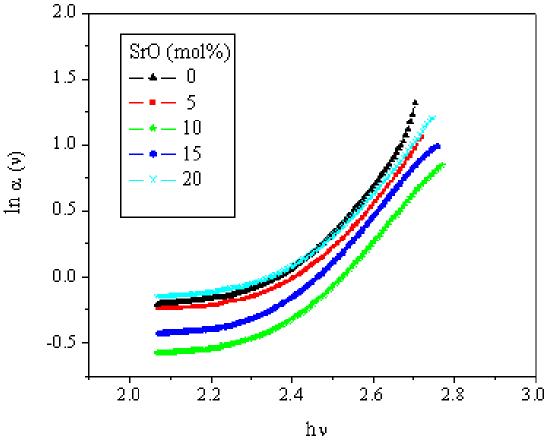

Fig. 7. Urbach plot for Vanadium doped SrO-Bi_2O_3-B_2O_3 glasses.

The width of the band tails *(ΔE)* associated with valance and conduction bands was believed to be originated from electron transition between localized states, where the density of these localized states is exponentially dependent on energy [27]. Also it was suggested that this energy *(ΔE)* arises from the random potential fluctuations in the material into the band gap and normally shows an exponential behavior [28]. It has been reported that the experimental tail observed in various materials with different structures have the same physical origin and this can be attributed to the phonon-assisted indirect electronic transition [29-30]. It is observed that the fundamental edge and cutoff wavelength shifted towards higher wavenumber i.e. to the lower photon energy could be attributed to the increase in NBO's [31]. These observations suggest that with increase in SrO, the shift of UV absorption edge to higher wavelength corresponds to transition to the NBO which binds an excited electron less tightly than a bridging oxygen and leading to a decrease in the value of band gap energy (E_g) and an increase in the value of Urbach energy *(ΔE)*. The calculated values of *ΔE* for the present glass system lie in between 0.25-0.29 eV. The obtained values are in well consistent with reported results [32].

The present glass system consists of TMIs (V^{4+} & V^{5+}) as well as alkaline earth ions (Sr^{+}) therefore conductivity should be mixed i.e. electronic and ionic. The vanadium ions have two oxidation states V^{4+} and V^{5+} and when a local structural deformation takes place due to a phonon, an electron may transform by hopping from the lower valance state to the higher valance state which gives rise to electronic conductivity and is described by small polaron hopping theory. The electronic conductivity can be expressed by

$$\sigma = \frac{\nu_o N e^2 R^2}{kT} C(1-C)\exp(-2\alpha l)\exp\left(\frac{-W}{kT}\right) \tag{5}$$

where ν_o is optical phonon frequency, W is activation energy for hopping conduction, R is mean distance between TMIs, C is fraction of reduced TMIs, α is ratio of wave function decay (tunneling factor) and N is the density of TMIs. The above equation can be simplified as

$$\sigma = \sigma_o e^{\frac{-W}{kT}} \tag{6}$$

where W is the activation energy, k is Boltzmann constant, T is temperature in Kelvin and σ_o is pre-exponential factor which is given by the relation

$$\sigma_0 = \frac{\nu_o N e^2 R^2}{kT} C(1-C)\exp(-2\alpha R) \tag{7}$$

The presences of Sr+ ions in the glasses under investigation give rise to ionic conductivity. It is usually accepted that positively charged interstitial pair, that is doubly occupied strontium sites, are responsible for ionic conductivity in the glasses [33-35]. The ionic conductivity is given by the expression

$$\sigma_i = \frac{\nu_0 N_{Sr} e^2 R^2}{6kT}\exp\left(\frac{-\frac{\Delta H_f}{2} - \Delta H_m}{kT}\right) \tag{8}$$

where N_{Sr} is the total concentration of strontium cation, ΔH_f and ΔH_m are the formation and migration enthalpy of the interstitial pair, R is the mean distance between cationic sites and ν_o is the ionic attempt frequency.

The temperature dependence of dc conductivity *(σ)* for the different glass compositions are shown in Fig. 8 and tabulated in Table 4. The activation energy calculated from the slope of the Fig. 8 is listed in Table 4. The behavior of electrical conductivity and activation energy with composition is shown in Fig 9. It is observed that for a given composition a transition occur in the conductivity curve which indicate a sudden increase in the conductivity at a particular temperature and is due to the conversion of electronic to ionic conductivity. This transition shifted to lower temperature region with increase in SrO content and is due to decrease in band gap energy as observed in Uv-Vis measurements.

Table 4. Electrical parameters as a function of x in xSrO (40-x) $Bi_2O_3.60B_2O_3$ glasses containing 2 mol % V_2O_5

Glass ID(*x*)	σ_{430K} (Ω m)$^{-1}$)	σ_{500K} (Ω m)$^{-1}$	Log σ_0	W (eV)
5	6.837×10^{-13}	1.759×10^{-9}	10.784	1.94
10	3.213×10^{-12}	4.045×10^{-9}	10.367	1.86
15	1.803×10^{-11}	1.588×10^{-8}	10.160	1.78
20	4.395×10^{-11}	2.878×10^{-8}	9.281	1.67

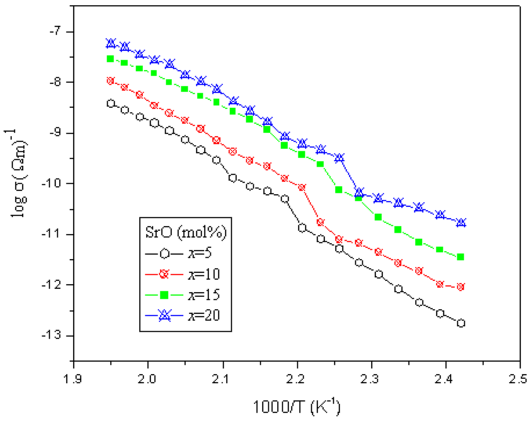

Fig. 8. Variation of log σ vs 1000/T for studied glasses.

These observations suggest that the glasses under study show mixed conductivity i.e. electronic as well as ionic.

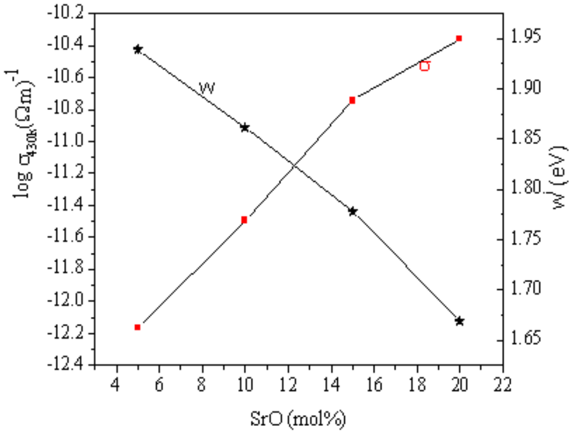

Fig. 9. Effect of SrO content on dc conductivity (430K) and activation energy W.

The results obtained are in good agreement with already reported results observed in alkaline doped bismuth borate glasses [27, 36].

4. Conclusions

The structural, physical, optical and electrical properties of the glass system with composition *x* SrO (40-*x*) Bi_2O_3 -60B_2O_3 containing 2 mol % V_2O_5, have been investigated. It was found that no boroxol ring formation observed in the glasses under study. On increasing SrO content, the frequency bands shifted from higher to lower wave number, suggesting the formation of NBO's. The density and molar volume is found to decrease with increases SrO content and is attributed to the structural changes occurred. It was found that the band gap energy decreases with increase in SrO content and is due to the increase in NBO's. On the basis of theoretical fitting of experimental absorption coefficient, it is concluded that the present glass system behaves as an indirect band gap semiconductor. The dc conductivity of the present glass system increases with strontium oxide content. A transition is observed in the conductivity curve which is due to the conversion of electronic to ionic conductivity. This transition shifted to lower temperature region with increase in SrO content and is attributed to decrease in band gap energy. The glasses under study exhibit the mixed conductivity.

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