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Effect of V_2O_5 on structural, physical and electrical properties of bismuth borate glasses

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The oxide glasses with composition xV_2O_5-(40-x) Bi_2O_3-60B_2O_3; (0≤x≤22.5) were prepared by rapid melt quench technique. The structural investigation of these glasses was performed by monitoring the infrared transmission spectra. It was found that the glass system under study consist of randomly connected BO_3 & BO_4 structural units. The density and molar volume of glasses were found to depend on V_2O_5 content. The conduction mechanism in these glasses was discussed in terms of small polaron hopping (SPH) theory proposed by Mott. It was observed that at 400 K, the dc conductivity increases with increasing vanadium content and ranging from 2.31×10^{-10} $(\Omega m)^{-1}$ to 9.97×10^{-6} $(\Omega m)^{-1}$.

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1. Introduction

The oxide glasses containing transition metal ions (TMIs) such as V, Fe, Co etc exhibits semiconducting properties [1-2]. Study of glass structure is a basic need to understand the behaviour of the material. Infrared spectroscopy becomes an important technique to study the structure of these glasses. The structure of oxide glasses can be expressed by the kind and type of oxygen coordination polyhedra in the structure and the way they interconnect to form the glass structure [3]. B_2O_3 is basic glass former and played a crucial role in the formation of glass network. It is generally used for the formation of dielectric and insulating material. The structure of borate glasses is mainly composed of BO_3 triangles forming six members boroxol ring connected by B-O-B linkage [4]. The boroxol group is composed of three corner sharing BO_3 triangles which form a very highly planar ring. The introduction of transition metal oxide (TMO) in the glass system modifies its structure and affects its electrical behavior, when the metal oxide is acting as a modifier [5-6]. It was reported that the addition of network modifier in borate glasses could produce the conversion of triangular BO_3 units to tetrahedral BO_4 structural units along with the formation of various cyclic units such as tri-borate B_3O_7, di-triborate B_3O_8, metaborate B_3O_9, and some more complicated units or to the formation of non bridging oxygens (NBOs) [7]. In semiconducting oxide glasses, SPH is the universally accepted transport mechanism as proposed by Mott [8], Greaves [9], Mott and Davis [10]. The glass former B_2O_3 has long been considered to be insensitive to the hopping process of semiconducting oxide glasses. Some work regarding the significant contribution of B_2O_3 to the semiconducting properties of vanadium based glasses has been reported [11-12].

The V_2O_5–B_2O_3 glasses have their potential applications in optical and electrical memory switching, cathode materials for making solid state and optical fiber [13]. The aim of the present paper is to study the role of V_2O_5 on the structure, physical and electrical properties of bismuth borate glasses. The interest for the present investigation arise due to presence of two network formers i.e., conventional B_2O_3 and unconventional Bi_2O_3.

2. Experimental

Glasses with composition; xV_2O_5 - (40-x) Bi_2O_3-60 B_2O_3; x = 0, 5, 10, 15 and 22.5 mol %, were prepared from analytical reagent grade chemicals. The batch materials were melted in porcelain crucibles placed in an electrically heated muffle furnace at 1373 K for about one hour. The glass melt was poured and subsequently pressed in a cooled carbon die held at room temperature. The glasses thus obtained were finally polished into a size 10 mm × 10 mm × 1mm (approx.). The glass powder was mixed with spectroscopically pure KBr. To obtain pellets, the mixed glass samples were pressed in a die and subjected to a pressure of 5tons/cm^2. The infrared (IR) transmission Spectra of these glass pellets were measured at room temperature using Perkin-Elmer FTIR Spectrophotometer in the range 500-3000 cm^{-1}.

The density *'d'* of glass Samples was determined by using Archimede's principle with xylene as an inert

buoyant liquid. The molar volume 'V_M' of each glass sample was calculated using the formula [14]

$$V_M = \sum_i \frac{x_i M_i}{d} \quad (1)$$

where x_i is the molar fraction and M_i is the molecular weight of *i*th component. The conductivity measurement was carried out by using Keithely electrometer (Model 617) in the temperature range 310-475 K. Silver paste electrodes were deposited on both faces of the polished samples and then *I-V* characteristic was recorded.

3. Results and discussion

Infrared transmission spectra of xV_2O_5 -(40-x) Bi_2O_3-$60B_2O_3$; ($0 \le x \le 22.5$) glass system are presented in Fig. 1. The spectra can be divided in to three infrared regions, which are similar to those reported earlier [15-17]. The first region in between 650-800 cm^{-1} is related to various borate arrangements and is due to the bending vibrations of B-O-B linkages. The second region from 800-1200 cm^{-1} is related to B-O stretching vibrations of tetrahedral BO_4 units. The third region lies between 1200-1600 cm^{-1} is related to B-O stretching vibrations of trigonal BO_3 units. The absorption peaks observed in infrared spectra are listed in Table 1. The appearance of broad bands in the present glasses is most probably due to combination of high degeneracy of vibrational states, thermal broadening of the lattice dispersion band and mechanical stretching from the powder samples. According to Krogh Moe's [18], the structure of B_2O_3 glass consists of a random network of planar BO_3 triangles with a certain fraction of six membered (boroxol) rings. X-ray and neutron diffraction studies suggest that structure of borate glass consists of random network of BO_3 triangles without boroxol rings. Similar findings have also been reported from molecular dynamic studies [19]. In B_2O_3 glasses, the absorption band at 806 cm^{-1} is the charactertics of boroxol ring [18]. The absence of this band in the present IR spectra signifies that no boroxol ring formation takes place in the glasses under study. The absence of boroxol ring suggests that the present glass system consist of randomly connected BO_3 & BO_4 groups.

It has been reported that Bi_2O_3 appears in bismuth-borate network as deformed [BiO_6] groups [20-21], both [BiO_6] and [BiO_3] polyhedral [7,22] or only as [BiO_3] pyramidal units [23]. The existence of [BiO_3] polyhedra must show its characteristic band at 830 cm^{-1} in IR spectra [21]. The absence of this band in Fig.1, indicates that the formation of [BiO_3] polyhedra does not occur, which suggest that only [BiO_6] octahedra form the bismuthate structure in present glasses. However the presence of [BiO_6] group which has characteristic absorption at 480 cm^{-1} could not be confirmed due to present measurement limits of IR spectra. In the present glass system, two broad band are observed for x= 0 and 5 (mol%), in the region 800-1600 cm^{-1}. On increasing V_2O_5 content (x > 5mol %),

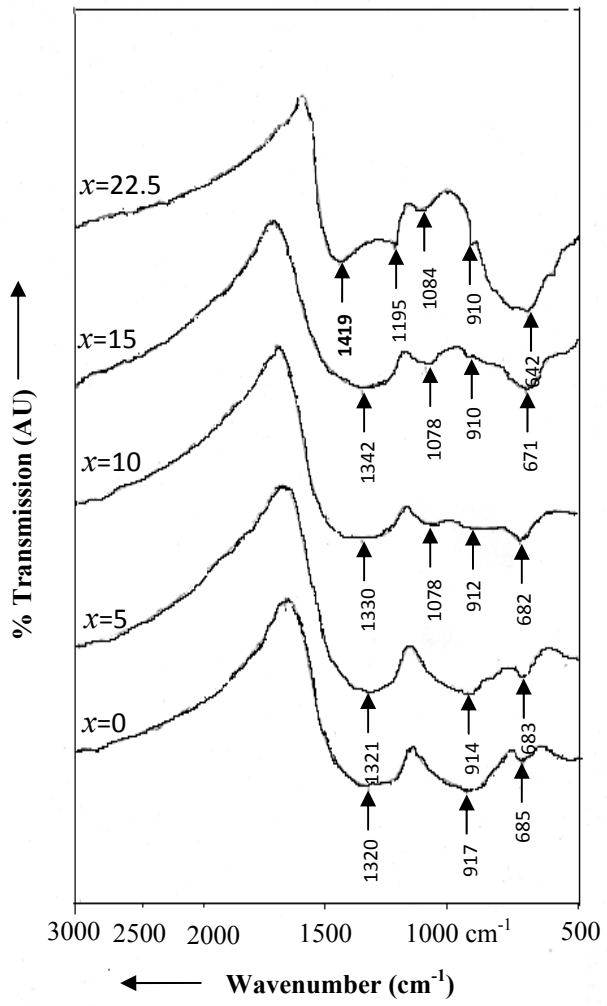

Fig. 1. IR Transmission spectra of xV_2O_5 -(40-x) Bi_2O_3-60 B_2O_3 glasses.

the band which lies in the region 800-1200 cm^{-1} splits into two broad bands whose intensity increases with further increase in vanadium content. The appearance of new band at 1078 cm^{-1} (x = 10 mol%), which is shifted to higher wave number with increase in V_2O_5 content is assigned to stretching vibrations of tetragonal BO_4 units in triborate, tetraborate and pentaborate groups [15]. A new sharp absorption peak is observed at 1195 cm^{-1} for x = 22.5 mol%, which is due to stretching vibrations of tetragonal BO_3 units from pyro- and ortho-borate groups [24], these groups containing a large number of NBOs. The broad band observed at 1320 cm^{-1} is due to stretching vibrations of B(III)-O-B(IV) units [25], on increasing V_2O_5 content this band is shifted to higher wave number (1419 cm^{-1}) and is assigned to B-O^- vibrations attached to large segment of borate network [17]. The band observed in the region 910-922 cm^{-1} is due to symmetric stretching vibrations of the isolated VO_2 group in [VO_4] polyhydra [26]. In the present glasses the band observed in the region 910-917 cm^{-1} is due to overlapping of both vibrations of tetrahedral BO_4 and VO_4 of the borate and vandate network. The absorption band at around 700 cm^{-1} was

assigned to B-O-B bending vibrations in borate networks [27]. A sharp dip

Table 1. FTIR spectral analysis of xV_2O_5-(40-x) Bi_2O_3- 60 B_2O_3 glasses.

Peak positions (cm^{-1})	Assignments
642	O-B-O bending [28]
671, 682, 683, 685	B-O-B bending [27]
910, 912, 914, 917	(i) B-O stretching vibrations of tetrahedral BO_4 units (ii)Symmetric stretching vibrations of the isolated VO_2 group in VO_4 polyhedra [26]
1078, 1084	B-O stretching vibrations of tetrahedral BO_4 units in tri-borate, tetraborate and penta-borate groups [15]
1195	Stretching vibrations of B-O bonds in BO_3 units from Pyro-ortho-borate groups [24]
1320, 1321, 1330, 1342	Stretching vibrations of B (III)-O-B (IV) units [25]
1419	$B\text{-}O^-$ vibrations attached to large segments of borate network [17]

at around 671-685 cm^{-1} observed in the entire glass system (except x = 22.5 mol%) is due to bending of B-O-B linkage in the borate network. The low frequency band observed at 642 cm^{-1} for composition x = 22.5 is due to O-B-O bending [28]. In the present glasses the frequency bands observed in the regions (685-643cm^{-1} and 917-910 cm^{-1}) shifted to lower wave number suggest the formation of NBOs i.e. conversion of BO_3 to BO_4 structural units.

The calculated values of density '*d*' and molar volume 'V_M' of the glass samples are listed in Table 2. Variation of density and molar volume with V_2O_5

Table 2. Chemical composition and physical properties of xV_2O_5-(40-x) Bi_2O_3- 60 B_2O_3 glasses

Glass ID (x)	Glass composition V_2O_5	Bi_2O_3	B_2O_3	Density d (g/cm^3)	Molar Vol. V_M (cm^3/mol)
0	0	40	60	5.15	44.30
5	5	35	60	4.84	44.20
10	10	30	60	4.65	42.95
15	15	25	60	4.41	42.70
22.5	22.5	17.5	60	4.05	42.30

content are shown in Fig. 2. It is observed that the density and molar volume decreases with increasing V_2O_5 contents. Although a small kink observed in both density and molar volume at x = 5 and 15 (mol%) which indicate that some structural changes takes place in the glasses under study.

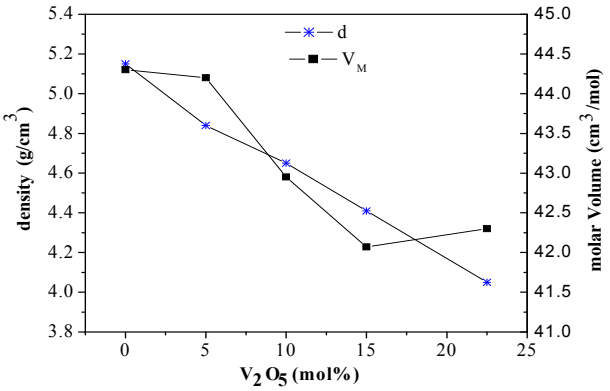

Fig. 2. *Variation of density and molar volume with V_2O_5 content.*

The observed changes in the structure are due to the conversion of BO_3 to BO_4 structural units i.e. increasing of NBO's as explained earlier in the IR spectra.

The dc conductivity 'σ' as a function of T^{-1} for different glass compositions is shown in Fig. 3. It is observed that conductivity 'σ' increases with increasing temperature, indicating temperature dependence of activation energy '*W*' which is a characteristic of small polaron hopping (SPH) conduction mechanism [5]. The logarithmic conductivity in the temperature range (310-475*K*) exhibits almost linear dependence on reciprocal temperature.

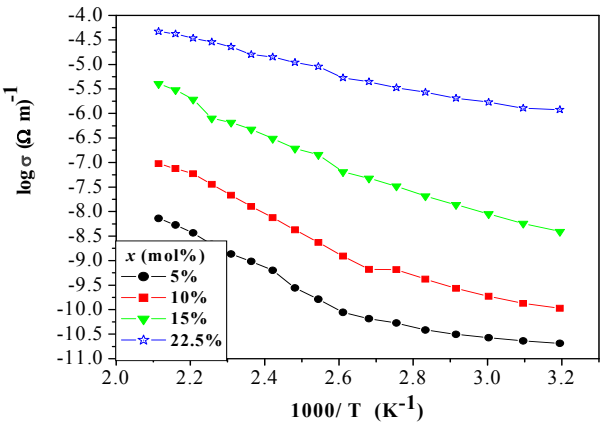

Fig. 3. Variation of log σ with $10^3/T$ (K^{-1}) for xV_2O_5 -(40-x) Bi_2O_3- 60 B_2O_3 glasses

The composition dependence of dc conductivity at constant temperature as shown in Fig. 4, indicates that the dc conductivity increases with increase in V_2O_5 concentration. It is also observed that the dc conductivity for all the glass samples increases with increase in temperature, indicating typical semiconducting behavior.

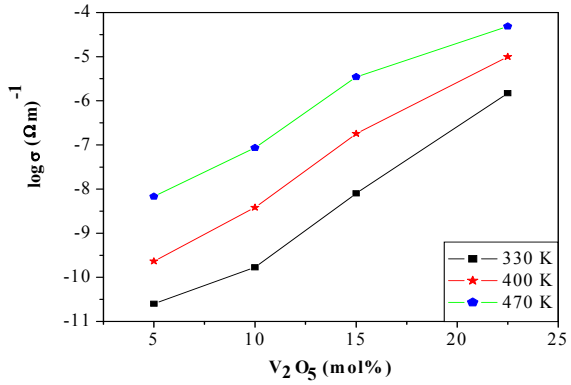

Fig. 4. Variation of log σ with Vanadium contents at different temperatures

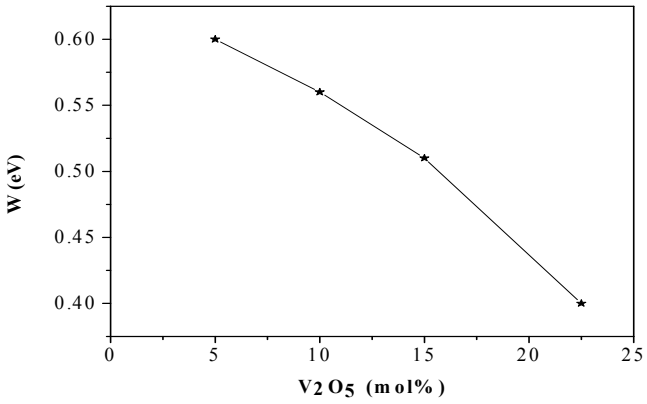

Fig. 5. Variation of activation energy with Vanadium contents.

In semiconducting oxide glasses the conduction mechanism at high temperature ($T > \theta_{D/2}$) is discussed by Mott-Holstein on the basis of small polaron hopping model [29-30]. In this model the conduction process is explained in terms of phonon assisted hopping of small polarons between localized states. The dc conductivity for the nearest neighboring hopping in non-adiabatic regime is given by the equation

$$\sigma = \frac{\nu_0 N e^2 R^2}{kT} C(1-C) \times e^{(-2\alpha R)} \times e^{\left(\frac{-W}{kT}\right)} \qquad (2)$$

where 'ν_0' is optical phonon frequency, 'W' is activation energy, '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. In TMO glasses, the conduction mechanism may be either adiabatic or non adiabatic based on the probability of successful jumps of carrier from one center to the other. For adiabatic conduction the term $e^{-2\alpha R} \approx 1$, therefore from equation (2), the conductivity can be expressed as

$$\sigma = \sigma_0 e^{\frac{-W}{kT}} \qquad (3)$$

where 'W' is the activation energy, 'k' is Boltzmann constant, 'T' is temperature in Kelvin and 'σ_0' is pre-exponential factor which is given by

$$\sigma_0 = \frac{\nu_0 N e^2 R^2}{kT} C(1-C) \qquad (4)$$

The activation energy is calculated from the slope of the log σ vs T^{-1} graph (Fig. 3) and listed in Table 4. The variation of activation energy with V_2O_5 concentration as shown in Fig. 5, indicates that the activation energy decreases with increasing V_2O_5 content.

The low value of activation energy and high value of electrical conductivity are similar to those V_2O_5-BaO-B_2O_3 glasses [31]. These results are in consistent with small polaron hopping theory [8]. In order to establish *W-R* relationship, the concentration of vanadium ions '*N*' was computed (listed in Table 4) using the formula [32].

$$N = 2\left[\frac{dW_t}{M_{W_t}}\right] N_A \qquad (5)$$

where 'd' is density, 'W_t' is the weight fraction, M_{Wt} is the molecular weight of vanadium ions and 'N_A' is the Avogadro number. The mean site separation 'R' between vanadium ions (assuming homogenous distribution of TMIs in the glass volume) was calculated (listed in Table 4) by using the relation [9-10]

$$R = \left(\frac{1}{N}\right)^{\frac{1}{3}} \qquad (6)$$

Table 4. Electrical parameters of xV_2O_5-(40-x) Bi_2O_3 - 60 B_2O_3 glasses.

x(mol%)	W (eV)	N ($\times 10^{23}$ cm^{-3})	R(nm)	r_p(nm)
5	0.60	0.0136	0.902	0.36
10	0.56	0.0280	0.709	0.28
15	0.51	0.0429	0.615	0.25
22.5	0.40	0.0569	0.560	0.23

The variation of activation energy '*W*' as a function of mean site separation '*R*' is shown in Fig. 6.

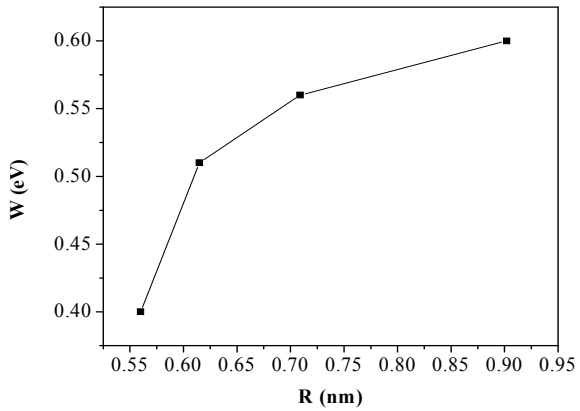

Fig. 6. Variation of activation energy 'W' with average ion separation 'R'.

It is observed that the activation energy increases with increase in site separation between vanadium ions. Bogomolov et al [33] have calculated the polaron radius 'r_P' for a non-dispersive system of frequency v_0 using the relation

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

The calculated values of electrical parameters (*N, R*, and r_p) listed in Table 4. are in good agreement with those reported earlier [34].

The transition metal oxide, V_2O_5 can enter in glass network either as a glass former or as a modifier or both. It was reported [35] that if V_2O_5 enters the structure as glass former then the conductivity should decrease due to increasing concentration of bridging oxygen ions. But in present glass system increase in conductivity due to increase in NBOs reveals that V_2O_5 acts as a network modifier.

4. Conclusions

The structural, physical and electrical properties of xV_2O_5 -(40-x) Bi_2O_3-$60B_2O_3$ glass system have been investigated. FTIR spectra of these glasses have been analyzed to identify spectral contribution of each component on the glass structure and find out the role of vanadium ions in the glass network. No boroxol ring formation was observed in these glasses. The structural units such as BO_3, BO_4 & VO_4 are the predominant coordination polyhedral in this glass system. The tri, tetra, peta, pyro and ortho-borate groups are observed in the glass system under study. Absence of boroxol ring and conversion of BO_3 to BO_4 units i.e. formation of NBOs suggest that V_2O_5 act as a modifier. Appearance of small kinks at x = 5 and 15 mol%, both in the density and molar volume curve is the signature of structural changes that occur due to the modifying nature of V_2O_5. The dc conductivity was found to increases with increasing temperature as well as V_2O_5 content and ranging from 2.31×10^{-10} $(\Omega m)^{-1}$ to 9.97×10^{-6} $(\Omega m)^{-1}$ at 400 K. The activation energy shows negative correlation with V_2O_5 concentration.

References

[1] G.S. Linsley, A.E. Owen, F.M. Hayatee, J. Non-Cryst. Solids. **4**, 208 (1970).
[2] M. Sayer, A. Mansingh, J.M. Reyes, G. Rosenblatt, J. Appl. Phys. **42**, 2857 (1971).
[3] Huaxin Li, Huixing Lin, Wei Chen, Lan Luo, J. Non-Cryst. Solids. **352**, 3069 (2006).
[4] J. Krogh Moe, J. Phys. Chem. Glasses. **3**, 101 (1962).
[5] I. Ardelean, Simona Cora, V. Ionco, J. Optoelect. Adv. Mater. **8**, 1843 (2006).
[6] I. Ardelean, Solid State Common. **27**, 697 (1978).
[7] L.Baia, R Steefan, J. Popp, S Simon, W. Kiefer, J. Non-Cryst. Solids. **324**, 109 (2003).
[8] N.F. Mott, J. Non-Cryst. Solids. **1,** 1 (1968).
[9] G.N. Greaves, J. Non-Cryst. Solids. **11**, 427 (1973).
[10] N.F. Mott, E.A. Davis, Electronic processes in Non- Cryst. Materials Clarendon, Oxford 1979.
[11] Noboru Ichinose, Yuichiro Nakai, J. Non-Cryst. Solids. **203**, 353 (1996).
[12] Virender Kundu, R.L. Dhiman, D.R.Goyal, A.S. Maan, Optoelect. Adv. Mater.-Rapid Comm. **2** 7 428 (2008).
[13] R.A. Montani, M. Levy, J.L. Souquest, J. Non-Cryst. Solids. **149,** 373 (1992).
[14] B.N. Meera, J. Ramakrishnana, J. Non Cryst. Solids. **159,** 1 (1993).
[15] E.I. Kamitsos, M.A. Karakassides, G.D. Chryssikos, J. Phys. Chem. Glasses. **91,** 1073 (1987).
[16] E.I. Kamitsos, A.P. Patsis, G.D. Chryssikos, J Non-Cryst. Solids. **152**, 246 (1993).
[17] C.P. Varsamis, E.I. Kamitos, G.D. Chryssikos, Phys. Rev. B. **60**, 3885 (1999).
[18] J. Krogh Moe, J Phys. Chem. Glasses. **6**, 46 (1965).
[19] F.L. Galeener, G. Lucovsky, J.C. Mikkelsen, Phys. Rev. B. **22,** 3983 (1980).
[20] L. Baia, D. Maniu, T. Iliescu, S. Simon, S. Schlucker, W. Kiefer, Asian J. Phys. **9**, 51 (2000).
[21] V.Dimitrov, Y. Dimitriev, A. Montenero, J. Non-Cryst. Solids. **180**, 51 (1984).
[22] H. Zheng, R. Xu, J. Mackenzie, J. Mater. Res. **4**, 911 (1989).
[23] S. Hazra, A. Gosh, Phys. Rev. B. **51**, 2, 881 (1995).
[24] Y.D. Yiannopoulos, G.D. Chryssikos, E.I. Kamitsos, Phys. Chem. Glasses. **42**, 164 (2001).

[25] B. Karthikeyan, Modern Physics Letter B, **20**, 6, 1 (2006).
[26] I.L. Botto, E.J. Baran, P.J. Aymonino, Monatsh. Chem. **107**, 1127 (1976).
[27] I. Ardelean, F. Ciorcas, M. Peteanu, I. Bratu, V. Ioncu, Mod. Phys. Let. B. **14**, 653 (2000).
[28] Roshan Lal, N.D. Sharma, Indian J. Pure & appl. Phys. **43,** 828 (2005).
[29] I.G.Austein, N.F.Mott, Adv. Phys. **18**, 41 (1969).
[30] T. Holstein, Ann. Phys. **8**, 343 (1959).
[31] E. Culea, A.Nicula, Solid State Commun. **58,** 545 (1986).
[32] H. Moi, T. Kitami, H. Sakata, J. Non-Cryst. Solids. **168,** 157 (1994).
[33] V.N. Bogmolov, E.K. Kudinev,U.N. Firsov, Sov. Phys. Solid State. **9**, 2501 (1968).
[34] M.M. Eldesoky, J. Mater. Sci. Mater. Electron. **14**, 215 (2003).
[35] H. Doweidar, A. Megahed, I.A.Gohar,J. Phys D: Appl. Phys. **19** 939(1986).

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