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Effect of Bi addition on dc, ac conductivity and dielectric properties of $Te_{15}(Se_{100-x}Bi_x)_{85}$ glassy alloys

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The present paper reports the dc, ac conductivity and dielectric properties viz. dielectric constant and dielectric loss of $Te_{15}(Se_{100-x}Bi_x)_{85}$ (x=0, 1, 2, 3, 4 at.%) glassy alloys at room temperature. The dc conductivity is calculated from the I-V characteristics curves of the pellets of bulk samples prepared by melt quenching technique. The samples obey Ohm's law in the lower (0-25V) voltage range whereas the behaviour in the higher (25-100V) voltage range is non-ohmic. The experimental results indicate that the conduction mechanism in these samples in the higher voltage range is Poole-Frenkel type. The increase in dc conductivity is probably due to Se-Bi bond concentration in the Se-Te-Bi glasses. The experimental results indicate that ac conductivity and the dielectric properties of the bulk samples are frequency dependent. The ac conductivity is found to obey the ω^s law. This increase in ac conductivity is probably due to relaxation caused by the motion of electrons or atoms. The ac conductivity is further found to increase with Bi content. The dielectric constant and dielectric loss are found to decrease with frequency and increase with Bi content.

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1. Introduction

The chalcogen elements S, Se and Te when doped with elements such as Bi, Ge, Sb and Ga etc. form the technologically important materials called chalcogenide glasses [1]. These materials have applications such as optical fibre memory devices, reversible phase change optical recording materials and memory switching [2-5]. Recently, the study of electron transport in disordered systems has gradually been developed and the investigation of density of defect states is of interest because of their effect on electrical properties of glassy semiconductors. The common feature of these glasses is the presence of localised states in the mobility gap because of the absence of long range order and various inherent defects. The significant localised states in mobility gap in chalcogenide glasses are the D^+ and D^- states [6]. The hopping conduction can be easily distinguished from that of band conduction by measuring the frequency dependence of ac conductivity. Therefore, the measurement of ac conductivity of amorphous chalcogenide glasses can be used to obtain information about these states. Generally, the undoped chalcogenide glasses show low values of electrical conductivity, which would mean a serious limit to their technological applications. Certain additives are used to improve these properties. Chalcogenide glasses are mostly selenium based because of its glass forming ability, unique property of reversible transformation and applications like switching, optical memory and xerography etc. [7,8]. Pure Se has disadvantages such as short life time and low photosensitivity. These problems can be overcome by alloying Se with impurities atoms like Te, Ge, Ga, As etc. [9,10]. It has been found that substitution of Te for Se breaks the Se_8 ring structure and slightly increases the chain fraction but reduces the chain length [11]. Se-Te glassy alloys have gained much importance because of their high photosensitivity, greater hardness, high crystallization temperature and smaller aging effects [12].

Addition of third element expands the glass forming area and also creates compositional and configurational disorder in the system. The energy band gap of the material plays an important role in preparing a device for a particular wavelength which can be modified by the addition of a dopant [13]. So the influence of additive on electrical properties has been an important issue in chalcogenide glasses. A systematic study of electrical properties of chalcogenide glasses provides useful information about the band gap, density of states, mechanism of conduction, type of dominant charge carriers, recombination kinetics and defect states etc. of the material [14,15]. We have chosen Bi as the third element because it produces remarkable changes in the optical and thermal properties of the Se-Te glasses, decreasing the optical band gap [16] and increasing the glass transition temperature [17]. The density is found to increase indicating the increase in rigidity and hence density of defect states [18]. Further, the addition of Bi to Se-Te glasses changes the conductivity from p type to n type [19-22]

The present work incorporates the study of composition dependence of I-V characteristics, the dc conductivity, the ac conductivity and dielectric properties such as dielectric constant and dielectric loss of the glassy pellets at room temperature of bulk glassy pellets.

2. Experimental procedure

Bulk multicomponent glassy materials of composition $Te_{15}(Se_{100-x}Bi_x)_{85}$ (x = 0, 1, 2, 3, 4 at.%) have been prepared by the melt quenching technique. Selenium, Telurium and Bismuth of high purity (99.999%) were weighed according to their atomic percentages and were sealed in cleaned quartz ampoules of length 10 cm and internal diameter 0.8 cm at a vacuum of 10^{-3} Pa. The ampoules were kept in a vertical furnace and heated to a temperature of 1073 K at a heating rate of 3-4 K/min. The ampoules were heated at this temperature for 12 hours. During heating the ampoules were frequently rocked to make the melt homogenous. The quenching was done in ice cold water. The ingots of glassy materials were obtained after breaking the ampoules. The ingots were grinded to get the powder of the materials. The pellets were made from the powder by applying a load of 5 tons. For the measurement of the I-V characteristics the samples were mounted in a specially designed sample holder, in which a vacuum of 10^{-3} Torr was maintained throughout the measurements. The pellets were coated with silver paste on both sides to confirm good electrical contact with the electrodes of the sample holder. A dc voltage (0-100V) was applied across the sample and the resulting current was measured by a digital picometer (Keithley, model 6487). An Impedance analyser (Wayne Kerr 6500B) was used for ac conductivity and dielectric properties measurements. The ac conductivity of the pellets was measured in the frequency range 10 k Hz to 100 kHz at room temperature.

3. Results and discussion

3.1 DC Conductivity

The I-V characteristics of glasses alloys recorded at room temperature in the voltage range (0-100V) are shown in fig.1. The curves show linear behaviour in the voltage range (0-25V) and in the higher voltage range there are deviations from the linearity means the samples show non Ohmic behaviour. The conductivity of the samples was found from the slope of I-V curves. It has been observed that the conductivity goes on increasing in the higher voltage range. The dc electrical conductivity of the samples in Ohmic region was calculated using the relation

$$\sigma_{DC} = 1/\rho_{DC} = (1/R)(L/A) \tag{1}$$

where R is resistance, L is thickness and A is area of cross-section and ρ_{DC} is the resistivity of the glassy pellets. The values of dc conductivity for all the samples in the different voltage ranges are given in table 1.The electrical conduction can take place by two parallel processes: 1) by band conduction and 2) by hopping conduction in the localized states. The band conduction occurs in the high temperature range. In this mode the carriers excited beyond the mobility edges into the localized states dominate the transport whereas in the hopping conduction the carriers excited into the localized states at the band edges dominate the transport [23]. The total conductivity is given by

$$\sigma = \sigma_i + \sigma_h \tag{2}$$

σ_i is the intrinsic conductivity and σ_h is the hopping conductivity. As pointed earlier the behaviour up to 25V is Ohmic but with further increase in voltage across the sample, the thermal effects may be induced resulting as increase in electrical conductivity. As a result the I-V characteristics change their behaviour towards the non-Ohmic region. For such behaviour conduction mechanism is proposed by Poole-Frenkel [24]. The linearity of ln(I) versus $V^{1/2}$ curve shown in fig. 2 suggest that the conduction mechanism in the samples is of Poole-Frenkel type. The relation between ln(I) and square root of the applied voltage given by Johncher and Hil [25] is

$$I = I_{PF} \exp(\beta V^{1/2} / KT) \tag{3}$$

where

$$\beta = (e^{3/2} / 4\pi\varepsilon\varepsilon_0 d)^{1/2} \tag{4}$$

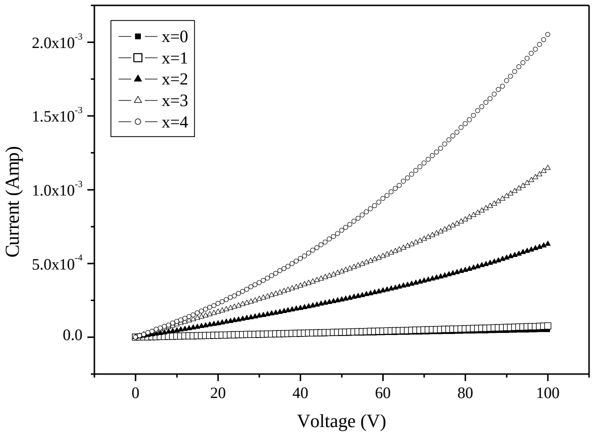

Fig. 1. I-V characteristics of $Te_{15}(Se_{100-x}Bi_x)_{85}$ (x=0, 1, 2, 3, 4 at.%) glassy alloys at room temperature.

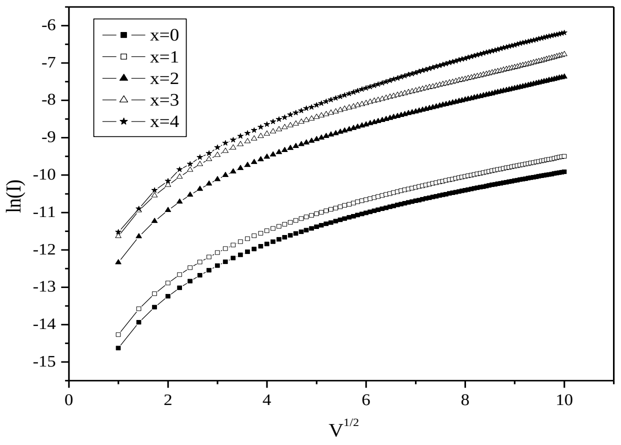

Fig. 2. Plot between ln(I) and $V^{1/2}$ verifying the Poole-Frenkel conduction mechanism.

Table 1. dc conductivity values of $Te_{15}(Se_{100-x}Bi_x)_{85}$ (x=0, 1, 2, 3, 4 at.%) glassy alloys at room temperature.

Composition	dc conductivity at different voltages ranges at room temperature	
	σ_{dc} $(\Omega\ cm)^{-1}$ (0-25V)	σ_{dc} $(\Omega\ cm)^{-1}$ (25-100V)
X=0	5.78×10^{-8}	5.82×10^{-8}
X=1	9.99×10^{-8}	1.04×10^{-7}
X=2	7.94×10^{-7}	$8.02. \times 10^{-7}$
X=3	1.38×10^{-6}	1.44×10^{-6}
X=4	2.60×10^{-6}	2.67×10^{-6}

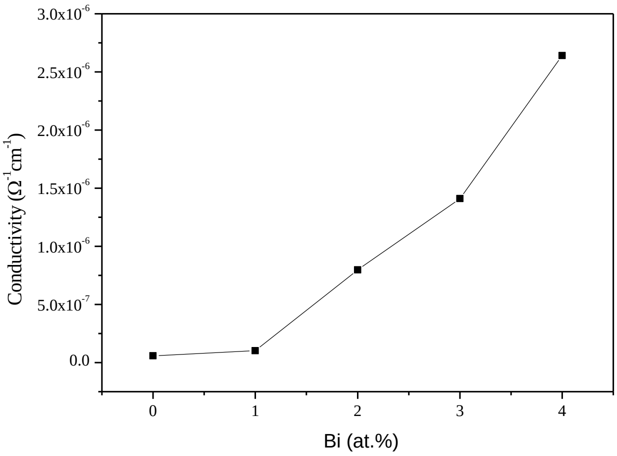

Fig.3. Composition dependence of dc conductivity of $Te_{15}(Se_{100-x}Bi_x)_{85}$ (x=0, 1, 2, 3, 4 at.%) glassy alloys at room temperature.

ε_0 is the permittivity of free space and ε is the relative permittivity of the sample d is the spacing between filled and empty sites. I_{PF} is given by

$$I_{PF} = I_0 \exp(\phi / KT) \qquad (5)$$

where ϕ is the trap depth and

$$I_0 = nAedv \qquad (6)$$

The Poole-Frenkel conduction mechanism deals with conduction in such materials where defect/impurity generated electron traps are involved. The structural defects in the material cause additional energy states close to the band edge called 'traps'. These traps restrict the current flow because of a capture and emission process, thereby becoming the dominant current mechanism. Fig. 3 shows the variation of average value of dc conductivity with Bi content over the entire voltage range. The increase in electrical conductivity of $Te_{15}(Se_{100-x}Bi_x)_{85}$ (x = 0,1, 2, 3, 4 at.%) glasses with Bi content could be explained on the basis of chemical bond theory of solids [26]. It is well established that in glasses containing Se there is a tendency to form polymerized network and the homopolar bonds are qualitatively suppressed [27]. The structure of Se-Te prepared by melt quenching is regarded as mixture of Se_8 rings, Se_6Te_2 mixed rings and Se-Se long chains [28]. A strong covalent bond exists between the atoms in the rings and between the chains only the Van der Waal's forces are dominant [29]. The addition of Bi to the Se-Te system leads to cross-linking of the chains. With the increase in Bi content the glassy network becomes heavily cross-linked and the steric hindrance increases. The strong Se-Se (184 kJ/mol) bonds are replaced by the weak Se-Bi (175.6 kJ/mol) bonds favouring an increase in thermal as well as electrical conductivity [30].

3.2 AC conductivity

The frequency dependence of ac conductivity in semiconductors and other disordered systems is due to conduction in localized states. The almost straight line graph between ln{$\sigma_{ac}(\omega)$} and ln(ω), fig.4, suggest that the a.c. conductivity has been found to obey the relation [31]

$$\sigma_{ac}(\omega) = A_0 \omega^s \qquad (7)$$

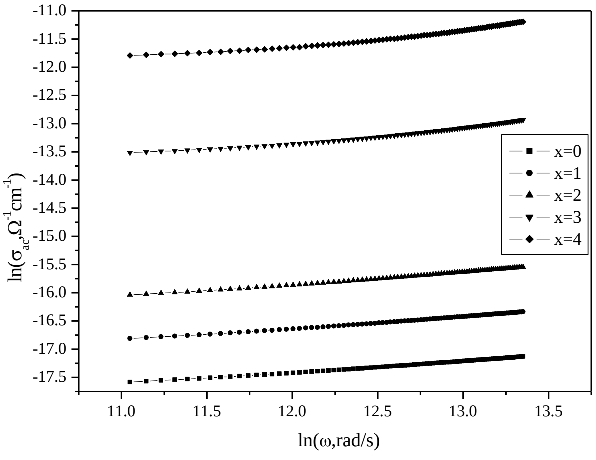

Fig. 4. Variation of ac conductivity with frequency of applied voltage for $Te_{15}(Se_{100-x}Bi_x)_{85}$ (x=0, 1, 2, 3, 4 at.%) glassy alloys at room temperature.

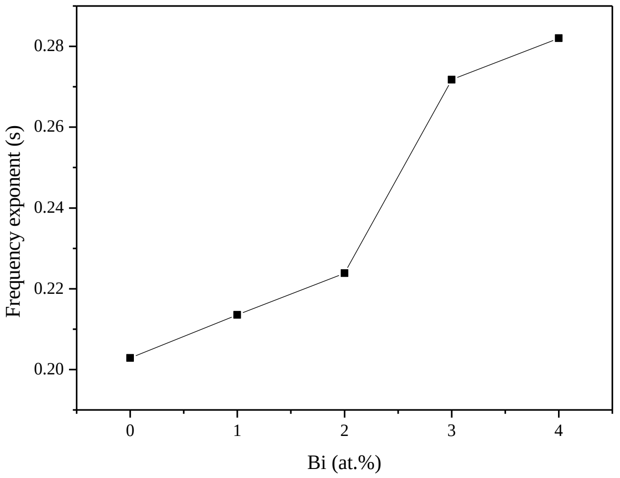

Fig. 5. Variation of frequency exponent with Bi content for $Te_{15}(Se_{100-x}Bi_x)_{85}$ (x=0, 1, 2, 3, 4 at.%) glassy alloys.

where ω is the angular frequency, A_0 is a constant and *s* is the frequency exponent. The value of a.c. conductivity is found to increase with frequency for all compositions. The values of ac conductivity measured at different frequencies are listed in table 2. Values of frequency exponent *s* were calculated from the slope of straight line graphs between $\ln\{\sigma_{ac}(\omega)\}$ and $\ln(\omega)$. The increase in ac conductivity with frequency has been ascribed to relaxation caused motion of electrons or atoms. Such motion can involve hopping or tunnelling between equilibrium sites. The plot of frequency exponent with Bi content for all compositions is shown in fig.5. Further, the frequency dependence of a.c. conductivity can be explained on the basis of correlated barrier hopping model (CBH) [32-34], according to which

$$\sigma_{ac}(\omega)=\frac{n}{24}\pi^{2}NN_{p}\varepsilon^{'}\omega R_{\omega}^{6} \tag{8}$$

where *n* is the number of polarons involved in hopping process, R_ω is the hopping distance for the condition $\omega\tau=1$ and is given by

$$R_{\omega}=\frac{ne^{2}}{\varepsilon^{'}\{\omega+K_{B}T\ln(\omega\tau)\}} \tag{9}$$

the value of frequency exponent is given by

$$s=1-\frac{6K_{B}T}{W_{M}+\left[K_{B}T\ln(\omega\tau)\right]} \tag{10}$$

where K_B is the Boltzman constant, τ is the characteristic relaxation time, W_M is the barrier height and T is the absolute temperature.

Table 2 ac conductivity values of $Te_{15}(Se_{100-x}Bi_x)_{85}$ (x=0, 1, 2, 3, 4 at.%) glassy alloys at different frequencies.

Composition	Ac conductivity at different frequencies $(\Omega\ \mathrm{cm})^{-1}$				
	σ_{ac} (10kHz)	σ_{ac} (25 kHz)	σ_{ac} (50 kHz)	σ_{ac} (75 kHz)	σ_{ac} (100 kHz)
X=0	2.31×10^{-8}	2.70×10^{-8}	3.11×10^{-8}	3.39×10^{-8}	3.63×10^{-8}
X=1	5.00×10^{-8}	5.88×10^{-8}	6.82×10^{-8}	7.48×10^{-8}	8.03×10^{-8}
X=2	1.08×10^{-7}	1.28×10^{-7}	1.50×10^{-7}	1.65×10^{-7}	1.77×10^{-7}
X=3	1.35×10^{-6}	1.56×10^{-6}	1.88×10^{-6}	2.15×10^{-6}	2.42×10^{-6}
X=4	7.55×10^{-6}	8.67×10^{-6}	1.04×10^{-5}	1.20×10^{-5}	1.37×10^{-5}

3.3 Dielectric properties

The complex dielectric constant of a material is represented by two terms

$$\varepsilon=\varepsilon_{1}+\varepsilon_{2} \tag{11}$$

where ε_1 is real part (dielectric constant) and ε_2 the imaginary part (dielectric loss). The frequency dependence of dielectric constant (ε_1) at room temperature for different compositions is shown in fig.6. The dielectric constant decreases with frequency for all compositions. The observation of dielectric effects in the glasses implies that dipoles exist, corresponding to polaron hopping between sites of different energies. Dielectric constant for a polar material is due to the contribution of electronic, ionic, orientation and space charge polarizations. The total polarization of the material is the sum of all type of polarizations [35]. When the applied field frequency is increased the dipoles will no longer be able to rotate sufficiently rapidly, so that their oscillations begin to lag behind those of the applied field. With a further increase in frequency the dipoles will be totally unable to follow the field and so the orientation polarization stopped. So, the dielectric constant decreases approaching a constant value due to space charge polarization. Larger values of dielectric constant are observed for increased Bi content. This behaviour can be explained on the basis of electrode polarization effects [36-38]. Further, with increase in Bi content the weak Bi-Se bonds increases where as the strong Se-Se bonds decreases. The weak bonds being more responsive to the electric field increases the dielectric constant with increase in Bi content.

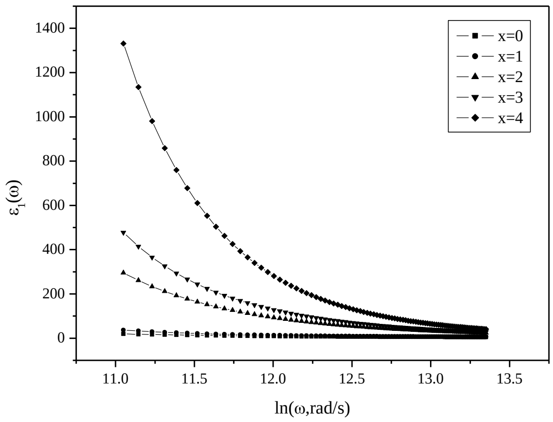

Fig. 6. Frequency dependence of dielectric constant for $Te_{15}(Se_{100-x}Bi_x)_{85}$ (x=0, 1, 2, 3, 4 at.%) glassy alloys at room temperature.

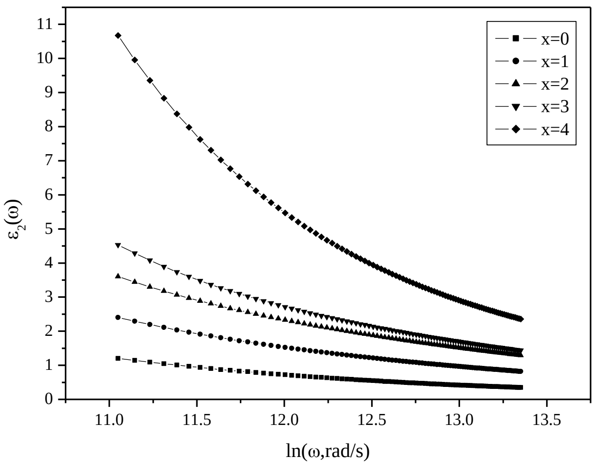

Fig. 7. Frequency dependence of dielectric loss for $Te_{15}(Se_{100-x}Bi_x)_{85}$ (x=0, 1, 2, 3, 4 at.%) glassy alloys at room temperature.

Fig. 7 shows frequency dependence of the dielectric loss (ε_2) at room temperature for all the compositions. The ε_2 obeys a power law with angular frequency (ω) for all compositions i.e. $\varepsilon_2 = B\omega^m$. This behaviour is confirmed by the straight line graph between $\ln(\varepsilon_2)$ and $\ln(\omega)$. The power *m* calculated from the slope of this graph is negative for all compositions. Guintini [39] have proposed a model to dielectric relaxation in chalcogenide glasses based on Elliot's [32] idea of hopping of charge carrier over the potential barrier between the charged defect states. According to this model the ε_2 at a particular frequency and the temperature range in which the dielectric dispersion occurs is given by

$$\varepsilon_2(\omega) = (\varepsilon_0 - \varepsilon_\infty) 2\pi^2 N \left(\frac{ne^2}{\varepsilon_0}\right)^3 k_B T \tau_0^m W_M^{-4} \omega^m \qquad (12)$$

where

$$m = -\frac{4k_B T}{W_M} \qquad (13)$$

here, n is the number of electrons that hop, N is the concentration of localized sites, ε_0 and ε_∞ are the static and optical dielectric constant respectively. W_M is the energy required to move the electron from a site to infinity. Thus a increase in frequency decreases the dielectric loss. Further, the decrease in dielectric loss with frequency may be due to migration of ions at low frequencies. The dielectric loss increases with Bi content indicates the increase in defect density of states.

4. Conclusions

The study of I-V characteristics of $Te_{15}(Se_{100-x}Bi_x)_{85}$ (x = 0,1, 2, 3, 4 at.%) glasses show that the glasses exhibit both the Ohmic and non-Ohmic behaviour in the studied voltage range. The dc conductivity of the glasses is found to increase with increase in Bi content. The linearity of graph between ln(I) and $V^{1/2}$ shows that the conduction mechanism is of Poole-Frenkel type in the higher voltage range. The ac conductivity is found to increase with frequency of applied voltage at room temperature. The increase of Bi content also increases the ac conductivity of the glasses. The dielectric constant and dielectric loss decreases with applied frequency and increases with increase in Bi content.

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References

[1] A. Zakery, S.R. Elliot, J. Non-Cryst. Solids **330**, 1 (2003).

[2] N. Suri, K.S. Bindra, R. Thangaraj, J. Phys. Condens. Matter **18**, 9129 (2006).

[3] M. S. Kamboj, G. Kaur, R. Thangraj, Thin Solid Films **350**, 420 (2002).

[4] E. R. Shaaban, M.T. Dessouky, A.M. Abousehly, J. Phys. Condens. Matter **19**, 096212 (2007).

[5] F.A. Lopez, M.C. Ramirez, J.A. Pons, A. Lopez-Delgado, F.J. Alguacil, J. Therm Anal. Calorim. **94**, 517 (2008).

[6] S.K. Tripathi, Vineet Sharma, A. Thakur, J. Sharma, G.S.S. Saini, N. Goyal, J. Non-Cryst. Solids **351**, 2468 (2005).

[7] J. Vazquez, D. Garcia-Barreda, P.L. Lopez-Alemany, P. Villares, R. Jimenez-Garay, J. Non-Cryst. Solids **142**, 345 (2004).

[8] G. Singh, J. Sharma, A. Thakur, N. Goyal, G.S.S. Saini, S.K. Tripathi, J. Optoelectron. Adv. Mater. **7**, 2069 (2003).

[9] M.A. Majeed Khan, M. Zulfequar, M. Hussain, J. Opt. Mater. **22**, 21 (2003).

[10] P. Sharma, S.C. Katyal, Physica B **403**, 3667 (2008).

[11] P. Sharma, S.C. Katyal, J. Non-Cryst. Solids **354**, 3836 (2008).

[12] S.O. Kasap, T.W. Auger, V. Aiyah, O. Krylouk, A. Berkirov, L. Tichy, J. Mater. Sci. **34**, 3779 (1999).

[13] E. Marquez, T. Wagner, J.M. Gonzalez-Leal, A.M. Bernal-Olive, R. Prieto-Aleton, R. Jimenez-Garay, P.J.S. Ewen, J. Non-Cryst. Solids **274**, 62 (2000).

[14] J.M. Marshall, Rep. Proj. Phys. **46**, 1235 (1983).

[15] Sanjeev Gautam, A. Thakur, S.K. Tripathi, N. Goyal, J. Non-Cryst. Solids **353**, 1315 (2007).

[16] Kameshwar Kumar, Pankaj Sharma, S.C. Katyal, Nagesh Thakur, communicated

[17] Kameshwar Kumar, Nagesh Thakur, S.S. Bhatt, Pankaj Sharma, Phil. Mag. **90**, 3907 (2010).

[18] Kameshwar Kumar, Nagesh Thakur, S.C. Katyal, Pankaj Sharma, Defect and diffusion forum **305-306**, 61 (2010).

[19] N. Tohge, T. Minami, M. Tanaka, J. Non-cryst. Solids **59-60**, 1015 (1983).

[20] N. Tohge, Y. Yamamoto, T. Minami, M. Tanaka, J. Appl. phys. lett. **34**, 640 (1979).

[21] P. Nagels, L. Tichey, A. Tiska and H. Ticha, J. Non-cryst. Solids **59-60**, 999 (1983).

[22] P Nagels, M. Rotti, W. Vikhrov, J.Phys. Paris, **42**, 907 (1981).

[23] N.F. Mott, E.A. Davis, Electronic processes in non-crystalline materials, Clarendon press Oxford, (1979).

[24] R.M. Abdel Latif, Physica B **254**, 273 (1998).

[25] A. K. singh, N. Mehta, K. Singh, chalcogenide letters **6**, 9 (2009).

[26] L. Pauling, Die Natur der Chemischen Binding, VCH Weinheim, (1976)

[27] M.K. Rabinal, N. Ramesh Rao, K.S. Sangunni, Phil. Mag. **70**, 89 (1994).

[28] M.A. Majeed Khan, M. Zulfequar, M. Hussain, J. Mater. Sci. **38**, 549 (2003).

[29] V.K. Saraswat, V. Kishore, N.S. Saxena, T.P. Sharma, Indian Journal of Pure and Applied Physics, **44**, 196 (2006).

[30] V.K. Saraswat, K. Singh, N.S. Saxena, V. Kishore, T.P. Sharma, P.K. Saraswat
Current Applied Physics **6**, 14 (2006).

[31] M. Pollak, T.H. Geballe, Phys.Rev. **22**, 1742 (1961).

[32] S.R. Elliot, Phil. Mag. **36**, 1291 (1977).

[33] K. Shimkawa, Phil. Mag. B **46**, 123 (1982).

[34] K. Shimkawa, Phil. Mag B **48**, 778 (1983).

[35] M. Pollak, T.H. Geballe, Phys. Rev. **22**, 1742 (1961).

[36] A.R. Long, J. Macmillan, N. Balkan, S. Summerfield, Phil. Mag. B **58**, 153 (1988).

[37] J.R. Macdonald, J.Non-Cryst. Solids **197**, 83 (1996).

[38] M. Cutroni, A. Mandanici, A. Piccols, C. Tomasi, Phil. Mag. B **71**, 843 (1995).

[39] J.C. Guintini, J.V. Zanchetta, D. Julien, R. Eholie, P. Houenou, J. non-Cryst. Solids **45**, 57 (1981).

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