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A.C. CONDUCTIVITY AND DIELECTRIC PROPERTIES OF $Se_{90}Cd_6Sb_4$ GLASSY ALLOY

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$Se_{90}Cd_6Sb_4$ chalcogenide semiconducting alloy was prepared by melt quench technique. The prepared glassy alloy has been characterized by techniques such as scanning electron microscopy (SEM) and energy dispersive X-ray (EDAX). The a.c. conductivity and dielectric properties of $Se_{90}Cd_6Sb_4$ chalcogenide semiconductor have been studied in the frequency range 5×10^2 Hz - 1×10^5Hz and in temperature range 303-328K. It is found that a.c. conductivity$\sigma_{ac}(\omega)$, dielectric constant (ε') and dielectric loss factor (ε'') depend on frequency and temperature. The frequency dependence of $\sigma_{ac}(\omega)$ is found to be linear and obey the power law $\omega^s$where $s\leq1$. A strong dependence of $\sigma_{ac}(\omega)$ and exponent s on temperature can be well interpreted in terms of correlated barrier hopping (CBH) model. The dielectric loss has been analysed to determine the barrier height W_m. It is found that the value of W_m agree with that proposed by theory of hopping of charge carriers over potential barrier between charged defect states as suggested by Elliott in case of chalcogenide glasses.

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1. Introduction

Chalcogenide glasses have attracted much attention over the last two decades due to their interesting physical properties such as chemical stability, high optical transparency and excellent electrical properties. Recently, a lot of work has been done in the field of chalcogenide glasses due their potential technological applications in the field of optoelectronics [1-4], optical and memory switching devices[4,5-6], solar energy conversion [7-8], infrared detectors[9], holography[10] and optical fibers[11]. Besides, the physical properties of these semiconducting glasses are strongly dependent on their composition [12-13].Chalcogenide glasses are known to be structurally disordered system and addition of impurities in the disordered system changes their structure, which leads to the change in conduction mechanism, which has been found to vary with different impurities [14-18]. The alloys produce characteristic effect which depends on the electronic structure of the alloying elements. Among various chalcogenide elements only Se is available in amorphous form, but it suffers from the disadvantage of short life time and low sensitivity [19]. However, the addition of impurities leads to relatively stable glasses with improved physical qualities [20-21].

Dielectric relaxation studies are important to understand the nature and the origin of dielectric loss which, in turn, may be useful in the determination of structure and defects in solids. As these materials are co-valently bonded solids, the dispersion is not expected at low frequencies. However, recent measurements have indicated [22-25] that dielectric dispersion loss does exists in these glasses even at very low frequency. The origin and nature of dielectric losses in these materials has therefore, become a matter of curiosity.

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Frequency dependent electrical conductivity of chalcogenide semiconductors is helpful to understand the conduction mechanism in their alloys. Therefore it is interesting to study the electrical behavior of these materials in a.c. fields which gives the important information about the transport process in localized state in the forbidden gap [26].

In our previous communication we have reported dielectric and a.c. conductivity of Indium doped chalcogenide glasses of Se-Cd-In system [27]. In the present work SEM and EDAX have been measured to analyze the surface morphology and elemental compositions of $Se_{90}Cd_6Sb_4$ glassy alloy. Dielectric and a.c. conductivity measurements of $Se_{90}Cd_6Sb_4$ glassy alloy has been carried out in the frequency range 5×10^2Hz - 1×10^5Hz and temperature range 303-328K.

2. Experimental details

Chalcogenide glassy alloys of $Se_{90}Cd_6Sb_4$was prepared from high purity (99.999%) Se, Cd and Sb elements by the melt quench technique. The exact amounts of alloying elements were weighed according to their atomic weight percentage using an electronic balance (LIBROR, AEG-120) with the least count of 10^{-4}gm and placed into ultra-cleaned quartz ampoules(length ≈ 5cm and internal diameter ≈ 8mm). The ampoules were evacuated and sealed under a vacuum of 10^{-5} Torr to avoid reaction of alloying elements with oxygen at a higher temperature. The sealed ampoules were heated in a furnace at rate of 4–5 K/min, the temperature raised up to 800°C and kept at that temperature for 12 h. During the heating process, the ampoules were constantly rocked by rotating ceramic rod to ensure the homogeneity of alloying materials. The ampoules with molten materials were rapidly quenched into ice-cooled water. The ingots of glassy materials were taken out from ampoules by breaking them. Surface morphology was studied using the JEOL, Japan JSM-6510 Model SEM. The magnification used was 2500×. The compositional analysis of the prepared alloy was studied by EDAX attachment to the above mentioned SEM model. Dielectric and electrical conductivity measurements have been done with Wayne Kerr Electronics, UK; model: 4255 in the frequency range from 5×10^2Hz - 1×10^5Hz and in temperature range 303-328K. For this, glassy samples were pressed into cylindrical pellet forms having diameter 10mm and thickness about 1.2mm under uniform load of 5 tons using hydraulic press. A pellet was sandwiched between two circular silver discs in order to ensure good electrical contact between sample and electrodes of the LCR meter. This whole assembly of sample and discs is placed between the electrodes of the LCR meter. The temperature measurement was facilitated by a copper constantan thermocouple close to sample. A vacuum of the order of 10^{-3}Torr was maintained over the entire temperature range. For determination of a.c. conductivity, the dissipation factor and capacitance were measured. All the measurements were carried out under dark condition in the cryostat. The signal voltage level was kept at 0.02 Volts.

The dielectric constant ε' was calculated using the relation:

$$\varepsilon' = Cd/A\varepsilon_o \qquad (1)$$

where C is the capacitance of the sample, d is thickness of the pellet, A is area of the pellet and ε_o is the free space permittivity.

The dielectric loss ε'' was calculated from the relation:

$$\varepsilon'' = \varepsilon' \mathrm{Tan}\delta$$

where $\delta=90^o-\theta$ and θ is the phase angle.

If ω is the frequency of applied signal and ϵ_o is the permittivity of free space, then AC conductivity is given as

$$\sigma_{ac}(\omega) = \omega\epsilon_o\epsilon'' \qquad (2)$$

$$\sigma_{ac}(\omega) = 2\pi f\epsilon_o\epsilon' \mathrm{Tan}\delta \qquad (3)$$

3. Results and Discussion

3.1 Surface morphological analysis

SEM is a promising technique for the topographic analysis, which gives important information regarding to growth mechanism, shape and size of the sample. Figure 1 shows the scanning electron micrograph of the studied sample. From SEM micrograph it is evident that image of the sample is uniform and without any pin holes or cracks and there is formation of conchoidal contours, which shows the presence of some micro-crystallites embeded in the glass matrix of the synthesized material.

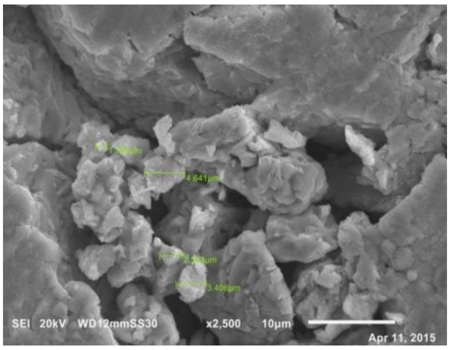

Fig.1: SEM images of $Se_{90}Cd_6Sb_4$ glassy alloys at 2500× magnification.

The elemental compositions of $Se_{90}Cd_6Sb_4$Glassy alloy were checked by energy despersive X-ray analysis (EDAX). The obtained percentage of the composition is $Se_{93}Cd_2Sb_5$as shown in Fig.2. EDAX analysis indicates the absence of impurity elements in the studied coposition.

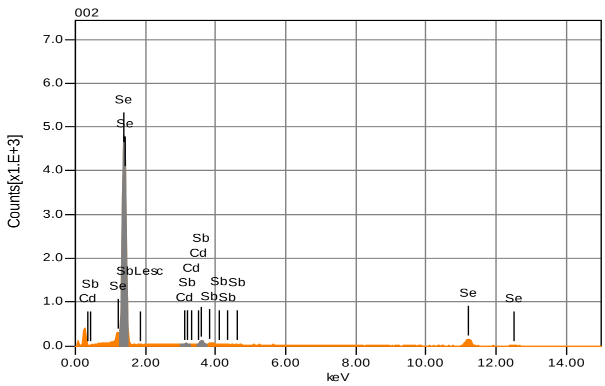

Fig.2: Energy dispersive X-ray analysis EDAX for $Se_{90}Cd_6 Sb_4$ glassy alloy.

3.2 Dielectric properties

Under dielectric studies, the electrical property of a material is studied as a function of frequency and temperature. Dielectric analysis helps to define, two fundamental electrical characteristics of materials. First the capacitive insulating nature, which represents its ability to store electrical charge and second the conduction nature, which represents its ability to transfer electric charge. In the succeeding section proper attention has been paid to investigate the dielectric properties of $Se_{90}Cd_6Sb_4$ glassy alloy in the frequency range 5×10^2Hz - 1×10^5Hz and in temperature range 303-328K. As a general features of the obtained results, the frequency and temperature dependence of dielectric constant (ϵ') and dielectric loss (ϵ'') are investigated.

3.2.1 The frequency and temperature dependences of dielectric constant (ϵ') and dielectric loss(ϵ")

Under dielectric measurement electrical properties of a material is measured as a function of frequency and temperature. This analysis reveal two fundamental electrical properties of materials, first the capacitive (insulating nature) which gives its ability for electrical charge storage and second the conduction nature which represent its ability to transfer electrical charge. However using these analysis the dielectric constant ε' and dielectric loss ε" of a material can be determined. Figure 3 shows the frequency dependence of dielectric constant (ε') of $Se_{90}Cd_6Sb_4$ glass alloy at different temperature.

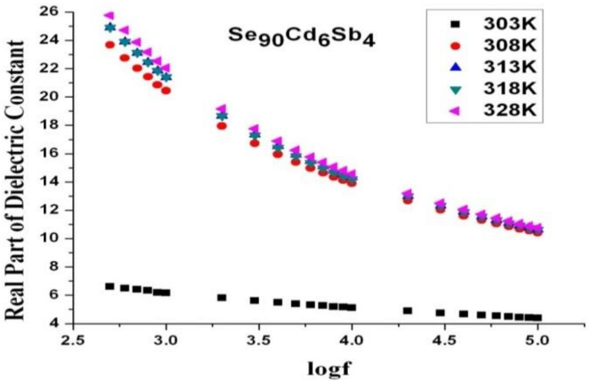

Fig.3: Variation of real part of dielectric constant with logf for $Se_{90}Cd_6Sb_4$ at different temperature.

It has been observed that ε' decreases with frequency and increases with temperature. The values of dielectric constant (ε') at different frequency and temperature are calculated and listed in table 1. The decrease of ε' with frequency can be attributed to the fact that at low frequencies ε' for polar material is explained by contribution of multi component of polarizability viz deformational (electronic and ionic) and relaxation (orientational and interfacial) polarization. The sum of above four type of polarization gives the total polarization of dielectric materials [28].

First of all electronic polarization arises due to displacement of valence electrons with respect to positive nucleus. Such type of polarization appears at frequencies upto 10^{16}Hz. The second type is the ionic polarization which appears due to displacement of positive and negative ions with respect to each other. Maximum frequency for ionic polarization is 10^{13} Hz. The third type is the dipolar polarization which appears in the materials having molecules with permanent electric dipole moments capable of changing orientation into the direction of applied electric field. Such polarization appears at frequencies upto 10^{10} Hz. The last one is the space charge polarization which appears due to the impedance mobile charge carriers by interfaces. Such type of polarization typically occurs in the frequency range 1-10^3 Hz. The ionic polarization does not play an important role in the total polarization. The orientational polarization decreases with increase in frequency because it takes more time then electronic and ionic polarization. This decreases the value of dielectric constant ε' with increase in frequency which ultimately reaches a constant value at higher frequency range, which correspond to interfacial polarization.

On the other hand the increase in ε' with temperature can be attributed to the fact that orientation polarization is dependent on thermal motion of molecule therefore, at low temperature dipoles can not orient themselves. With the increase in temperature there is favorable condition for orientation of dipoles, which increases the value of orientational polarization and ultimately results into increase of dielectric constant ε' with temperature.

Table 1.Values of dielectric constant (ε') of $Se_{90}Cd_6Sb_4$ at different frequencies and temperatures.

$Se_{90}Cd_6Sb_4$	Dielectric Constant (ε')			
	1×10^3Hz	1×10^4Hz	5×10^4Hz	1×10^5Hz
303K	6.16	5.11	4.58	4.38
308K	20.40	13.90	11.30	10.40
313K	21.38	14.30	11.60	10.60
318K	21.39	14.20	11.50	10.60
328K	22.04	14.56	11.71	10.77

Figure 4 shows the frequency dependence of dielectric loss (ε") of $Se_{90}Cd_6Sb_4$glassy alloy at different temperatures.

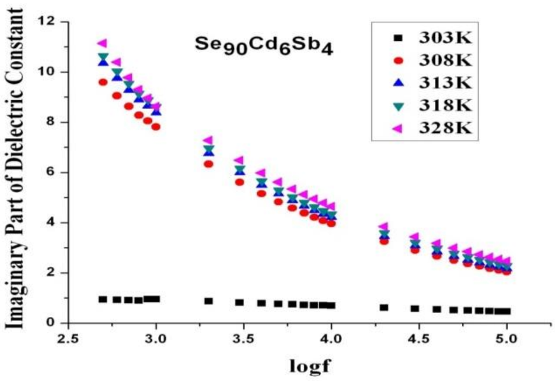

Fig.4: Variation of imaginary part of dielectric constant with logf for $Se_{90}Cd_6Sb_4$ at different temperature.

It has been observed that ε" decreases with frequency and increases with temperature. The values of dielectric loss (ε") at different frequencies and temperatures are calculated and listed in table 2.

Table 2.Values of dielectric loss (ε") of $Se_{90}Cd_6Sb_4$ at different frequencies and temperatures.

$Se_{90}Cd_6Sb_4$	Dielectric Loss(ε")			
	1×10^3Hz	1×10^4Hz	5×10^4Hz	1×10^5Hz
303K	0.95	0.68	0.514	0.45
308K	7.81	3.96	2.50	2.04
313K	8.38	4.21	2.66	2.17
318K	8.60	4.33	2.77	2.27
328K	8.63	4.65	2.99	2.47

The decrease of ε" with frequency can be attributed to the fact that, at low frequencies, the value of ε" is due to migration of ions in the material. At moderate frequencies ε" is due to the contribution of ion jumps, conduction loss of ion migration and ion polarization losses. At high frequencies ion vibration may be the only source of dielectric loss and therefore ε" has the minimum value [29].

On the other hand the increase of ε" with temperature can be explained according to steveles [30] who divided the relaxation phenomenon into three parts; first conduction losses, second dipole losses and third vibrational losses. When temperature is low it is found that conduction losses have minimum value and its value increases with increase in temperature which ultimately results into increase of ε" with temperature. The characteristic of low dielectric constant and dielectric loss with high frequency for given sample suggest that the sample possess enhanced optical quality with lesser defects and this parameter is of vital importance for various nonlinear optical materials and their applications in devices.

3.3. Frequency and temperature dependence of AC conductivity

Total conductivity of the material is the sum of a.c. and d.c. conductivity. Therefore a.c. conductivity $\sigma_{ac}(\omega)$is expressed as[31,32]

$$\sigma_{ac}(\omega)= \sigma_t(\omega)-\sigma_{dc} \quad (4)$$

where,$\sigma_t(\omega)$ is the total conductivity and σ_{dc} represents d.c. conductivity. Since d.c. component σ_{dc} is negligibly small as compared to $\sigma_t(\omega)$ in the studied sample, therefore $\sigma_t(\omega)$ is considered to be $\sigma_{ac}(\omega)$. The variation of $\sigma_{ac}(\omega)$ with frequency in the range 5×10^2Hz - 1×10^5Hz has been investigated for the temperature range 303K-328K. Variation of $\sigma_{ac}(\omega)$ with frequency at constant working temperature has been plotted in fig.5. From fig.5 it is evident that $\sigma_{ac}(\omega)$ increases linearly with frequency at a constant working temperature.

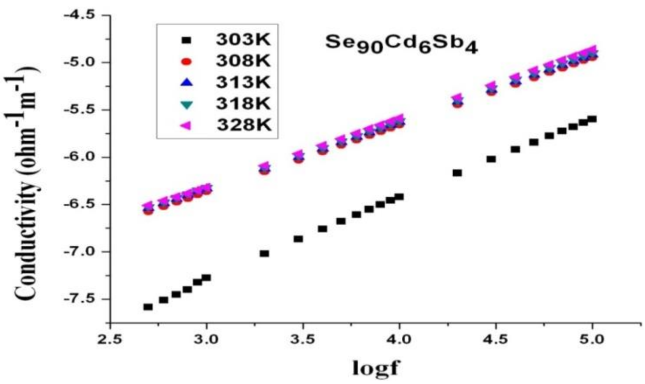

Fig.5: Frequency dependence of $\sigma_{ac}(\omega)$ for $Se_{90}Cd_6Sb_4$ glassy alloy at different temperature.

Generally a.c. conductivity in semiconductors is given as[32,33]

$$\sigma_{ac}(\omega)=A\omega^s \quad (5)$$

where, A is a constant, ω is the angular frequency and s is the frequency exponent. Value of frequency exponent s is obtained from the slopes of a.c. conductivity versus frequency plots. The dependence of frequency exponent s with temperature for the studied composition is shown in fig.6. It has been observed that s has values in the range 0.876 to 0.68, which is less then unity and decreases with increase of temperatures.

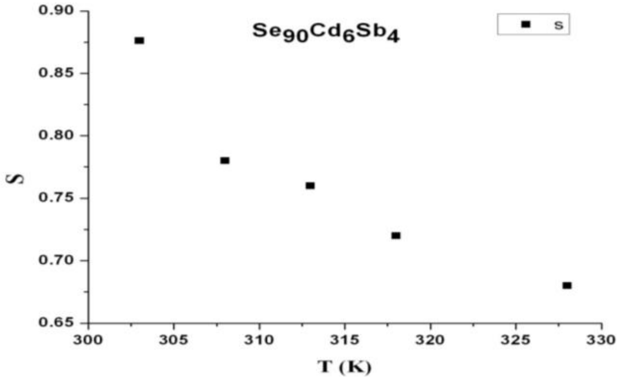

Fig.6: Temperature dependence of the frequency exponent s for $Se_{90}Cd_6Sb_4$ glassy alloy.

The observed behavior of s are in agreement with the correlated barrio hopping model(CBH) [33-35], such behavior have also been reported by other workers[36-39].

According to CBH model, the conduction occurs via bipolaron hopping process where two polaron simultaneously hop over the potential barrier between two charged defect states D^+ and D^- and barrier hight is correlated with the inter-site separation via a columbic interaction. Shimakava [40] further proposed that at higher temperature D^o states are produced by thermal excitation of D^+ and D^- states and a single polaron hopping (which includes one electron hopping between D^o and D^+ and hole between D^o and D^-) becomes dominant.

The frequency exponent s is given by the expression[34,41]

$$s=1-(6K_BT/W_m) \qquad (6)$$

Where, K_B is Boltzmann constant, T is absolute temperature,W_m is the barrier height which is energy needed to take two electrons from the D^- state to the conduction band in the absence of D^+centres.

Equation (3) can be arranged as

$$\alpha = 1-s = 6K_BT/W_m \qquad (7)$$

Knowing the value of s, $W_m$has been evaluated using eq.(7) for the studied composition. For the determination of W_m the parameter α is plotted as a function of temperature as shown in fig.(7). The slope of obtained straight line gives us the value of W_m and is found to be equal to 0.12eV. The obtained value of W_m is related to optical band gap of the material [42].

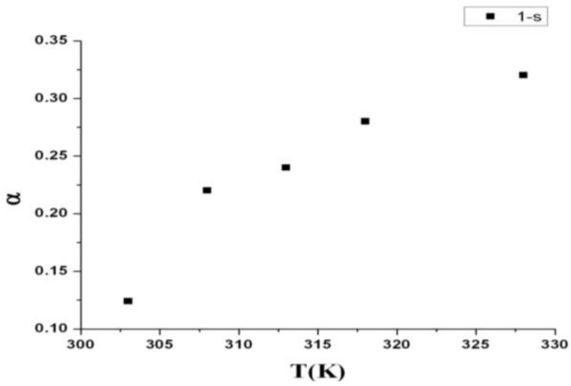

Fig.7: Temperature dependence of the value α for $Se_{90}Cd_6Sb_4$ glassy alloy.

Figure 8 shows the variation of $\sigma_{ac}(\omega)$ versus 1000/T for studied composition at different frequency values.

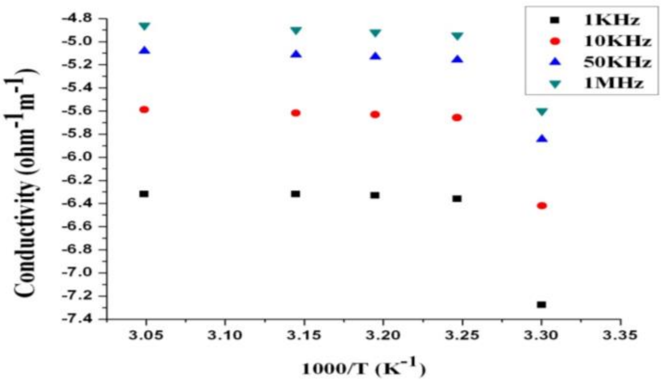

Fig.8: Temperature dependence of $\sigma_{ac}(\omega)$ for $Se_{90}Cd_6Sb_4$ glassy alloy.

It is evident from the figure that a.c. conductivity decreases non-linearly with reciprocal of temperature. From the shape of the curve it has been observed that the curve has two regions with different activation energies. The first region is week temperature dependent on the other hand second region is strongly temperature dependent region. Thus $\sigma_{ac}(\omega)$ can be expressed as sum of the two different conduction mechanism [43-46]

$$\sigma_{ac}(\omega)=\sigma_f+\sigma_s \quad (8)$$

Where, σ_f corresponds to weak temperature dependent mechanism which is attributed as due to hopping between localized state at fermi level.σ_s corresponds to strong temperature dependent component. Our present result is in good agreement with the recently reported results for other amorphous materials [43-46,38-39].

4. Conclusion

$Se_{90}Cd_6Sb_4$ chalcogenide glassy alloy has been prepared by melt quench technique. The prepared sample has been characterized by SEM, EDAX and impedance spectroscopic technique. Both dielectric constant ε' and dielectric loss ε" are found to have decreasing trend with increase in frequency and increasing trend with increase in temperature. It is found that both ε' and ε" show frequency dispersion at low frequency and show low values at high frequencies. The temperature and frequency dependence of a.c. conductivity $\sigma_{ac}(\omega)$ are studied in the frequency range5×10^2Hz - 1×10^5Hz and temperature range 303-328K. A.C. conductivity has been found to obey the power law ω^s, where $s\leq1$. $\sigma_{ac}(\omega)$ increases with increase of frequency in the measured temperature range while s decreases with increase of temperature. These results are in good agreement with the correlated barrier hopping (CBH) model. Value of maximum barrier height was estimated from the data of dielectric loss, which is in good agreement with the theory of hopping of charge carriers over a potential barrier between charge defect states. These calculations are performed according to Guintini equation based on Elliot model of chalcogenide glasses. The low value of ε' and ε" at high frequencies suggest that the prepared alloy possess enhanced optical quality with lesser defect and is therefore, suitable for nonlinear optical materials applications.

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References

[1] V.S.Shiryaev, C.Boussard-Pl'edel, P. Houizot, T. Jouan, J.L. Adam, J. Luacas, J. Mater. Sci.Eng. B **127,** 138 (2006).
[2] D. K. Dwivedi, N. Shukla, H. P. Pathak, K. Singh, Am. J. Mater. Sci.Eng.**2(2)**, 13 (2014).
[3] D. K. Dwivedi, H. P. Pathak, R. K. Shukla, A. Kumar, Optik Int. J. Light Electron Opt. **126**, 635 (2015).
[4] X.H. Zhang, Y. Guimond, Y. Bellec, J. Non-Cryst. Solids **326–327**,519 (2003).
[5] Y.Isbi,S.Sternklar,E.Garnet,V.Lyubin, M.Klebanov, A.Lewis, Opt.Commun. **171**, 219 (1999).
[6] H. P. Pathak, Nitesh Shukla, Vipin Kumar, D. K. Dwivedi, Optical Materials **52**,69 (2016).
[7] A.S.Arico,D.Silvestro,P.L.Antonucci,N.Giordano,V.Actonucci,J. Adv. Perf. Mater. **4**,115 (1987).
[8] J.S. Somghera,I.D.Agarwal,L.B.Shaw,L.E.Busse,V.Nauyen,P.Pureza,S.Bayya, F. Kung, J. Opt. Elect. Adv. Mater. **3**, 627(2001).

[9] D. K. Dwivedi, N. Shukla, H. P. Pathak,Materials Today: Proceedings **2(4-5)**, 2862(2015).
[10] A.K.Zakery,S.R.Elliot,J.Non-Cryst.Solids**330**, 1 (2003).
[11] D. Lezal,J.Pedlikova,J.Zavadil, Chalcogenide Lett.**1**, 11 (2004).
[12] S.A. Khan, M.Zulfequar, M.Hussain, Physica B **324**, 336 (2002).
[13] Suresh Kumar Sharma, R.K. Shukla, A. Kumar, Physica B **481**, 144 (2016).
[14] A Sharma, N Mehta,A Kumar, J. Mater. Sci., **46(13)**, 4509 (2011).
[15] M A M Khan, M Zulfequar, M Hussain, Curr. Appl. Phys., **2(5)**, 401 (2002).
[16] R M Mehra, S Kohli, APundir, V K Sachdev, P C Mathur, J. Appl. Phys.**81**, 7842 (1997).
[17] S Murugavel, S Asokan, Phys. Rev. B**58**, 4449 (1998).
[18] LA Wahab, Mater. Chem. Phys.**80(2)**, 401 (2003).
[19] S.A. Khan, M. Zulfequar, M. Hussain, Solid State Commun. **123**, 463 (2002).
[20] P. Sharma, S.C. Katyal, Physica B**403**, 3667 (2008).
[21] 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).
[22] M AAfifi, A E Bekheet, E AElwahhab, H E Atiya, Vacuum**61**, 9 (2001).
[23] A Abdel Aal, Egypt. J. Solids **29(2)**, 303 (2006).
[24] B S Rao, B R Kumar, V R Reddy, T S Rao, G V Chalapathi, Chalcogenide Letters **9(12)**, 517 (2012).
[25] H E Atyia, N A Hegab, M AAffi, M I Ismail, Journal of Alloys and Compounds **574**, 345 (2013).
[26] A.N.R. Long, Adv. Phys.**31**, 553 (1981).
[27] Nitesh Shukla, D.K.Dwivedi, Journal of Asian Ceramic societies, Accepted date (2016)19 February.
[28]M Barsoum "Fund. Ceram."McGraw Hill, New York (1977) p 543.
[29] N A Hegab, A E Bekheet, M A Afifi, L A Wahaba, H A Shehata, J. Ovonic Res.**3**, 71 (2007).
[30] T.M. Stevels, The Electrical Properties of Glasses, Handbuch der Physik, Ed. Flugged, Springer, Berlin 1957, 350.
[31] A.K. Jonscher, Nature **267**, 673 (1977).
[32] S.R. Elliott, Adv. Phys. **36**, 135 (1987).
[33]A.K Jonscher, Nature **267**, 673 (1977).
[34] S.R. Elliott, Philos. Mag. B **36**, 1291 (1977).
[35] A.R. Long, Adv. Phys. **31**, 553 (1982).
[36] A.M. Farid, H.E. Atyia, N.A. Hegab, Vacuum **80**,284 (2005).
[37] R.S. Kundu, K.L. Bhatia, N. Kishore, Philos. Mag. B **72**, 513 (1995).
[38] N.A. Hegab, H.M. EL-Mallah, ActaPhysicaPolonica A**116(6)**,1048 (2009).
[39]MohsinGanaie, M. Zulfequar, ActaphysicaPolonicaA**128(1)**, 59 (2015).
[40]K. Shimakawa, J. Phys. (Paris)**42C4**, 621 (1981).
[41] S.R. Elliott, Philos. Mag. B **37**, 553 (1978).
[42] R.A. Street, N.F. Mott, Phys. Rev. Lett.**35**, 1293 (1975).
[43] K. Shimakawa, Philos. Mag. B **46**, 123 (1982).
[44] H.K. Rockstad., Solid State Commun.**7** (1969) 1507.
[45] H.K.Rockstad., Solid State Commun.**7** (1971) 2233.
[46] H.K. Rockstad., J. Non-Solids **2** (1970) 192.