MODIFICATIONS IN BAND GAP & DC CONDUCTIVITY OF TERNARY CHALCOGENIDE GLASSES BY ADDITION OF LEAD

VIBHAV K. SARASWAT[a*], NAVEEN TANWAR[b], N.S. SAXENA[c]
[a]*Department of Physics, Oorja Mandir, Banasthali University, Banasthali – 304022 Tonk, Rajasthan, India.*
[b]*Deptt. of Physics, Ahir College, Rewari, Haryana, India.*
[c]*5-6, Vigyan Bhawan, University of Rajasthan, Jaipur- 302004 Rajasthan, India*

Effect of Lead (Pb) addition on Band gap (E_g) and Volume conductivity (σ) of Se-Te-Pb semi-conducting glasses has been discussed in this paper. The above said characterizations have been performed as a function of concentration of Pb at. wt.% proportion i.e. the composition of the glasses. Also, the temperature dependence of volume conductivity has been studied. These Chalcogenide glasses were prepared using rapid cooling of melt (Melt quenching) technique. The amorphous nature of these glasses has been confirmed by XRD patterns. Keithley Electrometer/High resistance meter 6517A was used in its FVMI mode to record I_V characteristics at different temperatures. Variation in conductivity, derived from I_V curves, as a function of composition of sample is explained on the basis of bonds formed in the system. Additionally, the Poole-Frenkel conduction mechanism has also been verified in order to investigate the good agreement with the established fact that most of Chalcogenide glasses obey Poole-Frenkel conduction mechanism. Absorption spectra were recorded using Ocean Optics USB2000 spectrophotometer in visible region. Analysis of these absorption spectra using Tauc relation reveals that this system is semiconducting and direct band gap material in nature. The observed results are found to be in good agreement with each other.

(Received August 28, 2012; Accepted October 3, 2012)

Keywords: Lead chalcogenide, DC volume conductivity, Absorption spectra, Poole-Frenkel conduction.

1. Introduction

To the best of our knowledge, every sector of scientific field, especially in material science, has gained remarkable improvements. Despite of several existing semiconducting materials (e.g. Si, Ge, GaAs and many more) and oxide semiconductors, the amorphous semiconductors or non oxide glasses have also proved their utility at technological level due to variety of special optical, electrical, dielectrical and thermo-physical properties [1-4]. Chalcogenide glassy alloys can be made easily either conventional or other suitable techniques by adding the one or more appropriate elements. Chalcogenide glassy materials are applicable in various technologies owing to adequate amorphous semiconducting features [5, 6].Ternary lead chalcogenide glasses have been interesting candidates among the researchers due to their potential application [7-12] in recent years. As per the evidences surveyed, very few attempts have been made to study chalcogenide glasses with one of the component as Pb. It may be due to the fact that lead is the last element in radioactive series, which is most stable, or lead is the one with which the formation of glass is most difficult deal. This motivated us to carry out dc electrical conductivity and optical band gap investigations on $Se_{85}Te_{15-x}Pb_x$ (x = 1, 2, 3 & 4) glasses.

[*]Corresponding author: vibhav.spsl@gmail.com

2. Experimental Techniques & Methods

Out of many well-known methods for glass preparations, Rapid cooling of melt technique [13] was used to obtain the series of glass with composition $Se_{85}Te_{15-X}Pb_X$ (X = 1, 2, 3 & 4). The synthesis conditions are widely varied: they depend on the glass composition, glass forming ability, and melting temperature of the constituent elements etc. Chalcogenide glasses belong to substances which have an incongruent melting point, exhibit a high partial vapor pressure during melting and are susceptible to oxidation and hydrolysis and therefore, the synthesis must be carried out in sealed quartz ampoule. The synthesis conditions are widely varied: they depend on the glass composition, glass forming ability, and melting temperature of the constituent elements etc. The necessary chemical and physical purity of the prepared glass should be about 10^{-5} mol% for the presence of OH, SH, SeH groups and the concentration of physical defects in the range $10^2 – 10^3$ /cm^3 [14]. Hence, the mixtures sealed in quartz ampoule under a pressure of 10^{-5} Torr, were slowly heated in a furnace upto 1100K for about 10-12 hrs. The heating rate was kept 3-4 K/min. During heating ampoules were frequently shaken to ensure the homogeneity of the melt. Quenching has been done in ice cooled water. The obtained ingots were taken out and gently grinded to fine powder [15].

The amorphous nature of these glasses was confirmed by X-ray diffraction patterns. The Bruker XRD machine was equipped with Cu K_α radiation (λ = 1.5406 Å). Pellets of 12 mm diameter and thickness ≈1mm were prepared, using a hydraulic pressure machine, under a load of 5 Tons to study the I_V characteristics and their temperature dependence in bulk. Keithley Electrometer/High resistance meter 6517Awas used to record I_V characteristics at different temperatures in its FVMI (Force Voltage & Measure Current) mode [16]. Further these curves were used to calculate dc conductivity (/Ω.mm) at 5V.

In order to study the band gap variation with respect to at.wt.% Pb content in these glasses, thin films [17] were deposited on a glass substrate using flash evaporation technique. These films were annealed at 323K, below its probable glass transition temperature for about 1 hr. The absorption spectra of these films were recorded using Ocean Optics USB 2000 spectrophotometer at room temperature. Further, these spectra were used to plot variation of $(\alpha h\nu)^2$ with respect to hν according to Tauc relation [18]. Finally, the band gap was calculated by these curves.

3. Results and discussions

The amorphous nature of obtained glasses was confirmed by XRD patterns. The absence of any sharp peak confirms amorphous nature. The large hump observed at lower angles is suggestive of the fact that some short range ordering is present in the system. Figure 1 shows the XRD patterns of $Se_{85}Te_{15-X}Pb_X$ (X = 1, 2, 3 & 4) glasses.

The pellets were used to record I_V characteristics at different temperatures. The increase in current with increase in temperature confirms the semi-conducting nature of these glasses.

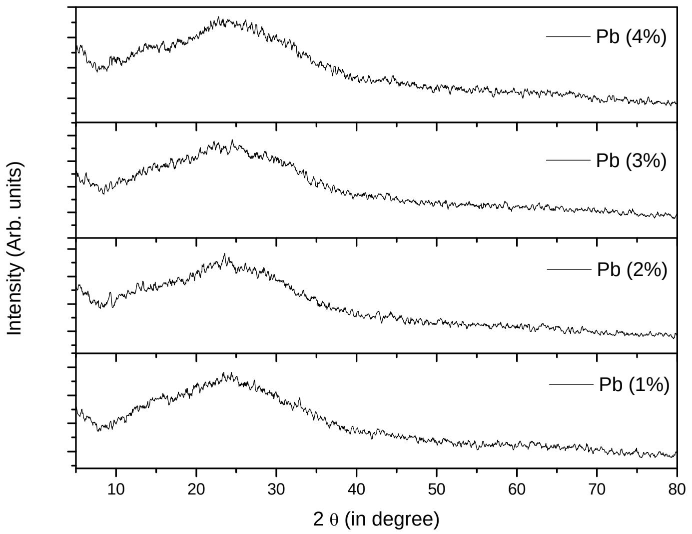

Fig.1: XRD patterns of $Se_{85}Te_{15-X}Pb_X$ (X = 1, 2, 3 & 4) glasses.

These I_V curves were used to calculate dc conductivity for 5V of these glasses [19]. Fig. 2 shows the I_V characteristics of $Se_{85}Te_{11}Pb_4$ glass at different temperatures as a representative case. Figure 3 shows the variation in conductivity of all candidates of the series under test at different temperatures as a function of Pb content in the sample.

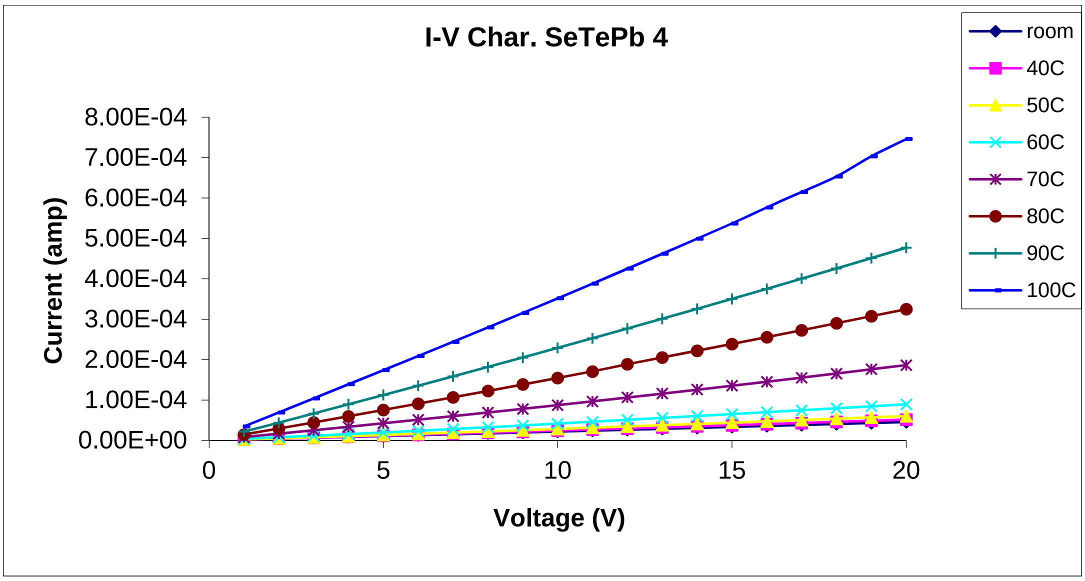

Fig.2: I_V characteristics of $Se_{85}Te_{11}Pb_4$ glass at different temperatures.

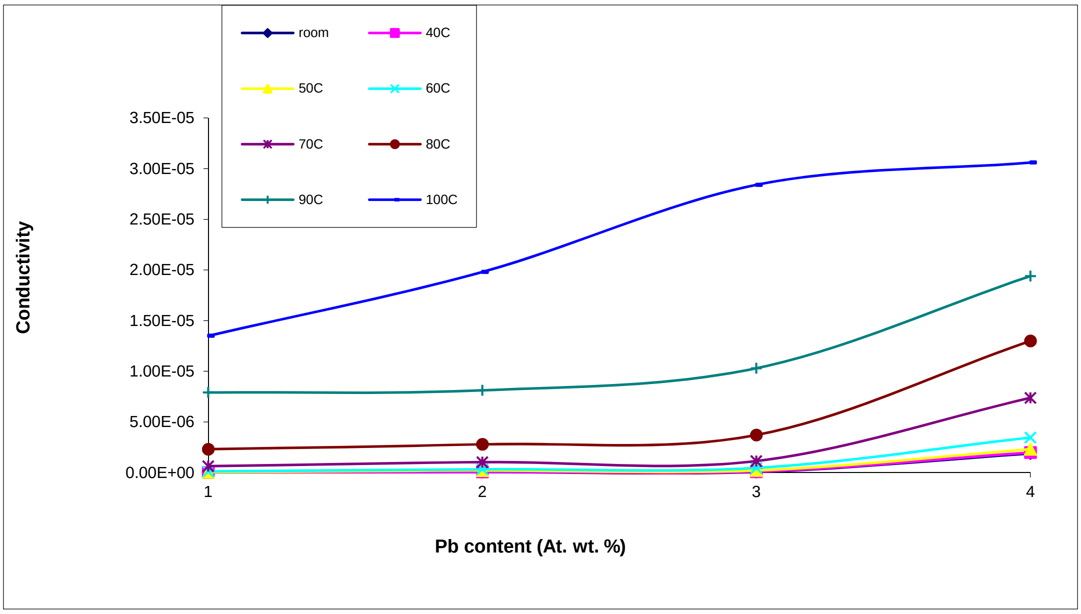

Fig.3: Conductivity vs Pb content for $Se_{85}Te_{15-X}Pb_X$ (X = 1, 2, 3 & 4) glasses at different temperatures.

The variation in conductivity with respect to Pb content (at.wt.%) in Se-Te-Pb system, as shown in figure 3, it is clear that the conductivity increases with the increase in temperature and also with the increase in Pb content in the sample. The conductivity curves retain its trend at all temperatures. This behavior of conductivity with temperature confirms the semi-conducting nature of the samples. The variation in conductivity with the respect to the Lead content in the specimen could be explained on the basis of structural changes and the bond formation occurring in the system during the addition of Pb in ternary glass.

In glassy Se, about 40% of the atoms have ring structure and 60% of the atoms are bounded as polymeric chains [20]. Tellurium (Te) enters as co-polymeric chain and tends to reduce the number of Se_8 member rings. Simultaneously, it increases the number of Se and Te atoms in the chain structure. The addition of Pb atoms in Se-Te system leads to the formation of bonds between Se & Pb and Te & Pb. The bond energy of Se-Pb bond is 304.1 kJ/mol and Te-Pb bond is 252.0 kJ/mol [21]. Since Pb is added at the cost of Te which increases the probability for the formation of Se-Pb bonds i.e. concentration of Se-Pb bonds increases with the increase of Pb content in SeTePb system resulting the more compact (theoretically dense) structure. Hence the conductivity increases with the increase of Pb content in the system.

There are plenty of evidences that Chalcogenide glasses obey Poole-Frenkel conduction mechanism [22]. In order to verify Poole-Frenkel conduction mechanism in Se-Te-Pb system, ln(I) vs $V^{1/2}$ plots were drawn at different temperatures as shown in figure 4 ($Se_{85}Te_{11}Pb_4$: representative case). Linearity of these plots suggests that the conduction mechanism in presented series is of Poole-Frenkel type. The observed linearity could be due to the absence of space charge resulting in a uniformity of field distribution between electrodes. The current in case of Poole- Frenkel effect will practically remain unchanged when polarities of the electrodes are reversed. This is due to the fact that current does not depend upon the potential barrier at the interface [19].

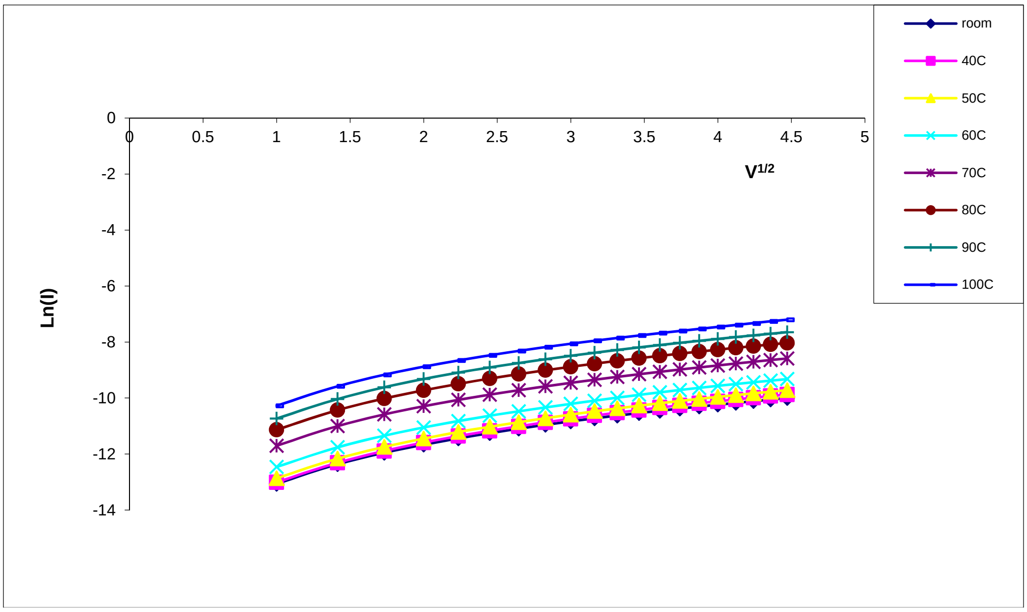

Fig.4: Verification of Poole-Frenkel conduction mechanism for $Se_{85}Te_{11}Pb_4$ glass.

In order to investigate optical band gap in the glassy series under test, absorption spectra were recorded at room temperature. Figure 5 shows the absorption spectra for $Se_{85}Te_{15-X}Pb_X$ glassy films, deposited on glass substrate. These spectra were further analyzed and $(\alpha h\nu)^2$ were plotted against hν according to Tauc relation [12] in order to calculate the band gap. Table 1 lists the band gap values (in eV) for different candidates of the presented series. It is quite evident from table 1 that as one increases Pb content in the system, band gap decreases. Since, Pb is metallic in nature; its addition in the system decreases the band gap. This decrease in band gap also supports increase in conductivity (figure 3) and the I_V measurements (figure 2).

Table 1: Band gap of $Se_{85}Te_{15-x}Pb_x$ (x = 1, 2, 3 & 4) glasses.

S. No.	**Composition of glass**	**Band gap (eV)**
1.	$Se_{85}Te_{14}Pb_1$	2.189
2.	$Se_{85}Te_{13}Pb_2$	2.126
3.	$Se_{85}Te_{12}Pb_3$	2.084
4.	$Se_{85}Te_{11}Pb_4$	2.035

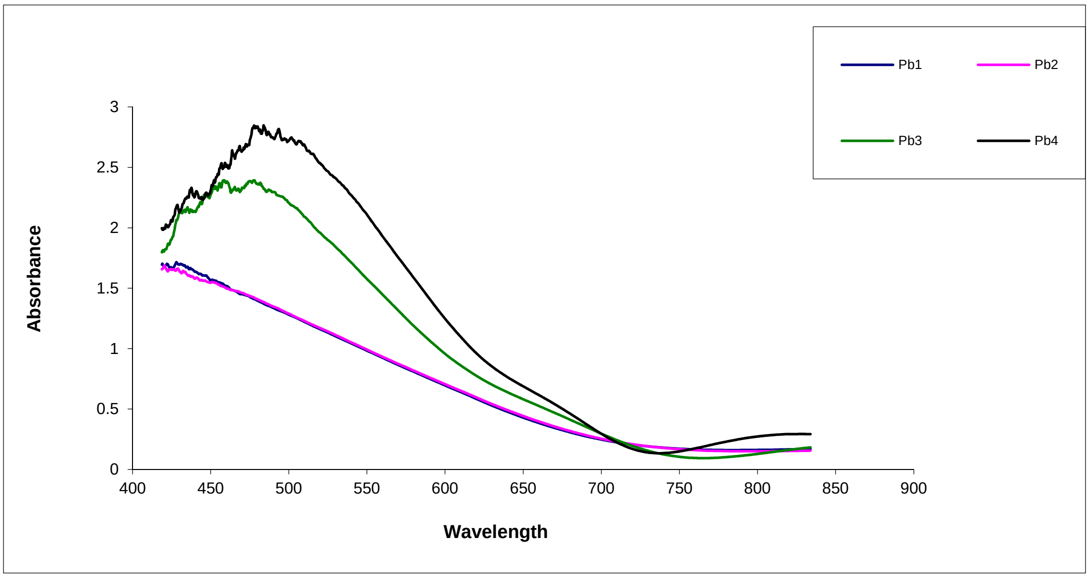

Fig.5: Absorption spectra of $Se_{85}Te_{15-x}Pb_x$ (x = 1, 2, 3 & 4) glasses.

4. Conclusions

The detailed discussions in the paper can conclude the facts that the presented series of Chalcogenide glasses is semi-conducting in nature. The increase in Pb content in the system forces the system towards more theoretically dense structure i.e. system contains 4 at.wt% of Pb possesses highest concentration of Pb-Se bonds, bonds with highest bond energy. This fact, finally, supports the increase in conductivity in these glasses. The linearity in ln(I) vs $V^{1/2}$ curves are in good agreement with the fact that these glasses obey Poole-Frenkel conduction mechanism. Lastly, the band gap study confirms the existence of direct band gap in these glassy materials, and the decrease in band gap with the increase in Pb content supports the conductivity variation in presented series.

References

[1] Pamukchieva V., Szekeres A., Todorova K., Svab E. and Fabian M., Optical Materials **32,** 45 (2009).
[2] Mahmoud E. A., El-Samanoudy M. M. and Abd Rabo A. S., J. Phy. Chem. Solids **63,** 2003 (2002).
[3] Sharma J. and Kumar S., J. Alloys and Comp., **506,** 710 (2010).
[4] Gunti S. R., Asokan S., J. Non-Cryst. Solids **356,** 1637 (2010).
[5] Singh A.K., J. of Non-oxide Glasses, **3(1)**, 1 (2012).
[6] Sharma N., Shukla S., Sharma J., Kumar S., J. of Non-oxide Glasses, **3(4)**, 121 (2011).
[7] Wieder J., Aronson S., J. Non-Cryst. Solids, **33**, 405 (1979).
[8] Kumar A., Goel S., Phys. Rev. B, **3(11)**, 5635 (1987).
[9] Mahadevan S., Giridhar A., J. Non-Cryst. Solids, **110**, 118(1989).
[10] Clavaguera-Mora M.T., Baro M.D., Surinach S., Saurina J., J. Non-Cryst. Solids, **131**, 479(1991).
[11] Mahadevan S., Giridhar A., J. Non-Cryst. Solids, **152**, 42(1993).
[12] Maharjan N.B., Saxena N.S., Bhandari D., Imran M.M., Paudyal D.D., Bull. Mater. Sci., **23**, 369 (2000).

[13] Zarzycki Jerry, Material Science and Technology, Vol 9 Glasses and Amorphous Materials, Eds: R.W. Cahn, P. Haasen, E.J. Kramer, VCH, Weinheim, Germany, Chap. 2, p. 95, (1991).
[14] Lezal D., Pedlikova J., Zavadil J., Kostka P., Poulain M., J. Non-cryst. Solids, **326 327**, 47 (2003).
[15] Saraswat Vibhav K., Kishore V., Saraswat Y.K., Saxena N.S., AIP Conf. Proc. OPTICS'11, **1391**, 504 (2011).
[16] Solanki D., Kishore V., Saraswat P.K., Mittal A.D., Gangwar S., Saraswat Vibhav K., Chalcogenide Letters, **7(4)**, 263 (2010).
[17] Saraswat Vibhav K., Kishore V., Deepika, Sharma Kananbala, Sharma T.P., Chalcogenide Letters, **4(5)**, 61 (2007).
[18] Saraswat Vibhav K., Kishore V., Saxena N.S., Sharma K, Sharma T.P., Mishra A., J. Optoelectron. & Adv. Mat., **8(4)**, 1349 (2006).
[19] Saraswat Vibhav K., Singh K., Saxena N.S., Kishore V., Sharma T.P., Saraswat P.K., Current Applied Physics, **6**, 14 (2006).
[20] Predeep P., Saxena N.S., Saksena M.P., Kumar A., Phys. Status Solidi A, **23**, 156 (1996).
[21] David R.R., CRC Handbook of Chemistry and Physics, Chemical Rubber Publishing, Cleveland, Ohio, (1977).
[22] Abdel Latif R.M., Physica B, **254**, 273 (1998).