

Bonding of third additive with Se & Te alters DC conductivity of ternary ChGs

Abstract

Presented paper investigates the effect of Pb and Cd as third additive in Se-Te based ternary chalcogenide glasses (ChGs). These glassy samples, prepared by rapid cooling of melt technique, of SeTePb and SeTeCd have been chosen to study of dc volume conductivity in chalcogenide glasses. The chosen compositions ($\text{Se}_{70}\text{Te}_{30-x}\text{Cd}_x$ ($x = 1, 2, 3, 4$ & 5) and $\text{Se}_{85}\text{Te}_{15-x}\text{Pb}_x$ ($x = 1, 2, 3$ & 4)) have been confirmed as amorphous using XRD. Bulk sample profile has been selected to study the volume dc conductivity and pellets of desired dimensions have been prepared under load of 5 tons. I-V characteristics of these pellets have been recorded using Keithley Electrometer / High resistance meter 6517A at different temperatures. This instrument was used in FVMI (Force Voltage Measure Current) mode, which provides the facility of use of single instrument to apply voltage and measure the current through sample. The decreasing nature of resistance with temperature confirms the semi conducting behavior of these glasses. The variation in conductivity with respect to concentration of the third element in ternary glass could be explained on the basis of formation of bonds of higher energy in the systems under test, which leads the system towards more theoretically dense structure. The observed linearity in $\ln(I)$ vs $V^{1/2}$ curves, as per Jonschere and Hill relation, is suggestive of Poole-Frenkel type conduction in these glasses. The results are helpful in better conceptual understanding of physics for the conduction mechanism in such glasses and may be used for tailoring the end user application.

Keywords: chalcogenide glasses, semi-conducting glass, dc conductivity, poole-frenkel conduction

Volume 3 Issue 1 - 2019

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Received: August 04, 2018 | **Published:** February 01, 2019

Introduction

Selenium (Se) has proved its potential in wide commercial applications. Its device applications like switching, memory and Xeroxing etc. made it attractive. It also exhibits a unique property of reversible transformation.¹ This property makes it very useful in optical memory devices. But in pure state it has some disadvantages because of its short lifetime and low sensitivity. To overcome these difficulties certain additives are used and binary and ternary chalcogenide glasses are obtained e.g. the addition of small percentage of Sb is sufficient to cause crystallization of Se.²⁻⁴

Ternary chalcogenide glasses, with third additive as Pb and Cd, have been interesting candidates among the researchers due to their potential applications in recent years.⁵⁻¹⁰ To the best of my knowledge, very few attempts have been made to study chalcogenide glasses with one of the component as Pb and Cd. 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. The addition of Cd also shows some interesting behavior, but it is hard to form glass with Cd because of its ductility.¹¹ This motivated us to carry out dc electrical conductivity investigations on $\text{Se}_{85}\text{Te}_{15-x}\text{Pb}_x$ ($x = 1, 2, 3$ & 4) and $\text{Se}_{70}\text{Te}_{30-x}\text{Cd}_x$ ($x=1, 2, 3, 4$ & 5) glasses.

Experimental

Glassy powders of $\text{Se}_{70}\text{Te}_{30-x}\text{Cd}_x$ ($x = 1, 2, 3, 4$ & 5) and $\text{Se}_{85}\text{Te}_{15-x}\text{Pb}_x$ ($x = 1, 2, 3$ & 4) have been obtained by grinding the ingots, prepared by melt quenching technique.¹²⁻¹⁵ Chalcogenide glasses belong to group of substances which have an incongruent melting point, exhibit

a high vapour pressure during melting and are susceptible to oxidation and hydrolysis and therefore, the synthesis must be carried out in sealed evacuated quartz ampoule. The synthesis conditions are widely varied: they depend on the glass composition, glass forming ability (GFA) and highest temperature achieved during synthesis etc. The necessary chemical and physical purity^{12, 16-18} of the prepared glass should be about 10^{-5} mol% for the presence of OH, SH, SHe groups and the concentration of physical defects in the range 10^2 - 10^3 per cm^3 . So, keeping all these in mind, the high purity constituent materials, purchased from Alfa Aesar, were weighed according to at.wt. % and mixed. This mixture was sealed in a quartz ampoule, evacuated at $\sim 10^{-5}$ torr then this ampoule was heated up to 950°C for about 8 hours. During this period the ampoule was frequently shaken to achieve better homogeneity of melt. Finally, the ingot of the glassy material under test, after the ice-cooled water quenching of the ampoule, were obtained. So obtained ingots were grinded into fine powders.

The amorphous nature of these powders was confirmed by XRD ($\lambda = 1.5406 \text{ \AA}$) machine, Bruker DX8 Advance. As a representative case XRD patterns of SeTePb glasses are shown in Figure 1. The pellets of 12mm diameter and 1mm thickness were prepared at 5 Ton load using a hydraulic machine, Metrex, New Delhi. These pellets were used to record I-V characteristics at different temperatures. I-V characteristics were recorded using Keithley Electrometer/ high resistance meter 6517A. The pellet was sandwiched between two copper electrodes with the help of pressure contact arrangement in an indigenously designed sample holder for the purpose.¹² The same meter was used, in its FVMI mode, to apply the voltage across the sample and to measure the current.¹²

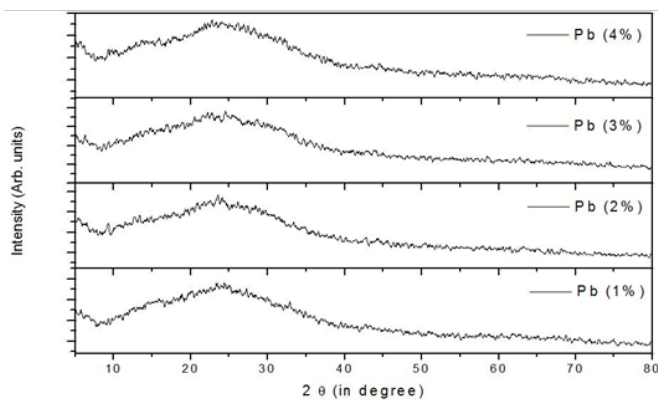


Figure 1 XRD patterns of $Se_{85}Te_{15-x}Pb_x$ ($x = 1, 2, 3$ & 4) glasses.

Results

As a case of representation, Figures 2 & 3 show the I-V characteristics of $Se_{70}Te_{25}Cd_5$ and $Se_{85}Te_{11}Pb_4$ at different temperatures, respectively. It is quite evident from figures 2 and 3 that the resistance decreases with the increase in temperature, which is suggestive of the fact that these samples are of semiconducting nature. It was also observed that the composition $Se_{70}Te_{25}Cd_5$ and $Se_{85}Te_{11}Pb_4$ show the maximum conduction at each temperature as compared to their counterparts in the respective series under test.

DC electrical conductivity has been calculated using a very basic relation¹²

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

where, symbols have their usual meanings.

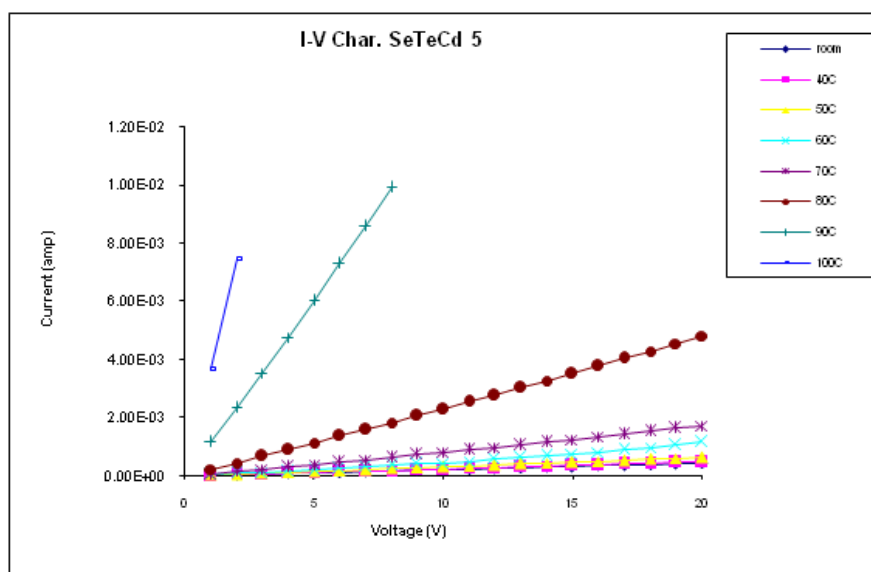


Figure 2 I-V Characteristics of $Se_{70}Te_{25}Cd_5$ glass at different temperatures

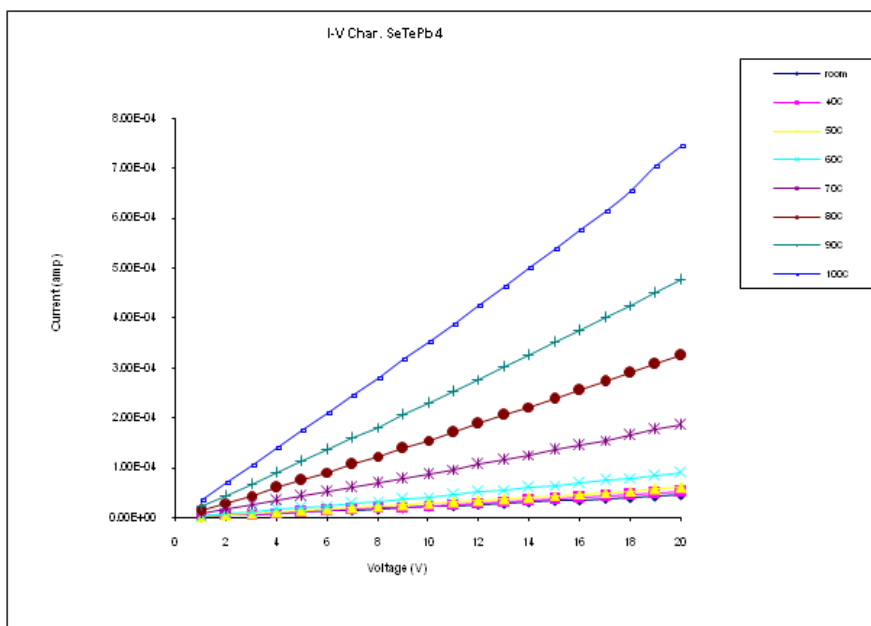


Figure 3 I-V Characteristics of $Se_{85}Te_{11}Pb_4$ glass at different temperatures.

Figures 4 & 5 show the variation in conductivity against the compositions of members of SeTeCd and SeTePb glassy series at different temperatures, respectively, as representative cases.

a consequence of relation between the current and the square root of the applied voltage as given by Jonschere¹⁹ for $Se_{70}Te_{25}Cd_5$ and $Se_{85}Te_{11}Pb_4$ glasses, respectively and the same trend has been obtained for other members of the series.

Figures 6 & 7 show the variation of $\ln(I)$ with respect to $V^{1/2}$,

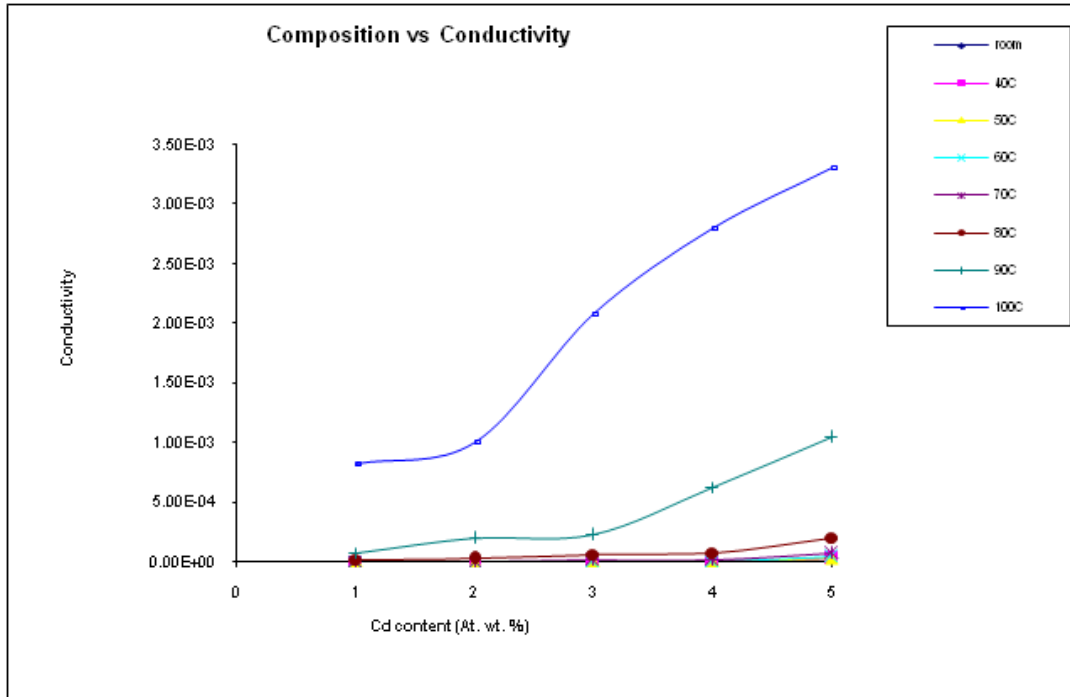


Figure 4 Variation of Conductivity ($\Omega.cm$) against composition at different temperatures.

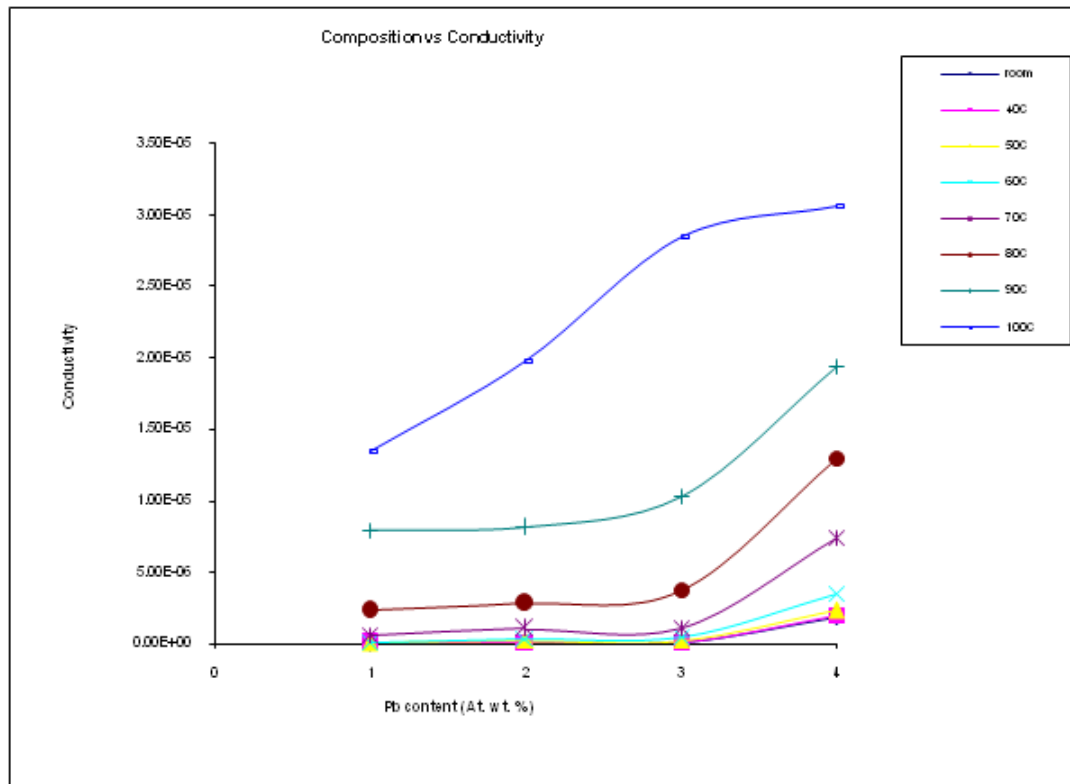


Figure 5 Variation of conductivity ($\Omega.cm$) against composition at different temperatures.

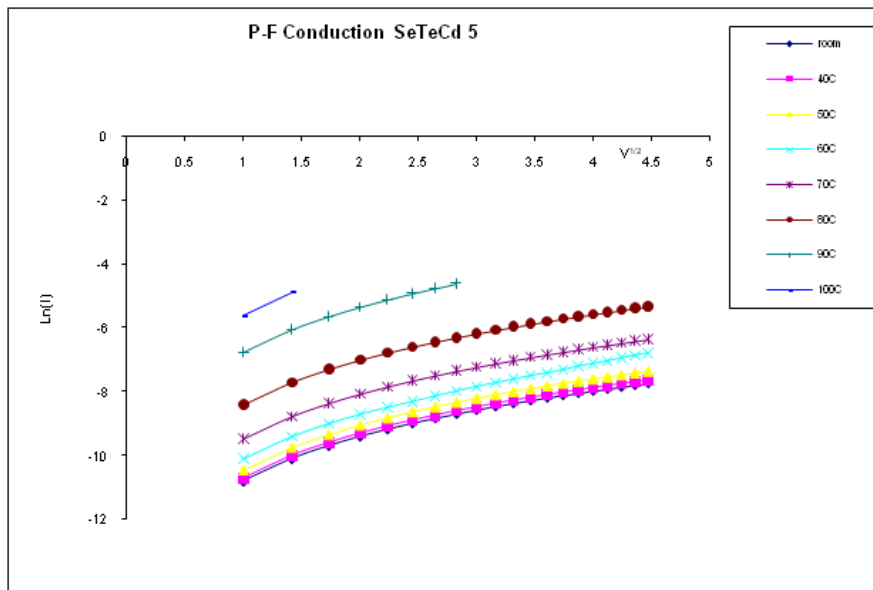


Figure 6 Verification of P-F conduction in $Se_{70}Te_{25}Cd_5$ glass at different temperatures.

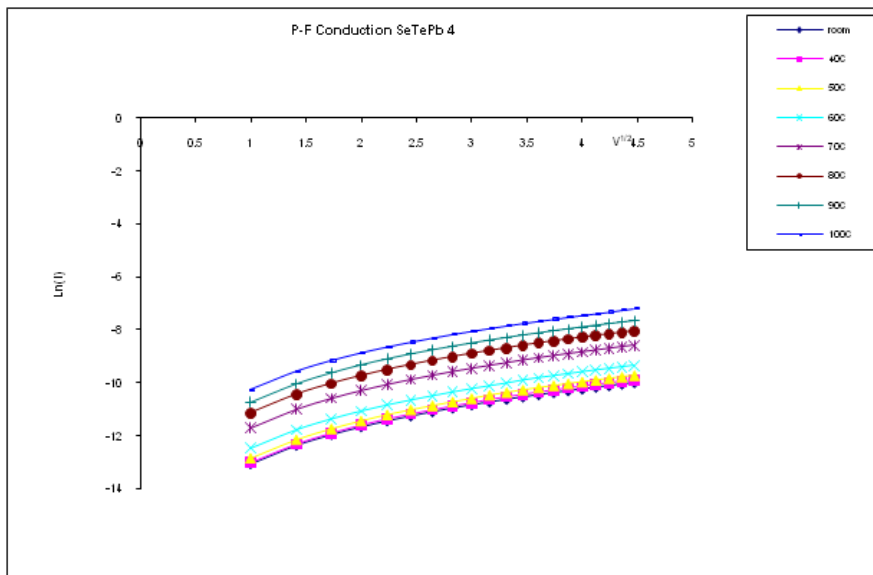


Figure 7 Verification of P-F conduction in $Se_{85}Te_{11}Pb_4$ glass at different temperatures.

Discussion

There are two fundamental processes occurring in such semi-conductors simultaneously namely, band conduction and hopping conduction. The band conduction occurs when the carriers are excited beyond the mobility edges into non-localized states at high temperatures. The excitation of the carriers into localized states at band edge causes the hopping conduction.^{12,20} Thus the total conductivity is given as,

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

where, σ_i is the intrinsic conductivity and σ_h is the hopping conductivity.

The variation in conductivity can be explained on the basis of bond formation between the third element (i.e. Cd or Pb, of the respective

series) and Se & Te. In glassy Se, about 40% of the atoms have ring structure and 60% of the atoms are bounded as polymeric chains.²¹ Tellurium enters as co-polymeric chains 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. Now, if one adds the third element to such system, the third element atoms; Cd or Pb in present case, in SeTe system leads to the formation of bonds between Se & Cd/Pb and Te & Cd/Pb. In first series, $Se_{70}Te_{30-x}Cd_x$ glasses, Cd is added at the cost of Te, which favours the formation of Cd-Se bonds in the system. The bond energy for Cd-Se bond is 127.6kJ/mol and for Cd-Te bond is 100.0kJ/mol²² and hence the concentration of higher energy bonds of Cd-Se is increased as one adds Cd in the system.

For the second series, $Se_{85}Te_{15-x}Pb_x$ glasses, the bond energy of Pb-Se bond is 304.1kJ/mol and Pb-Te bond is 252.0kJ/mol²³. Since, Pb is added at the cost of Te which increases the probability for the

formation of Pb-Se bonds i.e concentration of Pb-Se bonds increases with the increase of Pb content in SeTePb system resulting the more compact (theoretically dense) structure, also as in case of SeTeCd system. Hence, like first series, the conductivity increases with the increase of Pb content in the system.

Besides the formation of bond of higher energy, applied voltage, temperature and induced thermal effects due to higher voltage and other important factors contribute to the enhancement of electrical conduction in the samples.

Since chalcogenide glasses are semiconductors and the physical properties of these glasses strongly depend on various parameters, many researchers have floated ideas time to time to understand the conduction mechanism in such glasses. There are plenty of evidences that the conduction mechanism in chalcogenide glasses is of Poole-Frenkel type.^{3,6,12,24-28} To confirm this, results of this study have been used.

The linearity of these curves, Figures 6 & 7 are suggestive of the fact that these glasses obey the Poole-Frenkel conduction mechanism.²⁹ This linearity could be due to the absence of space charge resulting in a uniformity of field distribution between electrodes and practically, the current in such conduction remain unchanged if the polarities of the electrodes are reversed. This is due to the fact that current does not depend on the potential barrier at the interface.³⁰ The Poole-Frenkel conduction mechanism deals with the conduction in such materials where defect/impurity generated electrons & 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.^{12,20}

Conclusion

An important parameter, in electrical and sensing applications, DC electrical conductivity was calculated using I-V characteristics, recorded at different temperatures for both the glassy series i.e. $\text{Se}_{70}\text{Te}_{30-x}\text{Cd}_x$ and $\text{Se}_{85}\text{Te}_{15-x}\text{Pb}_x$ under test. It was found that the resistance decreases with the increasing temperature, which confirmed the semi-conducting nature of chosen samples. I-V characteristics and the conductivity variation with respect to the composition revealed that $\text{Se}_{70}\text{Te}_{25}\text{Cd}_5$ and $\text{Se}_{85}\text{Te}_{11}\text{Pb}_4$ composition are most conducting compositions among the samples in their respective series at all temperatures. The variation in conductivity with composition could be explained on the basis of bond formation between the third element (Cd/ Pb) and Se & Te. The formation of higher energy bonds eventually leads to theoretically dense system, which reflects as the increase in conductivity. A comparative study of figures 2 and 3 also reveals that SeTeCd system is more conducting than that of SeTePb system. The linearity observed in Figures 6 & 7 confirm that these glasses possess Poole-Frenkel conduction mechanism.

Acknowledgments

Author is thankful to Prof. N.S. Saxena, Emrt. Scientist, University of Rajasthan, Jaipur, India for his valuable suggestions and facilities provided at SPS laboratory, University of Rajasthan, Jaipur, India.

Conflicts of interest

Author declares that there is no conflicts of interest related to work presented in this paper.

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