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TITLE: Carrier Type Reversal in Pb sub x Ge sub 42-x Se58 and Pb20Ge sub y Se sub 80-y Glasses Exhibited in Thermal Diffusivity Measurements

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TITLE: International Workshop on Amorphous and Nanostructured Chalcogenides 1st, Fundamentals and Applications held in Bucharest, Romania, 25-28 Jun 2001. Part 1

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ADP011500 thru ADP011563

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CARRIER TYPE REVERSAL IN $Pb_xGe_{42-x}Se_{58}$ AND $Pb_{20}Ge_ySe_{80-y}$ GLASSES EXHIBITED IN THERMAL DIFFUSIVITY MEASUREMENTS

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Bulk $Pb_xGe_{42-x}Se_{58}$ ($x = 0, 2.5, 5, 7.5, 9, 10$ & 15 at.%) and $Pb_{20}Ge_ySe_{80-y}$ ($y = 17, 19, 21, 23$ and 25 at.%) homogeneous glasses have been prepared by melt quenching. The thermal diffusivity has been measured by the photoacoustic technique using a laboratory built non-resonant photoacoustic cell. The composition dependence of thermal diffusivity shows an anomalous behavior at $x = 9$ at% of Pb in $Pb_xGe_{42-x}Se_{58}$ and $y = 21$ at.% of Ge in $Pb_{20}Ge_ySe_{80-y}$ glasses, the composition at which a p- to n- conduction transition generally occurs. The reported electrical conductivity and optical band gap measurements are used to explain the minimum thermal diffusivity value obtained at the transition threshold in these glasses. These results have been explained with the Kolobov model on the basis of modification of the charged defect states due to the addition of metallic elements.

(Received May 31, 2001; accepted June 11, 2001)

Keywords: Disordered systems, Semiconductors, Thermodynamic

1. Introduction

The melt quenched chalcogenide glasses are semiconductors, which are useful in several potential applications like threshold and memory switching devices and the reverse phase change optical recording memories [1-3]. These glasses generally exhibit p- type electrical conduction due to the pinning of the Fermi level arising from the trapping of charge carriers at localized gap states [4,5]. Once it was believed that there is no possibility to prepare n- type chalcogenide bulk glasses. But in 1979, Tohge et al. [6,7] observed for the first time p- to n- type electrical conduction reversal in Bi doped Ge-Se glasses. After eight years, the same group [8] have observed the carrier type reversal in yet another system PbGeSe glasses. Since then, the mechanism of carrier type reversal has been in debate. There are two series in the PbGeSe glasses which exhibit p- to n- conduction change: one is $Pb_xGe_{42-x}Se_{58}$ (I) and the other is $Pb_{20}Ge_ySe_{80-y}$ (II). Apart from these two series, Murugavel and Asoken [9] have observed n-type conduction in $Pb_xGe_{42-x}Se_{48}Te_{10}$ glasses and Mehra et al. [10] have found the conduction change in $Pb_xIn_{25-x}Se_{75}$ glasses.

Over the past few years the photoacoustic (PA) technique has developed into a powerful tool for studying the optical and thermal properties of solids [11]. In PA technique [12], the sample to be studied is placed inside a closed cell containing air and a sensitive condenser microphone. The sample is then illuminated with a modulated beam of monochromatic light. The sample absorbs the incident energy; some of the energy levels in the sample are excited and subsequently de-excite through non-radiative relaxation processes. This periodic optical excitation of the sample results in a periodic heat flow from the sample to the surrounding gas. This in turn results in a periodic pressure oscillation within the cell, which is detected by a microphone as an acoustic signal. In recent years, a great deal of effort has been spent to understand the role of certain element in controlling the mechanism of electrical conduction in glassy chalcogenide semiconductors. Tohge et al. [7,8] have reported the results on electrical conductivity, thermoelectric power and drift mobility studies on both the series of PbGeSe glasses. Rabinal et al. [13,14] have carried out DSC measurements and optical properties on $Pb_xGe_{42-x}Se_{58}$ glasses. The ac conductivity and dielectric relaxation studies have been reported by Bhatia et al. [15,16]. Rahman et al. [17] have reported the dc conductivity measurements and current - voltage behavior of the $Pb_{20}Ge_ySe_{80-y}$ glasses and the origin of the carrier type reversal has been analysed by Vaidhyanathan et al. [18] using thermal, electrical and structural studies.

Many researchers [6-10,13-18] have analyzed the mechanism of carrier type reversal but no concrete explanation has been reached so far. A study of thermal properties is one of the techniques used to obtain an understanding of the conduction mechanism in chalcogenide glasses. It is established that the PA technique is highly sensitive to the topological threshold, rigidity percolation and carrier type reversal in chalcogenide glasses [19,20]. The composition dependence of the thermal diffusivity values on the glasses will help to reveal the mechanism of carrier type reversal [20]. To throw more light on understanding the electrical conduction changes in these glasses, we have undertaken thermal diffusivity measurements of both the series using the PA technique.

2. Experimental details

Many researchers have studied systematically the glass forming region of Pb-Ge-Se systems [8,21,22] and they found that the homogeneous glass formation is confined to two series of compositions. The I series is restricted around 58 at.% of Se, the maximum Pb content being 22.5 at.%. The II series is limited at 25 at.% of Ge with 20 at.% of Pb. In this study, we prepared $Pb_xGe_{42-x}Se_{58}$ ($x = 0, 2.5, 5, 7.5, 9, 10$ & 15 at.%) and $Pb_{20}Ge_ySe_{80-y}$ ($y = 17, 19, 21, 23$ & 25 at.%) homogeneous glasses by melt quenching.

Appropriate amount of high purity (99.999 %) elements of Pb, Ge and Se are sealed in quartz ampoule. The ampoule is evacuated to better than 5×10^{-5} Torr, then kept inside the tubular furnace. The ampoules are heated in two stages to avoid the sudden evaporation and deposition of the selenium to the inner wall of the quartz tube. The ampoules are heated slowly and maintained at 600°C for about 24 hours with continuous rotation. The temperature is then subsequently raised to 1000°C and kept under constant rotation for 36 hours to facilitate the homogenization of the sample. Then the ampoules are quenched rapidly in a continuous flow liquid Nitrogen bath, in order to avoid the vapour thermal isolating envelope around the ampoules, therefore increasing the efficiency and reproducibility of the fabrication process. The amorphous nature of the samples is verified by the absence of sharp peaks in X-ray diffraction spectra.

The thermal diffusivity measurement of various compositions of both the series have been carried out. The description of the photoacoustic cell developed here, the experimental setup and the procedure of the measurement have been reported elsewhere [20,23].

3. Results and discussion

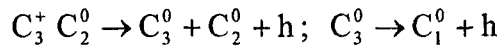
The log-log plot of chopping frequency versus PA signal amplitude is shown in Fig. 1 for the samples of different compositions. The thermal diffusion length at 100 Hz, thermal diffusivity and characteristic frequency with corresponding thickness of the samples have been listed in Table 1.

Borisova in 1981 [24] has suggested that the reason for the p-type electrical conduction in chalcogenide glasses is that the conduction band is formed by antibonding orbitals, whereas the valence band is formed by nonbonding orbital. The disorder is more dominant in antibonding states than in the nonbonding states, which results in a deeper tail for the conduction band states. So the electrons are localized stronger than the holes leading to p-type electrical conductivity.

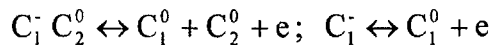
Table 1.

Composition	Sample thickness $l(\mu\text{m})$	Characteristic frequency $F_c(\text{Hz})$	Thermal diffusivity $\alpha = f_c l^2$ $\times 10^{-2} \text{ cm}^2 \text{ s}^{-1}$	Thermal diffusion length at 100 Hz $\mu = (2\alpha/\omega)^{1/2}$ $\times 10^{-2} \text{ cm}$
$Ge_{42}Se_{58}$	230	170.5	09.02	1.70
$Pb_{2.5}Ge_{39.5}Se_{58}$	280	140.8	11.04	1.88
$Pb_5Ge_{37}Se_{58}$	275	140.8	10.65	1.84
$Pb_{7.5}Ge_{34.5}Se_{58}$	275	150.6	11.39	1.90
$Pb_9Ge_{33}Se_{58}$	245	130.2	07.82	1.58
$Pb_{10}Ge_{32}Se_{58}$	273	190.0	14.16	2.12
$Pb_{15}Ge_{27}Se_{58}$	270	170.8	12.45	1.99
$Pb_{20}Ge_{17}Se_{63}$	265	120.9	08.49	1.64
$Pb_{20}Ge_{19}Se_{61}$	280	150.6	11.81	1.94
$Pb_{20}Ge_{21}Se_{59}$	270	130.5	09.51	1.74
$Pb_{20}Ge_{23}Se_{57}$	280	140.8	11.04	1.88
$Pb_{20}Ge_{25}Se_{55}$	275	140.4	10.62	1.84

The origin of p-type conduction has been explained with the charged defect states recently by Kolobov [25]. The lowest energy defects in a chalcogen are charged pairs consisting of a singly coordinated negative site (C_1^-) and a triply coordinated positive site (C_3^+). The subscript refers to the coordination, the superscript refers to the charge state and the C refers to the chalcogen. The charged defects C_3^+ and C_1^- have been called by Kastner [26] as a valence alteration pair (VAP). According to the Kolobov model [25], due to the thermal excitation of C_3^+ center with one of its neighbors C_2^0 , an electron-hole pair is created. The electron is attracted and trapped by the C_3^+ defect center and converts it into a C_3^0 center, which is unstable and easily decays to a C_1^0 center.



The hole created in the valence band is mobile and contributes to the conductivity. So, the process ends with the conversion of a C_3^+ center into a C_1^0 center with simultaneous creation of a hole in the valence band. In principle, the excited hole can recombine with its original C_3^+ and C_2^0 sites, but here the recombination is not possible because the structure of the defect has been modified. Hence, the process is irreversible and the excited hole is left in the valence band as a free carrier.



In the case of C_1^- center excited with its neighbor C_2^0 , the process becomes

In the singly coordinated defect, no structural reconstruction takes place in the defect site. So, the process is reversible since the created electron is recombined. As a consequence of these processes, the long-lived holes in the valence band due to the thermal excitation of positively charged defects become the origin of the p-type electrical conduction in the chalcogenide glasses. It is now fairly well established that the metallic additives such as Bi enters the network as charged species, altering the concentration of valence-alteration pairs [27,28]. When the concentration of charged additives exceeds that of valence-alteration pairs, the chalcogenide glasses exhibit the carrier type reversal.

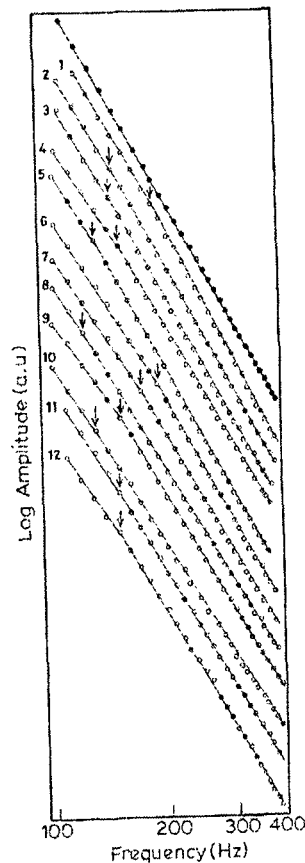


Fig. 1. Log - log plot of photoacoustic amplitude versus chopping frequency.

- (• - Thick sample, 1. $\text{Ge}_{42}\text{Se}_{58}$, 2. $\text{Pb}_{2.5}\text{Ge}_{39.5}\text{Se}_{58}$, 3. $\text{Pb}_5\text{Ge}_{37}\text{Se}_{58}$,
4. $\text{Pb}_{7.5}\text{Ge}_{34.5}\text{Se}_{58}$, 5. $\text{Pb}_9\text{Ge}_{33}\text{Se}_{58}$, 6. $\text{Pb}_{10}\text{Ge}_{32}\text{Se}_{58}$, 7. $\text{Pb}_{15}\text{Ge}_{27}\text{Se}_{58}$, 8. $\text{Pb}_{20}\text{Ge}_{17}\text{Se}_{63}$,
9. $\text{Pb}_{20}\text{Ge}_{19}\text{Se}_{61}$, 10. $\text{Pb}_{20}\text{Ge}_{21}\text{Se}_{59}$, 11. $\text{Pb}_{20}\text{Ge}_{23}\text{Se}_{57}$, 12. $\text{Pb}_{20}\text{Ge}_{25}\text{Se}_{55}$.

Fig. 2 and 3 show the variation of thermal diffusivity with Pb and Ge concentration respectively. It can be clearly seen from the figures that an anomalous behavior is observed, in $Pb_xGe_{42-x}Se_{58}$ glasses at 9 at.% of lead and in $Pb_{20}Ge_ySe_{80-y}$ glasses at 21 at.% of Ge, at the compositions showing a transition from p- to n- type conduction. The change is more prominent in I series than in the II series of glasses. This may be due to the difference in the way of changing the composition between the series. In II series Ge is substituted with Se atom, but in I series, Pb is substituted with Ge atom. The transition at the specific Pb and Ge composition in the glasses agrees well with the reported thermoelectric power measurements [8].

An attempt is made to explain the anomalous behavior of thermal diffusivity values with Pb and Ge addition of I and II series glasses respectively. Calculations of covalent bond concentrations of these series have been reported by Tohge et al. [8]. The reported radial distribution function [29] showed that Pb is present as Pb^{2+} ions in these glasses, necessarily accompanying nonbridging selenium ($-Se^-$). The possible bonds are Ge-Ge, Ge-Se, Pb-Se and Se-Se. In I series, the concentration of calculated covalent bonds Ge-Se and Ge-Ge changed gradually with relative increase in Pb-Se ionic bonds. But in II series, besides Pb-Se ionic bonds, the Se-Se bonds decreases and completely vanish at $x = 20$ at.% of Ge, while at this composition the concentration of Ge-Se bonds reaches maximum and Ge-Ge bonds start to appear. With further addition of Ge, the Ge-Ge bonds gradually increase and Ge-Se bonds decrease. It is speculated in this II series that the disappearance of Se-Se homopolar bonds causes the electrical conduction changes from p- to n- type. In I series the minimum value obtained at the transition can be attributed to the addition of Pb, where a decrease in the number of Ge-Se and Ge-Ge covalent bonds leads to an increase of Pb-Se ionic bonds. It is worth to mention here that the conduction change in both the series is at the specific compositions $Pb_9Ge_{33}Se_{58}$ and $Pb_{20}Ge_{21}Se_{59}$. The Pb and Ge concentrations are not the same but the Se at.% is almost equal in the two series.

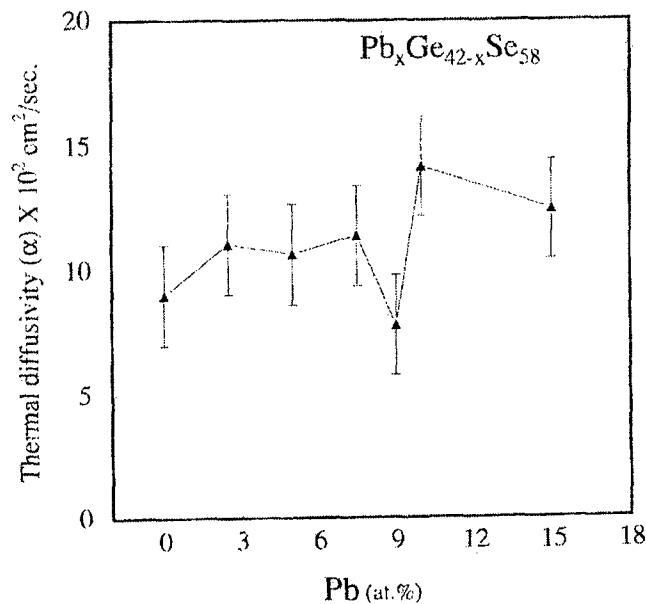


Fig. 2. Variation of thermal diffusivity with Pb concentration.

The similar trend of anomalous behavior of thermal diffusivity measurement with the composition of GeBiSe and Ge Bi Se Te glasses has already been observed by Thangaraju et al. [20]. The Ge Bi Se Te and I series glasses show the drastic change in thermal diffusivity value at the p- to n- transition. The changes are more prominent than in the GeBiSe and II series glasses. A perusal of these figures reveals that the thermal diffusivity value decreases at the time of transition then increases with increasing Bi in GeBiSe and Ge Bi Se Te glasses and, with Pb and Ge in I and II series glasses respectively. The electrical conductivity values [8] show that the specific composition where the electrical conductivity is a minimum agrees with that where the conduction type changes from p- to n-.

After the transition the conductivity increases with addition of respective Pb and Ge atomic concentration in I and II series glasses, which is reflected in the thermal diffusivity value also.

The minimum electrical conductivity during the p- to n- transition may be due to the maximum value of the optical band gap. Rabinal [30] has observed that the band gap value increases along with increasing Ge content in $Pb_{20}Ge_ySe_{80-y}$ glasses, the E_g value reaches maximum at $y = 21$ at.% and then decreases. We have reported the comparison of thermal diffusivity with electrical conductivity in the GeBiSe and Ge Bi Se Te glasses [20]. In solids, thermal conductivity is due to the heat transport by both phonons and charge carriers. The thermal diffusivity is directly proportional to the thermal conductivity [12]. Since at the p- to n- transition, the optical band gap is higher, the excited concentration of electrons from valence band to conduction band is appreciably low, which results in a lower carrier concentration. After the critical composition, the E_g value decreases and as a result the electrical conductivity and thermal diffusivity both increase. Further increasing the Pb and Ge concentration in I and II series respectively, the decreasing thermal diffusivity value may be due to a decrease in the phonon mobility arising out of scattering and phonon collisions due to the defects present in the 3-d structure.

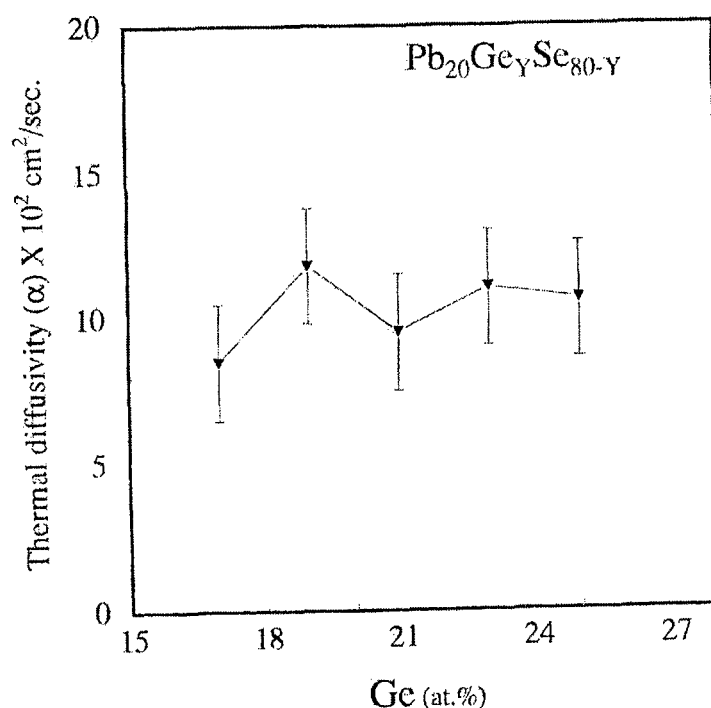


Fig. 3. Variation of thermal diffusivity with Ge concentration.

According to the Kolobov model [25] by the addition of Pb in Ge-Se glasses, the concentration of C_3^+ center decreases rapidly with a corresponding increase in C_1^- centers. So after a certain Pb and Ge composition in these glasses, C_1^- centers act as majority carriers, which result in n-type electrical conduction. From the above discussions, it is concluded that after the specific composition of Pb and Ge the Fermi level E_F moves towards the conduction band, which is assumed to be a consequence of the formation of Pb-Se ionic bonds. The addition of Pb atoms create the formation of negatively charged Se centers, which disturb the equilibrium between the Se^- and Se_3^+ centers by the law of mass action and hence causes the unpinning of Fermi level. Mehra et al. [10] have proved this unpinning of Fermi level in Pb added Se-In chalcogenide glasses with the studies of the activation energy of electrical conductivity and optical band gap.

4. Conclusion

The composition dependence of the thermal diffusivity of $Pb_xGe_{42-x}Se_{58}$ and $Pb_{20}Ge_ySe_{80-y}$ glasses has been studied by the photoacoustic technique. The measurements show an unusual behavior at p- to n- conduction changes. In $Pb_xGe_{42-x}Se_{58}$ glasses the change is more prominent than in the $Pb_{20}Ge_ySe_{80-y}$ glasses. Like the electrical conductivity measurements, the thermal diffusivity value shows minimum at the p- to n- transition threshold and then increases with corresponding increases of Pb and Ge concentration in I and II series glasses. The addition of Pb disturbs the equilibrium between Se_3^+ and Se^- centers, thus unlocking the Fermi level. This results in the E_F shifting toward the conduction band and in the p- to n- conduction changes in these glasses.

Acknowledgement

The authors thank Council of Scientific and Industrial Research (CSIR), India, for financial support.

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