JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 9, No. 10, October 2007, 3044 - 3048

AC conductivity in a-GeSePb glassy alloys

GURINDER SINGH, N. GOYAL, G. S. S. SAINI, S. K. TRIPATHI*
Department of Physics, Center of Advance Study in Physics, Panjab University, Chandigarh-160 014 India

The present paper reports the effect of Pb impurity (low ~ 2 at. % and high ~ 10 at. %) on the ac conductivity (σ_{ac}) of a-$Ge_{20}Se_{80}$ glassy alloy. Frequency dependent ac conductance and capacitance of the samples over a frequency range of 100 Hz - 50 kHz has been taken at different temperatures. At frequency 2 kHz and temperature 298 K, the value of σ_{ac} increases at low as well as at higher concentration of Pb. σ_{ac} is proportional to ω^s for undoped and doped samples. The value of frequency exponent (s) decreases as the temperature increases. These results have been explained on the basis of some structural changes after the Pb addition.

(Received July 3, 2007; October 1, 2007)

Keywords: Ge-Se-Pb, Chalcogenides, Hopping conduction, Defect states

1. Introduction

The chalcogenide glasses formed from selenium are considered most important semiconductors. Ge_xSe_{100-x} glassy alloys have been studied due to their glass-forming tendency. Their glass forming composition range is so extended, $0 \leq x \geq 43$ at. % that this system is ideal to study the dependence of the optic and transport properties on structure and composition. Amorphous semiconductors from Se based system such as Ge_xSe_{100-x} have attracted much attention in recent years. Ge_xSe_{100-x} (x= 15, 20 and 25) is being actively investigated as high efficiency semiconductors for xerography, switching and memory devices [1-4]. Exposure to light or heat that excites electron- hole pairs produces structural changes in nearly all chalcogenide glasses. The results change with atomic configuration, and a subsequent change in the physical properties such as structure, optical and electrical properties of the material [5, 6].

Chalcogenide glasses are generally p-type semiconductors [7]. In these materials, the valence band is constituted by the chalcogen lone-pair orbitals [8]. The effect of structural disorder is less on the lone-pair band compared to that on the antibonding orbitals (conduction band). Therefore, the range of localized tail states at the valence-band edge is smaller in comparison to the localized states at the conduction-band edge. As a consequence, the number of electrons excited above the conduction-band mobility edge is less than the number of holes excited below the valence-band mobility edge and the chalcogenide glasses behave as p-type semiconductors [9]. Chalcogenide glasses also contain positively and negatively charged defect states, known as valence-alternation pairs [10] (VAP's). During thermal excitation, the lifetime of free holes excited from the positively charged defect states are higher than the lifetime of free electrons excited from the negatively charged defects, which also account for the p-type conductivity [7]. Amorphous chalcogenides are generally insensitive to doping, because of the pinning of the Fermi level at midgap by the valence-alternation pairs [11]. Mott [12] has shown that charged additives could change the ratio of valence-alternation pairs to such an extent that the Fermi energy could become unpinned. Metallic additives such as Bi and Pb in chalcogenide glasses enter the network as charged species, altering the concentration of valence-alternation pairs [10]. When the concentration of charged additives exceeds that of valence-alternation pairs, the chalcogenide glasses can exhibit carrier-type reversal. p-n transition has been observed in Ge-Se and In-Se glasses, with the addition of Bi and Pb [13, 14].

The ac conductivity is one of the techniques that can be used to understand the conduction mechanism in chalcogenide glasses. ac conductivity (σ_{ac}) and dielectric constant (k) measurements of $(Ge_{20}Se_{80})_{100-x}Pb_x$; where x = 0, 2 and 10 at. % have been carried out. The present paper reports the temperature and frequency dependent σ_{ac} of $(Ge_{20}Se_{80})_{100-x}Pb_x$ glassy alloys. The results reported in the present study provide information about the effect of Pb alloying in $Ge_{20}Se_{80}$ glass. These interesting results have been explained on the basis of the structural changes occurring in the material due to the incorporaton of Pb metal. The modified Correlated Barrier Hopping model (CBH) [15, 16] has been used to explain the effect of Pb doping. Section 2 describes the experimental details. The results have been presented and discussed in section 3. The last section deals with the conclusion of this work.

2. Experimental

$(Ge_{20}Se_{80})_{100-x}Pb_x$ (x = 0, 2 and 10 at %) glassy materials have been prepared by taking the constituent elements (M/s Alfa Aesar, U.S.A.; purity ~ 99.999 %) in required atomic weight percentages. The materials were then mixed together and the mixture was sealed in a quartz

ampoule (length ~10cm, diameter ~1cm) under a pressure of ~10^{-5} Torr. These ampoules were mounted in a furnace for heating. In the beginning, the temperature of the furnace was raised slowly and kept constant at the melting temperature of each constituent element (600 K for Pb, 490 K for Se and 1210 K for Ge) for about two hours each. The temperature was then raised and maintained at about 50 K more than the highest melting point of the constituents (1260 K) for about 24 hours. The ampoules were immediately cooled in liquid nitrogen, for the materials to go into the glassy state. The glassy materials, in the form of ingots, were obtained by breaking the ampoules. To verify the amorphous nature of these glasses, X-ray diffraction (XRD) study on all samples was done (Philips X-Ray Generator, Model: PW1729 along with a PW1710 Diffractometer). No peaks have been observed for the materials prepared by above-mentioned technique, thereby, confirming the amorphous nature of the prepared materials.

Compressed pellets were prepared by grinding the bulk-ingots into fine powder and compressing the resulting powder in a die under a hydraulic press (pressure ~ 10^6 Kg/m^2). While making compressed pellets, one must ensure that the powder is compressed to maximum compaction so that there were no voids in the sample. A three terminal sample holder has been fabricated for the measurement of σ_{ac} of the pellet shaped samples. Provision was made for measuring the vacuum inside the sample holder. Cylindrical brass jacket was used as outer cover to provide excellent electromagnetic shielding. A built in micrometer was used for the measurement of sample thickness. Temperature of the sample was noted down with the help of a thermocouple which was kept close to the sample. A low temperature bath (Julabo F-70 VC/K) was used for controlling the temperature of the samples. Vacuum pumping system (Model: VS-65D, H.H.V India) was used to achieve a vacuum, up to 10^{-4} to 10^{-5} Torr inside the sample holder. A general Radio Bridge (Model 1615-A) was used for the measurements of frequency dependent ac conductivity and dielectric constant of the materials having large resistivity. The bridge consists of an audio oscillator (model 1311), a tuned amplifier (model 1232-A) and a null detector, which permits balance to a resolution of one part in a million. This bridge is designed for the precise measurements of capacitance and conductance. Its direct read-out system minimizes the reading errors and permits rapid operation.

3. Results and discussion

Figs. 1and 2 show the frequency dependence of measured conductivity (σ_{ac}) for the undoped $Ge_{20}Se_{80}$ and doped $(Ge_{20}Se_{80})_{90}Pb_{10}$ samples respectively at different temperatures. Similar results have been obtained for $(Ge_{20}Se_{80})_{98}Pb_2$ glassy alloy also (result not shown here). The conductivity data presented in these figures are fitted with the relation $\sigma_{ac} = A\omega^s$, where 's' is frequency exponent and A is a constant.

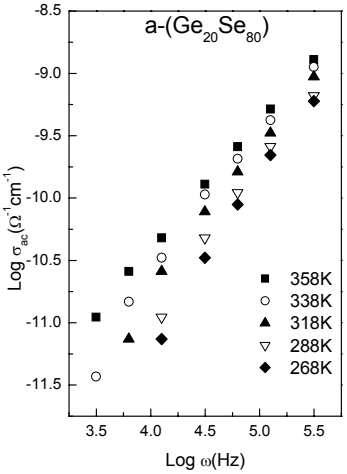


Fig.1. Frequency dependence of conductivity at different temperatures in a-$Ge_{20}Se_{80}$ alloy.

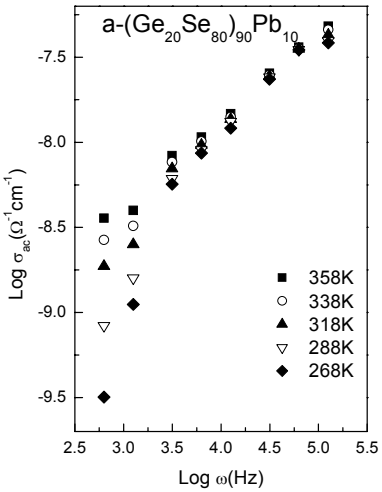


Fig.2. Frequency dependence of conductivity at different temperatures in a-$(Ge_{20}Se_{80})_{90}Pb_{10}$ alloy.

Fig. 3 shows the temperature dependence of the frequency exponent 's' for all three samples. It is clear from the figure that the value of 's' decreases with the increase in temperature and with the increase in Pb concentration also. This decrease is more in case of higher Pb (10 at. %) doping concentration as compared to the lower Pb (2 at. %) concentration. At temperatures below 300 K, the value of 's' of low Pb concentration approaches to the undoped sample. At high concentration of Pb, the value of 's' is always less compared to the undoped one irrespective of the temperature.

The decrease in slope with increasing temperature indicates that the value of 's' decreases with increasing temperature. Figures 4(a, b) show the temperature dependence of σ_{ac} of $Ge_{20}Se_{80}$, $(Ge_{20}Se_{80})_{96}Pb_2$ and $(Ge_{20}Se_{80})_{90}Pb_{10}$ glasses at frequencies 2 kHz and 10 kHz

respectively. From the figures, it is clear that the value of σ_{ac} increases with temperature more in

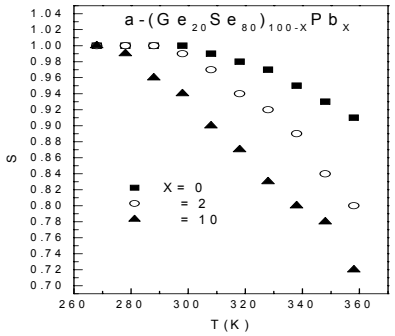
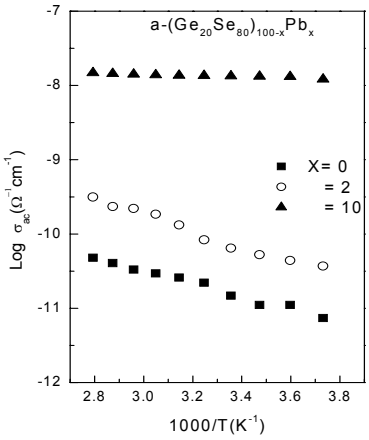
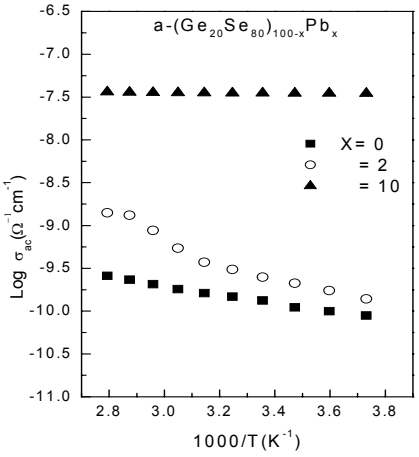


Fig.3. Variation of frequency exponent 's' with temperature

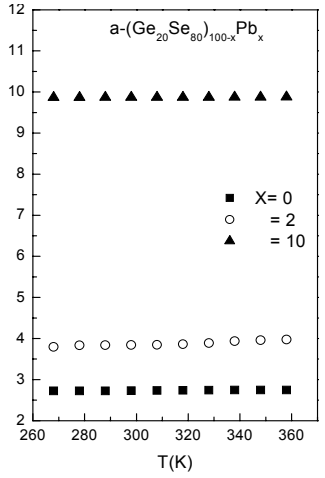


a

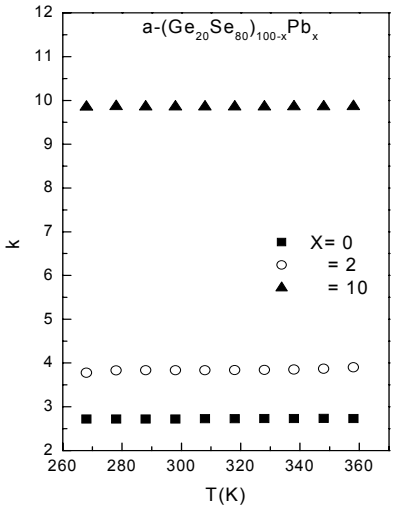


b

Fig. 4. Temperature dependence of ac conductivity (a) at 2 kHz (b) 10 kHz.



a



b

Fig. 5. Variation of dielectric constant k with temperature (a) at 2 kHz

case of pure and low doped (2 at %) than heavily doped (10 at %) samples. However, in case of higher doping concentration of Pb, the increase in σ_{ac} is small with temperature. The value of σ_{ac} of $Ge_{20}Se_{80}$ glass increases in both Pb concentrations. We observe a large increase in σ_{ac} at higher Pb concentration (10 at %) in all temperatures. Figures 5(a,b) show the temperature dependence of dielectric constant (k) at different frequencies 2 kHz and 10 kHz. From these figures, it is clear that the value of k increases at both concentrations of Pb at all temperatures. However, increase in the value of k is more in case of higher Pb concentration at all temperatures.

Using a modified Correlated Barrier Hopping Model (CBH) [15,16], the above results can be explained as discussed below. According to this model:

$$\sigma_{ac} = \frac{n\pi^3}{24} \; N^2 \omega \varepsilon \varepsilon_0 R_\omega^{\,6} \tag{1}$$

where n is the number of polaron involved in the hopping process, ω is the frequency, ε is the dielectric constant and R_ω is the hopping distance for the condition ωτ=1 and is given by [15]:

$$R_\omega = \frac{ne^2}{\pi \varepsilon \varepsilon_0 \{W_M + kT \ln(\omega \tau_0)\}} \tag{2}$$

The value of frequency exponent s is calculated from equations (1) and (2), and is equal to:

$$S = \frac{d(\ln \sigma_{ac})}{d(\ln \omega)} = 1 - \frac{6kT}{W - kT \ln[1/\omega\tau_0]} \tag{3}$$

where

$$NN_P = N_T^{\,2} \quad \text{(For bipolaron hopping)} \tag{4}$$

where N is the concentration of localized sites, N_P is the concentration of carriers and N_T is the number of density of states.

$$NN_P = N_T^{\,2} \exp(-U_{eff}/2kT) \quad \text{(For single polaron hopping)} \tag{5}$$

where U_{eff} is the effective correlation energy.

The total conductivity is the combined mechanism of these processes. These processes are bipolaron hopping between D^+ and D^- centers, single polaron hopping between D^0 and D^- centers and D^0 and D^+ centers. Here, W is equal to W_M, which is slightly less than the band gap for the bipolaron hopping. However, it is equal to W_1 and W_2 for the two types of single polaron hopping mechanisms, which are substantially less than W_M for bipolaron hopping. The smaller values of W_1 and W_2 for single polaron hopping means that the value of R_w is much greater for single polaron hopping as compared to bipolaron hopping Eq. (2).

Feltz [17] has reported from X-ray studies that Pb exists as Pb^{2+} in lead chalcogenide glasses. The radial distribution function reported by Tohge et al [18] also showed that Pb is present as Pb^{2+} ions in these glasses, necessarily accompanying nonbridging selenium ($-Se^-$). The possible bonds in these glasses are Ge-Ge, Ge-Se, Pb-Se and Se-Se. The concentration of calculated covalent bonds Ge-Se and Ge-Ge changed gradually with relative increase in the Pb-Se ionic bonds. The thermal conductivity as well as the heat capacity of Pb modified Ge-Se glasses have been measured simultaneously by Philip et al [19] using the photopyroelectric technique. They have shown carrier type reversal from p to n type at specific composition due to an increase in the electron concentration and the charged defect states. This change (p→n) brings about a decrease in the thermal conductivity due to the reduction in the phonon mean free path. The electronic contribution to heat capacity increases due to larger concentration of electrons in the medium consequent to p to n transition.

Rahman et al [20] have reported the carrier type reversal using dc conductivity measurements and current-voltage behaviour of the $Pb_{20}Ge_ySe_{80-y}$ glasses. It has been reported that the calorimetric properties of Pb modified chalcogenide glass [21,22], such as the glass transition temperature (T_g), crystallization temperature (T_c) and heat capacity drastically change at T_g. Activation energy and thermal diffusivity [23] have consistently shown anomalous features at the compositions at which change in the conduction type (p→n) takes place. Murugavel et al [22] have reported the majority charge carrier reversal, by electrical measurements, in $Pb_xGe_{42-x}Se_{48}Te_{10}$ glasses at x ≈ 9 at % of Pb.

From the above discussions, it is clear that in the case of the GeSePb system of glasses, the addition of Pb into Ge-Se glassy system converts some of Se_3^+ centers into Se_1^- centers. Hence, there is a decrease in the number of free holes formed by the conversion of Se_3^+ centers into Se_1^- centers. Moreover, with the decrease in the number of Se_3^+ centers, the number of traps that can capture electrons excited into the conduction band decreases. This results in an overall increase in the electron concentration in the medium. In addition, there is a simultaneous increase in the number of Se_1^- charged defect states, which enhances the number of shallow acceptors that capture holes from the valence band. These two effects together shift the Fermi level (E_F) towards the conduction band. The shift in the Fermi level, due to p→n transition, is a consequence of the formation of Pb-Se ionic bonds. Mehra et al [24] have also proved the unpinning of the E_F in Pb added Se-In chalcogenide glasses by electrical conductivity and optical band gap measurements. According to these authors, when Pb enters the network, the band picture changes drastically. Electron microscope studies on Pb-Ge-Se glasses do not show any noticeable inhomogeneties even at submicron scales. These results rule out the percolation of microcrystalline clusters as a plausible mechanism for the carrier type change in these glasses [25].

Hence, it is clear from the above discussions that the addition of Pb induces the carrier type reversal (p→n transition) in $Ge_{20}Se_{80}$ glass, when the Pb atoms enter the glassy network as positive defects. The Pb metal doping brings out a relative diminishing in D^+ (i.e. Se_3^+) defects as compared to D^- (i.e. Se_1^-) ones. The same effect has been observed in Bi doped $Ge_{20}Se_{80}$ glass [26]. As the Pb metal concentration increases, the bipolaron hopping contribution decreases due to the decrease in the density of defect states. But single polaron hopping contribution increases because of the shift of the Fermi level towards the conduction band as discussed earlier. Due to the shift of E_F towards conduction band, W_2 will decrease and it seems that single polaron hopping starts to dominate over bipolaron hopping as the concentration of Pb increases (i.e. 10 at. %).

4. Conclusions

Electrical conductivity measurements have been done in undoped $Ge_{20}Se_{80}$ and doped with Pb (low and high concentrations) metal. Frequency dependent ac conductivity (σ_{ac}) measurements at different temperatures show that the value of σ_{ac} increases at low concentration (2 at. %) as well as at high concentration of Pb (10 at. %). Dielectric constant (k) also follows the same pattern at both Pb concentrations. The value of 's' decreases at both concentrations at high temperature. It is observed that the addition of Pb brings out a reduction in the relative concentration of D^+ as compared to D^- defects. This imbalance accompanied by the contribution of extra electrons brings out n-type conduction in Pb doped glasses. Due to the shift of the Fermi level, single polaron hopping starts dominating over bipolaron hopping after adding different concentrations of Pb.

Acknowledgements

This work is financially supported by the C.S.I.R. (Major Research Project), New Delhi.

References

[1] K. Nakayama, K. Kojima, Y. Imai, T. Kasai, S. Fukushima, A. Kitagawa, M. Kumeda, Y. Kakimoto, M. Suzuki, J. Appl. Phys. **42**, 404 (2003).
[2] M. Lipinski, P. Panck, R. Ciach, J. Optoelectron. Adv. Mater. **5**, 1365 (2003).
[3] J. Teteris, J. Optoelectron. Adv. Mater. **4**, 687 (2002).
[4] A.K. Mairaj, et al., Appl. Phys. Lett. **81**, 3708 (2002).
[5] A.V. Kolobov, Hoyanagi, K. Tanaka, Ke Tanaka, J. Non-Cryst. Solids **198**, 709 (1996).
[6] Kojihayashi, D. Kato, K. Shimakawa, J. Non-Cryst. Solids **198**, 696 (1996).
[7] A.V. Kolobov, J. Non-Cryst. Solids **198-200**, 728 (1996).
[8] M. Kastner, Phys. Rev. Lett. **28**, 355 (1972).
[9] S. D. Baranovskii Sov. Phys. Semicond. **18**, 633 (1984).
[10] M. Kastner, D. Adler, H. Fritzsche Phys. Rev. Lett. **37**, 1504 (1976).
[11] D. Adler, C. J. Yoffa, Phys. Rev. Lett. **36**, 1197 (1976).
[12] N.F. Mott Philos. Mag. **34**, 1101 (1976).
[13] R.M. Mehra, S. Kohli, A. Pundir, V.K. Sachdev, P.C. Mathur, J. Appl. Phys. **81**, 7842 (1997).
[14] R.M. Mehra J. Appl. Phys. **81**, 7842 (1997).
[15] K. Shimakawa, Phil. Mag. B **46**, 123 (1982).
[16] K Shimakawa, Phil. Mag. B **48**, 778 (1983).
[17] A. Feltz, Amorphous Inorganic Materials and Glasses, VCH, Weinheim, pp: 275 (1993).
[18] N. Tohge, M. Matsuo, T. Minami, J. Non-Cryst. Solids **95-96,** 809 (1987).
[19] J. Philip, R. Rajesh, C. Preethy Menon, Appl. Phys. Letters **78,** 745 (2001).
[20] S. Rahman, M.V. Ramana, G.S. Sastry, Phys. Chem. Glasses **33,** 209 (1992).
[21] M.K. Rabinal, N. Ramesh Rao, K.S. Sangunni, E.S.R. Gopal, Phil. Mag. B **70,** 89 (1994).
[22] S. Murugavel, S. Ashokan, Phys. Rev. B **58,** 4449 (1998).
[23] S. Thomas, J. Philip, Solid State Commun. **107,** 423 (1998).
[24] R.M. Mehra, S. Kohli, A. Pundir, V.K. Sachdev, P.C. Mathur, J. Appl. Phys. **81**, 7842 (1997).
[25] J.C. Phillips, Phys. Rev. B **36,** 4265 (1987).
[26] G. Singh, J. Sharma, A. Thakur, N. Goyal, G. S. S. Saini, S. K. Tripathi, j. Optoelectron. Adv. Mater. **7**(4), 2069 (2005).

*Corresponding author: surya@pu.ac.in; surya_tr@pu.ac.in