OPTICAL AND CALORIMETRIC STUDYOF Pb₉Se₇₁Ge_{20-x}Sn_x (8≤x≤12) GLASS

V. MODGIL^{*}, V. S. RANGRA

Department of Physics, Himachal Pradesh University Summerhill Shimla (INDIA)-171005

Optical and calorimetric Study of $Pb_9Se_{71}Ge_{20-x}Sn_x$ ($8 \le x \le 12at$. %) glass has been taken. Thermal transition kinetic has been investigated under non-isothermal conditions by DSC technique. Phase separation has been observed in the material and is detected by examining the XRD of annealed bulk samples. Optical band gap and other optical constants such as refractive index, extinction coefficient has been determined. Material possesses good glass forming ability, high value of glass transition temperature, glass stability and refractive index.

(Received January14, 2014; Accepted November 10, 2014)

Keywords: Differential Scanning Calorimetry; Glass transition temperature; Activation energy; Band gap

1. Introduction

Among inorganic glassy materials, chalcogenide glasses occupy a unique place in material science towards advancement of technology. chalcogenide originates from the Greek word "chalcos" meaning ore and "gen" meaning formation. Chalcogenides can exist naturally as minerals; two of the most well-known being FeS₂ (pyrite) and AuTe₂ (calaverite). Generally these materials are weakly bonded materials than oxide glasses. But In comparison to amorphous silicon, halide glasses and other group IV tetrahedral bonded semiconductors these materials exhibit the superior properties which can be tailored by varying the composition. Among the chalcogenide materials, chalcogenide glasses have their unique technological significance and applications such as in rectifiers, photocells, memory and switching devices due to their unique electrical, thermal and optical properties [1,2]. Chalcogenide glasses are used as core materials in optical fibers for light transmission, especially when short lengths and flexibility are required. The selenium-based materials are preferred because of its unique property of reversible transformation, which makes these glasses useful as optical memory devices. Germanium based chalcogenides are identified as suitable materials for IR optical sensors in the biomedical process, gas detection [3] and data storing media [4] due to their long transmission window extending from $1-20\mu$ m. Crystallization studies of chalcogenide glasses are important in determining the transport mechanism, thermal stability and its practical applications

The better optical and thermal properties of these materials make them of potential use in the technological applications such as in photonics and phase change memories because of higher values of refractive index, lower value of phonon energy of these glasses[5-6]. The present Investigation on phase change memories (PCM) shows the possibility of obtaining multistate behavior, enhanced ability to withstand thermal cycling and use of lower voltages for achieving desired phase change response by using the bilayers of Ge-chalcogenide and Sn-chalcogenide[7].

Many researchers have carried out their work on this type of compositions such as Ge-Sb-Se,Ge-Sn-Se[8-9] and Ge-Sn-Sb-Se[10] to improve the optical properties.

^{*}Corresponding author: vivekmodgilphysics.hpu@gmail.com

These materials can be used in the photonic crystal applications due to their higher value of refractive index. Photonic crystals are the materials which are used in photonic applications, such as optical band-gap devices and omni-directional reflectors [6].

It is necessary to have the knowledge of thermal stability and glass-forming ability (GFA) of material to know its suitability for the particular technological application before crystallization takes place. The addition of elemental impurity such as Ge, Sn, In, Pb has a pronounced effect on structural, optical, electronic and thermal properties of material [11-15]. The Sn has been added in Pb-Se-Ge system to see the effect of Sn incorporation on thermal and optical behaviors of this material.

2. Experimental Details

2.1 Material synthesis and characterization

The chalcogenide materials $Pb_9Se_{71}Ge_{20-x}Sn_x$ ($8 \le x \le 12at$. %) are prepared by the melt quenching technique. Granules of Pb, and powder of Sn, Ge and Se having 99.999% purity are used .The material is then sealed in evacuated (~ 10^{-5} Torr) quartz ampoule (length ~ 15cm and internal diameter ~ 8 mm). The ampoules containing material are heated to 1000°C and held at that temperature for 10 hours. The temperature of the furnace is raised slowly at a rate of 3 - 4° C per minute. During heating, the ampoule is constantly rocked. The obtained melt is quenched in ice cool water. The nature of the material is ascertained by powder X-ray diffraction technique. For this, X-ray diffraction (XRD) patterns of sample are taken at room temperature by using an X-ray diffractometer Panalytical X'pert Pro (PW 3050/60, CuK_{a1} λ = 1.54 Å) shown in figure 1.

The thermal behavior of the material has been studied using differential scanning calorimetry(DSC) under non-isothermal conditions on approximately 15-20 mg quantity of each powdered samples by DSC instrument Mettler Star SW 9.01 model. Eachsample is heated at different heating rates 10, 15, 20 and 25° k/minute.We have found that material's samples at x=11, 12 have double crystallization peaks which are due to the phase separation in the material.We have annealed the bulk sample x=11 at temperatures 507K and 550K for 3 hoursto detect the phases separated in the material. Then XRD's of samples has been taken. figure. 4 shows the XRD patterns of the annealed samples (x=11). To find out the optical constants, thin films of chalcogenide glasses have been deposited by vacuum evaporation technique on thoroughly cleaned microscope glass substrate. The room-temperature optical-transmission and Reflection spectra of the samples, are recorded over the 200 nm to 2500 nm spectral region, by a double-beam UV/Vis/NIR spectrophotometer (Perkin-Elmer, model Lambda-750).

3. Results and discussions

3.1 Structural and thermal analysis

XRD diffractograms of the Pb9Se71Ge20-xSnx (x = 8, 9, 10, 11, 12 at. %) compositions are shown in figure 1 which confirm the amorphous nature of material.



Fig. 1 X- Ray Diffractograms of the chalcogenide glass $Pb_9Se_{71}Ge_{20-x}Sn_x(x=8,9,10,11,12)$

For thermal analysis material is heated under non-isothermal conditions at constant heating rate in DSC experiment, glass undergo the structural variations and crystallize. The variation of glass transition temperature, crystallization temperature with varying Sn concentration can be studied by comparing the DSC thermograms of all samples at same heating rate. Figure 2 shows the DSC thermograms of Pb₉Se₇₁Ge_{20-x}Sn_x ($8 \le x \le 12at$. %) material at a heating rate of 10 K min⁻¹. To know the thermodynamics of the material such as phase transformation, activation energy of glass transition and crystallization each sample is heated at four different heating rates.



Fig. 2 DSC thermograms of the samples at heating rate of 10K/min.

The glass upto atomic percentage x=10 of Sn shows the single crystallization peak and at x=11, 12 shows the double crystallization peaks. This appearance of double crystallization is because of partial phase separation in material. Phase separation is the unmixing of the initially homogeneous multicomponent material in to two or more amorphous phases. Comparatively smaller free energy of other phase or polyphase leads to phase separation of initially homogeneous single phase composition. For identification of the phases in material, the initial glassy sample Pb₉Se₇₁Ge₉ Sn₁₁ is annealed at 507Kand 550K for 3hours, which lies before the primary and secondary crystallization respectively. The annealed samples are then examined through XRD.

Figure 3 shows the XRD patterns of the annealed samples. After annealing the samples for 3 hours we have observed that two major phases $SnSe_2$ and $GeSe_2$ and minor phasePbSe in XRDdiffractograms. GeSe_2 has monoclinic structure and lattice parameters a=7.231Å, b= 16.748 Å, c=11.79 Å, [JCPDS file card no. 30-0595]. The $SnSe_2$ structure is formed in such a way that Sn layer is sandwiched between the two Se layers facing towards each other. The $SnSe_2$ has the hexagonal structure having a=3.84 Å, b=1.61 Å and c=6.18 Å [JCPDS file card no.38-1055] and Pb-Se crystallize in cubic structure and has a=6.089Å.



Fig. 3 X-Ray Diffractograms of sample Pb₉Se₇₁Ge₉Sn₁₁annealed at (a) 550K (b) 507K.

On the basis of chemical bond approach [16], with increase of Sn content, Ge-Se bonds got replaced by the Sn-Se bonds and glass transition temperature decrease. The glass at x=11,12 has been phase separated into two main phases, one Ge-rich and the other Sn-rich. The higher and lower T_c may be due to Ge rich and to the Sn-rich phase respectively.

3.2. Kinetics of phase transformations

3.2.1 Glass transition region

Glass forming ability (GFA) and thermal stability of vitreous materials can be established from the DSC measurement analysis. Usually unstable glass has crystallization peak close to glass transition temperature and stable glass has crystallization peak close to melting temperature. The difference T_p - T_g varies with alloy's structural units in compositions. T_p is peak crystallization temperature. Kauzmann[17] gave a criterion of good glass forming ability as reduced glass transition temperature, $T_{rg}=T_g/T_m$.

The ease of glass formation is determined by calculating the reduced glass transition temperature. Glass transition temperature has the compositional dependence. Hruby[18] described the glass forming ability (GFA) criterion as $H_r = \frac{T_p - T_g}{T_m - T_p}$. Higher value of T_p - T_g indicates the delay in the nucleation process and smaller value of T_m - T_p shows retardation to the growth process. The difference ($T_p - T_g$) is a strong indicator of both the thermal stability and the GFA. Higher the value of ($T_p - T_g$), higher is the thermal stability and GFA, because higher values of this difference indicate more kinetic resistance to the crystallization.

The value of T_{rg} is found to be of the order of about 2/3, indicating good glass forming ability for all the glassy compositions. For memory and switching materials, glass thermal stability and GFA parameters are of vital importance.

Heat Rate	$T(\mathbf{V})$	$T_p(K)$	T (K)	$T_c onset(K)$	Hruby	т	тт
(⁰ K/minute)	$I_g(\mathbf{K})$	T_{p1} T_{p2}	$I_{\rm m}(\mathbf{K})$	T_{c1} T_{c2}	Parameter	1 rg	1 p-1 g
$Pb_9Se_{71}Ge_{12}Sn_8$							
10	426.34	562.44	717.75	273.85	0.876	0.593	136.10
15	427.93	565.98	726.65	279.07	0.859	0.588	138.05
20	429.82	571.22	737.39	274.46	0.850	0.582	141.4
25	431.61	573.13	738.65	282	0.855	0.584	141.52
$Pb_9Se_{71}Ge_{11}Sn_9$							
10	425.72	558.2	724.36	276.12	0.797	0.587	132.48
15	425.28	563.5	729.97	281.18	0.830	0.582	138.22
20	428.12	566.32	731.48	281.21	0.836	0.585	138.2
25	430.11	566.53	733.51	283.22	0.816	0.586	136.42
$Pb_9Se_{71}Ge_{10}Sn_{10}$							
10	423.72	551	722.36	263.92	0.742	0.586	127.28
15	425.08	563.15	728.46	278.17	0.835	0.583	138.07
20	426.11	570.66	729.37	277.07	0.910	0.584	144.55
25	427.74	572.65	731.50	281.21	0.912	0.584	144.91
$Pb_9Se_{71}Ge_9Sn_{11}$							
10	421.21	536.72, 586.94	720.56	249.57, 298.96	0.628, 1.240	0.584	115.51,165.73
15	422.10	535.97, 588.98	722.13	249.96, 300.47	0.611, 1.253	0.584	113.87,166.88
20	422.98	537.59, 591	722.35	255.23, 304.12	0.620, 1.279	0.585	114.61,168.02
25	425.20	537.96, 590.58	720.53	253.07, 302.07	0.617, 1.272	0.590	112.76,165.38
Pb ₉ Se ₇₁ Ge ₈ Sn ₁₂							
10	419.10	528.51, 571.26	720.56	241.73, 286	0.569, 1.019	0.581	109.41,152.16
15	420.58	528.72, 567.47	699.13	245.43, 286.72	0.634, 1.115	0.601	108.14,146.89
20	422.06	529.23, 571.09	700.64	246.94, 288.82	0.625, 1.150	0.602	107.17,149.03
25	423.69	530.23, 573.62	706.77, 702.24	251.56, 288.50	0.603, 1.165	0.599, 0.603	106.54,149.93

Table 1 Values of glass transition temperature (T_g), peak crystallization temperature (T_p), onset crystallization temperature (T_c), melting temperature(T_m) and thermal stability parameters of Pb₉Se₇₁Ge_{20-x} Sn_x(8 \leq x \leq 12) at different heating rates.

х	Activation energies of crystallization(KJ/mol)					
	Kissinger		Mahadevan		Moynihan	
	Peak1	Peak2	Peak1	Peak2	Eg(KJ/mol)	
8	205.074		214.481		261.183	
9	249.723		259.072		231.656	
10	118.924		135.018		345.364	
11	204.919	313.630	216.852	341.42	321.182	
12	173.512	189.093	183.069	209.424	293.011	

 Table 2 The values of activation energies of crystallization calculated by Kissinger, Mahadevan approaches and activation energy of glass transition of samples by Moynihan approach.

3.2.2 Activation Energy of Glass Transition By Moynihan Approach

The one approach used for calculation of activation energy of glass transition is Moynihan's relation [19] Moynihan has found in his derivation of the dependence of T_g on heating rate $|\alpha|$. Accordingly for a given heating rate

$$\frac{dln|\alpha|}{d(\frac{1}{T_q})} \approx \frac{-\Delta E}{R} \quad (1)$$

Plots of ln α against 1000/T_g are plotted for various glassy alloys shown in figure 4. The values of activation energies found by Moynihan approach is tabulated in table 2.



Fig. 4 Plots of $\ln \alpha$ against 1000/ T_g glassy alloys from Moynihan equation.

Activation energy of glass transition decrease as x varies from 8 to 9. This is due to entrance of Sn in Pb-Se-Ge network, which weaken the network and decrease the activation energy of glass transition. Then after for x=10 this activation energy increase which might be due to replacement of Se-Se bonds by Sn-Se bonds(having large bond energy). The further addition of Sn to the glass matrix replace mostly the Ge-Se bonds by Sn-Se bonds. So it results in decrease in cohesive energy and mean bond energy of the glassy matrix as well as the activation energy of glass transition.

3.2.3 Activation energy of crystallization

Kissinger model.

The activation energy for crystallization, E_c , can be obtained from the dependence of peak crystallization temperature T_p on heating-rate, using the equation derived by Kissinger [20-21] as

$$ln\left(\frac{\alpha}{T_p^2}\right) = ln\left(\frac{ARnK_o}{E_c}\right) - \frac{E_c}{RT_p} \text{ and can be written as}$$
$$ln\left(\frac{\alpha}{T_p^2}\right) = \frac{-E_c}{RT_p} + \text{ constant}$$
(2)

Here α is the heating rate, Tp peak crystallization temperature, R gas constant.

The plot of $\ln\left(\frac{\alpha}{T_p^2}\right)$ vs 1000/T_p is shown in figure 5. The activation energy of crystallization is calculated from slope of the straight lines in the figure 5 and tabulated in table 2.



Fi.g 5 The plot of $ln\left(\frac{\alpha}{T_p^2}\right)$ vs 1000/ T_p for Kissinger approach.

Mahadeven Method

Mahadevan approximated the Kissinger approach, according to him the variation of $\frac{1}{T_p^2}$ with $\ln \alpha$ is much slower than that of $1/T_p$ with $\ln \alpha$, Mahadevan*et al* [22] have approximated Kissinger equation to the following form,

$$\ln(\alpha) \approx -\left(\frac{E_c}{RT_p}\right) + \text{constant}$$
 (3)

The activation energies for the present system can also be deduced from the slopes of the plots of $\ln\alpha$ against $1000/T_p$. in figure 6 and tabulated in table 2.



Fig. 6 The plot of $\ln(\alpha)$ versus 1000/ T_p for Mahadevan approach.

The addition of Sn creates the structural disorder in the material. Beyond x=10 phase separation in the material has been found. Mainly two phases GeSe₂ and SnSe₂ appear in the material which causes phase splitting and double crystallization peaks. We analyze from the table 2 that activation energies obtained from Mahadevan method is approximately around the activation energies obtained from the Kissinger's approach. However this slight difference in the activation energies obtained by these approaches may be attributed to the different formalism of the equations in these models based on approximations.

3.3. Optical and dielectric parameters

Optical band gap and refractive index (n) are required to know the material's optical behavior. The refractive index changes under the influence of light. The value of the refractive index of film in the spectral region of medium and weak absorption can be calculated by the expression [23].

$$n = \frac{1+R}{1-R} \pm \left[\left(\frac{R+1}{R-1} \right)^2 - (1+k^2) \right]^{0.5} (4)$$

The reflection spectra of material are shown in figure 7.



Fig. 7 The reflection spectra of chalcogenide glass thin filmsofPb₉Se₇₁Ge_{20-x}Sn_x.

The extinction coefficient (k) has been calculated using the relation $k = \frac{\alpha \lambda}{4\pi} (5)$

where α is the absorption coefficient [24] and is given by $\alpha = \frac{1}{d} \ln \left(\frac{1}{x} \right) \quad (6)$

where x is the absorbance.

x	n	k	Eg(eV)	\mathcal{E}_{i}	\mathcal{E}_{r}
8	2.35	0.0185	2.76	0.0876	5.6165
9	3.28	0.0219	2.71	0.1436	10.7579
10	3.32	0.0384	2.62	0.2549	11.0209
11	3.45	0.0515	2.56	0.3553	11.8998
12	3.63	0.0606	2.48	0.4399	13.1732

Table 3.Values of refractive index (n), extinction coefficient (k), optical energy gap (E_g) and real part (ε_r) , imaginary part (ε_i) of dielectric constant.

The optical absorption spectrum is the most productive tool for developing the energy band diagram. The absorption coefficient of an amorphous semiconductor in the high absorption region can be calculated by using Tauc's relation [24] $\alpha hv = B(hv - Eg)^m$ where *B* is a constant, E_g is the optical energy gap of the material and *m* determines the type of transition (m = 1/2 for the direct transition and m = 2 for the indirect allowed transition).



Fig.8 Plots of $(\alpha hv)^{0.5}$ versus (hv) for thin films of $Pb_9Se_{71}Ge_{20-x}Sn_x$.

The values of the optical energy gap (Eg) obtained for indirect allowed transition for thin films of Pb₉Se₇₁Ge_{20-x}Sn_x by making $(\alpha hv)^{0.5} \rightarrow 0$ are given in table 3 and shown in figure 8. The optical parameters refractive index (*n*)and extinction coefficient *k* has the compositional dependence as both increases with increasing Sn content. Optical constants in anisotropic media depend on electronic polarization of atoms, ions or molecules of the material when subjected to an electric field. The polarization does not respond instantly to an applied field and result in dielectric loss expressed as permittivity (ε), which is complex and frequency dependent and is given as $\varepsilon = \varepsilon_r$ + $i\varepsilon_i$, where(ε_r) and (ε_i) are real and imaginary parts of permittivity respectively. The real (ε_r) and imaginary (ε_i) parts of the dielectric constant of thin films were also calculated by using the value of *n* and *k* in the following relations [25]:

$$\varepsilon_r = n^2 - k^2 \qquad (7)$$

$$\varepsilon_i = 2nk \qquad (8)$$

It is evident from table 3 that the values of ε_r and ε_i increase on incorporating Sn into the Pb-Se–Ge system as Sn cause the more defect states in the glass matrix, which in turn can increase band tailing in gap and density of localized states which result in reduction of band gap.

4. Conclusion

The thermal and optical properties of the Pb-Ge-Se system have been greatly influenced by Sn addition. The phase transformation kinetics of $Pb_9Se_{71}Ge_{20-x}Sn_xglasses$ has been studied using Kissinger, Moynihan and Mahadavan apporaches. Samples at x=11,12 show a single glass transition and double crystallization peaks corresponding to $SnSe_2$ and $GeSe_2$ rich phases. Glass transition temperature decreases with increasing Sn concentration. The glassy material has high value of refractive index and decreasing optical band gap with increasing content of Sn in the glassy matrix.

References

- [1] A. B Seddon et al J. Non-Cryst. Solids 352, 2515 (2006)
- [2] E. R Shaaban, M A Kaid, El Sayed Moustafa and A. Adel J. Phys. D: Appl. Phys. 41, 125301 (2008)
- [3] A. A Wilhelm, Boussard-Pl'edel C, Q. Coulombier, J. Lucas, B. Bureau and P. Lucas *Adv. Mater.***19**, 3796 (2007),

[4]Kolobov A V, Fons P, Frenkel A I, Ankudinov A L, Tominaga J and Uruga T *Nature Mater.* **3**,703 (2004)

[5] C.Meneghini, A. Villeneuve, J.Opt.Soc.Am.B15, 2946 (1998).

- [6] K.Paivasaari, V. K. Tikhomirov, J. Turunen, Optics Express 15, 2336 (2007).
- [7] A.Devasia, S. Kurinec, K.A.Campbell and S. Raoux, App.Phy.Lett. 96,141908 (2010).
- [8] L.E. Mcneil, J.M.Mikrut, M .Peters, J. Sol.Stat. Commun.62, 101(1987).
- [9] J. M. Mikrut, L. E.Mcneil, J. Non-cryst. Solids.114, 127(1989).
- [10] E.A.Kislitskaya, V.F.Kokorina, Translated from ZhurnalPrikladnoiKhimii44, 646(1971).
- [11] M.M. Wakkad, E.Kh.Shokr, Sh. Mohamed, Phys. Stat.Sol. (a)183, 399(2001).
- [12] G.Mathew, K. N. Madhusudanan , J.Philip, Phys. Stat.Sol. (a) 168, 239 (1998) .
- [13] N.B. Maharajan, K.Singh, N. S. Sexena, Phys. Stat. Sol.(a) 195, 305 (2003).
- [14] G.Kaur, T. Komatsu J. Mater. Sci. 36, 4531(2001).
- [15] M.S. Kamboj , R. Thangaraj, Eur. Phys. J. Appl. Phys. 24, 33 (2003).
- [16] J.Bicerano and S. R. Ovshinsky J. Non-Cryst. Solids 74, 75 (1985).
- [17] W. Kauzmann Chem Rev. 43 219 (1948).
- [18] Hruby A. Czech J Phys B 22, 1187 (1972).
- [19] C. T. Moynihan, A. J. Easteal, J. Wilder, J. Tucker, J. Phys. Chem. 78, 2673 (1974).
- [20] H. E. Kissinger, J Res Nat Bur Stand. 57, 217 (1956).
- [21] H. E. Kissinger, Anal Chem. 29, 1702 (1957).
- [22] K.White, R. L. Crane, J. A. Snide, J. Non-Cryst. Solids 103, 210 (1988).
- [22] J S. Mahadevan, A Giridhar, A. K. Singh, J. Non-Cryst Solids. 88, 11(1986)..
- [23] El-Raheem MMAbd, J. Phys.: Condens. Matter 19, 216209 (2007).
- [24] J. Tauc, The Optical Properties of Solids (Amsterdam:North-Holland1970), pp171-180
- [25] M.M. Wakkad, E.K.H.Shoker, S. H. Mohamed, J. Non-Cryst. Solids 265, 157 (2000).