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A study of thermal crystallization in $\text{Se}_{70}\text{Te}_{30-x}\text{Sb}_x$ glassy alloys

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Abstract. — The time dependence of dc conductivity for different compositions of the amorphous semiconducting system $\text{Se}_{70}\text{Te}_{30-x}\text{Sb}_x$ ($0 \leq x \leq 10$) has been studied at various temperatures in the range 70-100 °C. An attempt is made to fit the experimental data to the crystallization theory of Avrami, giving the activation energy of crystallization and the order parameter. An increase in the activation energy of crystallization upto 4 at% of Sb is attributed to an increased disorder. However, at higher concentration of Sb, an ordered structure may be established due to the formation of micro-crystalline phases, as observed in X-ray diffraction patterns, which may result in the decrease of activation energy after 4 at% of Sb.

Introduction.

Se-Te alloys have gained much importance because of their higher photo-sensitivity, greater hardness, higher crystallization temperature, and smaller aging effects as compared to pure Se glass. The effect of incorporation of Sb on the electrical properties of these glasses has been studied by various workers [1-5]. In general it is observed that the dc conductivity increases, the activation energy for dc conduction decreases, thermoelectric power decreases, and the photoconductive decay becomes slower on incorporation of Sb to the binary Se-Te alloy. To explain the above results it is generally assumed that the addition of Sb in the Se-Te system leads to a cross-linking of the Se-Te chains which enhances the disorder in the system and hence leads to a deeper penetration of the localized states into the energy gap.

Crystallization studies may be useful in predicting the switching behaviour in these glasses as type of switching (threshold or memory) depends upon the rate of crystallization [6]. Apart from the technical importance, the knowledge of the crystallization process is important for the better understanding of the short range order in these materials.

In the present paper we report the crystallization studies in glassy $\text{Se}_{70}\text{Te}_{30-x}\text{Sb}_x$ where $0 \leq x \leq 10$. dc conductivity is measured as a function of time during crystallization. These studies have been carried out at different temperatures ranging from glass transition temperature and melting temperature. The crystallization kinetic parameters are calculated by fitting the extent of crystallization to the Avrami's theory of isothermal transformation. The

results indicate that the activation energy of crystallization increases monotonically with Sb concentration upto 4 atomic percent. However, at higher concentration of Sb, ΔE decreases with Sb concentration.

Theory of measurement.

Avrami's equation [7] relating the fraction of the crystalline volume (α) grown from the amorphous phase to the time of annealing, t , is given by

$$\alpha(t) = 1 - \exp(-Kt^n) \quad (1)$$

where K is the rate constant and n is the order parameter which depends upon the mechanism of crystal growth.

The rate constant K is given by the Arrhenius equation as

$$K = K_0 \exp\left(\frac{-\Delta E}{kT}\right) \quad (2)$$

where K_0 is a constant and ΔE is the crystallization activation energy.

The transformation process from the metastable phase (amorphous) to the stable one (crystalline) is accompanied by a continuous change of the electrical conductivity, σ , which is a sensitive structural parameter. The kinetics of the transformation process can thus be calculated by considering the electrical conductivity at any intermediate point during the transformation process as a characteristic quantity for a material containing two phases. El Monsly and Borisova [8], using dc conductivity as a parameter to study the crystallization kinetics, suggested an empirical relation for α , given by

$$\ln \sigma = \alpha \ln \sigma_c + (1 - \alpha) \ln \sigma_a \quad (3)$$

where σ_c and σ_a are the conductivities of the crystalline and amorphous phases having volume fractions α and $(1 - \alpha)$ respectively, and σ is the conductivity of a mixture during the amorphous to crystalline (a-c) transformation. Extensive investigations of the crystallization process from conductivity data for the amorphous phase of selenium and of selenium based alloys [9-11] have shown the validity of equation (3) subject to the limitation that σ changes by a large value during the growth stage.

In the present case, conductivity increases by several orders of magnitude on crystallization and hence equation (3) can be used to calculate α by measuring σ as a function of time during isothermal annealing at temperatures near the crystallization temperature. Once the values of α as a function of time are known at different isothermal temperatures of transformation, the kinetic parameters (ΔE and n) can be calculated using equations (1) and (2).

Experimental procedure.

Glassy alloys of $\text{Se}_{70}\text{Te}_{30-x}\text{Sb}_x$ ($x = 0, 2, 4, 6, 8, 10$) were prepared by quenching technique. 5N pure materials were sealed in quartz ampoules (internal diameter ~ 8 mm) in a vacuum of $\sim 10^{-5}$ Torr. The ampoules were kept inside the furnace where the temperature was raised slowly ($3-4^\circ\text{C min}^{-1}$) to 600°C . The ampoules were rocked frequently for 10 h at the maximum temperature to make the melt homogeneous. Quenching was done in ice water and the glassy nature of alloys was verified by X-ray diffraction.

The solidified glassy alloys thus prepared were ground to a very fine powder and the pellets (diameter ~ 6 mm and thickness ~ 0.5 mm) were obtained after compressing the powder in a die at a load of $(3-4) \times 10^4$ N.

The amorphous to crystalline transformation (a-c) was studied by measuring the d.c. conductivity (σ) as a function of time (2 min interval) at various temperatures between the glass transition and melting temperatures. The temperature was kept constant during the amorphous to crystalline transformation period. The remarkable increase of d.c. conductivity implies that the measured conductivity (σ) at any time (t) is the result of two conductivities σ_a and σ_c corresponding to double phase system, amorphous and crystalline.

The conductivity measurements were taken in a vacuum $\sim 10^{-3}$ Torr by mounting the samples in a specially designed metallic sample holder. The resistance was measured using Keithley Electrometer (model 614). The temperature was measured using a calibrated copper constant an thermocouple. Different pellets were taken for each temperature of annealing. The annealing temperature was obtained at a fast heating rate and then maintained constant till a saturation in the resistance was reached.

Results and discussions.

At any annealing temperature between glass transition and melting, σ varies with time. Figure 1 shows the variation in $\ln \sigma$ with the annealing time « t » of the amorphous to crystalline transformation of $\text{Se}_{70}\text{Te}_{28}\text{Sb}_2$, carried out in the temperature range 70-100 °C. The results for other glassy alloys, i.e., $\text{Se}_{70}\text{Te}_{30}$, $\text{Se}_{70}\text{Te}_{30-x}\text{Sb}_x$ ($2 \leq x \leq 10$), were also of the same nature.

During the transformation process, there appear to be three regimes of σ versus annealing time t . The part AB in figure 1 is linear and represents a gradual increase in σ as a result of the normal heating of the amorphous samples. The less-pronounced increase of σ during the

Fig. 1. — Annealing time dependence of the dc conductivity for $\text{Se}_{70}\text{Te}_{28}\text{Sb}_2$ sample during isothermal amorphous crystal phase transformations (the solid line is a guide for the eye).

second state BC is mainly accompanied by the formation of nuclei and their growth at the expense of the parent amorphous phase. The third stage CD, which covers a relatively large increase in σ , indicates the subsequent crystal growth of the new phase until maximum crystallization of the sample volume is attained, as signified by the limiting value, D, in figure 1. In the present study we are interested to understand the crystallization kinetics of crystal growth, i.e., part CD of the curve in figure 1.

The fraction transformed at different annealing times $\alpha(t)$ was calculated by using the relative increase in the electronic conduction during the crystallization growth (i.e. CD part on the curve of Fig. 1). σ_a is taken as the conductivity at point C and σ_c , that at point D in figure 1. The results are plotted in figure 2 for $\text{Se}_{70}\text{Te}_{28}\text{Sb}_2$. The results for other glassy alloys were also of the same nature (results not shown here).

The order parameter n of equation (1) characterizing the nucleation mechanism and the dimension of crystal growth has been calculated using the equation

$$\ln [\ln (1 - \alpha)^{-1}] = \ln K + n \ln t. \quad (4)$$

Fig. 2. — Extent of crystallinity vs. annealing time for $\text{Se}_{70}\text{Te}_{28}\text{Sb}_2$ crystallized for different isotherms.

According to equation (4), the plot of $\ln [\ln (1 - \alpha)^{-1}]$ versus $\ln t$ leads to a straight line of slope n and intercept $\ln K$. This has been verified for $\text{Se}_{70}\text{Te}_{28}\text{Sb}_2$ in figure 3. For other glassy alloys, similar results were obtained. Table I indicates the values of n at different temperatures in each glassy alloy.

The values of the temperature dependent crystallization rate constant (K), evaluated from the intercept of curves in figure 3, are plotted as a function of temperature in figure 4 for all the glassy alloys of the chosen system $\text{Se}_{70}\text{Te}_{30-x}\text{Sb}_x$ ($0 \leq x \leq 10$). The straight lines, thus

Fig. 3. — Avrami plots of the crystallization of $\text{Se}_{70}\text{Te}_{28}\text{Sb}_2$ for different isotherms.

Table I. — Temperature dependence of the order parameter (n), in $\text{Se}_{70}\text{Te}_{30-x}\text{Sb}_x$ glassy alloys.

$\text{Se}_{70}\text{Te}_{30}$		$\text{Se}_{70}\text{Te}_{28}\text{Sb}_2$		$\text{Se}_{70}\text{Te}_{26}\text{Sb}_4$		$\text{Se}_{70}\text{Te}_{24}\text{Sb}_6$		$\text{Se}_{70}\text{Te}_{22}\text{Sb}_8$		$\text{Se}_{70}\text{Te}_{20}\text{Sb}_{10}$	
Temp. (°C)	n	Temp. (°C)	n	Temp. (°C)	n	Temp. (°C)	n	Temp. (°C)	n	Temp. (°C)	n
75	1.0	80	1.6	80	1.6	70	1.3	80	1.1	70	1.4
80	0.9	85	1.8	85	1.7	75	1.2	85	0.9	75	1.2
85	0.9	90	1.9	90	1.6	80	1.1	90	0.9	80	1.4
90	1.1	100	2.0	95	2.0	85	1.4	95	0.9	85	1.3

Fig. 4. — Arrhenius plots of crystallization of $\text{Se}_{70}\text{Te}_{30-x}\text{Sb}_x$.

Table II. — Composition dependence of activation energy of crystallization in $\text{Se}_{70}\text{Te}_{30-x}\text{Sb}_x$ glassy alloy.

Composition	ΔE (kJ/mole)
$\text{Se}_{70}\text{Te}_{30}$	153
$\text{Se}_{70}\text{Te}_{28}\text{Sb}_2$	166
$\text{Se}_{70}\text{Te}_{26}\text{Sb}_4$	186
$\text{Se}_{70}\text{Te}_{24}\text{Sb}_6$	174
$\text{Se}_{70}\text{Te}_{22}\text{Sb}_8$	161
$\text{Se}_{70}\text{Te}_{20}\text{Sb}_{10}$	124

obtained, confirm the validity of equation (2). The activation energy of various compositions, obtained from the slope of $\ln K$ vs. $1000/T$ curves, is given in table II.

Figure 5 shows the variation of ΔE with Sb concentration in $\text{Se}_{70}\text{Te}_{30-x}\text{Sb}_x$ ($0 \leq x \leq 10$) glassy system. It is clear from this figure that ΔE is composition dependent and is maximum for $x = 4$.

A similar type of discontinuity at 4 at% Sb was also observed in our photoconductivity measurements [12] and a.c. conductivity measurements [13] in the same glassy system.

Fig. 5. — Composition dependence of activation energy of crystallization of $\text{Se}_{70}\text{Te}_{30-x}\text{Sb}_x$ system.

An increase in ΔE , upto 4 at% of Sb is expected if one considers that antimony enhances disorder upto 4 at% as mentioned earlier in this paper. However, for higher concentrations ($x \geq 6$) one can expect a reversal in the trend due to micro-crystalline phase formation.

This is confirmed by X-ray diffraction analysis where crystalline peaks were found to be superimposed on broad amorphous halos when Sb concentration reaches 6 at%.

Conclusion.

The amorphous to crystalline transformation process in the ternary system $\text{Se}_{70}\text{Te}_{30-x}\text{Sb}_x$ has been studied for six different compositions with $0 \leq x \leq 10$, using the electrical conductivity as a structural characteristic quantity to follow the growth of crystalline phases in the amorphous matrix. It is shown that Avrami equation correctly describes the crystallization process. Activation energy for crystallization of amorphous $\text{Se}_{70}\text{Te}_{30-x}\text{Sb}_x$ ($0 \leq x \leq 10$) determined from time dependence of electrical conductivity measured during isothermal annealing, shows a discontinuity at 4 at% of Sb, which is explained in terms of the formation of a micro-crystalline phase at higher concentrations of Sb ($x \geq 6$).

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References

- [1] Mehra R. M., Gurinder and Mathur P. C., International Conf. Semiconductor Materials (New Delhi, Dec. 1988) (Unpublished).
- [2] Sakai H., Shimakawa K., Inagaki Y. and Arizumi T., *Jpn J. Appl. Phys.* **13** (1974) 500.
- [3] Shimakawa K., Yoshida A. and Arizumi T., *J. Non-Cryst. Solids* **16** (1974) 258.
- [4] Nagels P., *Phys. Status Solidi (A)* **59** (1980) 505.
- [5] Jope J. K., *Ind. J. Pure Appl. Phys.* **20** (1982) 774.
- [6] Kumar A., Ph. D. thesis, Punjab Univ. (1979).
- [7] Avrami M., *J. Chem. Phys.* **8** (1940) 212.
- [8] El Monsly M. I. and Borisova Z. U., *Bull. Acad. Sci. USSR, Inorg. Mater.* **3** (1967) 923.
- [9] Kotkata M. F., Kamal G. M. and El-Mously M. K., *Ind. J. Tech.* **20** (1982) 390.
- [10] Kotkata M. F., Ayad F. M. and El-Mously M. K., *J. Non-Cryst. Solids* **33** (1979) 13.
- [11] Agarwal P., Goel S. and Kumar A., *J. Phys. III France* **1** (1991) 1429.
- [12] Dwivedi P. K., Srivastava S. K. and Kumar A., *Il Nuovo Cimento* (to be published).
- [13] Kumar S., Arora R. and Kumar A. (to be published).

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