



EFFECT OF ANTIMONY SUBSTITUTION ON THE CRYSTALLIZATION KINETICS OF Se70 Te30 GLASSY SYSTEM

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ABSTRACT

Crystallization kinetics has been studied in amorphous $Se_{70}Te_{30}Sb_x$ ($0 \leq X \leq 10$) by measuring the time dependence of electrical conductivity during the crystallization process. The samples have been annealed isothermally at various temperatures in the range of 70 -100°C. The experimental data has been fitted to the theory of surface induced crystallization process and various parameters have been calculated. The variation of these parameters with Sb concentration is found to be highly composition dependent.

The activation energy (E_c) the velocity of crystallization (V_c) and pre exponential factor of growth velocity (V_{co}) are found to increase up to 4 at % of Sb. However, a decrease is observed at higher concentration. The increase up to 4 at % may be associated with the increase in disorder. While, 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. This may be the reason for the decrease of the activation energy of crystallization after 4 at % of Sb.

An excellent correlation is found between V_{co} and E_c which is in accordance with the Meyer-Neldel relation. This is explained on the assumption that the viscosity of the melt controls the crystallization velocity in the aforesaid glassy system.

INTRODUCTION:

Se -Te glassy alloys have gained much importance because of their higher photosensitivity, greater hardness, higher crystallization temperature and smaller aging effects as compared to pure Se glass. The effect of incorporation of antimony (Sb) on the electrical properties of these alloys 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 photo -conductive 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 in amorphous Se-Te alloys has been studied using various techniques such as Differential Scanning Calorimetry (DSC) [6], Electron microscopy [7], Resistivity [8], Raman scattering [9] etc. The aim of the present work is to study the isothermal crystallization kinetics and discuss the effect of Sb substitution on the crystallization of amorphous Se-Te alloys. Since the conductivity of the amorphous state is much lower than that of the crystalline state, the electrical

measurements are expected to be very sensitive to phase changes in these materials [10]. The conductivity has also been used by a few workers to study crystallization in amorphous semiconductors [6-11].

In the present paper we report the crystallization studies in glassy Se₇₀Te_{30-x}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 (T_g) to melting temperature (T_m). The experimental data is fitted to the theory of surface induced crystallization process. Various parameters have been calculated and their variation with Sb concentration is discussed. The results indicate that the activation energy (E_c) and velocity of crystallization (V_c) along with pre-exponential factor of growth velocity (V_{c0}) increase up to 4 at% of Sb. However, a decrease is observed at higher concentrations.

2. Theory of Measurements:

2.1 Surface-Induced-crystallization Process:

When nuclei covers a surface of radius 'a' and when 'a' is large compared to the thickness of the sample layer, the crystallization occurs similar to an epitaxial growth, the crystalline phase reaching the opposite surface of the layer at a time $\tau = \frac{e}{V_c}$ where e is thickness of the sample and V_c is the growth rate

[12]. This is referred to as surface induced crystallization (SIC). It has been shown that at any given time 't' the conductance of the layer can be written in this case as [13] :-

$$\Sigma(t) = \Sigma(a) \left\{ 1 + \left(\frac{\sigma_m}{\sigma_a} - 1 \right) \frac{V_c t}{e} \right\} \dots \dots \dots (i)$$

where E(a) is the initial conductance of the amorphous layer, E(t) is the conductance at any time t, e is the thickness of the sample, V_c is crystallization velocity,

$$\sigma_m = \alpha_c \sigma_c + \alpha_a \sigma_a \dots \dots \dots (ii)$$

where α_a and α_c are the volume fractions for the amorphous and crystalline phases i.e. $(\alpha_a + \alpha_c = 1)$.

2.2 Procedure for obtaining crystallization velocity:

The amorphous to crystalline transformation (a - c) was studied by measuring the DC 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 DC 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 crystallization process occurs in three stages. During the first stage ($0 < t < t_0$), conductance increases quadratically with time as the fit of the data has predicted. The optical microscope observations by Nasu et. al. [8] have shown that the crystallization in a-Se-Te occurs in a two dimensional way at the interface. The crystallites grow in a disk-like form in this region along the substrate. According to Landauer [14], the above two dimensional crystallization leads to a quadratic variation of conductance with time.

During the second stage ($t_0 < t < t_1$), the conductance varies linearly as predicted by the model and the crystallization is completed at $t = t_1$, the growth of the crystallized area towards the free surface becomes dominant during second stage. The linear time dependence of the conductance up to a time t_1 was found to occur in all the samples. The process is termed as SIC. It is found that the conductance varies linearly with time, until $t = t_1$, at which SIC is completed ($t_1 = e/V_c$).

Finally, the conductance saturates for $t > t_1$, the saturation of the conductance ratio after time 't' results from the crystallization of the rest of the amorphous domains in the sample. This occurs when all the nucleation sites are exhausted and the growth of the crystallites stops.

In the analysis, σ_m is replaced by σ_t which refers to the conductivity of the mixture containing two phases at any given time between the amorphous and crystalline states.

The crystallization velocity was obtained through the measurement of (time at which the linearity of

$$\frac{\sum(t)}{\sum(a)} \text{ breaks off).}$$

3. 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 $\sim 8\text{mm}$) in a vacuum of $\sim 10^{-5}$ Torr. The ampoules were kept inside the furnace where the temperature was raised slowly ($3 - 4^\circ\text{C}/\text{min}$) to 600°C . The ampoules were rocked frequently for 10 hrs 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 $\sim 6\text{mm}$ and thickness $\sim 0.5\text{mm}$) were obtained after compressing the powder in a die at a load of $(3 - 4) \times 10^4\text{N}$.

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-constantan thermocouple. Different pellets were taken for each temperature of annealing near crystallization temperature. The annealing temperature was obtained at a fast heating rate and then maintained constant during measurements till saturation in the resistance was reached.

4. Results and Discussions:

The conductance variation during the isothermal annealing of amorphous $\text{Se}_{70}\text{Te}_{30-x}\text{Sb}_x$ ($0 \leq x \leq 10$) has been used to elucidate the crystallization process. The variation of the conductance ratio as a function of time for a- $\text{Se}_{70}\text{Te}_{28}\text{Sb}_2$ is shown in Fig.1. The crystallization time τ was obtained at each annealing temperature and corresponding growth rates V_c were calculated ($V_c = e / \tau$).

The crystallization velocities obtained using the above method are displayed as a function of temperature in Fig. 2 and given in Table-I.

It is evident from Fig. 2 that the crystallization velocities show a thermally activated behaviour with an Arrhenian dependence for each of the composition given by

$$V_c = V_{co} \exp\left(-\frac{E_c}{kT}\right) \dots\dots\dots\text{(iii)}$$

Fig. 3 shows the dependence of the activation energy E_c of crystallization on the Sb substitution in a- $\text{Se} : \text{Te}$. It is clear from this figure that E_c is highly composition dependent and is maximum for $x = 4$. The values of activation energy and $\ln V_{co}$, obtained from $\ln V_c$ versus $1000/T$ curves, are given in Table-II for various compositions used in the present study. It is clear from this table that a discontinuity in crystallization parameters occurs at 4 at % of Sb.

A similar type of discontinuity at 4 at % of Sb was also observed in our photoconductivity measurements [15] and a.c. conductivity measurements [16] in the same glassy system.

An increase in activation energy of crystallization E_c up to 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 ($x > 6$) 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 %.

5. The Meyer-Neldel relations in a- $\text{Se}_{70}\text{Te}_{30-x}\text{Sb}_x$ glassy Alloys:

Fig. 4 shows the plot of $\ln V_{co}$ versus E_c in the $\text{Se}_{70}\text{Te}_{30-x}\text{Sb}_x$ glassy system. It is clear from this figure that an excellent correlation exists between the V_{co} and E_c which is referred to as the well known Meyer-Neldel relation [17] and is described as

$$V_{\infty} = V_{\text{coo}} \exp\left[\frac{E_c}{E_{\infty}}\right] \dots\dots\dots (iv)$$

Where V_{coo} is a constant and $E_{\text{co}} \sim 0.0313$ eV as deduced from Fig. 4.

Although the Meyer-Neldel relation has been observed in various physical systems, there is still no satisfactory uniform explanation for its occurrence. We have tried to understand the origin of the above relation assuming that the crystallization velocity in amorphous materials is inversely proportional to the viscosity of the melt, which has a Vogel-Tammann-Fulcher (VTF) type of behaviour [10], i.e.,

$$\eta = \eta_0^{-1} \exp\left[\frac{E_0}{K(T - T_0)}\right] \text{ where } 0, E_0 \text{ and } T_0 \text{ are constants. This result has been reported by Kasap and}$$

Juhasz [18] in their experimental examination of the crystallization process of a-Se-Te alloys. Then the crystallization velocity is modified as

$$V_c = C \eta_0^{-1} \exp\left[-\frac{E_0}{k(T - T_0)}\right] \dots\dots\dots (v)$$

This eqn. is almost indistinguishable from eqn. (iv) in a narrow range of temperature studied in the present experiment, except for the vicinity of T_0 . Moreover, if we try to fit in the Arrhenian dependence of V_c in a temperature range T_1 to T_2 , we obtain:

$$V_{\text{co}} = C \eta_0^{-1} \exp\left[-\frac{E_0}{E_{\text{co}}}\right] \dots\dots\dots (vi)$$

$$E_{\text{co}} = k T \cdot \left[\frac{y_1 y_2 + y_2 y_3 - y_3 y_1}{y_2^2 - y_2 y_3 + y_3 y_4} \right] \dots\dots\dots (vii)$$

where $y_1 = a - b$, $y_2 = \ln(a/b)$, $y_3 = \ln\{(a-1)/(b-1)\}$, $y_4 = 1/b - 1/a$, $a = T_2/T_0$, $b = T_1/T_0$
The estimated E_{co} value of 0.0386 eV obtained using $T_1 = 343$ K, $T_2 = 373$ K and $T_0 = 290$ K [19] is in good agreement with the observed value. This seems to indicate that the crystallization velocity in a-Se₇₀Te₃₀-xSbx glassy system is controlled by the viscosity of the melt. The lack of viscosity data on the amorphous phase around the crystallization temperature does not allow us to directly link viscosity with crystallization velocity. However, the increase in T_g with Te concentration [19] is a good indicator of the increase in viscosity with Te and probably, the same may be in Sb substitution also.

6. Conclusion :

The amorphous to crystalline transformation process in the ternary system of Se₇₀Te₃₀-xSbx has been studied for six different compositions with 0

Table – 1
Temperature Dependence of the Crystallization Velocity in a-Se₇₀Te₃₀-xSb_x Glassy Alloys

Se ₇₀ Te ₃₀		Se ₇₀ Te ₂₈ Sb ₂		Se ₇₀ Te ₂₆ Sb ₄		Se ₇₀ Te ₂₄ Sb ₆		Se ₇₀ Te ₂₂ Sb ₈		Se ₇₀ Te ₂₀ Sb ₁₀	
Temp. (°C)	V _c (A°/Sec)	Temp (°C)	V _c (A°/Sec)	Temp (°C)	V _c (A°/Sec)	Temp (°C)	V _c (A°/Sec)	Temp (°C)	V _c (A°/Sec)	Temp (°C)	V _c (A°/Sec)
75	7.94x10 ²	80	8.33x10 ²	80	4.90x10 ²	70	3.62x10 ²	80	6.67x10 ²	70	3.26x10 ²
80	1.11x10 ³	85	1.11x10 ³	85	6.41x10 ²	75	5.21x10 ²	85	7.58x10 ²	75	5.95x10 ²
85	1.39x10 ³	90	1.28x10 ³	90	1.28x10 ³	80	9.26x10 ²	90	1.04x10 ²	80	6.41x10 ²
90	1.85x10 ³	100	1.39x10 ³	95	1.67x10 ³	85	1.85x10 ²	95	1.39x10 ²	85	7.58x10 ²

Table – II

Composition dependence of the activation energy of crystallization (E_c) in a-Se₇₀Te_{30-x}Sb_x Glassy alloys.

Glassy Alloys	E _c (eV)	In V _{co} (A ⁰ /sec.)
Se ₇₀ Te ₃₀	0.65	28.21
Se ₇₀ Te ₂₈ Sb ₂	0.80	33.03
Se ₇₀ Te ₂₆ Sb ₄	1.21	45.66
Se ₇₀ Te ₂₄ Sb ₆	1.08	42.29
Se ₇₀ Te ₂₂ Sb ₈	0.62	26.65
Se ₇₀ Te ₂₀ Sb ₁₀	0.32	17.05

Figure Captions:

Fig: 1. Variation of the conductance ratio as a function of annealing time for a- $\text{Se}_{70}\text{Te}_{28}\text{Sb}_2$ at an annealing temperature of 358 K.

Fig. 2. Crystallization velocities as a function of temperature for a- $\text{Se}_{70}\text{Te}_{30-x}\text{Sb}_x$ ($0 \leq x \leq 10$) system.

Fig. 3. The activation energy of crystallization as a function of Sb content in a- $\text{Se}_{70}\text{Te}_{30-x}\text{Sb}_x$ ($0 \leq x \leq 10$) system.

Fig. 4. The Meyer-Neldel relation in a- $\text{Se}_{70}\text{Te}_{30-x}\text{Sb}_x$ ($0 \leq x \leq 10$) system as a consequence of the dependence of the activation energy on the pre-exponential factor of crystallization velocity.

REFERENCES

1. Shimakawa K., Yoshida A., and Arizumi T., J. Non-cryst. Solids 16 (1974) 258.
2. Sakai H., Shimakawa K., Inagakiy., and Arizumi T., Jpn. J. Appl.Phys. 13 (1974) 500.
3. Nagels p., Phys. Status Solidi (A) 59 (1980) 505.
4. Mehra R.M., Gurinder and Mathur P.C., International conf. on semiconductor materials (New Delhi, Dec. 1988) (unpublished).
5. Jope, J. K., Ind. J. pure Appl. Phys. 20 (1982) 774.
6. Kotkata M.F., J. Non-cryst. Solids. 59 & 60 (1983) 891.
7. Damodara Das V., Laxmi P.J., Phys. Rev. B 37 (1988) 720.
8. Nasu T., Naito H., Kurosawa K., Matsushita T., Okuda M., Japan J. Appl. Phys. 28 suppl. 28(3) (1989) 285.
9. Safoula G, Suresh C., Napo K., Alimi K., Bernede J.C., Mevellec J.Y., J. Non-cryst. Solids 169 (1994) 126.
10. Elliott S.R., Physics of Amorphous Materials (Longman, Essex 1990).
11. Bhargava A., Jain I. P., J. phys. D 27 (1994) 830.
12. S Germain P., squelard S., Bourgoin J.C., Gheorghiu A., J. Non-cryst Solids 23 (1977) 93.
13. Bhargava A., Vijay Y.K., Jain I.P., Solid State Physics (India) 38 C (1995) 228.
14. Landauer R., J. Appl. phys. 23 (1952) 779.
15. Dwivedi P.K., Srivastava S. K., Kumar A., IL Nuovo Cimento. 15 D (1993) 1149.
16. Kumar S., Arora R., Kumar A., (to be published)
17. Meyer W., Neldel H., Z. Tech. phys. 12 (1937) 307.
18. Kasap S.O., Juhasz C., J. Mater. Sci. 21 (1986) 1329.
19. Reddy K.V., Bhatnagar A.K., J. phys. D: Appl. phys. 25 (1992) 1810.