

DETERMINATION OF THE NUCLEATION KINETIC PARAMETERS FOR A-Se BY DIFFERENTIAL SCANNING CALORIMETRY

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Nucleation parameters such as radius of critical nucleus, critical free energy change and interfacial tension have been determined for selenium by differential scanning calorimetry (DSC) using non-isothermal measurement with different heating rates. The interfacial tension values estimated using the DSC traces are found to varies from 1.241×10^{-8} to 1.271×10^{-8} N/m. The radius of the critical nucleus and critical free energy change as a function of both heating rate and supercooling temperature range were discussed.

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1. Introduction

Detailed knowledge of the kinetics of nucleation and crystal growth rate is useful for material design, since these kinetics control the phase formation and microstructure of the phases. The formation of the new phase is caused by fluctuations due to thermal agitations which bring the atoms to new positions corresponding to the product phase [1]. A large number of such fluctuations are unstable, since they are below a certain critical size (volume) and they cause a net increase of free energy [2-6]. Such an unstable minute region of the product phase is known as "embryo" of the new phase. When the size of embryos exceed a minimum critical size, they are capable of continued existence and are called "nuclei" of the product phase. The process of the formation of the nuclei is known as nucleation. The "growth" of nuclei requires transfer of atoms from the material in the interface on to these nuclei of the product phase [1]. Most phase changes occur by the growth of a limited number of nuclei. Nucleation is common to all types of solid state transformations.

In single-component systems the composition of such nuclei is identical to that of the parent phase, but the size and shape of the nuclei are different [1]. This is a basic assumption of the Volmer and Weber [2] and of Becker and Doring [3] (VWBD) theory. During the formation of nuclei, differences in shapes, sizes, and specific volumes create new surfaces, stresses, and strains. Therefore, nuclei will be formed only if the net free energy change during their formation is negative. Otherwise, the unstable embryo dissolves into the parent phase.

Let us assume that there is no difference between the specific volumes of the parent and the product phases and hence no strain at the interface. Furthermore, we shall assume that the interfacial energy between the two phases is σ and that σ is independent of crystallographic directions. The change in free energy, ΔG , due to the formation of spherical nuclei consists of two terms: (a) the bulk free energy decreases per unit volume, ΔG_v , and (b) the surface free energy increases per unit area of the surface (interfacial tension), σ . If the radius of a spherical embryo is r , then ΔG may be written as equal to [1,7,8]

$$\Delta G = -\frac{4\pi}{3}r^3\Delta G_v + 4\pi r^2\sigma \quad (1)$$

clearly, for small r , the second term will dominate (it is positive while the first term is negative) and the embryo will therefore be thermodynamically unstable. However, if the embryo reaches a critical size of radius r_c , ΔG will begin to decrease and further growth will be thermodynamically favorable. Let r_c be the critical radius (known as critical nucleus size) and ΔG_c the critical excess free energy. We can obtain r_c and ΔG_c by letting $(\partial\Delta G/\partial r)$ be equal to zero.

$$r_c = 2\sigma / \Delta G_v \quad (2)$$

$$\Delta G_c = \frac{16 \pi \sigma^3}{3 \Delta G_v^2} \quad (3)$$

One possible reference interfacial free energy value can be obtained from Turnbull's empirical rule [9,10] that relates solid-liquid interfacial free energy to the heat fusion per unit area at melting, i.e.,

$$\sigma = \frac{\beta \Delta H_m}{N_A^{1/3} V_{\text{mol}}^{2/3}} \quad (4)$$

where ΔH_m and V_{mol} represent the molar heat of fusion (the enthalpy of melting) and molar volume and N_A is Avogadro's number. The β value of 0.721 for Se compound has been used [11,12].

The driving force of crystallization, ΔG_v , given by the difference between the Gibbs free energy per mol of the amorphous and crystalline phases, can be calculated according to the relation[10,13,14]

$$\Delta G_v = \frac{\Delta H_m \Delta T}{T_m V_{\text{mol}}} \quad (5)$$

In the above equation, the supercooling, $\Delta T = T_c - T_g$, where T_c is the temperature at which the crystallization begins and T_g is the glass transition temperature.

Selenium was chosen for this study due to the fact that it is a single-component system which means that the nuclei of the parent (amorphous) phase and the product (crystal) phase are identical.

The goal of this paper is to demonstrate the validity of the analytical DSC method for measuring the critical size of crystal nucleus radius for selenium.

2. Experimental procedure

Pure Se (99.999 % purity) was sealed in a Pyrex ampoule (length 15 cm, internal diameter 12 mm) with a vacuum $\sim 10^{-3}$ Pa. The ampoule was kept in a furnace and heated up to 623 at a rate of 4-5 K/min. After that, ampoule was rocked frequently for a period of 2 hrs. at the maximum temperature to make the melt homogeneous. Quenching was done in air.

The amorphous nature and crystalline phases of Se glass were identified by X-ray diffraction (XRD) using X-ray diffractometer (Philips-PW1710) in the range 10-90 ° in 0.02° 2 θ steps with a counting time of 15s per step with Cu K_α radiation. Phases were identified by interrogation of the ICDD PDF-2 database incorporated in the program SEARCH/MATCH available in the PC software package PW1710 supplied by Philips.

The crystallization behavior of the amorphous Se was studied with a DSC Shimadzu DSC-50 on samples of ≈ 15 mg encapsulated in an Aluminum sample pans in an atmosphere of dry nitrogen at a flow of 30 ml/min. The instrument was calibrated with In, Pb, and Zn standards. The calorimetric sensitivity was 10 $\mu\text{W cm}^{-1}$ and the temperature precision was ± 0.1 K. Non-isothermal DSC curves

were obtained with selected heating rate 2-20 K/min in the range 300-610 K. The values of the glass transition temperature (T_g), the onset temperature of crystallization (T_c), the peak temperature of crystallization (T_p) and the melting temperature (T_m) were determined by using the microprocessor of the apparatus.

3. Results and discussion

Fig.1 shows a typical continuous DSC trace obtained for the amorphous Se glass at a heating rate of 10 K/min. The characteristic phenomena (endothermic and exothermic events) are evident in the DSC curves in the temperature range of investigation. From the analysis point of view, the DSC curves of the investigated Se glass is divided into three parts, the first one corresponds to the glass transition region which appears as one endothermic reaction at temperature T_g , the second part is related to the crystallization process of the considered glass indicated by exothermic crystallization peak T_p and the last corresponds to the melting region which appears as an endothermic reaction at temperature T_m . The glass transition temperature, T_g , the onset temperatures of crystallization T_c and the melting temperature T_m have been defined as temperatures corresponding to the intersection of two linear portions adjoining the transition elbow of the DSC trace in the endothermic and exothermic directions (see Fig.1). The peak temperature of crystallization T_p is the temperature at which the crystallization attains its maximum value and considered to be the peak temperature of the exothermic reaction in DSC curve. Values of the characteristic temperatures, T_g , T_c , T_p , T_m and supercooling temperature range, $\Delta T = T_c - T_g$ for the investigated Se glass are given in Table 1. It is observed that the values obtained agree with the quoted data in the literature for similar compound[15,16]. Table 1, reveals that the peak area for melting (melting endothermic peak) increase with increasing the heating rate.

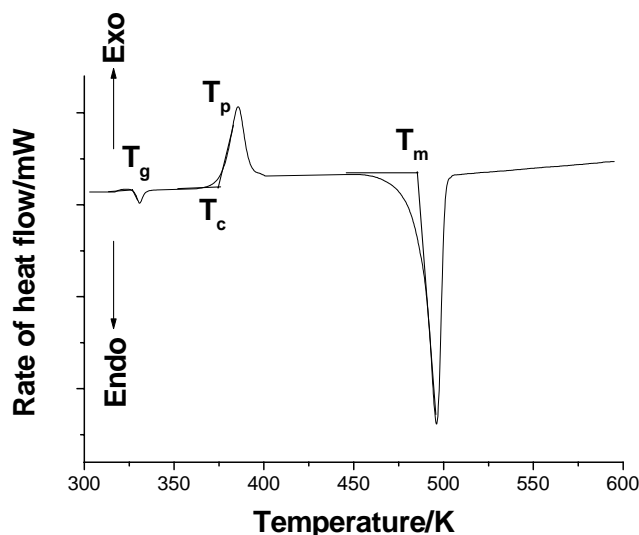


Fig.1. Typical DSC trace of Se glass at a heating rate of 10 K/min.

By definition, the molar heat of fusion (the enthalpy of melting) ΔH_m should be approximately constant for 100 % degree of crystallization which is not our case. This means that selenium glass is partially crystallizes from the amorphous matrix upon heating. To confirm this result, the crystallization products of amorphous Se after the thermal process (just after DSC run) were examined by XRD measurements (see Fig. 2). Typical two broad peaks located near $2\theta = 15-40^\circ$ and $40-70^\circ$ shown in Fig.2a for the as-prepared Se sample evidencing the amorphous nature of the structure, while several sharp Se diffraction peaks with broad peaks emerge for the just after DSC run Se sample are

shown in Fig.2b which reveals that the exothermic peak is attributed to the presence of microcrystallites of Se, remaining an residual amorphous phase. Annealing the amorphous Se, for a period of 3 hr. at 373 K, the broad peaks due to the amorphous structure completely disappears, and only sharp peaks appear, as shown in Fig.2c. This indicates that the Se has completely crystallized.

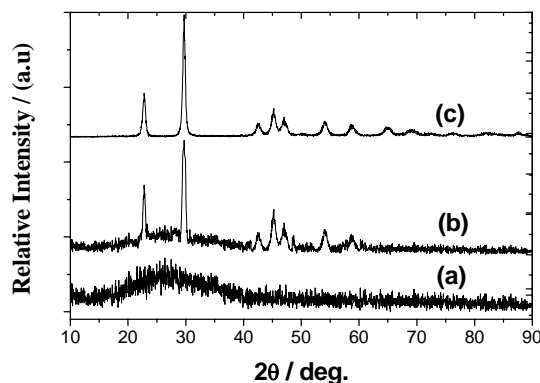


Fig.2. X-ray diffraction patterns recorded at room temperature for: (a) the as-prepared Se glass , (b) just after DSC run and (c) the sample annealed at 373K for 1 hr.

The enthalpy of melting ΔH_m for Se glass are evaluated using the formula

$$\Delta H = KA/M \quad (6)$$

where $K(=1.5)$ is the constant of the instrument used. The value of K was deduced by measuring the total area of the complete melting endotherm of high purity tin and used the well known enthalpy of melting of this standard material. A is the area of the melting peaks and M is the mass of the sample in g/mol. Integration of the melting endothermic on three DSC traces made at every heating rate yielded an average value for ΔH_m (see Table 1). Table 1 reveals that the values of the enthalpy of melting (heat of fusion) are shifted to higher values by increasing the heating rate. By using the values in Table1, The interfacial tension σ , the free energy change per unit volume, ΔG_v , the critical free energy change, ΔG_c and the radius of critical nucleus, r_c for Se can be determined from Eq.(4), Eq.(5), Eq.(3) and Eq.(2), respectively. The obtained values of σ , ΔG_v , ΔG_c , and r_c at different heating rates for Se are presented in Table 2. It is clear that, the measured interfacial tension, σ , varies from 1.241×10^{-8} to 1.271×10^{-8} N/m.

Table 1. Thermal parameters of the Se glass.

Rate (K/min)	T_g (K)	T_c (K)	T_p (K)	T_m (K)	ΔT (K)	ΔH_m (mJ/mol)
2	323.0	343.4	364.5	495.0	20.4	1.015
5	325.5	353.7	371.0	495.5	28.2	1.020
10	327.0	364.9	386.0	496.0	37.9	1.026
15	328.8	371.6	393.0	496.6	42.8	1.038
20	330.5	377.7	398.8	497.2	47.2	1.045

Table 2. The values σ , ΔG_v , ΔG_c and r_c at different heating rates for the Se glass.

Rate (K/min)	σ (N/m)	ΔG_v (J/m ³)	ΔG_c (J)	r_c (m)
2	1.241×10^{-8}	2.267	6.231×10^{-24}	1.09×10^{-8}
5	1.247×10^{-8}	3.145	3.284×10^{-24}	0.79×10^{-8}
10	1.254×10^{-8}	4.249	1.830×10^{-24}	0.59×10^{-8}
15	1.269×10^{-8}	4.848	1.456×10^{-24}	0.52×10^{-8}
20	1.277×10^{-8}	5.376	1.207×10^{-24}	0.47×10^{-8}

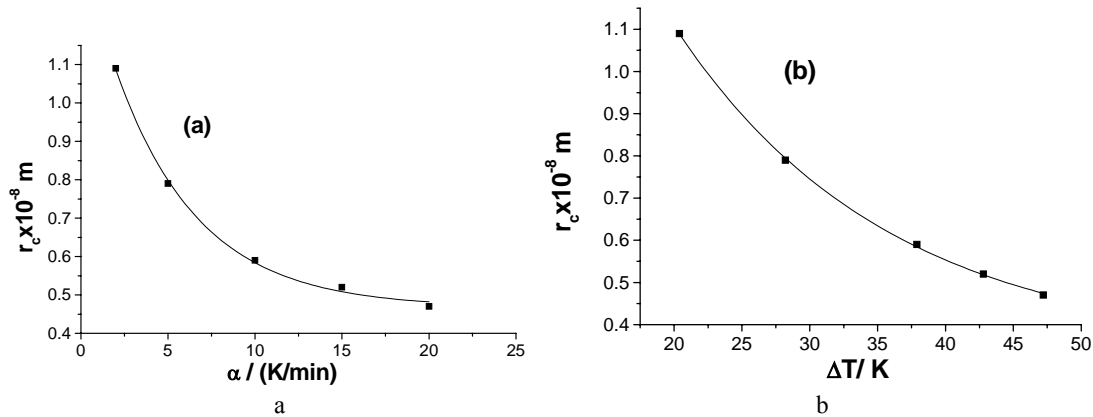


Fig.3. Relation between the radius of critical nucleus and (a) heating rate (α) and (b) supercooling (ΔT) for Se.

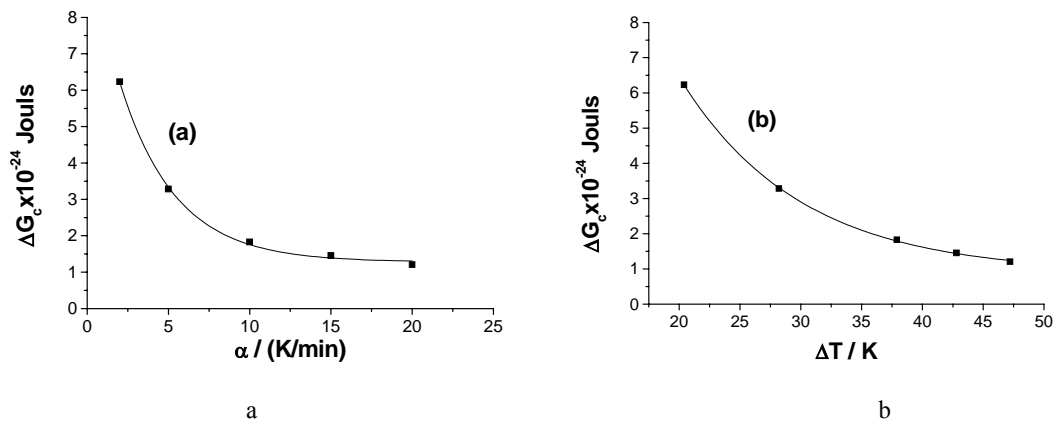


Fig.4. Relation between the critical free energy free change (ΔG_c) and (a) heating rate (α) and (b) supercooling (ΔT) for Se.

The evaluated radius of critical nucleus as a function of: (a) heating rate (α) and (b) supercooling temperature range, (ΔT) are depicted in Fig. 3. It is clear that the radius of critical nucleus exponentially decreases with increase in heating rate and supercooling. A Similar behavior is observed for the critical free energy change ΔG_c .

4. Conclusion

The differential scanning calorimetry has been applied successfully to determine the nucleation kinetic parameters for α -Se. Change in the heating rate from 2 K/min to 20 K/min increases the interfacial tension from 1.241×10^{-8} to 1.271×10^{-8} N/m. Both the critical radius of crystal nucleus r_c and critical free energy change (ΔG_c) vary exponentially with the heating rates and supercooling temperature range.

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