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Study of zinc incorporation on the non-isothermal crystallization in glassy selenium using iso-conversional approach



C. Dohare, N. Mehta*

Glass Science Laboratory, Department of Physics, Banaras Hindu University, Varanasi, India

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ABSTRACT

The crystallization kinetics of glassy Se (g-Se) and glassy $\text{Se}_{98}\text{Zn}_2$ alloy has been studied by means of differential scanning calorimetric (DSC) technique. Iso-conversional methods [Kissinger–Akahira–Sunose (KAS), Flynn–Wall–Ozawa (FWO), Tang and Straink] were used to determine the various kinetic parameters (i.e. crystallization temperature T_c , activation energy of crystallization E_c) of crystallization process in non-isothermal mode. The monotonous decrement in activation energy, E_c with the extent of conversion, α confirms the complex kinetic mechanism of g-Se and $\text{Se}_{98}\text{Zn}_2$ alloy. The reaction model, 'Avrami–Erofeev' $g(\alpha) = [-\ln(1-\alpha)]^{1/n}$ has been followed to describe the crystallization process with $n=1.5$ for g-Se and $n=2.0$ for $\text{Se}_{98}\text{Zn}_2$ alloy.

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1. Introduction

In selenium, each atom needs two neighbours to satisfy the valence requirements. This is achieved either by the formation of small molecules Se_8 or linear polymeric chains Se_n . Selenium can melt without appreciable change within these structural units, the required random arrangement of atoms being obtained by the breaking of weak bonding between units and by increasing flexibility of the chains [1]. The crystallization would appear to require some dissociation of the chains followed by their reformation in an ordered array.

The addition of Zn makes a catalytic effect on the crystallization of Se, due to weak bond over Se–Se. This makes crystallization easier, by facilitating the close packing of a few Se chains to form a nucleation centre. Chalcogenide semiconducting (ChS) glasses based on chemical modifier are valuable due to their greater hardness, high photosensitivity, higher crystallization temperature and smaller ageing effect and low viscosity as compared to g-Se [2]. The reason for the selection of Zn as chemical modifier in g-Se is based on its attractive and significant applications in chalcogenide glasses. There are reports of successful photo-doping of Zn in chalcogens in the literature that are suitable for the development of light-emitting diodes and lasers. Development of Zn-based p-type contact for high-efficiency tandem structure is recently reported for the tandem solar cell devices, which have been under development in various configurations because of

their promise of high efficiency [3]. The activation energy of crystallization (E_c) plays an important role in determining the utility of chalcogenide glasses as recording layer materials.

Although the description of model-free approach to kinetic analysis is the alternative of iso-conversional methods [4], it is more precise and less misleading. This misnomer does have attention on chief aspect of kinetic analysis, namely the influence that the choice of kinetic model has on the derivation of the Arrhenius parameters E and A for a rate process [5]. In this approach, the knowledge of the kinetic model describes the process having complexity of any extent. The objection to the 'model-free approach' is that the conversion function, $g(\alpha)$ or $f(\alpha)$ (where, α is the extent of conversion) [6], is not an essential piece of information in the kinetic analysis [7,8]. Iso-conversional methods are known to allow the calculation of model independent estimates of the activation energy, $E(\alpha)$, related to different extents of conversion, α . In contrast, the iso-conversional methods are highly recommended in order to obtain a reliable kinetics of the investigated course of action [9].

The aim of this work is to report the dependence of activation energy of crystallization over the extent of conversion by iso-conversional models and the implementation of order parameter, 'n' for the investigation of pre-exponential factor and reaction model of the same system.

2. Experimental and material preparation

g-Se and g- $\text{Se}_{98}\text{Zn}_2$ were prepared by the quenching technique [10]. The exact proportions of high purity elements sealed in

* Corresponding author. Tel.: +91 542 2307308x244; fax: +91 542 2368174.
E-mail address: dr_neeraj_mehta@yahoo.co.in (N. Mehta).

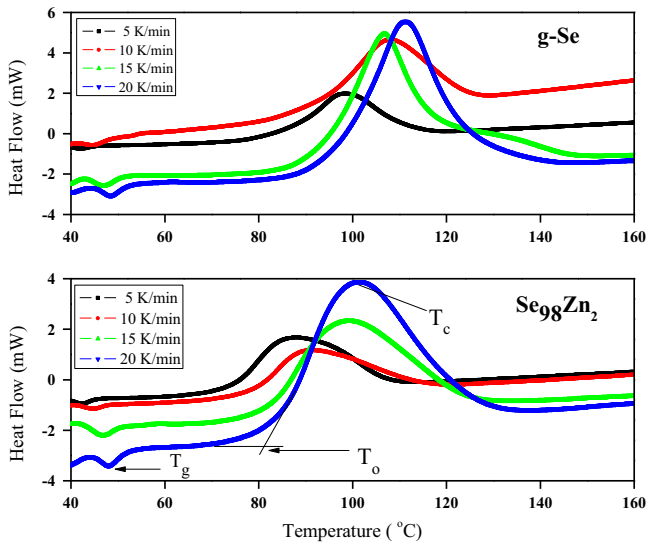


Fig. 1. DSC scans for g-Se and $\text{Se}_{98}\text{Zn}_2$ alloy at different heating rates ($\beta=5, 10, 15, 20$ K/min).

quartz glass ampoules were constantly rocked in a furnace to obtain homogeneous glassy materials. After rocking for about 12 h, the obtained melts were cooled rapidly by removing the ampoules from the furnace and dropping to ice-cooled water rapidly.

The thermal characterization was investigated using a differential scanning calorimeter (T.A. Instruments, USA; Model: Auto Q20). Temperature and enthalpy calibration were checked at all heating rates with zinc as a standard material supplied by TA Instruments. The accuracy of the heat flow in DSC was ± 0.01 mW and the temperature precision was ± 0.1 K. Measurements were made at same room temperature. Four heating rates (5, 10, 15 and 20 K/min) were used with nitrogen as purge gas. Fig. 1 shows the DSC scan of present samples at different heating rates.

3. Theoretical formulation

It has been investigated that model-free prediction, for thermally complex process, compares very well with the actual measurements and emphasizes the reaction complexity for iso-conversional dependence of E_α on α determined in support of curing process [11–13]. Iso-conversional methods are categorized as differential and integral form proposed by Freidman (FR), Flynn–Wall–Ozawa (FWO) and Kissinger–Kahira–Sunose (KAS) [14–20].

The kinetics of crystallization in amorphous material can be described by the following rate equation [15–17]:

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E_\alpha}{RT}\right) f(\alpha) \quad (1)$$

Here $f(\alpha)$ is the reaction model, which is related to the reaction mechanism. Under non- isothermal condition with a constant heating rate $\beta=(dT/dt)$, Eq. (1) may be written as:

$$\frac{d\alpha}{dT} = \frac{d\alpha}{dt} \left(\frac{1}{\beta}\right) = \frac{A}{\beta} \exp\left(-\frac{E_\alpha}{RT}\right) f(\alpha) \quad (2)$$

Here, ' α ' is the degree of cure (DOC), ' t ' is the time, $(d\alpha/dt)$ is the curing rate, ' R ' is the gas constant, and ' T ' is the absolute temperature, E_α is the apparent activation energy and ' A ' is the pre-exponential (frequency) factor.

The integral form of reaction model can be obtained by integrating Eq. (2) as:

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_{T_0}^T \exp\left(-\frac{E_\alpha}{RT}\right) dT = \frac{A}{\beta} I(E, T) \quad (3)$$

Here, ' T_0 ' is the initial temperature, and ' T ' is the temperature at an equivalent (fixed) state of transformation. Using an advanced iso-conversional method [21], numbers of experiments are carried out at different heating rates and, effective activation energy can be determined at any particular value of α . The temperature integral $I(E, T)$ in Eq. (3) is given as:

$$I(E, T) = \int_{T_0}^T \exp\left(-\frac{E_\alpha}{RT}\right) dt \quad (4)$$

Kissinger–Akahira–Sunose (KAS) method: In KAS method, the relation between the heating rate, β , and the temperature, $T_{\alpha i}$, at which a fixed fraction of α of the total amount is transformed, is given by [19,22,23]:

$$\ln\left(\frac{\beta}{RT_{\alpha i}^2}\right) = -\left(\frac{E_\alpha}{RT_{\alpha i}}\right) + \text{Constant} \quad (5)$$

Flynn–Wall–Ozawa (FWO) method: FWO method [24,25] has been used for the determination of non-isothermal analysis of crystallization in which the temperature integral in Eq. (4) is simplified by using the Doyle's approximation [26] and the relation is estimated as follows:

$$\ln(\beta_i) = -1.052 \left(\frac{E_\alpha}{RT_{\alpha i}}\right) + \text{Constant} \quad (6)$$

Tang method: Temperature integral relation has been suggested by Tang and is given as [27]:

$$\ln\left(\frac{\beta_i}{RT_{\alpha i}^{1.895}}\right) = -1.00145 \left(\frac{E_\alpha}{RT_{\alpha i}}\right) + \text{Constant} \quad (7)$$

Starink method: The method proposed by Starink is given as [17,28]:

$$\ln\left(\frac{\beta_i}{RT_{\alpha i}^{1.92}}\right) = -1.0008 \left(\frac{E_\alpha}{RT_{\alpha i}}\right) + \text{Constant} \quad (8)$$

4. Results and discussions

Evaluation of the reaction model, $g(\alpha)$ and pre-exponential factor, $\ln A_\alpha$: A suitable reaction model $g(\alpha)$ is chosen to describe the crystallization process of the mentioned alloys [29] by comparing the obtained experimental values of E_α and $\ln A_\alpha$ with those obtained from each model. The reaction model, 'Avrami–Erofeev' $g(\alpha) = [-\ln(1-\alpha)]^{1/n}$, has been followed to describe the crystallization process with $n=1.5$ for g-Se and $n=2.0$ for $\text{Se}_{98}\text{Zn}_2$ alloy at

Table 1

The value of pre-exponential factor, $\ln A_\alpha$, and reaction model, $\ln[g(\alpha)]$, for g-Se and $\text{Se}_{98}\text{Zn}_2$.

α	$\ln A_\alpha$ (min^{-1})		$\ln[g(\alpha)]$	
	g-Se	$\text{Se}_{98}\text{Zn}_2$	g-Se	$\text{Se}_{98}\text{Zn}_2$
0.1	35.9	28.7	-5.6	-2.9
0.2	34.5	27.9	-4.1	-2.2
0.3	33.5	27.5	-3.2	-1.7
0.4	32.8	27.1	-2.4	-1.4
0.5	32.2	26.8	-1.8	-1.1
0.6	31.7	26.5	-1.3	-0.8
0.7	31.1	26.3	-0.7	-0.5
0.8	30.5	25.9	-0.1	-0.2
0.9	29.8	25.6	0.6	0.1

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