STUDIES OF CRYSTALLIZATION KINETICS IN a-Se$_{80-x}$Te$_{20}$Cd$_x$ AND a-Se$_{80-x}$Te$_{20}$Ge$_x$ ALLOYS USING D.C. CONDUCTIVITY MEASUREMENTS

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The crystallization kinetics of a-Se$_{80-x}$Te$_{20}$Cd$_x$ (*x*=0, 5, 10, 15) and a-Se$_{80-x}$Te$_{20}$Ge$_x$ (*x*=5, 15, 20) alloys has been studied by an isothermal method. For this purpose, conductivity measurements are done during isothermal annealing at various temperatures between the glass transition and crystallization temperatures.

Avrami's equation is used to calculate the activation energy of crystallization (E_c) and order parameter (*n*). It is shown that Avrami's theory of isothermal crystallization correctly describes the crystallization kinetics in the present alloys. The composition dependence of E_c in these alloys has also been discussed.

Keywords: activation energy of crystallization, Avrami's equation, chalcogenide glasses, isothermal method

Introduction

Chalcogenide glasses exhibit many useful electrical properties. Numerous applications for these materials have been suggested and extended from well-established field of xerography to the very exciting field of threshold and memory switching [1–3]. The memory-switching phenomenon in chalcogenide glasses is related to amorphous to crystalline (a–c) phase transformation in them [4]. Chalcogenide glasses exhibiting an exothermic crystallization reaction above the glass transition temperature show a memory type switching. Such chalcogenide glasses, showing memory switching, have recently drawn great attention due to their application in phase change (PC) optical recording [5–8]. In this technique, the heat of a laser beam is used for thermal crystallization of amorphous films of chalcogenide glasses. The activation energy of crystallization (E_c) plays an important role in determining the utility of chalcogenide alloys as recording materials due to the fact that PC optical recording technique is based on the laser induced thermal crystallization of chalcogenide glasses.

The crystallization kinetics in chalcogenide glasses can be investigated using isothermal and non-isothermal methods. In isothermal method, the sample is brought near to crystallization temperature very quickly and then any physical quantity, which changes drastically, is measured as a function of time. In non-isothermal method, the sample is heated at a fixed rate and the physical parameter is recorded as a function of temperature. Any physical parameter, which changes drastically, can be taken as a measure of extent of crystallization as a function of time.

The present work is designed to study the crystallization kinetics of a-Se$_{80-x}$Te$_{20}$Cd$_x$ and a-Se$_{80-x}$Te$_{20}$Ge$_x$ alloys using DC conductivity as a physical parameter to be measured during a–c transformation. The kinetic parameters *n* and E_c are calculated by fitting the extent of crystallization to the Avrami's theory of isothermal transformation as used by other authors also [9–14].

Experimental

Materials

Glassy alloys of a-Se$_{80-x}$Te$_{20}$Cd$_x$ (*x*=0, 5, 10, 15) and a-Se$_{80-x}$Te$_{20}$Ge$_x$ (*x*=0, 5, 15, 20) were prepared by quenching technique. The exact proportions of high purity (99.999%) elements, in accordance with their atomic percentages, were weighed using an electronic balance (LIBROR, AEG-120) with the least count of 10^{-4} g. The materials were then sealed in evacuated (~10^{-5} Torr) quartz ampoules (length ~5 cm and internal diameter ~8 mm). Each ampoule was kept inside the furnace at 1000°C (where the temperature was raised at a rate of 3–4°C min^{-1}). During heating, all the ampoules were constantly rocked, by rotating a ceramic rod to which the ampoules were tucked away in the furnace. This was done to obtain homogeneous glassy alloys.

Methods

The glassy nature of alloys was checked by X-ray diffraction technique. The XRD pattern of glassy Se$_{80}$Te$_{20}$ is shown in Fig. 1. Absence of any sharp

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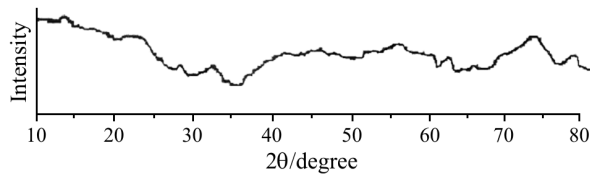
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Fig. 1 XRD pattern of a-Se$_{80}$Te$_{20}$ alloy

peak in XRD pattern in Fig. 1 confirms the glassy nature of Se$_{80}$Te$_{20}$ alloy. Similar XRD patterns were obtained for the other glassy alloys.

The glasses, thus prepared, were ground to make fine powder and the pellets (dia ~6 mm and thickness ~0.5–1 mm) were obtained after compressing the powder in a die at a load of 3–4·10^4 N.

The a–c phase transformation was studied by measuring the d.c. conductivity σ as a function of time (1–2 min intervals) at various annealing temperatures between the glass transition temperature and crystallization temperature. The annealing temperature T was kept constant during the a–c phase transformation period. The remarkable increase of σ implies that σ at any time t is the result of two conductivities σ$_a$ and σ$_c$ corresponding to a double phase system, amorphous and crystalline.

The conductivity measurements were taken in a vacuum ~10^{-2} Torr by mounting the samples in a specially designed sample holder. The sample holder has two parts 'a' and 'b' (Fig. 2). The upper part consists of two electrodes and an evacuation port. The samples were mounted between the jaws of two electrodes having a spring arrangement. At the end of two electrodes,
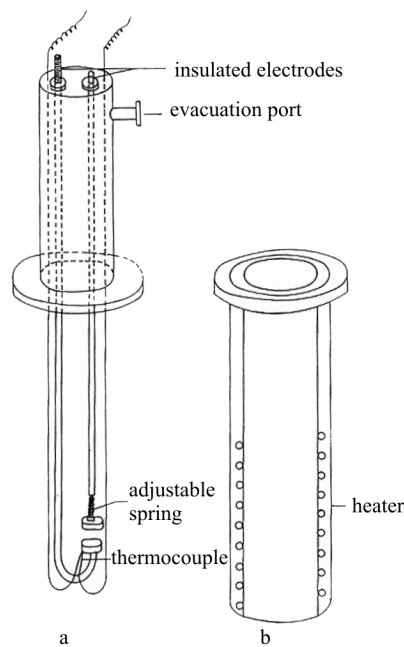

Fig. 2 Sample holder assembly for measurements of electrical conductivity in vacuum

two UHF connectors were used for the electrical connections of the sample. Canthal wire was wound as heating element on the outer covering of the sample holder assembly (Fig. 2b). Heating element was covered with plaster of Paris in order to avoid heat losses due to radiation. A calibrated copper-constantan thermocouple was mounted very near to the sample to measure the temperature of the sample. An O-ring was provided between the two parts of the sample holder for proper evacuations inside the chamber. The resistance was measured using Kiethely Electrometer (model 614). The temperature was measured using a calibrated constantan thermocouple. Different pellets were taken for each value of T. The annealing temperature T was attained at a fast heating rate and then maintained constant till saturation in the resistance was obtained.

Theory of measurements

During the isothermal transformation, the extent of crystallization (α) of a certain material is represented by the Avrami's equation [15]

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

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

The rate constant K is given by Arrhenius equation

$$K=K_0\exp[-E_c/RT] \qquad (2)$$

where K_0 is the pre-exponential factor and R is universal gas constant.

The a–c phase transformation in chalcogenide glasses is accompanied by a continuous change of the electrical conductivity (σ), which is a sensitive structural parameter.

Odelevsky [16] has suggested a power formula to calculate σ of a mixture during a–c phase change transition. According to him,

$$\sigma=\alpha\sigma_c^m+(1-\alpha)\sigma_a^m \qquad (3)$$

where σ$_c$ and σ$_a$ are the conductivities of crystalline and amorphous phases having volume fractions α and (1–α), respectively.

For the power m=1, the measured conductivity σ at a particular time during crystallization can be expressed as

$$\sigma=\alpha\sigma_c+(1-\alpha)\sigma_a \qquad (4)$$

On the other hand, when lnσ is considered to represent the sensitive parameter characterizing the dependence of conductivity on extent of crystallization, an empirical formula may be written in the following form:

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

or

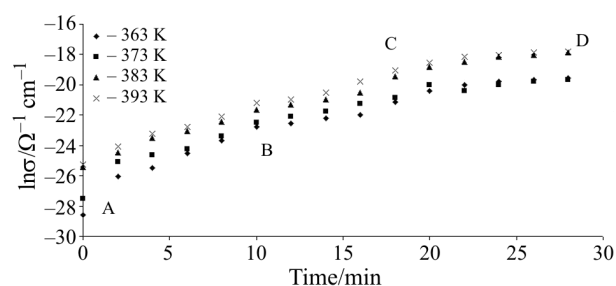$$\alpha = (\ln\sigma - \ln\sigma_a)/(\ln\sigma_c - \ln\sigma_a) \qquad (5)$$

Kotkata *et al.* [17] have used Eqs (4) and (5) to calculate the extent of crystallization in some Se based chalcogenide glasses and found that Eq. (5) is more satisfactory as $(\sigma_c - \sigma_a)$ is quite large in these glasses.

In the present case σ increases by several orders of magnitude on crystallization, hence Eq. (5) can be used to calculate α by measuring σ as a function of time during isothermal annealing at temperatures near crystallization temperature. Once the values of α as a function of time are known at different isothermal annealing temperatures, the kinetic parameters (n and E_c) can be calculated.

Results and discussion

Evaluation of n and E_c

Figure 3 shows the time dependence of $\ln\sigma$ during the a–c phase transformation of a-Se$_{65}$Te$_{20}$Ge$_{15}$ alloy carried out in the temperature range 90 to 120°C. The results for other glassy alloys were also of the same nature. During the transition process, there appears to be three regimes AB, BC and CD in σ *vs.* annealing time t curves. The part AB in Fig. 3 is linear and represents a gradual increase in σ as a result of the normal heating of the glassy alloys. The less pronounced increase of σ during the 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 new phase until maximum crystallization of the sample volume is attained,

as signified by the limiting value, D, in Fig. 3. In the present study our interest is in the part CD i.e., in the understanding of crystallization kinetics.
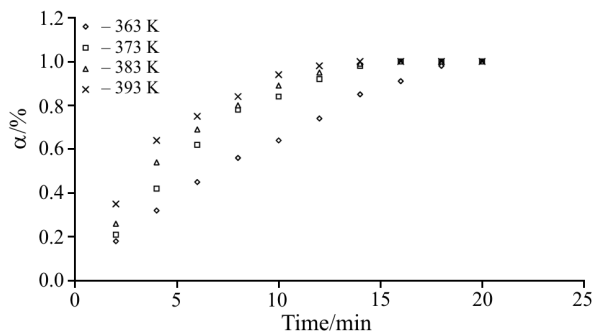
Using the measured value of conductivity, the extent of crystallization α at different annealing times is calculated at various annealing temperatures T using Eq. (5). Here, σ_a is taken as the conductivity at point C and σ_c, that at point D in Fig. 3. The variation of α as a function of time at different values of T is shown in Fig. 4 for a-Se$_{65}$Te$_{20}$Ge$_{15}$ alloy. The results for other glassy alloys were also of the same nature.

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

$$\ln[\ln(1-\alpha)^{-1}] = \ln K + n\ln t \qquad (6)$$

According to Eq. (6), the plot of $\ln[\ln(1-\alpha)^{-1}]$ *vs.* $\ln t$ leads to a straight line of slope n and intercept $\ln K$. This has been verified for a-Se$_{65}$Te$_{20}$Ge$_{15}$ alloy in Fig. 5. For other glassy alloys, similar results were obtained. The values of order parameter n at different values of annealing temperature T for a-Se$_{80-x}$Te$_{20}$Cd$_x$ and a-Se$_{80-x}$Te$_{20}$Ge$_x$ alloys are given in Table 1. From this table, it is clear that the average value of order parameter n in ternary alloys is found to be nearly equal to 1. This indicates that only one crystallization mechanism (one dimensional growth) may be responsible for the amorphous to crystalline (a–c) transformation of these alloys. The case of $n=1$ in Avrami's equation is also considered to be the case for random nucleation and growth with one nucleus on each particle.

The values of the temperature dependent crystallization rate constant K, evaluated from the intercepts of

Fig. 3 Annealing time dependence of d.c. conductivity for a-Se$_{65}$Te$_{20}$Ge$_{15}$ alloy during isothermal a–c phase transformations

Fig. 4 Extent of crystallization *vs.* annealing time for a-Se$_{65}$Te$_{20}$Ge$_{15}$ alloy

Table 1 Temperature dependence of order parameter

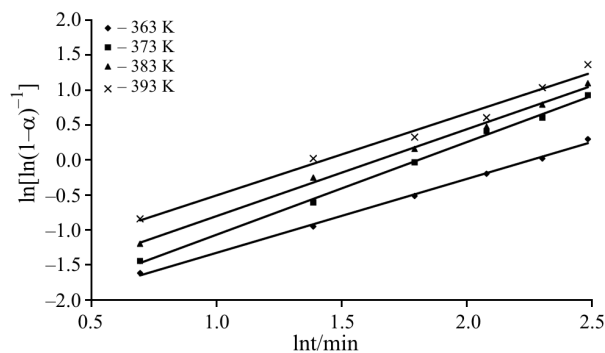| Se$_{80}$Te$_{20}$		Se$_{75}$Te$_{20}$Cd$_5$		Se$_{70}$Te$_{20}$Cd$_{10}$		Se$_{65}$Te$_{20}$Cd$_{15}$		Se$_{75}$Te$_{20}$Ge$_5$		Se$_{65}$Te$_{20}$Ge$_{15}$		Se$_{60}$Te$_{20}$Ge$_{20}$	
T/°C	n	T/°C	n	T/°C	n	T/°C	n	T/°C	n	T/°C	n	T/°C	n
70	1.6	80	1.1	90	1.2	90	1.1	90	1.0	90	1.1	90	1.0
80	1.6	90	1.2	100	1.2	100	1.2	100	1.0	100	1.2	100	1.0
90	1.4	100	1.1	110	1.1	110	1.2	110	1.0	110	1.2	110	1.0
100	1.2	110	1.3	120	1.0	120	1.1	120	1.1	120	1.1	120	0.9

Fig. 5 Avrami plots of the crystallization of a-$Se_{65}Te_{20}Ge_{15}$ alloy for different isotherms
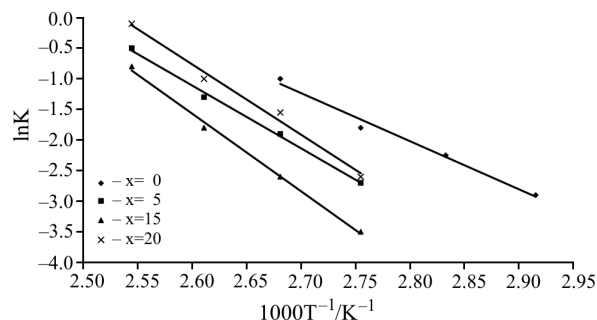

Fig. 6 Arrhenius plots of crystallization of a-$Se_{70-x}Te_{20}Ge_x$ (x=0, 5, 15, 20) alloys

Table 2 Activation energy of crystallization

Sample	E_c/kJ mol^{-1}
$Se_{80}Te_{20}$	71.7
$Se_{75}Te_{20}Cd_5$	99.7
$Se_{70}Te_{20}Cd_{10}$	120.5
$Se_{65}Te_{20}Cd_{15}$	91.4
$Se_{75}Te_{20}Ge_5$	99.3
$Se_{65}Te_{20}Ge_{15}$	92.6
$Se_{60}Te_{20}Ge_{20}$	99.5

$\ln[\ln(1-\alpha)^{-1}]$ *vs.* $\ln t$ curves are plotted as a function of temperature in Fig. 6 for a-$Se_{80-x}Te_{20}Ge_x$ alloys (x=0, 5, 15, 20). The straight line, thus obtained, confirms the validity of Eq. (2). Similar plots were obtained for a-$Se_{80-x}Te_{20}Cd_x$ alloys (x=5, 10, 15). The values of E_c for various alloys obtained from the slopes of $\ln K$ *vs.* $10^3/T$ curves are given in Table 2. It is interesting to note that E_c values calculated in a-$Se_{80-x}Te_{20}Cd_x$ alloys in the present work are in good agreement with the E_c values reported by Singh *et al.* in earlier paper [18] using non-isothermal DSC technique.

Composition dependence of E_c

From Table 2, it is clear that initially the value of E_c in a-$Se_{80-x}Te_{20}Cd_x$ (x=0, 5, 10, 15) and a-$Se_{80-x}Te_{20}Ge_x$ (x=0, 5, 15, 20) alloys increases with the concentra-

tion of third element M (M=Cd, Ge) and after a particular concentration it decreases. Thus, a reversal in the trend is observed in both glassy systems.

Many approaches have been proposed to explain the compositional dependence of various physical properties of chalcogenide glasses [19–27]. One of these approaches is the so-called chemically ordered network model (CONM) [19–22], in which the formation of heteropolar bonds is favored over the formation of homopolar bonds. In this model, the glass structure is assumed to be composed of cross-linked structural units of the stable chemical compounds (heteropolar bonds) of the system and excess, if any, of the elements (homopolar bonds). Due to chemical ordering, features (such as extremum, a change in slope or kink) occur for the various properties at the so-called tie line or stoichiometric compositions at which the glass structure is made up of cross-linked structural units consisting of heteropolar bonds only. The tie line compositions, where the features seen have chemical origin, are also referred as the chemical threshold of the system [28, 29].

Other approaches are the so-called topological models, which are based on the constraint theory [23–26] and on the structural dimensionality considerations [27]. In these models, the properties can be discussed in terms of the average coordination number ($<z>$), which is indiscriminate of the species or valence bond. In the constraints model [23–26], by equating the number of operating constraints to the number of degrees of freedom, $<z>$ of the most stable glass is shown to be ~2.4. At this value of $<z>$, the glass network changes from an elastically floppy (polymeric glass) type to a rigid (amorphous solid) type.

By extension of the topological model to the medium-range structures, other features at $<z>$~2.67 have also been observed [27]. However, the features observed at $<z>$~2.67 were attributed to a change from two-dimensional layered structure to a three-dimensional network arrangement due to cross-link.

In the present case, the co-ordination number of Se and Te is 2 and that of Cd and Ge is 4. A reversal in the trend of E_c in these glassy systems is observed at $<z>$=2.2 for a-$Se_{80-x}Te_{20}Cd_x$ system and at $<z>$=2.3 for a-$Se_{80-x}Te_{20}Ge_x$ system which are closer to topological models based on constraints theory described above.

Conclusions

The a–c transformation process in a-$Se_{80-x}Te_{20}Cd_x$ (x=0, 5, 10, 15) and a-$Se_{80-x}Te_{20}Ge_x$ (x=5, 15, 20) has been studied using the electrical conductivity as a structural characteristic quantity. It is shown that Avrami's theory of isothermal crystallization correctly describes the crystallization kinetics in the

present alloys. The composition dependence of E_c in a-Se$_{80-x}$Te$_{20}$Cd$_x$ (x=0, 5, 10, 15) and a-Se$_{80-x}$Te$_{20}$Ge$_x$ (x=5, 15, 20) alloys shows a reversal in the trend at a particular average coordination number. This is consistent with the theory of Phillips and Thorpe for the topological model in case of chalcogenide glasses.

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