JOURNAL OF MATERIALS SCIENCE 26 (1991) 4924–4930

Crystallization kinetics in glassy $Ge_{20}Se_{80-x}In_x$ alloys

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Crystallization kinetics is studied in glassy $Ge_{20}Se_{80-x}In_x$ $(0 \leq x \leq 20)$ using isothermal annealing at temperatures between the glass transition and melting. D.c. conductivity is taken as a parameter to estimate the extent of crystallization (α). The activation energy of crystallization (ΔE) and the order parameter (n) are calculated by fitting the values of α in the Avrami equations of isothermal crystallization. The results indicate that ΔE is highly composition-dependent, which is explained in terms of the stable phases in the Ge–Se–In system.

1. Introduction

The properties of the Ge–Se system have been studied in detail and it has been established that physical properties in this system are highly composition-dependent [1–5]. The addition of impurities as a third element has been quite useful in the understanding of the structure and transport properties in chalcogenide glasses. With this point of view, we have started a study of the Ge–Se system with some metallic additives. X-ray spectroscopic studies, photoconductivity and dielectric behaviour of Ge–Se–M (where M is a metal) have already been reported [6–9] from our laboratory. The present paper reports a study of crystallization kinetics in the Ge–Se–In system with varying In concentration. Such studies are quite important for a better understanding of the short-range order in these materials.

The extent of crystallization (α) of a certain material is represented by the Avrami equation [10] as follows:

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

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

The temperature dependence of K can be given by the Arrhenius equation

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

where K_0 is a constant, ΔE represents the activation energy of crystallization and k is the Boltzmann constant.

Any physical quantity which changes drastically upon crystallization can be used to monitor the extent of crystallization (α) and hence the kinetic parameters (ΔE and n) can be calculated using the above equations. Kotkata and co-workers [11–13] have used d.c. conductivity as a parameter to study the crystallization kinetics and have suggested an empirical relation to calculate α which is given by

$$\ln\sigma_m = \alpha \ln\sigma_c + (1-\alpha)\ln\sigma_a \qquad (3)$$

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_m is the conductivity of a mixture during the amorphous to crystalline (a–c) transformation. This equation is found to be most suitable when $(\sigma_c - \sigma_a)$ has quite a large value, as also found in the present case. We have, therefore, used the same equation to study the crystallization kinetics in glassy $Ge_{20}Se_{80-x}In_x$ where $x = 0$, 5, 10, 15 and 20. The results indicate that the kinetic parameters are composition-dependent, which is explained in terms of the stable phases in the Ge–Se–In system.

2. Experimental procedure

Glassy alloys of $Ge_{20}Se_{80-x}In_x$ with $x = 0$, 5, 10, 15 and 20 were prepared by quenching technique. 5N pure materials were sealed in quartz ampoules (internal dia ~ 8 mm) in a vacuum of ~ 10^{-5} torr. The ampoules were kept in a furnace where the temperature was raised slowly (3–4 °C min^{-1}) to 1000 °C. The ampoules were rocked for about 10 h at the maximum temperature to make the melt homogeneous and the quenching was done in air by an air blower.

The solidified substances were ground to a very fine powder and pellets (diameter ~ 6 mm and thickness ~ 0.5 mm) were obtained after compressing the powder in a die at a pressure of 3–4 t.

The (a–c) transformation was studied by measuring the d.c. conductivity (σ) as a function of time (0.5 min intervals) at various temperatures above the glass transition temperature (T_g).

The conductivity measurements were taken in a vacuum of ~ 10^{-3} torr by mounting the samples in a specially designed metallic sample holder. The current was measured using a Keithley electrometer model 614. The temperature was measured using a calibrated copper–constanton thermocouple.

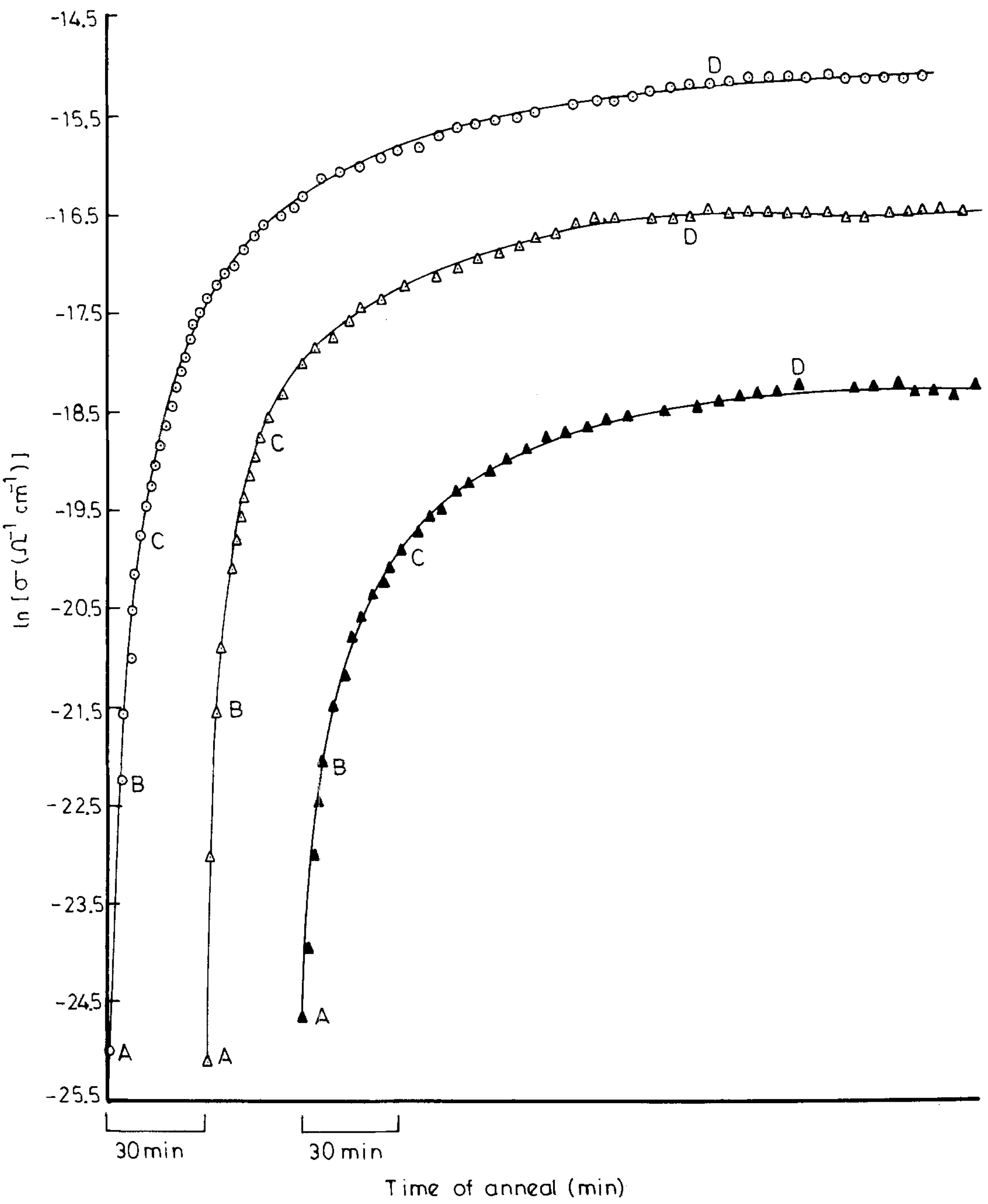

Figure 1 Annealing time dependence of d.c. conductivity for $Ge_{20}Se_{80}$ sample during different isothermal amorphous–crystalline phase transformations: (▲) 176 °C, (△) 186 °C, (⊙) 196 °C.

TABLE I Values of n at various annealing temperatures

$Ge_{20}Se_{80}$		$Ge_{20}Se_{75}In_5$		$Ge_{20}Se_{70}In_{10}$		$Ge_{20}Se_{65}In_{15}$		$Ge_{20}Se_{60}In_{20}$	
Temp. (°C)	n	Temp. (°C)	n	Temp. (°C)	n	Temp. (°C)	n	Temp. (°C)	n
176	0.97	166	0.72	156	1.01	146	0.87	141	0.46
186	0.89	176	0.82	166	1.00	156	0.91	151	0.46
196	0.89	186	0.77	176	1.04	176	0.89	161	0.59

3. Results and discussion

During isothermal annealing at temperatures between glass transition and melting, the electrical conductivity (σ) is found to vary with time (t). Figs 1 and 2 show the time dependence of σ at various annealing temperatures for glassy $Ge_{20}Se_{80}$ and $Ge_{20}Se_{60}In_{20}$, respectively. The results for other glassy alloys, i.e. $Ge_{20}Se_{75}In_5$, $Ge_{20}Se_{70}In_{10}$, and $Ge_{20}Se_{65}In_{15}$, were also of the same nature.

The transformation from amorphous to crystalline state occurs in three stages represented by AB, BC and CD in Figs 1 and 2. The part AB of these curves is

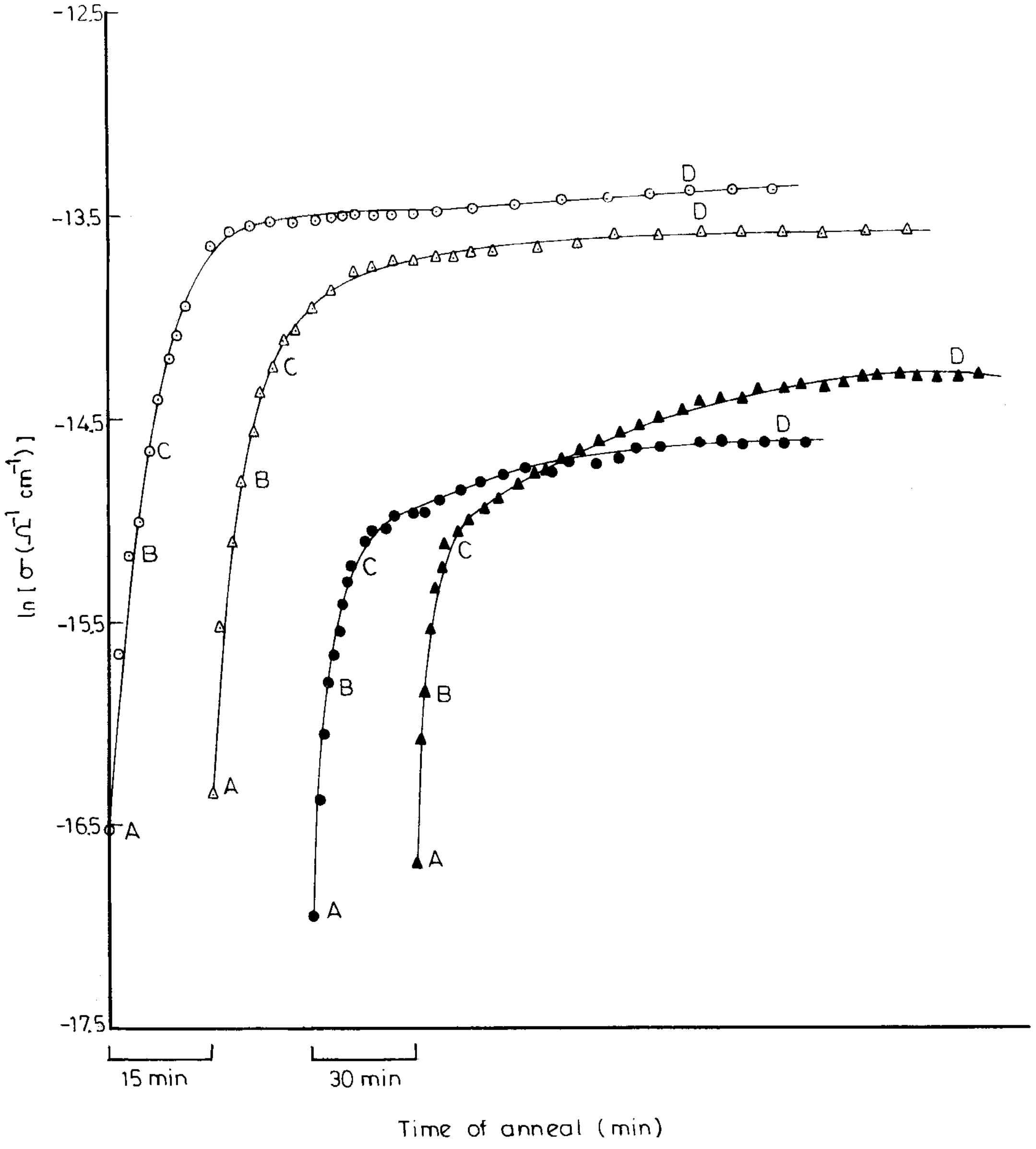

Figure 2 Annealing time dependence of d.c. conductivity for $Ge_{20}Se_{60}In_{20}$ sample during different isothermal amorphous–crystalline phase transformations: (▲) 141 °C, (●) 151 °C, (△) 161 °C, (⊙) 181 °C.

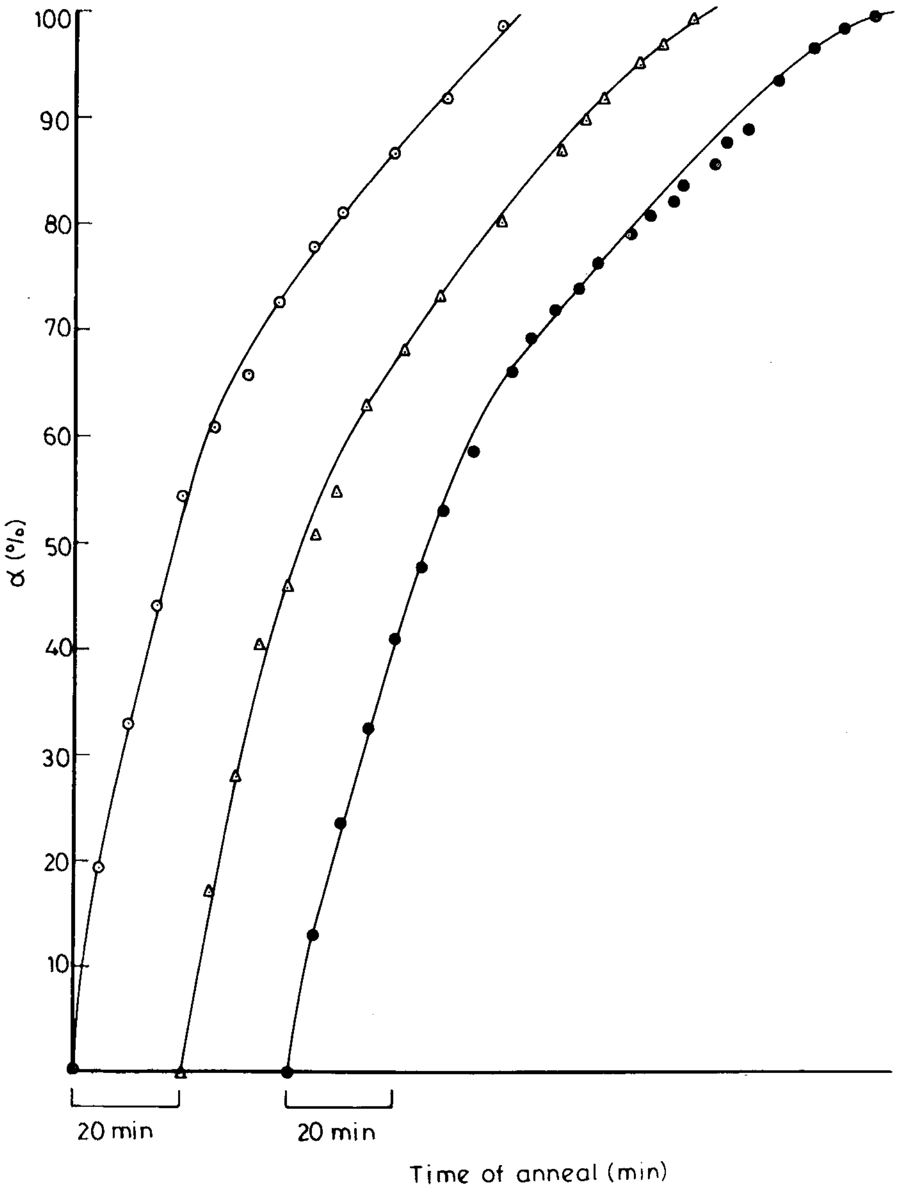

Figure 3 Crystallinity percentage versus annealing time for $Ge_{20}Se_{80}$ crystallized for different isotherms: (●) 176 °C, (△) 186 °C, (⊙) 196 °C.

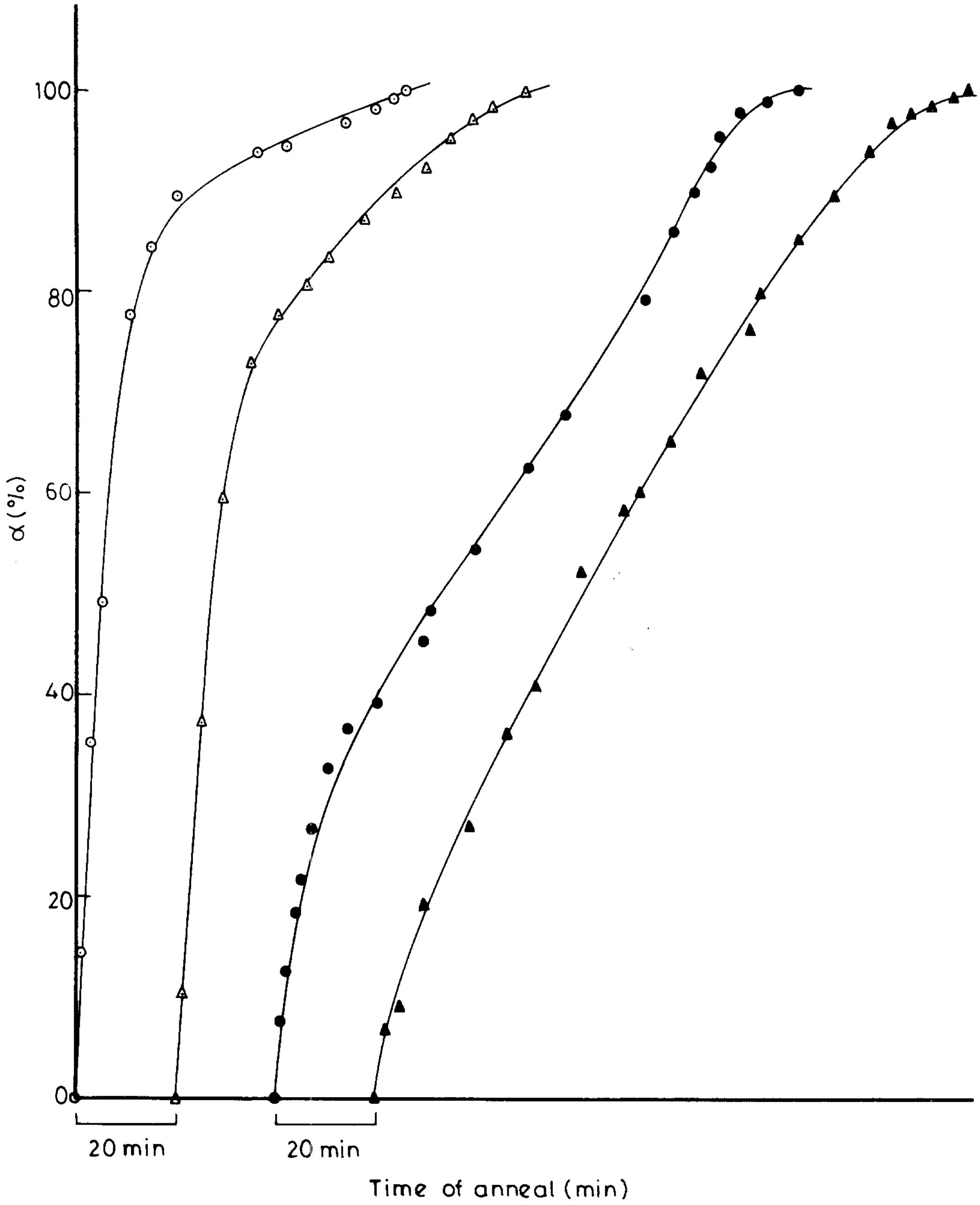

Figure 4 Crystallinity percentage versus annealing time for $Ge_{20}Se_{60}In_{20}$ crystallized for different isotherms: (▲) 141 °C, (●) 151 °C, (△) 161 °C, (⊙) 181 °C.

linear and represents a gradual increase of σ as a result of normal heating of the sample. The part BC shows a sharp rise of σ which may be due to the liberation of heat energy associated with the transition from a non-equilibrium to an equilibrium thermodynamic state. The third part represents the release of thermal energy, during the growth of the crystalline phase, which is being lost asymptotically from the sample and acquires a constant limiting value after a certain time. In the present study we are interested in understanding the crystallization kinetics during the growth process, i.e. the part CD of the curves in Figs 1 and 2.

As mentioned earlier, the extent of crystallization (α) can be calculated using Equation 1 where σ_a represents the conductivity at point C and σ_c that at point D in each curve in Figs 1 and 2. Using the measured value of conductivity (σ_m) at a given time, α is calculated as a function of time at various annealing temperatures for all the glassy samples studied. The results of these calculations are plotted in Figs 3 and 4 for $Ge_{20}Se_{80}$ and $Ge_{20}Se_{60}In_{20}$, respectively.The results for other glassy alloys were also of the same nature (results not shown here). Figs 5 and 6 show plots of $\ln[\ln(1-\alpha)^{-1}]$ versus $\ln t$ at various temperatures for $Ge_{20}Se_{80}$ and $Ge_{20}Se_{60}In_{20}$, respectively. Using Equation 1, the value of n can be determined at various temperatures from the slope of these curves. Table I shows the values of n at various temperatures for different glassy alloys.

From the intercepts of Figs 5 and 6, the values of K can be calculated at various temperatures for each glassy alloy. Fig. 7 shows that $\ln K$ versus $1000/T$ curves come out to be straight lines for all the glassy alloys, confirming the validity of Equation 2. From the slope of these curves, the values of ΔE are calculated for each glassy alloy; the results are given in Table II and plotted in Fig. 8. This figure indicates that ΔE

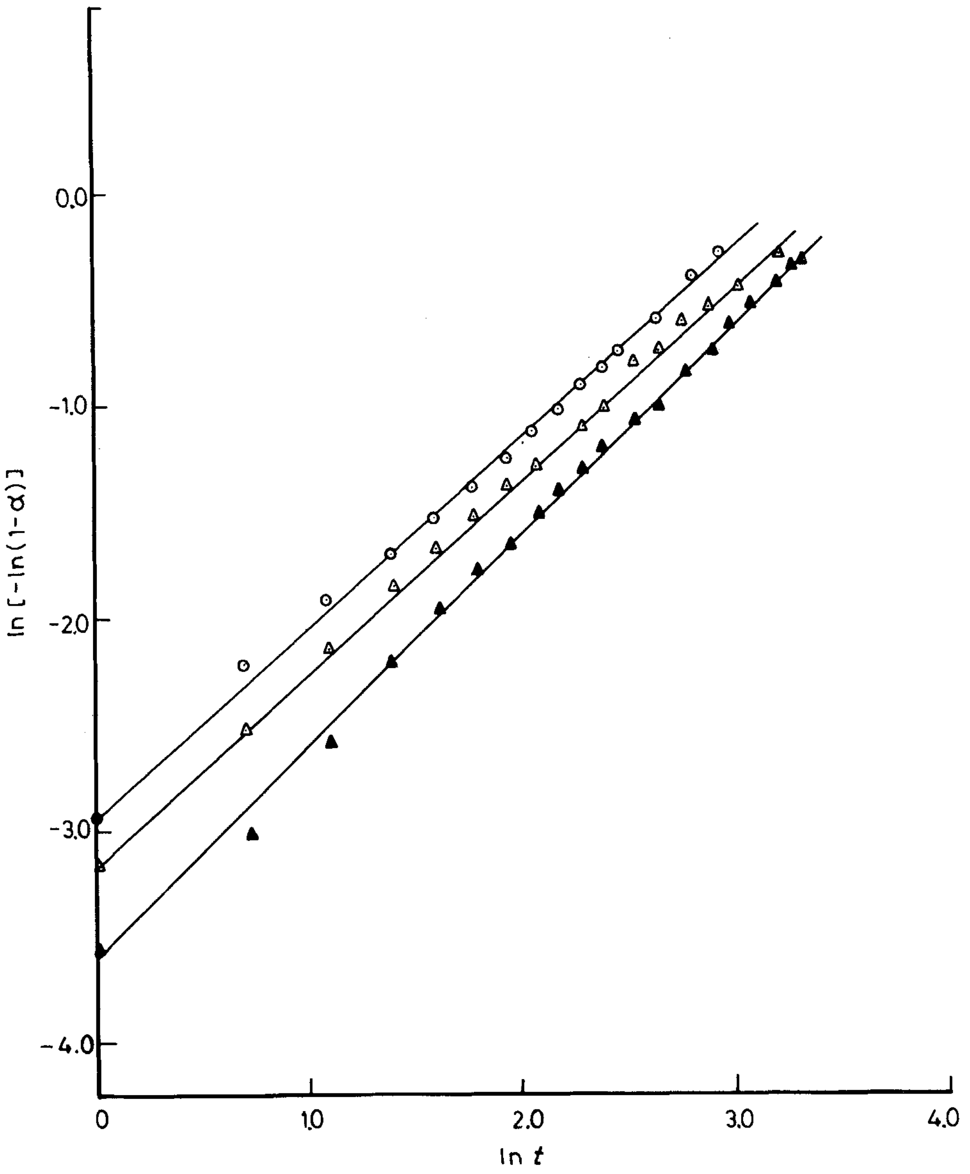

Figure 5 Avrami plots of the crystallization of $Ge_{20}Se_{80}$ for different isotherms: (▲) 176 °C, (△) 186 °C, (⊙) 196 °C.

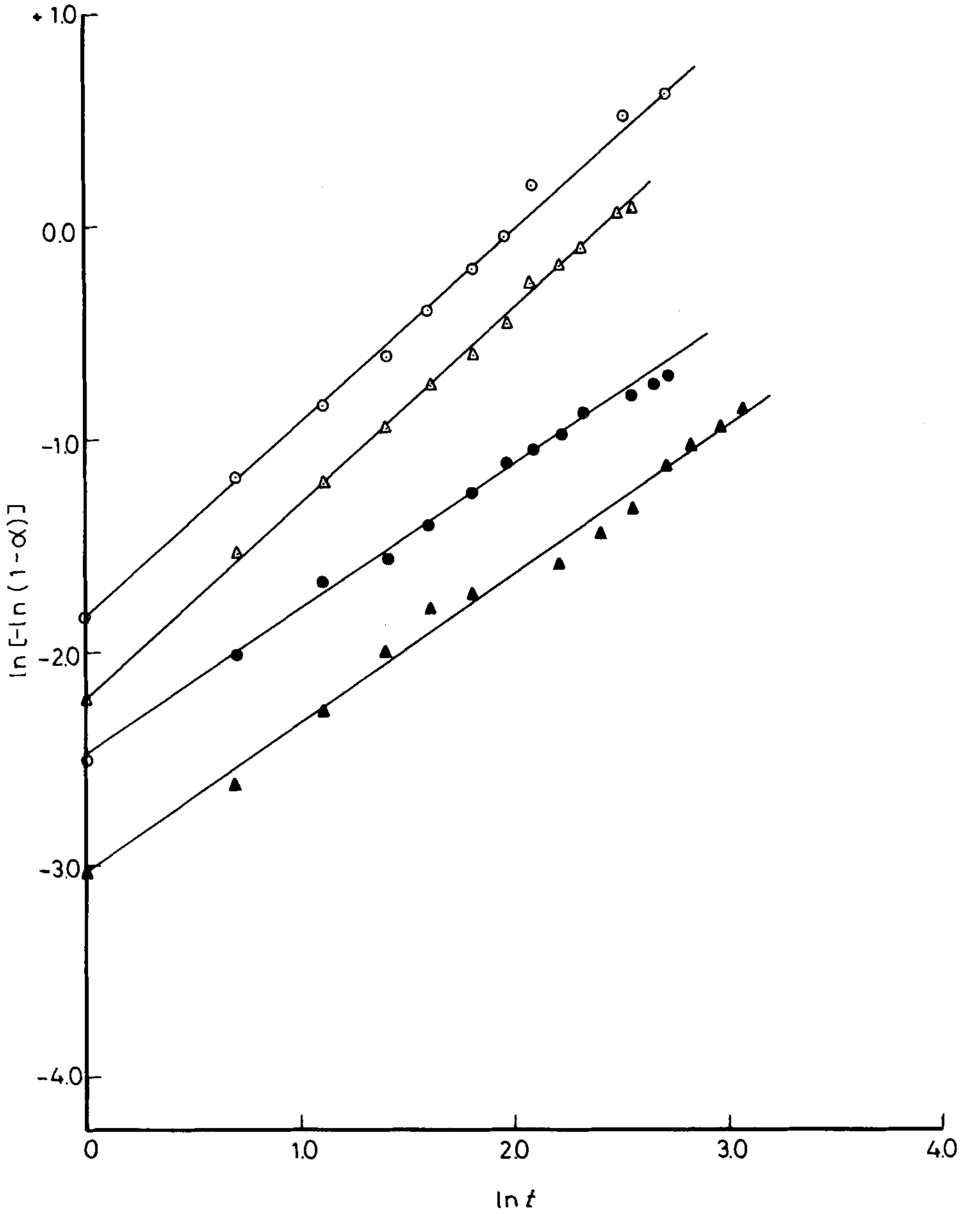

Figure 6 Avrami plots of the crystallization of $Ge_{20}Se_{60}In_{20}$ for different isotherms: (▲) 141 °C, (●) 151 °C, (△) 161 °C, (⊙) 181 °C.

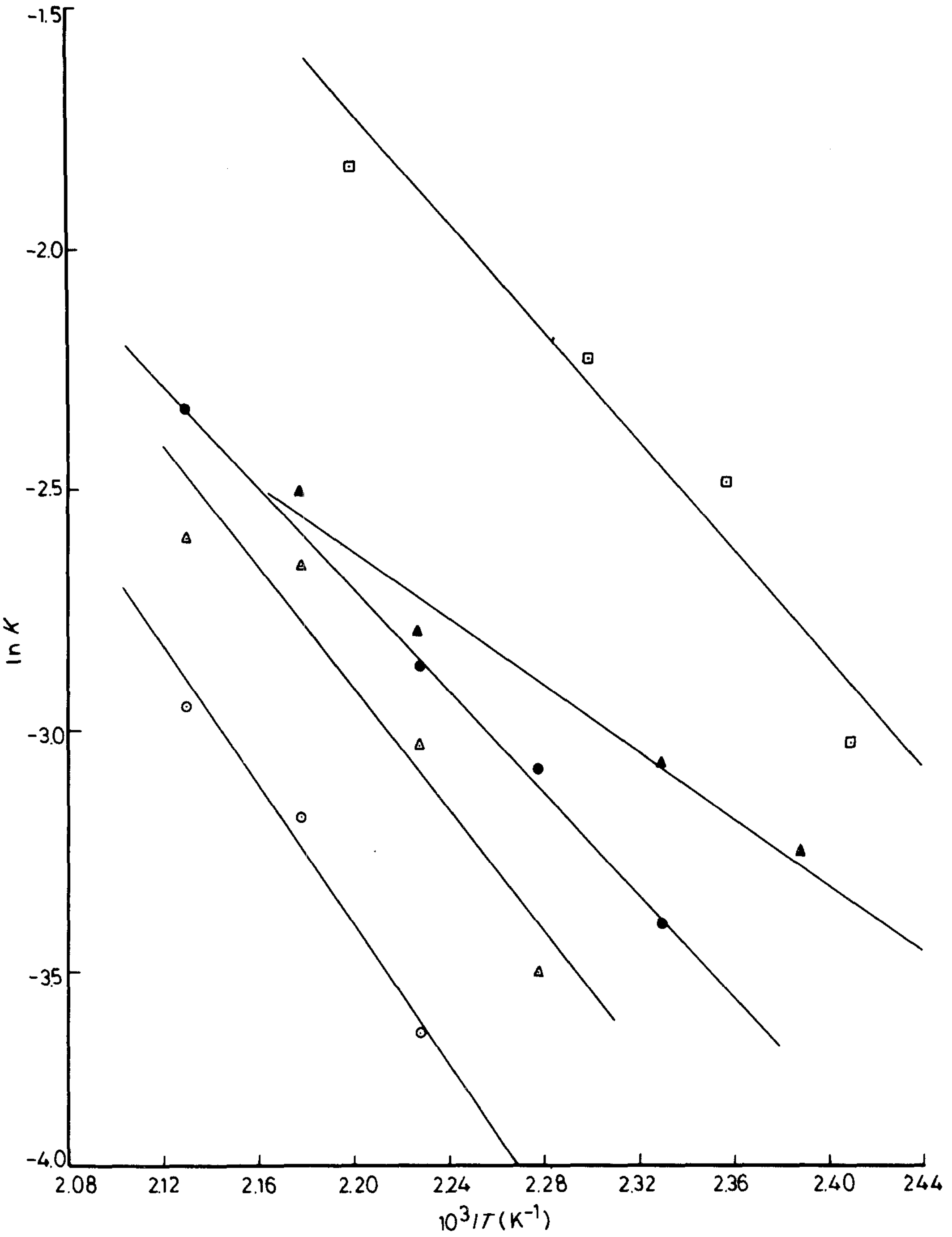

Figure 7 Arrhenius plots of crystallization of $Ge_{20}Se_{80-x}In_x$: (○) $Ge_{20}Se_{80}$, (△) $Ge_{20}Se_{75}In_5$, (●) $Ge_{20}Se_{70}In_{10}$, (▲) $Ge_{20}Se_{65}In_{15}$, (□) $Ge_{20}Se_{60}In_{20}$.

decreases on In incorporation in the Ge–Se system up to 15 at %. However, a further increase in In concentration increases the value of ΔE again.

A similar type of discontinuity at 15 at % In was also observed in our X-ray spectroscopic measurements in the same glassy system [6].

If one writes $Ge_{20}Se_{80-x}In_x$ as $Ge_{20}Se_{40}$ + $Se_{40-x}In_x$, then the largest value of x which contains In_2Se_3 + Se is $x = 16$. For higher concentration of In ($x > 16$), one can therefore expect the formation of In_2Se_3 + $GeSe_2$ + GeSe, which are the most stable phases as suggested by the phase diagrams. An increase in the activation energy of crystallization for $x > 15$ in the present case may, therefore, be a consequence of the formation of such stable phases in the Ge–Se–In system.

TABLE II Composition dependence of ΔE

Composition	ΔE (eV)
$Ge_{20}Se_{80}$	0.62
$Ge_{20}Se_{75}In_5$	0.53
$Ge_{20}Se_{70}In_{10}$	0.45
$Ge_{20}Se_{65}In_{15}$	0.30
$Ge_{20}Se_{60}In_{20}$	0.50

4. Conclusions

The crystallization kinetics of glassy $Ge_{20}Se_{80-x}In_x$ has been studied by the isothermal technique, i.e. by annealing the sample at certain fixed temperatures above the glass transition and measuring the d.c. conductivity with time during crystallization. The results

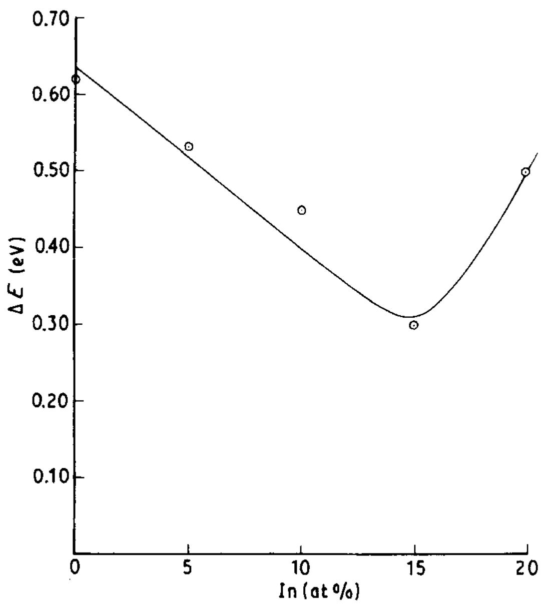

Figure 8 Composition dependence of the activation energy of crystallization in the system $Ge_{20}Se_{80-x}In_x$.

fit well with the Avrami equation of isothermal transformation. The kinetic parameters ΔE and n have been calculated for all the glassy alloys studied. A discontinuity in ΔE versus In concentration curve is observed for $x > 15$, which can be understood in terms of the formation of stable phases $In_2Se_3 + GeSe_2 + GeSe$ at higher concentration of In($x > 15$).

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Received 5 June
and accepted 20 December 1990