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RESIDUAL ENTROPY OF GLASSES AND THEIR RELATION WITH THE CRYSTALLIZATION BEHAVIOUR

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For the alloy of eutectic composition in the quasibinary $GeSe_2$–Sb_2Se_3 system the heat capacities of the glass, undercooled and stable liquid and crystalline phases have been measured using differential scanning calorimetry. Enthalpy, entropy and Gibbs free energy differences of vitreous and crystalline forms have been deduced for this alloy. The kinetic parameters of crystallization for glasses of nearby composition have been obtained by continuous heating experiments. The effective activation energy obtained has a value that accounts for the activation energy for nucleation calculated using simple nucleation theory formulae.

The phase diagram and glass forming region of the $GeSe_2$–Sb_2Se_3 system are known [1–3]. The eutectic composition and temperature are respectively 57.5 mol % $GeSe_2$ and 757 ± 1 K. The glass forming region extends from 35 to 98 mol % $GeSe_2$. In this paper we report on the determination of the heat capacity of a liquid, glassy and crystalline alloy of the eutectic composition of this system and also of the activation energy of crystallization of glasses of nearby composition. The nominal composition of these glasses is shown in Table 1. The residual values of thermodynamic quantities of the eutectic glass with respect to the crystalline stable phases are determined.

Table 1 Apparent activation energy for crystallization of $(GeSe_2)_x(Sb_2Se_3)_{100-x}$

x	E, kJ $(g\cdot at)^{-1}$
40	208 ± 6
50	209 ± 6
55	228 ± 6
60	187 ± 6

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Experimental

Bulk glasses were prepared by melting weighed amounts of elemental Ge, Sb and Se of 5N purity in evacuated and sealed quartz ampoules. The molten alloys were held at 1275 K for 12 h and constantly agitated to ensure homogeneity; subsequently they were quenched in air at room temperature. For the eutectic composition glass, melting and controlled quenching of the sample was performed directly in the calorimeter, because the critical cooling rate needed to avoid the crystallization of the melt is rather low compared to the maximum controlled cooling rate available in the DSC apparatus.

Calorimetric measurements were carried out in a Perkin–Elmer DSC 2 under pure argon atmosphere. The error in heat capacity measurement was 4% using a synthetic sapphire standard for calibration. The accuracy of the temperature measurements was within ±0.5 deg.

Results and discussion

Thermodynamic characterization of eutectic alloy

On heating the glass, the glass transition occurs at 540 K and the sample does not recrystallize if the heating rate is higher than 20 deg min^{-1}, that is, it passes continuously from undercooled liquid to stable liquid. However, crystallization

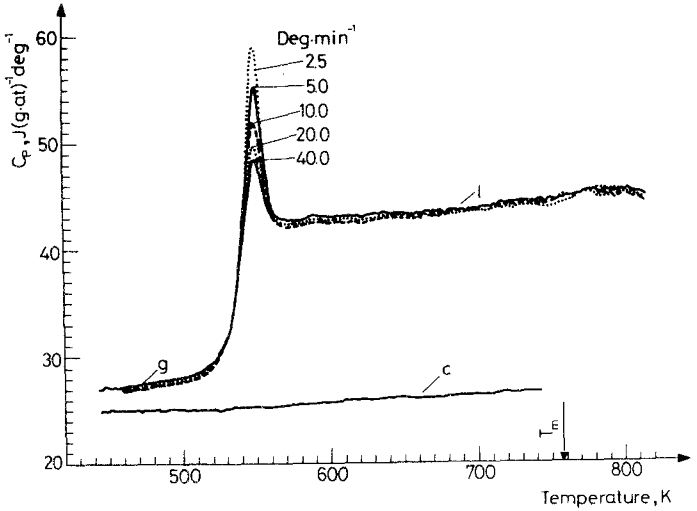

Fig. 1 Heat capacity versus temperature for glass (g), undercooled and stable liquid (l) and crystalline phases (c)

may be achieved on annealing the sample at temperature in the range 600–700 K. Figure 1 shows the heat capacity versus temperature for glass, undercooled and stable liquid and crystalline phases. In this figure are presented the heat capacity results on heating at a constant rate of 40 deg min^{-1} of glasses obtained at cooling rates ranging from 2.5 to 40 deg min^{-1}. There is a peak in the heat capacity at the glass transition which rises on lowering the cooling rate. A similar phenomenon is observed in other chalcogenide glasses [4–6]. The general behaviour of the heat capacity versus temperature on heating the glass is in agreement with that observed by other authors [6].

From the heat capacity determination the enthalpy and entropy values for glass, undercooled and stable liquid and crystalline phases have been calculeted relative to the stable liquid at the melting temperature T_m. These results are shown in Figs 2 and 3. The residual enthalpy and entropy (at 450 K) of the as-quenched glass with respect to the crystallized sample are respectively 2.2 kJ (g · at)$^{-1}$ and 1.9 J (g · at)$^{-1}$ deg^{-1}. The residual entropy obtained is of the same order of magnitude as those reported for other chalcogenide glasses [7].

The heat capacity measurements enables also the determination of the Gibbs free energy difference ΔG between undercooled liquid and crystalline solids. Figure 4 shows the value of ΔG obtained from experimental results.

Kinetic studies of crystallization

The high stability of the eutectic composition glass against crystallization prevents the crystallization kinetics study. This study has been done on nearby compositions

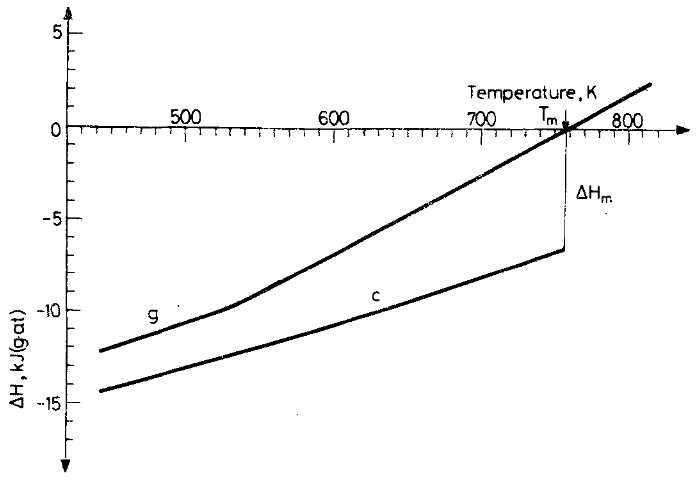

Fig. 2 Plot of enthalpy for glass (g), undercooled and stable liquid (l) and crystalline phases (c)

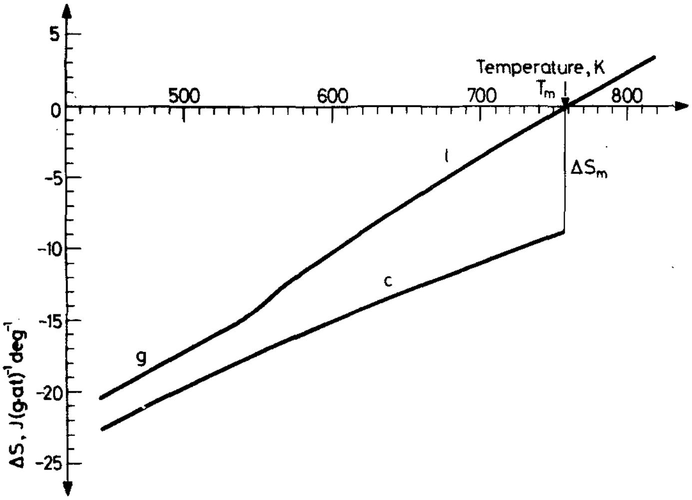

Fig. 3 Plot of entropy for glass (g), undercooled and stable liquid (l) and crystalline phases (c)

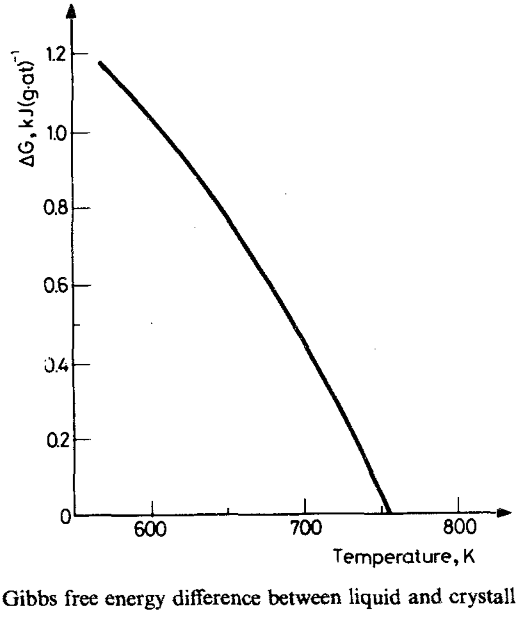

Fig. 4 Gibbs free energy difference between liquid and crystalline phases

of the $GeSe_2$–Sb_2Se_3 system. Experiments with constant heating rate were recorded from room temperature up to the temperature above the crystallization exotherm at scan rates ranging from 1.25 to 80 deg min^{-1}.

The fraction of crystallized material α, at given time, t, and the transformation rate $\frac{d\alpha}{dt}$ at the same time were determined from the DSC curve according to the method described previously [8]. To explain the crystallization we assume a transformation rate given by

$$d\alpha/dt = k(T)f(\alpha)$$

where $k(T)$ is the rate constant and $f(\alpha)$ is a function which reflects the mechanism of crystallization. For a fixed value of α, the plot of ln $(d\alpha/dt)$ versus $1/T$ obtained at different heating rates showed that $k(T)$ is given by the Arrhenius equation:

$$k(T) = k_0 \exp(-E/RT)$$

An example of such behaviour, for $\alpha = 0.3$ is presented in Fig. 5. The values deduced for the effective activation energy, E, are given in Table 1.

For simple nucleation theory [9–10] the activation energy for nucleation E_n, is expected to be $E_n \cong (\Delta H_m)^3/(\Delta G_c)^2$, where ΔG_c is the Gibbs free energy difference between the undercooled liquid and the crystalline phases at the onset of crystallization. From Fig. 4 a value of $\Delta G_c \cong 1.2$ kJ $(g \cdot at)^{-1}$ may be estimated for a

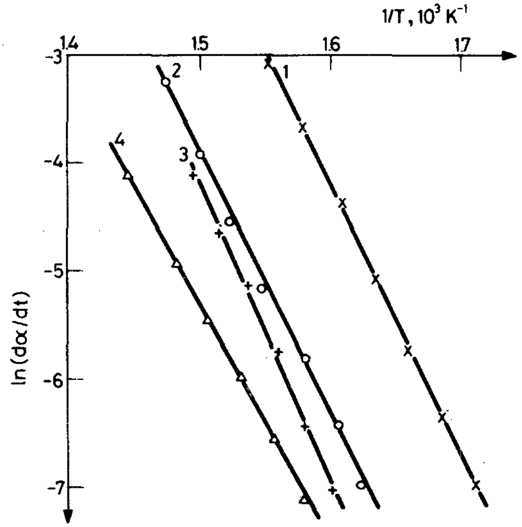

Fig. 5 Plots of $d\alpha/dt$, in logarithmic form, versus $1/T$ for a fixed fraction $\alpha = 0.3$ for $(GeSe_2)_x(Sb_2Se_3)_{100-x}$ samples with x: 40 (1), 50 (2), 55 (3), 60 (4)

temperature of 570 K. This gives a value of $E_n \cong 200$ kJ $(\text{g}\cdot\text{at})^{-1}$. Although the preceding calculation of E_n is very approximate it accounts nicely well for the values given in Table 1 for the effective activation energy. Morphological studies and microscopic examinations of the crystalline nuclei and their growth velocity are needed to further understand the crystallization mechanism.

Conclusions

Heat capacity measueements around the glass transition for glasses obtained at different cooling rates have shown that there is a peak at the upper part of glass transition that increases on decreasing cooling rate.

Due to the high resistance to crystallize of the eutectic composition it has been possible to measure the heat capacity of the undercooled liquid in all the range of temperatures between glass transition and melting.

The enthalpy and entropy of the glass, undercooled and stable liquid and crystalline phases have been calculated relative to the stable liquid at the melting temperature.

The Gibbs free energy difference between undercooled liquid and crystalline phases at the onset of crystallization accounts for the effective activation energy of crystallization obtained for nearby composition glasses.

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Zusammenfassung — Die Wärmekapazitäten von Glas, unterkühlter und stabiler Flüssigkeit und kristallinen Phasen von Mischungen der eutektischen Zusammensetzung des quasibinären Systems $GeSe_2$–Sb_2Se_3 werden mittels DSC gemessen. Aus den Ergebnissen werden Enthalpie, Entropie und freie Enthalpie der glasartigen und kristallinen Formen dieser Mischung abgeleitet. Die kinetischen Parameter der Kristallisation von Gläsern benachbarter Zusammensetzungen wurden durch temperaturprogrammierte Untersuchungen ermittelt. Die erhaltenen effektiven Aktivierungsenergien entsprechen dem für die Keimbildung nach einfachen theoretischen Formeln berechneten Wert.

Резюме — Методом дифференциальной сканирующей калориметрии определены теплоемкости стеклообразной фазы, переохлажденной и устойчивой жидкости, а также кристаллических фаз для сплава эвтектического состава в квазибинарной системе $GeSe_2$–Sb_2Se_3. Для стеклобразной и кристаллической форм этого сплава определены изменения энтальпии, энтропии и свободной энергии Гиббса. Путем непрерывного нагрева получены кинетические параметры кристаллизации стекол близкого состава. Полученная эффективная энергия активации имела значение принятое для энергии активации образования центров кристаллизации, вычисленной из простой теоретической формулы теории образования центров кристаллизации.