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A crystallization study of the $Ge_{25}Sb_{20}S_{55}$ glassy alloy

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Differential scanning calorimetry analysis was used to gain insight on the thermal stability and calorimetric behaviour on heating of the $Ge_{25}Sb_{20}S_{55}$ glassy alloy. The as-quenched glass shows a glass transition at $T_g = 570$ K. From the variation of T_g with the heating rate a value of $\Delta h = 240$ kJ mol^{-1} was obtained for the activation enthalpy of the mean relaxation time. On further heating an exothermic process appears ranging from 725 to 800 K giving rise to glassy GeS_2 and needle-like crystals of antimony. The microstructure of the crystallization product was obtained from X-ray diffraction and scanning electron microscopy. The resulting material shows two glass transitions. The crystallization process is explained correctly by the Johnson–Mehl–Avrami–Erofe'ev equation with a kinetic exponent of $n = 1.6$. The apparent activation energy of crystallization is evaluated as $E = 286$ kJ mol^{-1}.

1. Introduction

The structural relaxation and crystallization are important phenomena that characterize amorphous alloys [1] and, due to their exothermic character, they can be easily observed by differential scanning calorimetry (DSC). This is a suitable technique to gain insight into the thermal stability and crystallization behaviour of a chalcogenide glassy alloy [2–4]. In this paper DSC data reflecting the behaviour on a macroscopic scale are compared with those gathered from microscopic observations in an electron scanning microscope and in the X-ray diffraction spectra.

Some glassy alloys of the Ge–Sb–S system have been studied before [5–8]. Our aim was first of all to observe the thermal behaviour and to study the kinetics of the glass transformation and crystallization of glasses of the above system by isothermal and continuous heating methods [9]. Secondly, we planned to make observations of the as-quenched and heat-treated samples by optical and scanning electron microscopy (SEM) and X-ray diffraction. In this paper we report the calorimetric and morphological study of one alloy of the Ge–Sb–S system, namely the glassy alloy $Ge_{25}Sb_{20}S_{55}$.

2. Experimental procedure

The bulk glassy samples were prepared by direct synthesis from germanium and antimony (99.999% purity) and purified sulphur (mark DAB-6) in evacuated quartz ampoules in a rotary furnace. After synthesis and homogenization (10 h, $T = 1120$ K) the melts were rapidly cooled in water, the estimated cooling rate being $\sim 10^2$ K sec^{-1}.

The amorphous state and homogeneity were checked by optical microscopy and X-ray diffraction using Cu$K\alpha$ radiation. No trace of crystallization or phase separation was detected. The calorimetric experiments were performed in a Perkin–Elmer DSC-2 apparatus coupled with a data acquisition system. For each DSC run 15 to 20 mg powdered material was scanned under a pure argon atmosphere. Any spurious contribution to the specific heat resulting from baseline curvature was removed by substracting a reference curve (obtained by heating empty pans at the same rate or, in case of the isothermal measurements, with the crystallized material) from the curve obtained with the sample in place.

X-ray diffraction measurements using Cu$K\alpha$ radiation were used to identify the structural changes induced by heat treatment. Metallographic examination was performed on mechanically polished samples and scanning electron microscopical observations of the same sample were made using a Jeol JSM-840 scanning microscope with an energy dispersive spectrometer and backscattered electron image equipment.

3. Results and discussion

3.1. Differential scanning calorimetry

Fig. 1a shows a typical DSC curve at a scanning rate

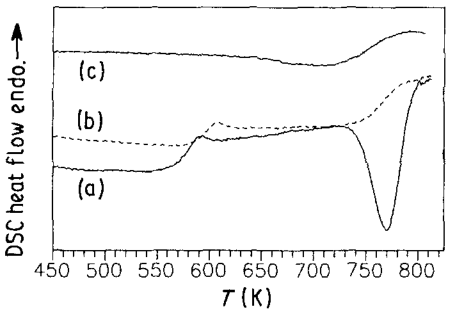

Figure 1 DSC scans of glassy $Ge_{25}Sb_{20}S_{55}$ at a heating rate of $10\ K\ min^{-1}$: (a) first heating scan; (b) second heating scan; (c) heating scan of glassy GeS_2.

of $10\ K\ min^{-1}$ with a glass transition temperature, T_g, at 570 K and a crystallization process ranging from 725 to 800 K. An apparent shift of the base-line location before and after the crystallization process is also observed. To analyse this shift, after the first heating up to 820 K, we cycled the sample down to room temperature and reheated it (at the same heating rate). The resulting DSC curve shows a second glass transition in the temperature range in which crystallization took place in the first heating of the glass (see Fig. 1b). The thermal decomposition of the sample hinders further heating to higher temperatures. To explain the appearance of two glass transitions in the reheated glass we assume that during the crystallization and simultaneous to it, a new glassy phase was produced. The composition of this new glass is most probably GeS_2 because of the similarity of part of the DSC curve with the DSC curve of glassy GeS_2, also measured and shown in Fig. 1c. This last result agrees with that already reported in the literature [10]. The difference between the first and second heating curves enabled us to evaluate the crystallization enthalpy (Fig. 2) associated with the crystallization peak obtaining a value of $\Delta H_c = 2.5\ kJ\ mol^{-1}$.

The glass transition temperature of the as-quenched glass exhibits a kinetic dependence on the heating rate, β. As expected, the glass transition temperature shifts to higher temperatures with increasing heating rates. The increase in T_g is nearly linear with the logarithm of the heating rate. Following Moynihan *et al.* [11] we attempted to determine the activation enthalpy, Δh, of the internal relaxation time from the variation of T_g with the heating rate. Using Equation 6 from [11], that is

$$d(\ln\beta)/d(1/T_g) = -(\Delta h/R) \qquad (1)$$

for different heating rates ($1.25 \leq \beta \leq 80\ K\ min^{-1}$), Δh was evaluated. The slope of the least squares fit yields a value for Δh equal to $240\ kJ\ mol^{-1}$. This value is of the same order of magnitude as that obtained for other glasses of the Ge–Sb–S system [8] and is of the order of the activation enthalpy for shear viscosity found in similar chalcogenide glasses [12].

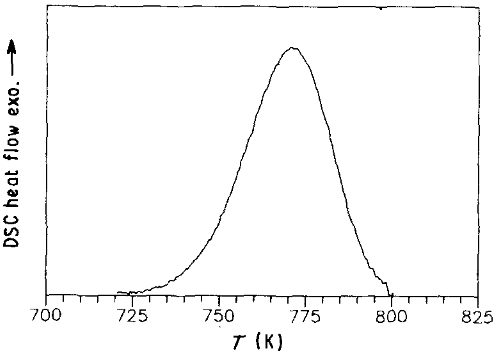

Figure 2 The crystallization peak obtained as a difference between the first (Fig. 1a) and second heating (Fig. 1b) DSC scans.

3.2. Crystallization kinetics

The crystallization kinetics study of the as-quenched glass was performed by combining both the isothermal and constant heating rate techniques [9]. The whole analysis of the results obtained with the constant heating rate technique was limited by the fact that the glass transition of GeS_2 glass is superimposed on the crystallization peak.

To analyse the crystallization process, we assume that the rate of crystallization, dx/dt, is given by the general equation

$$dx/dt = k(T)f(x) \qquad (2)$$

where x is the crystallized fraction at time t and temperature T, $k(T)$ is the rate constant generally given by the Arrhenius expression

$$k(T) = k_0 \exp(-E/RT) \qquad (3)$$

with E the effective activation energy and k_0 the pre-exponential factor. The function $f(x)$ reflects the mechanism of crystallization. In the Johnson–Mehl–Avrami–Erofe'ev (JMAE) model it has the form

$$f(x) = n(1-x)[-\ln(1-x)]^{(1-n)/n} \qquad (4)$$

where n is the kinetic exponent.

By relating Equations 2 and 3 and taking logarithms, we obtain

$$\ln(dx/dt) = \ln[k_0 f(x)] - E/RT \qquad (5)$$

Therefore, apart from a constant value, the experimental form of $f(x)$ can be obtained directly from the plot of $\ln(dx/dt)$ or (once E is known) $\ln[k_0 f(x)]$ against $\ln(1-x)$ obtained for an isothermal scan. For instance, such a plot is shown in Fig. 3 for an isothermal crystallization at 760 K. From the analysis of this

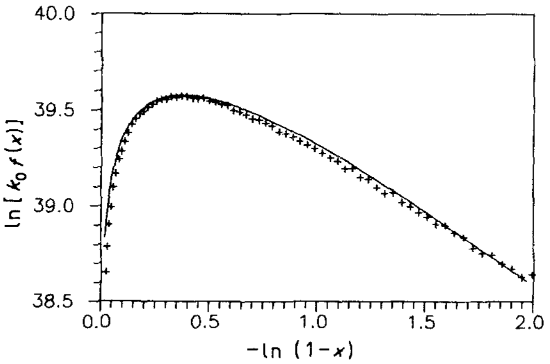

Figure 3 (+) Plot of $\ln[k_0 f(x)]$ against $\ln(1-x)$ obtained for the crystallization peak under isothermal treatment at 760 K. (——) The values calculated with the JMAE equation with $n = 1.6$.

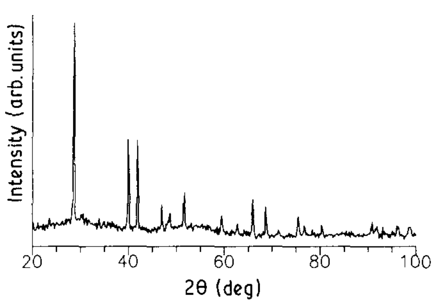

Figure 4 X-ray diffraction pattern of the crystallized specimen. (heated to 810 K at 10 K $\min^{-1}$).

curve the value of the kinetic exponent $n = 1.6$ was reached. This result suggests that we have an athermal nucleation of quenched-in embryos with limited three-dimensional growth diffusion [13]. The effective activation energy, E, was deduced by the peak method [14] and the value of 286 kJ mol^{-1} was obtained. Once the activation energy, E, and the kinetic exponent, n, are known, it is possible to estimate the pre-exponential factor, k_0: when measuring it in $\mathrm{seconds}^{-1}$, we obtain the value $\ln k_0 = 39.8$.

3.3. Structural and morphological analysis

The as-quenched as well as the heat-treated specimens were analysed by X-ray diffraction. The diffraction pattern obtained for the heat-treated sample shows reflection peaks corresponding in the main to hexagonal antimony, as can be seen in Fig. 4 and Table I.

The material (atomic number) contrast obtained by backscattered electron image is very useful for qualitative identification of phases and is especially suitable for quantitative evaluation of microstructural geometry [15, 16]. These images were obtained for the heat-treated material, slightly polished, and are shown in Figs 5a and b. As is known, in materials with high atomic number a large number of electrons is backscattered by atoms close to the surface, with little change in energy. Therefore, the antimony is seen to be lighter than the glassy matrix. A secondary electron image of the same sample is presented in Fig. 5c.

TABLE I Values of the X-ray diffraction angles (2θ) of a $Ge_{25}Sb_{20}S_{55}$ alloy heated to 810 K at 10 K $\min^{-1}$ and tentative assignation to crystalline antimony (as structure) after [19]

2θ (deg) experimental	*hkl*, Sb
23.60	003
28.65	102
40.06	014
42.00	110
47.04	105
48.76	006
51.66	022
59.46	204
62.75	017
65.96	116
68.74	212
71.45	108
75.50	124
76.79	300
80.43	215
90.77	119
91.78	220
96.19	306
98.65	132

The X-ray mapping or element distribution [15] of the same zone imaged in Fig. 5b is presented in Figs 5d to f. A semiquantitative analysis of the microstructural features can be obtained from these figures. Remembering that the intensity of each individual element mapping does not reflect the total amount of this element, it appears that, apart from the antimony needle-like crystals, the glassy matrix looks chemically homogeneous (at least at this level of accuracy). Results of semiquantitative analysis with energy dispersive X-ray spectroscopy (EDAXS) of both an antimony grain and the glassy matrix are in agreement with X-ray and element distribution results.

The fact that the primary crystallization of antimony occurs on heating the as-quenched glass can be understood because of the nominal composition of the glass. In fact a homogeneous glassy alloy of $Ge_{25}Sb_{20}S_{55}$ lies (in the Gibb's composition triangle) very close to the GeS_2–Sb line, in a region where there is, by analogy with the Ge–Sb–Se [17] and Ge–S–Te [18] systems, liquid–liquid stable or metastable immiscibility at intermediate temperatures. Therefore, at these temperatures the undercooled homogeneous liquid alloy obtained by heating the glass will be competing with a mixture of two immiscible liquid phases, one antimony and the other GeS_2. The first is expected to evolve to crystalline antimony as the second liquid changes to very good glass-forming stoichiometric GeS_2 alloy glass.

4. Conclusions

Coupling of the calorimetric, structural and morphological studies has proved to be very useful in obtaining a unified view of the thermal stability and crystallization behaviour of glasses of $Ge_{25}Sb_{20}S_{55}$.

The glassy alloy is thermally stable up to about 720 K. On further heating it partially decomposes, giving crystalline antimony and GeS_2 glassy alloy, which coexist with part of the initial glassy alloy.

The kinetic analysis of the glass transition of the homogeneous glassy alloy was carried out from the evolution of the glass transition temperature as a function of the heating rate. A value of 240 kJ mol^{-1} was obtained for the activation energy of the internal mean relaxation time. This value is of the same order of magnitude as those obtained in other Ge–Sb–S glasses [8].

By measurements in both isothermal and continuous heating modes it was possible to evaluate the crystallization kinetics. Isothermal results can be explained by the JMAE equation (with a kinetic exponent $n = 1.6$). Continuous heating results are in agreement with this model if it is further assumed that the rate constant follows the Arrhenius behaviour with an activation energy of 286 kJ mol^{-1} and a pre-exponential factor that has a logarithm of $\ln k_0 = 39.8$ (k_0 in $\sec^{-1}$).

On heating the glass, the primary crystallization of antimony occurred in the form of needle-like crystals.

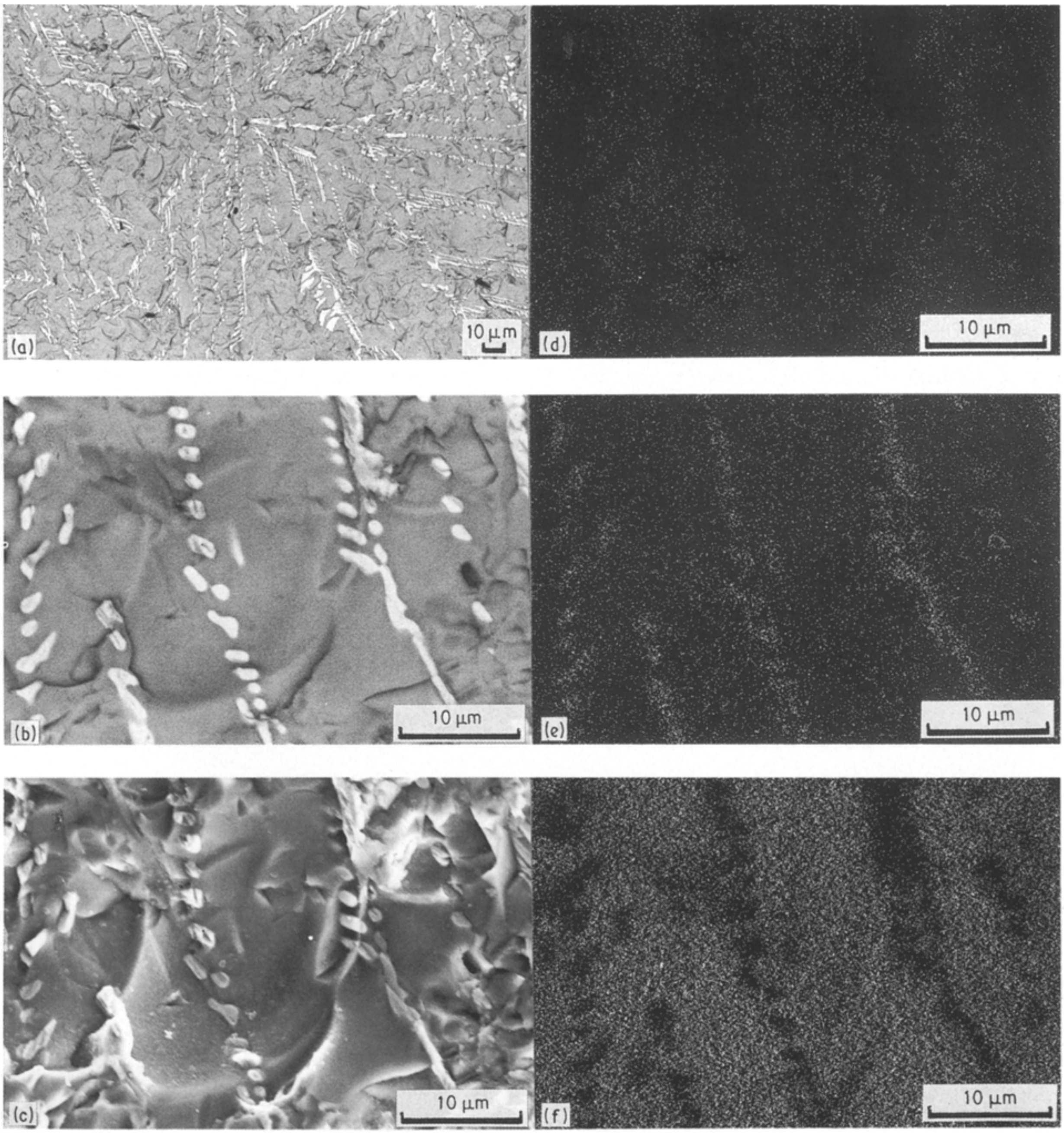

Figure 5 Scanning electron microscopy pictures of the $Ge_{25}Sb_{20}S_{55}$ glass annealed at 790 K for 1 h: (a) and (b) backscattered electrons; (c) SEM; (d) to (f) mappings of the same region as in (b); (d) germanium; (e) antimony; (f) sulphur.

X-ray and SEM observations demonstrate this partial crystallization in regions rich in antimony within a glassy matrix rich in sulphur.

Taking into account that this composition lies near the GeS_2–Sb line in the ternary composition diagram, the presence of elemental crystalline antimony and probably glassy GeS_2 on the heat-treated material could be explained by the combination of both the metastable liquid immiscibility of the alloy at intermediate temperatures and the high glass-forming ability of GeS_2-rich composition alloys.

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