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DSC study of some Ge–Sb–S glasses

M. D. BARÓ, N. CLAVAGUERA*, S. SURIÑACH
Departament de Física, Fac. Ciències, Universitat Autònoma de Barcelona, 08193 Bellaterra, Spain

Č. BARTA, N. RYŠAVÁ, A. TŘÍSKA
Institute of Physics, Czechoslovakian Academy of Science, 18040 Prague, Czechoslovakia

Differential scanning calorimetric analysis was made on three glasses of the Ge–Sb–S system in order to obtain insight into the kinetics of glass transition and of the inherent relaxation processes occurring in the glass transition region. The heat capacity of the supercooled liquid referred to as the glass was measured. The value of the heat capacity jump at the glass transition, ΔC_p, has been obtained for each glass. These values are in good agreement with those found for similar chalcogenide glasses. The relaxation process in the glassy alloy $Ge_{30}Sb_{10}S_{60}$ was investigated by measuring the excess heat capacity of the annealed glass in the glass transition region. A relaxation enthalpy of 2.7 meV for annealing at 595 K for 17 h was determined. A kinetic study of the glass transition in the $Ge_{20}Sb_{10}S_{70}$ glass was done. From the change in the glass transition temperature with scanning rate, an apparent activation energy of 3.9 eV was obtained. This value agrees with those measured for the apparent activation energy of the shear viscosity in similar glasses.

1. Introduction

The Ge–Sb–S system continues to receive the attention of many scientists as a potential system for optical applications. One of the most important advantages, from the ecological point of view, is that the glasses of this system do not contain poisonous elements. Another advantage of the antimony-containing materials is the fact that they are much more resistant to decomposition by reaction with air humidity than glasses of the Ge–S system [1]. Therefore, glasses of the Ge–Sb–S system are expected to be more useful in practice than those of the Ge–S system and many attempts to utilize them are in progress.

In the Ge–Sb–S system only one glass-forming region appears, shown in Fig. 1, located in the neighbourhood of the Ge–S side and sulphur-rich part of the Ge–Sb–S triangle, extending up to compositions with about 40 at. % Sb. Glassy materials of this system have a high transmittance in the infrared region in the range 1 to 22 μm and their absorption edge shifts towards longer wavelengths with increasing content of both antimony and germanium [2]. However, these properties are largely dependent on the thermal history of the sample.

One of the most convenient methods for the study of the thermokinetic characteristics of the glass transition is the differential scanning calorimetry (DSC). The dependence of the glass transition temperature on the heating temperature used for the measurement has been intensively studied from the theoretical point of view in connection with the relaxation processes that occur at the glass transition temperature [3–8]. Nevertheless, the question of the nature of the glass transition still remains open. In this paper we report the calorimetric behaviour through the glass transition of alloys with the compositions (1) $Ge_{10}Sb_{20}S_{70}$, (2) $Ge_{20}Sb_{10}S_{70}$ and (3) $Ge_{30}Sb_{10}S_{60}$. The location of these compositions in the glass forming region of the system is shown in Fig. 1. Our aim was to study both the kinetics of the glass transition and the relaxation process by continuous heating and/or isothermal anneals of the sample.

2. Experimental procedure

The bulk glassy samples were prepared by direct synthesis from germanium, antimony (purity 99.999%) and purified sulphur (mark DAB-6) in evacuated quartz ampoules in a rotatory furnace. After synthesis and homogenization (10 h, $T = 1120$ K) the melts were rapidly cooled in air. The glassy nature of the samples was confirmed by X-ray diffraction.

The calorimetric experiments were performed in a Perkin–Elmer DSC-2 apparatus coupled with a data acquisition system. For each DSC run, approximately 15 to 20 mg powdered material was used and scanned under a pure argon atmosphere. Any spurious contribution to the specific heat resulting from baseline curvature was removed by subtracting a reference curve (obtained by heating empty pans at the same rate) from the curve obtained with the sample in place. The error in heat capacity measurements was 2%

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* *Present address*: Departament Estructura i Constituients de la Materia, Facultat Física, Universitat Barcelona, Diagonal 647, 08028 Barcelona, Spain.

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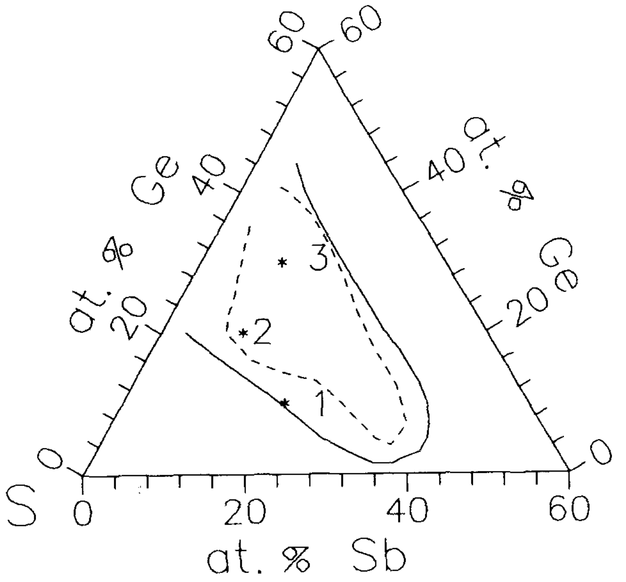

Figure 1 Glass-forming region of the Ge–Sb–S system: (——) glass-forming region for rapidly cooled samples [14], (---) glass-forming region for slowly cooled samples [15]. (1) $Ge_{10}Sb_{20}S_{70}$, (2) $Ge_{20}Sb_{10}S_{70}$, (3) $Ge_{30}Sb_{10}S_{60}$.

using a synthetic sapphire standard for calibration. The accuracy of the temperature measurements was within ± 0.5 K. X-ray diffraction measurements using CuK_α-radiation were used to identify the structural changes induced by heat treatment. Optical and electron scanning microscopical observations were made to elucidate the homogeneity of the samples. Metallographic examination was performed on mechanically polished samples and scanning electron microscopical observations of the same samples were made using the Jeol JSM-840 apparatus with an energy dispersive spectrometer.

3. Results

The DSC curve of a $Ge_{10}Sb_{20}S_{70}$ as-quenched glass in the temperature range 380 to 600 K is shown in Fig. 2. There are several thermal irregularities in it. We assume that the thermal effect at 440 K is caused by the great amount of sulphur in the glass. This is in accordance with a previous study on other sulphur-rich glasses [9] where an endothermic effect at 438 K was also observed. It is known [10] that at this temperature a variety of physical parameters of sulphur, such as viscosity and specific heat, show irregularities which are characteristic of the so-called λ transition. In general, it is believed that these changes are due to the formation of a long chain polymer of S_μ, so that the S_μ and S_8-rings are the main constituents in liquid sulphur at $T > 432$ K. Furthermore, the $Ge_{10}Sb_{20}S_{70}$ glass exhibits an apparent inhomogeneity once cross-sectioned, as can be seen in the photograph taken in the optical microscope (Fig. 3). Energy dispersive analysis of X-rays (EDAX) examination on the same

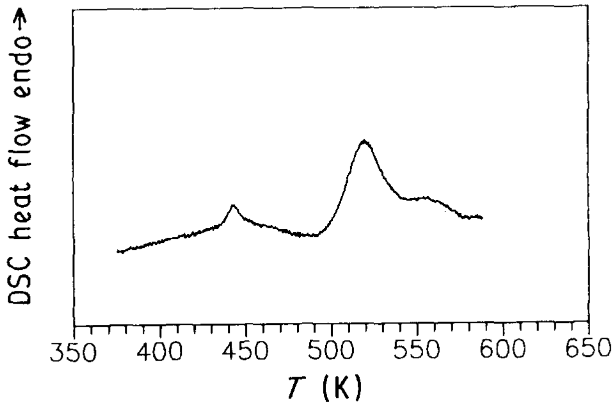

Figure 2 DSC scan of the low-germanium glass $Ge_{10}Sb_{20}S_{70}$ (1). Heating rate 20 K min^{-1}.

Figure 3 Photograph of the cross-section of $Ge_{10}Sb_{20}S_{70}$ glass.

TABLE I Values of the X-ray diffraction angles (2θ) and the respective indexes (*hkl*) of a $Ge_{30}Sb_{10}S_{60}$ glassy alloy thermally treated at 720 K for 10 h

2θ (deg)	*hkl*	
	GeS_2	Sb_2S_3
15.34	200	
16.18	$\bar{1}11$	
16.97	021	
18.21	130	
18.93	121, 220	
21.10	031	
23.51	$\bar{2}21$	
24.78		130
26.44	002	
28.65	330	230
30.40	241	
31.61	212	
32.39	340	221
33.35	060	301
34.18	$\bar{4}11$	
35.36		240
36.95	161, 260	231
39.11	$\bar{3}32$	
40.03		430
41.92	$\bar{5}11$	
42.86	530	421
44.78	$\bar{2}23$	
45.49		440
46.29	460	
47.03		002, 151
48.37		060
49.38		610
50.83	272	
52.97		351
54.53		132
59.42		720
62.72		370

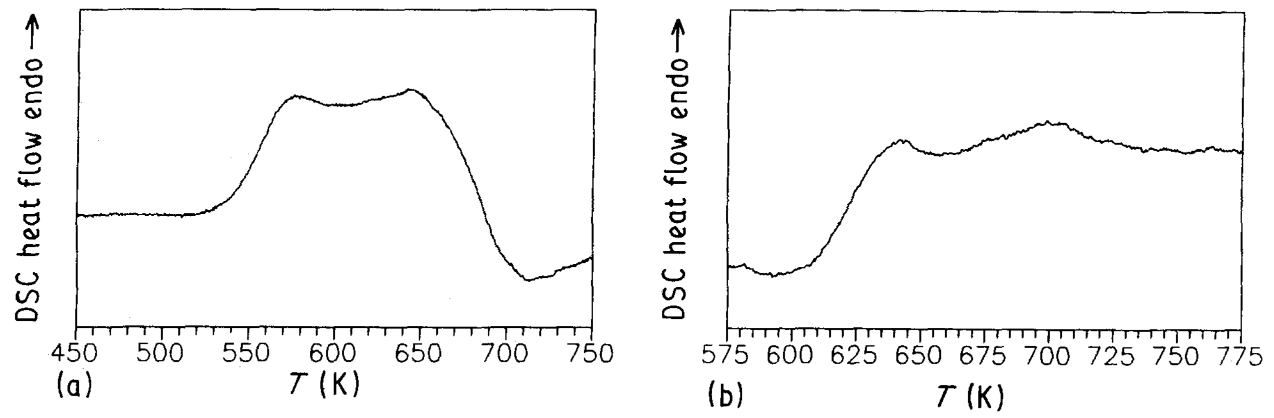

Figure 4 Differential scanning calorimetry scans at the heating rate 20 K min^{-1}: (a) $Ge_{20}Sb_{10}S_{70}$ (2) and (b) $Ge_{30}Sb_{10}S_{60}$ (3).

cross-section showed homogeneous distribution of the elements on the surface. The second thermal effect shown in Fig. 2, beginning at 500 K is due to the transition of the sample from the glassy to the supercooled liquid state and it is followed by crystallization (onset at 560 K).

Fig. 4a and b show the DSC curves obtained for the as-quenched glasses (1) $Ge_{20}Sb_{10}S_{70}$ and (3) $Ge_{30}Sb_{10}S_{60}$, respectively. The heat capacity changes due to the transition of the samples from the glassy to the supercooled liquid state and the beginning of crystallization are apparent in both curves. The above glasses were thermally treated by annealing at temperatures slightly higher than that of the onset of the crystallization. All such treated samples were X-ray analysed. The X-ray diffraction pattern of the initially glassy alloy, $Ge_{30}Sb_{10}S_{60}$, annealed once at 720 K for 10 h, is shown in Fig. 5. In the diffraction spectrum, not only peaks belonging to the orthorhombic antimony (III) sulphide but also those belonging to the monoclinic germanium (IV) disulphide appear. In Table I all the Bragg angles measured, as well as the respective indexes, are summarized. The X-ray diffraction analysis of the other alloy compositions treated in the same way did not give such clear results.

The variation of the heat capacity (referred to the value at 450 K) as a function of temperature in the glass transition region for the samples of the three compositions given is presented in Fig. 6. It is apparent that the glass transition temperature increases with the germanium content. At the glass transition, the heat capacity jump, ΔC_p, ranges from 8.5 (for low germanium content) to 21.3 J(g.at)$^{-1}$ (for high germanium content). Apart from this jump, alloys 1 and 3 show an endothermic peak at the end of glass transition. Similar values were obtained for other chalcogenide systems (see Table II). It would be interesting to study the viscosity of Ge–Sb–S melts in order to see if such large values of C_p at the glass transition temperature are accompanied by a corresponding non-Arrhenius behaviour of the viscosity in the vicinity of T with $T_g/T = 0.5$ [11].

The results of thermal cycles performed on an initially as-quenched $Ge_{30}Sb_{10}S_{60}$ glass are presented in Fig. 7. Curve a gives the C_p values obtained in the

TABLE II Heat capacity jump at the glass transition of some chalcogenide glasses

Glass	ΔC_p(J(g.at)$^{-1}$K^{-1})
$Ge_{10}Sb_{15}Se_{75}$	14.2 [16]
$Ge_{20}Sb_{10}Se_{70}$	8.8 [16]
$Ge_{28}Sb_{15}S_{57}$	18.8 [16]
$Ge_{10}Sb_{20}S_{70}$	8.6
$Ge_{20}Sb_{10}S_{70}$	9.7
$Ge_{30}Sb_{10}S_{60}$	21.3
$(GeSe_2)_{70}(GeTe)_{15}(Sb_2Te_3)_{15}$	15.0 [7]
$(GeSe_2)_{76}(Sb_2Te_3)_{24}$	16.3 [12]

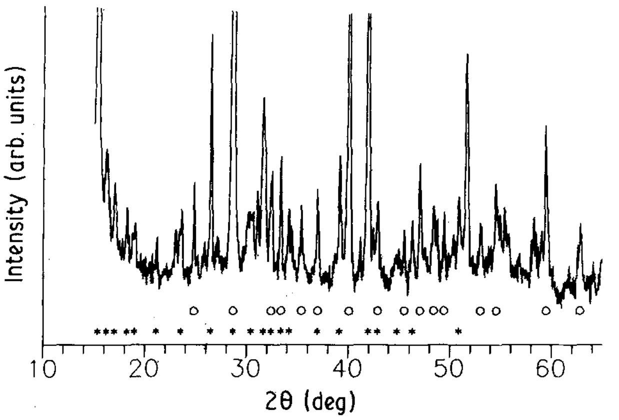

Figure 5 X-ray diffraction patterns of the $Ge_{30}Sb_{10}S_{60}$ (3) glassy alloy thermally treated at 720 K for 10 h. (*) GeS_2, (○) Sb_2S_3.

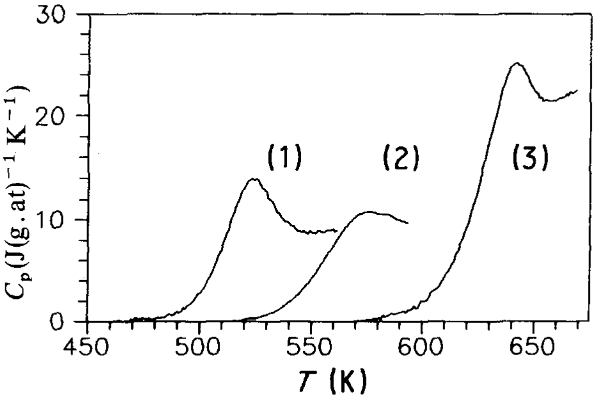

Figure 6 The composition dependence of the heat capacity in the glass transition region for the glassy alloy $Ge_{10}Sb_{20}S_{70}$ (1), $Ge_{20}Sb_{10}S_{70}$ (2) and $Ge_{30}Sb_{10}S_{60}$ (3), heating rate 20 K min^{-1}.

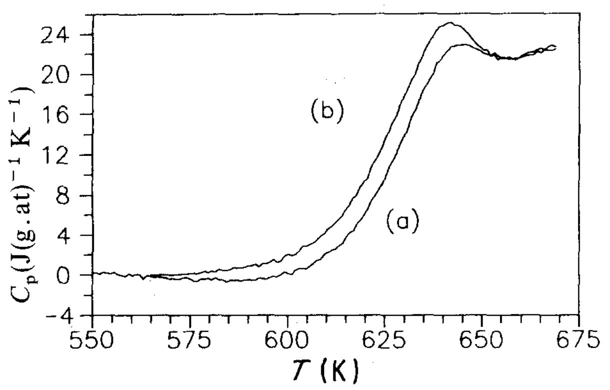

Figure 7 Heat capacity plotted against temperature for the as-quenched glass $Ge_{30}Sb_{10}S_{60}$ (3) at the heating rate 20 K min^{-1} (curve a) cycled by cooling below the glass transition and heating at the same rate (curve b).

heating of the as-quenched glass from room temperature to 660 K. After cooling to room temperature, curve b represents the second heating from room temperature to 660 K (heat-treated glass). Further cycling of the same sample by cooling and heating between 550 and 660 K gives heating results identical to curve b [12].

To analyse the influence on C_p of the thermal treatment on $Ge_{30}Sb_{10}S_{60}$ heat-treated glass, isothermal anneals of several hours were performed at temperatures inside the glass transition range. Once the isothermal treatment was finished the sample was quickly cooled to 550 K and its heat capacity measured in the temperature interval 550 to 660 K, with a heating rate of 20 K/min^{-1}. Instead of obtaining only a rapid change of C_p at the glass transition, there was also an increased endothermic effect which appeared as a peak in the excess C_p curve. The excess heat capacity curve obtained when annealing at 595 K for 17 hours is shown in Fig. 8. The area under the curve represents the relaxation enthalpy [13] and a value of $\Delta H_r = 2.7$ meV was obtained for the above anneal and may be due to small rearrangements of the atoms in the disordered network. In other chalcogenide glasses it has been shown that structural relaxation occurs over a wide temperature range and therefore consists of a large number of atomic processes, so that the whole phenomenon is ruled by a spectrum of activation energies [8].

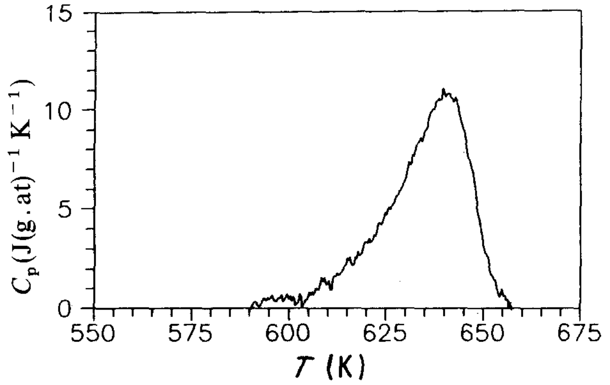

Figure 8 Excess heat capacity after annealing the glass $Ge_{30}Sb_{10}S_{60}$ (3) at 595 K for 17 h. Heating rate 20 K min^{-1}.

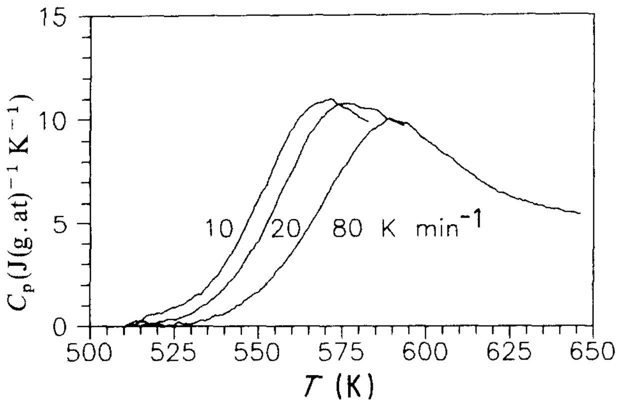

Figure 9 Heat capacity plotted against temperature for the $Ge_{20}Sb_{10}S_{70}$ (2) as-quenched glass subjected to different heating rates.

Fig. 9 shows the observed jump of C_p at the glass transition for alloy 2 and how it depends on the heating rate used for its measurement. All the curves were obtained for an initially as-quenched sample, heated through the glass transition region. Each curve corresponds to a particular heating rate. As expected, the glass transition temperature shifts to higher temperatures with increasing heating rates. The increase in T_g is nearly linear with logarithm of the heating rate. Moynihan *et al.* [3] have attempted to determine an activation enthalpy, Δh, of the internal relaxation time from the variation of T_g with the heating rate. Using the Equation 6 from [6] for the evaluation of this activation energy, Δh, that is

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

for the different heating rates β, Δh could be evaluated. The slope of the least squares fit yields a value for Δh equal to 3.9 eV. The value of Δh obtained is of the same order of magnitude as that of the activation enthalpy for shear viscosity found in similar chalcogenide glasses [17].

4. Conclusions

Some experimental determinations of the thermal behaviour of samples of the Ge–Sb–S system of nominal composition $Ge_{10}Sb_{20}S_{70}$, $Ge_{20}Sb_{10}S_{70}$ and $Ge_{30}Sb_{10}S_{60}$ have been performed. We have analysed the behaviour of the heat capacity in the glass transition region for the glassy alloys obtained by water-quenching and also subjected to several thermal treatments.

Cycled heat capacity measurements around these glass transitions demonstrate that the glass transition temperature increases with heating rate and decreases for slowly cooled glasses, but neither the value of C_p for the glass nor its jump, ΔC_p, at the glass transition varies. From the dependence of the glass transition temperature with heating rate, an average value for the activation energy for the internal relaxation time of 3.9 eV was obtained for the $Ge_{20}Sb_{10}S_{70}$ alloy glass.

The endothermic peak of the heat capacity observed on heating a glass heat-treated or after annealing at a temperature near and below that of the glass transition is assumed to account for the relaxation towards structures characterized by increasing stability compared to the initial state. The relaxation enthalpy associated with this endothermic peak referred to the as-quenched glass has been measured for an alloy of nominal composition $Ge_{30}Sb_{10}S_{60}$ once annealed at 595 K for 17 h. The value of $\Delta H_r = 2.7$ meV suggests that only small atomic rearrangements occur during relaxation.

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