Thermochimica Acta, 85 (1985) 175–178
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

THERMODYNAMIC AND KINETIC CHARACTERIZATION OF VITREOUS EUTECTIC $GeSe_2$-Sb_2Te_3 ALLOY*

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ABSTRACT

For the vitreous alloy of quasi-binary $GeSe_2$-Sb_2Te_3 eutectic composition heat capacities have been measured using differential scanning calorimetry. Enthalpy entropy and Gibbs free energy differences of vitreous and crystalline forms have been deduced and combined with the crystallization kinetic parameters in order to obtain a complete description of this glass.

INTRODUCTION

The phase diagram and glass forming ability of the $GeSe_2$-Sb_2Te_3 system have been reported earlier (ref. 1,2). The eutectic composition and temperature are, respectively, 24 mol% Sb_2Te_3 and 758±3K. The glass forming region extends from 5 to 30 mol% Sb_2Te_3.

In this paper we report on the determination of heat capacity around the glass transition of a chalcogenide glass of nominal composition $(GeSe_2)_{76}$ $(Sb_2Te_3)_{24}$ and the investigation of the residual values of thermodynamic quantities with respect to the stable state. The results are correlated to kinetic and morphological studies.

EXPERIMENTAL

Glassy samples were prepared by room temperature water quenching of the molten alloys. The thermal behaviour was investigated using a Perkin-Elmer DSC-2 coupled with a data acquisition system. We followed the normal procedure of calibrating measured temperature and energy values.

RESULTS

The DSC traces show the glass transition and two well-defined, through overlapped, exothermic crystallization peaks. In fig.1 the heat capacities are plot-

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* Work sponsored by Universitat de Barcelona (Ajut Investigació 1983).

0040-6031/85/$03.30

ted versus temperature for a glass heated (→), cooled (←) and then reheated (↠) through the glass transition region and for the crystalline phases, at a rate of 20 K min^{-1}. The points represent some of the data obtained by numerical treatment of a typical run and the bar the error for runs on different samples. As seen here a glass obtained by slow cooling has a smaller glass transition temperature T_g than the as-quenched one. Allowing for the kinetic nature of glass transition there is also an increase of T_g with heating rate. This fact is illustrated in fig.2 where are presented the results obtained for both as-quenched and slowly cooled glasses, at different scanning rates. Below T_g the C_p values agree with the classical limit of 3R. The change of C_p at the glass transition, ΔC_p, is 16.3 J $K^{-1}mol^{-1}$, a typical value in many chalcogenide systems (see table 1).

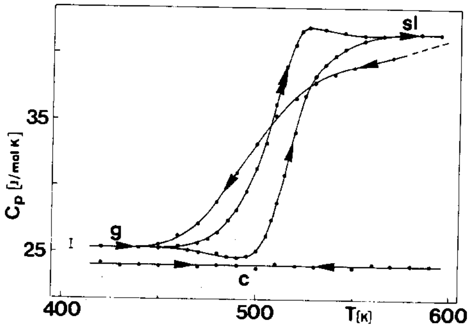

Fig. 1. Heat capacity versus temperature for glassy (g), supercooled liquid (sl) and crystalline (c) phases.

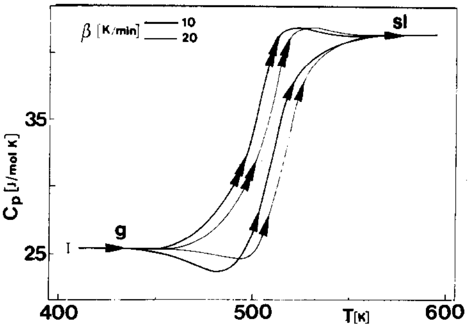

Fig. 2. Heat capacity curves in the glass transition region as a function of scan rate.

From heat capacity determination enthalpy and entropy values for glass, supercooled liquid and crystalline phases have been calculated relative to the standard state (crystalline phase at 298 K). Figure 3 shows the entropy changes of as-prepared glasses during heating (path: A→B→C), cooling (C→D→E), and reheating (E→D→C) at a scan rate of 10K min^{-1}.The temperature T_0 at which the entropy difference between the liquid and the crystalline phase vanishes defines, according to Kauzmann (ref. 7), the lower limit for the temperature of glass transition. Furthermore T_g would approach T_0 in the limit of low cooling or heating rates. We obtain T_0 = 457 K, T_g (as-quenched glass)= T_1 = 522 K while T_g (after cooling and reheating at 10K min^{-1})= T_2= 492 K. That is, extrapolating the liquid state through the glass transition region, the calculated T_0 reproduces the trends of the experimentally determined T_g values (T_1 and T_2). The residual entropy (at 298 K) of the as-quenched glass with respect to the crystalline sample is 2.0 J $mol^{-1}K^{-1}$. This value is much smaller than those obtained for

TABLE 1.

Heat capacity change at the glass transition and residual entropy of some glasses

Glass	As_2S_3	As_2Se_3	As_2Te_3	Se	P_4Se_4	$Ge_{25}Sb_{15}Se_{60}$	our Sample
ΔC_p(J g·at^{-1}K^{-1})	13.0[a]	14.6[a]	-	-	-	15.9[b]	16.3
ΔS^{res}(J g·at^{-1}K^{-1})	6.9[c] 7.0[d]	5.8[c] 8.5[d]	5.8[d]	7.2[d]	2.8[c]	-	2.0

a: from ref. 3; b: from ref. 4; c: from ref. 5; d: from ref. 6

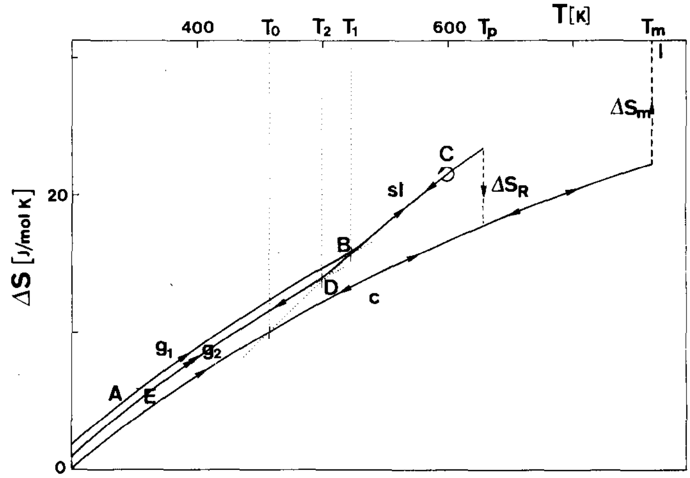

Fig. 3. Plot of entropy versus temperature for glasses (g_1,g_2), supercooled liquid (sl), crystalline (c) and liquid (l) phases. ΔS_R(ΔS_m) is the crystallization (melting) entropy at temperature T_p (T_m).

other chalcogenide glasses (see table 1). Furthermore, the residual entropy of the slowly cooled glass is about one half of that of the as-quenched one. These results further suggest that both glasses deviate little from the state of an ideal glass.

The heat capacity measurements allow also for the determination of the Gibbs free energy difference, ΔG, between supercooled liquid and crystalline solid. Curve 1 of fig. 4 shows the value of ΔG obtained from experimental results. Curve 3 gives the plot obtained using Turnbull (ref. 8) formula $\Delta G = \Delta S_m(T_m-T)$. A best fit is obtained with Hoffmann (ref. 9) equation (curve 2) which assumes that ΔG is T/T_m times Turnbull's value. This result supports the existence of associations in the supercooled liquid. The Gibbs free energy difference between the supercooled liquid and the crystalline phases at the onset of crystallization is ΔG_c = 1.2 kJ mol^{-1}. From simple nucleation theory (ref. 10) the activation energy for nucleation is then expected to be $E_N \sim (T_m \Delta S_m)^3/(\Delta G_c)^2 \sim 218$ kJ mol^{-1}. The crystallization process occurs in two well-defined, through overlapped peaks. The peak method (ref. 11) has been used to obtain the apparent activation energies. The values deduced are 150±5 and 230±7 kJ mol^{-1}, respectively, for the first and second peak. Although the preceding calculation of E_N is an approximate one it accounts for the values obtained for the apparent activation energies. Optical microscopic examinations show that nuclei grow in spherulitic form in the bulk. A surface nucleation density of 3 x $10^8 m^{-2}$ was observed for as-quenched glasses heated just to the onset of crystallization.

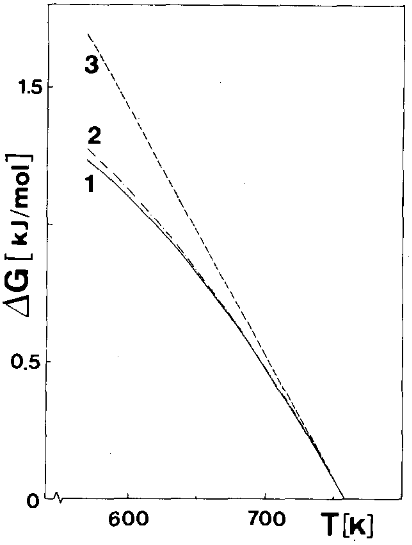

Fig. 4. Measured and estimated temperature dependence of the Gibbs free energy difference between liquid and crystalline phases.

CONCLUSIONS

Cycled heat capacity measurements around the glass transition demonstrate a "hysteresis-like" behaviour of the eutectic $GeSe_2$-Sb_2Te_3 vitreous alloy. 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 change ΔC_p at the glass transition vary. The decrease of residual entropy further evidences the thermal relaxation of the glass towards a more stable state. The Gibbs free energy difference between supercooled liquid and crystalline phases at the onset of crystallization accounts for the effective activation energy of crystallization obtained.

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