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GLASS FORMATION AND CRYSTALLIZATION IN THE $GeSe_2$-GeTe-Sb_2Te_3 SYSTEM

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ABSTRACT

The glass formation and crystallization of water-quenched $GeSe_2$-GeTe-Sb_2Te_3 molten alloys was investigated by means of differential scanning calorimetry and X-ray diffraction. The glass forming region for a cooling rate of the order of 10^3 K/min was deduced. The effective activation energy of the crystallization process was obtained. All the results were analysed in the light of the current empirical parameters that characterize glass formation. It is concluded that the best glass formers in that system are compositions of the type $(GeSe_2)_{73}(GeTe)_{15}Sb_2Te_3)_{12}$.

INTRODUCTION

As there is no absolute criterium for glass formation, empirical parameters are extensively used for quantitative characterization of the glass forming ability of molten alloys. Some parameters are related to the equilibrium phase diagram. One of them is the reduced glass temperature, $T_{g1}=T_g/T_1$, where T_g and T_1 are respectively the glass transition and the liquidus temperature. T_{g1} takes a value of about 2/3 for a large number of glassy substances [1]. Another parameter, introduced by Hruby [2] is K_{g1} defined as

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$K_{gl}=(T_r-T_g)/(T_l-T_r)$ where T_r is the temperature of the onset of the first crystallization peak. Good glass formers would, according to Hruby, have high K_{gl} values. Other parameters are fundamentally kinetic, as for instance the change in free energy in the crystallization of the liquid introduced by Turnbull [3] and subsequently developed by Uhlmann [4]. Another kinetic empirical parameter to give a measure of the glass forming ability was defined [5] as

$$\bar{A} = k_0 \exp(-E/RT_g)$$

where E is the effective activation energy of crystallization and k_0 the pre-exponential factor of the rate constant (assumed to have an Arrhenius form). Low values of $\bar{A}$ or $\ln(\bar{A})$ will be indicative of glass-forming ability. Other parameters are structural and deal with atomic geometrical arrangement, bonding and atomic size effects.

In this paper we present the results related to the glass formation and crystallization behaviour of $(GeSe_2)_{100-x-y}(GeTe)_y(Sb_2Te_3)_x$ molten alloys. The temperatures of the structural transformations characteristic of the glassy state and the effective activation energies of crystallization have been derived from differential scanning calorimetry (DSC).

EXPERIMENTAL RESULTS AND DISCUSSION

Details on the preparation of the glasses and the calorimetric procedure were given elsewhere [5]. The glassy state of the water-quenched samples (estimated cooling rate at 800 K of 10^3 K/min) was checked by X-ray diffraction. The glass forming region obtained by water quenching shown in Fig. 1 is roughly limited by the congruently melting compound $GeSe_2$ and the equicomposition lines of 48 mol % GeSe and 30 mol % Sb_2Te_3. Also shown in this figure is the experimentally determined eutectic valley connecting the binary eutectics of the systems $GeSe_2$-GeTe and $GeSe_2$-Sb_2Te_3.

There is certainly a relationship between the glass forming region and the microscopic arrangement of atoms. In the Ge-Sb-Se-Te system it is likely that some specific molecular structural units exist. The most significant of them, as deduced from radial distribution studies and spectroscopic analysis in the binaries, may be $GeSe_{4/2}$, $GeSe_{3/2}$, Sb_2Te_3 and, to a lesser extent, GeSe, $GeTe_{4/2}$ and $Sb_2Se_{4/2}$. Using these molecular units as the precursors of a fully cross-linked random glassy network we can guest the resulting glass forming compositions in the $GeSe_2$-GeTe-Sb_2Te_3 quasi-ternary section of the quaternary system. It is represented in Fig. 1 by the region inside the dashed lines and the limits of the composition triangle.

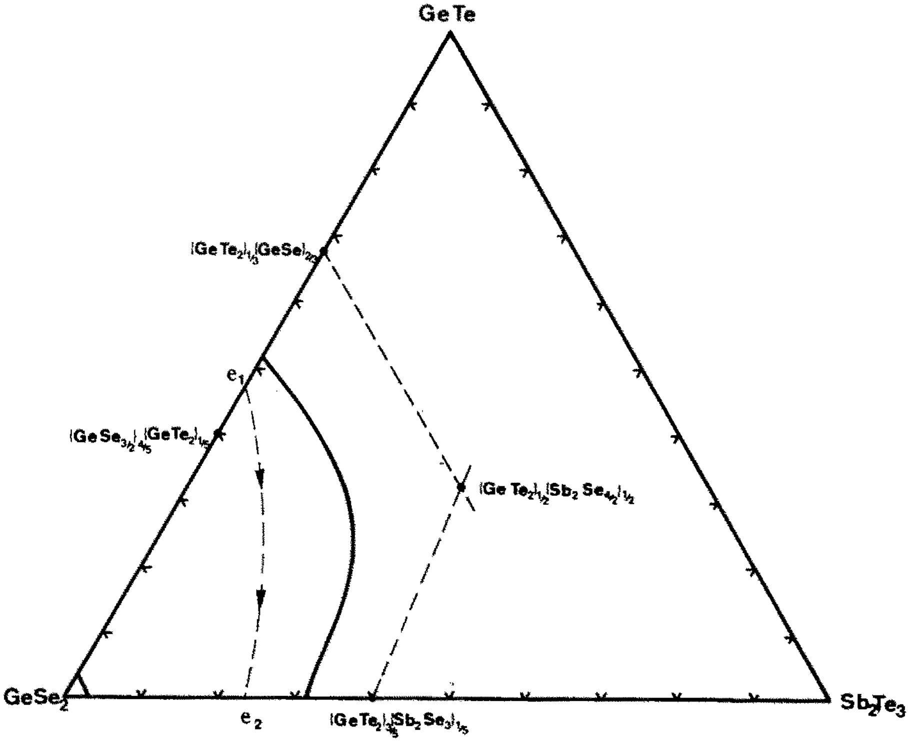

Figure 1 .- Glass forming region for $(GeSe_2)_{100-x-y}(GeTe)_y(Sb_2Te_3)$ alloys : (---) predicted by structural units , (——) obtained by quenching the melt in water . (--->) eutectic line .

The general conclusion on comparing this "theoretical" glass forming region with the experimental one, is that the aforementioned molecular units are probably present in the glasses studied.

To get an estimate of the glass forming ability we present in Table 1 the values of the temperatures of the glass transition and onset of crystallization, the reduced glass temperature and the K_{gl} parameter. The detailed study of the crystallization kinetics of most of the glasses was hindered because of the overlapping of the crystallization exotherms. However the peak method [6] has been used to obtain the effective activation energy, E, and to estimate the value of $\ln(k_{\theta})$ [5].

Therefore, the value of the parameter $\bar{A}$, was also estimated for each glass. The values obtained for $-\ln(\bar{A})$ are also shown in Table 1. Careful analysis of Table 1 allows to conclude that the best glass formers in the system, inside the glass forming region for a cooling rate of about 10^3 K/min, are those alloys with a composition of 15±5 mol % GeTe and 12±5 mol % Sb_2Te_3.

CONCLUSIONS

The glass formation and thermal behaviour on crystallization of water-quenched molten alloys of the quasi-ternary $GeSe_2$-GeTe-Sb_2Te_3 system have been analysed. First of all the glass-forming region for quenching in water was obtained. Then, the characteristic temperatures and effective activation energy for crystallization of the glasses were determined by DSC on continuous heating regime. From the values of these quantities the glass-forming ability of the $GeSe_2$ rich alloys of the quasi-ternary system was studied through the use of some thermal and kinetic parameters. The best glass formers of the system as deduced from the values of the K_{gl} parameter coincide with those deduced from the values of the $\bar{A}$

Table 1 .- Temperatures of structural transformations and kinetic parameters for glassy $(GeSe_2)_{100-x-y}(GeTe)_y(Sb_2Te_3)_x$ samples Glass transition (T_g)* and crystallization temperatures (T_r)*; effective activation energy of crystallization (E);reduced glass temperatures (T_{g1})* ; Hruby parameter (K_{g1})* and reduced parameter $\bar{A}$. (* Heating rate 20 K/min).

composition		temperatures (K)		activation energy	glass forming parameters		
x	y	T_g	T_r	E(kJ/g.at)	T_{g1}	K_{g1}	$-\log[\bar{A}]$ $\bar{A}$ in (s^{-1})
0	0	667	777		.656	.460	
5	0	613	725		.639	.477	
10	0	563	685	136	.628	.578	4.875
15	0	536	652		.648	.663	
20	0	526	630	148	.658	.612	5.176
24	0	501	593		.651	.520	
25	0	497	587	152	.639	.471	5.115
30	0	480	545	158	.608	.265	4.172
0	10	650	746	210	.659	.398	4.528
0	15	642	764	226			4.801
0	20	637	734	207	.692	.522	4.699
0	30	617	725	233	.690	.639	5.326
0	35	608	722		.694	.740	
0	40	595	710	240	.706	.865	6.024
0	45	585	686		.721	.808	
0	47	581	674		.733	.782	
0	50	579	652	270	.704	.427	5.306
5	15	572	701	163			5.334
10	10	552	683	171	.634	.701	5.644
10	15	547	682	211	.665	.957	6.471
10	20	542	680	176	.667	1.038	5.868
10	30	536	645	206	.693	.845	6.460
10	40	527	605	250	.633	.342	5.971
15	15	518	652	210	.653	.950	7.066
20	10	507	610	168	.659	.648	5.155
20	15	510	603	167	.638	.472	4.953
20	20	515	578	175	.640	.278	4.339
20	30	497	552	223	.605	.204	4.356
25	15	485	548	221	.600	.242	4.826
30	10	485	531	187	.594	.161	3.314

parameter. These best glass formers have a composition in the nearby of 15 mol % GeTe and 12 mol % Sb_2Te_3.

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