GLASS TRANSITION BEHAVIOR IN Se-RICH Ge-Se ALLOYS

J. Saurina[1]*, M. T. Mora*[2] *and N. Clavaguera*[3]

[1]Departamento Enginycria Industrial, Universitat de Girona, E-17071 Girona
[2]Grup de Física de Materials I, Universitat Autònoma de Barcelona, E-08193-Bellaterra
[3]Departamento ECM, Facultade Física, Universitat de Barcelona, E-08028-Barcelona, Spain

Abstract

Differential scanning calorimetry (DSC) was utilized to study the behavior of six Ge–Se glasses containing 0, 5, 10, 15, 17.5 and 20 at.% Ge during the glass transition. These alloys readily form glasses and can be prepared by quenching in air. Moreover, their behavior depends greatly on the composition. This work reveals that two additional properties must be considered: the variation in the glass transition temperature and different structural relaxation. The quantity used to quantify the relaxation was the enthalpy relaxation as this measures the heat lost by the glass during annealing. Given the complexity of the relaxation process, the experimental results were analysed by means of the empirical Kohlrausch-Williams-Watts relaxation model.

Keywords: alloys, glass transition, Se-rich Ge–Se alloys

Introduction

A liquid which has been undercooled to a temperature between the melting point and the glass transition is (except for very viscous liquids) in a metastable state of equilibrium. This state is the undercooled liquid state. At temperatures low enough below the glass transition, molecular movements are completely frozen. In this case, the glass is regarded as being in a metastable state. Since freezing is a gradual process, the glassy state finally reached depends on the cooling conditions in relation to the relaxational properties of the liquid. Our glassy samples are very stable against crystallization [1]. The $Ge_{10}Se_{90}$ glass can not be crystallized even after prolonged heat treatment at any temperature. The others samples undergo partial crystallization after heat treatment at temperatures above 600 K, but they can readily be observed in the undercooled liquid state [2]. The DSC technique allows convenient glass transition in many glasses. The reason is the high heat capacity C_p of the glass. In the short temperature interval in which the transition from glass to undercooled liquid occurs, the glass temperature climbs to a staggering value of even twice the initial one. No definitive the-

ory explaining the glass transition has been formulated so far. This may possibly be because the phenomenon may be due to both thermodynamic and kinetic effects. Beyond the glass transition temperature T_g, the undercooled liquid can attain any possible phase space thermodynamic configuration, whereas under T_g, the system is kinetically trapped in a configuration corresponding to a minimum of the potential energy. This implies that the existence of relatively high thermal potential energy barriers should be intrinsic to the glass state. Such a context allows the glass relaxation to take other configurations, which are more energetically favorable. In the alloys of our system, due to the low temperature of the Se component glass transition (T_g~326 K), the time elapsed between the quenching and analysis of the samples becomes the dominant factor in the study of structural relaxation. The significance of structural relaxation for a given sample is intimately linked to the size of the endothermic peak in the glass transition region temperature interval. Thus, it may be stated that the more energetic the peak is, the more relaxed is the studied sample.

Experimental procedure

Bulk glasses were obtained by the melt-quenching technique. Weighed amounts of elemental Ge and Se (5N purity) were sealed in fused quartz ampoules initially evacuated to 10^{-1} Torr. Each molten alloy was kept at a temperature of 1270 K for 20 h and constantly agitated to ensure homogeneity. Next, they were quenched in air. The slowly cooled glasses were prepared directly in the DSC from the initial melt-quenched glasses. First, they were heated up to the undercooled liquid state and next cooled at 20 K min^{-1} to 270 K. The glassy nature of the samples was confirmed by X-ray diffraction. The calorimetric experiments were performed in a Perkin-Elmer DSC 2 apparatus on about 10 mg of material under a dynamic argon atmosphere. The error in the heat capacity measurement was calibrated 20% with a synthetic sapphire standard. The accuracy of the temperature measurements was within 0.5 K.

Results

Glass transition

Samples which, after quenching in air, were kept at air temperature for a certain time before analysis are considered 'as-quenched'. To check the thermal treatment of the samples in a precise way, the structural relaxation effect due to air temperature annealing must be nullified. Consequently, the thermal history of the samples is eliminated by heating them with the DSC at 20 K min^{-1} until the endothermic peak associated with the structural relaxation has been completed. Next, the sample is cooled at 20 K min^{-1} until the initial temperature is reached.

We consider the other samples 'as-prepared'. Table 1 depicts the maximum temperature applied to the different alloys to eliminate their thermal history. Study of the DSC curves for 'as-quenched' temperatures will be useful to evaluate the influence of the preparation method on the glass transition, to establish whether crystallization occurs, and finally to know the structural changes in the samples during heating at 20 K min^{-1}. For each composition, the temperature interval within which the thermal capacity is measured ranges from 270 K to the temperatures provided in Table 1. Table 2 depicts, for each composition, the initial temperatures of the glass transition, T_g, for 'as-quenched' and 'as-prepared' samples. The values in Table 2 tell us that, whenever studied, the glass transition temperatures of 'as-quenched' samples shift towards greater valus than those of 'as-prepared' samples. Moreover, T_g increases in 'as-quenched' and 'as-prepared' samples as for Ge, except for the sample $Ge_{20}Se_{80}$. To depict the different behavior of the samples analysed, Fig. 1 records variations in thermal capacity of 'as-prepared' samples for every composition taken (from the total absence of Ge to 20% Ge) during the glass transition. These results are in agreement with those already published [4].

Table 1 Maximum temperature applied to different alloys to eliminate their thermal history

Sample	T/K
Ge_0Se_{100}	370
Ge_5Se_{95}	390
$Ge_{10}Se_{90}$	420
$Ge_{15}Se_{85}$	435
$Ge_{17.5}Se_{82.5}$	460
$Ge_{20}Se_{80}$	470

Table 2 Initial temperatures of glass transition, T_g, for 'as-quenched' and 'as-prepared' samples

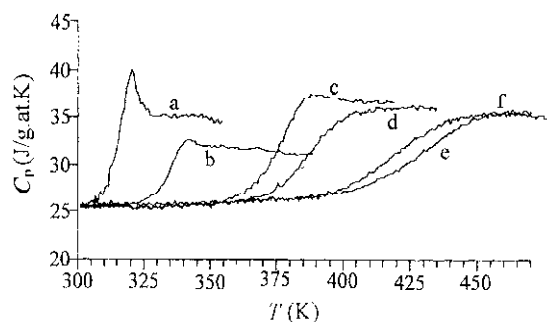| Sample	T_g/K	
	'As-quenched'	'As-prepared'
Ge_0Se_{100}	326	311
Ge_5Se_{95}	360	330
$Ge_{10}Se_{90}$	387	365
$Ge_{15}Se_{85}$	395	372
$Ge_{17.5}Se_{82.5}$	407	397
$Ge_{20}Se_{80}$	398	393

Fig. 1 Influence of Ge composition on glass transition for different 'as-prepared' alloys in the system Ge–Se. (a) 0% at. Ge, (b) 5% at. Ge, (c) 10% at. Ge, (d) 15% at. Ge, (e) 17.5% at. Ge, (f) 20% at. Ge

Structural relaxation

To study the recovery, the excess heat capacity induced by annealing was measured as the difference between the apparent heat capacity of the annealed glass and its true heat capacity. Isothermal and isochronal anneals were performed. Once the isothermal or isochronal experiment was finished. the sample was quickly brought to the beginning of the glass transition and its heat capacity was measured from there to the undercooled liquid state. The excess heat capacity is independent of the heating rate used to measure it [3]. The apparent heat capacity measured at a heating rate of 20 K min^{-1} for the sample $Ge_{10}Se_{90}$ at 323 K is shown in Fig. 2. The relaxation enthalpy, ΔH_r, is the area under the curve of the excess heat capacity versus temperature. It is equal to the enthalpy which was released by the sample during the annealing and which has to be re-absorbed by the sample to reach the undercooled liquid state. The relaxation enthalpy is independent of the heating rate [3], but depends on time and temperature [1]. Table 3 present the value of ΔH_r for the different annealing temperatures of the samples Ge_0Se_{100} and Ge_5Se_{95}.

Discussion

The first conclusion is that these materials form glasses easily since they can be prepared by quenching in air. Nevertheless, their behavior is dependent on various of their properties, and a deeper study shows that two different aspects must be taken into account: i) the glass transition temperature variation, and ii) different structural relaxation. As concerns the glass transition temperature, Table 2 shows that the beginning of the glass transition usually increases as a function of the presence of Ge. Two types of arguments can be evoked to justify such a variation. The first is macroscopic, originally thermodynamic, and refers to the
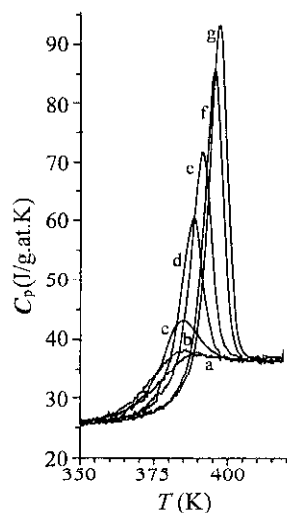
Fig. 2 Evolution of thermal capacity *vs.* temperature for $Ge_{10}Se_{90}$, after annealing at 323 K
during: a, 0 h; b, 1 h; c, 6 h; d, 48 h; e, 168 h; f, 744 h; g, 1344 h

liquid temperature variation depending on composition. An analysis of the
Ge–Se system phase diagram reveals that the temperature of the liquid ranges
from 217°C for the eutectic rich in Se to 740°C for the stoichiometric composi-
tion $GeSe_2$. Bearing in mind that glass is fundamentally a frozen liquid, it is not
surprising that the glass transition temperature behaves analogously to liquid
temperature, as happens for many glasses. Moreover, the transition of 'as-
quenched' samples begins later than that of 'as-prepared' ones. This may be due
to the cooling rate to obtain the glass, which is lower for 'as-prepared' samples
than for 'as-quenched' ones. The shift in temperature would then only show that
the lower the cooling rate, the lower the glass transition temperature will be. The
zone of undercooled liquid hence spreads towards lower temperatures. A second
type of argument to justify the general trend of the glass transition temperature
to increase has a microscopic origin. The structure of Ge–Se glasses is of a cova-
lent type and the coordination numbers for Se and Ge are respectively 2 and 4.
The structure is identical in the short scope to that displayed by the two elements
in the crystalline phase and also to that which the crystalline compound $GeSe_2$
exhibits. Consequently, pure Se in a glass state would be formed by microscopic
fibers obtained by putting Se atoms one after another. In the crystalline state,
these fibers also appear, but they are then well ordered and form a hexagonal
structure. Another possibility is that fibers close on themselves, forming rings.
The allotropic monoclinic variety of Se is built up on the basis of rings formed by
eight Se atoms each.

Table 3 Values of ΔH_r for different annealing temperatures of samples Ge_0Se_{100} and Ge_5Se_{95}

Ge_0Se_{100}	T=285 K	T=295 K	T=305 K
t/h	ΔH_r/J g^{-1}at	ΔH_r/J g^{-1}at	ΔH_r/J g^{-1}at
0	0	0	0
0.25	–	41	46
0.5	17	53	62
1	25	69	79
3	48	117	82
4	53	–	–
5	–	144	–
6	68	149	86
8	80	153	–
15	113	–	–
22	121	–	–

Ge_5Se_{95}	T=305 K	T=315 K
t/h	ΔH_r/J g^{-1}at	ΔH_r/J g^{-1}at
0	0	0
0.25	–	26
0.5	13	42
1	22	63
3	58	99
6	78	142
8	93	154
12	123	–
16	–	165
24	190	–
48	204	–

Let us again consider glass, but now not pure Se, but glass containing Ge atoms. The coordination number of these atoms is 4, and the fibers therefore join at a common point where the Ge atom is located. This implies that, as the amount of Ge increases, the network of intercrossing fibers becomes denser. Therefore, the resulting crystalline solid is more rigid. That is why the glass transition temperature, which somehow measures the glass network rigidity, increases as the amount of Ge does.

There is an exception to this general behavior of the glass transition temperature depending on composition. As we have seen in the experimental results, the

glassy alloy $Ge_{17.5}Se_{82.5}$ has a glass transition temperature higher than that of the alloy $Ge_{20}Se_{80}$ (Table 2 and Fig. 1). To explain this exception, one may consider two hypothesis: a) $Ge_{17.5}Se_{82.5}$ has a glass transition higher than normal, b) $Ge_{20}Se_{80}$ has a glass transition lower than normal. From a microscopic structural approach, the second explanation seems more reasonable because the order of the $GeSe_4$ stoichiometrics in the short scope could be explained on a single type of structural unity, which would explain the exceptional character of this alloy. On the other hand, Phillips [5] proved that GeSe glasses containing 20% or more Ge are mechanically unstable, which indicates that there is a modification in the rigidity of the linkage which may affect the value of the glass transition temperature for the composition $Ge_{20}Se_{80}$.

Figure 1 shows that C_p for the undercooled liquid of composition Ge_5Se_{95} is lower than those of the other compositons. This fact can be related to the eutectic composition of the $GeSe_2$–Se system, close to 5% (atomic) of Ge. In short, the undercooled liquid is much more stable at room temperature for this composition.

For a description of the structural recovery processes, we use the concept of a spectrum of activation energies $p_0(E)$, which was first proposed by Primak [6] and extended by Gibbs et al. [7]. We will assume that $p_0(E)$ is proportional to the total density of processes available for relaxation for each activation energy, E. In approximate form, $p_0(E_0) = -(1/RT)[d\Delta H_r/d \ln(t)]$ where $E_0 = RT \ln(At)$ and R is the gas constant. In order to calculate the form of $p_0(E)$, the frequency factor, A, was adjusted to obtain an activation energy spectrum independent of the annealing temperature. The method used is related to the utilization of the empirical Kohlrausch-Williams-Watts (K-W-W) relationship [8]. The pertient measures to perform this analysis are those obtained in the isothermal regime. The frequency factor $A = 7 \cdot 10^{11} s^{-1}$ is obtained for the sample $Ge_{10}Se_{90}$ for Ge_5Se_{95} it is $A = 4 \cdot 10^{12} s^{-1}$ and for Ge_0Se_{100} $A = 7 \cdot 10^{12} s^{-1}$. Figure 3 shows the activation energy spectra obtained at the temperatures analysed for the sample $Ge_{10}Se_{90}$. As we expected, the spectrum of every composition (and its respective temperatures) exhibits approximately the same shape. However, the values obtained are subject to
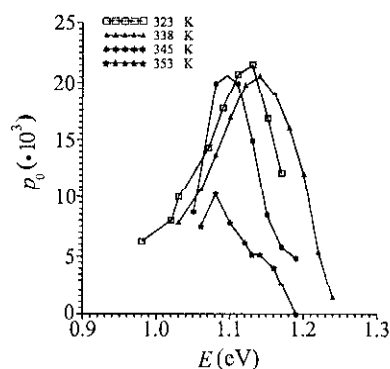

Fig. 3 Activation energy spectra for $Ge_{10}Se_{90}$ glass at different annealing temperatures

an uncertainty which is evaluated as 0.2 eV in the energy values. For the sample $Ge_{10}Se_{90}$, the interval is 1.00–1.25 eV and the peak energy is 1.14 eV. For Ge_5Se_{95}, the interval is 1.00–1.10 eV and the peak energy is 1.05 eV. For Ge_0Se_{100}, they are respectively 0.93–1.02 eV and 0.99 eV. The activation energy values agree with those obtained by the K-W-W method. The results are then hardly representative.

Conclusions

It has been shown that the true heat capacity as a function of temperature in the glass transition range can be measured for Ge_xSe_{100-x} glasses with x=0, 5, 10, 15, 17.5 and 20 by using DSC equipment. The measured T_g increases in 'as-quenched' and 'as-prepared' samples as for Ge, except for the sample $Ge_{20}Se_{80}$. The enthalpy released by the glass when annealed near the glass transition temperature, called the relaxation enthalpy, was deduced from the measurement of the apparent heat capacity of the annealed glass on heating it to the undercooled liquid state as compared to the true heat capacity of the sample in the same temperature interval.

For a description of the structural recovery processes, we use the concept of a spectrum of activation energies. As the relaxation rate increases with the annealing temperature, we conclude that structural relaxation is thermally activated. Full correspondence has been observed between the results obtained with the activation energy spectrum model and with the K-W-W model.

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