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Studies of structural relaxation and crystallization kinetics of $Se_x Te_{1-x}$ amorphous system by DTA measurements

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Differential thermal analysis studies of the binary system Se_xTe_{1-x} are reported and the phenomena accompanying the temperature-induced changes in amorphous samples are discussed. The enthalpy of crystallization of the samples is calculated from DTA measurements.

1. Introduction

Chalcogenide glasses have attracted a greal deal of attention in research because of their unusual electric properties [1–3], which are influenced by thermal effects associated with structural changes. It has been noted that in some chalcogenide systems, glasses which show no exothermic crystallization reaction above T_g are of threshold switching type. In some chalcogenide systems, glasses exhibiting an exothermic reaction above T_g show a memory type behaviour [4]. The memory effect was attributed to a reconstructive glass-to-crystal transformation [5].

The binary system Se–Te is of particular interest because the components are isomorphous and the phase diagram is very simple with total miscibility. Raman spectra measurements of vitreous Se–Te alloys near pure selenium [6] had indicated that tellurium enters co-polymer chains preferentially and tends to reduce the number of Se_8 rings.

The aim of the present contribution is to determine the nature of the thermal reactions during heating of some glassy Se–Te alloys and to relate the results to possible structural changes. The types of atomic movements certainly make a substantial contribution to the DTA curve observed. Therefore, DTA measurements may provide an understanding of the role played by structural changes in the electric behaviour of chalcogenide glasses. Moreover, it is hoped that these measurements may give some insight into the mode of return to the stable crystalline state.

2. Experimental details

The samples were prepared by melting the respective weight of the elements of high purity (99.999%) in evacuated quartz tubes (10^{-6} Torr) at 750° C for 6 h, homogenization was carried out under continuous agitation for 6 h, whereupon the resulting alloys were removed from the furnace and quenched in an ice-water bath to obtain the sample in the glassy state. Table I shows the composition of the samples prepared.

Differential thermal analysis was carried out using an automatic recording thermal analyser. A small amount of the sample was placed in an evacuated quartz ampoule, while an identical quartz ampoule was used as a reference. Measurements were carried out for each sample at different heating rates. The values obtained from DTA curves reflect the entire thermal history of the sample. The values of the crystallization peak temperature T_c are influenced by the sample heating rate, and are expected to be lower for slow heating rates than for fast ones [7].

TABLE I Composition of Se_xTe_{1-x} samples

Sample	Se_x (at %)	Te_{1-x} (at %)
Pure Se	100	0
$TeSe_{50}$	98.04	1.96
$TeSe_{20}$	95.24	4.76
$TeSe_{12.5}$	92.59	7.41
$TeSe_{10}$	90.91	9.09
$TeSe_9$	90	10
$TeSe_4$	80	20
$TeSe_{2.5}$	71.43	28.57

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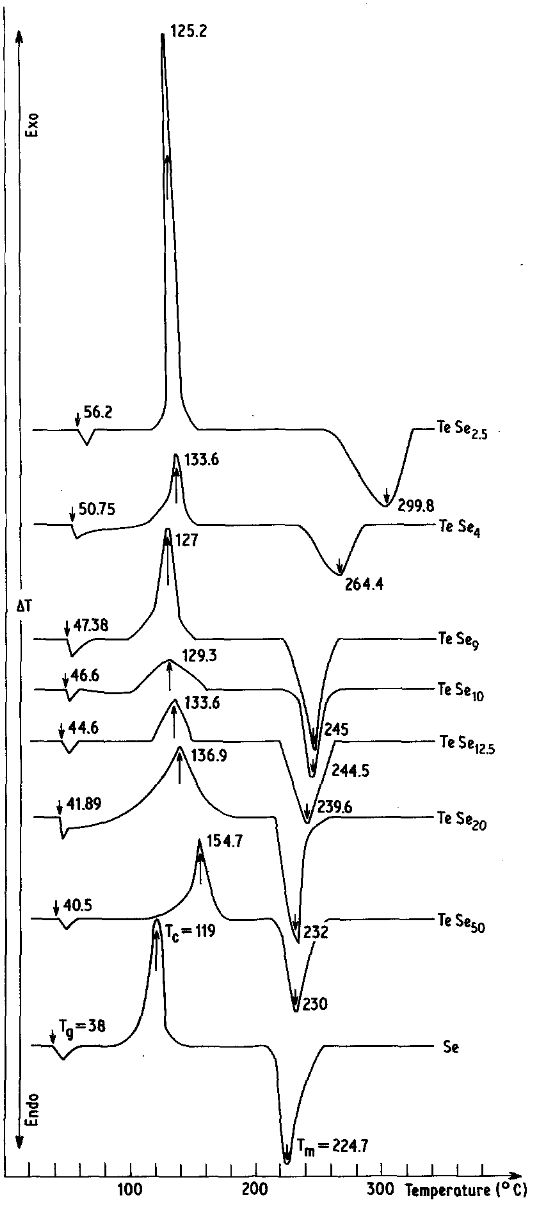

Figure 1 Differential thermal analysis thermograms for different Se_xTe_{1-x} samples at constant heating rate.

3. Results and discussion

3.1. General thermogram results

Fig. 1 shows the characteristic DTA thermograms during heating the samples at the same heating rate. The characteristic temperatures on the curves are: T_g, the glass transition temperature; T_c, the usual crystallization peak due to the exothermic reaction; and T_m, an endothermic peak temperature due to the melting of the crystalline material. T_g, T_c and T_m change markedly and become lower with slow heating rates.

The dependence of T_g, T_c, T_m and the ratio (T_g/T_m) on the tellurium content at a constant rate of heating are shown in Fig. 2. T_g and T_m increase with tellurium concentration; however, T_g increases slowly at high tellurium content. T_c has a maximum value near 1.96% Te, while it drops for higher Te concentrations. The ratio (T_g/T_m) increases rapidly for low tellurium content reaching a maximum value at 10% Te and decreases for higher concentrations.

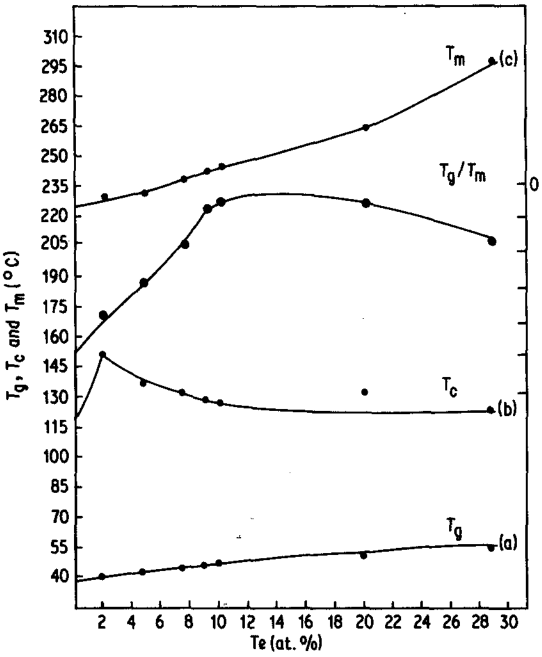

Figure 2 The dependence of the glass transition temperature (a), the crystallization peak temperature (b), the melting peak temperature (c) and the ratio T_g/T_m on tellurium concentration.

As the difference between T_g and T_m increases with tellurium concentration, the difference between T_c and T_g decreases. Since T_c depends not only on T_g but also on the equilibrium liquidus temperature and the mechanism of crystallite nucleation in a particular sample [8], one can deduce that both the nucleation rate and the growth rate of crystals in the metastable liquid phase just above T_g increase as the difference between T_g and the liquidus temperature increases, accounting qualitatively for the observed trend in T_c versus T_g. Approaching pure selenium in composition, the value of T_c drops slowly towards T_g, reflecting perhaps faster nucleation of a single component crystal as compared to an alloy crystal.

De Neufville [9] had proposed a model for the relationship between T_g, the optical gap E_g and the connectedness C, where the average connectedness for covalently bonded materials $C = 8 - N$, where N is the average number of outer electrons. According to this model, the Se–Te system ($C = 2$) should have a constant value of T_g independent of E_g. However, this result explicitly assumes that polymerization at any given composition is complete, which requires Se–Te alloys to consist of infinitely long chains. Tellurium glass appears to contain short chains [10], while selenium glass consists of a mixture of long chains and Se_8 rings [11]. Thus the variations of T_g observed with tellurium content appear to relate to the molecularity of the glass and the effect of molecularity on T_g. T_g should increase with increasing chain length and decrease with increasing ring concentration [12]. Thus, the slight increase in T_g near 28.57% Te may reflect the presence of shorter chains at higher tellurium content, while a low T_g value is indicative of more rings at higher selenium contents.

3.2. Kinetics of the crystallization process

The kinetics of crystallization of the Se–Te system can be determined from analysis of DTA data for each sample taken as a function of heating rate. A typical DTA thermogram for Te–Se_{20} sample at different heating rates is shown in Fig. 3. The method was derived by Kissinger [13] for first order rate processes. Prior studies on a-Cd–Ge–As_2 [14]. a-As_2–Se–Te_2 [15] and As_2Se_3 [16] have shown the utility of this technique for studying thermally activated crystallization phenomena. The activation enthalpy of crystallization h^* is given by

$$c \exp - \frac{h^*}{kT_c} = \frac{h^*\phi}{kT_c^2}$$

where T_c is the temperature of maximum rate and ϕ is the constant heating rate (K sec^{-1}). A plot of $\ln(h^*/T_c^2)$ versus $1/T_c$ yields a straight line from which h^* can be determined.

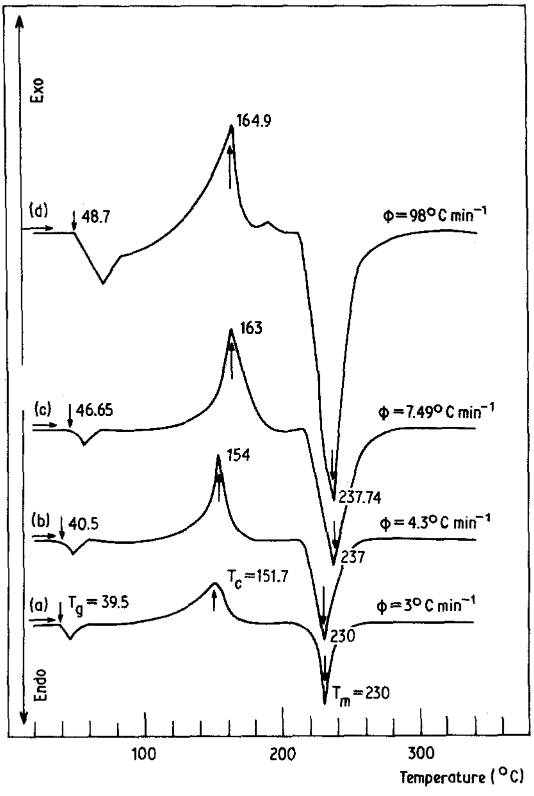

Figure 3 Diffenential thermal analysis thermograms for Te–Se_{50} sample at different heating rates.

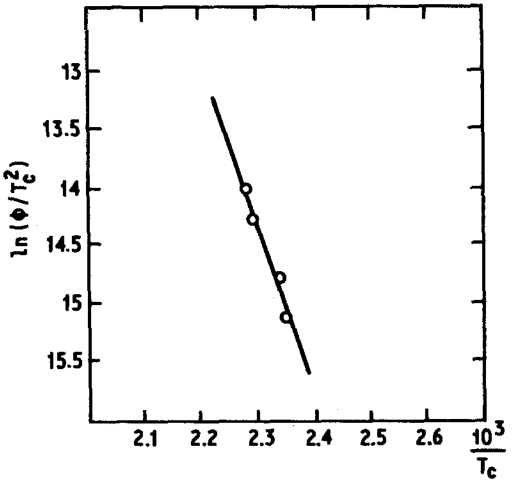

Figure 4 Plot of the crystallization data for Te–Se_{50} sample.

Crystallization data for a Te–Se_{20} sample are shown in Fig. 4. The straight line behaviour shows that the crystallization process obeys first order kinetics. This result is in accord with certain diffusion limited growth processes [17]. Fig. 5 shows the variations of the activation enthalpy of crystallization with tellurium content. The value of h^* increases near 1.96% Te, then it drops to a minimum value of 10% Te. On further increase of tellurium content, h^* increases again. The activation energy is relatively small on the selenium side. One of the reasons for the lower values of the activation energy is because Equation 1 is not always rigorous, as T_c does not necessarily correspond to the temperature of the maximum reaction rate as indicated by Reed [18]. Moreover, it was noticed that the activation energy depends on the holding temperature of the molten sample before

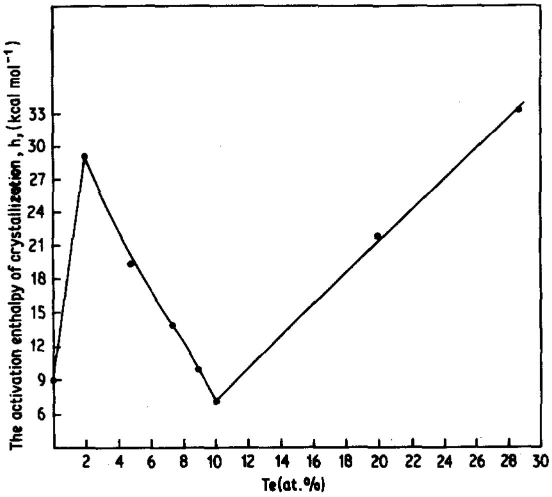

Figure 5 The dependence of the activation enthalpy of the crystallization process on the concentration of tellurium.

quenching: the lower the holding temperature the smaller the value of h^* becomes.

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