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Thermally induced transformations in $Ge_xAs_yTe_{100-x-y}$ glasses

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Chalcogenide glasses with compositions $Ge_{7.5}As_yTe_{92.5-y}$ ($y = 20, 40, 45, 47.5, 50, 52.5, 55$) and $Ge_{10}As_yTe_{90-y}$ ($y = 15, 20, 22.5, 35, 40, 45, 50$) have been prepared by the melt-quenching technique. The amorphous nature of these glasses has been confirmed by X-ray powder diffractometry. The thermal stability of these glasses has been studied using differential scanning calorimetry (DSC). The compositional dependence of the glass transition temperature, T_g, the crystallization temperatures, T_{c1} and T_{c2}, and the melting temperature, T_m, are reported. The glass-forming tendency, K_{gl}, and the activation energy of crystallization, E, are calculated. The activation energy decreases with increasing tellurium content for both sets of glasses.

1. Introduction

The switching phenomenon in chalcogenide glasses was first observed by Ovshinsky [1, 2]. Of the many glassy systems studied so far, the Ge–As–Te and Si–Ge–As–Te glasses appear to be promising for device applications. The Ge–As–Te glasses show "memory"-type switching action. These glasses can be switched from a high-resistance state to a high-conduction state by the application of an appropriate voltage, known as the threshold voltage. The voltage pulse presumably induces crystallization and a conducting filament is formed between the contacts [3, 4]. This crystalline filament can be locally melted and quenched to form glass by the application of a high current pulse with a rapidly trailing edge. Such bistable switching action in these glasses find applications in non-volatile electrically erasable programmable read only memory (EEPROM) cores [5]. The threshold voltage in memory switches is known to be dependent on the glass transition temperature [6]. Thus, the memory switching phenomenon depends on the ease of crystallization and other thermal behaviour of the glasses. After Savage [7], very little interest [4, 8–11] has been shown in investigating the physical properties of bulk Ge–As–Te glasses, although many papers have appeared on their switching behaviour. In this paper, we report the results of differential scanning calorimetry studies on two sets of Ge–As–Te glasses as part of a programme to investigate the physical properties of these technologically important glasses.

2. Experimental procedure

2.1. Glass preparation

The glass-forming region of the Ge–As–Te glasses [4, 7, 11] consists of two islands, one in the low-arsenic region and the other in the high-arsenic region. Although it has been reported [7, 11] that the two islands can be merged if high cooling rates are employed, our studies are mainly restricted to glass compositions in the larger island. The reaction tubes were made out of 8 mm i.d. fused silica tubes which were flattened to 3 mm. Appropriate amounts of high-purity (99.99%) elements were weighed (total weight being $\simeq 2$ g) and transferred into pre-cleaned fused silica tubes. The tubes were then evacuated to $< 10^{-5}$ mbar (1 mbar = 0.760 torr) and flame sealed. The ampoules were then loaded in a rotary furnace, heated to 1000 °C and rotated for 12 h at 1000 °C before quenching in a mixture of NaOH and ice–water. Glasses with compositions $Ge_{7.5}As_xTe_{92.5-x}$ ($x = 20, 40, 45, 47.5, 50, 52.5, 55$) and $Ge_{10}As_xTe_{90-x}$ ($x = 15, 20, 22.5, 35, 40, 45, 50$) have been prepared and studied.

2.2. X-ray diffraction studies

X-ray diffraction studies on powdered as-quenched glasses have been performed using a Philips PW 1140/90 X-ray powder diffractometer. CoK_α radiation ($\lambda = 0.179021$ nm) with a rating of 30 kV/20 mA was used at a fixed scan rate of $2° \text{ min}^{-1}$.

Fig. 1 shows a typical powder diffractogram where normalized intensity is plotted against twice the Bragg angle (2θ). The absence of sharp crystalline peaks in these diffractograms shows the non-crystalline nature of the samples. The three humps occurring between 2θ values of 10° and 70° appear to be the characteristic feature of these glasses.

2.3. Differential scanning calorimetry studies

The differential scanning calorimetry (DSC) studies were performed with a Stanton and Redcroft DSC 1500 system with a high-sensitivity DSC head. The experiments were done in alumina crucibles with

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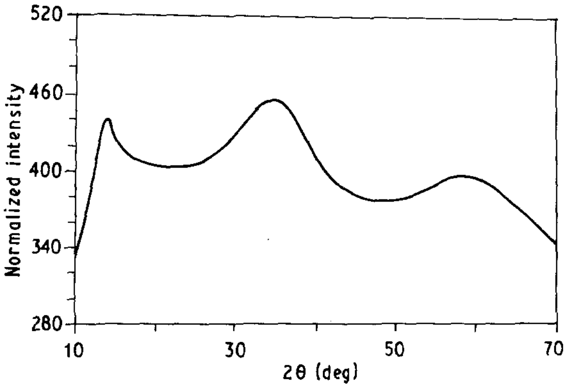

Figure 1 Typical X-ray powder diffractogram picture of as-quenched Ge–As–Te glass showing the amorphous nature of the samples.

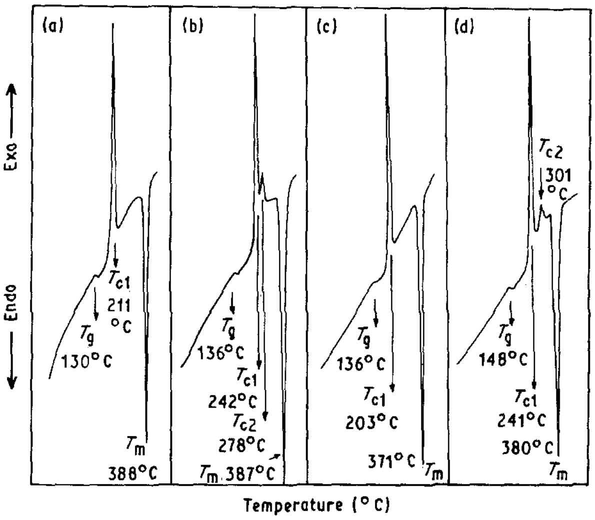

Figure 2 DSC curves of four Ge–As–Te glass compositions showing single or double crystallization behaviour when heated at 20 °C min^{-1}. (a) As-quenched $Ge_{7.5}As_{40}Te_{52.5}$ glass showing a single exothermic peak, (T_{c1}). (b) $Ge_{7.5}As_{45}Te_{47.5}$ glass showing two exothermic peaks (T_{c1} and T_{c2}). (c) $Ge_{10}As_{35}Te_{55}$ glass showing a single exothermic peak (T_{c1}). (d) $Ge_{10}As_{40}Te_{50}$ glass showing two exothermic peaks (T_{c1} and T_{c2}).

alumina powder (supplied by Stanton and Redcroft) as the standard reference material. Samples weighing about 10 mg were used and the values reported are the average of measurements that do not differ by more than ± 2 °C. The glasses have been studied under heating rates of 25, 20, 15, 10, and 5 °C min^{-1}.

A simple method of evaluating the glass-forming tendency by differential thermal analysis (DTA) was proposed by Hruby [12]. The coefficient

$$K_{gl} = (T_c - T_g)/(T_m - T_c) \qquad (1)$$

where T_c, T_g and T_m are the crystallization temperature, glass transition temperature and melting temperature, respectively, is a measure of the ease with which the glass can be formed.

The glass transition temperature and the crystallization temperatures shift when heated at different heating rates. The activation energy of any reaction in which the reaction temperature is dependent on the heating rate, can be calculated using the method of Kissinger [13], Augis-Bennett or Thakore [14]. Kissinger's equation,

$$d[\ln(\beta/T_r^2)/(1/T_r)] = -E/R \qquad (2)$$

where β is the heating rate, T_r is the reaction temperature (K), E is the activation energy for the reaction, and R is the universal gas constant, has been used to calculate the activation energy.

3. Results and discussion

Fig. 2a–d show the DSC curves of four glass compositions ($Ge_{7.5}As_{40}Te_{52.5}$, $Ge_{7.5}As_{45}Te_{47.5}$, $Ge_{10}As_{35}Te_{55}$ and $Ge_{10}As_{40}Te_{50}$) heated at 20 °C min^{-1}. The appearance of an endothermic peak at the glass transition temperature, T_g, and another endothermic peak at melting, T_m, are observed in all the glasses reported here. But some glass compositions show two exothermic peaks at temperatures T_{c1} and T_{c2}, whereas the rest show a single exothermic peak at T_{c1}. In Fig. 2a and c two glass compositions exhibiting single crystallization peaks are shown. Fig. 2b and d show two glass compositions that show double crystallization. When a multi-component glass is subjected to a constant heating rate as in a DSC experiment, the easily crystallizable phase in the glass composition crystallizes early in the experiment. In such cases, depending upon the stoichiometry of the composition, more than one crystallization peak is observed. There is also the possibility that two or more phases can crystallize together thereby showing only one crystallization peak. This may be the probable reason for the different crystallization behaviour exhibited by the above glasses. Double crystallization in Si_xTe_{100-x} for $x > 20$ [15, 16] and multiple crystallization in Si–Ge–AS–Te glasses [17] have been reported. But such behaviour has not been reported in Ge–As–Te glasses.

The glasses showing two crystallization peaks were air-quenched *in situ*, in the DSC after T_{c1}. The DSC curve of these glasses quenched after T_{c1} showed a single exothermic peak at T_{c2}, but no observable endothermic peak corresponding to a second glass transition temperature (T_{g2}) [18]. Either there is no second glass transition temperature or the thermal processes are too small to be detected. The small quantity of the second phase (as seen from the ratio of the peak heights T_{c1}/T_{c2} in Fig. 2) may be the reason for the non-observance of T_{g2} if present. The DSC was not used at very high sensitivities because of the high base-line shift at higher sensitivities. The X-ray analysis of the various phases crystallizing in the DSC experiment are being carried out and will be reported at a later date.

The T_g, T_{c1}, T_{c2} and T_m values for various compositions studied at 20 °C min^{-1} heating rate are given in Table I. The values correspond to the onset of T_g and the peak temperatures of T_{c1}, T_{c2} and T_m. The glass composition marked with the $ sign in Table I showed two crystallization peaks when heated at slow heating rates (< 15 °C min^{-1}), but the two peaks were unresolved at 20 °C min^{-1} heating rate. The glass transition temperature increases with decreasing tellurium at wt %. This agrees with the $Ge_{10}As_xTe_{90-x}$ data of Savage [7] (shown in parentheses in Table I),

TABLE I DSC data on Ge–As–Te glasses measured at 20 °C min^{-1} heating rate. (E_{c1} and E_{c2} are the activation energies of the first and second crystallization peaks, respectively)

Composition at wt % Ge:As:Te	T_g (°C)	T_{c1} (°C)	T_{c2} (°C)	T_m (°C)	K_{gl}	E_{c1} (eV)	E_{c2} (eV)
7.5:20:72.5	101	179	243	354	–	–	–
7.5:40:52.5	130	211	–	388	0.46	0.97	–
7.5:45:47.5	136	242	278	387	–	0.96	1.63
7.5:47.5:45	145	260	275	390	–	0.92	1.24
7.5:50:42.5	150	275	–	389	1.10	0.89	–
7.5:52.5:40	152	295	–	392	1.47	0.87	–
7.5:55:37.5	156	296	–	394	1.43	0.85	–
10:15:75	115 (123)	205	255 (244)	369	–	–	–
10:20:70	116 (127)	191	247 (234)	355	–	–	–
10:22.5:67.5	123	204	–	357	0.36	–	–
10:35:55	136	203	–	371	0.40	1.13	–
10:40:50	148 (173)	241	301 (300)	380	–	1.11	1.40
10:45:45	155	272	302	375	–	1.09	1.19
10:50:40	163 (195)	326 (300)	–	378	3.14	0.73	–

although the actual values show small differences in the two cases. The T_g increases with germanium at wt % for the same amounts of arsenic (or tellurium). This T_g dependence on germanium at wt % can be used to choose glass compositions with desirable T_g values. The K_{gl} values for glasses showing a single crystallization peak are also tabulated in Table I. Glasses with $K_{gl} < 0.5$ are difficult to form, requiring higher cooling rates, whereas glasses with $K_{gl} > 1$ can be easily formed with moderate quenching rates [12]. From the values of the coefficient of glass-forming tendency listed in Table I, one can infer that the glasses in the low-arsenic region are difficult to form as compared to the glasses with high-arsenic content.

The activation energies of crystallization for various crystallization peaks are listed in Table I. The compositions marked with the * sign in Table I gave ingots that are partially crystalline and partially glass and hence their activation energy values are not reported. The activation energy of both T_{c1} and T_{c2} decrease with decreasing tellurium at wt %, indicating that glasses with lower tellurium have a greater tendency to crystallize.

4. Conclusions

1. The T_g dependence on composition (increasing with germanium and arsenic content) can be used to prepare glasses of desired T_g values.

2. The glass forming tendency as denoted by K_{gl}, increases with increasing arsenic content.

3. The activation energy of crystallization decreases with increasing arsenic content (or decreasing tellurium) for both sets of glasses.

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