Journal of Thermal Analysis, Vol. 42 (1994) 1285-1297

THERMOANALYSIS OF QUASI-TERNARY $As_2(S, Se, Te)_3$ SEMICONDUCTOR GLASSES

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(Received April 7, 1993; in revised form December 8, 1993)

Abstract

In comparison with other chalcogenide glassy systems, less attention has been paid to the quasi-ternary (quaternary) system $As_2(S, Se, Te)_3$. In this paper, thermal methods were used to characterize ten different quaternary homogeneous semiconductor glasses that were prepared by mixing the stoichiometric binary systems As_2S_3, As_2Se_3 and As_2Te_3.

The ratios of the constituent binaries in the quasi-ternary glasses exerted a great influence on their thermal spectrum. The samples poor in As_2Te_3 showed neither the exothermic nor the endothermic peak due to crystallization (T_c) and melting (T_m), respectively, but only the glass transition (T_g). Three transition temperatures, T_g, T_c and T_m, were detected for other compositions. On the other hand, a phase separation was observed in the samples rich in As_2Te_3. A cyclic scanning technique was used to investigate the thermally-induced phases during two consecutive heating–cooling cycles covering the temperature range T_g–T_m.

The energy of decomposition E_d decreased on increase of the ratio As_2S_3/As_2Se_3 (at constant As_2Te_3), whereas it increased on increase of the ratio As_2Te_3/As_2Se_3 (at constant As_2Se_3 or As_2S_3).

Keywords: chalcogenide glassy system, semiconductor glasses

Introduction

The electrical, optical and thermal properties of amorphous As-chalcogenides in their stoichiometric binary and ternary (quasi-binary) systems have been well documented and reviewed, because of their usage in numerous semiconductor technological applications (cf. [1–6] and references therein). However, less attention has been paid to the quaternary (quasi-ternary) system $As_2(S, Se, Te)_3$. In a previous paper, the density, microhardness and electrical conduction have been reported for different glasses in that quasi-ternary system [7]. The structure of the corresponding crystalline phases was also studied [8].

Differential thermal analysis is known to demonstrate with ease the characteristic difference between a structurally stable material (exhibiting switching

0368–4466/94/ $ 4.00

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phenomena) and a reversible material (exhibiting memory phenomena). This communication reports a systematic investigation of the compositional dependence (S:Se:Te) of different thermal properties for ten arsenic quasi-ternary glasses.

Experimental

Sample preparation

In order to prepare glasses in the quasi-ternary system $As_2(S, Se, Te)_3$, the stoichiometric binaries As_2S_3, As_2Se_3 and As_2Te_3 were primarily prepared by placing the correct proportions into fused silica tubes under 10^{-5} Torr, and they were then heated up to 800°C in steps. The molten materials were quenched in ice-water. A quasi-ternary composition was prepared by mixing the correct ratios of the binaries in evacuated silica tubes at 500°C for 3 h. Quenching was then carried out in air for a few seconds, followed by immersion in an ice-water mixture. The glassy character of the quenched ingots was confirmed from their bright feature, X-ray diffraction (XRD) and differential thermal analysis (DTA) measurements.

The prepared homogeneous glasses of the system $As_2(S, Se, Te)_3$ are classified into four groups as follows:

Group A: $20As_2S_3\cdot(80-x)As_2Se_3\cdot xAs_2Te_3$ $(x = 30, 40, 50)$,

Group B: $20As_2Se_3\cdot(80-x)As_2S_3\cdot xAs_2Te_3$ $(x = 10, 30, 40)$,

Group C: $10As_2Te_3\cdot(90-x)As_2S_3\cdot xAs_2Se_3$ $(x = 20, 60, 80)$ and

Group D: $20As_2Te_3\cdot(80-x)As_2S_3\cdot xAs_2Se_3$ $(x = 10, 50)$.

Measurements technique

DTA experiments were carried out on a Shimadzu instrument (type DT-30). All measurements were referenced to α-Al_2O_3 powder in an Al-pan, and carried out in a nitrogen atmosphere flowing at 50 ml/min. Thermogravimetric (TG) measurements were performed to evaluate the activation energy of the decomposition process by the method proposed by Ozawa [9]. In this method, the TG curves obtained at different heating rates are required, where the following equation is valid:

$$\log \varphi_1 + 0.4567 \frac{E_d}{RT_1} = \log \varphi_2 + 0.4567 \frac{E_d}{RT_2} = \ldots,$$

where T (K) is the temperature at which the sample decomposes at heating rate φ. In the above equation, when the common logarithms of the heating rates are plotted against the reciprocal of absolute temperatures, a straight line will be obtained in the range where the decomposed ratios are equal. Accordingly, the activation energy of decomposition E_d can be evaluated.

Results and discussion

Compositional dependence of transition temperatures

Figure 1 shows typical DTA traces of freshly prepared $As_2(S, Se, Te)_3$ quenching materials at a constant heating rate φ = 10 deg·min^{-1}. The Figure shows an endothermic step on the lower temperature side, indicating that the glass transition (T_g) is present for all samples, i.e. all the examined compositions are in the glassy form. The Figure also indicates that the two peaks (the

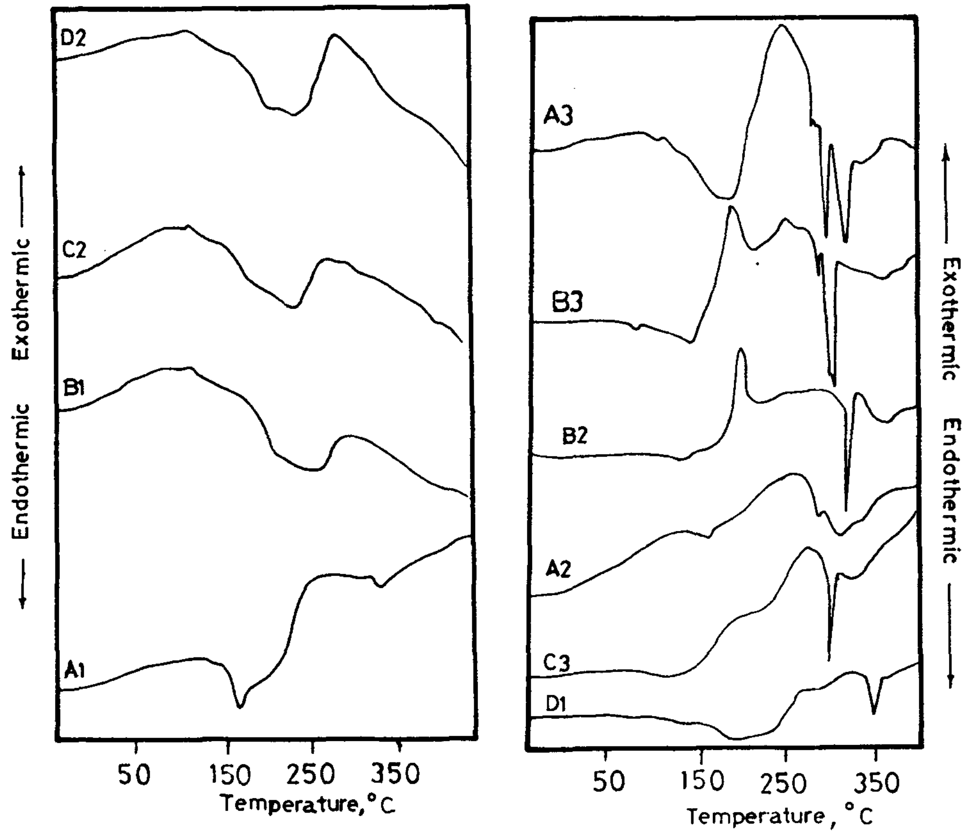

Fig. 1 DTA curves for the system $As_2(S, Se, Te)_3$ at a heating rate of 10 deg·min^{-1}

exotherm due to crystallization (T_c) and the endotherm due to melting (T_m) are absent for some compositions, and there is only T_g, pointing to a difficulty in crystallization of such glasses.

For the glasses exhibiting T_g, T_c and T_m, the T_g values lie in the range 61–152°C. An exothermic peak due to crystallization was observed for the samples having a small As_2Te_3/As_2Se_3 ratio. The values of T_c for such compositions lie in the range 178–280°C. The compositions A3 ($20As_2S_3{\cdot}30As_2Se_3{\cdot}50As_2Te_3$) and B3 ($40As_2S_3{\cdot}20As_2Se_3{\cdot}40As_2Te_3$), having $As_2Te_3/As_2Se_3 > 1$, with As_2S_3 concentrations of 20 and 40%, show two crystallization peaks; the first lies in the range 181–252°C, and the second in the range 245–275°C.

On melting, the crystalline material also yields one or two endothermic peaks, depending on the composition. For the compositions A2, B2, C3 and D1, which are characterized by one crystallization peak, one endothermic melting peak was observed in the range 288–321°C. Samples A3 and B3, rich in As_2Te_3, are characterized by more than one T_m. Sample A3 has two T_m's, the first at 270 and the second at 293°C. Sample B3 has three T_m's, at 270, 281 and 290°C.

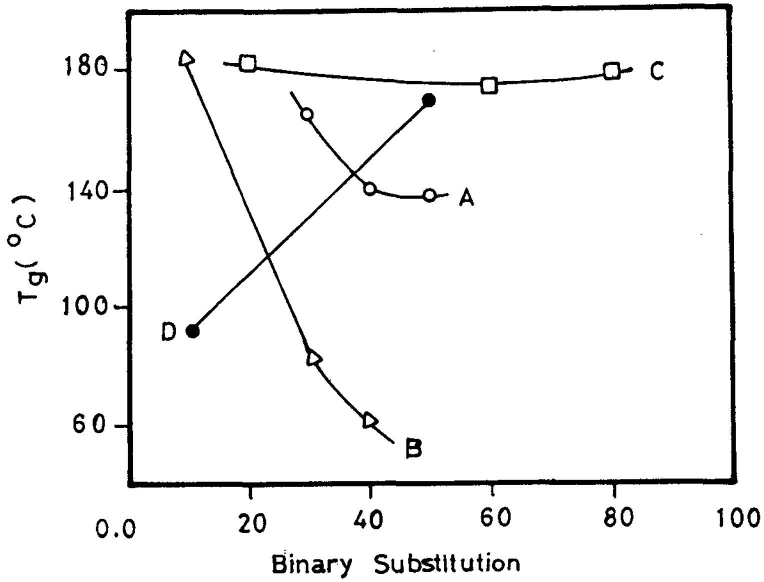

Fig. 2 Dependence of the glass transition temperature (T_g) on composition for glasses in the system $As_2(S, Se, Te)_3$

Figure 2 shows the compositional dependence of T_g. The effect of As_2S_3 or As_2Se_3 on T_g seems to be opposite to that of As_2Te_3. That is, increasing the substitution of As_2Te_3 in the glass leads to a decrease in the value of T_g. Such a composition dependence of T_g is similar to that of the microhardness (MH) [10].

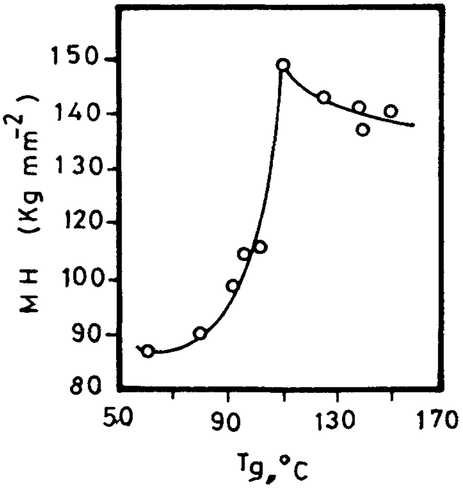

Fig. 3 Dependence of MH on T_g for the system $As_2(S, Se, Te)_3$

Here, it is interesting to note the discontinuity trend in the relation between MH and T_g in Fig. 3 as a result of the change in the relative molecular concentrations of the three binary components of the system. Accordingly, the compositions having the same percentage of selenium or tellurium are characterized by increased values of T_g (as well as MH) with increasing sulphur content. The values of T_g for the compositions with 20 mol% As_2Se_3 are 61, 68 and 110°C when their respective mole ratios As_2S_3:As_2Te_3 are 4:4, 5:3 and 7:1. The values of T_g for the compositions having the same concentration of tellurium (10 mol%) are 95, 102 and 110°C when their respective mole ratios As_2S_3:As_2Se_3 are 1:8, 3:6 and 7:2. Also glasses of 20 mol% As_2S_3 are characterized by decreased values of T_g with increasing tellurium content. The values of T_g are 125, 138 and 140°C for the glasses having ratios As_2Te_3:As_2Se_3 of 5:3, 4:4 and 3:5, respectively. For the compositions having the highest sulphur content (70 mol% As_2S_3), the value of T_g changes from 91 to 110°C on doubling the Se content at the expense of the Te content.

As an example, Fig. 4 shows a systematic study of the influence of the heating rate φ on thermally-induced transformations in composition B3 ($40As_2S_3\cdot 20As_2Se_3\cdot 10As_2Te_3$). This Figure indicates that the value of T_g is nearly rate-independent in the range 5–50 deg·min^{-1}. The start of the crystallization peak moves to higher temperatures on increase of φ, while the starting of T_m is rate-independent. At $\varphi = 15$ deg·min^{-1}, the third peak of melting is overlapped by the second peak, i.e. the melting of the two phases took place at nearly the same time. At φ = 20 deg·min^{-1}, crystallization starts before melting, i.e. during the heating process the glassy material arrives at the melting temperature before it is completely crystallized.

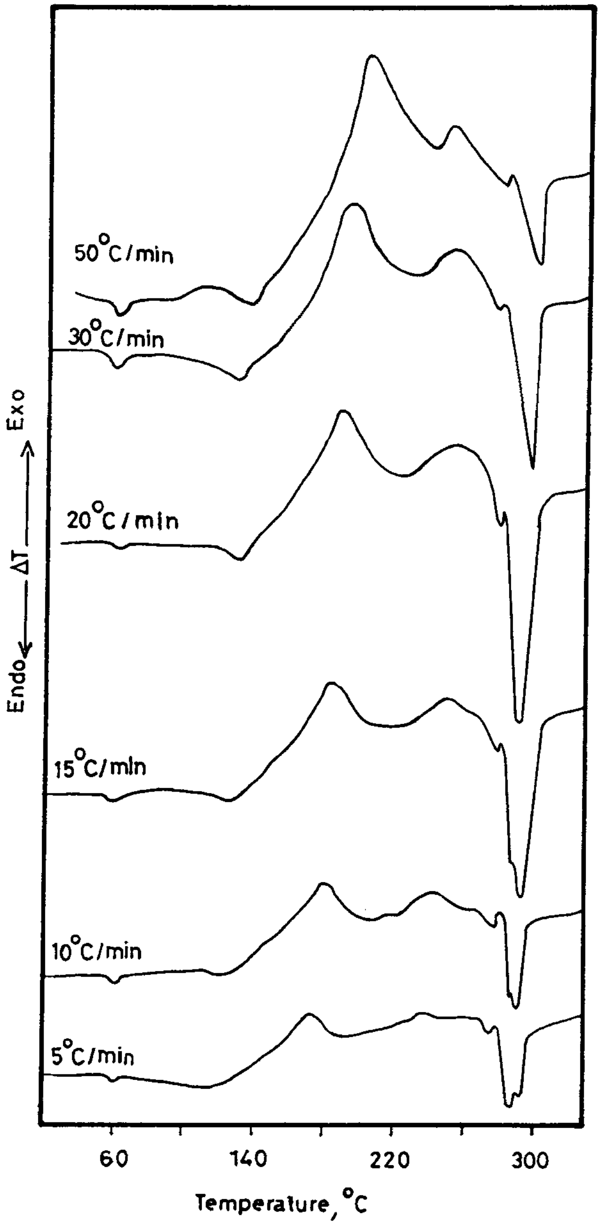

Fig. 4 DTA curves of $40As_2S_3 \cdot 20As_2Se_3 \cdot 40As_2Te_3$ at different heating rates

Table 1 Transition temperatures as a function of composition at heating rate 10 deg·min^{-1}

Composition	T_g / °C	T_c / °C			T_m / °C				T_{eva} / °C	K_{gl}
		1st		2nd	1st	2nd		3rd		
		T_b	$T_p - T_b$	T_p	T_b	$T_p - T_b$	$T_p - T_b$	T_p		
A1	164								368	
A2	139	175		255	288			310	341	0.12
A3	138	163	252–272	275	280	288–293		312	295	0.17
B1	183				289			381*	260	
B2	80	140		178	291			313	320	0.26
B3	61	122	181–210	245	270	277–281	288–290	293	285	0.28
C1	183				289			381*	260	
C2	175				228			273*	391	
C3	180	293		340	356			364	420	0.61
D1	91	211		280	303			320	410	0.52
D2	170								380	

T_b = begin of the peak, T_p = top of the peak
*T_m obtained after crystallization
T_{eva} = begin of evaporation

Table 1 summarizes the results on the transition temperatures T_g, T_c and T_m as a function of composition. The notation (*) indicates values obtained after heat treatment.

Glass-forming tendency

For the same quenching rate, the glass-forming tendency differs for different materials. This is related to the chemical bonds that determine the structure and all the properties of a body in any state of aggregation [6]. For chalcogenide glasses, chemical bonds with lone-pair electrons have a character of flexibility. This flexibility relies on the type, strength and concentration of the possibly existing chemical bonds in the glass.

Hruby and Stourac [12] suggested an appropriate measure for the glass-forming ability, which can be determined from a DTA scan:

$$K_{gl} = \frac{T_{c1} - T_g}{T_m - T_{c1}}$$

where T_{c1} and T_m represent the temperatures of the start of crystallization and melting, respectively. The values of K_{gl} of $As_2(S, Se, Te)_3$ glasses, obtained via their DTA scans at 10 deg·min^{-1}, are given in Table 1. This Table reveals that $K_{gl} > 0.1$ for all investigated glasses, and it increases with increase of both As_2S_3 and As_2Se_3 content, and decreases with increase of As_2Te_3. This means that the ability to form crystalline solids decreases with increasing As_2S_3 or As_2Se_3 content.

The chemically ordered (heteropolar) bonds As–S, As–Se and As–Te are favoured in the stoichiometric glasses investigated. This does not, of course, exclude the existence of disordered (homopolar) bonds that act as defects besides the disorder in the glass network. The presence of such broken chemical order represents a persistent difference between glasses and crystals [13, 14]. Crystalline networks are chemically ordered and are fully polymerized. Glassy networks, on the other hand, are both partially ordered and polymerized. These ideas have led to the notation of the phase separation [15] of glassy networks on a scale characterized by being of large molecular units (50≈100 Å). Table 1 also demonstrates the trend that the glass-forming tendency decreases from group $C \rightarrow D \rightarrow B \rightarrow A$, i.e. with increase of the concentration of As_2Te_3 in the quasi-ternary glassy materials.

Thermogravimetric analysis

The activation energy of decomposition is useful for evaluating the thermal stability of materials. A plot of log φ *vs.* $1/T$ is shown in Fig. 5 for all compo-

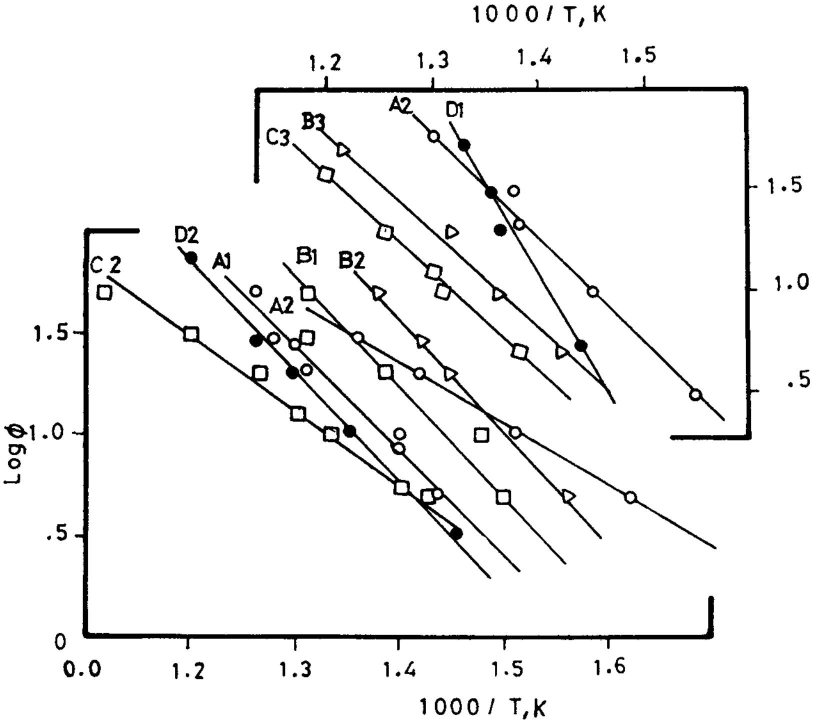

Fig. 5 Relation between log φ and $1/T$, obtained from TG of quasi-ternary $As_2(S, Se, Te)_3$ glasses

sitions investigated, where a least square fit could be applied to evaluate the values of E_d. Figure 6 shows the compositional dependence of E_d. It indicates a decrease in E_d with increasing As_2Te_3 % in groups A and B, and As_2Se_3 % in groups C and D.

The decomposition energy is correlated with the type and strength of the possible chemical bonds. The As–Te bond is longer than the As–Se bond, which is longer than the As–S bond. For Te-rich glasses, the covalent nature of the bond might be weakened by the presence of three-fold coordination Te sites. Accordingly, when As_2Te_3 % increases, the glass needs less energy to decompose. As the As–Se bond is longer than those in As_2S_3, when As_2S_3 % increases the glass needs more energy to decompose.

Heat-cooling cyclic scanning

The effects of heating and cooling on both the exothermic and endothermic peaks were examined, using DTA curves for all prepared quasi-ternary glasses. The normal procedure for the DTA cyclic scan was:

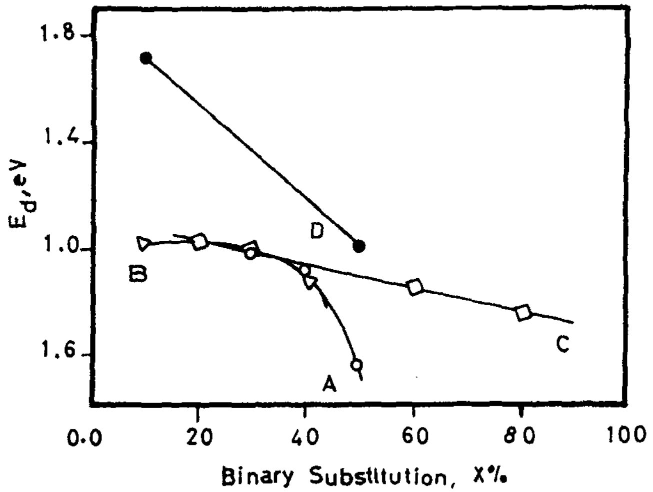

Fig. 6 Compositional dependence of energy of decomposition (E_d)

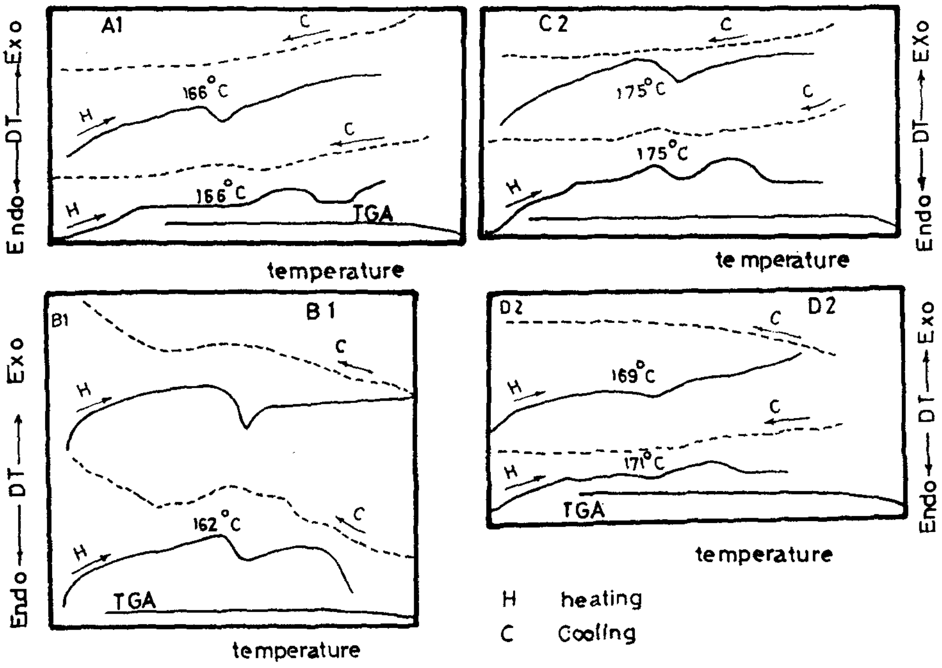

Fig. 7 DTA scanning of compositions A1, B1, C2 and D2. Full and dashed lines are the respective heating and cooling curves at 15 deg·min^{-1}

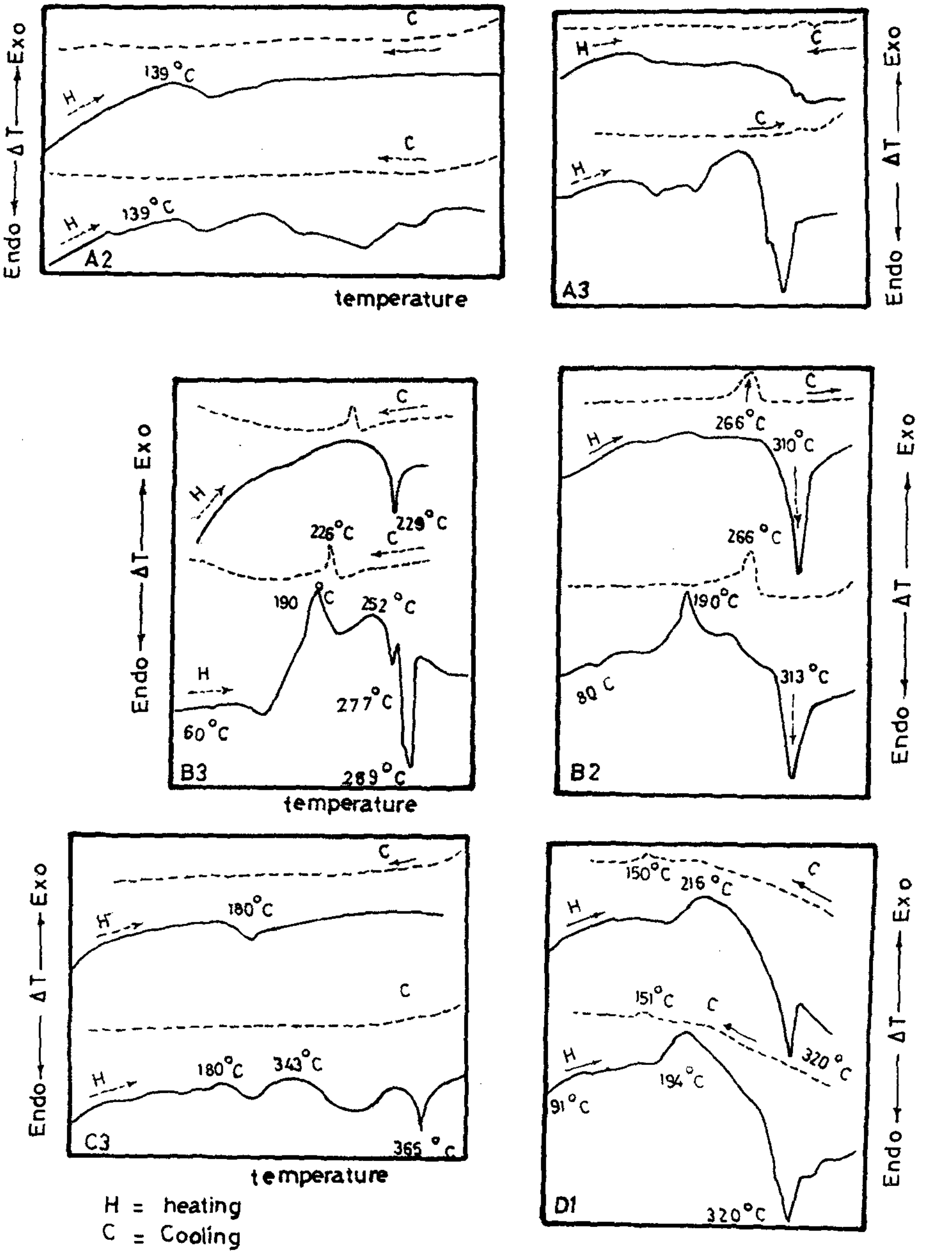

Fig. 8 DTA scanning of A2, A3, B3, B2, C3 and D1; heating and cooling rates are 15 deg·min^{-1}

(a) To raise the furnace temperature at a heating rate of 15 deg·min^{-1} to a maximum temperature that was chosen to be far from the decomposition temperature determined from the TG curves.

(b) To lower the temperature at a cooling rate of about 15 deg·min^{-1} to 50°C.

(c) To raise the temperature again as in step (a).

(d) To lower the temperature to 50°C.

The investigation of two consecutive cyclic scans of the examined glasses indicated some common features between the behaviours of different compositions.

i) The thermoanalytical curves of compositions A1, B1, D2 and C2 are shown in Fig. 7. In run a, the first heating cycle, only a glass transition T_g was observed. The only deviation from the baseline, after the endothermic step T_g, defined the starting point of decomposition, as indicated from the TG curve represented in the same Figure. Thus, no crystallization or melting peaks were observed before decomposition. In run b, during the first cooling cycle, no features of interest were observed. In run c, during the second heating cycle, no new observations were detected relative to run a. In run d, the second cooling cycle, no features of interest were observed, as in run b. From these results, it seems that the thermal behaviour of the material, either glass powder (run a) or massive glass (run c), is the same, indicating the difficulties with which these materials undergo crystallization.

ii) The value of T_g detected on the first heating (run a) lay in the range 155–193°C for the compositions A2, A3, B2, C3 and D1 (Fig. 8). Also, one melting peak in the range 281–303°C was observed for the compositions A2, A3, B2, C3 and D1, and two melting peaks, at 272 and 282°C, for B3. In run b, during the first cooling, one crystallization peak in the range 140–312°C was observed for the compositions A3, B2, B3, C3 and D1, whereas for the composition A2 there was no detectable deviation from the baseline. In run c, the second heating cycle, the composition A2 showed only T_g at 139°C, the two peaks due to crystallization and melting having disappeared. For the composition D1, T_g disappeared and T_c moved to a higher value. This is probably associated with the form of the material; before run a, the material was in powder form, but before run c, the material was in a massive (solid) form. It was observed that crystals grow more readily from powdered glass than from large solid pieces.

Conclusions

The systematic study of the thermoanalysis of different quasi-ternary $As_2(S, Se, Te)_3$ semiconductor glasses, using DTA and TG techniques, indicated that the two stoichiometric binaries As_2S_3 and As_2Se_3, and also their rich quasi-ternary compositions, display very little tendency to crystallize. The absence of any clear peak after T_g in the DTA scans of some compositions is a good indicator for the absence of structural changes, which is the case for the glassy compositions rich in As_2S_3 and As_2Te_3. In contrast, the glass-forming tendency is weak for the As_2Te_3-rich materials, so that a phase transition appears and this is related to the Te content, which prefers three-fold rather than two-fold coordination.

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Zusammenfassung — Verglichen mit anderen chalkogeniden glasartigen Systemen wurde dem quasi-ternären (quaternären) System $As_2(S,Se,Te)_3$ weniger Aufmerksamkeit geschenkt. Vorliegend werden thermische Methoden zur Beschreibung zehn verschiedener quaternärer homogener Halbleitergläser benutzt, die durch ein Mischen der stöchiometrischen binären Systeme As_2S_3, As_2Se_3 und As_2Te_3 hergestellt wurden.

Die Anteilsverhältnisse der binären Bestandteile in den quaternären Gläsern beeinflussen deren thermisches Spektrum in breitem Umfange. Proben mit einem geringen Gehalt an As_2Te_3 zeigen bei Kristallisation (T_c) und beim Schmelzen (T_m) weder exotherme noch endotherme Peaks. Es wird nur eine Glasumwandlung beobachtet (T_g). Für andere Zusammensetzungen können drei Umwandlungstemperaturen (T_g, T_c und T_m) beobachtet werden. Auf der anderen Seite wird bei Proben mit einem großen As_2Te_3-Gehalt eine Phasenseparierung beobachtet. Zur Untersuchung der thermisch induzierten Phasen innerhalb von zwei aufeinanderfolgenden Aufheiz- und Abkühlzyklen im Temperaturbereich T_g bis T_m wurde eine cyclische Scanningmethode eingesetzt.

Der Wert der Zersetzungsenergie E_d nimmt (bei konstantem As_2Te_3) mit zunehmendem As_2S_3/As_2Se_3-Quotienten ab und (bei konstantem As_2Se_3 oder As_2S_3) mit zunehmendem As_2Te_3/As_2Se_3-Quotienten zu.