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THERMAL CRYSTALLIZATION STUDIES ON Ga–Te GLASSES

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Abstract

Semiconducting Ga_xTe_{100-x} ($17 \leq x \leq 25$) glasses have been prepared by melt quenching method and thermal crystallization studies carried out using differential scanning calorimetry. On heating, virgin Ga_xTe_{100-x} glasses exhibit one glass transition and two crystallization reactions. The first crystallization reaction corresponds to the precipitation of hexagonal Te and the second one to the crystallization of the matrix into zinc blende Ga_2Te_3 phase. If Ga_xTe_{100-x} glasses are quenched to ambient temperature from T_{cr1} and reheated, they exhibit the phenomenon of double glass transition.

Keywords: DSC, Ga–Te glasses, thermal crystallization

Introduction

Thermal crystallization studies of glasses can yield useful information about the local structure of these materials. It has been reported by Cornet [1] and Asokan *et al.* [2, 3] that the crystallization behaviour of chalcogenide glasses depends on the short range order present in the material. In the chalcogenide glassy family, III-VI glasses are comparatively less explored, due to the difficulty in forming bulk glasses in these systems. There are earlier studies reported in literature, on the formation and thermal crystallization behaviour of Al–Te glasses [4]. In the present study, an effort is made to understand the thermal crystallization behaviour of Ga_xTe_{100-x} glasses of different compositions.

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Experimental

Bulk Ga_xTe_{100-x} ($17 \le x \le 25$) glasses were prepared by quenching from the melt. High purity elements were taken in desired proportions in evacuated quartz ampoules and sealed. The ampoules were heated above the melting tem-

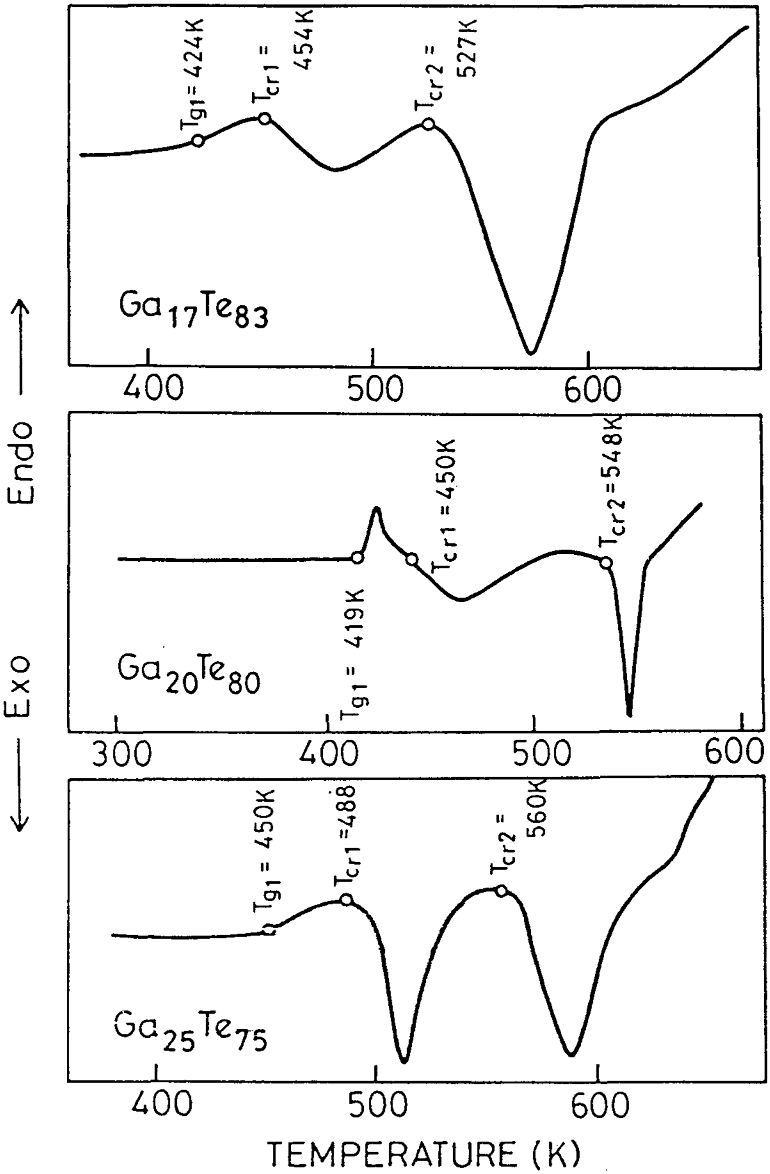

Fig. 1 DSC curve of Ga_xTe_{100-x} ($17 \le x \le 25$) glasses; heating rate 20 deg·min^{-1}

perature of the constituents and quenched into ice water. The glassy nature of the samples was confirmed by X-ray diffraction.

Thermal crystallization experiments were performed using Stanton Redcroft differential scanning calorimeter. About 20–30 mg of samples was used for each experiment and alumina was used as the reference material.

Results and discussion

Figure 1 shows the DSC curve of Ga_xTe_{100-x} ($17 \leq x \leq 25$) glasses. It is seen Fig. 1, that these glasses exhibit one endothermic glass transition (T_g) and two exothermic crystallization reactions on heating.

X-ray diffraction studies have been performed, on Ga_xTe_{100-x} samples, annealed at the two crystallization temperatures for about 2 h. Figure 2 shows the X-ray diffraction patterns of a representative $Ga_{20}Te_{80}$ sample under different thermal conditions. It can be seen from the diffraction pattern (Fig. 2a) that in samples annealed at the first crystallization reaction, hexagonal Te crystallizes out first, leaving behind a residual amorphous matrix. If $Ga_{20}Te_{80}$ glass is annealed at the second crystallization reaction T_{cr2}, the residual material also crystallizes into the equilibrium Ga_2Te_3 phase, as shown in Fig. 2b.

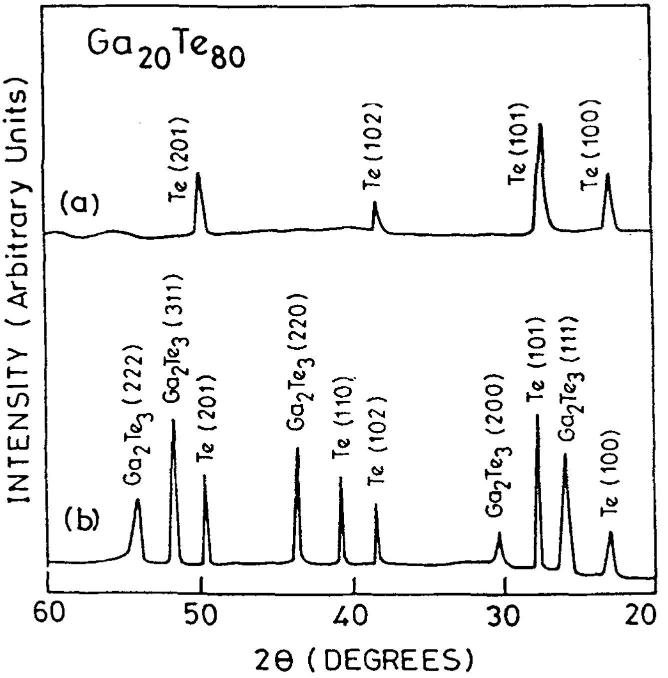

Fig. 2 X-ray diffraction patterns of $Ga_{20}Te_{80}$ sample under different thermal conditions: (a) after the first crystallization (b) after complete crystallization

The X-ray diffraction patterns of $Ga_{17}Te_{83}$ and $Ga_{25}Te_{75}$ samples annealed at T_{cr1} and T_{cr2} are similar.

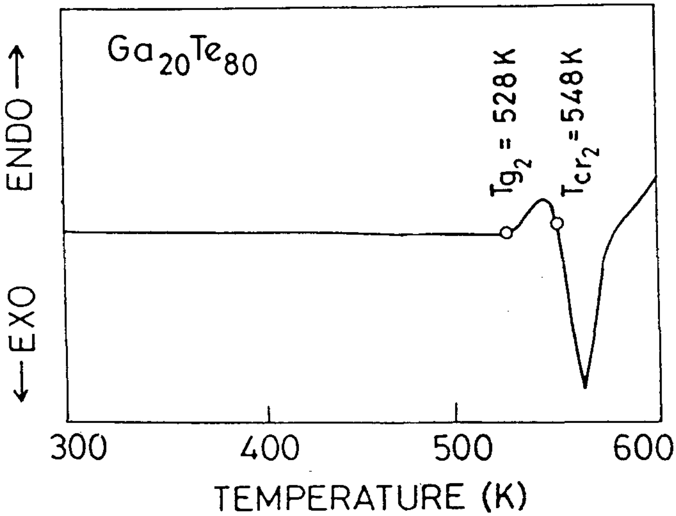

Fig. 3 DSC thermoanalytical curve of $Ga_{20}Te_{80}$, glass which has been previously heated up to the end of first crystallization and cooled back to room temperature

Ga_xT_{100-x} glasses were also heated up to the end of first crystallization reaction, quenched back to ambient and then reheated in a DSC run. These samples are found to exhibit the phenomenon of double glass transition. Figure 3 illustrates the DSC trace of $Ga_{20}Te_{80}$ sample, previously heated to the end of the first crystallization reaction (T_{cr1}) and cooled back to room temperature. It is seen from Fig. 3 that the reheated sample exhibits a second glass transition at T_{g2} with the second crystallization reaction at T_{c2} remaining unchanged. The other two glasses in the Ga–Te system ($Ga_{17}Te_{83}$ and $Ga_{25}Te_{75}$) also exhibit the second glass transition, if quenched to ambient from T_{cr1} and reheated. The second glass transition (T_{g2}) is observed in Ga–Te samples, only if they are quenched from temperatures between T_{cr1} and T_{cr2}. The presence of a second glass transition is a common feature among many Te based chalcogenide glasses like Si–Te [2], Ge–Te [3], Al–Te [5], etc., and this phenomenon is closely related to the chemical short range order present in the material.

The crystallization schemes for Ga_xTe_{100-x} ($17 \le x \le 25$) glasses, are as follows:

$$Ga_xTe_{100-x} \text{ (virgin glass, } 17 \le x \le 25) \xrightarrow{T_{g1}} \text{super cooled liquid} \xrightarrow{T_{cr1}}$$

$$\text{C–Te + amorphous matrix} \xrightarrow{T_{cr2}} \text{cryst. Te + cryst. } Ga_2Te_3$$

$$Ga_xTe_{100-x}\ (\text{virgin glass, } 17 \le x \le 25) \xrightarrow{T_{g1}} \text{super cooled liquid} \xrightarrow{T_{cr1}}$$

$$\text{C–Te + matrix} \rightarrow$$

quenched to ambient and reheated

$$\text{C–Te + glassy matrix} \xrightarrow{T_{g2}} \text{C–Te + super cooled liquid} \xrightarrow{T_{cr2}} \text{C–Te + C–}Ga_2Te_3$$

Here, C-denotes crystalline material.

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Zusammenfassung — Mittels der Abschreckmethode wurden halbleitende Ga_xTe_{100-x} ($17 \le x \le 25$) Gläser hergestellt und mit Hilfe von DSC thermische Kristallisationsuntersuchungen durchgeführt. Beim Erhitzen zeigen frischgefertigte Ga_xTe_{100-x}-Gläser eine Glasumwandlung und zwei Kristallisationsreaktionen. Die erste Kristallisationsreaktion entspricht der Präzipitation von hexagonalem Te und die zweite der Kristallisation der Matrix in die Zinkblendenphase Ga_2Te_3. Werden Ga_xTe_{100-x}-Gläser von T_{cr1} auf Umgebungstemperatur abgeschreckt und wieder erhitzt, zeigen sie die Erscheinung der Doppelglasumwandlung.