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Thermal crystallization behaviour of Ge-Te-Se glasses

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$Ge_{10}Te_{90-x}Se_x$ ($50 \leq x \leq 70$) and $Ge_{20}Te_{80-x}Se_x$ (x = 30, 50) glasses have been prepared by melt-quenching. The thermal crystallization behaviour of these samples has been studied by Differential Scanning Calorimetry (DSC), in order to characterise these glasses for memory-threshold switching applications. It is found that $Ge_{10}Te_{90-x}Se_x$ glasses have higher thermal stability and are more stable against devitrification. These samples may be suitable for threshold switching devices. $Ge_{20}Te_{80-x}Se_x$ glasses, on the other hand, phase separate on heating and exhibit a double stage crystallization. Based on this, it can be expected that $Ge_{20}Te_{80-x}Se_x$ samples will show memory behaviour. The activation energy for thermal crystallization of a representative $Ge_{10}Te_{40}Se_{50}$ glass belonging to the $Ge_{10}Te_{90-x}Se_x$ series has been found by the Kissinger's method to be 0.92 eV. The value of the activation energy obtained also indicates that $Ge_{10}Te_{90-x}Se_x$ samples are less prone to devitrification and more suitable for threshold behaviour.

1 Introduction

Differential Scanning Calorimetric (DSC) studies help in understanding the glass transition and crystallization behaviour of amorphous solids. Further, the thermal parameters of chalcogenide glasses, obtained from DSC experiments are useful for characterizing these materials for different applications, especially for electrical switching applications[1]. For example, the variation of electrical switching fields with composition of chalcogenide glasses is found to be directly related to the composition dependence of crystallization temperatures[2]. Also, there exists a correlation between the glass transition temperature and the switching fields of chalcogenide glasses[3]. Easy resettability of the memory state has been found to be intimately linked to the glass forming ability of chalcogenides[4] (estimated from thermal parameters). The thermal stability of chalcogenide glasses (given by the separation between the glass transition and crystallization temperatures) is found to be a deciding factor, in determining whether the sample will exhibit memory or threshold behaviour[5]. Further, as the memory (irreversible) switching in glassy chalcogenides is *thermal* in nature, involving the formation of conducting crystalline channels in the material[6], data on the activation energy for thermal crystallization is useful in selecting a suitable material for memory applications.

This paper deals with the differential scanning calorimetric studies on the glass transition and the crystallization behaviour of Ge-Te-Se glasses. In the Ge-Te-Se system, bulk, homogeneous glasses can be obtained in the composition range 10 to 30 atom percent of Ge, for varying Se and Te proportions[7,8]. Preparation and thermal characterization of Ge-Te-Se glasses of a few individual compositions have been reported earlier[9,10]. In the present work, DSC studies have been undertaken on Ge-Te-Se glasses of different compositions, with an idea to find the suitability of these materials for different switching applications.

2 Experimental Details

Bulk, semiconducting $Ge_{10}Te_{90-x}Se_x$ ($50 \leq x \leq 70$), $Ge_{20}Te_{80-x}Se_x$ (x = 30, 50) glasses have been prepared by the melt-quenching method. Constituent elements in desired proportions are sealed in evacuated quartz ampoules (10^{-6} torr). The sealed ampoules are heated to temperatures around 1100°C, in a tubular furnace. The ampoule containing the molten elements are rotated continuously at 10 rmp for about 48 hours, in order to homogenize the melt. Subsequently, the ampoules are quenched in a trough containing NaOH + ice-water mixture. The glassy nature of the samples is confirmed by X-ray diffraction. A Philips diffractometer with Cu K_α radiation is used for the X-ray studies.

A Stanton-Redcroft Differential Scanning Calorimeter is used for the thermal investigations. About 20-25 mg of sample is taken in quartz crucibles and alumina is used as the reference material. DSC studies are also undertaken as a function of heating rate on a representative sample, to evaluate the activation energy of crystallization.

3 Results and Discussion

3.1 Glass transition and crystallization behaviour

The Differential Scanning Calorimetric traces of $Ge_{10}Te_{90-x}Se_x$ ($50 \leq x \leq 70$) glasses, obtained at a heating rate of 15 deg/min, are shown in Figs 1 and 2. It can be seen from these Figs 1 and 2 that all the $Ge_{10}Te_{90-x}Se_x$ glasses studied exhibit one glass transition reaction on heating. However, the samples show different crystallization behaviour, depending on the composition; $Ge_{10}Te_{40}Se_{50}$ sample exhibits one exothermic crystallization reaction and an endothermic melting peak above the glass transition (Fig. 1). On the other hand, $Ge_{10}Te_{30}Se_{60}$ and $Ge_{10}Te_{20}Se_{70}$ samples do not exhibit any crystallization on heating (Fig. 2). These samples melt directly, after the glass transition. Fig. 3 shows the differential scanning calorimetric trace of a representative $Ge_{10}Te_{20}Se_{70}$ glass taken with a higher sensitivity (heating rate = 15 deg/min). It is evident from Fig. 3 that even with higher sensitivity, it has not been possible to detect any crystallization in this material.

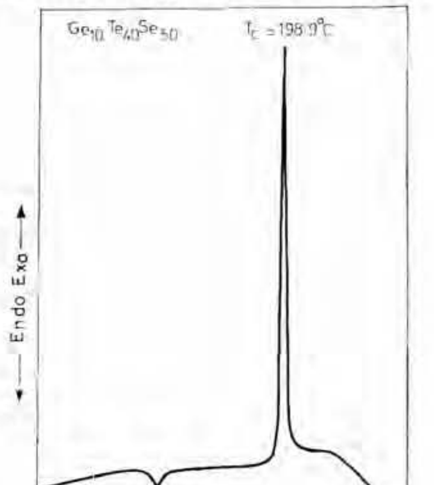

Fig. 1 — DSC thermogram of $Ge_{10}Te_{40}Se_{50}$ glass. Heating rate = 15 deg/min

In the case of $Ge_{10}Te_{30}Se_{60}$ sample, the melting occurs around 285°C. For $Ge_{10}Te_{20}Se_{70}$ sample, the melting starts just around 625°C and it has not been possible to observe the melting completely as the temperature limit of the DSC instrument in the high sensitivity mode is 650°C. It is also interesting to note that the glass transition reaction in $Ge_{10}Te_{20}Se_{70}$ sample is sharper than that for other glasses.

The thermal behaviour of $Ge_{20}Te_{80-x}Se_x$ (x = 30, 50) glasses is different from that of $Ge_{10}Te_{80-x}Se_x$ glasses. $Ge_{20}Te_{50}Se_{30}$ and $Ge_{20}Te_{30}Se_{50}$ samples exhibit two crystallization reactions, between the glass transition and melting reactions. Fig. 4 shows the DSC trace of the representative $Ge_{20}Te_{30}Se_{50}$ sample.

Telluride glasses which exhibit two crystallization reactions are usually found to show two glass transitions also. To observe the second glass transition, the samples

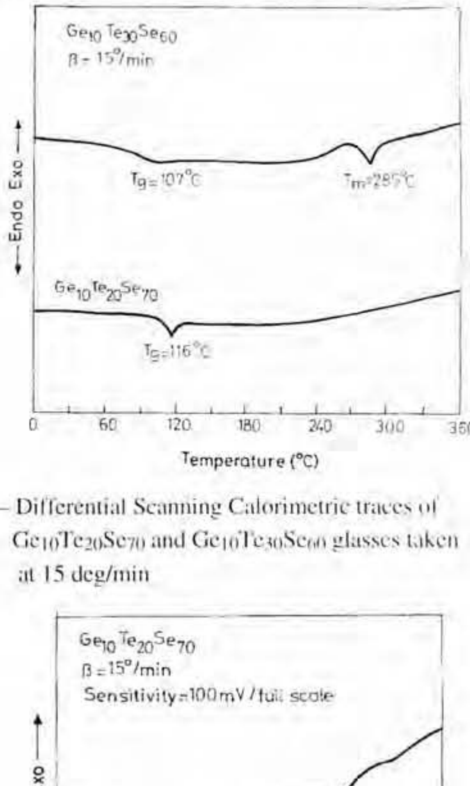

Fig. 2 — Differential Scanning Calorimetric traces of $Ge_{10}Te_{20}Se_{70}$ and $Ge_{10}Te_{30}Se_{60}$ glasses taken at 15 deg/min

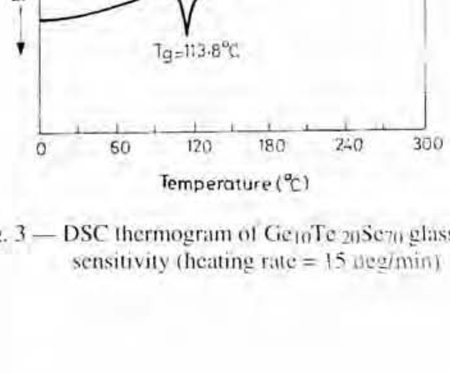

Fig. 3 — DSC thermogram of $Ge_{10}Te_{20}Se_{70}$ glass at higher sensitivity (heating rate = 15 deg/min)

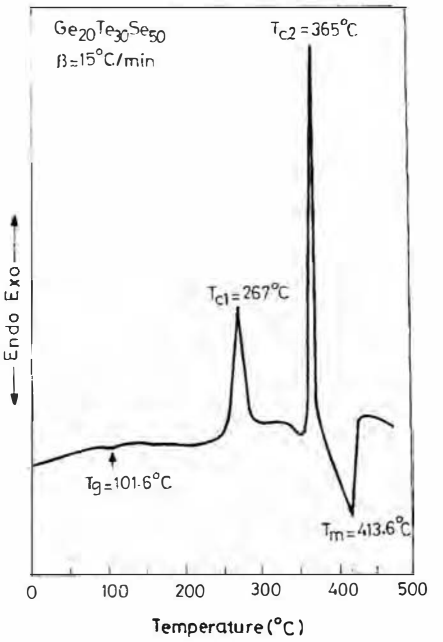

Fig. 4 — Differential Scanning Calorimetric trace of $Ge_{20}Te_{30}Se_{50}$ sample. Heating rate = 15 deg/min

are heated to the end of first crystallization reaction, quenched to ambient and reheated[11]. $Ge_{20}Te_{30}Se_{50}$ glasses also exhibits the phenomenon of double glass transition and double stage crystallization, when they are quickly cooled to room temperature and reheated in a DSC experiment[12].

The present DSC results indicate that the glass transition temperatures of $Ge_{10}Te_{90-x}Se_x$ glasses ($50 \leq x \leq 70$) increases with the composition x. Also, $Ge_{10}Te_{30}Se_{60}$ and $Ge_{10}Te_{20}Se_{70}$ glasses do not crystallize on heating. Even for the $Ge_{10}Te_{40}Se_{50}$ sample, the crystallization temperature is comparatively higher (198°C). Also, these samples have a high melting temperature. It can be concluded from the above that the $Ge_{10}Te_{90-x}Se_x$ samples ($50 \leq x \leq 70$), have a better thermal stability and hence will be more useful for threshold switching applications.

$Ge_{20}Te_{80-x}Se_x$ (x = 30, 50) glasses, which phase separate on heating and crystallize at lower temperatures (100°C) are more suitable for memory switching applications. In this context, it is interesting to note glasses as Al-Te and Ge-Te, which phase separate and exhibit a double stage crystallization, also show memory switching[3,11,13].

3.2 Activation energy for crystallization

DSC studies have been undertaken on a representative $Ge_{10}Te_{40}Se_{50}$ glass at different heating rate, to evaluate the activation energy for crystallization. Figs 5 and 6 give the differential calorimetric thermograms of $Ge_{10}Te_{40}Se_{50}$ sample, taken at 15, 20, 25 and 30 deg/min heating rates. The activation energy for crystallization E_c can be estimated using the Kissinger's method[14], from the following relation:

$$d\,[\ln(\beta/T_c^{\,2})]/d\,[1/T_c] = -E_c/R$$

where R is the gas constant; T_c the crystallization temperature; β is the heating rate. The plot of ln $(\beta/T_c^{\,2})$ versus $1/T_c$ is a straight line, the slope of which gives the activation energy of the crystallization (E_c). Fig. 7 shows the variation of ln $(\beta/T_c^{\,2})$ with $1000/T_c$ for a repre-

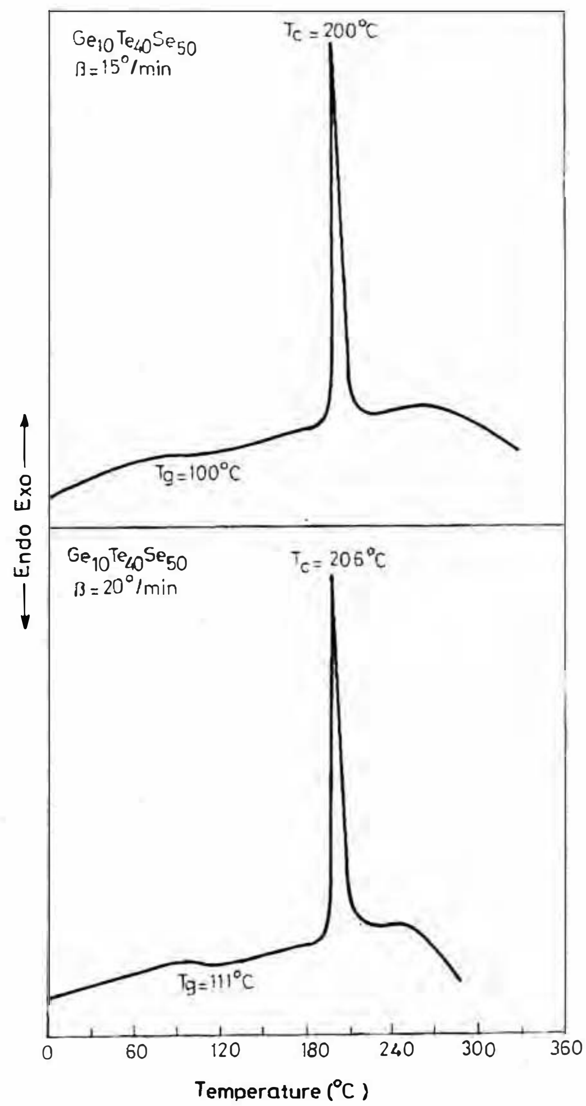

Fig. 5 — DSC thermogram of $Ge_{10}Te_{40}Se_{50}$ glass taken at 15 deg/min and 20 deg/min heating rates

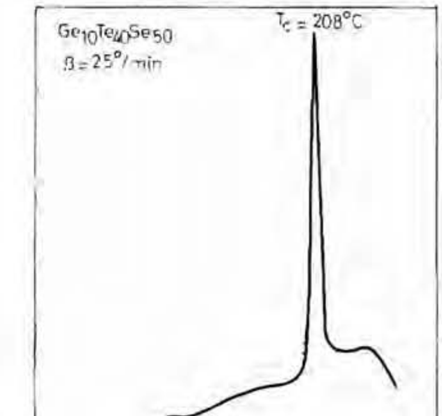

Fig. 6 — DSC thermogram of $Ge_{10}Te_{40}Se_{50}$ glass taken at 25 deg/min and 30 deg/min heating rates

sentative $Ge_{10}Te_{40}Se_{50}$ sample. The crystallization activation energy of this sample has been estimated from Fig. 7 as 0.92 eV. The crystallization activation energy of other glasses in the $Ge_{10}Te_{90-x}Se_x$ series, having higher Se content, will be even higher. Memory switching glasses such as As-Te, usually have the crystallization activation energy in the range[2,15] 0.1-0.3 eV. The comparatively larger activation energy (0.92 eV) of $Ge_{10}Te_{40}Se_{50}$ glass also corroborates the idea that $Ge_{10}Te_{90-x}Se_x$ glasses are less likely to show memory switching and more suited for threshold applications.

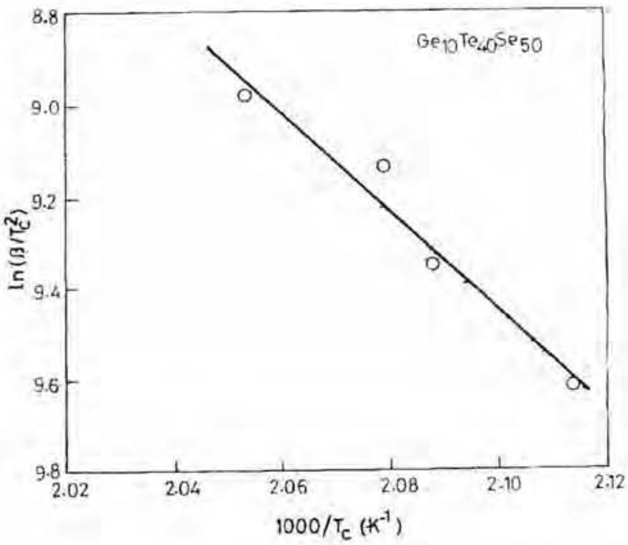

Fig. 7 — Kissinger's plot [ln (β/T_c^2) versus $1000/T_c$] of $Ge_{10}Te_{40}Se_{50}$ glass

4 Conclusion

Bulk, semiconducting $Ge_{10}Te_{90-x}Se_x$ ($50 \leq x \leq 70$) and $Ge_{20}Te_{80-x}Se_x$ ($x = 30, 50$) glasses have been prepared by melt-quenching. Differential Scanning Calorimetric studies on the thermal crystallization behaviour indicate that $Ge_{10}Te_{90-x}Se_x$ glasses have higher thermal stability and are more stable against devitrification. These samples may be more suitable for threshold switching applications. The higher activation energy for thermal crystallization of $Ge_{10}Te_{40}Se_{50}$ glass (0.92 eV) also supports the idea. $Ge_{20}Te_{80-x}Se_x$ glasses, on the other hand, phase separate on heating and exhibit a double stage crystallization. It may be expected that these samples will show memory behaviour.

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