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CHARACTERIZATION OF Ge-Se-Te GLASSES BY EMANATION THERMAL ANALYSIS AND DTA

S. Bordas and M. T. Clavaguera-Mora
Dept. Termología, Universidad Autónoma de Barcelona, Bellaterra, Spain

V. Balek
Nuclear Research Institute, 250 68 Řež, Czechoslovakia

ABSTRACT

The systematic study of the Ge-Se-Te system was carried out by emanation thermal analysis and DTA. The quenched samples were classified according to the thermal behaviour during heating and cooling. The glass transition, recrystallization and melting of the samples have been investigated. By means of the ETA supplementary information on these processes has been obtained. The differences in thermal behaviour of bulk and powdered samples have been characterized by ETA.

INTRODUCTION

Chalcogenide materials have been studied in the last decades because of their interesting properties and possible technological applications /1/.

The ETA is a sensitive method of objective characterization of solids /2,3/. The aim of this work is to show the possibilities of ETA in the study of the thermal behaviour of the Ge-Se-Te glasses. The ETA results are compared with the results of DTA.

EXPERIMENTAL

Around 100 samples (of about one gram) of different composition were prepared by melting mixtures of the required amounts of the elements of 5N purity in evacuated and sealed quartz ampoules. The melted alloys were held at 1000 °C for 12 h, constantly agitated and then quenched in air.

ETA is based on the measurement of the release of radioactive inert gas from the solid previously labeled by inert gas. The sample labeling was made by impregnation of the sample with an acetone solution containing ^{228}Th and ^{224}Ra isotopes /2/. The surface distribution of the inert gas was obtained in this way. The volume distribution of the inert gas in the sample was obtained by sample melting.

The Netzsch apparatus for ETA and DTA has been applied for the measurements, the heating and cooling was performed at a constant rate of 5 °C min^{-1} in dynamic atmosphere of argon.

The glassy state of the samples after these measurements was checked by X-ray powder diffraction.

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RESULTS AND DISCUSSION

The DTA and ETA heating curves shown in Fig. 1 represent the general types of curves observed with all powdered samples of the Ge-Se-Te system obtained as air quenched melts labeled in the surface.

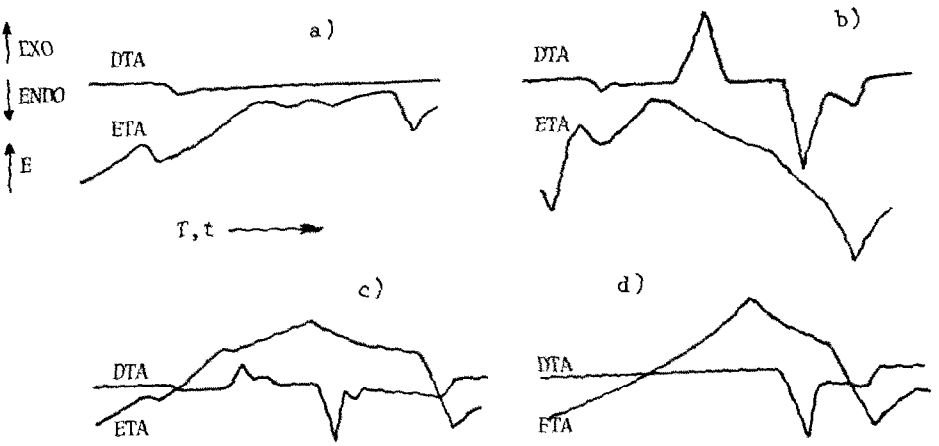

Fig. 1: Typical heating DTA and ETA curves of: a) glasses without recrystallization, b) glasses with recrystallization, c) partially crystalline samples, and d) crystalline samples

The DTA curve of type a) sample is typical for glasses which do not recrystallize but change continuously from glass to liquid and show only the glass transition (displacement of the baseline). The ETA curve of type a) sample shows: i) the onset of the solid matrix loosening of the glass transition by the decrease of the emanation release rate E (the beginning of the loosening process is several degrees before the onset of the glass transition determined by DTA); ii) some oscillation, at a temperature above the glass transition; that corresponds to the formation of the first stages of the new metastable phases involving small thermal effects; iii) the decrease of E which has been ascribed to the surface annealing of the sample, annealing of irregularities and cracks and other molecular defects; iv) an increase of the E, usually observed after the melting, corresponding to the increased mobility of the liquid and to the thermal diffusion of radon in the melt.

The glass transition observed by DTA and ETA of type b) /4/ and c) samples is revealed in a similar way as with the type a) sample. The DTA of samples b) and c) indicates recrystallization by one exothermic peak or even three peaks. The difference between these DTA curves lies in the fact that in the first case b) the heat evolved by recrystallization is approximately the same as that of melting, whilst in the second case c) it is much lower. This difference signifies that in the first case the sample was glassy before heating and that in the second case it was partially crystalline. Since the thermal behaviour varies

rather continuously with composition, the glassy or partially crystalline samples were characterized by X-ray diffraction.

On the ETA curves the recrystallization of samples b) and c) is indicated by: i) a peak of E (some tens of degrees before the onset of the process indicated by DTA), corresponding to the onset of the surface changes and formation of the first nuclei of the new crystalline or intermediate phases; ii) the decrease of the slope of E (at the same temperature as that of the recrystallization observed by DTA), corresponding to the onset of the bulk process; iii) the end of the bulk process, detected also by the change of the slope of E at the same temperature as on the DTA curve. These effects of ETA are less pronounced with the samples of type c) than with the samples of type b).

The melting of the samples of type b), c) and d) is indicated by DTA as one or several endothermic peaks corresponding to different regions of the phase diagram /5/. The DTA curve d) exhibits only melting endothermic peaks, it is a typical DTA curve of a crystalline sample. The onset and the end of the melting process are observed by ETA by a decrease and an increase of E, respectively. Moreover, by ETA it is possible to detect the pre-melting process, and the onset of total lattice distortion by a change of the slope of the ETA curve.

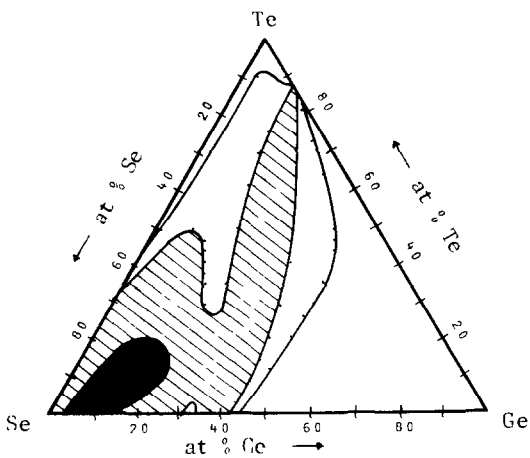

Fig. 2: Glass-forming regions for quenching in air. ■ glasses without recrystallization; ▨ glasses with recrystallization; ▦ partially crystalline; □ crystalline

Four different glass-forming regions found in air quenched melts are presented in Fig. 2, corresponding to the four types a) – d) of samples. The region of glasses without recrystallization is located in the Se-Te-$GeSe_2$ subsystem, around of the eutectic Ge_8Se_{92}. There exist extensive regions of glasses with recrystallization and partially crystalline in the Se-Te-$GeSe_2$, Te-$GeSe_2$-GeTe and $GeSe_2$-GeTe-GeSe subsystems. There exist also crystalline samples in the GeSe-GeTe-Ge subsystem and some regions in other the three nominate subsystems.

The bulk distribution of the radioactive label can be supposed in samples previously melted. Three different types of DTA curves (Fig. 3) were obtained during the cooling of the melts at 5 °C min^{-1}: the DTA curve e) is a baseline without any change (the melt is transformed into a glass); DTA curve f) exhibits

a broad exothermic peak which is always reproducible (a partially crystalline sample is formed); and the DTA curve g) exhibits well defined exothermic peaks (the liquid is nucleated heterogeneously and a crystalline sample is formed). The cooling ETA curves of these three types of melts represent a monotonous decrease of the E. By the evaluation of the temperature dependence of this decrease the defect state and its changes in the concerned samples can be characterized.

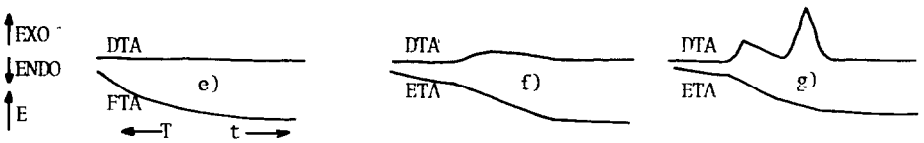

Fig. 3: Typical cooling DTA and ETA curves of: e) glass-forming samples, f) partially crystalline samples and g) crystalline samples.

The ETA curves obtained during the reheating of previously method samples differ from those of the initially surface labeled samples. Glass transition is not observed with melted samples as they possess a very small internal surface and the diffusion of radon is negligible. The recrystallization is indicated by a small increase of E. In the vicinity of the melting temperature the intense increase of E is due to radon diffusion in the solid, which is enhanced by pre-melting phenomena.

CONCLUSIONS

The DTA and ETA curves obtained for the Ge-Se-Te system were classified into four types. The ETA results agree with those of DTA, moreover the ETA provides a supplementary information about the first stages of the various structural changes. On the basis of these results the glass-forming region in the Ge-Se-Te system was determined.

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