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POSSIBILITIES OF EMANATION THERMAL ANALYSIS FOR THE CHARACTERIZATION OF SEMICONDUCTING GLASSES

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ABSTRACT

The evolution of structure and structural transformations taking place in representative specimens of semiconducting glasses in the system Ge–Sb–Se–Te during their thermal treatment were investigated by emanation thermal analysis.

INTRODUCTION

Semiconducting glasses have been studied in recent decades from both the technological (photoresistivity, xerography, solar cells, etc.) and theoretical points of view on account of the peculiarities of the non-crystalline state of solids. Many techniques have been applied in the study of glasses. Some provide information about the structure of solids (e.g., diffraction techniques) and others reflect processes that take place in the solids during heating and cooling (e.g., DTA and DSC) or characterize the macroscopic properties of solids (e.g., measurements of resistivity, optical absorption and commutation).

In this paper a brief description of the possibilities of emanation thermal analysis [1] (ETA) for the characterization of the evolution of structure and transformations taking place in semiconducting glasses during thermal treatment is presented. Representative specimens of the Ge–Sb–Se–Te system were selected for the ETA study on the basis of previous results concerning the crystallinity state of samples of various composition in this system [2–5].

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EXPERIMENTAL

The samples of semiconducting glasses were prepared by air quenching molten alloys of the Ge–Sb–Se–Te system of various composition. Before the ETA measurement the samples were crushed (pulverized) and labelled by impregnation with ^{228}Th and ^{224}Ra, giving ^{220}Rn by spontaneous radioactive decay [1].

RESULTS AND DISCUSSION

The principal processes taking place during heating of the glassy samples studied are glass transition, recrystallization and melting; some very stable glasses do not recrystallize on heating and change continuously from the glass to supercooled liquid and stable liquid [4,6]. These processes are characterized by effects on the ETA curves; the effects differ for crushed and monolithic (uncrushed) glass samples when heated at a constant rate.

A. Crushed samples superficially labelled

A typical ETA curve obtained during heating of a glass sample at a constant rate of 5°C min^{-1} is shown in Fig. 1. A few tenths of a degree before the glass transition (detected by DTA and dilatometry) there is an important and monotonous increase of the emanation rate, E, assumed to be an indication of the onset of loosening of the solid matrix before the glass transition. In the glass transition temperature interval the emanation rate decreases, and after the glass transition this decrease in E is smoother or may even increase.

Recrystallization is indicated on the ETA curve at temperatures a few tenths of a degree lower than the temperature of DTA effects. A decrease in

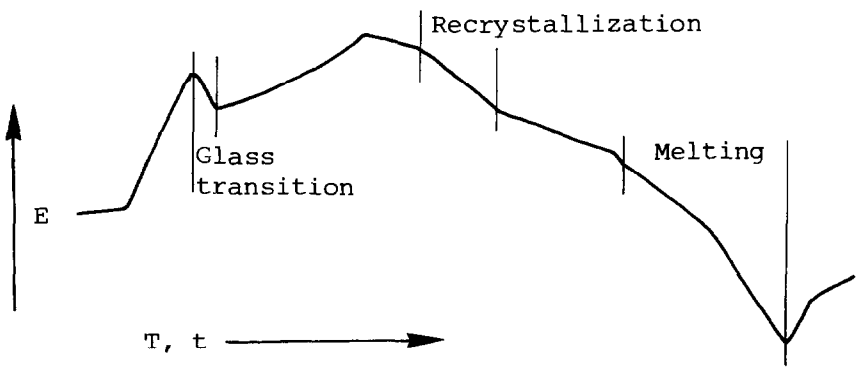

Fig. 1. Typical heating ETA curve of a semiconducting glass labelled in the surface.

the emanation rate is caused by the diminishing surface of the sample, when the formation of the first nuclei take place (surface sintering can be observed at this temperature) and by the migration of the parent isotopes ^{228}Th and ^{224}Ra from the surface to inside the sample. At the beginning of the exothermic process of recrystallization (as indicated by DTA or DSC) an enhanced decrease in the emanation rate is observed owing to the acceleration of the mentioned processes. At the end of the recrystallization the emanation rate increases again.

The melting is indicated by ETA regardless of whether the sample was initially in the glassy or crystalline state. On the other hand, the effects on the ETA depend on the morphology of the samples, i.e., the ETA curves for crushed and monolithic samples differ. For a crushed sample a few degrees before the melting temperature a sharp decrease in emanation rate related to the pre-melting phenomena and to the surface changes caused by the melting are observed. At the melting temperature the decrease in emanation rate slows, but at temperatures close to the end of melting a sharp decrease in emanation rate is observed, obviously associated with total distortion of the solid. The end of melting is indicated by ETA as an increase in emanation rate that corresponds to the increased mobility of the liquid and enhanced thermal diffusion of radon in the melt.

After this thermal treatment and melting of the glass sample, a bulk distribution of the radioactive label in the melt can be assumed. If the melt is cooled at a rate greater than the minimum quenching rate (MQR) needed to avoid crystallization of the solid, the sample becomes a supercooled liquid and finally a glass. This rapid cooling treatment (the rate is greater than 5°C min^{-1} for the samples in question) is accompanied by a continuous decrease in emanation rate, without noticeable effects on the ETA curves. When the melt is cooled at a rate slower than the MQR, i.e., less than 5°C min^{-1}, the samples recrystallize partially or totally during cooling. The ETA curve measured during cooling of the above-mentioned melt exhibits a faster decrease in emanation rate [2,3].

B. Monolithic samples labelled in the bulk

By heat treatment of the glassy sample initially labelled in the surface and subsequent cooling at a rate greater than the MQR, a glass labelled in the bulk was obtained. A typical ETA curve for such a sample obtained during heating at a constant rate of 5°C min^{-1} is shown in Fig. 2. It follows from Figs. 1 and 2 that the ETA curves of the superficially and bulk labelled samples differ significantly; glass transition of the bulk sample is not apparent on the ETA curve, which is obviously caused by the reduced surface compared with a powdered sample, the diffusion of radon in the bulk being negligible at these temperatures. The recrystallization is indicated by an increase in the emanation rate, which reflects the changes in the bulk

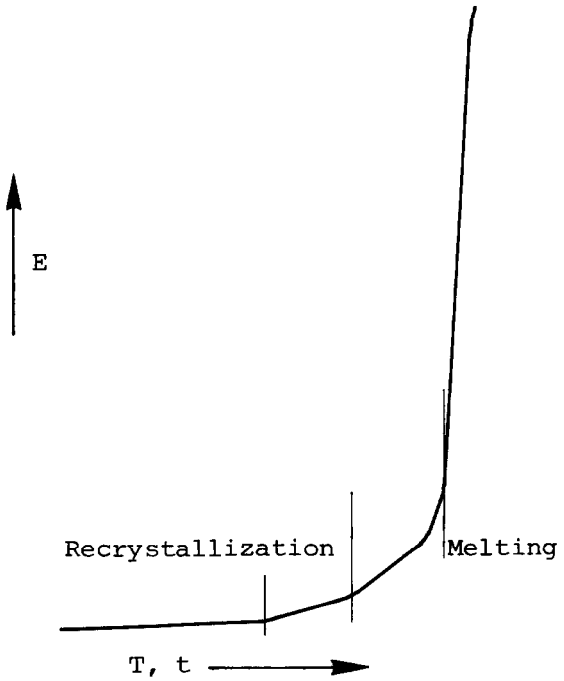

Fig. 2. Typical heating ETA curve of a semiconducting glass labelled in the bulk.

of the material. After recrystallization, a few degrees before melting, a sharp increase in emanation rate occurs, caused by thermal diffusion of radon in the lattice of the recrystallized solid. The pre-melting effects are not as pronounced with the bulk samples as with powdered samples. At the melting temperature a large increase in emanation rate is observed.

ETA has also been used for the study of the recrystallization of bulk samples under isothermal conditions. The homogeneously labelled bulk glass sample is characterized by a low emanation rate, which increases during recrystallization. After this increase, a slight decrease takes place at the end of recrystallization and surface sintering of the recrystallized sample.

CONCLUSIONS

ETA is an effective method for the study of the processes that take place during heating and cooling of semiconducting glasses. Additional information to that obtained by DTA is yielded by ETA. A good correlation between ETA and DTA results was found.

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