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THERMAL INVESTIGATION OF $GeSb_2Se_4$ CHALCOGENIDE ALLOY GLASS

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Differential thermal analysis measurements were performed between 115 and 550° on glass samples of $GeSb_2Se_4$ chalcogenide alloy, and the latent heats of structural transformations were obtained. Heat treatment was found to result in the appearance of an endothermic peak associated with the glass transition.

As part of a systematic study of the stability or the temperatures and latent heats of structural transformations of glasses of the Ge-Sb-Se system, this note reports on differential thermal analysis (DTA) measurements between 115 and 550° on alloys of composition $GeSb_2Se_4$.

The glass-forming area of the Ge-Sb-Se system has been established by Borisova and Pazin [1] and Haisty and Krebs [2]. Some physical properties of amorphous $GeSb_2Se_4$ were studied by Frumar et al. [3, 4], in particular the softening, recrystallization and melting temperatures.

The glassy samples were obtained by quenching of the melt, prepared by initial melting of the elements of 5 N purity. The material, sealed-off in an evaporated quartz ampoule, was heated at 1100° for 6 h and constantly agitated to make the melt homogeneous. The melt was then rapidly cooled to room temperature by immersion in water.

The amorphous state of the samples and their homogeneity were verified by X-ray analysis and scanning electron microscope observations.

A DTA plot of the previously-prepared glassy $GeSb_2Se_4$ (200 mg) is shown in Fig. 1. The measurements were performed at heating and cooling rates of 5°/min by means of an automatic apparatus (Netzsch Simultan Thermo Analyse Model 429).

Upon heating (Fig. 1/a), a glass transition is observed near 210°, which appears as a step in the DTA curve. An exothermic transformation –recrystallization– then takes place between 290 and 340° (ΔH = 8.6 cal/g), and finally above 400° a region of endothermic reactions (melting) is observed, with two wide peaks (ΔH = 8.9 cal/g). The general behaviour of this DTA curve agrees with that reported in [3].

On cooling from a temperature above the melting point (530°) an exothermic transformation (crystallization) is obtained (Fig. 1/b), formed by two overlapping

peaks, the first one beginning at about 440°, and the second one, more reproducible, always starting abruptly at 417°. On heating this transformed material, one obtains a DTA curve (Fig. 1/c) which shows only the endotherms of melting. Next, cooling of the sample (Fig. 1/d) gives a DTA curve analogous to that of Fig. 1/b.

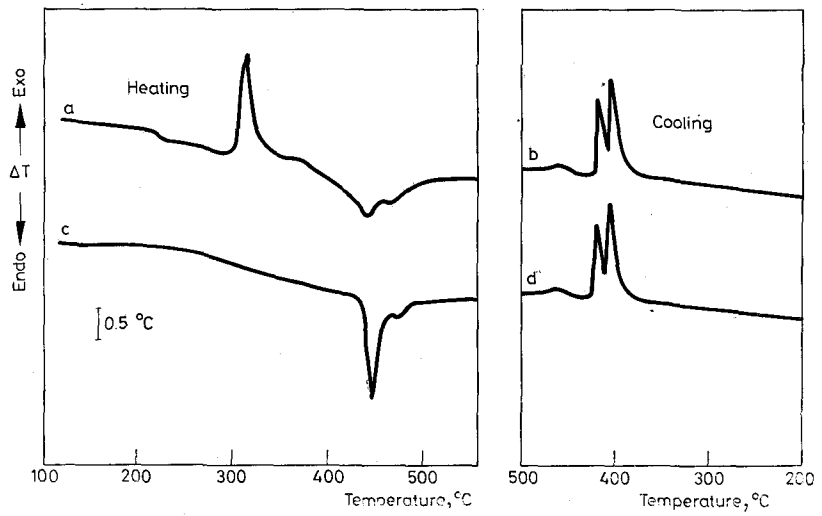

Fig. 1. DTA curves for a sample of $GeSb_2Se_4$ during two temperature cycles

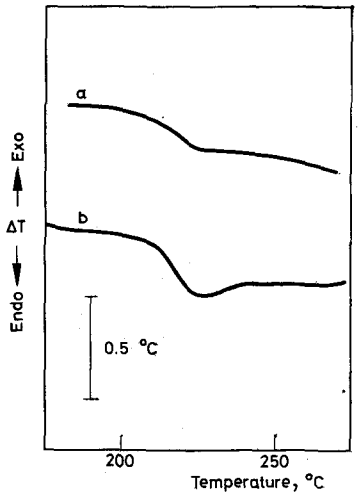

Fig. 2. DTA curves at the glass transition for two samples of $GeSb_2Se_4$: a) as-quenched glass, b) annealed glass

Annealing the glassy sample under vacuum at 200° during 60 h and then slowly cooling to room temperature yields the same DTA results, except for the behaviour of the glass transition DTA curve, as shown in Fig. 2. The endothermic peak associated, and concurrent, with the glass transition in the annealed glass (Fig. 2/b) is not present in the as-quenched glass (Fig. 2/a). The heat associated with the glass transition is about 0.98 cal/g. This kind of behaviour of the annealed glasses at the glass transition is similar to those previously reported for arsenic-selenium [5] and arsenic-antimony [6] alloy glasses, and may be characteristic of chalcogenide alloy glasses.

Heating the material to 250° at a rate of 5°/min and then cooling it at the same rate to room temperature does not destroy the glassy character of the sample, i.e. subsequent heating at 5°/min leads to a DTA curve like that of Fig. 1/a.

Very slow cooling of the glassy sample from 250° (for instance, at a rate of 0.1°/min) gives rise to a recrystallized sample like that obtained by heating up to 340°. That is, the heating DTA curve of the slowly-cooled sample shows only two wide endothermic peaks of melting, identical to the ones of Fig. 1/a. This result is confirmed by X-ray analysis, which shows [7] that the slowly-cooled sample, like the recrystallized one, has rather unresolved Debye–Scherrer lines, in contrast with the crystallized sample.

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