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THERMODYNAMIC DATA ON CHALCOGENIDE GLASSES

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The temperature-dependence of the specific heat near to the glass temperature was investigated for several Te- and As-based chalcogenide glasses, the latent heats of melting and crystallization of the former alloys also being measured. No thermal change could be detected in the transformation of the As-based alloys from the solid to the liquid state.

The present report describes some results of our investigations into the thermal properties of certain chalcogenide glasses. Electrical and optical switching and memory effects have been observed in many amorphous chalcogenides [1–2]. Pearson [3] and Eaton [4] suggested that thermally-induced phase changes were responsible for these phenomena. In glasses of appropriate composition, the amorphous material transforms to the crystalline modification upon being heated to the crystallization temperature. When the melted sample is cooled down, two different phases may be obtained depending on the cooling rate: slow cooling leads to crystallization, whereas if the sample is cooled down rapidly it solidifies in the amorphous state [5–8]. There is, however, a concentration region where even slow cooling produces amorphous material.

We measured the temperature-dependence of the heat capacities of the glassy and the crystalline material near to the glass temperature. In addition, the latent heats of melting and crystallization of the Te-based alloys were measured, and it was observed that these could be cycled repeatedly between the amorphous and the crystalline state.

Experimental

The required amounts of high-purity reactants were weighed out and approximately 2 g of the powder mixture was sealed in an evacuated glass tube. Six chalcogenide alloys of different compositions (see Table 1) were prepared by the usual melt-cool procedure.

The thermal parameters were determined with a Perkin–Elmer type DSC-2 differential scanning calorimeter. The encapsulated samples (~10 mg) were scanned from room temperature to 700 K at 20 K/min. The detailed theory of DSC can be found elsewhere [9–10].

Results and discussion

A list of the transition temperatures observed upon heating at 20 K/min may be found in Table 1.

Table 1

Transition temperatures of chalcogenide glasses

Sample No.	Composition	T_g, K	T_{Cr_1}, K	T_{Cr_2}, K	T_{m_1}, K	T_{m_2}, K
1	$Te_{81}Ge_{15}As_4$	403	468	494	647	667
2	$Te_{85}Ge_{15}$	404	445	489	655	680
3	$Te_{75}As_{25}$	360	404	—	636	—
4	$Te_{71}Ge_{15}Sb_2S_2$	386	445	469	633	674
5	$As_{40}Se_{50}Ge_{10}$	510	—	—	—	—
6	$As_{40}Se_{25}S_{25}Ge_{10}$	514	—	—	—	—

The samples can be divided into two different groups. Samples 1 – 4 show three types of thermal change:

a) a sudden increase in the heat capacity at $T = T_g$, the glass temperature T_g depends on the heating rate (Fig. 1);

b) an exotherm at $T = T_{Cr}$, which is interpreted as crystallization;

c) an endotherm at $T = T_m$, which is associated with the melting of the crystalline material.

In Table 2 we have collected the experimental and computed specific heat data near to the glass temperature.

Table 2

Specific heat in cal/g K

Sample No.	$C(T < T_g)$	$C(T > T_g)$	C_{comp}
1	0.055	0.10	0.053
2	0.051	0.07	0.051
3	0.075	0.10	0.054
4	0.054	0.09	0.051
5	0.091	0.12	0.082
6	0.097	0.14	0.092

$C(T < T_g)$ is the measured specific heat just below, and $C(T > T_g)$ just above T_g, while C_{comp} is the specific heat computed on the basis of the Neumann–Kopp rule, assuming that the heat capacity of the alloy can be approximated by the addition of the heat capacity of the constituents. The fact that the heat capacity below T_g is nearly equal to the heat capacity of the crystalline material (Fig. 1), which can be approximated to by the Neumann – Kopp rule, shows clearly that the extra degrees of vibrational freedom present in the amorphous state are almost completely frozen below T_g.

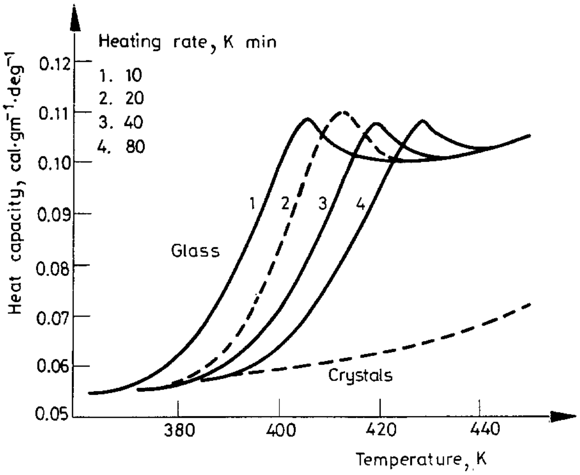

Fig. 1. Heat capacity of glassy and crystalline $Te_{85}Ge_{15}$ *vs.* temperature and heating rate

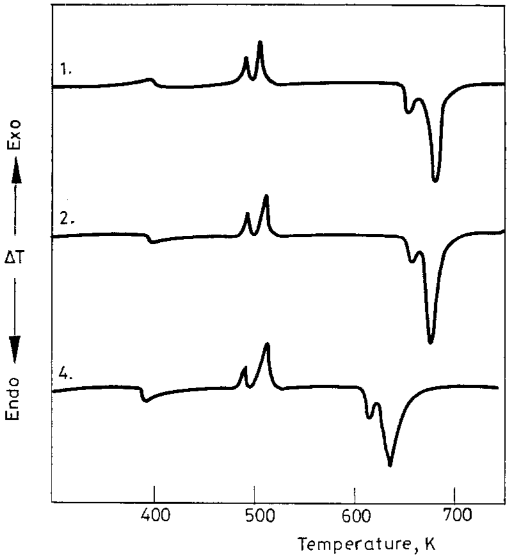

Fig. 2. DSC diagrams of samples 1, 2 and 4

T_g can be observed only in the samples quenched from $T > T_m$. When the sample is heated to T_{Cr} it goes through the exotherm, and after this the heat capacity shows no anomaly at $T = T_g$ (see Fig. 1). These facts together confirm that T_g is characteristic of the amorphous state, T_{Cr} is the crystallization and T_m the melting of the sample.

Samples 1, 2 and 4 show two distinct crystallization and two melting peaks (Fig. 2). The interpretation of these peaks is possible by assuming the crystallization of two different phases with different melting temperatures.

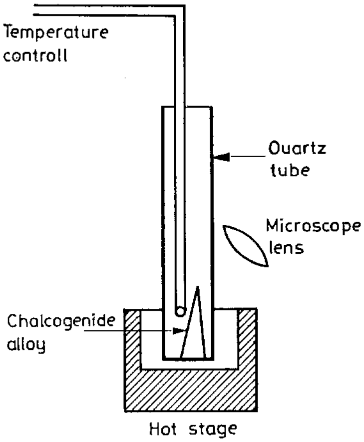

Fig. 3. A simple arrangement for determining the melting of chalcogenide glasses

The first exothermic transformation takes place between 440 and 470 K. This produced X-ray diffraction lines which were characteristic of Te crystallites [11]. The second exothermic transformation takes place between 470 and 500 K. X-ray diffraction identification of the heat-treated samples showed the presence of GeTe crystallites [11].

The latent heats of the transformations may be found in Table 3. The latent heat of crystallization is 2–5 times smaller than that of melting.

Table 3

Latent heat ΔH in cal/g

Sample No.	Crystallization	Melting
1	−9.3	17.9
2	−6.3	20.9
3	−5.5	26.1
4	−7.7	19.9

The magnitude of ΔH_{Cr} is dependent on the amount of glass crystallized at T_{Cr} for a given scan rate. Studies by Quinn and Johnson [12] on bulk chalcogenide glasses have shown that crystallization nucleates at the surface, and therefore the surface-to-volume ratio must be important in the process of converting from a non-crystalline to a crystalline state.

We carried out a simple experiment to determine whether the samples melt in the temperature range investigated by us. The experimental setup can be seen in Fig. 3. Visual observation shows that sample 5 begins to melt at 570 K. At 700 K the sample takes on a completely spherical shape, which means that the solid material transformed to the liquid state in the temperature range 570 – 700 K. A similar phenomenon could be observed in the case of sample 6, where the melting interval was estimated as 580 – 720 K.

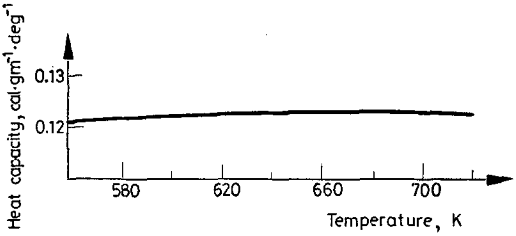

Fig. 4. Heat capacity of glassy $As_{40}Se_{50}Ge_{10}$ *vs.* temperature

Figure 4 proves that the samples show no significant thermal change (latent heat or heat capacity maximum) during melting. If there is any thermal anomaly, the associated energy must be smaller than the sensitivity of our instrument, i.e. less than 10^{-3} times the latent heat of melting observed with the crystalline material.

There is a structural difference between the thermal properties of samples 1 – 4 and samples 5 and 6. The first group can be characterized as "simple molecular

Table 4

Numerical values of the glass-forming tendency

Sample No.	K_{gl}
1	0.36
2	0.20
3	0.19
4	0.31

where $K_{gl} = \dfrac{T_{Cr_1} - T_g}{T_m - T_{Cr_1}}$.

glass forms" [13]. The numerical values of K_{gl} characteristic of the glass-forming tendency [14] are less than 0.4 (see Table 4); the glasses are therefore metastable and easily transform to the crystalline modification upon heating to the crystallization temperature.

Samples 5 and 6 have a high molecular polymer character [15, 16]. The glass is the most stable state of the substance. It is supposed that the temperature-dependence of the viscosity of the polymer glass form results in the absence of crystallization and melting effects.

The relationships between the thermodynamic data and the viscoelastic and dielectric properties are being studied further.

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Résumé — On a étudié au voisinage de la température de la transition vitreuse la variation de chaleur spécifique en fonction de la température pour différents verres à base de chalcogénures de Te et As, en mesurant la chaleur latente de fusion et de cristallisation. Pour les alliages à base d'arsenic on n'a pas détecté de changement thermique après la transformation de l'état solide à l'état liquide.

Zusammenfassung — Die Temperaturabhängigkeit der spezifischen Wärme verschiedener Te- und As-Chalkogenid Gläser wurde in der Nähe der Glastemperatur untersucht, indem die latente Schmelzwärme und die Kristallisation gemessen wurden. Bei den Legierungen auf As-Basis konnte nach dem Übergang von dem festen in den flüssigen Zustand keine thermische Veränderung nachgewiesen werden.

Резюме — Исследована температурная зависимость удельной теплоемкости нескольких халькогенидных стекол на основе Te и As около температуры стеклования. Для первого из двух сплавов была измерена скрытая теплота плавления и кристаллизации. Для халькогенидного стекла на основе As не было обнаружено термического изменения при переходе из твердого в жидкое состояние.