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DSC INVESTIGATION OF VITREOUS SELENIUM IN THE GLASS TRANSITION REGION

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The present paper describes the experimentally observed changes in the glass transition temperature T_g and the corresponding endothermic effect of a glassy Se with annealing at 10°. The changes were observed by the DSC method. During the annealing process the values of T_g and ΔH increase by 10° and 3 J/g, respectively, in comparison to the values of the samples as prepared. Both ΔH and T_g depend upon the scanning speed in the DSC measurements. The glass transition temperature as a function of heating rate a fits well the relation $1/T_g = C_1 - C_2 \ln a$; on the other hand, the value of ΔH with decreasing heating rate approaches zero (disappears).

Recently, much attention has been paid to the processes connected with changes of some physical parameters within the transformation region of glassy selenium [1–5], as well as some multicomponent chalcogenide glasses [6–11]. The results of these investigations are related to the previous time–temperature history of the glasses. Therefore, these results are of some practical use when dealing with operation of electronic and electronic-optical devices built from these glasses. In these investigations, the non-isothermal techniques are very useful and effective for measurement of various physical and, especially, thermophysical parameters. However, when interpreting the results of the non-isothermal measurements in the case of glassy materials, the possibility of temperature gradient formation (due to the low value of thermal conductivity) as well as the influence of the heating rate should be considered. These two factors seem to be especially important in the glass transition region. Because of various interpretations of effects within the glass transition region in glassy selenium, in our work we have concentrated on the experimental investigation of the influence of the kinetics of semi-micro-DSC measurements on the changes in glass transition temperature T_g and the corresponding endothermic effect (at temperature T_g).

Experimental

In the preparation of glassy selenium, highly-pure selenium in the form of pellets (99.9998%, produced by Koch Light Lab., Ltd.) was used as starting material. Small amounts of the selenium were put in quartz containers with a diameter of 2 mm and then evacuated to 2×10^{-5} torr. At this pressure the containers were sealed off and were then placed in an oven at 530° for two hours. Thereafter, the containers were quenched in water at 0°, in liquid nitrogen, and eventually were cooled by programme at a rate of 10°/min.

A commercial differential scanning calorimeter (Du Pont 900 Thermal Analyzer) was used in all DSC measurements. Applying this instrument, it was possible to use amounts of samples that were close to the semi-micro-DSC with the scanning speed ranging from 0.5°/min to 30°/min. The temperature scale was calibrated by means of the NBC-ICTA standard reference materials. The calibration coefficient for enthalpic measurements was determined from the heats of fusion of Ga and In, as well as from the measurement of the temperature-dependence of the specific heat in sapphire. In order to eliminate the possible "crucible effect", the powdered samples of glassy selenium were placed in suitable quartz pans. The empty quartz pan served as the reference material. The measurements were performed in argon.

The specimens were annealed for various times at 10 ± 0.5° in air and at 2×10^{-5} torr.

Results and discussion

In Figure 1 the DSC curves of glassy selenium samples within the transformation region are shown as a function of the annealing periods at 10°. The onset of the glass transition, defined in our work by the glass transition temperature T_g, occurs at 38° in a sample analyzed immediately after preparation. This sample is also characterized by a very small value of the endotherm enthalpy difference at T_g: $\Delta H \sim 2$ J/g.

From Fig. 1 one can see that the increasing annealing time is caused by two principal effects observable by the DSC method: a shift of the extrapolated temperature T_g to some higher value and the increase of enthalpy ΔH. Both these parameters, T_g and ΔH, relax during the annealing process to the saturated values $T_g = 48°$ and $\Delta H \sim 5$ J/g (Fig. 2). The maximum differences observed are 10° in the value of the transformation temperature and 3 J/g for the enthalpy.

In further work, we investigated the dependence of the relaxation properties of the parameters T_g and ΔH on factors that can substantially influence the structure of glassy selenium. It is known that by quenching melted selenium with various starting temperatures, it is possible to obtain glassy Se in which different proportions of built-up structural elements (polymeric chains and eightfold rings of Se atoms) are present. In the preparation of glassy Se we therefore varied the starting temperature of the liquid Se within the temperature range from 280° to 620°. Further, three cooling rates were employed (~100°/sec, ~1°/sec, and 10°/min). The samples of glassy Se were thermally worked up in various atmospheres. Both cooling rate and atmosphere drastically change the transport parameters of glassy Se [12, 13]. However, none of the above-mentioned factors substantially influence the relaxation character of either T_g or ΔH.

From the viewpoint of thermal analysis (i.e. a measurement under non-isothermal conditions), as a result of the annealing process a wide endothermic effect at T_g is demonstrated. It follows from the literature (there are some exceptions [3]) that the quasi-stationary measurements of thermophysical parameters (in contrast

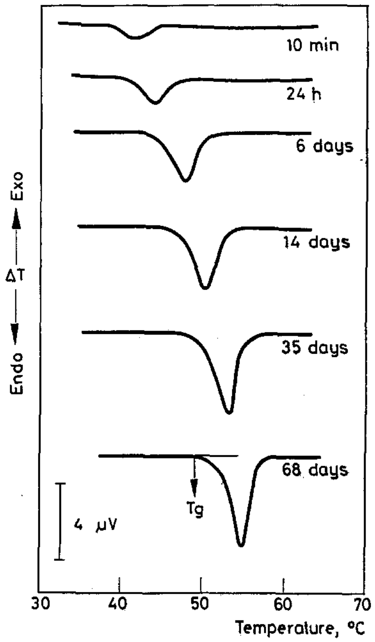

Fig. 1. Variation of DTA traces in the glass transition region for different annealing times at 01°. Heating rate: 10°/min; atmosphere: air

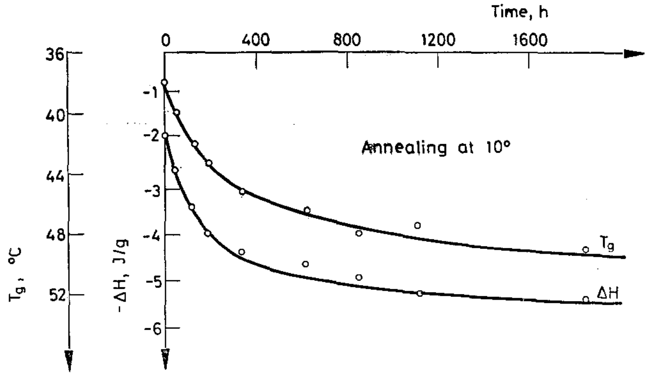

Fig. 2. Change in the glass transition temperature and in the endotherm enthalpy difference at T_g during annealing

with the dynamic, non-isothermal measurements) are not characterized by anomalies in their temperature-dependences (called "spurious maximum"by Moynihan and Schnaus). Therefore, our further investigations were directed towards a detailed kinetic study of a glassy Se that was characterized by saturated values of T_g and ΔH, i.e. it was minimal-annealed for 2 000 hours at 10°. The analysis that employs the DSC method shows two basic effects in such a well-annealed glassy Se:

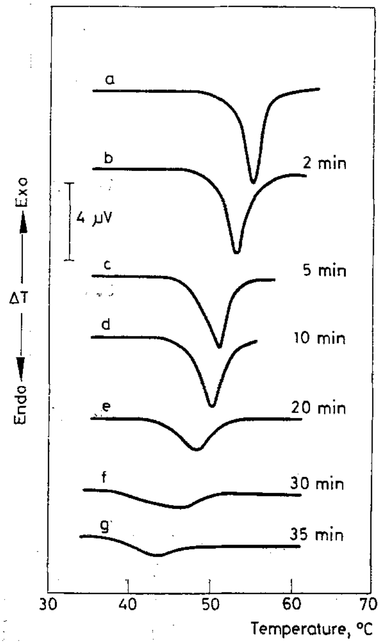

Fig. 3. a: DTA trace of the sample with saturated ΔH and T_g.b—g: DTA traces of this sample as a function of the annealing time at 40°. Atmosphere: air; heating rate: 10°/min

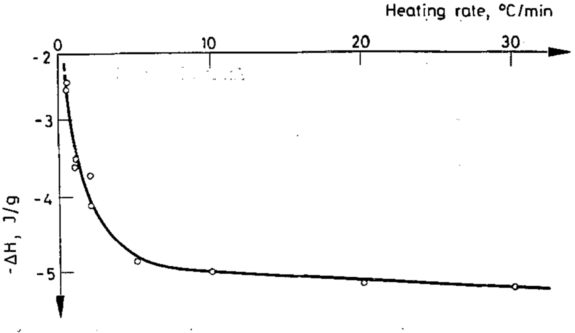

Fig. 4. Plot of endotherm enthalpy difference at T_g as a function of the heating rate

1. Gradual decrease of values of the parameters T_g and ΔH during further heat-treatment at temperatures higher than 30°. This is illustrated in Fig. 3, where a decrease of T_g and ΔH values during heat-treatment at 40° is shown. After a few minutes the samples are characterized by almost the same values as those immediately after preparation (Fig. 1).

2. Dependence of the effect at glass transition on the heating rate. The changes in ΔH and T_g due to some varying of the heating rate within the range 0.5°/min to 30°/min are shown in Figs 4 and 5.

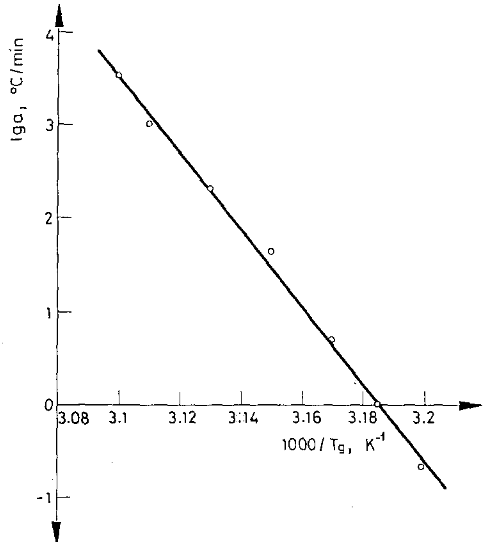

Fig. 5. A plot of ln a versus $1/T_g$

The glass transition temperature as a function of the sample heating rate a can be well extrapolated by the relation [17]

$$\frac{1}{T_g} = C_1 - C_2 \lg a$$

where the constants $C_1 = 3.08 \times 10^{-3}\ K^{-1}$ and $C_2 = 2.38 \times 10^{-5}\ K^{-1}$ were determined using the plot $1/T_g$ vs. lg a according to Fig. 5.

The decrease of the endotherm enthalpy difference at T_g with decreasing heating rate (Fig. 4) confirms that the observed endothermic effect is dependent on the applied non-isothermal measurement technique. Therefore, one can expect that at extremely small heating rates or in a quasi-isothermal measuring regime, respectively, the enthalpic effects at T_g disappear.

Thus, the existence of the glass transition endothermic effect according to our results can not be related to the structural changes formed in the annealing process [1]. The first stage in such a structural change in glassy Se (depolymerization of long Se chains) would be necessarily accompanied by some decrease of T_g according to the relation [14]:

$$T_g = T_g^{\infty} + \frac{A}{M}$$

where T_g^{∞} denotes the transition temperature for a polymer with infinitely long chain, A is a negative constant, and M is the molecular weight.

There are some other factors that may be considered in relation to the existence and the course of the glass transition endotherm during the annealing process, e.g. change in the local strain field, packing density [3], phase separation [15], decrease in the specific volume, fictive temperature and, especially, decrease in the molecular mobility [16], etc. Of course, the thermal measurements alone can not give an unambiguous decision about the mechanism. However, it seems to us to be very likely that the observed thermal effects in the range of T_g of glassy Se are due to the molecular mobility of the individual chain atoms and the free rotation of the chain segments. Therefore, the corresponding non-isothermal measurement with a properly chosen heating rate of the sample causes the formation of the "spurious maxima" just above the temperature T_g. On the basis of these ideas, the time development of the annealing effect follows the corresponding changes in molecular mobility.

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RÉSUMÉ — L'article décrit les variations observées expérimentalement par analyse calorimétrique différentielle (DSC) pour la température T_g de la transition vitreuse d'un Se vitreux recuit à la température de 10°, et pour l'effet endothermique correspondant. Pendant le recuit les valeurs de T_g et de ΔH augmentent respectivement de 10° et de 3 $J.g^{-1}$ par rapport aux valeurs des échantillons bruts de préparation. Les valeurs de ΔH et de T_g dépendent toutes deux de la vitesse de chauffage. La température de la transition vitreuse peut être représentée en fonction de la vitesse de chauffage a par l'équation $1/T_g = C_1 - C_2 \ln a$; d'autre part, la valeur de ΔH tend vers zéro lorsque la vitesse de chauffage diminue.

ZUSAMMENFASSUNG — Es werden die auf dem Versuchswege ermittelten Änderungen der Glas-Übergangstemperatur T_g und der entsprechende endotherme Effekt eines glasförmigen Se mit Mattätzung bei einer Temperatur von 10° beschrieben. Die Änderungen wurden mittels der DSC-Methode beobachtet. Während des Mattätzungsvorganges steigen die Werte von T_g und ΔH um 10° bzw. 3 J/g im Vergleich zu den Werten der ursprünglichen Proben. Sowohl ΔH wie T_g hängen von der Abtastgeschwindigkeit bei der DSC-Messung ab. Die Glas-Übergangstemperatur als Funktion der Aufheizgeschwindigkeit a kann mit der Gleichung $1/T_g = C_1 - C_2 \ln a$ gut beschrieben werden; andererseits nähert sich ΔH mit abnehmenden Aufheizgeschwindigkeiten dem Nullwert (verschwindet).

Резюме — Описаны экспериментально наблюдаемые изменения температуры перехода T_g в стекле и соответствующий эндотермический эффект стекловидного селена с отжигом при температуре Т = 10°. Эти изменения наблюдали с помощью метода дифференциальной сканируюущей калориметрии (ДСК). В процессе отжига значения T_g и ΔH увеличиваются соответственно на 10° и 3 дж/г по сравнению с значениями для исходных образцов. Обе величины ΔH и T_g зависят от скорости сканирования при ДСК измерениях. Температура разиягчемия стекла, как функция скорости нагрева a, хорошо описывается уравнением $1/T_g = C_1 — C_2, \ln a$. Однако, с другой стороны, значение ΔH с уменьшением скорости нагрева приближается к нулю (исчезает).