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STUDIES ON THE THERMAL CHARACTERIZATION OF VITREOUS CHALCOGENIDES

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The special position occupied by glasses amongst solids is again underlined by their thermal behaviour. This feature was studied using As_2Se_3 as model glass. The range of transformation characteristic of glass is less sharply defined than the freezing point. In the thermal characterization of glass the former is highly dependent on the rate of heating and the thermal history of the glass. The recrystallization and melting temperatures are subject to corresponding modifications.

The temperature of transformation is independent of grain size; the tendency to recrystallize however, increases with decreasing grain size and is displaced toward lower temperatures. Measurements obtained in thermal studies within the range of transformation are strictly reversible if the amorphous state is maintained. Comparative dilatometric measurements showed full agreement with the results obtained in the range of transformation of the glasses.

It is pertinent to explain briefly the glass formation process to understand the special problems of thermal investigations into glasses.

The classic formation process of vitreous solids is freezing a melt; hence the process is to be interpreted from the viewpoint of Frenkel's model of liquids. According to the model the near-order ranges of the melt have a dynamic arrangement and reorient steadily with regard to the excited degrees of freedom of the kinetic and potential energy. If the temperature falls steadily a corresponding energy distribution among all the degrees of freedom will occur.

The graph of the change of state connected with the temperature decrease can be seen in Figure 1; the change of state is expressed by the enthalpy function H or by volum V, respectively. The amount of the enthalpy decrease is ΔH at the crystallization point (T_s). In the further course the dependence of the enthalpy of the crystalline solid upon the temperature is illustrated. However, the crystallization may not occur because of inhibitions during the nucleation or during the growth of the new phase, respectively. Then the metastable range of the supercooled melt will be reached. The establishment of the equilibrium cannot follow the speed of the temperature fall below a point called T_E due to a high value of viscosity, which is resulting in the vitreous state. Thermodynamic transformations of the first order are missing in the range of T_E (freezing point). Hence it is also wrong to speak of a transformation point for more exact measurements revealed a wider transformation range again and again. For example, on heating the volume follows the course of the curve of the supercooled melt up to a point beyond the freezing point, where the volume will undergo a larger change within a certain temperature range and arrive at the range of the metastable equilibrium. Thus we

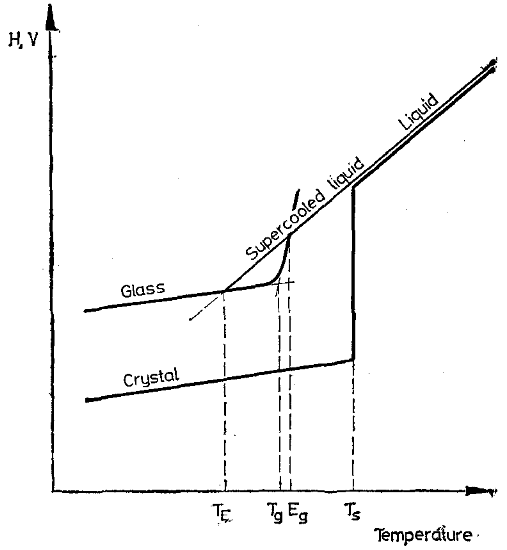

Fig. 1. Change of state of glasses with the temperature

obtain the T_g in shape of a discontinuity of the curve, which was already explained by Rötger [1] as a retardation effect. After passing the transformation the heating curve join the line of metastable equilibrium at the "junction temperature" E_g [2].

The T_g is less sharply defined than the freezing point and is to be found at a higher temperature. It is therefore strongly dependent upon the heating rate.

Experimental

Heat effects during thermal investigations in the transformation range are relatively small. Special care therefore must be practised in recording and utilizing these small heat effects reproducibly. The sample holder must have a maximal symmetry as it is an absolute premise for investigations of smallest heat effects with highly sensitive detection equipment.

These investigations have been carried out in an appropriate cylindrical silverbar with three symmetrical wells for the thermocouples and samples. The sample holes are coated with asbestos paper for preventing a heat transfer from the sample to sample holder. The sample holder has been closed with a lidwode from same material. To attain a favourable signal to underground response as prerequisite to registring these small heat-effects, recording of the thermoelectric voltage has been carried out with a light-spot follower recorder from Sefram (Paris).

As_2Se_3 was used as a model glass. The compound has a planar structure. It seems to be especially suitable, because it can be regarded as an intermediate compound, as to structure, between the predominantly linear organic polymers and the space lattice structure of silicate glasses.

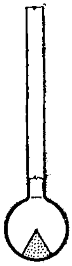

Fig. 2

The vitreous As_2Se_3 was prepared by weighting the 99.999 per cent pure elements of As and Se according to the composition in quartz ampoules, which were again and again evacuated, filled with inert gas (N_2) and finally closed in vacuo. This procedure was followed by melting for 8 hours at 700°. Then they were quenched in icewater or in air.

Afterwards 1/2000 mol of the pulverized glass sample was measured in a closed thinwall Rasothermglas ampoule (Fig. 2) filled with inert gas [3, 4].

Optimal heating rates

According to the previously explained special thermodynamic relations in glasses the temperature of characteristic effects depends greatly on the heating rate.

As mentioned above, the transformation range is obtained in form of a retardation effect, as Rötger [1] called it, resulting in a discontinuity in the graph being in shape and location markedly dependent upon the rate of heating.

Glass samples of uniform compositions, heat histories, and grain sizes were measured in order to clarify the existing relations. The sample quantity of 193 mg is relatively high compared with the international trend towards lesser amounts, but we had to make use of quantities like this because of the procedure necessarily connected with chalcogenide glasses in the ampoules due to the small heat-changes in the range of transformation.

In Fig. 3 we see the effect of heating rate on the important changes, based on many measurements. The shift of the temperatures of the characteristic ranges towards higher temperatures as the heating rate increases is obvious. The transformation range is more and more enlarged, and the maximum seems also to be shifted towards a higher temperature. The result underlines again the existence of the retarding effect occurring in the transformation range of glasses. The lowest heating rates used during the investigation (1.7, 3.5, and 5° per minute) resulted in shifts of 3 and 5°, respectively, towards higher temperatures in the transformation range of the glasses. However, the shift was more than 20°, when the heating rate was 10° per minute.

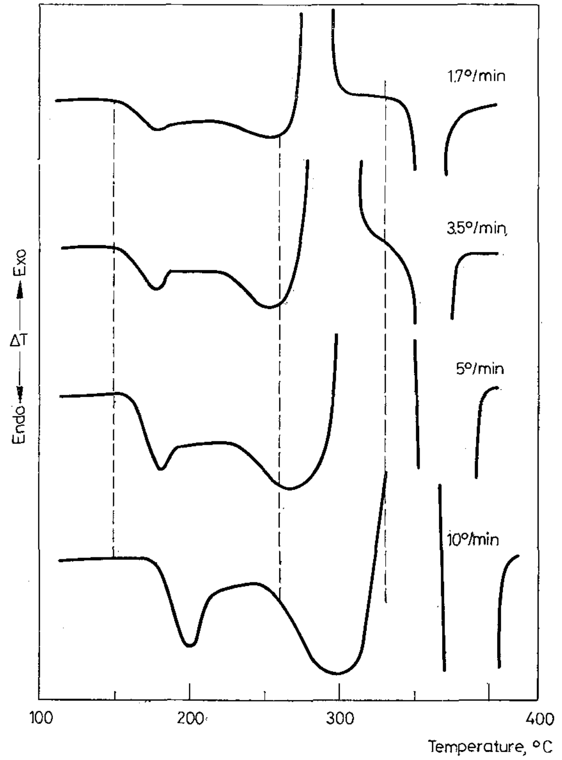

Fig. 3. DTA curves in function of the heating rate

The statements concerning the recrystallization temperature and the trend of recrystallization of glasses will change in the same way. An unrealistic assessment of the stability of corresponding glasses will be gained if too high heating rates are applied. Furthermore, considerable difficulties in the determination of melting points will occur, because the recrystallization of many glasses takes place within a relatively narrow temperature range below the melting point, and because a distinct separation of both effects is no longer possible at too high heating rates.

As a result of this investigation we recommend heating rates of 2 to 4° per minute, which we use successfully.

Thus the special thermodynamic situation with glasses is recognized and unduly great superheating effects are avoided. At the same time it is possible to evaluate reasonably the transformation ranges. Furthermore, suitable values of temperature are gained, permitting a realistic statement on the stability of glasses. In recent years we have found heating rates in the literature concerning thermal investigations into glasses that confirm our view.

The optimal grain size

The influence of the grain size on the DTA-curves of crystalline substances was thoroughly investigated. Except the general statement of a variable heat transport depending upon the grain size, in case of glasses no exact values were available. Measurements with compact samples are only possible in special measuring arrangements [5] according to the DTA principle. Owing to the condi-

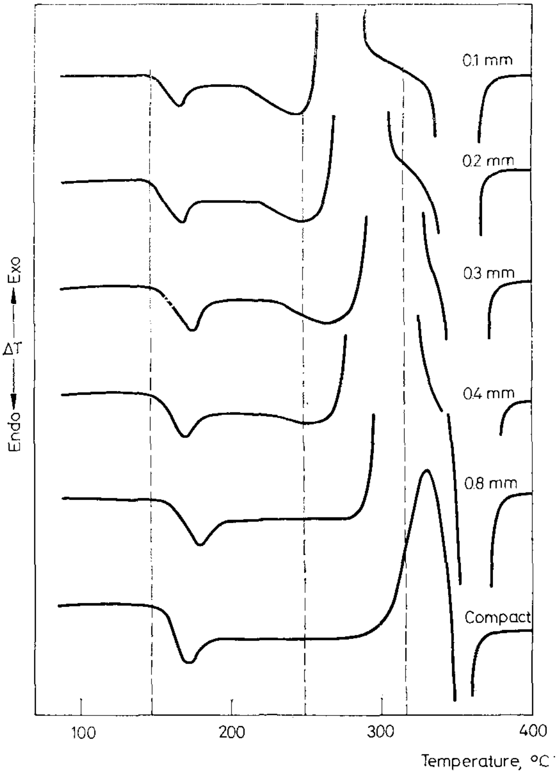

Fig. 4. DTA curves in function of the grain size

tions of preparation of glasses always larger compact pieces are obtained, which can only be measured in a finely powdered state.

The necessary pulverizing of glasses, however, leads to the formation of crystal nuclei, and thus influences the trend of recrystallization during the thermal investigation of glasses. The investigation was done with samples of the model glass with uniform heat histories at the heating rate of 3° per minute. The samples of different grain sizes were obtained by pulverizing the compact glass samples and passing them through sieves of different mesh apertures.

The results of the investigation are shown in Fig. 4. The measurements of samples of the grain sizes 0.1, 0.22, 0.28, 0.40, 0.75 mm are compared with the measurements of compact samples. The location of the temperature and the shape of the transformation range are not influenced by the grain size of the sample. However, as the grain size increases the trend of recrystallization decreases. The temperature of the beginning of recrystallization was maximally shifted by 35° compared with the compact sample.

The rise of the melting point results inevitably from the immediate connection of the recrystallization process with the subsequent melting of the model substance. The samples of the smallest grain size have a distinctly endothermic effect before the recrystallization takes place. The effect fades as the grain size increases. It is no longer perceptible at the grain size of 0.5 mm. The effect is the result of the change of the thermal conductivity of the sample due to sintering.

To summarize the results, it must be pointed out that some difficulties are involved in measuring compact samples. Bad thermal contact originates from the generally different expanding behaviour of the glasses compared with metallic sample vessels. The determination of the optimal grain size for DTA investigation into glasses aims at conditions being similar to the practical conditions under which glasses are used. On the basis of this investigation the grain size of 0.5 mm ± 0.1 mm seems still to meet the requirements.

Changes in thermal effects depending on the heat histories of the investigated glasses

The heat histories of glasses have a considerable effect on their properties.

Rötger [1] proved the considerable shift of the transformation range towards lower temperatures due to increasing cooling rates when preparing glasses. DTA investigations into glasses confirmed repeatedly Rötger's statement. Furthermore Yamamoto [6] drew attention to the occurrence of further effects in the DTA curves of differently cooled borosilicate glasses. The results of our investigation into the explained model glasses are shown in Fig. 5; the condition earlier described were used. An exothermic effect before the transformation range of the glasses must be pointed out. The quicker the cooling takes place, the greater is the effect. The effect arises from the amount of heat liberated by the glass relaxation. It complicates considerably a definite temperature determination of the transformation range. Therefore exact measurements are only possible with well annealed glasses.

Furthermore, the change of the transformation range towards a higher temperature is to be seen. At the same time a growing enthalpy effect occurs at the end of the transformation range. The latter peak is owing to the increasing stability of the glasses resulting in more effective relaxation phenomena in this dynamic investigation into glasses. Corresponding observations could also be made in case of analogously annealed glasses.

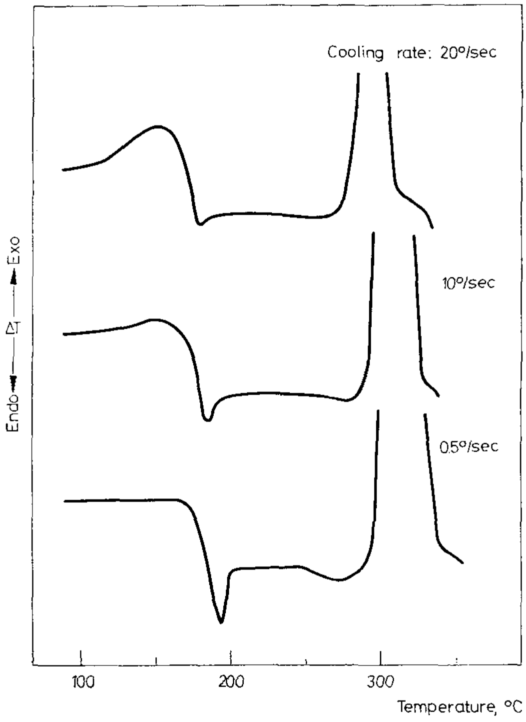

Fig. 5. DTA curves in function of the heat histories

To summarize it can be stated that the running down stabilizing process in the glass is evident in the DTA curves. The process originates from the different cooling rates involved in preparing glasses or subsequent heat treatment of the glasses.

If the glasses are extremely quenched, however, considerable difficulties may occur in evaluating the results.

Reversibility of the thermal investigations

The occurrence of the transformation range can be observed even if the sample is repeatedly heated, provided that during the heating process the vitreous state is kept up to beyond the transformation range and recrystallization does not happen in subsequent cooling. The process is reversible till recrystallization occurs. Some of such reversible measurements are illustrated in Fig. 6. The previously described shift of the transformation range can be observed because of the repeated heating and cooling processes representing an annealing process of the glasses at the same time. Generally a diminution of the difference of the basis lines before and after the transformation range occurs at the same time, because, owing to the proceeding disorder-order processes, a diminution of the Δc_p of the frozen undercooled liquid (disequilibrium) occurs, compared with the metastable equilibrium of the undercooled liquid.

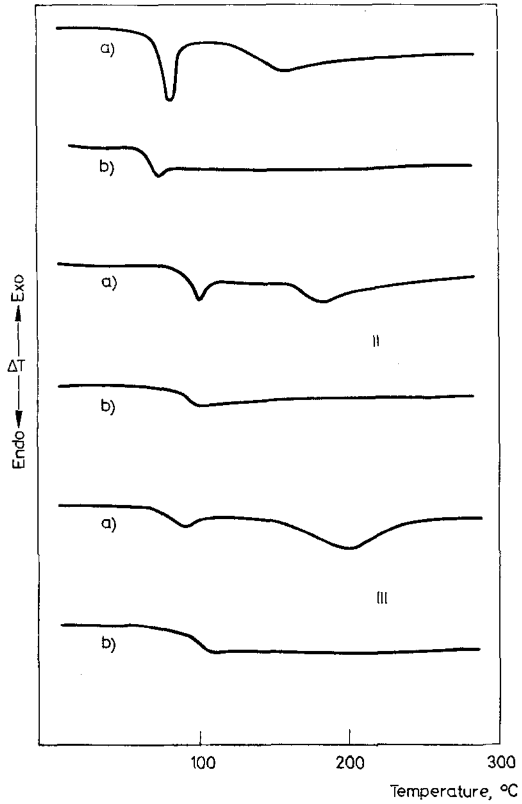

Fig. 6. DTA curves taken with repeated heating (b) and original tests (a)

It is of special interest to point out the second endothermic effect occurring in the original curves seen in the picture. According to the theory of the separation of glasses two glass phases must exist. The second endothermic effect should therefore be due to the transformation range of the second glass. Actually, possibilities like this do exist, although they are very rare. They should also occur in repeated heating processes according to the above described reversibility of the thermal measurements in the transformation range.

The measurement results shown in the figure reveal without doubt the non-existence of that second effect in repeated measurements. Hence the effect has to be assigned to the heat-consuming sintering process or to the "melting-down" of the non-crystallizing glasses, respectively. The samples were already completely compact after the first measurements, that is, the original grains could not be recognized.

Thus it was again confirmed that reproducibility and reversibility of the measurement results must be proved in any case.

Confirmation of the measurement results by applying a further method

The transformation range of the glasses can also be determined by means of dilatometric measurements.

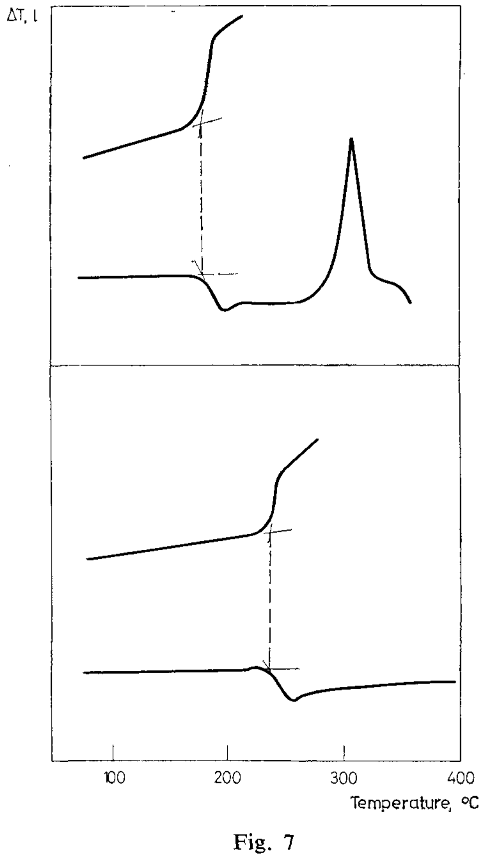

Fig. 7

The dilatometric measurements were carried out completely without touch with the help of an interference dilatometer; the samples had the length of 10 mm.

For the purpose of comparative measurements the glasses underwent both DTA and interference-dilatometric treatment at the same heating rates.

It is evident from Fig. 7 that the dilatometrically determined T_g-temperatures are in complete agreement with the correspondent temperatures in the DTA curves.

Keeping the special problems of the vitreous state in mind (Fig. 1) we can conclude from the measurement results that the DTA is a very suitable tool to investigate into glasses.

Conclusions

According to the special thermodynamic relations in glasses the thermal characterization is connected with special problems. Investigations on a typical model for vitreous chalcogenides suggest following assertions:

1. The temperature of transformation and recrystallization to a high degree is dependent on the heating rate. For interest to a realistic assessment of the stability of glasses heating rates of 2 – 4° per minute are recommended.
2. Actually the transformation range is not essentially influenced by the grain size, but the tendency of recrystallization is stronger with decreasing grain size. The grain size of 0.5 mm seems to meet the best requirements.
3. In consequence of the considerable dependence of the results on the thermal history of glasses, only measurements with well annealed samples are recommended.
4. Besides the observed reversible thermal effects of transformation range, additional irreversible processes are indicated by thermal investigations.

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Zusammenfassung — Die Sonderstellung der Gläser unter den Festkörpern wird auch durch ihr thermisches Verhalten besonders unterstrichen. Diese Besonderheiten wurden an einem Modellglas (As_2Se_3) untersucht. Der für die Gläser charakteristischen Transformationsbereich ist weniger scharf definiert als die Einfriertemperatur. Er ist bei der thermischen Charakterisierung der Gläser stark von der Aufheizgeschwindigkeit und der thermischen Vorgeschichte der Gläser abhängig. Entsprechenden Veränderungen unterliegen auch die Rekristallisations- und Schmelztemperaturen.

Unverändert bleibt die Transformationstemperatur bei wechselnder Korngröße; jedoch wird die Rekristallisationsneigung mit abnehmender Korngröße stärker ausgeprägt und nach niederen Temperaturen verschoben. Die thermischen Untersuchungen im Transformationsbereich sind bei Erhaltung des amorphen Zustandes streng reversibel.

Vergleichende dilatometrische Messungen zeigten eine völlige Übereinstimmung der Meßergebnisse im Transformationsbereich der Gläser.

RÉSUMÉ — La position particulière qu'occupent les verres parmi les corps solides est mise en relief par leur comportement thermique. Pour cette étude, on a choisi comme verre modèle (As_2Se_3). Pour les verres, l'intervalle de transformation est moins bien défini que leurs températures de solidification. Il dépend en effet fortement de la vitesse de chauffage et du traitement thermique préalable de même que les températures de recristallisation et de fusion.

La température de transformation n'est pas affectée par les variations de dimension des grains. La tendance à la recristallisation devient plus forte cependant quand la dimension des grains diminue et elle se déplace vers les températures plus faibles. Les réactions thermiques sont, dans l'intervalle des transformations et en maintenant l'état amorphe, strictement réversibles.

Des mesures dilatométriques comparées ont montré une concordance complète avec ces résultats dans l'intervalle de transformation des verres.

Резюме — Особое положение, занимаемое стеклами среди твердых тел, снова подчеркивается их термическим поведением. Эти свойства были изучены на примере As_2Se_3 в качестве модельного соединения. Область трансформационной характеристики стекла менее резко очерчена, чем точка замерзания. В термической характеристике стекла первый фактор в значительной степени зависит от скорости нагрева и термического поисхождения стекла. Температуры рекристаллизации и плавления подвергаются соответствующим изменениям. Температура превращения не зависит от размеров зерен. Однако, тенденция к рекристаллизации увеличивается с уменьшением размера зерен и смещается в сторону более низких температур. Величины, полученные при термическом исследовании в пределах области превращения, строго обратимы, если сохраняется аморфное состояние. Сравнительные дилатометрические измерения показали полное согласие с результатами, полученными в области превращения этих стекол.