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GLASS TRANSITION AND CRYSTALLIZATION EFFECTS DEMONSTRATED BY THERMAL ANALYSIS OF LIQUID-QUENCHED TERNARY GLASSES $Te_{80}Ge_{20-x}A^{V}_{x}$ (A^{V} = Sb, Bi)*

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In DSC studies of liquid-quenched ternary chalcogenide glasses $Te_{80}Ge_{20-x}A^{V}_{x}$ (A^{V} = Sb, Bi), the characteristic temperatures (glass transition and crystallization temperatures) were determined. Changes in the thermal stabilities of these glasses, depending on the element A (Sb, Bi) from group V of the periodic table and on its content in the alloy were evaluated. Moreover, the effect of changes in the glass composition on the glass formation ability expressed by the parameter K_{gl} was determined.

Preliminary studies of non-crystalline materials usually deal with glass state formation and thermal stability. For this purpose the glass transition temperature (T_g) and the crystallization temperature (T_x) are determined by differential thermal analysis. Recently the results of thermal analysis of liquid-quenched chalcogenide glasses belonging to the ternary Te-rich systems $Te-Ge-A^{IV}$ (A^{IV} = Sn, Pb) have been reported [1, 2]. The present studies concern Te-rich glassy alloys in which the element A^{V} is from group V of the periodic table (Sb, Bi). Differential scanning calorimetry studies of liquid-quenched ternary glasses $Te_{80}Ge_{20-x}A^{V}_{x}$ (A^{V} = Sb, Bi; x-at. % of A^{V}) were carried out.

Experimental

Alloys were prepared using high-purity components: Te-5N5 (VEB Halbleiterwerke, Frankfurt/Oder, GDR), Ge-6N and Sb-5N (Aluminium Foundry, Skawina, Poland), and Bi-5N (Koch-Light Laboratories, England). The components were weighed and sealed in silica ampoules after evacuation of air. The ampoules were then placed in a resistance furnace, where the components were melted with shaking at 900 K during 30 min. Subsequently the ampoules were cooled in air.

Non-crystalline samples for calorimetric studies were obtained by splat-cooling of the liquid alloy by the "gun" method (cooling rate 10^6-10^9 deg/s). The initial crystalline alloy (1–2 mg) was melted in a ceramic crucible placed in a resistance furnace heated to about 200 deg above the melting temperature of the alloy. Subsequently the alloy was blown out from the crucible with argon (pressure 12 atm) onto a copper plate cooled with liquid nitrogen.

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Calorimetric investigations were carried out in a Perkin-Elmer DSC-2 microcalorimeter with continuous heating, at heating rate $\beta = 20$ deg/min, sensitivity $\frac{dH}{dt} = 5$ mcal/s and sample mass $m = 10$ mg.

Temperatures of glass transition (T_g), crystallization onset (T_{x0}) and crystallization peak (T_{xp}) were read from the calorimetric curves. The bend in the DSC curve was interpreted as an effect of the glass transition, and the temperature of this transition was read at the inflection point of the curve. The temperature of crystallization onset (T_{x0}) was read at the intersection point of the base line and of the line tangential to the left side of the first crystallization peak. These temperatures were established from at least three DSC curves for each glass composition. The reproducibility of the results was better than 1 deg for T_g and 2 deg for T_{x0}.

Results

Figures 1 and 2 show fragments of the DSC curves representing the transition and crystallization effects in alloys $Te_{80}Ge_{20-x}Bi_x$ and $Te_{80}Ge_{20-x}Sb_x$. As concerns the bismuth-containing alloys, there is evidence of some thermal effects which can be attributed to the successive crystallization stages. The alloys containing Sb are characterized by only one distinct exothermic crystallization effect. Transition temperatures (T_g) and crystallization onset temperatures (T_{x0}) are shown in Fig. 3.

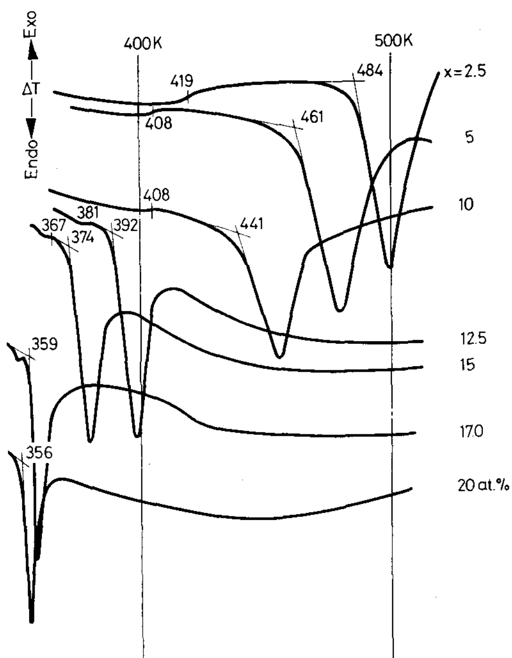

Fig. 1. Transition and crystallization effects in DSC curves for glassy alloys $Te_{80}Ge_{20-x}Bi_x$

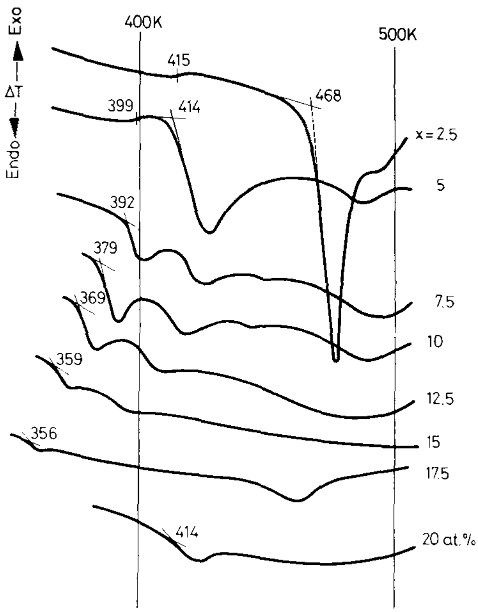

Fig. 2. Transition and crystallization effects in DSC curves for glassy alloys $Te_{80}Ge_{20-x}Sb_x$

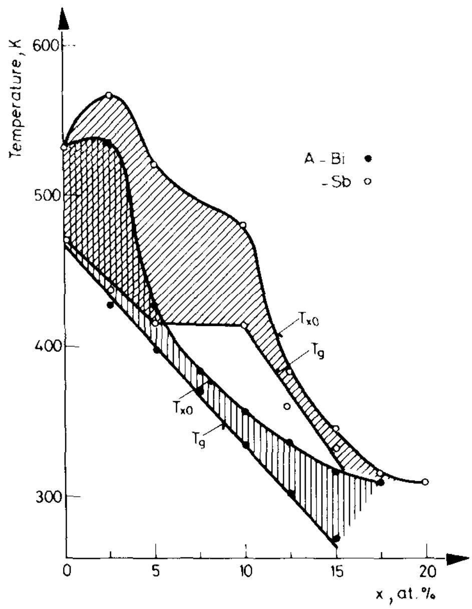

Fig. 3. Glass transition temperatures (T_g) and crystallization onset temperatures (T_{x0}) as functions of Bi and Sb contents for alloys $Te_{80}Ge_{20-x}Sb_x$ and $Te_{80}Ge_{20-x}Bi_x$

The hatched area represents the thermal stability region of the glassy alloys. The thermal stability expressed by the crystallization onset temperature T_{x0} reaches a maximum for both kinds of composition at 2.5 at.% of element A^V (Bi, Sb). Within the whole range of compositions, this stability is higher for $Te_{80}Ge_{20-x}Sb_x$ then for $Te_{80}Ge_{20-x}Bi_x$.

Discussion

Alloys of the Te – Ge binary system with a near-eutectic composition ($Te_{85}Ge_{15}$) were studied. Compositions of the investigated ternary alloys as well as the binary equilibrium diagrams of the component elements [3] are shown in Figs 4 and 5. Hruby's parameter K_{gl}, defined as $K_{gl} = \frac{T_{x0} - T_g}{T_m - T_{x0}}$ [4], is a coefficient describing the glass formation ability of the liquid-quenched alloy. The present results are comparable, because all measurements were taken at a constant heating rate (β = 20 deg/min). Figure 6 shows the changes in K_{gl} as functions of the changes in the bismuth or antimony contents. Parameter K_{gl} attains a maximum at 2.5 at.% of A^V (Bi, Sb) for both $Te_{80}Ge_{20-x}Bi_x$ and $Te_{80}Ge_{20-x}Sb_x$ alloys. This means that at such a content of A^V the glass formation ability is highest. Glass formation proceeds more easily for alloys containing Sb as compared with those containing Bi.

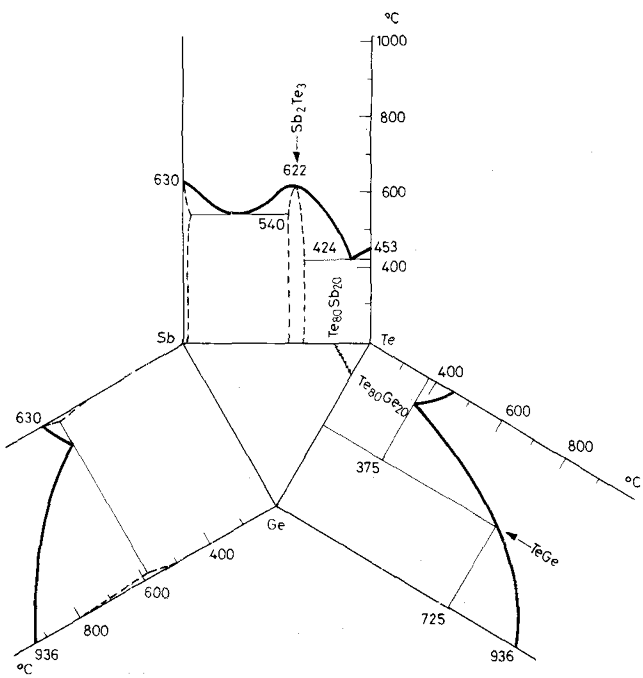

Fig. 4. Binary equilibrium diagrams [after [3]] and compositions of investigated ternary alloys Te-Ge-Sb

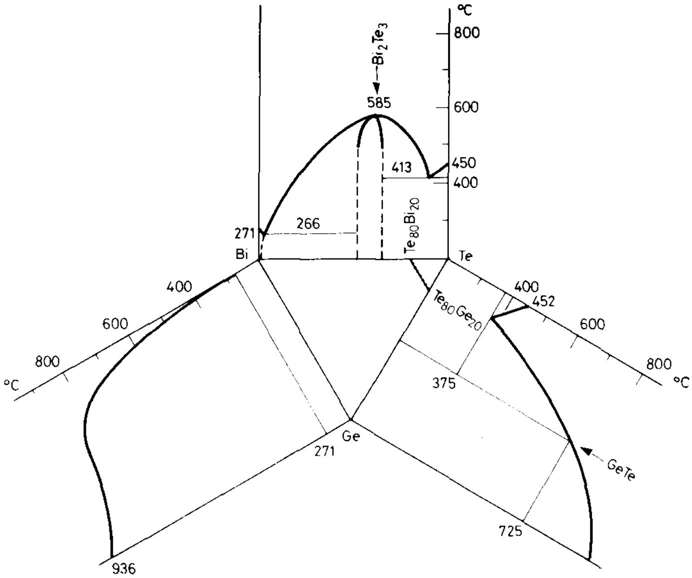

Fig. 5. Binary equilibrium diagrams [after [3]] and compositions of investigated ternary alloys Te-Ge-Bi

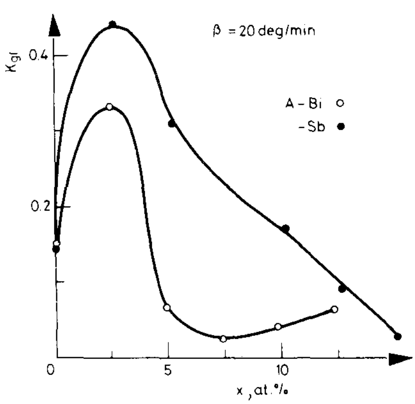

Fig. 6. The dependence of parameter K_{gl} on the alloy composition for alloys $Te_{80}Ge_{20-x}Sb_x$ and $Te_{80}Ge_{20-x}Bi_x$

Conclusions

1. Comparison of the thermal stabilities (described by the crystallization onset temperature, T_{x0}) of ternary liquid-quenched glasses $Te_{80}Ge_{20-x}Sb_x$ and $Te_{80}Ge_{20-x}Bi_x$ leads to the following conclusions:

a) the changes in the temperatures of the glass transition (T_g) and crystallization onset (T_{x0}), depending on the Sb or Bi contents, are different for the alloys, despite the similar stoichiometries of tellurides Bi_2Te_3 and Sb_2Te_3;

b) the thermal stability of the glassy alloy is higher in the presence of Sb, as compared with Bi;

c) the thermal stabilities of the alloys $Te_{80}Ge_{20-x}Bi_x$ and $Te_{80}Ge_{20-x}Sb_x$ are maximum at 2.5 at.% Bi or Sb.

2. The glass formation ability described by Hruby's parameter K_{gl} attains a maximum for both $Te_{80}Ge_{20-x}Sb_x$ and $Te_{80}Ge_{20-x}Bi_x$ at $x = 2.5$ at.% Bi or Sb.

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RÉSUMÉ — On a déterminé par analyse calorimétrique différentielle (DSC) les températures caractéristiques (températures de transition vitreuse et de cristallisation), des verres ternaires à chalcogénures formés par trempe à partir du liquide, du type $Te_{80}Ge_{20-x}A^V_x$ (A^V = Sb, Bi). On a évalué la variation de la stabilité thermique de ces verres en fonction de l'élément A (= Sb, Bi) du Vème groupe du tableau périodique et de sa teneur dans l'alliage. De plus, on a déterminé l'effet des variations de la composition du verre sur la capacité de formation du verre qui s'exprime par le paramètre K_{gl}.

ZUSAMMENFASSUNG — In DSC-Untersuchungen abgeschreckter ternärer Chalkogenidgläser des Typs $Te_{80}Ge_{20-x}A^V_x$ (A^x = Sb, Bi) wurden die charakteristischen Temperaturen (die Glas-Übergangs- und Kristallisationstemperaturen) bestimmt. Die Änderungen der Thermostabilität dieser Gläser wurden in Abhängigkeit von dem Element A (= Sb, Bi) aus der V Gruppe der Periodensystems und von seinem Gehalt in der Legierung ausgewertet. Ausserdem wurde der Einfluß der Änderungen in der Glaszusammensetzung auf die Glasbildungsfähigkeit, ausgedrückt durch den Parameter K_{gl}, bestimmt.

Резюме — При ДСК исследовании тройных халькогенидных стекол $Te_{80}Ge_{20-x}A^V_x$ (A^V=Sb, Bi), полученных резким охлаждением жидкостью, были определены температуры ст кло образования и температуры кристаллизации. Оценены изменения термической стабильности стекол в зависимости от элемена A (= Sb, Bi) в пятой группе периодической таблицы и его содержания в сплаве. Влияние изменений состава стекол на способность их к стеклообразованию, обозначаемое параметром K_{gl}, было определено.