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GLASS-FORMING ABILITY IN THE Ge–Sb–Te–Se QUATERNARY SYSTEM

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ABSTRACT

The glass-forming regions in the quaternary system Ge–Sb–Te–Se have been obtained for quenching in air and for a constant cooling rate of 5°C min^{-1}. The boundaries of the glass-forming regions and the thermal behaviour of the samples have been deduced from differential thermal analysis and X-ray diffraction. The results may be compared with some limited determinations of glass-forming ability in Te–Se, Ge–Te, Ge–Te–Se and Ge–Sb–Se systems, allowing for the fact that in the present work the experimental parameters for preparing and quenching the melts are identical for all the compositions studied. The formation and stability of glasses is discussed in terms of the obtained glass-forming regions and the observed thermal behaviour in differential thermal analysis measurements. Potential-device quality memory and switching compositions are suggested.

INTRODUCTION

The formation and stability of chalcogenide alloy glasses have been studied for a long time, and it is known that the glass-forming regions in multicomponent systems depend on the method of preparation.

In the present work, the glass-forming regions in the Ge–Sb–Te–Se system were deduced from differential thermal analysis (DTA) for both air-quenched and slowly-cooled (constant cooling rate = 5°C min^{-1}) melts. The vitreous regions were subdivided into several zones in an attempt to establish the glass-forming ability and stability in this system.

EXPERIMENTAL PROCEDURES

Samples of about 1 g were prepared by melting the required amounts of the elements of 5 N purity in evacuated (10^{-2} torr) and sealed quartz ampoules of 5 mm internal diameter and 1 mm thickness. The molten alloys were held at 1000 °C for 12 h, constantly agitated, and then quenched in air.

Differential thermal analysis was performed using a STA-429 Netzsch Thermal Analyzer, at a constant rate of 5 °C min^{-1}, on about 200 mg initially powdered samples in a dynamic argon atmosphere. On cooling, these samples from above the liquidus temperature, in the thermal analyzer we obtained the slowly cooled materials. The samples were referenced against carborundum.

CHARACTERIZATION OF GLASS-FORMING REGIONS BY DTA

The DTA curves shown in Figs. 1 and 2 represent the general types seen throughout the Ge–Sb–Te–Se quaternary system on heating and cooling, respectively. There are four different types of DTA curves on heating (Fig. 1). The first DTA curve (a) is typical of glasses which do not crystallize on heating but go continuously from glass to liquid and show only the glass transition at T_g. The two following DTA curves (b) and (c) show also recrystallization at T_c and melting at T_m. The difference between these DTA curves is that in the first one (b) the heat evolved in recrystallization is approximately the same as that of melting, whilst in the second one (c) it is much lower. This difference suggests that in the first case the sample was glassy before heating and that in the second case it was partially crystalline. Since the thermal behaviour varies rather continuously[1] with composition on going through the boundaries, the glassy or partially crystalline samples were characterized by X-ray diffraction. The last DTA curve (d) is typical of crystalline samples and shows only the melting transformation. On cooling, we obtained three different types of DTA curves (Fig. 2). The first DTA curve (e) corresponds to liquids for which the viscosity is very high and correspondingly a cooling rate of 5 °C min^{-1} is sufficient for bypassing

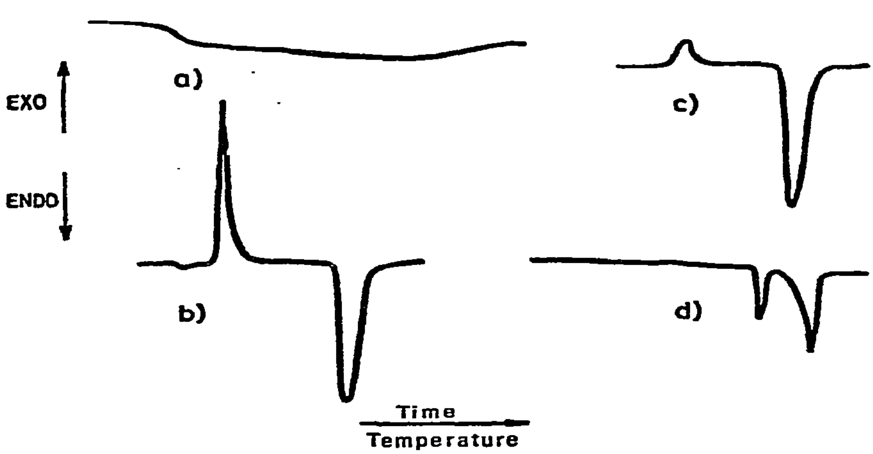

Fig. 1. Typical heating DTA curves of: (a) glasses without recrystallization; (b) glasses with recrystallization; (c) partially crystalline samples, and (d) crystalline samples.

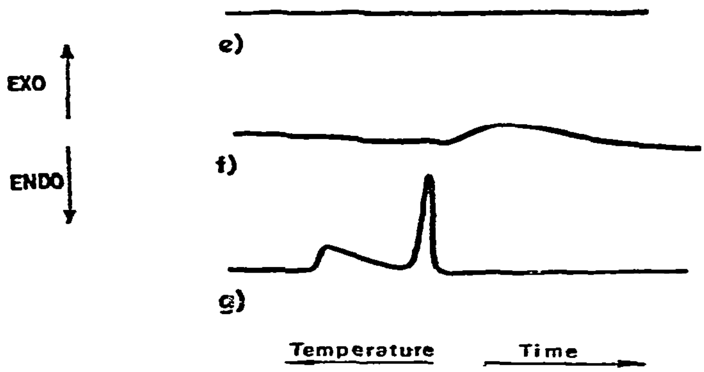

Fig. 2. Typical cooling DTA curves of: (e) glass-forming samples; (f), partially crystalline samples, and (g) crystalline samples.

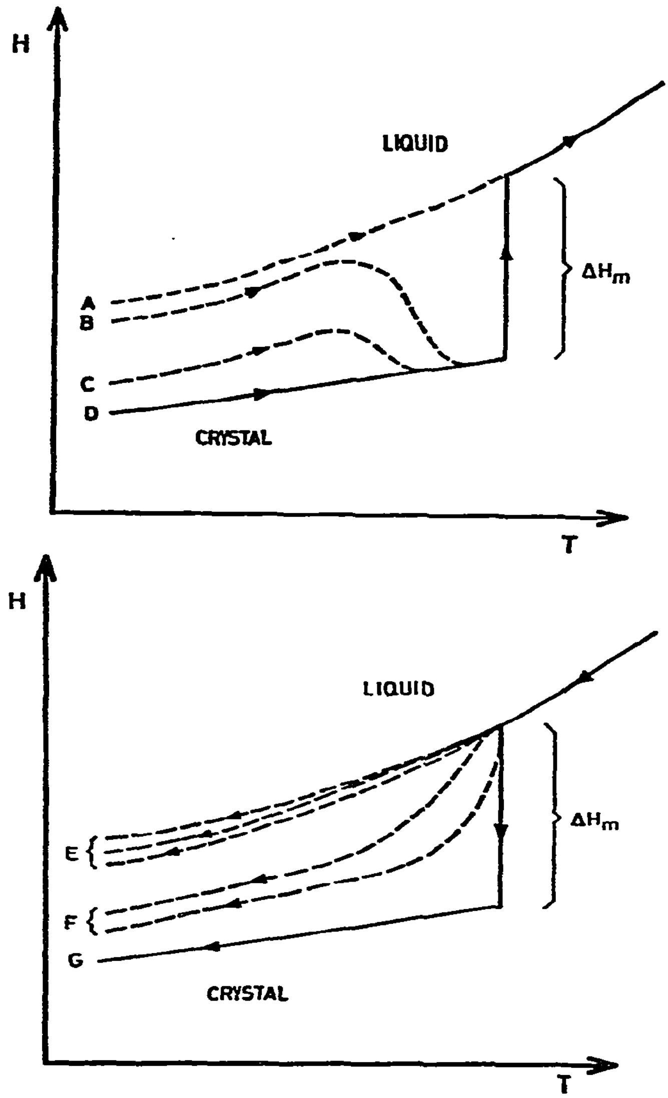

Fig. 3. Schematic representation of the enthalpy vs. temperature changes for the glass-forming system.

TABLE 1

CLASSIFICATION OF GLASS-FORMING ABILITY

Cooling DTA curve	*H–T diagram*	*Sample*	*Heating DTA curve*	*H–T diagram*
e	E	Glass without recrystallization	a	A
		Glass with recrystallization	b	B
f	F	Partially crystalline	c	C
g	G	Crystalline	d	D

crystallization[2]. DTA curve (f) is typical of samples which exhibit broad exothermic peaks not very reproducible either in temperature or in latent heat; that is, the viscosity of the melt is not so high to prevent the formation of nuclei, but since in most alloy glasses[3, 4] the temperature of the maximum nucleation frequency is lower than that of the maximum crystal growth rate, the molten alloy crystallizes only partially on cooling, even if the material crystallizes completely on heating. In DTA curve (g) the exothermic peaks are well defined and the latent heat associated with them reproducible*. These transformations correspond to the formation of crystalline phases.

The DTA structural transformations observed in the glass-forming quaternary system are schematically illustrated in the two H–T diagrams of Fig. 3. Combining the hypothetical paths represented there with the general types of DTA curves just discussed, we obtain the classification shown in Table 1.

This study has involved the use of 400 samples of different composition, all of them prepared using the same experimental conditions. The glass-forming regions obtained following the classification of Table 1 are presented in Figs. 4 and 5 for air-quenched and slowly cooled melts, respectively.

The region corresponding to glasses without recrystallization is larger for slowly cooled than for air-quenched melts because the second ones are powdered samples and then they show more tendency to crystallize.

DISCUSSION

The results for air-quenched samples agree generally with those reported for Ge–Sb–Se[5], Ge–Te–Se[6], Ge–Se[7], Ge–Te[8, 9] and Te–Se[10, 11] systems.

Comparing the regions of Figs. 4 and 5, a simple criterion of the importance of cooling rate can be deduced. Furthermore, associating increasing stability of glasses with the absence of recrystallization in the heating DTA curves, the most stable

* The temperature of the onset of the exothermic transformation is not always reproducible because the crystallization of the supercooled liquid is nucleated heterogeneously.

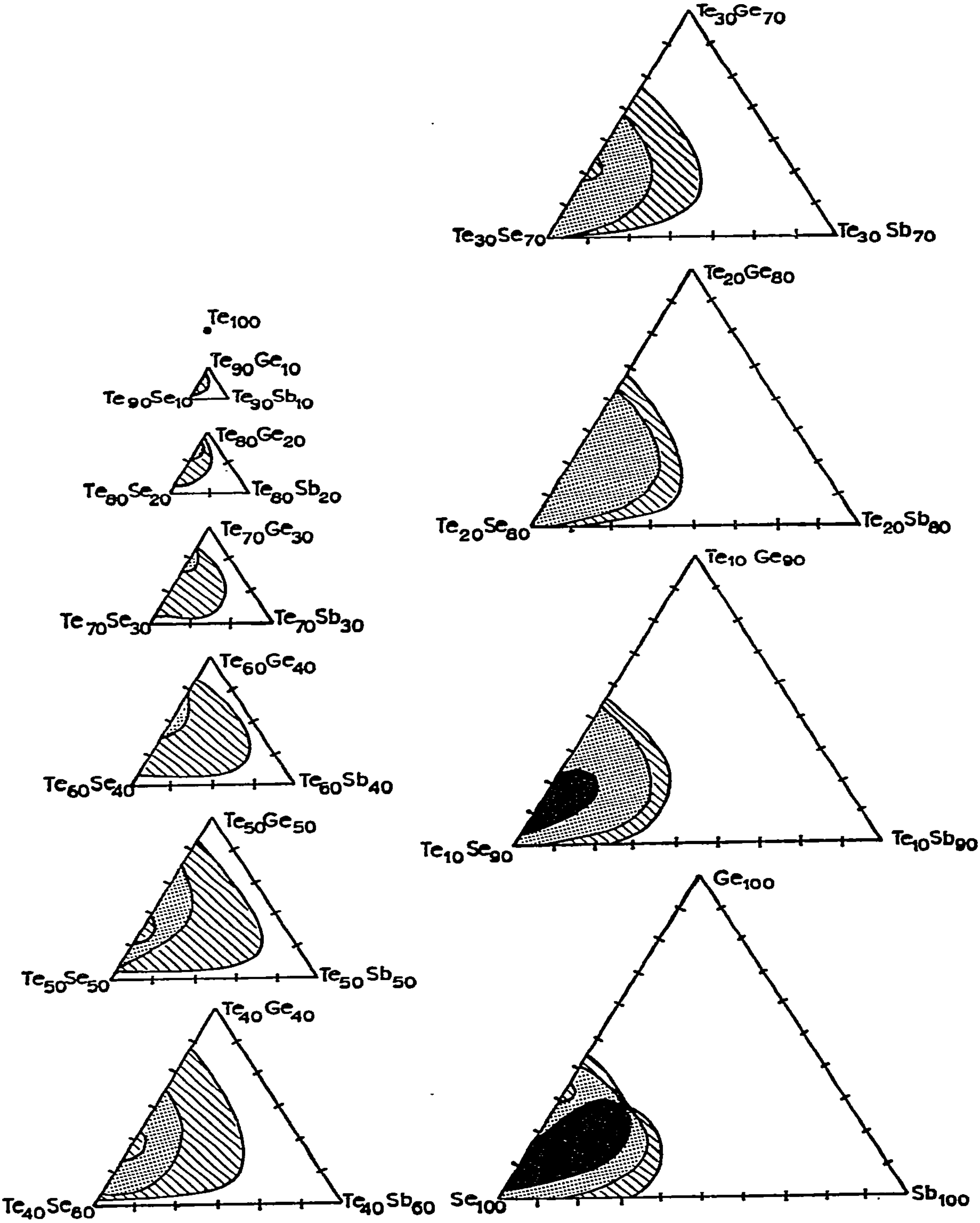

Fig. 4. Glass-forming regions for quenching in air. ■ Glasses without recrystallization; ▒ glasses with recrystallization; ▧ partially crystalline; □ crystalline.

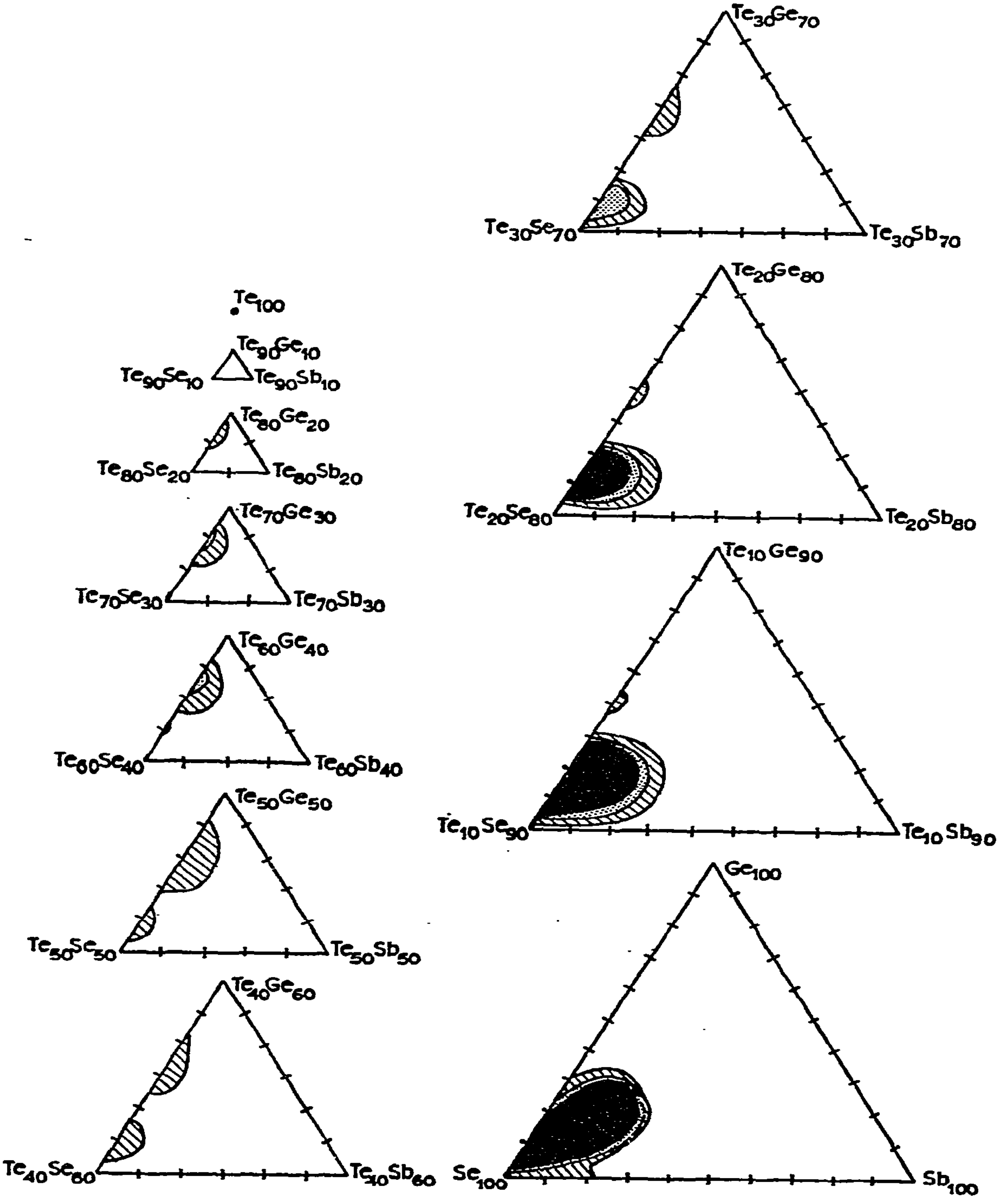

Fig. 5. Glass-forming regions for cooling at a constant rate of 5°C min^{-1}. ▪ : Glasses without recrystallization; ▒ glasses with recrystallization; ▧ partially crystalline; ☐ crystalline.

glasses of this quaternary system appear to be those of composition around the Ge_8Se_{92} eutectic of the Ge–Se system.

In order to identify potential-device quality memory and switching composition[12, 13], the thermal behaviour observed suggests[14] that compositions near $Ge_{19}Te_{72}Se_9$, $Ge_{44}Te_{16}Se_{40}$, $Ge_{13}Sb_{28}Se_{59}$ alloy glasses are the more interesting for switching (and even $Se_{1-x}Te_x$ with $x \ll 1$ if used at low temperatures) and those around $Ge_{15}Te_{85}$, $Ge_{32}Te_{43}Se_{25}$, $Sb_5Te_{35}Se_{60}$, $Ge_{13}Sb_{32}Se_{55}$ and $Ge_{10}Sb_{10}Te_{60}$-Se_{20} alloy glasses are promising as memory devices.

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