CENTRIFUGAL QUENCHING OF Pb–Se–As–Ge AND Ge–S–Cu MELTS

ЦЕНТРОБЕЖНОЕ ОХЛАЖДЕНИЕ ВЫПЛАВКА Pb–Se–As–Ge и Ge–S–Cu

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Phase separation was proved experimentally in many glassy materials consisting of two and more components. In such phase-separated systems the physical parameters can be changed to a great extend by controlled crystallization in a proper direction. Moreover, a suitable heat treatment enables to obtain a glass-crystalline material with various crystalline phases consequently influencing, e.g., infrared transmissivity [1], the values of the thermoelectric figure of merit (the Z-parameter) [2], and values of many other physical parameters [3].

Centrifugal separation of phases has been used in the study of phototropic and oxide glasses [4]; however, as far as we know it was not applied for chalcogenide glass-forming melts yet. In this work we have investigated the glasses produced by action of centrifugation of two chalcogenide glassforming melts, namely

I. Pb–Se Ge–As–Se, where phase separation was confirmed both by electron microscopy and the DSC method [5], and

II. Ge–S–Cu, where phase separation was confirmed by electron microscopy and DTA, with the composition of one separated phase indexed as Cu_2GeS_3 [6].

Sufficiently homogeneous glasses of the systems I (PbSe — $Ge_{1.5}As_{0.5}Se_3$) and II ($GeS_{1.375}$ + 3 at % Cu) were loaded in quartz ampoules, evacuated and sealed off, put in a ceramic cylinder heated up to 1230 K, and then cooled in a centrifuge in the centrifugal field of 700 g (2100 rpm) down to room temperature at a rate ~2 Ks^{-1}. The specimens prepared in this way had the shape of a cylinder of a diameter of 6 mm and a length of 13 mm (I) and 25 mm (II).

The DTA (DSC cell of the DuPont Thermal Analyzer 900), optical microscope and electron microprobe analyses (Jeol JXA 5A) were performed in the top, middle and lower parts of the longitudinal profiles of the glassy samples. Non-crystalline specimens were investigated only; the samples with crystalline inclusions were excluded from further investigation.

According to the optical investigation (Fig. 1) of the this-way-prepared system I glasses, the occurrence of the phase separation appeared as an existence of phase "a" embedded in the matrix of type "b". The distribution of a-phase is a function of location (Fig. 2) with ordering increasing from location 1 to 3. Such an arrangement of phases is revealed in the DTA thermogram (Fig. 3a) as changes of the specific heat jump Δc_p at T_g, the crystallization temperature T_c shift, and the appearance of a new glassy transition at the temperature T_{g2} at the maximum concentration of the phase "a" in location 1. In this system the distribution of initial elements measured by the microprobe in various parts of the specimen was found to be within the accuracy of measurement.

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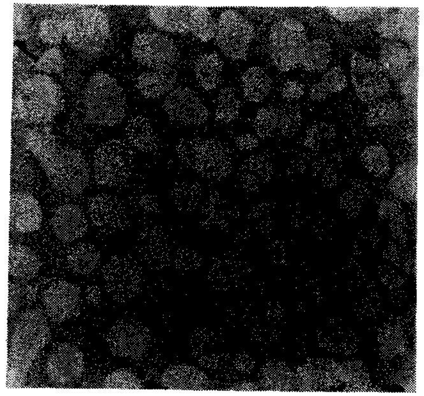
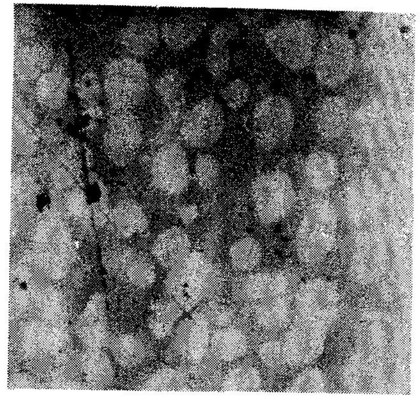


a



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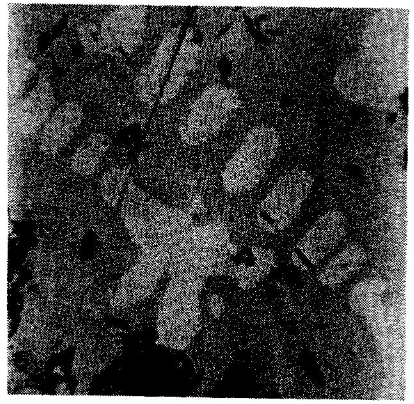

c

Fig. 1. Optical microscopy of system I at locations a. — 1, b. — 2, c. — 3 according to the Fig. 2.

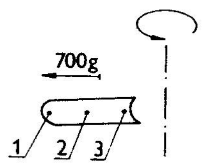

Fig. 2. Schematic diagram of the measured samples from the centrifugated bulk.

According to DTA of system II (Fig. 3b) a remarkable change of T_g *and* T_c values is observed together with changes in each separated phase represented by exothermic reactions at various temperatures. The exotherm corresponding to the crystallization region of the Cu_2GeS_3 phase is present in some parts of the specimen in location 1. Chemical analysis of the elements of the glass system II obtained by means of the electron microprobe results is in Table 1.

It follows from these measurements that the sulphur distribution in the whole profile is homogeneous. The drop in the amounts of the heavier elements Ge and Cu in location 1 confirms the existence of phases with a density higher than the others. One of these phases has been identified as Cu_2GeS_3 [6] with a density of 4.43 gcm^{-3} [7]. Supposing that the density of non-crystalline phase Cu_2GeS_3 is approximately the same, it justifies its presence at the "bottom" of the ampoule at location 1 due to the density of the surrounding matrix (3.1 gcm^{-3}).

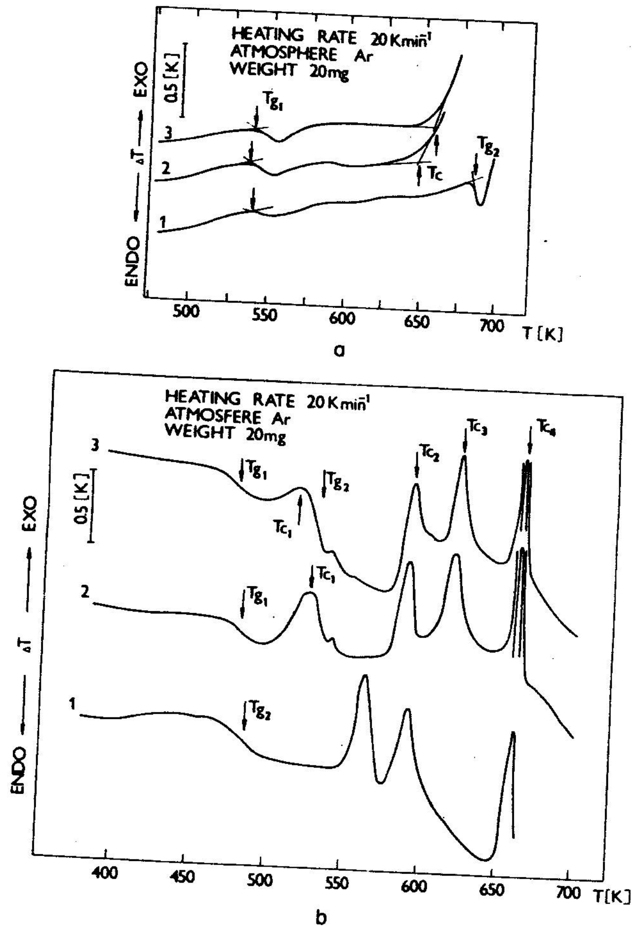

Fig. 3. DTA thermograms of systems I (a) and II (b), resp.

As it follows from our measurements, the method of bulk separation of phases of chalcogenide glasses melts by centrifuging represents a method suitable for the study of separated phases of glass systems. In a detailed study this method enables to obtain separated regions of specimens with maximum amounts per volume.

Table 1

Electron microprobe analysis of the glassy system II ($GeS_{1.375}$ + 3 at % Cu) as a function of location.

location	number of impulses Ge	S	Cu
1	145.026 ± 250	8.011 ± 120	7.521 ± 150
2	153.233 ± 250	8.337 ± 120	9.272 ± 150
3	159.323 ± 250	8.045 ± 120	9.770 ± 150

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