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THERMOELECTRICAL CONDUCTIVITY OF $Ge_{20}Bi_{15}S_{65}$ AS A COMPLEMENTARY METHOD TO DIFFERENTIAL THERMAL ANALYSIS

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ABSTRACT

As a complementary method to differential thermal analysis (DTA), thermoelectrometry has been used to follow the process of crystallization of Bi_2S_3 in $Ge_{20}Bi_{15}S_{65}$ chalcogenide glass. The step change in the temperature dependence of the d.c. electrical conductivity, usually ascribed to the crystallization process, occurs below the onset of the associated DTA peak and is probably a response to the nucleation process and/or to the crystallization of a thin surface layer of the sample. It was shown that the electrical properties of the studied glass during the crystallization of Bi_2S_3 cannot be described using the effective medium theory.

INTRODUCTION

Specific electrical, magnetic and optical properties of various types of glasses have attracted increasing attention particularly in order to make possible their practical utilization in electronics. One of the most important processes is that of recrystallization, which may occur on reheating a quenched glass and which is usually the aim of most thermoanalytical studies investigating the temperature-induced changes of thermal properties by DTA or DSC. Additional measurements of non-thermal properties are considered as a supplement to confirm the validity and/or to improve the distinguishability of thermometric data.

The temperature and the extent of crystallization are the desired characteristic quantities to be derived from the onset and the course of a measured property. It is usually assumed that coincidence exists between the thermal course of a particular measured property representing the crystalli-

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zation process as indicated by an individual technique. Possible discrepancies are ascribed to experimental factors arising, e.g., from the heating rate or applied external field, or are just listed without an explanation. Let us illustrate the situation with a few randomly selected examples of different types of glasses. Using d.c. resistivity measurements (ca. 1 K $\min^{-1}$), Šimšová et al. [1] found for the glassy system $31Mn_{1.5}Fe_{1.5}O_4 69B_2O_3$, splat quenched at 10^2–10^3 K s^{-1}, a crystallization temperature of $T_{cr} = 892$ K, while the corresponding value determined by DTA was 16 K higher. This difference was almost twice as great in the work of Arajs et al. [2], who investigated metallic glasses of binary alloys ($Fe_{84}B_{16}$, melt spinned at 10^5–10^6 K s^{-1} and reported T_{cr} values of 680, 680 and 650 K for DSC (10 K $\min^{-1}$), low-field magnetization (5 K $\min^{-1}$ at 100 Oe) and four-probe d.c. resistivity (1 K $\min^{-1}$), respectively. It is worth noting that the desired coincidence between DSC and magnetic measurements was achieved, whilst the lower value of T_{cr} obtained by resistivity measurements (somehow related to the heating rate) may be indicative of some prior crystallization processes (e.g., athermal behaviour of quenched-in nuclei). Other less common complementary measurements may provide even more extensive information about the possible pre-crystallization stages starting as low as the glass transformation, accomplished, e.g., by emanation thermal analysis for chalcogenide glasses (Bordas et al. [3]) or by thermosonimetry for metallic glasses (Lønvik and Holm [4]).

For our model system we used the data on the crystallization of Bi_2S_3 in $Ge_{20}Bi_{15}S_{65}$ chalcogenide glass [5], because the conductivity of crystalline Bi_2S_3 is an order of magnitude higher than that of the original glassy matrix. In addition, chalcogenide glasses are among the most often studied systems by DTA [6–11] and DSC [12] but there is surprisingly little information about complementary measurements of their non-thermal properties.

EFFECTIVE MEDIUM THEORY

Anomalous temperature dependences of d.c. electrical conductivity form a sensitive probe for experimental investigations of various phase transformations [13]. With respect to crystallization, a sample can be considered as a two-phase system: crystals of conductivity σ_c embedded in an amorphous matrix of conductivity σ_a. The average conductivity of this mixed phase with crystalline inclusions can be described by an effective medium theory (EMT) approximation, derived by Odelevskii [14] and Landauer [15]:

$$p\frac{\sigma_c - \sigma}{\sigma_c + 2\sigma} + (1 - p)\frac{\sigma_a - \sigma}{\sigma_a + 2\sigma} = 0 \qquad (1)$$

where p is the volume fraction of conducting (crystalline) inclusions. EMT predicted a percolation threshold at $p_c = 1/3$. A step change (conductivity jump) in the temperature dependence of the d.c. conductivity, $\sigma(T)$, is observed at temperatures where $p \approx p_c$. For the determination of p in a glassy matrix during crystallization, the EMT is often used [16–19]. However, it is necessary to take into consideration that eqn. (1) has been derived only for a spherical geometry of conducting inclusions. If the crystalline inclusions have different shapes (e.g., elliptical), the value of p_c will decrease. The step change in the $\sigma(T)$ dependence can be also caused by surface crystallization and thus $p_c \ll 1/3$. In these instances the assignment of the step change in the $\sigma(T)$ dependence to the percolation threshold of EMT could lead to erroneous results. For $p_c \neq 1/3$ it is possible to describe the d.c. electrical conductivity of an inhomogeneous medium by the following equations [20]:

$$\sigma = \sigma_a/(1 - p/p_c) \qquad \text{for } 0 \leqslant p < p_c \tag{2a}$$

$$\sigma = A(p - p_c)^{\gamma} \qquad \text{for } p_c < p < 0.4 \tag{2b}$$

$$\sigma = \sigma_c[(3/2)p - 1/2] \qquad \text{for } 0.4 \leqslant p \leqslant 1 \tag{2c}$$

where eqns. (2a) and (2c) are limiting cases of eqn. (1) for $\sigma_c \gg \sigma$ and for $\sigma_a \ll \sigma$. Equation (2b) is Kirkpatrick's power law [21], where A is a constant and $\gamma = 1.6$–1.7.

EXPERIMENTAL

The studied $Ge_{20}Bi_{15}S_{65}$ glass was prepared by melting a mixture of 5 N elements (total weight 8 g) in an evacuated ($p \approx 10^{-3}$ Pa) quartz ampoule (inner volume 5.5 cm^3, wall thickness 1 mm) in a rotary furnace. After annealing ($T \approx 710$ K, 4 h) and homogenization ($T \approx 1173$ K, 24 h), the ampoule was quenched in 10% KOH solution (at about 70 K s^{-1}).

The DTA trace of the bulk sample (ca. 10 mg) was obtained with a Du Pont 990 Thermal Analyser at a heating rate of 5 K min^{-1} [5], using Al_2O_3 as the reference material.

The identification of the crystalline phase in the studied glass was carried out by X-ray diffraction analysis (XRD) of recrystallized samples. These samples were obtained by annealing (30 min) of the bulk glass in cleaned, evacuated quartz ampoules. Powder XRD patterns of the annealed samples were obtained with Ni-filtered Cu $K\alpha$ radiation.

Conductivity measurements during the crystallization of the studied glass were carried out in a sandwich arrangement in an evacuated thermostat at heating rates of 5, 7 and 8.5 K min^{-1}. The recrystallized sample was measured using a four-probe method. In both instances aquadac contacts were used.

RESULTS AND DISCUSSION

Figure 1 shows the temperature dependence of the d.c. electrical conductivity, $\sigma(T)$, of glassy (curve 1) and recrystallized (curve 2) samples of composition $Ge_{20}Bi_{15}S_{65}$. It should be mentioned that the course of the $\sigma(T)$ dependence for the recrystallized sample can be affected by the non-stoichiometry [22–24] of Bi_2S_3 or by transport phenomena in a non-homogeneous system resulting, e.g., from barriers or leakage due to interfacial surfaces of microcrystallites, and thus will be excluded from further discussion.

From Fig. 1 it can be seen that at temperatures above 500 K the thermal dependence of the logarithm of conductivity departs from linearity, indicating the region of glass transformation, which is lower than the corresponding T_g obtained from complementary DTA and thermomechanometric (penetration measurements, T_s) results. At higher temperatures, the $\sigma(T)$ dependence shows a stepwise change of electrical conductivity within a relatively narrow temperature range, probably associated with the formation and growth of Bi_2S_3 crystals.

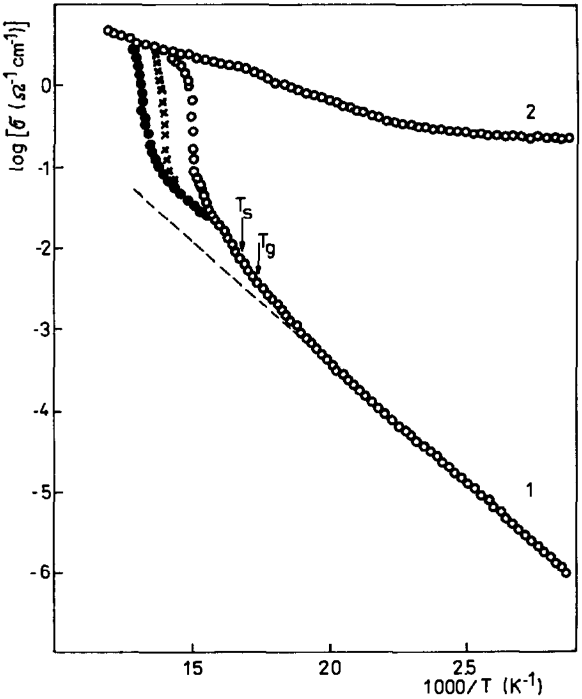

Fig. 1. Temperature dependence of the d.c. electrical conductivity of a $Ge_{20}Bi_{15}S_{65}$ glassy sample (curve 1) at heating rates of (○)5, (×)7 and (●)8.5 K min^{-1} and a recrystallized sample (curve 2). The transformation temperatures determined by DTA (T_g) and thermomechanometrically (penetration measurement, T_s) are marked by arrows.

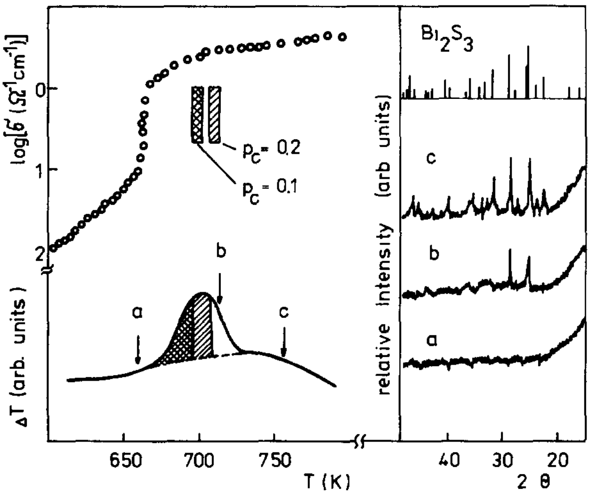

Fig. 2. Left: temperature dependence of the d.c. conductivity (upper curve) and DTA trace (lower curve) of $Ge_{20}Bi_{15}S_{65}$ glass during the crystallization of Bi_2S_3. The singly hatched area (DTA trace) indicates 20 vol.-% and the cross-hatched area 10 vol.-% of crystalline Bi_2S_3. Under the $\sigma(T)$ curve, the shaded areas show the approximate positions of the conductivity step change for $p_c = 0.2$ and 0.1, respectively. Right: XRD patterns of samples annealed at temperatures (a), (b) and (c). The data for pure crystalline Bi_2S_3 are shown for comparison.

The experimental dependences of ΔT_{DTA} and $\sigma(T)$ determined at comparable heating rates (5 K min^{-1}) are shown in Fig. 2. From XRD measurements on annealed glass at the temperature of the extrapolated start of the stepwise change of the $\sigma(T)$ dependence [temperature (a) in Fig. 2], no diffraction lines were determined. This is surprising because the stepwise change in $\sigma(T)$ should be caused by a percolation process due to the formation of conductive particles of Bi_2S_3 dispersed in a relatively low-conductivity glassy matrix [25]. According to the EMT, the concentration of crystalline Bi_2S_3 should reach 33.33 vol.%, which, however, contradicts our findings. To determine the actual Bi_2S_3 concentration we measured the dependence of the relative integral intensity of the $2\theta \approx 28.6°$ diffraction line of Bi_2S_3 on the volume concentration of crystalline Bi_2S_3 in homogenized mixtures with $Ge_{20}Bi_{15}S_{65}$ glass (Fig. 3). For the sample annealed at temperature (c) in Fig. 2, a concentration of 27.3 vol.-% * was established for crystalline Bi_2S_3 with a relative error not exceeding 3 vol.-%.

If follows that the whole area under the DTA curve in Fig. 2 corresponds to a concentration of 27.3 vol.-% of Bi_2S_3. Assuming, in a first approach,

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* The formal volume concentration of Bi_2S_3 in $Ge_{20}Bi_{15}S_{65}$ glass (with the assumption of additivity of molar volumes) is 35 vol.-%.

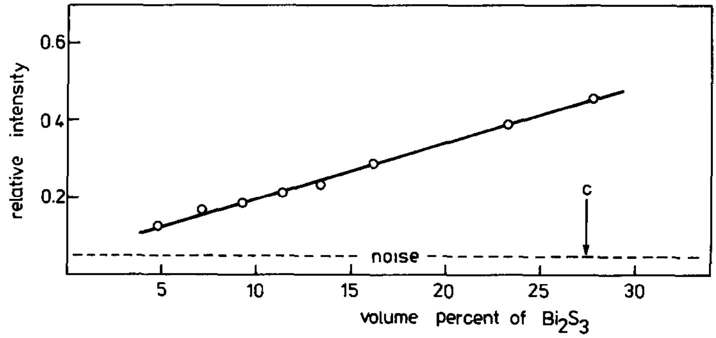

Fig. 3. Dependence of the relative integral intensity of the Bi_2S_3 diffraction line ($2\theta \approx 28.6°$) on the volume concentration of Bi_2S_3 in homogeneous powder mixtures of crystalline Bi_2S_3 and glassy $Ge_{20}Bi_{15}S_{65}$. The arrow indicates the sample annealed at temperature (c) in Fig. 2.

that the extent of crystallization, $\alpha(T)$, is expressed [26] by

$$\alpha(T) \approx \int_0^T (\mathrm{d}\alpha/\mathrm{d}T)\mathrm{d}T \tag{3}$$

the location of the stepwise change in electrical conductivity was determined for values of the percolation threshold p_c of 0.1 and 0.2 (Fig. 2).

It is likely that the stepwise change in $\sigma(T)$ is not associated with the volume growth of Bi_2S_3 crystals but rather that it is a response to the

Fig. 4. Scanning electron micrograph of the recrystallized sample annealed at temperature (c) in Fig. 2.

precrystallization stage of nucleation, whose thermal effects and crystallinity are beyond the detectability of ordinary DTA and XRD measurements. However, we should not exclude the possibility of a similarly undetectable interference of a simultaneous crystallization process taking place in the thin surface layer of the sample.

CONCLUSIONS

From the comparison of DTA and thermoelectrometry, it follows that the heat generated due to the crystallization of Bi_2S_3 in $Ge_{20}Bi_{15}S_{65}$ glass is indicated by DTA at higher temperatures than the change in electrical conductivity measured by thermoelectrometry which is usually associated with the same process. This is in general accord with other results [1–5], probably indicating a deeper insight into precrystallization processes associated with the formation of tiny domains available for the collective process of crystallization. In our case, nuclei of Bi_2S_3, even if otherwise undetectable, are then responsible for the change in the electrical conductivity of the sample.

The electrical properties of $Ge_{20}Bi_{15}S_{65}$ glass during the crystallization of Bi_2S_3 cannot be described within the framework of the classical effective medium theory, which assumes the percolation threshold at a volume concentration of conductive particles of 33.3 vol.-%.

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