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CRYSTALLIZATION IN $Ge_{20}Bi_{15}S_{65}$ GLASS

Jiří Málek[x], Jiří Klikorka, University of Chemical Technology,
Pardubice, Czechoslovakia
Nataša Ryšavá, Institute of Physics, Czechoslovak Academy of Sciences, Prague, Czechoslovakia

ABSTRACT

The prepared glass has been studied by DTA. The devitrification in this material is shown to be associated with crystallization of germanium disulfide and bismuth trisulfide. The crystallization of bismuth trisulfide can be described as two mutually independent nucleation-growth processes.

INTRODUCTION

In recent years much attention has been devoted to the study of both the preparation and the properties of the n-type chalcogenide bulk glasses. The kinetic of devitrification processes has not been studied in this type of glasses up to now. It was only shown[1] that a slow heating of the n-type $Ge_{20}Bi_{15}S_{65}$ glass leads to crystallization of Bi_2S_3 but a slow cooling (e.g. in air) of the melt of the same composition results in the crystallization of GeS_2. Thus at least two crystallization processes must exist in this type of glass. An investigation of the described processes could be useful for a better understanding of the properties of n-type chalcogenide bulk glasses.

EXPERIMENTAL

The studied glass $Ge_{20}Bi_{15}S_{65}$ was prepared in conventional way[1] and studied by differential thermal analysis (DTA). DTA thermograms were obtained with DuPont 990 thermal analyzer, the bulk and powder samples (~10 mg) being placed in an open quartz pan. The reference material was Al_2O_3. During the measurements the sample chamber was continuously flushed with dry Ar. The identification of crystalline phases in the studied glass was carried out by X-ray diffraction analysis (XRD) of crystallized samples. The crystallized samples were obtained by annealing (30 min) of the bulk $Ge_{20}Bi_{15}S_{65}$ glass in carefully cleaned evacuated quartz ampoules at temperatures marked by arrows in Fig.1. Powder XRD data of the annealed samples

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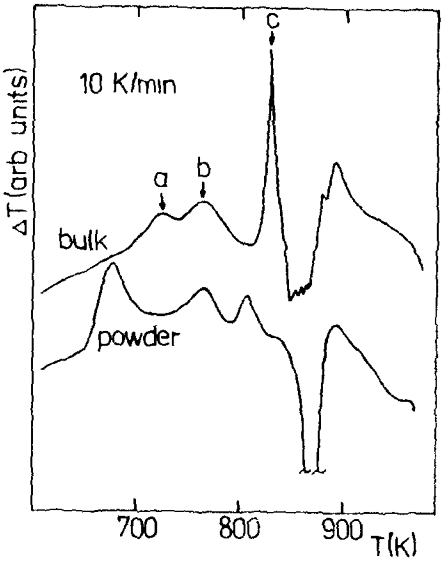

Fig.1 DTA curves of the bulk and powder samples of $Ge_{20}Bi_{15}S_{65}$ glass

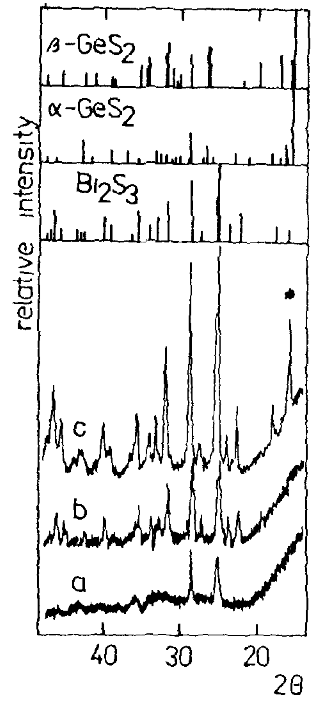

Fig.2 XRD patterns of the samples annealed at temperatures (a)-(c)

obtained with Ni-filtered $Cu_{K\alpha}$-radiation are presented in Fig.2 (the XRD data of crystalline Bi_2S_3 and GeS_2[2] are shown for comparison).

RESULTS AND DISCUSSION

DTA curves of both the bulk and powder samples of the studied glass are presented in Fig.1. Three crystallization peaks are observed before a strong endothermic effect corresponding to the melting of the glassy matrix. We have studied the crystallization corresponding to these three peaks only.

It is evident from Fig.2 that the annealing of the glass at temperatures (a) and (b) corresponding to the first two peaks leads to crystallization of Bi_2S_3. These crystallization peaks could be described by a theoretical approach based on the phenomenological Johnson-Mehl-Avrami (JMA) equation:

$$-\ln(1-\alpha) = (Kt)^n \quad \text{where} \quad K = A\exp(-E/RT)$$

α is the degree of crystallization after the time t, A is a frequency factor and E is the activation energy of the overall nucleation-growth process. The parameter n is related to the crystallization mechanism and the shape of crystals. It depends also on the ratio between the number of surface nuclei (N_S) and bulk nuclei (N_B) in quenched sample[3]. N_S is proportional to the specific surface area of the sample and N_B is proportional to the reciprocal of heating rate. In the powder sample of $Ge_{20}Bi_{15}S_{65}$ glass, surface nucleation can be dominant due to the higher specific surface area of the sample. Therefore, the corresponding first peak is larger and shifted to lower temperatures (see Fig.1). On the other hand, the second peak of the powder sample is not changed in comparison with the peak of the bulk sample, so the bulk nucleation seems to be dominant in this case. The theoretical values of the parameter n for both the surface nucleation and the bulk nucleation are 1 and 3, respectively[3]. Experimental DTA curves of the crystallization corresponding to the first two peaks at different rates of heating are denoted in Fig.3 by full lines. Dashed lines correspond to the calculated DTA curves of two mutually independent nucleation-growth processes. The calculation is based on JMA equation with Doyle approximation[4] for temperature integral. The influence of baseline drift correction (for heating rate 20 K/min) is shown by dotted line in Fig.3.

Table 1 Kinetic parameters of the crystallization of Bi_2S_3 in $Ge_{20}Bi_{15}S_{65}$ glass

peak	E(eV)	A(min^{-1})	n
exo(a)	1.66	$1.96\ 10^{11}$	1
exo(b)	0.84	$7.12\ 10^{4}$	3

The calculated parameters are summarized in table 1. The parameters n of both the first and the second peaks determined by calculation are 1 and 3, respectively. Thus the first peak seems to be related to the surface nucleation and the second peak to the bulk nucleation as we have assumed above. We remark that the calculations with consideration of two competitive processes led to unreal kinetic parameters. The differences between experimental and calculated curves are probably associated with temperature gradients in the sample holder and with a strong

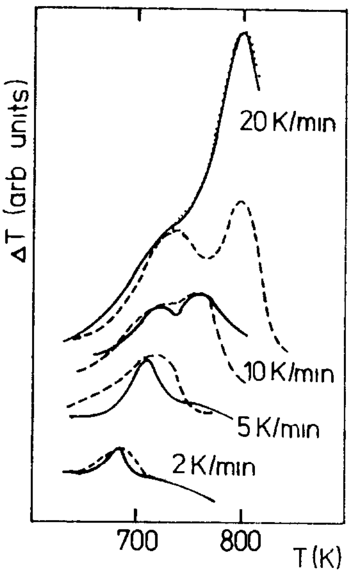

Fig.3 Experimental and calculated DTA curves (see text)

exothermic character of the process causing a delay in temperature programme with respect to the actual reaction temperature.

By annealing the $Ge_{20}Bi_{15}S_{65}$ glass at the temperature (c) a new diffraction peak (*) appears in XRD patterns corresponding to the crystallized fraction of GeS_2 (see Fig.1 and Fig.2). Germanium disulfide has two polymorphs^2, the high temperature, α, and the low temperature, β, modifications. These two modifications have very similar XRD patterns, so it is very difficult to determine which of these modifications crystallized in $Ge_{20}Bi_{15}S_{65}$ glass at the temperature (c).

We conclude that during the heating (10 K/min) of $Ge_{20}Bi_{15}S_{65}$ glass, Bi_2S_3 crystallized at temperatures 714 and 756 K and GeS_2 at temperature 818 K, respectively. After these crystallizations the melting of the glassy matrix is started. We suggest that the crystallization of Bi_2S_3 in studied glass can be described as two mutually independent nucleation-growth processes. The first and the second processes are probably related to the surface and to the bulk nucleation, respectively.

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