

# Determination of thermal parameters of glasses from the system $\text{Bi}_x(\text{As}_2\text{S}_3)_{100-x}$ based on DSC curves

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**Abstract** Thermal properties of glasses from the system  $\text{Bi}_x(\text{As}_2\text{S}_3)_{100-x}$  were studied by differential scanning calorimetry of a representative series of samples with  $x = 0.5, 2, 4, 6, 8,$  and  $10$  at.% Bi by determining the characteristic temperatures ( $T_g, T_{\text{onset}}, T_c, T_m$ ) and enthalpies ( $H_c, H_m$ ) of the processes taking place in the samples during their thermal treatment. Analysis of DSC recordings for the samples at the same heating rate allowed characterization of the phase transition temperature  $T_g$  as a function of the content of doping atoms in accordance with the criteria of chemical bonds formation in amorphous materials. Samples with 4 and 6 at.% Bi were thermally treated at different heating rates with the aim of determining, among the others, the parameters of their thermal stability. The assessment was done based on three different criteria. A higher tendency toward crystallization was observed with the glasses having a higher Bi content. Also, a trend of  $T_g$  shifting toward higher values, observed with increase in the heating rate, is in concordance with the Lasocka equation.

**Keywords** Chalcogenide glasses · Phase transition · Thermal stability

## Introduction

Modifications of the already well-known chalcogenide glasses doped by metal atoms, such as the As–S system, have been a subject of intensive research during the last

several decades thanks to the possibility of preparing materials with specific optical, electrical, and physico-chemical properties [1–4]. Doping of these amorphous glasses by bismuth atoms appeared especially interesting since it has been found that the dopant of this type induces changes in their behavior. This is evidenced as the change of the type of conductivity caused by the change in the concentration of charged states [5, 6], significant decrease in the optical band gap [7], memory switching [8], etc.

There are a number of works concerning theoretical considerations based on experimental measurements by calorimetric isothermal and non-isothermal analytical techniques for studying phase transformations in the material. Although isothermal methods are in the majority of cases more accurate, non-isothermal methods appeared as more attractive because of the possibility of determining thermal parameters in a simple and rapid way.

This work presents the results of a study of the thermal properties of the glasses from the system  $\text{Bi}_x(\text{As}_2\text{S}_3)_{100-x}$  ( $x = 0.5, 2, 4, 6, 8, 10$ ), as well as the analysis of the parameters of thermal stability of those glasses from the series which crystallized in the temperature range of measurements. Stability level of these glasses was assessed based on three standard criteria, whose values were determined from the experimentally obtained characteristic temperatures on the DSC curves. The shift of the phase transition temperature as a function of bismuth content was discussed in the light of the criteria of Bicerno and Ovshinski [9].

## Experimental

Glasses of the system  $\text{Bi}_x(\text{As}_2\text{S}_3)_{100-x}$  were synthesized from high purity elementary components (99.99%) by the

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method of cascade heating. Masses were measured on a METTLER B-6 analytical balance, with an accuracy of  $5 \times 10^{-8}$  kg. The measured amounts were sealed in the cylindrical quartz ampoules evacuated to a pressure of the order of magnitude  $10^{-2}$  Pa. The synthesis was carried out in a semiautomatic horizontal tube furnace Carbolite, Model CTF 12/65. After heating the elementary components from room temperature to a temperature of 523 K at a rate of 50 K/h, the 4-h temperature plateau was maintained in order to reduce the vapor pressure of sulfur and intensify its reaction with arsenic and bismuth. The process of heating was then continued at a rate of 25 K/h up to 573 K, and a new plateau was established in order to intensify the reaction of melted bismuth with other components. Maximum temperature of the synthesis was 873 K, and it was the last temperature plateau at which the ampoules were held for a long time, to allow better homogenization of the material. Cooling was carried out with powder alumina, reducing the mechanical stress in the sample.

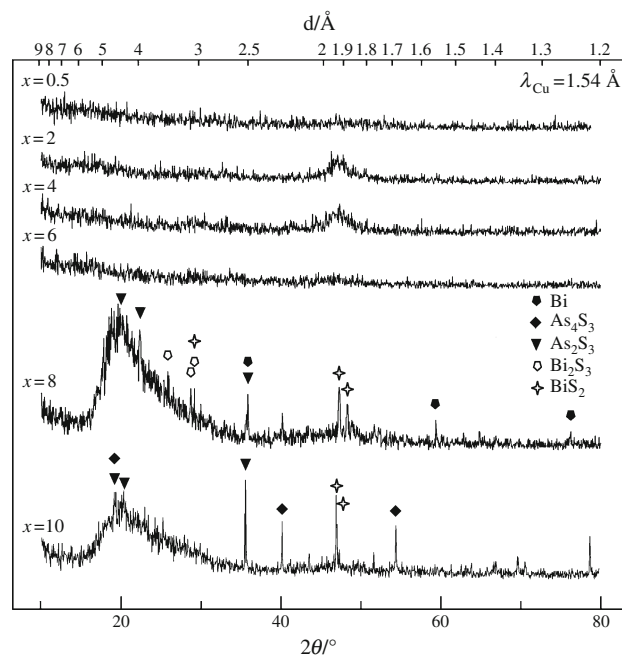
Measurements of thermal characteristics of the investigated glass samples were carried out on a DSC METTLER TOLEDO 822 differential scanning calorimeter in non-isothermal regime. Bulk samples were placed in standard aluminum vessels and heated at a rate of 10 K/min in the temperature range 300–770 K. Samples with  $x = 4$  and 6 at.% Bi were thermally treated at additional three heating rates. X-ray diffraction method was used to check the structural character of investigated glasses. Measurements were carried out on a powder diffractometer Bruker D8 on as prepared samples and also on thermally treated samples with  $x = 0.5$  and 4 at.% Bi, which were annealed at temperatures beyond the peak of crystallization temperature, at a heating rate of 10 K/min for 2 h.

## Results and discussion

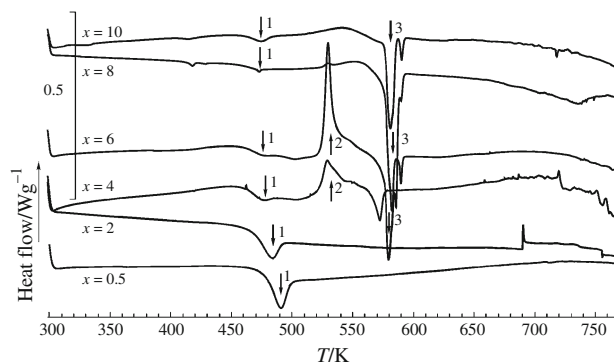
Figure 1 shows the diffractograms of samples from the system  $\text{Bi}_x(\text{As}_2\text{S}_3)_{100-x}$  recorded at room temperature. Amorphous character is predominant in samples with  $x = 0.5, 2, 4,$  and 6 at.% Bi. In samples with 8 and 10 at.% Bi it was possible to register crystalline centers of the type Bi, Bi–S, and As–S. Identification of some crystalline centers was made by comparison with data files PDF [10]: for Bi—card No 26-214, for  $\text{As}_4\text{S}_3$ —card No 26-126, for  $\text{As}_2\text{S}_3$ —card No 19-84, for  $\text{Bi}_2\text{S}_3$ —card No 17-320 and for  $\text{BiS}_2$ —card No 17-267.

The DSC curves given in Fig. 2 show the dependence of heat flow (normalized with respect to the sample mass) as a function of temperature rise for the glasses of the investigated system at a heating rate of 10 K/min.

The first maximum (peak 1) is related to the kinetic effect of softening, characterized by an enthalpic relaxation



**Fig. 1** Diffractograms of the samples from the system  $\text{Bi}_x(\text{As}_2\text{S}_3)_{100-x}$



**Fig. 2** DSC curves for the samples from the system  $\text{Bi}_x(\text{As}_2\text{S}_3)_{100-x}$

peak due to the molecular restructuring in the material. The second maximum (peak 2) stands for the exothermic reaction of crystallization. It can be noticed that the crystallization processes are clearly defined only for the glasses  $\text{Bi}_4(\text{As}_2\text{S}_3)_{96}$  and  $\text{Bi}_6(\text{As}_2\text{S}_3)_{94}$ .

A complete lack of a crystallization peak in the investigated temperature range for the samples with lower Bi percentage can be explained by the insignificant effect of doping atoms at this level on the structure of the arsenic–sulfide matrix, since the DSC curve for the glass  $\text{As}_2\text{S}_3$  is also lacking the signal of the crystallization process in the given temperature interval.

On the other hand, an extremely small change of the slopes of DSC curves for the samples with  $x = 8$  and 10 at.% Bi in the temperature interval corresponding to the crystallization process in samples with 4 and 6 at.% Bi, as

shown by X-ray measurements, is a consequence of the already existing crystallization phase (Fig. 1).

For the glasses with  $x = 6, 8$  and  $10$  at.% Bi, the change of the enthalpy of melting of crystalline phase, accompanied by two or even three peaks, indicates the formation of different crystalline centers in these samples in the course of their heating.

The determination of the parameter  $T_g$  is of great practical importance bearing in mind that its position on the temperature scale indicates the temperature range in which the given material can be used, as well as its thermal stability.

Figure 3 shows the dependence of the values of  $T_g$  for the investigated glasses on Bi content. The values of this parameter for all the investigated compositions were determined from the DSC curves (Fig. 2) by the onset point method, and are given in Table 1; the  $T_g$  value of glass  $As_2S_3$  was taken from the literature [11].

The highest glass transition temperature corresponds to the composition with the lowest concentration of Bi,

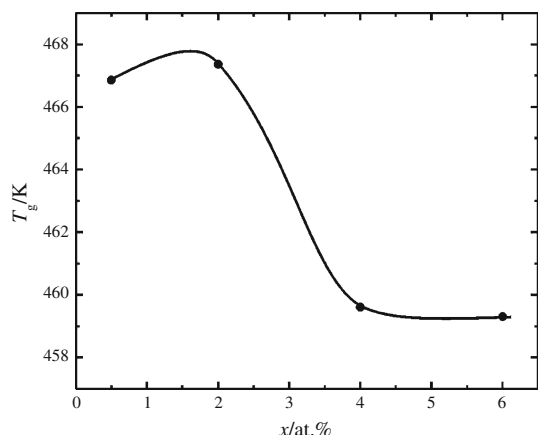


Fig. 3 Dependence of  $T_g$  on Bi content in the system  $Bi_x(As_2S_3)_{100-x}$

whereas the glasses with higher Bi content have constantly lower  $T_g$  values compared to that characterizing the softening process without Bi.

It is not possible to discuss the influence of Bi atoms on  $T_g$  value for the samples with  $x = 8$  and  $10$  at.% Bi, since these glasses are partly crystallized, and therefore their glass transition temperature is a complex parameter. Hence these values are not shown in Fig. 3.

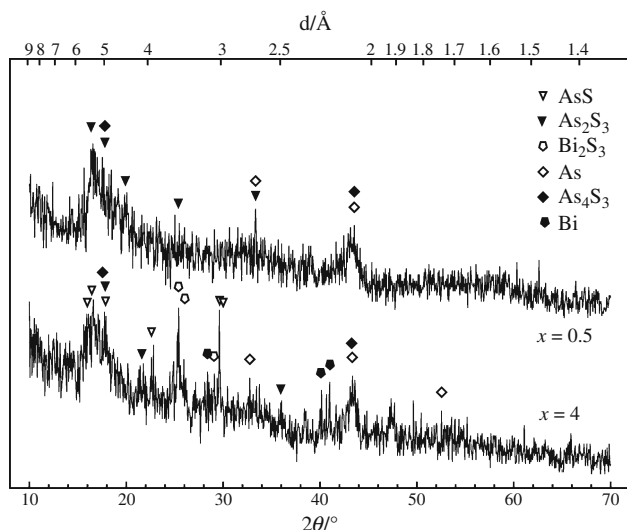
In the process of doping the As-S system with Bi at low concentration (e.g., 0.5 at.%) one can not expect the effect of building-in of doping atoms in the pyramidal structural units because of the existence of strong covalent bonds between them. On the other hand, the S-S chains are dominated by the van der Waals interactions, so that it can be expected that the doping atoms readily bind to these bridging sulfur atoms. Such way of modifying the amorphous matrix doped with Bi atoms has also been observed in the case of glasses from Se-Te system [12].

In the composition with higher dopant content the incorporation of Bi atoms in the pyramidal units by the replacement of As atoms is more probable and more favorable from the energy aspect. In this way, in concordance with the criterion of Bicerno and Ovshinski [9], the energetically more favorable Bi-S bonds are formed (bond energy 315.3 kJ/mol) on account of the As-S bonds and the homopolar As-As bond, whose energy (382 kJ/mol) [13] is insignificantly larger than that of the As-S bond. Hence, the overall energy balance of the system is smaller, which is evidenced as a decrease in the phase transition temperature  $T_g$ .

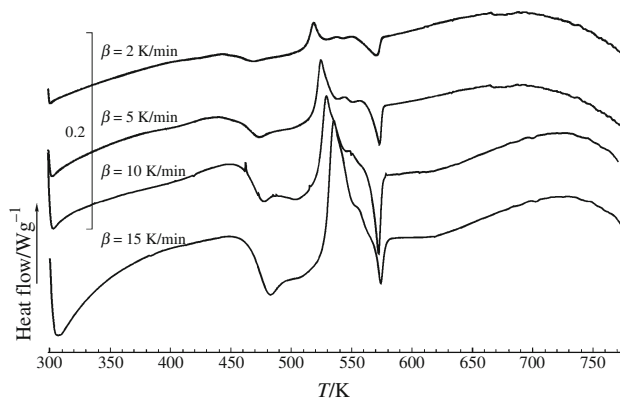
The diffractogram of the annealed glass  $Bi_4(As_2S_3)_{96}$  (Fig. 4) confirms the presence of the structural units of the type  $Bi_2S_3$ . Identification of some crystalline centers was made by comparison with data files PDF [10]: for AsS—card No 24-78, 33-127, for  $As_2S_3$ —card No 27-28, 19-84, for  $Bi_2S_3$ —card No 17-320, for As—card No 30-100<sup>†</sup>, for  $As_4S_3$ —card No 26-126 and for Bi—card No 5-519.

Table 1 Characteristic temperatures ( $T_g$ ,  $T_p$ , and  $T_m$ ) and enthalpies ( $H_{cr}$  and  $H_m$ ) of the thermal treatment process of the glasses  $Bi(As_2S_3)_{100-x}$

x/at. %	$\beta/K \text{ min}^{-1}$	$T_g/K$	$T_{ons}/K$	$T_p/K$	$T_{m1}/K$	$T_{m2}/K$	$H_{cr}/J \text{ g}^{-1}$	$H_{m1}/J \text{ g}^{-1}$	$H_{m2}/J \text{ g}^{-1}$
4	2	451.7(5)	512.6(5)	518.1(5)	571.3(5)	–	7.61	7.35	–
	5	455.6(5)	518.1(5)	524.4(5)	572.8(5)	–	8.26	3.49	–
	10	459.6(5)	521.2(5)	528.8(5)	572.0(5)	–	10.4	3.06	–
	15	464.0(5)	527.1(5)	534.8(5)	573.9(5)	–	10.27	1.15	–
6	10	459.3(5)	524.8(5)	529.3(5)	579.5(5)	589.5(5)	18.06	10.27	0.81
	15	460.8(5)	529.0(5)	533.8(5)	582.3(5)	591.2(5)	15.49	12.97	–
	20	462.0(5)	531.2(5)	536.0(5)	582.7(5)	591.1(5)	17.04	12.13	–
	30	463.2(5)	534.4(5)	540.4(5)	582.8(5)	591.8(5)	15.83	10.56	–
0.5	10	476.5(5)	–	–	–	–	–	–	–
2	10	467.4(5)	–	–	–	–	–	–	–
8	10	460.5(5)	–	–	581.2(5)	585.4(5)	–	21.0	–
10	10	460.3(5)	–	–	581.2(5)	588.1(5)	–	8.16	0.81



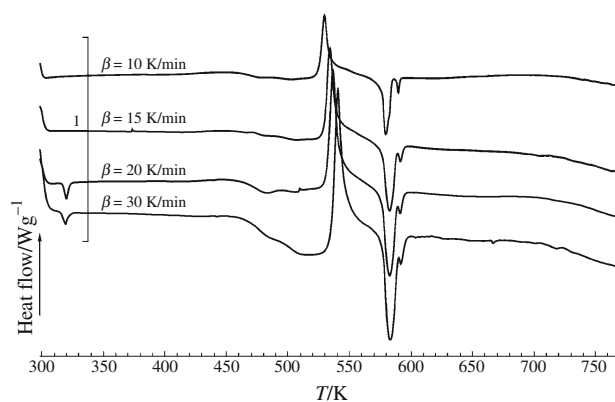
**Fig. 4** Diffractograms of annealed samples from the system  $\text{Bi}_x(\text{As}_2\text{S}_3)_{100-x}$



**Fig. 5** DSC curves for the glass  $\text{Bi}_4(\text{As}_2\text{S}_3)_{96}$  recorded at different heating rates

Figures 5 and 6 show the DSC curves for the samples in which crystallization was observed ( $x = 4$  and 6 at.% Bi, Fig. 2), recorded at the different heating rates. Because of the overlapping of the crystallization and melting processes, lower heating rates were applied in the thermal treatment of the glass  $\text{Bi}_4(\text{As}_2\text{S}_3)_{96}$ . Samples of the  $\text{Bi}_6(\text{As}_2\text{S}_3)_{94}$  glass were treated at higher heating rates to enhance the enthalpic relaxation peak (because of the lagging of the rate of equilibrium attainment with respect to the heating rate), i.e. to ensure more precise reading of the value of  $T_g$ .

Table 1 gives the values of temperatures, characteristic for the crystallization processes:  $T_{\text{ons}}$  (crystallization onset temperature) and  $T_p$  (crystallization peak temperature) at different rates of sample heating for the samples with  $x = 4$  and 6 at.% Bi, as well as the melting onset temperature of the previously crystallized fraction  $T_m$ . Besides,



**Fig. 6** DSC curves for the glass  $\text{Bi}_6(\text{As}_2\text{S}_3)_{94}$  recorded at different heating rates

the table contains the values of enthalpies, i.e., the energies liberated in the crystallization processes  $H_{\text{cr}}$  and energies absorbed in the melting processes  $H_m$ .

The data given in Table 1 also indicate that the increase in the heating rate  $\beta$  in the thermal treatment of samples with  $x = 4$  and 6 at.% Bi caused a shift of  $T_g$  to higher values, which is in agreement with the behavior described by Lasocka's equation.

As can be seen from the literature, a number of quantitative methods have been proposed for assessing the stability level of glasses on the basis of the characteristic temperatures of the processes that take place in the glasses in the course of their thermal treatment.

In this respect, one can single out the following quantities:

- $H_r = \frac{T_{\text{ons}} - T_g}{T_m - T_p}$  according to the Hruby criterion [14];
- $S = \frac{(T_p - T_{\text{ons}})(T_{\text{ons}} - T_g)}{T_g}$  according to the so-called  $S$ -criterion of Saad and Poulain [15].
- $K(T_p) = K_0 \exp\left(-\frac{E}{RT_p}\right)$  according to the Surinach–Hu criterion [16]

A higher thermal stability and higher tendency to melt vitrification exhibit the glasses for which the values of the parameters  $H_r$  and  $S$  are larger, i.e., the parameter  $K(T_p)$  smaller.

Table 2 gives the numerical values characterizing the thermal stability of the glasses  $\text{Bi}_4(\text{As}_2\text{S}_3)_{96}$  and  $\text{Bi}_6(\text{As}_2\text{S}_3)_{94}$  according to the above criteria. The effect of Bi on the lowering of the thermal stability of glasses, observed in this investigation, has also been found for the systems Ge–Se–Bi [17] and Se–Te–Bi [18]. Namely, it is evident that the sample with smaller Bi content is characterized by higher values of the parameters  $H_r$  and  $S$ , i.e., by a smaller value of the parameter  $K(T_p)$  compared to the values obtained at the same rate of heating of the samples

**Table 2** Thermal stability parameters ( $H_r$ ,  $S$ , and  $K(T_p)$ ) for different heating rates  $\beta$  obtained on the basis of characteristic temperatures on the DSC curves

$x/\text{at.}\%$	$\beta/\text{K min}^{-1}$	$H_r$	$S/\text{K}$	$K(T_p)/\text{s}^{-1}$
4	2	1.145	1.874	$1.64 \times 10^{-8}$
	5	1.290	2.156	$3.48 \times 10^{-8}$
	10	1.424	2.504	$5.85 \times 10^{-8}$
6	15	1.617	2.546	$11.73 \times 10^{-8}$
	10	1.304	1.576	$1.89 \times 10^{-5}$
	15	1.407	1.751	$2.94 \times 10^{-5}$
	20	1.482	1.772	$3.62 \times 10^{-5}$
	30	1.680	2.255	$5.5 \times 10^{-5}$

with a higher Bi content. Hence, it can be concluded that the sample with a lower doping atom concentration is thermally more stable. A higher tendency toward crystallization with the glasses having a higher Bi content is in concordance with the previous results [19].

## Conclusions

The processes that take place in the glasses of the system Bi–As–S in the course of their thermal treatment were analyzed on the basis of the characteristic temperatures. The shift of the glass transition temperature was correlated to the concentration of doping atoms. Based on  $T_g$  vs. Bi content behavior and results of X-ray measurements of thermally treated samples, the conclusions were drawn about the network modification due to the introduction of doping atoms. For two samples whose DSC curves were characterized by crystallization peaks, thermal stability was assessed based on the variation of the heating rate. It was found that the glass with a higher Bi content exhibited lower thermal stability and higher tendency to crystallization.

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