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Mechanical Characteristics of As_2S_3 Glasses Induced by Doping with Bismuth

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This paper presents and discusses the results of the instrumented indentation test of the samples of the system $Bi_x(As_2S_3)_{100-x}$, $x = 1.5$, 3, 5, and 7 at.%. Measurements of mechanical parameters were performed using a Fischerscope HM2000 S nanoindentation device. The experimental data obtained by measuring the microhardness parameters were used to determine some other mechanical quantities that are important for the characterization of the examined materials in terms of their potential applications. For the first three compositions, the results indicated an increase in the microhardness with the increase in the content of doping atoms, which can be interpreted as an enhancement of the strength and stiffness of the structural network. The lower value of microhardness of the sample with the maximum content of Bi can BE associated with the specific structure of this composition. The pronounced indentation size effect was also detected on the indentation curve in the range of smaller loads. According to the model of elastic-plastic deformation, applied for the description of indentation size effect measured for the investigated chalcogenides, the largest value of the elastic recovery was observed for the sample $Bi_7(As_2S_3)_{93}$. The calculated values of the elasticity modulus show that the glass with $x = 5$ at.% Bi is characterized with the highest atomic packing density.

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1. Introduction

Mechanical properties of chalcogenide glasses, which are closely correlated with their structure and other physical and chemical properties, play an important role in their practical applications [1, 2]. It should be borne in mind that these glasses suffer from high brittleness, which makes the fabrication and manipulation of their structural parts very delicate and decreases their service life. Hence, it is of paramount importance to study the resistance of chalcogenide glasses against surface damage due to sharp mechanical contacts [3, 4]. Among the various experimental techniques, indentation hardness testing is frequently used for the determination of mechanical properties of these materials, since it enables the determination of elastic and plastic properties of the material. The Fisherscope HM2000 is a computer-controlled measuring system for microhardness testing and determination of material parameters according to ISO 14577 [5]. This experimental technique enables simultaneous determination of a number of mechanical quantities from the indentation curve, which are important for the characterization of the material from the aspect of its practical application and establishment of correlation with the structural elements.

This work presents the results of the analysis of the mechanical parameters of chalcogenide samples from the system of $Bi_x(As_2S_3)_{100-x}$. Also, it discusses the effect of phase separation and crystalline centers dispersed in the amorphous matrix on the values of the mechanical parameters for the composition with the highest Bi content.

2. Experimental

Measurements of the mechanical parameters of the chalcogenides from the system $Bi_x(As_2S_3)_{100-x}$, $x = 1.5$, 3, 5 and 7 at.% were carried out on a Fischerscope HM2000 S system, calibrated according to the DIN EN ISO 14577-3 standard using a BK7 type reference block. The glass samples were embedded into polyester resin and polished with abrasive powders of the appropriate grain size to a mirror finish. For each value of the load applied, measurements were performed at least in three cycles. The force change rate during the cycle was 0.5 mN/s, and the samples were subjected to a series of loads in the interval of 20–400 mN.

3. Results and discussion

The indentation curves shown in Fig. 1, recorded for the investigated materials at the maximum load of $F =$ 300 mN in three measurement cycles, indicate a high reproducibility of the experimental data. The curves recorded for the maximum Bi content ARE missing from the figure since they partly overlapped with the $F = f(h)$ curves corresponding to those for the composition with $x = 3$ at.% Bi. The results of measuring the Vickers microhardness are presented in the form of the functional dependence of the applied load (Fig. 2).

The fact that the microhardness is a measure of the chemical bonds strength and that glass transition tem-

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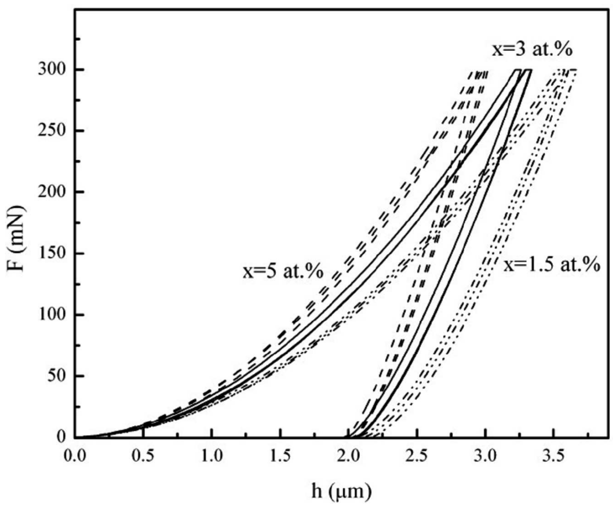

Fig. 1. Dependence of the load force on the imprint depth for samples from the $Bi_x(As_2S_3)_{100-x}$ system.

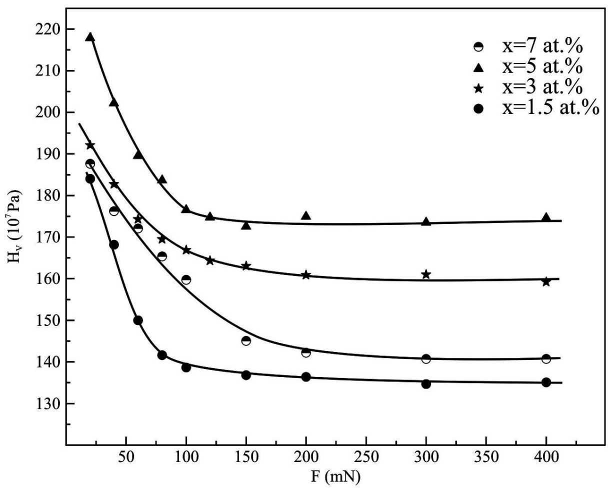

Fig. 2. Dependence of H_V on the load force for samples of the $Bi_x(As_2S_3)_{100-x}$ system.

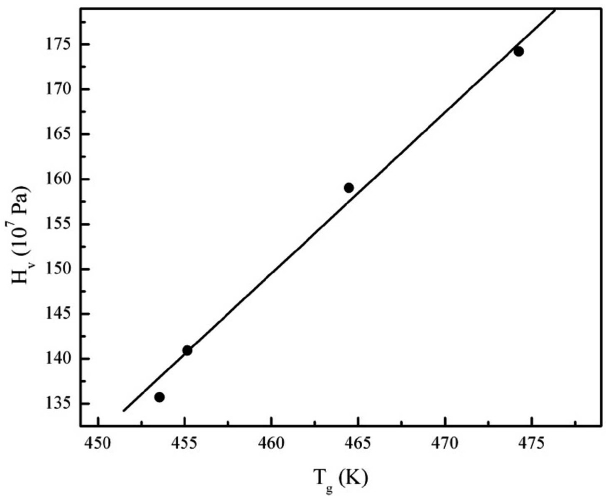

Fig. 3. Dependence of H_V on the glass transition temperature for samples of the $Bi_x(As_2S_3)_{100-x}$ system.

perature T_g is determined primarily by short-range ordering while the contribution of intermolecular interactions in the analyzed samples is negligible is confirmed by the correlation between these quantities (Fig. 3). The increase in the glass transition temperature for the first three doped composition is accompanied by increase in the parameter H_V and indicates the strengthening of glass material and increase in the stiffness of structural network at these concentrations of doping atoms. The analogy in the trend behavior of these two parameters also exists in the composition $Bi_7(As_2S_3)_{93}$, considering that its T_g value is lower than those for the glasses $Bi_3(As_2S_3)_{97}$ and $Bi_5(As_2S_3)_{95}$.

Since the microhardness can be interpreted as a measure of the strength of chemical bonds the increase in the quantity H_V as a function of the content of the dopant atoms for the first three compositions indicates the strengthening of the glass structure. This means that the solidity and rigidity of the structural network at these Bi contents show an increase due to the induction of structural units of the type Bi–S. This conclusion is confirmed with the results of the Raman spectroscopy of the sample $Bi_5(As_2S_3)_{95}$, which showed the domination of Bi_2S_3 and As_2S_3 bonds [6]. The compound with the highest Bi content shows, however, a deviation from this trend. Namely, the limiting concentration of Bi in this composition is critical for the preservation of the amorphous nature of the material, which is characterized by phase separation [7]. Thus, it is obvious that Bi doping in this concentration caused a decrease in the strength of the network due to the appearance of structural inhomogeneity and formation of homopolar atomic bonds. This is also pointed out by the analysis of the Raman spectrum of composition $Bi_7(As_2S_3)_{93}$, when it was concluded the existence of realgar and orpiment phase as well as As–As bonds [6].

The fact that phase separation is negatively reflected on the value of microhardness indicates the necessity of controlled induction of crystalline centers in the technological procedure of the synthesis. Namely, the presence of crystalline centers dispersed in the amorphous matrix As_2S_3 has as a consequence the accumulation of charge carriers at the boundary surfaces, leading to a significant increase in dielectric properties of this compound [8]. The effect of the decrease in the microhardness with the increase in the applied force (that is the normal indentation size effect, ISE) [9, 10], is pronounced with all compositions in the force range of 20–200 mN. At the same time, the ISE phenomenon indicates that the microhardness of the investigated chalcogenides cannot be characterized by only one measured parameter. In the procedure for correcting the experimentally obtained H_V values the model of elastic-plastic deformation (EPD) was used. This model is based on the correction of the dimensions of the imprint due to the elastic recovery of the material upon the removal of the indentor [11]. The relation describing this correction has the form [12]:

$$B = \frac{F}{(d + d_0)^2}, \quad (1)$$

where $B = H_T/k$ is the parameter denoting the so-called real hardness, independent of the load, and d_0 represents the correction for the imprint diagonal d, i.e. the susceptibility of the material in respect of ISE. The value of the imprint diagonal for a given load F is calculated on the basis of the indentor surface area A_s (Table I), which is determined from the indentation curve. Table I shows also the values of the other mechanical parameters obtained from the F–h curve: indentation hardness H_{IT}, indentation modulus $E_{IT}/(1 - \nu^2)$, elastic deformation work W_e, as well as the maximal (h_{max}), finite (h_f), and contact (h_c) depth of the indentor. Their determination is important for establishing the correlation between the mechanical quantities and the structure. It should be noted that there is a similarity in the behavior of these quantities in dependence of the Bi content, and the deviation of the values for the composition with maximum content of Bi atoms. The application of the EPD model on the glasses from the system $Bi_x(As_2S_3)_{100-x}$ is illustrated in Fig. 4.

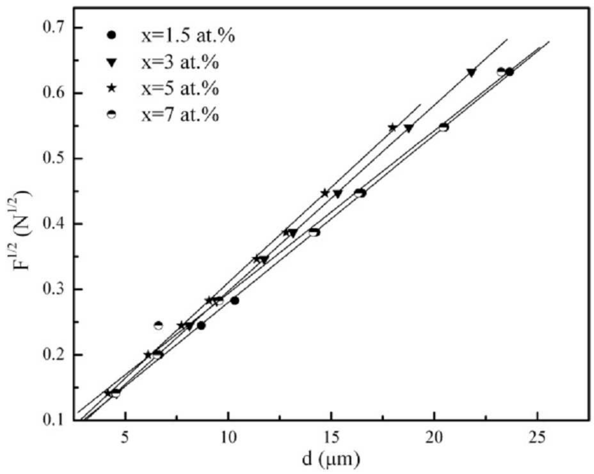

Fig. 4. Dependence of $F^{1/2}$ on the calculated value of the imprint diagonal d for samples of the system $Bi_x(As_2S_3)_{100-x}$.

TABLE I

Characteristic quantities determined from the $F-h$ curves at the load of $F = 300$ mN for samples of the system $Bi_x(As_2S_3)_{100-x}$.

x [at.%]	H_M [N/mm^2]	H_V [10^7 Pa]	H_{IT} [N/mm^2]	$E_{IT}/(1-\nu^2)$ [GPa]	W_e [μJ]	A_s [μm^2]	h_{max} [μm]	h_f [μm]	h_c [μm]
1.5	819.62	134.68	1425.23	16.51	0.18	336.34	3.62	2.13	2.93
3	971.31	160.96	1703.33	19.57	0.17	282.66	3.31	2.0	2.68
5	1158.96	175.87	1861.04	26.83	0.13	236.21	3.02	2.04	2.57
7	907.7	135.85	1437.58	20.66	0.15	303.09	3.45	2.02	2.92

Linear fitting of the functional dependence $F^{1/2} = f(d)$ was used to determine the values of the parameters B and d_0, shown in Table II. By comparing the calculated H_T values with the measured H_V values (Table I) one may notice that the difference between them is about 7–18%. The shift of the calculated H_T toward lower values is the largest for the maximum Bi content, for which there was also observed a significantly larger value of elastic recovery, i.e. the largest value of the diagonal correction. On the other hand, the lowest diagonal correction corresponds to the sample with $x = 3$ at.% Bi, for which the difference between the measured and calculated values of hardness is the smallest, so that it could be concluded that the ISE for the chalcogenide system $Bi_x(As_2S_3)_{100-x}$ is to a significant extent influenced by the elastic recovery of the material. Based on the values of h_{max} and h_c (Table I), the contact hardness S of the investigated compositions can be calculated from the relation

$$h_c = h_{max} - \varepsilon \frac{F_{max}}{S} \quad (2)$$

and then the elasticity modulus E is determined according to the following relation [13]:

$$\frac{F}{S^2} = \frac{\pi}{(2\beta)^2} \frac{H_V}{E^2}, \quad (3)$$

where β is the correction factor for the absence of the indentor symmetry, which for the Vickers indentor is $\beta = 1.0124$.

The values of the elasticity modulus calculated for the maximum load $F = 400$ mN (Table II) correspond to the values that are typical for chalcogenide glasses [14, 15]. The behavior of this parameter as a function of Bi content should be interpreted bearing in mind that it also depends on the atomic packing density, and not only on the strength of the bonds between the constituents.

This means that the composition with the greatest recovery after the indentation need not correspond to the highest value of the elasticity modulus if the packing den-

TABLE II

Parameters of the EPD model and elasticity module E for samples of the system $Bi_x(As_2S_3)_{100-x}$.

x [at.%]	B [10^8 Pa]	d_0 [μm]	H_T [10^7 Pa]	E [GPa]
1.5	6.55	0.95	121.43	17.8
3	8.09	0.45	150.10	21.7
5	8.50	0.64	157.68	31.8
7	6.19	1.83	114.79	25.3

sity C_g of its structural units is lower compared to the other investigated compositions. On the other hand, based on the values presented in Table II, one may assume that the densest atomic arrangement in the investigated system is characteristic for the glass with $x = 5$ at.% Bi, and this assumption is in accordance with the results of the Raman spectroscopy [6]. Also, it should be pointed out that the sample with the highest value of the estimated modulus corresponds to the smallest value of the elastic deformation work, W_e (Table I), and vice versa.

4. Conclusion

The results of the instrumented indented tests of the samples from the $Bi_x(As_2S_3)_{100-x}$, $x = 1.5$, 3, 5 and 7 at.% System indicated an increase in the microhardness as a function of the doping element content for the first three compositions, as well as a pronounced normal ISE phenomenon in the range of lower indentation loads. According to the correlation with glass transition temperature, the value of the H_V was interpreted as a measure of the strength of the chemical bonds in the structure, i.e. as an indicator of the strength and rigidity of the structural network. The deviation observed for the sample with the maximum content of Bi atoms is associated with the phase separation in the structure of this composition, also observed on the Raman spectra [6]. The application of the EPD model in the process of correcting experimental data enabled the determination of the parameters B and d_0, and, based on their values, it was possible to estimate the influence of the effect of elastic recovery of the investigated materials on the measurement results. Based on the estimated values of the elasticity modulus one concludes that the glass with $x = 5$ at.% Bi is characterized by the densest atomic packing, which is in accordance with analysis of its Raman spectra [6].

Acknowledgments

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