

THERMAL COEFFICIENT OF LINEAR EXPANSION OF NON-CRYSTALLINE CHALCOGENIDES IN THE As–S–Se–Te–I SYSTEM

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Abstract

The object of the paper is an investigation of the glasses of the $(As_2S_3)_x(AsSe_{0.5}Te_{0.5}I)_{100-x}$ type for $65 \leq x \leq 95$, using methods of thermomechanical analysis. Values of the thermal coefficients of linear expansion in solid and visco-plastic phase were determined. It was shown that introducing arsenic-sulfide in glass-matrix AsChI, i.e. $(AsSe_{0.5}Te_{0.5}I)$, leads to an increasing stability of these glasses.

The characteristic temperatures of softening T_g and the temperature of the beginning of deformation T_ω increase by increasing content of As_2S_3 . The analytical forms of dependence of four significant physical values α_g , α_l , T_g , T_ω , as a function of As_2S_3 content in the structure of glasses were fitted.

Keywords: amorphous chalcogenides, glass transition temperature, temperature of beginning of deformation, thermal coefficient of linear expansion

Introduction

The quality, different applicative characteristics and many important physical characteristics of binary systems As–S, As–Se and As–Te [1] would be enriched by the structure combination, introducing two or even three chalcogenide elements to the system. In addition, introducing halogen elements in the material leads to the changes in structure, i.e. the chain-structure transforms into space-defined or layer-chain structure.

Considering significant characteristics of ternary system As–S–Se, As–S–Te, As–Se–Te [2–5] and also results which are related to specific characteristics of Cu–As–Se–I and Ge–As–Se–S–I [6, 7], samples of the $(As_2S_3)_x(AsSe_{0.5}Te_{0.5}I)_{100-x}$ type for $65 \leq x \leq 95$ were synthesized, using method described in our previous paper [8].

This paper describes the results of thermomechanical study of bulk glassy chalcogenide material of complex structure. As it is very well known, the coefficient of thermal expansion is related to the temperature of softening. It depends strongly on strength and the type of chemical bond in structural units and on the bonds interconnecting the structural units themselves.

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The thermal coefficient of linear expansion of the solid and visco-plastic phase, α_g and α_1 , [9, 10] respectively, were determined as a slope of straight-line parts of the functional dependence of the relative changes in the sample height vs. temperature. The characteristic temperatures in area of phase transition, glass-transition temperature T_g and temperature of the beginning of deformation T_ω were also determined. The value of thermal coefficient of linear expansion α and its characteristic change in range of transformation, could help in understanding of the internal structure of the glassy skeleton and the influence of some structural units to glass-stability.

Experimental

Dilatometric studies of amorphous samples of the $(As_2S_3)_x(AsSe_{0.5}Te_{0.5}I)_{100-x}$ type for $65 \leq x \leq 95$, were carried out on a Perkin Elmer TMA 7 thermomechanical analyzer in the range from the room temperature to the temperature of the beginning of the material deformation by its own mass. The samples were prepared in a form of parallelepiped (thickness was 0.8–4.4 mm) by using abrasive powder and special carrier (holder). The changes in sample length were measured within accuracy of $\pm 10^{-4}$ mm. The rate of sample heating was 2 K min^{-1} , and the furnace was cooled using water. Measurements were carried out in the air atmosphere at probe loads of 10 mN. The results of these measurements are statistically treated.

Results and discussion

The results of measuring expansion of the sample $(As_2S_3)_x(AsSe_{0.5}Te_{0.5}I)_{100-x}$ are presented in Fig. 1. The thermal coefficients of linear expansion of solid and visco-plastic phase, α_g and α_1 , respectively, i.e. below and above the temperature T_g , were determined based on the slope of straight-line parts of the functional dependence of the relative changes in the sample height vs. temperature.

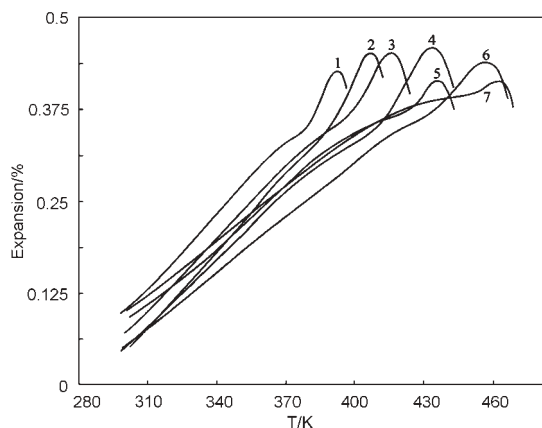


Fig. 1 Relative changes in the sample height of glasses of the $(As_2S_3)_x(AsSe_{0.5}Te_{0.5}I)_{100-x}$ system with temperature: 1 – $x = 65$; 2 – $x = 70$; 3 – $x = 75$; 4 – $x = 80$; 5 – $x = 85$; 6 – $x = 90$; 7 – $x = 95$

Table 1 Thermomechanical parameters of glasses in the $(\text{As}_2\text{S}_3)_x(\text{AsSe}_{0.5}\text{Te}_{0.5}\text{I})_{100-x}$ system

$x/\%$ As_2S_3	$\alpha_g/10^{-6} \text{ K}^{-1}$	$\alpha_l/10^{-6} \text{ K}^{-1}$	T_g/K	T_w/K
65	36.6±0.3	80±6	380.7±2.0	389.9±1.4
70	34.0±0.6	73±5	389.3±1.8	404.3±0.5
75	32.8±0.3	64±5	400.9±0.3	416.7±0.8
80	30.0±0.3	53±2	412.7±1.1	430.6±0.6
85	28.3±0.3	46±6	423.7±1.0	435.2±0.8
90	26.2±0.3	35±5	437.3±0.4	455.4±0.8
95	24.5±0.3	24±3	455.2±0.5	463.6±1.1

The errors of obtained values of α_g are not higher than 2%, and less than 5% for α_l . In Table 1, statistically treated results for α_g , α_l , T_g and T_w including corresponding deviations are presented.

As it is known, the thermal expansion of glass material is caused by changes in lengths of relatively weak intermolecular forces between the existing structural units. It manifests in terms of relatively high values of α .

The chemical bonds inside structural units of AsSe , As_2Se_3 , As_2S_3 , As_2Te_3 ,... type, which are the most probably formed in these glasses, are of covalent type. These bonds are much stronger than intermolecular bonds between structural units and they are practically not influenced by the expansion. In other words, the change in the interatomic distance within the structural units involved make only a small portion in the value of α .

Figures 2 and 3 show correlation between α_g and α_l , T_g and T_w , and content of As_2S_3 structural units. By extrapolating assumed functional dependence of α_g and T_g vs. content of As_2S_3 for $x=100$, i.e. in the case of As_2S_3 glass, we got the values of α_g and T_g , which are very close to the values found in literature ($\alpha_g=(23.9\pm 1.3)\cdot 10^{-6} \text{ K}^{-1}$ and $T_g=(463\pm 5) \text{ K}$) [11]. These literature values are marked at figures as open square. It can be concluded that the values of coefficient α for investigated samples (Table 1) are in the range of characteristic values for chalcogenide glasses [11].

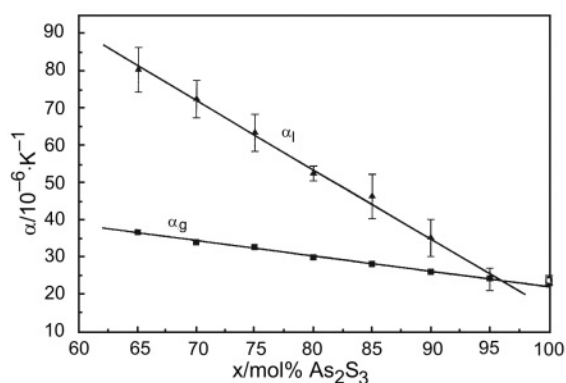


Fig. 2 The thermal coefficient of linear expansion of solid phase (α_g) and visco-plastic phase (α_l) as function of As_2S_3 content

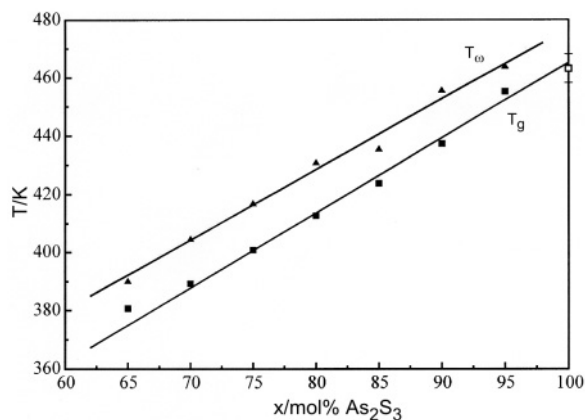


Fig. 3 The glass-transition temperature (T_g) and the temperature of the beginning of deformation (T_ω) as function of As_2S_3 content

The values of T_g and T_ω are increased, and the values of thermal coefficient of linear expansion are decreased by increasing the content of As_2S_3 which shows that those structural units contribute to the strength of glassy skeleton and enhance stability of glass. Namely, one expects that higher values of glass transition temperature T_g imply higher degree of interconnection of structural elements in the network. For this reason, the increase of T_g with increase of As_2S_3 contents in glass matrix, indicates to higher thermal stability of the material.

It should be noticed that observed decreasing trend of α coefficient with increasing content of As_2S_3 in the glasses, is also preserved above the temperature T_g , i.e. it is also related to the coefficient of visco-plastic phase α_1 . Increasing trend of α coefficient and at the same time decreasing trend of temperatures T_g and T_ω by increasing content of As_2S_3 has monotonous character which attributed to solid solution character.

Analytical forms of these functions were fitted as follows:

$$\alpha_g = 63 - 0.41x \quad [10^{-6} \text{ K}^{-1}]$$

$$\alpha_1 = 202 - 1.86x \quad [10^{-6} \text{ K}^{-1}]$$

$$T_g = 207 + 2.58x \quad [\text{K}]$$

$$T_\omega = 235 + 2.42x \quad [\text{K}]$$

where x is content of As_2S_3 in the sample.

These expressions enable successful estimation of expected values of these important parameters, while synthesizing new materials inside the defined range of concentrations. It has been shown (Fig. 4) that, within the experimental errors, relation between the thermal expansion coefficients and the reciprocal value of the glass transition temperature can be represented by a linear function.

The same correlation between thermal coefficients α_g and α_1 is noticed. The linearity of the function $\alpha_1 = f(\alpha_g)$, which has been confirmed for many inorganic and organic glasses [12], has also been found for the glasses of the investigated system (Fig. 5).

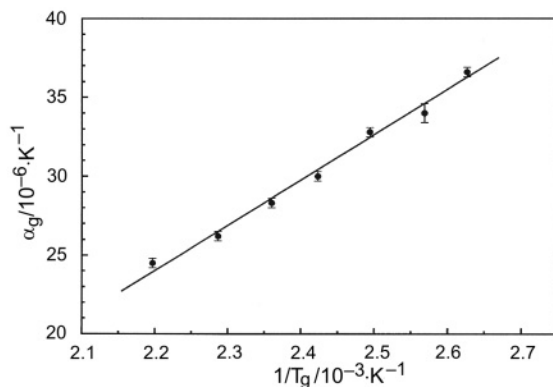


Fig. 4 Correlation between the thermal expansion coefficient α_g and glass transition temperature $1/T_g$ for the glasses $(\text{As}_2\text{S}_3)_x(\text{AsSe}_{0.5}\text{Te}_{0.5}\text{I})_{100-x}$

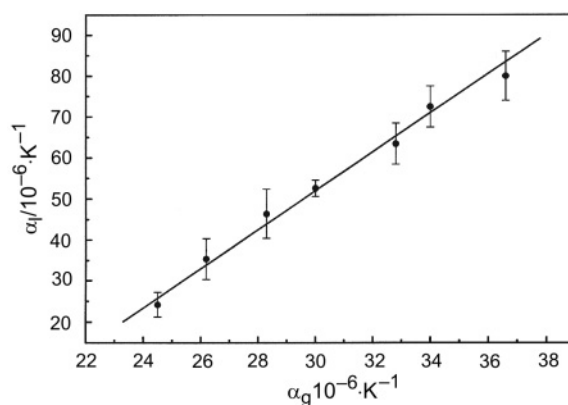


Fig. 5 Correlation between the thermal coefficients of linear expansion of the visco-plastic (α_l) and solid (α_g) phase for glasses of the $(\text{As}_2\text{S}_3)_x(\text{AsSe}_{0.5}\text{Te}_{0.5}\text{I})_{100-x}$ type

This could be an indirect proof that the corresponding α_l/α_g ratio is the function of the Poisson coefficient μ [13] only, which is approximately constant for the glasses of the same system, i.e. of the same structural composition.

Conclusions

It was shown that the glass transition temperature and the temperature of the beginning of deformation show a linear increase with As_2S_3 content in the $(\text{As}_2\text{S}_3)_x(\text{AsSe}_{0.5}\text{Te}_{0.5}\text{I})_{100-x}$ glasses. The first parameter changes in the range from 380 to 456 K and the second parameter in the 390 to 464 K range.

At the same time coefficients of thermal expansion in solid and visco-plastic phase decrease in the range from 36.6 to $24.5 \cdot 10^{-6} \text{ K}^{-1}$ and in the 80 to $24 \cdot 10^{-6} \text{ K}^{-1}$ range, respectively.

Presented results show that the presence of As_2S_3 in the sample leads to stronger glassy network and also improved stability of glass.

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