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Influence of antimony on thermal stability of bulk chalcogenides from $Sb_xAs_{37-x}S_{48}I_{15}$ system

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The paper describes the results of determining the thermomechanical properties of chalcogenide glasses from $Sb_xAs_{37-x}S_{48}I_{15}$ system for x=0, 12, 22, 32 and 37 at%. The glass transition temperatures, i.e. the softening temperatures t_g, thermal coefficients of linear expansion α_g and temperatures of the beginning of deformation t_ω were determined by the methods of thermomechanical analysis. The glass transition temperatures were also determined by DSC method. It was found that the glass transition temperatures, temperatures of beginning of deformation and thermal coefficients of linear expansion α_g depend on the percentage of Sb content in the glasses. The glass transition temperatures and temperatures of the beginning of deformation increase with increase of Sb content. The coefficients of linear expansion decrease with the increase of Sb content.

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1. Introduction

Investigations of mechanical, electrical, optical and other physical properties of amorphous semiconducting materials have shown that these properties depend substantially on the system composition. Four and five – component systems offer special possibilities regarding the possibility of varying and even programming the relevant properties of these systems because one can influence the properties of the system simply by changing the ratio of their components [1-4].

The investigated system is $Sb_xAs_{37-x}S_{48}I_{15}$ for the x=0, 12, 22, 32 and 37 at%. The samples were synthesized and investigated in order to determine the influence of substitution of As atoms with Sb atoms on thermally induced SbSI ferroelectric centers, i.e. on expected ferroelectric characteristics of glass-ceramics material (sital). It is known that obtaining at least partialy amorphous SbSI is possible only under the special conditions [5]. On the other hand presence of arsenic should improve the process of obtaining the amorphous matrix in investigated system.

The results of determining the thermomechanical properties of these chalcogenides were described. The glass transition temperatures, i.e. the softening temperatures t_g, thermal coefficients of linear expansion α_g and temperatures of the beginning of deformation t_ω were determined by the methods of thermomechanical analysis. The glass transition temperatures were also determined by differential scanning calorimetry (DSC) method.

2. Experiment

According to phase diagrams of two ternary systems As-S-I and Sb-S-I shown in Fig. 1 [5, 6], melting temperature of each element and compounds that can be formed, technological card for obtaining the glasses of $Sb_xAs_{37-x}S_{48}I_{15}$ type, for x= 0, 12, 22, 32 and 37 at% was projected.

The investigated glasses were synthesized from high purity elementary components (99.99%). Masses were measured by analytical balance METTLER B-6 with an accuracy of $\pm 5\times10^{-8}$ kg. The measured quantities were sealed in cylindrical quartz ampoules evacuated to a pressure of the order of magnitude of 1×10^{-3} Pa. The ampoule length was usually about 15 cm, its diameter 15 mm, and the wall thickness 1.5 mm, in order to be able to withstand the relatively high pressures in the ampoule during the synthesis. The synthesis was carried out in semiautomatic horizontal tube furnaces Carbolite, Model CTF 12/65, with a temperature controller Eurotherm 91-3. The melts were air-quenched.

Compositions on the border of glass-forming regions, i.e. three-component samples $Sb_{37}S_{48}I_{15}$ and $As_{37}S_{48}I_{15}$, were obtained in modified processes that were adjusted according to the present elementary components.

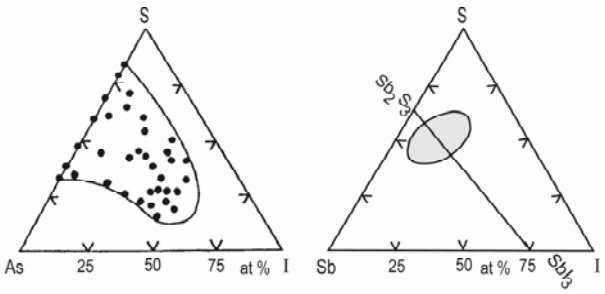

Fig. 1. Phase diagram of ternary system: a) As-S-I and b) Sb-S-I.

Amorphous character of the samples was determined by using standard optical and X-ray techniques.

Dilatometric studies of samples were carried out on a Perkin Elmer TMA 7 thermomechanical analyzer in the range from room temperature to the temperature of the beginning of the material deformation by its own mass. Changes in sample length were measured with an accuracy of $\pm 10^{-4}$ mm, rate of sample heating was 2 ^{o}C /min, and the furnace was cooled with water.

The calorimetric measurements were carried out using DSC822^e Mettler Toledo with a temperature accuracy of ±2 ^{0}C. Bulk glass samples (~5 mg) were sealed in aluminium pans and scanned under pure nitrogen atmosphere at the heating rate of 10 ^{0}C/min.

3. Results

Fig. 2 presents dilatometric curves, i.e. the results of thermal linear expansion recording of the investigated glass system.

The glass transition point, i.e. the softening temperature t_g was determined as a temperature of the first slope changes in linear functional dependence of the relative changes in the sample height versus temperature. The termination of the process of thermal expansion of the glass is characterized by the temperature of the beginning of deformation t_ω. After this temperature glass starts to change its dimension due to its own mass.

Thermal coefficients of linear expansion of solid (α_g) for $Sb_xAs_{37-x}S_{48}I_{15}$ samples for x=0, 12, 22, 32 and 37 at % Sb were determined from the slope of straight - line parts of the functional dependence $\Delta\ell=f(t)$ (Fig. 2).

The determined values for both of characteristic temperatures and thermal coefficients of linear expansion of solid (α_g) for investigated samples are given in Table 1.

Relatively high values of thermal coefficients of linear expansion of investigated samples indicate that thermal expansion is dominantly due to the changes of bonds length between expected structural units. Strong covalent bonds, which are formed inside the expected structural units, can not have significant influence on thermal expansion effects [1].

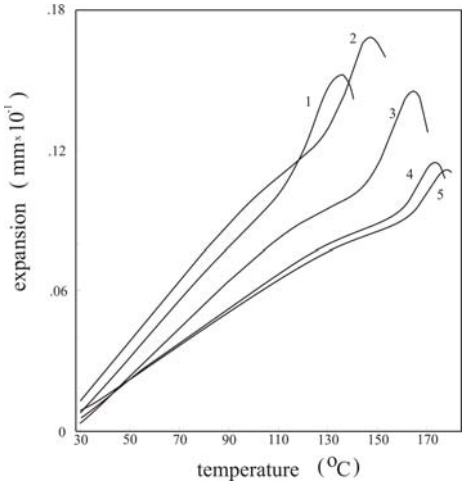

Fig. 2. Changes in the sample height of: 1) $As_{37}S_{48}I_{15}$; 2) $Sb_{12}As_{25}S_{48}I_{15}$: 3) $Sb_{22}As_{15}S_{48}I_{15}$: 4) $Sb_{32}As_5S_{48}I_{15}$; 5) $Sb_{37}S_{48}I_{15}$.

Fig. 3 shows correlation between glass transition point and the temperature of the beginning of thermomechanical deformation and content of Sb in $Sb_xAs_{37-x}S_{48}I_{15}$ glasses.

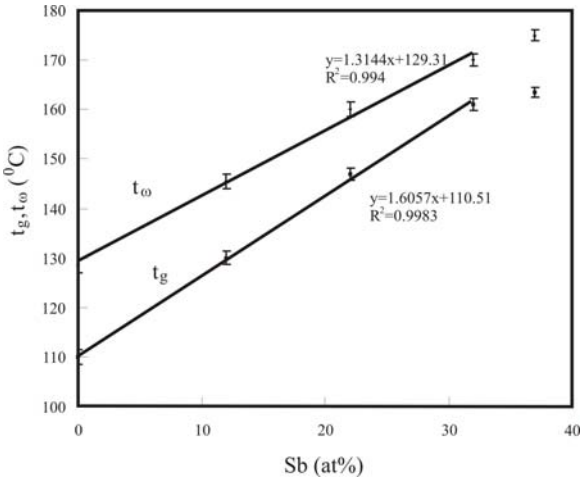

Fig. 3. Dependence of glass transition point and temperature of the beginning of deformation on Sb content determined by thermomechanical analysis.

Fig. 4 presents the dependence of thermal coefficients of linear expansion of glass samples (α_g) on Sb content. Linear dependence of this parameter on antimony content indicates that samples have the character of solid solutions [7].

It can be seen that increase in Sb content in glass composition has significant influence on presented parameters. The coefficient of linear expansion of solid phase α_g, decreases and the softening temperature t_g increases with increase in Sb content in the material, indicating thus the strengthening of the structural network of the glass.

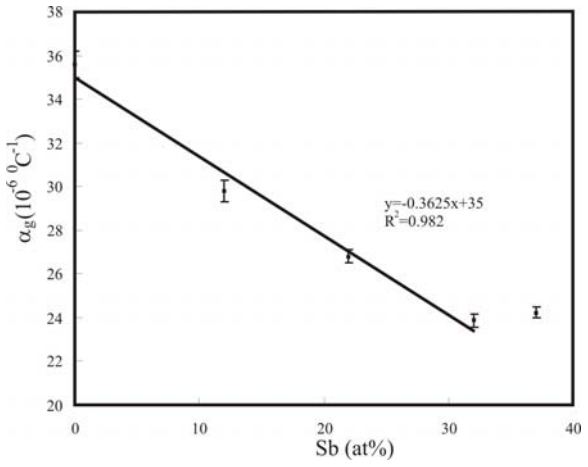

Fig. 4. Dependence of thermal coefficients of linear expansion (α_g) on Sb content.

The stronger structural skeleton and higher softening temperatures mean a better thermal stability of the material. The temperature of the beginning of deformation t_ω, follows the change in the softening temperature and also increases linearly with increase in Sb content.

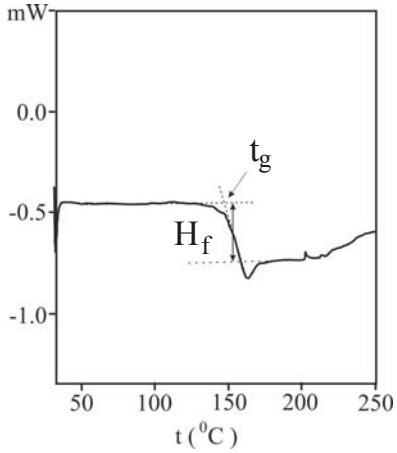

Fig. 5. DSC curve for the $Sb_{22}As_{15}S_{48}I_{15}$.

Only the $Sb_{37}S_{48}I_{15}$ composition does not fit in plotted linear dependence of determined parameters on Sb content within the error limits, although this composition also shows increase of obtained temperatures with increase of Sb percentage in investigated glasses.

Fig. 5 presents DSC curve for the $Sb_{22}As_{15}S_{48}I_{15}$ sample as a representative of the investigated glasses.

The glass transition temperatures and jump of heating capacity ΔC_p were determined.

The values for glass transition temperatures and jump of heating capacity ΔC_p, which were determined by DSC measurements are shown in Table 1.

ΔC_p is evaluated using the relation [8]:

$$\Delta C_p = (\frac{H_f}{m})(\frac{1}{\beta})$$

where H_f is the change of heat flow through a sample of mass m and β is the heating rate.

Table 1. Results of dilatometric measurements of glasses $Sb_xAs_{37-x}S_{48}I_{15}$: t_g-softening temperature, t_ω-temperature of beginning of deformation, α_g-thermal coefficient of linear expansion of solid phase and the values for glass transition temperatures and jump of heating capacity, ΔC_p obtained from DSC records.

sample	TMA results				DSC results	
	l (mm)	α_g ($\cdot 10^{-6}$ ^{0}C^{-1})	t_g (^{0}C)	t_ω (^{0}C)	t_g (^{0}C)	ΔC_p (J/gK)
$As_{37}S_{48}I_{15}$	3.457	35.6(6)	110.0(14)	128.5(14)	110(1)	0.175(9)
$Sb_{12}As_{25}S_{48}I_{15}$	4.265	29.8(5)	130.0(14)	145.5(14)	130(1)	0.202(10)
$Sb_{22}As_{15}S_{48}I_{15}$	3.968	26.8(3)	147.0(12)	160.0(14)	146(1)	0.283(6)
$Sb_{32}As_5S_{48}I_{15}$	3.330	23.87(29)	161.0(12)	170.0(12)	160(1)	0.216(15)
$Sb_{37}S_{48}I_{15}$	3.053	24.23(23)	163.5(10)	175.0(10)	164(1)	0.244(24)

Fig. 6 shows dependence of glass transition point and temperature of the beginning of deformation on Sb content determined by DSC.

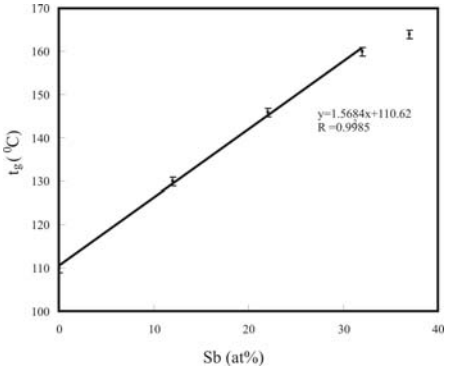

Fig. 6. Dependence of glass transition point and temperature of the beginning of deformation on Sb content determined by DSC.

Glass transition temperature dependence on Sb content in glass composition, which had been noticed in dilatometric shifts, has been confirmed in DSC measurements. Considering that glass transition temperature depends on heating rate it must be emphasized that measurements were carried out with different values of this parameter.

4. Conclusions

For glasses from $Sb_xAs_{37-x}S_{48}I_{15}$ system for x=0, 12, 22, 32 and 37 at% determined values of the softening temperatures were in range from 110.0(14) ^{0}C to 163.5(10) ^{0}C, temperatures of the beginning of

deformation from 128.5(14) ^{0}C to 175.0(10) ^{0}C and thermal coefficients of linear expansion from 35.6(6) × 10^{-6} $^0C^{-1}$ to 23.87(29) × 10^{-6} $^0C^{-1}$. It was determined that increase of Sb content in glass matrix significantly influences the increase in values of softening temperatures and temperatures of the beginning of deformation and decrease of thermal coefficient of linear expansion, and therefore also influences thermal stability of investigated system.

DSC measurements in region of glass transition temperature have confirmed the results of dilatometric measurements.

Acknowledgements

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