

EFFECT OF COPPER ON THERMOMECHANICAL CHARACTERISTICS OF AMORPHOUS AsSe_yI_z

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Abstract

The paper describes results of a study of glasses of the type $\text{Cu}_x(\text{AsSe}_{1.4}\text{I}_{0.2})_{100-x}$ for $x=0, 1, 5, 10, 15, 20$ and 25 at% Cu, by the methods of thermomechanical analysis. Values of the thermal coefficients of linear expansion in solid and visco-plastic phase were determined and the dependence of this parameter on copper concentration was established. The experimental method used enabled the determination of characteristics glass transition temperature and the temperature of the beginning of deformation, and it was found that these parameters increase with increase in the copper content.

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

Introduction

As is known, thermal expansion of solid bodies is a consequence of the anharmonic oscillations of atoms (molecules) of the structural network. Dilatometric measurements can be the way to determine several quantities important for disordered systems. By measuring the effects of linear change of dimensions of the material in the course of its heating it is possible to determine the thermal coefficient of linear expansion, α . Its value and the characteristic change in the range of transformation can bring about a better understanding of the internal relationships in the structural skeleton of glasses. The higher the coefficient α , the lower the strength of the bonds interconnecting the structural units, i.e. the smaller the short-range ordering [1]. Weaker bonds between these domains means a lower vitrification (or softening) point.

It is possible to distinguish two coefficients of thermal expansion α [2]:

α_g – related to the solid phase of the disordered material, i.e. conditioned by increase of the mean distance between the particles;

α_l – related to visco-plastic state and may be represented in the form $\alpha_l = \alpha_g + \Delta\alpha$.

The value $\Delta\alpha$, representing the difference between the two coefficients ($\alpha_l - \alpha_g$), is a consequence of gradual breaking of chemical bonds between the domains of

short-range ordering and increase of their mobility [2, 3]. The termination of the process of thermal expansion of the glass is characterized by the temperature T_{ω} the so-called temperature of the beginning of deformation. After this temperature the glass starts to change its dimensions due to its own mass.

Previous investigations by different thermal methods showed that the glass transition temperature (T_g) of the glasses in the chalcogenide system Cu–As–Se–I depends on the copper ratio in the material [4].

In this work we present results of the research carried out with the aim of establishing the effect of copper content in the glasses of the type $\text{Cu}_x(\text{AsSe}_{1.4}\text{I}_{0.2})_{100-x}$ for $y=1.4$ and $z=0.2$ on the value of thermal expansion coefficient, glass transition point, as well as the temperature of the beginning of thermomechanical deformation.

Experimental

Dilatometric studies of amorphous samples of the type $\text{Cu}_x(\text{AsSe}_{1.4}\text{I}_{0.2})_{100-x}$ for $x=0, 1, 5, 10, 15, 20$ and 25 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, and the temperature changes with ± 2 K. The rate of sample heating was 2 K min^{-1} , and the furnace was cooled with water. Measurements were carried out in the air atmosphere at probe loads of 10 mN.

In view of the fact that the measuring equipment required a defined form of samples, they were prepared mechanically in the form of plates whose initial thicknesses were 2–7 mm.

Results and discussion

In Fig. 1 the results of measuring expansion of the samples are presented. The thermal coefficients of linear expansion of the solid and visco-plastic phase, α_g and α_i , respectively, determined on the basis of the slope of straight-line parts of the functional

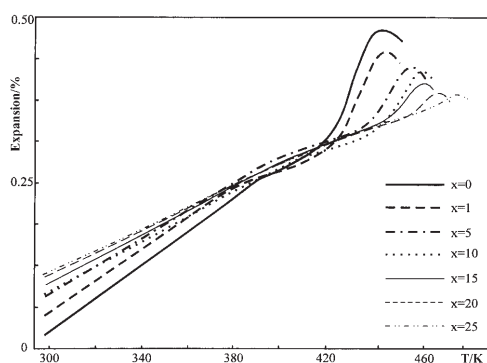


Fig. 1 Relative changes in the sample height of glasses of the $\text{Cu}_x(\text{AsSe}_{1.4}\text{I}_{0.2})_{100-x}$ system with temperature

dependence of the relative changes in the sample height with temperature. The errors of particular results for α_g are not higher than 2%, and less than 5% for α_l (the higher error is a consequence of the narrow range of the existence of visco-plastic phase in which α_l is determined). In Table 1 the statistically treated results for α_g , α_l , T_g , and T_w with the corresponding deviations are presented.

Table 1 Thermomechanical parameters of glasses in the $\text{Cu}_x(\text{AsSe}_{1.4}\text{I}_{0.2})_{100-x}$ system

| Contents of copper $x/\text{at.}\%$ | $\alpha_g/10^{-6} \text{ K}^{-1}$ | $\alpha_l/10^{-6} \text{ K}^{-1}$ | T_g/K | T_w/K |
|--|-----------------------------------|-----------------------------------|----------------|----------------|
| 0 | 25.8±0.2 | 95.9±3.2 | 420.4±0.4 | 439.7±0.5 |
| 1 | 23.9±0.2 | 78.6±3.5 | 424.8±0.4 | 440.6±0.9 |
| 5 | 21.3±0.3 | 63.3±6.0 | 436.4±0.7 | 449.5±1.0 |
| 10 | 20.1±0.2 | 53.7±2.9 | 442.1±0.3 | 456.2±0.7 |
| 15 | 18.8±0.1 | 42.8±2.4 | 445.7±0.5 | 457.4±1.2 |
| 20 | 17.3±0.1 | 31.8±2.7 | 452.8±0.7 | 463.7±1.1 |
| 25 | 16.3±0.2 | 21.8±3.3 | 461.8±1.0 | 473.5±1.1 |

α_g, α_l – thermal coefficients of linear expansion of the solid and visco-plastic phase, respectively;
 T_g – glass transition temperature, T_w – temperature of the beginning of deformation

It can be seen that the obtained values of thermal coefficient of linear expansion of these glasses in solid state are relatively high compared with, let's say, vitreous SiO_2 ($\alpha_g=2\cdot 10^{-6} \text{ K}^{-1}$ [5]). The reason for the behaviour of such materials should be connected with characteristics of structural units. Namely, the previous results show that at the temperatures below T_g , the thermal expansion of glass material was determined, a priori with intermolecular forces between the elements of the glass structure [3, 6, 7]. On the other hand, it is known that in the materials of this type the atoms in the domain of short-range ordering, i.e. the atoms in the existing structural units are prevailing bound by the covalent type of bonding [8, 9]. The energy of this strong bond changes very little with the change in its length, i.e. with the change of the interatomic distance, as a consequence of heating. By using an approximate expression for the potential energy the atom possesses in the field of action of elastic forces of the other atoms [1] it is possible to express the thermal coefficient of linear expansion as a function of the derivative of this energy [10]. The mentioned large changes in the energy for small changes of interatomic distances, characteristic of strong homopolar bonds, imply high values of the second derivative of the potential energy, the consequence being a small value of the component of the coefficient α characterizing the domain of short-range ordering. In other words, the change in the interatomic distance within the structural units involved makes only a small portion in the value of α . As the energy of intermolecular interaction between structural units, and which, by their nature, are not so weak, changes little with the distance, it is clear that the thermal expansion of the investigated glasses occurs, mainly, due to the change in the intermolecular bonds.

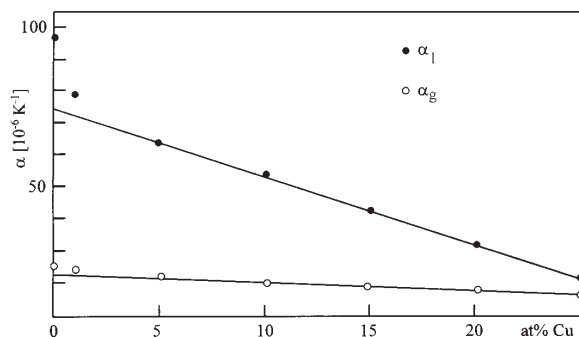


Fig. 2 Dependence of thermal coefficients of linear expansion of the $\text{Cu}_x(\text{AsSe}_{1.4}\text{I}_{0.2})_{100-x}$ glasses on copper concentration; α_g – for the solid phase; α_l – for the visco-plastic phase

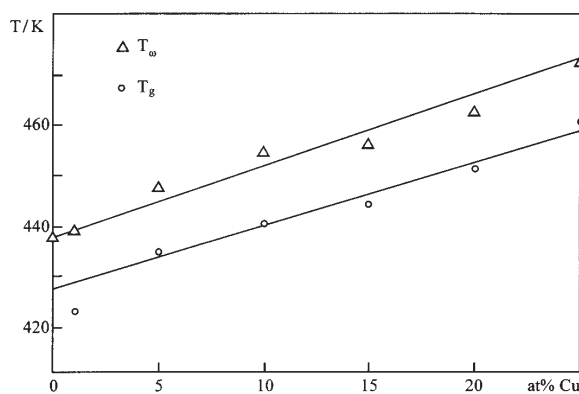


Fig. 3 Dependence of the glass transition temperature T_g and the temperature of the beginning of deformation T_w for the glasses $\text{Cu}_x(\text{AsSe}_{1.4}\text{I}_{0.2})_{100-x}$ on copper concentration

Another obvious result is the decrease of the thermal coefficient of linear expansion of the solid phase α_g and the increase in the glass transition temperature T_g with the increasing content of copper in the investigated system. Thus, it could be said that copper strengthens the glass network and a possible way for this is the formation at increased concentrations of the new structural units of the form CuAsSe_2 , Cu_3AsSe_3 , and Cu_3AsSe_4 , compositions of which have already been established [9, 11–13]. The stronger structural skeleton (which is characterized by smaller α_g values) and higher glass transition temperature T_g mean a wider temperature range of the existence of the disordered phase, which explicitly means an increased thermal stability. The stronger internal binding in the glass network, i.e. the stronger intermolecular forces cause the energies of these bonds change less with distance, which explains the lowering of the coefficient. The evidence that copper strengthens the internal glass structure is confirmed by the behaviour of the microhardness with the change of copper concentra-

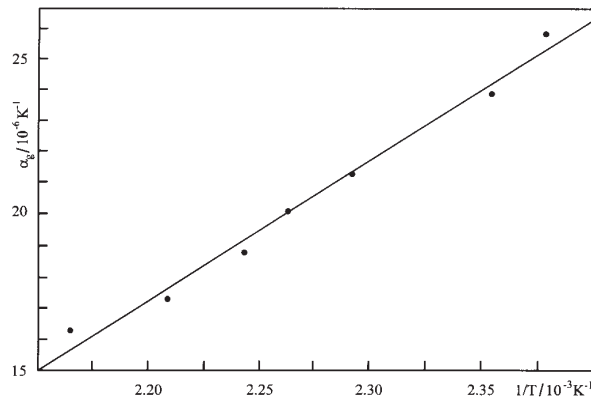


Fig. 4 Correlation between the thermal expansion coefficient α_g and glass transition temperature T_g for the glasses $\text{Cu}_x(\text{AsSe}_{1.4}\text{I}_{0.2})_{100-x}$

tion in the materials [14]. It should be pointed out that this tendency reaches saturation at a copper concentration of 21.44% [9, 13, 14], which corresponds to the percentage of its participation in the stoichiometric ratio CuAsSe_2 .

Also, it should be noticed that the decreasing trend observed for the α coefficient with increasing copper content 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 (Table 1). In Fig. 2 the concentration dependence on the thermal coefficient of linear expansion of solid and visco-plastic phase is presented. In the case of the investigated glasses, the abrupt change in α_1 with the introduction of small amounts of copper is a consequence of the appearance of domains of short-range ordering in the copper-containing structure. In other words, the initial nonlinearity of the function $\alpha_1 = f(\text{at\% Cu})$ at increased copper concentration is probably due to the absence of essential changes in the lattice ordering, i.e. the existing structural units are only accumulated in the material.

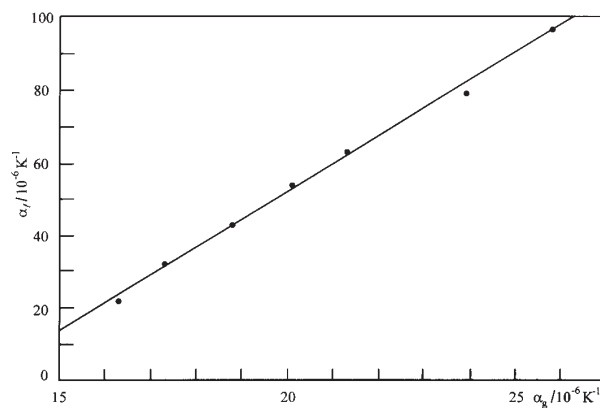


Fig. 5 Correlation between the thermal coefficients of linear expansion of the visco-plastic (α_1) and solid (α_g) phase for glasses of the $\text{Cu}_x(\text{AsSe}_{1.4}\text{I}_{0.2})_{100-x}$ type

Figure 3 shows the concentration dependence on the glass transition temperature T_g and temperature of beginning of transformation T_ω .

By using least squares method and taking into account the standard deviations, the corresponding linear dependence were derived for α_g and T_g . After excluding the results for the samples without copper and with 1% of copper, which showed larger deviations, the analytic forms of these functions are as follows:

$$\alpha_g = 22.6 - 0.256x \quad (10^{-6} \text{ K}^{-1})$$

$$T_g = 429 + 1.23x \quad (\text{K})$$

where x is the atomic percentage of copper in the investigated glass.

It has been shown that, within the experimental errors, the relationship between the thermal expansion coefficients and the reciprocal value of the glass transition temperature can be represented by a linear function (Fig. 4).

Besides, within the obtained results the correlation of the same type is observed for the coefficients α_l and α_g . The linearity of the function $\alpha_l = f(\alpha_g)$, which has been confirmed for many inorganic and organic glasses [15] has also been found for the glasses of the investigated system, which is evident from Fig. 5. This could be an indirect proof that the corresponding α_l / α_g ratio is only a function of the Poisson coefficient μ [3], 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 the copper content in the $\text{Cu}_x(\text{AsSe}_{1.4}\text{I}_{0.2})_{100-x}$ glasses. The former parameter changes in the range from 420 to 462 K, and the latter one in the 440 to 474 K range. At the same time, the coefficient of thermal expansion of the material in the solid and visco-plastic phase changes in the interval from 25.8 to $16.3 \cdot 10^{-6} \text{ K}^{-1}$ and 95.9 to $21.8 \cdot 10^{-6} \text{ K}^{-1}$, respectively. Such tendencies are preserved to the maximum copper content of 21.44 at%, after which crystalline centers inevitably appear, which essentially change the character of the physical parameters.

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