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DEPENDENCE OF THERMAL STABILITY AND THERMOMECHANICAL CHARACTERISTICS OF NON-CRYSTALLINE CHALCOGENIDES IN THE Cu–As–Se SYSTEM ON COPPER CONTENT

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The paper describes the results of a study of glasses of the type $Cu_xAs_{50}Se_{50-x}$ for x=5, 10 and 15 at.% Cu, by the method of thermomechanical analysis. Values of the thermal coefficients of linear expansion in solid (α_g) and visco-plastic (α_ω) phase were determined. On the basis of the results obtained using the mentioned methods it was possible to determine the specific temperature of the beginning of the softening process of the glass (T_g), as well as the temperature of the beginning of the deformation (T_ω). It was shown that coefficients of linear expansion decrease with the increase of Cu content. On the other hand, the increase of Cu content caused the increase of the temperatures. The analytical forms of dependence of four physical parameters α_g, α_ω, T_g, T_ω as a function of the Cu content were fitted.

Keywords: *chalcogenides, thermal coefficient of linear expansion, thermomechanical analysis*

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. The investigated materials are based on binary system As–Se, and copper introduced in chosen cut. It has been found that the presence of Cu in amorphous arsenic-selenides leads to the increase of density, microhardness, and softening temperature and to the decrease of activation energy of electroconductivity [1–3]. Arsenic selenide As_2Se_3 is a typical representative of chalcogenide glassy semiconductors, with a wide range of applications in optoelectronics, information storage and acusto-optics. A special interest for those applications is connected with doping of the glasses by active impurities, which alter the optical and electrical properties of the host material [4–6]. When copper is introduced in system As–Se, it forms compounds with both arsenic and selenium. There are four known compounds of copper with selenium: Cu_2Se, $CuSe$, $CuSe_2$, Cu_3Se_2, four with arsenic: Cu_2As, Cu_3As, Cu_6As_2, and Cu_5As_2 [7] and some compounds of copper, arsenic and selenium ($CuAsSe_2$, Cu_3AsSe_3 and Cu_3AsSe_4) [8].

The aim of this paper is to study the effect of metal impurity on thermal stability and thermomechanical characteristics of the As–Se glasses doped with copper.

Experimental

According to phase diagram of ternary system Cu–As–Se (Fig. 1), melting temperature of each element and compounds that can be formed, technological card of obtaining glasses $Cu_xAs_{50}Se_{50-x}$ type, for x=0, 5, 10 and 15 was projected.

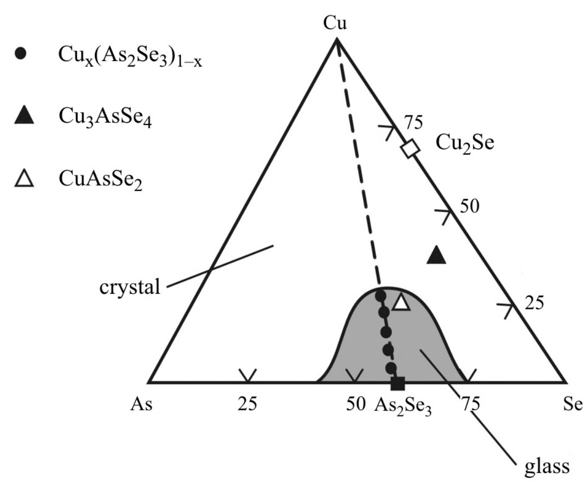

Fig. 1 Phase diagram of ternary system Cu–As–Se

The investigated glasses were synthesized from high purity elementary components. The process was conducted according to a special program, in cylindrical quartz ampoules evacuated to a pressure of the order of magnitude of $1x10^{-3}$ Pa. The ampoule

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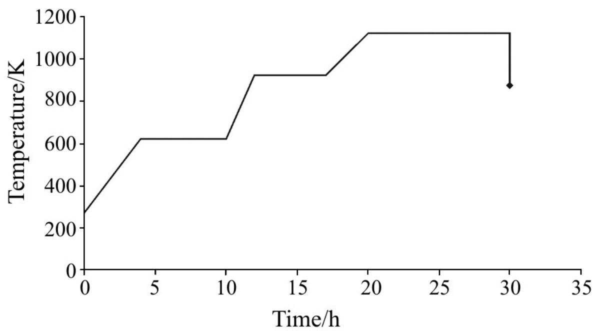

Fig. 2 Diagram of process for obtaining glasses $Cu_xAs_{50}Se_{50-x}$

length was usually about 15 cm, its diameter 15 mm, and the wall thickness 2 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, according to the empirically defined regime shown in Fig. 2.

By using the optical stereo microscope and polarizing microscope, checking of homogeneity of samples was performed. Amorphous character of samples was determined by using the conoscopic technique of polarizing microscope and X-ray diffraction.

For determining the thermal characteristics and defining the range of existence of each individual phase a Paulik-Paulik-Erdey Derivatograph, type 1000 was used. Samples were heated to 1273 K in open ceramic crucibles in air atmosphere, using Al_2O_3 as inert standard. The heating rate was 10 K min^{-1} and the mass of the samples was 100 mg. Before measurement the samples were powdered.

Dilatometric studies of samples were carried out on a PerkinElmer 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 $\pm10^{-4}$ mm, rate of sample heating was 2 K min^{-1}, and the furnace was cooled with water.

In view of the fact that the measuring equipment required a defined form of samples, they were prepared mechanically by using abrasive powders with different grain size. The ultimate forms of samples were plates whose thickness were from 1 to 1.5 mm.

Results and discussion

In order to study the effect of copper in possibly shifting the maxima corresponding to different thermal effects, Fig. 3 presents DTA curves of the investigated glasses. From this curves we note some points, which may correspond to the following processes: initial softening of the amorphous phase; softening

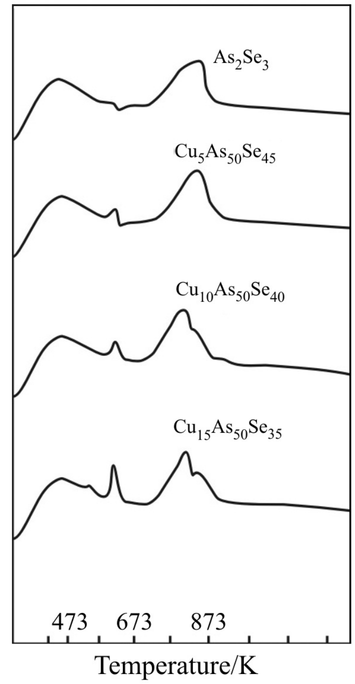

Fig. 3 DTA curves of the samples

region of the glasses; partial crystallization and the beginning of the thermal decomposition. By analyzing these curves for the whole series of samples, the complexity of their patterns can be observed as a consequence of the increase in copper content.

In Fig. 4 are presented the results of linear expansion of $Cu_5As_{50}Se_{45}$, $Cu_{10}As_{50}Se_{40}$ and $Cu_{15}As_{50}Se_{35}$ glasses.

Dilatometric curves for samples with 5 at% and 15 at% Cu have shown a standard shape for amorphous systems, so parts indicating linear dependence of expansion on temperature and softening, are easy to notice. On the other hand, curve relating to sample with 10 at% Cu has three critical points before the beginning of deformation. Those characteristic temperatures (372, 427 and 448 K) are indicating the

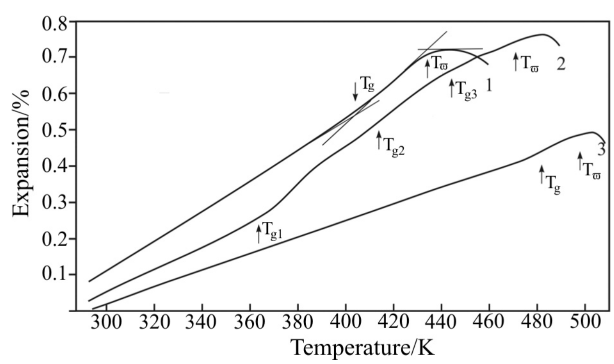

Fig. 4 Relative changes in the sample height:
curve 1 – $Cu_5As_{50}Se_{45}$, curve 2 – $Cu_{10}As_{50}Se_{40}$,
curve 3 – $Cu_{15}As_{50}Se_{35}$

existence of different areas in the glass samples with different local structural units in amorphous net.

Considering that melting temperature of crystal selenium is 373 K, first registered temperature for $Cu_{10}As_{50}Se_{40}$ could indicate the existence of such form. Bearing in mind that crystal selenium exists in six allotropic modifications, even more than one of detected critical points can represent this component. On the other hand, the variety of structural units that can be found in glasses of investigated type, allows other possibilities as well. Namely, the analysis of the diffraction spectra shows that increase in copper content in a given glass yields an increase in the number of formed structural units [8, 9]. The number and the nature of different structural elements are normally a consequence of the composition, but also of the subsequent thermal treatment of the material.

Thermal coefficients of linear expansion of solid (α_g) and visco–plastic phase (α_ℓ) for $Cu_xAs_{50}Se_{50-x}$ samples for x=5, 10 and 15 at% Cu were determined from the slope of straight-line parts of the functional dependence $\Delta\ell/\ell=f(t)$ from Fig. 4. It can be concluded that the values of coefficient α for investigated samples are in the range of characteristic values for chalcogenide glasses [10, 11].

The errors of particular results for 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_ω, including corresponding standard deviations of the mean values of not less than 5 measurements, are presented. It can be considered that α_g depends mostly on bonds length between structural units, during the heating process. Strong chemical bonds inside structural units of type Cu_2Se, As_2Se_3, and AsSe, which can be found in glasses from investigated system, are mostly covalent and therefore have a small influence on thermal expansion effects.

On the other hand, intermolecular forces are much weaker; they show more dilatometric changes during the heating and therefore have the dominant role in α_g value. Previous investigations of the glassy systems Cu–As–Se (with copper content from 10 to 25 at%) indicated that the three-component elementary compound Cu_3AsSe_4 has the main role in bonding and improving the structural network of the amorphous systems [8, 12–14].

Table 1 Results of dilatometric measurements of glasses $Cu_xAs_{50}Se_{50-x}$: T_g – softening temperature, T_ω – temperature of the beginning of deformation, α_g and α_ℓ – thermal coefficient of linear expansion of solid and viscoplastic phase, respectively

Copper content x/at%	T_g/K	T_ω/K	$\alpha_g/10^{-6}$ K^{-1}	$\alpha_\ell/10^{-6}$ K^{-1}
5	406±1.9	439±1.8	32.7±1.0	43.4±1.1
10	448±2.0	471±2.0	26.1±1.5	36.8±1.5
15	482±1.8	498±1.8	15.6±1.0	29.6±1.1

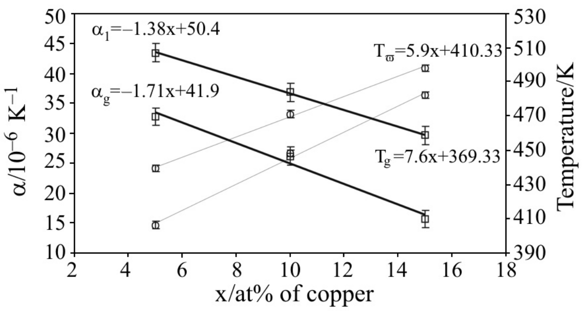

Fig. 5 Dependence of α_g, α_ℓ, softening temperature T_g and temperature of the beginning of deformation T_ω on copper content

In Fig. 5 is presented the dependence of α_g and α_ℓ on copper content and the analogous concentration dependence of the softening temperature T_g and temperature of the beginning of deformation T_ω.

It can be seen that the coefficient of linear expansion of solid phase, α_g, decreases and the softening temperature T_g increases with increase in copper content in the material, indicating thus the strengthening of the structural network of the glass.

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 (T_g) and also increases linearly with increase in copper content. At the same time, it can be also noticed that the coefficient of viscoplastic phase α_ℓ has a trend of linear decrease with increase in copper concentration, like that observed for α_g.

Similar monotonous dependence has also been noticed at some other chalcogenide systems [10, 15] and some magnesium aluminum silicate mass glasses in contrast to magnesium aluminum silicate glass-ceramics [16].

Conclusions

The three-component, amorphous system $Cu_xAs_{50}Se_{50-x}$, for x=5, 10 and 15 at.% Cu is investigated. The results of complex thermal measurements made it possible to determine characteristic points connected to thermal treatment. It was established that softening temperature (T_g) and temperature of the beginning of deformation (T_ω) are increasing, and those thermal coefficients of linear expansion of solid state and visco-plastic phase (α_g and α_l) decreases as copper content rises in investigated system.

Acknowledgements

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