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# Influence of the Introduction of Copper into Amorphous $As_2Se_3$ Matrix on Its Thermal and Structural Characteristics

G. Štrbac[a], S. Lukić-Petrović[a,*], D. Štrbac[a], K. Čajko[a] and I.I. Turyanytsa[b]

[a]University of Novi Sad, Faculty of Sciences, Department of Physics
Trg Dositeja Obradovića, 421000 Novi Sad, Serbia

[b]Uzhhorod National University, Faculty of Engineering, 14-a Universytetska Str., Uzhhorod, 88000 Ukraine

This paper describes the results of the determination of some thermal and structural parameters of glasses from the $Cu_x(As_2Se_3)_{100-x}$ system for $x = 0$, 1, 5, 10 and 15 at.%. Based on the differential scanning calorimetry curves taken at different heating rates, glass transition temperature $T_g$, onset temperature of crystallization $T_{onset}$, and melting temperature $T_m$ of crystalline units formed are determined. The values of activation energy $E_g$ of glass transition process are calculated. These characteristic temperatures served as the basis for the calculation of the parameters of thermal stability of the glasses towards crystallization.

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## 1. Introduction

Previous investigations of amorphous semiconducting materials formed by copper, arsenic, chalcogen, and halogen elements have shown that the increase of copper content in the glass changes significantly their physical properties [1–3].

Thermal stability of an amorphous system is a term related to the glass resistance to crystallization, and it is commonly used while ascertaining the potential of a glass for its practical applications. On the other hand, there is a general tendency to find a best possible correlation between the parameters of thermal stability and parameters determining the ability to form different glasses [4, 5].

The aim of this work was to study the characteristics of glass transition process and determine the parameters that describe thermal stability of the glasses from the investigated system.

## 2. Experiment

The investigated glasses of $Cu_x(As_2Se_3)_{100-x}$ type, for $x = 0$, 1, 5, 10, and 15 at.% were synthesized from high-purity elementary components by cascade heating method. The melts were air-quenched.

Differential scanning calorimetry (DSC) was used to measure the caloric manifestation of the phase transformation and study of the kinetics parameters under non-isothermal conditions. Measurements were carried out using a DSC822e Mettler Toledo instrument.

Bulk glass samples (weight ≈ 15 mg) were sealed in the aluminum pans and scanned under pure nitrogen atmosphere (gas flow 50 ml min$^{-1}$). Recordings were performed at different heating rates of 2, 5, 7.5, 10, 20, and 30 K min$^{-1}$. The choice of heating rates depended on the degree of overlapping of the processes on the thermograms.

Since $T_g$ and $T_{onset}$ were determined indirectly, the determination error was larger than in the directly read $T_m$.

## 3. Results and discussion

Figure 1 shows the DSC curves for the glasses of $Cu_x(As_2Se_3)_{100-x}$ type for $x = 0$, 1, 5, 10, and 15 at.%, recorded at the heating rate of 10 K min$^{-1}$.

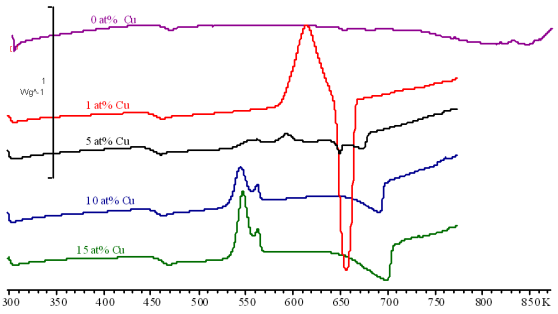


Fig. 1. DSC curves for the glasses of $Cu_x(As_2Se_3)_{100-x}$ type, recorded at the heating rate of 10 K min$^{-1}$.

A basic parameter characterizing the process of softening is the glass transition temperature $T_g$. The dependence of $T_g$ on the copper content is shown in Fig. 2.

As can be seen from Fig. 2, the introduction of 1 at.% of copper decreased significantly the value of $T_g$ compared to the $As_2Se_3$ composition. By forming bonds with Se and/or As, copper forms units that disturb the coherence of the glass network. Already at this concentration, the share of the structural units with copper is about 5%. The decrease in the $T_g$ cannot be related to the appearance of new structural units consisting of As and Se, since their ratio did not shift significantly from 2:3.

*corresponding author; e-mail: svetlana@df.uns.ac.rs

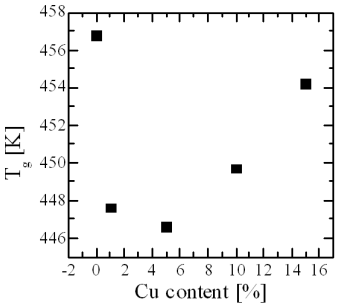


Fig. 2. Dependence of $T_g$ (for heating rate of 10 K min$^{-1}$) on the copper content.

At the copper content of 10 and 15 at.% in the glass composition an increase is observed in the glass transition temperature, that is in the structural compactness of the glass network. It has been shown that this trend accompanies the increase in copper content up to 30 at.%, and that the $T_g$ value for such high copper contents is higher than that determined for $As_2Se_3$ [6].

The change in the trend of the dependence of the glass transition temperature on the copper content in the glass composition can be explained by the dominant formation of the structural units in which copper coordination is higher. The situation is made more complex due to the fact that copper, by forming units with As and Se, binds more Se, thus shifting the glass matrix to the area which is richer in As, yielding the formation of new structural units, probably $As_4Se_4$. $As_4Se_4$ molecular species can exist as an ethylene-like polymerized unit in addition to forming cage-like molecules [7]. Also, it is possible to expect the formation of the units $As_4Se_3$.

The experimental results obtained for the dependence of the glass transition temperature on the heating rate, correspond to the empirical linear functional dependence proposed by Lasocka [8], with the worst factor of correlation of $R^2 = 0.96$ for the composition of 10 at.% Cu. The values of the parameter $A$, free term and the parameter $B$ which is determined by the slope of the linear dependence and represents the response of the material to the configuration changes in the area of its softening, are given in Table I.

TABLE I

Values of the parameters $A$ and $B$ of the linear Lasocka function and $E_g$ determined by the methods of Kissinger and Mahadevan.

| $x$ [at.%] | Lasocka | | $E_g$ [kJ mol$^{-1}$] | |
|---|---|---|---|---|
| | $A$ [K] | $B$ [K] | Kissinger | Mahadevan |
| 1 | 457.6(11) | 5.9(5) | 267(20) | 274(20) |
| 5 | 455.8(4) | 5.21(22) | 311(14) | 318(14) |
| 10 | 458.7(12) | 4.9(6) | 320(40) | 328(40) |
| 15 | 464.9(3) | 5.81(18) | 289(8) | 297(8) |

The activation energy of the glass transition process, $E_g$, was determined according to the modified relations of Kissinger [9, 10] and Mahadevan [11]. The modification was made by introducing the glass transition temperature $T_g$ instead of the crystallization peak temperature $T_c$. The $E_g$ values are presented in Table I.

Thermal stability was estimated according to the parameters proposed by different authors [12–14], and which are often used in the analysis of thermal stability. A number of parameters have been proposed in view of the fact that there is a general tendency to find a best possible correlation between the parameters of thermal stability and the parameters determining the ability to form different glasses [4, 5]. The calculated values of the parameters are given in Table II.

TABLE II

Values of the parameters of thermal stability: $\Delta T$ — Dietzel's criterion, $K_H$ — Hruby's criterion, $H$ — criterion of Saad and Poulain, $S$ — criterion of Saad and Poulain.

| $x$ [at.%] | $\beta$ [K/min] | $\Delta T$ [K] | $K_H$ | $H$ | $S$ [K] |
|---|---|---|---|---|---|
| 1 | 10 | 141.9(7) | 2.138(26) | 0.3171(12) | 7.67(17) |
| 5 | 10 | 91.1(7) | 0.822(9) | 0.2040(11) | |
| 10 | 10 | 81.9(7) | 0.514(6) | 0.1822(11) | 2.24(10) |
| 15 | 10 | 81.7(7) | 0.502(6) | 0.1799(11) | 1.81(10) |

The introduction of copper leads to a decrease of the thermal stability of the investigated system. An abrupt decrease of thermal stability of the composition with 5 and more at.% Cu compared to the composition with 1 at.% Cu is a consequence of the crystallization of new structural units at lower temperatures.

It can be seen that there is only a mild decrease in the thermal stability of the composition with 15 at.% Cu compared to that of 10 at.% Cu, and this is also seen from the similarity of the obtained DSC curves for these compositions. Hence it can be concluded that at these compositions the crystallization results in the identical structural units, and no significant changes in the glass structure are observed.

## 4. Conclusions

It has been shown that $T_g$ is essentially dependent on the Cu content in the glass composition and that the form of this functional dependence is determined by the Cu concentration. The values of $E_g$ were also determined.

The introduction of Cu into the $As_2Se_3$ matrix leads to a decrease in the thermal stability of the system.

Finally, it should be pointed out the fact that the DSC investigations showed that Cu is actively built in into the glass matrix and, thanks to its high coordination and formation of new structural units, influences essentially the thermal characteristics of the investigated glasses.

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