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THERMAL ANALYSIS AND X-RAY DIFFRACTION INVESTIGATION OF THE COPPER(I) SELENOARSENATE (Cu_3AsSe_4)

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The compound Cu_3AsSe_4 was studied. Differential thermal analysis studies and X-ray powder diffraction of crystalline samples at room and higher temperatures have been carried out. The characteristics of the decomposition process of the compound were determined. As_2Se_3 and Cu_2Se were identified as products of thermal decomposition. The copper oxides, Cu_2O and CuO, were found to be the compounds formed in the last stage of the thermal treatment.

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1. Introduction

Previous investigations of amorphous semiconducting materials formed by copper, arsenic, chalcogen and halogen elements have shown that increase of copper content in the glass changes significantly their physical properties [1-5]. The interpretation of the main results has been based on the assumption that the change in the concentration of elementary components produces a change in the structural elements of the solid amorphous structure. Studies of chemical stability, mechanical and thermophysical properties [6-8] have directly confirmed the existence of a correlation between the percentage of copper and the stability of the material. It appeared that positive effects are achieved at the copper content of 20-25 wt. %, when a maximum strength of the atomic lattice and matrix of the amorphous systems of the type $Cu_x(As_2Se_3)_{1-x}$ and $Cu_x(AsSe_{1.4}I_{0.2})_{1-x}$ is reached.

Starting from the fact that the crystalline compound $CuAsSe_2$ contains 21.44 wt. % Cu, 25.28 wt. % As, and 53.28 wt. % Se, the observed properties of the glass could be ascribed to the newly-formed structural units which in the amorphous matrix would have the spatial arrangement analogous to that in the mentioned crystal. However, the X-ray studies [9] have shown that subsequent thermal treatment of these amorphous systems leads to the formation of the compound Cu_3AsSe_4, which has been mentioned as an alternative [10], in which copper content amounts to 32.79 wt. %.

Due to the importance of the structuro-chemical units based on Cu_3AsSe_4 for the glass properties, a deeper insight into the physics of this compound became necessary. This work describes some of the relevant thermophysical characteristics of Cu_3AsSe_4.

2. Experimental

Samples for the experiment were obtained by two technological procedures. One of the procedures was analogous to that used for preparation of non-crystalline chalcogenides with copper along the cuts $Cu_x(As_2Se_3)_{1-x}$ and $Cu_x(AsSe_{1.4}I_{0.2})_{1-x}$ [11]. The other technological process (Fig. 1) was the cascade heating to the maximal chosen temperature reproducing the way used in the synthesis of complex glasses, followed by cooling in ambiental conditions according to well - known Newton's law:

$$t = t_r + (t_m - t_s)e^{-k\tau} \quad (1)$$

where t_r – room temperature, t_m – maximum melting temperature, τ - time, k – coefficient dependent of the furnace characteristics.

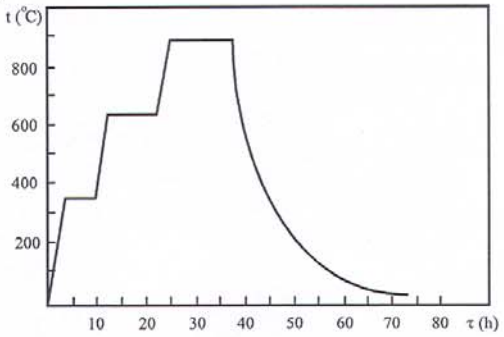

Fig. 1 Temperature regime for getting the crystalline compound.

In view of the geometry, capacity and other specific features of the heating system, as well as the temperature at which the process started (t_m~900^{0}C), sample cooling lasted about 40 hours.

The composition of the prepared bulk samples corresponded to the compounds $CuAsSe_2$ and Cu_3AsSe_4, as well as to As_2Se_3 and Cu_2Se, which were prepared with the aim of enabling experimental verification of the expected transformations of copper(I) selenoarsenate. Elementary components used for the synthesis were of high purity: Cu – 99.998%, As, Se – 99.999%.

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

The X-ray diffraction (XRD) measurements were performed on a conventional X-ray diffractometer PW 1373-PW 1065/50 (Philips) with a $\theta - 2\theta$ geometry, using step scanning mode and monochromatized CuK_α radiation (λ=0.15418 nm). XRD spectra at higher temperatures were recorded using a high temperature attachment HTK 10 (Paar) and automatic control bar HTK 2 – HC (Paar). Experiments were carried out up to maximum temperature of 650 °C. The heating rate was 1 or 2 °C/min.

3. Results and discussion

Density of bulk samples was 5203(3)kg/m^3 for $CuAsSe_2$ and 5512(3) kg/m^3 for Cu_3AsSe_4. Irrespective of the mode of melt cooling, the compound Cu_3AsSe_4 always showed characteristics of a crystalline phase. Namely, although all the conditions were ensured for accomplishing the process of glass synthesis, crystallization has always taken place. The samples obtained by annealing in air showed somewhat lower degree of crystallinity (about 75%), which could be improved by additional thermal treatment. Fig. 2 shows the course of increasing crystallinity on the basis of the change of the diffraction maximum registered in the X-ray spectrum for the value of Bragg's angle of $2\theta = 28.15^0$ (for CuK_α radiation).

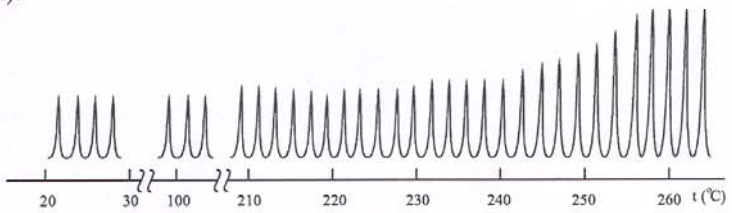

Fig. 2 Temperature dependence of the intensity of diffraction maxima in the vicinity of $2\theta = 28^0$.

A similar effect appeared also as a result of the synthesis of the Cu_2Se compound. Such results are a consequence of the fact that the position of the points representing Cu_3AsSe_4 and Cu_2Se in the concentration phase triangle of the Cu-As-Se system (Fig. 2, [12]) shows that these compounds can be obtained only in an ordered phase.

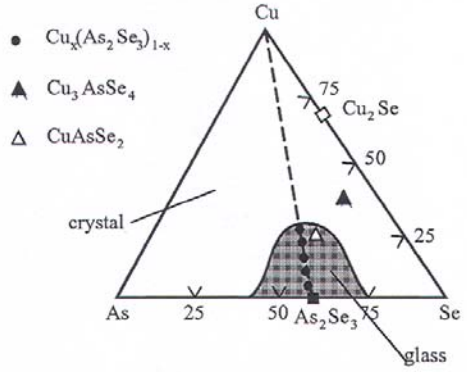

Fig. 3 Phase diagram of the system Cu-As-Se.

The results that will be discussed here are related to the samples obtained in the process which enabled the formation of the energetically most favourable state of the system, i.e. the solid phase with the crystal lattice characteristics.

The diffractograms recorded at room temperature for $CuAsSe_2$ and Cu_3AsSe_4 (Fig. 4) showed high coincidence of the values of interplanar distances, which could be a consequence of different degree of distortion of the identical elementary cells [10]. Some literature data suggest the possibility that the compound Cu_3AsSe_4 is not formed *ab initio* but appears in the process of normal cooling of the amorphous AsSe matrix.

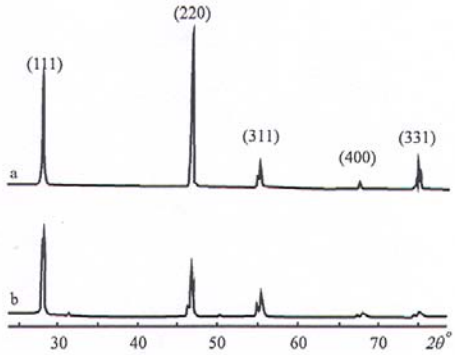

Fig. 4 X-ray spectra of $CuAsSe_2$ (a) and Cu_3AsSe_4 (b) at room temperture.

The positions of the diffraction maxima (Fig. 4) enabled us to determine the following values of the interplane distances (in nm): 0.317; 0.195; 0.166; 0.138; 0.127, and 0.133. By analogy with modifications of copper(I) thiosulphate which crystallize so that their structure could be considered as a modification of ZnS in which 1/4 Zn is replaced with Cu and 3/4 Zn with As, i.e. that Zn_4S_4 is transformed into Cu_3AsSe_4 [14], the diffraction picture for the compound Cu_3AsSe_4 suggests the elementary cell formed on the basis of a sphalerite configuration (Fig. 5) with the parameter a = 0.549 nm.

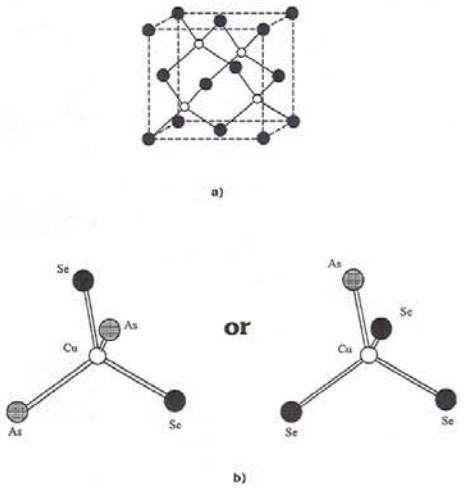

Fig. 5 Structure of sphalerite (a) and the case of atom substitution (b).

In Fig. 6a are presented the results of derivatographic analysis of copper(I) selenoarsenate and in Fig. 6b the characteristic decomposition curves for two selenides of copper and arsenic, which enabled a correct identification of the processes occuring in the thermal decomposition of the three-component crystals.

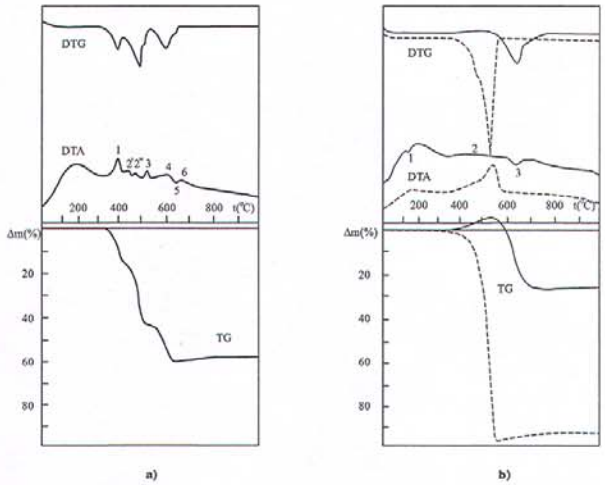

Fig. 6 DTA, TG and DTG curves of crystals: (a) Cu_3AsSe_4, (b) Cu_2Se (full line) and As_2Se_3 (broken line).

The analysis of the recorded DTA, TG and DTG curves indicates that the whole process of thermal decomposition of Cu_3AsSe_4 could be schematically presented in the following way:

$$2Cu_3AsSe_4 \xrightarrow[395^o]{Se_2\uparrow} As_2Se_3 + 3Cu_2Se \xrightarrow[520^o]{As_2Se_3\uparrow} 3Cu_2Se \xrightarrow[600^o]{1.5O_2\downarrow} 3Cu_2O + 1.5Se_2 \rightarrow$$

$$\xrightarrow[640^o]{1.5Se_2\uparrow} 3Cu_2O \xrightarrow[655^o]{O_2\downarrow} Cu_2O + 4CuO$$

The TG curve for the Cu_2Se crystal clearly points to a mass increase during heating in the temperature range 400-580 ^{0}C, which was ascribed to the reaction with the oxygen from air:

$$2Cu_2Se \xrightarrow[520^o]{2O_2\downarrow} 4CuO + Se_2 \xrightarrow[620^o]{Se_2\uparrow} 4CuO$$

The results of the thermal analysis are also presented in Table 1.

Table1
The characteristics of the thermal decomposition of Cu_3AsSe_4.

No.	Temperature (°C)	Type of effect	Fragment elimination	Δm_{obs}, (%)	Δm_{cal}, (%)
1	395	endo+exo	$-0.5Se_2$ and recrystallization	12	13.58
2',2''	420,470	exo	crystallization of Cu_2Se and As_2Se_3		
3	520	exo	$-0.5As_2Se_3$	32	33.26
4	600	exo	$+0.75\ O_2$	2	4.1
5	640	endo	$-0.75Se_2$	18	20.37
6	655	exo	$+0.5O_2$	2	3.7
residue	$0.5Cu_2O+2CuO$			38	39.6

Table 2
The characteristics of the thermal decomposition of Cu_2Se.

No.	Temperature (°C)	Type of effect	Fragment elimination	Δm_{obs}, (%)	Δm_{cal}, (%)
1	120	endo	melting	-	-
2	400-580	exo	$+O_2$	5	5.16
3	620	endo	$-0.5Se_2$	32	33.17
residue	2CuO			68	66.83

The end products of thermal treatment of both crystalline compounds were analyzed by X-ray diffraction and it was found that they are copper oxides.

These results were confirmed by X-ray diffraction at higher temperatures. In Fig. 7 are presented spectra of the crystalline Cu_3AsSe_4 recorded at several temperatures.

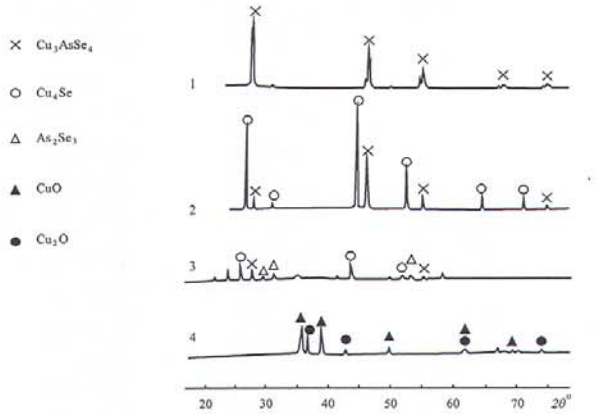

Fig. 7 Difractograms of the crystalline form Cu_3AsSe_4 at several temperatures: (1) - 20°C, (2) - 400°C, (3) - 450°C, (4) - 650°C.

4. Conclusions

The aim of the study was to examine some relevant thermophysical characteristics of the three-component compound Cu_3AsSe_4, which represents the basical phase in glassy semiconducting chalcogenides involving copper.

By combining complex physical methods it was possible to resolve the question of the decomposition of this crystalline form. Thermogravimetric measurements and differential thermal analysis in combination with high-temperature X-ray diffraction showed that the structural units Cu_3AsSe_4 (sphalerite type) are formed during thermal treatment as transition forms of the crystalline phase Cu_2Se and As_2Se_3 and the end products on the temperature scale are copper oxides Cu_2O and CuO.

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