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THERMAL STABILITY AND PHOTORECORDING IN AMORPHOUS $Cu_x(As_2Se_3)_{1-x}$ SYSTEM

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ABSTRACT

Investigations of mechanical, electrical, optical and other physico-chemical properties of amorphous semiconducting materials have shown that these properties depend substantially on the system composition.

In view of the known fact that the introduction of copper into arsenic selenide influences substantially its conducting characteristics, this work gives an analysis of the effect of an increased copper content in $Cu_x(As_2Se_3)_{1-x}$ on its optical energy gap. In addition, changes in thermal stability of the system are investigated, the interval between phase transitions points is determined, and the most probable mechanism of thermal decomposition is proposed.

A series of thin films obtained by evaporation of the investigated materials was used to investigate the photorecording effect caused by prolonged laser irradiation. Changes in transparency were studied as a function of exposure and concentration change of the components at room temperature. Finally, it was investigated the possibility to erase reversibly the dark traces caused by irradiation, by a prolonged heating of films at characteristics temperatures.

EXPERIMENTAL

Samples of the investigated system were synthesized and their films prepared by evaporation according to the known procedures [1,2].

A MOM derivatograph served to record simultaneously the DTA, DTG, TG and T curves. The samples were heated in air atomsphere from room temperature to 1000°C at a rate of 10°C/min. As standard served α-Al_2O_3.

The photorecording effect was studied using a He-Ne laser (wavelength 632 nm, power 1 mW) for irradiation of films of thickness about 2 μm. The measurements were carried out from room temperature to 200°C.

RESULTS AND DISCUSSION

The region of glass formation in the As-Se system is relatively wide (from pure Se to 60 at.% As) [3,4,5]. If copper is included in the As_2S_3 system, the $CuAsSe_2$ structural units are formed [6]. For this stoichiometric ratio, the copper content is 21.44%, which means that until this value is reached the Cu-As-Se system contains also the As_2Se_3 structural units.

At the crystallization temperature [7] a phase having Cu_3AsSe_4 structural units is formed, which corresponds to the reaction:

$$3CuAsSe_2 \rightarrow Cu_3AsSe_4 + As_2Se_2$$

In Figure 1 are shown DTA and DTG curves for $Cu_{10}(As_2Se_3)_{90}$ which can be regarded as the representative of the given system, whereas in Table 1 is given the most probable mechanism of its thermal decomposition.

TABLE 1

Ordinal number of the process	*Temeprature (°C)*	*Type of the process*
1	160	begining of amorphous phase softening
2	260	crystallization of Cu_3AsSe_4
3	360	decomposition of $As_{4/2}Se_{4/2}$ structural units
4	410	melting of crystalline phase
5 6	500 550	thermal decomposition of $CuAsSe_2$ and Cu_3AsSe_4 structural units
7	580	thermal decomposition of As_2Se_3 structural units

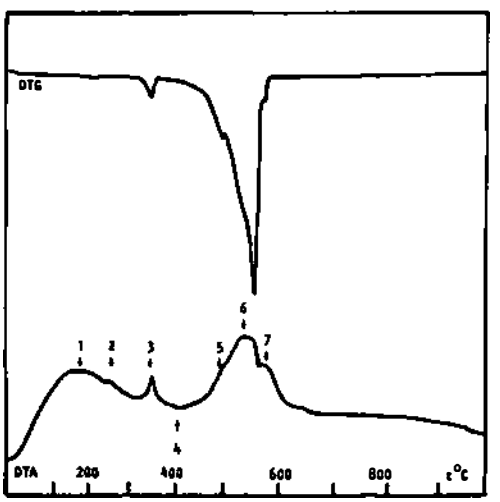

Fig. 1. DTA and DTG curves for $Cu_{10}(As_2Se_3)_{90}$

Such an approach enables the percentual mass loss in process 3 to be calculated as a function of copper content up to 21.44%, according to the relation:

$$\Delta m(\%) = k(n\%Cu)1.495$$

where k is a factor characterizing degree of crystallization and it represents an empiric quantity related to the technology of synthesis.

In Table 2 are presented the calculated values for Δm and those obtained by thermogravimetric measurements.

Figure 2 shows the DTA curves of all the investigated samples of the system $Cu_x(As_2Se_3)_{1-x}$ (x = 0, 5, 10, 15, 20, 25).

TABLE 2

n%Cu	0	5	10	15	20
Δm_{cal}	0	2.2	4.4	6.6	8.8
Δm_{obs}	0	2	4.5	7	9

The complete derivatographic analysis of the system containing 25% of copper is illustrated in Figure 3. When thermal decomposition is completed, the residue mass is 33%, which corresponds to formation of CuO as the final product (Δm_{cal}=31.25%). It is obvious that under conditions of „presaturation" with copper some new structural units appear which are characterized by the crystallization temperature of 300 C (peak 2'), their effect on decomposition of $As_4/_2Se_4/_2$ structural units (3'), and by their decomposition (5').

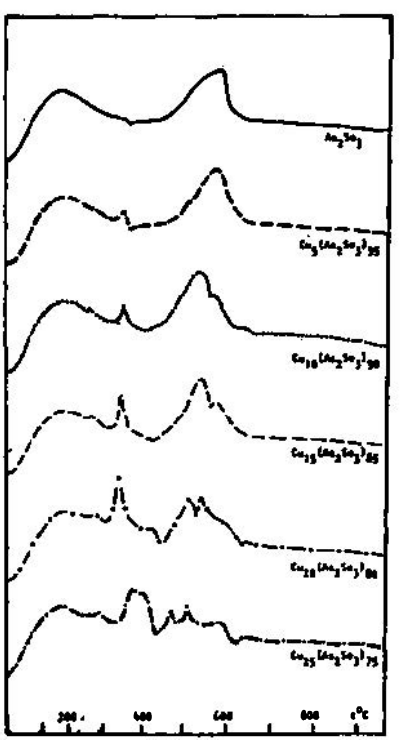

Fig. 2. DTA curves of samples of $Cu_x(As_2Se_3)_{1-x}$ system

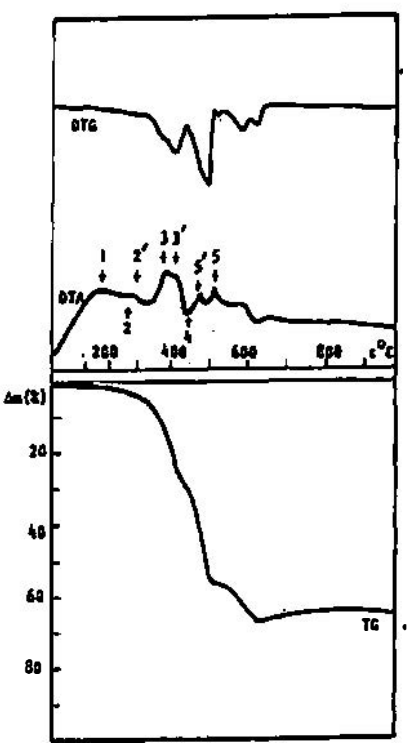

Fig. 3. DTA, DTG and TG curves for $Cu_{25}(As_2Se_3)_{75}$

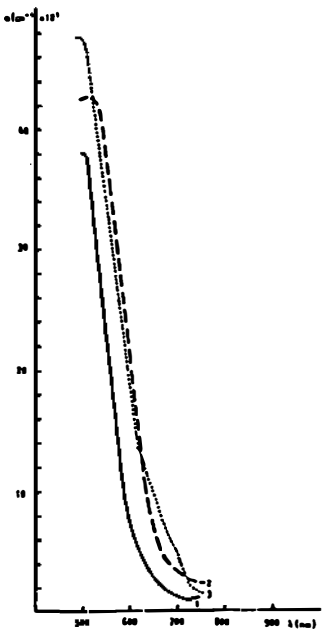

Fig. 4. The absorption coefficients: curve 1-$Cu_5As_{50}Se_{45}$, curve 2-$Cu_{10}As_{50}Se_{40}$, curve 3-$Cu_{15}As_{50}Se_{35}$.

Figure 4 illustrates the change of absorption coefficients in the region of short wavelength limit. These coefficients served as the basis for calculation of the corresponding optical energy-gaps (Table 3).

TABLE 3

Ord. N°	*Sample*	λ_g *(nm)*	E_g *(eV)*
1	$Cu_5As_{50}Se_{45}$	582	2.131
2	$Cu_{10}As_{50}Se_{40}$	630	1.969
3	$Cu_{15}As_{50}Se_{35}$	650	1.908

The photorecording effect is illustrated in Figure 5, where the relative transparencies (T/T_0) are shown as a function of exposure time.

The smaller changes of darkening intensity corresponding to higher copper concentrations are expectable if it is borne in mind the behaviour of absorption coefficients (Figure 4). The discussed specifictly concerning structural units that are formed in the presence of copper indicate that this effect is related to changes in capture centres in the As-Se bonds. This point of view on photostructural changes is supported by the observed effects related to the change of drift mobilities and which are a direct consequence of the electric properties [8].

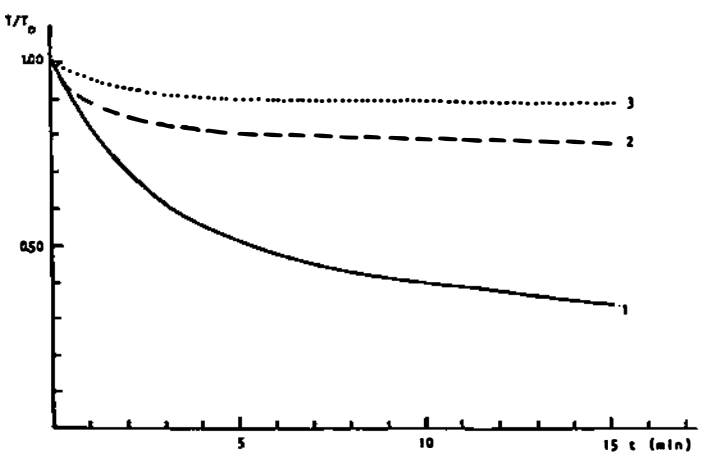

Fig. 5. Dependence of darkening on time: curve 1-$Cu_5As_{50}Se_{45}$, curve 2-$Cu_{10}As_{50}Se_{40}$, curve 3-$Cu_{15}As_{50}Se_{35}$.

By heating of samples to a temperature approaching their softening points (between 140 and 160°C) their transparency is practically brought up to the original level. Each further protorecording is almost completely reversible.

REFERENCES

|1| D.M. Petrović, S.R. Lukić, M.I. Avramov, V.V. Khiminets, J. Mat. Sci. Lett., 5, 290-292 (1986)

|2| I.D. Turyanitsa, G.D. Semak, A.A. Kikineshi, V.V. Khiminets, I.I. Turyanitsa, Zh. V. Kh. O. im. D.I. Mendeleeva, 5, 592-593 (1975)

|3| S.C. Rowland, S. Narasimhan, A. Bienenstock, J. Appl. Phys., vol 43, Nº 6, 2741-2745 (1972).

|4| Z.U. Borisova, R.L. Müler, Tzin-Chen-Tsai, Zh. Prikl. Khim., 35, 774-777 (1962)

|5| L.A. Boydakov, Z.U. Borisova, R.L. Müler, Zh. Prikl. Khim., 34, Nº 12, 2446-2454 (1961)

|6| G.M. Orlova, N.A. Alimbarashvili, I.I. Kozhina, A.P. Dologokuptseva, Zh. Prikl. Khim., vol 45, Nº 11, 2285-2289 (1972)

|7| S. Abdulla, M. Dongol, M.M. Ibrahim, Phys. Stat. Sol. (b), 144, 745-752 (1987)

|8| L. Toth, L.P. Kozakova, J. Non-Crist. Sol., 90, 429-432 (1987).