JOURNAL OF MATERIALS SCIENCE 25 (1990) 3557–3560

Thermal stability and electrical conductivity of $Ge_{20}As_{14}(Se_xS_{1-x})_{52}I_{14}$ glasses

D. M. PETROVIĆ, M. I. AVRAMOV, S. R. LUKIĆ
Institute of Physics, Faculty of Sciences, University of Novi Sad, Yugoslavia

V. V. KHIMINETS, M. V. DOBOSH
Department of Microelectronics, State University, Uzghorod, USSR

Investigations of five-component glasses of the $Ge_{20}As_{14}(Se_xS_{1-x})_{52}I_{14}$ type are reviewed for the temperature interval from room temperature to 1273 K. Thermogravimetric analyses enable the determination of the mechanism of thermal decomposition, as well as the range of amorphous phase existence. Electroconductivity was followed by the method of four points under a direct current regime. Semiconductive character was evaluated, as well as the energies of the corresponding energy gaps. The effect of sulphur (i.e. selen) concentrations on the electrical characteristics was also discussed, along with some of the elements significant for determining the mechanisms of electrical conductivity. Results on optical energy gaps were also redetermined.

1. Introduction

According to a preliminary optical investigation of the $Ge_{20}As_{14}(Se_xS_{1-x})_{52}I_{14}$ system [1], the variations of selenium and sulphur indicate different energy gaps in the scope of some expected ranges. The linear dependence of the energy gap on the concentration of these elements was also proved. It was simultaneously shown that even in this system, it is possible to retain high transparency characteristics for a wide range of wavelength intervals.

These investigations continue the study of this system in relation to electrical conductivity characteristics. Particular attention is payed to the behaviour of the material on thermal treatment at a wide range of temperature intervals.

2. Experimental procedures

The semi-conductive glasses investigated were synthesized from elementary components according to a method already published [1]. The amorphous character of the investigated samples was controlled by X-ray diffractometer PW 1965/50 (Philips) and the application of CuK_α radiation.

Thermogravimetric measurements were carried out by derivatograph (Paulik-Paulik-Erdey) under air atmosphere and Al_2O_3 as standard, at temperature intervals from room temperature to 1273 K. Heating was at a rate of $10^\circ C\,min^{-1}$. The equipment and the methodology applied for recording DTA and DDTA curves have been described earlier [2].

Registration of the dependence of electric current on temperature characteristics was carried out from room temperature to 403 K, with the error increasing 5%. Samples were prepared in the shape of plates with dimensions $7 \times 7 \times 0.5$ mm, while the contacts were obtained in In–Ge paste. Samples were stored in a cryostat with a vacuum at 10^{-4} Pa. The temperature was regulated by a copper–constantan thermic element with an accuracy of ± 0.5 K.

Electroconductivity was measured for a wide temperature interval (from 293 to 1223 K) by the four points method. In order to eliminate the effect of thermoelectromotive force, which may appear between electrodes due to the possible appearance of a temperature gradient along the sample, the voltage decrease was measured for both current directions through the sample. In this way, the effect of electrical asymmetry of the electrodes is simultaneously eliminated. The powdered sample was stored in a quartz cell with four graphite electrodes. After vacuation, the cell was sealed and before measuring stored in a furnace in order to carry out sample sintering and to realize contacts with the electrodes, as well as to homogenize the sample.

3. Results and discussion

In our preliminary note on the $Ge_{20}As_{14}(Se_xS_{1-x})_{52}I_{14}$ system [1], the linear absorption coefficient was calculated neglecting the effect of regular reflection. This led to an insufficiently exact determination of the energy gap, that is, of its dependence on the concentration of sulphur (selenium). Fig. 1 shows the results for linear absorption coefficients obtained by taking into account the correction for regular reflection, using the relation [3]

$$\alpha = \frac{1}{d} \ln \frac{(1 - R)^2 + \sqrt{(1 - R)^4 + 4T^2R^2}}{2T} \qquad (1)$$

where α is the linear absorption coefficient, n is the refraction index, d is the thickness of the sample, T is the transmittance and the reflectance (R) was

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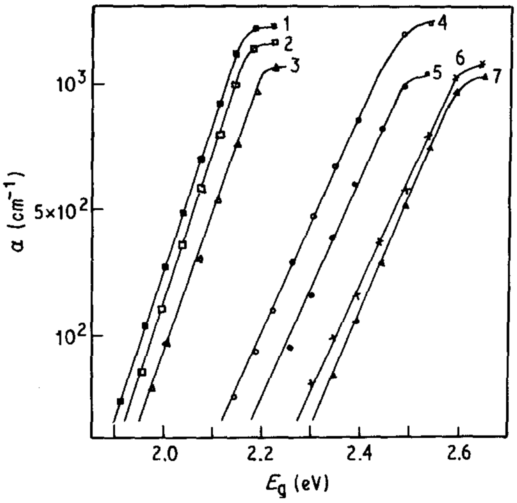

Figure 1 The absorption coefficients for (1) $Ge_{20}As_{14}Se_{52}I_{14}$; (2) $Ge_{20}As_{14}Se_{48}S_4I_{14}$; (3) $Ge_{20}As_{14}Se_{42}S_{10}I_{14}$; (4) $Ge_{20}As_{14}Se_{12}S_{40}I_{14}$; (5) $Ge_{20}As_{14}Se_8S_{44}I_{14}$; (6) $Ge_{20}As_{14}Se_2S_{50}I_{14}$; (7) $Ge_{20}As_{14}S_{52}I_{14}$.

calculated from the relation:

$$R = \left(\frac{n-1}{n+1}\right)^2.$$

The refraction index dispersion, determined on the basis of experimental results, is presented in Fig. 2. On choosing $\alpha \simeq 10^3\,\text{cm}^{-1}$ as the reference value [4], the redetermined analytical expression for the dependence of the optical energy gap on the concentration changes of selenium (sulphur), is of the form

$$E_g\,(\text{eV}) = 2.56 - 0.008x \qquad (2)$$

Aiming to give the general characterization of the material for a wider temperature interval, Fig. 3 shows the typical results of derivatographic analyses. The figure also shows the results for the sample of $Ge_{20}As_{14}(Se_xS_{1-x})_{52}I_{14}$ composition, although the other samples of this system indicate the same behaviour, involving only some quantitative differences for particular effects. Treatment was carried out practically in an open atmosphere, with the possibility of partial oxidation with oxygen from air. Although it is necessary to give a detailed analysis of DTA curves, it is preferable to use the treatment which is presented and discussed later. Nevertheless, from this DTA curve we note four important points, which may correspond to the following processes:

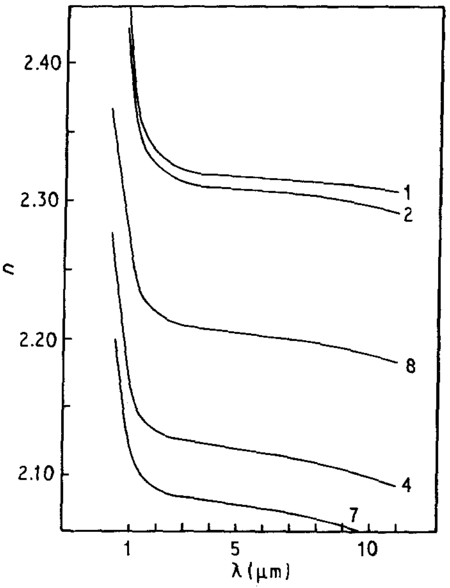

Figure 2 The refraction index dispersion for (1) $Ge_{20}As_{14}Se_{52}I_{14}$; (2) $Ge_{20}As_{14}Se_{48}S_4I_{14}$; (4) $Ge_{20}As_{14}Se_{12}S_{40}I_{14}$; (7) $Ge_{20}As_{14}S_{52}I_{14}$; (8) $Ge_{20}As_{14}Se_{26}S_{26}I_{14}$.

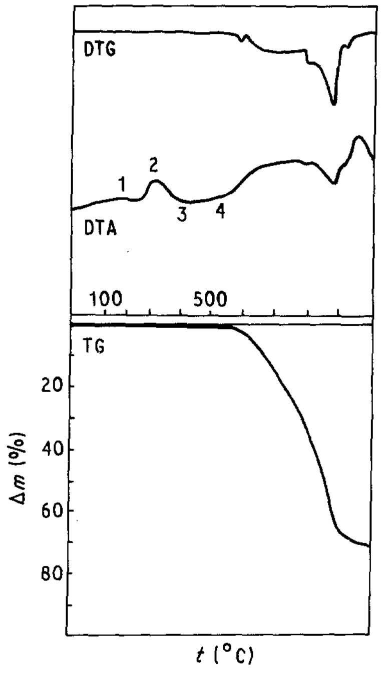

Figure 3 TG, DTG and DTA curves of the sample $Ge_{20}As_{14}Se_{26}S_{26}I_{14}$.

1. Initial softening of the amorphous phase;
2. partial crystallization;
3. softening and the beginning of crystalline phase melting;
4. the beginning of thermal decomposition.

Particular significance is ascribed to the temperature of the latter effect, $T_0 = 853\,\text{K}$, as it represents the boundary of thermal stability of the system.

The DTG curve indicates clearly that the weight decrease takes place in two steps. The first is in the interval from 853 to 1063 K, whereas the evaporation of all components from the amorphous phase proved to be uniform creating a monostructural vapour above the liquid. In the second stage, the interval from 1063 to 1223 K, material is intensively dissociated involving decomposition not only of intermolecular but also of interatomic bonds. It is significant to notice that in order to attain high optical homogeneity, the system must be hardened at a temperature slightly lower than 853 K in the course of cooling.

Activation energies (ΔE) and orders of reaction (n) were determined using the general equation of reaction kinetics [5]. They are $\Delta E_1 = 10\,\text{kJ}\,\text{mol}^{-1}$ and $n_1 = 1.03$ for the first decomposition, and $\Delta E_2 = 5\,\text{kJ}\,\text{mol}^{-1}$ and $n_2 = 3.60$ for the second stage, respectively.

Fig. 4 shows DTA and DDTA analysis of a sample with the same composition as in Fig. 3, but treated under a vacuum of 1.33×10^{-5} kPa. Due to different conditions it is hard to compare these results, although the curve of first derivation is fairly instructive (Fig. 4, DDTA). It indicates two extremes in the course of softening of the amorphous phase ($T_{g_1} = 398\,\text{K}$ and

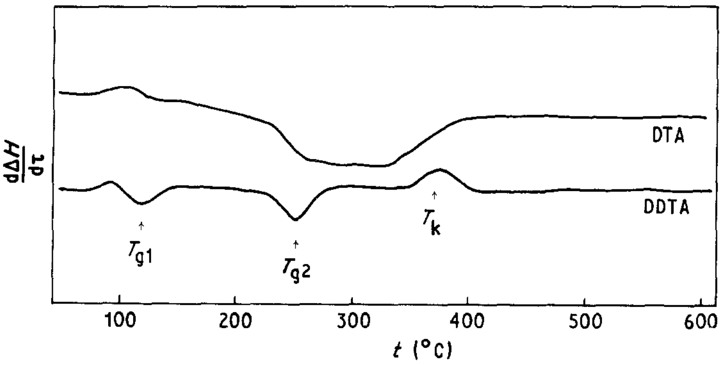

Figure 4 DTA and DDTA curves of the sample $Ge_{20}As_{14}Se_{26}S_{26}I_{14}$ treated under vacuum of 1.33×10^{-5} kPa.

T_{g_2} = 528 K). This due to the fact that the character of glass softening is complex, caused probably by the existence of two different structural units. An exothermic effect (T_k = 623 K) refers approximately to point 2 above, already indicated as crystallization temperature.

Fig. 5 gives the dependence of the values for electrical current forces on reciprocal temperature values in the interval from 293 to 403 K for samples with x = 0.05 and 1. The linearity obtained shows the dependence of $I \sim \exp(-E_a/kT)$ which enables the evaluation of energy gaps without knowing specific conductivity itself (which was impossible to measure because of the problem of making proper contacts with the sample).

Fig. 6 refers to the samples for x = 0.77 and x = 1, giving the dependence of the logarithms of the specific conductivities on the reciprocal temperature values from 293 to 1173 K. According to these measurements it is also possible to determine the widths of the energy gap E_a, and the constants of specific conductivity σ_0. From Fig. 6 it is obvious that conductivity in the greatest portion is changed according to the relation

$$\sigma > \sigma_0 \exp\left(-\frac{E_a}{kT}\right) \qquad (3)$$

where σ_0 is the constant characteristic for the given material and E_a unique activation energy [6]. σ_0 is determined by extrapolation of the linear portion of the curve for $T \to \infty$. The values given in Table I are obtained this way.

Analysing the behaviour of the conductivity for the regime of direct current, it is noticed that at temperatures T_{g_1} and T_{g_2} no change of curve slopes is detected. This sometimes happens with halcogenide glasses [7], indicating slow increase of the width energy gap with temperature. It may be that this is effected by the procedure used in this experiment, which at higher temperatures makes impossible the realization of the mechanism of thermal decomposition in the manner evaluated by derivatographic analysis. However, at higher temperatures above 960 K an increase of conductivity is noticed, probably the result of the beginning of the last transition toward the metallic type of conductivity [8]. At T_k temperature there are no changes in the behaviour, which speaks in favour of the idea that the system may be classified together with materials with a low tendency towards crystallization [9].

As illustrated in Fig. 7, the change in the energy gap with selenium (sulphur) concentration is linear and follows density changes characteristic of solid

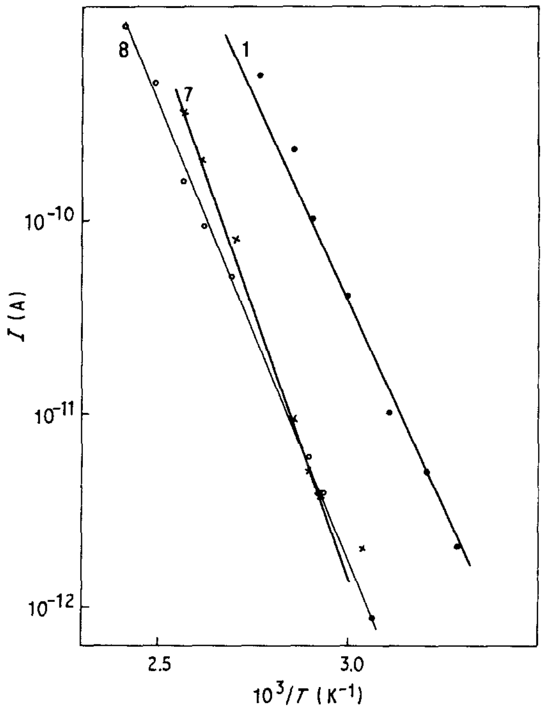

Figure 5 The dependence of electrical current forces of temperatures of $Ge_{20}As_{14}(Se_xS_{1-x})_{52}I_{14}$. (1) x = 1; (7) x = 0; (8) x = 0.5.

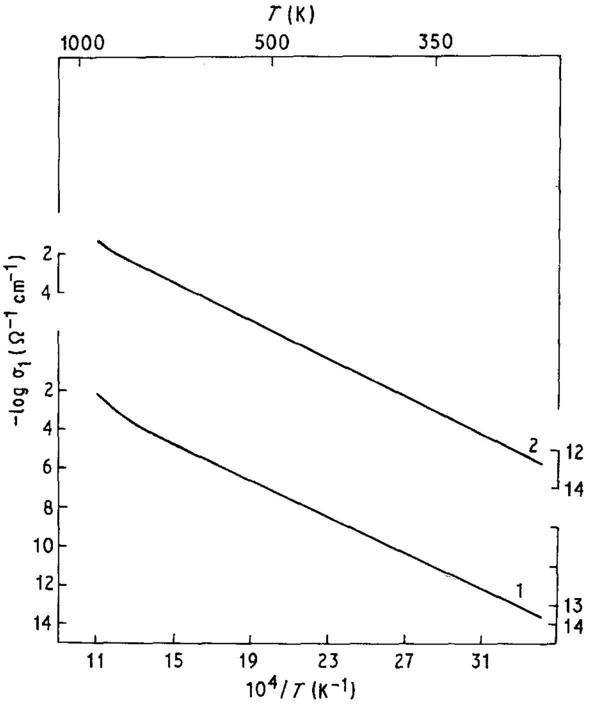

Figure 6 The dependence of the specific conductivity of temperatures of $Ge_{20}As_{14}(Se_xS_{1-x})_{52}I_{14}$. (1) x = 1; (2) x = 0.77.

TABLE I Values

Sample	E_a(eV)	E_g(eV)	$\sigma_0/\Omega^{-1}\,\mathrm{cm}^{-1}$
$Ge_{20}As_{14}S_{52}I_{14}$	1.05	1.21	–
$Ge_{20}As_{14}S_{26}Se_{26}I_{14}$	1.00	1.08	–
$Ge_{20}As_{14}S_{12}Se_{40}I_{14}$	0.93	1.04	2344.2
$Ge_{20}As_{14}Se_{52}I_{14}$	0.88	0.99	114.8

solutions. However, one half of the optical energy gap ($E_g/2$) [1] for all concentrations retains the relation $E_a < E_g/2 \simeq 2\,\mathrm{eV}$, which is characteristic of p-type conductivity for such materials [6].

Of course, these conclusions refer to measurements carried out for the behaviour of the materials at direct currents. However, only further conductivity investigations at currents of different frequencies would enable more detailed conclusions concerning the conductivity mechanisms.

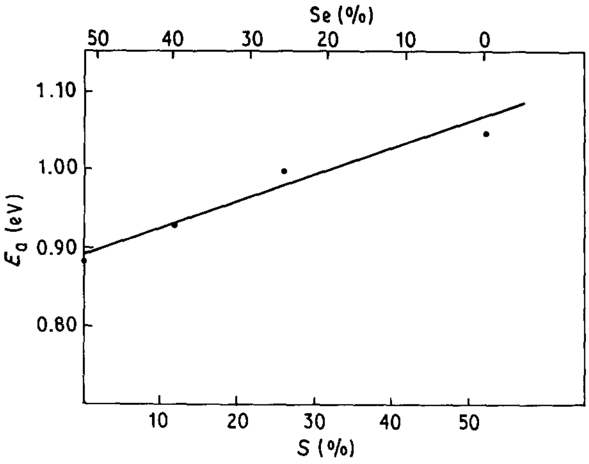

Figure 7 Dependence of energy gap on concentration of selenium sulphur.

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Received 13 March
and accepted 30 August 1989