

PHOTOLUMINESCENCE AND ABSORPTION EDGE OF THE AMORPHOUS SEMICONDUCTING
SYSTEM $\text{Ge}_{20}\text{As}_{14}(\text{S}_x\text{Se}_{1-x})_{52}114$

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ABSTRACT

Depending on the concentration of sulphur (selenium), the absorption edge of the amorphous semiconducting system $\text{Ge}_{20}\text{As}_{14}(\text{S}_x\text{Se}_{1-x})_{52}114$ is substantially shifted, which is due to the change in the optical energy gap. As the same time, the photoluminescence maximum is also shifted. Changes of the both effects exhibit a linear dependence, suggesting the type of structural units of the glass is preserved when sulphur is being replaced with selenium. A comparison of photoluminescence spectra of the binary (As_2S_3 , As_2Se_3 , GeS_2) and ternary (AsSeI , AsSI) compounds, suggests the presence of the same basic structural units in the five-component system. In addition, the mechanism of photoluminescence capture is discussed.

INTRODUCTION

Previous investigations of the complex glasses Ge-As-Se-S-I indicated a series of advantages, from the physical-technology point of view, of the system $\text{Ge}_{20}\text{As}_{14}(\text{S}_x\text{Se}_{1-x})_{52}114$ /1/. Its properties are essentially dependent on the concentration ratio of sulphur and selenium /2/. In the present work we have investigated the photoluminescence properties of this system for $x = 0, 12, 26, 40$ and 52 .

EXPERIMENTAL

Semiconducting glasses of the system $\text{Ge}_{20}\text{As}_{14}(\text{S}_x\text{Se}_{1-x})_{52}114$ were synthesized from the high-purity elementary components, as described earlier /1/. Photoluminescence spectra were taken by the monochromator UKM-1 (USSR), using the excitation lamp DKSSh-1000 (USSR). Samples were in the form of the polished plates of dimensions $8 \times 6 \times 1$ mm. All measurements were carried out at 77 K.

RESULTS AND DISCUSSION

Figure 1.a. shows the excitation spectra of luminescence (ES) and photoluminescence (PS) of the investigated glasses.

Figure 1.b. shows the dependence of photoluminescence maxima on the sulphur concentration. The $h\nu$ values should correspond to the quantity $(1/2)E_g^a/3$, which can be obtained on the basis of the characteristic absorption edge.

The dependence analogous to that in Fig. 1.b. was also established for the characteristics of the change in optical energy gap, determined on the basis of the absorption edge /1/. This could be expected because of the relation $h\nu_{PS} \approx (1/2)E_g^a/3$. These results showed that, due to an increase in the selenium concentration, the absorption edge is shifted towards higher wavelengths, i.e. due to the increase in the energy gap. At the same time, photoluminescence measurements showed the peak in-

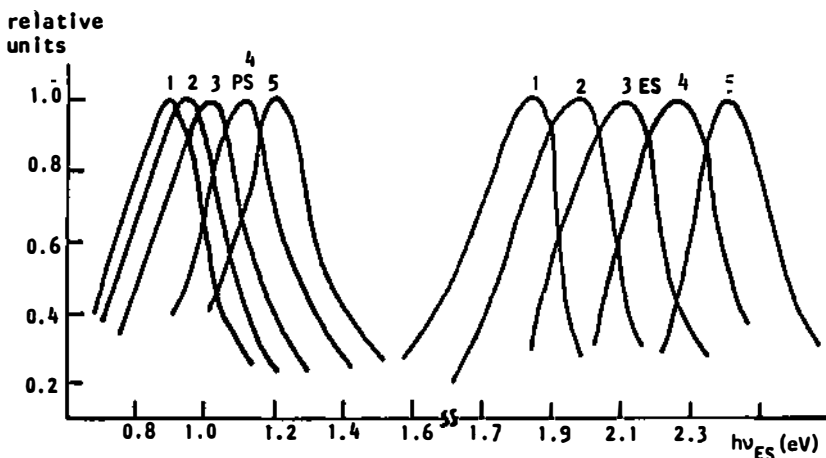


Fig. 1.a.

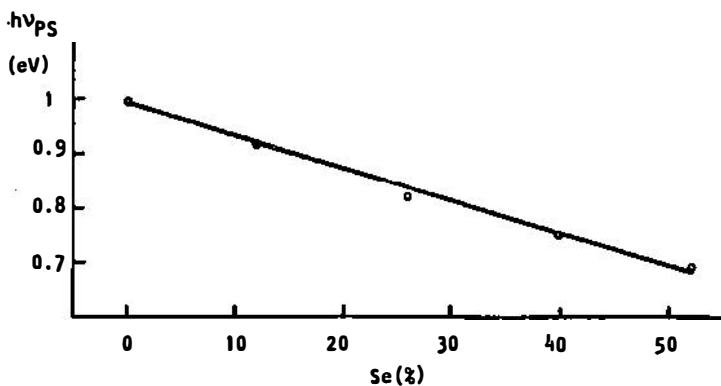


Fig. 1.b.

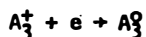
tensity is practically independent of the S/Se ratio. The linear dependence suggests the presence of solid solution /4/ and the absence of structural changes when sulphur and selenium are interchanged.

In the interpretation of the results, it could be started from defect pairs which are in the ground state oppositely charged, and represent the centres responsible for emission /5/. Here, the following pairs could be expected:

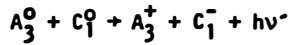
- a) $C_3^+ - C_1^-$, formed by the triply-bonded arsenic atoms and single-bonded iodine atoms;
- b) $C_3^+ - A_3^-$, where A_3^- is the defect due to the rupture of the arsenic atom bond;
- c) $A_3^+ - C_1^-$, where A_3^+ is a positively charged defect due to the rupture of the arsenic atom bond.

It can be assumed that the emission centres are primarily the $A_3^+ - C_1^-$ /6/, though photoluminescence spectra may be related to other defect pairs.

As a result of excitation, the charged centres are neutralized according to the scheme:



Photoluminescence is probably due to tunnelling effect involving the neutral centres:



The energy of emission is significantly lower than the energy of excitation (Table 1), because a great part of the energy of charge carriers is spent on the deformation of structural network of the glass.

TABLE 1

SAMPLE	$(h\nu)_{PS}$ (eV)	$(h\nu)_{ES}$ (eV)
$Ge_{20}As_{14}Se_{52}I_{14}$	0.69	1.73
$Ge_{20}As_{14}Se_{40}S_{12}I_{14}$	0.75	1.87
$Ge_{20}As_{14}Se_{26}S_{26}I_{14}$	0.82	2.01
$Ge_{20}As_{14}Se_{12}S_{40}I_{14}$	0.92	2.16
$Ge_{20}As_{14}S_{52}I_{14}$	1.00	2.30

Figure 2 shows excitation and photoluminescence spectra at 77 K of some two- and three-component glasses. The interval of their occurrence justifies the supposition that the corresponding elementary units are present in a certain ratio in the structure of the five-component glass under investigation.

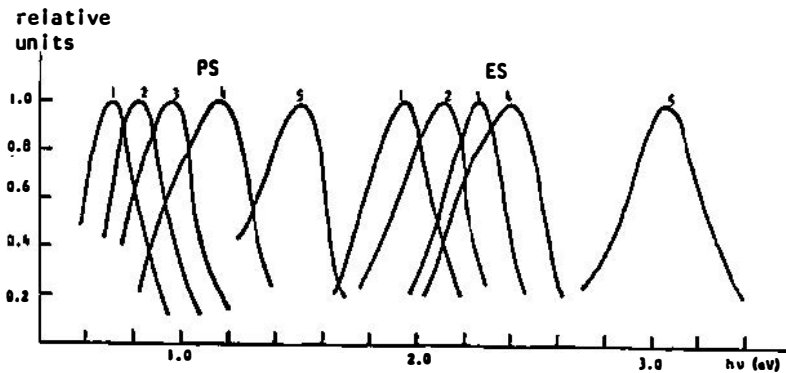


Fig. 2.

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