Radiative recombination in the vitreous semiconductors Ge_2S_3, Ge_2Se_3, and Ge–Pb–S

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We report the first investigations of recombination radiation in a new group of vitreous semiconductors. We demonstrate the presence of two groups of radiative levels in these materials.

The rapid development of research on radiative recombination in the vitreous arsenic chalcogenides As_2S_3 and As_2Se_3, which started in recent years, has yielded much valuable information on the energy spectrum of localized states in their forbidden bands. It became known, for example, that the photoluminescence spectra of these materials are characterized by rather broad emission bands at energies approximately equal to half the optical width of the forbidden bands. The observed emission bands are due, in the opinion of many authors,[1–7] to transitions through deep recombination centers, which are connected with structure defects of the bond-breaking type.

In this article we present the first results of an investigation of recombination radiation in a new group of vitreous semiconductors based on germanium chalcogenides, namely Ge_2S_3, Ge_2Se_3, and Ge-Pb-S.

The spectral distribution of the recombination radiation was investigated on freshly cleaved surfaces of bulky samples photoexcited in the energy interval 2–3 eV and at the temperature 77 °K. The spectral characteristics were measured after a stationary irradiation regime set in, i.e., 500–1000 sec after the instant of excitation.[7,8]

The results of these measurements are shown in Fig. 1 for Ge_2S_3 and Ge_2Se_3. We see that, just as in the arsenic chalcogenides, there is a broad emission band. The difference is that a tendency to splitting into two bands is observed. A similar splitting is observed also in the photoluminescence spectra of the glasses of the Ge-Pb-S system (Fig. 2).

The main parameters of the spectral characteristics shown in Figs. 1 and 2 are listed in the table.[1)] A comparison of the parameters indicates that the energy position of the less intense band (E_2) remains the same

TABLE I.

Material / Parameter	Energy position of emission bands		Intensity ratio E_2/E_1, relative units	Radiation intensity, relative units
	E_1, eV	E_2, eV		
Ge_2S_3	1.10	0.85	0.45	1.00
Ge_2Se_3	1.00	0.85	0.65	0.17
$Ge_{40.5}Pb_3S_{56.5}$	0.97	0.85	0.65	0.18
$Ge_{33.5}Pb_{10}S_{56.5}$	0.97	0.86	0.65	0.10
$Ge_{28.5}Pb_{15}S_{56.5}$	0.97	0.86	0.70	0.10
$Ge_{25.5}Pb_{18}S_{56.5}$	0.95	0.86	0.75	0.10
$Ge_{23.5}Pb_{20}S_{56.5}$	0.95	–	–	0.04

in all the germanium chalcogenides. On the other hand, the energy position of the more intense band (E_1) varies with the composition. Thus, for example, when the Pb content is increased and the Ge content is decreased, the (E_1) band shifts towards lower energies. The intensities of the bands (E_1) and (E_2), as seen from the table, also change.

The results, in our opinion, offer direct evidence that two groups of radiative recombination centers are present in the forbidden band of a vitreous germanium calcogenide. The nature of these centers requires further study, which will contribute to the understanding of the energy spectrum of the forbidden band and of the electronic processes of disordered semiconductors.

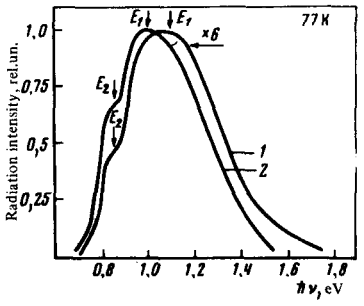

FIG. 1. Recombination-radiation spectra of vitreous semiconductors: 1—Ge_2S_3, 2—Ge_2Se_3.

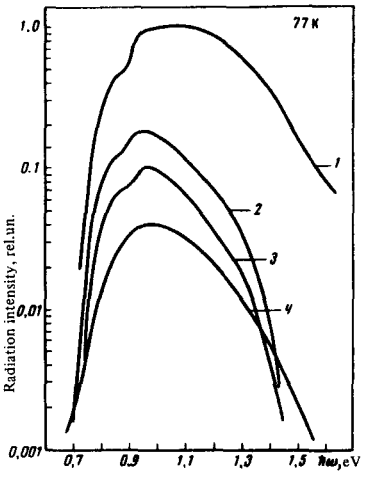

FIG. 2. Recombination emission spectra of the vitreous system Ge-Pb-S: 1—Ge_2S_3, 2—$Ge_{40.5}Pb_3S_{56.5}$, 3—$Ge_{33.5}Pb_{10}S_{56.5}$, 4—$Ge_{23.5}Pb_{20}S_{56.5}$.

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[1)]The optical thicknesses of the Ge_2S_3 and Ge_2Se_3 forbidden bands are ~ 2.4 and 1.9 eV, respectively, at 77 °K.

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