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Relaxation and thermoinduced processes in glassy $\text{HgSe}_{(x)}\text{-GeSe}_{2(1-x)}$ alloys

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Abstract. Spectra of absorption in glassy $\text{HgSe}_{(x)}\text{-GeSe}_{2(1-x)}$ ($x = 42, 46, 54$) alloys were studied. Sustained relaxation processes – a shift of the optical absorption edge to longer wavelength – were detected. Also observed was a thermoinduced reversible process when the absorption edge is shifted in the same direction after the samples have been annealed at 100 °C.

Keywords: glassy alloys, optical absorption, thermodarkening, relaxation process, metastable state.

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One of the characteristic features of chalcogenide glasses is photoinduced changes of their structure. These materials exhibit a wide variety of photostimulated processes such as absorption coefficient change, reversible and irreversible photostructural changes, luminescence fatigue, phenomenon of laser annealing etc. This enables them to be used for optical recording of information (with a high-density of recording and high resolution) or for creating holographic images. Such phenomena as reversible and irreversible optical darkening and bleaching are of special interest. It appears that these phenomena are closely related to the structural properties of glasses, but the underlying mechanism has not yet been established.

The phase diagram and technology of synthesis of HgSe-GeSe_2 alloys is presented in publications [1, 2, 3]. The mount for examining absorption spectra has been assembled using IKS-12 spectrometer and a usual circuit of synchronized detection. In alloys presented in this work the phenomenon of optical darkening has been discovered. Figure 1 shows the shift of the optical absorption edge (OAE) for three samples. Processes 1–2, 1'–2', and 1''–2'' represent a change in OAE after a six-month interval without external influence. This, in fact, means a free relaxation of the system into a more stable state. In

addition to relaxation processes, we detected a change in OAE under the influence of temperature as shown by 2–3, 2'–3', and 2''–3''. In all samples the magnitude of optical absorption increased at the temperature exceeding 80 °C. Graphs 3, 3', and 3'' represent OAE of alloys after 30 minutes of annealing at 100 °C. The process of thermodarkening is a reversible one. After an interval of three to four days without external influence on the samples OAE returns to the state 2, 2' and 2'' respectively. As it can be seen at the graphs and the table a maximum shift in OAE to the infrared part of the spectrum is demonstrated by the $\text{HgSe}_{(42)}$ sample. It decreases with the increase of the content of HgSe .

One can see that there are two components in the process that leads to a change of OAE in chalcogenide glassy semiconductors (CGS): the reversible and irreversible ones. Authors of [4] related the irreversible component to the presence of the so-called irregular homopolar bonds in CGS. In the case of alloys of the HgSe-GeSe_2 system, these may be bonds like Se–Se. But as a result of thermal processing these bonds sever, and energetically more beneficial heteropolar bonds such as Hg–Se or Ge–Se may be formed.

In [5, 6] induced structural changes are associated with interband correlation of potential. Different types

of correlation may be represented by correlation coefficient γ .

In the conduction and valence bands in spatially different points of a semiconductor γ takes the values +1 and -1 for parallel and antiparallel fluctuations, respectively (Fig. 2).

In the case of optical darkening, the share of the antiparallel component of the potential fluctuation increases. When OAE shifts in the direction of the high-energy part of the spectrum, the share of the parallel component increases. Maximum possible shift is observed with the switch of coefficient γ from +1 to -1. The magnitude of the maximum shift is determined by the following formula [5, 7]:

$$\Delta E_{\max} = h\nu(\gamma = -1) - h\nu(\gamma = +1) = -2W^2/B$$

where $h\nu$ is the photon energy at the absorption edge at a fixed value of absorption coefficient α ; W is the average value of potential fluctuation; B is the half-width of the band.

In the theory of approximate coherent potential [6, 8] the fuzziness of the absorption edge (or its slope) is determined by the following formula:

$$E_0 \approx W^2/2B$$

With E_0 known, maximum magnitude of the absorption edge shift ΔE_{\max} may be evaluated. Using the values of E_0 from [9] for alloys of the HgSe-GeSe₂ system, we will calculate ΔE_{\max} . The results are shown in Table 1. As one can see, as a result of the experiment we received the value of reversible thermoinduced changes of OAE (ΔE) for HgSe_(42, 46) samples that constitutes 11-13% of the maximum value (ΔE_{\max}). Such comparatively low values of ΔE may be accounted for in the following way. Together with the "direct" process of strengthening of the antiparallel component share in potential fluctuation in the material, a "reverse" process may concurrently take place during which metastable antiparallel fluctuation

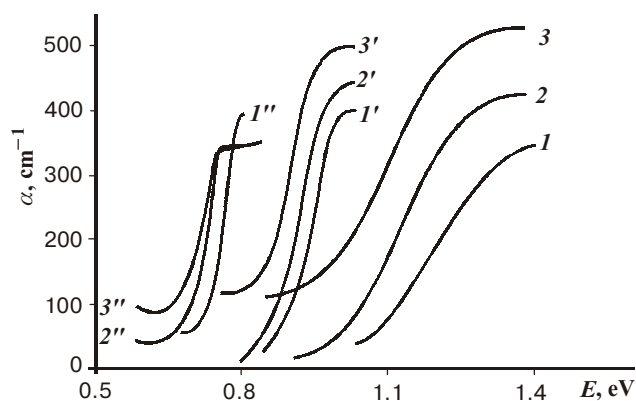


Fig. 1. Shift of the absorption edge in the alloys of the HgSe-GeSe₂ system (1, 2, 3 42%; 1', 2', 3' 46%; 1'', 2'', 3'' 54% HgSe).

slowly change and parallel fluctuation is formed. In HgSe₍₅₄₎ alloy, the shift of OAE is only 6 % of the maximum. In addition to that, thermoinduced processes in this sample change its OAE, which is represented at the graph by the change in the slope of the curve (curves 2''-3'', Fig. 1). That means that E_0 is functionally dependent on temperature. This fact is confirmed also in [9], where the authors show that HgSe₍₅₄₎ alloy is characterised by the crystal modification of general Urbach's rule. According to the theory of interband correlation of potential [5], a parallel or almost parallel shift of OAE has to take place in photoinduced or thermoinduced processes. Therefore, it is not expedient to apply this theory to HgSe₍₅₄₎ sample.

Table 1. Parameters of thermodarkening (determined at 250 cm⁻¹) and of the absorption edge.

HgSe content, mol. %	42	46	54
ΔE , eV	0.082	0.035	0.01
E_0 , eV [8]	0.18	0.068	0.039
ΔE_{\max} , eV	0.72	0.272	0.156

Phenomenologically more general model for explanation of photoinduced and thermoinduced processes is the configurational model. According to conceptions presented in [4, 10, 11], a structural element of CGS may be represented by adiabatic potential (Fig. 3). Lower-energy state A is primary, whereas higher-energy state B is metastable.

Thermal energy is absorbed by a structural element that is in the primary state. After that the structural element relaxes into the new state of equilibrium. To transfer from state B into state A, a structural element has to overcome potential barrier E_p . Transition into the primary state A takes place without any external influence. It is clear that the newly formed bonds are so weak that the thermal fluctuation of atoms suffices for the switching of the bonds and the transfer of the system into a new state. Having increased the temperature or the annealing time, we may be able to fix structural elements in state B. This is a promising object of further research of glassy alloys.

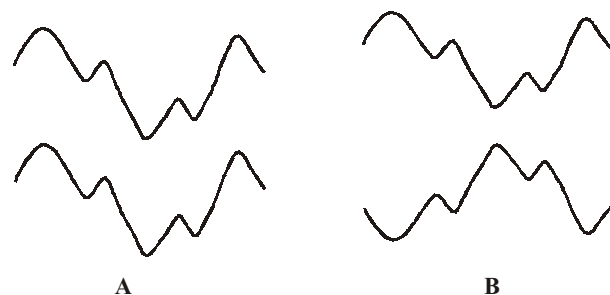


Fig. 2. Types of the potential fluctuation: A - parallel; B - antiparallel.

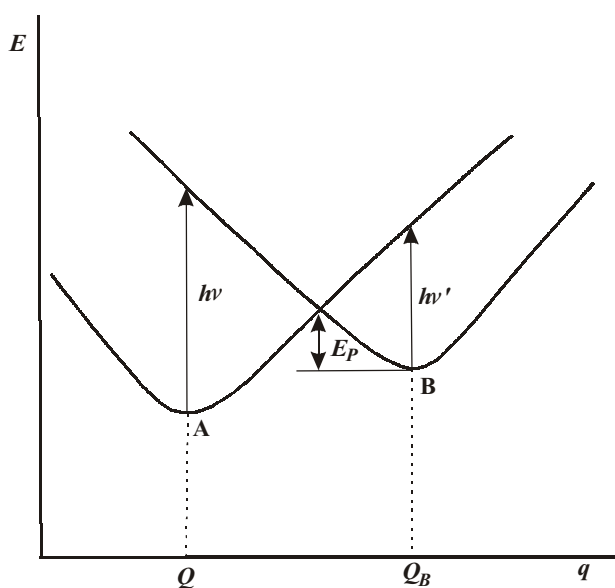


Fig. 3. Configurational coordinate diagram ($h\nu$, $h\nu'$ – energy absorption before and after darkening, respectively)

In conclusion, in alloys of HgSe–GeSe₂ system we observed sustained relaxation processes, i.e. a shift of the optical absorption edge to longer wavelength. We also detected thermoinduced reversible shift of OAE in the same direction. Explanation of these phenomena was given within the theory of interband correlation of potential and with the help of the configurational model.

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