On the Temperature Behaviour of Optical Transmission Spectra of γ-Modified Vitreous As_2S_3

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Abstract

Temperature behaviour of the optical transmission of γ-irradiated vitreous v-As_2S_3 is studied for the first time in the absorption edge region. It is shown that temperature dependences of the main transmission characteristics are different for γ-irradiated and non-irradiated glasses. The difference is associated with the existence of specific coordination topological defects appearing in the As_2S_3 network due to γ-irradiation.

Keywords: chalcogenide glass, gamma-irradiation, optical transmission, temperature behaviour

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Introduction

Owing to excellent transparency of vitreous chalcogenide semiconductors in the IR spectral region, they are especially attractive for different applications in modern optoelectronics [1-3]. These glasses reveal another unique feature, a high sensitivity to influence of external irradiation [4-6]. In sulphur-based chalcogenide glasses, this is a reason for a long-wave shift of the fundamental optical absorption edge or a so-called darkening effect, which makes them important for industrial dosimetric applications [4]. Thus, the stoichiometric quasi-layered vitreous v-As_2S_3 has been suggested as one of the most efficient media for Co^{60} γ-ray sensors operating in 0.5–10 MGy range of the absorbed doses [7].

It is worthwhile to note that v-As_2S_3 could be used repeatedly because of good reversibility in the observed optical changes resulted from subsequent cycles of γ-irradiation and thermal annealing just below the glass transition temperature T_g [8]. The process of thermal restoration has been typically studied using a step-wise heating/cooling procedure [8]. With this aim, the γ-irradiated sample should be placed into a furnace and maintained there at a certain temperature during some period of time (e.g., 30 min). Then the sample is cooled to the ambient temperature and, finally, its optical transmission spectrum is recorded in the region of fundamental optical absorption edge. Each next cycle of heating/cooling should be performed at still higher (by ~5–10 K) furnace temperatures, until we reach the temperature ~20 K lower than T_g. The process of thermal restoration has revealed a typical threshold character, the corresponding onset temperature being about 390–400 K and the activation energy ~0.3–0.5 eV [8]. The microstructural mechanism of these transformations has been explained in terms of γ-induced coordination topological defects [4,9].

Unfortunately, the optical measurements according to the mentioned experimental scheme have been performed after thermal annealing only, while the changes in the optical transmission occurring just during the annealing process have not been recorded. As a consequence, real temperature behaviour of the fundamental optical absorption edge after γ-irradiation still remains unclear, thus leading to uncertainties in the dose value determination in case when As_2S_3-based dosimeters are operated at higher temperatures.

In the present paper we study the temperature dependence of the optical transmission for γ-irradiated v-As_2S_3 near the fundamental absorption edge and in a wide range of temperatures varying from the room one up to near-T_g temperatures.

Experimental

Thick (1–2 mm) rectangular samples of v-As_2S_3 synthesised with conventional melt-quenching technique were used in our experiments. They had high-quality, plane-parallel polished surfaces. Some of them were γ-irradiated with a power of several Gy/s in a closed cylindrical cavity of concentrically arranged Co^{60} sources (the so-called 'stationary radiation field' conditions). The temperature did not exceed ~310 K and the accumulated dose approached 2 MGy. For the reference, the rest of samples were stored in darkness under the natural conditions.

Optical transmission spectra τ(λ) were measured before and after γ-irradiation, using double-beam Perkin-Elmer spectrophotometer Lambda-35 possessing the accuracy of about ±0.2 %. The air-flow heating of samples was provided directly in the measuring chamber of spectrophotometer. Two thermocouples were placed on different facets of the sample with the purpose of controlling the temperature gradient (<1 K/cm) along its length. The temperature was changed by 5 K per 3 min steps, the first two minutes being used for stabilizing a next temperature and the last minute for taking the optical spectrum. The deviation of temperature during the measurements did not exceed ±1 K.

The experiments were carried out on a number of both γ-irradiated and non-irradiated samples in order to clarify reproducibility of the results.

Results and discussions

The temperature behaviour of the optical transmission for non-irradiated v-As_2S_3 in their fundamental optical absorption edge region is shown in Fig. 1a. Both the qualitative and quantitative characteristics of this behaviour turn

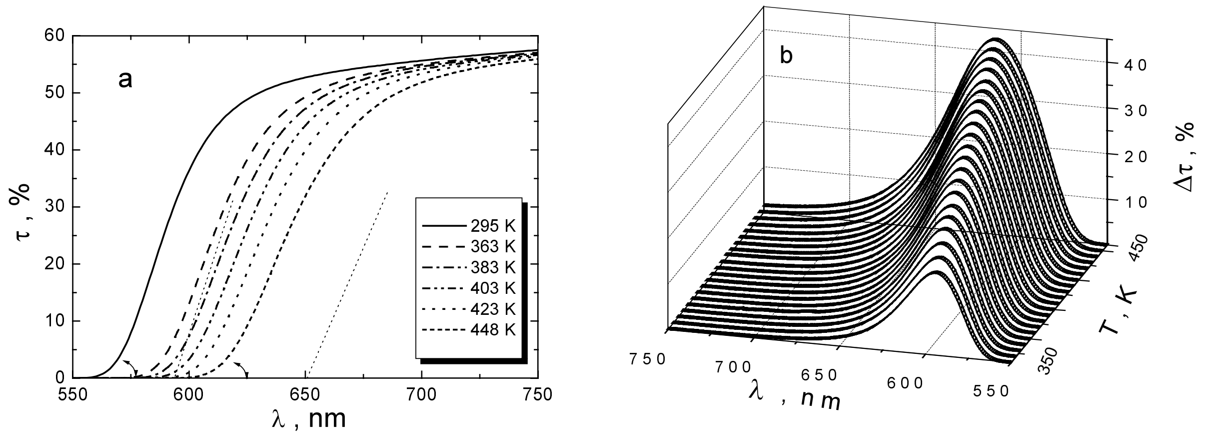

Fig. 1. Optical transmission spectra (τ(λ), a) and their thermally-induced changes (Δτ(λ), b) for the non-irradiated v-As_2S_3 measured at different temperatures.

out to be the same in the heating and cooling regimes, depending only on the temperature in the spectrophotometer chamber: the higher the temperature, the larger the long-wave shift of the transmission spectrum and the less the corresponding slope is, as indicated in Fig. 1a. This effect can be conveniently presented in the form of $\Delta\tau(\lambda)$ differences between the transmission spectrum at the room temperature and the spectra taken at higher sample temperatures (see Fig. 1b). It is clearly seen that every $\Delta\tau(\lambda)$ curve is characterised by a well-defined maximum, whose shape, magnitude ($\Delta\tau_{max}$) and position (λ_{max}) are fully determined by the current sample temperature. So, $\Delta\tau_{max}$ and λ_{max} values may be used as adequate descriptive parameters for further characterization of the observed optical effects in v-As_2S_3. For the non-irradiated v-As_2S_3, the above parameters exhibit almost linear dependence on temperature (see Fig. 1b). This agrees completely with the near-linear temperature behaviour known for the optical gap of the glass under test [10-12].

The effect of γ-irradiation manifests itself through the long-wave shift of the transmission $\tau(\lambda)$ measured in the region of fundamental optical absorption edge at the room temperature, accompanied by decrease in its slope (see Fig. 2). The main features of this phenomenon, the corresponding dose dependences and the mechanisms are described elsewhere [4,7-9]. Here we focus our attention only on the temperature behaviour of the optical changes produced by γ-irradiation.

Heating of γ-irradiated sample leads to additional long-wave shift in the transmission spectrum, which runs up to ~50 nm at the maximal annealing temperature of 448 K (see Fig. 2). This temperature is close to T_g in v-As_2S_3 (~460 K) and it is enough to erase all the reversible optical changes produced by γ-irradiation in the glass [8]. As a result, after the point of 448 K is reached during heating, one can consider further temperature behaviour of the fundamental absorption edge in v-As_2S_3 as that peculiar for a non-irradiated sample. Therefore, in our further consideration we label the temperature dependences of the optical properties obtained during heating of γ-irradiated v-As_2S_3 as I-type behaviour, whereas the dependences obtained during cooling or those for the non-irradiated glasses will be referred to as N-type behaviour.

If γ-irradiation did not affect the temperature behaviour of the optical characteristics, we should have observed no essential difference in the transmission spectra of γ-irradiated v-As_2S_3 taken at the same temperatures in the heating and cooling runs, like in the case of non-irradiated samples. However, these spectra prove to be not coincident (see the data of Fig. 2 referred to 353 K), giving rise to difference in the appropriate $\Delta\tau(\lambda)$ curves.

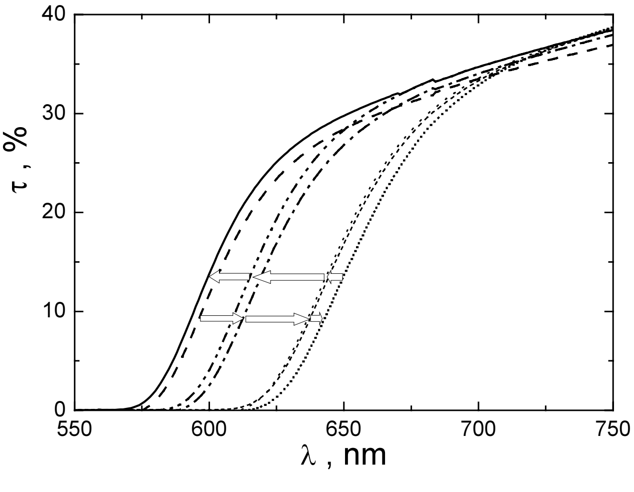

Fig. 2. Optical transmission spectra of γ-irradiated v-As_2S_3 measured during heating-cooling thermal cycling according to the following scheme: room temperature (dash) – 353 K (dash-dot) – 433 K (short dash) – 448 K (short dot) – 433 K (dot) – 353 K (dash-dot-dot) – room temperature (solid). Notice that the last spectrum coincides with the $\tau(\lambda)$ curve measured for v-As_2S_3 immediately before γ-irradiating.

Fig. 3 shows the temperature dependences of the maximal transmission changes $\Delta\tau_{max}$ and their positions λ_{max} acquired for non-irradiated and γ-irradiated samples from the $\Delta\tau(\lambda)$ characteristics. The N-type behaviour of the optical transmission has been repeatedly obtained in the subsequent heating/cooling cycles for the previously γ-irradiated and then annealed sample, as well as for the non-irradiated v-As_2S_3 (see inserts in Fig. 3). The I-type behaviour has been observed only while heating the γ-irradiated v-As_2S_3.

It is evident (see Fig. 3a) that the $\Delta\tau_{max}(1/T)$ dependences plotted on a semilogarithmic scale split into two specific parts that correspond to the regions located before (A) and after (B) the 'threshold region'. In the A region the I- and N-type behaviours differ, while in the B region they coincide, exhibiting a near-linear dependence on the reciprocal temperature. The threshold region is roughly defined as the range of 370–400 K, where the N- and I-type $\Delta\tau_{max}(1/T)$ behaviours change their character. We notice here that the 'step-wise' heating/cooling investigations on the γ-irradiated v-As_2S_3, Ge-Sb-S and Ge-As-S glasses have also given the region of ~370–400 K as the threshold one, where the optical changes produced by γ-irradiation start to vanish rapidly [8,13]. In our case, the semilogarithmic $\Delta\tau_{max}(1/T)$ curve for the γ-irradiated v-As_2S_3 does not exhibit such a rough perturbation in this region and changes in the slope are merely seen. Contrary to the N-type, the I-type behaviour manifests itself in almost linear dependence on the reciprocal temperature peculiar for the A region. This means that, contrary to non-irradiated v-As_2S_3, the temperature shift of the absorption edge in this region for γ-irradiated v-As_2S_3 is characterised by a single activation energy, thus supporting idea of a single mechanism causing such the shift. Hence, one can conclude that, in addition to reduction of temperature sensitivity of the optical properties in the low-temperature region, the γ-treatment of v-As_2S_3 also suppresses the N-type mechanisms of the temperature edge shift characteristic for non-irradiated or annealed glass.

The temperature behaviour of the spectral position λ_{max} changes due to γ-irradiation, too (see Fig. 3b). These results testify that the position of the maximal transmission changes $\Delta\tau_{max}$ shifts with increasing temperature towards longer wavelengths for both the γ-irradiated and non-irradiated v-As_2S_3, showing again a near-linear temperature dependence. However, the I-type behaviour for this case begins to coincide

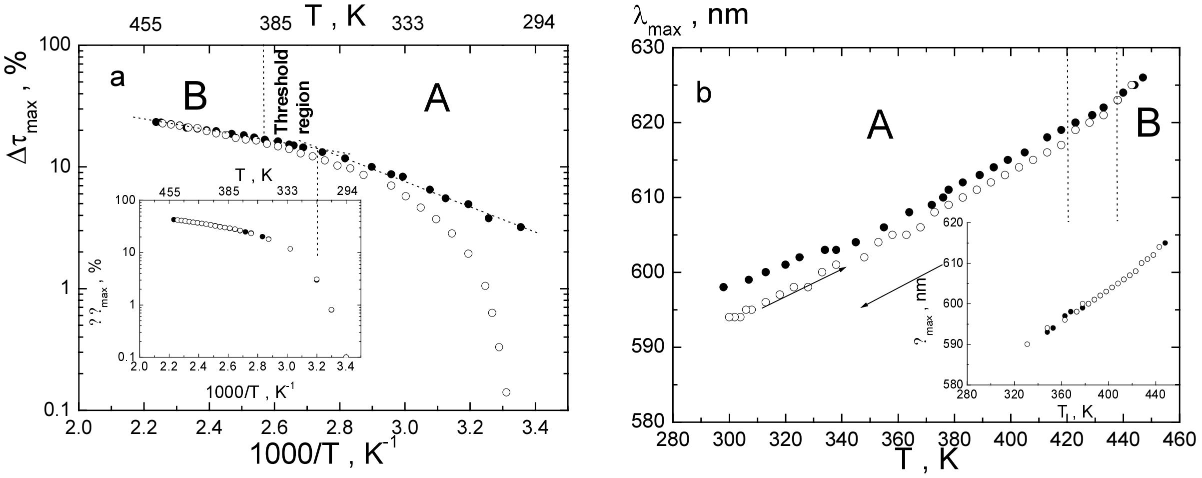

Fig. 3. Temperature dependences of maximal changes in the optical transmission ($\Delta\tau_{max}$, a) and their spectral positions (λ_{max}, b) for γ-irradiated v-As_2S_3 measured during the heating (full circles) and cooling (open circles) thermal cycles. The inserts show the same dependences for the non-irradiated v-As_2S_3.

with the N-type one at higher temperatures (a roughly estimated threshold region being equal to 420–440 K), when compare with those characteristic for $\Delta\tau_{max}(1/T)$. Despite the nature of this peculiarity is still unclear, we can assume it to be attributed to a different temperature stability of the two components of γ-induced effect in the region of fundamental absorption edge, the long-wave shift of the optical characteristic and the decrease in its slope.

According to the model of formation of coordination defects, which has been previously developed for explaining reversible γ-induced optical effects in v-As_2S_3 [4,9], the long-wave shift in the fundamental optical absorption edge is attributed to γ-induced switch from stronger heteropolar covalent As-S bonds to weaker homopolar As-As ones. The slope decrease after the γ-irradiation is associated with the appearance of charged defects (pairs of over- and under-coordinated As and S atoms, or so-called D^+-D^- centres) in the glass structure. The thermal restoration effect is caused by thermally-activated backward switching (As-As to As-S) and the processes of annihilation of the charged defects. They represent a ground for explaining reversibility in the γ-induced optical phenomena [4,8,9].

The developed model does not contradict the present results, too. The existence of wrong homopolar bonds and charged defects is a reason for different temperature behaviour of the fundamental absorption edge observed for the γ-irradiated sample in the A region. The presence of coordination defects also enables one to explain a single activation mechanism for the temperature shift of the optical absorption edge occurring in γ-irradiated v-As_2S_3. The annihilation of these defects in the 380–430 K interval and the backward switching processes are obviously responsible for the appearance of threshold regions in the $\Delta\tau_{max}(1/T)$ and $\lambda_{max}(T)$ dependences. After the processes are fully completed, the I- and N-type dependences in the B region coincide.

Conclusions

- The temperature dependence of the optical transmission in the fundamental absorption edge region measured for γ-irradiated v-As_2S_3 differs from that peculiar for the non-irradiated compound in its low-temperature part (A) and fully coincides with the latter in its high-temperature part (B). The threshold region between the A and B parts is distinguished.
- The character of $\Delta\tau_{max}(1/T)$ curves in the A region testifies a lower temperature sensitivity of the optical absorption edge in γ-irradiated sample, when compare to non-irradiated v-As_2S_3, thus revealing a single activation mechanism of the temperature shift.
- γ-ray dosimeters based upon v-As_2S_3 can be operated in the temperature region A with losing no information about the absorbed dose, though the dose evaluation procedure should include additionally the temperature correction according to the obtained results.

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