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IR OPTICAL PROPERTIES OF $As_{32}Sb_8S_{60}$ CHALCOGENIDE GLASS AND EFFECT OF γ-IRRADIATION

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Abstract. In this paper, impact of γ-irradiation on the transmittance of $As_{32}Sb_8S_{60}$ chalcogenide glass in the near and mid IR spectral range is investigated. The radiation-induced changes in the main IR impurity absorption bands are discussed to be taken into account in IR optical devices based on the glass composition studied to work in the conditions of high energy radiation fields.

Keywords: chalcogenide glasses, impurity absorption, radiation modification, IR optics

ВПЛИВ γ-ОПРОМІНЕННЯ НА ІЧ ОПТИЧНІ ВЛАСТИВОСТІ ХАЛЬКОГЕНІДНОГО СКЛА $As_{32}Sb_8S_{60}$

Т. С. Кавецький, О. Й. Шпотюк, Г. І. Довбешко, І. В. Блонський, В. М. Цмоць

Анотація. В статті представлено результати вивчення впливу γ-опромінення на прозорість халькогенідного скла $As_{32}Sb_8S_{60}$ в ближньому та середньому ІЧ діапазоні спектру. Обговорюються радіаційно-індуковані зміни основних смуг ІЧ домішкового поглинання, які слід врахувати при використанні скла даного хімічного складу в ІЧ оптичному приладобудуванні для роботи в умовах високоенергетичних радіаційних полів.

Ключові слова: халькогенідні стекла, домішкове поглинання, радіаційна модифікація, ІЧ оптика

ВЛИЯНИЕ γ-ОБЛУЧЕНИЯ НА ИК ОПТИЧЕСКИЕ СВОЙСТВА ХАЛЬКОГЕНИДНОГО СТЕКЛА $As_{32}Sb_8S_{60}$

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Аннотация. В статье представлены результаты по изучению влияния γ-облучения на прозрачность халькогенидного стекла $As_{32}Sb_8S_{60}$ в ближнем и среднем ИК диапазоне спектра. Обсуждаются радиационно-индуцированные изменения основных полос ИК примесного поглощения, которые следует учитывать при использовании стекла данного химического состава в ИК оптическом приборостроении для работы в условиях высокоэнергетических радиационных полей.

Ключевые слова: халькогенидные стекла, примесное поглощение, радиационная модификация, ИК оптика

1. Introduction

Chalcogenide glasses based on sulphur, selenium, and tellurium and doped by rare-earth elements are widely used in modern optoelectronics with passive and active applications for IR optical devices [1]. A very significant property for such applications is a high IR transmittance of these materials, but impurity absorption processes in the near and mid IR range must be taking into account during fabrication and exploitation of chalcogenide glass optical fibers and waveguides [2].

Another problem is preparation of host glass matrix with optimal properties. The chemical-technological modification methods have been developed to resolve it, but their possibilities are practically exhausted. Besides, sufficient complication in chemical-technological modification exists due to additional and very expensive procedures such as multi-state distillation, homogenized vacuum melting, vapour filtration, thermal decomposition, dissociate evaporation, melt centrifugation and fractioning, etc. The real problem appeared recently is connected with development of alternative energy-conserved and ecologically-save methods of post-technological modification of chalcogenide glass. One of the most suitable ways to successfully resolve the above problem is connected with possibilities of structural modification of glass in the conditions of high energy γ-irradiation. The principal advantages of this post-technological route were discussed elsewhere [3].

In the present study we report recent results on impact of post-technological radiation modification on the IR impurity absorption in bulk samples of $As_{32}Sb_8S_{60}$ chalcogenide glass.

2. Experimental

$As_{32}Sb_8S_{60}$ glass was prepared by the conventional melt-quenching procedure [4]. After synthesis, the ingot was cut to the disks of the same thickness (~ 1 mm) and polished to a high optical quality. Before experimental measurements, the samples were annealed at a temperature of 20-30 K below the glass transition temperature (T_g = 455-460 K [4]) to remove possible mechanical strains formed after preparation.

Post-technological radiation treatment of the samples was performed by γ-quanta with average energy of 1.25 MeV and accumulated dose of 0.76 MGy at normal conditions of stationary radiation field created in a closed cylindrical cavity by a number of concentrically established ^{60}Co radioisotope capsules. No special measures were taken to prevent uncontrolled thermal annealing of the samples, but maximum temperature in the irradiating camera did not exceed 320-330 K during prolonged γ-irradiation (more than 10 days), providing absorbed dose power $P < 5$ Gy/s.

IR spectra were recorded in the transmission geometry in the region of 4000-400 cm^{-1} by using Fourier spectrometer Bruker IFS-66 (Germany). The spectra measured were treated with standard programmes Opus-4.2 and Opus-5.5, included into Bruker IFS-66 software, and also with special programme OMNIC for spectra processing.

3. Results and discussion

Fig. 1 shows the IR transmittance spectra measured for the non-irradiated and γ-irradiated samples. It is seen that the glass composition studied possesses a high transmittance, being a good candidate for applications in IR optical devices. The remarkable changes in IR transmittance upon γ-irradiation are found in the vicinity of 3500, 3000, and 1500 cm^{-1} and marked by dashed circles in the figure.

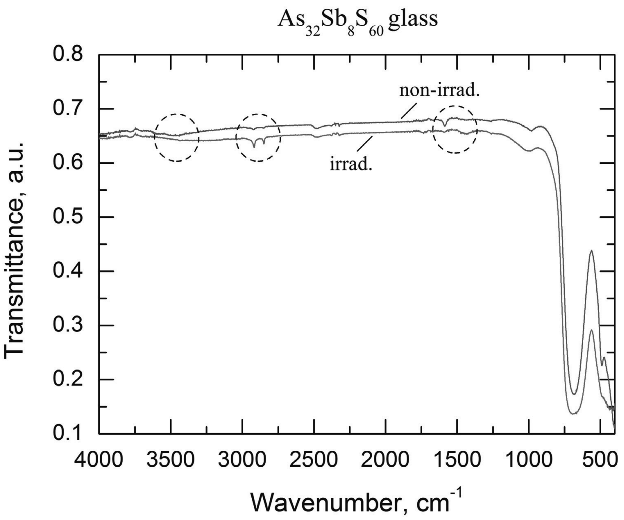

Fig. 1. IR transmission spectra for the investigated non-irradiated and γ-irradiated samples of $As_{32}Sb_8S_{60}$ glass. The remarkable radiation-induced changes in IR transmittance in the vicinity of 3500, 3000, and 1500 cm^{-1} are marked by dashed circles.

In order to make comparative analysis between the non-irradiated and γ-irradiated samples, the IR transmittance spectra were transformed to the optical density spectra by using OMNIC programme and than were normalized as shown in Fig. 2. The wavenumbers of the main impurity absorption bands were identified by Opus programmes. The dashed circles in the figure are cited in the spectral ranges corresponding to those marked in Fig. 1.

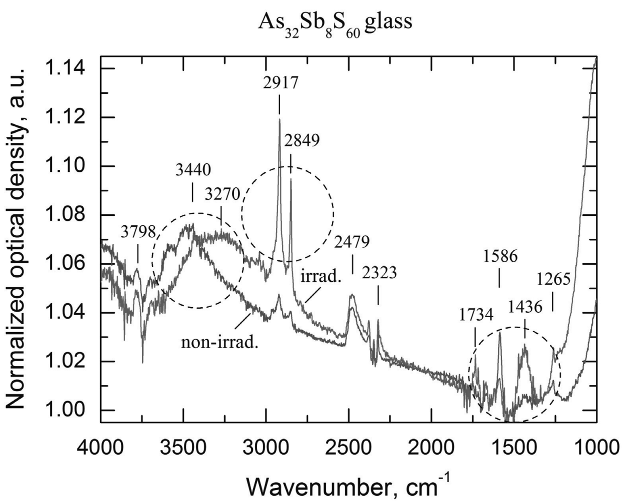

Fig. 2. Normalized optical density spectra for the investigated non-irradiated and γ-irradiated samples of $As_{32}Sb_8S_{60}$ glass. The dashed circles are cited in the spectral ranges corresponding to those marked in Fig. 1.

Several very weak absorption bands are identified, being related to the impurity complexes of [2,5-7]: isolated (free) molecular water H_2O (band at 3789 cm^{-1}); hydroxyl =As–OH groups (band at 3440 cm^{-1}); hydroxyl –S–OH groups (band at 3270 cm^{-1}); hydrocarbon CH_2 groups (bands at 2917 and 2849 cm^{-1}); sulphur-hydrogen –S–H complexes (band at 2479 cm^{-1}); molecular H_2S (band at 2323 cm^{-1}); molecular-adsorbed water H_2O (band at 1586 cm^{-1}); oxide –S–O– complexes and/or molecular As_4O_6 (bands at 1436 and 1265 cm^{-1}).

After post-technological radiation modification of the glass matrix the picture in the impurity absorption becomes some different from one proper for the non-irradiated sample. The main radiation-induced changes detected are (i) the decrease amount of molecular-adsorbed water H_2O, and (ii) increase amounts of hydroxyl –S–OH, hydrocarbon CH_2, oxide –S–O– and/or molecular As_4O_6 groups.

First process is probably connected with radiolysis of molecular-adsorbed water H_2O under irradiation and joining of the created products with intrinsic structural units of a glass network. The main products formed as a result of this radiolysis are hydroxyl –S–OH complexes that explain in part the second process. Also, the radiation-induced oxidation takes place upon irradiation with additional appearance of oxide –S–O– complexes and/or molecular As_4O_6 groups due to implantation of air-adsorbed oxygen into a glass network through mechanisms described earlier in the case of g-As_2S_3 [5]. The largest effect, however, is observed on the hydrocarbon CH_2 complexes (so-called 'radiation-induced hydrocarbonization') which seems to be originated from chemical interaction of γ-destructed intrinsic structural units with absorbed hydrocarbon C_nH_m groups in a good agreement with laser mass spectroscopy data for g-As_2S_3 [5].

The above mentioned post-technological radiation modification effects should be taken into account from the practical viewpoint for controlling/monitoring of impurity absorption processes in chalcogenide glass used in IR optical devices. It is interesting whether these effects are reversible or irreversible with annealing of glass. This problem and also compositional investigations are now in progress.

4. Final remarks

It is established g-$As_{32}Sb_8S_{60}$ possesses a high transmittance in the 4000-1000 cm^{-1} range that makes it a good candidate for IR optical applications. Post-technological radiation modification effects are found to be connected with radiolysis of molecular-adsorbed water, implantation of air-adsorbed oxygen into a glass network and chemical interaction of γ-destructed intrinsic structural units with absorbed hydrocarbon groups. The features observed should be used during fabrication and exploitation of IR optical fibers and waveguides based on the glass composition studied to work in the conditions of high energy radiation fields.

Acknowledgments

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