Gamma-Induced Changes in Optical Transmission of As-S Semiconductor Glasses

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Abstract – Compositional trends of γ-induced optical changes in chalcogenide glasses are studied with the binary As-S system. Effects of γ-irradiation and annealing are compared using to the changes measured in the fundamental optical absorption edge region.

Key words – glass, chalcogenide glass, As-S, γ-irradiation, optical spectroscopy, optical transmission.

I. Introduction

Rapid development of telecommunication technologies at the beginning of the third Millennium has increased the search for new functional media for effective transfer of wide-spectra electro-magnetic radiation and development of novel miniaturization approach for passive and active photonics [1]. One of the most promising material systems for inclusion in such multifunctional applications is the semiconductor chalcogenide glasses (SChG), glassy materials with high content of the chalcogens (S, Se, Te).

The SChG system consisting of binary arsenic sulphide (As-S) has been known since the earliest stages of glass science and technology [2]. Owing to their excellent transparency in infrared spectral region, As-S glasses are especially attractive for different applications in modern optoelectronics and photonics [1]. Unfortunately, their optical properties are not fully suitable for some specific applications governed by high technological reliability and reproducibility requirements. So, the leading manufactures in this field have been engaged in the development and improvement of SChG to obtain materials with optimal characteristics. Under such conditions, the technologies that exploit the property consisting of externally-induced structural modification can be especially useful, as is clearly demonstrated for stoichiometric As_2S_3 prepared in the form of thin films and bulk glasses exposed to absorbed light and γ-irradiation [3]. Compositional behavior of photo-induced modification has been well studied in thin As_xS_{100-x} films, while effects produced by γ-irradiation in bulk glasses of the same system have not yet been investigated comprehensively.

The main aim of this paper is to investigate compositional trends of γ-induced optical changes in bulk As_xS_{100-x} SChG in a wide compositional range and determine their feedback on γ-induced modification in dependence on the prehistory of the specimens.

II. Experimental Procedure

The homogeneous As_xS_{100-x} samples with x = 30, 33, 36, 40, 42 were prepared by conventional rocking-melting-quenching technique. The samples were synthesized using respective quantities of high-purity As and S in evacuated and sealed fused quartz ampoules. The mixture of high-purity precursors was melted in a rocking furnace at 720–790 K for 12–24 hours. The ingots were then air-quenched to a glassy state. After synthesis, the samples were annealed 30-40 K below the respective glass transition temperature (T_g) for each composition. Then, specimens were cut from the bulk samples as plane-parallel plates and polished to high optical quality.

The γ-irradiation treatment was carried out at the ambient conditions in a closed cylindrical cavity of concentrically established ^{60}Co sources (the mean energy of γ-quanta 1.25 MeV) with 0.7 kGy/h dose rate at the temperature not exceeding 300 K. The overall duration of γ-irradiation treatment was 6 months and total accumulated dose during this period was near ~3 MGy.

The optical transmission spectra in the fundamental absorption edge region were recorded using *AvaSpec-2048* spectrometer (*Avantes*, Netherlands) with a maximum associated error of ± 1%. The heating and cooling of specimens was provided in a specially adjusted temperature chamber with a constant 5 K/min rate and an uncertainty in the temperature control of ± 0.5 K. Optical transmission spectra were recorded for each γ-irradiated, further annealed and rejuvenated samples (characteristic temperatures T_{ann} and T_{rej} are given in Table 1). So, investigations under such protocol were performed in a so-called *backward-measuring chronology*.

TABLE 1

PARAMETERIZATION OF EXPERIMENTAL MEASURING PROTOCOL

SChG composition	Thickness, mm	T_g, K [28]	T_{ann}, K	T_{rej}, K
$As_{30}S_{70}$	1.54	425	390	455
$As_{33}S_{67}$	1.53	430	395	465
$As_{36}S_{64}$	1.53	440	405	475
$As_{40}S_{60}$	1.44	465	425	495
$As_{42}S_{58}$	1.50	460	425	495

III. Results and Discussion

Optical transmission spectra of γ-irradiated, subsequently annealed, and rejuvenated As-S specimens are presented in Fig. 1. Two effects could be determined from these spectra: (i) effect of annealing on rejuvenated specimens and (ii) effect of γ-irradiation on annealed specimens. Additionally, under the assumption that the total effect of γ-irradiation in saturation does not depend on thermal history, we could determine the third effect in our investigations, (iii) the effect of γ-irradiation on rejuvenated specimens (Fig. 1). This assumption seems to be quite reasonable assuming that only the latest treatment determines the final thermodynamic state of the SChG, similar to the assumption presented elsewhere [30].

The effect of γ-irradiation on the annealed SChG is revealed long-wave shift of the optical transmission spectra (*darkening effect*) of near-stoichiometric As_xS_{100-x} specimens (x = 36, 40, 42). Corresponding shifts in the annealed S-rich As_xS_{100-x} specimens with x = 30 and 33 are of under-margin intensity. The well-defined γ-induced short-wave shift of the optical transmission spectra (*bleaching effect*) could be observed for rejuvenated As-deficient specimens, the ΔT_{max} value reaching 9, 5 and 2% in the specimens with x = 30, 33 and 36, respectively (Fig. 2). At the same time, the rejuvenated $As_{40}S_{60}$ and $As_{42}S_{58}$ SChG still exhibit γ-induced darkening effect, similarly to the annealed ones.

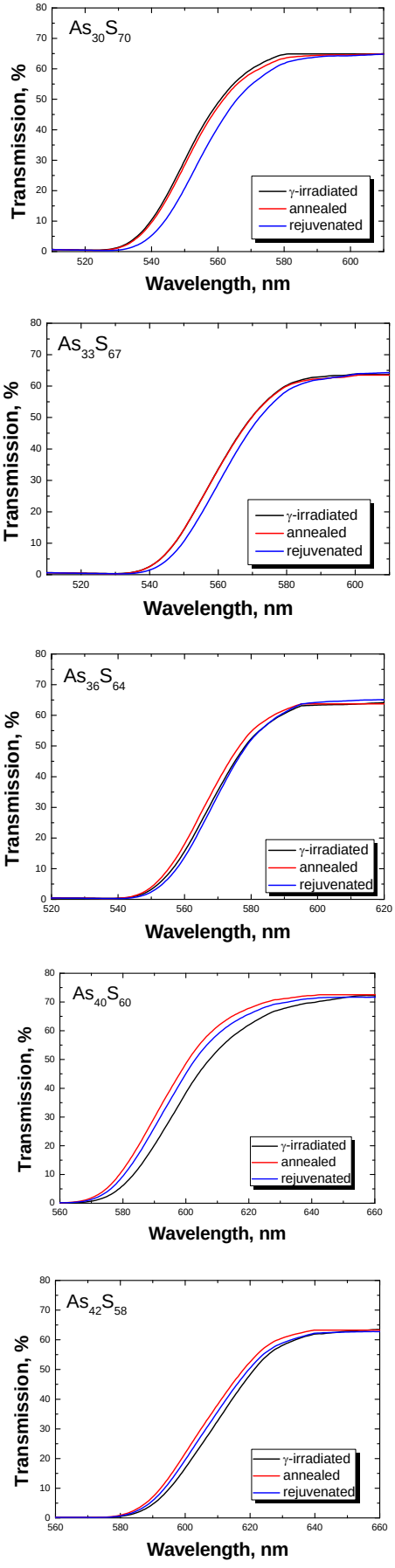

Fig. 1. Optical transmission spectra of γ-irradiated, annealed and rejuvenated As-S SChG

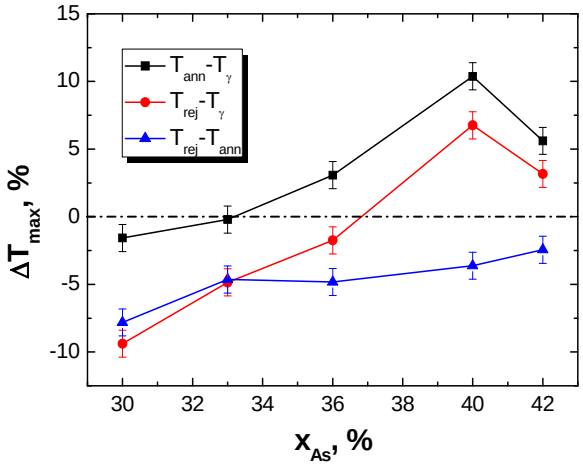

Fig. 2. Maximal intensities of subtractive optical transmission spectra relevant to different effects in As-S SChG: black squares – γ-induced effect in annealed specimens; red circles – γ-induced effect in rejuvenated specimens; blue triangles – annealing effect in rejuvenated specimens

A possible explanation for the observed γ-induced darkening effect in studied SChG can be given in terms of destruction-polimerization transformations (DPT) concept via structural rearrangement accompanied by switching of heteropolar As–S covalent bonds into homopolar As–As ones.

For the S-rich rejuvenated specimens, the bleaching effect of γ-irradiation is anticipated according to the obtained results. It is attributed to the physical ageing stimulated by γ-irradiation. The difference in the positions of the fundamental optical absorption edge of annealed and rejuvenated SChG confirms this supposition, showing bleaching as a result of thermally-induced physical ageing. Thus, the γ-induced changes in the position of the fundamental optical absorption edge of As-S SChG should be considered as a balance between two independent competitive processes – DPT (including defect formation) and γ-induced physical ageing.

Conclusions

Compositional trends of γ-induced optical changes in chalcogenide glasses of binary As-S system are studied by *in-situ* optical spectroscopy arranged in *backward measuring chronology*. The compositional dependence of γ-induced changes in the annealed specimens and anticipated γ-induced changes in the rejuvenated SChG are shown to have similar character with maxima at the $As_{40}S_{60}$ stoichiometric composition. Any deviations from stoichiometry towards both S- and As-rich compositions reduce the value of γ-induced darkening. In general, the obtained results demonstrate the complex nature of radiation-induced optical effects in As-S SChG and their dependence on glass composition and thermal history.

References

[1] J. S. Sanghera, I. D. Aggarwal, J. Non-Cryst. Solids. 256-257 (1999) 6
[2] C. Schultz-Sellack, Ann. Phys. 139 (1870) 182.
[3] O. I. Shpotyuk, Opto-Electronics Rev. 11 (2003) 19.