

PACS 61.43.Fs, 61.80.Ed, 78.40.Fy, 78.40.Pg

## **Radiation-induced optical darkening and oxidation effects in As<sub>2</sub>S<sub>3</sub> glass**

**T.S. Kavetskyy**

*Ivan Franko Drohobych State Pedagogical University,  
24, I. Franko str., 82100 Drohobych, Ukraine*

**Abstract.** The long-wave shift of fundamental optical absorption edge with decreasing the sample's transparency in the saturation region in the As<sub>2</sub>S<sub>3</sub> bulk glass (~2 mm thick) due to radiation treatment by <sup>60</sup>Co  $\gamma$ -quanta with the average energy  $E = 1.25$  MeV and accumulated dose  $\Phi = 2.41$  MGy is reported. The red shift (radiation-induced optical darkening effect) is detected within the period of 2-3 months after  $\gamma$ -irradiation able to cause the well-known static radiation-induced optical effect. The detected decrease in the slope of  $\tau(\lambda)$  curve in the fundamental optical absorption edge region after  $\gamma$ -irradiation, resulting in the maximum difference of optical transmittance for the unirradiated and  $\gamma$ -irradiated samples  $\Delta\tau(h\nu)_{\max}$  at the level 33.5%, can be interpreted within the radiation-induced defect formation processes occurring in the structural network of glass. At the same time, as expected from literature, the observed decrease in the sample's transparency at the level 33% upon radiation is plausibly caused by the accompanying radiation-induced oxidation processes that are the most probably related with appearance of As<sub>2</sub>O<sub>3</sub> (arsenolite) crystals and S phases at the surface of  $\gamma$ -irradiated sample, forming a white oxidized layer visible to the eye. The disadvantage of As<sub>2</sub>S<sub>3</sub> glass to be selected as the best model object for X-ray diffraction study of  $\gamma$ -radiation-structural changes, especially in respect to the first sharp diffraction peak, is considered.

**Keywords:** chalcogenide glass, optical properties, radiation modification, radiation oxidation.

Manuscript received 19.02.14; revised version received 28.07.14; accepted for publication 16.09.14; published online 30.09.14.

### **1. Introduction**

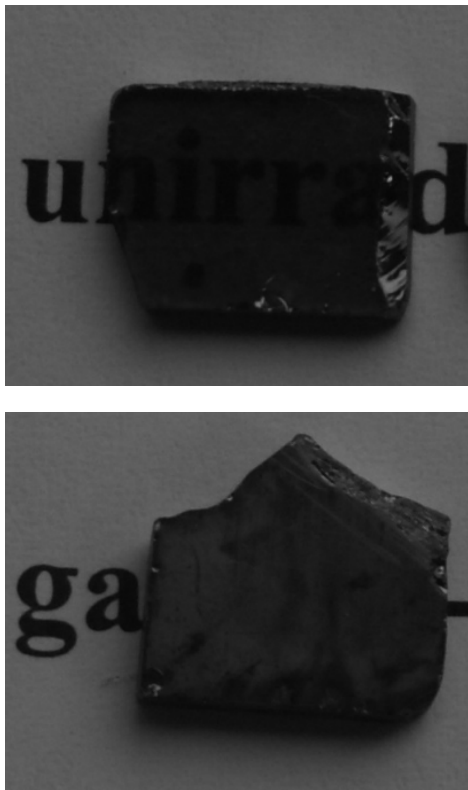
Recently, Shpotyuk *et al.* [1] investigated the influence of high-energy  $\gamma$ -irradiation on the first sharp diffraction peak (FSDP) in X-ray diffraction (XRD) pattern in As<sub>2</sub>S<sub>3</sub> bulk glasses from the viewpoint of uncontrolled changes in chemistry of the samples owing to environmental impurities, first of all, oxygen. Indeed, formation of crystalline As<sub>2</sub>O<sub>3</sub> (arsenolite) and S phases at the surface of g-As<sub>2</sub>S<sub>3</sub> (g- for glassy) after prolonged <sup>60</sup>Co  $\gamma$ -irradiation with ~3 MGy dose has evidently been proved by the authors, and the impact of these products on the

FSDP shape as well as on the next XRD peak (as seen from Figs. 4 and 5 [1]) has reasonably been shown.

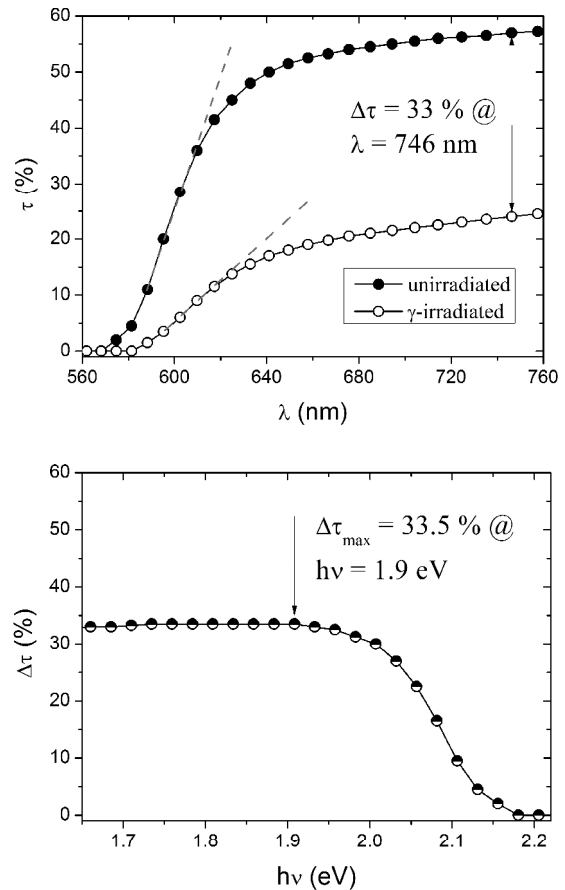
The oxidation processes due to decomposition of As<sub>2</sub>S<sub>3</sub> and further formation of As<sub>2</sub>O<sub>3</sub> and S phases were reported in the case of prolonged photo-exposure of As<sub>2</sub>S<sub>3</sub> thin films as well [2, 3]. But regarding photostructural changes, the possibility of *in-situ* experiment, i.e. when the samples are illuminated *in-situ* on goniometers, can be applied to resolve XRD pattern upon illumination more precisely, excluding impact of oxidation processes [4, 5]. So, using the detailed XRD measurements of annealed and illuminated g-As<sub>2</sub>S<sub>3</sub> bulk

samples, Tanaka [4, 5] concluded that the photoinduced FSDP changes are as follows: (i) the angular shifts of the peak position, which are prominent for samples illuminated at low temperatures [6, 7], are not detected or very small, and (ii) the peak becomes weaker and broader with illumination, and at peak tails asymmetric intensity enhancement occur. The photostructural changes observed in g-As<sub>2</sub>S<sub>3</sub> bulk samples have plausibly been interpreted [5] within the distortion model.

Unfortunately, it is not possible to perform *in-situ* experiment in the case of  $\gamma$ -irradiation, and, thus, the impact of oxidation processes in  $\gamma$ -irradiated g-As<sub>2</sub>S<sub>3</sub> cannot be excluded during measurements. The radiation-induced oxidation results in formation of oxidized layer, but using mechanical treatment, when  $\gamma$ -irradiated sample is washed and polished, this oxidized layer can be removed [1]. One of the methods to verify its removing is measurement of optical transmission spectrum in the fundamental optical absorption edge region. No significant changes in saturation region of optical transmittance between the  $\gamma$ -irradiated and annealed (in sense as unirradiated) samples would be a signature on the disappearance of oxidized layer (see Fig. 2 [1]).



**Fig. 1.** Photos of g-As<sub>2</sub>S<sub>3</sub> samples in the unirradiated (top) and  $\gamma$ -irradiated (bottom) states. The white oxidized layer at the surface of  $\gamma$ -irradiated sample is visible to the eye (see the text for details).



**Fig. 2.** Optical transmission spectra,  $\tau(\lambda)$ , of g-As<sub>2</sub>S<sub>3</sub> samples in the unirradiated (closed circles) and  $\gamma$ -irradiated (open circles) states (top) and the differential spectrum,  $\Delta\tau(h\nu)$ , between optical transmittance for the unirradiated and  $\gamma$ -irradiated samples (bottom). Dashed lines, showing the slope of  $\tau(\lambda)$  curves, are drawn as a guide to the eye. The numerical values in percentage inside figures indicate the radiation-induced changes in the optical transmittance at the corresponding wavelength and photon energy marked by arrows (see the text for details).

On the other hand, the uncontrolled radiation-induced oxidation means that the As<sub>2</sub>O<sub>3</sub> crystals and S phases have to be always deleted in order to examine carefully the radiation-structural changes in g-As<sub>2</sub>S<sub>3</sub>; while, other chalcogenides, for example, the glasses of Ge-As-S system, do not show oxidized layer at the surface upon radiation [8-13], and, thus, they do not need washing and polishing procedure to be measured in the  $\gamma$ -irradiated state. In other words, the g-As<sub>2</sub>S<sub>3</sub> cannot be considered as the best model object for identification of radiation-structural changes using XRD, despite a high sensitivity of glassy arsenic trisulphide to  $\gamma$ -irradiation [14]. In this case, the As-enriched glasses in chalcogenide glassy systems, not showing oxidized layer upon radiation and with structure mainly built by AsS<sub>3/2</sub> pyramids likely to g-As<sub>2</sub>S<sub>3</sub>, can be chosen as better

candidates for structural studies by XRD in respect to the FSDP-related correlations, first of all. For instance, the investigation of radiation/annealing-induced structural changes in  $\text{Ge}_x\text{As}_{40-x}\text{S}_{60}$  glasses ( $x = 16, 24, 32, 36$ ), which can be also presented as  $(\text{As}_2\text{S}_3)_y(\text{Ge}_2\text{S}_3)_{1-y}$  non-stoichiometric system ( $y = 0.6, 0.4, 0.2, 0.1$ ), using high-energy synchrotron XRD is found to be quite informative regarding the FSDP-related correlations in the As-S sub-system [15]. Namely, the radiation-induced FSDP changes mainly occur in the As-enriched glass composition ( $x = 16$ ) to be in a good agreement with the photoinduced FSDP changes in the g- $\text{As}_2\text{S}_3$  bulk samples reported by Tanaka [4, 5]. Obviously, the g- $\text{Ge}_{16}\text{As}_{24}\text{S}_{60}$ , possessing also a high sensitivity to  $^{60}\text{Co}$  gamma radiation influence [8-13], can be considered as a good representative for investigation of the FSDP-related correlations in  $\gamma$ -irradiated chalcogenide glasses.

The present work is aimed at verifying the expected radiation-induced optical darkening effect (i.e., the long-wave shift of fundamental optical absorption edge) accompanying the oxidation processes (to be seen through decreasing the sample's transparency) in the g- $\text{As}_2\text{S}_3$  studied in the unirradiated and  $\gamma$ -irradiated states, showing, therefore, the disadvantage of glassy arsenic trisulphide to be selected as the best model object for XRD study of radiation-structural changes, especially in respect to the FSDP.

## 2. Experimental

The investigated g- $\text{As}_2\text{S}_3$  bulk samples were prepared by conventional melt-quenching technique [16]. To remove the mechanical strains formed during synthesis procedure, the samples were annealed at the temperature  $433 \pm 1$  K (below the glass transition temperature  $T_g = 456\text{--}465$  K [16, 17]) for 1 hour.

Radiation treatment of the samples by  $\gamma$ -quanta with the average energy  $E = 1.25$  MeV and accumulated dose  $\Phi = 2.41$  MGy was performed at the normal conditions of stationary radiation field, created in a closed cylindrical cavity by a number of concentrically mounted  $^{60}\text{Co}$  radioisotope capsules as shown schematically in [18]. 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  $\gamma$ -irradiation (more than 30 days), providing absorbed dose power  $P < 5$  Gy/s [18, 19].

Optical transmission spectra were recorded using "Specord M-40" (200-900 nm) double-beam spectrophotometer. The special marks were drawn on the sample surface in order to prevent experimental error related with a sample position in the device camera. The accuracy of the measurements was  $\pm 0.5\%$ . The optical transmission spectrum was firstly measured for the g- $\text{As}_2\text{S}_3$  sample in the unirradiated state. After that, the sample was subjected to  $\gamma$ -irradiation. Within the period

of 2 to 3 months after  $\gamma$ -irradiation, the optical transmission spectrum was measured again for the g- $\text{As}_2\text{S}_3$  sample in the  $\gamma$ -irradiated state. These measurements were performed to examine only the well-known static radiation-induced optical effects, which are stable in the long period of time starting from 2 months after  $\gamma$ -irradiation, as revealed for various systems of chalcogenide vitreous semiconductors [8-11, 13, 20-24].

## 3. Results and discussion

Fig. 1 shows the photos of g- $\text{As}_2\text{S}_3$  bulk samples in the unirradiated and  $\gamma$ -irradiated states. Both pieces of the glass were cut from the same ingot. The samples were polished and thermally annealed after cutting procedure. The piece of the glass in the  $\gamma$ -irradiated state corresponds to the investigated g- $\text{As}_2\text{S}_3$  measured, at first, as unirradiated and, after, as  $\gamma$ -irradiated. The white oxidized layer at the surface of  $\gamma$ -irradiated sample is visible to the eye. As expected from literature, the radiation-induced oxidation is the most probably related with appearance of  $\text{As}_2\text{O}_3$  (arsenolite) crystals and S phases at the surface of  $\gamma$ -irradiated sample through decomposition-oxidation reactions well described in [1].

The optical transmission spectra,  $\tau(\lambda)$ , of g- $\text{As}_2\text{S}_3$  samples in the unirradiated and  $\gamma$ -irradiated states are shown in Fig. 2. The long-wave shift of fundamental optical absorption edge with decreasing the slope upon radiation, that is the radiation-induced optical darkening effect, is clearly identified. It is also seen that this red shift is accompanied by the essential decreasing the sample's transparency, i.e.  $\Delta\tau = 33\%$  at  $\lambda = 746$  nm. The differential spectrum  $\Delta\tau(h\nu)$  in the photons' energy scale between the optical transmittance for the unirradiated and  $\gamma$ -irradiated samples indicates the maximum change  $\Delta\tau_{\text{max}} = 33.5\%$  at  $h\nu = 1.9$  eV, as also given in Fig. 2. As the slope of fundamental optical absorption edge decreases upon radiation, the  $\gamma$ -induced disorder takes place as related with intrinsic structural changes in the glass network (see, e.g., [8-11] and references therein). Thus, the detected reduction of the slope of  $\tau(\lambda)$  curve in the fundamental optical absorption edge region after  $\gamma$ -irradiation, resulting in the maximum radiation-induced optical darkening effect  $\Delta\tau(h\nu)_{\text{max}}$ , can be interpreted as caused by the radiation-induced defect formation processes occurring in the structural network of glass. At the same time, the observed decreasing the sample's transparency is plausibly caused by the above mentioned radiation-induced oxidation processes at the surface of glass.

Because of the radiation-induced oxidation products, i.e.  $\text{As}_2\text{O}_3$  crystals and S phases, impact on the FSDP and next XRD peak [1], it is understandable that this disadvantage makes the  $\gamma$ -irradiated g- $\text{As}_2\text{S}_3$  sample to be as not the best model object at XRD studying the radiation-structural changes, including the FSDP-related correlations, first of all, in glassy chalcogenides. As

noted, the As-enriched Ge-As-S chalcogenide glasses, not showing the white oxidized layer upon radiation due to decomposition-oxidation reactions [8-13], can be selected as better candidates for this purpose. As shown in [15], the XRD study of  $\gamma$ -irradiated/annealed g-Ge<sub>16</sub>As<sub>24</sub>S<sub>60</sub>, which corresponds to (As<sub>2</sub>S<sub>3</sub>)<sub>0.6</sub>(Ge<sub>2</sub>S<sub>3</sub>)<sub>0.4</sub> alloy, with a dominant structure based on AsS<sub>3/2</sub> pyramids likely to g-As<sub>2</sub>S<sub>3</sub> [25], allows plausibly detecting the radiation-structural changes, including the FSDP-related ones, in the As-S sub-system of chalcogenide glasses. Finally, from the positive point of view, the radiation-induced oxidation observed could be considered as protection procedure to be used in practice. For instance, it may be important for advanced chalcogenide photonics [26].

#### 4. Conclusions

The long-wave shift of fundamental optical absorption edge or radiation-induced optical darkening effect in the g-As<sub>2</sub>S<sub>3</sub> bulk sample (~2 mm thick) due to <sup>60</sup>Co  $\gamma$ -radiation treatment (average energy  $E = 1.25$  MeV and accumulated dose  $\Phi = 2.41$  MGy) has been detected in the period of 2-3 months after  $\gamma$ -irradiation (static radiation-induced optical effect). The maximum radiation-induced changes at  $\Delta\tau(h\nu)_{\max}$  at the level 33.5%, owing to the intrinsic structural transformations, and decreasing the sample's transparency at the level 33% have been identified. The observed changes in the saturation region upon radiation have been referred to the accompanying oxidation processes, which are the most probably related with appearance of As<sub>2</sub>O<sub>3</sub> (arsenolite) crystals and S phases at the surface of  $\gamma$ -irradiated sample, forming the white oxidized layer visible to the eye. These oxidation products, resulting in satellite peaks in the XRD patterns in the FSDP region [1], show the disadvantage of glassy arsenic trisulphide to be selected as the best model object at XRD studying the radiation-structural changes, especially in respect to the FSDP. As alternative, the As-enriched Ge-As-S glasses, not showing such oxidized layer upon radiation, can be used as better candidates for diffraction investigations of  $\gamma$ -radiation-induced FSDP changes in the As-S sub-system of glassy chalcogenides. However, in the positive sense, the radiation-induced oxidation processes revealed in the g-As<sub>2</sub>S<sub>3</sub> could be considered as a protection procedure for application in chalcogenide photonics.

#### Acknowledgments

The author would like to thank Prof. V.M. Tsmots for stimulating discussions. The investigated samples used for measurements were prepared within joint research projects (#0106U007386 and #0109U007446c) between DSPU (Drohobych, Ukraine) and SRC "Carat" (Lviv, Ukraine) supported by the MES of Ukraine (#0106U007385 and #0109U007445). Optical spectroscopy experiments were performed within the

above projects as well. Support of DAAD (Germany) and MES of Ukraine (projects #0111U001021 and #0114U002616) is also gratefully acknowledged.

#### References

1. M. Shpotyuk, O. Shpotyuk, R. Golovchak, P. Demchenko, FSDP-related correlations in  $\gamma$ -irradiated chalcogenide semiconductor glasses: The case of glassy arsenic trisulphide g-As<sub>2</sub>S<sub>3</sub> revised // *J. Phys. Chem. Solids*, **74**, p. 1721-1725 (2013).
2. J.S. Berkes, S.W. Ing, Jr., W.J. Hillegas, Photodecomposition of amorphous As<sub>2</sub>Se<sub>3</sub> and As<sub>2</sub>S<sub>3</sub> // *J. Appl. Phys.*, **42**(12), p. 4908-4916 (1971).
3. S.A. Keneman, J. Bordogna, J.N. Zemel, Evaporated films of arsenic trisulfide: Physical model of effects of light exposure and heat cycling // *J. Appl. Phys.*, **49**(9), p. 4663-4673 (1978).
4. K. Tanaka, Photoexpansion in As<sub>2</sub>S<sub>3</sub> glass // *Phys. Rev. B*, **57**(9), p. 5163-5167 (1998).
5. K. Tanaka, Photoinduced structural changes in amorphous semiconductors // *Semiconductors*, **32**(8), p. 861-866 (1998).
6. K. Tanaka, Reversible photoinduced change in intermolecular distance in amorphous As<sub>2</sub>S<sub>3</sub> network // *Appl. Phys. Lett.*, **26**(5), p. 243-245 (1975).
7. H. Hamanaka, S. Minomura, K. Tsuji, Comparative studies of pressure and photo induced structural changes in As<sub>2</sub>S<sub>3</sub> glass // *J. Non-Cryst. Solids*, **137&138**, p. 977-980 (1991).
8. O.I. Shpotyuk, E.R. Skordeva, R.Ya. Golovchak, V.D. Pamukchieva, A.P. Kovalskii, Radiation-stimulated changes in transmission of chalcogenide glasses of As<sub>2</sub>S<sub>3</sub>-Ge<sub>2</sub>S<sub>3</sub> // *Journal of Applied Spectroscopy*, **66**(5), p. 749-753 (1999).
9. O.I. Shpotyuk, A.P. Kovalskiy, E. Skordeva, E. Vateva, D. Arsova, R.Ya. Golovchak, M.M. Vakiv, Effect of gamma-irradiation on the optical properties of Ge<sub>x</sub>As<sub>40-x</sub>S<sub>60</sub> glasses // *Physica B*, **271**, p. 242-247 (1999).
10. O.I. Shpotyuk, N.M. Vakiv, A.P. Koval'skii, E. Skordeva, E. Vateva, D. Arsova, R.Ya. Golovchak, R.V. Lutsiv, Radiation-induced effects in Ge-As-S chalcogenide glasses // *Glass Physics and Chemistry*, **26**(3), p. 260-264 (2000).
11. E. Skordeva, D. Arsova, V. Pamukchieva, E. Vateva, R. Golovchak, A. Kovalskiy, O. Shpotyuk,  $\gamma$ -induced changes in Ge-As-S glasses // *J. Optoelectron. Adv. Mater.*, **2**(3), p. 259-266 (2000).
12. O.I. Shpotyuk, R.Ya. Golovchak, T.S. Kavetsky, A.P. Kovalskiy, M.M. Vakiv, Radiation-optical effects in glassy Ge-As(Sb)-S systems // *Nucl. Instrum. Meth. Phys. Res. B*, **166-167**, p. 517-520 (2000).
13. V. Balitska, R. Golovchak, A. Kovalskiy, E. Skordeva, O.I. Shpotyuk, Effect of Co<sup>60</sup>  $\gamma$ -irradiation on the optical properties of As-Ge-S glasses // *J. Non-Cryst. Solids*, **326&327**, p. 130-134 (2003).

14. O.I. Shpotyuk, A.O. Matkovskii, Radiation-stimulated processes in vitreous arsenic trisulphide // *J. Non-Cryst. Solids*, **176**, p. 45-50 (1994).
15. T.S. Kavetsky, V.M. Tsmots, A.L. Stepanov, Radiation/annealing-induced structural changes in  $\text{Ge}_x\text{As}_{40-x}\text{S}_{60}$  glasses as revealed from high-energy synchrotron X-ray diffraction measurements // *Semiconductor Physics, Quantum Electronics & Optoelectronics*, **15**(4), p. 310-320 (2012).
16. A. Feltz, *Amorphous and Vitreous Inorganic Solids*. Moscow, Mir, 1986 (in Russian).
17. M. Popescu, *Non-Crystalline Chalcogenides*. Dordrecht-Boston-London, Kluwer Academic Publishers, 2000.
18. T. Kavetsky, I. Kaban, O. Shpotyuk, W. Hoyer, V. Tsmots, On the structural-optical correlations in radiation-modified chalcogenide glasses // *J. Phys.: Conf. Ser.*, **289**, p. 012007(1-6) (2011).
19. T. Kavetsky, O. Shpotyuk, I. Kaban, W. Hoyer, Atomic- and void-species nanostructures in chalcogenide glasses modified by high-energy  $\gamma$ -irradiation // *J. Optoelectron. Adv. Mater.*, **9**(10), p. 3247-3252 (2007).
20. V. Balitska, J. Filipecki, O. Shpotyuk, J. Swiatek, M. Vakiv, Dynamic radiation-induced effects in chalcogenide vitreous compounds // *J. Non-Cryst. Solids*, **287**, p. 216-221 (2001).
21. O.I. Shpotyuk, T.S. Kavetsky, A.P. Kovalskiy, V. Pamukchieva, Gamma-irradiation effect on the optical properties of  $\text{Ge}_x\text{As}_{40-x}\text{S}_{60}$  chalcogenide glasses // *Proc. SPIE*, **4415**, p. 278-283 (2001).
22. O.I. Shpotyuk, T.S. Kavetsky, A.P. Kovalskiy, R.V. Lutziv, V. Pamukchieva, Radiation-induced changes in optical transmission in vitreous semiconductors of the  $\text{Ge}_x\text{As}_{40-x}\text{S}_{60}$  system // *Ukr. Fiz. Zh.*, **46**(4), p. 495-498 (2001).
23. O.I. Shpotyuk, R.Ya. Golovchak, A.P. Kovalsky, T.S. Kavetsky, Time and temperature stability of radiation-induced changes in optical properties of ternary chalcogenide glassy semiconductor systems // *Functional Materials*, **10**(2), p. 317-321 (2003).
24. T.S. Kavetsky, Impact of the sample thickness and  $\gamma$ -irradiation dose on the occurrence of radiation-induced optical effects in chalcogenide vitreous semiconductors of the Ge-Sb-S system // *Semiconductors*, **45**(4), p. 499-502 (2011).
25. D. Arsova, E. Skordeva, D. Nesheva, E. Vateva, A. Perakis, C. Raptis, A comparative Raman study of the local structure in  $(\text{Ge}_2\text{S}_3)_x(\text{As}_2\text{S}_3)_{1-x}$  and  $(\text{GeS}_2)_x(\text{As}_2\text{S}_3)_{1-x}$  glasses // *Glass Physics and Chemistry*, **26**(3), p. 247-251 (2000).
26. B.J. Eggleton, B. Luther-Davies, K. Richardson, Chalcogenide photonics // *Nature Photonics*, **5**, p. 141-148 (2011).