

УДК 539.213;535.21

G. Lovas¹, V. Mitsa¹, R. Holomb¹, I. Rosola¹, E. Borkach²

¹Uzhhorod National University, Institute for Solid State Physics and Chemistry, Uzhhorod, Ukraine
e-mail: v.mitsa@gmail.com

²II. Rákóczi Ferenc Transcarpathian Hungarian Institute, Beregovo, Ukraine

THE ROOM TEMPERATURE VISIBLE PHOTOLUMINESCENCE IN g-As₂S₃ AND Ge-BASED GLASSES

PL radiation from long term aged fractured surfaces of GeS₂-based glasses was assigned to the surface contaminant effect from native oxidized layer, which might have formed in the air. When have been used for PL measuring the freshly fractured surface of g-GeS₂(T₃V₂) all PL peaks which was connected with GeO_x species where disappeared in PL spectrum.

Keywords: visible photoluminescence, chalcogenide glass, oxide phase, edge absorption, GeS₂.

Introduction

Wide band chalcogenide glassy semiconductors (ChGS) have been studied as host materials for different types of ions due to potential applications as optical amplifiers for the telecommunications window and nonlinear optical media for high-speed all-optical signal processing [1-4]. Nowadays optical and electronic properties of nanostructured ChGS have attracted much attention because they exhibit useful phenomena and have potentials for becoming novel media for future photonic devices [5]. Earlier we have measured low temperature photoluminescence (PL) in nanostructured wide band ChGS by using a projector lamp as excitation light source [6]. The position of peak energies near 1.1-1.3 eV in measured PL spectra in this case were corresponding to so called “half-gap” rule [7-9]. During last decades for exciting PL and Raman spectra of ChGS a different laser lines were intensively used [2-4, 10-18] and some deviation from above mentioned rule in PL spectra of some ChGS was found [11, 12]. The low temperature PL spectrum of g-GeS₂ obtained with two different excitation energies at 2.7 and 2.81 eV each has two peaks with position of main peak energies at 2.20 and 2.28 eV correspondingly. The shape of this luminescence bands was dependent on the excitation wavelength [11]. The low temperature PL spectrum of nanostructured

(GeS₂)_{100-x}(GeO₂)_x glasses excited by 3.1 eV laser line is blue shifted from 1.3 to 2.1 eV when x increases from x=0 to x=80 [12]. Room temperature PL in the visible range of nanocrystalline (nc) nc-Ge was reported in literature and attributed to different origins [15-18]. From chemically etched Ge the 2.3-2.3 eV visible PL (excited photon energy, E_{ex}=2.8 eV) was assigned to GeO_x species [16]. The PL results presented in [17] shows that visible luminescence (E_{ex}=3.81 eV) of the porous Ge thin films originated from the germanium oxide. A number of mentioned above results show that exact mechanism of luminescence in nc-Ge is still under discussion. Nanostructured ChGS are known to be susceptible to oxide impurities [19]. Presented here new results of experimental investigation of Ge-free binary g-As₂S₃, g-GeS₂ glass and ternary (GeS₂)_x(As₂S₃)_{100-x} glasses at high energy of PL excitation might add new information about the nature of luminescence in nanostructured materials.

Materials and methods

Glasses were prepared from the mixture of high-purity germanium (99.999 wt. %), elemental sulfur and arsenic refined by vacuum distillation. The mixture was synthesized in the evacuated (~10⁻³ Pa) quartz ampoules by step-wise gradual heating up to 973 K for g-As₂S₃ sample and 1223 K for Ge-containing samples in a rocking furnace.

The g-GeS₂ samples for PL measuring were synthesized by melt quenching from different temperatures ranging from 1173 K (T₁) to 1473 K (T₄) and quenching rate from 100 K/s (V₁) and 150 K/s (V₂) (hereafter be denoted T_iV_j). The long term aged (9 years) of samples fractured surfaces were excited by cw laser illumination of 3.03 eV. From comparison of PL spectra a fresh fractured surfaces was used. An exiting diode laser scattering was filtering by cut-off filter at E>2.75 eV. To study the light absorption of these glasses by convenient method, transmittance and reflectance spectra from polished samples have been used to extract the absorption coefficient (α).

Results and discussion

When the fresh fractured surface of bulk glass of g-As₂S₃ with inclusion of realgar-type As₄S₄ molecules was chosen [13] it gives in PL spectrum an intensive narrow symmetric PL signal which maximum is centered at E₁=2.43 eV with low energy side band at E₂=1.7 eV (Figure 1). The excitation energy (3.03 eV) was higher than optical band-gap energy (E₀) of g-As₂S₃ (E₀=2.4 eV). The position of PL maximum E₁ is in good agreement with value of optical band-gap edge absorption E₀ in region of Tauc-rule absorption (Figure 1), LUMO-HOMO energy width of 12-member rings based on AsS_{3/2} pyramids ($\Delta E=2.41$ eV) [13] and earlier found in this region the “hot luminescence” of g-As₂S₃ [14]. But from compare with the theoretical consideration of luminescence [15] in our case energy dependent intensity of luminescence (Fig.1) is not proportional of $\alpha = \alpha(E)$ of edge absorption and not clear is high energy PL the surface contaminant or photostructural effect. It needs further investigations and detail analysis will be further performed.

The position of a good separated low intensive wide band near E₂=1.7 eV is in excellent agreement with the position of intensive PL band in PL spectrum of natural crystal realgar β -As₄S₄ [20]. Raman scattering measuring by varying of excitation photon energy combined with computer simulation experiments in order to obtain detailed images of structure of g-As₂S₃ has shown existing of

realgar-type molecules As₄S₄ in g-As₂S₃ [4, 13]. Therefore, we consider in first approximation that E₂ maximum could be connected with realgar-type As₄S₄ molecules inclusions in g-As₂S₃. [13].

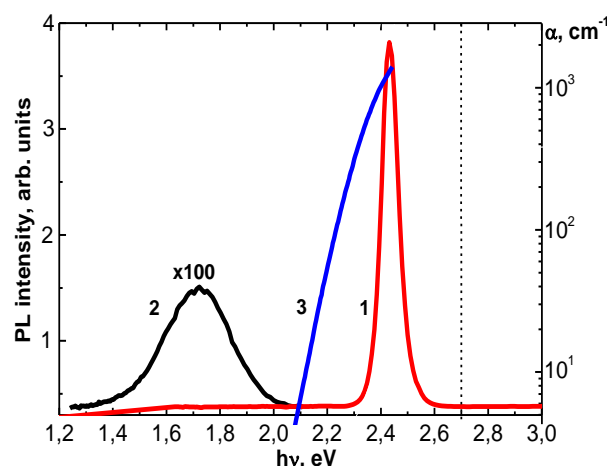


Fig. 1. PL and edge absorption spectra of g-As₂S₃: 1,2 - PL; 3 - edge absorption.

PL spectra g-GeS₂(T_iV_j) are shown in Figure 2. They have on high energy side of wide band almost the same peak position near E*₁=2.6-2.7 eV, shoulder near E*₂=2.2-2.3 eV and the tail of each the spectrum is extending beyond 2 eV. The peak position will be indicated E*₁ and E*₂ hereafter. In general, depending on the excitation wavelength the PL energy in GeO_x shows variations. Usually a blue PL band (2.8 -3.1 eV) is observed when the PL is excited in the near UV [21], and when the excitation wavelength is longer than the blue wavelengths, the other PL bands (i. e. 1.6-1.9 eV, 2.1-2.3 eV bands) are observed [21]. From the variety of oxygen-deficient defects the theoretical modeling shows that X₃Ge-GeX₂ (X=OH, OAH₃, A=Ge) defect gives only a red/orange PL band at 2.0–2.1 eV [22].

In order to determine the origin of the low energy E*₂ photoluminescence spectra of GeS₂(T_iV_j) glasses the luminescence spectra from ternary (As₂S₃)_x(GeS₂)_{1-x} glasses having various Ge to As ratios were examined (Figure 3). With the shift of the optical band gap of (GeS₂)_x(As₂S₃)_{100-x} to lower energy by decreasing x, E*₂=2.2-2.3 eV peak did not change position (Figure 3). The intensity of the luminescence E*₂ peak decreased with increasing arsenic content in ternary glasses, which indicates that the E*₂ luminesc in

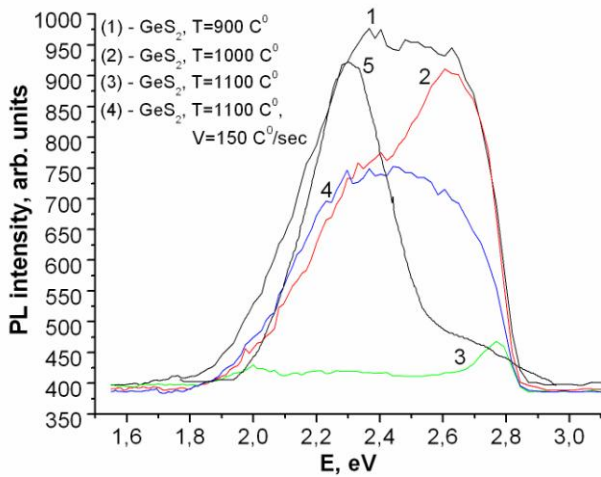


Fig. 2. PL spectra g-GeS₂(T_iV_j) (curves 1-4), curve 5 for PL of GeO_x was taken from [21].

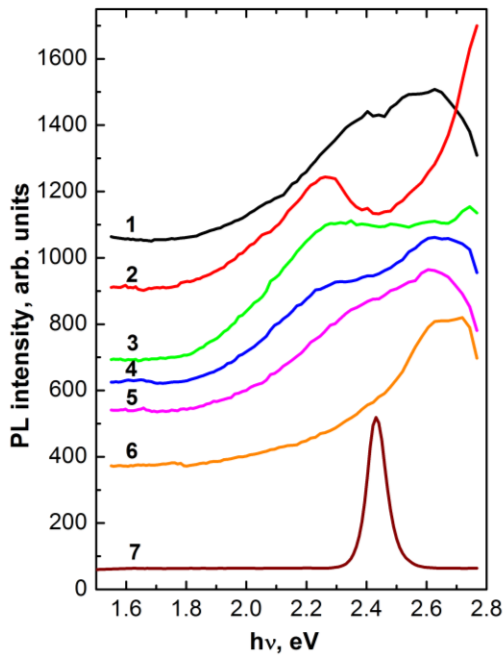


Fig. 3. PL spectra of (As₂S₃)_x(GeS₂)_{1-x} glasses: 1) x=0.1; 2) x=0.2; 3) x=0.3; 4) x=0.4; 5) x=0.6; 6) x=0.7; 7) x=0.

GeS₂-based glasses could be associated with Ge-containing centers. Oxygen related bands in the PL spectrum of an as-synthesized GeO_x nanowire (fig. 2, curve 6) which was excited at the O K-edge (536.5 eV), showed during fitting procedure four components at 1.90, 2.17, 2.42, and 2.70 eV [21]. Thermal annealing of the GeO_x nanowire leads to the disappearance of the high energy bands at 2.42

and 2.70 eV and decreasing intensity of PL yield [21]. It would be more reasonable to ascribe this peaks (Fig. 2 and Fig.3) like previous PL studies of nc-Ge [15-17, 21] to presence of GeO_x species. We consider the possibility that the PL radiation in GeS₂-based glasses is a surface contaminant effect from native oxidized layer, which might have formed in the air. Argument for this conclusion is fact when we have used for PL measuring the freshly fractured surface of g-GeS₂(T₃V₂) all PL peaks which we connected with GeO_x species where disappeared in PL spectrum of g-GeS₂(T₃V₂) (Figure 2, curve 3).

Luminescence of unknown origin peaking near 2.8 eV from the freshly fractured surface of g-GeS₂(T₃V₂) (Figure 2, curve 3) is lying in the region of exponential part of edge absorption. We suggest that this high-energy emission could be due to the presence some types of Ge_nS_m clusters in native matrix of GeS₂-based glasses. This suggestion based on our findings of increasing intensity of bands connected with 4-member rings in resonant Raman spectra of g-GeS₂ [23]. LUMO-HOMO energy gap for four-member ring is near 3 eV and it is very close to energy of excitation PL of investigated wide band glasses. Role of closed clusters in processes of luminescence in ChGS was theoretically analyzed in [24].

Conclusion

We observed visible photoluminescence in wide band gap binary and ternary chalcogenide glasses. The position of PL maximum E₁=2.43 in g-As₂S₃ is in good agreement with early found [14] g-As₂S₃ “hot luminescence in this region”. PL radiation from long term aged fractured surfaces of GeS₂-based glasses was assigned to the surface contaminant effect from native oxidized layer. Argument for such assigned is PL spectrum of g-GeS₂ freshly fractured surface where PL peaks connected with GeO_x centers are disappeared.

REFERENCES

- Zalkovsij M., Bisgaard C. Zoffman, Novitsky A., Malureanu R., Savastru D., Popescu A., Jepsen P.U., Lavrinenko A.V. Ultrabroadband terahertz spectroscopy of

- chalcogenide glasses // *Applied Physics Letters*. 2012. - vol. 100. - P. 031901-1-031901-6.
2. Mitsa V., Holomb R., Veres M., Marton A., Rosola I., Fekeshgazi I., Koós M. Non-linear optical properties and structure of wide band gap non-crystalline semiconductors // *Phys. Stat. Sol. C*. - vol. 8. - № 9. – 2011. - P. 2696-2700.
 3. Liu X., Naftaly M., Iha A. Spectroscopic evidence for oxide dopant sites in GeS₂-based glasses using visible photoluminescence from Pr³⁺ probe ions // *Journal of Luminescence*. - vol. 96. - 2002. - P. 227-238.
 4. Gamulin O., Ivanda M., Mitsa V., Balarin M., Kosovic M. Monitoring structural phase transition of (Ge₂S₃)_x(As₂S₃)_{1-x} chalcogenide glass with Raman spectroscopy // *Journal of Molecular Structure*. - vol. 993. - 2011. – P. 264–268.
 5. Eggleton B.J., Luther-Davies B., Richardson K. Chalcogenide photonics // *Nature Photonics*. - vol. 5. – 2011. - P. 141-148.
 6. Mitsa V., Babinets Y., Gvardionov Y. and Yermolovich I. Photoluminescence in Ge_xAs_yS_{1-x-y} by varying the average coordination number // *J. of Non-Crystalline Solids*. - vol. 137&138. – 1991. - P. 959-962.
 7. Popescu M. *Non-Crystalline Chalcogenides* // KluwerAcademic Publishers. – New York. – 2000.
 8. Kolobov A.V. *Photo-induced metastability in amorphous semiconductors* // Wiley-VCH. - 2003.
 9. Fairman R. and Ushkov B. *Semiconducting Chalcogenide Glass. P.I–III. P.I. Glass formation, structure, and simulated transformations in chalcogenide glass; P. II. Properties of glasses* // Elsevier. - 2004.
 10. Davydova N.A., Bondar N.V., Tyschenko V.V. Photoinduced effects in luminescent spectra of chalcogenide glasses // *Journal of Applied Spectroscopy*. - vol. 69. – 2002. - P. 258-262.
 11. Nakanishi S.T., Tomii Y., Hachiya K. Temperature dependence of the photoinduced fatigue-recovery phenomena of photoluminescence under prolonged irradiation in GeS₂ chalcogenide glass // *J. of Non-Crystalline Solids*. - vol. 354. – 2008. - P. 1627-1632.
 12. Terakado N., Tanaka K. Does the charged defect exist in nano-structured chalcogenide glass? // *Applied Physics Express*. - vol. 1. – 2008. - P. 081501-1-081501-3.
 13. Holomb R., Mitsa V., Petrachenkov O., Veres M., Stronski A. and Vlček M. Comparison of structural transformations in bulk and as-evaporated optical media under action of polychromatic or photon-energy dependent monochromatic illumination // *Phys. Stat. Sol. C*. - vol. 8. - № 9. – 2011. - P. 2705-2708.
 14. Murayama K., Bösch M.A. Radiative recombination in crystalline As₂S₃ // *Physical Review B*. - vol. 23. – 1981. - P. 6810-6812.
 15. Tanaka K. Excitation-energy-dependent photoluminescence in glassy As–S and crystalline As₂S₃ // *Phys. Status Solidi B*. - vol. 1–6. – 2013. - DOI 10.1002/pssb.201248519.
 16. Kartopu G., Bayliss S.C., Karavanskii V.A., Curry R.J., Turan R., Sapelkin A.V. On the origin of the 2.2-2.3 photoluminescence from chemically etched germanium // *J of Luminescence*. - vol. 101. – 2003. - P. 275-283.
 17. Ko T.S., Shieh J., Yang M.C., Lu T.C., Kuo H.C., Wang S.C. Phase transformation and optical characteristics of porous germanium thin films // *This Solid Films*. - vol. 516. – 2008. - P. 2934-2938.
 18. Sun K.W., Sue S.H., Liu C.W. Visible luminescence from Ge quantum dots // *Physica E*. - vol. 28. – 2005. - P. 525-530.
 19. Lezal D. Chalcogenide glasses – survey and progress // *Journal of Optoelectronics and Advanced Materials*. - vol. 5. -2003. - P. 23–34.
 20. Bishop S.G., Shanabrook B.V., Strom U. and Taylor P.C. Comparison of optically induced localized states in chalcogenide glasses and their crystalline counterparts //

- J. De Phisque E. - vol. 42. – 1981. - P. C4-383-C4-386.
21. Mingfa Peng, Yang Li, Jing Gao, Duo Zhang, Zheng Jiang, Xuhui Sun. Electronic Structure and Photoluminescence Origin of Single-Crystalline Germanium Oxide Nanowires with Green Light Emission // J. Phys. Chem. C. - vol. 115. – 2011. - P. 11420–11426.
22. Zyubin A.S., Mebel A.M., Lin S.H. Photoluminescence of oxygen-deficient defects in germanium oxides: A quantum chemical study // The Journal of Chemical Physics. - vol. 125. – 2006. - P. 064701-0647011.
23. Holomb R., Johansson P., Mitsa V., Rosola I. Local structure of technologically modified g-GeS₂: resonant Raman and absorption edge spectroscopy combined with ab initio calculations // Philosophical Magazine. - 2005. - vol. 85.- P. 2947-2960.
24. Banik I. On photoluminescence in chalcogenide glasses based on barrier-cluster model // J. of Non – Oxide and Photonic Glasses. - vol. 1. – 2009. - P. 29-33

Стаття надійшла до редакції 03.06.2013

Г. Ловас¹, В. Міца¹, Р. Голомб¹, І. Росола¹, Є. Боркач²

¹Ужгородський національний університет, Ужгород, Україна
e-mail: v.mitsa@gmail.com

²Закарпатський угорський інститут ім. Ф.Ракоці II, м. Берегово, Україна

ВИДИМА ФОТОЛЮМІНЕСЦЕНЦІЯ ПРИ КІМНАТНІЙ ТЕМПЕРАТУРІ В g- As₂S₃ ТА В СТЕКЛАХ НА ОСНОВІ Ge

Фотолюмінесцентне випромінювання, що спостерігалось зі сколу стекел на основі GeS₂ при старінні, віднесено до окисної фази, що утворилася на поверхні стекел під час тривалого зберігання зразків на повітрі. Усі ФЛ максимуми пов'язані з центрами GeO_x, зникли з фотолюмінесцентного спектру, коли фотолюмінесцентний спектр був знятий зі свіжесколотої поверхні з об'ємного скла g-GeS₂(T₃V₂).

Ключові слова: видима фотолюмінесценція, халькогенідне скло, окисна фаза, край поглинання, GeS₂.

Г. Ловас¹, В. Мица¹, Р. Голомб¹, И. Росола¹, Е. Боркач²

¹Ужгородский национальный университет, Ужгород, Украина
e-mail: v.mitsa@gmail.com

²Закарпатский венгерский институт им. Ф. Ракоци II, Берегово, Украина

ВИДИМАЯ ФОТОЛЮМИНЕСЦЕНЦИЯ ПРИ КОМНАТНОЙ ТЕМПЕРАТУРЕ В g- As₂S₃ И СТЕКЛАХ НА ОСНОВЕ Ge

Фотолюмінесцентное излучение которое наблюдалось со скола стекел на основе GeS₂ при старении, отнесено к окисной фазе, которая образовалась на поверхности стекел в течении длительного хранения образцов на воздухе. Все ФЛ максимумы, связанные с центрами GeO_x, исчезли с фотолюмінесцентного спектра, когда фотолюмінесцентный спектр был снят со свежесколотої поверхности об'ємного стекла g-GeS₂(T₃V₂).

Ключевые слова: видимая фотолюмінесценция, халькогенідное стекло, окисная фаза, край поглощения, GeS₂.