

Room Temperature Visible Luminescence in Wide Band Gap Chalcogenide Glasses

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Abstract – Visible photoluminescence (PL) was observed in binary $g\text{-As}_2\text{S}_3$, technologically modified $g\text{-GeS}_2(\text{T}_i\text{V}_j)$ and ternary glasses along $(\text{As}_2\text{S}_3)_x(\text{GeS}_2)_{1-x}$ line. PL maximum in $g\text{-As}_2\text{S}_3$ at 2.43 eV was assigned to band-to-band transitions and its position is in good agreement with value of optical band-gap edge absorption ($E_0=2.4$ eV). It is suggested that the peak at 2.2-2.3 eV in $g\text{-GeS}_2(\text{T}_i\text{V}_j)$ and GeS_2 -based ternary glasses may be attributed to presence of GeO_x species. Complex PL peak at 2.6-2.7 eV in GeS_2 -based glasses was identified with germanium sulfur sites.

I. INTRODUCTION

Recently the PL results presented in [1-3] show that visible luminescence of the nanostructured Ge thin films originated from the germanium oxide. Nanostructured chalcogenide glasses (ChG) are known to be susceptible to oxide impurities [4]. The extrinsic absorption in Ge-containing ChGS can be caused by non controlled GeO and GeO_2 impurities [4]. Presented here new results of experimental investigation of Ge-free binary $g\text{-As}_2\text{S}_3$, $g\text{-GeS}_2$ glass and ternary $(\text{GeS}_2)_x(\text{As}_2\text{S}_3)_{100-x}$ glasses at high energy of PL excitation might add new information about the nature of luminescence in nanostructured materials.

II. MATERIALS AND METHODS

The binary and ternary glasses were prepared by direct synthesis from appropriate amount of the elements with 5N purity using a standard method. Than the $g\text{-GeS}_2$ samples for PL measuring were synthesized by melt quenching from different temperatures ranging from 1173 K (T_1) to 1473 K (T_4) and quenching rate from 100 K/s (V_1) and 150 K/s (V_2) (hereafter be denoted T_iV_j). The samples were excited by cw laser illumination of 3.03 eV. An exiting diode laser scattering was filtering by cut-of filter at $E>2.75$ eV. To study the light absorption of these glasses by convenient method, transmittance and reflectance spectra have been used to extract the absorption coefficient (α).

III. RESULTS AND DISCUSSION

When the bulk glass of $g\text{-As}_2\text{S}_3$ with inclusion of realgar-type As_4S_4 molecules was chosen [5,6] it gives in PL spectrum an intensive narrow symmetric PL signal which maximum is centered at $E_1=2.43$ eV with low energy side band at $E_2=1.7$ eV (Figure 1). The excitation energy (3.03 eV) was higher than optical band-gap

energy (E_0) of $g\text{-As}_2\text{S}_3$ ($E_0=2.4$ eV). The position of PL maximum E_1 is in good agreement with value of optical band-gap edge absorption E_0 in region of Tauc-rule absorption (Figure1) and LUMO-HOMO energy width of 12-member ring based on $\text{AsS}_{3/2}$ pyramids ($\Delta E=2.41$ eV) [7]. Therefore we conclude that luminescence E_1 in $g\text{-As}_2\text{S}_3$ originates from band-to-band transitions.

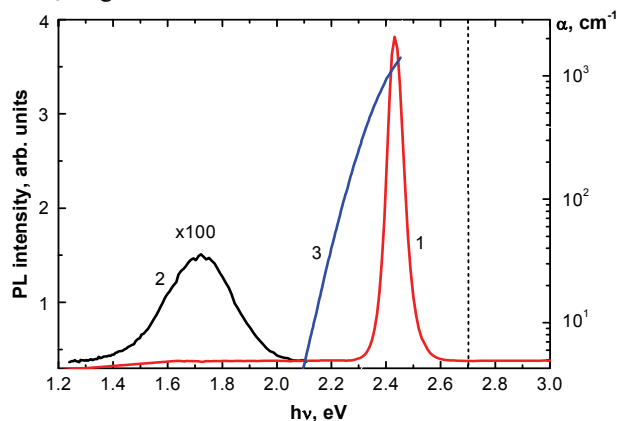


Figure 1. PL and edge absorption spectra of $g\text{-As}_2\text{S}_3$: 1,2 - PL; 3 - edge absorption.

The position of a good separated low intensive wide band near $E_2=1.7$ eV is in excellent agreement with the position of intensive PL band in PL spectrum of natural crystal realgar $\beta\text{-As}_4\text{S}_4$ [8]. Raman scattering measuring performed by varying of excitation photon energy combined with computer simulation experiments in order to obtain detailed images of structure of $g\text{-As}_2\text{S}_3$ has shown existing of realgar-type molecules As_4S_4 in $g\text{-As}_2\text{S}_3$ [6]. Therefore, we consider in first approximation that E_2 maximum could be connected with realgar-type As_4S_4 molecular inclusions in $g\text{-As}_2\text{S}_3$.

Edge absorption spectra of $g\text{-GeS}_2(\text{T}_2\text{V}_2)$ and $g\text{-GeS}_2(\text{T}_3\text{V}_2)$ together with their PL spectra are shown in Figure 2. PL spectra of $g\text{-GeS}_2(\text{T}_i\text{V}_j)$ 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.

High energy E^*_1 peak position is corresponding to steep rise of the absorption in range of Urbach edge absorption. In order to determine the origin of the low

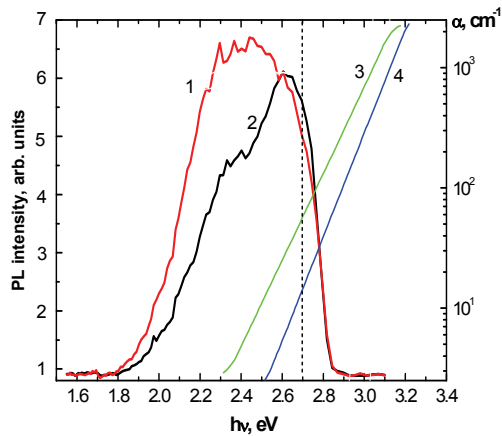


Figure 2. PL and edge absorption spectra: 1,4 - $\text{g-GeS}_2(\text{T}_3\text{V}_2)$; 2,3 - $\text{g-GeS}_2(\text{T}_2\text{V}_2)$

energy E^*_2 photoluminescence spectra of $\text{GeS}_2(\text{T}_i\text{V}_j)$ glasses the luminescence spectra from ternary $(\text{As}_2\text{S}_3)_x(\text{GeS}_2)_{1-x}$ glasses having various Ge to As ratios were examined (Figure 3). With the shift of the optical band gap of $(\text{GeS}_2)_x(\text{As}_2\text{S}_3)_{100-x}$ to lower energy by decreasing x [5], $E^*_2=2.2\text{-}2.3$ eV peak did not change position (Figure 3) but E^*_2 intensity decreases with increasing arsenic content, which indicates that the E^*_2 luminescence in GeS_2 -based glasses could be associated with Ge-containing centers. It would be more reasonable to ascribe this peak to presence of GeO_x species like in previous PL studies of nc-Ge [1-3]. The average concentration of oxide impurities in the structure of Ge-containing chalcogenide glasses may be around 10^{-3} mol. % [4,9].

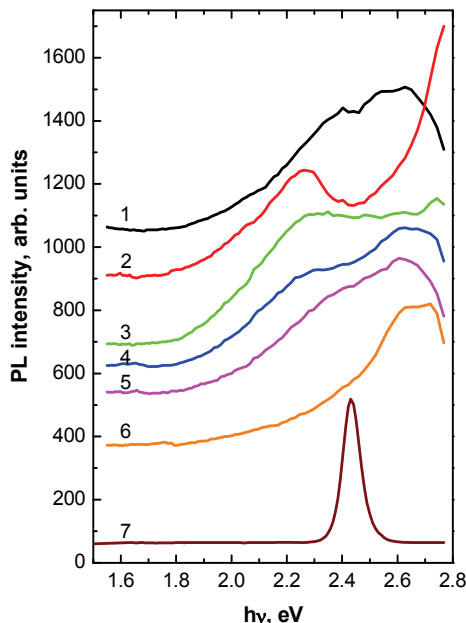


Figure 3. PL spectra of $(\text{As}_2\text{S}_3)_x(\text{GeS}_2)_{1-x}$ glasses: 1) $x=0.1$; 2) $x=0.2$; 3) $x=0.3$; 4) $x=0.4$; 5) $x=0.6$; 6) $x=0.7$; 7) $x=0$.

Luminescence of unknown origin peaking near $E^*_1=2.6\text{-}2.7$ eV overlaps with $E^*_2=2.2\text{-}2.3$ eV on its high energy side (Figure 2 and 3). High energy PL peak E^*_1 is lying in the region of exponential part of edge

absorption of binary (Figure 1,2) and ternary glasses [5] and could be connected with band-to-band transition. We suggest that this high-energy emission could be due to the presence of some types of Ge_nS_m nanoclusters in native matrix of GeS_2 -based glasses. This suggestion based on our findings of increasing intensity of bands connected with 4-member rings in resonant Raman spectra of g- GeS_2 [10]. 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 [11]. Now experimental investigations of energy structure of wide band glasses are in progress.

IV. CONCLUSION

We observed visible photoluminescence in wide band gap binary and ternary chalcogenide glasses. The position of PL maximum in g- As_2S_3 is in good agreement with value of optical band-gap edge absorption $E_0=2.4$ eV. We assumed that 2.2-2.3 eV visible PL might arise from GeO_x impurities in the structure of GeS_2 -based glasses.

REFERENCES

- [1] E.Nogales, A.Montone, F.Cardellini, B.Mendez, J. Piqueras*, Visible cathodoluminescence from mechanically milled germanium”, *Semicond. Sci. Technol.*, vol.17, pp. 1267-1271, 2002.
- [2] G.Kartopu, S.C.Bayliss, V.A.Karavanskii, R.J.Curry, R.Turan, A.V.Sapelkin, “On the origin of the 2.2-2.3 photoluminescence from chemically etched germanium. *J of Luminescence*, vol.101, pp.275-283, 2003.
- [3] T.S.Ko, J.Shieh, M.C.Yang, T.C.Lu, H.C.Kuo, S.C.Wang, “Phase transformation and optical characteristics of porous germanium thin films”, *This Solid Films*, vol.516, pp. 2934-2938, 2008.
- [4] D. Lezal, “Chalcogenide glasses – survey and progress”, *Journal of Optoelectronics and Advanced Materials*, vol. 5, pp. 23 – 34, 2003.
- [5] V. Mitsa, R. Holomb, M. Veres, A. Marton, I. Rosola, I. Fekeshgazi, M. Koós, “Non-linear optical properties and structure of wide band gap non-crystalline semiconductors”, *Phys. Stat. Sol. C.*, vol.8, №9, pp. 2696-2700, 2011.
- [6] O. Gamulin, M. Ivanda, V. Mitsa, M. Balarin, M. Kosovic, “Monitoring structural phase transition of $(\text{Ge}_2\text{S}_3)_x(\text{As}_2\text{S}_3)_{1-x}$ chalcogenide glass with Raman spectroscopy”, *Journal of Molecular Structure*, vol.993, pp. 264–268, 2011.
- [7] R. Holomb, V. Mitsa, O. Petrachenkov, M. Veres, A. Stronski, and M. Vlček, “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, pp. 2705-2708, 2011.
- [8] S.G. Bishop, B.V. Shanabrook, U. Strom and P.C. Taylor, “Comparison of optically induced localized states in chalcogenide glasses and their crystalline counterparts”, *J. De Physique E*, vol.42, pp.C4-383-C4-386, 1981.
- [9] A.R.Hilton, “Optical properties of chalcogenide glass”, *J. of Non-Crystalline Solids*, vol.2, pp.28-39, 1970.
- [10] R. Holomb, P. Johansson, V. Mitsa, I. Rosola, Local structure of technologically modified g- GeS_2 : resonant Raman and absorption edge spectroscopy combined with ab initio calculations, *Philosophical Magazine*, vol.85 pp. 2947-2960, 2005.
- [11] I.Banik, On photoluminescence in chalcogenide glasses based on barrier-cluster model, *J. of Non – Oxide and Photonic Glasses*, vol.1, pp. 6–18,