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The visible photoluminescence from aged and freshly fractured surfacees of chalcogenide glasess

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Abstract: The position of PL maximum at E_1=2.43 in PL spectrum of freshly fractured g-As_2S_3 is in good agreement with early found “hot luminescence” g-As_2S_3 and illumination of elemental sulfur species on the surface of the ZnS nanobelts in this region. PL radiation from long term aged fractured surfaces of GeS_2-based chalcogenide 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-GeS_2(T_3V_2) all PL peaks which was connected with GeO_x species where disappeared in PL spectrum.

Keywords: visible photoluminescence, chalcogenide glass, oxide phase, edge absorption, glassy GeS_2

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 exiting 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-GeS_2 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 $(GeS_2)_{100-x}(GeO_2)_x$ glasses exited 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 (exited 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-As_2S_3, g-GeS_2 glass and ternary $(GeS_2)_x(As_2S_3)_{100-x}$ 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-As_2S_3 sample and 1223 K for Ge-containing samples in a rocking furnace. The g-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 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-As_2S_3 with inclusion of realgar-type As_4S_4 molecules was chosen[13] 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-As_2S_3 (E_0=2.4 eV). The position of PL maximum E_1 is in good agreement with value E_0 in region of Tauc-rule absorption (Figure 1), LUMO-HOMO energy width of 12-member rings based on $AsS_{3/2}$ pyramids (ΔE=2.41 eV) [13] and earlier found in this region the "hot luminescence" of g-As_2S_3 [14] . The origin of the green PL band at about 2.4 eV was related to elemental sulfur species on the surface of the ZnS nanobelts, enrich in sulfur [15]. In our case in Raman spectra of g-As_2S_3 was found the band which is responsible to S-S vibration [13]. Secondly, the energy dependent intensity of luminescence (Fig.1) is not proportional of α=α(E) of edge absorption [15] and not clear is high energy PL in g-As_2S_3 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 E_2= 1.7 eV is in excellent agreement with the position of intensive PL band in PL spectrum of natural crystal realgar β-As_4S_4 [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-As_2S_3 has shown existing of realgar-type molecules As_4S_4 in g-As_2S_3 [4,13]. Therefore, we consider in first approximation that E_2 maximum could be connected with realgar-type As_4S_4 molecules inclusions in g-As_2S_3. [13].

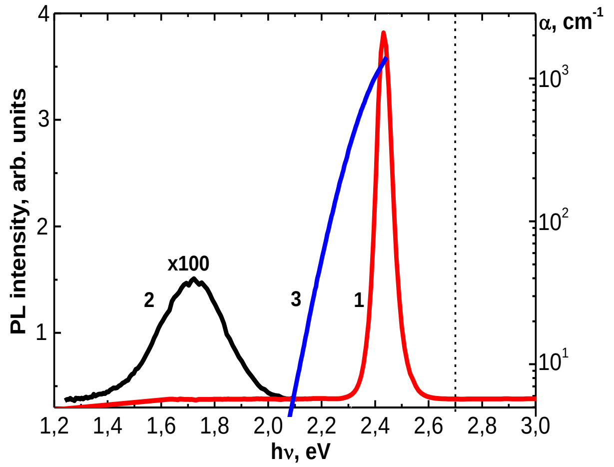

Figure 1. PL and edge absorption spectra of g-As_2S_3: 1,2 - PL; 3 - edge absorption.

PL spectra g-$GeS_2(T_iV_j)$ 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 $X_3Ge–GeX_2$ (X=OH, OAH_3, A=Ge) defect gives only a red/orange PL band at 2.0–2.1 eV [22].

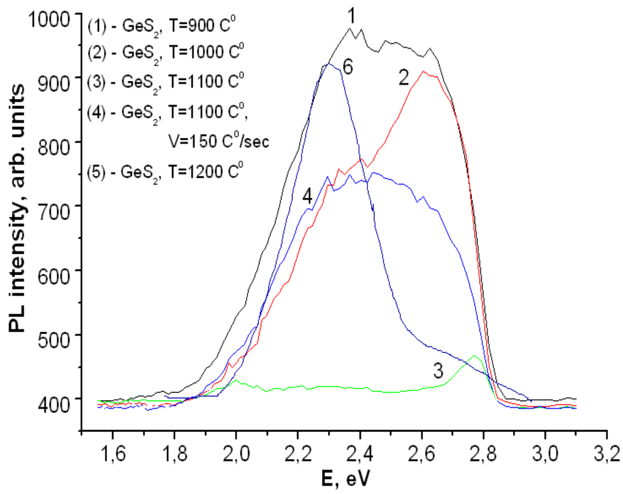

Figure 2. PL spectra g-$GeS_2(T_iV_j)$, curve 6 for PL of GeO_x was taken from [21].

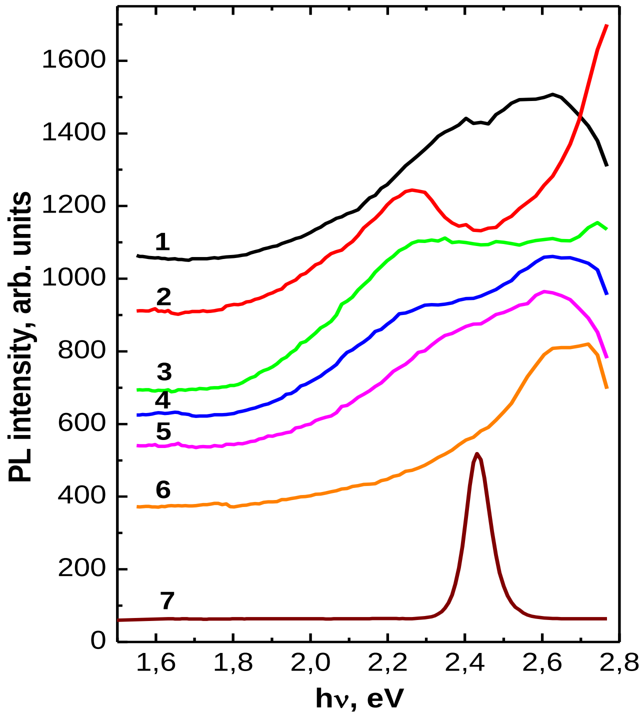

Figure 3. PL spectra of $(As_2S_3)_x(GeS_2)_{1-x}$ glasses: 1) x=0.1; 2) x=0.2; 3) x=0.3; 4) x=0.4; 5) x=0.6; 6) x=0.7; 7) x=0.

In order to determine the origin of the low energy E^*_2 photoluminescence spectra of $GeS_2(T_iV_j)$ glasses the luminescence spectra from ternary $(As_2S_3)_x(GeS_2)_{1-x}$ glasses having various Ge to As ratios were examined (Figure 3). With the shift of the optical band gap of $(GeS_2)_x(As_2S_3)_{100-x}$ 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 luminescence in GeS_2-based glasses could be associated with Ge-containing centers. Oxygen related bands in the PL spectrum of an as-synthesized GeO_x nanowire (figure 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 [17,21] to presence of GeO_x species. We consider the possibility that the PL radiation in GeS_2-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-$GeS_2(T_3V_2)$ all PL peaks which we connected with GeO_x species where disappeared in PL spectrum of g-$GeS_2(T_3V_2)$ (Figure 2, curve 3).

Luminescence of unknown origin peaking near 2.8 eV from the freshly fractured surface of g-$GeS_2(T_3V_2)$ (Figure 2, curve 3) is lying in the region of exponentional 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 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 [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 E_1=2.43 in g-As_2S_3 is in good agreement with early found [14] "hot luminescence" g-As_2S_3 in this region. PL radiation from long term aged fractured surfaces of GeS_2-based glasses was assigned to the surface contaminant effect from native oxidized layer. Argument for such assigned is PL spectrum of g-GeS_2 freshly fractured surface where PL peaks connected with GeO_x centers are disappeared.

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Мица В., Боркач Е., Ловас Г., Голомб Р., Росола И., Рудько Г., Гуле Е., Фекешхази И.

Видимая фотолюминесценция старой и свежеобразованной поверхности халькогенидных стекол

Аннотация: В спектре фотолюминесценции стеклообразного с-As_2S_3, возбужденной со свежесколотой поверхности, спектральное положение полосы при 2,43 эВ, находится в хорошем согласии с положением раннее обнаруженной в этом стекле полосой «горячей фотолюминесценции». Природу полосы в этой области в ZnS, обогащенном серой, относят к излучению ФЛ центров, связанных с элементарной серой. Фотолюминесцентное излучение наблюдаемое со скола бинарных и тройных стекол на основе стеклообразного с-GeS_2 при старении, отнесено к окисной фазе GeO_x, что образовалась на поверхности стекол в течении длительного хранении образцов на воздухе. Все ФЛ максимумы, связанные, с центрами GeO_x, исчезли с фотолюминесцентного спектра, когда спектр был снят со свежесколотой поверхности объемного стекла g-GeS_2(T_3V_2).

Ключевые слова: видимая фотолюминесценция, халькогенидное стекло, окисная фаза GeO_x, край поглощения, с-GeS_2, с-As_2S_3