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Photoluminescence of As_2S_3 doped with Cr and Yb

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Abstract. The results of experimental researches of photoluminescence spectra in As_2S_3 glasses obtained by doping of Cr and Yb ions to As–S host matrix followed by Raman and calorimetric studies as well as low-temperature magnetization measurements have been given. Possible mechanisms of obtained effects are discussed.

Keywords: chalcogenide glass, photoluminescence, Raman spectra, thermal property, magnetization.

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1. Introduction

Chalcogenide glasses (ChGs) exhibit a number of interesting optical properties with various potential applications as reviewed in, for example [1, 2], etc. As frequently pointed out by various researchers, ChGs are promising materials for various applications because they are transparent over a wide range of wavelengths in the infrared region, they possess high refractive indices, low phonon energies and are easy to fabricate. Chalcogenide glasses can be used in applications in sensorics, infrared optics and optoelectronics. The glasses can be used for preparation of optical fibers both for passive and active applications.

The refractive index and its wavelength dependence, luminescent properties are among important parameters that determine the suitability of materials as optical media. The photoluminescence (PL) spectrum of arsenic chalcogenides when excited by light with $\hbar\omega \approx E_g$ (E_g is an optical bandgap energy) lies at about half the optical gap, which means that PL undergoes a strong Stokes shift, and it appears as a broad Gaussian-shaped spectrum with a peak energy E_{PL} approximately at $E_{PL} \approx E_g/2$ [3-5]. Developments in photonics applications highlighted the chalcogenide glass as a host for rare-earth ions [1, 6-9].

Tanaka [10] proposed a new model for the half-gap PL. The latter arises from recombination of electrons, being trapped by anti-bonding states of wrong (and strained) bonds at around the mid-gap Fermi level, and holes in Urbach-edge states at the valence-band top. The wrong bond seems to be the most dominant defect in covalent chalcogenide semiconductors such as $\text{As}_2\text{S}(\text{Se})_3$, irrespective of glass and crystal, and accordingly, this model can be applied to the corresponding crystals as well. The PL fatigue, which is more prominent in the glass, may arise from momentary trapped electrons (type I) and broken chemical bonds (type II) in disordered flexible lattices. However, complete understandings of the PL fatigue remain difficult as caused by some experimental limitations.

In this work, photoluminescence of As_2S_3 doped with Cr and Yb was investigated.

2. Experimental

The glasses of compositions As_2S_3 , As_2S_3 :Cr 0.5 wt.% and As_2S_3 :Cr 0.75 wt.%, As_2S_3 , As_2S_3 :Yb 0.5 wt.%, As_2S_3 :Yb 1 wt.% and As_2S_3 :Yb 2 wt.% were prepared using the standard melt-quenching technique with constituent elements of 6N purity, which were melted in vacuum-sealed silica ampoules for 10...12 hours and

subsequently quenched in air. Room temperature Raman spectra were recorded using a Fourier spectrophotometer Bruker IFS-55 Equinox with FRA-106 attachment.

Photoluminescence of As_2S_3 doped with Cr was studied within the 800...1600-nm region ($T = 77 \text{ K}$, $\lambda_{\text{ex}} = 514 \text{ nm}$) using a HORIBA Jobin-Yvon T64000 spectrometer. Photoluminescence of As-S glasses modified with Yb was excited by a laser diode at the 980-nm wavelength with the radiation intensity 150 mW and was registered at room temperature using a Zolix SBP 300 monochromator (resolution $\sim 1 \text{ nm}$) with Zolix CR131 attachment.

Thermal properties were studied using the DSC technique, T_g values for undoped and doped glasses were obtained. NETZSCH DSC 404 calorimeter (with accuracy $\pm 0.5 \text{ K}$) was used in DSC measurements. Calorimetric measurements were carried out using powder samples ($m \sim 20 \text{ mg}$) in argon atmosphere under temperature changes within 40...250 °C. The heating rate $q = 10 \text{ K/min}$. Calibration of the calorimeter was carried out by melting pure metals In, Sn, Bi, Pb, Al, Cu with known values of temperature and enthalpy of melting.

Magnetization of the samples was measured with a Cryogenic S600 Super-conducting Quantum Interference Device (SQUID) magnetometer within the temperature range 5...400 K and in magnetic fields up to 5 T. A cryogenic system was completed with automated instrument control, data acquisition and analysis using the National Instrument's LabVIEW software.

3. Results

Raman spectra

Introduction of Cr impurity (Fig. 1) leads to the intensity increase of the bands at 192, 227, 236, 365 cm^{-1} , which correspond to the presence of non-stoichiometric molecular fragments of the As_4S_4 nanophase. The intensity of the 496 cm^{-1} band, characteristic for the vibrations of S-S bonds, is decreased with the Cr introduction. The difference spectra (Fig. 2) reveal the changes occurred in the glass structure upon variation of composition. From these spectra, one can be see that addition of Cr leads to intensity increase of the 150 cm^{-1} band that corresponds to vibrations of phase-decomposed S_8 rings and the 317 cm^{-1} band, which can be attributed to pyramidal structural AsS_3 units with additional sulfur atoms involved into (-S-S-) chains and joined pyramidal fragments. The main observed effect under introduction of chromium into As_2S_3 is the change of the relative concentration of the main and non-stoichiometric structural units characteristic for As_2S_3 glasses.

Chalcogenide glasses As_2S_3 doped with ytterbium were investigated using Raman spectroscopy to obtain information regarding incorporation of impurity metal

ions into the host glass structure. Introduction of Yb leads (Figs 3a and 3b) to the intensity increase of the bands at 192, 227, 236, 365 cm^{-1} that correspond to the presence of the As_4S_4 nanophase. The intensity of the 496 cm^{-1} band characteristic for the vibrations of S-S bonds is decreased with the Yb introduction. The difference spectra reveal changes occurred in the glass structure upon variation of composition. From these spectra, it can be seen that addition of Yb leads to the intensity increase in the 150 cm^{-1} band that corresponds to vibrations of phase-decomposed S_8 rings and the 317 cm^{-1} band, which can be attributed to pyramidal structural AsS_3 units with additional sulfur atoms involved into (-S-S-) chains and joined pyramidal fragments. Doping of As_2S_3 glasses with small amount of Yb ions, up to 1 wt.%, only slightly affect the short-range order structure of the host matrix. The main observed effect after introduction of ytterbium into As_2S_3 is the change of the relative concentration of the main and non-stoichiometric structural units characteristic for As_2S_3 glasses.

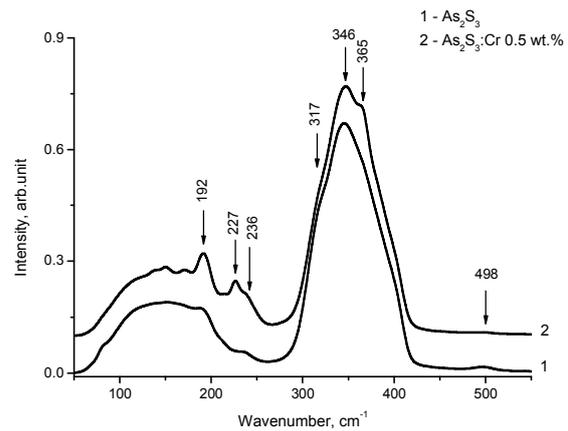


Fig. 1. Raman spectra of As_2S_3 and $\text{As}_2\text{S}_3\text{:Cr}$ 0.5 wt.%.

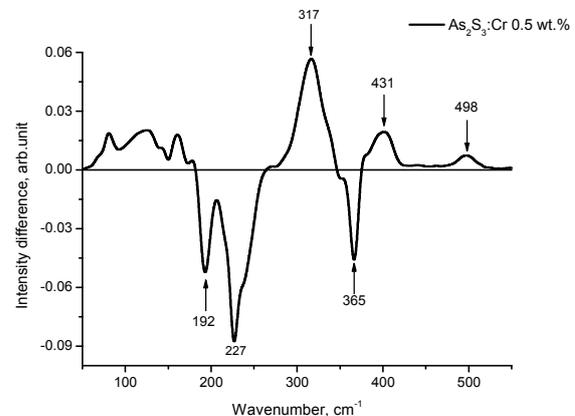


Fig. 2. Differential Raman spectra of As_2S_3 doped with Cr 0.5 wt.% (relatively to As_2S_3).

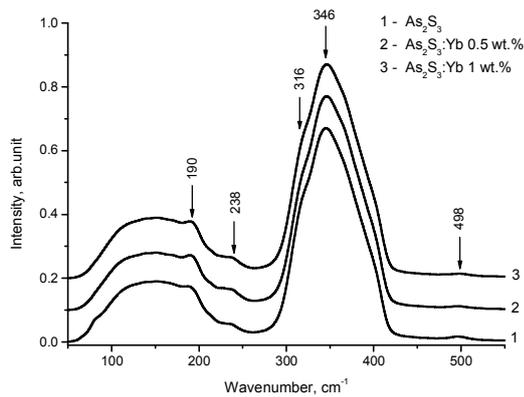


Fig. 3a. Raman spectra of As_2S_3 , $\text{As}_2\text{S}_3:\text{Yb}$ 0.5 wt.% and $\text{As}_2\text{S}_3:\text{Yb}$ 1 wt.%. Spectra are normalized by intensity of the 346 cm^{-1} peak and shifted by equal distances in order of appearance.

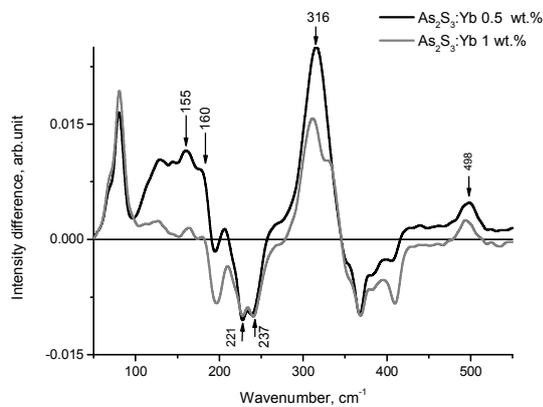


Fig. 3b. Difference Raman spectra of chalcogenide glasses: $\text{As}_2\text{S}_3:\text{Yb}$ 0.5 wt.% and $\text{As}_2\text{S}_3+\text{Yb}$ 1 wt.% (relatively to As_2S_3).

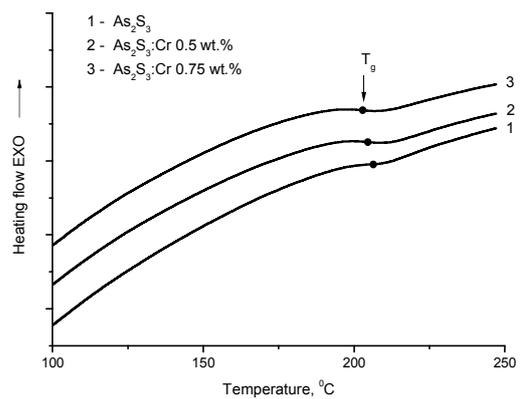


Fig. 4a. Thermograms of As-S:Cr glass with Cr content 0, 0.5 and 0.75 wt.% at the heating rate 10 K/min.

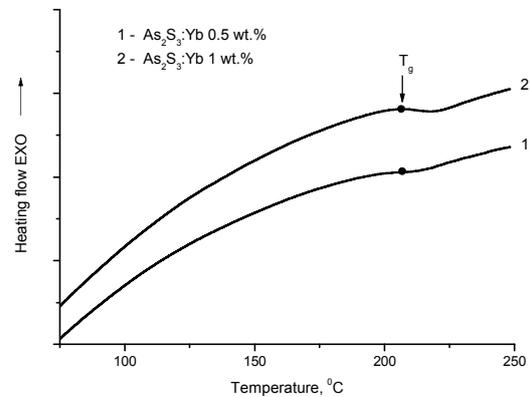


Fig. 4b. Thermograms of As_2S_3 with content of Yb 0.5 wt.% and 1 wt.% at the heating rate 10 K/min.

Thermal properties

Thermogram for As-S:Cr with Cr content 0.75 wt.% (heating rate 10 K/min) is shown in Fig. 4. It is necessary to note that with increase of the heating rate, T_g value is shifted towards higher temperatures. Kissinger's expression was used for estimating the activation energy of glass transition. The obtained T_g values for As_2S_3 with various concentrations of Cr and Yb are presented in Table.

Table. Glass transition temperature T_g of doped As-S glasses ($q = 10\text{ K/min}$).

Composition	$T_g, \text{ }^\circ\text{C}$
As_2S_3	208.3
$\text{As}_2\text{S}_3:\text{Cr}$ 0.5 wt.%	204.5
$\text{As}_2\text{S}_3:\text{Cr}$ 0.75 wt.%	202.8
$\text{As}_2\text{S}_3:\text{Yb}$ 0.5 wt.%	207
$\text{As}_2\text{S}_3:\text{Yb}$ 1 wt.%	206.2

Luminescence

Photoluminescence spectra for glasses $\text{As}_2\text{S}_3:\text{Cr}$ with different Cr composition are presented in Fig. 5. It can be seen from the figure that the photoluminescence intensity increases with the Cr concentration, thus, showing the increased level of defects with the chromium introduction having small effect on its shape.

Rare-earth luminescence As-S glasses modified by Yb have two luminescence bands in the near IR range, which are placed near 980 and 1060 nm (Fig. 6). In this case, transitions from the excited state $^2F_{5/2}$ to the main state $^2F_{7/2}$ that are characteristic for ion Yb^{3+} are pronounced. The intensity of photoluminescence increases with increase of the ytterbium concentration.

Magnetic properties

Pure chalcogenide glasses are diamagnetics. Introduction of transitional and rare earth impurities changes magnetic properties of the investigated chalcogenide glasses [13]. In the fields near 5 T, the $M(T)$ dependence was observed (Fig. 7), which is characteristic for paramagnetics and ferromagnetics in the paramagnetic temperature range

[13]. Measurements of magnetic properties (temperature dependence of the specific magnetic moment) were performed under various conditions of sample cooling. A sample was cooled in zero external magnetic field, then the magnetic field with specified magnitude was set. In what follows, this magnetic field was maintained constant during the sample heating. The interval of temperature variation was chosen in such a way that the maximal value of temperature exceeded the temperature of transition into the paramagnetic state. Hereinafter, such dependences are denoted as ZFC. Further, the sample was cooled in the magnetic field and $M = M(T)$ was obtained. It is denoted as FC in figures.

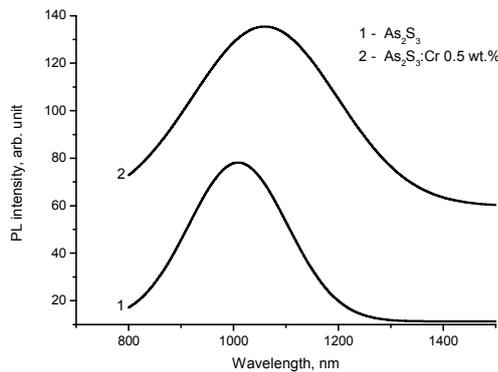


Fig. 5. Luminescence spectra of undoped As_2S_3 and doped with Cr 0.5 wt.%.

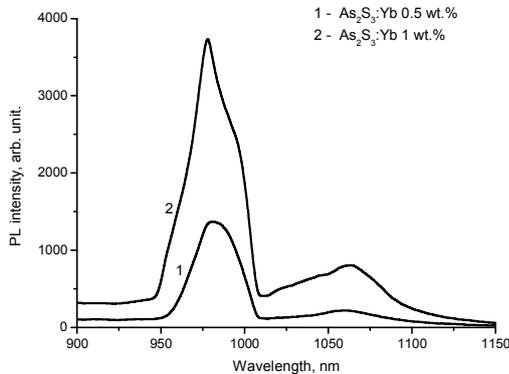


Fig. 6. Luminescence spectra of As_2S_3 doped with Yb: 0.5 and 1 wt.%.

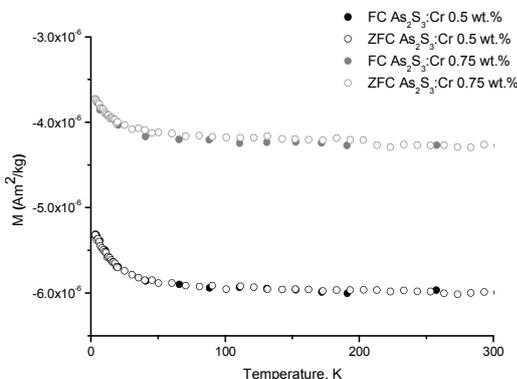


Fig. 7. Temperature dependence of mass magnetization (M) in As_2S_3 doped with Cr 0.5 and 1 wt.% ($B = 5$ T).

4. Discussion

Results on photoluminescence spectra for glasses $As_2S_3:Cr$ with different Cr content are in agreement with the model proposed by Tanaka [10]. According to Tanaka's model, half-gap photoluminescence arises from recombination of electrons, being trapped by anti-bonding states of wrong (and strained) bonds at around the mid-gap Fermi level, and holes in Urbach-edge states at the valence-band top. The wrong bonds are considered as the most dominant defects in covalent chalcogenide semiconductors such as $As_2S(Se)_3$. The wrong-bond density in As_2S_3 is markedly affected by the preparation condition [11]. Also, it is necessary to note that the density of the wrong bond in $As_2S(Se)_3$ is estimated at a few atomic percent, which is consistent with the insensitivity of photoluminescence on impurity concentrations up to ~ 0.1 at.%. At this level, the wrong bond concentration change can be tracked by Raman spectroscopy as was shown above. Raman measurements show that the intensity of bands that correspond to the presence of As_4S_4 nanophase is increased with the growth of the Cr concentration, that is, the number of the wrong As-As bonds is increased. And due to increase of the number (concentration) of the wrong As-As, the luminescence intensity must be increased, which can be seen in Fig. 5.

Developments in photonics applications of chalcogenide glasses have highlighted them as a matrix-host for rare-earth ions [7-9]. Bishop et al. [12] demonstrated the so-called broad-band excitation, i.e., excitation of rare-earth ions, not directly, but through exciting the host chalcogenide glass having a broad Urbach-edge spectrum. Chalcogenide glasses can be doped by significant amounts of impurities (up to the level of several atomic percents) without essential changing the optical quality [14]. This feature can be connected with the flexibility of the glass network, lesser density of glass as compared to the crystal, presence of nanovoids (which sizes can be estimated from positron annihilation lifetime spectra using different formula [15, 16]). It is necessary to note that introduction of rare earth elements can change not only luminescent but also magnetic properties of chalcogenide glasses.

5. Conclusions

Optical, thermal, luminescent and magnetic properties of chalcogenide glasses can be changed by doping of transitional and rare-earth metals. Photoluminescence of As_2S_3 doped with Cr is well explained by the model proposed by Tanaka [10]. Chalcogenide glasses can be host for rare-earth metals, which provides a possibility to simultaneously change both luminescent and magnetic properties of glasses.

Acknowledgements

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