

## Photoluminescence and phonon spectrum studies of arsenide sulfide compound doped with rare earth elements

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### Abstract

The phonon spectrum and photoluminescence properties of  $(\text{La}_2\text{O}_3)_{0.05}(\text{As}_2\text{S}_3)_{0.90}(\text{Er}_2\text{O}_3)_{0.05}$  compound were studied in a broad aspect. The energy difference between the two-component maxima of photoluminescence located at the value of energy  $E \approx 1.4\text{eV}$  was 41 meV, which corresponded to the energy of the most intense transverse optical (TO) phonon determined from the general radiation spectrum in the phonon spectrum region. In other words, the first photoluminescence line was observed simultaneously with the emission of a TO phonon with an energy of 41 meV. By changing the concentration of the erbium atom in different percentages in the infrared region of the spectrum and at the same time doping it with the lanthanum element, which plays the role of a sensitizer, a sharp increase in the intensity of photoluminescence was achieved in the intracentral ( $^4\text{J}_{2/11} - ^4\text{J}_{15/2}$ ) transition of the erbium atom. All these results show that the compound is suitable for wide application in various fields of optoelectronics.

**Keywords:** arsenide sulfide, photoluminescence, phonon spectrum, energy transfer, cross relaxation mechanism.

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### 1. Introduction

The practical application of glasses doped with rare earth elements (NTE) in optoelectronic devices (including lasers, displays, white light diodes) creates interest in the study of their optical properties. Thus, energy transfer between glasses (NTE) allows the creation of highly efficient radiation sources [1]. In work [2] the  $\alpha$ - $\text{As}_2\text{S}_3$  compound is considered an important material with its optical properties in the infrared region of the spectrum. The low melting temperature of these substances ( $T \approx 583\text{K}$ ) makes it quite simple to obtain thin optical fibers from them. One of the first photoluminescence studies on glass chalcogenides was performed by Kolomiets. In this study, it was explained that the recombination process is related to deep-dwelling levels near the Fermi level [3]. In [4], it was clarified that the radiation in the  $\text{As}_2\text{S}_3$  compound doped with various lanthanoids is related to the transitions of these lanthanoids, respectively. Due to the fact that some of the optical transitions of the  $\text{As}_2\text{S}_3$  compound overlap with the radiation lines of the rare earth ions, the energy of the photon absorbed in the wide area of the  $\text{As}_2\text{S}_3$  compound is transferred

to the rare earth elements, which increases the efficiency of photoluminescence [6]. This important fact is used in practice in fiber-optic amplifiers [7-9]. The band gap of  $\text{As}_2\text{S}_3$  lies in the visible region of the spectrum ( $E_g \approx 2.4$  eV), and thus optical transitions involving conduction bands and edge tail states overlap with some absorption/emission bands due to the discrete levels of the rare-earth ions [10,11]. PL properties of  $(\text{La}_2\text{O}_3)_{0.05}(\text{As}_2\text{S}_3)_{0.90}(\text{Er}_2\text{O}_3)_{0.05}$  compounds are investigated in detail in the near-infrared ranges. The mechanism of the increase of the infrared luminescence intensity with increasing  $\text{Er}^{3+}$  concentration is explained according to interaction between the activator ions [12].

## 2. Experiments

Photoluminescence (PL) measurements were performed using PL/PLE/Raman spectrometer (Tokyo Instruments, Inc.). The emission of the samples was excited 325 nm (HeCd) wavelength laser beams. Photoluminescence from the sample was dispersed through a grating ( $100 \text{ g/mm}^{-1}$ ) monochromator MS 5207 I (SOL Instruments, Inc) and detected by CCD multiplier DU 491A-1.7 (Tokyo Instruments, Inc.). PL spectra were plotted after correcting the spectral sensitivity of the detection system.

The Raman spectra of the same samples were measured on a Nanfinder 30 confocal Raman microspectrometer (Tokyo Instr., Japan). An Nd: YAG laser with an output radiation wavelength 532 nm. As an excitation source, a maximum power of 10 mW was used. The spectral resolution was no worse than  $0.5 \text{ cm}^{-1}$ . The scattered radiation detector was a cooled CCD camera (1024 by 12 pixels) operating in the photon counting mode. Raman spectra were measured in backscattering geometry.

## 3. Results and discussion

Taking into account that the glasses doped with rare earth elements are interesting from the point of view of practical application, the photoluminescence properties of the compound  $(\text{La}_2\text{O}_3)_{0.05}(\text{As}_2\text{S}_3)_{0.90}(\text{Er}_2\text{O}_3)_{0.05}$  is widely studied in this study.

In our experiments,  $^4\text{J}_{2/11}$ - $^4\text{J}_{15/2}$  (1000nm) and C- $\text{Er}_2\text{O}_3$  were used as initial components. In the studied system, the samples taken from the primary components in stoichiometric composition are ground into powder in an agate mortar, placed in a quartz ampoule, and poured into a glass graphite bush. The synthesis is carried out in stages. First, the quartz ampoule is kept at a temperature of 850 K for 3 hours. Then the temperature is raised to 875-1050 K and the synthesis is continued for 4 hours. The rapid cooling process is carried out in air.

Luminescence studies were performed on a PL/PLE/Raman spectrometer (Tokyo Instruments, Inc.). 532nm (Nd YAG), 642nm, 785nm lasers were used as the excitation source. MS3507I (800-2000nm) spectrometer was used to record the spectra. (SOL Instruments, Inc.).

The PL lines depicted in Figure 1 are mainly related to the Fermi level and defect states located in the center of the band gap. Photoluminescence spectra in this region (at 800-950nm) were also observed in our previous work [12-24].

While the intensity of the PL line at the value of 1.359eV changes weakly with the decrease in temperature, the intensity line of the PL corresponding to the value of  $E \approx 1.4$ eV decreases sharply with the decrease in temperature. It can be concluded from this that it was observed with the emission of a TO phonon with an energy equal to 1.36eV and a maximum energy of 41meV.

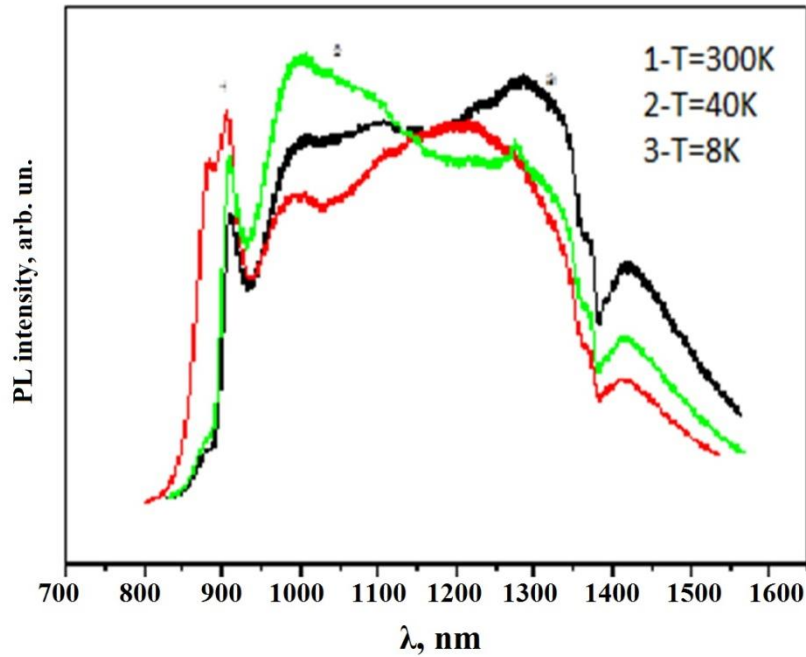


Figure 1. Temperature dependence of PL emission spectra of  $\text{As}_2\text{S}_3$

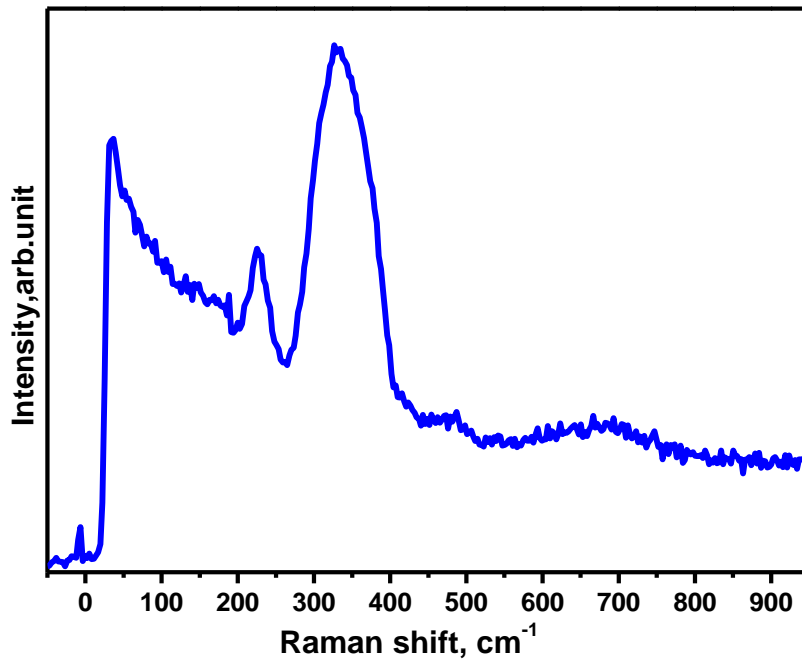
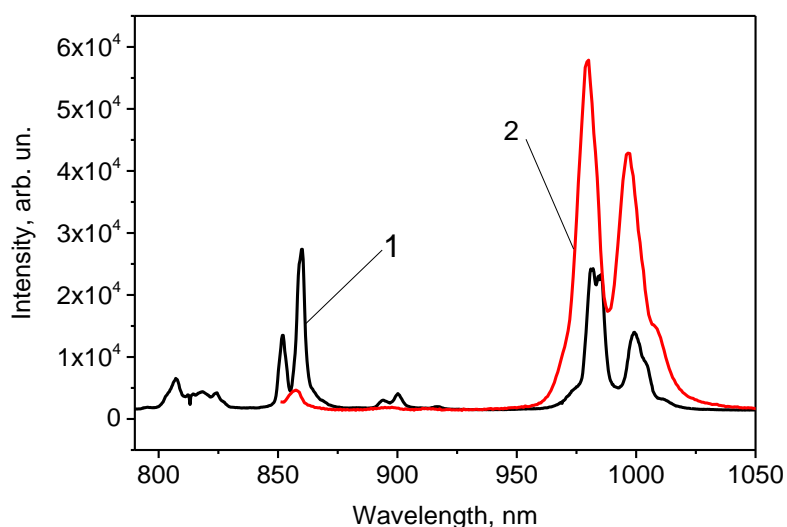


Figure 2. Raman spectrum of  $\text{As}_2\text{S}_3$

As a continuation of the research, the luminescence spectra of other compounds were studied. During the study of the photoluminescence of the  $\text{As}_2\text{S}_3:\text{Er}_2\text{O}_3$  compound, we observe a relative decrease in the intensity of the broad peak in the  $\text{As}_2\text{S}_3$  compound and weak luminescence maxima ( ${}^4\text{J}_{2/11}-{}^4\text{J}_{15/2}$  and  ${}^4\text{J}_{2/13}-{}^4\text{J}_{15/2}$ ) caused by internal transitions of the erbium atom on this peak.

With the addition of  $\text{La}_2\text{O}_3$  to this compound ( $(\text{La}_2\text{O}_3)_{0.05}(\text{As}_2\text{S}_3)_{0.90}(\text{Er}_2\text{O}_3)_{0.05}$ ) we observe a sharp increase in the luminescence intensity due to the intraatomic transition of erbium  ${}^4\text{J}_{2/11}-{}^4\text{J}_{15/2}$  (1000nm) (Figure 3).



**Figure 3.** PL spectra of compounds  $(\text{La}_2\text{O}_3)_{0.07}(\text{As}_2\text{S}_3)_{0.90}(\text{Er}_2\text{O}_3)_{0.03}$  and  $(\text{La}_2\text{O}_3)_{0.05}(\text{As}_2\text{S}_3)_{0.90}(\text{Er}_2\text{O}_3)_{0.05}$  (curve 1 and 2, respectively)

Thus, different lasers (532nm, 642nm, 785nm) are used as an excitation source. Although the intensity of this peak increases relatively in all cases, when the 532 nm (Nd:YAG) laser is used as the excitation source, the intensity of this peak increases by about 20 times. Strong emission peaks belonging to  $\text{La}_2\text{O}_3$  completely disappear during this time. It is likely that the photoluminescence efficiency increases when using different excitation sources, the energy of the absorbed photon is transferred to this atom in a wide area of the  $\text{As}_2\text{S}_3$  compound due to the overlap of the optical transitions of the  $\text{As}_2\text{S}_3$  compound with the radiation lines of the Er atom, and at the same time, as is known, Lanthanum is a sensitizer for all rare earth elements. (As La ions do not have 4f electrons, we cannot say that energy can be transferred from lanthanum to Er atom).

However, to clarify the reason for the sharper increase in intensity during excitation with a 532nm laser, by changing the concentration of Er additive  $(\text{La}_2\text{O}_3)_{0.07}(\text{As}_2\text{S}_3)_{0.90}(\text{Er}_2\text{O}_3)_{0.03}$  the luminescence spectrum of the compound was studied. It was observed that as the concentration decreased, the intensity of the peak at 850 nm ( $^4\text{S}_{3/2} \rightarrow \text{I}_{12/3}$ ) increased, and the intensity of the peak at 1000 nm ( $^4\text{S}_{3/2} \rightarrow \text{I}_{12/3}$ ) decreased sharply. The location and shape of the peaks have not changed. Considering the studied excitation spectrum, we can say that the energy transfer of one Er atom to another neighboring Er atom occurs through the cross relaxation mechanism.

#### 4. Conclusion

For the first time, we have analyzed pairs of PL lines corresponding to 1.4 eV and 1.35 eV in low-energy excitations identified in the IR region, which have no information about these PL maxima in other works. The first two-component lines of the PL located at the energy value  $E \approx 1.4\text{eV}$  has 41 meV less energy than the second line corresponding to the energy  $E \approx 1.359\text{ eV}$ . This difference corresponds to the energy of the most intense TO phonon determined from the total radiation spectrum in the phonon spectral region. The luminescence spectrum of  $(\text{La}_2\text{O}_3)_{0.07}(\text{As}_2\text{S}_3)_{0.90}(\text{Er}_2\text{O}_3)_{0.03}$  compound was studied by changing the concentration of Er additive. It was observed that as the concentration decreased, the intensity of the peak at 850 nm ( $^4\text{S}_{3/2} \rightarrow \text{I}_{12/3}$ ) increased, and the intensity of the peak at 1000 nm ( $^4\text{J}_{2/11} - ^4\text{J}_{15/2}$ ) decreased sharply. The location and shape of the peaks have not changed. The studied excitation spectrum suggests that the energy transfer of one Er atom to another neighboring Er atom occurs through the cross-relaxation mechanism.

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