

Absorption and Emission Spectra of Ga_{0.017}Ge_{0.25}As_{0.083}S_{0.65} Glasses Doped with Dy³⁺

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Abstract: The absorption spectra in the visible and near IR regions for Ga_{0.017}Ge_{0.25}As_{0.083}S_{0.65} are investigated. The visible luminescence from Dy³⁺, and co-doped with Ho³⁺ and Dy³⁺ ions embedded in Ga_{0.017}Ge_{0.25}As_{0.083}S_{0.65} glass hosts at room temperature and at T=10 K is reported, when pumping with an Ar⁺-ion laser at λ=488 nm. Fluorescence emissions at around 1300 nm was observed for Dy³⁺ doped glasses with wavelength pumping at 950 nm. Energy transfer from Ho³⁺:⁵F₃ level to Dy³⁺:⁴F_{9/2} level increase the visible emission efficiency at 650 nm and at ~1300 nm in the co-doped glasses. The investigated Ga_{0.017}Ge_{0.25}As_{0.083}S_{0.65} glasses doped with Dy³⁺ are promising amplifier materials for 1300 and 1500 nm fiber optic telecommunication windows.

Keywords: Chalcogenide glasses, optical absorption, photoluminescence, rare-earth ions

I. INTRODUCTION

Rare earth doped chalcogenide glasses are intensively investigated due to their possible potential applications as optical amplifiers for 1.3 and 1.5 μm telecommunication windows and fiber lasers. Chalcogenide glasses are characterized by high rare earth solubility, chemical stability, high refractive index (≥2.4), and a broad transmission window. Due to very low phonon energy of the Ge-based chalcogenide glasses was obtaining an increasing in the radiative efficiencies of the rare earth transitions. The Ga₂S₃-GeS₂ glassy system is a good host material for the rare-earth ions [1], has a large glass-forming region, high transmission in the visible region and high and high values of the glass transition temperature T_g ~ 425 °C [2]. The chalcogenide glasses doped with rare-earth ions exhibit fluorescence at fixed wavelengths [3]: Nd³⁺ (0.786, 0.919, 1.08, 1.37 μm); Er³⁺ (0.822, 0.869, 0.987, 1.54, 2.7, 3.5, 4.5 μm); Ho³⁺ (0.76, 0.91, 1.2, 2.9, 3.9 μm); Pr³⁺ (1.3, 1.6, 2.9, 3.4, 4.5, 4.8, 4.9, 7.2 μm); Dy³⁺ (1.3, 1.8, 2.3, 4.3 μm).

Visible photoluminescence from Pr-doped (GeS₃)₈₀(Ga₂S₃)₂₀ pumped by Ar⁺-laser was reported in [4]. The authors explain the photoluminescence and its temperature dependence by the presence of energy transfer from tail states of the host glass to Pr³⁺ ions. Some papers were dedicated to investigation of the transfer mechanism and increasing of the fluorescence efficiency for Tm³⁺/Ho³⁺ co-doped Ge₂₅Ga₅S₇₀ glasses [5], for Pr³⁺/Er³⁺ co-doped Ge₃₀As₈Ga₅S₆₁ glasses [6], and for Er³⁺/Tm³⁺ in different compositions of Ge-Ga-As-S glasses [2]. The aim of this paper is to investigate the visible and at 1.3 (1.5 μm) photoluminescence from Ga_{0.017}Ge_{0.25}As_{0.083}S_{0.65} glasses doped with Dy³⁺ and co-doped with Ho³⁺/Dy³⁺ rare earth ions.

II. EXPERIMENTAL

The glasses used in this study was Ga_{0.017}Ge_{0.25}As_{0.083}S_{0.65} doped with 0.05 and 0.2 at.% Dy³⁺, and co-doped glasses: Ga_{0.017}Ge_{0.25}As_{0.083}S_{0.65} +0.07 at.% Ho³⁺ + 0.13 at.% Dy³⁺ and Ga_{0.017}Ge_{0.25}As_{0.083}S_{0.65} +0.13 at.% Ho³⁺ + 0.07 at.% Dy³⁺. Bulk glasses were prepared from high purity (6N) elemental Ga, Ge, As, S and rare earth sulfides Dy₂S₃, which were loaded into fused silica ampoules and evacuated, flame sealed, and heated at 1200 K for 30 h in a rocking furnace, than quenched in water.

The absorption and photoluminescence spectra were carried out on 1-2 mm thick polished samples of the respective glasses. An Ar⁺-ion laser provided pumping radiation at 488 nm for fluorescence measurements. Emission spectra were taken by an SDL-1 double grating spectrograph (spectral slit width 10 Å) supplied with an FEU-106 photomultiplier in the photon count regime. The luminescence spectra also was investigated, when excited by an infrared LED 90RTM 5070 (λ = 950 nm).

III. EXPERIMENTAL RESULTS AND DISCUSSION

The transmittance region of the investigated glasses extends from the fundamental absorption edge region near 0.5 μm up to the lattice vibration threshold at about 8.0 μm. Fig.1 shows the absorption spectra of Ga_{0.017}Ge_{0.25}As_{0.083}S_{0.65} glasses (1), doped with 0.05 at.% Dy³⁺, and with 0.2 at.% Dy³⁺ (3) at room temperature T=300 K. The absorption edge in the glasses doped with Dy³⁺ is shifted in the region of higher photon energies and makes it more transparent (Fig.1). The observed weak absorption tail in most chalcogenide glasses is due to the effect of impurities and defects in the glasses.

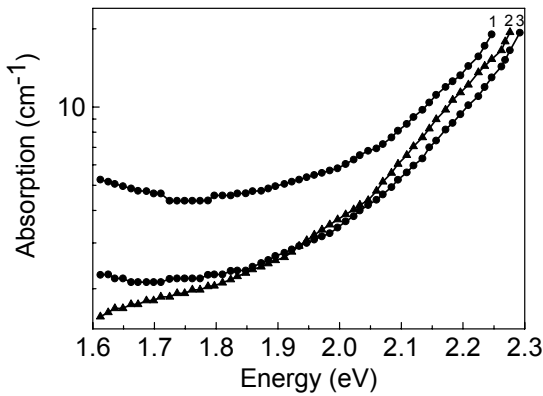


Fig.1. The absorption spectra of $\text{Ga}_{0.017}\text{Ge}_{0.25}\text{As}_{0.083}\text{S}_{0.65}$ glasses (1), doped with 0.05 at.% Dy^{3+} , and with 0.2 at.% Dy^{3+} (3) at room temperature $T=300$ K.

Introduction of Dy^{3+} in the host glass results in strong absorption bands of Dy^{3+} ions located in the near infrared (IR) parts of the transparency region (Fig.2). The position of the absorption bands of Dy^{3+} -ions is similar to previously published data, and the intensity of the bands increased in proportion to the rare earth content. The nature of these bands is associated with optical excitation of electrons from the basic levels to upper Stark manifold states.

In the Fig.2 also are indicated the possible electron transitions when the light is absorbed by the chalcogenide glass doped with Dy^{3+} ions.

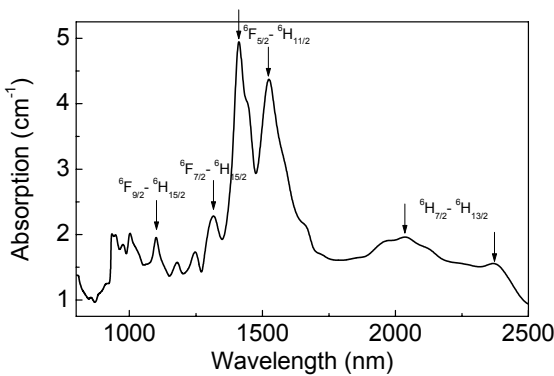


Fig.2. The absorption spectra of $\text{Ga}_{0.017}\text{Ge}_{0.25}\text{As}_{0.083}\text{S}_{0.65}$ glasses doped with 0.2 at.% Dy^{3+} at room temperature $T=300$ K.

For the $\text{Ga}_{0.017}\text{Ge}_{0.25}\text{As}_{0.083}\text{S}_{0.65}$ glasses doped with Dy^{3+} the optical absorption measurements were used by the authors [7] for calculation of the Judd-Ofelt parameters, for determining the branching ratio and the excited state lifetimes. The values of the Judd-Ofelt parameters are the following:

$$\Omega_2=9.3 \cdot 10^{-20} \text{ cm}^2$$

$$\Omega_4=3.2 \cdot 10^{-20} \text{ cm}^2$$

$$\Omega_6=1.41 \cdot 10^{-20} \text{ cm}^2$$

The fluorescence lifetime was experimentally determined using different methods by pumping the discrete levels of Dy^{3+} ions by 1064 nm, and are the following [7]:

For the level ${}^6\text{H}_{9/2}$, $\tau=29 \mu\text{s}$

For the level ${}^6\text{F}_{11/2}$, $\tau=29 \mu\text{s}$

For the level ${}^6\text{H}_{11/2}$, $\tau=640 \mu\text{s}$

For the level ${}^6\text{H}_{13/2}$, $\tau=29 \mu\text{s}$

It was mentioned that the radiative decay rate from this pair of levels depends not only on the Judd-Ofelt parameters, but also on the energy splitting of the levels.

Fig.3 shows the photoluminescence spectra in the visible region excited at 488 nm for some of the $\text{Ga}_{0.017}\text{Ge}_{0.25}\text{As}_{0.083}\text{S}_{0.65}$ glasses doped with 0.05 at.% Dy^{3+} , and 0.2 at.% Dy^{3+} at $T=10$ K. The more intensive luminescence bands were observed for the 0.05 at.% Dy^{3+} , and situated at 603 nm (${}^4\text{G}_{11/2} \rightarrow {}^6\text{H}_{9/2}$), 650 nm (${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{11/2}$), and 710 nm (${}^4\text{G}_{11/2} \rightarrow {}^6\text{F}_{9/2}$). At the same time for the $\text{Ga}_{0.017}\text{Ge}_{0.25}\text{As}_{0.083}\text{S}_{0.65}$ glasses doped with 0.2 at.% Dy^{3+} only one luminescence band situated at 745 nm (${}^6\text{F}_{3/2} \rightarrow {}^6\text{F}_{9/2}$) was observed.

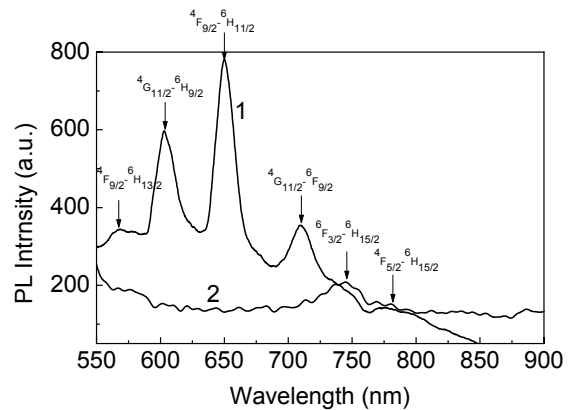


Fig.3. PL spectra at $T=10$ K excited at $\lambda=488$ nm for $\text{Ga}_{0.017}\text{Ge}_{0.25}\text{As}_{0.083}\text{S}_{0.65}$ glasses doped with 0.05 at.% Dy^{3+} (1), and 0.2 at.% Dy^{3+} (2).

Fig.4. represents the photoluminescence spectra at $T=10$ K excited at $\lambda=950$ nm for $\text{Ga}_{0.017}\text{Ge}_{0.25}\text{As}_{0.083}\text{S}_{0.65}$ glasses doped with 0.05 at.% Dy^{3+} (1) and with 0.2 at.% Dy^{3+} . In comparison with the visible photoluminescence, in this region of spectra more intensive luminescence can be observed for the $\text{Ga}_{0.017}\text{Ge}_{0.25}\text{As}_{0.083}\text{S}_{0.65}$ glass doped with 0.2 at.% Dy^{3+} . A broad luminescence band situated around 1300 nm can be assigned to the electron radiative transition ${}^6\text{F}_{11/2} \rightarrow {}^6\text{H}_{15/2}$. For the $\text{Ga}_{0.017}\text{Ge}_{0.25}\text{As}_{0.083}\text{S}_{0.65}$ glass doped with 0.05 at.% Dy^{3+} a broad luminescent band located around 1600 nm is observed, while when the concentration of Dy^{3+} increase up to 0.5 at.% this luminescent band is quenched. The intensity of photoluminescence at the low temperature strongly increase ($\sim 10^3$ times) in respect with the intensity of

photoluminescence at the room temperature. The concentration of rare-earth ions and temperature effects suggest that at high concentrations of rare earth ions and elevated temperatures some interaction between the separate rare earth ions take place, as well as between the rare earth ions and the host lattice which lead to the effect of quenching of photoluminescence [7-9].

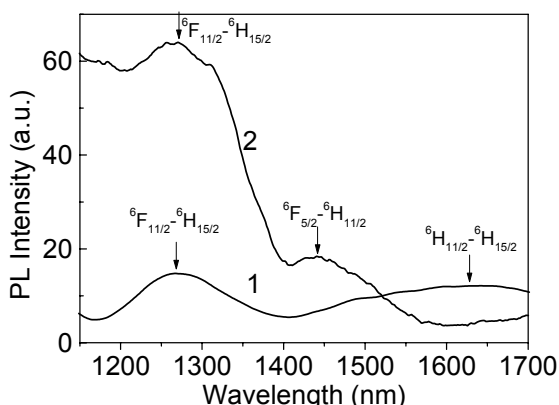


Fig.4. PL spectra at T=10 K excited at $\lambda=950$ nm for $\text{Ga}_{0.017}\text{Ge}_{0.25}\text{As}_{0.083}\text{S}_{0.65}$ glasses doped with 0.05 at.% Dy^{3+} (1) and with 0.2 at.% Dy^{3+} .

A very narrow luminescence peak in the visible region was detected in co-doped glasses $\text{Ga}_{0.017}\text{Ge}_{0.25}\text{As}_{0.083}\text{S}_{0.65} + 0.07$ at.% $\text{Ho}^{3+} + 0.13$ at.% Dy^{3+} and $\text{Ga}_{0.017}\text{Ge}_{0.25}\text{As}_{0.083}\text{S}_{0.65} + 0.13$ at.% $\text{Ho}^{3+} + 0.07$ at.% Dy^{3+} by pumping with $\lambda=488$ nm (Fig.5). The observed luminescence peak around 650 nm is characteristic for Ho^{3+} ions (${}^5\text{F}_5 \rightarrow {}^5\text{I}_8$).

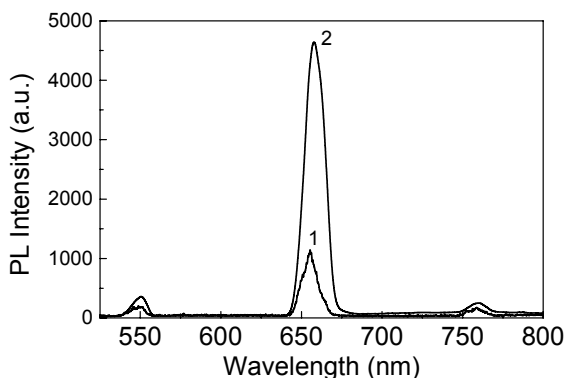


Fig.5. PL spectra at T=10K excited at $\lambda=488$ nm for $\text{Ga}_{0.017}\text{Ge}_{0.25}\text{As}_{0.083}\text{S}_{0.65}$ glasses codoped with 0.07 at.% $\text{Ho}^{3+} + 0.13$ at.% Dy^{3+} (1) and 0.13 at.% $\text{Ho}^{3+} + 0.07$ at.% Dy^{3+} (2).

We suggest that increasing of the photoluminescence intensity for the $\text{Ga}_{0.017}\text{Ge}_{0.25}\text{As}_{0.083}\text{S}_{0.65} + 0.13$ at.% $\text{Ho}^{3+} + 0.07$ at.% Dy^{3+}

is due to the energy absorbed by the glass matrix and transferred to Ho^{3+} ions. In the co-doped $\text{Ho}^{3+}/\text{Dy}^{3+}$ glasses an increase of the intensity photoluminescence of the bands located at 1300 nm also take place (Fig.5), and which are characteristic for the electron transitions of Dy^{3+} levels (${}^6\text{F}_{11/2} \rightarrow {}^6\text{H}_{15/2}$), or Ho^{3+} levels (${}^4\text{F}_4({}^5\text{S}_2) \rightarrow {}^5\text{I}_6$). For optical fiber amplifiers is important to obtain in chalcogenide glasses doped with rare earth ions the luminescence at the 1300 and 1500 nm. For a reason the investigated glasses were excited with the LED at $\lambda=950$ nm. Fig.6 shows the typical photoluminescence spectra at T=10K excited at $\lambda=950$ nm for $\text{Ga}_{0.017}\text{Ge}_{0.25}\text{As}_{0.083}\text{S}_{0.65}$ glasses co-doped with 0.07 at.% $\text{Ho}^{3+} + 0.13$ at.% Dy^{3+} (1) and 0.13 at.% $\text{Ho}^{3+} + 0.07$ at.% Dy^{3+} (2). In this case, when the investigated sample is excited with light $\lambda=950$ nm (${}^6\text{F}_{7/2}({}^6\text{F}_{5/2}) \rightarrow {}^6\text{H}_{15/2}$), we can observe the emission bands located at around 1300, and 1650 nm, that are characteristic for the Dy^{3+} ions electron transitions: ${}^6\text{F}_{11/2} \rightarrow {}^6\text{H}_{15/2}$ (1300 nm) and ${}^6\text{H}_{11/2}({}^6\text{H}_{13/2}) \rightarrow {}^6\text{H}_{15/2}$ (1650-1700 nm). In such way it was shown that the absorbed light by the host glass excite certain of the rare earth emission lines in the visible and near IR region.

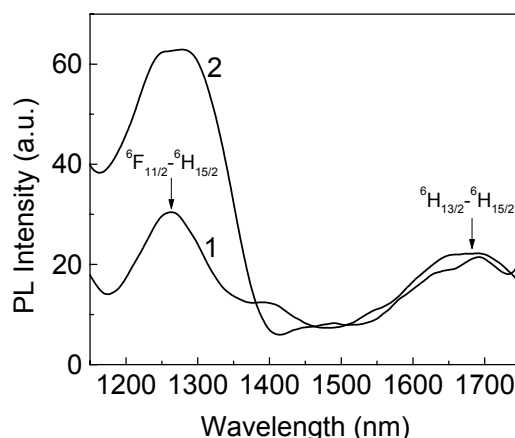


Fig.6. PL spectra at T=10K excited at $\lambda=950$ nm for $\text{Ga}_{0.017}\text{Ge}_{0.25}\text{As}_{0.083}\text{S}_{0.65}$ glasses codoped with 0.07 at.% $\text{Ho}^{3+} + 0.13$ at.% Dy^{3+} (1) and 0.13 at.% $\text{Ho}^{3+} + 0.07$ at.% Dy^{3+} (2).

Some possible energy transfer mechanisms (*resonant energy transfer, stepwise up conversion, cooperative luminescence, cooperative energy transfer and simultaneous photon absorption*) as well as *from the host glass to the rare earth ions*, as well as from two different rare earth ions are discussed in [8-12]. According to [8] some native defects of the host glass also can be responsible for broad-band photoluminescence excitation. The authors outline that the principles involved in the non-radiative transfer of energy from the defect related site in the host glass to the rare earth dopant are quite similar to those of “sensitized of luminescence”. In this mechanism the luminescence is excited from an emitter impurity through the absorption of the light in the Urbach edge of

the glass and non-radiatively the energy is transferred to the emitter (activator). In our case the rare earth atoms ions are the emitters (activators) and the native defects in chalcogenide glasses (dangling chalcogen bonds) play the role of sensitizers. This model was used by us for interpretation of the photoluminescence spectra in Ga-La-S:O glasses doped with Pr³⁺ ions [13] and in As₂S₃ glasses doped with Pr³⁺ and Dy³⁺ ions [14].

The broad band excitation process in chalcogenide glasses doped with rare earth ions was interpreted in terms of the Mott, Davis, Street model for the optical and electronic properties of native defect states [15]. According to this model the exciting light absorbed in the Urbach tail of the absorption edge creates an electron-hole pair in the glass. The hole is then captured by a nearby defect state (a charged dangling bond in the Mott, Davis, Street model) thereby changing the charge state of the defect. Capturing of the hole on the defect state leads to relaxation of the lattice around the defect and shifts the defect energy state deeper into the gap. The electron can then either recombine radiatively with the bound hole, giving rise to the host glass luminescence, or recombine non-radiatively, transferring its energy to a nearby rare earth atom and placing it in an excited state. Another possibility is that the pair could recombine non-radiatively, transferring its energy to the host lattice resulting in no luminescence. The third process of non-radiative recombination leads to lack of luminescence. This model explains the decrease in the host glass photoluminescence intensity with increasing of rare earth concentration in the all spectral range [8].

IV. SUMMARY

In conclusion, the photoluminescence spectra of Ga_{0.017}Ge_{0.25}As_{0.083}S_{0.65} glasses doped with Dy³⁺, and co-doped with Ho³⁺/Dy³⁺ rare earth ions at room temperature and at T=10K in the visible and near infrared (IR) spectral regions were investigated. In the visible region the glasses show bright luminescence due to the presence of rare-earth ions similar to that in other glasses. The observed photoluminescence is associated with the electron transitions between the levels of the rare earth ions due to the energy transfer mechanism including broad band absorption of the light by the tail state of the host glass and transfer of energy to the rare earth ions. Lowering the temperature increase the intensity and make the luminescence bands more narrows. The effect of co-doping on the luminescence spectra is determined by increasing of the intensity of the emission bands due to the effect of transfer of energy between two rare-earth ions.

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