

# Photoluminescence of $\text{Ga}_{0.017}\text{Ge}_{0.25}\text{As}_{0.083}\text{S}_{0.65}$ glasses doped with rare-earth ions

M. S. IOVU\*, N. N. SYRBU, YU. S. TVER'YANOVICH<sup>a</sup>, G. J. ADRIAENSSENS<sup>b</sup>

*Center of Optoelectronics, IAP, ASM, Str. Academiei 1, MD-2028 Chisinau, R. Moldova*

*<sup>a</sup>Russian Center of Laser Physics, St. Petersburg State University, St. Petersburg, Russia*

*<sup>b</sup>Laboratorium voor Halfgeleiderfysica, University of Leuven, B-3001 Leuven, Belgium*

The visible luminescence from  $\text{Pr}^{3+}$ ,  $\text{Dy}^{3+}$ ,  $\text{Nd}^{3+}$ ,  $\text{Sm}^{3+}$  and codoped with  $\text{Ho}^{3+}$  and  $\text{Dy}^{3+}$  ions embedded in  $\text{Ga}_{0.017}\text{Ge}_{0.25}\text{As}_{0.083}\text{S}_{0.65}$  glass hosts at room temperature and at  $T=10$  K is reported, when pumping with an  $\text{Ar}^+$ -ion laser at  $\lambda=488$  nm. Fluorescence emissions at  $1.3 \mu\text{m}$  was observed for  $\text{Dy}^{3+}$  and both at  $1.3$  and at  $1.5 \mu\text{m}$  for  $\text{Pr}^{3+}$  doped glasses with wavelength pumping at  $950$  nm. Energy transfer from  $\text{Ho}^{3+}$   $^5\text{F}_3$  level to  $\text{Dy}^{3+}$   $^4\text{F}_{9/2}$  level increase the visible emission efficiency at  $650$  nm in the codoped glasses. The investigated  $\text{Ga}_{0.017}\text{Ge}_{0.25}\text{As}_{0.083}\text{S}_{0.65}$  glasses doped with  $\text{Pr}^{3+}$  are promising amplifier materials for  $1.3$  and  $1.5 \mu\text{m}$  fiber optic telecommunication windows.

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## 1. Introduction

Rare-earth doped chalcogenide glasses are intensively investigated due to their possible potential applications as optical amplifiers for the  $1.3$  and  $1.5 \mu\text{m}$  telecommunication windows and for fiber lasers [1-5]. Chalcogenide glasses are characterized by high rare-earth solubility, chemical stability, high refractive index ( $\geq 2.4$ ), and a broad transmission window [6-8]. Due to the very low phonon energy of the Ge-based chalcogenide glasses an increase in the radiative efficiencies of the rare earth transitions is obtained. The  $\text{Ga}_2\text{S}_3$ - $\text{GeS}_2$  glassy system is a good host material for the rare-earth ions [9], has a large glass-forming region, high transmission in the visible region and high values of the glass transition temperature  $T_g \sim 425$  °C [10]. The chalcogenide glasses doped with rare-earth ions exhibit fluorescence at the following fixed wavelengths [11]:  $\text{Nd}^{3+}$  (0.786, 0.919, 1.08,  $1.37 \mu\text{m}$ );  $\text{Er}^{3+}$  (0.822, 0.869, 0.987, 1.54, 2.7, 3.5,  $4.5 \mu\text{m}$ );  $\text{Ho}^{3+}$  (0.76, 0.91, 1.2, 2.9,  $3.9 \mu\text{m}$ );  $\text{Pr}^{3+}$  (1.3, 1.6, 2.9, 3.4, 4.5, 4.8, 4.9,  $7.2 \mu\text{m}$ );  $\text{Dy}^{3+}$  (1.3, 1.8, 2.3,  $4.3 \mu\text{m}$ ). Even visible photoluminescence from Pr-doped  $(\text{GeS}_3)_{80}(\text{Ga}_2\text{S}_3)_{20}$  pumped by  $\text{Ar}^+$ -laser was reported in [12]. The authors explain this photoluminescence and its temperature dependence by the presence of energy transfer from tail states of the host glass to  $\text{Pr}^{3+}$  ions. Some papers were dedicated to the investigation of the transfer mechanism behind the increase of the fluorescence efficiency for  $\text{Tm}^{3+}/\text{Ho}^{3+}$  co-doped  $\text{Ge}_{25}\text{Ga}_5\text{S}_{70}$  glasses [13], for  $\text{Pr}^{3+}/\text{Er}^{3+}$  co-doped  $\text{Ge}_{30}\text{As}_8\text{Ga}_5\text{S}_{61}$  glasses [14], and for  $\text{Er}^{3+}/\text{Tm}^{3+}$  in different compositions of Ge-Ga-As-S glasses [10]. The aim of this paper is to investigate the visible and the  $1.3$  ( $1.5$ )  $\mu\text{m}$  photoluminescence from  $\text{Ga}_{0.017}\text{Ge}_{0.25}\text{As}_{0.083}\text{S}_{0.65}$

glasses doped with  $\text{Pr}^{3+}$ ,  $\text{Dy}^{3+}$ ,  $\text{Nd}^{3+}$ ,  $\text{Sm}^{3+}$  and co-doped with  $\text{Ho}^{3+}/\text{Dy}^{3+}$  rare-earth ions.

## 2. Experimental

The glasses used in this study were  $\text{Ga}_{0.017}\text{Ge}_{0.25}\text{As}_{0.083}\text{S}_{0.65}$  doped with 0.05 and 0.2 at.%  $\text{Pr}^{3+}$ , 0.05 and 0.2 at.%  $\text{Dy}^{3+}$ , 0.05 and 0.2 at.%  $\text{Nd}^{3+}$ , 0.05 and 0.2 at.%  $\text{Sm}^{3+}$ , and 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.%  $\text{Dy}^{3+}$  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.%  $\text{Dy}^{3+}$ . Bulk glasses were prepared from high purity (6N) elemental Ga, Ge, As, S and rare earth elements (Pr, Dy, Nd, Sm and Ho) 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 photoluminescence was measured on  $1$ - $2$  mm thick polished samples of the respective glasses. An  $\text{Ar}^+$ -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  $10 \text{ \AA}$ ) supplied with an FEU-106 photomultiplier in the photon count regime. The luminescence spectra also were investigated, when excited by an infrared LED 90RTM 5070 ( $\lambda = 950$  nm).

## 3. Experimental results and discussion

Fig. 1a and 1b show the PL spectra in the visible region excited at  $488$  nm for some of the investigated glasses.

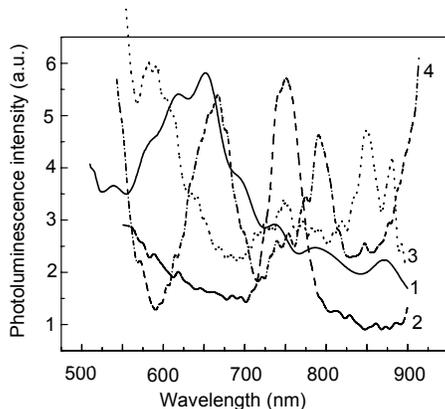


Fig. 1. PL spectra at room temperature excited at 488 nm for  $Ga_{0.017}Ge_{0.25}As_{0.083}S_{0.65}$  glasses (1) and doped with 0.2 at.%  $Sm^{3+}$  (2), 0.2 at.%  $Pr^{3+}$  (3), and 0.2 at.%  $Dy^{3+}$  (4).

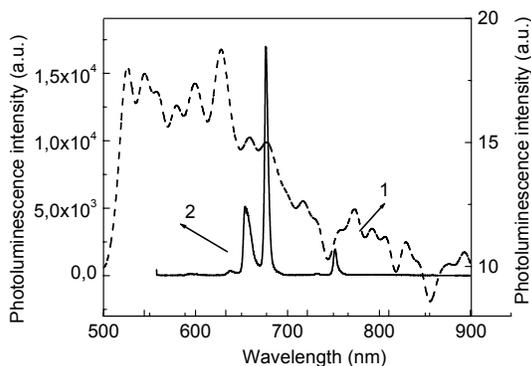


Fig. 1b. PL spectra excited at 488 nm for  $Ga_{0.017}Ge_{0.25}As_{0.083}S_{0.65}$  glasses doped with 0.05 at.%  $Sm^{3+}$  at 300 K (curve 1, right scale), and at 10 K (curve 2, left scale).

In  $Ga_{0.017}Ge_{0.25}As_{0.083}S_{0.65}$  glasses doped with 0.2 at.%  $Sm^{3+}$  the strong room-temperature photoluminescence band situated around 750 nm when excited at 488 nm ( ${}^6H_{5/2} \rightarrow {}^4G_{7/2}$ ) may be caused by the non-radiative transition  ${}^4G_{7/2} \rightarrow {}^4G_{5/2}$  followed by the radiative transition  ${}^4G_{5/2} \rightarrow {}^6H_{13/2}$  (Fig. 2a). Lowering of the temperature from  $T=300$  K to  $T=10$  K does not change the intensity of photoluminescence band, but does shift it from  $\lambda=750$  nm to  $\lambda=650$  nm, i.e. to the ( ${}^4G_{5/2} \rightarrow {}^6H_{9/2}$ ) transition. For low concentrations of Samarium (0.05 at.%  $Sm^{3+}$ ), a broad band of photoluminescence situated in the spectral range 550–800 nm was observed at room temperature (Fig. 1b). The photoluminescence band at  $\lambda=650$  nm that appears at low temperatures ( $T=10$  K) in  $Ga_{0.017}Ge_{0.25}As_{0.083}S_{0.65}$  glass doped with 0.2 at.%  $Sm^{3+}$ , splits into two narrow bands located at  $\lambda=625$  nm and  $\lambda=650$  nm in  $Ga_{0.017}Ge_{0.25}As_{0.083}S_{0.65}$  glass doped with 0.05 at.%  $Sm^{3+}$  (Fig. 1b, curve 2). For this  $Ga_{0.017}Ge_{0.25}As_{0.083}S_{0.65}$  glass with the low doping concentration of 0.05 at.%  $Sm^{3+}$ , the photoluminescence intensity at low temperature ( $T=10$  K)

strongly increases ( $\sim 10^3$  times) with respect to the intensity at room temperature. These effects of rare-earth concentration and temperature suggest that at high concentrations of rare-earth ions and elevated temperatures quenching of photoluminescence is observed due to interactions between the separate rare-earth ions and between the rare-earth ions and the host lattice [15-17].

For  $Ga_{0.017}Ge_{0.25}As_{0.083}S_{0.65}$  glasses doped with 0.2 at.%  $Dy^{3+}$ , the two luminescence bands situated at 665 nm and 790 nm can be attributed to the electron transitions of  $Dy^{3+}$  ion,  ${}^4F_{9/2} \rightarrow {}^6H_{11/2}$  and  ${}^4F_{5/2} \rightarrow {}^6H_{15/2}$ , respectively (Fig. 2b).

For  $Ga_{0.017}Ge_{0.25}As_{0.083}S_{0.65}$  glasses doped with 0.2 at.%  $Pr^{3+}$  the luminescence spectra are more complicated. In the visible region the spectra contain four well distinguishable bands at 590 nm, 750 nm, 850 nm and 880 nm. When the luminescence is excited at 488 nm the energy is transferred to the  $Pr^{3+}$  ion at the  ${}^3P_0$  level, and then the following electron transitions with light emission take place:  ${}^3P_0 \rightarrow {}^3H_6$  ( $\sim 600$  nm),  ${}^3P_0 \rightarrow {}^3F_4$  ( $\sim 700$  nm),  ${}^3P_0 \rightarrow {}^1G_4$  ( $\sim 900$  nm).

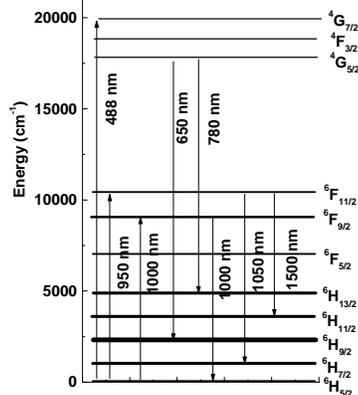


Fig. 2a. Energy level diagram for  $Sm^{3+}$  ions.

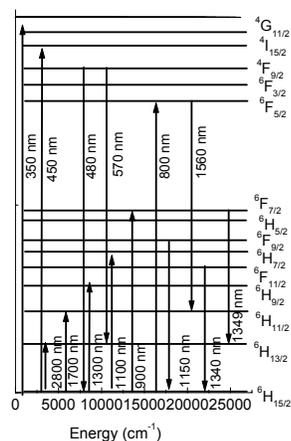


Fig. 2b. Energy level diagram for  $Dy^{3+}$  ions.

A very narrow luminescence peak was detected in co-doped glasses:  $\text{Ga}_{0.017}\text{Ge}_{0.25}\text{As}_{0.083}\text{S}_{0.65} + 0.07 \text{ at.}\% \text{ Ho}^{3+} + 0.13 \text{ at.}\% \text{ Dy}^{3+}$  and  $\text{Ga}_{0.017}\text{Ge}_{0.25}\text{As}_{0.083}\text{S}_{0.65} + 0.13 \text{ at.}\% \text{ Ho}^{3+} + 0.07 \text{ at.}\% \text{ Dy}^{3+}$  (Fig.3a). The observed luminescence peak around 650 nm is characteristic for  $\text{Ho}^{3+}$  ions ( ${}^5\text{F}_5 \rightarrow {}^5\text{I}_8$ ). We suggest that the increase of the photoluminescence intensity for the  $\text{Ga}_{0.017}\text{Ge}_{0.25}\text{As}_{0.083}\text{S}_{0.65} + 0.13 \text{ at.}\% \text{ Ho}^{3+} + 0.07 \text{ at.}\% \text{ Dy}^{3+}$  is due to the energy absorbed by the glass matrix and transferred to  $\text{Ho}^{3+}$  ions. In the same  $\text{Ho}^{3+}/\text{Dy}^{3+}$  co-doped glasses, an increase of the photoluminescence intensity of the bands located at 1300 nm also takes place (Fig.3b). These bands are characteristic for the electron transitions of  $\text{Dy}^{3+}$  levels ( ${}^6\text{F}_{11/2} \rightarrow {}^6\text{H}_{15/2}$ ), or  $\text{Ho}^{3+}$  levels ( ${}^4\text{F}_4({}^5\text{S}_2) \rightarrow {}^5\text{I}_6$ ).

For optical fiber amplifiers it is important to obtain in chalcogenide glasses doped with rare-earth ions the luminescence at the 1300 and 1500 nm. For that reason the investigated glasses were excited with the LED at  $\lambda=950$  nm. Fig.4a shows a typical luminescence spectrum for  $\text{Ga}_{0.017}\text{Ge}_{0.25}\text{As}_{0.083}\text{S}_{0.65}$  glasses doped with 0.2 at.%  $\text{Pr}^{3+}$  when excited at  $\lambda=950$  nm. In this case, when the investigated sample is excited with light of  $\lambda=950$  nm ( ${}^3\text{H}_4 \rightarrow {}^1\text{G}_4$ ), we can observe the emission bands located at 1300, 1500 and 1650 nm that are characteristic for the  $\text{Pr}^{3+}$  ion electron transitions:  ${}^1\text{G}_4 \rightarrow {}^3\text{H}_8$  (1300 nm) and  ${}^3\text{F}_3 \rightarrow {}^3\text{H}_4$  (1500-1650 nm) (Fig. 4b). It was thus shown that light absorbed by the host glass excited certain of the rare-earth emission lines in the visible and near-IR region. Some possible energy transfer mechanisms (*resonant energy transfer, stepwise upconversion, cooperative luminescence, cooperative energy transfer and simultaneous photon absorption*) as well from the host glass to the rare earth ions, as between two different rare earth ions, are discussed in [16-20]. According to [16] some native defects of the host glass can also be responsible for broad-band photoluminescence excitation. We used this model for interpreting the photoluminescence spectra in Ga-La-S:O glasses doped with  $\text{Pr}^{3+}$  ions [21] and in  $\text{As}_2\text{S}_3$  glasses doped with  $\text{Pr}^{3+}$  and  $\text{Dy}^{3+}$  ions [22].

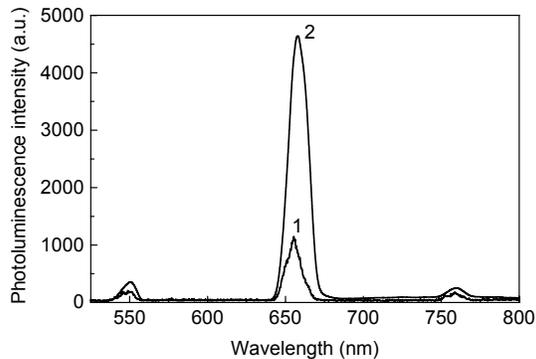


Fig. 3a. PL spectra at  $T=10\text{K}$  excited at  $\lambda=488$  nm for  $\text{Ga}_{0.017}\text{Ge}_{0.25}\text{As}_{0.083}\text{S}_{0.65}$  glasses codoped with 0.07 at.%  $\text{Ho}^{3+} + 0.13 \text{ at.}\% \text{ Dy}^{3+}$  (1) and 0.13 at.%  $\text{Ho}^{3+} + 0.07 \text{ at.}\% \text{ Dy}^{3+}$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

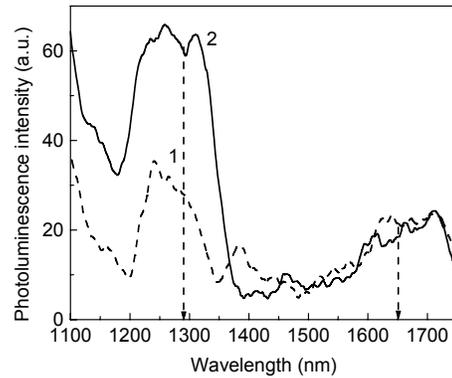


Fig. 3b. PL spectra at room temperature when excited at  $\lambda=950$  nm for  $\text{Ga}_{0.017}\text{Ge}_{0.25}\text{As}_{0.083}\text{S}_{0.65}$  glasses codoped with 0.07 at.%  $\text{Ho}^{3+} + 0.13 \text{ at.}\% \text{ Dy}^{3+}$  (1) and 0.13 at.%  $\text{Ho}^{3+} + 0.07 \text{ at.}\% \text{ Dy}^{3+}$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

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 [23-25]. 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 transfer 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 without accompanying luminescence. The second process of non-radiative energy transfer from the excited electron-hole pair is supposed to give rise to a broad-band excitation of the rare-earth dopants. This model explains the decrease in the host glass photoluminescence intensity with increasing rare-earth concentration in the whole spectral range [16].

#### 4. Summary

In conclusion, the photoluminescence spectra of  $\text{Ga}_{0.017}\text{Ge}_{0.25}\text{As}_{0.083}\text{S}_{0.65}$  glasses doped with  $\text{Pr}^{3+}$ ,  $\text{Dy}^{3+}$ ,  $\text{Nd}^{3+}$ ,  $\text{Sm}^{3+}$ , and co-doped with  $\text{Ho}^{3+}/\text{Dy}^{3+}$  rare-earth ions were investigated at room temperature and at  $T=10$  K, in the visible region and at 1.3 (1.5)  $\mu\text{m}$ . In the visible region the glasses show bright luminescence due to the presence of rare-earth ions similar to that in other glasses. The effect of co-doping on the luminescence spectra is marked by an increase of the intensity of the emission bands due to an energy transfer process between the two rare-earth ions.

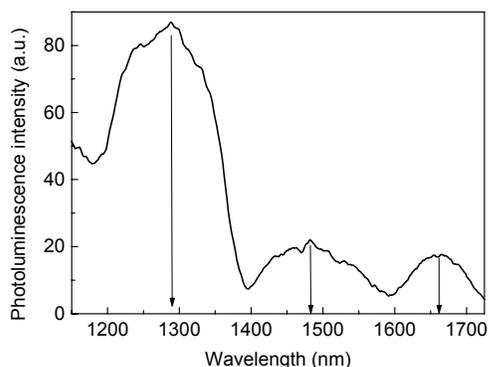


Fig. 4a. PL spectra at room temperature when excited at 950 nm for  $Ga_{0.017}Ge_{0.25}As_{0.083}S_{0.65}$  glasses doped with 0.2 at.%  $Pr^{3+}$ .

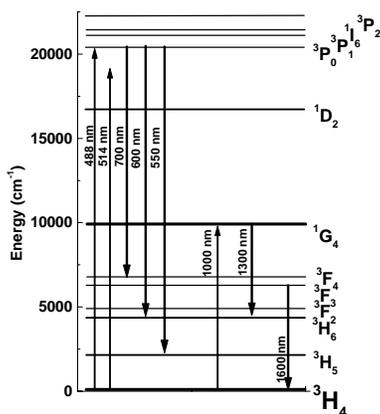


Fig. 4b. The possible electron transitions for the  $Pr^{3+}$  ions.

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\*Corresponding author: iovu@as.md