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EMISSION SPECTRA OF $Ge_{25}Ga_{1.7}As_{8.3}S_{65}$ Glass DOPED WITH Sm^{3+} AND Nd^{3+}

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The absorption spectra in the visible and near IR regions for $Ga_{0.017}Ge_{0.25}As_{0.083}S_{0.65}$ doped with Sm^{3+} and Nd^{3+} ions are investigated. The visible luminescence from Sm^{3+} and Nd^{3+} 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. The fluorescence emission in near infrared region was investigated when pumping with LED at 950 nm. The energy transfer of the absorbed light in the broad band Urbach region of the host glass to the Sm^{3+} and Nd^{3+} is suggested for increasing the emission efficiency. The investigated $Ga_{0.017}Ge_{0.25}As_{0.083}S_{0.65}$ glasses doped with Pr^{3+} Nd^{3+} are promising materials for optical amplifiers operating at 1000, 1300 and 1500 nm 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 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 (less than 340 cm^{-1}) was obtaining an increasing in the radiative efficiencies of the rare earth transitions (e.g., for the $^1G_4 \rightarrow {}^3H_5$ transition at 1300 nm for Pr^{3+} ions). The Ga_2S_3-GeS_2 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 $T_g \sim 425\ ^oC$ [2]. The chalcogenide glasses doped with rare-earth ions exhibit fluorescence at fixed wavelengths [3]: Nd^{3+} (0.786, 0.919, 1.08, 1.37 μm); Er^{3+} (0.822, 0.869, 0.987, 1.54, 2.7, 3.5, 4.5 μm); Ho^{3+} (0.76, 0.91, 1.2, 2.9, 3.9 μm); Pr^{3+} (1.3, 1.6, 2.9, 3.4, 4.5, 4.8, 4.9, 7.2 μm); Dy^{3+} (1.3, 1.8, 2.3, 4.3 μm).

Visible photoluminescence from Pr-doped $(GeS_3)_{80}(Ga_2S_3)_{20}$ pumped by Ar^+-laser was reported in [4]. The authors explain the photoluminescence and it temperature dependence by the presence of energy transfer from tail states of the host glass to Pr^{3+} ions. Some papers were dedicated to investigation of the transfer mechanism and increasing of the fluorescence efficiency for Tm^{3+}/Ho^{3+} co-doped $Ge_{25}Ga_5S_{70}$ glasses [5], for Pr^{3+}/Er^{3+} co-doped $Ge_{30}As_8Ga_5S_{61}$ glasses [6], and for Er^{3+}/Tm^{3+} in different compositions of Ge-Ga-As-S glasses [2].

Non-oxide chalcogenide glasses with typical highest energy phonon of 250-350 cm^{-1} are extremely attractive as hosts for Pr^{3+} doping (compare with highest-energy phonon of about 1100 cm^{-1} in silica glass, in which no measurable emission at 1.3 mm is observed). The neodymium ions Nd^{3+} has not been studied intensively as rare earth dopant for chalcogenide glasses because the main fluorescent level $^4F_{3/2}$ is separated by a large gap from the next lower lying level $^4I_{15/2}$. For $70Ga_2S_3$:$28.5La_2S_3$:$1.5Nd_2S_3$ glass in the absorption spectrum a strong absorption band located at 600 nm ($^4I_{9/2} \rightarrow {}^2G_{7/2}$) was observed compared to the band at 815 nm ($^4I_{9/2} \rightarrow {}^2H_{9/2}$) [5]. The composition dependence of the environmenent of Nd^{3+} and Sm^{3+} in chalcogenide glasses containing Ga, Ge and S, Se and Te was investigated in [7]. It was shown that the spectral shift in absorption bands of Nd^{3+} is a linear function of the mean electronegativity of chalcogens involved in the glasses, and which indicates the coincidence between the average composition of the first coordination sphere of Neodymium ions and the composition of anionic subsystem in the investigated glasses. Regarding Samarium, the spectral shift in absorption bands of Sm^{3+} ions is non-linear function of the mean electronegativity of the chalcogens.

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 Nd^{3+} and Sm^{3+} ions. These rare earths ions has a rich spectrum of transitions in the infrared wavelength region from 1000 to 7000 nm, which offers the promise of lasers, amplifiers and high brightness sources for remote sensing. The advantage of optical fibers fabricated from chalcogenide glasses doped with rare-earth ions as fiber amplifiers is that in this case the upper levels of rare-earth ions are populated not only by the resonance excitation, but also due to the light absorption in the host chalcogenide glass, the energy of which than is transferred to the rare-earth ions.

2. Experimental

Bulk glasses of $Ga_{0.017}Ge_{0.25}As_{0.083}S_{0.65}$ doped with 0.05 and 0.2 at.% Sm^{3+} and with 0.05 and 0.2 at.% Nd^{3+} were prepared from high purity (6N) elemental Ga, Ge, As, S and rare earth sulfides Sm_2S_3 and Nd_2S_3, 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. For optical transmission a UV/VIS (300÷800 nm) and 61 NIR (800÷3500 nm) Specord's CARLZEISS Jena production were used. 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 ($\lambda = 950$ nm).

3. Experimental results and discussion

Nd^{3+} -doped glass lasers have been studied extensively because of their high efficiency and room temperature operation. These desirable characteristics result from the 4f-level nature of the Nd^{3+} ion. The levels denoted $^2H_{9/2}$ and $^4F_{5/2}$ could be used to absorb light from a pumping source at about 800 nm. Ions excited into the pump band decay, usually non-radiatively, to the upper lasing level $^4F_{3/2}$. From this upper laser level, there are two four-level transitions with high gain, $^4F_{3/2} \rightarrow {}^4I_{11/2}$ at 1.06 μm and $^4F_{3/2} \rightarrow {}^4I_{13/2}$ at 1.35 μm (Fig.1a). In addition, there is still a further non-radiative transition from the lower lasing level to the ground state. This situation allows heavy population of the upper laser level. The energy level position of extrinsic lanthanide centers in energy band structure of the vitreous semiconductor depends of the composition of the anionic environment of the lanthanide atoms. The absorption spectra of some glasses doped with Nd^{3+} ions was investigated: $70Ga_2S_3:28.5La_2S_3:1.5Nd_2S_3$ [9], $(Ga_2S_3)_x$-$(Na_2S)_{1-x}$ [10], and $70Ga_2S_3:30La_2S_3$ [11]. Some results regarding the $Ge_{0.25}Ga_{0.05}As_{0.05}S_{0.65}$ glasses doped with Nd^{3+} and Sm^{3+} ions are published in [12]. The luminescence bands and the peak intensities deduced from Raman experiments correspond to 1360 nm for Nd^{3+} ions and 1476 nm for Sm^{3+} ions, respectively.

For the glasses $Ge_xGa_5Se_{95-x}$ system because of limited transparency in the visible spectral region, only absorption bands connected with electron transitions from $^6H_{5/2}$ ground level to higher energy levels of manifolds ^6F_J (J=11/2, 9/2, 7/2, 5/2, 3/2, 1/2) and ^6H_J (J=15/2, 13/2, 11/2, 9/2, 7/2) of Sm^{3+} ions (Fig.1b), which are located in infrared region, were observed at room temperature [8]. The transmittance region of the investigated glasses $Ga_{0.017}Ge_{0.25}As_{0.083}S_{0.65}$ extends from the fundamental absorption edge region near 0.5 μm up to the lattice vibration threshold at about 8.0 μm. In Sm-free samples this region is transparent, with only weak traces of OH (~2.9 μm) and CO_2 (~4.3 μm). Introduction of Sm^{3+} results in strong absorption bands of Sm^{3+} -ions located in the visual and near infrared (IR) parts of the transparency region (Fig.2a). The position of the absorption bands of Sm^{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.

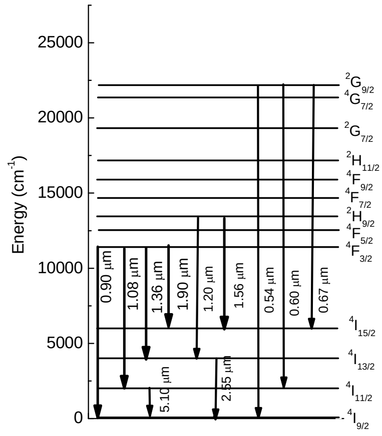

Fig.1a. Energy levels diagram of Nd^{3+} ion.

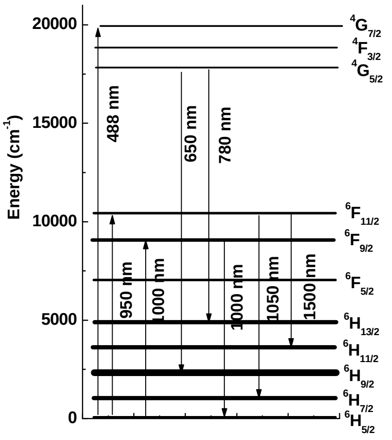

Fig.1b. Energy levels diagram of Sm^{3+} ion.

From Fig.2a it is seen that the absorption bands in $Ga_{0.017}Ge_{0.25}As_{0.083}S_{0.65}$ doped with Sm^{3+} are connected with electron transitions from $^6H_{5/2}$ ground level to higher energy levels of manifolds ^6F_J (J=11/2, 9/2, 5/2) and ^6H_J (J=15/2, 13/2 of Sm^{3+} ions: $^6H_{5/2}\rightarrow{}^6F_{11/2}$ (960 nm), $^6H_{5/2}\rightarrow{}^6F_{9/2}$ (1101 nm), $^6H_{5/2}\rightarrow{}^6H_{15/2}$ (1269 nm), $^6H_{5/2}\rightarrow{}^6F_{5/2}$ (1422 nm), $^6H_{5/2}\rightarrow{}^6H_{13/2}$ (2015 nm).

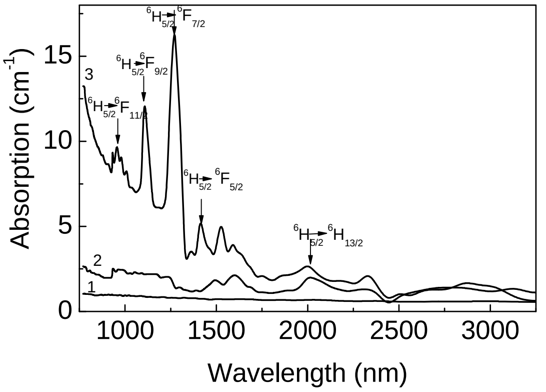

Fig.2a. The absorption spectra of $Ga_{0.017}Ge_{0.25}As_{0.083}S_{0.65}$ glasses (1), and doped with 0.05 at.% Sm^{3+} (2) and with 0.2 at.% Sm^{3+} (3) at room temperature T=300 K.

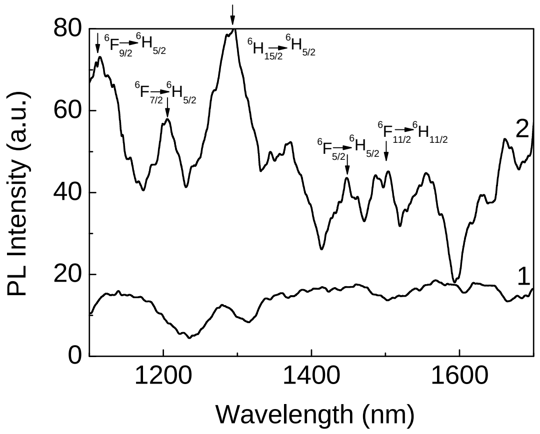

Fig.2b. Photoluminescence spectra for $Ga_{0.017}Ge_{0.25}As_{0.083}S_{0.65}$ glasses doped with 0.05 at.% Sm^{3+} (1) and with 0.2 at.% Sm^{3+} (2) measured at room temperature. λ_{exc}=950 nm.

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 exited with the LED at λ=950 nm. Fig.2b shows a typical luminescence spectra for $Ga_{0.017}Ge_{0.25}As_{0.083}S_{0.65}$ glasses doped with 0.05 and 0.2 at.% Sm^{3+} when excited at λ=950 nm. In this case, when the investigated sample is excited with light λ=950 nm ($^6H_{5/2}\rightarrow{}^6F_{11/2}$), we can observe the emission bands located at around 1100, 1300 and 1500 nm, that are characteristic for the Sm^{3+} ions electron transitions: $^6F_{9/2}\rightarrow{}^6H_{5/2}$ (1100 nm), $^6H_{15/2}\rightarrow{}^6H_{5/2}$ (1300 nm), and $^6F_{11/2}\rightarrow{}^6H_{11/2}$ (1500 nm).

For low concentrations of Samarium (0.05 at.% Sm^{3+}) at room temperature a broad band of photoluminescence situated in the spectral range 550÷800 nm was observed (Fig.3a).In $Ga_{0.017}Ge_{0.25}As_{0.083}S_{0.65}$ glasses doped with 0.2 at.% Sm^{3+} at the room temperature the strong photoluminescence band situated around 750 nm when excited at 488 nm ($^6H_{5/2}\rightarrow{}^4G_{7/2}$) may be caused with the non-radiative transition $^4G_{7/2} \rightarrow {}^4G_{5/2}$ and than with the radiative transition $^4G_{5/2} \rightarrow {}^6H_{13/2}$ (Fig.3b). Lowering of the temperature from T=300 K to T=10 K for $Ga_{0.017}Ge_{0.25}As_{0.083}S_{0.65}$ doped with 0.05 at.% Sm^{3+} increase the intensity of photoluminescence bands, but only shifts it from λ=655 nm to λ=700 nm, respectively. The photoluminescence band which appear at low temperatures (T=10 K) in $Ga_{0.017}Ge_{0.25}As_{0.083}S_{0.65}$ glass doped with 0.05 at.% Sm^{3+} situated at λ=650 nm is splinted in two narrow bands located at λ=625 nm and λ=650 nm (Fig.3b, curve 2). For $Ga_{0.017}Ge_{0.25}As_{0.083}S_{0.65}$ glass doped with 0.05 at.% Sm^{3+} the intensity of photoluminescence at low temperature (T=10 K) strongly increase (~10^3 times) in respect with the intensity of photoluminescence at room temperature. The concentration of rare-earth ions and temperature effects suggest that at high concentrations of rare-earth ions and elevated temperatures is caused by some interaction between the separate rare-earth ions, as well as by the interaction between the rare-earth ions and the host lattice which lead to the effect of quenching of photoluminescence [1].

To quantitatively comprehend optical phenomena of rare earth ions in glasses, it is of great importance to evaluate radiative and non-radiative decay process of related *4f* levels. The Judd-Ofelt theory is usually adopted to obtain the transition probabilities including radiative decay rate by utilizing the data of absorption cross sections of several *f-f* electric-dipole transitions [13,14].

According to the Judd-Ofelt theory the line strength of the electric dipole transition between an initial J manifold $\left|(S,L)J\right\rangle$ and final manifold $\left|(S',L')J'\right\rangle$, is given as

$$S_{JJ'} = \sum_{t=2,4,6} \Omega_t \left| \left\langle (SL)J \right\| U^{(t)} \left\| (S'L')J' \right\rangle \right|^2, \tag{1}$$

where $\left\langle \left\| U^{(t)} \right\| \right\rangle$ terms are the reduced matrix elements of the unit tensor operators calculated in the intermediate-coupling approximation, and the coefficients $\Omega_t (t = 2,4,6)$ are the intensity parameters that contain the effects of the crystal field terms, the radial integrals of electrons, and so on.

The line strength of the absorption band $S_{JJ'}$ was calculated with the experimental value of the integrated absorbance from the relation

$$\int_{band} \alpha(\lambda) d\lambda = \frac{8\pi^3 e^2 \bar{\lambda} \rho}{2hc(2J+1)} \frac{1}{n} \left[\frac{(n^2+2)^2}{9} \right] S_{JJ'} \tag{2}$$

where:
$\alpha(\lambda)$ - is the absorption coefficient at wavelength λ;
$\bar{\lambda}$ - is the mean wavelength at absorption band;
ρ - is the concentration of Er^{3+} ions per cm^3;
J - is the total angular momentum for the initial state;
h = *6.62·10⁻²⁷ erg/s* – the Plank's constant;
c = *3·10¹⁰ cm/s* – the light velocity;
e = *4.8·10⁻¹⁰ ESU (Electrostatic Units)* – elementary electric charge;
n - is the refractive index.

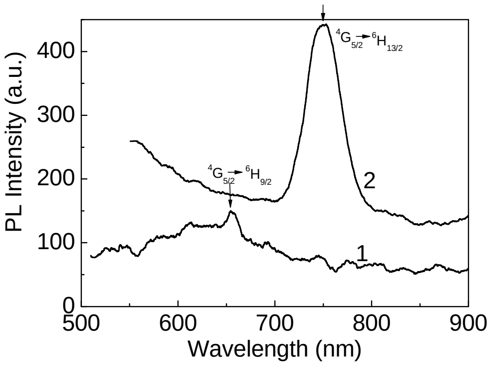

Fig.3a. PL spectra excited at 488 nm for $Ga_{0.017}Ge_{0.25}As_{0.083}S_{0.65}$ glasses doped with 0.05 at.% Sm^{3+} (curve 1), and with).2 at.% Sm^{3+} (curve 2) at 300 K.

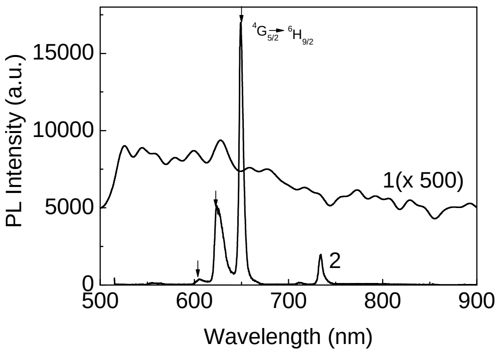

Fig.3b. PL spectra excited at 488 nm for $Ga_{0.017}Ge_{0.25}As_{0.083}S_{0.65}$ glasses doped with 0.05 at.% Sm^{3+} at 300 K (curve 1), and at 10 K (curve 2).

The factor $\frac{(n^2+2)^2}{9n}$ - is the local field correction for the ion in a dielectric medium. Each value of $\int \alpha(\lambda)d\lambda$ is determined by numerical integration of the various absorption bands obtained from spectrophotometer measurements. By using (1) and (2), the measured absorption peak area can be written in terms of the Ω_t parameters: if there are *i* bands used than for each measured absorption band B_i^m an equation of the form

$$B_i^m = a_i\Omega_2 + b_i\Omega_4 + c_i\Omega_6 \tag{3}$$

where

$$a_i = \frac{8\pi^3 e^2 \rho}{3ch(2J+1)} \frac{(n^2+2)^2}{9n} \bar{\lambda}_i \left|\langle (S,L) \| U^{(2)} \| (S',L')J' \rangle\right|^2 \tag{4}$$

and similarly for B_i and C_i can be written.

The Judd-Ofelt parameters for the GaGeAsS and other Chalcogenide glasses doped with Nd^{3+} ions are reported in [9]:

$\Omega_2=4.42\cdot10^{-20}$ cm^2
$\Omega_4=9.10\cdot10^{-20}$ cm^2
$\Omega_6=6.79\cdot10^{-20}$ cm^2

For the glasses GaGeAsS doped with Sm^{3+} ions in the literature does not exist, but some data are for the $Ge_xGa_5Se_{95-x}$ glasses doped with Sm^{3+} ions [8]. The Judd-Ofelt parameters depend on the glass composition, and the ratio Ω_2/Ω_6 takes the values between 1.8 to 2.2 and the parameter $\Omega_6=(1.9\div7.3)\cdot10^{-24}$ m^2, respectively.

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 [12, 15-18]. According to [15] 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 Pr^{3+} ions [19] and in As_2S_3 glasses doped with Pr^{3+} and Dy^{3+} ions [20].

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 [21]. 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 [15].

4. Summary

The absorption spectra at room temperature and the photoluminescence spectra of $Ga_{0.017}Ge_{0.25}As_{0.083}S_{0.65}$ glasses doped with Pr^{3+} 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.

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