$Ge_{25}Ga_{1.7}As_{8.3}S_{65}$ GLASS DOPED WITH Pr^{3+}
FOR 1.3 μm OPTICAL AMPLIFIERS

E. LUPAN[*], V. CIORNEA, M. IOVU
Institute of Applied Physics of the Academy of Sciences of Moldova
Str. Academiei 5, MD-2028 Chisinau, R. Moldova

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 Pr^{3+} ions are investigated. The visible luminescence from Pr^{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. Fluorescence emissions at around 1300 and 1500 nm was observed for Pr^{3+} doped glasses with wavelength pumping at 950 nm. The energy transfer of the absorbed light in the broad band Urbach region of the host glass to the Pr^{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+} are promising materials for optical amplifiers operating at 1300 and 1500 nm telecommunication windows.

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 °C [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].

Selection of the host glass is very critical in case of Pr because of the proximity of the next lower-lying level to the $^1G_4$. From the energy diagram (Fig.1b) the energy gap between $^1G_4$ manifold and the $^3F_4$ manifold is approximately 3000 cm^{-1}. Therefore a host with low phonon energy is highly desirable to decrease the non-radiative transition between these levels. Non-oxide chalcogenide glasses with typical highest energy phonon of 250-350 cm^{-1} are extremely attractive as hosts for Pr 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).

---

[*]Corresponding author: elena_lupan@yahoo.com

Pr^{3+} -doped Ge-Ga-S- glasses have been successfully prepared with good optical quality. Because of the low phonon energy of the host glass, a fluorescence lifetime of about 360 ms for the $^{1}G_4$ level was obtained, which, together with the large stimulated emission cross-section, makes Pr-doped Ge-Ga-S glass a very promising material for 1.3 mm fiber amplifier applications. The concentration of Pr for such a deviuce should be less than 500 ppm by weight to supress the concentration quenching [1].

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 Pr^{3+} ions. Praseodymium 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.% Pr^{3+} were prepared from high purity (6N) elemental Ga, Ge, As, S and rare earth sulfides Pr_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 (λ = 950 nm).

3. Experimental results and discussion

The transmittance region of the investigate d glasses extends from the fundamental absorption edge region near 0.5 μm up to the lattice vibration threshold at about 8.0 μm. Fig.1a shows the absorption spectra of $Ga_{0.017}Ge_{0.25}As_{0.083}S_{0.65}$ glasses doped with 0.05 at.% Pr^{3+} (1) and with 0.2 at.% Pr^{3+} (2) at room temperature T=300 K. The absorption edge in the glasses doped with Pr^{3+} is shifted in the region of higher photon energies and makes it more transparent. The observed weak absorption tail in most chalcogenide glasses is due to the effect of impurities and defects in the glasses.
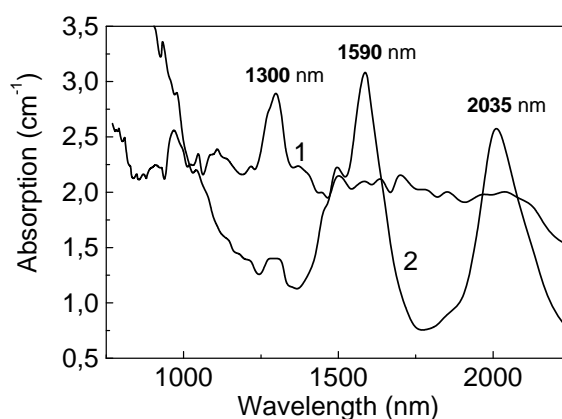

Fig.1a. The absorption spectra of $Ga_{0.017}Ge_{0.25}As_{0.083}S_{0.65}$ glasses doped with 0.05 at.% Pr^{3+} (1) and with 0.2 at.% Pr^{3+} (2) at room temperature T=300 K.
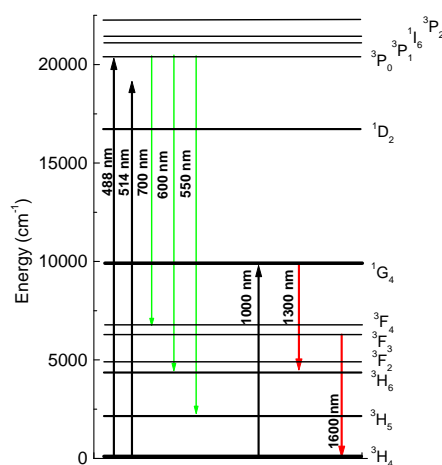
Fig.1b. Energy levels diagram of Pr³⁺ ion.

Introduction of Pr^{3+} in the host glass results in strong absorption bands of Pr^{3+} ions located in the near infrared (IR) parts of the transparency region. The position of the absorption bands of Pr^{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.1b are indicated the possible electron transitions when the light is absorbed by the chalcogenide glass doped with Pr^{3+} ions.
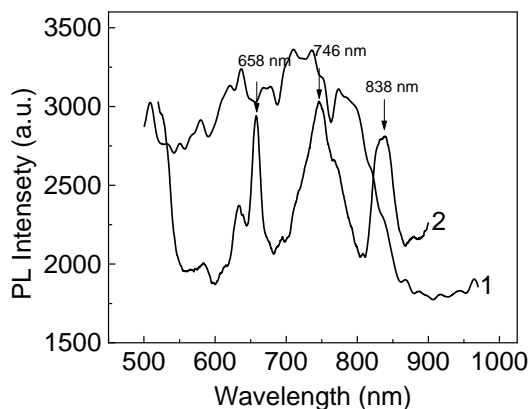

Fig.2a. Visible photoluminescence spectra for $Ga_{0.017}Ge_{0.25}As_{0.083}S_{0.65}$ glasses doped with 0.05 at.% Pr^{3+} (1) and with 0.2 at.% Pr^{3+} (2) measured at T=10 K. . λ_{exc}=488 nm.
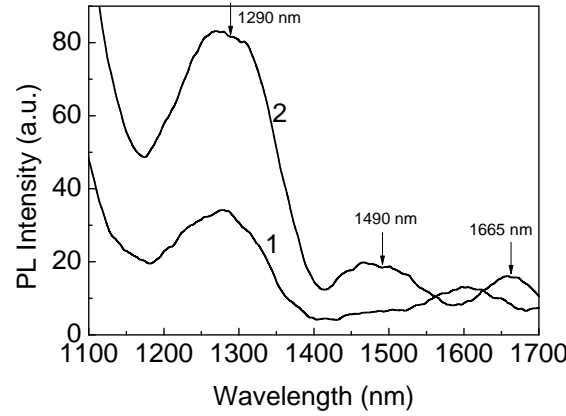
Fig.2b. Photoluminescence spectra for $Ga_{0.017}Ge_{0.25}As_{0.083}S_{0.65}$ glasses doped with 0.05 at.% Pr^{3+} (1) and with 0.2 at.% Pr^{3+} (2) measured at room temperature. λ_{exc}=950 nm.

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 [7,8].

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

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

where $\langle\|U^{(t)}\|\rangle$ 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

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

where: $\alpha(\lambda)$ - is the absorption coefficient at wavelength λ;

λ - 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 $= 6.62 \cdot 10^{-27}$ *erg/s* – the Plank's constant;

c $= 3 \cdot 10^{10}$ *cm/s* – the light velocity;

e $= 4.8 \cdot 10^{-10}$ *ESU (Electrostatic Units)* – elementary electric charge;

n - is the refractive index.

The factor $\dfrac{(n^2+2)^2}{9n}$ - 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

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

and similarly for B_i and C_i can be written.
For the $Ga_{0.017}Ge_{0.25}As_{0.083}S_{0.65}$ glasses doped with Pr^{3+} the optical absorption measurements were used by the authors [9] for calculation of the Judd-Ofelt parameters, for determining the brunch ratio and the excited state lifetimes. The values of the Judd-Ofelt parameters are the following:

$$\Omega_2 = 10.4 \cdot 10^{-20} \ cm^2$$
$$\Omega_4 = 4.8 \cdot 10^{-20} \ cm^2$$
$$\Omega_6 = 10.4 \cdot 10^{-20} \ cm^2$$

The fluorescence lifetime was experimentally determined for the discrete level $^1G_4$ of the Pr^{3+} ion of 180 mksec with the quantum efficiency 0f 0.7.

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 [10-14]. According to [10] 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 [15] and in As_2S_3 glasses doped with Pr^{3+} and Dy^{3+} ions [16].

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 [17]. 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 [10].

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.

Acknowledgement

References

[1] K.Wei, D.P.Machevirth, J.Wenzel, E.Smitzer, G.H.Sigel, J. Non-Cryst. Solids **182**, 257 (1995).
[2] Y.G.Choi, K.H.Kim, B.J.Lee, Y.B.Shin, Y.S.Kim, J.Heo. J. Non-Cryst. Solids **278**, 137 (2000).
[3] J.S.Sanghera, I.D.Aggarwal, J. Non-Cryst. Solids, **256 &257**, 6 (1999).
[4] V.K.Tikhomirov, I.Iakoubovskii, P.W.Hertogen, G.J.Adriaenssens, Appl. Phys. Lett. **71**, 2740 (1997).
[5] Properties, Processing and Applications of Glass and Rare Earth Doped Glasses for Optical Fibers, Ed. D.Hewak, INSPEC, London, UK, 1998.
[6] S.H.Park, D.C.Lee, J.Heo, J.Am.Ceram.Soc., **3**(5), 1284 (2000).
[7] B.R.Judd, Phys. Rev., **127**, 750 (1963).
[8] G.S.Ofelt, J. Chem. Phys, **37**, 511 (1963).
[9] R.S.Quimby, B.G.Aitken, J. of Non-Cryst. Solids, **320**, 100 (2003).
[10] S.G.Bishop, D.A.Turnbull, B.G.Aitken, J. of Non-Cryst. Solids, **266-269**, 876 (2000).
[11] R.S.Quimby, B.G.Aitken, J. Appl. Phys., **82**, 3992 (1997).
[12] Erbium-Doped Fiber Amplifiers, Eds. P.C.Becker, N.A.Olsson, J.R.Simpson, Academic Press, 1999.
[13] D.Lezal, M.Poulain, J.Zavadil, Ceramics – Silikaty, **45**, 105 (2001).
[14] A. Tverjanovich, Ya.G.Grigoriev, S.V.Degtyarev, A.V.Kurochkin, A.A.Man'shina, Yu.S.Tver'yanovich, J. of Non-Cryst. Solids, **286**, 89 (2001).
[15] A.B.Seddon. D.Furniss, M.S.Iovu, S.D.Shutov, N.N.Syrbu, A.M.Andriesh, P.Hertogen, G.J. Adriaenssens, J. Optoelectron. Adv. Mater. **5**, 1107 (2003).
[16] M. Iovu, A.Andriesh, I,Culeac, J. Optoelectron. Adv. Mater. **7**, 2323 (2005).
[17] N. F. Mott, E. A. Davis, Electronic Processes in Non-Crystalline Materials, Clarendon Press, Oxford, 1979.