The spontaneous emission probabilities for Ga-La-S:Pr³⁺ glass

A. NISTREANU[a*], N. ENACHI[a], M. IOVU[a], V. KOROLI[b], D. FURNISS[c], A. SEDDON[c]

[a]Institute of Applied Physics, Academy of Science of Moldova, Str. Academiei 5, MD- 2028 Chisinau, R. Moldova
[b]Institute of Chemistry, Academy of Science of Moldova, Str. Academiei 3, MD- 2028 Chisinau, R. Moldova
[c]Novel Photonic Glasses Group, University of Nottingham, Nottingham N67 2RD, UK

The absorption and emission spectra of chalcogenide glasses (Ga-La-S:O) doped with trivalent Praseodymium were experimentally investigated and theoretically discussed. The glasses show bright luminescence due to Pr³⁺ ion emission. The effect of oxygen on the luminescence spectra is determined by decreasing of host glass self-absorption of the short-wavelength bands. In order to obtain the good agreement between the theoretical model and experimental results we apply the Judd-Ofelt theory for this glass matrix. Radiative transition rates are calculated and compared with measured experimental parameters. The radiative and non-radiative transition processes between the energy levels of the Pr³⁺ ions stimulated by optical and acoustical vibration modes are proposed in order to obtain the quantitative correlation between the proposed theoretical model and experimental results.

1. Introduction

Gallium lanthanum sulfide (Ga-La-S) glass was investigated intensively last years as perspective host materials for development of active optical elements for optoelectronics (solid state laser materials). The trivalent Praseodymium ion (Pr³⁺) in glasses presents an intricate energy level scheme Fig. 1, with energy gaps of various magnitudes, and several metastable levels emitting multi-colored light. The complex spectral output Pr³⁺ has made this system a good candidate for such various applications as a laser ion [1,2], and low cost integrated photonic devices [3-5]. Chalcogenide glasses doped with rare earth elements present great interest both as perspective materials for development of light amplifiers as well as laser sources for IR spectral range [5]. Typical examples of the active components include the optical amplifiers based on the Er³⁺ doped silica fibers, which are commercially available in the wavelength region of 1.53 to 1.56 μm. Other potential applications are oscillators, super luminescent and laser sources. Among the advantages of rare earth doped chalcogenide glasses one should mention: high transmission in IR (up to 12 μm), high refractive index (n ≈ 2.4), low phonon energy, good chemical stability, easy fiber fabrication and large glass formation regions, promising host materials to enhance the emission efficiency of the luminescence at mid-infrared wavelengths.

The electronic configuration of the ion Pr³⁺ is (closed shells + 4f²). The total number of the ion 4f² quantum states is 91. The electron-electron interaction creates the LS terms ³H, ³F, ¹G, ¹D, ¹I, ³P and ¹S. The spin orbit interaction splits the LS terms into J sublevels, but mixes

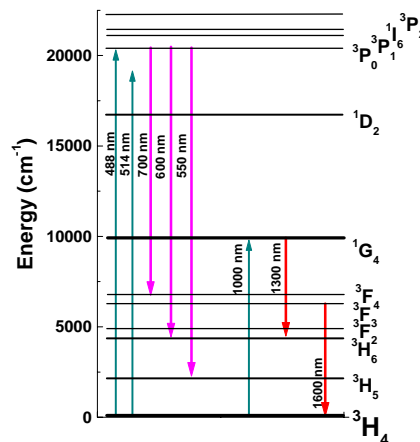states with the same J and different L and S. An energy level scheme is presented in Fig. 1.

Fig. 1 Energy level scheme of Pr³⁺ in glasses.

Trivalent praseodymium is indeed a spectral entity that can benefit from the application of a theoretical tool explaining the observed data and pointing the search for a complete and satisfactory picture in the right direction.

The Judd-Ofelt (J-O) theory [6, 7, and 13] has had a remarkable success in the characterization of radiative transitions in rare earth doped glasses. In the standard Judd-Ofelt technique, the three Judd-Ofelt parameters $\Omega_2, \Omega_4, \Omega_6$ are determined by measuring the integrated absorption coefficient for a number of ground state

transitions, and requiring that the differences between the measured and calculated integrated absorption coefficient be minimized. These parameters can then be used to calculate the emission or absorption between any pair of excited states, which allows a quantitative estimate of stimulated emission or exited-state absorption cross sections. So the purpose of this paper is to review the applications of the J-O theory to the Pr^{3+} ion and to use this system to clarify its limits and validity.

2. The Praseodymium ion in gallium lanthanum sulfide

2.1. IR transmission region

Our data for the absorption spectra of Pr^{3+} in Ga-La-S:O glass were taken from [4,5]. We briefly summarize that the GLS glasses were prepared by melting from standard sulphides (Merck Ltd) at 1150°C, 5 hours, in a vitreous carbon crucible inside an evacuated silica ampoule. Oxygen was introduced in the form of La_2O_3 at the expense of La_2S_3. Samples of the type 70/30GLSx%[O]y%[Pr] have been examined, where 70/30 GLS denotes the $0.70Ga_2S_3:0.30La_2S_3$ composition with the cationic ratio Ga/Ln=0.70/0.30, x and y are weight percentage of oxygen and praseodymium, respectively. The one compositions with 2.95 wt %[O] was chosen as core/clad glass materials stable against crystallization. Pr concentration y was 1.0 wt %.
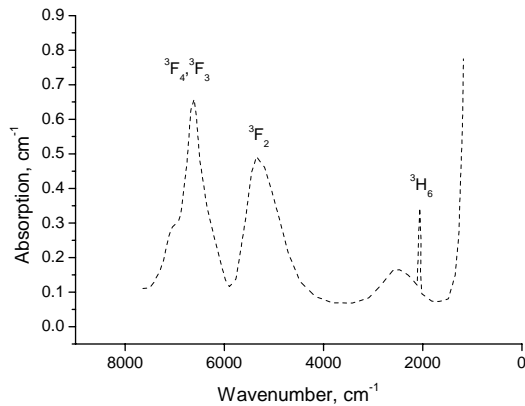

Fig. 3. Absorption spectra of 70/30GLS 2.95%[O] sample with Pr content 1% in the wavelength regions of 0.54-0.66 μm.

Fig.2. IR absorption spectra of 70/30GLS 2.95%[O] samples with Pr content 1.0%
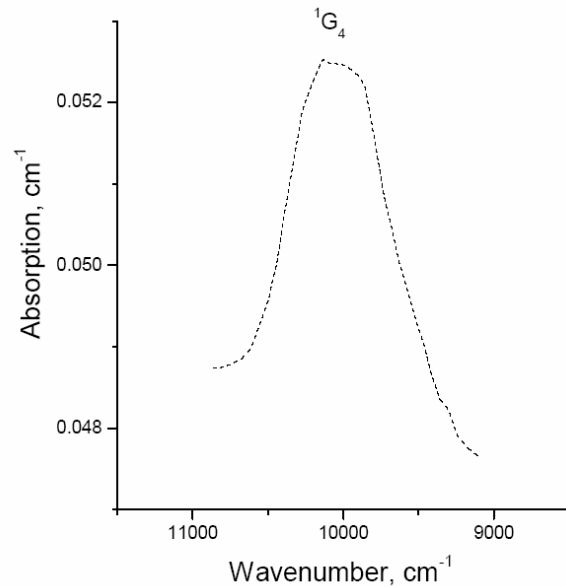
Fig. 4. Absorption spectra of 70/30GLS 2.95%[O] sample with Pr content 1% in the wavelength regions of 0.87-1.1 μm.

The composition (mol %) of this sample is 70Ga2S3·30La₂S₃·2.95%[O]·1.0%[Pr] with the concentration $\approx 8 \times 10^{19}$ cm⁻³. Where the concentration was calculated taking into account the molar percentage of a sample ant its density. The absorption spectrum of the 1% -doped sample is shown in Fig. 2-4 and summarized in Table I.
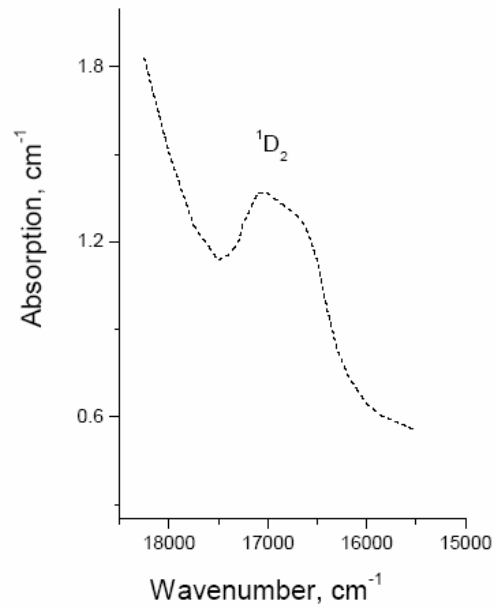
In accord with these experimental data we have calculated the theoretical value of Judd-Ofelt parameters $\Omega_2, \Omega_4, \Omega_6$ that were determined by measuring the integrated absorption coefficient for a number of ground

state transitions represented in the figures above with their absorption spectra(see below Judd-Ofelt theory).

2.2. Photoluminescence measurements

Photoluminescence spectra were recorded with a computer driven monochromator. The spectra were recorded for each sample in the wavelength region of 500-1200 nm. Figure 2 illustrates a typical photoluminescence spectrum of the Ga-La-S glasses doped with 1.0 wt% Pr^{3+}. A very strong band is observed at approximately 655 nm. The wavelength at which this PL occurs is consistent with results reported in other papers for Pr ions [4, 5]. Several other PL bands occur at around 540, 620, 637, 700 and 740 nm. The intensity of the PL band at 655 nm increases strongly with increasing the excitation light intensity. The previous study of PL in Pr-doped Ga-La-S glasses [4, 5] detected almost the same strong PL bands in the visible spectra.
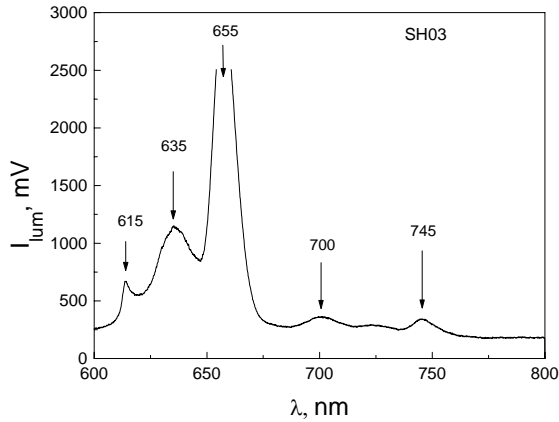

Fig. 5. Spectral distribution of photoluminescence on Pr^{3+}-doped Ga:La:S glass (70/30 GLS 2.95%[O] 1.00% [Pr].

3. Judd-Ofelt theory

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.

According to the Judd-Ofelt theory the line strength of the electric dipole transition between an initial 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 $\left\langle \|U^{(t)}\| \right\rangle$ 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 or integrated absorption coefficient from the relation [10,11]

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

where:
$\alpha(\nu)$ - is the absorption coefficient in cm^{-1};
$\overline{\nu}$ - is the mean frequency (wavenumber) in cm^{-1} at absorption band;
N - is the concentration of Pr^{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(n $\approx$ 2.404 for 2.95 wt.%[O]).

The factor $\frac{(n^2+2)^2}{9n}$ - is the local field correction for the ion in a dielectric medium.

Each value of $\int_i \alpha(\nu)d\overline{\nu}$ is determined by numerical integration of the various absorption bands obtained from spectrophotometer measurements. By using (1) and (2), the measured absorption peak area (see fig. 2-4) can be written in terms of the Ω_t parameters: if there are i bands used than for each experimental (measured) absorption band B_i^{exp} an equation of the form

$$\int_i \alpha(\nu)d\overline{\nu} = B_i^{exp} = a_i\Omega_2 + b_i\Omega_4 + c_i\Omega_6 \qquad (3)$$

where

$$a_i = \frac{8\pi^3 e^2 N\overline{\nu}}{3hc(2J+1)} \left[\frac{(n^2+2)^2}{9n} \right] \left| \langle (SL)J | U^{(2)} | (S'L')J' \rangle \right|^2$$

$$b_i = \frac{8\pi^3 e^2 N\overline{\nu}}{3hc(2J+1)} \left[\frac{(n^2+2)^2}{9n} \right] \left| \langle (SL)J | U^4 | (S'L')J' \rangle \right|^2 \quad (4)$$

$$c_i = \frac{8\pi^3 e^2 N\overline{\nu}}{3hc(2J+1)} \left[\frac{(n^2+2)^2}{9n} \right] \left| \langle (SL)J | U^{(6)} | (S'L')J' \rangle \right|^2$$

The set of i equations obtained overdetermines the Ω_t parameters and can be solved using a last squares fitting method.

The forms of the equations used in the least squares fitting procedure are [12, 13, and 14]:

$$\sum_i a_i B_i^{exp} = \sum_i a_i^2 \Omega_2 + \sum_i a_i b_i \Omega_4 + \sum_i a_i c_i \Omega_6$$

$$\sum_i b_i B_i^{exp} = \sum_i a_i b_i \Omega_2 + \sum_i b_i^2 \Omega_4 + \sum_i b_i c_i \Omega_6 \qquad (5)$$

$$\sum_i c_i B_i^{exp} = \sum_i a_i c_i \Omega_2 + \sum_i b_i c_i \Omega_4 + \sum_i c_i^2 \Omega_6$$

which can be solved using conventional matrix methods. The object of the procedure is to minimize the sum of the squares of the differences between the measured band area and that which is calculated (the residuals) i.e.

$$\frac{\partial \sum_i (B_i^{exp} - B_{calc})^2}{\partial \Omega_{2,4,6}} = 0 \qquad (6)$$

Once the Ω_t parameters have been calculated, various radiative properties of the Lanthanide ion in that particular host can be evaluated.

The measured integrated absorption coefficient for the five absorption bands lying between 500nm and 5000nm for the Pr^{3+} in GaLaS:O are given in table I. The mean frequency in cm^{-1} of each band and the $\langle (SL)J |$ designation of the terminal J manifolds involved are also listed.

Table 1. Integrated absorption coefficients for Pr^{3+} in GaLaS:O

$\langle (SL)J |$	Wavenumber $\bar{\nu}$,cm^{-1}	B_{exp}^i ,cm^{-2}	B_{calc}^i ,cm^{-2}	ΔB
$^1D_2$	17000	134.9	69.9	65
$^1G_4$	10136	5.2	5.5	-0.3
$^3F_4, ^3F_3$	6609	399.1	403.0	-3.9
$^3F_2, ^3H_6$	5348	369.5	379.0	-9.5
$^3H_5$	2060	101.4	44.8	56.6

The quality of the fit of the model to Pr^{3+} in GaLaS:O integrated absorption coefficients can be expressed in terms of the rms-B deviation in integrated absorptions and in rms-ΔB deviation that are defined as[10]

$$\Delta B_{rms} = \left[\frac{\sum_i (\Delta B)^2}{N-3} \right]^{\frac{1}{2}} = \left[\frac{\sum_i (\Delta B_{exp}^i - B_{calc}^i)^2}{N-3} \right]^{\frac{1}{2}} = 61.316$$

$$\Delta B_{rms} = \left[\frac{\sum_i (B_{calc}^i)^2}{N-3} \right]^{\frac{1}{2}} = 395.68$$

The percent error for the study is

$$100\% \frac{\Delta B_{rms}}{B_{rms}} = 100\% \frac{61.316}{395.68} \approx 15\%$$

The ratio $\dfrac{B_{calc}}{B_{exp}}$ also gives useful information about the reliability of the calculations. This error is comparable to the errors reported for the intensities fitting of rare-earth ions in Y$_2$O$_3$ [9].

The intensity parameters $\Omega_t (t = 2,4,6)$ can be obtain from more than three measured absorption cross sections by using the method of least squares fitting reported above.

These parameters in our case for the trivalent praseodymium ion (Pr^{3+}) doped (Ga-La-S:O) glasses are

$$\Omega_2 = 0.61378 \times 10^{-20} cm^2$$
$$\Omega_4 = 2.8076 \times 10^{-20} cm^2 \qquad (7)$$
$$\Omega_6 = 0.73805 \times 10^{-20} cm^2$$

We can compare our parameters with those from [8] that are

$$\Omega_2 = 7.3 \times 10^{-20} cm^2$$
$$\Omega_4 = 6.2 \times 10^{-20} cm^2 \qquad (7^1)$$
$$\Omega_6 = 3.9 \times 10^{-20} cm^2$$

We see that in [8] we have the same material Pr^{3+} doped Ga-La-S, the unique differences is that in our sample we have a small concentration of 2.95 wt.%[O] that change the behavior in absorption spectra. The reason of differences of intensities parameters (7) and (7^1) is due to area measurements, where the IR absorption spectra from [8] are four or three times higher than our plot-data. The physical meaning of these results is due to addition of lanthanum oxide into GaLaS glass that reduces the quantum efficiency and introduces pump wavelength dependence. The idea is that lanthanum oxide substituted into the glass matrix creates new sites for the rare earth ion (see above that oxygen was introduced in the form of La$_2$O$_3$), and the new sites cause large inhomogeneous broadening.

Also we can compare with another rare earth elements so we have that the transition probabilities in Nd^{3+} ions are dominated by the Ω_6 value, that in Dy^{3+} ion is dominated mainly by the Ω_2 value, which is strongly dependent on the ligand field symmetry or the host composition, and often takes the largest value among three parameters. The Ω_2 value increases with increasing covalence of rare-earth and ligand bond.

The spontaneous emission probability A from an initial manifold $|(S,L)J\rangle$ to a final manifold $|(S',L')J'\rangle$ can be calculated using the following equation:

$$A(J,J') = \frac{64\pi^4 e^2 \bar{\nu}^3}{3h(2J+1)} n \left[\frac{(n^2+2)^2}{9} \right] \times \sum_{t=2,4,6} \Omega_t \left| \langle (SL)J \| U^{(t)} \| (S'L')J' \rangle \right|^2$$

(8)

Table 2. Spontaneous emission probabilities, radiative lifetimes from Judd-Ofelt parameters for ion (Pr^{3+}) doped (Ga-La-S:O) glasses

Transition	E, cm^{-1}	$\bar{\lambda}$, nm	A_{JJ} s^{-1}	τ, s
$^3P_0 \rightarrow {}^1D_2$	3900	2564	6	
$\rightarrow {}^1G_4$	10800	925.9	1742	
$\rightarrow {}^3F_4$	13850	722.0	10486	
$\rightarrow {}^3F_2$	15700	636.9	8102	
$\rightarrow {}^3H_6$	16400	609.7	2739	
$\rightarrow {}^3H_4$	20650	484.2	49083	
			72158	1.38×10^{-5}
$^1D_2 \rightarrow {}^1G_4$	6950	1438	341	
$\rightarrow {}^3F_4$	10000	1000	760	
$\rightarrow {}^3F_3$	10450	956.9	157	
$\rightarrow {}^3F_2$	11850	843.8	912	
$\rightarrow {}^3H_6$	12550	796.8	854	
$\rightarrow {}^3H_5$	14750	677.9	42	
$\rightarrow {}^3H_4$	16800	595.2	1044	
			4110	2.4×10^{-4}
$^1G_4 \rightarrow {}^3F_4$	3050	3278	21	
$\rightarrow {}^3F_3$	3500	2857	2	
$\rightarrow {}^3F_2$	4900	2040	3	
$\rightarrow {}^3H_6$	5600	1785	179	
$\rightarrow {}^3H_5$	7800	1282	285	
$\rightarrow {}^3H_4$	9850	1015	27	
		2042	517	1.93×10^{-3}
$^3F_4 \rightarrow {}^3F_3$	450	22222	0.02	
$\rightarrow {}^3F_2$	1850	5405	0.62	
$\rightarrow {}^3H_6$	2550	3921	57	
$\rightarrow {}^3H_5$	4750	2105	187	
$\rightarrow {}^3H_4$	6800	1470	211	
			455.6	2.19×10^{-3}
$^3F_3 \rightarrow {}^3F_2$	1380	7246	0.7	
$\rightarrow {}^3H_6$	2100	4761	23	
$\rightarrow {}^3H_5$	4300	2325	179	
$\rightarrow {}^3H_4$	6350	1574	212	
			414.7	2.41×10^{-3}
$^3F_2 \rightarrow {}^3H_6$	700	14285	0.2	
$\rightarrow {}^3H_5$	2900	3448	20	
$\rightarrow {}^3H_4$	4950	2020	432	
			452.2	2.21×10^{-3}
$^3H_6 \rightarrow {}^3H_5$	2200	4545	11	
$\rightarrow {}^3H_4$	4250	2352	13	
			24	4.16×10^{-2}
$^3H_5 \rightarrow {}^3H_4$	2050	4878	9.8	1.02×10^{-1}

where $\bar{\nu}$ - is the mean wavenumber of the particular emission band (the peak).

However, there have been few reports on the relationship between the structure and Ω_t (t=2,4,6) in glasses: only a semiimperical relation between Ω_6 and the ligand field asymmetry has been reported.

Among three Ω_t parameters of Pr^{3+} obtained by Judd-Ofelt analysis in glasses Ω_4 is most sensitive to the overlap integrals of *4f* and *5d* orbitals.

The total radiative rate of a manifold is the sum of the intermanifold spontaneous emission rates [15]

$$A_J = \sum_{J'} A_{JJ'}$$

(9)

Or in other words by summing the $A_{JJ'}$ coefficient over all final states, we can find the radiative lifetimes of individual levels. We have

$$\tau_{rad} = \frac{1}{\sum A_{JJ'}}$$

(10)

Taking into account all this formula we can calculate theoretically the spontaneous probabilities, the radiative rate, and radiadive lifetimes for various levels. The reduced matrix elements that appear in (1) can be taken from tables such as the ones reported in Kaminskii's books [1,2]. The data for the trivalent praseodymium ion (Pr^{3+}) doped (Ga-La-S:O) glasses are reported in Table II.

4. Discussion

From the Fig. 5 and Table II we conclude that the fluorescence centered at 655 nm can be attributed with $^1D_2 \rightarrow {}^3H_5$ transition and is quite smooth over this band. Fluorescence at 635 nm is associated with the $^3P_0 \rightarrow {}^3F_2$ transition. The emission in the 480-615 nm bands is associated with $^3P_0 \rightarrow {}^3H_6$, $^3P_0 \rightarrow {}^3H_4$, $^1D_2 \rightarrow {}^3H_4$, and the emissions in the 745-850 nm is associated with $^1D_2 \rightarrow {}^3H_6$, $^1D_2 \rightarrow {}^3F_2$ and $^3P_0 \rightarrow {}^1D_2$. Since emission from these transitions overlap, it is not possible to separate under 488 nm pumping where all initials states are populated.

The results obtained for the application of Judd-Ofelt theory to (Ga-La-S-O):Pr^{3+} presents an outcome: that the large uncertainty with the Judd-Ofelt parameters, have been obtained. Error estimate for the rates of Table I are $\pm 15\%$ and are based upon rms deviation between calculated and experimental integrated absorbaces in the Judd-Ofelt least square fit, also error Pr^{3+} concentration determination. This outcome should be examined vis-à-vis the approximations that have been introduced: (i) all the states of the *4f5d* configuration are assumed to have the same energy, and (ii) the energy –spreading of the $4f^2$ states is considered to be much smaller than the difference between their average energy and that of *4f5d* configuration.

5. Conclusions

(1) We have theoretical calculated the intensities parameters Ω_2, Ω_4, Ω_6 that were determined by measuring the integrated absorption coefficient for five ground state transitions of Pr^{3+} in Ga-La-S:O glass. For these

calculations we can conclude that for obtaining a good agreement with experiment one must have at least 5-6 absorption area bands. Also the errors in determining the areas under the $\alpha(\nu)$ curves affect the relative intensities as well, and arise not only from errors in measuring a prescribes area, but also in determining the base line for zero rare-earth absorption when two or more transitions groups lie close to one another. When the overlap area between two groups exceed 5% of the total area for the two groups, the total area was measured and the matrix elements corresponding to the two transitions were combined and treaded as a single experimental point in the fitting process.

(2) We have spectroscopically characterized the transitions of Pr^{3+} in Ga-La-S:O glass. The fluorescence spectra were taken and decay lifetimes of the lower lying states measured. A Judd-Ofelt analysis was performed to characterize the radiative rates of these manifolds.

(3) Also one concludes that the photoluminescence of Pr^{3+} in Ga-La-S chalcogenide glass samples can be seen red with naked eye. The excitation at 0.488 μm populates the P manifold and provides radiative transitions to lower lying terms. The room temperature emission presents broad and unresolved bands characteristic of inhomogenously disordered glass matrix. The strong photoluminescence bands in the visible region of the spectra confirm the perspective of Ga-La-S glasses for application in optoelectronics.

References

[1] A. Kaminskii, B. M. Antipenco, Multilevel Operating Schemes of Crystals Lasers, Moscow: Nauka (1989)

[2] A. Kaminskii, Crystalline Lasers, CRC Press, Boca Raton (1996)

[3] S. Ramachandran, E. Reuter, D. Turnbull, J. Verdeyen, S. Bishop, J.Appl. Phys. **77**(7), p.3365-3371 (1995)

[4] A. B. Seddon D. Furniss, M. S. Iovu, S. D. Sutov, N. N. Syrbu, A. M. Andriesh, P. Hertogen, G. J. Adriaenssens, J. Optoelectron. Adv. Mater. **5**(5), 1107 (2003).

[5] A. B. Seddon, D. Furniss, M. S. Iovu, S. D. Sutov, N. N. Syrbu, A. M. Andriesh, P. Hertogen, G. J. Adriaenssens, Journ. of Non-Crystalline Solids, **326&327**, 279 (2003).

[6] B. R. Judd Optical absorption in rare earth ions Phys Rev **127**, 750 (1962).

[7] G. S. Ofelt, Intensities of crystal spectra of rare earth ions, J. Chem. Phys, **37**, 511 (1962).

[8] D. W. Hewak, 1. A. Medeiros Neto, B. Samson, R. S. Brown, K. P. Jedrzejewski, IEEE Phot. Techn. Letters **6**, 5 (1994).

[9] W. F. Krupke, Phys. Rev. **145**, 325 (1966).

[10] W. F. Krupke, "IEEE J. Quant. Electron. **7**, 153 (1971).

[11] W. F. Krupke, IEEE J. Quant. Electron. **10**, 450 (1974).

[12] R. S. Quimby, J. Appl. Phys. **75,** 613 (1994).

[13] K. Gschneider, "Handbook on the physics and chemistry of rare earth", **25**, 165 (1998).

[14] J. Hoffman, "Numerical methods for engineers and scientists", p. 237, New-York (2001)

[15] L. B. Shaw , B. B. Haribson, Optics Express **1**(4), 87 (1997).

[16] B. E. Bowlby, J. of Luminescence **100**, 131 (2002).

_____

[*]Corresponding author: nistreanuandrei@gmail.com