

SPECTROSCOPIC PROPERTIES OF Pr³⁺ IONS IN Ge-In-S CHALCOGENIDE GLASSES

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The Judd-Ofelt parameters (Ω_2 , Ω_4 , Ω_6) of Pr³⁺ ions in ((GeS₂)₈₀(In₂S₃)₂₀)_{100-x}(Pr₂S₃)_x glasses (x=0.5-7) were determined from the values of experimentally obtained electric dipole oscillator strengths of intra-f configuration electron transitions. Absolute as well as normalized minimization fitting procedures using five or six transitions were applied for the determination of Judd-Ofelt parameters. Obtained values of Judd-Ofelt parameters, root mean square deviations, and other optical parameters (probabilities of spontaneous radiative electron transitions, emission cross-sections) are discussed in relation with different concentration of Pr³⁺ ions in studied glasses and with the type of calculation.

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1. Introduction

Rare-earth (RE) – doped chalcogenide glasses (ChG) are prospective inorganic materials for photonic applications such as fiber amplifiers and lasers [1,2]. Over oxide and halide glasses, ChG are favourable due to lower phonon energy, higher index of refraction, and broader transmission window in infrared (IR) spectral region [1-3]. In detail, Pr³⁺-doped ChG are applicable in near-IR spectral region (XS-band \cong 1.3 μ m using ¹G₄ \rightarrow ³H₅ and U-band \cong 1.6 μ m using (³F₄, ³F₃) \rightarrow ³H₄ intra-f-configuration electron transitions, respectively) [3,4]. In mid-IR, for applications is interesting broad-band emission in 3-5 μ m spectral region originating from ¹G₄ \rightarrow (³F₄, ³F₃), ³F₄ \rightarrow ³F₂, (³F₄, ³F₃) \rightarrow ³H₆, (³F₂, ³H₆) \rightarrow ³H₅, and ³H₅ \rightarrow ³H₄ transitions of Pr³⁺ ions [5,6].

Spectroscopic properties of RE³⁺ ions are usually evaluated using phenomenological approach based on Judd-Ofelt theory [7,8]. Evaluation of Judd-Ofelt parameters Ω_t (t = 2, 4, 6) in sulphide and even more in selenide glasses is a difficult task. The main problem is that the position of short-wavelength absorption edge (optical band gap) is often located in the red or in near-IR and the number of absorption bands of RE³⁺ ions available for calculations is drastically limited. Low number of absorption bands used in the calculations results in less confidence of obtained Judd-Ofelt parameters [2].

It is well-known that simple binary ChG can contain only small amount of RE³⁺ ions (compounds) without crystallization, segregation or clustering [9]. On the other hand, modification of binary ChG with some elements (for example Ga) leads to significantly higher solubility of RE resulting from structural changes (modifications) of the amorphous matrix [10]. In this study, Ge-In-S glassy matrix was selected as host for RE³⁺ doping in order to evaluate the solubility of Pr.

In order to estimate and discuss the validity of Judd-Ofelt parameters for different concentrations of Pr³⁺ ions, Judd-Ofelt calculation for Pr³⁺ ion embedded in selected chalcogenide glass from Ge-In-S system was performed, applying absolute as well as relative minimization fitting procedures using five or six absorption lines.

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2. Experimental

Glass samples were prepared by well-established melt-quenching method. The starting materials were used in their element forms: Ge, In, and S all of ~ 5N-purity and Pr of 3N-purity. Batches placed inside sealed and evacuated silica ampoules were melted in a rocking furnace at 970 °C for 8 hours. The ampoules with the melt were subsequently quenched in undercooled water with salt.

The obtained glasses were optically homogeneous, of orange to dark red color. The homogeneity of the individual samples and absence of any crystalline phase was confirmed by optical transmission measurements, optical, electron microscopy and by X-ray diffraction.

The transmission spectra of cut and polished plan-parallel plates of prepared glasses were measured using spectrophotometers Perkin-Elmer Lambda 9 (VIS, NIR) and BIORAD FTS 175C (NIR, MID). Room-temperature photoluminescence spectra were obtained by pumping the samples at 1064 nm with continuous-wave Nd:YAG laser (20 mW). The emission spectra were detected with a liquid nitrogen cooled Ge detector. In the spectral region 500-1500 nm, the index of refraction of studied glasses was determined by the analysis of ellipsometric data (measured at three different angles of incidence - 65, 70, and 75 degrees, variable angle spectral ellipsometer WOOLLAM) using simple Cauchy dispersion formula.

3. Results

The prepared glasses of composition $((\text{GeS}_2)_{80}(\text{In}_2\text{S}_3)_{20})_{100-x}(\text{Pr}_2\text{S}_3)_x$, where $x \leq 7$ mol.% were homogeneous according to the methods mentioned in experimental part and well transparent. The density of studied glasses increased with increasing Pr^{3+} content, $\rho = 3.28\text{-}3.65 \text{ g}\cdot\text{cm}^{-3}$.

The optical transmission of studied glasses was high in broad spectral range from visible to infrared region. The position of short-wavelength absorption edge is located between 500-600 nm in the visible region of the spectrum. The short-wavelength absorption edge is shifted to lower energies with increasing of Pr^{3+} content. The long-wavelength absorption edge of prepared samples was found near 900 cm^{-1} and can be assigned to the multiphonon Ge-S vibrations. The presence of Pr_2S_3 does not influence the position of the long-wavelength absorption edge.

Because of limited transparency window in the visible part of the spectra due to fundamental absorption of the glassy host, only four absorption bands connected with electron transitions from $^3\text{H}_4$ ground state to $^3\text{H}_5$, ($^3\text{H}_6$, $^3\text{F}_2$), ($^3\text{F}_3$, $^3\text{F}_4$) and $^1\text{G}_4$ higher energy levels of Pr^{3+} ions ($\cong 4.32$, 2.03, 1.59 and 1.02 μm) were observed in room-temperature transmission spectra. Absorption band corresponding to the $^3\text{H}_4 \rightarrow ^1\text{D}_2$ transition ($\cong 0.62 \mu\text{m}$) was observable, but hidden in the short-wavelength absorption edge.

Two emission bands ($\cong 1.34$ and 1.61 μm) were observed in the photoluminescence spectra of Pr^{3+} -doped Ge-In-S glasses. The emission band $\cong 1.34 \mu\text{m}$ has a full width at half maximum of the intensity of the emission band (FWHM) of ~70 nm, the second emission band $\cong 1.61 \mu\text{m}$ has a FWHM of ~90 nm.

For the analysis of ellipsometric data, simple model consisting of bulk material (with Cauchy dispersion in refractive index values) and surface roughness layer (described using effective medium approximation) was utilized. Refractive index values obtained using mentioned model increased with increasing content of Pr^{3+} ions; for example at 1.0 μm refractive index increased from 2.17 (for parent glass) to 2.28 (for glass with $x = 7$). Further in IR ($>1.5 \mu\text{m}$), refractive index values were extrapolated using A, B, and C parameters of Cauchy dispersion formula.

4. Discussion

For the testing of the suitability for RE doping, the Ge-In-S glass family was selected. We assumed that the presence of In atoms could increase the RE solubility similarly like Ga atoms in Ge-Ga-S(Se) glasses. On the basis of thermal stability criteria (will be published elsewhere), $(\text{GeS}_2)_{80}(\text{In}_2\text{S}_3)_{20}$ parent composition was selected for Pr doping. This composition is located near the centre of glass-forming region in Ge-In-S system, which predicts easy preparation of stable and homogeneous glasses. Selected parent glass can be also described as stoichiometric compound

consisting of GeS₂ and In₂S₃. Using stoichiometric glassy matrix for RE doping was already shown to be important for values of optical parameters of Sm³⁺ and Dy³⁺ ions; stoichiometric glasses from Ge-Ga-Se system have very high values of Judd-Ofelt parameters. From the spectroscopic quality factor (given by Ω_4/Ω_6 ratio) point of view, the best optical glass (from Ge-Ga-Se glassy system doped with Sm³⁺ ions) is also the stoichiometric one [11].

We have found that in (GeS₂)₈₀(In₂S₃)₂₀ glass one can incorporate unexpectedly high content (up to 7 mol.%, i.e. 1.63×10^{21} Pr atoms.cm⁻³) of Pr₂S₃ without any observable crystallization or segregation. The integrated areas of absorption bands of Pr³⁺ ions are increasing with increasing content of praseodymium nearly linearly up to 3 mol.% of Pr₂S₃ (Fig. 1). We believe that the optical activity of Pr³⁺ ions does not change with their concentration in glassy matrix up to mentioned content.

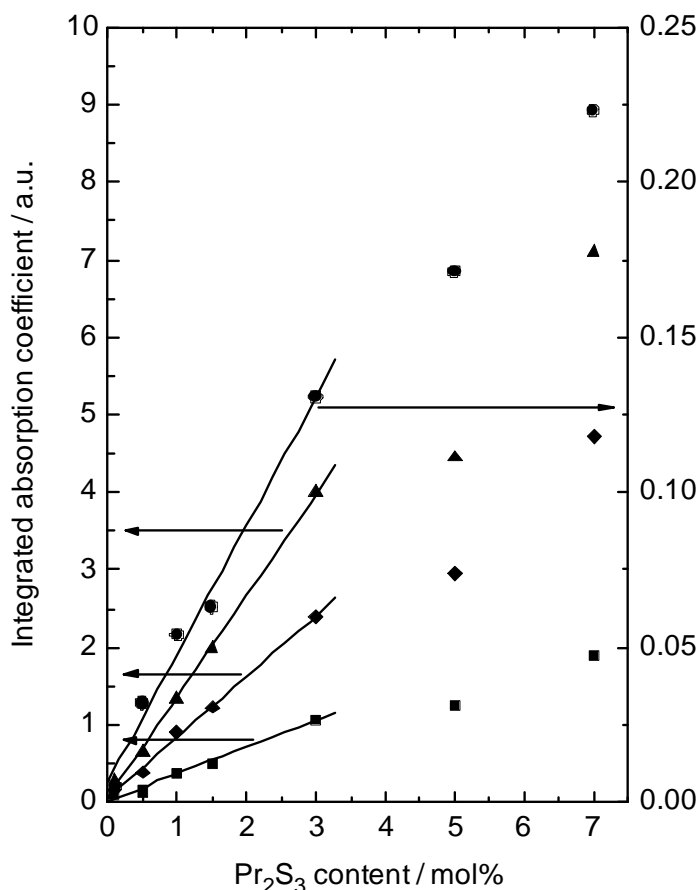


Fig. 1. Concentration dependencies of areas of absorption bands assigned to electron transitions of Pr³⁺ ions. Absorption bands connected with transitions: ${}^3\text{H}_4 \rightarrow {}^3\text{H}_5$ (squares), ${}^3\text{H}_4 \rightarrow ({}^3\text{H}_6, {}^3\text{F}_2)$ (diamonds), ${}^3\text{H}_4 \rightarrow ({}^3\text{F}_3, {}^3\text{F}_4)$ (triangles), and ${}^3\text{H}_4 \rightarrow {}^1\text{G}_4$ (circles).

For Judd-Ofelt calculations [7,8], the experimental oscillator strengths of electric dipole transitions (f_{ed}^{exp}) of Pr³⁺ ions in ((GeS₂)₈₀(In₂S₃)₂₀)_{100-x}(Pr₂S₃)_x glasses were calculated from the room temperature transmission spectra. The experimental oscillator strength of ${}^3\text{H}_4 \rightarrow {}^3\text{H}_5$ pure electric-dipole transition was obtained after subtraction of the magnetic dipole contribution, S-H and CO₂ absorption. Because of strong overlap in case of absorption bands assigned to ${}^3\text{H}_4 \rightarrow ({}^3\text{H}_6, {}^3\text{F}_2)$ and ${}^3\text{H}_4 \rightarrow ({}^3\text{F}_3, {}^3\text{F}_4)$ transitions, the individual absorption bands (${}^3\text{H}_4 \rightarrow {}^3\text{H}_6$, ${}^3\text{H}_4 \rightarrow {}^3\text{F}_2$, ${}^3\text{H}_4 \rightarrow {}^3\text{F}_3$, and ${}^3\text{H}_4 \rightarrow {}^3\text{F}_4$) were determined by fitting of these bands using Voigt profiles of individual

transitions assuming spectral line shapes resulting from a superposition of independent Lorentzian (homogeneous) and Doppler (inhomogeneous) line broadening mechanisms in real systems.

The electric dipole oscillator strength between states $|a\rangle$ and $|b\rangle$ is

$$f_{ed} = \frac{8\pi^2 mc\sigma}{3h(2J+1)} \chi \sum_{t=2,4,6} \Omega_t \left| \langle a \| U^{(t)} \| b \rangle \right|^2, \quad (1)$$

where m is electron mass, c is the speed of light, σ is transition's wavenumber, h is Planck's constant, J is angular momentum of the initial level in the transition, χ is the field correction factor ($\chi = (n^2+2)^2/9n$ where n is the refractive index of the material), and $\langle a \| U^{(t)} \| b \rangle$ are doubly reduced matrix elements of the tensor operator $U^{(t)}$. Doubly reduced matrix elements of the tensor operator, $U^{(t)}$, are assumed to be independent of the host and, therefore, we have used their values calculated by Weber [12]. Judd-Ofelt parameters Ω_2 , Ω_4 , and Ω_6 are commonly evaluated by the least square fit to a set of M experimental values of electric dipole oscillator strengths. The standard (absolute) least square method minimizes the sum of the absolute differences $\sum_i (f_i^{\text{exp}} - f_i^{\text{calc}})^2$ using so-called root mean square (RMS) as follows [13]:

$$RMS = \sqrt{\frac{\sum_i (f_i^{\text{exp}} - f_i^{\text{calc}})^2}{M-3}}. \quad (2)$$

Normalized method minimizes the sum of the relative differences $\sum_i [(f_i^{\text{exp}} - f_i^{\text{calc}}) / f_i^{\text{exp}}]^2$ [13,14]:

$$RMS_{\text{norm}} = \sqrt{\frac{1}{M-3} \sum_i \left(\frac{f_i^{\text{exp}} - f_i^{\text{calc}}}{\sigma_i} \right)^2}, \quad (3)$$

where σ_i is standard deviation in determination of f_i^{exp} and is assumed to be constant fraction of f_i^{exp} : $\sigma_i = k \cdot f_i^{\text{exp}}$ with k set to 0.025 (corresponding to 5% error on measured oscillator strengths) [13].

Judd-Ofelt parameters calculated by standard method depend strongly on the magnitude of data included in the fit, i.e. small discrepancy on large f_i^{exp} increases the sum in Eq. (2) as much as large error on small f_i^{exp} . On the other hand, Judd-Ofelt parameters estimated by normalized method (Eq. (3)) should be independent of the magnitude of f_i^{exp} . Because of large differences between the magnitude of f_i^{exp} for Pr^{3+} in some cases (${}^3\text{H}_4 \rightarrow {}^3\text{H}_6$ or ${}^3\text{H}_4 \rightarrow {}^1\text{G}_4$, i.e. weak transitions vs. ${}^3\text{H}_4 \rightarrow {}^3\text{F}_2$ or ${}^3\text{H}_4 \rightarrow {}^3\text{F}_3$, i.e. strong transitions), one can predict more reliable results obtained using normalized method.

We also examined the influence of the number of absorption lines used in the calculations of Judd-Ofelt parameters (6 vs. 5 excluding ${}^3\text{H}_4 \rightarrow {}^1\text{G}_4$ or ${}^3\text{H}_4 \rightarrow {}^3\text{H}_5$ lines). The reason for excluding ${}^1\text{G}_4$ absorption line is that this line is usually the weakest one among observed absorption bands, so the error on measured oscillator strength should be highest. ${}^3\text{H}_4 \rightarrow {}^3\text{H}_5$ lines were not used in some calculations because of uncertainty of their oscillator strengths due to spectral overlap with CO_2 as well as S-H absorption.

The results of absolute and normalized calculations of Judd-Ofelt parameters together with obtained RMS values as well as ${}^1\text{G}_4 \rightarrow {}^3\text{H}_5$ electric-dipole transition characteristics (probabilities (A) and emission cross-sections (σ_e ; calculated using measured line shape of the emission band and Füchtbauer-Ladenburg equation [15])), and ratios between calculated and experimental oscillator strengths are summarized in Table 1 and 2.

From the comparison of obtained Judd-Ofelt parameters, $A({}^1\text{G}_4 \rightarrow {}^3\text{H}_5)$, and $\sigma_e({}^1\text{G}_4 \rightarrow {}^3\text{H}_5)$ values (Tables 1,2) one can observe that the samples can be divided into two groups. First group (glasses doped up to 3 mol.% of Pr_2S_3 , Nr. 1-4) returned higher values of Ω_t ($t = 2, 4, 6$), A , and σ_e parameters, respectively. On the other hand, second group (heavily doped glasses Nr. 5 and 6) has

significantly lower values of mentioned parameters (Tables 1, 2). We believe that this behaviour of samples with very high content of RE can be connected with clustering of RE ions [16]. This hypothesis is supported by lower optical activity of heavily doped glasses (Fig. 1).

It should be noted that there are clear differences in individual Ω_t parameters in glasses of first group. Nevertheless, parameters A and σ_e , that (generally speaking) take into account all three Ω_t values, are well comparable for all glasses in first group: $A(^1G_4 \rightarrow ^3H_5) \sim 1240 \pm 80 \text{ s}^{-1}$, $\sigma_e(^1G_4 \rightarrow ^3H_5) \sim 1.53 \pm 0.08 \times 10^{-20} \text{ cm}^2$ and $A(^1G_4 \rightarrow ^3H_5) \sim 1220 \pm 140 \text{ s}^{-1}$, $\sigma_e(^1G_4 \rightarrow ^3H_5) \sim 1.49 \pm 0.18 \times 10^{-20} \text{ cm}^2$ using absolute and normalized minimization procedures, respectively. Clear differences in values of Judd-Ofelt parameters (glass Nr. 1 vs. glasses Nr. 2-4, Tables 1,2) are probably connected with the overestimation of areas of absorption bands related to S-H/CO₂ absorption in case of $^3H_4 \rightarrow ^3H_5$ absorption line resulting in lower f^{exp} value.

The confidence on the Ω_t parameters (first group; glasses Nr. 1-4) has been analysed on the basis of standard deviation values (σ). We have found that Ω_6 parameter is pretty well determined: $\pm 2\sigma/\Omega_6 \sim 10\%$ and $\sim 13\%$ for absolute and normalized method, respectively. This results from high values of $U^{(6)}$ coefficients in most of the Eq. (1). The $U^{(2)}$ and $U^{(4)}$ coefficients have significantly lower values and that is why the Ω_2 and Ω_4 parameters are determined with less confidence (2σ four times higher in some cases when compared with Ω_6 values).

RMS values obtained using absolute minimization procedure are fairly independent on the number of used absorption lines (6 vs. 5) neither on omitted absorption line ($^3H_4 \rightarrow ^3H_5$, $^3H_4 \rightarrow ^1G_4$) (Table 1). In principle, for absolute method are crucial the strongest absorption lines, which were taken into account in all calculations. The explanation for mentioned independence of RMS is that omitted absorption lines are weak and, in fact, they influence the minimization procedure only marginally.

Table 1. Glass description, Pr₂S₃ content, Judd-Ofelt Ω_t ($t = 2, 4, 6$) parameters, absolute root mean square deviations (RMS), $^1G_4 \rightarrow ^3H_5$ spontaneous emission probabilities (A), $^1G_4 \rightarrow ^3H_5$ emission cross-section (σ_e), and ratios between calculated and experimental oscillator strengths (all transitions are from the ground state 3H_4 to those specified in the table). Sections A, B, and C are for calculations using 6 absorption lines, 5 absorption lines (excluding $^3H_4 \rightarrow ^3H_5$ transition), and 5 absorption lines (excluding $^3H_4 \rightarrow ^1G_4$ transition).

Glass Nr.	Pr ₂ S ₃ content mol.%	Ω_2 10 ⁻²⁰ cm ²	Ω_4 10 ⁻²⁰ cm ²	Ω_6 10 ⁻²⁰ cm ²	RM		A s ⁻¹	σ_e 10 ⁻²⁰ cm ²	$f^{\text{calc}}/f^{\text{exp}}$					
					S 10 ⁻⁷	S			3H_5	3H_6	3F_2	3F_3	3F_4	1G_4
A	1	0.5	7.1	8.5	6.3	6.9	1178	1.45	1.26	0.77	0.99	1.00	0.97	0.34
	2	1	11.9	6.8	6.9	3.2	1238	1.55	0.96	0.99	1.00	1.00	1.01	0.42
	3	1.5	11.9	4.9	7.3	3.2	1261	1.56	1.00	1.45	1.00	1.00	0.99	0.54
	4	3	9.9	5.9	6.9	3.9	1301	1.55	0.91	1.35	1.00	1.00	1.01	0.53
	5	5	7.0	4.9	4.4	2.5	852	1.03	0.91	1.02	1.00	1.01	1.00	0.45
	6	7	7.6	5.5	4.9	1.7	947	1.14	0.96	0.90	1.00	1.00	1.01	0.54
B	1	0.5	7.6	8.0	6.6	5.6	1207	1.49		0.79	1.00	1.00	1.01	0.35
	2	1	11.8	6.9	6.9	3.6	1232	1.54		0.99	1.00	1.00	1.00	0.42
	3	1.5	11.9	4.9	7.3	3.9	1261	1.56		1.45	1.00	1.00	0.99	0.54
	4	3	9.7	6.2	6.8	3.5	1286	1.53		1.34	1.00	1.00	1.00	0.52
	5	5	7.0	4.9	4.4	2.2	846	1.02		1.01	1.00	1.00	0.99	0.45
	6	7	7.5	5.5	4.8	1.9	943	1.13		0.90	1.00	1.00	1.00	0.54
C	1	0.5	7.1	8.5	6.3	6.9	1177	1.45	1.26	0.77	0.99	1.00	0.97	
	2	1	11.9	6.8	6.9	1.5	1237	1.55	0.96	0.99	1.00	1.00	1.01	
	3	1.5	11.9	4.9	7.3	3.2	1261	1.56	1.00	1.45	1.00	1.00	0.99	
	4	3	9.9	5.9	6.9	4.2	1300	1.55	0.91	1.35	1.00	1.00	1.01	
	5	5	7.0	4.9	4.4	2.2	852	1.03	0.91	1.02	1.00	1.01	1.00	
	6	7	7.6	5.5	4.9	1.3	947	1.14	0.96	0.90	1.00	1.00	1.01	

In contrast, RMS values based on normalized minimization procedure are much more sensitive to absorption lines used in the calculations (Table 2). Lowest values of RMS calculated by normalized method (and thus the most reliable results) were obtained using five absorption lines excluding ${}^3\text{H}_4 \rightarrow {}^1\text{G}_4$ transition. When ${}^3\text{H}_4 \rightarrow {}^1\text{G}_4$ line was included in fitting of the data, RMS values significantly increased (Table 2). The problem is that f^{calc} of discussed absorption line is markedly underestimated; it is 35-59 % of f^{exp} , which indeed agrees approximately with published data [13,17]. On the other hand, one can see that determination of f^{calc} (${}^3\text{H}_4 \rightarrow {}^1\text{G}_4$) is using Judd-Ofelt parameters questionable. However, larger set of experimental data should be analyzed in order to solve this problem.

Table 2. Glass description, Pr_2S_3 content, Judd-Ofelt Ω_t ($t = 2, 4, 6$) parameters, normalized root mean square deviations (RMS), ${}^1\text{G}_4 \rightarrow {}^3\text{H}_5$ spontaneous emission probabilities (A), ${}^1\text{G}_4 \rightarrow {}^3\text{H}_5$ emission cross-section (σ_e), and ratios between calculated and experimental oscillator strengths (all transitions are from the ground state ${}^3\text{H}_4$ to those specified in the table). Sections A, B, and C are for calculations using 6 absorption lines, 5 absorption lines (excluding ${}^3\text{H}_4 \rightarrow {}^3\text{H}_5$ transition), and 5 absorption lines (excluding ${}^3\text{H}_4 \rightarrow {}^1\text{G}_4$ transition).

Glass	Pr ₂ S ₃ Nr.	Pr ₂ S ₃ content mol. %	Ω_2 10 ⁻²⁰ cm ²	Ω_4 10 ⁻²⁰ cm ²	Ω_6 10 ⁻²⁰ cm ²	RMS	A s ⁻¹	σ_e 10 ⁻²⁰ cm ²	$f^{\text{calc}}/f^{\text{exp}}$					
									${}^3\text{H}_5$	${}^3\text{H}_6$	${}^3\text{F}_2$	${}^3\text{F}_3$	${}^3\text{F}_4$	${}^1\text{G}_4$
A	1	0.5	4.5	10.9	6.2	17.0	1202	1.48	1.29	0.82	0.95	1.07	0.98	0.35
	2	1	11.5	8.2	7.1	13.0	1299	1.62	1.01	1.05	1.04	1.08	1.05	0.45
	3	1.5	13.9	4.9	6.4	13.8	1154	1.43	0.94	1.28	1.10	0.93	0.88	0.51
	4	3	11.5	6.0	6.4	13.4	1240	1.48	0.89	1.26	1.10	0.97	0.94	0.51
	5	5	7.5	5.1	4.7	12.5	903	1.09	0.96	1.08	1.06	1.07	1.06	0.48
	6	7	6.7	6.9	5.1	10.1	1013	1.22	1.03	0.99	1.03	1.11	1.07	0.58
B	1	0.5	5.9	10.3	7.3	18.4	1341	1.65		0.90	1.02	1.15	1.12	0.39
	2	1	11.6	8.1	7.2	15.9	1302	1.63		1.06	1.05	1.08	1.05	0.45
	3	1.5	13.6	5.0	6.2	16.8	1140	1.41		1.27	1.09	0.92	0.87	0.50
	4	3	11.0	6.2	6.1	16.0	1210	1.44		1.24	1.07	0.95	0.92	0.50
	5	5	7.4	5.1	4.6	15.3	896	1.08		1.07	1.05	1.06	1.05	0.47
	6	7	6.9	6.8	5.2	12.3	1021	1.23		0.99	1.03	1.11	1.08	0.59
C	1	0.5	5.6	9.1	6.2	9.5	1157	1.43	1.23	0.77	0.93	1.00	0.96	
	2	1	11.9	6.9	7.0	1.2	1247	1.56	0.96	1.00	1.01	1.01	1.02	
	3	1.5	13.9	3.9	6.2	9.0	1108	1.37	0.90	1.22	1.06	0.87	0.85	
	4	3	11.8	4.9	6.2	8.2	1190	1.42	0.85	1.20	1.06	0.90	0.91	
	5	5	7.9	4.1	4.6	2.6	868	1.05	0.92	1.02	1.02	1.00	1.03	
	6	7	7.2	5.9	5.0	2.4	972	1.17	0.98	0.94	1.00	1.04	1.04	

In spite of absolute differences in Judd-Ofelt parameters, both methods (absolute or normalized) allow one to estimate most of the transitions' intensities (oscillator strengths) of Pr^{3+} ions in studied ChG with a confidence interval better than $\sim 25\%$ (Tables 1, 2). Unfortunately, few transitions are worse predictable; error in their intensities should be $\sim 60\%$.

Parameters of ${}^1\text{G}_4 \rightarrow {}^3\text{H}_5$ transition ($\cong 1.3 \mu\text{m}$ (spontaneous emission probabilities, radiative lifetimes, etc.) can probably be estimated within $\sim 10\%$ error limit. Satisfactory standard deviation values are connected with larger and better determined $\Omega_6 U^{(6)}$ product coefficient for this transition, resulting from high value of $U^{(6)}$ and the stability of Ω_6 parameter, respectively.

Photoluminescence spectra of studied Pr^{3+} -doped Ge-In-S glasses in near-IR consist of two emission bands $\cong 1.34$ (${}^1\text{G}_4 \rightarrow {}^3\text{H}_5$) and $1.61 \mu\text{m}$ ($({}^3\text{F}_4, {}^3\text{F}_3) \rightarrow {}^3\text{H}_4$), that are typical for ChG doped with Pr^{3+} ions [3,5,18]. The peak emission cross-section values ($\cong 1.34 \mu\text{m}$; glasses Nr. 1-4, Tables 1,2) are approximately 4.3 times that for Pr^{3+} in ZBLAN, 1.8 times that for Pr^{3+} in Ga-La-S [19], and 1.1 times that for Pr^{3+} in Ge-Ga-S glasses [20], respectively. Significantly higher values of σ_e for Pr^{3+} in Ge-In-S glasses can be attributed to different refractive index and/or lower FWHM values.

5. Conclusions

Studied ChG from Ge-In-S family can contain unexpectedly high content (up to 7 mol.%) of Pr₂S₃ without any observable crystallization or segregation. Clustering effects of RE ions in heavily doped glasses (> 3 mol.% of Pr₂S₃) were indicated by lower optical activity in terms of absorption, spontaneous emission probabilities, and emission cross-sections. Absolute minimization as well as normalized minimization fitting procedures using five or six transitions were applied for the determination of Judd-Ofelt parameters and optical parameters (spontaneous emission probability, emission cross-section) of ¹G₄ → ³H₅ transition. The confidence analysis of the Ω_t parameters for glasses doped up to 3 mol. % of Pr₂S₃ showed that Ω₆ parameter is well determined (error limit 13%), while Ω₂ and Ω₄ parameters are determined with less confidence (2σ four times higher in some cases when compared with Ω₆ values). RMS values obtained using absolute minimization procedure are fairly independent on the number of used absorption lines (6 vs. 5) neither on omitted absorption line (³H₄ → ³H₅, ³H₄ → ¹G₄). In opposition, lowest RMS values based on normalized minimization procedure (and thus the most reliable results) were obtained using five absorption lines excluding ³H₄ → ¹G₄ transition. In spite of absolute differences in Judd-Ofelt parameters, most of the transitions' intensities of Pr³⁺ ions in studied ChG can be estimated with a confidence interval better than ~ 25% using both calculation methods (absolute or normalized). Optical parameters of ¹G₄ → ³H₅ transition ≅ 1.3 μm (interesting for applications) can probably be estimated within ~ 10% error limit. Values of emission cross-section for 1.3 μm transition of Pr³⁺ in Ge-In-S glasses are significantly higher than that in other fluoride or sulphide compositions.

In conclusion, we have shown that Judd-Ofelt calculations for Pr³⁺ ions can be performed with satisfactory error limits and reliable results even for ChG with limited number of available absorption bands.

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