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Optical Transitions and Excited State Absorption Cross Sections of SrLaGaO₄ Doped with Ho³⁺ Ions

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Abstract: The spectroscopic properties of SrLaGaO₄ (SLO) crystal doped with Ho³⁺ ions were studied in this work. Absorption, emission spectra and decay dynamics of excited states have been measured and discussed using the Judd–Ofelt model. Photoluminescence emissions were attributed to transitions from the excited ³D₃, ⁵S₂, ⁵F₅, ⁵I₆ and ⁵I₇ multiplet manifolds. The experimental lifetimes for five excited states have been compared to the theoretical values, calculated using Judd–Ofelt theory, allowing for the determination of the multiphonon relaxation rates (W_{nr}) of the respective states. The experimental data were approximately on a line expressed by $W_{nr} = W_0 \exp(-\alpha\Delta E)$ with $W_0 = 0.5 \times 10^7 \text{ s}^{-1}$ and $\alpha = 2.6 \times 10^{-3} \text{ cm}$. To discuss the excited state absorption (ESA) pathways, that originated from several excited levels, we used the Judd–Ofelt formalism allowing determination of the integrated cross section for ESA transitions.

Keywords: holmium; luminescence; SrLaGaO₄:Ho³⁺; excited state absorption (ESA)

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1. Introduction

The strontium lanthanum gallate SrLaGaO₄ (SLO) and its solid solutions have been extensively investigated since they were considered as a promising substrate for high temperature superconducting (HTSc) films [1]. SLO doped with transition metal (TM) or rare earth (RE) ions was also considered as laser active media [2]. Recently, SLO has been investigated as a host lattice for phosphors, which exhibit unusual and interesting properties when activated by RE or TM ions [3,4]. In particular, when Tb³⁺ is introduced into SrLaGaO₄, long persistent green emission has been reported [3]. The duration of green afterglow was observed even after more than 3.5 h. A novel, far-red emitting SrLaGaO₄:Mn⁴⁺ phosphor with high brightness and excellent luminescent properties has been synthesized by the simple solid-state reaction and investigated in [5]. In addition, the luminescence spectra of SLO activated by Cr³⁺ were reported in [4]. It was shown that Cr³⁺ ions occupy more than four different sites in the SLO lattice, which is related to the random distribution of Sr²⁺ and La³⁺ ions.

The interest in studying RE³⁺ doped SLO strongly results both from its structural disorder, and the resulting inhomogeneous broadening of the optical transitions [6], as well as from the ability of this matrix to accept high concentrations of activator [1,2]. Such a broadening helps the generation of ultrashort pulses by mode locking. Thus, due to its good thermal properties and broad gain spectrum, Yb³⁺-doped strontium lanthanum aluminate crystal was reported as a promising material for power-scalable, broadly tunable CW and sub-100 fs mode-locked lasers at ~1 μm [7].

Holmium ion activated solids have been the subject of extensive investigations for the development of laser materials, phosphors and color displays [8–10]. The use of Ho³⁺ as a potential candidate for temperature sensing has been confirmed, and thermal-coupled levels of Ho³⁺ ions, ⁵F₄ and ⁵S₂, ⁵S₂ and ⁵F₅, have been investigated in temperature measurement applications [11].

In particular, much attention has been dedicated to the studies of up-conversion processes in Ho^{3+} doped low-energy phonon crystals, optical glasses [12] and glass ceramics [13]. Up-conversion materials have wide applications, such as for bio-imaging, photo-therapies, photo-catalysis, solar conversion, temperature sensing, etc. Generally, energy transfer up-conversion (ETU), excited state absorption (ESA), and photon avalanche (PA) are the three main channels for up-conversion fluorescence. The Ho^{3+} ion is very suitable for use in up-conversion processes because it has many long-lived intermediate metastable levels, from which ESA can take place resulting in a strong, green anti-Stokes luminescence from $^5\text{S}_2$ level which has been demonstrated in a number of Ho^{3+} doped materials after red and infrared excitation [14]. It was also demonstrated that ESA has an important influence on the performance of Ho-doped fiber lasers [15]. Thus, for the modeling of these up-conversion excitation processes the ESA cross sections have to be known.

Although the optical properties of Nd^{3+} , Pr^{3+} , Eu^{3+} , Yb^{3+} and Tm^{3+} doped SLO crystals have been reported [3,6,7,16], the spectroscopic data on Ho^{3+} doped SLO have not, to our knowledge, been presented in detail. In [17] we reported on the nature of strong spectral lines broadening in Ho^{3+} doped $\text{SrLaGa}_3\text{O}_7$ and SrLaGaO_4 crystals which have been investigated by using the non-resonant fluorescence line narrowing (FLN) technique. Also, up-conversion ultraviolet emission from $^3\text{D}_3$ level in these compounds was observed in [18]. The partial energy diagram of Ho^{3+} ions in the SLO host, together with the strongest observed emission transitions, is illustrated in Figure 1.

Figure 1. The partial energy diagram of Ho^{3+} ions in SrLaGO_4 crystal. Arrows indicate the emission transitions.

Recently, we studied ESA processes that involve the $^5\text{I}_6$ and $^5\text{I}_7$ energy levels of Ho^{3+} in singly Ho^{3+} -doped $\text{ZrF}_4\text{--BaF}_2\text{--LaF}_3\text{--AlF}_3\text{--NaF}$ (ZBLAN) glass [12] and also YAlO_3 (YAP), $\text{Y}_3\text{Al}_5\text{O}_{12}$ (YAG), LiYF_4 (YLF) and $\text{SrLaGa}_3\text{O}_7$ (SLG) crystals [14]. In the present investigation, we extend this work by identifying and quantifying a range of pump excited state absorption ESA processes in SLO that may affect the functioning of Ho^{3+} -doped SLO green phosphor or laser.

2. Materials and Experiment

A $\text{SrLaGaO}_4\text{:Ho}^{3+}$ crystal with activator concentrations of 0.3 at % was grown using the Czochralski technique at ITME Laboratory in Warsaw. The samples used were monocrystalline of good optical quality which, after orientation, were cut into $10 \times 5 \times 2 \text{ mm}^3$ plates and polished carefully in order to meet the requirements for spectroscopic measurements. Polarized absorption spectra were measured in the 200–2900 nm range of

wavelength at room temperature on a Cary-50 UV–Vis–NIR spectrophotometer (Varian, Inc., Palo Alto, CA, USA) equipped with Glan–Taylor polarizers.

Luminescence from the sample was excited using both pulsed and CW laser sources. For the pulsed measurements an optical parametric oscillator Surelite OPO (Continuum, Santa Clara, CA, USA) with YAG:Nd laser (Surelite II, Continuum Santa Clara, CA, USA) as a pumping source was used. CW excitation was performed with tunable Ti-sapphire laser (Coherent 899 Ring Laser, (Santa Clara, CA, USA)) pumped by argon laser (Coherent Innova 300, (Santa Clara, CA, USA)). Optical signal from the sample was analyzed using DK480 monochromator (CVI Laser Corporation, Albuquerque, NM, USA) and detected by cooled photomultiplier tubes (EMI C1034-02 GaAs (EMI Electronics Ltd., London, England) or Hamamatsu 7102 (Hamamatsu Photonics K.K., Hamamatsu, Japan)) and PbS detector for visible and infrared range, respectively. Stanford SR 400 photon-counting system (Stanford Research Systems Sunnyvale, CA, USA) controlled by PC was used to perform data acquisition. Measurements of luminescence decays were recorded using Stanford SR 430 multichannel analyzer (Stanford Research Systems Sunnyvale, California, USA). Low temperatures of the samples were obtained with a Displex Model CSW-202 cryostat (Apd Cryogenics Inc., Allentown, PA, USA).

SrLaGaO₄ belongs to a large family of compounds of general chemical formula ABCO₄ where A = Ca, Sr, Ba; B = Y, La–Gd; C = Al, Ga. SLO crystallizes in a perovskite-like, tetragonal structure, space group I4/mmm with unit cell parameters of $a = b = 0.38437(3)$ nm and $c = 1.26880(15)$ nm, the volume of the unit-cell $V = 178.27(1)$ Å³ and the number of structural units $Z = 2$ [19,20]. The crystal structure is built from CO₆ (GaO₆) layers formed in the ab plane. The Sr²⁺ and La³⁺ cations are distributed randomly between the layers, taking positions in nine coordinated sites with distorted C_{4v} symmetry. The C cations have a coordination of six and are in a slightly distorted octahedral environment, while Sr and La ions are surrounded by nine oxygens. The elementary cell of SrLaGaO₄ is shown in Figure 2 with the crystal built along the c-axis.

Figure 2. Schematic crystal structure of SrLaGaO₄.

Since the radius of the Ho³⁺ ion (0.172 Å) is comparable to those of the La³⁺ (0.126 Å) and Sr²⁺ (0.131 Å), it can be assumed that both La³⁺ and Sr²⁺ sites can be occupied by Ho³⁺ in SrLaGaO₄. It has been shown that the random distribution of the A and B cations over different lattice positions leads to a disordered structure of these crystals resulting in the strong inhomogeneous broadening of the spectral lines.

3. Results and Discussion

3.1. Absorption Spectra and Optical Transition Intensity Analysis

The structure makes SrLaGaO₄ uniaxially anisotropic where the strength of the absorption lines is dependent on the direction of the incident light. Bearing in mind that the optical axis is parallel to the crystallographic c-axis, two orthogonal light polarizations, π ($E \parallel c$) and σ ($E \perp c$), should be taken into account. Thus, in our spectroscopic study, we have measured the absorption characteristics for two principal light polarizations for a-cut 0.3 at% Ho³⁺ doped SrLaGaO₄ crystal. The measured spectra in the 300–2200 nm range are presented in Figure 3.

Figure 3. (a) Visible and (b) Infrared part of the polarized absorption spectrum of SrLaGaO₄:Ho³⁺ crystal recorded at room temperature.

Once the polarized absorption spectra had been measured, integrated absorbances $\bar{\Gamma}$ were calculated according to Equation (1) [21]:

$$\bar{\Gamma} = \int_{band} \bar{\alpha}(\lambda) d(\lambda) = -\frac{1}{L} \int_{band} \ln \left[\frac{1}{3} \exp(-\alpha_{\pi}(\lambda)L) + \frac{2}{3} \exp(-\alpha_{\sigma}(\lambda)L) \right] d(\lambda) \quad (1)$$

where L is the distance the light has traveled inside the sample, $\alpha_{\pi}(\lambda)$ and $\alpha_{\sigma}(\lambda)$ are the absorption coefficients for π and σ polarizations and λ is wavelength. Integrated absorbances determined in this way were used to obtain the experimental line strengths needed to perform the Judd–Ofelt [22,23] intensity analysis. Because the drawbacks and precision of the Judd–Ofelt theory have been analyzed in detail elsewhere [24], only the essential results have been included in this article. The main point of this approach is that the oscillator strength f_{calc} of the electric dipole transition between multiplets of lanthanide ion ($J \rightarrow J'$) is described as:

$$f_{calc} = \frac{8\pi^2 mc}{3h(2J+1)} \frac{1}{\lambda} \chi \sum_{t=2,4,6} \left| U_{JJ'(c)}^{(t)} \right|^2 \Omega_t \quad (2)$$

where h is Planck's constant, J is the angular momentum of the initial level, $\bar{\chi} = \frac{1}{3}(\chi_{\pi} + 2\chi_{\sigma})$ is an average local field correction factor, where for electric dipole transition $\chi_{\pi,\sigma} = \frac{(n_{\pi,\sigma}^2 + 2)^2}{9n_{\pi,\sigma}}$, $U^{(t)}$ are the doubly reduced matrix elements and Ω_t are empirically determined parameters. The value of oscillator strength can be also obtained from experimentally measured absorption or emission spectra. For the absorption line, the experimental oscillator strength f_{exp} , can be defined as

$$f_{exp} = \frac{mc^2 \epsilon_0}{\pi e^2 N} \bar{\Gamma} \quad (3)$$

where e and m are the electron charge and mass respectively, $\bar{\Gamma}$ is the integrated absorbance obtained from Equation (1) and c represents the light velocity.

From the least-square fit of calculated (f_{calc}) and measured (f_{exp}) oscillator strengths the three Ω_t intensity parameters were obtained. The reduced matrix elements needed for this calculation were taken from [25]. The values of calculated and measured oscillator strengths together with the average wavelengths for all measured absorption lines are presented in Table 1. The Judd–Ofelt intensity parameters were evaluated to be $\Omega_2 = 1.25 \times 10^{-20} \text{ cm}^{-1}$, $\Omega_4 = 0.42 \times 10^{-20} \text{ cm}^{-1}$, $\Omega_6 = 1.80 \times 10^{-20} \text{ cm}^{-1}$ with RMS deviation between the calculated and measured oscillator strength values of 5.3×10^{-6} . The obtained measure of the quality of the fit is closed to values found by applying the Judd–Ofelt approach to other materials doped with holmium ions [26].

Table 1. Oscillator strengths (f_{exp} —measured, f_{theor} —calculated) of absorption transitions for Ho^{3+} ion in SrLaGaO_4 crystal.

Transition $^5\text{I}_8 \rightarrow$	Wavelength λ [nm]	Oscillator Strengths	
		$f_{exp} [10^{-6}]$	$f_{theor} [10^{-6}]$
$^5\text{I}_7$	2011	2.19	1.73
$^5\text{I}_6$	1169	1.13	1.34
$^5\text{I}_5$	902	0.33	0.24
$^5\text{I}_4$	748	0.03	0.02
$^5\text{F}_5$	647	3.37	2.29
$^5\text{S}_2 + ^5\text{F}_4$	541	3.86	4.04
$^5\text{F}_3$	488	0.92	1.58
$^5\text{F}_2$	476	0.10	0.92
$^3\text{K}_8$	470	0.29	0.84
$^5\text{G}_6 + ^5\text{F}_1$	454	20.7	6.68
RMS = 5.3×10^{-6}			

Comparison of Judd–Ofelt parameters between $\text{Ho}^{3+}:\text{SLO}$ and other Ho^{3+} —doped hosts is shown in Table 2.

Table 2. Calculated Judd–Ofelt intensity parameters for $\text{SrLaGaO}_4:\text{Ho}^{3+}$ compared with several Ho^{3+} ion activated solids.

Material	Ω_2 [10^{-20} cm^2]	Ω_4 [10^{-20} cm^2]	Ω_6 [10^{-20} cm^2]	Ref.
SrLaGaO_4 (SLO)	1.25	0.42	1.80	This work
$\text{SrLaGa}_3\text{O}_7$ (SLG)	2.23	0.85	1.81	[27]
ZBLAN glass	2.46	2.02	1.71	[12]
$\text{Y}_3\text{Al}_5\text{O}_{12}$ (YAG)	0.10	2.09	1.72	[28]
LiYF_4 (YLF)	1.16	2.24	2.09	[29]

From the calculated set of Ω_t intensity parameters the electric dipole transition probabilities $A_{JJ'}$ for emissions between J and J' manifolds of Ho^{3+} were calculated using the equation:

$$A_{JJ'} = \frac{64\pi^4 e^2}{3h(2J+1)} \frac{1}{\lambda^3 \bar{\chi}} \sum_{t=2,4,6} \left| U_{JJ'}^{(t)} \right|^2 \Omega_t \quad (4)$$

Evaluated probabilities $A_{JJ'}$ of the radiative transitions from the excited states, the branching ratios β_{calc} and resulting radiative lifetimes are presented in Table 3. The values of radiative lifetimes of the $^3\text{D}_3$, $^5\text{F}_3$, $^5\text{S}_2$, $^5\text{F}_5$, $^5\text{I}_4$, $^5\text{I}_5$, $^5\text{I}_6$ and $^5\text{I}_7$ were calculated to be: 477 μs , 217 μs , 211 μs , 372 μs , 5.34 ms, 3.37 ms, 2.83 ms and 8.02 ms, respectively.

Table 3. Probabilities of radiative transitions, branching ratios and radiative lifetimes of excited states of Ho^{3+} in SrLaGaO_4 crystal.

Transition	$\text{SrLaGaO}_4\text{:Ho}^{3+}$		
	A [1/s]	β	τ_R
$^3\text{D}_3 \rightarrow ^3\text{G}_5$	22	0.011	
$^5\text{G}_5$	70	0.034	
$^3\text{K}_7$	32	0.015	
$^5\text{G}_6$	20	0.009	
$^3\text{K}_8$	821	0.374	
$^5\text{F}_3$	25	0.011	
$^5\text{F}_4$	35	0.016	
$^5\text{F}_5$	11	0.005	
$^5\text{I}_4$	50	0.023	
$^5\text{I}_6$	106	0.141	
$^5\text{I}_7$	794	0.361	
$^5\text{I}_8$	87	0.039	
$\Sigma A = 2097$		1	477 μs
$^5\text{F}_3 \rightarrow ^5\text{F}_4$	0	0.000	
$^5\text{S}_2$	0	0.000	
$^5\text{F}_5$	1	0.000	
$^5\text{I}_4$	112	0.024	
$^5\text{I}_5$	50	0.011	
$^5\text{I}_6$	265	0.057	
$^5\text{I}_7$	761	0.165	
$^5\text{I}_8$	3427	0.742	
$\Sigma A = 4615$		1	217 μs
$^5\text{S}_2 \rightarrow ^5\text{F}_5$	0	0.000	
$^5\text{I}_4$	64	0.013	
$^5\text{I}_5$	64	0.014	
$^5\text{I}_6$	256	0.054	
$^5\text{I}_7$	1835	0.388	
$^5\text{I}_8$	2511	0.531	
$\Sigma A = 4731$		1	211 μs
$^5\text{F}_5 \rightarrow ^5\text{I}_4$	0	0.000	
$^5\text{I}_5$	11	0.004	
$^5\text{I}_6$	140	0.052	
$^5\text{I}_7$	471	0.175	
$^5\text{I}_8$	2068	0.769	

Table 3. Cont.

Transition	SrLaGaO ₄ :Ho ³⁺		
	A [1/s]	β	τ_R
$\Sigma A = 2690$		1	372 μ s
$^5I_4 \rightarrow ^5I_5$	9	0.050	
5I_6	70	0.371	
5I_7	90	0.478	
5I_8	19	0.100	
$\Sigma A = 187$		1	5.34 ms
$^5I_5 \rightarrow ^5I_6$	9	0.031	
5I_7	173	0.583	
5I_8	115	0.386	
$\Sigma A = 297$		1	3.37 ms
$^5I_6 \rightarrow ^5I_7$	30	0.084	
5I_8	324	0.916	
$\Sigma A = 353$		1	2.83 ms
$^5I_7 \rightarrow ^5I_8$	125	1	8.02 ms

The emission characteristic of the crystal was measured at room temperature in the 250 nm–2.5 μ m spectral range after CW excitation. All experimentally observed emission lines corresponding to transitions from the 3D_3 , 5F_3 , 5S_2 , 5F_5 , 5I_6 and 5I_7 excited states of SrLaGaO₄:Ho³⁺ are presented in Figure 4. The emission spectrum is dominated by $^5S_2 \rightarrow ^5I_8$ transition, resulting in the strongest luminescence line at about 550 nm.

Figure 4. (a) UV-Vis and (b) IR part of polarized emission spectrum of SrLaGaO₄: Ho³⁺ recorded at room temperature.

3.2. Luminescence Dynamics

Fluorescence decay curves were registered after wavelength selective pulsed excitation. Figure 5 shows decay profiles of the 3D_3 , 5S_2 , 5F_5 , 5I_6 and 5I_7 emissions in 0.3% Ho³⁺ doped SrLaGaO₄ measured at 300 K. The fluorescence lifetimes of 3D_3 , 5S_2 , 5F_5 , 5I_6 and 5I_7 manifolds were determined with estimated relative errors of 1% to be of 35 μ s, 98 μ s, 6 μ s, 1 ms and 4 ms, respectively. Due to the large energy gap to the next lying lower level of about 4000 cm^{−1} the 5I_6 and 5I_7 decays could be considered as being predominantly radiative which was confirmed by its temperature independence.

Figure 5. Decay profiles of the 3D_3 , 5S_2 , 5F_5 , 5I_6 and 5I_7 emission in Ho^{3+} doped SrLaGaO_4 crystal measured at 300 K.

Knowing values of radiative and measured lifetimes, the rates of multiphonon relaxations can be simply calculated using the equation:

$$W_{nr} = \frac{1}{\tau_{obs}} - \frac{1}{\tau_R} \quad (5)$$

Calculated radiative lifetimes, measured at low temperature lifetimes, the energy gaps to the next lower level and the multiphonon transition rate for excited states of Ho^{3+} in SrLaGaO_4 are shown in Table 4.

Table 4. Calculated radiative lifetimes τ_R , lifetimes observed at $T = 10$ K τ_{obs} , energy gaps ΔE , and obtained multiphonon transition rates W_{nr} for excited states of Ho^{3+} in SrLaGaO_4 crystal.

Manifold	$\text{SrLaGaO}_4:\text{Ho}^{3+}$			
	τ_R [μs]	τ_{obs} [μs]	$\Delta E_{i(i-1)}$ [cm ⁻¹]	W_{nr} [s ⁻¹]
3D_3	477	35	2100	26,500
5S_2	211	151	2794	1883
5F_5	372	7	~1950	140,169
5I_6	2833	1200	3426	480
5I_7	8015	4000	4225	125

Dependence of the multiphonon transition probability W_{nr} on the energy gap to the next lower level ΔE can be described as an exponential function [30]:

$$W_{nr} = W_0 \times \exp(-\alpha \Delta E) \quad (6)$$

The $W_{nr}(\Delta E)$ dependence, together with the data for low phonon ZBLAN glass [31], is shown in Figure 6. The values of W_0 and α in Equation (6) were calculated as $0.5 \times 10^7 \text{ s}^{-1}$ and $2.6 \times 10^{-3} \text{ cm}$, respectively.

Figure 6. The multiphonon relaxation rate W_{nr} as a function of energy gap ΔE for the excited states of Ho^{3+} ion in SrLaGaO_4 —red line. Open circles denote experimental points. For comparison the data for ZBLAN glass are also presented—blue solid line.

As can be observed from Figure 6 the nonradiative decay rates in SLO are about one order of magnitude higher than in ZBLAN. The difference in results from higher in the case of SLO of the the phonon frequency distribution function, which is approximately $\hbar\omega_{\max} = 707 \text{ cm}^{-1}$ [32], than in ZBLAN matrix, which is 580 cm^{-1} [3].

3.3. Excited State Absorption Transitions

The high number of long-lived multiplets present in Ho^{3+} acting as good population reservoirs leads to the possibility of ESA transitions into higher lying energy levels. The intermediate levels for ESA are therefore 5I_J states ($J = 5, 6, 7$). Using the Judd–Ofelt formalism it is possible to estimate the ESA integrated cross sections by means of the following expression:

$$\sigma_{int} = \int_{\lambda_1}^{\lambda_2} \sigma(\lambda) d\lambda = \frac{8\pi^3 e^2}{3hc (2J+1)} \chi \sum_{t=2,4,6} |U_{JJ'}^{(t)}|^2 \Omega_t \quad (7)$$

where λ is the mean wavelength corresponding to the ESA transition.

With this method, the ESA transition cross sections in the spectral range between 400 and 5000 nm in Ho^{3+} -doped SLO were calculated and are presented in Figure 7, together with the GSA cross sections.

Figure 7. Spectrum of calculated ground state absorption (GSA) and excited state absorption (ESA) integrated cross sections σ in $\text{SrLaGaO}_4:\text{Ho}^{3+}$ crystal.

Figure 7 also illustrates that several infrared excitation wavelengths could lead to population of the 5S_2 state from which green anti-Stokes emission results. These processes for excitation in the 720–750, 870–920 and 960–1000 nm spectral ranges are interpreted in Figure 8 and are confirmed by the excitation spectrum of up-converted 5S_2 green emission presented in Figure 9. Similar spectra were also reported for other Ho^{3+} activated systems [14].

Figure 8. Energy level diagram of Ho^{3+} presenting different paths of populating the 5S_2 state of Ho^{3+} involving GSA and ESA processes.

Figure 9. Excitation spectra of $\text{SrLaGaO}_4:\text{Ho}^{3+}$ crystal when monitoring the strongest $^5S_2 \rightarrow ^5I_8$ emission transition at 550 nm, $T = 300$ K.

On the other hand, the energy level diagram in Figure 8 illustrates that in the up-conversion excitation of 5S_2 emission several near-resonant transitions, with participation of low energy phonons, are involved. It can also be observed that energies of GSA and ESA transitions are in close proximity, so it is difficult to indicate one responsible process. We have focused our attention on the 750 nm excitation band, as it was reported to be responsible for the efficient photon avalanche process that occurs in Ho^{3+} activated solids [33].

As results from Figure 8, after 750 nm excitation, the first step is the weak quasi-resonant GSA $^5I_8 \rightarrow ^5I_4$ absorption, followed by non-radiative de-excitation to the 5I_6 and 5I_7 metastable levels which act as intermediate levels. The next steps are: a strong resonant ESA $^5I_7 \rightarrow ^5S_2, ^5F_4$ and non-resonant ESA $^5I_6 \rightarrow ^5G_6, ^5F_1$ transitions followed by

non-radiative de-excitation to the 5S_2 , 5F_4 levels from which an intense green emission is obtained.

Calculated GSA and ESA absorption cross section values for transitions involved in the 750 nm excitation process for SrLaGaO₄ and several other Ho³⁺ activated materials are summarized in Table 5. The cross-sections of the non-resonant transitions from 5I_7 and 5I_6 to the multi-phonon side bands were calculated in the framework of formalism developed by Auzel [34] who showed that the probability for Stokes excitation with respect to an energy gap ΔE to the electronic level is given by:

$$W_S = W_S(0) \exp(-\alpha_S \Delta E) \quad (8)$$

where α_S is related to the multi-phonon nonradiative decay parameter α_{NR} by

$$\alpha_{NR} = \alpha_S - (h\omega) - 1/N \ln(N/S_0) \quad (9)$$

where $N = E/h\omega$ is the average order of the multi-phonon process, S_0 is the Huang–Rhys electron–phonon coupling parameter at 0 K and $h\omega$ is the highest phonon frequency of the host.

Table 5. Calculated GSA and ESA absorption cross section values for transitions involved in the 750 nm excitation process for SrLaGaO₄ and several other Ho³⁺ activated materials.

Material	$^5I_8 \rightarrow ^5I_4$	$^5I_7 \rightarrow ^5S_2 + ^5F_4$	$^5I_6 \rightarrow ^5G_6 + ^5F_1$	Ref.
	σ (GSA) [10 ^{−20} cm ²]	σ (ESA) [10 ^{−20} cm ²]	σ (ESA) [10 ^{−20} cm ²]	
SLO	0.0053	1.242	0.903	This work
SLG	0.0037	1.318	0.116	[27]
ZBLAN	0.0025	1.220	0.942	[12]
YAG	0.0036	1.309	1.202	[28]
YLF	0.0037	1.405	1.080	[29]

The values of the integrated cross sections calculated according to Equation (7) are proportional to the line strength of the electric-dipole transition $S_{ed}(JJ') = \sum_{t=2,4,6} |U_{JJ'}^{(t)}|^2 \Omega_t$.

Considering the 750 nm excitation conversion to 5S_2 green emission following values of squared matrix elements, $|U_\lambda|^2$ should be considered. In Figure 10 the S_{ed} values' dependence on Ω_t is presented.

Figure 10. S_{ed} values' dependence on Ω_t parameters for transitions involved in 750 nm up-conversion excitation.

It thus results that in the considered 750 nm excitation, the ESA ($^5I_7 \rightarrow ^5S_2 + ^5F_4$) is the most important process and that for its cross-section to be large, materials with a high

value of the Ω_6 parameter should be chosen. Thus, according to the Judd–Ofelt parameters presented in Table 2, the highest ($^5I_7 \rightarrow ^5S_2 + ^5F_4$) ESA cross-sections could be expected for $\text{Ho}^{3+}:\text{LiYF}_4$ crystal. This is confirmed by the data reported by Kuck et al. [35]. From Table 6 and Figure 10 it can also be seen that the $^5I_8 \rightarrow ^5I_4$ GSA is only Ω_6 dependent.

Table 6. Doubly reduced matrix elements for selected transitions in Ho^{3+} ions.

$ U_t ^2$	$^5I_8 \rightarrow ^5I_4$	$^5I_7 \rightarrow ^5F_4$	$^5I_7 \rightarrow ^5S_2$	$^5I_7 \rightarrow ^5S_2 + ^5F_4$	$^5I_6 \rightarrow ^5G_6$	$^5I_6 \rightarrow ^5F_1$	$^5I_6 \rightarrow ^5G_6 + ^5F_1$
$ U^2 ^2$	0	0	0	0	0.0093	0	0.0093
$ U^4 ^2$	0	0.1965	0	0.1965	0.0837	0	0.0837
$ U^6 ^2$	0.0082	0.0349	0.4195	0.4544	0.1094	0.2383	0.3477

The ratio between the GSA and ESA cross sections ($\beta = \text{GSA}/\text{ESA}$) is an important parameter for establishing the photon avalanche process. It was proposed in [36] that a β value lower than 10^{-4} is necessary to expect avalanche up-conversion. Above this limit, the up-conversion emission does not exhibit any pump threshold. Evaluated here $\beta = \text{GSA}/\text{ESA}$ is about 4×10^{-3} and is beyond the limit for photon avalanche up-conversion to occur.

4. Conclusions

The spectroscopy and the fluorescence dynamics of SrLaGaO_4 crystal doped with Ho^{3+} ions have been studied in detail and analyzed. Based on polarized absorption spectra, the Judd–Ofelt intensity parameters were determined and radiative transition probabilities for several Ho^{3+} excited states were calculated. This, together with the measured fluorescence lifetimes, allowed evaluation of the multiphonon relaxation parameters for SLO matrix.

Several ESA mechanisms which generate the green emission from the 5S_2 level in SLO under 750, 900 and 980 nm band excitations have been proposed. The Judd–Ofelt analysis, which is usually performed for transitions from the ground-state manifold, was used to determine the integrated cross-sections of the ESA transitions and to predict the possibility of photon avalanche up-conversion occurring under 750 nm pumping.

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