# Judd Ofelt analysis of Ho<sup>3+</sup> and CdS co-doped Sol-Gel Silica glasses

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Ho<sup>3+</sup> doped in CdS: SiO<sub>2</sub> glasses with good optical quality were fabricated by sol-gel technique. The glass samples were studied by X-ray diffraction, optical absorption and photoluminescence spectroscopy. Phenomenological Judd–Ofelt theory was applied to obtain the three intensity parameters  $\Omega_2$ ,  $\Omega_4$  and  $\Omega_6$ . Comparatively higher values of  $\Omega_2$ , smaller value  $\Omega_4 / \Omega_6$  as well as efficient radiative transitions reveal the prospect of the studied glass as potential optical material in the blue and green regions.

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### 1. Introduction

Glasses and semiconductors find immense importance in photonics from both technological and fundamental research point of view [1]. Between these, glass integrated optics has attracted the attention of material scientists and photonic device engineers who seek to take the advantage of its robustness, appealing optical properties and compatibility with established silicon manufacturing protocols [2]. There has been growing interest in rare earth (RE) doped glass matrices because of its numerous applications in optoelectronics and photonics. RE ions as such possess small absorption coefficients due to parity forbidden f-f transitions leading to less efficient excitation by UV-light. However if the RE ions are doped in suitable glass matrices, the excitation efficiencies of RE ions are enhanced yielding very good luminescence behavior in the visible (Vis), infrared (IR), and near infrared (NIR) regions thus making them potential candidate for solid state lasers, optoelectronic devices, colour displays etc [3-5].

In the development of RE doped optical glasses, the host glass matrix plays a very crucial role. It is well established that the radiative parameters associated with luminescence transitions of lanthanide  $(Ln^{3+})$  ions in glasses are highly sensitive to the chemical environment. The transition probabilities for emission from  $Ln^{3+}$  ions are expected to increase with increase in covalency that depends upon the network forming ions. Network modifiers also change the local environment of  $Ln^{3+}$  ions to some extent [6]. Hence, the choice of suitable glass former and glass modifier systems plays a decisive role in tailoring the glass matrix to meet their specific requirements. So far, much effort has been spent on fluoride systems due to their lower phonon energy as compared to oxide systems [5]. On the other hand, the

oxide glasses like phosphate and silica glasses possess high chemical durability and thermal stability and hence bear potential as host material for practical applications as compared to fluoride glasses. Silica glasses also possess superior chemical resistance and are optically transparent at the excitation and lasing wavelengths [7].

 $\mathrm{Ho}^{3+}$  is one of the most efficient RE ions that have been used extensively for lasing applications. The transitions between numerous electronic levels of  $\mathrm{Ho}^{3+}$ ions occur in the UV, Vis as well as IR region of the electromagnetic spectrum [8, 9]. Consequently there are many lines in the emission spectrum which are used as laser transitions [10]. A good number of research activities on the spectroscopic behavior of  $\mathrm{Ho}^{3+}$  doped in various hosts have been going on around the globe [11-20].

Both direct and indirect band gap semiconductors doped in the glass matrix behave as sensitizing centers since their excitation co-efficient is very high due to band to band absorption [21]. CdS, a II-VI semiconductor, is one of the extensively used sensitizer for RE emissions. Also, there are reports of enhancement of RE excited state lifetime due to addition of CdS [22]. The incorporation of CdS in glass matrix changes the structural features of the network as well [21, 23], and hence could be treated as potential glass modifier. Although CdS has been used by several workers as codopant in RE doped glass matrices [24-26], to our knowledge, no such comprehensive study on Ho<sup>3+</sup> ions co-doped with CdS silica glasses has been carried out.

Studies on the enhancement of spectroscopic efficiency of RE ions have been an important area of research from their application perspective. In our earlier communications, we have reported the spectroscopic studies of  $\text{Ho}^{3+}$  and  $\text{Er}^{3+}$  ions in Al(NO<sub>3</sub>)<sub>3</sub>-SiO<sub>2</sub> [27, 28] and  $\text{Er}^{3+}$  ion in CdS-SiO<sub>2</sub> [6] sol-gel glasses and found

improved efficiencies of Al(NO<sub>3</sub>)<sub>3</sub> and CdS co-doped silica glasses. In the present work, in order to study the effect of CdS on the Ho<sup>3+</sup> transitions in silica glasses, the spectroscopic behavior of Ho<sup>3+</sup> doped CdS-SiO<sub>2</sub> glasses is studied. The glasses were fabricated by the sol-gel technique and were characterized by UV-Vis absorption and photoluminescence measurements. Phenomenological J.O. theory [29-31] is used to analyze the f-f transitions of Ho<sup>3+</sup> ions by using the absorption spectrum. Oscillator strengths for different f-f transitions and J. O. intensity parameters are calculated. Important radiative parameters viz. transition probability, radiative life time of the excited states, emission cross-sections of different emission levels and branching ratios are evaluated from the recorded photoluminescence spectrum.

# 2. Experimental

The glass samples were prepared by the sol-gel method. Ho<sub>2</sub>O<sub>3</sub> as the source of Ho<sup>3+</sup> and CdS as the codopant were used. Tetraethylorthosilicate (TEOS) (Merck >98%) as organo metallic precursor, methanol (Merck 99%) as solvent and nitric acid (Merck 70%) as catalyst were used together with doubly distilled water in proportion of 16:70:4:10. All the chemicals used in the preparation method were of analytical grade and were used as received. Dopants in above concentrations were mixed with methanol, nitric acid, doubly distilled water and were stirred by a magnetic stirrer for about 30 minutes. To this solution TEOS was added and the mixture was further stirred for about 1 hour or till gelation begins. The gel was then put in plastic container and dried at room temperature to densify the mass into an amorphous, porous solid matrix called xerogel. Dopants in sol-gel glasses got impregnated into these pores. After about 100 hours the gel shrunk to about half its original volume and solidified. Further densification is accomplished by leaving it to dry at room temperature for 21 days followed by annealing in ambient at 150° C for two hours to obtain the final glass. The refractive indices (n) of the glass samples were measured by Almico Abbe refractometer. Optical absorption spectra of the samples were recorded by a Hitachi U-2001 double beam UV-VIS spectrophotometer (spectral resolution of 0.1 nm) in the scanning range from 350 to 1000 nm using undoped glass as reference. X-Ray diffraction (XRD) spectra for the sample was recorded by Seifert XRD 3003 T/T with Cu K<sub>a</sub> radiation (1.541 Å) operated at an acceleration voltage of 40 kV and tube current of 30 mA. The scanning was done in the  $2\theta$  range of 5-65° at a rate of 0.05° per second. Photoluminescence spectrum for the glass was recorded by a Fluoromax 4P spectrofluorimeter (spectral resolution of 1 nm) using excitation wavelength of 378 nm. All the measurements were done at room temperature.

## 3. Results and discussions

# 3.1. Judd Ofelt analysis

The room temperature optical absorption spectrum of  $Ho^{3+}$  (0.01 M) in CdS -SiO<sub>2</sub> glass is shown in fig. 1.



Fig. 1. Optical absorption spectrum for 0.01M  $Ho^{3+}$ doped CdS-SiO<sub>2</sub> glass. Inset shows the magnified portion for the ground state to  ${}^{3}K_{8}$ ,  ${}^{5}F_{2}$  and  ${}^{5}F_{3}$  transitions.

Nine absorption bands arising due to the transitions from  ${}^{5}I_{8}$  ground state to  ${}^{3}H_{6}$ ,  ${}^{5}G_{5}$ ,  ${}^{5}G_{6}$ ,  ${}^{3}K_{8}$ ,  ${}^{5}F_{2}$ ,  ${}^{5}F_{3}$ ,  ${}^{5}F_{4}$ ,  ${}^{5}F_{5}$ and  ${}^{5}I_{5}$  states ascribed to electric dipole (e-d) transitions were observed. Assignments of the absorption peaks are done by comparing the absorption spectrum with earlier published works [32-34]. Presence of an envelope instead of a flat baseline on the absorption spectrum is ascribed to the presence of CdS in the glass network [6,35,36].The signature of CdS crystals in the glass network is also revealed by the XRD spectrum as shown in figure 2. Small intensity peak at 36.2° corresponding to (102) planes of CdS crystals [37] superimposed on the harrow like pattern indicates that CdS particles are dispersed throughout the glass network. Using the Debye Scherrer formula the size of the CdS crystallites were estimated to be ~ 4 nm.



Fig. 2. XRD spectrum of co-doped  $Ho^{3+}$  (0.01M) and CdS (0.01M) SiO<sub>2</sub> glass.

Using J.O. theory, the experimental oscillator strengths  $(f_{exp})$  of the observed e-d transitions are determined from the relation

$$f_{exp} = 4.318 \times 10^{-9} \int \varepsilon(v) dv$$
 (1)

where,  $\epsilon(v)$  is the molar extinction co-efficient at wave no (cm<sup>-1</sup>) determined from Lambert Beer's law. To determine the J.O. parameters T<sub>t</sub> for t = 2, 4 & 6, oscillator strengths measured experimentally (f<sub>exp</sub>) were co-related with its corresponding Judd's [29] expression for oscillator strengths (f<sub>cal</sub>) of e-d transitions between initial and terminal states given by

$$\mathbf{f}_{cal} = \sum_{t=2,4,6} \mathbf{T}_{t} \mathbf{v} (\left\langle \Psi \mathbf{J} \| \mathbf{U}(t) \| \Psi' \mathbf{J}' \right\rangle)^{2}$$
(2)

using the least square fit analysis. In equation (2), U(t) is a tensor operator of rank t calculated in an intermediate coupling approximation [33]. Since the values of these operators are essentially independent of hosts, values calculated by Carnall et al. [34] for Ho<sup>3+</sup> (aquo) ions are used in these calculations. Moreover, for solid glass matrix the refractive index (n) of glass plays an important role. Therefore, the original J.O. parameters ( $T_t$ ) are transformed into J.O. intensity parameters,  $\Omega_t$  through the following expression [38],

$$\Omega_{t} = \frac{3h}{8\pi^{2}mc} \frac{9n}{(n^{2}+2)^{2}} (2J+1)T_{t}$$
(3)

In equation (3),  $^{2}J+1^{2}$  is the multiplicity of the lower state, 'm' the mass of the electron while the rest of the symbols have their usual meaning.

The measured experimental  $(f_{exp})$  and calculated theoretical  $(f_{cal})$  oscillator strengths of the observed Ho<sup>3+</sup> transitions are compiled in table1 along with the J.O. intensity parameters  $(\Omega_t)$ . The values of experimental and theoretical oscillator strengths are in good agreement with an r.m.s. deviation of 3.96 x 10<sup>-6</sup> between them. For some of the transitions the difference between calculated and experimental values of oscillator strengths is little higher which may be because of 4f–5d mixing [39] contributing to intensities with odd values of t in U(t) matrix elements which are neglected in the J.O. model.

Table 1. Oscillator strengths ( $f_{exp}$  and  $f_{cal}$ ) and J.O. Intensity parameters for  $Ho^{3+}$ : CdS-SiO<sub>2</sub> sol-gel glass.

Transition	Peak	Oscillator	Strength			
	Wavelength	$(x10^{-6})$				
	(nm)	Calculated	Measured			
		(f <sub>cal</sub> )	(f <sub>exp</sub> )			
${}^{5}I_{8} \xrightarrow{3} H_{6}$	360	9.20	19.7			
<sup>5</sup> G <sub>5</sub>	417	12.2	12.4			
${}^{5}G_{6}$	450	72	72.1			
$^{3}K_{8}$	469	6.67	4.01			
${}^{5}F_{2}$	474	6.44	7.13			
<sup>5</sup> F <sub>3</sub>	485	11.3	7.78			
${}^{5}F_{4}$	537	25.2	24.2			
<sup>5</sup> F <sub>5</sub>	643	20.4	17.4			
<sup>5</sup> I <sub>5</sub>	890	1.78	0.565			
r.m.s. deviat	ion (10 <sup>-6</sup> )	3.96				
$\Omega_2 (x 10^{-20} \text{ cm})$	n <sup>2</sup> )	16.7				
$\Omega_4 (x 10^{-20} cr)$	n <sup>2</sup> )	10.9				
$\Omega_6 (x 10^{-20} \text{ cm})$	$n^2$ )	18.2				
$\Omega_4/\Omega_6$		0.59				

The J.O. intensity parameters ( $\Omega_t$ ) are important for analysis of local structure and bonding in the vicinity of the RE ions. It is well known that the  $\Omega_2$  parameter depends on the structure and is associated with the asymmetry and covalency of the lanthanide sites [40]. The  $\Omega_4$  and  $\Omega_6$  parameters depend on bulk properties of the host such as viscosity and dielectric property of the medium and are also affected by the vibronic transitions of the RE ions bound to the ligand atoms [41]. Moreover, the values of the J.O. intensity parameters can be used to calculate the spectroscopic quality factor  $\Omega_4/\Omega_6$ , which is critically important in predicting the stimulated emission for the laser active medium [40,42].

Host Glasses	$ \begin{array}{c} \Omega_2 \\ (\text{cm}^2) \end{array} (10^{-20}) $	$\Omega_4$ (10 <sup>-20</sup> ) (cm <sup>2</sup> )	$\Omega_6 (10^{-20})$ (cm <sup>2</sup> )	$\Omega_4/\Omega_6$	Reference
Al(NO <sub>3</sub> ) <sub>3</sub> -SiO <sub>2</sub>	6.07	6.10	9.83	0.62	[27]
Pure SiO <sub>2</sub>	5.15	7.39	9.65	0.77	Present work
CdS-SiO <sub>2</sub>	16.7	10.9	18.2	0.59	Present work
PbO-Al <sub>2</sub> O <sub>3</sub> -B <sub>2</sub> O <sub>3</sub>	5.38	17.15	26.50	0.65	[27]
PbO-ZnO-B <sub>2</sub> O <sub>3</sub>	5.26	4.13	2.48	1.67	[27]
Li <sub>2</sub> O-CaO-B <sub>2</sub> O <sub>3</sub>	6.83	3.15	2.53	1.25	[27]
LKBBT	4.37	1.91	1.45	1.32	[27]
NaPO <sub>3</sub> -BaF <sub>2</sub>	3.78	2.97	2.05	1.45	[27]
ZBLAN	1.90	2.09	1.56	1.34	[27]
Fluorohafnate	1.53	3.19	4.93	0.65	[27]
Oxyfluoroborate	1.22	12.11	9.96	1.22	[27]
Fluoroindate	1.37	2.35	2.22	1.06	[27]
ZnF <sub>2</sub> -CdF <sub>2</sub>	0.80	2.60	2.00	1.30	[27]

Table 2. Comparative Judd Ofelt intensity parameters and the spectroscopic quality factors for  $Ho^{3+}$  in different hosts.

The J.O. intensity parameters obtained in the present glass is compared with other glass hosts and is presented in table 2. Comparatively higher value of  $\Omega_2$  parameter for the studied glass indicates higher asymmetry and stronger covalent environment between RE and ligand ions in Ho<sup>3+</sup> doped CdS -SiO<sub>2</sub> glass. The result is significant since the transition probabilities for emission of Ln<sup>3+</sup> ions are expected to increase with increase in covalency [7, 43].

#### 3.2. Photoluminescence analysis

The photoluminescence spectrum for the Ho<sup>3+</sup>: CdS -SiO<sub>2</sub> sol-gel glass under 378 nm excitation is shown in figure 3. Four major emission bands centered at 437, 463, 495 and 552 nm arising due to the transitions from the excited  ${}^{5}G_{5}$ ,  ${}^{5}F_{3}$ ,  ${}^{5}F_{4}$  and  ${}^{5}S_{2}$  to the ground  ${}^{5}I_{8}$  state [24, 32, 40, 44] were observed. Figure 4 describes the emission transitions in terms of the energy level diagram. Using the emission spectrum and the values of  $\Omega_{t}$ , important radiative parameters for the observed emission transitions were estimated with the help of formulae mentioned in ref. [45].

The spontaneous emission probability for an excited state is given by

$$A(\Psi J, \Psi' J') = \frac{64\pi^4 e^2 n (n^2 + 2)^2}{3h\lambda^3 (2J + 1)9} \sum_{t=2,4,6} \Omega_t \left| \left\langle \Psi J \right\| U(t) \| \Psi' J' \right\rangle \right|^2$$
(4)

The total spontaneous emission probability for all transitions from that state is

$$A_{T} = \sum A(\Psi J, \Psi' J')$$
<sup>(5)</sup>

and  $A_T^{-1}$  gives the radiative lifetime  $\tau_{rad}$  that determines the rate of depopulation of the given state.

The fluorescence branching ratio of transitions from the initial to the lower levels is given by

$$\beta_{\rm r} = \frac{A(\Psi J, \Psi' J')}{A_{\rm T}(\Psi J)} \tag{6}$$

Combination of J–O theory of electric-dipole transitions with the fluorescence line shapes provides a convenient way to determine the stimulated emission cross-sections,  $\sigma$  ( $\lambda_p$ ), of the emissive levels which is calculated as

$$\sigma\left(\lambda_{\rm p}\right) = \frac{\lambda_{\rm p}^{4}}{8\pi {\rm cn}^{2}\Delta\lambda} A \tag{7}$$

where,  $\lambda_p$  is peak emission wavelength and  $\Delta\lambda$  is the effective band width of the emission band.



Fig. 3. Photoluminescence spectrum for  $0.01M \text{ Ho}^{3+}$ doped CdS -SiO<sub>2</sub> glass under 378 nm excitation.



Fig. 4. Emission energy level scheme of  $Ho^{3+}$  in CdS codoped SiO<sub>2</sub> glass.GSA and NR represent respectively ground state absorption and non-radiative transition.

Initial state	Final state	Energy (cm <sup>1</sup> )	U(2) <sup>2</sup>	U(4) <sup>2</sup>	U(6) <sup>2</sup>	A (s <sup>-1</sup> )	β <sub>r</sub>	τ <sub>rad</sub> (μs)
${}^{5}G_{5}$	<sup>5</sup> I <sub>8</sub>	22883	0	0.5257	0	16654.041	0.426	25.58
	${}^{5}I_{7}$	17758	0.5889	0.0273	0.1133	16563.567	0.424	
	${}^{5}I_{6}$	14324	0.1329	0.1768	0.0791	3982.203	0.102	
	<sup>5</sup> I <sub>5</sub>	11712	0.0034	0.0662	0.0576	711.823	0.018	
	${}^{5}I_{4}$	9639	0	0.0094	0.0421	188.700	0.005	
	${}^{5}F_{5}$	7304	0.3494	0.0385	0.1183	794.649	0.020	
	${}^{5}S_{2}$	4470	0	0.11	0.0006	26.212	0.001	
	${}^{5}F_{4}$	4275	0.2867	0.0236	0.1429	144.895	0.004	
	${}^{5}F_{3}$	2273	0.1868	0.1031	0.0331	13.803	0.0004	
${}^{5}F_{3}$	<sup>5</sup> I <sub>8</sub>	21598	0	0	0.3465	24217.324	0.614	25.34
	${}^{5}I_{7}$	15485	0.0000	0.2472	0.2275	9673.459	0.245	
	${}^{5}I_{6}$	12051	0.0000	0.0892	0.2167	3279.529	0.083	
	<sup>5</sup> I <sub>5</sub>	9439	0.0000	0.2185	0.0179	867.853	0.022	
	${}^{5}I_{4}$	7366	0.0002	0.0982	0.3953	1259.552	0.032	
	${}^{5}F_{5}$	5031	0.0397	0.0807	0.0846	149.608	0.004	
	${}^{5}S_{2}$	2197	0.0070	0.0001	0.0000	0.477	0.000	
	${}^{5}F_{4}$	2002	0.0969	0.0313	0.0957	11.320	0.0003	
${}^{5}F_{4}$	<sup>5</sup> I <sub>8</sub>	20202	0	0.2421	0.7087	37977.217	0.879	23.14
	<sup>5</sup> I <sub>7</sub>	13483	0	0.196	0.0322	1978.265	0.046	
	${}^{5}I_{6}$	10049	0.0011	0.2576	0.1721	1792.532	0.042	
	<sup>5</sup> I <sub>5</sub>	7437	0.0016	0.1327	0.4651	1211.874	0.028	
	${}^{5}I_{4}$	5364	0.0002	0.0237	0.2585	227.233	0.005	
	${}^{5}F_{5}$	3029	0.2001	0.0919	0.0075	36.909	0.001	
${}^{5}S_{2}$	<sup>5</sup> I <sub>8</sub>	18116	0	0	0.2091	12074.004	0.513	42.47
	<sup>5</sup> I <sub>7</sub>	13288	0	0	0.4208	9588.815	0.407	
	${}^{5}I_{6}$	9854	0	0.0248	0.1421	1458.535	0.062	
	${}^{5}I_{5}$	7242	0	0.0057	0.0932	356.389	0.015	
	${}^{5}I_{4}$	5169	0.0015	0.0325	0.0285	66.181	0.003	
	${}^{5}F_{5}$	2834	0	0.0131	0.0058	3.017	0.0001	

Table 3. Calculated spontaneous emission probabilities, branching ratios and radiative lifetimes for  $Ho^{3+}$  in CdS -SiO<sub>2</sub> sol-gel

Table 3 shows the spontaneous emission probabilities (A), branching ratios ( $\beta_r$ ) and radiative lifetimes ( $\tau_{rad}$ ) for the observed emissions in Ho<sup>3+</sup> doped CdS -SiO<sub>2</sub> glass. The branching ratios as calculated for these transitions are 42.6, 61.4, 87.9 and 51.2 % respectively which indicates that  ${}^{5}F_{3} \rightarrow {}^{5}I_{8}$  and  ${}^{5}F_{4} \rightarrow {}^{5}I_{8}$  blue transitions contribute the majority of the photoluminescence emissions of Ho<sup>3+</sup> in the CdS -SiO<sub>2</sub> glass.

The  $\Omega_4$  parameter together with  $\Omega_6$  has very important effect on some transitions of Ho<sup>3+</sup>, such as the  ${}^5F_3 \rightarrow {}^{5}I_8$ and  ${}^5S_2 \rightarrow {}^5I_8$  transitions [5], because these transitions depend only on the  $\Omega_4$  and  $\Omega_6$  parameters as the reduced matrix elements of the unit tensor U(2)<sup>2</sup> is equal to zero (as listed in Table 3). Furthermore, for these transitions, U(4)<sup>2</sup> is also equal to zero; but U(4)<sup>2</sup> still has contribution on the other branching ratios for the  ${}^{5}F_3$  and  ${}^{5}S_2$ luminescence. Thus the smaller  $\Omega_4$  and larger  $\Omega_6$  are favorable for the  ${}^{5}F_{3} \rightarrow {}^{5}I_{8}$  and  ${}^{5}S_{2} \rightarrow {}^{5}I_{8}$  luminescence of Ho<sup>3+</sup>. In order to enhance the luminescence intensity of these two transitions in comparison to  ${}^{5}F_{3} \rightarrow {}^{5}I_{7,6,5,4}$ ,  ${}^{5}F_{5,4}$ ,  ${}^{5}S_{2}$  and  ${}^{5}S_{2} \rightarrow {}^{5}I_{6,5,4}$ ,  ${}^{5}F_{5}$  transitions, one therefore requires  $\Omega_{4} \ll \Omega_{6}$ . Therefore,  $\Omega_{4} / \Omega_{6}$  factor becomes critical [46] while measuring the efficiency of the visible laser transition  ${}^{5}F_{3} \rightarrow {}^{5}I_{8}$  and  ${}^{5}S_{2} \rightarrow {}^{5}I_{8}$  of Ho<sup>3+</sup>. From table 2 it is seen that the magnitude of  $\Omega_{4} / \Omega_{6}$  parameter for the Ho<sup>3+</sup>: CdS -SiO<sub>2</sub> glass is least among the compared glasses. This significant result indicates that these transitions in the studied CdS-SiO<sub>2</sub> glasses could be very potential transitions for blue and green lasing applications.

From the emission spectra of the glass, the emission level peak wavelength ( $\lambda$ ), effective band width ( $\Delta \lambda$ ) as well as full width at half maximum (FWHM) and stimulated emission cross-sections ( $\sigma(\lambda_p)$ ) were calculated and documented in table 4.

Emission Transition	λ (nm)	Δλ (nm)	FWHM (nm)	$\frac{\sigma(\lambda_p)}{(10^{-20} \text{cm}^2)}$	$ \sigma (\lambda_p) x \tau_{rad} (10^{-24} \text{ cm}^2 \text{s}) $	σ (λ <sub>p</sub> ) x FWHM (10 <sup>-26</sup> cm <sup>3</sup> )
${}^{5}G_{5} \rightarrow {}^{5}I_{8}$	437	13.87	16.93	2.48	0.6348	4.2027
${}^{5}\mathrm{F}_{3} \rightarrow {}^{5}\mathrm{I}_{8}$	463	18.47	15.46	3.42	0.8654	5.2814
${}^{5}\mathrm{F}_{4} \rightarrow {}^{5}\mathrm{I}_{8}$	495	24.66	40.25	5.24	1.2126	21.095
${}^{5}S_{2} \rightarrow {}^{5}I_{8}$	552	21.01	63.35	3.02	1.2845	19.159

Table 4. Calculated radiative parameters of  $Ho^{3+}$  doped CdS-SiO<sub>2</sub> glass.

Jorgensen et al. [47] and Sharma et. al. [48] reported that transitions having spontaneous emission probability greater than 500 s<sup>-1</sup>, fluorescence branching ratio ~ 0.5 and ~ 6000 cm<sup>-1</sup> of energy separation between the energy level under consideration and terminating level are considered to be good radiative transitions. The last requirement is generally essential in order to circumvent the nonradiative rates. Calculated radiative parameters of the observed emission bands for the present glass reveals that the transitions are efficient radiative transitions as these transitions obey the above mentioned conditions required for a good radiative transition. The estimated peak stimulated emission cross-sections obtained for the four observed radiative transitions for the Ho<sup>3+</sup> in CdS-SiO<sub>2</sub> glass are found to be 2.48 x10<sup>-20</sup>, 3.42 x10<sup>-20</sup>, 5.24 x10<sup>-20</sup> and 3.02 x10<sup>-20</sup> cm<sup>2</sup>. Comparison of these parameters (shown in table 5) with that in GdVO<sub>4</sub> crystal, oxyfluoroborate glass, PbO–Al<sub>2</sub>O<sub>3</sub>–B<sub>2</sub>O<sub>3</sub> glass and leadzinc-borate glass [24,40,41,49] suggests that the studied glass possesses significantly higher values of emission cross sections which indicates that the CdS-SiO<sub>2</sub> glass is an efficient host material for Ho<sup>3+</sup> green and blue lasing operations under upconversion and downconversion pump. Comparison of the figure of merit parameter  $\sigma$  ( $\lambda_p$ ) x  $\tau_{rad}$ for the present glass with other hosts reveal that the parameter is of same order with PbO-Al<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> [49], lead silicate and lead zinc borate glasses [24] but inferior to oxyfluoroborate glass [41] and GdVO<sub>4</sub> crystals [40].

*Table 5. Comparison of stimulated emission cross sections and radiative lifetimes of the observed Ho*<sup>3+</sup> *transitions in different hosts.* 

$\sigma(\lambda_{\rm p}) (10^{-20} {\rm cm}^2)$								
	CdS-SiO <sub>2</sub>	GdVO <sub>4</sub>	Oxyfluoroborate	PbO-Al <sub>2</sub> O <sub>3</sub> -	Lead	Lead Zinc		
		crystals	glass	B <sub>2</sub> O <sub>3</sub> glass	silicate	Borate glass		
${}^{5}G_{5} \rightarrow {}^{5}I_{8}$	2.48							
${}^{5}F_{3} \rightarrow {}^{5}I_{8}$	3.42		0.56			0.46		
${}^{5}F_{4} \rightarrow {}^{5}I_{8}$	5.24		0.40			0.31		
${}^{5}S_{2} \rightarrow {}^{5}I_{8}$	3.02	1.83	0.38	0.42	0.343	0.21		
τ <sub>rad</sub> (μs)	$ au_{rad}(\mu s)$							
${}^{5}G_{5} \rightarrow {}^{5}I_{8}$	25.58							
${}^{5}F_{3} \rightarrow {}^{5}I_{8}$	25.34	146	2080			418		
${}^{5}F_{4} \rightarrow {}^{5}I_{8}$	23.14	144			240	421		
${}^{5}S_{2} \rightarrow {}^{5}I_{8}$	42.47	250	1070	340	400	687		
$\sigma (\lambda_p) x \tau_{rad} (10^{-24} \text{ cm}^2 \text{s})$								
${}^{5}G_{5} \rightarrow {}^{5}I_{8}$	0.6348							
${}^{5}F_{3} \rightarrow {}^{5}I_{8}$	0.8654		11.85			1.92		
${}^{5}F_{4} \rightarrow {}^{5}I_{8}$	1.2126					1.31		
${}^{5}S_{2} \rightarrow {}^{5}I_{8}$	1.2845	4.57	4.06	1.42	1.36	1.44		

Present study shows that  $Ho^{3+}$  doped CdS-SiO<sub>2</sub> glass possess improved J.O. intensity parameters and yields very efficient green and blue photoluminescence. The result is attributed to the change in structural modifications of the glass network because of the addition of CdS. Studies have revealed that the absorption and photoluminescence intensity of RE doped in glasses depend strongly on the network formers and network modifiers. Yang et al. [50] proposed that the doping of CdS can increase concentration of Si dangling bonds and oxygen vacancy in the network of the silica xerogel. This means that CdS is thought to introduce non-bridging oxygens (NBOs) into the mix, which are oxygens that form only one bond with silica, leaving another open to bond with a RE. In this

way, CdS surrounds each RE ion, distancing each ion from the other. This in turn reduces cross-relaxation and increases photoluminescence.

### 4. Conclusions

In this communication, co-doped Ho<sup>3+</sup> and CdS in silica glasses were prepared by the sol-gel technique. The prepared glasses were analyzed from the absorption and photoluminescence spectra by using the phenomenological J.O. theory. The calculated J.O. intensity parameter  $\Omega_2$  for the present glass host is observed to be significantly higher than the compared glasses which are very critical for application of the glass as host for lasers and other optical devices. The smaller value of spectroscopic quality factor  $\Omega_{4}/\Omega_{6}$  for the glass is very encouraging for the  ${}^{5}F_{3} \rightarrow {}^{5}I_{8}$ , and  ${}^{5}S_{2} \rightarrow {}^{5}I_{8}$  lasing transitions of Ho<sup>3+</sup>. The higher values of emission cross sections possessed by the present glass indicates that the CdS-SiO<sub>2</sub> glass acts a promising host material for Ho<sup>3+</sup> green and blue lasing transitions.

#### References

- [1] P. Bettotti, Advances in Optics **2014**, 1 (2014).
- [2] M. P. Andrews, S. I. Najafi, Proceeding of. SPIE, San Diego, CA, Aug 1997.
- [3] J J. Li, R. Wei, X.Y. Liu, H. Guo, Opt. Express 20(9), 10122 (2012).
- [4] M. Reddy, G.R. Dillip, K. Mallikarjuna, B. Sudhakar Reddy, K. Vemasevana Raju, D. P. Raju, Photonics Letters of Poland 3 (1), 32 (2011).
- [5] X. Qiao, X. Fan, J. Wang, M. Wang, J. Appl. Phys. 99, 0743021 (2006).
- [6] P. Dutta, Optoelectron. Adv. Mat. 6(3-4), 427 (2012).
- [7] S. R. Elliott, Physics of Amorphous Materials, Longman Science and Technology, Essex, 1990, Section 3.
- [8] V. Lavin, F. Lahoz, I.R. Martin, U.R. Rodriguez-Mendoza, J. M. Caceres, Opt. Mater. 27, 1754 (2005).
- [9] J. C. Boyer, F. J. Vetrone, A. Capobianco, A. Speghini, M. Bettinelli, J. Appl. Phys. 93, 9460 (2003).
- [10] E. Rukmini, C.K. Jayasankar, Opt. Mater. 4, 529 (1995).
- [11] A.V. Kiryanov, V. Aboites, A.M. Belobolov, M.J. Damzen, A. Minasian, M.I. Timoshechkin, M.I. Belobolov, J. Lumin. **102-103**, 715 (2003).
- [12] J.C. Boyer, F. Vetrone, J.A. Capobianco, A. Speghini, M. Bettinelli, J. Appl. Phys. 93, 9460 (2003).
- [13] B. Karmakar, J. Solid State Chem. 178, 2663 (2005).
- [14] L. Feng, J. Wang, Q. Tang, L.F. Liang, H.B. Liang, Q. Su, J. Lumin. **124**, 187 (2007).
- [15] X. Wang, H. Lin, D. Yang, L. Lin, E.Y.B. Pun, J. Appl. Phys. 101, 1135351(2007).
- [16] F. Lahoz, I.R. Martin, A. Briones, J. Appl. Phys. 95, 2957 (2004).
- [17] A.K. Singh, S.B. Rai, V.B. Singh, J. Alloy Compd. 403, 97 (2005).
- [18] X. Zhang, X. Liu, J.P. Jouart, G. Mary, Chem. Phys. Lett. 287, 659 (1998).
- [19] J.C. Boyer, F. Vetrone, J.A. Capobianco, A. Speghini, M. Zambelli, M. Bettinelli, J. Lumin. 106, 263 (2004).
- [20] E. Osiac, I. Sokolska, S. Kuck, J. Alloys Compd. 323-324, 283 (2001).
- [21] D. Chen, Y. Wang, E. Ma, F. Bao, Y. Yu, Scripta Mater. 55, 891(2006).
- [22] T. Hayakawa, S. Tamil Selvan, M. Nogami, J. Sol-Gel Sci. Tech. 19, 779 (2000).
- [23] J.P. Arago, B.J. Lopez, E. Cordoncillo, P. Escribano, F. Pelle, B Vianab, B. Sanchez, J. Mater. Chem. 18(43), 5169 (2008).
- [24] S. T. Selvan, T. Hayakawa, M. Nogami, J. Phys. Chem. B. 103, 7064 (1999).

- [25] N. S. Hussain, N. Ali, A. G. Dias, M. A. Lopes, J. D. Santos, S. Buddhudu, Thin Solid Films 515, 318 (2006).
- [26] S. T. Selvan, T. Hayakawa, M. Nogami, J. Non-Cryst. Solids 291, 137 (2002).
- [27] P. Dutta, S. Rai, Optik 122, 858 (2011).
- [28] S. Rai, P. Dutta, AIP Conference Proceedings for International Conference on Transport and Optical Properties of Nanomaterials—ICTOPON - p 475, 2009.
- [29] B.R. Judd, Phys. Rev. 127(3), 750 (1962).
- [30] G.S. Ofelt, J. Chem. Phys. 37(3), 511 (1962).
- [31] R.D. Peacock, The intensities of lanthanide f-f transitions, In Rare Earths Structure and Bonding 22, Dunitz, J.D. Hemmerich, P, Eds.; Springer-Verlag Berlin and Heidelberg, p.83, 1975.
- [32] N. Rakov, G. S. Maciel, C. B. de Araujo, Y. Messaddeq, J. Appl. Phys. 91(3), 1272 (2002).
- [33] G.H. Dieke, Spectroscopic Observations on Maser Materials, In Advances in Quantum Electronics, Singer, J.R. Ed; Columbia University Press, New York, p.164, 1961.
- [34] W.T. Carnall, P.R. Fields, K. Rajnak, J. Chem. Phys. 49, 4424 (1968).
- [35] R. Das, S. Pandey, International Journal of Material Science 1(1), 35 (2011).
- [36] K. Susumu, I.L. Medintz, H. Mattoussi, Colloidal Quantum Dots, Synthesis, photophysical properties and Biofunctionalisation Strategies Mattoussi, H.; Cheon, J. Eds Inorganic Nanoprobes for Biological Sensing and Imaging, Artech House, p1, 2009.
- [37] X. Ma, X. Zhang, J. Gong, N. Wang, B. Fan, L. Qu, Cryst.Eng. Commun. 14, 246 (2012).
- [38] H. Lin, E. Y. B. Pun, X. R. Liu, J. Non-Cryst. Solids 283, 27 (2001).
- [39] M. Eyal, E. Greenberg, R. Reisfeld, N. Spector, Chem. Phys. Lett. 117, 108 (1985).
- [40] Y. Yang, B. Yao, B. Chen, C. Wang, G. Ren, X. Wang, Opt. Mater. 29, 1159 (2007).
- [41] S. B. Rai, Spectrochim. Acta Part A, 58(8), 1559 (2002).
- [42] R. R. Reddy, Y. N. Ahammed, P. A. Azeem, K. R. Gopal, T. V. Rao, S. Buddhudu, N. S. Hussain, J. Quant. Spectrosc. Radiat. Transfer 77, 149 (2003).
- [43] V. Ravi Kumar, M. Rami Reddy, N. Veeraiah, Phys. Status Solidi A 147(2), 601 (1995).
- [44] F. Fermi, G. Ingletto, C. Aschieri, M. Bettinelli, Inorg. Chim. Acta 163, 123 (1989).
- [45] C. Guery, J. L. Adam, J. Lucas, J. Lumin. 42, 181 (1988).
- [46] A. A. Kaminskii, Laser Crystals: Their Physics and Properties, 4th ed.; Springer-Verlag: New York, p.142,1996.
- [47] C. K. Jørgensen, R. Reisfeld, Journal of Less Common Metals 93, 107 (1983).
- [48] Y. K. Sharma, S. S. L. Surana, R. K. Singh, R. P. Dubedi, Opt. Mater. 29, 598 (2007).
- [49] M. R. Reddy, S. B. Raju, N. Veeraiah, J. Phys. Chem. Solids 61, 1567 (2000).
- [50] P. Yang, C. F. Song, M. K. Lu, X. Yin, G. J. Zhou, D. Xu, D. R. Yuan, Chem. Phys. Lett. 345, 429 (2001).

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