International Journal of Current Research in Science and Technology
Volume 2, Issue 1 (2016), 29–32. (Special Issue)
ISSN: 2394-5745
Available Online: http://ijcrst.in/

International Journal of Current Research in Science and Technology

Judd Ofelt Theory: A Suitable Tool to Study Rare Earth Spectra

Seminar Paper*

Pankaj Dutta[1]

1 Laser and Spectroscopy Laboratory, Department of Physics, Dibrugarh University, Dibrugarh, Assam, India.

Abstract: Rare earths are a very important class of optical materials that have been used in diverge areas of science and technology. The application domains of rare earths are mainly based on their optical absorption and luminescence spectra that arise because of the 4f electronic transitions. In this work, Judd Ofelt theory has been successfully applied for analyzing absorption spectra for a very efficient rare earth, Holmium in silica glasses. The physical significance of the obtained Judd Ofelt intensity parameters was highlighted.

Keywords: Judd Ofelt, Analyzing absorption spectra, physical significance.

1. Introduction

Rare-earth (RE) ions have been the subject of intensive investigations for last several decades. A unique combination of their partially filled 4f^n-electron shell ($1 < n < 14$) (which has a large number of possible energetic states) and screening effect produced by their completely filled 5s^{2}5p^6-electron shells (which weakens the influence of external electric and magnetic fields on 4f-electrons) makes them very attractive for numerous applications, e.g. as activator ions in solid state lasers and phosphors covering a wide spectral range from infrared (IR) to ultraviolet (UV) spectral regions [1]. They are chiefly trivalent and it is principally the properties of the trivalent ions which are important rather than neutral atoms. Their trivalent salts have absorption spectra and in some cases fluorescence spectra with sharp lines in the visible or neighboring spectral regions which is why they are important as optical materials [2].

RE ions are used as dopants mainly for two reasons. The first one is their well defined and sharp energy levels, which may serve as structural probes for the environment of the dopants and the other one is the modification of the energy level structure of the RE ions caused by the host environment may lead to interesting applications e.g. solid state lasers [3]. The optical spectroscopy of RE laser materials is mainly concerned with the interaction of electronic centres (ions of RE metals) with optical radiation in insulating solids (crystals and glasses). The energy levels associated with 3d^n and 4f^n electronic configurations (of ions of RE elements) are the most important active ions for laser materials.

The Judd Ofelt (J.O.) theory [4, 5] is the most suitable theory to characterize the intensities of forced electric-dipole transitions between 4f states of lanthanide ions, where, the absorption and emission probabilities for an ion matrix combination

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[*] *Proceedings : UGC Sponsored National Seminar on* `Value and Importance of Mathematical Physics` *held on 05.12.2015, organized by Department of Mathematics and Physics, Government Rajeev Lochan College, Rajim, Gariaband (Chhattisgarh), India.*

are given as a function of a set of three parameters, i.e. the intensity or J.O. parameters. The theory has been successfully applied to account for the optical properties of lanthanide ions in solid matrices [6].

Before Judd and Ofelt work, the main emphasis in theoretical interpretation of trivalent lanthanide and actinide absorption spectra had been upon the correlation of the experimentally observed energy levels with those calculated by diagonalisation of the complete energy matrices of the appropriate f^nelectron configurations [6-12]. These calculations were surprisingly successful and led to the establishment of reasonably reliable intermediate coupling eigenvectors for most of the low lying energy levels. Early estimates of the relative importance of the different modes by which electronic transitions can occur within the f^n configuration were made by Van Vleck [13]. Subsequently, Broer et al [14] revised and extended these estimates and presented as well a considerable amount of experimental data on the intensities of lanthanide spectra in aqueous solutions. The actual calculation of intensities has been made feasible by the classic work of Judd [1] and Ofelt [2].

In the present work, the Judd Ofelt parameters for a very important RE Holmium in silica glasses have been calculated from the observed absorption and PL spectra. The significance of the Judd Ofelt intensity parameters related to absorption and PL characteristics of the RE in the glassy environment is also highlighted.

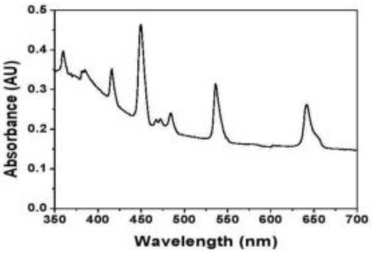
2. Experimental

The glass samples for the present study were prepared by the sol-gel method as described in earlier papers [7]. Ho_2O_3 (0.01M) as the source of Ho^{3+} were used. All the chemicals used in the preparation method were of analytical grade and were used as received. 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) at the scanning range from 350 to 1000 nm using undoped glass as reference. All the measurements were done at room temperature.

3. Results and Discussions

3.1. Absorption Spectra and Judd Ofelt Analysis

The room temperature optical absorption spectrum of Ho^{3+} doped -SiO_2 glasses in the region of 400-1000 nm, ascribed to electric dipole (e-d) transitions is shown in figure 1. The final states of the electronic transitions from the Ho^{3+} ground states associated with the absorption bands are indicated in the figure. Ten bands for the transitions from $^5I_8$ ground state to $^3H_6$, $^5G_4$, $^5G_5$, $^5G_6$, $^3K_6$, $^3K_8$, $^5F_3$, $^5F_4$, $^5F_5$ and $^5I_5$ states respectively, are observed. Assignments of the peaks are done by comparing with earlier works [8, 9].



The experimental oscillator strengths ($f_{\exp}$) of the observed e-d transitions are determined from the following relation

$$f_{\exp} = 4.318 \times 10^{-9} \int \varepsilon(\nu) d\nu \tag{1}$$

Where, $\varepsilon(\nu)$is the molar extinction co-efficient at wave no $\nu(\mathrm{cm}^{-1})$ determined from Lambert Beer's law. To determine the Judd-Ofelt parameters (T_t) for t = 2, 4 & 6, oscillator strengths measured experimentally are co-related with its corresponding Judd's [4] expression for oscillator strengths of e-d transitions between initial ΨJ and terminal $\Psi' J'$ states, by

$$f_{cal} = \sum T_t \nu \left(\left\langle \Psi J \parallel U(t) \parallel \Psi^{/} J^{/} \right\rangle \right)^2 \tag{2}$$

using the least square fit analysis. In Equation (2), $U(t)$is a tensor operator of rank t calculated in an intermediate coupling approximation [10]. Since the values of these operators are essentially independent of hosts, values calculated by Carnall et al [11] for Ho^{3+}(aquo) ions are used in these calculations. The summation in Equation (2) is over the three values of t = 2, 4 & 6. In the characterization of spectral intensities of the absorption bands, the glass refractive index (n) plays an important role. Therefore, the original J.O. parameters (T_t) are transformed into Ω_t through the following expression,

$$\Omega_t = \frac{3h}{8\pi^2 mc} \frac{9n}{(n^2+2)^2} (2J+1) T_t \tag{3}$$

In Equation (3), n is the refractive index of material,$(2J+1)$ 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^{3+} transitions are compiled in table I along with the J.O. intensity parameters (Ω_t).

Grnd. state	Exctd. state	Energy,(cm^{-1})	Oscillator Strength (10^{-6})	
			Calctd. (f_{cal})	Exptl., (f_{exp})
$^5I_8$	$^3H_6$	27778	2.63	3.35
	$^5G_4$	25974	2.75	2.45
	$^5G_5$	24031	3.65	2.70
	$^5G_6$	22227	1.61	1.60
	$^3K_6$	21403	4.16	4.89
	$^3K_8$	21187	1.82	6.78
	$^5F_3$	20661	3.20	1.82
	$^5F_4$	18657	7.17	6.60
	$^5F_5$	15588	5.85	8.48
	$^5I_5$	11249	5.03	6.93
r.m.s deviation (10^{-6})			1.11	
$\Omega_2(10^{-20}cm^2)$			5.15	
$\Omega_4(10^{-20}cm^2$			7.39	
$\Omega_6(10^{-20}cm^2)$			9.65	
Ω_4/Ω_6			0.77	

Table 1. The experimental and theoretical oscillator strengths with Judd Ofelt intensity parameters for Ho^{3+} transitions in pure-$\mathrm{SiO_2}$ glass.

The values of experimental and theoretical oscillator strengths are in good agreement with an r.m.s deviation of ± 1.11 x 10^{-6} between them which suggests the reliability of the calculation process. The larger differences observed between the calculated and the experimental values of oscillator strengths for some of the transitions is because of 4f–5d mixing [12] which may contribute to intensities with odd values of t in $\|U(t)\|$ matrix elements which are neglected in the J.O. model.

Host Glasses	$\Omega_2(10^{-20}\ \mathrm{cm}^2)$	$\Omega_4(10^{-20}\ \mathrm{cm}^2)$	$\Omega_6(10^{-20}\ \mathrm{cm}^2)$	$\Omega_4/\ \Omega_6$	Reference
Pure- $\mathrm{SiO_2}$	5.15	7.39	9.65	0.77	Present work
$\mathrm{Al(NO_3)_3}$- $\mathrm{SiO_2}$	6.07	6.10	9.83	0.62	[7]
CdS-$\mathrm{SiO_2}$	16.7	10.9	18.2	0.59	[13]

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

The J.O. intensity parameters obtained in the present glass is compared with other silica glass hosts with addition of $Al(NO_3)_3$ and CdS as co-dopant and is presented in table II. The Ω_2 parameter of the pure SiO_2 glass is found to be less than the other silica glasses which indicates that asymmetry and covalent environment between RE and ligand ions in Ho^{3+} single doped pure-SiO_2 glass are stronger than those in other compared glasses.

4. Conclusions

The J.O. intensity parameters (Ω_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 [14]. The $\Omega_4$and$\Omega_6$parameters depend on bulk property 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 [15]. Moreover, the values of the J.O. intensity parameters can be used to calculate the spectroscopic quality factorΩ_4/Ω_6, which is critically important in predicting the stimulated emission for the laser active medium [14, 16] . Another important parameter that can be evaluated from the Judd Ofelt theory is the magnitude of the spectroscopic quality factorΩ_4/Ω_6 which is very critical for some transitions of RE ions. The comparison of this parameter for the compared glasses indicate that CdS co-doped glass hosts recognizes this to be a better optical glass for Ho^{3+} transitions in silica host.

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