SPECTROSCOPIC STUDIES OF Er^{3+} DOPED IN SOL-GEL SILICA GLASS

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Abstract: Trivalent Erbium ions (Er^{3+}) doped in silica glass was prepared by sol-gel technique which relies on the chemical reaction of liquid precursors to form the glass. Absorption spectrum was recorded in the visible region which shows several peaks resulting from the transition from ground state $^4I_{15/2}$ to various excited states. The optical absorption has been investigated using Judd-Ofelt (J-O) theory. J-O parameters were obtained from the absorption spectrum. Large value of the parameter Ω_2 shows that the bonding of the dopant to the host network is more covalent than ionic.

Keywords: sol-gel; erbium; absorption; Judd-Ofelt

1. Introduction:

Rare earth (RE) ions embedded into glasses and crystals and nano particles via sol-gel process enables the design of photonic and Opto-electronic materials. Since the f- orbital is strongly shielded from the outside ligands, the position of the spectral lines vary only slightly with the environment, however their intensities are strongly dependent on the host where the RE ions is embedded. Currently there is a growing interest in the study of new photonic materials prepared by sol-gel technique. Study of trivalent rare earth ions doped materials for their possible applications in optical amplifiers, display devices, communication fields and solid state lasers [1, 2]. Glasses are well suitable hosts for the rare-earth ions as they provide a long composition range, good rare earth solubility and cost effective. Silica glass has many favorable properties as a host for rare earth (RE) ions as it has high transparency, good chemical and thermal stability, low thermal expansion and good mechanical strength [3,4-6]. In this sense, glass has proved to be useful as host materials for rare-earth ions, because of their high transparency composition and easy mass production. This is explained by the presence of a large concentration of radiation-induced color centers [7].The optical properties of RE ions with transitions between different $4f^n$ energy states [8]. Among the RE ions $Er^{3+}$is the most favorable and extensively studied [9-11].
In this paper we investigate the Optical properties of Er^{3+} doped with sol-gel silica glass. The optical absorption has been investigated using the Judd-Ofelt theory. J-O parameters Ω_2, Ω_4, Ω_6 were obtained from the absorption spectrum and used to study the optical properties of the prepared glass sample [12-14].

2. Experimental method:

2.1. Glass sample preparation:

The silica glass samples were prepared by the procedure similar to that described in our previous paper [15, 16]. The sol-gel silica glass containing in ratio of TEOS, H_2O, C_2H_5OH and HNO_3 is 1:5.5:3.5:0.1 and in this present work Erbium oxide is used as source of Er^{3+}in place of $Pr(NO_3)_3$.$6H_2O$ and $HoCl_3.6H_2O$. The samples were dried by slow heating to 90℃ then annealed in an electric muffle furnace up-to 1000℃ with heating rate 1℃ per 1 minute to form dense glass samples with thickness 0.2cm, diameter 1.6cm, density 2.06 g/cm^3 and refractive index 1.62.

2.2. Experimental setup:

Absorption spectra were recorded in the visible region at room temperature using iHR320 imaging spectrometer in the spectral range of 400-900nm, using Syner JY™ software from Horiba Scientific fully integrated data acquisition.

3. Results and discussions:

3.1. Absorption and Judd-Ofelt analysis:

Absorption Spectra:

The spectral intensities of f-f transitions of RE have been treated using phenomenological approach of Judd-Ofelt theory [12, 13]. The electronic dipole line strength is expressed as a sum of product of experimentally derived intensity parameters and matrix elements of tensor operators connecting states of $4f^n$ configuration. Intensity parameters determined for a given ion host are used to calculate the probability of transitions between any $4f^n$ level of interest for laser action. This includes adsorption and fluorescence intensities, excited state absorption, radiative lifetime and branching ratios. Since the J-O parameters do not differ greatly for adjacent ions in the lanthanide series elements can be made using extrapolated values. In glasses, transition probabilities as well as energy levels vary from site to site.

By Judd-Ofelt (J-O) theory, the analysis of the radiative transition in the 4f states of Er^{3+} is performed. According to J-O Theory, the calculated oscillator strength (f_{cal}) of the electric dipole transition between two states $|l^N SLJ> \rightarrow |l^N S'L'J'>$ can be expressed as,

$$f_{cal}^{ed} = \frac{8\pi^2 mc\bar{v}(n^2+2)^2}{3h(2J+1)9n} \sum_{\lambda=2,4,6} \Omega_\lambda |\langle l^N SLJ \| U^{(\lambda)} \| l^N S'L'J'\rangle|^2 \tag{1}$$

where, m=9.10904×10^{-28} g is the mass of electron, c=2.9979×10^{10}cms^{-1} is the velocity of light, h=6.6261×10^{-27} erg is Planck's constant, J is the total angular momentum of the initial state, n=1.62 is the refractive index, Ω_λ are the J-O intensity parameters and $\|U^{(\lambda)}\|$ are the reduced matrix elements evaluated in the intermediate coupling approximation for transition $|l^N SLJ> \rightarrow |l^N S'L'J'>$ at energy $\bar{v}$ expressed in cm^{-1}. The reduced matrix elements $\| U^\lambda \|$ are known to be relatively host independent, so the values obtained by Carnall et al. [17], are used in the calculations.

The experimental oscillator strengths for transitions from the ground state to the excited states are determined from the absorption spectrum, using the following relation,

$$f_{exp} = \frac{8\pi^2 m_e c\, v}{he^2} \int \varepsilon(\bar{v})\, dv \tag{2}$$

where, e = 4.803×10^{-10}esu (elementary charge), m_e = 9.10904×10^{-28} g (mass of electron), c = 2.9979×10^{10}cms^{-1} (speed of light), h = 6.6261×10^{-27} erg (Planck's constant) v = wave no. at the absorption maximum (cm^{-1}). Using the constants:

$$f_{exp} = 4.319 \times 10^{-9} \int \varepsilon(\bar{v})\, dv \tag{3}$$

where, $\varepsilon(\bar{v})$ is the molar absorptivity at energy $(\bar{v})$ cm^{-1}. The molar absorptivity, ε values can be calculated from the absorbance A by use of Lambert Beer Law:

$$A = \varepsilon.d.c \tag{4}$$

where ε is the molar absorptivity [dim: L^2, units: mol^{-1}[cm-1]], c is the concentration [dim:L^{-3},units:mol^{-1}], d is the optical path length [dim: L, units: cm]. The area can be determined by integrating the peak which is equivalent to the calculation of the integral

$$\int \varepsilon(\bar{v})\, dv \tag{5}$$

The Judd-Ofelt intensity parameters are evaluated using least square fitting and the oscillator strengths obtained from equation (3) which is experimentally determined values and co-related with the theoretical expression given in Eq. (1).

Fig1 shows the absorption spectrum of Er^{3+}doped glass which has been recorded in the 400-900nm region. Absorption bands observed at different wavelengths of 795nm, 653nm, 543nm, 521nm, 488nm and 433nm corresponding to the transitions $^4I_{15/2} \rightarrow ^4I_{9/2}$, $^4I_{15/2} \rightarrow ^4F_{9/2}$, $^4I_{15/2} \rightarrow ^4S_{3/2}$, $^4I_{15/2} \rightarrow ^4H_{11/2}$, $^4I_{15/2} \rightarrow ^4F_{7/2}$, $^4I_{15/2} \rightarrow ^4F_{5/2} + ^4F_{3/2}$ from the ground state to different excited states. Among these transitions $^4I_{15/2} \rightarrow ^4H_{11/2}$ transition at 521nm has maximum intensity.
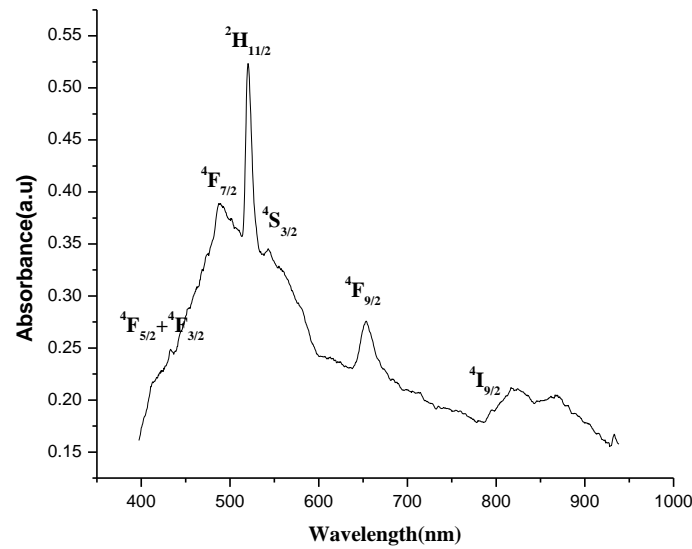
Figure 1: Absorption spectra of Er^{3+} doped glass.

The J-O intensity parameters along with the experimental and calculated oscillator strengths of Erbium doped sample heated to 1000^0C with the refractive index of glass sample, n=1.62 is given below in Table 1 and 2.

Table 1: Shows oscillator strengths for the absorption bands of Erbium doped sample.

Transition $^4I_{15/2} \rightarrow$	Wavelength (nm)	Energy (Cm^{-1})	Area	Concentration	Thickness (cm)	$f_{exp}(\times 10^{-6})$	$\|U^{(2)}\|^2$	$\|U^{(4)}\|^2$	$\|U^{(6)}\|^2$	$f_{cal}(\times 10^{-6})$
$^4I_{9/2}$	795	12578	6.59	1	0.2	0.17	0	0.1733	0.0099	0.10344
$^4F_{9/2}$	653	15313	17.185	1	0.2	0.44	0	0.5354	0.4618	0.4575
$^4S_{3/2}$	543	18416	2.679	1	0.2	0.069	0	0	0.2211	0.0422
$^2H_{11/2}$	521	19193	52.094	1	0.2	1.347	0.7125	0.4125	0.0925	1.347
$^4F_{7/2}$	488	20491	10.595	1	0.2	0.274	0	0.1469	0.6266	0.27429
$^4F_{5/2}+^4F_{3/2}$	433	23094	1.324	1	0.2	0.0342	0	0	0.1272	0.0304

Table2: Shows the Judd-Ofelt intensity parameters for the absorption bands of Erbium doped sample.

Transition $^4I_{15/2} \rightarrow$	$\|U^{(2)}\|^2$	$\|U^{(4)}\|^2$	$\|U^{(6)}\|^2$	$f_{cal}(\times 10^{-6})$	$f_{exp}(\times 10^{-6})$	$\Omega_2(cm^2)$	$\Omega_4(cm^2)$	$\Omega_6(cm^2)$	SQF= $\frac{\Omega_4}{\Omega_6}$
$^4I_{9/2}$	0	0.1733	0.0099	0.10344	0.17				
$^4F_{9/2}$	0	0.5354	0.4618	0.4575	0.44				
$^4S_{3/2}$	0	0	0.2211	0.0422	0.069	0.704×10^{-20}	0.471×10^{-20}	0.104×10^{-20}	4.4
$^2H_{11/2}$	0.7125	0.4125	0.0925	1.347	1.347				
$^4F_{7/2}$	0	0.1469	0.6266	0.27429	0.274				
$^4F_{5/2}+^4F_{3/2}$	0	0	0.1272	0.0304	0.0342				

The J-O intensity parameters Ω_λ (λ=2, 4, 6) are found by comparing experimentally and theoretically calculated oscillator strengths, but in our present studies have found some trend that relates the parameters to the local environment of the Er^{3+}ions. From table-1 it is found that J-O intensity parameters have the following trends $\Omega_2 > \Omega_4 > \Omega_6$. The large value of Ω_2 indicates the presence of covalent bonding between the rare earth ions and glass host. The J-O intensity parameter Ω_2 is very sensitive to the structure and it is associated with the symmetry and covalency of lanthanide sides. On the other hand Ω_4 and Ω_6 values show the viscosity and dielectric properties of the media and also affected by the vibronic transition of the rare earth ions bond to the ligand atoms. J-O intensity parameters can be used to calculate the spectroscopic quality factor (SQF $= \frac{\Omega_4}{\Omega_6}$) = 4.4 which determines the stimulated emission for the laser active medium.

4. Conclusions:

In this work Er^{3+}doped in sol-gel silica glass is characterized. The optical absorption of the prepared sample is used to study the spectroscopic properties and to obtain Judd-Ofelt intensity parameters. The Judd-Ofelt intensity parameters in the prepared samples are in the order of trends $\Omega_2 > \Omega_4 > \Omega_6$.

References:

[1] E. S. Nurbaisyatula, K. Azmanb , H. Azhanb , W. A. W. Razalib , A. Noranizaha , S. Hashimc and Y. S. M. Alajerami, Journal of Optics and Spectroscopy 116(3), 413, 2014.
[2] I. Kostova, G. Patronov and D. Tonchev, *Journal of Chemical* Technology and Metallurgy 53(6), 1087, 2018.
[3] H. Lian, Z. Hou, M. Shang, D. Geng, Y. Zhang and J. Lin, Journal of Energy 57, 270, 2013.
[4] W. Yang, X. Li, D. Chi, H. Zhang and X. Liu, Journal of Nanotechnology 25, 482001, 2014.
[5] M. Vega, P. Alemany, I.R. Martin and J. Llanos, Journal of RSC Advances 7 , 10529, 2017.
[6] S. Rai and A.L. Fanai, Journal of Luminescence 170, 325, 2016.
[7] B. H. Babu, N. Ollier, M. L. Pichel, H. El Hamzaoui, B. Poumellec, L. Bigot, I. Savelii, M. Bouazaoui, A. Ibarra and M. Lancry, Journal of Applied Physics 118, 123107, 2015.
[8] R. D Peacock, The Intensities of Lanthanide f↔f Transitions, in Rare Earths: Structure and Bonding edited by J.D. Duunitz, Z.P. Hemmerich, R.H. Holm, J.B.Ibers, D. Reinen and R.J.P. Williums, (Springer, Berlin, 1975) Vol.22.
[9] M.J. Weber, Journal of Physical Review 157, 262, 1967.
[10] M. Ferrari and C. Armellini, Journal of Sol-Gel Science and Technology 19, 569, 2000.
[11] A. Biswas, G.S. Maciel, R. Kapoo, C. S. Friend and P.N. Prasad, Journal of Applied Physics Letters 82, 2389, 2003.
[12] B.R. Judd, Journal of Physical Review 127, 750, 1962.
[13] G.S. Ofelt, Journal of Chemical Physics 37, 511, 1962.
[14] M.P. Hehlen, M.G. Brik and K.W. Kramer, Journal of Luminescence 136, 221, 2013.
[15] A. L. Fanai, U. Khan and S. Rai, Journal of Non-Crystalline Solids 503, 89, 2019.
[16] S. Rai and A. L. Fanai, Journal of Non-Crystalline Solids 449, 113, 2016
[17] W. T. Carnall, P.R. Fields and K. Rajnak, Journal of Chemical Physics 49(10), 4424, 1968.