Absorption Spectral Studies of Er^{+3} Ions in Sol–Gel Derived Silica Glass

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***Abstract*—Er^{3+} doped Silica glass (SGS01) has been prepared by Sol-Gel technique. The absorption spectral studies of doped Sol-Gel derived Silica glass has been performed to compute the phenomenological Judd-Ofelt parameters (Ω_λ) and various spectroscopic parameters like Slater-Condon parameter (F_k) k=2,4,6, Lande. parameter (ζ_{4f}), Racah parameter (E^k) k=1,2,3, nephelauxetic ratio ($\beta^{'}$) and bonding parameters ($b^{1/2}$) to study the local structure of the ligands around the rare earth ion. The result of the investigations with essential discussions and conclusions has been reported in this paper.**

Keywords*— *Sol–gel silica glass, Absorption Spectra, Judd-Ofelt parameter, Laser parameter, Doped glass.

I. INTRODUCTION

The sol-gel process actually offers unique opportunity for the synthesis of optical materials with composition stoichiometrically controlled. The homogeneous mixture of several components in liquid state makes it possible to vary the optical materials over a wide range of compositions at molecular level, therefore the optical properties of the materials are tailored, such as Ge dopants to change the refractive index [1], P dopants to increase nonlinear gain coefficient of silica and rare earth dopants to create gain in the host materials [2]-[4]. In summary, the sol-gel method provides an efficient and cost-effective platform for us to explore the effects of different dopants on the properties of the micro-cavities. Sol–gel glasses doped with rare-earth (RE) ions are of interest for various applications including solid state lasers, optical waveguides and fibre amplifiers. Rare earth ions can be incorporated into a variety of host materials. In the early years of solid state lasers crystalline hosts doped with rare earths were used to fabricate laser devices [5]. Here, lithium niobate, rare earth aluminates or fluoride crystals may serve as examples. However, for utilizing the luminescence properties in combination with optical waveguides amorphous materials have to be used. Among them, silica glasses are of superior significance due to their application with optical fibers [6]. Also other materials such as alumina [7]-[11], sodalime [7] or fluoride glasses [12]-[16] as well as chalcogenides [17] have come under consideration. Also silicon has been doped with rare earth elements, namely erbium [18], as there is a great desire for photonic components to be integrated together with electronic devices. Especially for the fabrication of integrated optical amplifiers a high amplification is required together with short waveguides. Hence, a high level of optically active dopants has to be achieved. This means, that the ions do not only have to be incorporated into the host material in an arbitrary manner, but they have to be soluble in the solid phase and must not form clusters or show segregation effects. Normally, rare earth ions are bound to non-bridging oxygen atoms within a glass matrix [6].

II. EXPERIMENTAL

Silica sols containing 1mol% Er_2O_3 was prepared using tetraethyl orthosilicate, $ErNO_3$, deionized water, HCl and C_2H_5 OH. The chemicals used were all AR (analytical reagent) grade. Calculated amount of dopant salts were poured in TEOS under stirring condition at room temperature. The molar ratio of TEOS : C_2H_5OH : H_2O : HCl was 1: 4: 14: 0.01 respectively. TEOS and ethanol were magnetically stirred thoroughly till both were in well mixed state. To this well-mixed solution the remaining water was added in which the desired acid was mixed. Again the solution was magnetically stirred to get a clear solution. The sols were cast in polypropylene dishes and were sealed to avoid intercalation of external impurity. The gels were aged for one month at room temperature to obtain the sol-gel. The samples taken in silica crucibles were sintered in a Muffle furnace at 600 ºC for 3 h and then the furnace was cooled to room temperature at a rate of 0.5 ºC per minute. The highest temperature required to obtain a silica glass prepared by sol gel method is about 1000 ºC, which is lower by about 1000 ºC compared to the temperature required for the melt-quenching process. Transparent and bubble free glass was prepared reproducibly. The spectral measurements were carried out by spectrophotometer method. The Absorption spectra in the spectral range 200-800 nm were recorded on UV-Visible double beam spectrophotometer model Perkin Elmer spectrophotometer model lambda 35.

The Absorption spectra has been recorded in terms of wavelength (nm) vs. optical density (a.u.). The absorption spectra of Er^{+3} doped Silica glass has been investigated. From these spectral data Judd-Ofelt parameters (Ω_λ), Slater-Condon parameter (F_k), k=2,4,6, Lande parameter (ζ_{4f}), Racah parameter (E^k), k=1,2,3, nephelauxetic ratio ($\beta^{'}$) and bonding parameters ($b_{1/2}$) have been calculated to study the nature of bonding in these glasses. Intensities of the f-f transitions in the absorption spectra have been analyzed by the application of the Judd-Ofelt theory.

III. RESULTS AND DISCUSSION

Spectral intensities

From the absorption spectra, it is observed that 10 absorption peaks are clearly observed in the wavelength range 200-800 nm and can be attributed to transitions from

the ground state $^4I_{15/2}$ to the higher energy states. The oscillator strengths for electric dipole transitions from the ground state $^4I_{15/2}$ to upper energy levels can be experimentally determined using the equation.

$$P_{\exp} = 4.6\times10^{-9}\times\frac{1}{cl}\log\frac{I_0}{I}\times\Delta\upsilon^{1/2} \quad \text{(I)}$$

Where c is the concentration of the absorbing ion per unit volume, l is the path length and log (I_0/I) is the absorbance and $\Delta\nu^{1/2}$ is half band width. However for a solid material it is generally expressed in terms of line strength S_{exp}.

$$P_{\exp} = \frac{8\pi^2 mc\nu}{3h(2J+1)}\left[\frac{(n^2+2)^2}{9n}\right]S_{\exp} \quad \text{(II)}$$

Where (2J + 1) is the degeneracy of the ground state of the rare-earth ions, n is the refractive index of the medium, m is the mass of the electron, ν is the mean energy of the transition, the factor $(n^2+2)^2/9$ represents the local field correction for an ion embedded in a dielectric medium. Since the bands produced by the magnetic dipole mechanism have very low spectral intensity compared to that of the electric dipole bands, S_{md} could be neglected in comparison to S_{ed} which is given by

$$S_{ed}\left[(S,L)J:(S',L')J'\right] = \sum_{\lambda=2,4,6}\Omega_\lambda\left|\left\langle(S,L)J\left\|U^{(\lambda)}\right\|(S',L')J'\right\rangle\right|^2$$

(III)

Oscillator strengths calculated from the absorption spectra and using the values of reduced matrix elements and other parameters, Ω_λ (λ = 2,4,6) can be calculated by a least squares method. The experimental oscillator strengths, experimental line strength (S_{exp}) and calculated line strength (S_{cal}) with their differences (ΔS) of all the observed bands of Er^{3+} doped glass is presented in TABLE 1.

To find out the Judd-Ofelt intensity parameters we substitute the values of oscillator strengths from TABLE 1 in Eq. 3 and consider these relations as equations of unknowns Ω_2, Ω_4 and Ω_6.Using least squares fit method and using 10 linear equations, best set of Judd-Ofelt intensity parameters are obtained. Using these Judd-.Ofelt intensity parameters, the oscillator strengths are calculated. The rms deviations between experimental and calculated oscillator strengths are very small indicating the validity of Judd-Ofelt theory.

TABLE2 : Judd-Ofelt intensity parameters for Er^{+3} doped hosts

$\Omega_2(10^{-20})$	$\Omega_4(10^{-20})$	$\Omega_6(10^{-20})$
2.1121	1.6735	1.2171

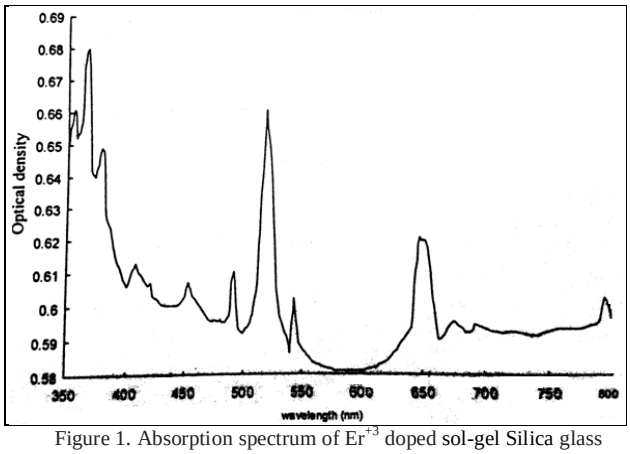
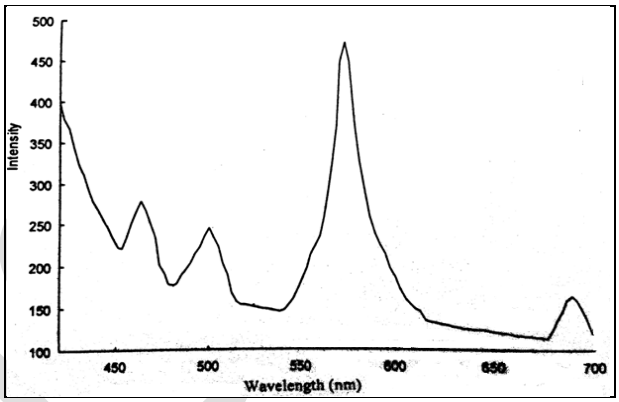


Figure 1. Absorption spectrum of Er^{+3} doped sol-gel Silica glass



.Figure 2. Fluorescence spectrum of Er^{+3} doped sol-gel Silica glass

TABLE1 : Experimental oscillator strengths, experimental line strength (S_{exp}) and calculated line strength (S_{cal}) with their differences (ΔS) for various absorption levels in Sol-Gel silica glass

Absorption levels	**λ (nm)**	**$P_{exp.}$ (10^{-6})**	**S_{exp} (10^{-20})**	**S_{cal} (10^{-20})**	**ΔS (10^{-20})**
$^4I_{15/2}\rightarrow{}^4I_{9/2}$	794	0.30	0.2273	0.3390	-0.112
$^4F_{9/2}$	655	2.37	1.4813	1.4003	0.081
$^4S_{3/2}$	545	0.51	0.2652	0.2586	0.006
$^2H_{11/2}$	522	5.33	2.6549	2.1442	0.511
$^4F_{7/2}$	490	2.05	0.9585	0.9968	-0.038
$^4F_{3/2}$, $^4F_{5/2}$	454	1.25	0.5415	0.4264	0.115
$^2H_{9/2}$	404	0.78	0.3007	0.3248	-0.024
$^4G_{11/2}$	378	9.61	3.4663	3.1087	0.357
$^2G_{9/2}$, $^2K_{15/2}$	366	2.89	1.0093	0.7086	0.301
$^2G_{7/2}$	353	0.55	0.1852	0.1706	0.014

Goodness of fit = 1.211

The Judd-Ofelt intensity parameters (Ω_2, Ω_4 and Ω_6) depend on the host glass composition [19].Generally Ω_2 parameter is an indicator of the covalency and crystal field asymmetry of the rare earth ion and Ω_4 and Ω_6 are related to the rigidity of host matrix. In present case the values of Ω_4 and Ω_6 are almost equal. The Judd-Ofelt theory does not permit an easy calculation of these parameters and it is very difficult to predict the behavior of the host around the rare earth ion on the basis of their values. In Silica glass it seems that the rare earth ions gets surrounded by $[SiO_4]^{4-}$ tetrahedra. The negative charge of $[SiO_4]^{4-}$ tetrahedra is not properly

balanced thereby decreasing the covalent character between the rare earth ions and oxygen atoms. In most of the glasses the Ω_4 parameter seems to follow the trend set by Ω_2 parameter. But the Ω_4 parameter is less sensitive to the environment than the Ω_2 parameter.

Spectroscopic parameters

From the data of absorption spectra of Er^{3+} doped Silica glass and using the method of Wong [20] (and Taylor series expansion) and using the observed band energies as E_J, zero order energies E_{OJ} and partial derivatives of rare earth ion [21], the correction factors ΔE^K, $\Delta\zeta_{4f}$ are evaluated by least squares fit method.

TABLE 3 : Calculated values of slater-condon, lande., nephelauxetic ratio, racah and bonding parameters for Er^{+3} doped Silica glass.

Parameters	SGS01	Parameters	SGS01
F_2 (cm^{-1})	431.422	E^3 (cm^{-1})	617.629
F_4 (cm^{-1})	68.673	F_4/F_2	0.159
F_6 (cm^{-1})	7.871	E^1/E^3	11.121
ζ_{4f} (cm^{-1})	2466.291	E^2/E^3	0.050
E^1 (cm^{-1})	6868.972	β'	0.9948
E^2 (cm^{-1})	31.166	$b^{1/2}$	0.050

From the known free ion parameters E^K, ζ^0_{4f}, the Racah (E^1, E^2, E^3) and spin orbit (ζ^{4f}) parameters in Silica glass matrices are obtained. These values are presented in TABLE 3. The hydrogenic ratios E^1/E^3 and E^2/E^3, which indicate radial properties, are also presented in TABLE 3. It is observed that the hydrogenic ratios are nearly constant indicating that radial properties are same in the glass matrix. Using the correction factors ΔE^K, $\Delta\zeta_{4f}$ and using the partial derivatives, calculated energy values are obtained. The rms deviations between the experimental and calculated energies are reasonable and they are within the experimental error.

In Er^{+3} doped Silica glass specimen the relation among different F_k parameters are found as $F_2 > F_4 > F_6$. The ratios of $F_4/F_2 \sim 0.159$ and parameter $E^1/E^3 \sim 11.121$ and $E^2/E^3 \sim 0.050$ are in good approximation with the corresponding hydrogenic ratios.

IV. CONCLUSIONS

The Absorption spectral studies of Silica glass doped with Er^{+3} ions have been carried out from the absorption spectra oscillator strengths of various absorption bands are evaluated. The higher value of Ω_2 parameter indicates a higher asymmetry around Er^{+3} ions in this glass. The low values of goodness of fit indicate the validity of the Judd-Ofelt theory. In Silica glass it seems that the rare earth ions gets surrounded by $[SiO_4]^{4-}$.The negative charge of $[SiO_4]^{4-}$ tetrahedra is not properly balanced thereby decreasing the covalent character between the rare earth ions and oxygen atoms. The high value of spectroscopic quality factor (Ω_4/Ω_6 = 1.37) indicates that the present glass is more rigid as compared to other oxide glasses.

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