Optical Absorption Study of Nd^{+3} Ion in Silica Glass

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***Abstract*—Nd^{3+} doped Silica glass (SGS01) has been prepared by Sol-Gel technique. The amorphous nature of the prepared glass samples was confirmed by X-ray diffraction. The absorption spectra of Nd^{+3} doped Silica glass has been recorded at room temperature. Ten bands in the region 200-800 nm have been observed. Slater-Condon parameters (F_k) (k=2, 4 and 6), Lande's parameter (ζ_{4f}) and Racah parameters (E^k) k=1,2,3, have been computed. Using these parameters energies and intensities of these bands has been calculated. To study the nature of bonding in doped glasses nephelauxetic ratio (β') and bonding parameter ($b^{1/2}$) have also been computed. The intensities of the f-f transitions in the absorption spectra have been analyzed by the application of the Judd-Ofelt theory. J-O parameters (Ω_λ) have been computed. The spectroscopic quality factor related with the rigidity of the glass system is also discussed.**

***Keywords*— Nd^{+3} doped Silica glass, Energy interaction parameters, optical properties, Judd-Ofelt analysis.**

I. INTRODUCTION

Sol gel glass preparation has been extensively studied since Dislich [1] reported the formation of borosilicate glass by hot-pressing granules of dehydrated gel [2]. Glasses synthesised by the sol gel method are promising matrices for the formation of optical nano-composites. The use of these nano-composites in optoelectronics, photonics, and fiber optics has opened up a new way for the development of unique information systems with tuneable characteristics over a wide frequency range [3]. In the present work, the absorption spectra of Nd^{3+}doped Silica glass have been investigated. From the spectral data various energy interaction parameters like Slater-Condon parameters F_k (k=2, 4 and 6), Lande parameter ζ_{4f} and Racah parameters E^k (k=1, 2 and 3) have been computed. Nephelauxetic Ratio (β') and Bonding Parameters ($b^{1/2}$) have also been computed from these parameters to study the nature of bonding in doped glasses. The intensity of the transition for the rare-earth ions has been calculated in term of Judd-Ofelt theory [4],[5]. This theory is known for a set of three intensity parameter Ω_λ (λ = 2, 4 and 6) which are useful to the environment of trivalent rare earth ions. To understand the laser efficiency of these materials, the value of spectroscopy quality factor (Ω_4/Ω_6) has been evaluated.

II. EXPERIMENTAL

Nd^{+3} doped Silica glass was synthesized by the Sol-Gel method [6]. The starting chemicals used were all AR (analytical reagent) grade. Silica sols containing 1mol% Nd_2O_3 was prepared using tetraethyl orthosilicate, $NdNO_3$, deionized water, HCl and C_2H_5OH. 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. Transparent and bubble free glass was prepared reproducibly. The refractive indices of the glass (n=1.681) has been measured at λ = 589.3 nm on an Abbe refractometer with an accuracy of ±0.001. The sample being glassy, it requires an adhesive coating on its surface, preferably 1-monobromonaphthalene as the contact layer between the sample and prism of the refractometer by using a sodium vapor lamp.

X-ray diffractogram of glass sample was studied. The absorption spectra of these glasses were recorded between wavelength ranges 200-800 nm with a Perkin-Elmer Lambda 750 Spectrophotometer at room temperature. The Absorption spectra has been recorded in terms of wavelength (nm) vs. optical density (a.u.).

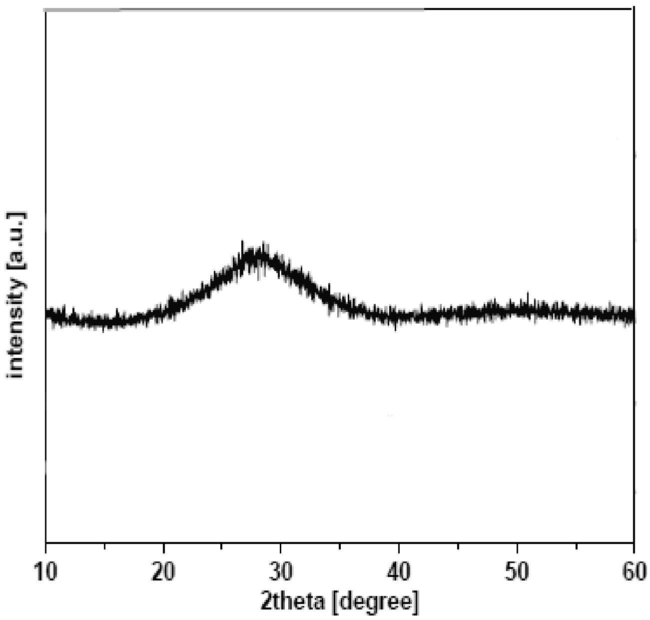

Figure 1. X-Ray diffraction patterns of SGS01 Glass Specimen

III. RESULTS AND DISCUSSION

The XRD patterns of the glass is shown in Fig.1, which confirmed its amorphous nature. The absorption spectra of Nd^{3+} doped Silica glass specimens have been presented in Fig. 2.

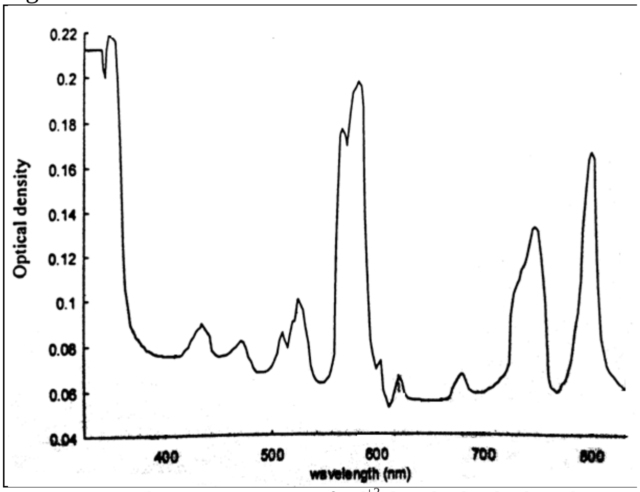

Figure 2. Absorption spectrum of Nd^{+3} doped sol-gel Silica glass

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 $^4I_{9/2}$ to the higher energy states.

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})
$^4I_{9/2}\rightarrow{}^4F_{5/2},{}^2H_{9/2}$	797	4.22	2.0191	2.3713	-0.352
$^4F_{7/2},{}^4S_{3/2}$	753	5.38	2.4293	2.3199	0.109
$^4F_{9/2}$	681	1.20	0.4901	0.1650	0.325
$^2H_{11/2}$	622	0.88	0.3282	0.0419	0.286
$^4G_{5/2},{}^2G_{7/2}$	583	9.82	3.4336	3.8296	0.396
$^2K_{13/2},{}^4G_{7/2}$	526	6.75	2.1295	0.7115	1.418
$^4G_{9/2}$	512	1.85	0.5681	0.3040	0.264
$^2K_{15/2},{}^2G_{9/2},{}^2D_{3/2},{}^2P_{3/2}$	469	2.21	0.6216	0.2387	0.382
$^2P_{1/2},{}^2D_{5/2}$	432	0.36	0.0932	0.1034	-0.011
$^4D_{3/2},{}^4D_{1/2}$	350	7.52	1.5786	1.5442	0.034

Goodness of fit = 2.851

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

$\Omega_2(10^{-20})$	$\Omega_4(10^{-20})$	$\Omega_6(10^{-20})$
2.1244	2.6133	3.3356

From the observed absorption spectra, the intensities of the observed bands have been calculated in terms of oscillator strengths, P_{exp}, and line strengths, S_{exp}, spectral region wise and have been collected in Table 1. The Judd-Ofelt [4], [5] intensity parameters Ω_λ (λ = 2, 4 and 6) for the glass have been computed using line strengths and matrix element values by partial regression method [7] and have been presented in Table 2. The intensities of all the ten observed bands have been included in this calculation. Computation of Ω_λ parameters is very important since they have been further used in the calculation of different radiative properties. The calculated line strengths agree well with the experimental values. For Nd^{3+} doped Silica glass, Ω_λ values vary as $\Omega_2<\Omega_4<\Omega_6$. The Ω_2 parameter is affected by the covalency, the Ω_6 parameter is related to the rigidity of the glass hosts, and Ω_4 parameter is determined by Ω_2 and Ω_6 parameters [8], [9].

In Nd^{3+} doped glass the contribution to Ω_6 parameters are mainly due to the hypersensitive transition $^4I_{9/2}\rightarrow{}^4G_{5/2}$. The bonding environment surrounding the rare earth ion has been discussed on the basis of the value of Ω_λ parameters. The success of Judd-Ofelt theory has been shown by low value of goodness of fit between the measured (S_{exp}) and calculated (S_{cal}) line strengths.

The spectroscopic quality factor (Ω_4/Ω_6) related with the rigidity of the glass system has been found to 0.783 in the present glasses. This shows that this glass are fairly rigid as compared to CdBiB [11] and zinc fluoride borophosphate [12] glasses.

Spectroscopic parameters

From the data of absorption spectra of Nd^{3+} doped Silica glass and using the method of Wong [10] (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 [13], 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})	329.61	E^3 (cm^{-1})	480.91
F_4 (cm^{-1})	48.105	F_4/F_2	0.1459
F_6 (cm^{-1})	5.428	E^1/E^3	10.408
ζ_{4f} (cm^{-1})	908.234	E^2/E^3	0.053
E^1 (cm^{-1})	5005.756	β'	0.9953
E^2 (cm^{-1})	25.921	$b^{1/2}$	0.048

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 Nd^{+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 ~ 0.1459 and parameter E^1/E^3 ~ 10.408 and E^2/E^3 ~ 0.053 are in good approximation with the corresponding hydrogenic ratios.

IV. CONCLUSIONS

In summary, it is concluded that we have successfully developed transparent and moisture resistant Silica Glass by Sol-Gel technique. The calculated energies of the transitions using least square fit method are exactly coinciding with the experimentally obtained energies of the transitions, reflecting the good accuracy of the experimentation. The hypersensitive transition $^4I_{9/2} \rightarrow ^4G_{5/2}$ exhibits high intensity as a function of Judd-Ofelt intensity (Ω_6) parameter in the case of 1 mol% Nd^{3+} glass system. The spectroscopic quality factor related with the rigidity of the glass system has been found to 0.783 in the present glass, which is fairly large as compared to other glasses. The large values of spectroscopic quality factor (Ω_4/Ω_6) make them suitable for optical devices.

REFERENCES

[1]. Dislich H., (1971). 'Preparation of multicomponent glasses without fluid melts'. Glastech.Ber. **44 (1)**, p 1-8.

[2]. Masayuki Yamane and Yoshiyuki Asahara (2000). 'Glasses for photonics'. Cambridge University Press, Cambridge, UK. 271pp.

[3]. Khimich N. N., Berdichevskii G. M., Poddenezhnyi E. N., Golubkov V. V., Boiko A. A., Ken'ko V. M., Evreinov O. B. and Koptelova L.A., (2007). 'Sol–Gel Synthesis of an Optical Silica Glass Doped with Rare-Earth Elements'. Glass Phys. Chem. **33 (2)**, p 152–155.

[4]. Judd B.R., (1962), Phys. Rev., **127**, 750.

[5]. Ofelt G.S., (1962), J. Chem. Phys., **37**, 511.

[6]. Reisfeld R. and Jorgensen C. K., (1992), "Chemistry, Spectroscopy and Applications of Sol-Gel Glasses", Springer-Verlag, New York.

[7]. Carnall W.T., Fields P. R., and Rajnak K., (1968), J. Chem. Phys. (USA), **49**, 4412, 4424, 4443, 4447, 4450.

[8]. Lin H.E.Y., Pun B. and Liu X.R., (2001), J. Non-Cryst. Solids, 283, 27.

[9]. Rolli R., Gatterer K. and Wachtler M., (2001), Spectrochim. Acta Part A, **57**, (2001).

[10]. Wong E.Y., (1961), J. Chem. Phys., Vol. **35**, 544.

[11]. Nageswara Raju C., Adinarayana Reddy C., Sailaja S., Jin Seo H. and Sudhakar Reddy B., (2012). J. Matter. Sci., Vol.**47**, 772.

[12]. Sharma Y.K., Dubedi R.P., Joshi V., Karnataka K.B. and Surana S.S.L., (2005). Indian J. Eng. Mater. Sci., Vol **12**, 65.

[13]. Ratnakaram Y.C.; (1987), Ph.D. Thesis, SV University, Tirupati.