Structural, optical and non-linear investigation of Eu^{3+} : $\text{Al}(\text{NO}_3)_3$ – SiO_2 sol–gel glass

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Abstract. Optical absorption and fluorescence spectra of Eu^{3+} ions in $\text{Al}(\text{NO}_3)_3$ – SiO_2 sol–gel glass have been investigated using the Judd–Ofelt theory. JO intensity parameters (Ω_J) and subsequent radiative properties for $^5D_0 \rightarrow ^7F_{1,2,4,6}$ transitions are determined. The lifetime (τ_r) of 5D_0 state is computed and along with JO parameters are compared with their corresponding values in other glasses prepared by conventional technique. A structural analysis, using IR and XRD spectra and non-linear parametrization of the silica gel glass is carried out. The study reveals the glass to be a very good third order non-linear amorphous optical material.

Keywords. Judd–Ofelt parameters; optical properties; non-linear properties; lifetime; sol–gel glass.

1. Introduction

The use of sol–gel technique in preparation of inorganic oxides and glasses of high purity and homogeneity for various electro-optic and photonic applications is relatively new. But it has emerged of late as a popular synthesizer of inorganic polymers like glass, ceramic because of its simple chemistry and variations in applications (Reisfeld 1990; Beckers and Leeuw 2000). Rare earth ions incorporated into glasses, thin films and nano particles via sol–gel process enable the design of photonic materials. Currently there is a growing interest in the study of new photonic materials prepared by sol–gel technique. The technique utilizes simple low temperature reactions like hydrolysis and polycondensation and has many advantages over the conventional quench technique apart from being cost effective. Being a low temperature synthesizer of glass, it enables doping of inorganic/organic molecules at high concentration in glasses. The dopant molecules may be impregnated in the pores of these glasses. The technique further provides wide chemical possibilities of controlling the nature of host matrix, prevention of ionic aggregation and hydroxyl content that affect the luminescence efficiency of optical materials.

Spectroscopic study of rare earth ions in glasses provides information with regard to transition probability, lifetime, branching ratio, etc for the excited states of rare earth ions that are essential in design of various electro-optic and optical devices like lasers, colour displays and amplifiers. The spectra of trivalent lanthanide in solution or crystal lattice arise(s) from forbidden transitions within the $4f^n$ -configuration (Wybourne 1965) to which

the Judd–Ofelt (JO) (Judd 1962; Ofelt 1962) theory has been successfully applied in quantitative determination of its optical properties. Optical properties of Eu^{3+} ions in glasses have been extensively studied to prepare materials for good optical devices (Oomen and Dongen 1989; Nageno *et al* 1994; Dejneka *et al* 1995). Eu^{3+} ion is also used as a probe ion to determine the structure surrounding the rare earth ions in host matrix. In the first ever reported work on rare earth doped glass prepared by sol–gel technique, Eu was used as the rare earth. Eu^{3+} being the only lanthanide ion in which the ground state has $J = 0$, special restrictions come into force on the induced electric–dipole transitions originating from the ground state.

In this paper we investigate the optical properties of Eu^{3+} ions in silica gel glass in presence of Al taken as $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ using the Judd–Ofelt approach. The JO intensity parameters for Eu^{3+} : $\text{Al}(\text{NO}_3)_3$ – SiO_2 sol–gel glass are computed and compared with results in other glasses prepared by conventional quench technique to study its variation. Radiative properties of 5D_0 state of Eu are determined using the JO phenomenological parameters in the glass and its lifetime compared. Further, a structural analysis and non-linear parametrization of the silica gel glass has been carried out in this work. XRD and IR spectroscopy have been utilized for structure–composition relation study of the glass.

2. Experimental

2.1 Glass preparation

Eu^{3+} : $\text{Al}(\text{NO}_3)_3$ – SiO_2 glass was prepared by sol–gel technique where tetraethylorthosilicate (TEOS) was taken as

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the glass precursor. The ratio of TEOS to other constituents used in the preparation viz. doubly distilled H_2O , methanol and dilute HNO_3 , was 16:10:70:4, respectively. 0.044 g of Eu_2O_3 along with 0.14 g $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was dissolved in 10.5 ml mixture of methanol, distilled water and dilute nitric acid and stirred for about 10 min. Distilled water was added to initiate the process. To this solution 2 ml of TEOS was added and further stirred for about an hour till gelation started. The resulting gel was then poured into plastic moulds and left to dry and solidify at room temperature. In 3–4 days the stiff mass of gel solidified to form glass. Several authors processed the gel at around 1100°C (Patra *et al* 1998; Patra and Ganguly 1999) during solidification, which is not carried out here. The sample was however, treated at $150\text{--}200^\circ\text{C}$ prior to fluorescence recording to reduce hydroxyl quenching of fluorescence intensity. On solidification, a colourless, transparent glass sample measuring $1 \times 1 \times 0.15$ cm in dimension, 0.853 g in weight and 1.472 g/cm^3 in density, was obtained. The composition of the glass was worked out in mol% as: 3 $\text{Al}(\text{NO}_3)_3$ –96 SiO_2 –1 Eu_2O_3 .

TEOS and Eu_2O_3 used in the fabrication of the sample under study were from Merck (Germany) and Aldrich (Germany), respectively with 99.9% purity.

2.2 Measurement and spectra recording

The fluorescence of the glass sample was excited by 488 nm line of Ar-ion laser operated at 50 mW whereas the UV-VIS absorption spectra was recorded with a Analytik Jena (model Specord 200) spectrophotometer. Refractive index (n) of the glass was measured using a Almico ABBE refractometer with monobromonaphthelene as the contact liquid. A Cd–Hg lamp with filters was used to illuminate the refractometer to measure refractive indices at $I_e = 5461 \text{ \AA}$, $I_F = 4800 \text{ \AA}$ and $I_{C'} = 6438 \text{ \AA}$ required for non-linear parametrization. Density (d) of the glass was measured using xylene as the immersion fluid by Archimedes method. XRD spectra was recorded in a PDX-11P3A, JEOL (Japan) diffractometer using $\text{CuK}\alpha$ radiation, operating at 30 kV and 10 mA, while the IR spectra in $4000\text{--}200 \text{ cm}^{-1}$ range was recorded using KBr technique with a Jasco FT/IR–300E spectrophotometer. All the measurements and recordings were carried out at room temperature (27°C).

3. Results and discussion

3.1 XRD and IR spectra

XRD spectra (figure 1) of the sample reveal its amorphous nature. A typical hallow like pattern observed between 5° and 18° of 2θ is attributed to the amorphous structure of silica gel. Similar patterns are observed when rare earth dopants are changed in the same gel matrix. But XRD

patterns of silica gel treated at 1050°C and above are reported (Battisha 2002) to show peaks indicative of crystallization in gel structure. Bouajaj and Ferreri (1997) suggested that in gels treated at 1050°C , crystallization begins and at 1300°C crystallization occurs.

The use of X-ray diffraction in determination of glass structure is limited because of the absence of long-range order in glasses. Techniques such as the one that determines the radial distribution functions of electron densities about specific atom too has its limitations, as the symmetry and extent of short range order cannot be resolved adequately. IR absorption spectroscopy using KBr technique is, however, successful in the study of structure–composition relation in glasses and ceramics (El Batal *et al* 2000). Moreover, it can be used to identify low concentration impurities, such as water, hydroxyl ions, etc in glasses (Dunken and Doremus 1987). The IR spectra of Eu^{3+} : $\text{Al}(\text{NO}_3)_3$ – SiO_2 sol–gel glass are shown in figures 2(A) (air dried) and (B) (treated at 150°C). Spectra are marked by bands associated with network vibrational modes centred around 475, 800, 960, 1080, 1390, 1640 and 3435 cm^{-1} .

The broad band at 3435 cm^{-1} corresponds to the fundamental stretching vibrations of –OH groups and reveals the presence of hydroxyl groups in the glass. In addition to this, the band around 1640 cm^{-1} assigned to the bending mode of water molecules indicates the presence of adsorbed water. The peak at 1390 cm^{-1} is assigned to vibrations of TEOS ethoxy group (Chul and Chung 1991) and is very unstable. The strong band at 1080 cm^{-1} , the most prominent in the IR spectra is due to Si–O–Si asymmetric stretching mode. Two more small bands observed at 960 cm^{-1} and 800 cm^{-1} are assigned to Si–O stretching and Si–O–Si symmetric stretching or vibrational modes of ring structure, respectively. The band at 475 cm^{-1} is due to Si–O–Si bending modes (Brinker *et al* 1986). In between 400 and 200 cm^{-1} only small inflections are observed. Absence of strong absorption structure in this region suggests of a feeble modifying effect of Al and Eu ions on the glass.

Figure 1. XRD spectra of Eu^{3+} in $\text{Al}(\text{NO}_3)_3$ – SiO_2 sol–gel glass.

Figure 2. IR spectra of Eu^{3+} in $\text{Al}(\text{NO}_3)_3$ - SiO_2 sol-gel glass: (A) air dried and (B) treated at 150°C .

In figure 2(B) the most striking feature is the disappearance or merger of unstable ethoxy group and Si-O stretching bands with the Si-O-Si asymmetric stretching vibrational band. However, there is no significant change in -OH and H_2O content (indicated by the bands) in the glass treated at 150°C .

3.2 Absorption and fluorescence spectra

Absorption profile of Eu^{3+} in $\text{Al}(\text{NO}_3)_3$ - SiO_2 sol-gel glass is given in figure 3A. Absorption bands resolved in the UV-VIS range (350–480 nm) correspond to ${}^7F_0 \rightarrow {}^5D_{2,4}$, ${}^5G_{2,3,4}$, 5L_6 transitions. The ${}^7F_1 \rightarrow {}^5D_3$ transition band is not well resolved. All assignments of transitions are based on assignments of lanthanide spectra of Dieke (1968) and Carnall *et al* (1968). The close proximity of ${}^7F_{1,2}$ states of Eu^{3+} to its ground state 7F_0 , their separation being $\sim 250 \text{ cm}^{-1}$ and $\sim 1000 \text{ cm}^{-1}$, respectively from the ground state, makes these states adequately populated even at room temperature. This enables absorption from ${}^7F_{0,1,2}$ states of Eu^{3+} to excited states.

The ${}^7F_0 \rightarrow {}^5D_2$ induced electric-dipole transition is hypersensitive in nature and is known to exhibit wide variation in its band intensity (Carnall *et al* 1968). ${}^7F_0 \rightarrow {}^5L_6$ transition band is the most intense among all absorption bands in the glass. Although forbidden by ΔS and ΔL selection rule, the transition (${}^7F_0 \rightarrow {}^5L_6$) is allowed by ΔJ rule.

The fluorescence spectrum of Eu^{3+} in the sol-gel glass is given in figure 3B. Four bands corresponding to transi-

tions ${}^5D_0 \rightarrow {}^7F_{1,2,3,4}$ are observed in between 580 and 700 nm. The ${}^5D_0 \rightarrow {}^7F_0$ transition, one of the weakest rare earth transitions (Dejneka *et al* 1995), known as non-degenerate ($J = 0$, for both levels), is not resolved here. A close analysis reveals that ${}^5D_0 \rightarrow {}^7F_1$ transition is a magnetic-dipole allowed, whereas ${}^5D_0 \rightarrow {}^7F_{2,3,4}$ transitions are electric-dipole allowed transitions. The intensity of ${}^5D_0 \rightarrow {}^7F_2$ transition is the most intense among the resolved transitions. Fluorescence intensity gives a measure of the interaction strength between host and dopant ions that result in a host dependent perturbation. This perturbation modifies the selection rules, permitting transitions in ions trapped in host lattice(s) which otherwise are forbidden by selection rule in free ion(s) (Boulon *et al* 1985). ${}^5D_0 \rightarrow {}^7F_0$ transition (not resolved in figure 3(B)) is one such case. The relative fluorescence intensity ratio (R) of ${}^5D_0 \rightarrow {}^7F_2$ to ${}^5D_0 \rightarrow {}^7F_1$ transition allows one to estimate the deviations from site symmetries of Eu^{3+} ions. The ${}^5D_0 \rightarrow {}^7F_1$ magnetic-dipole allowed transition is quite independent of local site symmetry (Gallagher *et al* 1965; Blasse *et al* 1966). A small quantity of Al or B used as codopant is known to increase the absorption and fluorescence intensity of rare-earth ions in silica sol-gel glasses (Patra *et al* 1998). The reason for such an increase is lowering of site symmetry of rare-earth ions in vicinity of Al or B ions. The presence of Al ions in the silica gel glass under investigation has effectively countered the fluorescence quenching by hydroxyl groups present in the gel matrix. The measured R value (3.38) is an indication of the fact.

3.3 Oscillator strength—Judd-Ofelt analysis

Quantitative analysis of $f-f$ transitions in rare-earth is provided by the Judd-Ofelt theory. According to it the spectral intensity (f_{cal}) of absorption band corresponding to transition $\Psi J \rightarrow \Psi' J'$ depends on three parameters ($\Omega_{I=2,4,6}$) known as the Judd-Ofelt parameters.

$$f_{\text{cal}} = \frac{8p^2 mc(n^2 + 2)^2}{3h\bar{I} (2J + 1)9n} \times \sum \Omega_I |\langle \Psi J \| U^I \| \Psi' J' \rangle|^2, I = 2, 4, 6, \quad (1)$$

$\bar{I}$ is the mean wavelength of transition.

The experimental oscillator strengths (f_{exp}) or absorption band intensities are determined using the relation

$$f_{\text{exp}} = 4.318 \times 10^{-9} \int e(n) dn, \quad (2)$$

where $e(n)$ is the molar absorptivity at frequency n in cm^{-1} . The experimentally determined values of band intensity are correlated to the theoretical expression for oscillator strength derived by Judd (1962)

Figure 3. A. Absorption spectra of Eu^{3+} in $\text{Al}(\text{NO}_3)_3$ - SiO_2 sol-gel glass and B. fluorescence spectra of Eu^{3+} in $\text{Al}(\text{NO}_3)_3$ - SiO_2 sol-gel glass.

Table 1. JO intensity parameter (Ω_I) and oscillator strengths (f_{exp} and f_{cal}) in $\text{Eu} : \text{Al}(\text{NO}_3)_3$ - SiO_2 glass.

Transitions	Energy (cm^{-1})	$f_{\text{exp}} (\times 10^{-6})$	$f_{\text{cal}} (\times 10^{-6})$
${}^7F_0 \rightarrow {}^5D_4$	27657	0.155	0.155
${}^7F_0 \rightarrow {}^5G_4$	26678	0.306	—
${}^7F_0 \rightarrow {}^5G_2$	26318	0.074	—
${}^7F_0 \rightarrow {}^5G_3$	25990	0.150	0.221
${}^7F_0 \rightarrow {}^5L_6$	25368	1.689	1.689
${}^7F_1 \rightarrow {}^5D_3$	NR	—	—
${}^7F_0 \rightarrow {}^5D_2$	21514	0.123	0.123
JO intensity parameters ($\Omega_I \times 10^{-20} \text{cm}^2$):			
	Ω_2	Ω_4	Ω_6
	5.61	3.47	2.91

* $d_{\text{rms}} = [(\text{sum of the square of the deviations})/(\text{no. of transitions} - \text{no. of parameter})]^{1/2}$, root-mean-square deviation of f_{exp} and f_{cal} .

$$f_{\text{cal}} = n \sum T_l |(\Psi J \| U^l \| \Psi' J')|^2, \quad l = 2, 4, 6, \quad (3)$$

to evaluate T_l , the Judd–Ofelt (JO) parameters. These are usually determined by least square fit analysis. In expressions (1) and (3) $\|U^l\|^2$, the doubly reduced matrix elements evaluated in the intermediate coupling approximation for a transition $\Psi J \rightarrow \Psi' J'$ at energy $n(\text{cm}^{-1})$ are independent of the host. Thus values of $\|U^l\|^2$ used in our calculations are taken from Carnall *et al* (1968).

In Eu^{3+} doped sol-gel glass, T_l for $l = 2, 4$ and 6 are determined directly from the absorption bands of ${}^7F_0 \rightarrow {}^5D_2$, ${}^7F_0 \rightarrow {}^5D_4$ and ${}^7F_0 \rightarrow {}^5L_6$ transitions, respectively (Deun *et al* 1999). And subsequently JO intensity parameters (Ω_I) are obtained from (Augel 1987)

$$\Omega_I = \frac{3h}{8p^2 mc} \times \frac{[9n](2J+1)}{(n^2+2)^2} T_l, \quad (4)$$

n is the refractive index of the glass and J the ground state total angular momentum. This simplicity in the determination of Ω_I in Eu^{3+} : glass is because, for ${}^7F_0 \rightarrow {}^5D_2$ transition, matrix elements $\|U^4\|^2$ and $\|U^6\|^2$ are zero. Similarly the matrix elements $\|U^2\|^2$ and $\|U^6\|^2$ are zero for ${}^7F_0 \rightarrow {}^5D_4$ transition and for ${}^7F_0 \rightarrow {}^5D_6$ transition $\|U^2\|^2$ and $\|U^4\|^2$ are zero. The JO intensity parameter (Ω_I) along with the experimental (f_{exp}) and calculated (f_{cal}) oscillator strengths evaluated are compiled in table 1.

The JO intensity parameters give an insight into the local structure and bonding in vicinity of rare earth ions (Jorgensen *et al* 1983). The environment sensitive parameter (Ω_2) indicates an amount of covalent bonding and the vibronic dependent parameter (Ω_6) is related to the rigidity of the material. A compilation of Judd–Ofelt intensity parameters and radiative lifetimes of 5D_0 state of Eu: glasses are presented in table 3 for comparison. The magnitude of Ω_2 in sol-gel glass, which is smaller than all the glasses, except the ZBLA glass, indicates bonding in the sol-gel glass to be more ionic (less covalent) than the glasses compared to, except ZBLA glass, with respect to which it is more covalent. The covalent bonding is strongest in L4BE glass amongst the glasses compared. The rigidity of the gel glass (indicated by Ω_6) is only lower than the fluoroborate glass (L5FBE). One should be careful in comparing Ω_I values in different systems as JO parameters depend on the constraints under which they are evaluated (Babu and Jayasankar 2000). This is exhibited in the evaluation of Ω_I in K-fluoride and Li-fluoroborate (L4BE) glasses. In L4BE glass Ω_4 could not be evaluated, as the ${}^7F_0 \rightarrow {}^5D_4$ transition was not well resolved in the absorption spectra where the parameters were determined as in the sol-gel glass. Ω_6 in the K-fluoride glass could not be evaluated as absorption bands resolved (used in Ω_I calculation) in the range of 400–520 nm were all independent of $\|U^6\|^2$. It resulted in very high values of Ω_2 and Ω_4 in L4BE and K-fluoride glasses, respectively.

3.4 Radiative properties from W_l

The JO intensity parameters (Ω_l), referred to as the phenomenological parameters are used to predict important radiative properties of Ln^{3+} ions in host matrix. Peak emission cross-section [$S(I_p)$] between states ΨJ and $\Psi' J'$ are calculated from (Chamarro *et al* 1991)

$$S(I_p) = \frac{I_p^4 A(\Psi J, \Psi' J')}{8\pi c n^2 \Delta I_{\text{eff}}}, \quad (5)$$

where I_p is the peak emission wavelength and ΔI_{eff} the effective bandwidth of a transition. $A(\Psi J, \Psi' J')$ is the radiative transition probability between states, ΨJ and $\Psi' J'$ and is

$$A(\Psi J, \Psi' J') = A_{\text{ed}} + A_{\text{md}}.$$

The electric-dipole transition probability (A_{ed}) is calculated from

$$A_{\text{ed}} = \frac{64\pi^4 e^2 n(n^2 + 2)^2}{3h\bar{I}^3 (2J+1)9} \times \sum_{p=2,4,6} \Omega_l |\langle \Psi J \| U^l \| \Psi' J' \rangle|^2, \quad (6)$$

$\bar{I}$ is the average wavelength of transition. A_{md} , the magnetic-dipole transition probability is

$$A_{\text{md}} = \frac{64\pi^4 n^3 e^2}{3h\bar{I}^3 (2J+1)4m^2 c^2} \times |\langle \Psi J \| L + 2S \| \Psi' J' \rangle|^2. \quad (7)$$

A_{md} for the ${}^5D_0 \rightarrow {}^7F_1$ transition has been calculated from values reported in Babu and Jayasankar (2000) with refractive index correction. The sum of $A(\Psi J, \Psi' J')$ for the states involved gives the total radiative probability (A_T),

$$A_T = \sum A(\Psi J, \Psi' J'), \quad (8)$$

and A_T^{-1} gives the radiative lifetime that determines the rate of depopulation of any given state. Another important radiative property, the fluorescent branching ratio (b_r), is calculated from

$$b_r = \frac{A(\Psi J, \Psi' J')}{A_T(\Psi J)}, \quad (9)$$

and is used to predict relative intensity of lines originating from a given excited state.

Using expressions (5)–(9) radiative transition probability, $A(\text{s}^{-1})$, branching ratio (b_r), effective bandwidth (ΔI_{eff}) and peak emission cross-section [$S(I_p)$] are predicted for the ${}^5D_0 \rightarrow {}^7F_{1,2,4}$ transitions. Further A_T and t_r of 5D_0 state of Eu^{3+} in sol-gel glass is predicted and compared with values in other glasses. These values are presented in table 2.

Knowledge of non-linear properties is necessary to understand the optical quality of materials. These properties are estimated from refractive indices of materials at three different wavelengths (I_F , I_e and $I_{c'}$ in this case). Theoretical formulation to predict the non-linear refractive index (n_2) changes in optical material was given by Boling and Glass (1978). They suggested the necessity of small non-linear refractive index to minimize environmental effect on dopant ions. Glass (1975), on the other hand, defined materials to be optically active on the basis of their dispersive power. Accordingly, materials possessing Abbe number (n_e), the popular way to define dispersive power, between 50 and 100 are regarded as optically active.

3.5 Non-linear properties

The mathematical expression for Abbe number, the optical quality defining factor is (Weber *et al* 1983)

$$n_e = \frac{n_e - 1}{n_F - n_{c'}}, \quad (10)$$

where n_e , n_F and $n_{c'}$ are refractive indices at $I_e = 5461 \text{ \AA}$, $I_F = 4800 \text{ \AA}$ and $I_{c'} = 6438 \text{ \AA}$, respectively. Values of the refractive indices in the $\text{Eu}:\text{Al}(\text{NO}_3)_3\text{-SiO}_2$ sol-gel glass are, $n_e = 1.504$, $n_F = 1.508$ and $n_{c'} = 1.499$. The reciprocal of n_e gives the dispersive power ($1/n_e$) of materials. The non-linear refractive index (n_2) is evaluated from Abbe number and n_e using the expression (Glass 1975)

$$n_2 (10^{-13} \text{ esu}) = \frac{68(n_e - 1)(n_e^2 + 2)^2}{n_e [1.517 + [(n_e^2 + 2)(n_e + 1)n_e / 6n_e]]^{1/2}}. \quad (11)$$

Table 2. Calculated radiative parameters along with measured peak emission wavelength and fluorescence intensity ratio R of Eu^{3+} in $\text{Al}(\text{NO}_3)_3\text{-SiO}_2$ sol-gel glasses.

Transitions	$A(\text{s}^{-1})$	b_r (%)	$I_p[\text{\AA}]$	ΔI_{eff} (nm)	$S(I_p) \times 10^{-22} \text{ cm}^2$
${}^5D_0 \rightarrow {}^7F_1$	48	17.78	6000	11	2.19
${}^5D_0 \rightarrow {}^7F_2$	174	64.44	6230	10	13.95
${}^5D_0 \rightarrow {}^7F_4$	46	17.04	7049	18	3.33
${}^5D_0 \rightarrow {}^7F_6$	02	0.74	nr	–	–
$A_T(\text{s}^{-1})$	270				
t_r of 5D_0 (ms)	3.70				
R	3.38				

Table 3. JO parameters ($\Omega_I \times 10^{-20} \text{ cm}^2$) and radiative lifetime (t_r in ms) for 5D_0 state in Eu^{3+} : glasses.

JO parameters	Present work			Reported work			
	$\text{Al}(\text{NO}_3)_3\text{-SiO}_2$	L5FBE (2)	L4BE (2)	ZBLA (15)	PbSi (19)	KMgSi (26)	K-Fluoride (22)
Ω_2	5.61	5.64	11.62	0.64	6.44	6.36	8.63
Ω_4	3.47	4.44	—	4.87	4.13	3.94	10.51
Ω_6	2.91	5.38	2.82	2.84	1.44	0.51	—
t_r of 5D_0 state (ms):	3.70	3.12	2.11	6.56	1.91	3.14	2.27

(2) Babu and Jayasankar (2000); (15) Dejneka *et al* (1995); (19) Fermi *et al* (1988); (22) Hazarika and Rai (2002); (26) Ofelt (1962).

Table 4. Abbe number (n_e), dispersive power ($1/n_e$), non-linear ref. index (n_2), coefficient (g) and susceptibility ($c^{e(3)}$) of Eu^{3+} : $\text{Al}(\text{NO}_3)_3\text{-SiO}_2$ sol-gel glass.

$n_{F'}$	$n_{c'}$	$n_{F'} - n_{c'}$	n_e	n_e	$1/n_e$	$n_2 (10^{-13} \text{ esu})$	$g (\text{cm}^2/\text{W})$	$w_0 \times 10^{-13}$	$N \times 10^{-16}$	$c^{e(3)}$
1.508	1.499	0.009	1.504	56	0.018	1.351	0.3761	114.46	674.197	18.77

Once n_2 is estimated, the non-linear refractive index coefficient (g) can be evaluated from (Milam and Weber 1976)

$$g (\text{cm}^2/\text{W}) = \frac{4p \times 10^7}{cn_e} n_2, \quad (12)$$

where c is the velocity of light. The expression for third order non-linear susceptibility ($c^{e(3)}$) is (Brown 1985)

$$c^{e(3)} = \frac{g}{4} \times \frac{(n_e^2 + 2)^2}{9} \times \frac{(n_e^2 - 1)^2}{16p^2} \times \frac{2p}{Nhw_0}. \quad (13)$$

$g = 3$ for glassy materials. The other non-linear factors, N and w_0 , are given by

$$N = \frac{p(n_e^2 - 1)(n_e^2 + 1)(X_{F'} - X_{c'})n_e}{r_0 2n_e}, \quad (14)$$

$$r_0 = 0.528 \times 10^{-8},$$

and

$$w_0 = [X_e + [(n_e^2 + 2)(n_e + 1)(X_{F'} - X_{c'})n_e/6n_e]]^{1/2}, \quad (15)$$

where $X_{F'} = 10^{16}/I_{F'}^2$, $X_e = 10^{16}/I_e^2$, and $X_{c'} = 10^{16}/I_{c'}^2$.

Using expressions (10)–(15) non-linear properties and susceptibility of Eu^{3+} : sol-gel glass have been estimated (table 4). Low non-linear refractive index (n_2), coefficient (g) and reasonably high Abbe number (n_e) indicates the high optical quality of the silica gel glass.

4. Conclusions

In the present work Eu^{3+} : $\text{Al}(\text{NO}_3)_3\text{-SiO}_2$ sol-gel glass is fabricated and characterized. Various absorption and ra-

diative properties of the glass are evaluated using the Judd–Ofelt theory. Moreover, a structural analysis and non-linear parametrization are also undertaken. Calculated radiative properties like $S(I_P)$ and b_r , that characterize lasing transition are very encouraging for the potential laser transition ($^5D_0 \rightarrow ^7F_2$) in the sol-gel glass, far better than in fluoride and fluoroborate glasses (Babu and Jayasankar 2000; Hazarika and Rai 2002), respectively obtained with same mol% of EuF_3 (fluoride) and Eu_2O_3 (fluoroborate).

IR spectra of the sol-gel glass indicate the presence of quite a significant $-\text{OH}$ and H_2O content. The $-\text{OH}$ and water content can be effectively reduced by treating the gel during solidification at around 1000°C . Reduction in these contents can further enhance the fluorescence intensity. Lifetime predicted for Eu ions in silica gel is also relatively high.

In addition to the radiative properties, the relatively high Abbe number (n_e) and low non-linear refractive index (n_2) and the non-linear susceptibility ($c^{e(3)}$) value confirm the glass to be of a high optical quality and a very good third order non-linear amorphous material.

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