SPECTROSCOPIC PROPERTIES OF ERBIUM IONS DOPED IN BISMUTH BORO-SILICATE GLASSES

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Glasses with composition $20\text{B}_2\text{O}_3 \cdot (79.5-x)\text{Bi}_2\text{O}_3 \cdot x\text{SiO}_2$ ($10 \leq x \leq 40$) containing 0.5mol% of Er^{3+} ions were prepared by melt-quench technique. Optical absorption and fluorescence spectra were recorded at room temperature for all glass samples. Based on the Judd-Offelt theory, spectroscopic properties of Er^{3+} ions are discussed by changing the host glass compositions. The intensity parameters Ω_2 , Ω_4 , and Ω_6 are determined by applying least square analysis method. The variation of Ω_2 and Ω_6 with Bi_2O_3 content has been attributed to changes in the asymmetry of the ligand field at the rare earth ion site and to the changes in the rare earth oxygen (RE-O) covalency. The variation of Ω_4 with Bi_2O_3 content has been attributed to rigidity of the samples. Using these intensity parameters various radiative properties like spontaneous emission probability, branching ratio, radiative life time and stimulated emission cross-section of various emission lines have been evaluated. An intense green luminescence bands with maximum around 516 nm and 536 nm are assigned to the ${}^2\text{H}_{11/2} \rightarrow {}^4\text{I}_{15/2}$ and ${}^4\text{S}_{3/2} \rightarrow {}^4\text{I}_{15/2}$ transitions respectively has been obtained.

Keywords: Spectroscopic property; Rare earth metal; Optical absorption.

1. Introduction

Over the past several decades, optical and spectroscopic properties of various trivalent lanthanides have been extensively investigated for various host materials to apply optical devices. After showing laser action of Er^{3+} by Snitzer and Woodcock in 1965 [1] considerable efforts are made on the research of Er^{3+} ions doped oxide glasses. Due to their rich energy level structure, the trivalent erbium doped glasses have been used as media of the up-conversion laser, wave-guide laser, and erbium-doped fiber amplifier (EDFA) which is one of the key elements used in the wavelength-division-multiplexing (WDM) network for optical communication. Recently, much attention has been given to the research of the Er^{3+} ions doped glasses [2-4] due to the $1.5\mu\text{m}$ emission from the ${}^4\text{I}_{13/2} \rightarrow {}^4\text{I}_{15/2}$ transition is eye safe and located in the optical third communication window where the losses are minimum. The most stable ionization state is the trivalent one, with 5s & 5p electrons remaining untouched and acting to screen the energy levels of the 4f

electrons from the effect of surrounding environment. The transition probability between 4f states, however are sensitive to the ions surrounding the rare earth ions.

In general, the optical and spectroscopic properties are strongly dependent on host materials. Many potential host materials for rare earth ions have been developed. It was found that the oxide glasses have small absorption coefficient, high chemical and thermal durability, therefore they are suitable material for technology applications [5-6]. Silicate glasses are chemically durable, thermally stable and optically transparent at the excitation and lasing wavelength. Bismuth oxide glasses are more suitable due to its high refractive index, low phonon energy and good chemical suitability [7-8]. The efforts to improve quantum efficiency of the luminescence bands have paid attention to heavy metal host materials [9-10]. The Judd-Ofelt theory [11-12] is usually adopted to calculate, by assuming certain approximation, transitions probability from the data of absorption cross-section of several f-f transitions. According to this theory, the strength of an f-f transitions may be expressed by the sum of the products of three intensities parameters Ω_λ ($\lambda = 2, 4, 6$) times the squared matrix elements $U^{(i)}$ between the initial J-states and the terminal J* state. Once the phenomenological parameters Ω_λ have been calculated, it is possible to derive the strength of any absorption or emission transmission, as well as the stimulated cross-section, the fluorescence branching ratio from level J to J*, and the radiative life time of an excited level. Such spectral studies give valuable information about the structure and bonding in glass and radiative and non radiative properties of rare earth ions doped in glass matrix. This information is essentially required while developing new optical devices [13].

Oxide glasses are stable hosts for obtaining efficient luminescence in rare earth ions. Therefore, the purpose of the present study is to introduce the upgraded lasing material by including the heavy metals Bi_2O_3 in silicate glasses using Judd-Ofelt theory.

2. Theoretical Details

The Judd-Ofelt [11-12] parameters Ω_λ ($\lambda = 2, 4, 6$) can be determined from the experimental ground state oscillator strength (f_{expt}) of the absorption spectral transitions via an integration of the absorption coefficients for each band according to the following equation:

$$f_{\text{expt.}} = 4.318 \times \int \epsilon(\nu) d\nu \quad (1)$$

where $\epsilon(\nu)$ is the molar extinction coefficient at average energy (ν) in cm^{-1} . The measured line strength is used to calculate the intensity parameters Ω_λ by solving a set of equations for the corresponding transitions between initial to terminal manifold ($\Psi J \rightarrow \Psi' J'$) expressed by calculated oscillator strengths (f_{cal}) and is given by

$$f_{\text{cal}}(\Psi J; \Psi' J') = \frac{8\pi^2 m c \nu}{3h(2J+1)} \left[\frac{(n^2+2)^2}{9n} \right] \times \sum_{\lambda=2,4,6} \Omega_\lambda (\Psi J \| U^\lambda \| \Psi' J')^2 \quad (2)$$

where $(n^2+2)^2/9n$ is a factor for the effective field at the well-localized center in a medium of isotropic refractive index, m is the mass of electron, c is the velocity of light in vacuum, h is the Planck's constant, n is the refractive index of glass, ν is the frequency of the $\Psi J \rightarrow \Psi' J'$ transition, Ω_λ ($\lambda = 2, 4, 6$) are the J-O intensity parameters and $\|U^\lambda\|$ are the doubly reduced matrix elements of the unit tensor operator of the rank $\lambda = 2, 4$ and 6 which are calculated from the intermediate coupling approximation for a transition $\Psi J \rightarrow \Psi' J'$.

In order to determine the accuracy of the intensity parameters, the root-mean-square deviation (δ_{RMS}) is also calculated using the relation .

$$\delta_{RMS} = \left[\frac{\sum (f_{cal} - f_{expt})^2}{\sum f_{expt}^2} \right]^{1/2} \quad (3)$$

Where summation is taken over the bands used to calculate Ω_λ parameters.

The spontaneous emission probability for a transition from an initial state (ΨJ) to a particular final state ($\Psi' J'$) is given by

$$A_R(\Psi J; \Psi' J') = \frac{64\pi^4 \nu^3}{3h(2J+1)} \left[\frac{n(n^2+2)^2}{9} S_{ed} + n^3 S_{md} \right] \quad (4)$$

where S_{ed} and S_{md} are electric and magnetic dipole line strengths, respectively. The selection rules for the electric dipole transitions S_{ed} from the f -configuration mixing include $\Delta l = \pm 1$, $\Delta S = 0$, $|\Delta L|$ and $|\Delta J| \leq 6$. The total radiative transition probability (A_T) of an excited state is given by the sum of the $A_R(\Psi J; \Psi' J')$ terms calculated over all the terminal states and is related to radiative life time (τ_R) as

$$\frac{1}{\tau_R} = A_T(\Psi J) = \sum_{\Psi' J'} A_R(\Psi J; \Psi' J') \quad (5)$$

And the branching ratio is given by

$$\beta_R(\Psi J; \Psi' J') = \frac{A_R(\Psi J; \Psi' J')}{A_T(\Psi J)} \quad (6)$$

The peak stimulated emission cross-section, $\sigma_e(\lambda_p)$, is an essential parameter to predict the laser performance of the glass and can be determined using the following expression

$$\sigma_e(\lambda_p) = \frac{\lambda_p^4}{8\pi c n^2 \Delta \lambda_{eff}} A_R(\Psi J; \Psi' J') \quad (7)$$

where λ_p is the wavelength of the fluorescence peak and $\Delta \lambda_{eff}$ is the line width obtained by dividing the area of the emission band by its average height. The large value of

stimulated emission cross-section and high branching ratio determine the suitability of the materials for good optical devices.

3. Experimental

Glasses having compositions $20\text{B}_2\text{O}_3 \cdot (79.5-x)\text{Bi}_2\text{O}_3 \cdot x\text{SiO}_2$ ($10 \leq x \leq 40$, mol%) doped with 0.5 mol% of Er^{3+} ions were prepared by melt quench technique. Appropriate amount of AR grade chemicals (B_2O_3 , Bi_2O_3 , SiO_2 and Er_2O_3) having purity above 99.99% were weighed on 0.001% accuracy and mixed thoroughly. The raw mixed materials were melted in a muffle furnace in air (at 1150°C for 40 min). The crucible was shaken frequently after every 10 minutes for the homogeneous mixing of all the constituents. The melt was quenched at room temperature by pouring between two stainless steel plates. The quenched samples were annealed to minimize the internal strain and then allowed to cool slowly to room temperature. The samples were polished for spectral and other investigations. The amorphous nature of the glasses was confirmed by recording the X-ray diffraction pattern using Mini Flex Desktop X-ray Diffractometer with $\text{Cu-K}\alpha$ line of wavelength at the scanning rate of $2^\circ/\text{min}$ and 2θ was varied from 10° to 80° .

The refractive index (n) of the prepared samples was measured by the Brewster angle method using He-Ne laser (633 nm). The density (D_g) of all the glasses was measured by using Archimedes principle with xylene as immersing liquid. The relation used is

$$D_g \left(\text{gm} / \text{cm}^3 \right) = \frac{W_a}{W_a - W_b} D_x \quad (8)$$

Where W_a is the weight of glass sample in air, W_b is the weight of glass sample when immersed in xylene and D_x is the density of xylene ($0.86 \text{ gm}/\text{cm}^3$).

The Optical absorption spectra of all the polished samples were recorded on a Varian-Carry 5000 spectrophotometer in the range 300-3200 nm. The emission spectra were recorded using Fluoro-max-3 Fluorimeter with Xe arc lamp as the excitation source at wavelength of 800 nm.

4. Result and Discussion

The optical absorption spectrum of BBSE1 is shown in Fig. 1. From these spectra, absorption bands at 488, 520, 538, 650, 816 and 976nm are observed, which predict the Er^{3+} ions transition from the ground state $^4\text{I}_{15/2}$ to various excited states within 4f shell which were assigned as $^4\text{F}_{7/2}$, $^2\text{H}_{11/2}$, $^4\text{S}_{3/2}$, $^4\text{F}_{9/2}$, $^4\text{I}_{9/2}$, and $^4\text{I}_{11/2}$ respectively. The experimental and calculated values of oscillator strength are presented in Table1.

FIG. 1. Optical absorption of BBSE1 glass

FIG. 2. Fluorescence spectra of BBSE1 glass

Table 1. Oscillator strength ($\times 10^{-6}$) for the transitions from ground level $^6I_{5/2}$ and root mean square (δ_{RMS}) of various Er^{3+} doped BBSE glasses.

Transitions $^4I_{15/2} \rightarrow$	λ	BBSE1		BBSE2		BBSE3		BBSE4	
		fexp	fcal	Fexp	fcal	fexp	fcal	Fexp	fcal
$^4F_{7/2}$	488	0.80	1.02	0.73	0.87	0.70	0.92	0.61	0.54
$^2H_{11/2}$	520	2.37	3.02	1.72	2.25	1.57	1.64	1.08	0.87
$^4F_{9/2}$	650	1.34	1.83	1.34	1.41	1.52	0.98	1.26	1.09
$^4I_{9/2}$	816	2.72	3.14	2.36	2.68	1.91	1.80	1.57	0.93
$^4I_{11/2}$	976	1.39	0.99	2.93	2.80	0.97	0.89	1.29	1.59
$\delta_{RMS} (10^{-6})$		0.97		1.32		1.17		1.32	

According to the Judd-Ofelt theory, the effect of the crystal field can be described by three intensity parameters Ω_{λ} ($\lambda = 2, 4, 6$). These parameters are obtained from the experimental oscillator strengths and the calculated double reduced matrix elements by using least square analysis method [14]. The variation of Ω_2 with Bi_2O_3 content has been attributed to changes in the asymmetry of the ligand field at the rare earth ion site and to the changes in their rare earth oxygen (RE-O) covalency [15]. The shift in the hypersensitive band shows that the covalency of the RE-O bond decreases with decrease of Bi_2O_3 content, and it is attributed to the increased interaction between the rare earth ions and the non-bridging oxygen's (NBO's). Therefore the covalency of the rare-earth oxygen decreases with the increase in SiO_2 content in the host glasses.

Table 2 Refractive index (n), Judd-Ofelt intensity parameters (Ω_2 , Ω_4 , Ω_6) and SQF of various Er^{3+} doped BBSE glasses.

Intensity	BBSE1	BBSE2	BBSE3	BBSE4
n	2.12	1.84	1.73	1.68
$\Omega_2(10^{-20}\text{cm}^2)$	2.32	2.83	3.22	3.69
$\Omega_4(10^{-20}\text{cm}^2)$	1.42	1.32	1.48	1.56
$\Omega_6(10^{-20}\text{cm}^2)$	1.17	1.22	1.11	1.43
(SQF) Ω_4/Ω_6	1.21	1.08	1.33	1.09

Where as the intensity parameters Ω_4 and Ω_6 are related to the rigidity of the host [16]. A measure of the accuracy of the fitted values of the Ω_λ parameters are given by δ_{RMS} deviation which is also given in table 1.

Fig. 2, shows three peaks of emission spectrum at 475, 516, 536 nm that assigned the following emission transitions $^4\text{F}_{7/2} \rightarrow ^4\text{I}_{15/2}$, $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$, $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ respectively.

Table 3 The peak wavelength (λ_p), radiative transition probability (A_{rad}), branching ratio (β_r), stimulated emission cross-section (σ), total radiative transition probability (A_T) and radiative life time (τ_r) of Er^{3+} ion doped BBSE glasses

Transitions	λ_p	BBSE1			BBSE2			BBSE3			BBSE4		
From	(nm)	A_{rad}	β_r	σ	A_{rad}	β_r	σ	A_{rad}	β_r	σ	A_{rad}	β_r	σ
		(s^{-1})	(%)	(10^{-20}cm^2)	(s^{-1})	(%)	(10^{-20}cm^2)	(s^{-1})	(%)	(10^{-20}cm^2)	(s^{-1})	(%)	(10^{-20}cm^2)
$^4\text{F}_{7/2} \rightarrow ^4\text{I}_{15/2}$	475	419	0.367	4.95	406	0.370	4.34	394	0.380	3.92	381	0.392	3.57
$^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$	516	331	0.290	2.14	313	0.285	2.11	288	0.280	1.08	267	0.275	1.76
$^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$	536	392	0.343	3.41	376	0.343	2.97	354	0.342	2.69	323	0.332	2.34
$A_T(\text{s}^{-1})$		1142			1095			1036			971		
$\tau_r(\mu\text{s})$		875			913			965			103		

From table 3, it is observed that the value of stimulated emission cross-section (σ) decreases with the decrease in Bi_2O_3 content in the host glass. The trend observed in the present study follows the same pattern as reported by S Sanghi et al. [17] in Er^{3+} ion doped zinc bismuth borate glass.

From the figure 2 two green luminescence bands with maximum around 516 nm and 536 nm are assigned to the $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$ and $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ transitions respectively. Another emission band is identified as due to $^4\text{F}_{7/2} \rightarrow ^4\text{I}_{15/2}$ electronic transition. The most intense emission (easily seen by naked eyes) corresponds to the green emission from the $^4\text{S}_{3/2}$ level. Further-more, these emissions are in agreement with previous investigations on erbium-doped glasses [18-20]. The high values of stimulated emission cross-section suggest that the prepared glasses are potential candidates for the lasing host materials and for low threshold, high gain applications.

5. Conclusion

The refractive index of the glass reduces from 2.12 to 1.68 with the decrease in $\text{Bi}_2\text{O}_3 / \text{SiO}_2$ ratio. The spectroscopic properties of Er^{3+} doped glass has been analyzed on the basis of Judd-Ofelt theory. The covalent nature of the prepared glass decreases with the decrease in Bi_2O_3 content in the host glass. The branching ratio for the transition $^4\text{F}_{7/2} \rightarrow ^4\text{I}_{15/2}$ is 40% therefore the radiative transition probability is high as 419 s^{-1} as shown in Table 3. From here it concluded that the prepared glasses are suitable host for the lasing materials. It shows lasing emission in the visible range.

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