International Journal of Engineering Science Invention
ISSN (Online): 2319 – 6734, ISSN (Print): 2319 – 6726
www.ijesi.org ||Volume 6 Issue 10|| October 2017 || PP. 42-47

Spectroscopic Properties of Tb^{3+} Doped in Zinc Lithium Bismuth Borate Glasses

S.L.Meena
Ceremic Laboratory, Department of physics, Jai Narain Vyas University, Jodhpur 342001(Raj.) India
*Corresponding Author: *S.L.Meena*

Abstract: *Glass sample of Zinc Lithium Bismuth Borate (25-x) Bi_2O_3:20Li_2O:20ZnO:35 B_2O_3: x Tb_2O_3. (where x=1,1.5,2 mol%) have been prepared by melt-quenching technique. The amorphous nature of the prepared glass samples was confirmed by X-ray diffraction. The absorption spectra of three Tb^{3+} doped zinc lithium bismuth borate glasses have been recorded at room temperature. The various interaction parameters like Slater-Condon parameters F_K (k=2, 4, 6), Lande parameter (ξ_{4F}), nephelauexetic ratio (β'), bonding parameter ($b^{1/2}$) and Racah parameters E^K (k=1, 2, 3) have been computed. Judd-Ofelt intensity parameters Ω_λ (λ = 2, 4, 6) and laser parameters have also been calculated. The spectroscopic quality factor related with the rigidity of the glass system is also discussed.*

Keywords: *Bismuth borate glasses, Energy interaction parameters, Optical properties, Judd-Ofelt analysis.*

Date of Submission: 29-09-2017 Date of acceptance: 25-10-2017

I. Introduction

Among all oxide glasses, borate glasses have been studied the most because of their compositional versatility, good physical and chemical properties and well developed melting and casting technology. The performance and relatively low cost of borate glasses make them attractive for most of the ordinary laser applications [1-4]. Bismuth oxide contained host glass matrix improves chemical durability of the glass [5, 6].

It has been shown that the heavy metal oxide (HMO) glasses are very attractive hosts for rare earth ions because of the high refractive index, lower transition temperature than phosphate and silicate glasses and low phonon energy [7-9].Bismuth borate glasses are of great importance for their industrial and special applications as low-loss fiber optics, infrared transmitting materials or as active medium of Raman fiber optical amplifiers [10, 11].

Bismuth borate glasses have the advantages of low melting temperature, extensive glass formation range, high physical and chemical stability [12-14]. Furthermore, rare earth ion doped bismuth borate glasses posses large stimulated emission cross section and high fluorescence quantum efficiency [15, 16]. In the present form of zinc lithium bismuth borate glasses the oxide such as Bi_2O_3 could be found as the network modifiers(NWM) and B_2O_3 can be used as the network former(NWF).

The aim of the present study is to prepare the Tb^{3+} doped zinc lithium bismuth borate glass with different Tb_2O_3 concentrations. The absorption spectra, fluorescence spectra of $Tb^{3+}$of the glasses were investigated. The Judd-Ofelt theory has been applied to compute the intensity parameters Ω_λ (λ=2, 4, 6).These intensity parameter have been used to evaluate optical properties such as spontaneous emission probability, branching ratio, radiative life time and stimulated emission cross section.

II. Experimental Techniques

Preparation of glasses

The following Tb^{3+} doped bismuth borate glass samples (25-x) Bi_2O_3:20Li_2O:20ZnO:35 B_2O_3: x Tb_2O_3. (where x=1,1.5, 2) have been prepared by melt-quenching method. Analytical reagent grade chemical used in the present study consist of Bi_2O_3, Li_2O, ZnO, and $B_2O_3$and Tb_2O_3. They were thoroughly mixed by using an agate pestle mortar. then melted at 1050^0C by an electrical muffle furnace for 2h., After complete melting, the melts were quickly poured in to a preheated stainless steel mould and annealed at temperature of 350^0C for 2h to remove thermal strains and stresses. Every time fine powder of cerium oxide was used for polishing the samples. The glass samples so prepared were of good optical quality and were transparent. The chemical compositions of the glasses with the name of samples are summarized in Table 1.

Table 1

Chemical composition of the glasses

Sample	Glass composition (mol %)
ZnLiBiB (UD)	25 Bi_2O_3:20Li_2O:20ZnO: 35 B_2O_3
ZnLiBiB (TB1)	24 Bi_2O_3:20Li_2O:20ZnO: 35 B_2O_3: 1 Tb_2O_3
ZnLiBiB (TB1.5)	23.5 Bi_2O_3:20Li_2O:20ZnO: 35 B_2O_3: 1.5 Tb_2O_3
ZnLiBiB (TB 2)	23 Bi_2O_3:20Li_2O:20ZnO: 35 B_2O_3: 2 Tb_2O_3

ZnLiBiB (UD) -Represents undoped Zinc Lithium Bismuth Borate glass specimen.
ZnLiBiB (TB) -Represents Tb^{3+} doped Zinc Lithium Bismuth Borate glass specimens.

III. Theory

3.1 Oscillator Strength

The spectral intensity is expressed in terms of oscillator strengths using the relation [17].

$$f_{expt.} = 4.318 \times 10^{-9} \int \varepsilon(\nu)\, d\nu \qquad (1)$$

Where, ε (*ν*) is molar absorption coefficient at a given energy *ν* (cm^{-1}), to be evaluated from Beer–Lambert law.

Under Gaussian Approximation, using Beer–Lambert law, the observed oscillator strengths of the absorption bands have been experimentally calculated [18], using the modified relation:

$$P_m = 4.6 \times 10^{-9} \times \frac{1}{cl} \log \frac{I_0}{I} \times \Delta\upsilon_{1/2} \qquad (2)$$

Where c is the molar concentration of the absorbing ion per unit volume, *l* is the optical path length, $\log I_0/I$ is optical density and $\Delta\upsilon_{1/2}$ is half band width.

3.2. Judd-Ofelt Intensity Parameters

According to Judd [19] and Ofelt [20] theory, independently derived expression for the oscillator strength of the induced forced electric dipole transitions between an initial J manifold $|4f^N$ (S, L) J> level and the terminal J' manifold $|4f^N$ (S',L') J'> is given by:

$$\frac{8\Pi^2 mc\bar{\upsilon}}{3h(2J+1)}\frac{1}{n}\left[\frac{(n^2+2)^2}{9}\right] \times S(J, J') \qquad (3)$$

Where, the line strength S (J, J') is given by the equation

$$S(J, J') = e^2 \sum_{\lambda=2,4,6} \Omega_\lambda \langle 4f^N(S, L) J \| U^{(\lambda)} \| 4f^N(S', L') J' \rangle 2$$

In the above equation m is the mass of an electron, c is the velocity of light, *ν* is the wave number of the transition, h is Planck's constant, n is the refractive index, J and J' are the total angular momentum of the initial and final level respectively, Ω_λ (λ = 2, 4, 6) are known as Judd-Ofelt intensity parameters which contain the effect of the odd-symmetry crystal field terms, radial integrals and energy denominators. $\| U^{(\lambda)} \|^2$ are the matrix elements of the doubly reduced unit tensor operator calculated in intermediate coupling approximation. Ω_λ parameter can be obtained from least square fitting method [21] (Table 4). The matrix element $\| U^{(\lambda)} \|^2$ that are insensitive to the environment of rare earth ions were taken from the literature [22].

3.3 Radiative Properties

The Ω_λ parameters obtained using the absorption spectral results have been used to predict radiative properties such as spontaneous emission probability (A) and radiative life time (τ_R), and laser parameters like fluorescence branching ratio (β_R) and stimulated emission cross section (σ_p).

The spontaneous emission probability from initial manifold $|4f^N$ (S', L') J'> to a final manifold $|4f^N$ (S, *L) J* >| is given by:

$$A[(S', L') J'; (S, L) J] = \frac{64\pi^2\nu^3}{3h(2J'+1)}\left[\frac{n(n^2+2)^2}{9}\right] \times S(J', \bar{J}) \qquad (4)$$

Where, $S(J', J) = e^2 [\Omega_2 \| U^{(2)} \|^2 + \Omega_4 \| U^{(4)} \|^2 + \Omega_6 \| U^{(6)} \|^2]$

The fluorescence branching ratio for the transitions originating from a specific initial manifold $|f^N$ (S', L') J'> to a final many fold $|f^N$ (S, *L)* J > is given by

$$\beta[(S',L')J';(S,L)J] = \sum_{SLJ} \frac{A[(S'\ L')]}{A[(S'\ L')\ J'(\bar{S}\ \bar{L})]} \quad (5)$$

Where, the sum is over all terminal manifolds.

The radiative life time is given by

$$\tau_{rad} = \sum_{SLJ} A[(S',L')J';(S,L)] = A_{Total}^{-1} \quad (6)$$

Where, the sum is over all possible terminal manifolds. The stimulated emission cross -section for a transition from an initial manifold $|f^N(S',L')J'>$ to a final manifold $|f^N(S,L)J>|$ is expressed as

$$\sigma_p(\lambda_p) = \left[\frac{\lambda_p^4}{8\pi c n^2 \Delta\lambda_{eff}}\right] \times A[(S',L')J';(\bar{S},\bar{L})\bar{J}] \quad (7)$$

Where, λ_p the peak fluorescence wavelength of the emission band and $\Delta\lambda_{eff}$ is the effective fluorescence line width.

3.4 Nephelauxetic Ratio (β') and Bonding Parameter ($b^{1/2}$)

The nature of the R-O bond is known by the Nephelauxetic Ratio (β') and Bonding Parameter ($b^{1/2}$), which are computed by using following formulae [23, 24]. The Nephelauxetic Ratio is given by

$$\beta' = \frac{\nu_g}{\nu_a} \quad (8)$$

Where, ν_g and ν_a refer to the energies of the corresponding transition in the glass and free ion, respectively. The values of bonding parameter ($b^{1/2}$) is given by

$$b^{1/2} = \left[\frac{1-\beta'}{2}\right]^{1/2} \quad (9)$$

IV. Result And Discussion

4.1 XRD Measurement

Figure 1 presents the XRD pattern of the sample contain - B_2O_3 which is show no sharp Bragg's peak, but only a broad diffuse hump around low angle region. This is the clear indication of amorphous nature within the resolution limit of XRD instrument.

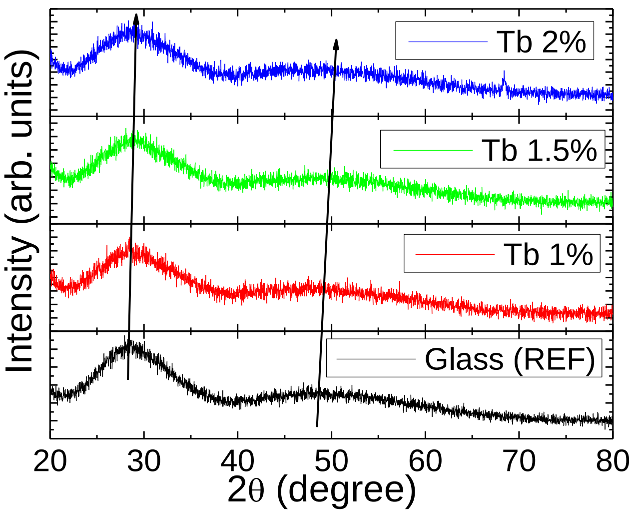

Fig. 1: X-ray diffraction pattern of Bi_2O_3: Li_2O: ZnO: B_2O_3: Tb_2O_3.

4.2 Thermal Property

Figure 2 shows the thermal properties of ZnLiBiB glass from 300^0C to 1000^0C. From the DSC curve of present glasses system, we can find out that no crystallization peak is apparent and the glass transition temperature T_g are 352,455 and 585 respectively. The T_g increase with the contents of Tb_2O_3 increase. We could conclude that thermal properties of the ZnLiBiB glass are good for fiber drawing from the analysis of DSC curve.

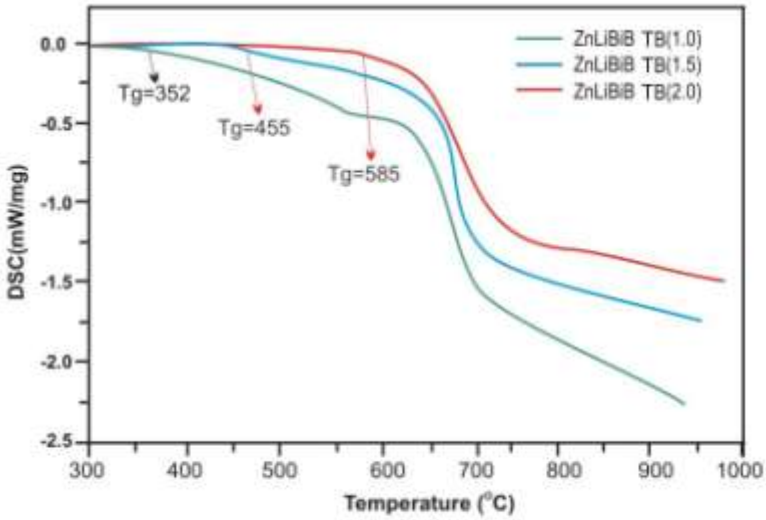

Fig.2: DSC curve of ZnLiBiB (TB) glasses.

4.3 Absorption Spectrum

The absorption spectra of Tb^{3+} doped ZnLiBiB (TB 01) glass specimen has been presented in Figure 3 in terms of optical density versus wavelength (nm). Five absorption bands have been observed from the ground state $^7F_6$ to excited states $^5D_4$, ($^5D_3$, $^5G_6$), $^5L_{10}$, ($^5D_2$, $^5G_4$, $^5G_5$) and $^5L_9$ for Tb^{3+}doped ZnLiBiB glasses.

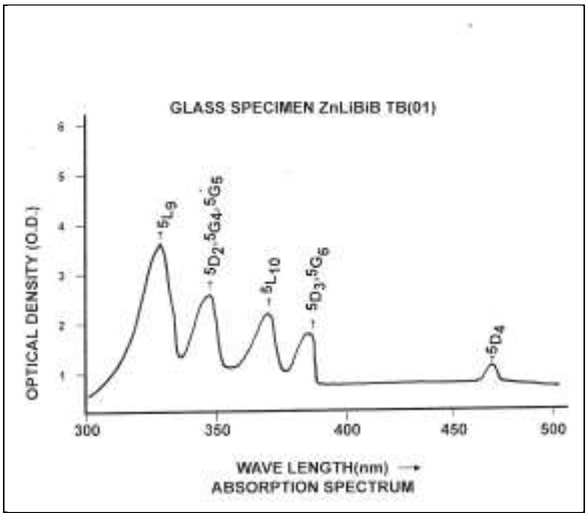

Fig.3: Absorption spectrum of Tb^{3+}doped ZnLiBiB (01) glass

The experimental and calculated oscillator strengths for Tb^{3+}ions in zinc lithium bismuth borate glasses are given in Table 2.

Table 2: Measured and calculated oscillator strength ($P_m \times 10^{+6}$) of Tb^{3+}ions in ZnLiBiB glasses.

Energy level from $^7F_6$	**Glass ZnLiBiB(TB01)**		**Glass ZnLiBiB(TB1.5)**		**Glass ZnLiBiB(TB02)**	
	$P_{exp.}$	$P_{cal.}$	$P_{exp.}$	$P_{cal.}$	$P_{exp.}$	$P_{cal.}$
$^5D_4$	0.44	0.069	0.42	0.075	0.41	0.071
$^5D_3$,$^5G_6$	0.80	0.48	0.78	0.50	0.76	0.49
$^5L_{10}$	1.50	1.23	1.47	1.24	1.45	1.23
$^5D_2$,$^5G_4$,$^5G_5$	1.78	0.64	1.76	0.65	1.75	0.64
$^5L_9$	2.08	1.12	2.05	1.12	2.04	1.11
r.m.s. deviation	±0.6849		±0.6849		±0.7128	

Computed values of F_2, Lande's parameter (ξ_{4f}), Nephlauxetic ratio(β') and bonding parameter($b^{1/2}$) for Tb^{3+} doped ZnLiBiB glass specimen are given in Table 3.

Table 3. F_2, ξ_{4f}, β' and $b^{1/2}$ parameters for Terbium doped glass specimen.

Glass Specimen	F_2	ξ_{4f}	β'	$b^{1/2}$
Tb^{3+}	400.26	1820.87	0.9703	0.1219

Judd-Ofelt intensity parameters Ω_λ (λ=2, 4, 6) were calculated by using the fitting approximation of the experimental oscillator strengths to the calculated oscillator strengths with respect to their electric dipole contributions. In the present case the three Ω_λ parameters follow the trend $\Omega_2 > \Omega_4 > \Omega_6$. The spectroscopic quality factor (Ω_4 /Ω_6) related with the rigidity of the glass system has been found to lie between 1.615 and 1.631in the present glasses.

The value of Judd-Ofelt intensity parameters are given in Table 4

Table4: Judd-Ofelt intensity parameters for Tb^{3+} doped ZnLiBiB glass specimens

Glass Specimen	**$\square_2$(pm^2)**	**$\square_4$(pm^2)**	**$\square_6$(pm^2)**	**$\square_4$ /$\square_6$**	**References**
ZnLiBiB(TB01)	4.276	3.890	2.405	1.617	P.W.
ZnLiBiB(TB1.5)	5.154	3.895	2.412	1.615	P.W.
ZnLiBiB(TB02)	4.556	3.899	2.390	1.631	P.W.
SBS(ER)	6.99	2.04	2.08	0.981	[25]
CdBiB(SM)	0.04	2.84	6.03	0.471	[26]

The values of Ω_4 /Ω_6 for glasses studied are given in Table 4. Tb^{3+} doped ZnLiBiB glasses are having larger value of (Ω_4 /Ω_6) than [SBS (ER) and CdBiB(SM)].It shows that ZnLiBiB (TB) glasses are a kind of better optical glass.

4.4. Fluorescence Spectrum

The fluorescence spectrum of Tb^{3+}doped in zinc lithium bismuth borate glass is shown in Figure 4. There are four broad bands observed in the Fluorescence spectrum of Tb^{3+}doped zinc lithium bismuth borate glass. The wavelengths of these bands along with their assignments are given in Table 5. Fig. (4).Shows the fluorescence spectrum with four peaks ($^5D_4 \rightarrow {}^7F_6$), ($^5D_4 \rightarrow {}^7F_5$), ($^5D_4 \rightarrow {}^7F_4$) and ($^5D_4 \rightarrow {}^7F_3$), respectively for glass specimens.

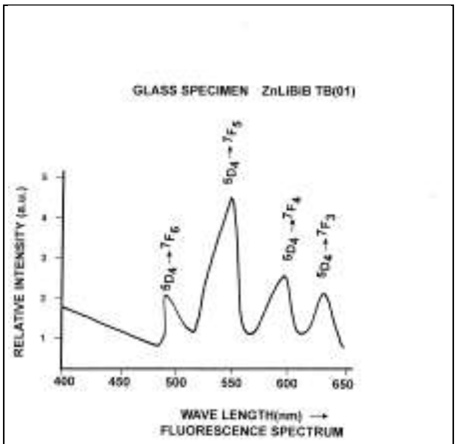

Fig.4: fluorescence spectrum of Tb^{3+}doped ZnLiBiB (01) glass

Table 5. Emission peak wave lengths (λ_{max}),radiative transition probability (A_{rad}),branching ratio (β),stimulated emission cross-section(σ_p) and radiative life time(τ_R) for various transitions in Tb^{3+}doped ZnLiBiB glasses.

Transition		ZnLiBiB TB 01				ZnLiBiBTB 1.5				ZnLiBiBTB 02			
	λ_{max} (nm)	$A_{rad}(s^{-1})$	β	σ_p (10^{-20} cm^2)	$\tau_R(\mu s)$	$A_{rad}(s^{-1})$	β	σ (10^{-20} cm^2)	$\tau_R(\mu s)$	$A_{rad}(s^{-1})$	β	σ_p (10^{-20} cm^2)	$\tau_R(\mu s)$
$^5D_4 \rightarrow {}^7F_6$	488	3297.337	0.1166	0.4774		3570.035	0.1103	0.50100		3565.521	0.1194	0.5053	
$^5D_4 \rightarrow {}^7F_5$	550	18054.849	0.6382	2.6342		21229.365	0.6559	3.0856		19133.896	0.6407	2.7543	
$^5D_4 \rightarrow {}^7F_4$	582	3310.755	0.1170	1.2163	33.48	3380.648	0.1045	1.2112	35.35	3344.920	0.1120	1.1775	30.90
$^5D_4 \rightarrow {}^7F_3$	625	3627.589	0.1282	0.8472		4185.861	0.1293	0.4058		3819.976	0.1279	0.8799	

V. Conclusion

In the present study, the glass samples of composition (25-x) Bi_2O_3:20Li_2O:20ZnO:35 B_2O_3: x Tb_2O_3 (where x=1, 1.5, 2mol %) have been prepared by melt-quenching method. Judd-Ofelt intensity parameters Ω_λ (λ=2, 4, 6) are evaluated from the intensities of various absorption bands of optical absorption spectra. The spectroscopic quality factor (Ω_4 /Ω_6) related with the rigidity of the glass system has been found to lie between 1.615 and 1.631in the present glasses. The radiative transition probability, branching ratio are highest for ($^5D_4\rightarrow{}^7F_5$) transition and hence it is useful for laser action. The stimulated emission cross section (σ_p) has highest value for the transition ($^5D_4\rightarrow{}^7F_5$) in all the glass specimens doped with Tb^{3+} ion. This shows that ($^5D_4\rightarrow{}^7F_5$) transition is most probable transition.

References

[1]. Alajerami, Y.S.M., Hashim,S.,Hassan, W.M.,Ramil, T.A.andKasim,A.(2012).Optical properties of lithium magnesium borate glass doped with Dy^{3+} and Sm^{3+} ions, Physics B: Condensed Matter, 13,2398.

[2]. Doualan,J.L.,Girared,S.,Haquin,H.,andAdam,J.L.andMontagne,J.(2003).Spectroscopic properties and laser emission of Tm^{3+} doped ZBLAN glass at 1.8 µm, Optical Materials, 24,563.

[3]. Rajesh, D., Naidu, M.D., Ratnakaram, Y.C. and Balakrishna, A.(2014). Ho^{3+}doped strontium-aluminium-bismuthborateglassesfor green light emission,Luminescence,29,854

[4]. Laczka,M., Stoch, L. and Gorecki,J.(1992). Bismuth containing glasses as materials for optoelectronics. J. Alloy Compd., 186,291.

[5]. Lin, J.J., Huang, W., Sun, Z., Ray. C.S. and Day, D.E. (2004). Structure and non- linear optical performance of TeO_2-Nb_2O_3-ZnO glasses, J. Non- Cryst. Solids, 336, 194.

[6]. Dumbaugh, W.H. and Lapp, J.C. (1992). Heavy-Metal Oxide Glass, J. Am. Cer. Soc., 75, 2315.

[7]. Heo, J., Shin, Y.B. and Jang, J.N.(1995).Spectroscopic analysis of Tm^{3+} in Pbo-Bi_2O_3-Ga_2O_3 glass, Appl.Opt.34,4289.

[8]. Nachimuthu P., Jagannthan R. (1995).Tb^{3+} fluorescence as a probe of cluster formation in lead oxyfluoride glasses, Journal of Non-Crystalline Solids 183, 211.

[9]. Motke, S.G., Yowale, S.P. and Yawale,S.S.(2002).Infrared spectra of zinc doped lead borate glasses. Bull.Mater.Sci. 25, 78.

[10]. Araj, Y., Suzuki, T., Ohishi,Y., Morimoto, S.and Khonthon,S.(2007).Ultrabroadband near-infrared emission from a colorless bismuth doped glass.Appl.Phys.lett.90,261110-1-3.

[11]. Truong,V.G., Bigot,L., Lerouge,A.,Douay,M. and Razdobreev,I.(2008). Study of thermal stability and luminescence quenching properties of bismuth doped silicate glasses for fiber laser applications. Appl.Phys.lett, 92, 041908-1-3.

[12]. Opera.I., Hesse, H. and Betzler,K.(2004). Optical properties of bismuth borate glasses.Opt.Mater.26, 237.

[13]. Ardelean,I., Cora,S. and Rusu, D.(2008). EPR and FT-IR Spectroscopic studies of Bi_2O_3-B_2O_3-CuO glasses.Physica B, 403, 3685.

[14]. Kamitsos,E.I.,Karakassides,M.A.,and Chryssikos, G.D.(1987). Vibrational spectra and structure of heavy metal oxide glasses.J. Non-cryst.solids, 202,240.

[15]. Sun,H., Wen, L., Xu,S., Dai, S., Hu, L., and Jiang, Z.(2005). Novel lithium barium lead bismuth glasses. Mater.lett., 59,962.

[16]. Altaf, M., Chaudhry, M.A., Zahid, M. (2005). Study of optical band gap of zinc borate glasses,J.Research(Science). 14,259.

[17]. Gorller-Walrand, C. and Binnemans, K. (1988). Spectral Intensities of f-fTransition. In: Gshneidner Jr., K.A. and Eyring,L., Eds., Handbook on the Physics and Chemistry of Rare Earths, Vol. 25, Chap. 167, North-Holland, Amsterdam, 101.

[18]. Sharma, Y.K., Surana, S.S.L. and Singh, R.K. (2009). Spectroscopic Investigations and Luminescence Spectra of Sm^{3+} Doped Soda Lime Silicate Glasses. J.Rare Earths, 27, 773.

[19]. Judd, B.R. (1962). Optical Absorption Intensities of Rare Earth Ions. Physical Review, 127, 750.

[20]. Ofelt, G.S. (1962) Intensities of Crystal Spectra of Rare Earth Ions. J.Chemical Physics, 37, 511.

[21]. Goublen, C.H. (1964). Methods of Statistical Analysis. Asian Publishing House, Bombay, Chap. 8, 138.

[22]. Babu, P. and Jayasankar, C.K. (2001). Spectroscopy of Pr^{3+} Ions in Lithium Borate and Lithium Fluoroborate Glasses.Physica B: Condensed Matter, 301, 326.

[23]. Sinha, S.P. (1983).Systematics and properties of lanthanides, Reidel,Dordrecht.

[24]. Krupke, W.F. (1974). IEEE J.Quantum Electron QE, 10,450.

[25]. Jamalaiah, B.C., Rao, S., Kumar, M.V., Gopal, K.R. and Reddy, R.R.(2015). Enhanced 1.53 µm luminescence in Er^{3+} doped sodium boro silicate glasses. App.Sci.Lett.3, 85.

[26]. Sailaja, S.,Nageswara, R.,Adinarayana,R.,Prasad,B.D., Jho, Y.D. and Reddy, B.S. (2013). Optical properties of Sm^{3+} doped cadmium bismuth borate glasses.J.Mol.Structure.1038, 34.

International Journal of Engineering Science Invention (IJESI) is UGC approved Journal with Sl. No. 3822, Journal no. 43302.