The International Journal of Engineering and Science (IJES)
|| Volume || 6 || Issue || 10 || Pages || PP 30-36 || 2017 ||
ISSN (e): 2319 – 1813 ISSN (p): 2319 – 1805

Spectroscopic Properties of Eu^{3+}Doped in Yttrium ZincLithium Bismuth Borate Glasses

S.L.Meena
Ceremic Laboratory, Department of physics, Jai NarainVyas University, Jodhpur 342001(Raj.) India
E-mail address:shankardiya7@rediffmail.com

ABSTRACT
Glass sample of Yttrium Zinc Lithium Bismuth Borate (20-x) Bi_2O_3:15Li_2O:15ZnO:10Y_2O_3:40 B_2O_3: xEu_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 Eu^{3+} dopedyttrium zinc lithium bismuth borate glasses have been recorded at room temperature. The various interaction parameters likeSlater-Condon parameters F_K (k=2,4,6),Lande' parameter (ξ_{4f}),nephelauexetic ratio (β'), bonding parameter ($b^{1/2}$) andRacah parametersE^K (k=1,2 3) have been computed.Judd-Ofelt intensity parameters and laser parameters have also been calculated.The large stimulated emission cross-section in bismuth borate glasses suggests the possibility of utilizing these systems as laser materials.

Keywords: Yttrium Zinc lithium bismuth borate glasses,Energy interaction parameters,Optical properties,Judd-Ofelt analysis.

Date of Submission: 03-10-2017 Date of Acceptance: 23-10-2017

I. INTRODUCTION

Oxide glasses doped with rare earth active ions are important for a variety of applications such as amplifier, demultiplexers, lasers and memory devices. Oxide glasses in particular have proven favorable as host materials for rare earth elements because of their high transparency, compositional variety and are easy to mass produce. Most of these applications utilize the intra 4f-4f transitions of trivalent rare earth ions and the efficiency of the transition is strongly dependent on the host materials where these ions are embedded [1-6].

Bismuth borate glasses have high refractive index, good physical and chemical stability and large transmission windows in the near infrared regions [7-10].Addition of network modifier (NWF) Li_2O to the bismuth borate glasses improves both electrical and mechanical properties of such glasses.ZnO is also added due to its specific chemical and microstructure properties. Bismuth glasses are very useful for exploiting as lead free high density radiation shielding window (RSW), as lead free low softening point dielectric glasses for plasma display panel, thick film conductors, sealing glasses for metals [11].

The stimulated emission cross-section (σ_p) parameter is the most important parameter. Its value signifies the rate of energy extraction from the laser material and is generally used to predict laser action in different rare earth doped glass specimens. For laser applications, the values of the stimulated emission cross-section are of great interest. High refractive index of the host material, large line strength and small fluorescence line widths are required to obtain large stimulated emission cross-section favorable for high gain and rapid energy extraction[12-15]

The aim of the present study is to prepare the Eu^{3+} doped yttrium zinc lithium bismuth borate glass with different Eu_2O_3 concentrations. The absorption spectra, fluorescence spectra of $Eu^{3+}$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 Eu^{3+} doped bismuth borate glass samples (20-x) Bi_2O_3:15Li_2O:15ZnO:10Y_2O_3:40 B_2O_3: xEu_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,Y_2O_3 and $B_2O_3$and Eu_2O_3. They were thoroughly mixed by using an agate pestle mortar. then melted at 1080^0C 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 380^0C 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 Table1.

Table 1
Chemical composition of the glasses

Sample	Glass composition (mol %)
YZnLiBiB(UD)	20 Bi_2O_3:15Li_2O:15ZnO:10Y_2O_3:40 B_2O_3
YZnLiBiB(EU1)	19 Bi_2O_3:15Li_2O:15ZnO:10Y_2O_3:40 B_2O_3: 1 Eu_2O_3
YZnLiBiB(EU1.5)	18.5 Bi_2O_3:15Li_2O:15ZnO:10Y_2O_3:40 B_2O_3: 1.5 Eu_2O_3
YZnLiBiB(EU 2)	18 Bi_2O_3:15Li_2O:15ZnO:10Y_2O_3:40 B_2O_3: 2 Eu_2O_3

YZnLiBiB(UD) -Represents undopedYttrium Zinc Lithium Bismuth Borate glass specimen.
YZnLiBiB(EU) -Represents Eu^{3+} dopedYttriumZinc Lithium Bismuth Borate glass specimens.

III. THEORY

3.1Oscillator Strength

The spectral intensityis expressed in terms of oscillator strengths using the relation [16].

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

Where, ε (*v)* is molar absorption coefficient at a given energy v (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 [17], 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 [18] and Ofelt [19] theory, independently derived expression for the oscillator strength of the induced forced electric dipole transitions between an initial J manifold $|4f^N (S, L) J\rangle$ level and the terminal J' manifold $|4f^N (S', L') J'\rangle$ 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, v 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 [20].

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 $|4f^N (S', L') J'\rangle$ to a final manifold $|4f^N (S, L) J\rangle|$ is given by:

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

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 $|4f^N (S', L') J'>$ to a final many fold $|4f^N (S,L)J>$ is given by

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

Where, the sum is over all terminal manifolds.

The radiative life time is given by

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

Where, the sum is over all possible terminal manifolds. The stimulated emission cross -section for a transition from an initial manifold $|4f^N (S', L') J'>$ to a final manifold $|4f^N (S,L)J>|$ is expressed as

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

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

3.4Nephelauxetic Ratio (□) 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 [21, 22]. The Nephelauxetic Ratio is given by

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

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

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

IV. RESULT AND DISCUSSION

4.1XRD 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.

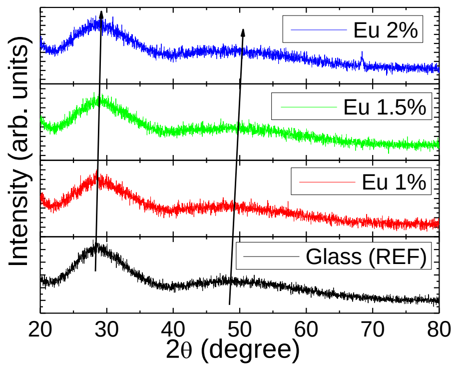

Fig. 1: X-ray diffraction pattern of Bi_2O_3: Li_2O: ZnO: B_2O_3: Y_2O_3: Eu_2O_3

4.2 Thermal Property

Figure 2 shows the thermal properties of YZnLiBiB 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 351,453,583 respectively. The T_g increase with the contents of Eu_2O_3 increase. We could conclude that thermal properties of the YZnLiBiB glass are good for fiber drawing from the analysis of DSC curve.

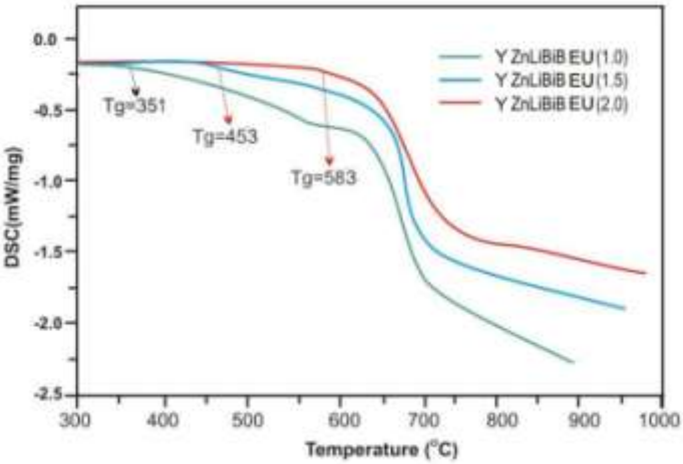

Fig.2: DSC curve ofYZnLiBiB (EU) glasses.

4.3 Absorption Spectrum

The absorption spectra of Eu^{3+} doped YZnLiBiB(EU 01) glass specimen has been presented in Figure 3 in terms of optical density versus wavelength (nm).Four absorption bands have been observed from the ground state $^7F_0$ to excited states $^5D_2$,$^5L_6$,$^5G_2$and ($^5G_6$,$^5G_4$)for Eu^{3+}dopedYZnLiBiB glasses.

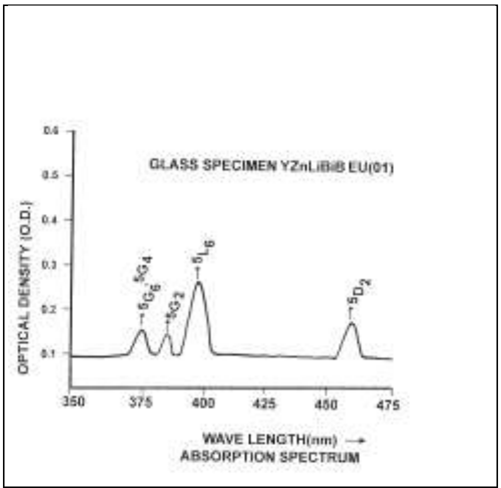

Fig.3: Absorption spectrum of Eu^{3+}doped YZnLiBiB(01)glass

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

Table2: Measured and calculated oscillator strength ($P_m \times 10^{+6}$) of Eu^{3+}ions in YZnLiBiB glasses.

Energy level from $^7F_0$	Glass YZnLiBiB(EU01)		Glass YZnLiBiB(EU1.5)		Glass YZnLiBiB(EU02)	
	P_{exp}.	P_{cal}.	P_{exp}.	P_{cal}.	P_{exp}.	P_{cal}.
$^5D_2$	1.66	1.38	1.65	1.37	1.63	1.33
$^5L_6$	3.25	3.18	3.20	3.15	3.10	3.03
$^5G_2$	0.50	0.40	0.48	0.43	0.45	0.41
$^5G_6$,$^5G_4$	0.55	0. 42	0.53	0.48	0.50	0.44
r.m.s. deviation	±0.324		±0.314		±0.304	

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

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

Glass Specimen	F_2	ξ_{4f}	β'	$b^{1/2}$
Eu^{3+}	372.63	1445.73	0.9645	0.1332

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 $\Omega_\lambda$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 1.203 and 1.371in the present glasses.

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

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

Glass Specimens	**Ω_2(pm^2)**	**Ω_4(pm^2)**	**Ω_6(pm^2)**	**Ω_4 / Ω_6**
YZnLiBiB(EU01)	2.483	2.061	1.713	1.203
YZnLiBiB(EU1.5)	2.479	2.178	1.696	1.284
YZnLiBiB(EU02)	2.473	2.424	1.768	1.371

4.4. Fluorescence Spectrum

The fluorescence spectrum of Eu^{3+}doped in yttrium zinc lithium bismuth borate glass is shown in Figure 4. There are two broad bands observed in the Fluorescence spectrum of Eu^{3+}doped yttrium 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 two peaks ($^5D_0 \rightarrow {^7F_2}$) and ($^5D_0 \rightarrow {^7F_4}$) for glass specimens.

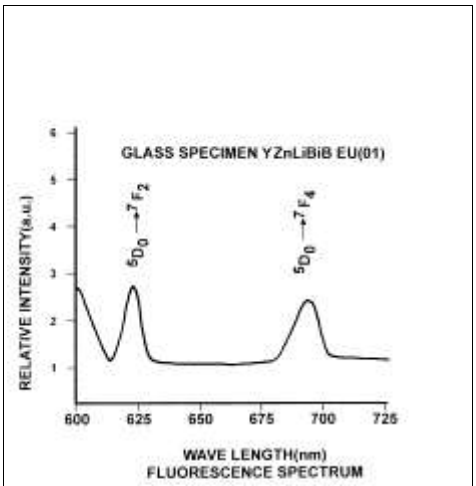

Fig.4:fluorescence spectrum of Eu^{3+}doped YZnLiBiB (01) glass

Table5. 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 Eu^{3+}doped YZnLiBiB glasses

Transition		YZnLiBiB EU 01				YZnLiBiB EU 1.5				YZnLiBiBEU 02			
	λ_{max} (nm)	A_{rad}(s^{-1})	β	σ_p ($10^{-20}cm^2$)	τ_R(μs)	A_{rad}(s^{-1})	β	σ ($10^{-20}cm^2$)	τ_R(μs)	A_{rad}(s^{-1})	β	σ_p ($10^{-20}cm^2$)	τ_R(μs)
$^5D_0 \rightarrow {^7F_2}$	619	30.053	0.2389	0.01260	7948.49	30.032	0.2286	0.01250	7611.86	30.059	0.2099	0.01231	6984.26
$^5D_0 \rightarrow {^7F_4}$	700	95.76	0.7611	0.04814		101.342	0.7714	0.05037		113.12	0.7901	0.05586	

V. CONCLUSION

In the present study, the glass samples of composition 20 Bi_2O_3:15Li_2O:15ZnO:10Y_2O_3:40 B_2O_3: x Eu_2O_3 (where x=1, 1.5, 2mol %) have been prepared by melt-quenching method. The Judd-Ofelt theory has been applied to calculate the oscillator strength and intensity parameters Ω_λ(λ=2, 4, 6). The stimulated emission cross section (σ_p) has highest value for the transition ($^5D_0 \rightarrow {}^7F_4$) in all the glass specimens doped with Eu^{3+} ion. This shows that ($^5D_0 \rightarrow {}^7F_4$) transition is most probable transition and it is useful for laser action.

REFERENCES

[1] Subhadra,M. and Kistaiah, P. (2012).Infrared and Raman spectroscopic studies of alkali bismuth borate glasses: Evidence of mixed alkali effect, Vibrational Spectroscopy, 62(9), 27.

[2] Wang, Y., Dai, S. Chen, F. Xu, T. and Nie, Q. (2009). Physical properties and Optical Band Gap of New Tellurite Glasses within the TeO2-Nb2O5-Bi2O3 System. Mater.Chem.Phys. 113,407.

[3] Anjaiah, J. and Laxmikanth, C. (2015). Optical Properties of Neodymium Ion Doped Lithium Borate Glasses, 5173.

[4] Lin, H., Pun, E.V.B. and Wang, X.J. (2005). Intense visible fluorescence and energy transfer in Dy^{3+}, Tb^{3+}, Sm^{3+} and Eu^{3+} doped rare-earth borate glasses. J. Alloy. Compd., 390:201.

[5] Ramteke, D.D., Annapurna, K. and Deshpande, V.K.andGedam, R.S. (2014). Effect of Nd^{3+} on spectroscopic properties of lithium borate glasses, J. Rare earths 32, 1153.

[6] Pascuta, P.,Pop, L., Rada, S.,Bosca,M. and Culea, E.(2008). The local structure of bismuth borate glasses doped with europium ions evidenced by FTIR spectroscopy, J. Mater.Sci. Mater. Electron, 19,428.

[7] Minakova, N.A.,Zaichuk, A.V. and Belyi, Y.I.(2008). The structure of borate glass, J. Glass and Ceramics, 65, 70.

[8] Peng, M., and Wondraczek, L. (2009). Bismuth-Doped Oxide Glasses as Potential Solar Spectral Converters and Concentrators. J. Mater. Chem., 19, 630.

[9] Laczka M, Stoch L and Gorecki J, (1992). Bismuth- containing glasses as materials for optoelectronics, J. Alloys Comp., 186,279.

[10] Devi,Renuka, Jayasankar, C. K.(1995) Optical properties of Nd^{3+} ions in lithium borateglasses,Materials chemistry and physics, 42,106.

[11] Becker. (2003). Thermal and optical properties of glasses of the system Bi_2O_3-B_2O_3, Crystal research and technology, 38, 82.

[12] Xue,D.,Betzler,K,Hesse,H and Lammers, D.(2000).Non-linear optical properties of borate crystals,solid state communications,114,25.

[13] Gautam, C.,Yadav,A.K. and Kumar,A.(2012).A Review on infraredspectroscopy of borate glasses with effect of different additives,ISRNCeramics Article ID428497,17

[14] Sharma, V., Singh, S.P.,Mudahar, G.S. and Thind,K.S.(2012). Synthesis and characterization of cadmium containing sodium borate glasses, New,J. Glass ceram,2,155

[15] Ivankov, A.,Seekamp,J. and Bauhofer, W. (2006). Optical properties ofEu^{3+}doped zinc borate glasses,Journal of luminescence,121,131.

[16] Gorller-Walrand, C. and Binnemans, K. (1988). Spectral Intensities of f-f Transition. 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, 101-264.

[17] 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. Journal of Rare Earths, 27, 773-780.

[18] Judd, B.R. (1962). Optical Absorption Intensities of Rare Earth Ions. PhysicalReview, 127, 761.

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

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

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

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

[23] Rajesh,D., Balakrishna, A and Ratnakaram, Y.C.(2012).Luminescence,structural and dielectric properties of Sm^{3+} impurities in strontium lithium bismuth borate glasses. Opt.Mat. 35,108.

[24] Gedam,R.S.,Ramteke, D.D.(2013). Influence of CeO_2 addition on the electrical and optical properties of lithium borate glasses. J.Phys. Chem.Solids, 74, 1399.

[25] Som,T. and Karmakar,B.(2008). Infrared-to-Red Upconversion Luminescence in Samarium-Doped Antimony Glasses.J.of Luminescence, 12, 1989.

[26] Shen,L.F.,Chen,B.J.,Pun,Y.B. and Lin,H.(2015).Sm^{3+} doped alkaline earth borate glasses as UV-Visible photon conversion for solar cells. J.of Luminescence, 160, 138.

[27] Opera,I,Hesse,H.,Betzler,K.(2004).Optical properties of bismuth borate glasses.Optical Materials,26,235.

[28] Agarwal,A.,Pal,I.,Sanghi,S.andAgarwal,M.P.(2009).Sanghi,S.

[29] Wagh, A., Ajithkumar,M.P. and Kamath,S.D.(2013). Composition dependent structural and thermal properties of Sm_2O_3 doped zinc fluoro borate glasses, Energy research J.4, 52.

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

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

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

[33] Rajesh, D.,Naidu,M.D., Ratnakaram, Y.C. and Balakrishna, A.(2014).Ho^{3+}doped strontium-aluminium-bismuth borate glasses for green lightemission,Luminescence,29,854.

[34] Gorller-Walrand, C. and Binnemans, K. (1988) Spectral Intensities of f-f Transition. 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.

[35] 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. *Journal of Rare Earths*, 27, 773.

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

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

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

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

[40] Sinha, S.P. (1983).Systematics and properties of lanthanides,Reidel,Dordrecht.
[41] Krupke,W.F.(1974).IEEE J.Quantum Electron QE,10,450.
[42] Coelho,J.,Freire, C.andHuussain,N.S.(2012).Structral studies of lead lithium borate glasses doped with silver oxide,Spectrochim.Acta A,86,392.
[43] Naresh,V. and Buddhudu,S.(2012).Structural,thermal,dielectric and ac conductivity properties of lithium fluoro-borate optical glasses.Ceram. Int., 38, 2325.