International Journal in Physical and Applied Sciences
Volume 07 Issue 11, November 2020 ISSN: 2394-5710 Impact Factor: 5.578
Journal Homepage: http://ijmr.net.in, Email: irjmss@gmail.com
Double-Blind Peer Reviewed Refereed Open Access International Journal

SPECTRAL AND THERMAL PROPERTIES OF SM^{3+} DOPED IN ZINC LITHIUM TUNGSTEN ZIRCONIUM PHOSPHATE GLASSES

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

Abstract

Glass sample of Zinc Lithium Tungsten Zirconium Phosphate: (50-x) P_2O_5:10ZnO:10Li_2O:10WO_3:20ZrO_2:xSm_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 Sm^{3+} doped zinc lithium tungsten zirconium phosphate glasses have been recorded at room temperature. The various interaction parameters like Slater-Condon parameters F_k (k=2,4,6), Lande parameters (ξ_{4f}), nephelauexetic ratio (β'),bonding parameters ($b^{1/2}$)and Racah parameters E^k(k=1,2 3) have been computed. Judd-Ofelt intensity parameters and laser parameters have also been calculated.

Keywords: ZLTZP Glasses, Thermal Properties , Optical properties, Judd-Ofelt analysis.

I. Introduction

Glasses are easy to make and at the same time they can be tailored to specific applications. Rare- earth ion doped glasses have attracted much attention as potential materials for various optical devices such as lasers, up-converters, optical fibers [1-5]. Photoluminescence of Ho^{3+}, Nd^{3+}, Dy^{3+}, $Er^{3+}$and Sm^{3+} ions are investigated for application in high-energy particle detector, optical data storage, bar-code reading, laser printing and satellite communication, and solid- state lighting [6-8]. Glasses having zirconium oxide have attained great attention, since they are used in the wide area of applications. The glasses containing rare earth in various forms such as network formers luminescent ions are of great deal of interest for their unique optical and electrical properties [9, 10]. Glass treated with rare earth ions can be well developed as luminescent material due to high emission efficiency, according to the 4f-4f and 4f-5d electron transitions . Phosphate glasses are considered as prominent materials because of their verity of applications in several areas of interest such as low glass transition temperature, lower melting temperature, high thermal expansion coefficient [11, 12]. A survey of literature shows that there are many reports available on phosphate glasses [13-15].

The aim of the present study is to prepare the Sm^{3+} doped zinc lithium tungsten zirconium phosphate glass with different Sm_2O_3 concentrations. The absorption spectra, fluorescence spectra of $Sm^{3+}$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 optical properties such as spontaneous emission probability, branching ratio, radiative life time and stimulated emission cross section. Large stimulated emission cross section is one of the most

important parameters required for the design of high peak power solid state lasers.

II. Experimental Techniques

Preparation of glasses

The following Sm^{3+} doped zinc lithium tungsten zirconium phosphate glass samples (50-x) P_2O_5:10ZnO:10Li_2O:10WO_3:20ZrO_2:xSm_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 P_2O_5, ZnO, Li_2O, WO_3, ZrO_2 and Sm_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 250^0C 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 %)
ZLTZP (UD)	50 P_2O_5:10ZnO:10Li_2O:10WO_3:20ZrO_2
ZLTZP (SM1)	49 P_2O_5:10ZnO:10Li_2O:10WO_3:20ZrO_2: 1 Sm_2O_3
ZLTZP (SM 1.5)	48.5 P_2O_5:10ZnO:10Li_2O:10WO_3:20ZrO_2 1.5 Sm_2O_3
ZLTZP (SM 2)	48 P_2O_5:10ZnO:10Li_2O:10WO_3:20ZrO_2: 2 Sm_2O_3

ZLTZP (UD) -Represents undoped Zinc Lithium Tungsten Zirconium Phosphate glass specimens.
ZLTZP (SM) -Represents Sm^{3+} doped Zinc Lithium Tungsten Zirconium Phosphate glass specimens.

III. Theory

3.1 Oscillator Strength

The intensity of spectral lines are 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, $\varepsilon(\nu)$ 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 [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, I is the optical path length, $\log I_0/I$ is optical density and $\Delta\upsilon_{1/2}$ is half band width.

International Journal in Physical and Applied Sciences
Volume 07 Issue 11, November 2020 ISSN: 2394-5710 Impact Factor: 5.578
Journal Homepage: http://ijmr.net.in, Email: irjmss@gmail.com
Double-Blind Peer Reviewed Refereed Open Access International Journal

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 $|4f^N (S, L) J>$ 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 (S', L') is given by the equation

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

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 .

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:

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

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

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

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 Parameters ($b^{1/2}$), which are computed by using following formulae [20, 21]. The Nephelauxetic Ratio is given by

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

where, ν_a and ν_g refer to the energies of the corresponding transition in the glass and free ion, respectively. The values of bonding parameter $b^{1/2}$ are 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 - P_2O_5 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.

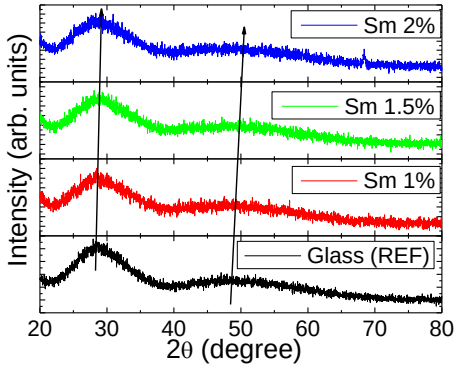

Fig. 1: X-ray diffraction pattern of P_2O_5:ZnO:Li_2O:WO_3:ZrO_2:Sm_2O_3

International Journal in Physical and Applied Sciences
Volume 07 Issue 11, November 2020 ISSN: 2394-5710 Impact Factor: 5.578
Journal Homepage: http://ijmr.net.in, Email: irjmss@gmail.com
Double-Blind Peer Reviewed Refereed Open Access International Journal

4.2 Thermal Properties

Figure 2 shows the thermal properties of ZLTZP 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 352^0C, 456^0C and 586^0C respectively. The T_g increase with the contents of Sm_2O_3 increase. We could conclude that thermal properties of the ZLTZP glass are good for fiber drawing from the analysis of DSC curve.

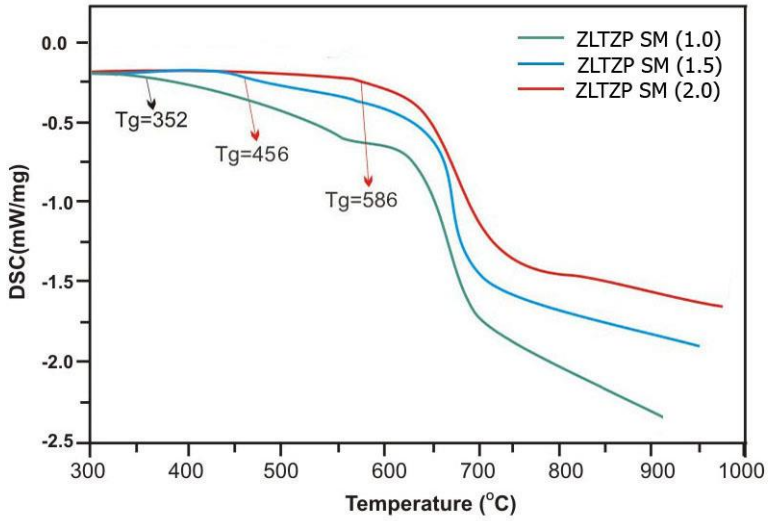

Fig.2: DSC curve of ZLTZP (SM) glasses.

4.3 Absorption Spectrum

The absorption spectra of Sm^{3+} doped ZLTZP (SM 01) glass specimen has been presented in Figure 3 in terms of optical density versus wavelength (nm). Ten absorption bands have been observed from the ground state $^6H_{5/2}$ to excited states $^6F_{1/2}$, $^6F_{7/2}$, $^6F_{9/2}$, $^4G_{7/2}$,$^4I_{9/2}$, $^4M_{7/2}$, $(^6P,^4P)_{5/2}$, $^4F_{7/2}$, $^4D_{1/2}$, and $(^4D,^6P)_{5/2}$ for Sm^{3+} doped ZLTZP glasses

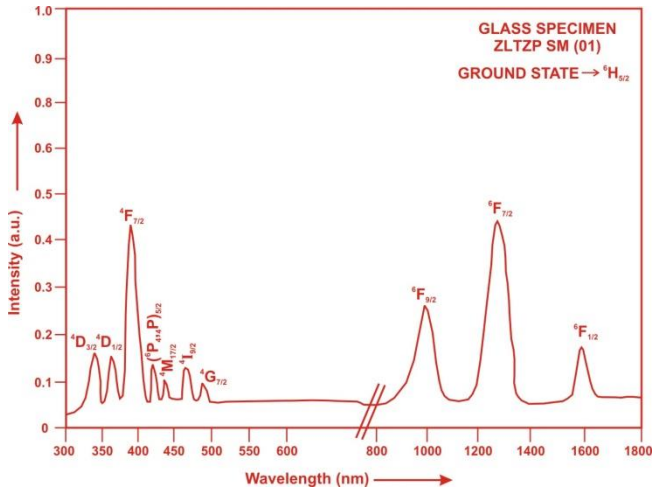

Fig.3: Absorption spectrum of Sm^{3+}doped ZLTZP (01) glass

The experimental and calculated oscillator strengths for Sm^{3+} ions in zinc lithium tungsten zirconium phosphate glasses are given in Table 3

Table3: Measured and calculated oscillator strength ($P_m \times 10^{+6}$) of Sm^{3+}ions in ZLTZP glasses.

Energy level from $^6H_{5/2}$	**Glass ZLTZP (SM01)**		**Glass ZLTZP (SM1.5)**		**Glass ZLTZP (SM02)**	
	$P_{exp.}$	$P_{cal.}$	$P_{exp.}$	$P_{cal.}$	$P_{exp.}$	$P_{cal.}$
$^6F_{1/2}$	1.56	1.61	1.52	1.58	1.48	1.55
$^6F_{7/2}$	5.47	5.53	5.44	5.52	5.41	5.49
$^6F_{9/2}$	3.82	3.87	3.78	3.84	3.72	3.82
$^4G_{7/2}$	0.16	0.12	0.13	0.117	0.1	0.12
$^4I_{9/2}$,$^4M_{15/2}$,$^4I_{11/2}$	1.16	1.89	1.12	1.87	1.08	1.87
$^4M_{17/2}$,$^4G_{9/2}$,$^4I_{15/2}$	0.26	0.25	0.23	0.246	0.17	0.24
(^6P,$^4P)_{5/2}$,$^4L_{13/2}$	1.28	1.30	1.24	1.302	1.2	1.30
$^4F_{7/2}$,$^6P_{3/2}$,$^4K_{11/2}$	5.52	5.60	5.48	5.60	5.42	5.61
$^4D_{1/2}$,$^6P_{7/2}$,$^4L_{17/2}$	2.42	2.45	2.38	2.44	2.34	2.42
$^4D_{3/2}$, (^4D,$^6P)_{5/2}$	2.55	3.46	2.52	3.46	2.46	3.45
r.m.s. deviation	0.3726		0.3863		0.4105	

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

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

Glass Specimen	F_2	ξ_{4f}	β'	$b^{1/2}$
Sm^{3+}	358.82	1258.16	0.9337	0.1821

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 1.081 and 1.099 in the present glasses.

The value of Judd-Ofelt intensity parameters are given in **Table 5**

Table5: Judd-Ofelt intensity parameters for Sm^{3+} doped ZLTZP glass specimens

Glass Specimen	**Ω_2(pm^2)**	**Ω_4(pm^2)**	**Ω_6(pm^2)**	**Ω_4 /Ω_6**	**Ref.**
ZLTZP (SM01)	4.537	4.195	3.880	1.081	P.W.
ZLTZP (SM1.5)	4.445	4.197	3.855	1.089	P.W.
ZLTZP (SM02)	4.362	4.203	3.825	1.099	P.W.
ZnLiBiB(SM)	4.137	3.847	3.528	1.091	[22]

4.4. Fluorescence Spectrum

The fluorescence spectrum of Sm^{3+}doped in zinc lithium tungsten zirconium phosphate glass is shown in Figure 4. There are four broad bands observed in the Fluorescence spectrum of Sm^{3+}doped zinc lithium tungsten zirconium phosphate glass. The wavelengths of these bands along with their assignments are given in Table 6. Fig. (4).Shows the fluorescence spectrum with four peaks ($^4G_{5/2}\rightarrow{}^6H_{5/2}$), ($^4G_{5/2}\rightarrow{}^6H_{7/2}$), ($^4G_{5/2}\rightarrow{}^6H_{9/2}$) and ($^4G_{5/2}\rightarrow{}^6H_{11/2}$), respectively for glass specimens.

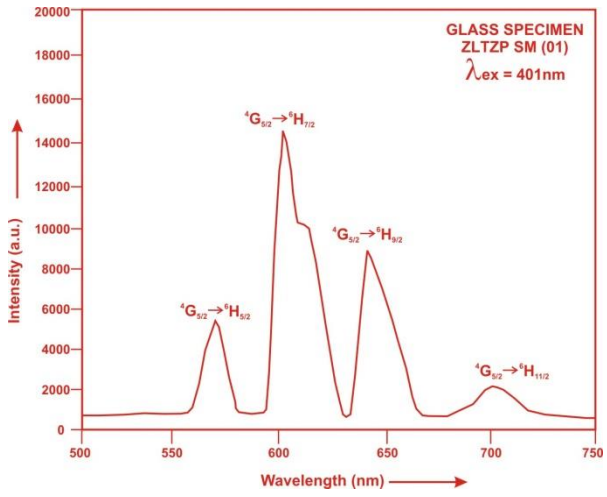

Fig.4: fluorescence spectrum of Sm^{3+}doped ZLTZP (01) glass

Table 6. Emission peak wave lengths (λ_p),radiative transition probability (A_{rad}),branching ratio (β),stimulated emission cross-section(σ_p) and radiative life time(τ_R) for various transitions in Sm^{3+} doped ZLTZP glasses

Transition		ZLTZP SM 01				ZLTZP SM 1.5				ZLTZP SM 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)	$\tau_R(\mu s)$
$^4G_{5/2}\rightarrow{}^6H_{5/2}$	562	11.96	0.4116	0.00402	3442.43	11.91	0.4121	0.0044	3460.05	11.89	0.4136	0.0048	3475.97
$^4G_{5/2}\rightarrow{}^6H_{7/2}$	602	126.85	0.4367	0.0451		126.69	0.2281	0.0483		126.44	0.4395	0.0522	
$^4G_{5/2}\rightarrow{}^6H_{9/2}$	645	120.62	0.4152	0.0428		119.35	0.2422	0.0448		118.27	0.4111	0.0469	
$^4G_{5/2}\rightarrow{}^6H_{11/2}$	705	31.07	0.1069	0.0134		31.061	0.9305	0.0141		31.08	0.1080	0.0146	

V. Conclusion

In the present study, the glass samples of composition (50-x) P_2O_5:10ZnO:10Li_2O:10WO_3:20ZrO_2:xSm_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 radiative transition probability, branching ratio are highest for ($^4G_{5/2}\rightarrow{}^6H_{7/2}$) transition and hence it is useful for laser action. The stimulated emission cross section (σ_p) has highest value for the transition ($^4G_{5/2}\rightarrow{}^6H_{7/2}$) in all the glass specimens doped with Sm^{3+} ion. This shows that ($^4G_{5/2}\rightarrow{}^6H_{7/2}$) transition is most probable transition.

References:

[1]. Kothandan, D., Kumar, R. J. (2015).Optical properties of rare earth doped borate glasses," International Journal of chemTech Research 8(6), 310-314.
[2]. Monisha, M., Nancy,A. , Souza, D., Nimitha ,V. L., Prabhu, S , Sayyed, M.I.(2020). "Dy^{3+} doped SiO_2- B_2O_3-Al_2O_3-NaF-ZnF_2 glasses : An exploration of optical and gamma radiation shielding features," Current Applied Physics 20(11), 1207-1210.
[3]. Dousti, M.R. , Poirier, G.Y., de Camargo, A.S.S.,(2020).Tungsten Sodium Phosphate glasses doped with trivalent rare earth ions (Eu^{3+}, Tb^{3+}, Nd^{3+}, Er^{3+}) for visible and near infrared applications, Journal of Non- Crystalline Solids 530, 119838.

[4]. Jianberi,Q.I.U., Qing, J.I.A.Q., Dacheng, Z.H.O.U., Zhengwen, Y.A.N.G.(2016). Recent progress on up conversion enhancement in rare earth doped transparent glass ceramics, Journal of Rare Earths 34(4), 341-367.
[5]. Kaur, A., Khanna, Khanna, A., Aleksandrov, L.I. (2017).Structural, thermal, optical and photo luminescent properties of barium tellurite glasses doped with rare earth ions, Journal of Non-Crystalline Sollids 476,67-74
[6]. Dutebo, M. T., Shashikala, H.D. (2020).Influence of (Er^{3+}, La^{3+}, Ce^{4+}) additions on physical and optical properties of 50 CaO- 50 P_2O_5 glasses," Physica B: Condensed Matter 597, 412358.
[7]. Alqarni, A. S., Hussin, R., Alamri, S.N., Ghoshal, S.K.(2020). "Tailored structures and dielectric traits of holmium ion-doped zinc-sulpho-boro-phosphate glass ceramics," Ceremics International 46(3), 3282-3291.
[8]. Yannick, L., Mohammed, E.l., Amradoui, J. L. F., Fortin,P.L.,Sidney, R. , Youne, M.(2013). "Infrared to Visible Up-Conversion Emission in Er^{3+}/ Yb^{3+} codoped Fluoro phosphate Glass Ceramics," Journal of the American Ceramic Society 96(3),825-832.
[9]. Haijian Li, Jianhua Yi, Zhao Qin, Zhihua Sun, Yi Xu, Changjian Wang, Fengqi Zhao, Yucheng Hao, Xiaofeng L. (2019). "Structures, Thermal expansion, chemical stability and crystallization behavior of phosphate based glasses by influence of rare earth," Journal of Non-Crystalline Sollids 522,119602.
[10] Dimitrov, V. and Komatsu, T. (2005). "Classification of Oxide Glasses: A polarizability Approach," Journal of Solid State Chemistry, 178,831-846.
[11]. Lin.H. 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," Journal of Alloys and Compounds,390,197-201.
[12]. Shanmuga, S. S., Marimuthu, K., Sivraman, M. and Babu, S. S.(2010). Composition dependent structural and optical properties of Sm^{3+}-doped sodium borate and sodium fluoroborate glasses," Journal of Luminescence, 130, 1313–1319.
[13]. Babu,S. S., Babu,P., Jayasankar,C.K. , Sievers,W., Wortmann, G. (2007).Optical absorption and photolumibescence studies of Eu^{3+} doped phosphate and flurophosphate glasses, Journal of luminescence,126,109-120.
[14]. Deopa,N., Rao, A. S., Gupta,M., Vijay Prakash, G. (2018).Spectroscopic investigation of Nd^{3+} doped lithium lead Alumino Borate glasses for 1.06 µm laser Applications, Optical materials 75, 127-134 (2018).
[15]. Dousti, M. R., Ghoshai, S. K., Amjad, R. J. ,Sahar, M. R. and Namaz, R. F.(2013). Structural and optical study of samarium doped lead zinc phosphate glasses, Optics Communications,300, 204–209.
[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.
[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.

[18]. Judd, B.R. (1962). Optical Absorption Intensities of Rare Earth Ions. Physical Review, 127, 750.
[19]. Ofelt, G.S. (1962) Intensities of Crystal Spectra of Rare Earth Ions. The Journal of Chemical Physics, 37, 511.
[20].Sinha, S.P. (1983).Systematics and properties of lanthanides, Reidel, Dordrecht.
[21].Krupke, W.F. (1974).IEEE J. Quantum Electron QE, 10,450.
[22]. Meena, S.L.(2017).Spectroscopic Properties of Sm^{3+} Doped in Zinc Lithium Bismuth Borate Glasses, International Journal of Pure and Applied Physics.13,3,485-494.