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Spectral and Raman Analysis of Pr^{3+} Doped Zinc Lithium Alumino Tungsten Borophosphate Glasses

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ABSTRACT: Zinc lithium alumino tungsten borophosphateglasses containing Pr^{3+} in (40-x)P_2O_5:10ZnO:10Li_2O:10Al_2O_3:10WO_3:20B_2O_3:xPr_6O_{11} (where x=1, 1.5,2 mol %) have been prepared by melt-quenching method. The amorphous nature of the glasses was confirmed by x-ray diffraction studies. Optical absorption, fluorescence spectra and Raman spectra were recorded at room temperature for all glass samples. Judd-Ofelt intensity parameters Ω_λ (λ=2, 4, 6) are evaluated from the intensities of various absorption bands of optical absorption spectra. 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.

KEYWORDS: ZLATBP Glasses, Optical Properties, Judd-Ofelt Theory, Raman analysis.

I. INTRODUCTION

Rare earth ions doped in different glass hosts to achieve favourable potential applications in a variety of optical devices such as lasers, fiber amplifiers, optical, liner , high refractive index, high density, large third order nonlinear optical susceptibility and nonlinear properties [1-5].Phosphate glass is an extremely promising material for laser and nonlinear applications in optics due to some of its essential characteristic features, such as low phonon maxima, low melting temperature and excellent transparency in the far infrared region [6-10].

Phosphate glasses are very important because of the possibility of their application in optoelectronic and optic device fields, such as lasers, fiberopticand solar cells [11-13].An important characteristic of these materials is the relatively low cutoff phonon energy compared with other oxide glasses such as silicate or tellurite glasses. The addition of network modifier (NWF) Li_2O is to improve both electrical and mechanical properties of such glasses. Zinc oxide is added in the glass matrix to increase glass forming ability and to ensure low rates of crystallization in the glass system [14, 15].

In this work, the spectroscopic properties of Pr^{3+}-doped (40-x)P_2O_5:10ZnO:10Li_2O:10Al_2O_3:10WO_3:20B_2O_3:xPr_6O_{11}(where x=1, 1.5,2 mol %) glasses were investigated. The absorption spectra, fluorescence spectra and Raman spectra of $Pr^{3+}$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.

II. EXPERIMENTAL TECHNIQUES

A. PREPARATION OF GLASSES

The following Pr^{3+} doped Zinc lithium alumino tungsten borophosphateglasssamples(40-x)P_2O_5:10ZnO:10Li_2O:10Al_2O_3:10WO_3:20B_2O_3:xPr_6O_{11}(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,Al_2O_3,WO_3, $B_2O_3$and Pr_6O_{11}. All weighed chemicals were powdered by using an Agate pestle mortar and mixed thoroughly before each batch (10g) was melted in alumina crucibles in silicon carbide based an electrical furnace.

Silicon Carbide Muffle furnace was heated to working temperature of 1055^0C, for preparation of Zinc lithium alumino tungsten borophosphateglasses, for two hours to ensure the melt to be free from gases. The melt was stirred several times to ensure homogeneity. For quenching, the melt was quickly poured on the steel plate & was immediately

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inserted in the muffle furnace for annealing. The steel plate was preheated to100^{0}C.While pouring; the temperature of crucible was also maintained to prevent crystallization. And annealed at temperature of 350^{0}C 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 %)
ZLATBP (UD)	$40P_2O_5$:10ZnO:$10Li_2O$:$10Al_2O_3$:$10WO_3$:$20B_2O_3$
ZLATBP (PR1)	$39P_2O_5$:10ZnO:$10Li_2O$:$10Al_2O_3$:$10WO_3$:$20B_2O_3$:$1Pr_6O_{11}$
ZLATBP(PR 1.5)	$38.5P_2O_5$:10ZnO:$10Li_2O$:$10Al_2O_3$:$10WO_3$:$20B_2O_3$: 1.5 Pr_6O_{11}
ZLATBP (PR2)	$38P_2O_5$:10ZnO:$10Li_2O$:$10Al_2O_3$:$10WO_3$:$20B_2O_3$: 2 Pr_6O_{11}

ZLATBP (UD)—Represents undopedZinc Lithium Alumino Tungsten Borophosphate glass specimen.
ZLATBP(PR) -Represents Pr^{3+} dopedZinc Lithium Alumino Tungsten Borophosphateglass specimens.

III. THEORY

A. OSCILLATOR STRENGTH

The intensity of spectral lines are expressed in terms of oscillator strengths using the relation [16].

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

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, using the modified relation [17].

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

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

B. 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:

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

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

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

$\lambda = 2, 4, 6$

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 and 6) are known as Judd-Ofelt intensity parameters.

C. 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).

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

$$A[(S', L')\ J'; (S,L)J] = \frac{64\pi^2\nu^3}{3h(2J'+1)}\left|\frac{n(n^2+2)^2}{9}\right| \times S(J', \bar{J}) \quad (5)$$

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

$$\beta[(S', L')\ J'; (S, L)\ J] = \sum_{S\ L\ J} \frac{A[(S'L)]}{A[(S'L')J'(\bar{S}L)]} \quad (6)$$

where, the sum is over all terminal manifolds.

The radiative life time is given by

$$\tau_{rad} = \sum_{S\ L\ J} A[(S', L')\ J'; (S,L)\ ] = A_{Total}^{-1} \quad (7)$$

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

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

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

D.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

$$\beta' = \frac{\nu_g}{\nu_a} \quad (9)$$

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

$$b^{1/2} = \left|\frac{1-\beta'}{2}\right|^{1/2} \quad (10)$$

III. RESULT AND DISCUSSION

A. XRD Measurement

Figure 1 presents the XRD pattern of the samples containing show no sharp Bragg's peak, but only a broad diffuse hump around low angle region. This is the clear indication of amorphous nature with in the resolution limit of XRD instrument.

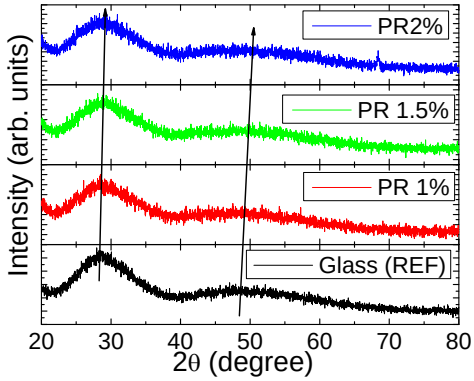

Fig.1:X-ray diffraction pattern of ZLATBP (PR) glasses.

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B. Raman spectra

The Raman spectrum of Zinc Lithium Alumino Tungsten Borophosphate(ZLATBP) glass specimens is recorded and is shown in Fig. 2. The spectrum peaks located at 397 and 777 cm^{-1}. The band at 397 $cm^{-1}$is is related to the bending motion of phosphate polyhedral PO_4 units with cation like ZnO as the modifier. The broad band at 777cm^{-1} is due to symmetric stretching of (P–O–P) bridging oxygen bonds in $(P_2O_7)_4$ units.

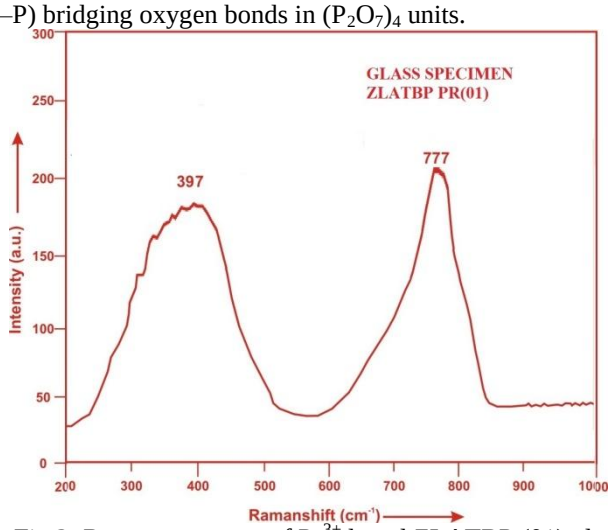

Fig.2: Raman spectrum of Pr^{3+}doped ZLATBP (01) glass.

C. Absorption spectra

The absorption spectra of ZLATBP (PR) glasses, consistsof absorption bands corresponding to the absorptions from the ground state $^3H_4$ of Pr^{3+} ions. Eight absorption bands have been observed from the ground state $^3H_4$ to excited states $^3F_2$,$^3F_3$,$^3F_4$,$^1G_4$,$^1D_2$,$^3P_0$,$^3P_1$ and$^3P_2$ for Pr^{3+} doped ZLATBP (PR) glasses.

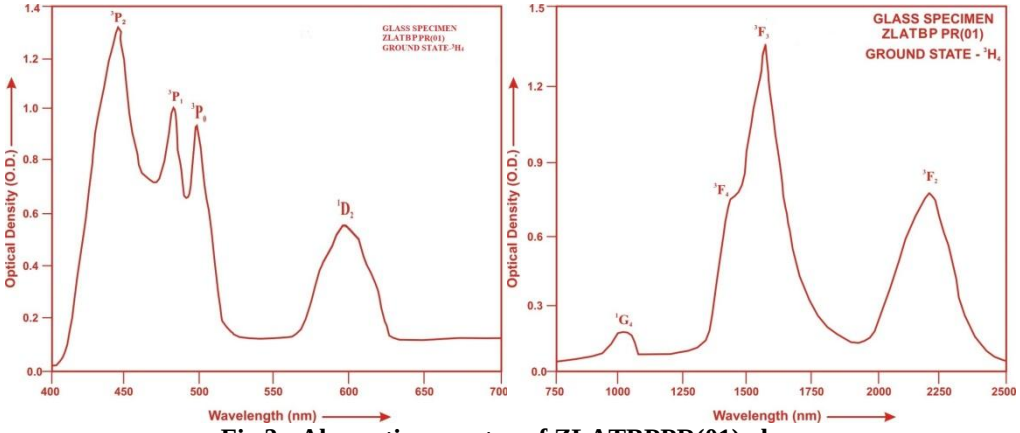

Fig.3: Absorption spectra of ZLATBPPR(01) glass.

The experimental and calculated oscillator strengths for Pr^{3+} ions Zinc lithium alumino tungsten borophosphateglasses are given in **Table 2**

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Table 2.Measured and calculated oscillator strength ($P^m \times 10^{+6}$) of Pr^{3+} ions in ZLATBP glasses.

Energy level $^3H_4$	Glass ZLATBP (PR01)		Glass ZLATBP (PR1.5)		Glass ZLATBP (PR02)	
	$P_{exp.}$	$P_{cal.}$	$P_{exp.}$	$P_{cal.}$	$P_{exp.}$	$P_{cal.}$
$^3F_2$	4.24	3.63	3.75	3.29	2.87	2.46
$^3F_3$	7,73	6.78	6.44	5.64	4.86	4.16
$^3F_4$	4.25	4.09	3.25	3.35	2.36	2.50
$^1G_4$	0.48	0.35	0.38	0.29	0.29	0.21
$^1D_2$	3.35	1.19	2.24	0.99	1.45	0.73
$^3P_0$	4.48	2.17	3.48	1.89	2.68	1.33
$^3P_1$	4.88	3.52	3.77	3.05	2.79	2.17
$^3P_2$	11.39	3.97	10.43	3.26	9.39	2.42
R.m.s.deviation	2.9227		2.6667		2.5488	

The various energy interaction parameters like Slater-Condon parameters F_k(k=2, 4, 6), Lande′ parameter ξ_{4f} and Racah parameters E^k(k=1, 2, 3) have been computed using partial regression method. The ratio ofRacah parameters E^1/E^3 and E^2/E^3 are about 9.79 and 0.048respectively. Computed values of Slater-Condon, Lande, Racah,nephelauexetic ratio and bonding parameter for Pr^{3+}dopedZLATBPglassspecimens are given in **Table 3**.

Table3.Computed values of Slater-Condon, Lande, Racah, nephelauexetic ratio and bonding parameter for Pr^{3+} doped ZLATBP glass specimens.

Parameter	Free ion	ZLATBPPR01	ZLATBPPR1.5	ZLATBPPR02
$F_2(cm^{-1})$	322.09	300.03	299.99	300.02
$F_4(cm^{-1})$	44.46	44.28	44.25	44.28
$F_6(cm^{-1})$	4.867	4.414	4.410	4.413
$\xi_{4f}(cm^{-1})$	741.00	858.25	858.70	858.28
$E^1(cm^{-1})$	4728.92	4451.77	4450.22	4451.45
$E^2(cm^{-1})$	24.75	22.01	22.01	22.01
$E^3(cm^{-1})$	478.10	454.73	454.72	454.72
F_4/F_2	0.13805	0.14751	0.14751	0.14758
F_6/F_2	0.01511	0.01471	0.01470	0.01471
E^1/E^3	9.8911	9.7899	9.7867	9.7894
E^2/E^3	0.0518	0.0484	0.0484	0.0484
β'		0.88887	0.88849	0.88879
$b^{1/2}$		0.23573	0.23613	0.23580

Judd-Ofelt intensity parameters $\Omega_\lambda(\lambda$ = 2, 4 and 6) were calculated by using the fitting approximation of the experimental oscillator strengths to the calculated oscillator strengths with respect to their electric dipolecontributions. In the present case the three $\Omega_\lambda$parameters follow the trend $\Omega_2<\Omega_4<\Omega_6$.

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

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Table 4.Judd-Ofelt intensity parameters for Pr^{3+} doped ZLATBP glass specimens.

Glass Specimen	$\Omega_2(pm^2)$	$\Omega_4(pm^2)$	$\Omega_6(pm^2)$	Ω_4/Ω_6
ZLATBP (PR01)	2.127	3.265	6.140	0.5318
ZLATBP(PR1.5)	2.064	2.847	5.005	0.5688
ZLATBP(PR02)	1.609	2.003	3.732	0.5367

D. Fluorescence Spectrum

The fluorescence spectrum of Pr^{3+}doped in zinc lithium alumino tungsten borophosphateglass is shown in Figure 4. There areeightbroad bands ($^3P_0\rightarrow{}^3H_4$), ($^3P_1\rightarrow{}^3H_5$), ($^1D_2\rightarrow{}^3H_4$), ($^3P_0\rightarrow{}^3H_6$),($^3P_0\rightarrow{}^3F_2$), ($^3P_1\rightarrow{}^3F_3$), ($^1D_2\rightarrow{}^3H_5$) and ($^3P_0\rightarrow{}^3F_4$)respectively for glass specimens.

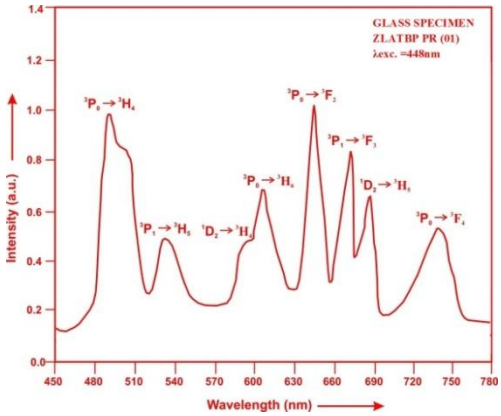

Fig.4:Fluorescence spectrum of ZLATBP PR (01) glass.

Table 5.Emission peak wave lengths (λ_p), radiative transition probability (A_{rad}), branching ratio (β_R), stimulated emission crosssection (σ_p), and radiative life time (τ) for various transitions in Pr^{3+} doped ZLATBP glasses.

Transition		ZLATBPPR 01				ZLATBPPR 1.5				ZLATBPPR 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_p (10^{-20} cm^2)	τ_R (μs)	$A_{rad}(s^{-1})$	β	σ_p (10^{-20} cm^2)	$\tau_R(10^{-20}$ $cm^2)$
$^3P_0\rightarrow{}^3H_4$	485	1716.00	0.1693	1.062		1500.02	0.1656	1.216		1057.45	0.1579	1.055	
$^3P_1\rightarrow{}^3H_5$	532	2818.32	0.2781	0.6708		2401.69	0.2651	0.618		1730.48	0.2583	0.492	
$^1D_2\rightarrow{}^3H_4$	599	588.02	0.0580	0.2843		486.35	0.05369	0.258		360.39	0.05380	0.207	
$^3P_0\rightarrow{}^3H_6$	602	495.43	0.0488	0.3472	98.687	404.45	0.04465	0.328	110.39	302.18	0.04511	0.274	149.29
$^3P_0\rightarrow{}^3F_2$	643	1483.96	0.1464	2.053		1442.87	0.1593	2.514		1127.03	0.1683	2.439	
$^3P_1\rightarrow{}^3F_3$	676	2706.43	0.2671	1.817		2539.33	0.2803	1.884		1920.72	0.2867	1.529	
$^1D_2\rightarrow{}^3H_5$	685	7.72	0.00076	0.0117		6.618	0.00073	0.0127		4.74	0.00071	0.0106	
$^3P_0\rightarrow{}^3F_4$	730	317.18	0.0313	0.2857		277.13	0.0306	0.271		195.46	0.0292	0.208	

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V. CONCLUSION

In the present study, the glass samples of composition (40-x):P_2O_5:10ZnO:10Li_2O:10Al_2O_3:10WO_3:20B_2O_3:xPr_6O_{11}(where x=1, 1.5, 2 mol %) have been prepared by melt-quenching method. The value of stimulated emission cross-section (σ_p) is found to be maximum for the transition ($^3P_0 \rightarrow {}^3F_2$) forglassZLATBP(PR 01), suggesting that glass ZLATBP(PR01) is better compared to the other two glass systemsZLATBP(PR1.5) and ZLATBP(PR02).

REFERENCES

[1].Hraiech, S.,Bouzidi, C.,Férid, M. (2017). Luminescence properties of Er^{3+}doped phosphate glasses, Physica B: Condensed Matter 522, 15–21.
[2].Hu,J. Y.,Yang, H. W.,Chen, Y. J.,Lin, J. S.,Lai, C. H.,Lee, Y. M. andZhang, T.(2011). Properties and structure of Yb^{3+} doped zinc aluminum silicate phosphate glasses, J. Non-Cryst. Solids 357, 2246–2250.
[3].Sene,F.F.,Martinelli, J.R. andGomes, L.(2004). Optical and structural characterization of rare earth doped niobium phosphate glasses, J. Non-Crystalline Solids 348, 63–71.
[4].Shih, P.Y. (2004). Thermal, chemical and structural characteristics of erbium-doped sodium phosphate glasses, Materials Chemistry and Physics 84, 151–156.
[5].Seneschal, K.,Smektala, F.,Bureau, B.,Floch, M.,Jiang, S.,Luo, T.,Lucas, J. andPeyghambarian, N. (2005). Properties and structure of high erbium doped phosphate glass for short optical fibers amplifiers, Materials Research Bulletin 40, 1433–1442.
[6].Jiang,S., Luo,T., Hwang,B.C.,Smektala, F., Seneschal,K.,Lucas, J. andPeyghambarian, N. (2000). Er^{3+}-doped phosphate glasses for fiber amplifiers with high gain per unit length, J. Non. Cryst. Solids 263–264, 363–368.
[7].Reddy,A. A.,Babu, S. S.,Pradeesh, K., Otton,C. J. andPrakash, G. V. (2011). Optical properties of highly Er^{3+}doped sodium-aluminiumphosphate glasses for broadband 1.5 µm emission, Journal of Alloys and Compounds 509, 4047–4052.
[8].Ajroud, M.,Haouari, M. Ben,O.,Maaref, H.,Brenier A. and Garapon,C.(2000). Investigation of the spectroscopic properties of Nd^{3+}-doped phosphate glasses, Journal of Physics: condensed Matters, vol. 12, no. 13, 3181.
[9].Ebendorff-Heidepriem H. andEhrt, D. (1998). Optical spectroscopy of rare-earth ions in glasses, GlastechBer : Glasses Sci Tech, vol. 71, no. 10, 289.
[10].Rao, T.V.R., Reddy, R.R., NazeerAhammed, Y.andParandamaiah, M. (2000). Luminescence properties of Nd^{3+}, TeO_2-B_2O_3–P_2O_5–Li_2O glass.Infrared Physics and Technology, 41: 247. phatefibers and fiberlasers,IEEE Photon Technol . Lett. 18(4), 574-576.
[11]. Santos, C.C., Guedes, I., Loong, C.-K., Boatner, L.A., Moura, A.L., de Araujo, M.T., Jacinto, C.andVermelho, M.V.D.(2010).Spectroscopic properties of Er^{3+}-doped lead phosphate glasses for photonic application, J. Phys. D: Appl. Phys. 43, 025102.
[12].Brito, T.B., Vermelho, M.V.D., Gouveia, E.A., de Araujo, M.T., Guedes, I., Loong, C.-K. andBoatner, L.A.(2007).Optical characterization of Nd^{3+} and Er^{3+}doped lead-indium-phosphate glasses, J. Appl. Phys. 102, 043113.
[13].Veasey,D. L.,Funk, D. S., Peters,P. M.,Sanford, N. A., Obarski,G. E.,Fontaine, N.,Young, M.,Paskin, A. P., Liu,W.,Houde -Walter, S. N.andHayden, J. S.(2000).Yb/Er -codoped and Yb -doped waveguide lasers in phosphate glass, J. Non -Cryst. Solids 263 and 264, 369 -388.
[14].Pavani, P. G., Sadhana, K. and Mouli, V. C. (2011). Optical, physical and structural studies of boro-zinc telluriteglasses,Physica B:Condensed Matter, vol. 406, no. 6-7, 1242–1247.
[15]. Durga, D.K. and Veeraiah, N. (2003). Role of manganese ions on the stability of ZnF_2–P_2O_5–TeO_2 glass system by the study of dielectric dispersion and some other physical properties.J. Phys. Chem. Solids,64, 133–146.
[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.
[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.