IOSR Journal Of Applied Physics (IOSR-JAP)
e-ISSN: 2278-4861.Volume 16, Issue 5 Ser. 1 (Sept. – Oct. 2024), PP 28-34
www.Iosrjournals.Org

Photoluminescence and Raman analysis of Nd^{3+} doped in Ytterbium Zinc Lithium Sodium Barium Calcium Aluminophosphate glasses

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

Abstract
Glass of the system:(30-x)P_2O_5:10ZnO:10Li_2O:10Na_2O:10BaO:10CaO:10Al_2O_3: 10Y_2O_3: x Nd_2O_3. (where x=1, 1.5,2 mol %) have been prepared by melt-quenching method. (where x=1,1.5 and 2 mol%) have been prepared by melt-quenching technique. The amorphous nature of the prepared glass samples was confirmed by X-ray diffraction. Optical absorption, Excitation, fluorescence and Raman spectra have been recorded at room temperature for all glass samples. Judd-Ofelt intensity parameters Ω_λ (λ=2, 4 and 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: *YZLSBCAP Glasses, Optical Properties, Judd-Ofelt Theory, Raman Spectra.*

Date of Submission: 27-09-2024 Date of Acceptance: 09-10-2024

I. Introduction

The rare earth doped glasses are the promising candidates for the advanced technological applications including the optoelectronic devices, up-converters, optical amplifications. Amongst many other glasses the phosphate glasses find many applications in optical data storage, high energy particle detector, solid state ionic devices, white LEDs, optical waveguide and optical telecommunications [1-5].Phosphate glasses are very well known for their suitable physical, optical and chemical properties, good thermal stability and excellent mechanical properties phosphate glasses. Phosphate glasses act as good hosts for large concentrations of doping rare earth ions with good homogeneity [6-8]. These glasses possess high refractive index, density, good photothermal properties and low phonon phonon losses.

Phosphate glasses have has become the most prominent choice as host materials due to its high rare earth solubility, high color purity of the emitting light, high quantum efficiency, long life-time of metastable state and low non-linear refractive index. The addition of oxide such as ZnO,Li_2O and BaO are used for improves the chemical durability of phosphate glasses. The presence of Al_2O_3 in host matrix enhances the mechanical strength and increase the devitrification [9-11]. Recently Nd^{3+} ions doped glasses found important in the area of wave guide laser, laser action and Telecommunications optical fibers [12-16].

I have studied on the Optical absorption, Excitation, Fluorescence and Raman spectra of Nd^{3+} doped ytterbium zinc lithium sodium barium calcium aluminophosphate. The intensities of the transitions for the rare earth ions have been estimated successfully using the Judd-Ofelt theory. The laser parameters such as radiative probabilities (A), branching ratio (β_R), radiative life time (τ_R) and stimulated emission cross section(σ_p) are evaluated using J.O. intensity parameters (Ω_λ, λ=2,4 and 6).

II. Experimental Techniques

Preparation of glasses

The following Nd^{3+} doped aluminophosphate glass samples :(30-x)P_2O_5:10ZnO:10Li_2O:10Na_2O:10BaO:10CaO:10Al_2O_3: 10Y_2O_3:xNd_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, Na_2O, BaO, CaO,Al_2O_3,Y_2O_3 and Nd_2O_3. They were thoroughly mixed by using an agate pestle mortar. Then melted at 1075˚C by an electrical muffle furnace for 2 hours. After complete melting, the melts were quickly poured in to a preheated stainless steel mould and annealed at temperature of 350˚C for 2 h 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.**

Table1.

Sample	Glass composition (mol %)
YZLSBCAP (UD)	$30P_2O_5$:10ZnO:$10Li_2O$:$10Na_2O$:10BaO:10CaO:$10Al_2O_3$:$10Y_2O_3$
YZLSBCAP (ND1)	$29P_2O_5$:10ZnO:$10Li_2O$:$10Na_2O$:10BaO:10CaO:$10Al_2O_3$:$10Y_2O_3$:$1Nd_2O_3$
YZLSBCAP (ND1.5)	$28.5P_2O_5$:10ZnO:$10Li_2O$:$10Na_2O$:10BaO:10CaO:$10Al_2O_3$:$10Y_2O_3$:$1.5Nd_2O_3$
YZLSBCAP (ND2)	$28P_2O_5$:10ZnO:$10Li_2O$:$10Na_2O$:10BaO:10CaO:$10Al_2O_3$:$10Y_2O_3$: $2Nd_2O_3$

YZLSBCAP (UD) - Represents undoped Ytterbium Zinc Lithium Sodium Barium Calcium Aluminophosphate specimens.
YZLSBCAP (ND) - Represents Nd^{3+} doped Ytterbium Zinc Lithium Sodium Barium Calcium Aluminophosphate glass specimens.

III. Theory

3.1 Oscillator Strength

The intensity of spectral lines 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, I 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

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

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=2,4and 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:

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

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

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

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.

IV. Result and Discussion

4.1. XRD Measurement

Figure 1 presents the XRD pattern of the samples shows 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.

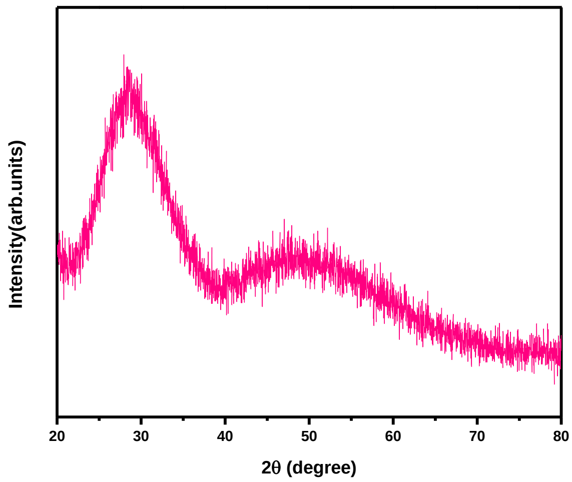

Fig.1: X-ray diffraction pattern of YZLSBCAP ND (01) glass.

4.2 Raman spectra

The Raman spectrum of Ytterbium Zinc Lithium Sodium Barium Calcium Aluminophosphate (YZLSBCAP) glass specimens is recorded and is shown in Fig. 2. The spectrum peaks located at 395 and 775 cm^{-1}. The band at 395 cm-1is is related to the bending motion of phosphate polyhedral PO_4 units with cation like ZnO as the modifier. The broad band at 775cm^{-1} is due to symmetric stretching of (P–O–P) bridging oxygen bonds in $(P_2O_7)_4$ units.

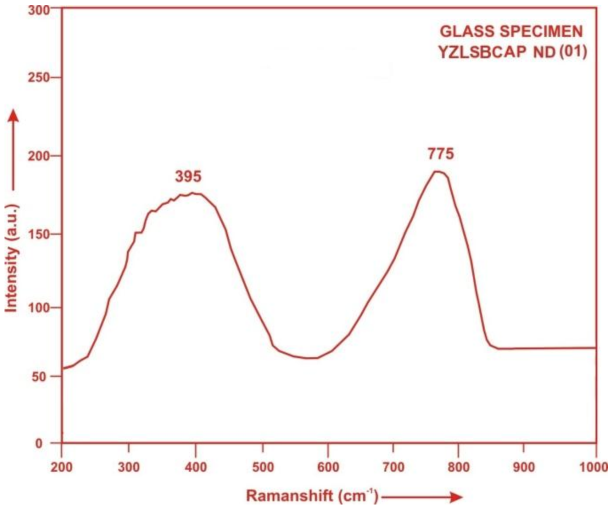

Fig. (2): Raman spectrum of YZLSBCAP ND (01) glass.

4.2. Absorption spectra

The absorption spectra of YZLSBCAP (ND01) glass, consists of absorption bands corresponding to the absorptions from the ground state $^4I_{9/2}$ of Nd^{3+} ions. Nine absorption bands have been observed from the ground state $^4I_{9/2}$ to excited states $^4F_{3/2}$, $^4F_{5/2}$, $^4F_{7/2}$, $^4F_{9/2}$, $^2H_{11/2}$, $^4G_{5/2}$, $^4G_{7/2}$, $^4G_{9/2}$, and $^2G_{9/2}$ for Nd^{3+} doped YZLSBCAP (ND 01) glass.

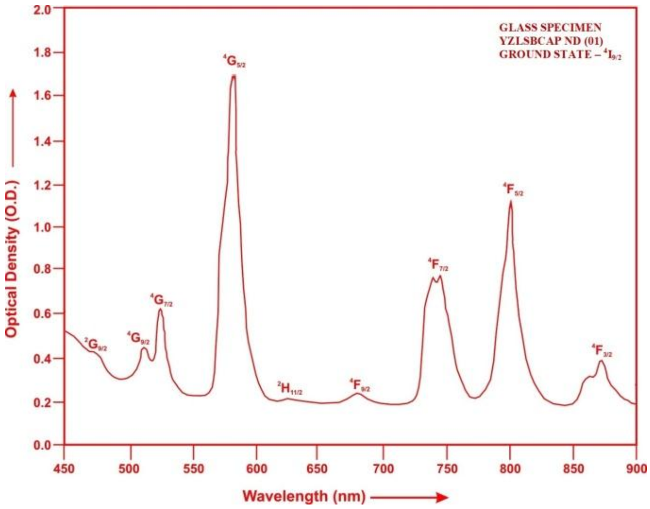

Fig.3: Absorption spectra of YZLSBCAP ND(01) glass.

The experimental and calculated oscillator strength for Nd^{3+} ions in YZLSBCAP glasses are given in **Table 2.**

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

Energy level from $^4I_{9/2}$	Glass YZLSBCAP (ND01)		Glass YZLSBCAP (ND1.5)		Glass YZLSBCAP (ND02)	
	$P_{exp.}$	$P_{cal.}$	$P_{exp.}$	$P_{cal.}$	$P_{exp.}$	$P_{cal.}$
$^4F_{3/2}$	4.88	4.41	3.82	3.55	2.80	2.69
$^4F_{5/2}$	8.57	8.83	7.45	7.58	6.46	6.31
$^4F_{7/2}$	8.89	8.95	7.85	8.06	6.82	7.12
$^4F_{9/2}$	0.68	0.52	0.64	0.45	0.61	0.39
$^2H_{11/2}$	0.30	0.15	0.27	0.13	0.22	0.11
$^4G_{5/2}$	26.25	26.40	24.15	24.36	23.25	23.39
$^4G_{7/2}$	4.68	5.79	3.65	4.92	2.45	4.12
$^4G_{9/2}$	3.32	2.56	3.28	2.12	2.15	1.69
$^2G_{9/2}$	0.99	3.37	0.96	2.76	0.92	2.14
r.m.s.deviation	0.9336		0.7532		0.7220	

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

Parameter	Free ion	YZLSBCAP (ND01)	YZLSBCAP (ND1.5)	YZLSBCAP (ND02)
$F_2(cm^{-1})$	331.16	324.41	324.48	324.49
$F_4(cm^{-1})$	50.71	50.75	50.73	50.75
$F_6(cm^{-1})$	5.154	5.032	5.034	5.035
$\xi_{4f}(cm^{-1})$	884.0	882.81	883.05	882.77
$E^1(cm^{-1})$	5024.0	4945.11	4945.61	4946.35
$E^2(cm^{-1})$	23.90	23.04	23.06	23.06
$E^3(cm^{-1})$	497.0	489.56	489.56	489.57
F_4/F_2	0.1531	0.1564	0.1563	0.1564
F_6/F_2	0.0155	0.0155	0.0155	0.0155
E^1/E^3	10.1086	10.1010	10.1021	10.1034
E^2/E^3	0.0481	0.04706	0.04710	0.04709
β'		0.99542	0.99548	0.99568
$b^{1/2}$		0.04788	0.04751	0.04649

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

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

Glass Specimen	$\Omega_2(pm^2)$	$\Omega_4(pm^2)$	$\Omega_6(pm^2)$	Ω_4/Ω_6	Ref.
YZLSBCAP (ND01)	1.391	9.046	2.833	3.193	P.W.
YZLSBCAP (ND1.5)	2.121	7.203	2.623	2.746	P.W.
YZLSBCAP (ND02)	3.198	5.353	2.394	2.236	P.W.
SLBB (ND)	7.530	10.070	8.860	1.137	[21]
TZ (ND)	3.829	4.353	4.247	1.025	[22]

4.3 Excitation Spectrum

Excitation spectra of YZLSBCAP ND (01) glass recorded at the emission wavelength 1065 nm is depicted as figure 4. The excitation spectra consists of two peaks corresponding to the transitions from the ground state $^4I_{9/2}$ to the two excited states $^4F_{5/2}$ and $^4F_{3/2}$ at the wavelengths of 808 and 887 nm respectively. Among these, a prominent excitation band at 808 nm has been selected for the measurement of emission spectrum of Nd^{3+} glass.

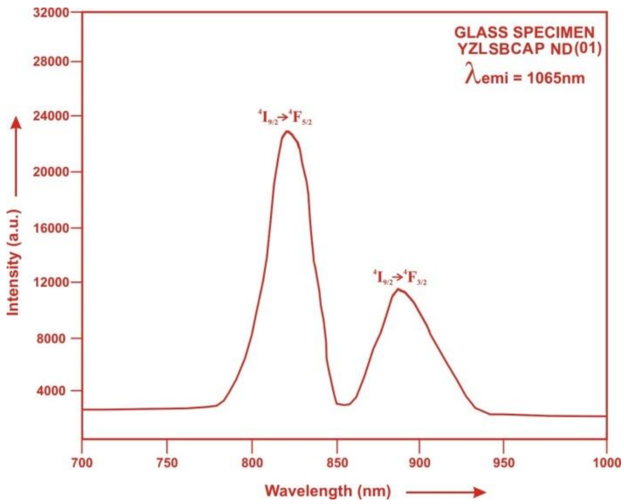

Fig.4: Excitation Spectrum of YZLSBCAP ND (01) glass.

4.4. Fluorescence Spectrum

The fluorescence spectrum of Nd^{3+}doped in ytterbium zinc lithium sodium barium calcium aluminophosphate is shown in Figure 5. There are six broad bands ($^4G_{7/2}\rightarrow{}^4I_{9/2}$),($^4G_{7/2}\rightarrow{}^4I_{11/2}$), ($^4F_{3/2}\rightarrow{}^4I_{9/2}$), ($^4F_{3/2}\rightarrow{}^4I_{11/2}$), ($^4F_{3/2}\rightarrow{}^4I_{13/2}$) and ($^4F_{3/2}\rightarrow{}^4I_{15/2}$) respectively for glass specimens.

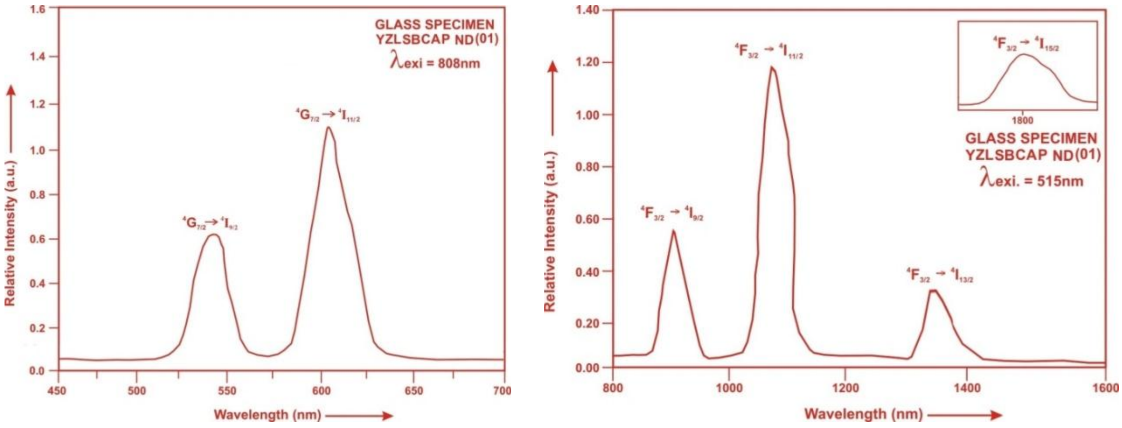

Fig.5: Fluorescence spectrum of YZLSBCAP ND (01) glass.

The wavelengths of these bands along with their assignments are given in **Table 5**.

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_R) for various transitions in Nd^{3+} doped YZLSBCAP glasses.

Transition		YZLSBCAP (ND 01)				YZLSBCAP (ND 1.5)				YZLSBCAP (ND 02)			
	λ_{max} (nm)	$A_{rad}(s^{-1})$	β	σ_p (10^{-20} cm^2)	τ_R(μs)	$A_{rad}(s^{-1})$	β	σ_p (10^{-20} cm^2)	τ_R (μs)	$A_{rad}(s^{-1})$	β	σ_p (10^{-20} cm^2)	τ_R (10^{-20} cm^2)
$^4G_{7/2}\rightarrow{}^4I_{9/2}$	532	3955.32	0.4546	0.548	114.92	3342.65	0.4309	0.485	128.92	2779.91	0.3947	0.421	141.98
$^4G_{7/2}\rightarrow{}^4I_{11/2}$	595	3126.58	0.3593	1.107		3072.30	0.3961	1.183		3204.11	0.4549	1.314	
$^4F_{3/2}\rightarrow{}^4I_{9/2}$	905	1033.34	0.1188	0.917		833.82	0.1075	0.769		632.30	0.0898	0.597	
$^4F_{3/2}\rightarrow{}^4I_{11/2}$	1075	514.74	0.0592	2.174		441.48	0.0569	1.989		366.20	0.0520	1.699	
$^4F_{3/2}\rightarrow{}^4I_{13/2}$	1320	69.89	0.0080	0.367		64.84	0.0084	0.356		59.32	0.0084	0.339	
$^4F_{3/2}\rightarrow{}^4I_{15/2}$	1800	1.67	0.0002	0.022		1.55	0.0002	0.020		1.42	0.0002	0.019	

V. Conclusion

In the present study, the glass samples of composition :(30-x)P_2O_5:10ZnO:10Li_2O:10Na_2O:10BaO:10CaO:10Al_2O_3: 10Y_2O_3:xNd_2O_3. (where x =1, 1.5, 2 mol %) have been prepared by melt-quenching method. From Raman spectra the broad band at 775cm^{-1} is due to symmetric stretching of (P–O–P) bridging oxygen bonds in $(P_2O_7)_4$ units.The stimulated emission cross section (σ_p) has highest value for the transition ($^4F_{3/2}\rightarrow{}^4I_{11/2}$) in all the glass specimens doped with Nd^{3+} ion. This shows that ($^4F_{3/2}\rightarrow{}^4I_{11/2}$) transition is most probable transition.

References

[1]. Ahmadi,F.,Mallawany,R.El.,Papanikolaou,S.,Asteris,P.G(2024). Prediction of optical properties of rare-earth doped phosphate glasses using gene expression programming, Scientifc Reports, 14:15505.

[2]. Meena, S.L. (2024).Spectral and Thermal analysis of praseodymium doped bismuth borate glasses for thermionic applications. IOSR J.Appl.Phys.16,20-27.

[3]. Zhou,L.,Zhu,Z.(2021).Magneto-optical and luminescent properties of Tb^{3+} ions doped GBPZ magneto-optical glass,J.Non-Cryst.Solids,574,121165.

[4]. Li,H.,Zou,H.,Sun,Z.,Xu,Y.,Wang,C.,Xie,X.,Yi,J.,Zhao,F.(2022).Spectroscopic and Surface crystallization characterizations of yttrium doped phosphate glasses,Crystals,12,109,1-9

[5]. Dogan,A.,Erden,M.,Esmer,K.,Eryurek,G.(2021).Upconversion luminescence and temperature sensing characteristics of Ho^{3+}/Yb^{3+} co-doped tellurite glasses,J.Non-Cryst.Solids,571,121055.

[6]. Meena,S.L.(2023).Structural and FTIR analysis of Sm^{3+} ions doped ytterbium zinc lithium lead sodalime cadmium phosphate glasses,Int.J.Inno.Res.Sci.Eng.Tech.12,10811-10820.

[7]. Khan,M.A.,Amjad,R.J.,Ahmad,M.A.,Sattar,A.,Hussain,S.,Yasmeen,S.,Dousti,M.R.(2020).Structural and optical study of erbium doped borophosphate glass. Optic,206, 16370.

[8]. Han,L.,Zhang,Q.,Song,J.Xiao,Z.,Qiang,Y.,Ye,X.You,W.,Lu,A.(2020).A novel Eu^{3+} doped phosphate glass for reddish orange emission: Preparation, structure and fluorescence properties,J.Lumin.221,117041.

[9]. Kolobkova,E.,Alkhlef,A.,Mironov,L.Yu.,Bogdanov,O.(2020).Effect of the phosphate content on the spectroscopic and lasing properties of Er^{3+}/Yb^{3+} doped fluorophosphates glasses,Ceram.Int.46,26396-26402.

[10]. Rao,Ch.S.,Kukar,K.U.,Babu,P.,Jayasankar,C.K.(2012).Optical properties of Ho^{3+} ions in lead phosphate glasses,Opt.Mat.35,102-107.

[11]. Marzouk,M.A.,ElBatal,H.A.,Hamdy,Y.M.,Ezz-Eldin,F.M.(2019).Collective Optical, FTIR and Photoluminescence spectra of CeO_2 and or Sm_2O_3-doped Na_2O-ZnO-P_2O_5 glasses,10.1155,6527327,1-11.

[12]. Singh,H., Singh, T., Singh,D., Bhatia, V., Kumar, D., Singh S.P.(2023).Up-conversion and down conversion studies of Nd^{3+} doped borophosphate glasses, Opt.Mat.137,113586.

[13]. Ismail,M.M.,Batisha,I.K.,Zur,L.,Chiasera,A.,Ferrari,M.,Lukowiak,A.(2020).Optical properties of Nd^{3+} doped phosphate glasses,99,109591.

[14]. Yusof,N.N.,Ghoshal,S.K.,Jupri,S.A.,Azlan,M.N.(2020).Synergistic effects of Nd^{3+} and Ag nanoparticle doping on spectroscopic attributes of phosphate glass,Opt.Mat.110,110403.

[15]. Muniz,R.F.,Zanuto,V.S.,Gibin,M.S.,Gunha,J.V.,Novatski,A.,Rohling,J.H.,Medina,A.N.,Baesso,M.L.(2023).Down and upconversion processrs in Nd^{3+}/Yb^{3+} codoped sodium calcium silicate glasses with concomitant Yb^{2+} assessment,41(3),342-348.

[16]. Kumar,K.U.,Babu,P.,Basavapoornima,Ch.,Praveena,R.,Rani,D.S.,Jayasankar,C.K.(2022).Spectroscopic properties of Nd^{3+} doped boro-bismuth glasses for laser applications,Phys.B.Condens.Matter,646,414327.

[17]. 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.

[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. Journal of Rare Earths, 27, 773.

[19]. Judd, B.R.(1962).Optical absorption intensities of rare earth ions,Phys.Rev.127,750-761.

[20]. Ofelt,G.S. (1962). Intensities of crystal spectra of rare earth Ions, Chem.Phys37, 511-520.

[21]. Rajesh,D.,Balakrishna,A.,Seshadri,M.,Ratnakaram,Y.C.(2012).Spectroscopic investigations on Pr^{3+} and Nd^{3+} doped strontium-lithium-bismuth borate glasses,Mol.Bio.Mol.Spect.97,963-974.

[22]. Moreira,L.M.,Anjos,V.,Bell,M.J.V.,Ramos,C.A.R.,Kassab,L.R.P.,Doualan,D.J.L.,Camy,P.,Moncorge,R.(2016).The effects of Nd^{3+} concentration in the laser emission of TeO_2-ZnO glasses,Opt.Mat.58,84-88.