Spectral and Transmittance Properties of Nd^{3+} Doped Lead Lithium Potassium Niobium silicate Glasses

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***Abstract*: Glass of the system: (45-x)SiO_2:10PbO:10Li_2O:10K_2O:25Nb_2O_5:xNd_2O_3. (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. The amorphous nature of the prepared glass samples was confirmed by X-ray diffraction. Optical absorption, Excitation, fluorescence and Transmittance spectra were 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 (A), branching ratio (β), radiative life time (τ_R) and stimulated emission cross–section (σ_p) of various emission lines have been evaluated.**

***Keywords*: LLPNS Glasses, Optical Properties, Judd-Ofelt Theory, Transmittance Properties.**

I. Introduction

Transparent glass–ceramic as host materials for active optical ions have attracted great interest recently due to their potential application in optical devices such as frequency-conversion materials, lasers and optical fiber amplifiers [1–5]. The oxide glasses generally possess a good mechanical strength, chemical durability, and thermal stability. Glasses containing rare earth ions in various forms such as network formers, modifiers or luminescent ions receive great deal of interest for their unique optical, electrical and various other properties [6-10]. Glasses doped with trivalent rare earth ions are also considered to be promising materials for optical amplifiers. Silicate glass exhibit very important physical, mechanical and chemical properties such as low melting temperature, high thermal expansion coefficient and good thermal stability. They have high thermal stability, high transparency, a low melting point, a high gain density [11-14]. Nd_2O_3 improve the chemical resistance of the glass matrix, and its optical characteristics.

In the present work, the absorption spectra of Nd^{3+} doped LLPNS glasses have been investigated. From the spectral data 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. The Judd-Ofelt theory has been applied to compute the intensity parameters Ω_λ (λ=2, 4, 6). These intensity parameters have been used to evaluate optical properties such as spontaneous emission probability, branching ratio, radiative life time and stimulated emission cross section.

II. Experimental

The following Nd^{3+} doped Silicate glass sample (45-x)SiO_2:10PbO:10Li_2O:10K_2O:25Nb_2O_5: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 SiO_2, PbO, Li_2O, K_2O, Nb_2O_5 and Nd_2O_3. They were thoroughly mixed by using an agate pestle mortar. Then melted at 1055˚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.**

Table 1. Chemical composition of the glasses.

Sample	Glass composition (mol %)
LLPNS (UD)	45SiO_2:10PbO:10Li_2O:10K_2O:25Nb_2O_5.
LLPNS (ND1)	44SiO_2:10PbO:10Li_2O:10K_2O:25Nb_2O_5: 1Nd_2O_3.
LLPNS (ND1.5)	43.5SiO_2:10PbO:10Li_2O:10K_2O:25Nb_2O_5:1.5Nd_2O_3.
LLPNS (ND2)	43SiO_2:10PbO:10Li_2O:10K_2O:25Nb_2O_5:2Nd_2O_3.

LLPNS (UD)—Represents undoped Lead Lithium Potassium Niobium Silicate glass Specimens.
LLPNS (ND)—Represents Nd^{3+} doped Lead Lithium Potassium Niobium Silicate glass Specimens.

III. Theory

3.1 Oscillator Strength

The intensity of spectral lines are expressed in terms of oscillator strengths using the relation [15].

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

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 [16], 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 [17] and Ofelt [18] 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

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

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 angularmomentum of the initial and final level respectively, Ω_λ (λ=2,4and 6) are known as Judd-Ofelt intensity

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:

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

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

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

where, the sum is over all terminal manifolds.

The radiative life time is given by

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

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

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

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 [19, 20]. The Nephelauxetic Ratio is given by

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

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

$$b^{1/2} = \left[\frac{1-\beta'}{2}\right]^{1/2} \qquad (10)$$

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.

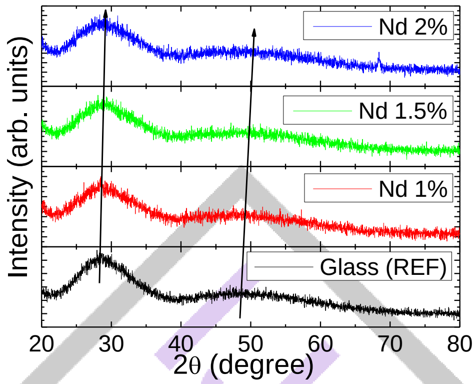

Fig.1: X-ray diffraction pattern of SiO_2: PbO: Li_2O: K_2O: Nb_2O_5 :Nd_2O_3 glasses.

4.2 Transmittance Spectrum

The Transmittance spectrum of Nd^{3+}doped in lead lithium potassium niobium silicate glass is shown in Figure 2.

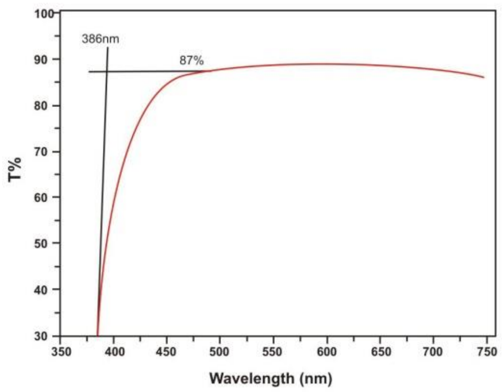

Fig. (2) Transmittance spectrum of Nd^{3+} doped LLPNS glasses.

4.3 Absorption spectra

The absorption spectra of LLPNS (ND 01) 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 LLPNS (ND 01) glass.

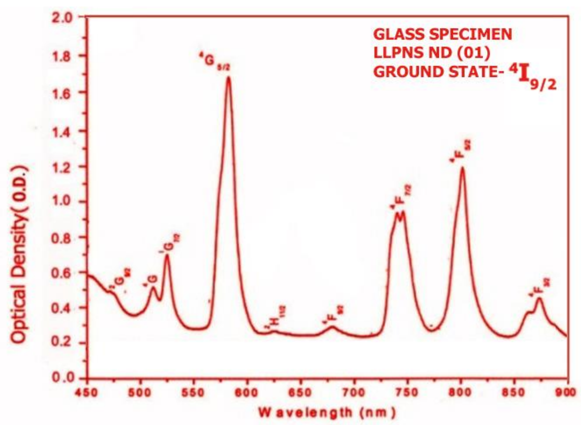

Fig.3: Absorption spectra of LLPNS (ND 01) glass.

The experimental and calculated oscillator strengths for Nd^{3+} ions in lead lithium potassium niobium silicate glasses are given in **Table 2**.

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

Energy level from $^3H_4$	Glass LLPNS (ND01)		Glass LLPNS (ND1.5)		Glass LLPNS (ND02)	
	$P_{exp.}$	$P_{cal.}$	$P_{exp.}$	$P_{cal.}$	$P_{exp.}$	$P_{cal.}$
$^4F_{3/2}$	4.53	4.28	3.84	3.58	2.83	2.79
$^4F_{5/2}$	8.68	8.90	7.68	7.89	6.84	6.86
$^4F_{7/2}$	9.13	9.13	8.43	8.62	7.66	8.04
$^4F_{9/2}$	0.64	0.53	0.59	0.48	0.43	0.43
$^2H_{11/2}$	0.30	0.15	0.22	0.14	0.20	0.12
$^4G_{5/2}$	25.96	26.21	24.78	25.02	23.42	23.72
$^4G_{7/2}$	4.99	5.70	3.98	5.03	2.64	4.28
$^4G_{9/2}$	2.73	2.52	2.41	2.17	1.99	1.78
$^2G_{9/2}$	0.96	3.30	0.82	2.80	0.69	2.24
R.m.s.deviation	0.8355		0.7668		0.7741	

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 and formula described elsewhere [21].

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

Parameter	Free ion	LLPNS (ND01)	LLPNS (ND1.5)	LLPNS (ND02)
$F_2(cm^{-1})$	331.16	324.575	324.6023	324.423
$F_4(cm^{-1})$	50.71	50.719	50.71915	50.3239
$F_6(cm^{-1})$	5.154	5.0384	5.0399	5.03286
$\xi_{4f}(cm^{-1})$	884.0	882.803	882.8114	883.117
$E^1(cm^{-1})$	5024.0	4947.0206	4947.594	4944.968
$E^2(cm^{-1})$	23.90	23.07634	23.0805	23.0487
$E^3(cm^{-1})$	497.0	489.565	489.5624	489.5301
F_4/F_2	0.1531	0.15626	0.156250	0.156392
F_6/F_2	0.0155	0.01552302	0.0155266	0.01551181
E^1/E^3	10.1086	10.10492	10.10616	10.10146
E^2/E^3	0.0481	0.047136	0.047145	0.04708334
β'		0.9801	0.9802	0.9797
$b^{1/2}$		0,099750	0.099499	0.010075

Judd-Ofelt intensity parameters Ω_λ (λ = 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 dipole contributions. In the present case the three Ω_λ parameters follow the trend $\Omega_2 < \Omega_6 < \Omega_4$.

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

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

Glass Specimen	$\Omega_2(pm^2)$	$\Omega_4(pm^2)$	$\Omega_6(pm^2)$	Ω_4/Ω_6	Ref.
LLPNS (ND01)	1.626	9.178	3.159	2.905	[P.W.]
LLPNS (ND1.5)	2.416	7.586	2.992	2.535	[P.W.]
LLPNS (ND02)	3.328	5.769	2.893	1.994	[P.W.]
TBZN(ND)	1.574	2.368	1.768	1.339	[22]

4.4 Excitation Spectrum

The Excitation spectra of Nd^{3+}doped LLPNS glass specimens have been presented in Figure 4 in terms of Excitation Intensity versus wavelength. The excitation spectrum was recorded in the spectral region 700–1000 nm fluorescence at 1065nm having different excitation band centered at 808 nm and 888 nm are attributed to the ($^4I_{9/2}\rightarrow{}^4F_{5/2}$) and ($^4I_{9/2}\rightarrow{}^4F_{3/2}$) transitions, respectively. The highest absorption level is $^4F_{5/2}$ and is at 808 nm. So this is to be chosen for excitation wavelength.

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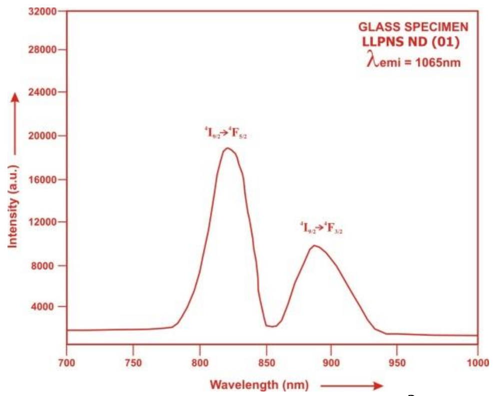

Fig. (4) Excitation spectrum of doped with Nd^{3+} LLPNS glasses.

4.5 Fluorescence Spectrum

The fluorescence spectrum of Nd^{3+}doped in lead lithium potassium niobium silicate glass is shown in Figure 5. There are three broad bands ($^4F_{3/2}\rightarrow{}^4I_{9/2}$), ($^4F_{3/2}\rightarrow{}^4I_{11/2}$), ($^4F_{3/2}\rightarrow{}^4I_{13/2}$) and ($^4F_{3/2}\rightarrow{}^4I_{15/2}$) respectively for glass specimens.

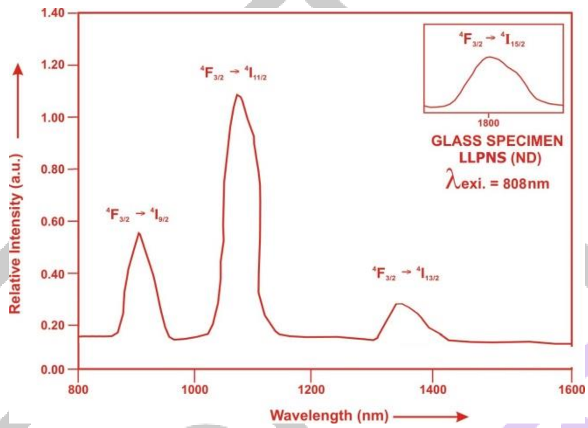

Fig.5: Fluorescence spectrum of LLPNS glasses doped with Nd^{3+} LLPNS glasses.

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

		LLPNS (ND01)				LLPNS (ND01)				LLPNS (ND01)			
Transition	λ_p(nm)	$A_{rad}(s^{-1})$	β_R	σ_p ($10^{-20}cm^2$)	τ_R(µs)	$A_{rad}(s^{-1})$	β_R	σ_p ($10^{-20}cm^2$)	τ_R(µs)	$A_{rad}(s^{-1})$	β_R	σ_p ($10^{-20}cm^2$)	τ_R(µs)
$^4F_{3/2}\rightarrow{}^4I_{9/2}$	905	931.45	0.6277	0.9266	673.93	780.27	0.6122	0.7971	784.69	608.33	0.5824	0.6434	957.32
$^4F_{3/2}\rightarrow{}^4I_{11/2}$	1075	481.98	0.3248	2.4554		427.27	0.3353	2.3206		371.49	0.3556	2.2426	
$^4F_{3/2}\rightarrow{}^4I_{13/2}$	1320	68.77	0.0463	0.3949		65.28	0.0512	0.3880		63.24	0.0605	0.3898	
$^4F_{3/2}\rightarrow{}^4I_{15/2}$	1800	1.64	0.00111	0.0235		1.56	0.00122	0.0228		1.51	0.00145	0.02269	

V. Conclusion

In the present study, the glass samples of composition (45-x) SiO_2:10PbO:$10Li_2O$:$10K_2O$:$25Nb_2O_5$:xNd_2O_3 (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 ($^4F_{3/2}\rightarrow{}^4I_{11/2}$) for glass LLPNS (ND 01), suggesting that glass LLPNS (ND 01) is better compared to the other two glass systems LLPNS (ND1.5) and LLPNS (ND02). On the basis of spectrophotometric, transmittance reaches about 87% for all silicate glasses doped with Nd^{3+} ions.

References

[1]. Murty, V. R. L., Rekha rani, P., Venkateswarlu, M., Swapna, K., Mahamuda, Sk, Srinivas Prasad, M. V. V. K.(2019). Absorption And Energy Band Gap Studies Of Nd^{3+} -Er^{3+} Ions Doped Zinc Alumino Bismuth Borate Glasses, Int.J.Sci.andTech.8, 12, 3367-72.

[2] Shelby,J. E.(2005). Introduction to Glass Science and Technology, TJ International Padstow, New York, NY, USA, 2nd edition, 2005.

[3] Becker, P. (2003).Thermal and optical properties of glasses of the system Bi_2O_3—B_2O_3, Crystal Research and Technology, 38, 74–82.

[4]. Deopa, N., Rao, A.S., Gupta, M., Prakash, G. V. (2018). Spectroscopic investigations of Nd^{3+} doped Lithium Lead Alumino Borate glasses for 1.06 μm laser applications, Optical Materials 75, 127-134.

[5].Shaaban, K.S., Wahab, E.A.A., Shaaban, E.R., et al. (2020). Electronic polarizability, optical basicity, and mechanical properties of aluminum lead phosphate glasses. Opt Quant Electron 52, 125, 1-16.

[6]. Kolobkova, E., Yasukevich, A., Kuleshov, N., Nikonorov, N., Babkina, A. (2019). Concentration dependence of spectroscopic properties and energy transfer analysis of the fluorophosphate glasses with small phosphates content doped with Nd^{3+} ions. Journal of Non-Crystalline Solids 526, 11970.

[7] Sharma, Ritu, Rao, A.S., Deopa, Nisha, Venkateswarlu, M., Jayasimhadri, M., Haranath, D., Vijaya Prakash, G.(2018).Spectroscopic study of Pr^{3+} ions doped Zinc Lead Tungsten Tellurite glasses for visible photonic device applications‖, Optical Materials 78,457-464.

[8] Linganna,K., Rathaiah, M., Vijaya, N., Basavapoornima, C., Jayasankar, C.K., Ju, S., Han, W.T., Venkatramu,V.(2015). 1.53 lm luminescence properties of Er^{3+}-doped K Sr–Al phosphate glasses, Ceram. Int. 41, 5765–5771.

[9]. Pan, Z., Ueda, A., Mu, R., Morgan, S.H.(2007).Upconversion luminescence in Er^{3+}-doped germanate-oxyfluoride and tellurium-germanate-oxyfluoride transparent glass-ceramics, Journal of Luminescence 126 , 251–256.

[10].Guan,Y., Wei,Z., Huang, Y., Maalej, R. and Seo, H. J. (2013).1.55μm emission and upconversion luminescence of Er^{3+} - doped strontium borate glasses. Ceramics International, 39, 7023.

[11].Zhou, S., Jiang, N., Zhu, B., Yang, H., Ye, S., Laksminarayana, G., Hao, J. and Qiu, J. (2008). Multifuction Bismuth-Doped Nanoporous Silica Glass: From Blue Green, Orange, Red and White Light Sources to Ultra-Broadband Infrared Amplifiers.Adv.Funct.Mater, 18, 1407.

[12]. Manasa, P., Ran, F., Basavapoornima, Ch., Depuru, S. R., Jayasankar, C.K. (2020). Optical characteristics of (Eu^{3+}, Nd^{3+}) co-doped leadfluorosilicate glasses for enhanced photonic device applications, Journal of Luminescence 223, 117210.

[13]. Deepa, M., Doddoji, R., Viswanath, C.S. D., Chandrasekhar, A.V. (2019). Optical and NIR luminescence spectral studies: Nd^{3+}-doped borosilicate glasses, Journal of Luminescence 213, 191-196.

[14]. Qiao,Y., Da, N., Chen, D. , Zhou, Q., Qiu, J. and Akai, T.(2007).Spectroscopic properties of neodymium doped high silica glass and aluminum codoping effects on the enhancement of fluorescence emission, Appl. Phys. B87, 717–722 .

[15]. 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.

[16]. 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.

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

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

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

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

[21] Sharma, Y.K. (1991) .Spectral and Electoral Properties of Lanthanide Ions in Different Environment. PhD Thesis, University of Jodhpur.

[22]. Marzuki, A., Pramuda, A., Fausta, D.E. (2020).Effect of Nd_2O_3 and Na_2O concentration on physical and spectroscopic properties of TeO_2–Bi_2O_3–ZnO–Na_2O–Nd_2O_3 glasses, Mater. Res. Express 7, 065201.