Spectroscopic Properties of Nd^{3+} Doped Lead Lithium SodiumTungsten Borophosphate Glasses

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Abstract

Glass of the system: (40-x) P_2O_5:10PbO:10Li_2O:10Na_2O: 10WO_3:20 B_2O_3: 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. Optical absorption spectra were recorded at room temperature for all glass samples. 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 these parameters energies and intensities of these bands has been calculated. 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 (A), branching ratio (β_R), radiative life time (τ_R) and stimulated emission cross–section (σ_p)) of various emission lines have been evaluated.

Keywords: LLSTBP Glasses, Optical Properties, Judd-Ofelt Theory, Rare earth ions.

Introduction:

Amongst many other glasses the P_2O_5 based glasses find wide spread applications in optical data transmission, detection and laser technologies .Phosphate glasses are very well known for their suitable mechanical and chemical properties, homogeneity, good thermal stability, and excellent optical properties phosphate glasses show an enhancement of rare earth radiative emission properties due to their variety of sites available for the doping ions [1-5].

Phosphate glasses are potentially important host materials for developing rare earth doped optical devices. Phosphate glasses have excellent transparency, good mechanical and thermal stability. Borophosphate glass has low phonon energy, chemical and thermal stability. Thus, it can be widely used in visible and infrared laser, fiber amplifier and optical data storage devices. They present superior properties like that high transparency, low melting point, high gain density, high solubility for rare-earth ions and low dispersion [6-10].The host matrix compose of PbO, a glass modifier/glass farmer a heavy metal oxide along with P_2O_5, Li_2O, Na_2O, WO_3 and B_2O_3.The addition of Na_2O to the glass mixture improves the rare earth ion solubility leading to the possibility of using even higher concentrations of ions [11].

The present work reports on the absorption and emission properties of Nd^{3+} doped lead lithium sodium tungsten borophosphate. 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).

Experimental:

Preparation of glasses:

The following Nd^{3+} doped borophosphate glass samples (40-x) P_2O_5:10PbO:10Li_2O:10Na_2O: 10WO_3:20 B_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, PbO, Li_2O, Na_2O, WO_3, B_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.**

Table 1: Chemical composition of the glasses

Sample	Glass composition (mol %)
LLSTBP (UD)	$40P_2O_5:10PbO:10Li_2O:10Na_2O:10WO_3:20B_2O_3$
LLSTBP (ND1)	$39P_2O_5:10PbO:10Li_2O:10Na_2O:10WO_3:20B_2O_3:1Nd_2O_3$
LLSTBP (ND1.5)	$38.5P_2O_5:10PbO:10Li_2O:10Na_2O:10WO_3:20B_2O_3:1.5Nd_2O_3$
LLSTBP (ND2)	$38P_2O_5:10PbO:10Li_2O:10Na_2O:10WO_3:20B_2O_3: 2Nd_2O_3$

LLSTBP (UD) - Represents undoped Lead Lithium Sodium Tungsten boro phosphate glass specimens.
LLSTBP (ND) - Represents Nd^{3+} doped Lead Lithium Sodium Tungsten borophosphate glass specimens.

Theory:

Oscillator Strength:

The intensity of spectral lines is expressed in terms of oscillator strengths using the relation [12].

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

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 [13], 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.

Judd-Ofelt Intensity Parameters:

According to Judd [14] and Ofelt [15] 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

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

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

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:

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

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

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

The radiative life time is given by

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

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.

Results and Discussion:

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.

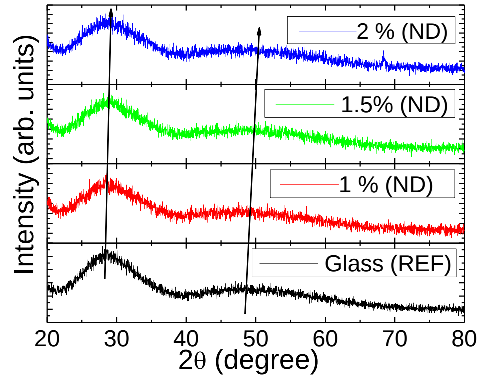

Fig.1: X-ray diffraction pattern of P_2O_5: PbO: Na_2O: WO_3:B_2O_3:Nd_2O_3 glasses.

Absorption spectra:

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

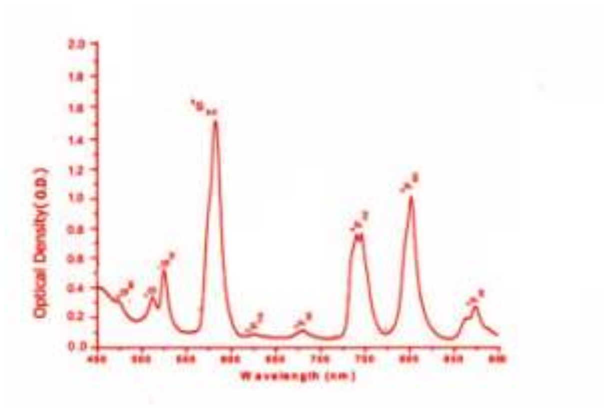

Fig.2: Absorption spectra of LLSTBP (ND 01) glass.

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

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

Energy level from $^4I_{9/2}$	**Glass LLSTBP (ND01)**		**Glass LLSTBP (ND1.5)**		**Glass LLSTBP (ND02)**	
	$P_{exp.}$	$P_{cal.}$	$P_{exp.}$	$P_{cal.}$	$P_{exp.}$	$P_{cal.}$
$^4F_{3/2}$	4.982	4.617	4.63	4.54	3.84	4.079
$^4F_{5/2}$	9.62	9.56	9.52	9.63	8.63	8.72
$^4F_{7/2}$	9.88	10.02	9.72	10.32	8.85	10.54
$^4F_{9/2}$	0.884	0.566	0.764	0.575	0.672	0.528
$^2H_{11/2}$	0.426	0.163	0.384	0.165	0.292	0.151
$^4G_{5/2}$	26.82	26.88	25.58	26.11	24.64	25.27

$^4G_{7/2}$	4.92	6.056	3.88	5.97	2.92	5.49
$^4G_{9/2}$	3.92	2.712	2.18	2.69	1.98	2.44
$^2G_{9/2}$	0.98	3.56	0.82	3.51	0.64	3.17
r.m.s.deviation	1.0391		1.1841		1.2717	

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

Parameter	Free ion	LLSTBP (ND01)	LLSTBP (ND1.5)	LLSTBP (ND02)
$F_2(cm^{-1})$	331.16	327.46	327.45	327.37
$F_4(cm^{-1})$	50.71	49.89	49.88	49.92
$F_6(cm^{-1})$	5.154	5.144	5.143	5.140
$\xi_{4f}(cm^{-1})$	884.0	889.09	889.39	889.04
$E^1(cm^{-1})$	5024.0	4971.86	4971.05	4970.72
$E^2(cm^{-1})$	23.90	23.76	23.76	23.73
$E^3(cm^{-1})$	497.0	489.52	489.49	489.55
F_4/F_2	0.1531	0.1524	0.1523	0.1525
F_6/F_2	0.0155	0.0157	0.0157	0.01570
E^1/E^3	10.1086	10.1567	10.1555	10.1537
E^2/E^3	0.0481	0.04850	0.04853	0.04848
β'		0.98884	0.98879	0.98856
$b^{1/2}$		0.07470	0.07488	0.07565

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.

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

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

Glass Specimen	$\Omega_2(pm^2)$	$\Omega_4(pm^2)$	$\Omega_6(pm^2)$	Ω_4/Ω_6	Ref.
LLSTBP(ND01)	1.293	9.860	3.389	2.909	P.W.
LLSTBP (ND1.5)	1.173	9.638	3.529	2.731	P.W.
LLSTBP (ND02)	1.661	8.631	3.267	2.642	P.W.
LBB(ND)	1.577	4.483	3.333	1.35	[16]
GLB(ND)	2.95	5.01	3.93	1.27	[17]
LTNd10	4.54	5.79	5.69	0.75	[18]

Fluorescence Spectrum:

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

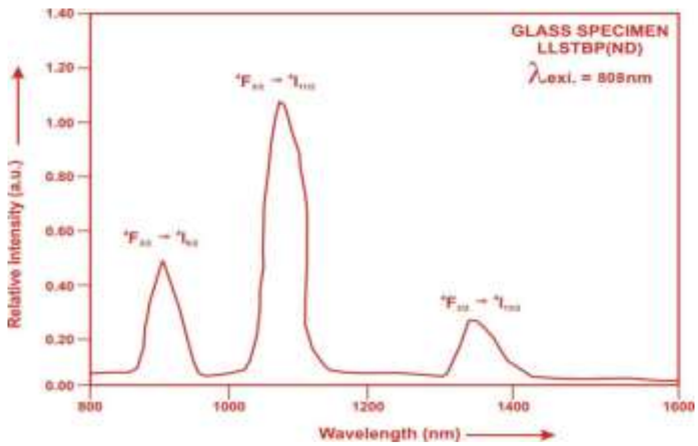

Fig.3: Fluorescence spectrum of LLSTBP glasses doped with Nd^{3+}.

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

Conclusion:

In the present study, the glass samples of composition (40-x) P_2O_5:10PbO:10Li_2O:10Na_2O: 10WO_3:20 B_2O_3: xNd_2O_3. (where x =1, 1.5, 2 mol %) have been prepared by melt-quenching method. 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.

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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 LLSTBP glasses.

Transition		LLSTBP(ND 01)				LLSTBP(ND 1.5)				LLSTBP(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)
$^4F_{3/2}\rightarrow{}^4I_{9/2}$	905	1046.02	0.6309	0.930	603.17	889.42	0.6295	0.813	707.82	724.06	0.6083	0.687	840.10
$^4F_{3/2}\rightarrow{}^4I_{11/2}$	1075	536.21	0.3234	2.449		458.33	0.3244	2.290		403.49	0.3390	2.205	
$^4F_{3/2}\rightarrow{}^6H_{13/2}$	1320	75.69	0.0457	0.385		65.05	0.0460	0.345		62.79	0.0528	0.349	