

Spectral and Thermal Properties of Pr³⁺ Doped Lead Lithium Sodium Tungsten Borophosphate Glasses

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Abstract

Lead lithium sodium tungsten borophosphate glasses containing Pr³⁺ in (40-x):P₂O₅:10PbO:10Li₂O:10Na₂O:10WO₃:20B₂O₃:xPr₆O₁₁ (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, Excitation spectra and fluorescence spectra were recorded at room temperature for all glass samples. Judd-Ofelt intensity parameters Ω_{λ} ($\lambda=2, 4, 6$) 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: LLSTBP Glasses, Optical Properties, Judd-Ofelt Theory, Thermal Properties.

Date of Submission: 27-08-2021

Date of Acceptance: 11-09-2021

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 [1–8]. Phosphate glasses possess easier preparation, large transparency window, low phonon energy, better thermal stability, high refractive index, good mechanical, high density and chemical durability [9-13]. Pr³⁺ doped glasses are very important because of the possibility of their application in optoelectronic, optic device fields, such as lasers, fiber optic large bandwidth, high emission and absorption cross-section and solar cells [14-16]. The addition of network modifier (NWF) Li₂O is to improve both electrical and mechanical properties of such glasses. Recently, rare earth doped phosphate glass has attracted much interest because of high rare earth ion solubility, optical data transmission, detection, sensor and catalysts [17, 18].

In this work, the spectroscopic properties of Pr³⁺ -doped (40-x):P₂O₅:10PbO:10Li₂O:10Na₂O:10WO₃:20B₂O₃:Pr₆O₁₁ (where x=1, 1.5,2 mol %) glasses were investigated. absorption, Excitation spectra and fluorescence spectra, The absorption, Excitation and fluorescence spectra of Pr³⁺ of the glasses were investigated. The J-O intensity parameters render significant information regarding local structure and bonding in the vicinity of rare- earth ions.

II. Experimental Techniques

Preparation of glasses

The following Pr³⁺ doped lead lithium sodium tungsten borophosphate glass samples (40-x):P₂O₅:10PbO:10Li₂O:10Na₂O:10WO₃:20B₂O₃:Pr₆O₁₁ (where x=1, 1.5,2) have been prepared by melt-quenching method. Analytical reagent grade chemical used in the present study consist of P₂O₅, PbO, Li₂O, Na₂O, WO₃, B₂O₃ and Pr₆O₁₁. 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 1050⁰C, for preparation of Lead lithium sodium tungsten borophosphate glasses, 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 inserted in the muffle furnace for annealing. The steel plate was preheated to 100⁰C. While pouring; the temperature of crucible was also maintained to prevent crystallization. And annealed at temperature of 350⁰C 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 %)
LLSTBP (UD)	40P ₂ O ₅ :10PbO:10Li ₂ O:10Na ₂ O:10WO ₃ :20B ₂ O ₃
LLSTBP (PR 1)	39P ₂ O ₅ :10ZnO:10Li ₂ O:10CdO:10MgO:20B ₂ O ₃ :1 Pr ₆ O ₁₁
LLSTBP (PR 1.5)	38.5P ₂ O ₅ :10PbO:10Li ₂ O:10Na ₂ O:10WO ₃ :20B ₂ O ₃ : 1.5 Pr ₆ O ₁₁
LLSTBP (PR 2)	38P ₂ O ₅ :10PbO:10Li ₂ O:10Na ₂ O:10WO ₃ :20B ₂ O ₃ : 2 Pr ₆ O ₁₁

LLSTBP (UD)—Represents undoped Lead Lithium Sodium Tungsten Borophosphate glass specimen.

LLSTBP (PR) -Represents Pr³⁺ Lead Lithium Sodium Tungsten Borophosphate glass specimens.

III. Theory

3.1 Oscillator Strength

The intensity of spectral lines are expressed in terms of oscillator strengths using the relation [19].

$$f_{\text{expt}} = 4.318 \times 10^{-9} \int \epsilon(v) dv \quad (1)$$

where, $\epsilon(v)$ 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 [20].

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

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

3.2. Judd-Ofelt Intensity Parameters

According to Judd [21] and Ofelt [22] theory, independently derived expression for the oscillator strength of the induced forced electric dipole transitions between an initial J manifold $|4f^N(S, L) J\rangle$ level and the terminal J' manifold $|4f^N(S', L') J'\rangle$ is given by:

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

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

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

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} ($\lambda = 2, 4$ and 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 $|4f^N(S', L') J'\rangle$ to a final manifold $|4f^N(S, L) J\rangle$ 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 $|4f^N(S', L') J'\rangle$ to a final many fold $|4f^N(S, L) J\rangle$ is given by

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

where, the sum is over all terminal manifolds.

The radiative life time is given by

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

where, the sum is over all possible terminal manifolds. The stimulated emission cross -section for a transition from an initial manifold $|4f^N(S', L') J'\rangle$ to a final manifold $|4f^N(S, L) J\rangle$ 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.

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 [23, 24]. 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

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

IV. Result and Discussion

4.1. 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.

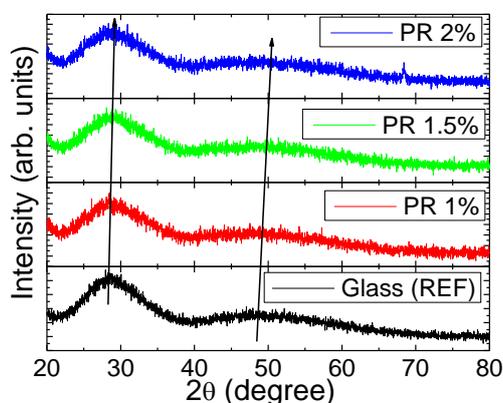


Fig.1: X-ray diffraction pattern of LLSTBP (PR) glasses.

4.2 Thermal Properties

Figure 2 shows the thermal properties of LLSTBP (PR) glass from 300^oC to 1000^oC. 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 355^oC, 450^oC and 580^oC respectively. The T_g increase with the contents of Pr₆O₁₁ increase. I could conclude that thermal properties of the LLSTBP (PR) glass are good for fiber drawing from the analysis of DSC curve.

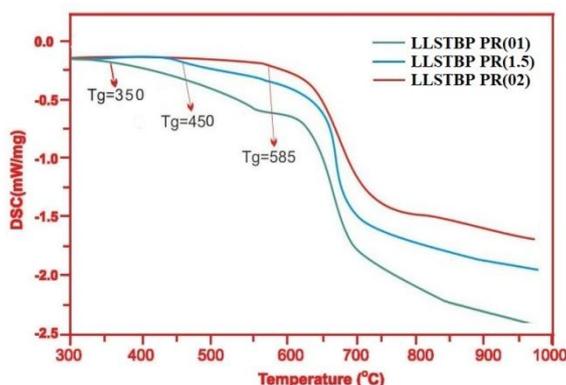


Fig.2: DSC curve of LLSTBP (PR) glasses.

4.3. Absorption spectra

The absorption spectra of LLSTBP (PR) glasses, consists of absorption bands corresponding to the absorptions from the ground state ³H₄ of Pr³⁺ ions. Eight absorption bands have been observed from the ground state ³H₄ to excited states ³F₂, ³F₃, ³F₄, ¹G₄, ¹D₂, ³P₀, ³P₁ and ³P₂ for Pr³⁺ doped LLSTBP (PR) glasses.

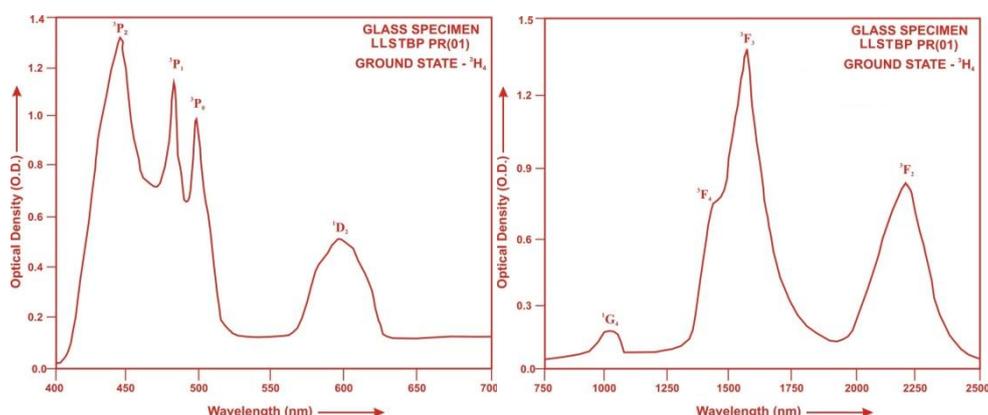


Fig.3: Absorption spectra of LLSTBP PR (01) glass.

The experimental and calculated oscillator strengths for Pr³⁺ ions in lead lithium sodium tungsten borophosphate glasses are given in **Table 2**

Table 2. Measured and calculated oscillator strength ($P^m \times 10^{+6}$) of Pr³⁺ ions in LLSTBP glasses.

Energy level ³ H ₄	Glass LLSTBP (PR01)		Glass LLSTBP (PR1.5)		Glass LLSTBP (PR02)	
	P _{exp.}	P _{cal.}	P _{exp.}	P _{cal.}	P _{exp.}	P _{cal.}
³ F ₂	4.33	3.68	3.75	3.23	2.85	2.37
³ F ₃	7.93	6.88	6.37	5.52	4.86	4.06
³ F ₄	4.28	4.17	3.26	3.33	2.35	2.48
¹ G ₄	0.58	0.36	0.38	0.28	0.29	0.21
¹ D ₂	3.45	1.21	2.14	0.97	1.44	0.72
³ P ₀	4.48	2.13	3.48	1.71	2.67	1.16
³ P ₁	4.88	3.49	3.76	2.81	2.79	1.94
³ P ₂	12.14	4.03	11.29	3.21	10.64	2.38
R.m.s.deviation	3.1564		2.9905		3.0132	

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. The ratio of Racah parameters E¹/E³ and E²/E³ are about 9.79 and 0.048 respectively. Computed values of Slater-Condon, Lande', Racah, nephelauxetic ratio and bonding parameter for Pr³⁺ doped LLSTBP glass specimens are given in **Table 3**.

Table3. Computed values of Slater-Condon, Lande', Racah, nephelauxetic ratio and bonding parameter for Pr³⁺ doped LLSTBP glass specimens.

Parameter	Free ion	LLSTBP PR01	LLSTBP PR1.5	LLSTBP PR02
F ₂ (cm ⁻¹)	322.09	300.01	300.02	300.01
F ₄ (cm ⁻¹)	44.46	44.26	44.28	44.27
F ₆ (cm ⁻¹)	4.867	4.4116	4.413	4.412
ξ_{4f} (cm ⁻¹)	741.00	858.40	858.26	858.41
E ¹ (cm ⁻¹)	4728.92	4451.02	4451.48	4450.98
E ² (cm ⁻¹)	24.75	22.01	22.01	22.01
E ³ (cm ⁻¹)	478.10	454.74	454.73	454.74
F ₄ /F ₂	0.13804	0.14753	0.147577	0.14755
F ₆ /F ₂	0.01511	0.01470	0.01471	0.014706
E ¹ /E ³	9.8911	9.7879	9.7893	9.7881
E ² /E ³	0.0518	0.0484	0.0484	0.0484
β'		0.88868	0.88880	0.888675
b ^{1/2}		0.235924	0.2357949	0.235929

Judd-Ofelt intensity parameters Ω_λ ($\lambda = 2, 4$ and 6) were calculated by using the fitting approximation of the experimental oscillator strengths to the calculated oscillator strengths with respect to their electric dipole contributions. In the present case the three Ω_λ parameters follow the trend $\Omega_2 < \Omega_4 < \Omega_6$. The variation of Ω_2

with P₂O₅ content has been attributed to changes in the asymmetry of the ligand field at the rare earth ion site and to the changes in their rare earth oxygen covalence.

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

Table 4. Judd-Ofelt intensity parameters for Pr³⁺ doped LLSTBP glass specimens.

Glass Specimen	$\Omega_2(\text{pm}^2)$	$\Omega_4(\text{pm}^2)$	$\Omega_6(\text{pm}^2)$	Ω_4/Ω_6
LLSTBP (PR01)	2.233	3.257	6.373	0.5111
LLSTBP (PR1.5)	2.160	2.616	5.068	0.5162
LLSTBP (PR02)	1.646	1.769	3.795	0.4661

4.4 Excitation Spectrum

Excitation spectra of LLSTBP PR (01) glass recorded at the emission wavelength 395 nm is depicted as figure 4. The excitation spectra consists of three peaks corresponding to the transitions from the ground state ³H₄ to the various excited states ³P₂, ³P₁ and ³P₀ at the wavelengths of 448, 465 and 486 nm respectively. Among these, a prominent excitation band at 448 nm has been selected for the measurement of emission spectrum of Pr³⁺ glass.

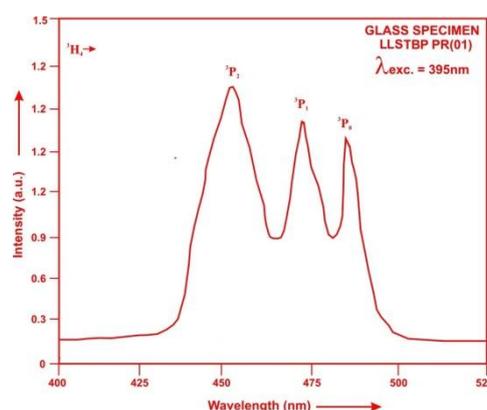


Fig.4: Excitation Spectrum of LLSTBP PR (01) glass.

4.5. Fluorescence Spectrum

The fluorescence spectrum of Pr³⁺ doped in lead lithium sodium tungsten borophosphate glass is shown in Figure 5.

There are nine broad bands (³P₀→³H₄), (³P₀→³H₅), (¹D₂→³H₄) (³P₀→³H₆), (³P₀→³F₂), (³P₁→³F₃), (¹D₂→³H₅), (³P₀→³F₄) and (¹G₄→³H₅) respectively for glass specimens.

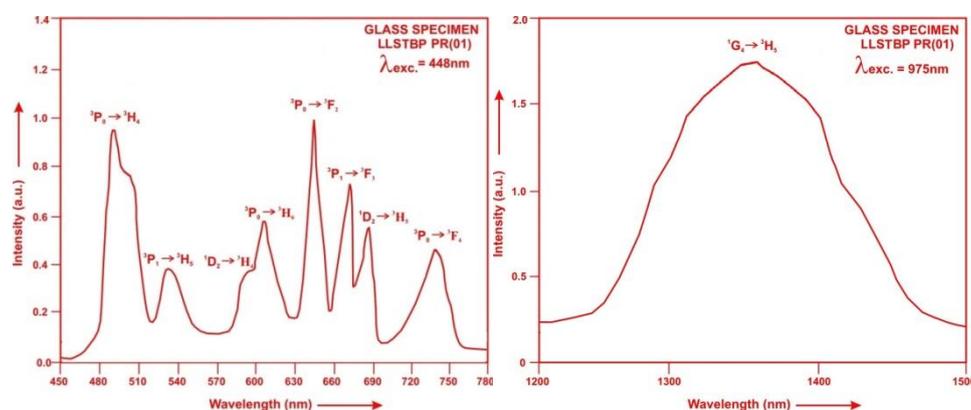


Fig.5: Fluorescence spectrum of LLSTBP PR (01) glass.

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 Pr³⁺ doped LLSTBP glasses.

Transition	LLSTBP PR 01					LLSTBP PR 1.5				LLSTBP PR 02			
	λ_{max} (nm)	$A_{rad}(s^{-1})$	β	σ_p ($10^{-20} cm^2$)	$\tau_R(\mu s)$	$A_{rad}(s^{-1})$	β	$\sigma_p(10^{-20} cm^2)$	$\tau_R(\mu s)$	$A_{rad}(s^{-1})$	β	σ_p ($10^{-20} cm^2$)	τ_R ($10^{-20} cm^2$)
³ P ₀ → ³ H ₄	485	1648.19	0.1608	1.974		1326.46	0.1512	0.979		8987.78	0.1415	0.883	
³ P ₁ → ³ H ₂	529	2747.49	0.2681	0.665		2202.87	0.2511	0.572		1552.98	0.2445	0.438	
¹ D ₂ → ³ H ₄	599	584.32	0.0570	0.282		467.48	0.0533	0.249		345.91	0.0545	0.203	
³ P ₀ → ³ H ₅	602	495.13	0.0483	0.351		394.53	0.0449	0.319		296.02	0.0466	0.278	
³ P ₀ → ³ F ₂	645	1500.02	0.1464	2.199	97.57	1453.88	0.1658	2.592	114.01	1110.13	0.1748	2.393	157.43
³ P ₁ → ³ F ₃	676	2688.67	0.2623	1.809		2456.16	0.2800	1.785		1814.96	0.2857	1.441	
¹ D ₂ → ³ H ₂	685	7.50	0.00073	0.0112		6.016	0.00069	0.0103		4.20	0.00066	0.0082	
³ P ₀ → ³ F ₄	730	304.65	0.0297	0.275		245.18	0.02795	0.235		166.13	0.0262	0.169	
¹ G ₄ → ³ H ₂	1350	272.80	0.0266	0.956		218.90	0.02496	0.782		162.82	0.0256	0.596	

V. Conclusion

In the present study, the glass samples of composition (40-x):P₂O₅:10PbO:10Li₂O:10Na₂O:10WO₃:20B₂O₃:xPr₆O₁₁ (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 (³P₀→³F₂) in all the glass specimen doped with Pr³⁺ ion. This shows that (³P₀→³F₂) transition is most probable transition and it useful for laser action.

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S.L.Meena. "Spectral and Thermal Properties of Pr³⁺ Doped Lead Lithium Sodium Tungsten Borophosphate Glasses." *IOSR Journal of Applied Physics (IOSR-JAP)*, 13(5), 2021, pp. 01-07.