Spectroscopic Properties of Pr^{3+} Doped in Zinc Lithium CalciumPotassiumniobatePhosphate Glasses.

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Abstract- *Glass of the system: (45-x) P2O5:10ZnO:10Li2O:10CaO:10K2O:15Nb2O5:xPr6O11. (Where x=1, 1.5,2 mol %) have been prepared by melt-quenching method. The amorphous nature of the prepared glass samples was confirmed by X-ray diffraction. Optical absorption, Excitation and fluorescence 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 (τR) and stimulated emission cross–section (σp) of various emission lines have been evaluated.*

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

Introduction

Rare earth glasses have attracted much attention, because they have large practical and potential applications in many fields, such as infrared sensors, glass lasers, optical fiber amplifiers, phosphors, electro-luminescent devices, memory devices and flat-panel displays [1–5].Phosphate glass is an extremely promising material for laser, mechanical sensors, reflecting windows 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].They have high thermal stability, high transparency, a low melting point, a high gain density and low dispersion rates [11-15]. The addition of ZnO increases both the tendency of glass formation, refractive index while decreases the optical energy band gap[16].Among active rare-earth ions Pr^{3+} exhibits high solubility in ceramic glasses, which also possess excellent optical and physical properties [17-22].

The present work reports on the preparation and characterization of rare earth doped heavy metal oxide (HMO) glass systems for lasing materials. We have studied on the Optical absorption and fluorescence properties of Pr^{3+} doped Zinc Lithium Calcium Potassiumniobate Phosphateglasses. 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), 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 Techniques

Preparation of glasses

The following Pr^{3+} doped Zinc Lithium Calcium Potassiumniobate Phosphate glass samples(45-x)P_2O_5:10ZnO:10Li_2O:10CaO:10K_2O:15Nb_2O_5: 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,CaO,K_2O,$Nb_2O_5$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 1175^0C, for preparation of Zinc Lithium Calcium Potassiumniobate Phosphate 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 100^0C. While pouring; the temperature of crucible was also maintained to prevent crystallization. And annealed at temperature of 350^0C 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 %)
ZLCPNP (UD)	45P_2O_5:10ZnO:10Li_2O:10CaO:10K_2O:15Nb_2O_5
ZLCPNP (PR1)	44P_2O_5:10ZnO:10Li_2O:10CaO:10K_2O:15Nb_2O_5:1 Pr_6O_{11}
ZLCPNP(PR 1.5)	43.5P_2O_5:10ZnO:10Li_2O:10CaO:10K_2O:15Nb_2O_5: 1.5 Pr_6O_{11}
ZLCPNP (PR2)	43P_2O_5:10ZnO:10Li_2O:10CaO:10K_2O:15Nb_2O_5: 2 Pr_6O_{11}
ZLCPNP (UD)- RepresentsundopedZinc Lithium Calcium Potassiumniobate Phosphateglass specimen.	
ZLCPNP(PR) -Represents Pr^{3+} dopedZinc Lithium Calcium Potassiumniobate Phosphate glass specimens.	

Theory

Oscillator Strength

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

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

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 [24].

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

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

Judd-Ofelt Intensity Parameters

According to Judd [25] and Ofelt [26] 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:

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

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

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

$\lambda = 2, 4, 6$

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.

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:

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

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

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

S L J

where, the sum is over all terminal manifolds.

The radiative life time is given by

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

S L J

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

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

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 [27, 28]. The Nephelauxetic Ratio is given by

$$\beta' = \frac{\nu_g}{\nu_a} \tag{9}$$

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

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

Result and Discussion

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.

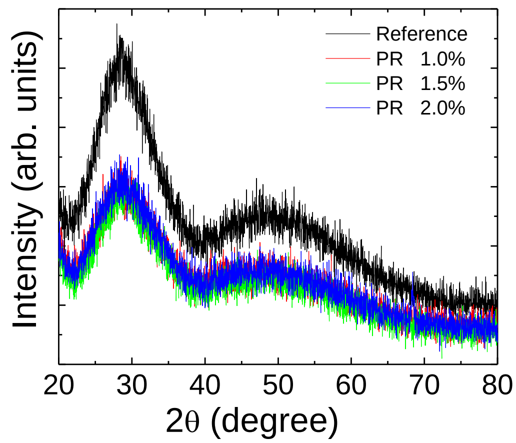

Fig.1: X-ray diffraction pattern of ZLCPNP (PR) glasses.

Absorption spectra

The absorption spectra of ZLCPNP (PR) glasses, consists of 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 ZLCPNP PR(01) glass.

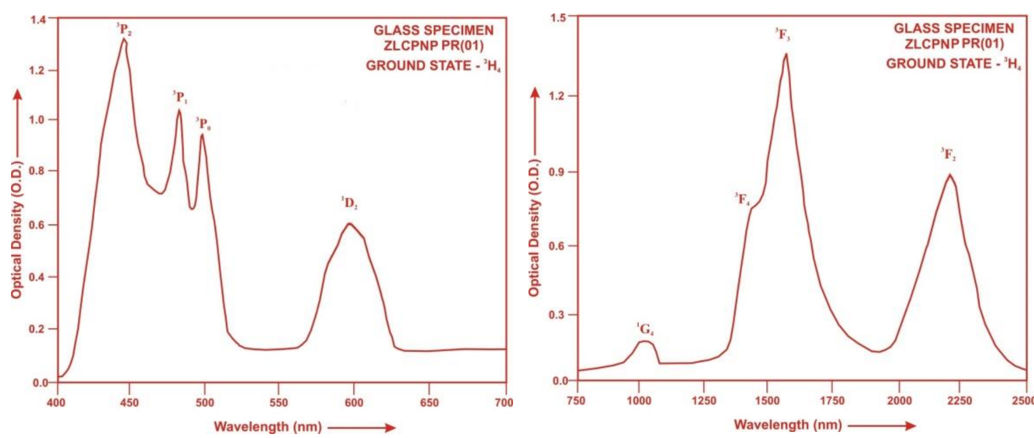

Fig.2: Absorption spectra of ZLCPNP (PR01) glass.

The experimental and calculated oscillator strengths for Pr^{3+} ions in zinc lithium calcium potassium iodate phosphate glasses are given in Table 2

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

Energy level $^3H_4$	**Glass ZLCPNP (PR01)**		**Glass ZLCPNP (PR1.5)**		**Glass ZLCPNP (PR02)**	
	$P_{exp.}$	$P_{cal.}$	$P_{exp.}$	$P_{cal.}$	$P_{exp.}$	$P_{cal.}$
$^3F_2$	5.758	4.858	5.648	4.828	5.436	4.725
$^3F_3$	8.325	7.284	8.243	7.304	7.843	7.075
$^3F_4$	5.568	4.597	5.478	4.568	5.268	4.405
$^1G_4$	0.486	0.381	0.372	0.380	0.284	0.367
$^1D_2$	4.225	1.296	4.186	1.295	3.642	1.252
$^3P_0$	4.455	1.515	4.278	1.649	3.825	1.649
$^3P_1$	5.648	1.537	5.536	1.672	5.342	1.672
$^3P_2$	12.768	4.274	11.849	4.270	10.642	4.125
R.m.s.deviation	3.6932		3.3545		2.9206	

The ratio of Racah parameters E^1/E^3 and E^2/E^3 are about 9.78 and 0.048 respectively. Computed values of Slater-Condon, Lande′, Racah, nephelauexeticratio and bonding parameter for Pr^{3+}dopedZLCPNP glass specimens are given in Table 3.

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

Parameter	**Free ion**	**ZLCPNP(PR01)**	**ZLCPNP (PR1.5)**	**ZLCPNP (PR02)**
$F_2(cm^{-1})$	322.09	299.99	300.00	300.02
$F_4(cm^{-1})$	44.46	44.25	44.27	44.29
$F_6(cm^{-1})$	4.867	4.410	4.412	4.414
$\xi_{4f}(cm^{-1})$	741.00	858.77	858.44	858.18
$E^1(cm^{-1})$	4728.92	4450.06	4450.94	4452.07
$E^2(cm^{-1})$	24.75	22.013	22.01	22.01
$E^3(cm^{-1})$	478.10	454.70	454.73	454.74
F_4/F_2	0.13805	0.14750	0.14755	0.14762
F_6/F_2	0.01511	0.01470	0.01471	0.01471
E^1/E^3	9.8911	9.78689	9.7881	9.7905
E^2/E^3	0.0518	0.04841	0.04840	0.04839
β'		0.88846	0.88867	0.88895
$b^{1/2}$		0.23616	0.23593	0.23564

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

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

Glass Specimen	$\Omega_2(pm^2)$	$\Omega_4(pm^2)$	$\Omega_6(pm^2)$	Ω_4/Ω_6
ZLCPNP(PR01)	2.871	1.315	4.001	0.3287
ZLCPNP(PR1.5)	2.789	1.429	3.962	0.3607
ZLCPNP(PR02)	2.714	1.428	3.811	0.3747

Fluorescence Spectrum

The fluorescence spectrum of Pr^{3+}doped in zinc lithium calcium potassiumniobatephosphate glass is shown in Figure 3. 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.

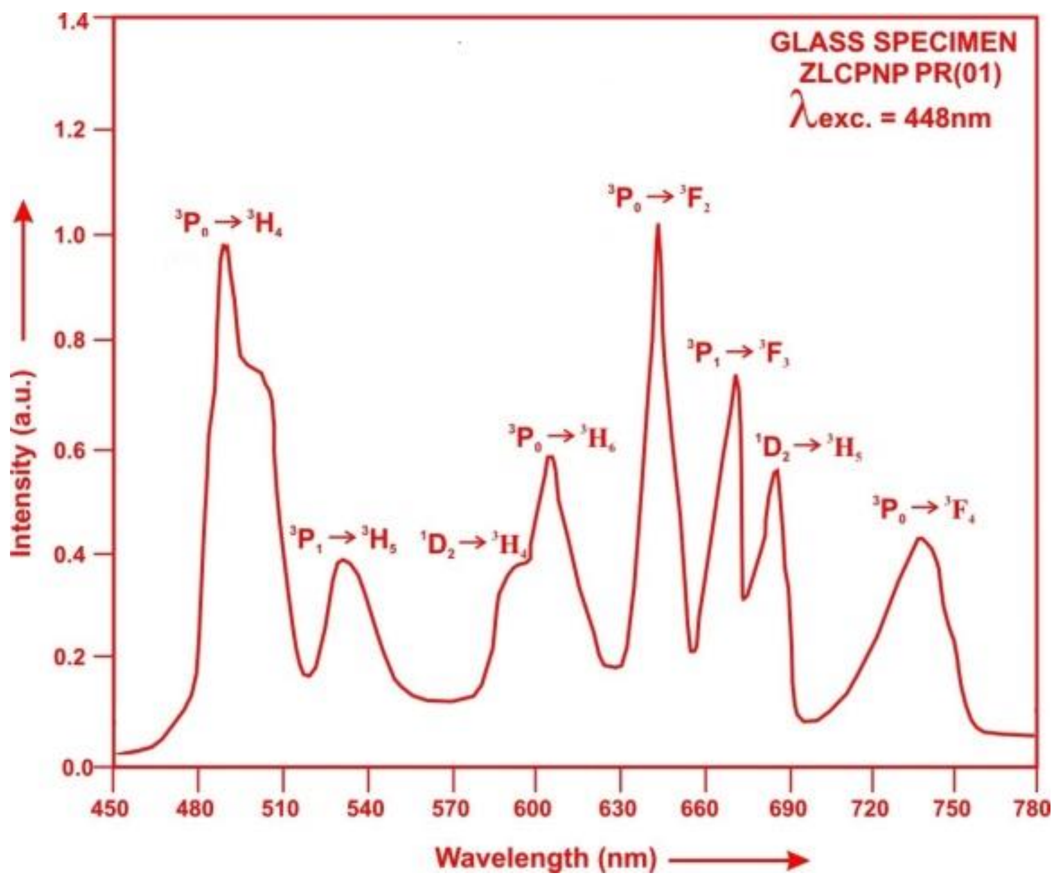

Fig.3: Fluorescence spectrum of ZLCPNP (PR01) glass.

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 ZLCPNP glasses.

Transition		ZLCPNP(PR 01)				ZLCPNP(PR 1.5)				ZLCPNP (PR 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)
$^3P_0 \rightarrow ^3H_4$	485	980.67	0.0900	0.378		1068.37	0.0975	0.491		1068.99	0.0995	0.666	
$^3P_1 \rightarrow ^3H_5$	532	1978.71	0.1817	0.368		2061.22	0.1881	0.405		2027.85	0.1888	0.422	
$^1D_2 \rightarrow ^3H_4$	599	519.56	0.0477	0.188		520.07	0.0475	0.200		503.39	0.0469	0.214	
$^3P_0 \rightarrow ^3H_6$	602	458.09	0.0421	0.240	91.81	454.48	0.0415	0.272	91.27	437.99	0.0408	0.301	93.12
$^3P_0 \rightarrow ^3F_2$	643	2840.83	0.2608	2.820		2764.94	0.2524	3.175		2695.70	0.2510	3.672	
$^3P_1 \rightarrow ^3F_3$	676	3927.40	0.3606	1.988		3884.17	0.3545	2.126		3802.17	0.3541	2.299	
$^1D_2 \rightarrow ^3H_5$	685	5.185	0.00048	0.0055		5.45	0.00050	0.0071		5.381	0.0050	0.0081	
$^3P_0 \rightarrow ^3F_4$	730	181.26	0.0166	0.127		197.35	0.0180	0.147		197.59	0.0184	0.1554	

Conclusion

In the present study, the glass samples of composition (45-x):P_2O_5:10ZnO:10Li_2O:10CaO:10K_2O:15Nb_2O_5: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 ($^3P_0 \rightarrow ^3F_2$) forglass ZLCPNP(PR 01), suggesting that glass ZLCPNP(PR01) is better compared to the other two glass systems ZLCPNP(PR1.5) and ZLCPNP(PR02).

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