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ABSORPTION AND EMISSION PROPERTIES OF PR(III) DOPED CALCIUM BORAX GLASSES

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ABSTRACT:

Optical absorption and photoluminescence spectra of Pr(III) doped calcium borax glasses are presented. The observed spectra have been analyzed to calculate oscillator strengths (f), the Judd-Ofelt intensity parameters (Ω_λ). The radiative parameters namely, transition probabilities (A, Aτ), branching ratios (β_R %), lifetimes (τ_R µsec) and stimulated emission cross-sections (σ_P λcm^2) are also evaluated for the different glass compositions and shown to change with chemical compositions.

Keywords — Praseodymium ions, borax glass, Judd-Ofelt

INTRODUCTION:-

Optical properties like optical absorption and luminescence spectra of various rare earth (RE) ions doped calcium and mixed borate glasses have been extensively investigated in the recent years [1–5]. Glasses doped with trivalent rare earth praseodymium ion have become important optical materials for use in the field of optical devices such as optical fibre lasers, as amplifiers [6-7]. The trivalent state of praseodymium in calcium borax glass provides rich emission spectrum from UV to visible due to radiative transitions from the excited $^5d_1$, $^3P_1$, $^3P_0$ and $^1D_2$ states to the ground $^3H_4$ state. , moreover the quantum efficiency of the radiative transition $^5d_1 \rightarrow {}^3H_4$ and $^1D_2 \rightarrow {}^3H_4$ transitions is unity and concentration independent. More interestingly there lies the possibility of up-conversion process populating $^3P_1(^3P_0)$ from $^1D_2$ state , the phenomenon can be utilized in the construction of up-conversion laser system. The potential application of calcium borax glass has led us to further studying the effect of borate groups on the spectral properties of trivalent praseodymium doped in such glass. In this paper we have reported the results of our investigations, characteristics have been investigated.

EXPERIMENTAL-

Samples of calcium borax glasses doped with Pr(III) and undoped borax glass concentration series of Pr3+ varying was prepared by melting a batch of $CaCO_3$ (Merck Chemical, 99.9%). The concentrations cited here were measured by chemical balance.

The glasses were melted in borosilicate glass crucibles in a electric furnace at around 650^0C for undoped borax glass and at around 750^0C for calcium doped borax glasses in air. The resulting melts were held for 1h, to ensure complete polymerization. The molten glasses were poured into a glass plate, chilled; the glass samples removed from the mould, and annealed at an appropriate temperature and to release strains and then cooled to room temperature. Glass disc of diameter 2cm were used for spectral studies. All absorption spectra at room temperature were recorded in a UV-VIS recording spectrophotometer (Perkin Elmer Lambda 3B) by photon counting techniques. The emission measurement was done in ratio mode (emission signal/reference signal) useful to compensate for changes in the intensity of excitation radiation. The emission spectra thus obtained is termed corrected emission spectra. The OH contents are usually determined by the absorption coefficient at 3000 cm^{-1} which was calculated from absorption spectra measured in a FTIR spectrometer (Perkin-Elmer, model no. 1615). Density measurements were made by Archimedes method using benzene as the immersion liquid.

THEORY- The observed intensities of the corresponding absorption peaks were determined in terms of oscillator strengths (f_{exp}) from the expression[8,9]

$$P = 4.318 \times 10^{-9} \times \frac{Sa.\ M_x.\ M_Y}{l.C} \qquad \text{----------(1)}$$

Where

P = Calculated oscillator strength for a specific f-f transition.

l = Thickness of the glass sample.

S = Area in sq. cm of the band in cm^2 .

M_x = Rate of change of energy along base line with unit length (in cm)

i.e. ($\Sigma\Delta E$/cm).

ΔE = Difference in energy of beginning and end of the peak.

M_Y = Rate of change of intensity of absorption per sq. cm.

The calculated value of oscillator strength is used to evaluate the τ_λ values. This involves making of ψ (in cm^{-1}) values for each spectral band and obtaining a sum of these products with the tensor operators $(U^\lambda)^{(R)}$ for each λ wave i.e. 2,4,6 for Pr (III). The oscillator strength and the E^*U^λ product subjected to matrix calculation Ω_λ (Judd-ofelt intensity)

$$P = \Omega_2 U^2 + \Omega_4 U^4 + \Omega_6 U^6 \qquad \text{---------- (2)}$$

These values have been determined using three and four-parameter expression, which was evaluated using self devised PASCAL compiled computer program [18].

In the Judd-Ofelt theory the electric dipole line strength (S_{ed}) of a transition is given by(8)

$$S_{ed} = e^2 \sum_{2,4,6} \Omega_\lambda \langle \psi j || U^\lambda || \psi' j' \rangle^2 \qquad \text{---------- (3)}$$

Where Ω_λ is given by

$$\Omega_\lambda = \frac{3h}{8\pi^2 mc} \cdot \frac{9n\,(2j+1)T_\lambda}{(n^2+2)^2} \qquad \text{---------- (4)}$$

Ω_λ (λ= 2,4,6) are the judd-ofelt intensity parameters and T_λ(λ= 2,4,6) are the adjustable judd-ofelt parameters obtained from least square analysis of experimental oscillator strengths and the matrix elements are composed of U^λ the unit tensor operator connecting the initial and final states of ψj and $\psi' j'$ respectively arising from the electronic configuration f^N. The reduced matrix elements of the unit tensor operator U^λ evaluated in the intermediate coupling scheme are almost insensitive to the ion environment (9-10). We have used the U^λ values give in the literature (11).

The matrix values of $\langle \psi j || L+2S || \psi' j' \rangle^2$ were evaluated from following carnall et al (12). The theoretical oscillator strength (f_{cal}) of a transition at wave number υ is given by

$$f_{cal} = \frac{8\pi^2 m c \ddot{u}}{3 h e^2 (2J+1)} \left[\frac{(n^2+2)^2}{9h} S_{ed} \right] \text{ ---------- (5)}$$

Where ü is the energy difference in wave number(cm^{-1}) between the two levels concerned.

The radiative transition probability A(ψJ, ψ'J') between the state ψJ and ψ'J' is given by (8)

$$A(\psi j, \psi' j') = \left[\frac{64\pi^4 v^3}{3h(2J+1)} \right] X \left[\frac{n(n^2+2)^2}{9} \right] S_{ed} \text{ ---------- (6)}$$

Where n is refractive index

The total radiative transition probability A_T (ψJ) is

$$A_T(\psi j) = \sum_{\psi' j'} A(\psi j, \psi' j')$$

Where the sum runs over all ψ'j' lower energy levels than ψj.

Since fluorescence level relaxation involves transition to several low-lying levels, therefore, the total radiative transition is calculated from the formula.

$$A_T(f^n \psi j) = \Sigma A(f^n \psi j + f' \psi' j)$$

The fluorescent branching ratio β_R are obtained from the relaxation state ψj to a particular final value is calculated using equation;

$$\beta_R(\psi J, \psi' J') = [A(\psi j, \psi' j') / A_T(\psi j)]$$

The total radiative life time of a state is given as

$$\tau_R(\psi j) = [A_T(\psi j)]^{-1}$$

The experimental branching ratios were obtained from the areas under the emission bands. The stimulated emission cross section (σ_P) of a given emission transition is calculated using the relationship (13)

$$\sigma_P(\lambda_P) = \frac{\lambda_P^4}{8\pi c n^2 \Delta\lambda_P} A(\psi j, \psi' j')$$

Where (λ_P) is the average emission wavelength, ($\Delta\lambda_P$) is the effective emission band width taken as the full width half maximum bandwidth at the corresponding emission peak and A (ψj, $\psi' j'$) the radiative transition probability.

RESULTS AND DISCUSSION-

The various physical parameters like the density, Refractive index and volume values for given glass composition are given table (1) and the absorption spectra at room temperature of Pr(III) doped glasses are shown in fig (1). The spectral lines are assigned in analogy with given in literature (14). There are several groups of line characteristics of 4f-4f absorption of trivalent Pr(III) which corresponds to $^3H_4$ ground state to the $^3P_0$, $^3P_1$, $^3P_2$ and $^1D_2$ states respectively. The experimental f values obtained are listed in table (1), have been used to determine in JO parameters. In this calculation the reduced matrix elements for three transitions are taken into account. The JO parameters values calculated with these parameters are also listed in table (1). The experimental and calculated oscillator strength values shows a very good agreement according to Jorgensen and Reisfeld (15), the Ω_2 parameter is indicative of the account of covalent bonding from the table (1), it can be concluded that calcium borax glass is more ionic in character compare to glasses doped with borate group. The experimental f values obtained are given in table (1). Considering the RE ions in the center of the cube an average RE-O distance is calculated to be 2.07 A^0 for borate, 2.22 A^0 for phosphate and 2.29 A^0 for silicate (16). Hence the size of the cube will be silicate > phosphate> borate. Hence oscillator strength will also follow the above sequence.

Table (1):- Physical properties of calcium Borax glass sample doped with Pr(III) ions.

Glass Composition	Density (gm/cm^3)	Refractive Index	Transition	S_{ed}	F_{exp}	F_{cal}	w_λ
Calcium Borax (Base)	2.52	1.51	-	-	-	-	-
Calcium Borax with Pr(III) Doped	2.60	1.53	$^3H_4$-$^3P_2$ -$^3P_1$ -$^3P_0$ -$^1D_2$	71.2 20.3 23.2 19.3	11.1 5.2 2.1 1.8	10.1 2.8 2.1 1.8	Ω_2=20.3 Ω_4= 7.23 Ω_6= 21.5

The radiative properties such as the radiatve transition ($Asec^{-1}$), total radiative relaxation rate (A_T μsec) of florescent levels and stimulated emission cross-section (σ_P^λ cm^2) have been evaluated for all the recorded emission bands and are given in table (2) along with the measured emission peak wavelength (λ_P nm) and effective half bandwidths ($\Delta\lambda_P$ nm). The radiative properties of Ln(III) ions in glasses doped on a number of factors such as the network former and modifier in the glass and the refractive index (17).

Table (2):- Some measured spectral Parameter of Pr(III) doped calcium borax glasses:-

Emission transition	Measured emission	Effective bandwidth	Radiative Transition Probability	Total radiative Relaxation rate	Branching ratio	Stimulated Emission cross section	Radiative lifetime
$^3P_0$- $^3H_4$	463	20	263	13057	23	4.2	359
$^3P_0$- $^3H_5$	520	28	1665	13057	15	3.2	547
$^3P_0$- $^3H_6$	571	26	7131	13057	57.7	25.7	143
$^3P_0$- $^3F_2$	619	14	1013	13057	9.3	8.9	1031

The experimental values of radiative lifetime is found to be sometimes less than the calculated values. The difference between the calculated and measured lifetimes arises due to multiphonon relaxation and cross relaxation between pars of RE ions. The β_R values obtained here is quite large and with the introduction of borax group, it increases enormously. From the very high value of branching ratios together with the higher values of stimulated emission cross sections it seems to be that the matrix can found potential application in the field of laser.

CONCLUSION –

the increment of Ω_2 values with the introduction of borax, indicates the increment of covalence of glass matrices. The borax group has tremendous effects on the radiative properties. All the spectral parameters suggest that calcium borax glasses doped with rare earth can have potential application in the field of lasers.

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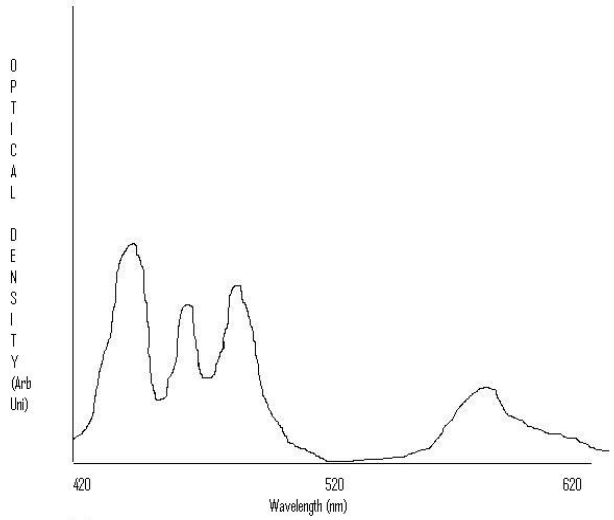
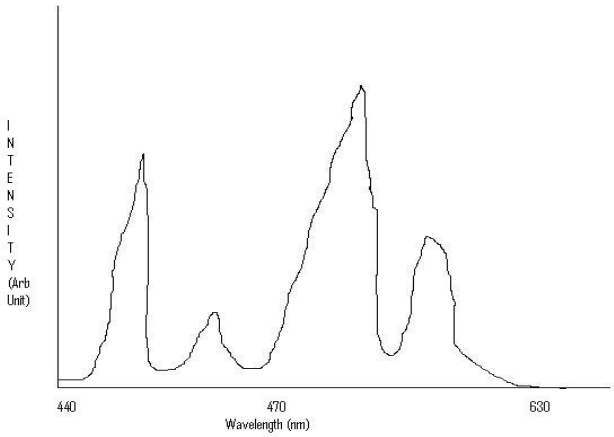


Fig (1) :- Absorption Spectra of Pr(III) Doped Calcium Borax Glasses



Fig(2):- Emission spectra of Pr(III) Doped borax Glasses.