

## Correlation of radiative properties of rare earth ions ( $\text{Pr}^{3+}$ and $\text{Nd}^{3+}$ ) in chlorophosphate glasses—0.1 and 0.5 mol% concentrations

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**Abstract.** Optical properties of chlorophosphate glasses of the type  $50\text{P}_2\text{O}_5-30\text{Na}_2\text{HPO}_4-20\text{RCl}$  (R = potassium and lead) activated by 0.1 and 0.5 mol% of  $\text{Pr}^{3+}$  and  $\text{Nd}^{3+}$  have been investigated. Optical band gaps ( $E_{\text{opt}}$ ) have been reported for 0.1 and 0.5 mol% concentrations of  $\text{Pr}^{3+}$  and  $\text{Nd}^{3+}$  doped potassium and lead chlorophosphate glasses. Energy levels and optical transitions of  $\text{Pr}^{3+}$  and  $\text{Nd}^{3+}$  are assigned. Spectroscopic parameters ( $E^1$ ,  $E^2$ ,  $E^3$ ,  $x_{\text{if}}$  and  $a$ ), spectral intensities ( $f_{\text{expt}}$ ), Judd–Ofelt intensity parameters ( $\Omega_2$ ,  $\Omega_4$  and  $\Omega_6$ ) and radiative lifetimes ( $t_{\text{R}}$ ) are correlated for 0.1 and 0.5 mol% concentrations of these two ions in potassium and lead chlorophosphate glasses.

**Keywords.** Optical band gaps; spectroscopic parameters; intensity parameters; radiative lifetimes.

### 1. Introduction

Generally phosphate glasses possess low refractive index and low dispersion and so they are good candidates to minimize self-focusing effects of laser radiation (Weber 1990; Peng and Day 1991). Several authors reported the spectroscopic investigations of rare earth ions in different phosphate and fluorophosphate glasses (Joshi and Joshi 1992; Balda *et al* 1994; Binnemans *et al* 1998; Jiang *et al* 1998). Optical absorption spectra and energy band gaps in praseodymium borophosphate glasses were reported by Sharma *et al* (1995). Neto *et al* (1995) reported the optical properties of praseodymium doped fluoride glasses. Jurdyc *et al* (1997) studied the laser spectroscopy of  $\text{Pr}^{3+}$  doped germanium sulphide based glasses. Judd–Ofelt analysis and multiphonon relaxations of rare earth ions in fluorohafnate glasses were given by Cases and Chamarro (1991). Spectroscopic properties of rare earth doped calcium aluminate based glasses were reported by Uhlmann *et al* (1994).

Cases *et al* (1991) studied the optical properties of  $\text{Nd}^{3+}$  ions in  $\text{ZnF}_2\text{--CdF}_2$  based glasses. Optical properties of  $\text{Nd}^{3+}$  in tellurite and phosphotellurite glasses were studied by Weber *et al* (1981). Details of preparation of  $\text{Nd}^{3+}$  doped fluorozirconate glass laser fibre were given by Hu *et al* (1995). Gatterer *et al* (1998) reported the suitability of Nd(III) absorption spectroscopy to probe the structure of glasses from the ternary system  $\text{Na}_2\text{O--B}_2\text{O}_3\text{--SiO}_2$ . Previously Ratnakaram and Viswanadha Reddy (2000a, b) reported the spectroscopic investigations of  $\text{Pr}^{3+}$  and  $\text{Nd}^{3+}$  doped different chlorophosphate glasses in 0.5 mol%

concentrations of rare earth ions. These results included optical band gaps, spectral intensities, intensity parameters, radiative lifetimes and branching ratios. These results stimulated the present investigation of spectroscopic studies of  $\text{Pr}^{3+}$  and  $\text{Nd}^{3+}$  ions in 0.1 mol% concentration in potassium and lead chlorophosphate glasses.

In this paper, we report the spectral studies of  $\text{Pr}^{3+}$  and  $\text{Nd}^{3+}$  ions in potassium and lead chlorophosphate glasses in 0.1 and 0.5 mol% concentrations. These glasses are of the type  $50\text{P}_2\text{O}_5-30\text{Na}_2\text{HPO}_4-20\text{RCl}$  (R = potassium and lead). The aim of this study is to investigate the influence of the concentration of rare earth ions on optical band gaps, spectral intensities and radiative lifetimes.

### 2. Experimental

The analar grades of  $\text{P}_2\text{O}_5$ ,  $\text{Na}_2\text{HPO}_4$ ,  $\text{KCl}$  and  $\text{PbCl}_2$  were purchased from E. Merck India Ltd., Bombay and  $\text{PrCl}_3$  and  $\text{NdCl}_3$  were obtained from M/s Indian Rare Earth Ltd., Kerala. All these chemicals were of 99.9% purity. The general composition of the glass was  $50\text{P}_2\text{O}_5$ ,  $30\text{Na}_2\text{HPO}_4$  and  $20\text{RCl}$  (R = K and Pb). The rare earths were added in 0.1 and 0.5 mol% concentrations to the above glass composition. The glass samples were prepared by melting the required amounts of above chemicals in a specially made clay crucible at a temperature of  $1100^\circ\text{C}$ . The details of preparation of these glasses were explained elsewhere (Ratnakaram and Viswanadha Reddy 2000a). Density of the glass samples was determined by Archimedes principle using xylene as the immersion liquid with an accuracy of  $\pm 0.005 \text{ g/cm}^3$ . The glass refractive indices were measured using Abbe's refractometer with an accuracy of  $\pm 0.001$ . The absorption spectra were recorded at room temperature in UV–VIS–

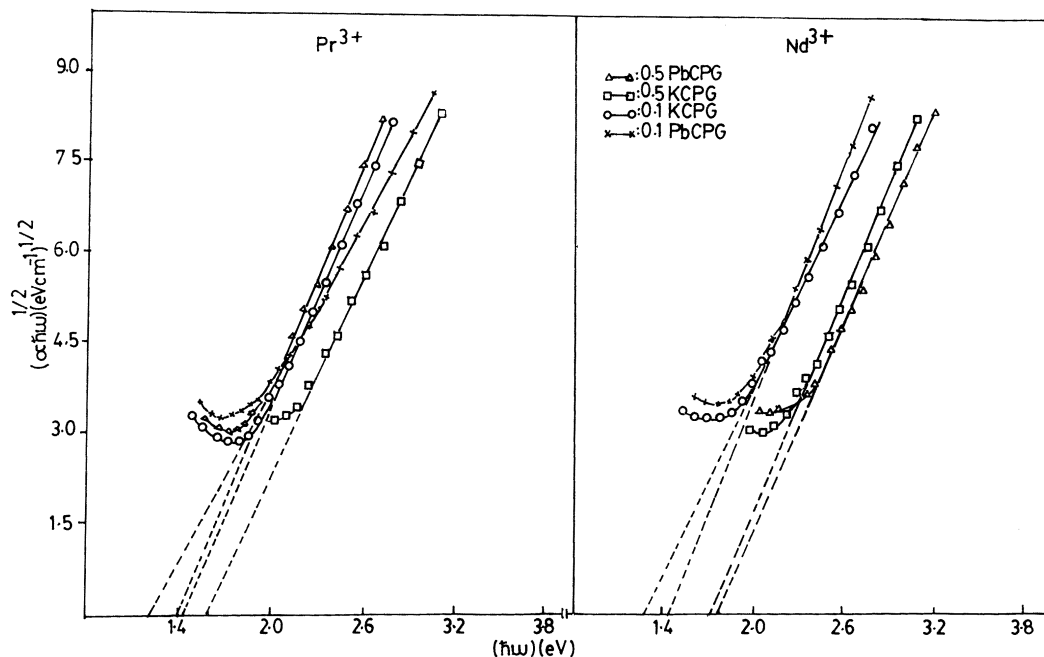
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NIR region using Hitachi U-3400 UV-VIS-NIR double beam spectrophotometer.

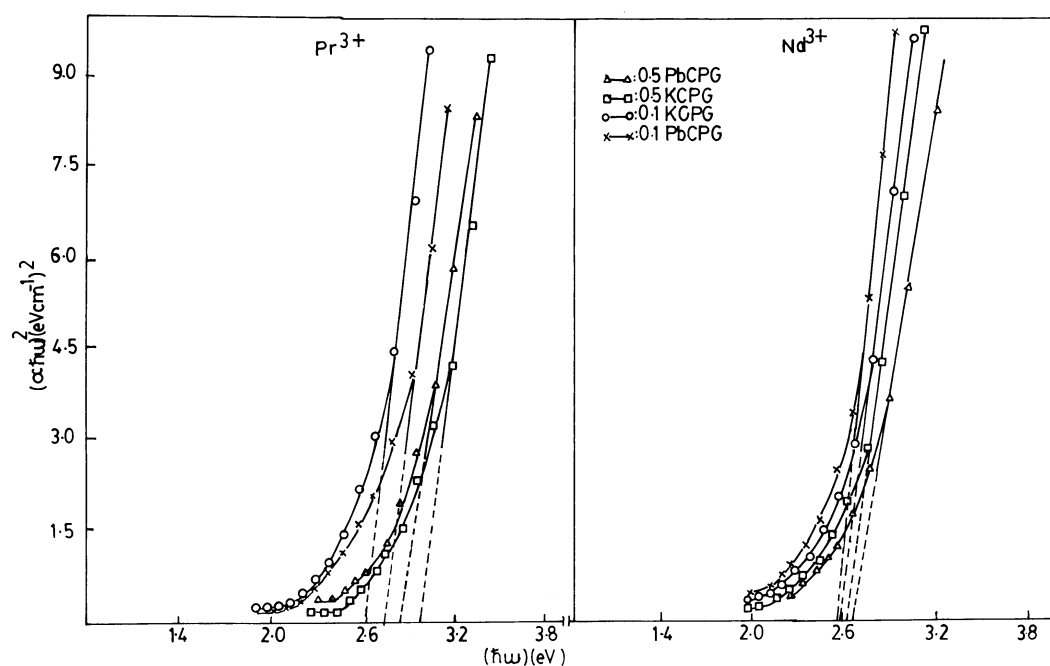
### 3. Results and discussion

Using Davis and Mott (1970) theory, the optical data are analysed for higher values of  $a(w)$  above the exponential

region by plotting  $(a\hbar w)^{1/2}$  as a function of photon energy,  $\hbar w$  for indirect transitions and by plotting  $(a\hbar w)^2$  as a function of  $\hbar w$  for direct transitions for  $\text{Pr}^{3+}$  and  $\text{Nd}^{3+}$  ions as shown in figures 1 and 2, respectively. The optical band gap, ' $E_{\text{opt}}$ ' values are obtained by extrapolation to  $(a\hbar w)^{1/2} = 0$  and  $(a\hbar w)^2 = 0$  and are presented in table 1 for both  $\text{Pr}^{3+}$  and  $\text{Nd}^{3+}$  ions in potassium and lead



**Figure 1.** Variation of  $(a\hbar w)^{1/2}$  with  $\hbar w$  for  $\text{Pr}^{3+}$  and  $\text{Nd}^{3+}$  doped potassium and lead chlorophosphate glasses (0.1 and 0.5 mol% concentrations).



**Figure 2.** Variation of  $(a\hbar w)^2$  with  $\hbar w$  for  $\text{Pr}^{3+}$  and  $\text{Nd}^{3+}$  doped potassium and lead chlorophosphate glasses (0.1 and 0.5 mol% concentrations).

chlorophosphate glasses. From the table, it is observed that optical band gap values increased with increasing concentration of lanthanide ion for both direct and indirect transitions in the two glasses.

The absorption spectra of  $Pr^{3+}$  and  $Nd^{3+}$  ions in potassium and lead chlorophosphate glasses are shown in figures 3–6. The energy,  $E_J$ , of the  $J$ th level may be written in Taylor's series expansion (Wong 1961, 1963) as

$$E_J = E_{0J} + \sum_{k=1}^3 \frac{dE_J}{dE^k} \Delta E^k + \frac{dE_J}{dx} \Delta x_{4f} + \frac{dE_J}{da} \Delta a, \quad (1)$$

where  $E_{0J}$  is the zero order energy of the  $J$ th level and  $dE_J/dE^k$ ,  $dE_J/dx$  and  $dE_J/da$  are partial derivatives. Using experimental energies as  $E_J$ , the numerical values of zero order energies and partial derivatives, a number of linear

equations equal to the number of observed levels are formed and the  $\Delta$  values are calculated by using the least squares fit method. The  $E^k$ ,  $x_{4f}$  and  $a$  parameters are evaluated from

$$E^k = E_0^k + \Delta E^k, \quad (2)$$

$$x_{4f} = x^0 + \Delta a, \quad (3)$$

and

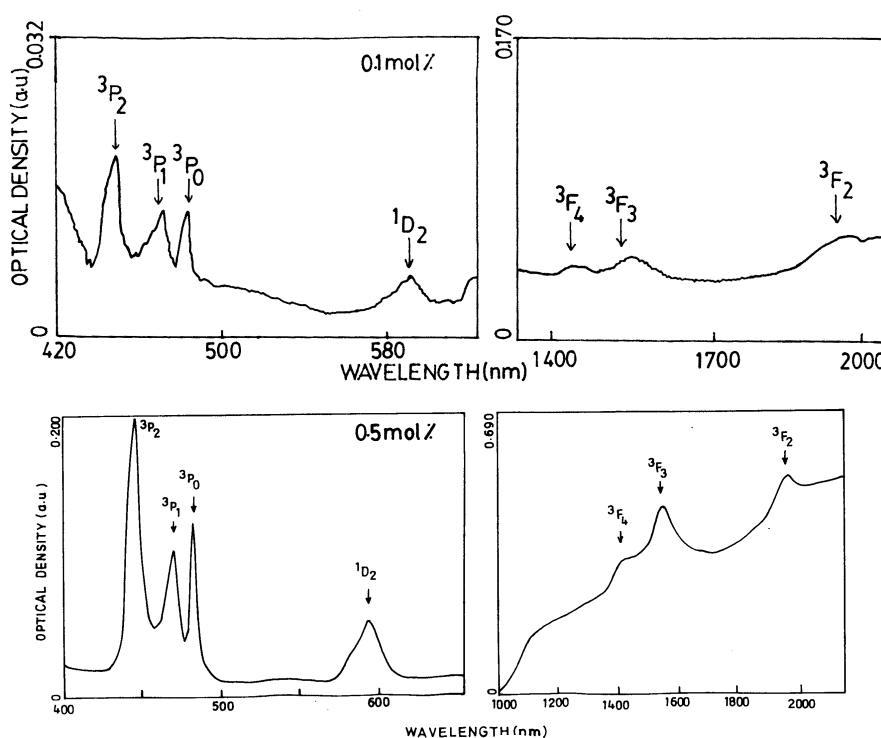
$$a = a^0 + \Delta a, \quad (4)$$

where  $E_0^k$ ,  $x^0$  and  $a^0$  are the aquo ion parameters with which the partial derivatives are evaluated. The experimental energies of  $Pr^{3+}$  and  $Nd^{3+}$  ions in 0.1 and 0.5 mol% concentrations of rare earth ion for both

**Table 1.** Optical band gaps ( $E_{opt}$ , eV) for indirect and direct transitions of  $Pr^{3+}$  and  $Nd^{3+}$  doped potassium (KCPG) and lead (PbCPG) chlorophosphate glasses in different concentrations (concentration values are in mol%).

Sl. no	Glass	$Pr^{3+}$				$Nd^{3+}$			
		Indirect		Direct		Indirect		Direct	
		0.10	0.50	0.10	0.50	0.10	0.50	0.10	0.50
1.	KCPG	1.42	1.59	2.62	2.94	1.30	1.71	2.60	2.65
2.	PbCPG	1.23	1.39	2.76	2.84	1.45	1.78	2.60	2.68

Glass composition:  $50P_2O_5-30Na_2HPO_4-20RCl$  (R = potassium and lead).



**Figure 3.** Optical absorption spectra of  $Pr^{3+}$  doped potassium chlorophosphate glass (0.1 and 0.5 mol% concentrations).

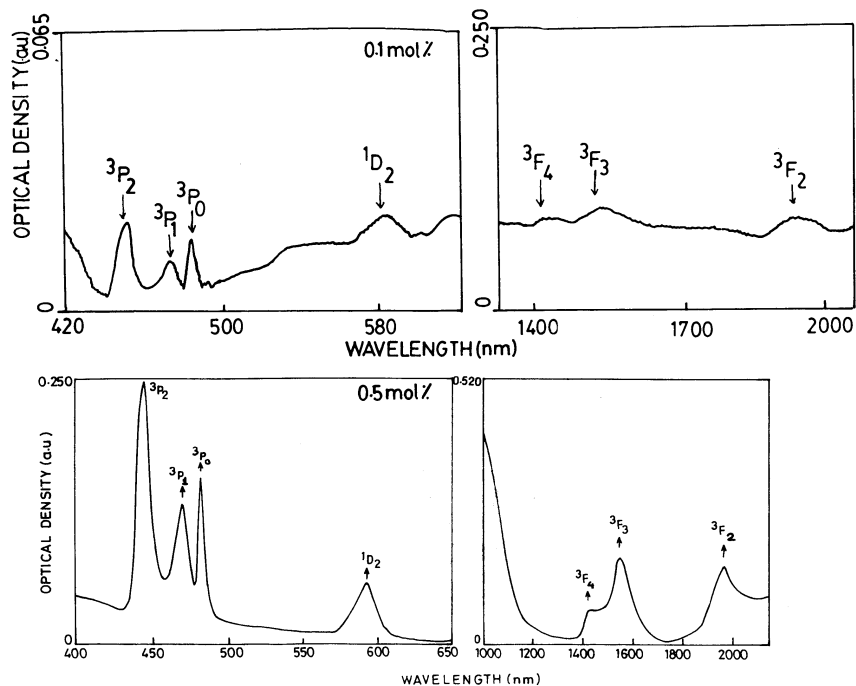


Figure 4. Optical absorption spectra of Pr<sup>3+</sup> doped lead chlorophosphate glass (0.1 and 0.5 mol% concentrations).

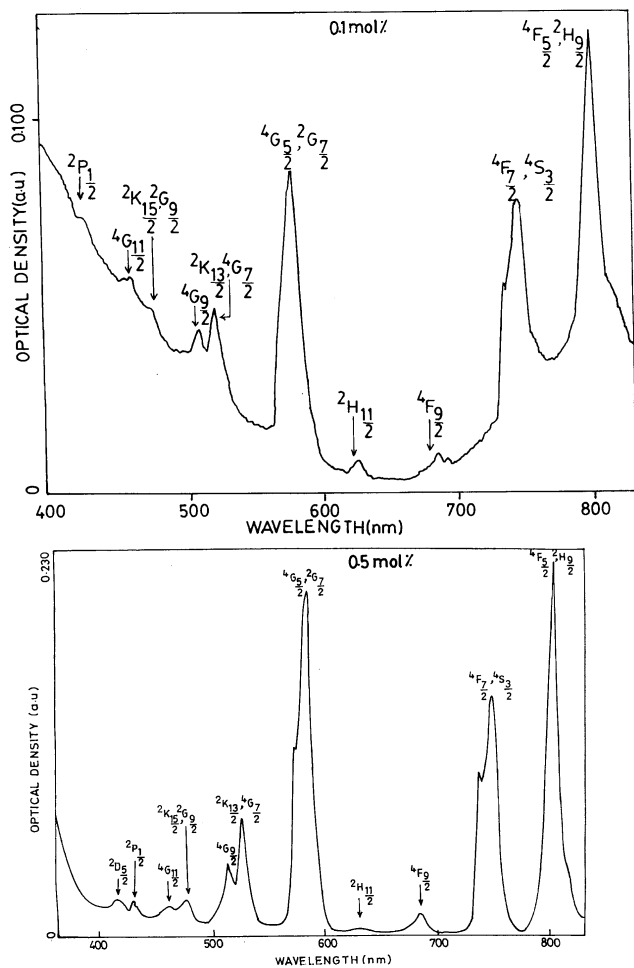


Figure 5. Optical absorption spectra of Nd<sup>3+</sup> doped potassium chlorophosphate glass (0.1 and 0.5 mol% concentrations).

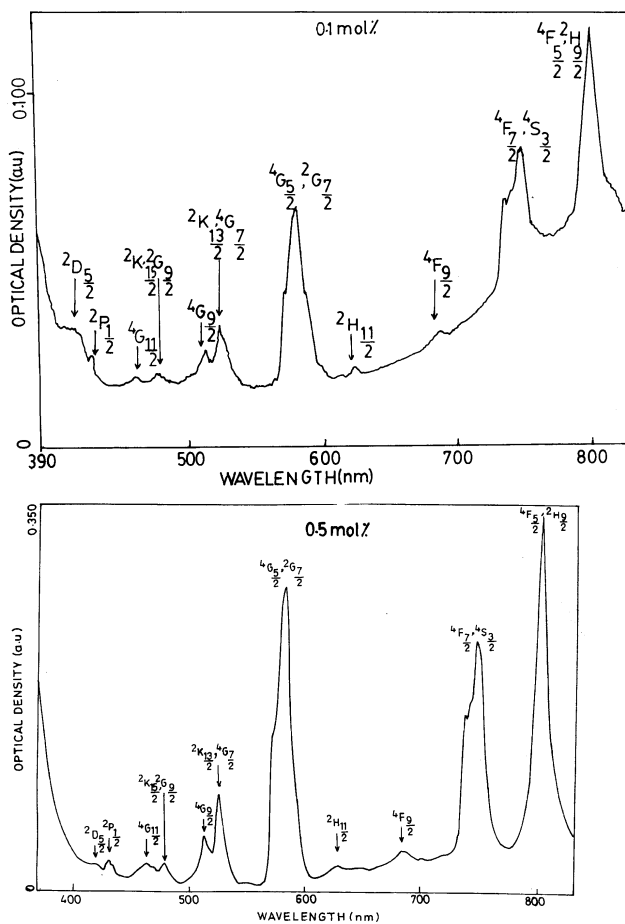


Figure 6. Optical absorption spectra of Nd<sup>3+</sup> doped lead chlorophosphate glass (0.1 and 0.5 mol% concentrations).

potassium and lead chlorophosphate glasses and various spectroscopic parameters ( $E^1$ ,  $E^2$ ,  $E^3$ ,  $x_{4f}$  and  $a$ ) are presented in table 2. In the case of Pr<sup>3+</sup> ion, as the observed levels are less in number, the parameter  $a$  is not evaluated. The rms deviations between experimental and calculated energies are also presented in table 2 and these values are within experimental error.

The intensities of the absorption bands are determined using the formula

$$f_{\text{exp}} = 4.32 \times 10^{-9} \int e(\nu) d\nu, \quad (5)$$

where  $e(\nu)$  is molar extinction coefficient corresponding to the energy of the transition  $\nu$ . It is calculated from the Beer–Lambert's law

$$e(\nu) = \frac{1}{cl} \log \frac{I_0}{I}, \quad (6)$$

where  $c$  is the concentration of the lanthanide ion in mol/l,  $l$  the optical path length and  $\log(I_0/I)$  the optical density. In the present work, the intensity of all the bands are measured by taking the area of the each absorption band.

According to Judd–Ofelt (1962) theory

$$f_{\text{ed}} = \sum_{l=2,4,6} T_l \nu (f^N \psi J \| U^\lambda \| f^N \psi' J')^2, \quad (7)$$

the three parameters  $T_2$ ,  $T_4$  and  $T_6$  are evaluated using the experimental data employing least squares fit. The

squared reduced matrix elements  $\|U^\lambda\|^2$  in the above equation are calculated in the intermediate coupling case. As these values are insensitive to the environment, we have used the values given by Carnall *et al* (1978). With these  $T_2$ ,  $T_4$  and  $T_6$  parameters and squared reduced matrix elements, ' $f_{\text{cal}}$ ' values are obtained. The experimental spectral intensities for all the transitions of Pr<sup>3+</sup> and Nd<sup>3+</sup> ions in 0.1 and 0.5 mol% concentrations of rare earth ion in potassium and lead chlorophosphate glasses are presented in table 3. The rms deviations which show agreement between experimental and calculated spectral intensities are also presented in this table and these values are very low. From the table, it is observed that the spectral intensities are slightly higher for certain transitions in the case of 0.5 mol% of rare earth ion for both Pr<sup>3+</sup> and Nd<sup>3+</sup> ions in the two glasses. From the rms deviation values, it is observed that the Judd–Ofelt theory works less on Pr<sup>3+</sup> ion.

The Judd–Ofelt intensity parameters ( $\Omega_l$ ) are calculated from the formula

$$\Omega_l = \frac{3h}{8\pi^2 mc} \frac{9n}{(n^2 + 2)^2} (2J + 1) T_l, \quad (8)$$

where  $n$  is the refractive index of the medium. The calculated Judd–Ofelt intensity parameters  $\Omega_2$ ,  $\Omega_4$  and  $\Omega_6$  are also presented in table 3. Generally,  $\Omega_2$  parameter indicates the amount of covalent bonding between rare earth anion and chloride cation and  $\Omega_4$  and  $\Omega_6$  parameters indicate the rigidity of the host. From the table, it is observed that  $\Omega_2$  parameter is negative for Pr<sup>3+</sup> ion, which indicates

**Table 2.** Energies and various spectroscopic parameters of Pr<sup>3+</sup> and Nd<sup>3+</sup> doped potassium (KCPG) and lead (PbCPG) chlorophosphate glasses in different concentrations (energy values are in cm<sup>-1</sup> and concentration values are in mol%).

Sl. no.	Energy level	Pr <sup>3+</sup>				Energy level	Nd <sup>3+</sup>			
		KCPG		PbCPG			KCPG		PbCPG	
		0.1 $E_{\text{expt}}$	0.5 $E_{\text{expt}}$	0.1 $E_{\text{expt}}$	0.5 $E_{\text{expt}}$		0.1 $E_{\text{expt}}$	0.5 $E_{\text{expt}}$	0.1 $E_{\text{expt}}$	0.5 $E_{\text{expt}}$
1.	<sup>3</sup> F <sub>2</sub>	5105	5100	5110	5110	<sup>4</sup> F <sub>5/2</sub> , <sup>2</sup> H <sub>9/2</sub>	12470	12474	12474	12465
2.	<sup>3</sup> F <sub>3</sub>	6485	6470	6476	6480	<sup>4</sup> F <sub>7/2</sub> , <sup>4</sup> S <sub>3/2</sub>	13394	13390	13379	13390
3.	<sup>3</sup> F <sub>4</sub>	6916	6944	6957	6870	<sup>4</sup> F <sub>9/2</sub>	14575	14611	14596	14611
4.	<sup>1</sup> D <sub>2</sub>	16844	16884	16895	16885	<sup>2</sup> H <sub>11/2</sub>	16008	15965	15926	15863
5.	<sup>3</sup> P <sub>0</sub>	20771	20754	20780	20767	<sup>4</sup> G <sub>5/2</sub> , <sup>2</sup> G <sub>7/2</sub>	17171	17183	17183	17153
6.	<sup>3</sup> P <sub>1</sub>	21293	21307	21302	21307	<sup>2</sup> K <sub>13/2</sub> , <sup>4</sup> G <sub>7/2</sub>	19049	19071	19097	19057
7.	<sup>3</sup> P <sub>2</sub>	22455	22455	22455	22471	<sup>4</sup> G <sub>9/2</sub>	19491	19522	19514	19510
8.						<sup>2</sup> K <sub>15/2</sub> , <sup>2</sup> G <sub>9/2</sub>	20985	20976	20976	20936
9.						<sup>4</sup> G <sub>11/2</sub>	21671	21604	21625	21615
10.						<sup>2</sup> P <sub>1/2</sub>	23309	23200	23330	23260
11.						<sup>2</sup> D <sub>5/2</sub>	24008	24083	–	23905
rms deviation:		± 227	± 225	± 229	± 221		± 74	± 98	± 89	± 100
	$E^1$	4675	4640	4725	4651		4961	5052	4973	5029
	$E^2$	20.9	21.3	20.8	21.2		24.7	23.5	24.3	23.6
	$E^3$	455	455	455	455		494	490	494	490
	$x_{4f}$	791	788	788	791		900	862	888	864
	$a$						6.64	– 1.98	4.90	– 2.12

that Judd–Ofelt theory works less well on  $\text{Pr}^{3+}$  ion. It is also observed that in the case of  $\text{Nd}^{3+}$  ion, the variation of  $\Omega_2$  parameter is more when compared with  $\Omega_4$  and  $\Omega_6$  parameters by varying the concentration. But for  $\text{Pr}^{3+}$  ion there is much variation in both  $\Omega_2$  and  $\Omega_6$  parameters. It indicates that in the case of  $\text{Nd}^{3+}$ , surrounding environment of the rare earth ion is different for different concentrations, but for  $\text{Pr}^{3+}$  ion, both the environment and rigidity changes with concentration. In the calculation of different radiative properties of rare earth ions, we have considered the magnitudes of intensity parameters.

The electric dipole line strengths are calculated employing the formula

$$S_{\text{ed}} = e^2 \sum_{l=2,4,6} \Omega_l (\psi J \| U^l \| \psi' J')^2, \quad (9)$$

The radiative transition probability is given by

$$A = \frac{64\pi^2 n^3}{3h(2J+1)} \frac{n(n^2+2)}{9} S_{\text{ed}}, \quad (10)$$

and is related to the radiative lifetime  $t_R$ , of an excited state by the expression

$$t_R = A_T(\psi J)^{-1}, \quad (11)$$

where  $A_T(\psi J)$ , is the total radiative transition probability.

Using the above expressions, the radiative lifetimes are estimated for certain excited states  ${}^3P_1$ ,  ${}^3P_0$ ,  ${}^1D_2$  and  ${}^3F_3$  of  $\text{Pr}^{3+}$  and  ${}^4G_{9/2}$ ,  ${}^4G_{7/2}$ ,  ${}^4G_{5/2}$ ,  ${}^2H_{11/2}$ ,  ${}^4F_{9/2}$ ,  ${}^4F_{5/2}$  and  ${}^4F_{3/2}$  of  $\text{Nd}^{3+}$  and are presented in table 4 for both 0.1 and 0.5 mol% concentrations in potassium and lead chlorophosphate glasses. From the table it is observed that the

**Table 3.** Spectral intensities and Judd–Ofelt intensity parameters ( $\Omega_2$ ,  $\Omega_4$ ,  $\Omega_6$ ,  $\times 10^{-20}$   $\text{cm}^2$ ) of  $\text{Pr}^{3+}$  and  $\text{Nd}^{3+}$  ions in potassium (KCPG) and lead (PbCPG) chlorophosphate glasses in different concentrations (concentration values are in mol%).

Sl. no.	Energy level	$\text{Pr}^{3+}$				Energy level	$\text{Nd}^{3+}$			
		KCPG		PbCPG			KCPG		PbCPG	
		0.1 $E_{\text{expt}}$	0.5 $E_{\text{expt}}$	0.1 $E_{\text{expt}}$	0.5 $E_{\text{expt}}$		0.1 $E_{\text{expt}}$	0.5 $E_{\text{expt}}$	0.1 $E_{\text{expt}}$	0.5 $E_{\text{expt}}$
1.	${}^3F_2$	2.621	3.346	4.262	4.219	${}^4F_{5/2}$ , ${}^2H_{9/2}$	3.804	3.946	2.306	2.548
2.	${}^3F_3$	5.435	15.359	5.270	11.374	${}^4F_{7/2}$ , ${}^4S_{3/2}$	2.981	3.905	1.853	2.678
3.	${}^3F_4$	1.882	10.659	1.360	6.542	${}^4F_{9/2}$	0.336	0.262	0.110	0.216
4.	${}^1D_2$	4.204	5.361	5.502	4.645	${}^2H_{11/2}$	0.055	0.249	0.114	0.604
5.	${}^3P_0$	3.858	7.083	3.157	5.329	${}^4G_{5/2}$ , ${}^2G_{7/2}$	7.931	9.079	3.919	5.667
6.	${}^3P_1$	7.206	11.363	3.734	11.514	${}^2K_{13/2}$ , ${}^4G_{7/2}$	2.171	2.368	1.058	1.276
7.	${}^3P_2$	16.439	22.887	12.028	21.642	${}^4G_{9/2}$	1.469	1.668	0.797	1.192
8.						${}^2K_{15/2}$ , ${}^2G_{9/2}$	0.335	0.807	0.037	0.346
9.						${}^4G_{11/2}$	0.095	0.343	0.164	0.354
10.						${}^2P_{1/2}$	0.110	0.235	0.063	0.151
11.						${}^2D_{5/2}$	1.262	0.195	–	0.068
rms deviation:		$\pm 7.01$	$\pm 6.85$	$\pm 5.31$	$\pm 7.79$		$\pm 0.53$	$\pm 0.31$	$\pm 0.23$	$\pm 0.33$
	$\Omega_2$	– 2.168	– 5.988	3.571	– 2.263		0.631	1.491	0.193	1.091
	$\Omega_4$	9.375	12.285	7.161	12.532		3.619	2.840	1.931	1.451
	$\Omega_6$	3.621	17.301	3.325	10.759		1.868	2.487	1.192	1.173

**Table 4.** Radiative lifetimes ( $t_R$ ,  $\mu\text{s}$ ) of certain excited states of  $\text{Pr}^{3+}$  and  $\text{Nd}^{3+}$  ions in potassium (KCPG) and lead (PbCPG) chlorophosphate glasses in different concentrations (concentration values are in mol%).

Sl no.	Excited level	$\text{Pr}^{3+}$				Excited level	$\text{Nd}^{3+}$			
		KCPG		PbCPG			KCPG		PbCPG	
		0.1	0.5	0.1	0.5		0.1	0.5	0.1	0.5
1.	${}^3P_1$	23	13	25	15	${}^4G_{9/2}$	219	196	438	317
2.	${}^3P_0$	21	13	24	15	${}^4G_{7/2}$	263	229	616	362
3.	${}^1D_2$	345	145	332	209	${}^4G_{5/2}$	170	150	332	239
4.	${}^3F_3$	1727	634	1933	876	${}^2H_{11/2}$	7358	6586	13965	10732
						${}^4F_{9/2}$	768	648	1247	703
						${}^4F_{5/2}$	568	532	954	844
						${}^4F_{3/2}$	702	665	1185	878

lifetime values decrease for all excited levels as the concentration increases for both  $\text{Pr}^{3+}$  and  $\text{Nd}^{3+}$  ions in these two glasses. Similar results have been reported by Balda *et al* (1999) and Adam *et al* (1999) in the case of  $\text{Pr}^{3+}$  doped fluorophosphate glasses and  $\text{Nd}^{3+}$  doped fluoroarsenate glasses, respectively.

#### 4. Conclusions

The optical band gaps ( $E_{\text{opt}}$ ) increase with the increase of concentration of rare earth ions for both indirect and direct transitions. Except for 0.5 mol% of  $\text{Pr}^{3+}$  ion in potassium chlorophosphate glass ( $\Omega_2 < \Omega_4 < \Omega_6$ ), the variation of magnitude of Judd–Ofelt intensity parameters is  $\Omega_2 < \Omega_6 < \Omega_4$  for 0.1 and 0.5 mol% concentrations. The variation of  $\Omega_2$  is more in the case of  $\text{Nd}^{3+}$  ion, whereas in the case of  $\text{Pr}^{3+}$ , both  $\Omega_2$  and  $\Omega_6$  parameters vary with concentration. The estimated radiative lifetimes for all the excited states of  $\text{Pr}^{3+}$  and  $\text{Nd}^{3+}$  ions decrease as the rare earth ion concentration increases. Similar results have been reported in fluorophosphate and fluoroarsenate glasses.

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#### References

- Adam J L, Balda R, Melscoet I, Smektala F, Lacha L M and Fernandez J 1999 *J. Non-Cryst. Solids* **256 & 257** 390
- Balda R, Fernandez J, Menidioroz A, Adam J L and Boulard B 1994 *J. Phys. Condens. Matter* **6** 913
- Balda R, Fernandez J, Adam J L, Mendioroz A and Arriandiaga M A 1999 *J. Non-Cryst. Solids* **256 & 257** 299
- Binnemans K, Van Deun R, Gorller-Walrand C and Adam J L 1998 *J. Non-Cryst. Solids* **238** 11
- Carnall W T, Cross White H and Cross White H M 1978 Energy level structure and transition probabilities of the trivalent lanthanides in  $\text{LaF}_3$ , Argonne National Laboratory Report, ANL-78-XX
- Cases R and Chamarro M A 1991 *J. Solid State Chem.* **90** 313
- Cases R, Chamarro M A, Alcala R and Rodriguez V D 1991 *J. Lumin.* **48** 509
- Davis F A and Mott N F 1970 *Philos. Mag.* **22** 903
- Gatterer K, Pucker G, Jantscher W, Fritzer H P and Arafa S 1998 *J. Non-Cryst. Solids* **231** 189
- Hu H, Yi G, Lin F, Qi C, Yu Y, Ye A and Gan F 1995 *J. Non-Cryst. Solids* **184** 218
- Jiang S, Myers M and Peyghambarian N 1998 *J. Non-Cryst. Solids* **239** 143
- Joshi B C and Joshi M C 1992 *J. Non-Cryst. Solids* **142** 171
- Judd B R 1962 *Phys. Rev.* **127** 750
- Jurdyc A M, Garapon C, Jacquier B, Meresse Y, Fonteneau G and Adam J L 1997 *J. Non-Cryst. Solids* **213 & 214** 231
- Neto J A M, Hewak B W and Tate H 1995 *J. Non-Cryst. Solids* **183** 201
- Ofelt G S 1962 *J. Chem. Phys.* **37** 511
- Peng Y B and Day D E 1991 *Glass Technol.* **32** 166
- Ratnakaram Y C and Viswanadha Reddy A 2000a *J. Non-Cryst. Solids* **277** 142
- Ratnakaram Y C and Viswanadha Reddy A 2000b *Phys. Chem. Glasses* **41** 121
- Sharma Y K, Mathur S C, Dube D C and Tandon S P 1995 *J. Mater. Sci. Lett.* **14** 71
- Uhlmann E V, Weiberg M C, Kreidl N Y, Burgner L L, Zanoni R and Church K H 1994 *J. Non-Cryst. Solids* **178** 15
- Weber M J 1990 *J. Non-Cryst. Solids* **123** 208
- Weber M J, Myers J D and Blackburn D H 1981 *J. Appl. Phys.* **52** 2944
- Wong E Y 1961 *J. Chem. Phys.* **35** 544
- Wong E Y 1963 *J. Chem. Phys.* **38** 976