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A study of electron paramagnetic resonance and optical absorption in calcium chromium phosphate glasses containing praseodymium

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Abstract

This paper reports on the EPR and optical absorption studies of Cr^{3+} ions in praseodymium calcium chromium phosphate glasses. The effect of concentration of Cr^{3+} ions and rare earth oxide praseodymium on resonance signals have been studied. The temperature dependence of EPR signals was studied. The intensity of the resonance signals increases with decrease of temperature whereas the linewidths are found to be independent of temperature. The coupling constant J between Cr^{3+} ion pairs was calculated. The crystal-field parameters and optical band gap energy were evaluated. From the results, the values of the optical band gap energy are found to depend quite sensitively on added chromium content. It is observed that the crystal-field at the Cr^{3+} ion site becomes weak with increase in praseodymium content. The theoretical values of optical basicity were also evaluated.

Keywords: EPR; Cr^{3+} ions; Optical absorption studies; Temperature effects; Crystal-field parameters; Phosphate glasses

1. Introduction

In the last three decades a great effort has been devoted to the study of glasses containing transition metal and rare earth element impurities [1–5]. In recent years glasses doped with rare earth and transition metal ions have attracted a great deal of attention because the rates at which and the mechanism by which excited states of rare earth ions form and decay are of great importance for the application of these ions in phosphors. One of the most investigated transition metal impurity ions is Cr^{3+} and the large number of review articles and papers testifies to the high level of interest in this field [5–11], even in connection with the development of lasers. Moreover, in applications ranging from new optical material research to optoelectronic and integrated optical devices, there has been increasing interest in glasses due to their lower production costs with respect to single crystals. Currently the basic features of Cr^{3+} in a large number of crystalline matrices are so well established that this ion is extensively used as a probe for studying the structure and the local symmetry of new and exotic materials.

Phosphate systems have been chosen mainly for three reasons. (a) Phosphate systems are usually low melting. (b) Phosphates being highly acidic produce a reasonable concentration of the reduced state (Fe^{2+}, V^{4+} etc) of the transition metal ions even on ordinary melting in air, thus an additional reducing atmosphere during melting is not required and (c) the glass forming region in binary transition metal oxide phosphate systems is usually larger than that in oxide, silicate, borate or germanate systems. Thus very high concentrations of transition metal oxides can be dissolved in phosphate melts, consequently a higher electrical conductivity may be obtained [12].

Zakharov and Yudin [13] have studied the EPR spectrum of Cr^{3+} ions in a complex phosphate glasses at 9.3 GHz and found that $g_{\parallel}=5.0\pm0.2$ and $g_{\perp}=1.78\pm0.05$. Landry et al. [14] studied the EPR and optical absorption spectra of Cr^{3+} ions in zinc aluminum phosphate glasses to which controlled amounts of Cr_2O_3 were added and found a pronounced dependence of EPR spectrum on Cr^{3+} concentration. We are interested in studying the EPR at different temperatures and the optical absorption at room temperature for Cr^{3+} ions in praseodymium calcium phosphate (here afterwards referred to as Pr Ca P) glasses. In the present investigation we have examined the effects of added amounts of rare earth oxide (up to 6 mol%) to calcium chromium phosphate glasses.

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Table 1
Composition of glasses studied in the present work

System	Composition
1. Ca Cr P	$24CaCO_3+1Cr_4(SO_4)_5(OH)_2+75P_2O_5$
2. Pr Ca Cr P	$1Pr_6O_{11}+(24-x)CaCO_3+xCr_4(SO_4)_5(OH)_2+75P_2O_5$ ($x=1$, 3, 5 and 7)
3. Pr Ca Cr P	$xPr_6O_{11}+(24-x)CaCO_3+1Cr_4(SO_4)_5(OH)_2+75P_2O_5$ ($x=1$, 2, 4 and 6)

2. Experimental techniques

All batch materials (Pr_6O_{11}, $CaCO_3$, P_2O_5) used were of analar quality. Chromium was added to the batch as $Cr_4(SO_4)_5(OH)_2$. Table 1 lists the batch composition in mol% of glasses studied in the present work. The chemicals were weighed accurately in an electrical balance and ground to fine powder and mixed thoroughly. The batches were then placed in porcelain crucibles and melted in electrical furnace in air at 1340°C. The melt was then quenched to room temperature in air by pouring it onto a polished porcelain plate and pressing it quickly with another porcelain plate. The glasses thus obtained were green in colour.

The EPR spectra were recorded at room as well as at different temperatures on an ESR Spectrometer (JEOL-FE-1X) operating in the X-band frequency ($\approx$9.205 GHz) with a field modulation frequency of 100 kHz. The magnetic field was scanned from 0 to 500 mT and the microwave power was set at 20 mW. A powdered glass specimen of 100 mg was taken in a quartz tube for EPR measurements. Polycrystalline DPPH with an effective g value of 2.0036 was used as a standard field marker.

EPR spectra of 1 $Pr_6O_{11}+19CaCO_3+5Cr_4(SO_4)_5(OH)_2+75P_2O_5$ glass sample was recorded at different temperatures (123–423 K) using a variable temperature controller (JES-UCT-2AX). A temperature stability of ±1 K was easily maintained throughout the measurement.

The optical absorption spectrum for the glass samples was recorded at 300 K on a Hitachi spectrophotometer (model 3600) in the wavelength region 400 to 800 nm. The

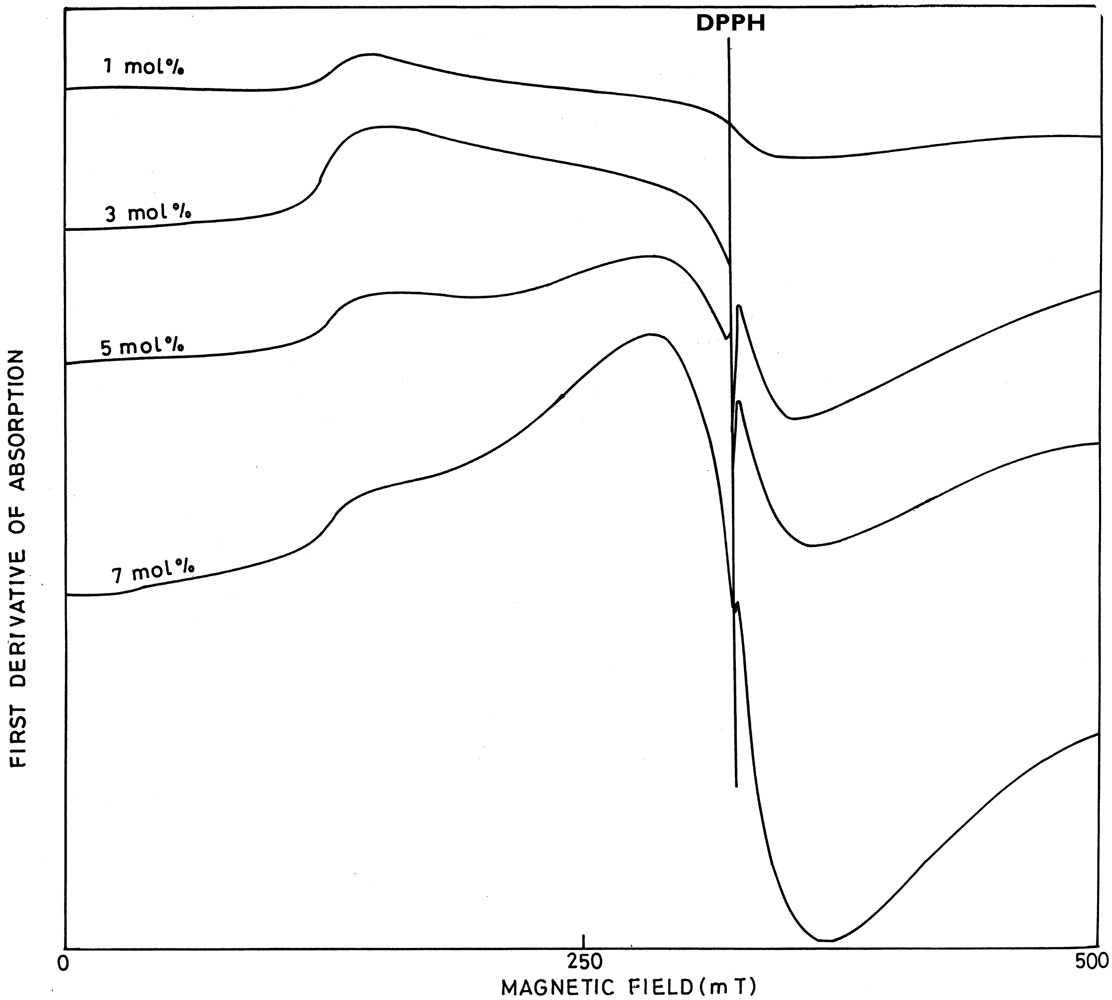

Fig. 1. EPR spectra of various mol% of Cr^{3+} ions doped in 1 Pr Ca Cr P Glasses at room temperature.

accuracy with which the peaks were measured is ±10 cm^{-1}.

3. Results and discussion

3.1. EPR studies

No EPR signal was detected in the spectra of undoped glasses. When various mol% of Cr^{3+} ions were added to Pr Ca P glasses (See Table 1), the EPR spectra of all investigated samples exhibit resonance signals as shown in Fig. 1. The EPR spectra of all the glasses studied exhibit a broad resonance line at $g_{\|}=4.64\pm0.05$ and an intense resonance line centered at $g_{\perp}=2.01\pm0.03$. The spectrum at low field i.e., the EPR absorption at $g\approx5$ resonance is attributed to isolated Cr^{3+} ions in strongly distorted sites, characterized by $\Delta>h\nu$. The resonance at $g\approx2$ is generally observed and attributed to exchange coupled Cr^{3+} ion pairs and is related to weakly distorted sites, characterized by $\Delta<h\nu$. The EPR spectrum exhibits a marked concentration dependence. In high chromium content glasses the EPR spectrum is dominated by the build up of a line in the vicinity of $g\approx2$. Thus the EPR spectrum gradually modifies from an initial low field absorption to one at high field with increase in chromium content. The change in EPR spectrum with concentration is attributed to a combination of isolated octahedrally coordinated Cr^{3+} ions and exchange-coupled pairs of Cr^{3+} ions which are individually sixfold coordinated.

Fig. 2 shows the EPR spectra for Cr^{3+} ions with various mol% of praseodymium in Pr Ca P glasses (see Table 1). The EPR spectra of all investigated samples exhibit resonance signals at $g_{\|}=4.64\pm0.05$ and at $g_{\perp}=2.01\pm0.03$ which are characteristic of Cr^{3+} ions. In all cases the intensity of EPR signals decreased with increase in praseodymium content. Even the use of 1 mol% of rare earth oxide resulted in significant reduction of the signal. The reduction of the signal in these type of glasses is due to various reasons, such as paramagnetic ions coupled by strong exchange interactions [15] spin–spin interaction between neighboring paramagnetic ions of different elements [16] and process involving redox phenomena [17]. At low concentrations of Pr^{3+} ions the last of the above three may be the dominant mechanism. At higher concentrations of rare earth oxide the loss of the chromium resonance signal may be due to relaxation process involving interaction between Cr^{3+} and Pr^{3+} ions.

The number of spins participating in resonance of each EPR signal is assumed to be proportional to the product of peak to peak height (I_{pp}) and square of its width $(\Delta B_{pp})^2$ [18]

$$N\alpha I_{pp}(\Delta B_{pp})^2 \qquad (1)$$

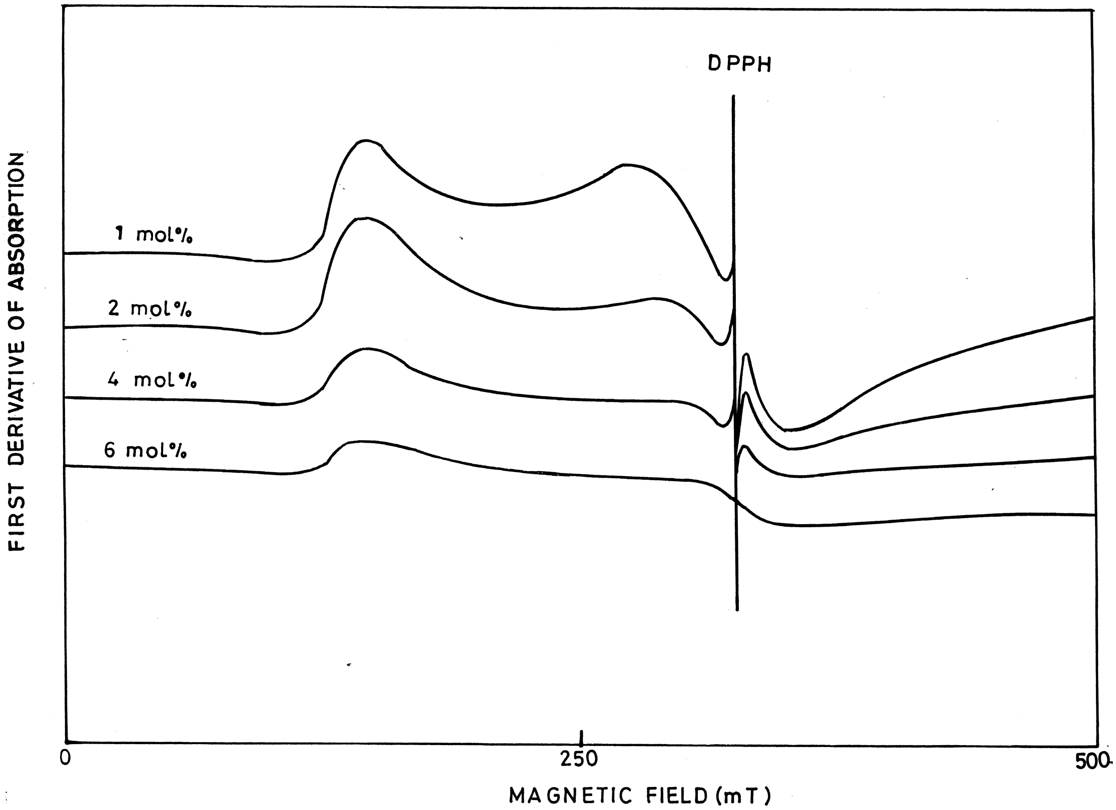

Fig. 2. EPR spectra of 1 mol% of Cr^{3+} ions with different mol% of Praseodymium ions in calcium chromium phosphate glasses.

Fig. 3 shows the plot of number of spins participating in resonance in Pr Ca Cr P glasses (see Table 1) with various mol% of chromium as well as praseodymium content. From Fig. 3 it is seen that number of spins participating in resonance increases with chromium content whereas it decreases with praseodymium content. The increase in number of spins due to exchange-coupled Cr^{3+} ion pairs whereas the decrease in number of spins due to the relaxation process.

The EPR spectra of 1 $Pr_6O_{11}+19CaCO_3+5Cr_4(SO_4)_5(OH)_2+75P_2O_5$ glass sample were studied at different temperatures (123 to 423 K) and the spectra are shown in Fig. 4. The peak to peak width of the $g\approx2$ resonance line is found to be independent of temperature between 123 to 423 K, whereas the intensity of the resonance line decreases with increase in temperature. Fig. 5 shows the dependence of logarithmic intensity $\log(N)$ on inverse temperature $(1/T)$ for the resonance signal at $g\approx2$ for 5 mol% of Cr^{3+} ions in 1 Pr Ca P glass. From Fig. 5 it is clear that the intensity of resonance line decreases with increase in temperature. This is in accord with the expectations $(I\alpha 1/T)$ for paramagnetic centers.

Duffy and Ingram [19] reported that the ideal values of optical basicity can be predicted from the composition of the glass and basicity moderating parameters of various cations present. The theoretical values of optical basicity of the glass can be estimated using the formula [19]

$$\Lambda_{\mathrm{th}} = \sum_{i=1}^{n} \frac{Z_i r_i}{2\gamma_i} \tag{2}$$

where n is the total number of cations present, Z_i is the oxidation number of the i^{th} cation, r_i is the ratio of number of i^{th} cations to the number of oxides present and γ_i is the basicity moderating parameter of the i^{th} cation. The basicity moderating parameter γ_i can be calculated [19] from the following equation:

$$\gamma_i = 1.36(x_i - 0.26) \tag{3}$$

where x_i is Pauling electronegativity [20] of the cation. The theoretical values of optical basicity (Λ_{th}) calculated for the glass samples (see Table 1) are listed in Table 2. It is interesting to see that the optical basicity decreases with chromium concentration for a fixed value of

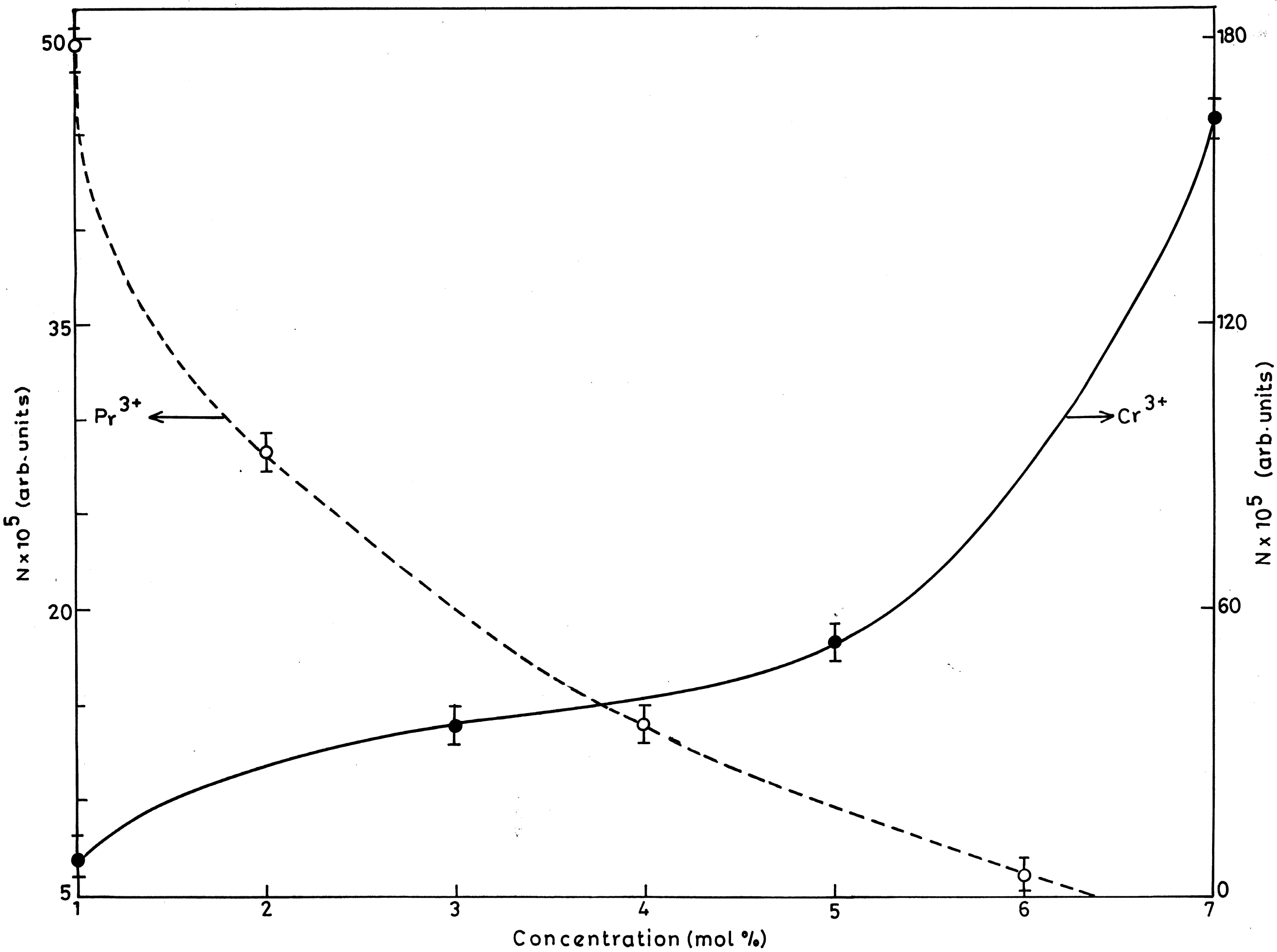

Fig. 3. The number of spins participating in resonance for different mol% of chromium as well as praseodymium ions at room temperature.

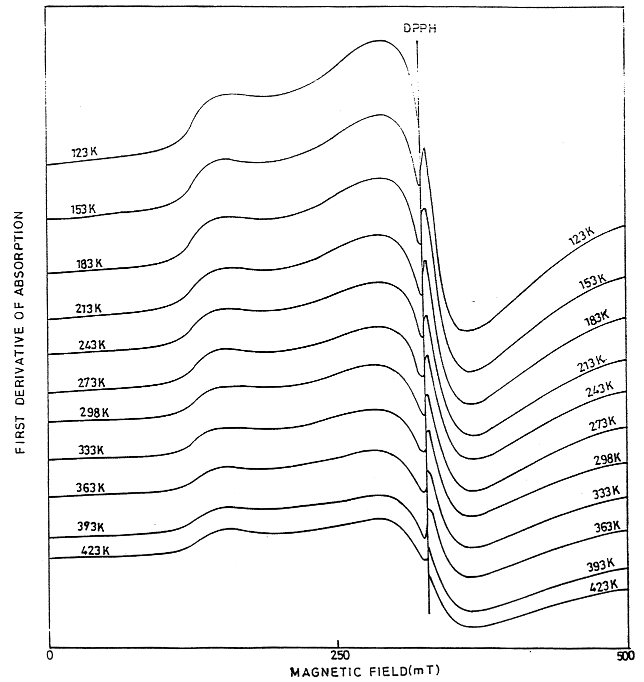

Fig. 4. EPR spectra for 5 mol% of chromium content in 1 Pr Ca P glass at different temperatures.

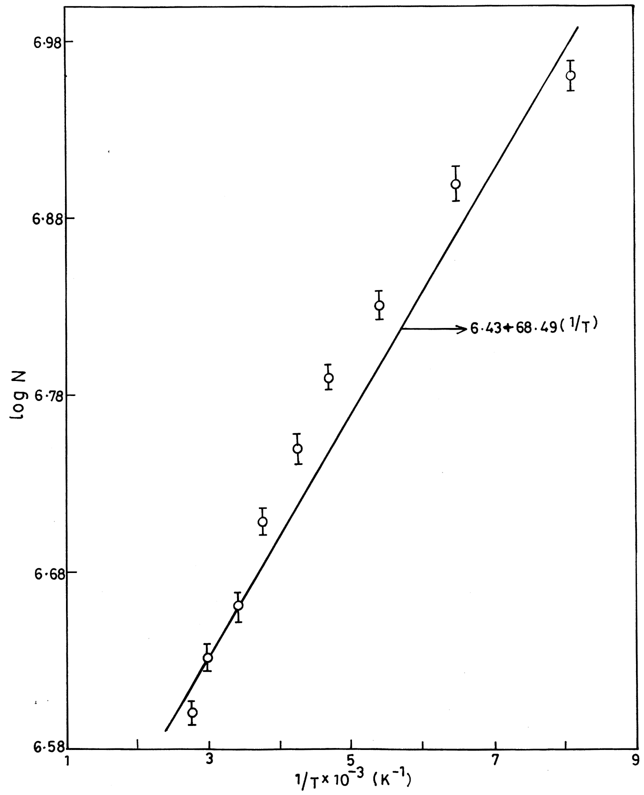

Fig. 5. A plot of logarithmic intensity (log N) versus $1/T$ at different temperatures for 5 mol% of chromium in 1 Pr Ca P glasses.

praseodymium, whereas the optical basicity increases with praseodymium concentration for a fixed value of chromium which are shown in Fig. 6. This increase in optical basicity with praseodymium content may be due to the weak crystal-field at the chromium site which is confirmed from our Dq/B values in optical absorption studies.

3.2. Coupling constant 'J' between Cr^{3+} ion pairs

Fournier et al. [21] gave the following expression to calculate the relative intensity of EPR line at various temperatures.

$$RI(T) = \frac{4\exp(-J/kT) + 20\exp(-3\,J/kT) + 56\exp(-6\,J/kT)}{1 + 3\exp(-J/kT) + 5\exp(-3\,J/kT) + 7\exp(-6\,J/kT)} \quad (4)$$

where J is anti-ferromagnetic coupling constant between the Cr^{3+} ion pairs, k is the Boltzmann constant and T is absolute temperature.

The intensities were determined by double integrating the EPR first derivative curve. Fig. 7 shows a graph between $RI(T)$ versus kT for different J values calculated using Eq. (4). Fig. 7 also shows the experimental values superimposed on theoretical curves (obtained by Eq. (4)). Fournier et al. [21] have taken a spin 1/2 sample as standard for measuring the relative intensities. In the present work, the relative intensities were measured with respect to the intensity at room temperature. Hence all the curves have been scaled to a factor of ten at room temperature (corresponding to $kT \approx 209$ cm^{-1}). From Fig. 7 we can observe that the experimental data is very close to the curve for $J = 75$ cm^{-1}. This value is in the same order as reported by Fournier et al. [21].

3.3. Optical absorption studies

The optical absorption spectra of chromium in calcium phosphate and praseodymium calcium phosphate glasses were recorded at room temperature and are shown in Fig. 8. The absorption spectra of chromium in calcium phosphate glasses are similar to that of lead fluorophosphate glass [22]. If the praseodymium content is increased the crystal-field at the Cr^{3+} ion becomes weak which is confirmed by our Dq/B values.

Cr^{3+} ions have the d^3 configuration and have a larger octahedral site preference energy (OSPE) [23]. The ground state is always $^4A_2$ irrespective of the strength of the crystal-field. In general for chromium doped glasses we expect three broad bands in the increasing order of energy as $^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$, $^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ and $^4A_{2g}(F) \rightarrow {}^4T_{1g}(P)$. The highest energy band $^4A_{2g}(F) \rightarrow {}^4T_{1g}(P)$ transition occurs at above 30,000 cm^{-1}

Table 2
Theoretical values of optical basicity for the Pr Ca Cr P glasses (see Table 1) with increasing concentration of chromium and praseodymium

Concentration of chromium (mol%)	Optical basicity Λ_{th}.	Concentration of Praseodymium (mol%)	Optical basicity Λ_{th}.
1	0.428	1	0.428
3	0.423	2	0.434
5	0.419	4	0.445
7	0.416	6	0.454

and it will be obscured by intense charge transfer band [24].

Cr^{3+} ions have strong visible absorption bands due to the spin allowed but parity forbidden $^4A_{2g}(F)\rightarrow{}^4T_{2g}(F)$ and $^4A_{2g}(F)\rightarrow{}^4T_{1g}(F)$ transitions. These $^4A_{2g}(F)\rightarrow{}^4T_{2g}(F)$ broad bands are of interest for applications in lasers [25,26] and solar concentrators [8,27].

The widths of these bands imply strong electronic coupling to vibrations of the local environment. When a broad vibronic band and sharp absorption line overlap interference between two types of transitions can occur. First given by Fano for helium [28], the qualitative interpretation of this effect has been found to apply successfully to other systems. For instance Fano antiresonances have been observed for $3d^3$ ions (V^{2+} or Cr^{3+}) in oxide glasses [3]. In our system we favor Fano antiresonance interpretation [3]. In this scheme the sharp t_2^3 intra-configurational transitions undergo destructive interference causing a cancellation of absorptive intensity. This structure has been attributed to the spin forbidden transitions $^4A_{2g}(F)\rightarrow{}^2E_g(G)$ and $^4A_{2g}(F)\rightarrow{}^2T_{1g}(G)$. These transitions acquire their spin allowed character via spin–orbit interaction with the broad $^4A_{2g}(F)\rightarrow{}^4T_{2g}(F)$ transition. They appear negative because of destructive interfer-

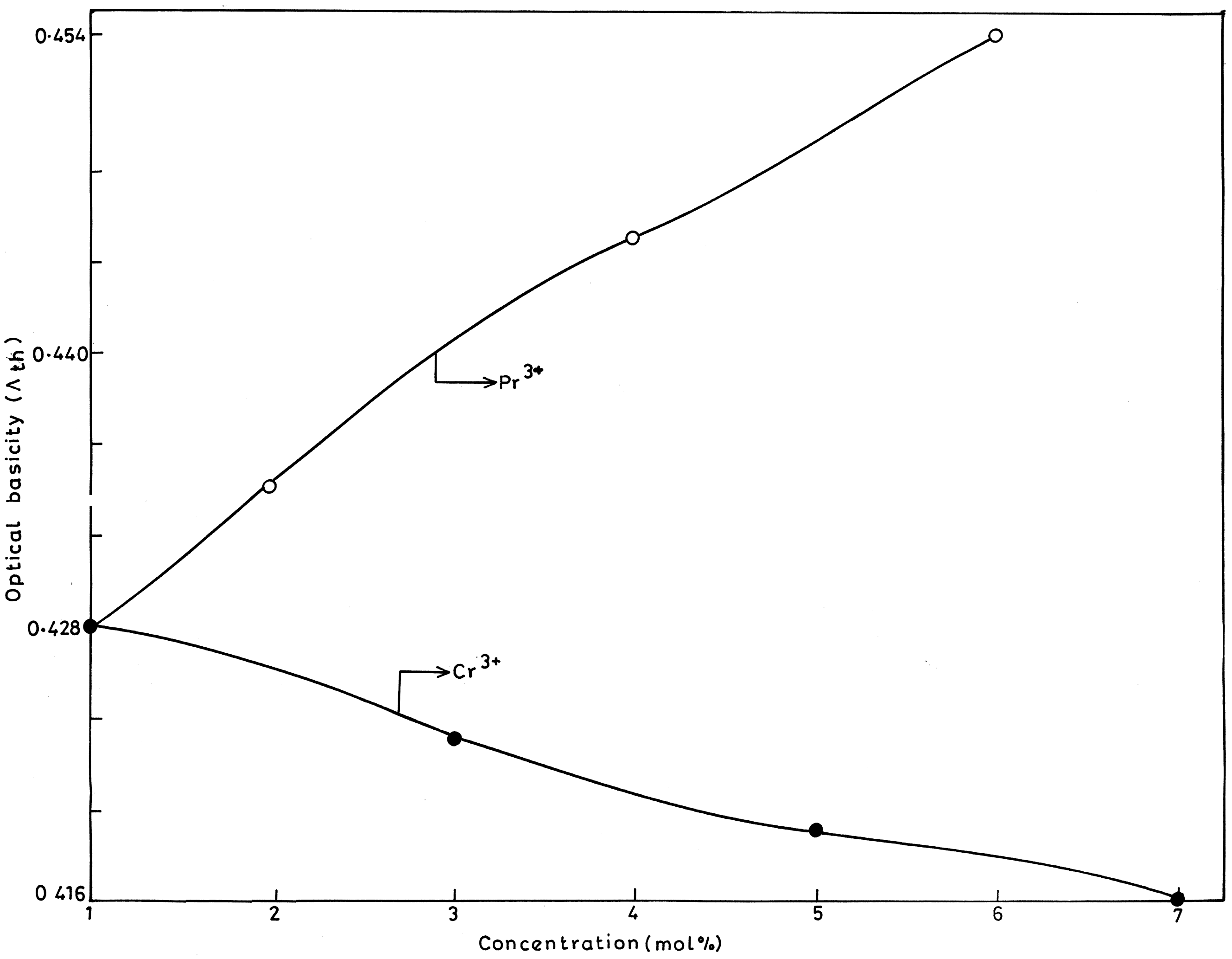

Fig. 6. A plot of optical basicity in Pr Ca Cr P glasses for various mol% of Cr^{3+} and Pr^{3+} ions at room temperature.

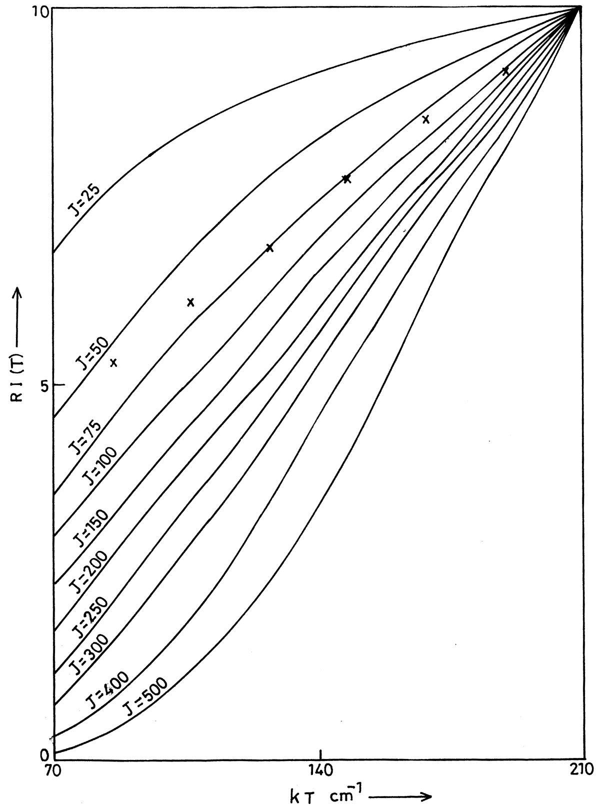

Fig. 7. A graph between relative intensities *RI*(*T*) versus *kT* for different *J* values.

ence with $^4T_{2g}$ vibronic quasi-continuum, which causes cancellation of observed intensities as well as a change in the original peak position and shape [29]. They are sharp because there is no exchange in the electronic configuration (t_2^3) [29,30].

The crystal-field *Dq* and Racah parameters *B* and *C* for the investigated glass samples were estimated from the optical absorption studies. In particular, the value of the crystal-field parameter *Dq* is given by the energy difference between the ground state and first excited state of Cr^{3+}, $^4A_2$ and $^4T_2$ respectively. The value of Racah B-parameter is evaluated by using the relations given by Casalboni et al. [9].

$$Dq = \frac{E(^4A_2) - E(^4T_2)}{10}$$

$$Dq/B = \frac{15(x-8)}{x^2 - 10x}$$

Where

$$x = \frac{E(^4A_{2g} \rightarrow {}^2T_{1g}) - E(^4A_{2g} \rightarrow {}^4T_{2g})}{Dq}$$

From the energy position of the ^2E level we can evaluate the C-parameter following Rasheed et al. [6].

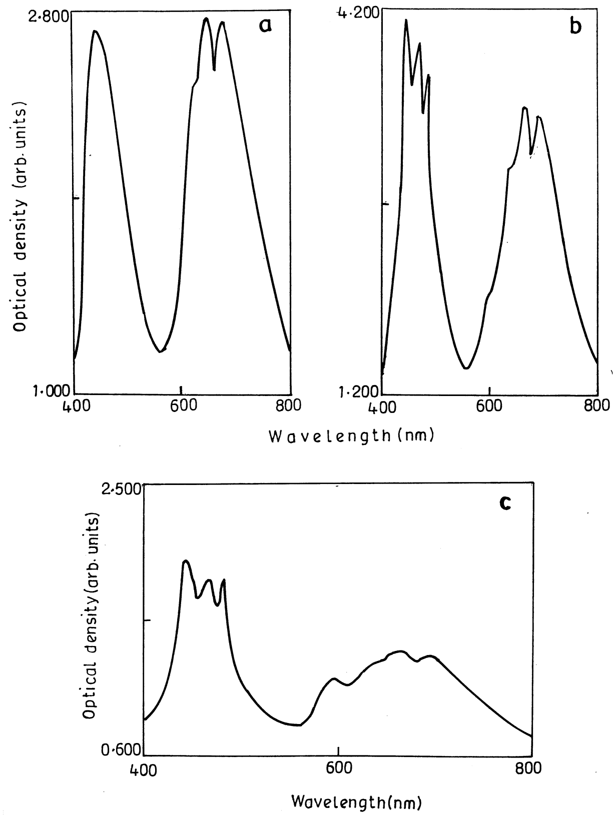

Fig. 8. Room temperature optical absorption spectra of 1 mol% of Cr^{3+} ions in (a) Calcium phosphate glass. (b) one praseodymium calcium phosphate glass. (c) six praseodymium calcium phosphate glass.

$$\frac{C}{B} = \frac{1}{3.05}\left[\frac{E(^2E)}{B} - 7.9 + 1.8\left(\frac{B}{Dq}\right)\right]$$

The observed band positions and level splitting are in good agreement with the values reported in literature and are compared with other systems and are also included in Table 3. In weak crystal-field sites the values of $Dq/B \ll 2.3$ and for strong fields the values of $Dq/B \gg 2.3$ are found. For intermediate crystal-fields the value of $Dq/B \approx 2.3$. The Dq/B values obtained in the present work are in the following order.

System	Ca Cr P	1 Pr Ca Cr P	6 Pr Ca Cr P
Dq/*B* values	2.12	> 1.98	> 1.86

which clearly indicates that as the concentration of praseodymium increases the bands becomes broader and the crystal-field at the Cr^{3+} ion site become weak. The other bands in the absorption spectra at 590 nm, 480 nm, 470 nm and 445 nm are due to the transitions from the ground state $^3H_4$ to the excited states $^1D_2$, $^3P_0$, $^3P_1$ and $^3P_2$ of praseodymium, respectively [31].

3.4. Optical band gap energy (E_{opt})

The absorption coefficient 'α' can be determined as a

Table 3
Absorption band positions and level splittings for some Cr^{3+} ion doped glasses

Glass type	^2E cm^{-1}	$^2T_1$ cm^{-1}	$^4T_2$ cm^{-1}	$^4T_1$ cm^{-1}	B cm^{-1}	Dq/B cm^{-1}	C cm^{-1}
Fluorozirconate[b]	14600	15050	15300	22150	850	1.80	2925
Fluoride	14860[b]	15530	15385	23040	850	1.84	2948
Lithium borate[b]	14674	15570	15750	23050	700	2.25	3090
Tellurite[b]	14124	14925	15385	21739	699	2.20	3143
Ca phosphate[a]	14515	15625	15060	21835	710	2.12	3103
1Pr Ca 1Cr P[a]	14495	15875	15270	22470	771	1.98	2984
6Pr Ca 1Cr P[a]	14470	15725	15060	22520	810	1.86	2884

[a] Present work.
[b] F. Rasheed et al. [7].

function of frequency using the formula:

$$\alpha(\omega) = \frac{A}{d} \times 2.303 \tag{5}$$

where A is absorbance at frequency ω and d is the thickness of the glass sample. The optical band gap for an indirect transition can be determined using the relation [32]

$$E_{\mathrm{opt}} = h\upsilon - \frac{(\alpha h\upsilon)^{1/2}}{B} \tag{6}$$

Thus $(\alpha h\upsilon)^{1/2}$ is plotted against $h\upsilon$. The graphs obtained are shown in Fig. 9 for 1Pr Ca 1Cr P and 1Pr Ca 5Cr P glasses. The optical band gap is obtained by extrapolating the linear region of the curve to the $h\upsilon$-axis. From the graph it is clear that the addition of chromium to the glass causes a reduction in the optical energy gap and this is consistent with the initiation of band tailing suppressed to occur at lower values of $N(E)$, the density of states function, as reported by Hogarth and Novikov [33]. The optical band gap obtained in the present work is 3.4–3.2 eV which is in the same order as reported in literature for phosphate glasses [33–36].

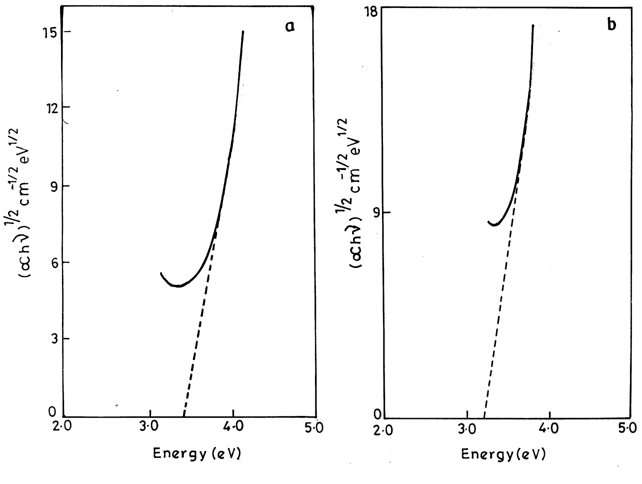

Fig. 9. A plot of $(\alpha h\upsilon)^{1/2}$ versus $h\upsilon$ for 1 mol% and 5 mol% of chromium in one praseodymium calcium phosphate glass at room temperature.

4. Conclusions

1. In all the investigated samples the EPR spectra of Cr^{3+} ions in praseodymium calcium chromium phosphate glasses exhibit resonance signals. The spectra exhibit a marked concentration dependence on both chromium and on praseodymium contents.
2. The number of spins participating in resonance increases with chromium concentration whereas it decreases with increasing praseodymium content. The increase of the number of spins is most probably due to exchange-coupled pairs whereas we attribute the decrease to the relaxation process.
3. The intensity of the resonance signals decreases for higher temperatures according to 1/T law. The linewidths are found to be independent of temperature.
4. It is observed that the crystal-field at the Cr^{3+} ion site becomes weak with increase in praseodymium content, which is confirmed from our Dq/B values.
5. Fano anti-resonances observed in $^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ broad band of Cr^{3+} ion are interpreted as being due to interference between $^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ broad vibronic band and sharp absorption lines $[^4A_{2g}(F) \rightarrow {}^2E_g(G)$ and $^4A_{2g}(F) \rightarrow {}^2T_{1g}(G)]$.
6. It is observed that the optical band gap decreases with increase in concentration of chromium.

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