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

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This paper reports on electron paramagnetic resonance (EPR) and optical absorption studies for Mn^{2+} ions in praseodymium calcium manganese phosphate glasses. The EPR spectra exhibit three resonance signals at $g \approx 2.0$, $g \approx 3.3$ and $g \approx 4.8$. A six line hyperfine structure spectrum centered at $g \approx 2.0$ has been observed in the EPR spectra of all the glasses at lower concentration of Mn^{2+} ions. The effects of the concentration of Mn^{2+} ions and praseodymium oxide on resonance signals have been studied. The temperature dependence of EPR signals were also studied. The intensity of the resonance signals decreases with increase in temperature whereas the linewidths are found to be independent of temperature. As temperature is increased small fluctuations in hyperfine splitting are observed. From the optical absorption spectrum, the crystal field parameters and optical band gap energy were evaluated. The optical band gap energy is found to depend quite sensitively on added manganese content. The theoretical values of optical basicity were also evaluated. © *2000 Kluwer Academic Publishers*

1. Introduction

Over the last few decades, great importance has been attached to glasses doped with rare-earth and transition-metal ions because of the interesting spectroscopic properties of their 4 f^N and 3 d^N electrons. In recent years, research on common glasses and other less common non-crystalline solids containing transition metal and rare earth ions has attracted considerable interest because the rate at which and the mechanism by which excited states of these ions are formed and decay are of great importance in the application of these ions in phosphors, lasers, solar energy concentrators and other currently developed electronic devices [1]. Moreover, in applications ranging from new optical material research to optoelectronics and integrated optical devices, there has been increasing interest in glasses due to their lower production costs with respect to single crystals.

Among oxide glasses, phosphate glasses are very important from the point of view of technological effectiveness and preservation of the useful properties of the material upon introduction of a significant content of active ions [2]. Phosphate glasses usually possess low melting temperature, high thermal expansion coefficient, low glass transition temperature, low softening temperature and are of increasing interest for many applications. e.g. glass to metal seals, thick film plate, the molding of optical elements and low temperature enamels for metals [3–5]. They are also relatively easy to prepare and offer an important range of compositional possibilities with which it is possible to control the physical and chemical properties of interest for specific technological applications. High quantum efficiencies (91%) have been reported, for the luminescence of Mn^{2+} ions in phosphate glasses [6].

Electron paramagnetic resonance (EPR) and optical absorption techniques are recognized as powerful tools for probing the local environment of a paramagnetic impurity and mapping the crystal field [7, 8]. This paper reports on the EPR and optical absorption studies for Mn^{2+} ions in praseodymium calcium manganese phosphate (here afterwards referred to as Pr Ca Mn P) glasses. The effect of concentration of Mn^{2+} ions and praseodymium oxide on resonance signals has been studied. The temperature dependence of EPR signals was also studied.

2. Experimental techniques

The starting materials (Pr_6O_{11}, $CaCO_3$, $MnCO_3$ and P_2O_5) used in the preparation of glasses were of Analar quality. Table I 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 an electrical furnace in air at 1473 K. 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 EPR spectrometer

TABLE I Composition of glasses studied in the present work (x in mol %)

System	Composition
1. Pr Ca Mn P	1 $Pr_6O_{11} + (24 - x)$ $CaCO_3$ $+ x$ $MnCO_3 + 75$ P_2O_5 ($x = 0.5, 0.75, 1, 1.25, 3$ and 5)
2. Pr Ca Mn P	x $Pr_6O_{11} + (24 - x)$ $CaCO_3$ $+ 1$ $MnCO_3 + 75$ P_2O_5 ($x = 0.5, 1, 1.25, 2, 2.5, 3$ and 5)

(JEOL-FE-1X) operating in the X-band frequency (≈ 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 10 mW. A powdered glass specimen of 100 mg was taken in a quartz tube for EPR measurements. Polycrystalline Diphenyl Picryl Hydrazyl (DPPH) with an effective g value of 2.0036 was used as a standard field marker.

The EPR spectrum of a 1 $Pr_6O_{11} + 23.5$ $CaCO_3 + 0.5$ $MnCO_3 + 75$ P_2O_5 glass sample was recorded at different temperatures (123 to 433 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 U3400) in the wavelength region 340 to 800 nm. The 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 quantities of Mn^{2+} ions were added to praseodymium calcium phosphate glasses (see Table I), the EPR spectra of all the investigated samples exhibit three resonance signals, at $g \approx 2.0$, $g \approx 3.3$ and $g \approx 4.8$ and are shown in Fig. 1. The EPR spectrum is very similar to others reported for Mn^{2+} ions in various glass systems [9–14]. The resonance signal at $g \approx 2.0$ shows a six line hyperfine structure superimposed on a rather broad back ground signal. The characteristic hyperfine structure (hfs) is due to the interaction of electron spin with the nuclear spin $I = 5/2$ and was resolved for the $g \approx 2.0$ resonance line. The EPR spectra of Mn^{2+} ions in glasses show a remarkable concentration dependence. At lower concentrations of Mn^{2+} ions (less than 3 mol % of Mn^{2+} ions) the spectrum shows a sextet. The six resolved hyperfine lines spread over a region of approximately 500 G in width. The ability to observe the ^{55}Mn hyperfine structure has two tangible benefits: (i) It generally allows unambiguous assignments of positions of complex resonance lines to manganese and (ii) The magnitude of the hyperfine constant provides a measure of covalent bonding between Mn^{2+} ions and its surrounding ligands [15, 16]. Their relative intensities vary with the glass structure and composition. When the concentration of Mn^{2+} ions is increased by more than 3 mol %, the sextet hyperfine structure disappears leaving behind a single broad line due to ligand field fluctuations in the Mn^{2+} ion vicinity and also due to the dipolar interactions [17].

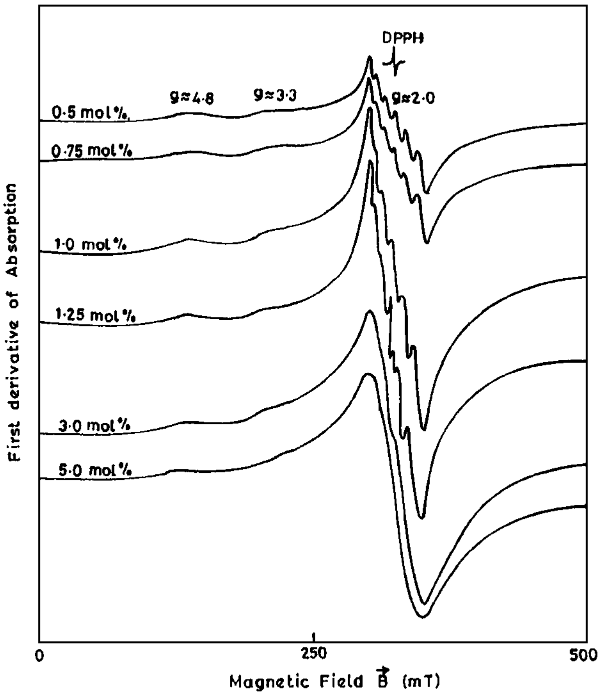

Figure 1 EPR spectra for various mol % of Mn^{2+} ions in 1 Pr Ca Mn P glasses at room temperature.

In case of d^5 transition metal ions, it is known that axial distortion of octahedral symmetry gives rise to three Kramers doublets $|\pm 5/2\rangle$, $|\pm 3/2\rangle$ and $|\pm 1/2\rangle$ [7]. Application of the Zeeman field splits the spin degeneracy of the Kramers doublets. As the crystal field splitting is normally much greater than the Zeeman field, the resonances observed are due to transitions within the Kramers doublets split by the Zeeman field. The resonances at $g \approx 3.3$ and $g \approx 4.8$ are attributed to the rhombic surroundings of the Mn^{2+} ions. The resonance at $g \approx 2.0$ is due to Mn^{2+} ions in an environment close to octahedral symmetry and is known to arise from the transition between the energy levels of the lower doublet, while the resonances at $g \approx 3.3$ and $g \approx 4.8$ arise from the transition between the energy levels of the middle Kramers doublet. The difference between these levels in the case of the resonance at $g \approx 4.8$ is higher than the transition energy at 9.205 GHz klystron frequency. Thus the observed intensity of this line is low and often decreases or falls to zero at higher temperatures.

Fig. 2 shows the EPR spectra of Mn^{2+} ions with various contents of praseodymium in Pr Ca Mn P glasses (see Table I). The EPR spectra of all the investigated samples exhibit resonance signals at $g \approx 2.0$, $g \approx 3.3$ and $g \approx 4.8$ which are characteristic of Mn^{2+} ions. At higher concentrations of praseodymium, the intensity of the EPR signals of Mn^{2+} ions decreases. The reduction of the signal in these type of glasses is due to various reasons, such as paramagnetic ions coupled by strong exchange interactions [18], spin-spin interaction between neighbouring paramagnetic ions of different elements [19] and a process involving redox phenomena [20]. The reduction of the signal in the present study at higher concentrations of Pr^{3+} may be due to relaxation

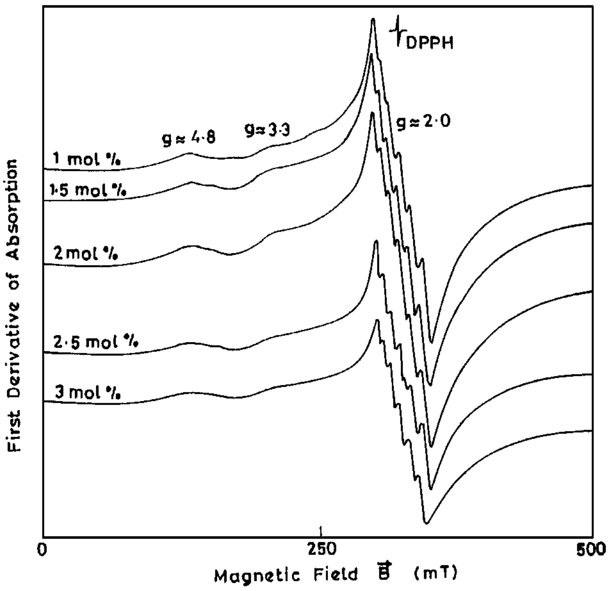

Figure 2 EPR spectra of 1 mol % of Mn^{2+} ions with different mol % of praseodymium ions in Pr Ca Mn P glasses.

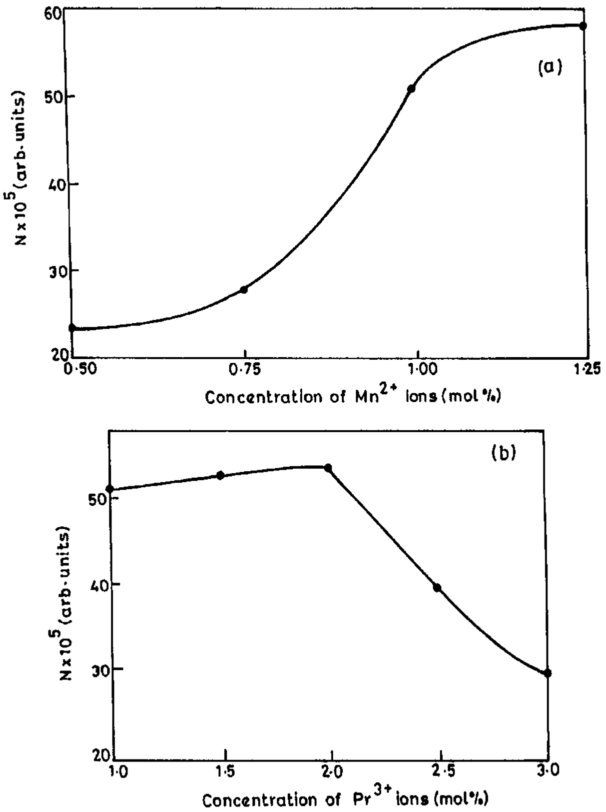

Figure 3 The number of spins participating in resonance for different mol % of manganese as well as praseodymium ions in Pr Ca Mn P glass at room temperature.

process involving interactions between Mn^{2+} ions and praseodymium ions.

The number of spins participating in the resonance of each EPR signal is approximated as proportional to the product of peak to peak height (I_{pp}) and square of its width $(\Delta B_{pp})^2$ [21]

$$N \propto I_{pp}(\Delta B_{pp})^2 \tag{1}$$

Fig. 3 shows the plot of number of spins participating in resonance in Pr Ca Mn P glasses (see Table I) with various contents of manganese as well as praseodymium content. From Fig. 3a it is clear that the number of spins participating in the resonance increases with manganese content (the number of spins for 3 mol % and above are not shown in the figure), whereas from Fig. 3b it slightly increases up to 2 mol % and afterwards decreases with increase in praseodymium content. The increase in number of spins is due to exchange-coupled Mn^{2+} ion pairs whereas the decrease in number of spins may be due to the relaxation process between Mn^{2+} and the Pr^{3+} ions.

The EPR spectrum of a 1 $Pr_6O_{11} + 23.5\ CaCO_3 + 0.5\ MnCO_3 + 75\ P_2O_5$ glass sample was recorded at different temperatures (123 to 433 K) and the spectra are shown in Fig. 4. The peak to peak width of the $g \approx 2$ resonance line is found to be independent of temperature between 123 to 433 K, whereas the intensity of the resonance line decreases with increase in temperature. Fig. 5 shows the dependence of logarithmic intensity $\log(N)$ versus inverse temperature $(1/T)$ for the resonance signal at $g \approx 2$ for 0.5 mol % of Mn^{2+} ions in 1 Pr Ca Mn P glass. From Fig. 5 it is clear that the intensity of resonance line decreases with increase in temperature according to the Boltzmann law.

Duffy and Ingram [22] reported that the ideal values of optical basicity can be predicted from the composition of the glass and the basicity moderating parameters of the various cations present. The theoretical values of optical basicity of the glass can be estimated using the formula [22]

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

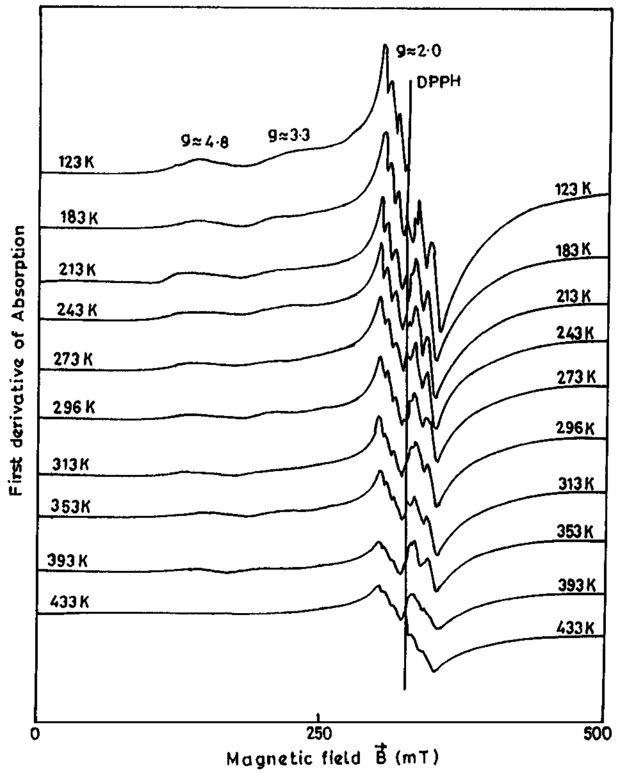

Figure 4 EPR spectra for 0.5 mol % of manganese content in 1 Pr Ca Mn P glass at different temperatures.

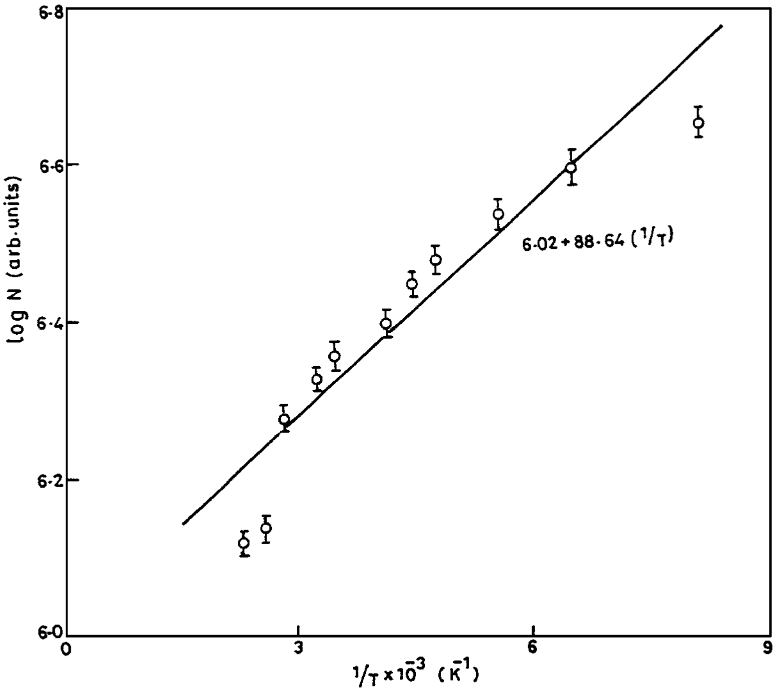

Figure 5 A plot of logarithmic intensity (log N) versus $1/T$ at different temperatures for 0.5 mol % of manganese ions in 1 Pr Ca Mn P glass.

where n is the total number of cations present, Z_i is the oxidation number of the ith cation, r_i is the ratio of number of ith cations to the number of oxides present and γ_i is the basicity moderating parameter of the ith cation. The basicity moderating parameter γ_i can be calculated [22] from the following equation:

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

where x_i is the Pauling electronegativity [23] of the cation. The theoretical values of optical basicity (Λ_{th}) calculated for the glass samples (see Table I) are listed in Table II. It is interesting to note that the optical basicity decreases with increase in manganese concentration for a fixed value of praseodymium, whereas the optical basicity increases with increase in praseodymium concentration for a fixed value of manganese and are shown in Fig. 6. The increase in optical basicity with increase in praseodymium content may be due to the weak crystal field at a Mn^{2+} site.

Table III gives some typical values of the hyperfine splitting and g values for 0.5 mol % of Mn^{2+} ions in 1 Pr Ca Mn P glass at different temperatures. It is apparent from different average values of A measured from peak to peak, A_{pp}, and trough to trough, A_{tt}, that the individual lines are strain broadened, leading to an asymmetry in the absorption spectrum [24]. The first derivative spectrum as a consequence, shows larger values of A, when measured trough to trough, rather than peak to peak. An overall average was calculated from:

$$A_{\text{avg}} = \left[\frac{(\Delta_{\text{Opp}} + \Delta_{\text{Ott}})}{5} + \frac{(\Delta_{\text{Mpp}} + \Delta_{\text{Mtt}})}{3} + \frac{(\Delta_{\text{Ipp}} + \Delta_{\text{Itt}})}{1}\right] \tag{4}$$

TABLE II Theoretical values of optical basicity for the Pr Ca Mn P glasses (see Table I) with increasing concentration of manganese and praseodymium

Concentration of manganese (mol %)	Optical basicity, Λ_{th}	Concentration of praseodymium (mol %)	Optical basicity, Λ_{th}
0.5	0.4423	0.5	0.4389
0.75	0.4421	1	0.4418
1	0.4418	1.25	0.4449
1.25	0.4416	2	0.4479
3	0.4399	2.5	0.4506
5	0.4379	3	0.4534
		5	0.4638

TABLE III The hyperfine splitting and g values for 0.5 mol % of Mn^{2+} ions in Pr Ca Mn P glass at different temperatures

Temperature (K)	g	Δg	A_{pp} $\times 10^{-4}$ T	A_{tt} $\times 10^{-4}$ T	A $\times 10^{-4}$ T
123	2.035	−0.033	79.0	89.9	84.4
153	2.039	−0.037	81.8	87.2	84.5
183	2.039	−0.037	83.1	94.0	88.5
213	2.039	−0.037	84.5	91.2	87.8
243	2.037	−0.035	87.2	95.4	91.3
273	2.039	−0.037	85.8	94.0	89.9
296	2.035	−0.033	87.2	92.6	89.9
313	2.033	−0.031	81.8	92.6	87.7
393	2.039	−0.037	81.8	92.6	87.7
433	2.037	−0.035	81.8	92.6	87.7

where Δ_{Opp} and Δ_{Ott} represent the differences between the first and sixth peak positions, measured peak to peak and trough to trough respectively. Δ_{Mpp} and Δ_{Mtt} represents difference in positions between second and fifth peaks and Δ_{Ipp} and Δ_{Itt} between second and third peaks. It is interesting to note that, in all of the glass samples, $\Delta_{\text{Opp}}/5 \approx \Delta_{\text{Mpp}}\ /3 \approx \Delta_{\text{Ipp}}$ and $\Delta_{\text{Ott}}/5 \approx \Delta_{\text{Mtt}}\ /3 \approx \Delta_{\text{Itt}}$. This indicates that the g-value in each case is well behaved [24].

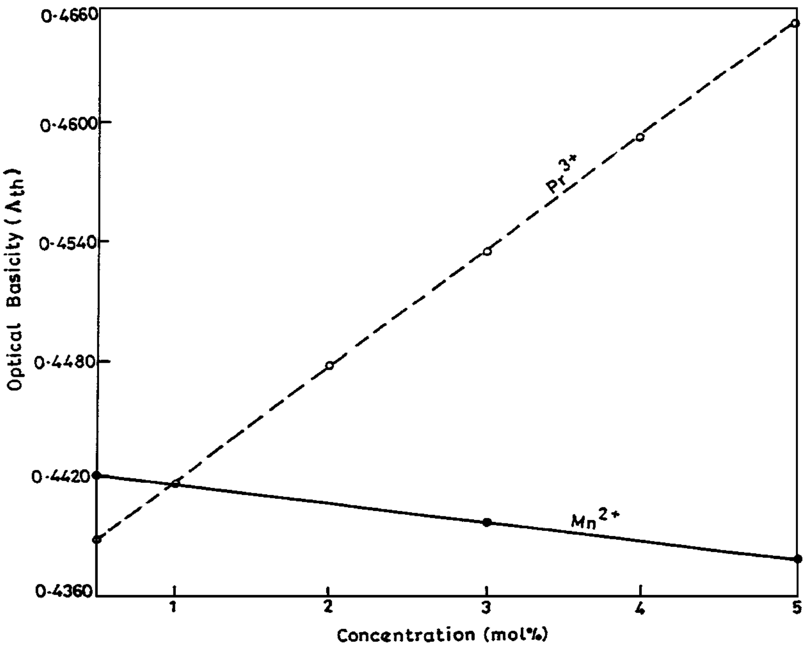

Figure 6 A plot of optical basicity in Pr Ca Mn P glasses for various mol % of Mn^{2+} and Pr^{3+} ions at room temperature.

The Mn^{2+} signal is very similar in all of the glasses, the major difference appearing in magnitude of the hyperfine splitting. Van Wieringen [15] has noted that the strength of the hyperfine splitting depends on the matrix into which the ion is dissolved and is mainly determined by the electronegativety of the neighbours. This means a qualitative measure of the covalency of the bonding in the matrix which can be determined from the value of A; the smaller the splitting, the more covalent the bonding of the anion. It was also noted [15] that the g-value for the hyperfine splitting was indicative of the nature of bonding in the glass. If the g-value shows a negative shift with respect to 2.0023, then the bonding is ionic and conversely, if the shift is positive, then the bonding is more covalent in nature. From the measured negative shift in the g-value, with respect to 2.0023, it is apparent that the Mn^{2+} ion is in an ionic environment [15]. This supports the conclusion drawn from the observed A value.

3.2. Optical absorption studies

Fig. 7 shows the optical absorption spectra of (a) 1 Pr Ca 5 Mn P glass, (b) 1 Pr Ca 1 Mn P glass and (c) 5 Pr Ca 1 Mn P glass at room temperature. Mn^{2+} (d^5) ions gives rise to free ion terms ^6S, ^4G and several other quartet and doublet states of which ^6S is the ground state. In an octahedral environment, in a weak crystal field ^6S transforms into $^6A_{1g}(S)$ as the ground state, where as ^4G splits into $^4T_{1g}(G)$, $^4T_{2g}(G)$, $^4E_g(G)$ and $^4A_{1g}(G)$ states. In the present study, we observed only two bands for Mn^{2+} ions in Pr Ca Mn P glass. From Fig. 7a and b we see that as the concentration of Mn^{2+} ions decreases from 5 to 1 mol % the intensity of the Mn^{2+} band decreases. We also observe from Fig. 7b and c that as the concentration of rare earth oxide praseodymium increases from 1 to 5 mol % the intensity of the band due to Mn^{2+} ion is suppressed.

TABLE IV Comparision of crystal field parameters for Mn^{2+} ions in different host lattices

Complex	B (cm^{-1})	C (cm^{-1})	Dq (cm^{-1})	Reference
Mn^{2+} : $NaMnF_3$	845	3040	775	[28]
Mn^{2+} : NaF	845	3040	760	[29]
Mn^{2+} : ZBLAF	715	3575	630	[30]
Mn^{2+} : $NaSO_4$:$ZnSO_4$	780	3081	700	[31]
Mn^{2+} : PrCaMnP	800	3000	715	Present study

TABLE V Observed and calculated wavenumbers for the bands observed at room temperature for Mn^{2+} ions in Pr Ca Mn P glass ($B = 800$ cm^{-1}; $C = 3000$ cm^{-1} and Dq $= 715$ cm^{-1})

Transition from $^6A_{1g}(S)$ to	Observed band position (cm^{-1})	Calculated band position (cm^{-1})
$^4T_{1g}(G)$	18865	18850
$^4E_g(G)$	24500	24490

The bands at 408 nm and at 530 nm are identified as due to Mn^{2+} ions. These two bands have been assigned due to the transitions $^6A_{1g}(S) \rightarrow {}^4E_g(G)$ and $^6A_{1g}(S) \rightarrow {}^4T_{1g}(G)$ respectively. With these assignments the cubic field energy matrices of Tanabe and Sugano [25], including Tree's polarization correction term α [26] given by Mehra [27] are solved for different sets of B, C and Dq. Since the correction term α is relatively small, it is fixed at the free ion value of 76 cm^{-1}. The values of B, C and Dq obtained in the present investigation are given in Table IV along with those of Mn^{2+} ions in other complexes [28–31]. The values of B, C and Dq give a good fit between the experimentally observed bands at room temperature. The observed and calculated wavenumbers for the bands observed at room temperature for Mn^{2+} ions are given in Table V. The other bands in the absorption spectra at 590, 480, 470 and 445 nm are due to the transitions from the ground

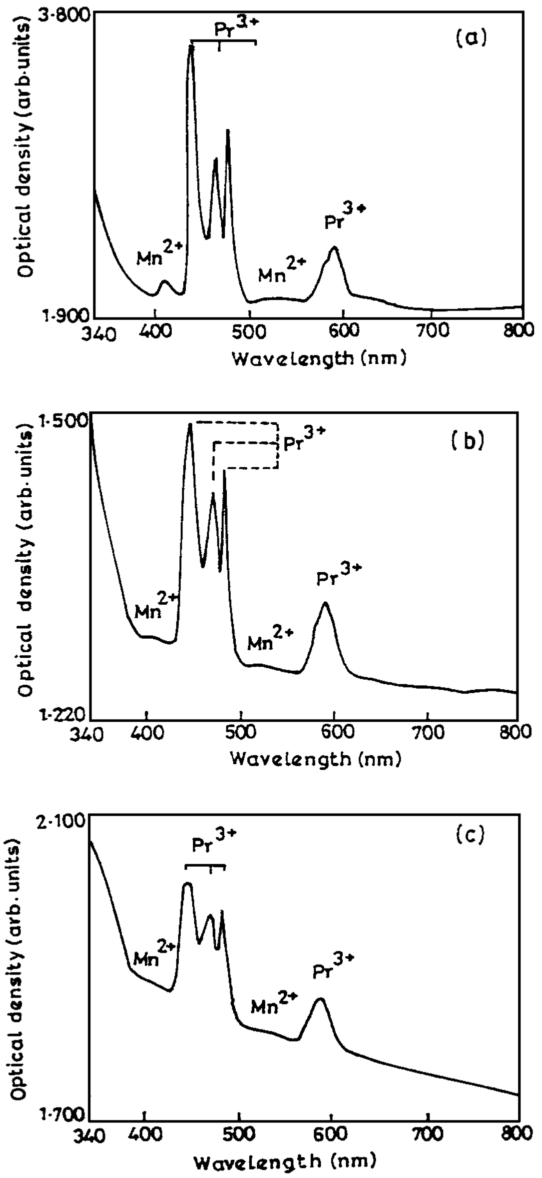

Figure 7 Room temperature optical absorption spectra for: (a) 1 praseodymium calcium 5 manganese phosphate glass; (b) 1 praseodymium calcium 1 manganese phosphate glass and; (c) 5 praseodymium calcium 1 manganese phosphate glass.

state $^3H_4$ to the excited states $^1D_2$, $^3P_0$, $^3P_1$ and $^3P_2$ of Pr^{3+} ion respectively [32].

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

The absorption coefficient 'α' can be determined as a function of frequency using the formula

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

where 'A' is the 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 [33]

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

Thus $(\alpha h\upsilon)^{1/2}$ is plotted against $h\upsilon$. The graphs obtained are shown in Fig. 8 for 1 Pr Ca 1 Mn P and 1 Pr Ca 5 Mn 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 manganese content 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 [34]. The optical band gap obtained in the present work is 3.50–3.25 eV which is in the same order reported in literature for phosphate glasses [34–37].

4. Conclusions

(1) In all the investigated samples, the EPR spectra for Mn^{2+} ions in praseodymium calcium manganese phosphate glasses exhibit three resonance signals and these are attributed to Mn^{2+} ions in rhombic and octahedral symmetry. The spectra exhibit a marked concentration

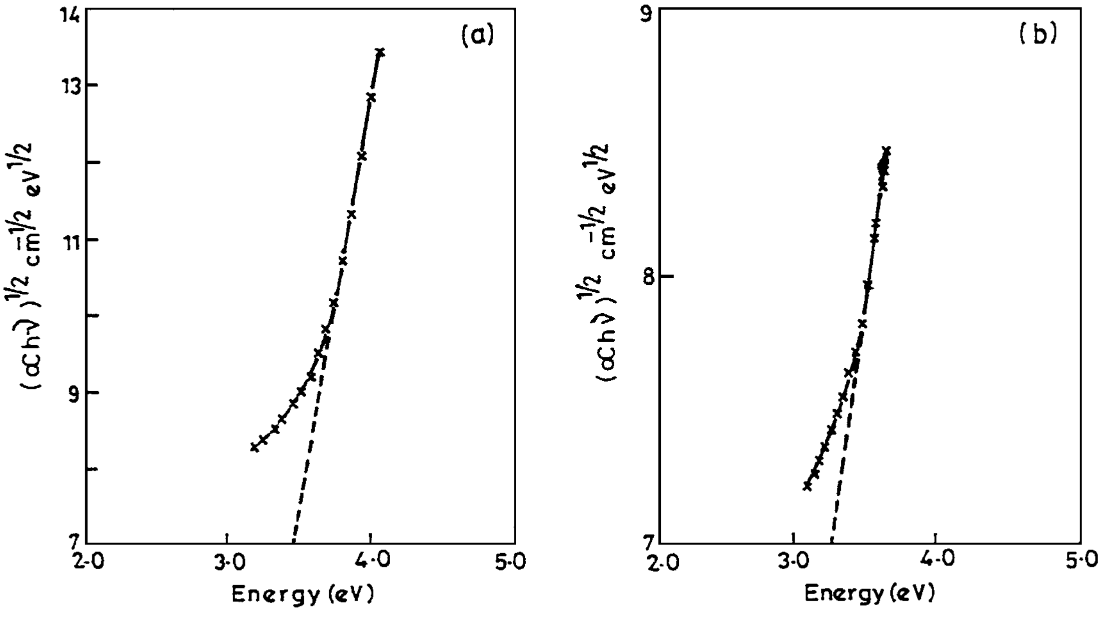

Figure 8 Plots of $(\alpha h\upsilon)^{1/2}$ versus $h\upsilon$ for: (a) 1 mol % and; (b) 5 mol % of manganese ions in 1 Pr Ca Mn P glass at room temperature.

dependence on both manganese and as well as on praseodymium content.

(2) The number of spins participating in the resonance increases with manganese concentration whereas it decreases at high concentration of praseodymium. The increase in spins is due to exchange-coupled pairs whereas for decrease in spins is attributed due to the relaxation process.

(3) The intensity of the resonance signals decreases with increase in temperature according to the Boltzmann law. The linewidths are found to be independent of temperature. Small fluctuations were observed in hyperfine splitting when the temperature is varied.

(4) From the observed g and A values it is concluded that the Mn^{2+} ions are in an ionic environment.

(5) It is observed that the optical band gap energy decreases with increase in concentration of manganese.

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