This thesis deals with the results of "EPR and optical spectral investigations on certain transition metal and rare-earth ions in alkali barium phosphate and alkaline earth alumino borate glasses and in phosphors", carried out by the author during the course of the present research work. The thesis runs as follows.

Chapter I deals with a brief introduction to glassy state and phosphors. The principles of electron paramagnetic resonance (EPR) and optical absorption spectra, with necessary theory, are presented. The general method of obtaining the spin-Hamiltonian parameters from EPR spectrum is outlined. The ligand field theory, necessary for the analysis of optical absorption spectra is also included.

Chapter II describes the experimental techniques employed by the author in the present investigations. The preparation of glasses and phosphors, used in the present work are briefly described. A brief introduction of the JEOL FEI X ESR spectrometer is presented and its major components are explained. A brief description of the JASCO UV-VIS-NIR spectrophotometer used for optical absorption studies is also included.

The contributions made by the author to the existing knowledge are presented in two parts. 'Part A: Glasses' comprises of Chapters III to V, which deal with the results of the investigations on certain transition metal ions (VO^{2+}, Cr^{3+} and Cu^{2+}) doped in glasses. 'Part B: Phosphors' comprises of
Chapters VI and VII, which deal with the results of the investigations on Mn$^{2+}$ and Eu$^{3+}$ ions doped in phosphors.

**Part A: Glasses**

Chapter III reports the results of the electron paramagnetic resonance (EPR) and the optical spectral investigations of VO$^{2+}$ ions in different alkali barium phosphate glasses. The EPR spectra of the samples exhibit eight-line hyperfine structure, characteristic of VO$^{2+}$ ions in octahedral sites with tetragonal distortion. The EPR spectrum is found to exhibit a marked concentration dependence. From the observed EPR spectra, the spin-Hamiltonian parameters, the Fermi contact interaction parameter (k) and the dipolar hyperfine coupling constant (P) have been evaluated. The EPR spectra have also been recorded at different temperatures. The temperature variation EPR studies show that the number of spins participating in the resonance decreases with the increase of temperature, in accordance with the Boltzmann law. From the EPR data, the paramagnetic susceptibility ($\chi$) has been calculated at different temperatures (T). From the plot of $1/\chi$ versus T, Curie constant has been evaluated.

The optical absorption spectrum exhibits two bands, characteristic of VO$^{2+}$ ions in octahedral symmetry with tetragonal distortion. These bands have been assigned to the transitions $^2B_{2g} \rightarrow ^2E_g$ and $^2B_{2g} \rightarrow ^2B_{1g}$ in the order of increasing energy. From the ultraviolet absorption edges, the optical band gap ($E_{opt}$) and the Urbach energy ($\Delta E$) have been evaluated. By correlating the EPR and optical absorption data, the molecular orbital coefficients have been
evaluated. The values of theoretical optical basicity \((A_{db})\) of the glasses have also been calculated.

Chapter IV reports the results of the investigations on electron paramagnetic resonance (EPR) and optical absorption studies of \(Cr^{3+}\) ions in different alkaline earth alumino borate glasses. The EPR spectra of \(Cr^{3+}\) ions doped in calcium alumino borate (CaAB) glasses show a weak resonance signal at \(g \approx 4.50\) and an intense resonance signal at \(g \approx 1.98\). These signals have been attributed to the isolated \(Cr^{3+}\) ions at rhombic sites and the contributions from both the exchange coupled \(Cr^{3+}\) ion pairs and the isolated \(Cr^{3+}\) ions at nearly octahedral sites. The concentration dependence of the linewidth of the resonance signal at \(g \approx 1.98\) suggests the formation of \(Cr^{3+}\) ion clusters by magnetic superexchange interactions. The EPR spectra have also been recorded at different temperatures. The temperature dependence of the resonance signal at \(g \approx 1.98\) suggests that the exchange interaction between \(Cr^{3+}\) ions is antiferromagnetic in nature with Néel temperature 233 K. The number of spins, participating in the resonance at \(g \approx 1.98\) has been calculated at different temperatures. From the EPR data, the paramagnetic susceptibility \((\chi)\) has been calculated at different temperatures \((T)\). The plot of \(1/\chi\) and \(T\) is found to obey Curie-Weiss law, with negative Curie temperature. By measuring the relative intensities of the resonance signal at \(g \approx 1.98\), at different temperatures, the value of antiferromagnetic coupling constant \((J)\) has been estimated.

The optical absorption spectrum shows four bands, characteristic of \(Cr^{3+}\) ions in nearly octahedral symmetry. These bands have been attributed to the transitions \(^4A_{2g}(F) \rightarrow ^4T_{2g}(F), ^4A_{2g}(F) \rightarrow ^4T_{1g}(F), ^4A_{2g}(F) \rightarrow ^2A_{1g}(G)\) and
\[ {^4A_{2g}(F) \rightarrow ^4T_{1g}(P) \text{ of } Cr^{3+} \text{ ions, in the order of increasing energy. From the positions of band maxima, the crystal field splitting parameter (Dq) and the Racah interelectronic repulsion parameters (B and C) have been evaluated. From the ultraviolet absorption edges, the optical band gap (E_{opt}) and the Urbach energy (\Delta E) have been evaluated. The values of theoretical optical basicity (\Lambda_{rb}) of the glasses have also been calculated.} \]

Chapter V reports the results of the investigations on electron paramagnetic resonance (EPR) and optical absorption spectra of Cu$^{2+}$ ions in different alkaline earth alumino borate glasses. The EPR spectra of Cu$^{2+}$ ions in calcium alumino borate (CaAB) glasses exhibit resonance signals, characteristic of Cu$^{2+}$ ions in axially elongated octahedral sites. From the EPR spectra, the spin-Hamiltonian parameters have been evaluated. The observed g values (\(g_1 > g_2 > g_3\)) suggest that the Cu$^{2+}$ ions, in the present sample, occupy tetragonally distorted octahedral sites with \(d_{x^2-y^2}\) orbital (\(^2B_{1g}\)) as the ground state. The EPR spectrum exhibits a marked concentration dependence. The EPR spectra of Cu$^{2+}$ ions doped in CaAB glass have also been recorded at different temperatures. The number of spins (N) participating in the resonance has been calculated as a function of temperature T. From the EPR data, the paramagnetic susceptibility (\(\chi\)) has been evaluated at different temperatures (T). From the plot of \(1/\chi\) versus T, the Curie temperature and the Curie constant have been evaluated.

The optical absorption spectra of all the glasses exhibit a single broad band. This band has been attributed to the transition \(^3B_{1g} \rightarrow ^3B_{2g}\) of Cu$^{2+}$ ions in axially elongated octahedral sites. By correlating the EPR and optical absorption
data, the nature of in-plane σ bonding between Cu$^{2+}$ ions and ligands is estimated. From the ultraviolet absorption edges, the optical band gap ($E_{opt}$) and the Urbach energy ($\Delta E$) have been evaluated. The values of theoretical optical basicity ($A_{th}$) of the glasses have also been calculated.

**Part B: Phosphors**

*Chapter VI* reports the results of the investigations on electron paramagnetic resonance (EPR), luminescence and infrared (IR) spectra of Mn$^{2+}$ ions doped in zinc gallate powder phosphor. The EPR spectrum, at room temperature, exhibits a sextet hyperfine pattern centered at $g_{eff} = 2.00$, characteristic of Mn$^{2+}$ ion. The EPR spectrum exhibits a marked concentration dependence. The EPR spectra have also been recorded at different temperatures. The number of spins (N) participating in the resonance has been calculated as a function of temperature. From the EPR data, the paramagnetic susceptibility ($\chi$) has been calculated at different temperatures (T). From the plot of $1/\chi$ versus T, the Curie temperature and the Curie constant have been evaluated.

The emission spectrum exhibits two bands centered at 468 nm and 502 nm. The low energy band has been attributed to $^4T_1 \rightarrow ^6A_1$ transition of Mn$^{2+}$ ions. The high energy band has been attributed to the trap-state transitions. The excitation spectrum exhibits two bands at 228 nm and 280 nm. The high energy band is attributed to host-lattice absorption and the low energy band is attributed to the charge-transfer absorption or $d^5 \rightarrow d^4$'s transition band. The FT-IR spectrum shows the bands corresponding to the stretching vibrations of Mn-O and Zn-O groups in the presence of Ga$^{3+}$ ions in the spinel lattice.
Chapter VII reports the results of the investigations on electron paramagnetic resonance (EPR) and luminescence studies of Eu$^{2+}$ ions doped in BaFCl powder phosphor. The BaFCl phosphor doped with different concentrations of Eu$^{2+}$ ions has been prepared by solid state reaction in carbon atmosphere. The EPR spectrum exhibits a well resolved hyperfine structure (hf) of $^{151}$Eu and $^{153}$Eu isotopes at $g_{\text{eff}} \approx 1.988$ due to the fine structure transition $| \pm 1/2 \rangle \leftrightarrow | \mp 1/2 \rangle$. The EPR spectra have also been recorded at different temperatures. The number of spins (N) participating in the resonance has been calculated as a function of temperature. From the EPR data, the paramagnetic susceptibility ($\chi$) is calculated at various temperatures (T). The Curie temperature and the Curie constant have been evaluated from the plot of $1/\chi$ versus T.

The emission spectrum of Eu$^{2+}$ ions doped BaFCl phosphor exhibits a strong band, which has been attributed to $4f^6 5d^1 \ell_2 \rightarrow ^6S_{7/2}$ transition of Eu$^{2+}$ ions. The weak bands observed at lower energy side could be due to the transitions of oxygen-vacancy centers isolated and perturbed by Eu$^{2+}$ ions. The excitation spectrum exhibits three bands with a staircase structure superposed on the low energy band. The band observed at 282 nm is attributed to $^6S_{7/2} \rightarrow 4f^6 5d^1 \ell_2$ transition and the bands observed at 216 nm and 250 nm are attributed to oxygen-vacancy centers. The staircase structure with seven peaks has been attributed to the transitions from $^6S_{7/2}$ to the spin-orbit multiplets of $4f^6 [^{3}F_{J}, J = 0 \text{ to } 6]$. 

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