PREFACE

The thesis presents the results of the investigations carried out during the last three years on the optical absorption and electron paramagnetic resonance of transition metal ions in solids. The main objective of the study is to investigate the splitting of the energy levels of the transition metal ions doped into zinc potassium phosphate hexahydrate (ZPPH) crystals and thereby ascertain the site symmetry of the dopant ions.

The results of the optical absorption spectra of VO$^{2+}$, Cu$^{2+}$, Cr$^{3+}$, Co$^{2+}$ and Ni$^{2+}$ in ZPPH are presented in the thesis and form a definite contribution to the existing knowledge of the transition metal ion spectroscopy. In the case of VO$^{2+}$ & Cu$^{2+}$ ions, the EPR spectra of the both single crystal and polycrystalline samples are analysed to supplement the optical absorption data and these results are also presented in the respective chapters.

Chapter 1 presents a brief introduction of the theoretical background necessary for the investigations. Understanding and analyses of the optical absorption and EPR spectra of the transition metal ions in solids. The notations of the energy levels in free ions and crystal fields have been specified. The basic concepts of the crystal fields, molecular orbital and ligand field theories have been delineated. Fundamental concepts of paramagnetic resonance and the general technique for evaluation of spin-Hamiltonian parameters are presented. Various text books, monographs and research publications have been liberally used in
developing the subject matter of this chapter. The results of the each individual ion are summarised in the subsequent chapters. The details of the instruments that are used in the present investigations are outlined in the Annexure. Most of the material of the annexures is collected from the manufacturer's manuals and form a very useful ready reference.

Chapter 2 depicts the results of optical absorption and EPR spectra of vanadyl doped ZPPH. The optical absorption spectrum exhibits three bands and is characteristic of tetragonal site symmetry. The EPR spectrum of powdered sample reveals two set eight-line pattern, which supports the same. Single crystal rotation confirms that the vanadyl impurity has entered the lattice in place of Zn²⁺. From the relevant formulae, the following crystal field and spin-Hamiltonian parameters are evaluated.

\[
\begin{align*}
D_q &= 1492, \quad D_s = -3854, \quad D_t = 186 \text{ cm}^{-1} \\
g_I &= 1.936, \quad g_\perp = 1.976, \quad A_I = 201 \times 10^{-4} \text{ cm}^{-1}, \quad A_\perp = 76 \times 10^{-4} \text{ cm}^{-1} \\
P &= -129 \times 10^{-4} \text{ cm}^{-1}, \quad K = 0.75, \quad \beta^{2+} = 0.73, \quad \epsilon^{-2} = 0.95
\end{align*}
\]

The results are communicated for publication in Solid State Communications.

Chapter 3 describes the results and analyses of the copper doped ZPPH. Optical absorption spectrum exhibits four bands characteristic of Cu²⁺ in rhombic symmetry. EPR spectrum of the polycrystalline sample exhibits four lines each in low, mid and high field regions and supports the optical absorption results. Single crystal rotations have done in all the three planes and analysis indicates that.
this case also Cu$^{2+}$ entered the lattice replacing Zn$^{2+}$. The following spin Hamiltonian and bonding parameters are evaluated:

\[
g_1 = 2.372; \quad g_2 = 2.188; \quad g_3 = 2.032;
\]
\[
A_1 = 78 \times 10^{-4} \text{ cm}^{-1}; \quad A_2 = 48 \times 10^{-4} \text{ cm}^{-1}; \quad A_3 = 63 \times 10^{-4} \text{ cm}^{-1};
\]
\[
\alpha^2 = 0.55.
\]

The results of the investigations indicate that the site symmetry of Cu$^{2+}$ ions in ZPPH is rhombically distorted octahedral with the ground state $^2A_1(d^9)$. Some of the results of the investigations on Cu$^{2+}$ doped ZPPH are published in Indian Journal of Chemistry, vol. 35 A. p.590-591 (1999). Single crystal results are communicated for publication in Solid State Communications.

Chapter 4 contains the results of optical absorption spectra of the chromium doped ZPPH. The optical absorption spectrum is characteristic of Cr$^{3+}$ in trigonally distorted octahedral symmetry. The crystal field parameters are evaluated:

\[
D_q = 1580, \quad B = 780 \quad \text{and} \quad C = 3000 \text{ cm}^{-1}
\]

Since only one band exhibits splitting due to trigonal distortion, the trigonal field parameters could not be evaluated.

The IR spectrum of the sample is characteristic of water and phosphate ions of the host.

Chapter 5 presents the results and analyses of the optical absorption spectra of cobalt doped ZPPH. The optical absorption spectrum of Co\(^{2+}\) doped ZPPH crystal does not exhibit any splittings even at low temperatures and is characteristic of Co\(^{2+}\) in near octahedral symmetry. The following crystal field parameters are evaluated, by solving the relevant matrices:

\[\begin{align*}
D_q &= 930, \quad B = 925 \text{ and } C = 3790 \text{ cm}^{-1}.
\end{align*}\]

Chapter 6 embodies the results and analyses of optical absorption spectra of the nickel doped ZPPH crystals both at RT and LNT. The spectrum at RT does not show any splittings and is characteristic of octahedral symmetry. At LNT the band corresponding to the transition \(^3\)A\(_{2g}\)(F) \(\rightarrow\) \(^3\)T\(_{1g}\)(P) splits into four components and these splittings are attributed to the spin-orbit interaction. Therefore the site symmetry of the Ni\(^{2+}\) ion in ZPPH is ascribed to the octahedral symmetry associated with spin-orbit interaction. The following crystal field parameters are evaluated, by solving the relevant energy matrices:

\[\begin{align*}
D_q &= 900, \quad B = 890 \text{ and } C = 3800 \text{ cm}^{-1}.
\end{align*}\]