ABSTRACT

In the thesis, the electron paramagnetic resonance investigations of the following crystals have been carried out;

i) Sodium Formate (NaHCOO:VO$^{2+}$)

ii) Sodium Formate (NaHCOO:Mn$^{2+}$)

iii) Potassium Oxalate Monoperhydrate (K$_2$C$_2$O$_4$.H$_2$O:VO$^{2+}$)

iv) Potassium Oxalate Monoperhydrate (K$_2$C$_2$O$_4$.H$_2$O:Cu$^{2+}$)

v) Lithium Hydrogen Sulphate (LiHSO$_4$:VO$^{2+}$)

vi) Lithium Hydrogen Sulphate (LiHSO$_4$:Cu$^{2+}$)

Wherever, the dopant is VO$^{2+}$ or Cu$^{2+}$, the optical absorption spectra have also been studied. Wherever, the dopant is Mn$^{2+}$, the superposition model analysis (SKM) has been carried out. All experimental works have been done at room temperature and therefore, the dopants chosen were VO$^{2+}$, Mn$^{2+}$ and Cu$^{2+}$ ions which could give EPR spectra at this temperature.

Sodium formate crystal was chosen in order to compare the results obtained in this crystal with those of formates of second group elements (Ca, Sr, Ba---), investigated widely in our laboratory.

In NaHCOO:VO$^{2+}$, when the dopant concentration was kept low, VO$^{2+}$ ion was found to replace one of the Na$^+$ substitutional sites and when the dopant concentration was increased, VO$^{2+}$ ion was found to replace Na$^+$ ion at two substitutional sites. Reason has been advanced to explain why one site is more favourable in comparison to the other. Spin-Hamiltonian parameters, polar
angles ($\theta, \phi$), molecular bonding coefficients ($\beta^2, \epsilon^2$). Fermi contact term ($k$), dipolar hyperfine coupling parameter ($p$) and crystal field parameters ($D_q, D_g, D_l$) have been evaluated with the help of EPR and Optical spectra.

In NaBCO$_3$:Mn$^{2+}$, two substitutional sites for Mn$^{2+}$ have been found. They are magnetically equivalent but oriented differently. When Mn$^{2+}$ ion substitutes Na$^+$ ion, there has been some rearrangement in the immediate neighbourhood, which has been estimated by SPM analysis.

As far as the values of spin-Hamiltonian parameters and other parameters obtained by optical spectroscopy are concerned, there was not found any simple rule to differentiate between the values obtained in formates of monovalent cation and those obtained in formates of divalent cations.

EPR spectra of K$_2$C$_2$O$_4$•H$_2$O had been earlier studied with Mn$^{2+}$ and Cu$^{2+}$ ions as the dopants. It was thought to be interesting to extend this study to K$_2$C$_2$O$_4$•H$_2$O$_2$ and thus assess the effect of an additional oxygen ion associated with each molecule.

In K$_2$C$_2$O$_4$•H$_2$O: Mn$^{2+}$, two interstitial sites have been found and the principal axes of the complexes are directed towards K$^+$-K$^+$ (vacancy) direction. In K$_2$C$_2$O$_4$•H$_2$O$_2$:Mn$^{2+}$, two sites have been found, but Mn$^{2+}$ ion occupies a position in between the two nearest K$^+$ sites and the principal axes are oriented towards Mn$^{2+}$-O direction. The reasons for the observed differences are assigned. SPM analysis explains the relaxation effects in the
vicinity of Mn$^{2+}$ ion.

In $K_2C_2O_4 \cdot H_2O:Cu^{2+}$, there are two magnetically inequivalent sites and it has been proved that the Cu$^{2+}$ has entered the lattice as an oxalate moiety rather than in a substitutional K$^+$ site. In $K_2C_2O_4 \cdot H_2O_2:Cu^{2+}$, there are two sites but Cu$^{2+}$ occupies position between two nearest K$^+$ sites and the principal axes are directed towards Cu$^{2+}$$\cdot$$-0$ direction. The reasons for these differences are given. Covalency parameters ($\alpha', \alpha''$), the mixing coefficients ($\alpha$ & $\beta$) and the Fermi contact term ($K$) have been calculated. The ground state wave function has been evaluated.

LiHSO$_4$ crystal was chosen because there was no EPR data. No XRD was also available, which made it more challenging.

In LiHSO$_4:VO^{2+}$, two VO$^{2+}$ sites were found. They were found to occupy tetrahedral voids (120° inclined to each other). The angular variation of the spectra suggests that the LiHSO$_4$ might belong to hexagonal close-packed crystal structure. Data from EPR and optical spectra were combined to estimate spin-Hamiltonian parameters and other parameters.

EPR spectra of LiHSO$_4:Cu^{2+}$ was very interesting and unusual. It extended from near zero field region to $g \simeq 2$ region. It could be tentatively interpreted as arising due to $S = 2$ system obtained by super-exchange among four copper ions mediated by intervening oxygen ions. Such spectra have been observed recently by us in many other systems. There are earlier references also to the spectra of $S = 2$ system. The optical spectrum of LiHSO$_4:Cu^{2+}$
is also unusual and five absorption signals are observed in the region 23000 cm\(^{-1}\) to 35000 cm\(^{-1}\) instead of usual three signals in the region 70000 cm\(^{-1}\) to 100000 cm\(^{-1}\). More work in this system is planned in our laboratory.

The present thesis has been divided into six chapters. The first chapter gives a brief outline of the phenomenon of EPR, a short description of the experimental set up and theories related to VO\(^{2+}\), Mn\(^{2+}\) & Cu\(^{2+}\) ions, since these dopants have been used in the studies carried out in this thesis. In the second chapter, EPR and optical absorption studies on NaHCOO:VO\(^{2+}\) is presented. In third chapter, EPR and SPM analysis of NaHCOO:Mn\(^{2+}\) is given. Fourth chapter includes EPR and SPM investigations on K\(_2\)C\(_2\)O\(_4\).H\(_2\)O \(\cdot\) Mn\(^{2+}\). Fifth chapter presents EPR study of K\(_2\)C\(_2\)O\(_4\).H\(_2\)O \(\cdot\) Cu\(^{2+}\) single crystal. In sixth chapter, EPR and optical absorption studies of LiHSO\(_4\):VO\(^{2+}\) and LiHSO\(_4\):Cu\(^{2+}\) are described.

In all the cases, the crystals have been grown by slow evaporation of the aqueous solution of the compounds in which a little amount of the dopant is added. The EPR spectrometer used is JES-RE2X, JEOL (JAPAN) with 100 KHz field modulation. The optical absorption spectra have been recorded on CIBA-CORNIG 2800 UV -visible spectrophotometer. The results of our investigations have been published in various journals, a list of publications is given at the end of the thesis.