Spectroscopic Investigations of Mn (II) Doped Ni L-Histidine Hydrochloride Monohydrate Crystals

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ABSTRACT: *The main focus of this work had been to grow good quality crystals from amino acids and amino acid based materials for spectroscopic applications. Growth of crystals from aqueous solution is one of the methods of crystal growth which is extremely popular in the production of technologically important crystals. For the first time, Mn(II) doped Ni L-Histidine Hydrochloride monohydrate, Mn-NiLHICL crystals were grown from aqueous solution at room temperature by slow evaporation technique. The Mn(II) doped crystals were characterized by spectroscopic techniques such as X-Ray diffraction studies, Electron Paramagnetic Resonance(EPR), Optical absorption and FTIR studies. From the powder diffraction patterns of the grown crystals, lattice cell parameters were evaluated, a = 1.5186 nm, b = 0.8917 nm and c = 0.6889 nm. Values calculated from EPR studies for 'g' and Hyperfine Splitting factor for Mn(II) ion in the host crystal, g = 2.071, A= 103 x 10^{-4} cm^{-1} indicated octahedral symmetry. Optical absorption studies confirmed the octahedral symmetry of Mn(II) ions in the host crystal. Crystal field and inter electronic parameters were evaluated for Mn^{2+} ion as Dq = 855cm^{-1}, B = 810 cm^{-1}and C = 2480 cm^{-1}. Characteristic vibrations of the structure in the crystal confirmed the nature of bonding between the doped metal ion and the amino acid complex.*
Keywords: Crystal growth, XRD, EPR, Optical, FTIR studies.

I. INTRODUCTION

Amino acid crystals doped with transition metal ions are suitable model systems to understand the basic aspects of role of metal ions in proteins.The critical role that dopants play in semiconductor devices stimulated the research on the potential applications of doped crystals. Doping is a well-chosen and widely accepted technique for incorporating the required physical properties in a bulk material for technological applications [1–4]. The technique has been extensively explored to modify the properties like electro optical (photoluminescence), conductivity and crystal growth [5,6]. It has also been demonstrated that metal ions, specially the transition metal ions are the most versatile in modifying the properties of a compounds dopant ions[7-9].It is also well known that doping of a paramagnetic ion in a paramagnetic or diamagnetic host lattice of known symmetry helps one to understand the symmetry and covalency around the embedded ion. Doped amino acids and amino acid complexes were reported to exhibit NLO properties as they combine the advantages of organic and inorganic materials [[10,11]. L-Histidine is a protein forming amino acid, playing a fundamental role in several biological mechanisms including the formation of haemoglobin and is being used in the treatment of allergic diseases and anaemia [12]. Multi-dentate complexes of amino acids with metal ion dopants are at present considered as novel materials for second harmonic generation (SHG) properties [13]. Mn(II) is a well-known paramagnetic probe for both NMR and EPR investigations of metal ion binding sites and ligand interactions in enzymes and other proteins [14]. Studies were reported on Cu(II),Ni(II), Cr(III)and Zn(II) ion doped crystalline structures of pure L-Histidine hydrochloride monohydrate. In all these cases, dopant ions occupied interstitial positions in the crystal lattice of L-Histidine hydrochloride monohydrate and exhibited very good NLO properties. [4,15,16].

As far as our literature search goes, little attention has been paid to doped amino acid complexes and few investigations have been carried out on this class of compounds[16]. Thus there is a great need to explore their full potential by undertaking studies on these materials and the present study is one in this direction. Various transition metal ion doped amino acid complexes were grown in our laboratory in crystalline form and were characterized initially to understand the structure, site symmetry and nature of bonding. Mn(II) ion doped NiLHICl complex was one such system whose growth aspects were studied by slow evaporation technique. The grown crystals were characterized by X-Ray Diffraction, EPR, FTIR and Optical absorption studies to understand the site symmetry and the nature of bonding.

II. Experimental Section

Nickel L-Histidine Hydrochloride Monohydrate (here after called as Ni-LHICL) crystals were grown by slow evaporation technique at room temperature from aqueous, equimolar and equivolume solutions of Nickel Chloride Hexahydrate (NiCl$_2$6H$_2$O) and L-Histidine Hydrochloride Monohydrate (C$_6$H$_{10}$N$_3$O$_2$Cl.H$_2$O). For the preparation of Mn(II) doped crystals, an amount of 0.01 mol% of Manganese Chloride was added to the growth solution and yields Mn(II) doped Ni-LHICL crystals about fifteen days during the slow evaporation process. Powder X-Ray diffraction patterns of the prepared Mn(II) doped Ni-LHICL crystals are recorded on PHILLIPS PW1830 X-ray diffractometer. A suitable crystal was selected for optical absorption spectrum and taken from JASCO V-670 Spectrophotometer. Electron Paramagnetic Resonance spectrum was recorded on JEOL- JES-FA 200 Spectrophotometer. Fourier Transformed-Infra Red (FT-IR) spectrum was recorded using KBr pellets on Thermo Nicolet 6700 FT-IR spectrophotometer in the region 400-4000 cm^{-1}.

III.   Results and Discussion

3.1 Crystal Structure:

Mn(II) doped Nickel L-histidine Hydrochloride monohydrate single crystals are Orthorhombic with space group $P2_12_12_1$. The unit cell dimensions are a = 1.5186, b = 0.8917 and c = 0.6889 nm. L-Histidine molecule consists of two groups of very nearly co-planar atoms. In the unit cell, these two groups are turned towards each other and the molecule is said to exist in the closed form [17] .

3.2. Powder X-ray diffraction data:

Powder X-ray diffraction pattern of Mn(II) doped Ni-LHICL crystals is shown in the Fig. 1 and it contains sharp, clean patterns which indicates the highly crystalline phases. The prepared crystal system belongs to orthorhombic system and the corresponding lattice cell parameters are evaluated by using POWD programme. The obtained lattice cell parameters are, a = 1.5186, b = 0.8917 and c = 0.6889 nm. These values agreed well with the reported values of pure LHICL crystal cell parameters, a = 1.5317, b = 0.8929, c = 0.6851 nm [23]. The powder X-ray diffraction data for Mn(II) doped Ni-LHICL crystals are given in the Table 1.

3.3. EPR spectrum of Mn(II) doped NiLHICL crystals:

EPR Spectra of Mn(II) at room temperature are well resolved due to long spin lattice relaxation times in its ground state [18-20]. The EPR spectrum of Mn(II) ions in general can be analyzed using the spin Hamiltonian.

$$H = g\ \beta\ BS + SAI + SDS$$

Where 'g' is the isotropic factor, 'β' the Bohr magneton, 'B' is External magnetic field, 'S' is the vector operator of the electron spin momentum and 'A' is the hyperfine interaction parameter, 'I' is the vector operator of nuclear spin momentum and 'D' is the   zero field splitting parameter. The isotropic signal at g = 2.071 is due to Mn(II) in an environment close to octahedral symmetry. The value of 'A' in the range of 103.84×10^{-4} cm-1 is consistent with Mn(II) in octahedral co-ordination [21]. It has been shown by Van Wieringen[22] that there is a regular variation of hyperfine coupling constant with covalency.

3.4. Optical absorption studies of Mn(II) doped NILHICL crystals:

The five d-electrons of Mn(II) ions are distributed in the t2g and eg. orbitals, with three in the former and two in the later. Thus the ground state configuration is t2g,eg.This configuration gives rise to the ^6A_1g, ^4A_1g, ^4Eg, ^4T_1g, ^4T1g and a number of doublets states of which ^6A_1g lies lowest according to Hund's rule. The free ion level for of Mn(II) in the order of an energy increasing are ^6S,^4G,^4P,^4D and ^4F etc. The energy levels of Mn(II) ion in octahedral environment i.e. coordination number 6 are $^6A_1g(S)$, $^4T_1g(G)$, $^4T_2g(G)$,^4Eg, $^4A_1g(G)$, $^4T_2g(D)$ and $^4Eg(D)$. The $^4Eg + ^4A_1g(G)$ and $^4Eg(D)$ levels have relatively less influence compared to the other levels by crystal field. It means that the relative sharp lines can be expected in the absorption or excitation spectrum, which is the criterion for assignments of levels for Mn(II) ion [23,24]. Manganese free ion ground term is $^6S_{5/2}$ therefore no spin-allowed absorptions are possible. The electronic d-d transitions from a high spin d^5 configuration must necessarily involve the pairing of some electron spins. Such transitions are both spin-forbidden and orbitally forbidden therefore the bands are weak these transitions are assigned using Tanabe-Sugano diagram[25].

The spectrum recorded in the optical absorption region is shown in Fig.3. The observed bands at 685 nm corresponds to $^6A_1g(S) \rightarrow ^4T_1g(G)$, the band at 405 nm is assigned to $^6A_1g(S) \rightarrow ^4T_2g(D)$ for Mn(II) ions in the Mn(II) doped NiLHICL crystals [26-29]. The optical absorption spectrum also exhibited three characteristic bands at 1185,720 and 422 nm for Ni(II) ion in the host lattice. These three intense bands observed are 6 assigned to the three spin allowed transitions $^3A_2g(F) \rightarrow ^3T_2g(F)$, $^3A_2g(F) \rightarrow ^3T_1g$ (F) and $^3A_2g(F) \rightarrow ^3T_1g(P)$ will be intense. Based on these assignments energy matrices (d^5 and d^8) are solved for different values of inter-electronic repulsion parameters B, C and Crystal field parameter Dq. The following values are for Mn(II) ion Dq = 855, B = 810 and C = 2480 cm-1. For Ni(II) ion Dq = 840, B = 820 and C = 2950 cm-1. The observed and calculated band head positions of Mn(II) doped NiLHICL crystals are shown in Table 2.

3.5. FT-IR spectra of Mn(II) doped NiLHICL crystals:

FT-IR spectroscopy was effectively used to identify the functional groups in the grown crystal. FT-IR spectrum of the Mn(II) doped NiLHICL crystals is shown in Fig. 4. The NH_3^+ stretching and characteristic of hydrogen bonding region shows broad bands in the range 3500-2500 cm-1.The N-H stretching vibration of the amino group in L-Histidine gives rise to an amide band between 3310 and 3270 cm-1. The amide band is usually part of a Fermi resonance doublet with the second component absorbing weakly between 3100 and 3030 cm-1 [30]. The CH2 group of Histidine produces peaks at 2602 and 3035cm-1 due to its symmetric and asymmetric stretching modes. The peak at 1574 cm-1 is attributed to the skeletal vibrations of Histidine ring. The values are shown in Table 3. The FT-IR spectral study reveals the presence of various functional groups and confirms the slight distortion of the structure of the crystal due to doping. These values are compared with the values of pure L-Histidine [31]and doping of L-Histidine hydrochloride monohydrate crystal [32].

IV.   Conclusion

Mn (II) NiLHICL Crystals are grown at room temperature and are characterized using Powder XRD, EPR, Optical absorption and FT-IR studies. The following conclusions are drawn

Powders XRD pattern confirms the pure LHICL crystal structure. The deviation of evaluated cell parameter with the pure crystals may confirm the incorporation of transition metal ions in the host lattice. The analysis of the optical absorption spectra confirms the coordination of Ni(II) and Mn(II) ions is octahedral site symmetry in the host lattices. The crystal field and Racah parameters are determined. From the EPR spectral studies, spin-Hamiltonian and hyperfine splitting parameters also suggests the octahedral sites for Mn(II) ions in the host lattice. By correlating EPR and optical results, the evaluated parameters indicate the partial covalence between Mn(II) ions and its ligands. From FT-IR studies, the prepared Mn(II)-NiLHICL crystals shows different vibrational bands related to stretching modes of NH_3^+, COO- groups, and in plane C-H deformation imidazole ring which confirms the presence of amino acid. A five membered ring is formed with the metal, amine nitrogen and the carboxylic oxygen.

Acknowledgments

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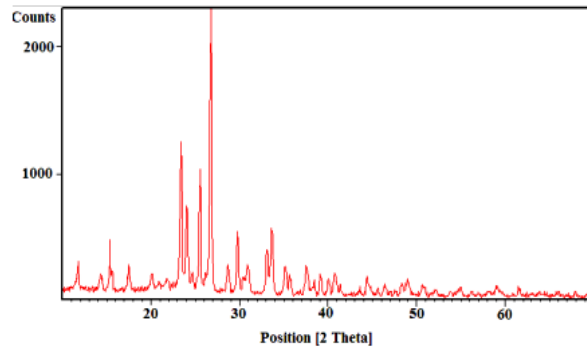
Figures

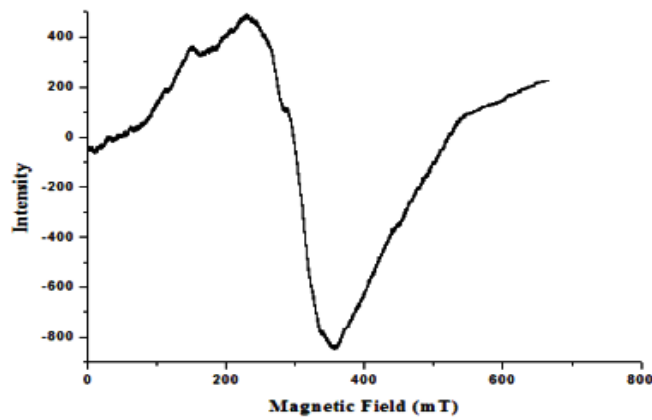**Fig.1 XRD spectrum of Mn (II) doped Ni L-HICl crystal.**

Fig.2 EPR spectrum of Mn(II) doped Ni L-HICl.
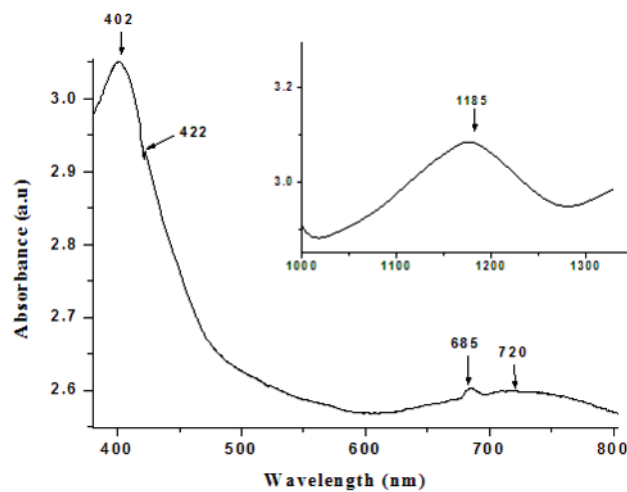

Fig.3 Optical spectrum of Mn (II) doped Ni L-HICl
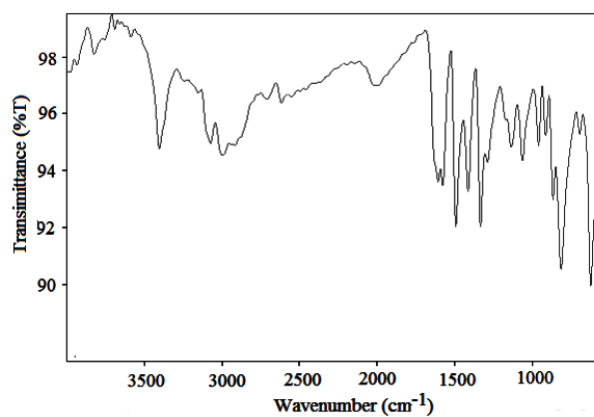

Fig.4 FTIR of Mn(II) doped Ni L-HICl

Table :1 d-spacing and h k l values obtained for of Mn(II) doped NiLHICL Crystal.

Sys: Orthorhombic   P Lambda= 1.540600   F30= 2.0(.032,464)   X30= 0

Lo30/ Lc464 M20= 2.8 A= 21.36 B= 104.63 C= 159.43 D= 41.10 E=   1.80 F= 30.

a=1.5186 nm , b= 0.8917nm, c= 0.6889 nm

| d-spacing A | | Indices | | | 2θ | |
obs.	calc.	h	k	l	obs.	calc
7.5306	7.5306	0	1	0	11.74	11.74
6.1630	6.1630	1	1	0	14.36	14.36
5.7576	5.7576	1	0	1	15.38	15.38
5.1587	5.1587	0	1	1	17.17	17.17
4.4096	4.4096	0	1	1	20.12	20.12
4.0681	4.0681	1	1	1	21.83	21.83
3.8002	3.7653	0	2	0	23.39	23.61
3.6983	3.7174	3	2	0	24.04	23.92
3.4875	3.4890	5	1	0	25.52	25.51
3.3306	3.3336	5	0	0	26.75	26.72
3.1086	3.1068	5	1	1	28.69	28.71
2.9970	2.9980	0	1	2	29.79	29.78 .
2.8894	2.8947	1	1	2	30.92	30.87
2.7039	2.7031	1	1	2	33.10	33.11
2.6621	2.6566	3	0	2	33.64	33.71
2.5496	2.5498	6	2	1	35.17	35.17
2.5139	2.5136	6	0	1	35.69	35.69
2.3933	2.3896	3	2	1	37.55	37.61
2.3005	2.3035	3	1	2	39.13	39.07
2.2118	2.2114	6	3	1	40.76	40.77
2.0731	2.0698	6	0	2	43.63	43.70
2.0368	2.0361	5	3	2	44.44	44.46

Table : 2 Optical transitions for the Mn(II) doped NiLHICL crystals

Transitions From $^6A_{1g}(S)$	Observed		Calculated
	Wavelength (nm)	Wavenumber (cm^{-1})	Wavenumber (cm^{-1})
ForMn(ll) $^6A_{1g}(S)\square\ ^4T_{1g}(G)$	405	24685	24881
$^6A_{1g}(S)\square\ ^4T_{2g}(D)$	685	14594	14558
For Ni(ll) $^3A_{2g}(F)\square\ 3T_{1g}\ (F)$	422	23690	23696
$^3A_{2g}(F)\square\ 3T_{1g}\ (P)$	720	13885	13803
$^3A_{2g}(F)\square\ 3T_{2g}\ (F)$	1185	8436	8400

Table : 3 Observed Vibrational modes of Mn(II) doped Ni L-Histidine Hydrochloride Monohydrate Crystals

Wavenumber (cm^{-1})	Assignments
3403	O-H stretching of water
2997	N-H Symmetrical stretching
2616	C-H Symmetrical stretching
1635	C=O stretching
1605	Asymmetric bend of NH_3^+ and C=N stretching
1575	Asymmetric mode of –COO$^-$ and C=C stretching
1491	Symmetric bend of NH_3^+
1416	Symmetric mode of –COO$^-$ and C-N stretching
1070	C-O stretching of corboxylic group
863	C-H out of plane bending