Research Article

Effect of Ni^{2+} Doping on the Growth and Properties of Mn-L-Histidine Hydrochloride Monohydrate Crystals

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The main focus of this work had been to grow good quality crystals from amino acids and amino acid-based materials for nonlinear optics (NLO) applications. For the first time, a series of amino acid complexes doped with transition metal ions were grown in our laboratory from aqueous solutions by slow evaporation technique. Ni(II) ion doped Manganese L-Histidine hydrochloride monohydrate (Ni(II)-MnLHICl) crystals were grown on the same lines and were characterized by powder X-ray diffraction (XRD), optical absorption, electron paramagnetic resonance, and infrared absorption studies. From Powder XRD, the unit cell lattice parameters were calculated as $a = 1.5301$ nm, $b = 0.8928$ nm and $c = 0.6851$ nm. From electron paramagnetic resonance (EPR) spectra, isotropic “ g ” factor and spin hamiltonian parameter A all were calculated as 2.0439 and 20×10^{-4} , respectively. From optical absorption studies, crystal field splitting value (D_q) and the interelectron repulsion parameters B and C were calculated for Ni^{2+} and Mn^{2+} as $D_q = 850 \text{ cm}^{-1}$, $B = 725 \text{ cm}^{-1}$, $C = 2640 \text{ cm}^{-1}$ and $D_q = 915 \text{ cm}^{-1}$, $B = 810 \text{ cm}^{-1}$, $C = 2780 \text{ cm}^{-1}$, respectively. The presence of various functional groups and the modes of vibrations were confirmed by FTIR studies.

1. Introduction

Doping is a well-chosen and widely accepted technique for incorporating the required physical properties in a bulk material for technological applications [1–3]. The technique has been extensively explored to modify the properties like electrooptical (photoluminescence), conductivity and crystal growth [4]. It has also been demonstrated that metal ion dopants are the most versatile in modifying the properties of a compound [5]. Metal amino acid interactions have been widely studied because of their biological importance. Metal amino acid complexes constitute very important model systems in order to understand the electronic properties of metal ions in biologically important macromolecules [6]. Amino acid complexes doped with transition metal ions are suitable model systems for understanding the basic aspects of role of metals in proteins [7, 8].

L-Histidine is an optically active α -amino acid in its laevo-form and is a tridentate ligand that has an imidazole

ring, amino, and carboxylate groups. It is also a protein-forming amino acid playing a fundamental role in several biological mechanisms including the formation of hemoglobin and is being used in the treatment of allergic diseases and anemia [9]. Complexes of amino acids with metal ion dopants combine the advantage of organo amino acid with that of inorganic metal ions [10]. Multidentate complexes of amino acids with metal ion dopants are at present considered as novel materials for second harmonic generation (SHG) properties and for nonlinear optics NLO applications too [11]. Effects of Cu(II), Ni(II), Cr(II) and Zn(II) ion doping on pure L-Histidine hydrochloride monohydrate crystal structures were reported [12–15]. In all these cases, dopant ions occupied interstitial positions in the crystal structure of L-Histidine hydrochloride monohydrate and exhibited very good NLO (Nonlinear optics) properties. 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 complex crystals were grown in our laboratory and were characterized to understand the structure, site symmetry, and nature of bonding in them. Ni(II) ion doped MnLHICl complex was one such system, synthesized and characterized by various techniques such as X-ray diffraction XRD, electron paramagnetic resonance (EPR), Fourier transform infrared (FTIR), and optical absorption studies. The growth aspects of the crystals were studied using slow evaporation technique. The photographs of as-grown crystals of Ni(II) ion doped MnLHICl is shown in Figure 1.

2. Material and Methods

2.1. Ni(II) Doped MnLHICl Crystal Growth by Slow Evaporation Technique. Crystals of Ni^{2+} ion doped MnLHICl were grown by slow evaporation at room temperature from the aqueous, equimolar, and equivolume solutions of manganese chloride hexahydrate ($\text{MnCl}_2 \cdot 6\text{H}_2\text{O}$) and L-Histidine hydrochloride monohydrate ($\text{C}_6\text{H}_{10}\text{N}_3\text{O}_2\text{Cl} \cdot \text{H}_2\text{O}$) containing 0.01 mol% of nickel chloride dihydrate ($\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$) added as dopant to the growth solution. Crystals of Ni(II) doped MnLHICl appeared in about 45 days.

The Powder X-Ray Diffraction studies of the crystal were carried out using PHILIPS MAKE PW1830 X-Ray Diffractometer. Ni(II)-MnLHICl crystals were powdered and X-Ray powder diffraction patterns were recorded at room temperature. All the diffraction patterns were obtained using $\text{K}\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$) at 30 kV and 15 mA from $2\theta = 8^\circ$ to 70° with steps of 0.05° . Polycrystalline EPR spectrum of the sample was recorded at room temperature on JEOL JES-FA 200 EPR Spectrometer. The optical absorption spectrum was recorded in the range of 200–1400 nm using JASCO V670 Spectrophotometer and the FTIR spectrum was recorded using KBr pellets on THERMO NICOLET 6700 FTIR Spectrophotometer in the region 400–4000 cm^{-1} .

2.1.1. Crystal Structure. The unit cell of pure L-Histidine hydrochloride monohydrate ($\text{C}_6\text{H}_{10}\text{N}_3\text{O}_2 \text{ HCl} \cdot \text{H}_2\text{O}$) has four molecules per unit cell, belonging to orthorhombic system. The reported values of cell parameters for pure LHICl crystal were $a = 1.5275 \text{ nm}$, $b = 0.8929 \text{ nm}$, $c = 0.6851 \text{ nm}$ with space group $\text{P}_{2_1}2_12_1$ [17]. Ni^{2+} doped MnLHICl crystals were also orthorhombic with space group $\text{P}_{2_1}2_12_1$. The unit cell dimensions for the crystal were evaluated as $a = 1.5301 \text{ nm}$, $b = 0.8928 \text{ nm}$, and $c = 0.6851 \text{ nm}$ which were presented in Table 1. Thus, the observed values of cell dimensions for Ni(II) doped MnLHICl were in good agreement with the reported values of pure L-Histidine. A comparative account of the X-Ray diffraction data of the Ni^{2+} doped Mn LHICl crystal with that of pure LHICl was presented in Table 1.

FIGURE 1: Ni(II) doped MnLHICl crystals.

TABLE 1: XRD data of pure LHICl and Ni(II) doped MnLHICl crystals.

Sample	Cell parameters/nm	Volume/ $\text{\AA}^3$	Space group
Pure LHICl	$a = 1.5285$	933.71	$\text{P}_{2_1}2_12_1$
	$b = 0.8884$		
	$c = 0.6876$		
Ni(II) doped MnLHICl	$a = 1.5301$	935.97	$\text{P}_{2_1}2_12_1$
	$b = 0.8928$		
	$c = 0.6851$		

3. Results and Discussion

Ni(II) doped crystal of MnLHICl complex (Figure 2) had a different growth habit and color from those of Ni(II) doped LHICl [13].

3.1. X-Ray Spectral Studies. From powder X-ray diffraction data, Ni(II) doped MnLHICl crystal was orthorhombic with lattice parameters $a = 1.5301 \text{ nm}$, $b = 0.8928 \text{ nm}$, and $c = 0.6851 \text{ nm}$ and space group $\text{P}_{2_1}2_12_1$ was analyzed and the results were presented in Table 1. The computer program POWD (an Interactive Powder Diffraction Data Interpretation and Indexing Program, Version 2.2) was used to calculate hkl values which were presented in Table 2 and found to be in good agreement with the JCPDS values.

3.1.1. EPR Studies. The powder EPR spectrum of the Ni^{2+} doped MnLHICl was recorded at room temperature and was shown in Figure 3. The crystals gave a well-resolved EPR spectrum, even though very few d^8 systems that exhibit room temperature EPR spectra are known in the literature. The Spin-Hamiltonian parameters were determined. The resonance peak that appeared at $g = 2.0033$ and the value of hyperfine splitting factor, $A = 20 \times 10^{-4}$, indicated octahedral site symmetry for Ni^{2+} in the host lattice [18, 19].

3.1.2. Optical Absorption Studies. The UV-VIS spectrum was recorded for the grown crystals in the wavelength range 200–1400 nm and shown in Figure 4. The UV-VIS calculations are carried out by energy matrices. Three intense, spin-allowed transitions due to ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$, ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$, and ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$ and two weak, spin-forbidden transitions due to ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^1\text{E}_g(\text{D})$ and ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$ are expected for Ni^{2+} ion in an octahedral field [20].

FIGURE 2: Powder XRD spectrum of Ni(II) doped MnLHICl crystal.

FIGURE 3: EPR spectrum of Ni(II) doped MnLHICl crystal.

FIGURE 4: UV-VIS spectrum of Ni(II) doped MnLHICl crystal.

TABLE 2: d-Spacings and hkl values of Ni(II) doped MnLHICl crystal.

d-Spacing		Indices			2 θ Deg.	
Obs	Calc	h	k	l	Obs	Calc
7.7126	7.7113	1	1	0	11.46	11.47
7.6555	7.6505	2	0	0	11.55	11.56
6.2534	6.2532	1	0	1	14.15	14.15
5.8115	5.8094	2	1	0	15.23	15.24
5.1220	5.1219	1	1	1	17.30	17.30
5.1051	5.1039	2	0	1	17.36	17.36
4.4640	4.4648	0	2	0	19.87	19.87
4.4318	4.4315	2	1	1	20.02	20.02
4.4308	4.4286	3	1	0	20.02	20.03
4.2856	4.2853	1	2	0	20.71	20.71
4.0928	4.0912	3	0	1	21.70	21.70
3.8563	3.8556	2	2	0	23.04	23.05
3.8277	3.8252	4	0	0	23.22	23.23
3.7401	3.7402	0	2	1	23.77	23.77
3.7205	3.7193	3	1	1	23.90	23.91
3.6333	3.6332	1	2	1	24.48	24.48
3.5181	3.5161	4	1	0	25.29	25.31
3.4255	3.4258	0	0	2	25.99	25.99
3.3601	3.3591	3	2	0	26.51	26.51
3.3428	3.3439	1	0	2	26.64	26.64
3.3415	3.3419	4	0	1	26.65	26.67
3.1981	3.1984	0	1	2	27.87	27.87
3.1306	3.1307	1	1	2	28.49	28.49
3.1267	3.1266	2	0	2	28.52	28.52
3.0168	3.0161	3	2	1	29.59	29.59
2.9512	2.9509	2	1	2	30.26	30.26
2.9213	2.9213	1	3	0	30.58	30.58
2.9058	2.9047	4	2	0	30.74	30.76
2.8442	2.8438	3	0	2	31.43	31.43
2.7956	2.7942	5	0	1	31.99	32.01
2.7738	2.7735	2	3	0	32.25	32.25
2.7296	2.7296	0	3	1	32.78	32.78
2.6872	2.6872	1	3	1	33.31	33.31
2.5712	2.5709	2	3	1	34.87	34.87
2.5612	2.5609	2	2	2	35.01	35.01
2.5252	2.5241	5	2	0	35.52	35.54
2.4542	2.4537	4	1	2	36.58	36.59
2.4070	2.4066	3	3	1	37.33	37.33
2.3913	2.3916	6	0	1	37.58	37.62
2.3693	2.3684	5	2	1	37.94	37.96
2.3494	2.3489	4	3	0	38.28	38.29
2.3099	2.3087	6	1	1	38.96	38.98
2.2832	2.2822	5	0	2	39.44	39.45
2.2586	2.2588	1	0	3	39.88	39.88
2.2466	2.2467	0	3	2	40.10	40.15
2.2325	2.2329	0	4	0	40.38	40.38
2.2228	2.2228	1	3	2	40.55	40.55

TABLE 3: Optical values of Ni(II) doped MnLHCl crystal. Observed and calculated energies of various bands in the optical absorption spectrum of Ni(II) doped MnLHCl.

Transition	Wavelength (nm)	Observed wavenumber (cm ⁻¹)	Calculated wavenumber (cm ⁻¹)
For Ni ²⁺ ion			
³ A _{2g} → ³ T ₂ (F)	510	19602	19628
³ A _{2g} → ³ T ₁ (F)	680	14594	14618
³ A _{2g} → ³ T ₁ (P)	1090	9171	9150
	$D_q = 915 \text{ cm}^{-1}$	$B = 725 \text{ cm}^{-1}$	$C = 2640 \text{ cm}^{-1}$
For Mn ²⁺ ion			
⁶ A _{1g} → ⁴ T ₁ (G)	425	23523	23520
⁶ A _{1g} → ⁴ A ₁ (G)	610	16371	16388
	$D_q = 850 \text{ cm}^{-1}$	$B = 810 \text{ cm}^{-1}$	$C = 2780 \text{ cm}^{-1}$ $[\alpha] = 76$

TABLE 4: IR values for Ni(II) doped MnLHCl crystal.

Band in cm ⁻¹	Assignment
3587	O–H stretch of H ₂ O
3265	Symmetrical stretching (ν_1) of H ₂ O
2988	Asymmetric stretching of NH ₃ ⁺
2597	Symmetric stretching of NH ₃ ⁺
2358	Stretching of C–H
1605	Asymmetric bend of NH ₃ ⁺ and C=N stretching
1494	Symmetric bending of NH ₃ ⁺
1411	Symmetric mode of COO ⁻ and C–N stretching
1285	O–H in-plane bending
1061	O–H stretching of carboxylic acid
864	C–H out-of-plane bending
693	CH ₂ bending
620	Torsional NH oscillation of NH ₃ ⁺

The three observed strong peaks at 510 nm, 680 nm, and 1090 nm were assigned to ³A_{2g}(F) → ³T_{2g}(F), ³A_{2g}(F) → ³T_{1g}(F) and ³A_{2g}(F) → ³T_{1g}(P) transitions. The crystal field splitting value (D_q) and the interelectron repulsion parameters B and C were calculated as $D_q = 915 \text{ cm}^{-1}$, $B = 725 \text{ cm}^{-1}$, and $C = 2640 \text{ cm}^{-1}$. Peaks corresponding to Mn²⁺ (d^5) ion in an octahedral environment at 425 nm and 610 nm from ⁶A_{1g}(S) → ⁴A_{1g}(G) and ⁶A_{1g}(S) → ⁴T_{1g}(G) transitions were also observed in the host lattice which coincide with the reported values for divalent manganese ion [21]. The crystal field splitting value (D_q) and the inter electron repulsion parameters B and C were found to be $D_q = 850 \text{ cm}^{-1}$, $B = 810 \text{ cm}^{-1}$ and $C = 2780 \text{ cm}^{-1}$. The band assignments indicated the presence of both the ions in the crystal lattice of Ni (II) doped MnLHCl and were shown in Table 3.

3.1.3. FTIR Spectral Studies. FTIR spectrum and the characteristic assignment of peak values for Ni²⁺ doped MnLHCl crystal in the range of 4000–500 cm⁻¹ were shown in Figure 5 and Table 4, respectively, and were in good agreement with the absorptions reported in the literature for LHCl and its complexes [22–24].

FIGURE 5: FTIR spectrum of Ni(II) doped MnLHCl crystal.

4. Conclusion

For the first time, Ni²⁺ ion doped manganese L-histidine hydrochloride monohydrate crystals were grown by slow evaporation technique at room temperature in a period of 45 days. X-ray diffraction studies confirmed that the grown crystals belong to orthorhombic system with the space group P2₁2₁2₁. A close observation of the crystallographic data showed very slight changes in the values indicating negligible changes in the crystal structures. The Racah parameters (B and C) and crystal field parameter (D_q) were calculated. From the EPR and optical studies, it was concluded that octahedral site symmetry existed for the Ni(II) ion in the host lattice. The presence of various functional groups and the modes of vibrations were identified by FTIR studies.

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