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Structure and Characterization of Mn(II) DOPED Zn(II) L-Histidine Hydrochloride Monohydrate Complex Crystals

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Abstract: **- The present study focuses on characterisation of Mn(II) doped Zn(II) L-Histidine hydrochloride complex crystals grown from aqueous solutions, using slow evaporation technique at room temperature. Characterization of grown crystals was carried by 13C NMR, Thermal, SEM, Chemical etching studies. The measured NLO activity of the grown crystals is encouraging.**

Index Terms— L-Histidine, NLO, Thermal, optical, SEM.

INTRODUCTION

The influence doping on several crystals has gained importance as it can modify the electrical and optical properties of materials used in advanced technological applications [1- 4]. Amino acids are interesting compounds which exhibit molecular chirality, absence of strongly conjugated bonds and zwitter ionic nature making them potential candidates for NLO applications [5]. Over the past few decades, metal ion–amino acid interactions gained technological importance in the form of non-linear optical materials. Amino acids complexes with the incorporation of metal ions as dopants are found advantageous due to derived properties of organo amino acid and inorganic metal ions. These are considered as novel materials for the property of second harmonic generation (SHG) [6].

Amino acid L-Histidine contains an atom of chiral carbon atom which forms crystal in non-centro symmetric space group, an essential condition for the compounds to exhibit NLO properties [7]. L-Histidine had been widely studied as it shows nonlinear optical (NLO) activity in L-Histidine tetrafloroborate [8]. Several compounds of L-Histidine were found to have high SHG efficiency [9]. In view of amino acids potential ability to bind to metal ions, L-Histidine complexes are reported to play a prominent role in biological processes [10, 11]. Zinc is a trace element biologically and participates in diverse processes in animal and human physiology [12]. It is essential for catalytic activity of about 100 enzymes [13, 14] and plays pivotal role in immunisation, healing wounds, synthesis of proteins and DNA [15, 16]. Zinc-Histidine complex, [Zn (His) 2] was found to possess greater biological potency, enhanced bioavailability with an antioxidant potential compared to other zinc salts and hence protects cortical neurons from induced damage of oxidative stress [17]. Manganese is an important element which helps in various physiological activities. It integrates many metalloproteinase that are vital in metabolic processes. Reports of Mn (II) doped amino acids are available. Reported EPR studies on manganese incorporated into L-Alanine crystals indicated that Mn (II) ions were at magnetically equivalent interstitial sites [18].EPR studies of Mn(II) doped monohydrated L-Asparagine crystals also indicated the incorporation of Mn(II) ions into two distinct chemically active sites in asparagine crystals [19].According to our survey two crystal systems, Zinc (D,L-Histidine)$_2$ complex with the incorporation of Cu(II) ion as dopant [20] and Zinc L-Histidine complex with Mn(II) ion as dopant [21] were reported. The later was also characterised by EPR, X-ray diffraction and calorimetric studies. Histidine ligand was reported as bound to Zn(II) ion through imidazole and amino nitrogens and carboxylate oxygen. ESR studies of Zinc L-Histidine complex with Mn(II) ion as dopant are available. No other transition metal ions were reported as dopants on L-Histidine complexes. Hence Mn(II) doped Zn(II) L-Histidine hydrochloride monohydrate complex is a novel crystal system grown and characterized in our laboratory.

In the present study, Mn(II) ion doped Zn L-Histidine complex crystals were developed by slow evaporation of aqueous solution at room temperature and characterized by various spectroscopic techniques like powder X-Ray diffraction analysis, Electron paramagnetic resonance (EPR) FT-IR ,UV-Vis spectral and micro hardness studies. Nd: YAG laser study confirmed the second harmonic generation (SHG) efficiency of the grown crystals. Scanning electron microscopic, thrmogravimetric and differential thermal analysis (TG and DTA) and etching studies were also performed to ascertain their thermal and mechanical stabilities.

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2. EXPERIMENTAL DETAILS

Material and Method

Zn(II) L-Histidine hydrochloride monohydrate crystals, here after called ZnLHICl, were developed from equimolar and equivolume solutions of Zinc chloride hexahydrate (ZnCl2.6H2O) [0.244g, 0.1mol] and L-Histidine hydrochloride monohydrate (C6H12ClN3O3) [0.209g, 0.1mol] using slow evaporation method at room temperature. Mn (II) doped Zn(II)LHICl crystals were grown by adding 0.01mol % of Mn(II) chloride solution to the growth solution.

General procedure

The solution was constantly agitated with a magnetic stirrer for about two hours to obtain a homogeneous mixture and was filtered through a whattman filter paper. The solution was then poured into a fresh 100 ml beaker, and covered at the brim with a porous aluminum foil and was left for slow evaporation at room temperature. Colorless crystals of Mn(II) doped ZnLHICl shown in Fig .1 with good external morphology and of various sizes were obtained in about 40 to 45 days. The crystals were washed with acetone and dried. Dimensions of the well grown crystal were 10 x 9 x 6 mm3.

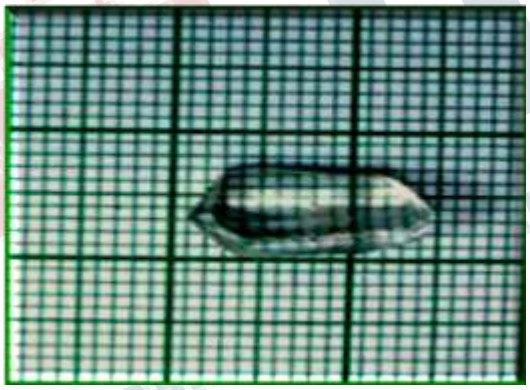

Fig.1 Mn(II) doped ZnLHICl crystal

Analytical Discussion

XRD spectrum was recorded on PHILIPS Make PW1830 X-RAY Diffractometer with Kα (λ = 1.54056 Å) radiation, EPR spectrum on JEOL Make JES-FA 200 EPR Spectrometer at room temperature, FT-IR spectrum on thermo Nicolet 6700 within the range 400- 4000 cm-1 using KBr pellets, UV-VIS spectrum in the range of 200–1400 nm on JASCO V670 Spectrophotometer, 13CNMR spectrum on Bruker AvII-400 MHz, TG/DTA analysis on SII Nano Technology model TG/DTA 6200. SEM studies by SEM Hitachi-S520, Micro hardness studies by HM-210 Vicker's micro hardness tester, Chemical Etching studies by Metallurgical microscope (Axioskop 40 MAT), NLO activity by Q switched High energy Nd: YAG Laser- Quanta Ray : Model Lab-170-10 - Energy – 850 mJ /1064 nm.

2.1 ^{13}C NMR Spectral studies :

^{13}C NMR spectral study was carried out to identify the carbon atoms present in various chemical environments in the grown crystals. 13C NMR spectrum of Mn(II) doped ZnLHICl shown in Fig.2 also has six resonance peaks. A comparison of these peak positions with the positions of LHICl crystal revealed up field shifts for all the positions. The resonance peak at δ = 172.99 ppm assigned to the presence of CO group of side chain, two consecutive signals at δ = 134.02 and 127.41 ppm assigned to the CH groups of imidazole ring and the peak at 117.73 ppm assigned to the ring C atoms showed up field shifts. Resonance peaks resolved at δ = 53.64 and 25.75 ppm due to the CH and CH2 groups of L-Histidine in Mn (II) doped ZnLHICl crystal also exhibited up field shifts. These changes observed in the positions of resonance peaks may be because of complex formation and and doping of metal ions on L-Histidine crystals [21]. The chemical shifts recorded in the 13C NMR in LHICl and Mn(II) doped ZnLHICl crystals are presented in Table.1.

Table: 1 ^{13}C NMR Chemical shifts in LHICl and Mn (II) doped ZnLHICl crystals

Spectrum	Signals of δ(ppm)		Functional groups
	LHICl	Mn(II) doped ZnLHICl	
^{13}C NMR	176.86	172.57	CO of side chain
	139.20,135.21	134.02,127.41	CH of imidazole ring
	119.23	117.73	C of imidazole ring
	54.43	53.64	CH of side chain
	27.14	25.75	CH_2 of side chain

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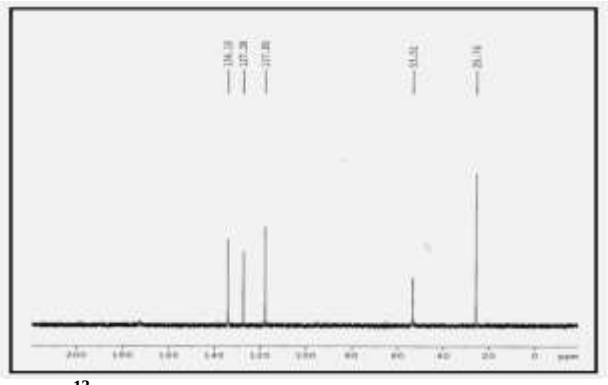

Fig. 2^{13}C NMR spectrum of Mn(II) doped ZnLHICl crystal

2.2 THERMAL STUDIES: TG/DTA studies

Thermal analysis shows thermal stability of the grown crystals and monitoring this property is important in the fabrication technology [22]. Thermo grams of TG/DTA for Mn(II) doped ZnLHICl crystals as shown in Fig .3

In simultaneously recorded TG/DTA curves for Mn(II) doped ZnLHICl crystals, first stage of weight loss corresponding to 5.9% occurred at 175oC was found to be due to the loss of water molecules and the next is also due to major weight loss in the temperature range 287-381°C. Weight loss continued further up to 800oC due to decomposition and volatilisation of the crystal. In line with TG study, DTA curve of Mn(II) doped ZnLHICl recorded two sharp endothermic peaks, one at 175°C attributed for removal of water from crystal lattice and the second at 287°C was related to the melting point of the Mn (II) doped ZnLHICl crystal. Third stage of decomposition was at 381°C with 42% weight loss, the products of decomposition being NH_3, CO, CO_2 and CH_4. Enhanced thermal stability was observed for the Mn(II) doped ZnLHICl crystals due to inclusion of metal ions over LHICl due to doping. The shifting in peaks to higher temperatures could be seen clearly in the grown doped crystals.

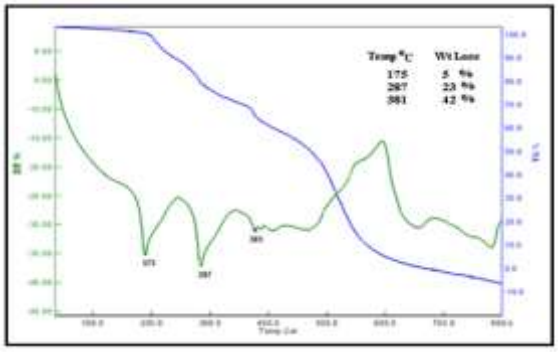

Fig.3 TG/DTA analysis of Mn(II) doped ZnLHICl crystal

2.3 Scanning electron microscopic (SEM) and EDAX Analysis :

Scanning Electron Microscopy (SEM) was useful in investigating the surface morphology of Mn (II) doped ZnLHICl . Images at two different magnifications are shown in Fig.4. This technique is useful to find the presence of imperfections in the grown crystals. The SEM image of LHICl crystal given in Fig.5 shows a smooth surface, free from inclusions and scattered centres [23].

The SEM image of Mn(II) doped ZnHICL crystals indicate clearly affected external morphology of the LHICl crystal due to formation of complex and doping. Rough surface with visible inclusions on the surface of the doped crystal was also due to different growing patterns of the crystal. These visible inclusions were assumed to the incorporation of dopant in the crystal.

Energy dispersive X-ray analysis (EDAX) is an important tool for identification of elements present in. EDAX spectrum of Mn(II) doped ZnHICL crystals is shown in Fig.6. The constituent elements were indicated in the quantitative results for the doped crystals as shown in the Fig.6. Presence of weak peak for Mn in the crystals is a clear indication of its presence as a dopant in the lattice of host.

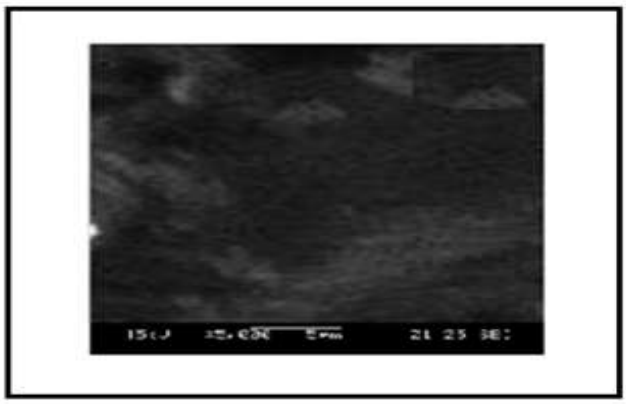

Fig.4 SEM image of LHICl crystal

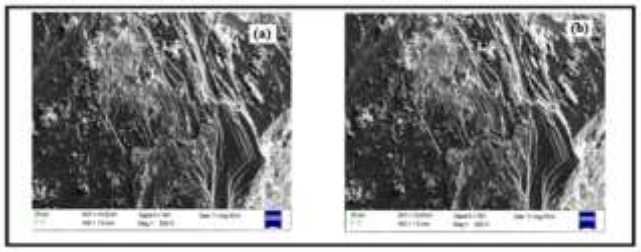

Fig.5 SEM images of Mn(II) doped ZnLHICl crystals at two different magnifications

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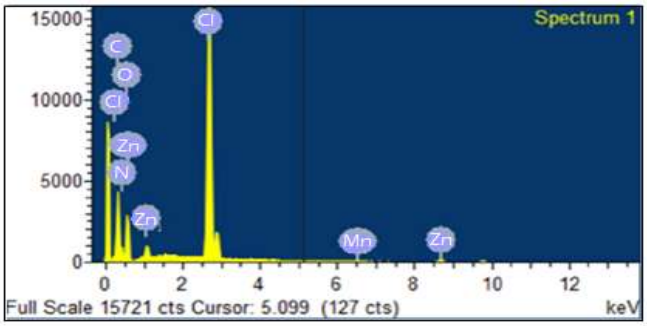

Fig. 6 EDAX spectrum of Mn(II) doped ZnLHICl crystal

2.4 Microhardness studies:

Hardness is one of the important factor in selection of bulk crystals in fabrication of devices Hence it is important to understand the mechanical properties of the crystals [24]. Higher hardness value of a crystal indicates application of higher stress to form dislocation, which confirms more perfection in the processes of crystallisation. [25]. Hardness was measured using the relation, Hv = 1.8544 P/d2.

Micro hardness, measured in terms of vicker's hardness number Hv, indentation load is P in Kg and d, the diagonal length, taken as an average of several impressions made. Micro hardness results showed that hardness increased with increasing loads up to a load of P = 52.2 g with a value for Hv = 46 kg/mm2. After applying a load of P = 52.2 g, Hv value showed a decreasing trend, cracks were formed due to the release of internal stress generated locally by indentation ,decreasing the hardness value [26] as shown in Fig. 7.

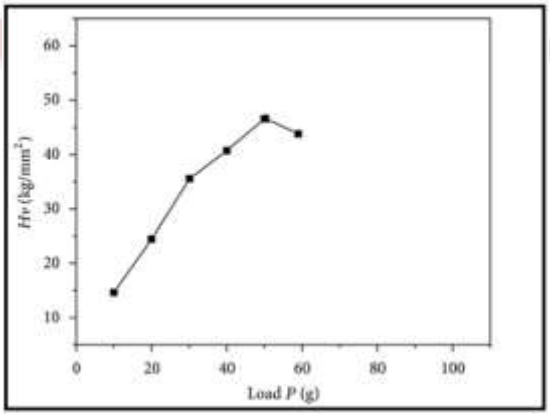

Fig.7 Microhardness studies on Mn(II) doped ZnLHICl crystal

2.5 Chemical etching studies : Chemical etching which was carried out on doped crystals with water as etchant . It is one of the simple and powerful tools to find the symmetry of the crystal face from the shape of etch pit and the distribution of structural defects in the grown crystals [27. Surface of the grown crystal was dipped in water for etching and the etched samples were immediately examined and their microstructures are shown in Fig 8. The existence of etch pits even after continuous etching suggests that they are due to dislocation. The increased size of etch pit formed on these doped crystals can be due to crystalline perfection when compared to LHICl [28, 23].

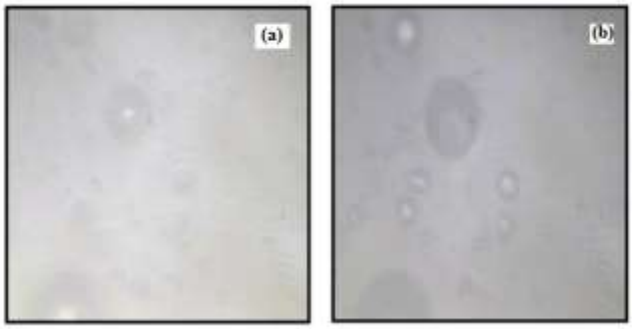

Fig. 8 Etch patterns of Mn(II) doped ZnLHICl crystal for (a) 5 Sec and (b) 10 Sec

2.6 Nonlinear optical activity of Mn(II) doped Zn LHICl crystals

The nonlinear optical conversion efficiency test was carried out using the Kurtz Powder technique [29]. In this experiment Q switched pulses were obtained from a Q switched Nd - YAG laser of wave length 1064 nm. The crystals were reduced to a particle size of 125-150 mm and packed in bore of uniform size with micro capillary nature and then subjected to laser radiation.

The output from the crystal was monochromatic which reflects the property of fundamental waveof 532nm. The generated second harmonic radiation was focused by a lens and detected by a photo multiplier tube. A reference material KDP was used for the present measurement with an incident beam of power 0.68 J/P. The SHG efficiency of the crystal was confirmed by observing the emission of green light. The SHG efficiency of Mn(II) doped ZnLHICl crystal was found to be 5.8 mJ, higher than that of many organic NLO crystals but slightly lower than KDP value (8.8 mJ).

CONCLUSIONS

13C NMR showed up field shifts for all the positions indicating a change of carbon atom environment of functional groups due to complex formation. The melting point of the Mn(II) doped ZnLHICl crystal is 287 °C, greater than LHICl. SEM studies indicate visible inclusions on the surface due to the incorporation of dopant ion and EDAX analysis confirmed the presence of metal ions in the lattice of crystal. Crystals are mechanically stable with crystalline

perfection and with minimum deformations.The SHG effiency of Mn(II) doped ZnLHICl crystal is equal to 5.8 mJ.

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REFERENCES

[1] X. Lai, K.J. Roberts, L.H. Avanci, L.P. Cardoso and J.M. Sasaki; J. Appl. Crystallogr., 2003; 36: 1230.

[2] D.A.H. Cunningham, R.B Hammond, X. Lai and K.J. Roberts; Chem. Mater., 1995; 7:1690.

[3] X. Lai, K.J. Roberts, J.M. Bedzyk, P.F. Lyman, L.P. Cardoso and J.M. Sasaki; Chem. Mater., 2005; 17: 4053.

[4] C.M.R. Remedios, W. Paraguassu, P.T.C. Freire, J. Mendes-Filho, J.M. Sasaki and F.E.A. Melo; Phys. Rev. B., 2005; 72: 014121.

[5] M.L. Caroline, R. Sankar, R.M. Indirani and S.Vasudevan; Mater Chem Phys., 114 (2009) 490.

[6] P.C. Thomas, S. Aruna, J. Madhavan, Reena Ittyachan, Joseph Arul Pragasam, Joe G M Jesudurai, K.Prabha and P.Sagayaraj; Ind. J. Pure and Appl.Phy., 45 (2007) 591.

[7] Ittyachan Reena, S. X. Jesu Raja, S. A. Rajasekar and P. Sagayaraj; Mater. Chem. Phys., 90 (2005)10.

[8] H.O. Marcy, M.J. Rosker, L.F. Warren, P.H. Cunningham and C.A. Thomas; Opt. Lett., 20 (1995) 252.

[9] S. Goma, C.M. Padma, C.K. Mahadevan; Mater. Lett., 60 (2006) 3701.

[10] M. Vazquez, D. Rothman and B. Imperiali; Org.Biomol. Chem., 2 (2004) 1965.

[11] L.Antolini, G. Marcotrigiano, L. Menabue and G.C. Pellacani; Inorg. Chem., 22 (1983)141.

[12] C.A. Heyneman; Ann. Pharmacother., 30(1996)186.

[13] H.H. Sandstead; J. Lab. Clin. Med., 124 (1994) 322.

[14] Institute of Medicine, Food and Nutrition Board Dietary Reference Intakes, National Academy Press., Washington D.C, 1-28 (2001).

[15] N.W. Solomons; J.Nutr. Rev., 56 (1998) 27.

[16] A.S. Prasad; J. Nutrition., 11(1995) 93.

[17] R.J. Williams, J.P. Spencer and F.M. Goni and Rice-Evans CA, Neurosci. Lett., 371 (2004) 106.

[18] J. R. Pinheiro, E. W. S. Caetano, V. N. Freire, G. A. Farias, K.Krambrock, M. C. F. de Oliveira, J. A. Pinheiro, B. S. Cavada and J. L. de Lima Filho; Appl. Phys. Lett. (Submitted)

[19] K. Krambrock, K. J. Guedes, L. O. Ladeira M. J. B. Bezerra, T. M. Oliveira, G. A. Bezerra, B. S. Cavada, M. C. F. de Oliveira, M. Z. S. Flores, G. A. Farias and V. N. Freire; Physical review., 75 (2007) 104205.

[20] D. Sergio Dalosto, Rafael Calvo, L.J.Pizarro and I. Mari Arriortua; J.Phy. Chem. A., 105 (2001) 1074.

[21] P.Anandan, Ph.D Thesis; Studies on the growth aspects and Characterization of some amino acids based semiorganic nonlinear optical single crystals, (2010) 82.

[22] P.Anandan, Ph.D Thesis; Studies on the growth aspects and Characterization of some amino acid based semiorganic nonlinear optical single crystals, (2010) 85.

[23] C. Alosious Gonsago, Helen Merina Albert, P.Malliga and A. Joseph Arul Pragasam; Mat. Man. process., 27 (2012) 355.

[24] P. Rajesh and P. Ramasamy; Physica B., 404 (2009)1611.

[25] G. Anandha Babu; J. Crys. Growth., 310 (2008)1228.

[26] P. Anandan, G. Parthipan, T. Saravanan, R. Mohan Kumar, G. Bhagavan narayana and R. Jayavel; Physica B: Cond. Matter., 405 (2010) 4951.

[27] K. Sangwal; Etching of Crystals: Theory, Experiment and Application, North Holland Physics Publishing, Amsterdam, The Netherlands (1987).

[28] V. Renuga; Adv. Res., 2 (2014) 1159.

[29] SK Kurtz and TT. Pery; J.Appl. Phys., 39 (1968) 3798.