

## **Synthesis, growth and studies of undoped and magnesium chloride doped L-histidine hydrochloride single crystals**

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### **ABSTRACT**

*Undoped and magnesium chloride doped L-Histidine Hydrochloride single crystals were synthesized and grown by solution method with slow evaporation technique. Solubility of the samples was measured at different temperatures. The grown crystals were subjected by X-ray diffraction techniques to identify the crystal structure. Fourier Transform Infra-Red (FT-IR) spectra to identify the functional groups. The UV-Vis-NIR spectral studies were carried out to find the transmittance and other optical parameters. The presence of elements in the grown crystals was identified by EDAX studies. The Vicker's microhardness test was carried out to test the mechanical stability and the hardness parameters are determined. The TG/DTA and DSC studies confirm the thermal stability of the grown crystals. The second Harmonic generation (SHG) efficiency of the crystals was found by Kurtz and Perry technique.*

**Keywords:** single crystal, crystal growth, NLO, thermal analysis, hardness

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### **INTRODUCTION**

In the last decade, organic nonlinear optical crystals with aromatic rings have attracted much attention because of their high nonlinearity, fast response and tailor made flexibility. However, the short comings of aromatic crystal, such as poor physico-chemical stability, low hardness and cleavage tendency hinder their device application. In order to keep the merits and overcome the shortcomings of organic materials, some new classes of NLO crystals such as metal organic or semi organic crystals have been developed [1]. Amino acids are interesting materials for NLO applications. Complexes of amino acids with inorganic salts are promising materials for optical Second Harmonic Generation (SHG). In recent years semiorganic crystals have emerged as extremely promising building blocks for NLO materials. They share the properties of both organic and inorganic materials. Hybrid crystals substantial may have acoustically induced birefringent effects as it was established for the Ru-complexes [2,3]. These materials can be used as better alternative for KDP crystals in frequency doubling and laser fusion experiments due to their higher values of laser damage threshold [4,5]. L – Histidine analogs have attracted attention as promising NLO materials after it was found that L – Histidine tetrafluoroborate have higher NLO properties than LAP by Marcy et. al [6].

L-Histidine Hydrochloride(LHHC) is one such promising semiorganic nonlinear optical material and through scan on literature reveals that only a limited work on various properties of this complex has been reported [7,8]. Magnesium chloride is one of many substances used for dust control, soil stabilization, wind erosion, mitigation, its second – most common use is ice control. Magnesium chloride is also used in fertilizer, water treatment, several medical and topical (skin related) applications. If magnesium chloride is used as a dopant, it may alter the properties of L – Histidine Hydrochloride crystals. In the present investigation, the growth aspects of bulk crystals of undoped and MgCl<sub>2</sub> doped LHHC were studied using slow evaporation technique. The grown crystals were characterized by single crystal XRD, FT – IR, EDAX and UV – Vis – NIR, thermal, microhardness and SHG studies.

## MATERIALS AND METHODS

### 2.1. Synthesis of the sample

Undoped and magnesium chloride ( $\text{MgCl}_2$ ) doped L-Histidine Hydrochloride (LHHC) salts were synthesized by L-Histidine (Merck 99%) and Hydrochloric acid (AR grade) in the equimolar ratio 1:1 in aqueous solution. The solution was stirred well at a constant rate to get homogeneity. Prepared solution was then filtered twice using whatmann filter paper, the solution was transferred to a petri dish and it was allowed to evaporate isothermally at  $40^\circ\text{C}$  in a constant temperature water bath for few days to get the undoped LHHC salt. 1mole % magnesium chloride was added to the solution of LHHC and similar procedure was followed as the synthesis of undoped LHHC salt. After synthesizing the salts, solubility studies of the samples were carried out.

### 2.2. Solubility studies

Solubility study was carried out using a hot plate magnetic stirrer and a digital thermometer. Initially the temperature of solvent was maintained at  $30^\circ\text{C}$ . The synthesized salt of LHHC was added systematically to 50 ml of deionized water in an air-tight container kept on the hot-plate magnetic stirrer and stirring was continued till a small precipitate was formed. This gave confirmation of supersaturated condition of the solution. Then, 25ml of the solution was pipetted out and taken in a petri dish and it was warmed up at  $40^\circ\text{C}$  till the solvent was evaporated out and solubility was determined by gravimetric method [9]. The same procedure was followed to find the solubility of undoped and  $\text{MgCl}_2$  doped LHHC samples at other temperatures. Variation of solubility with temperature for undoped and magnesium chloride added LHHC salts are presented in the fig.1. It is observed from the results that the solubility increases with temperature for the both samples and it is found to be more for  $\text{MgCl}_2$  doped LHHC sample compared to the undoped sample.

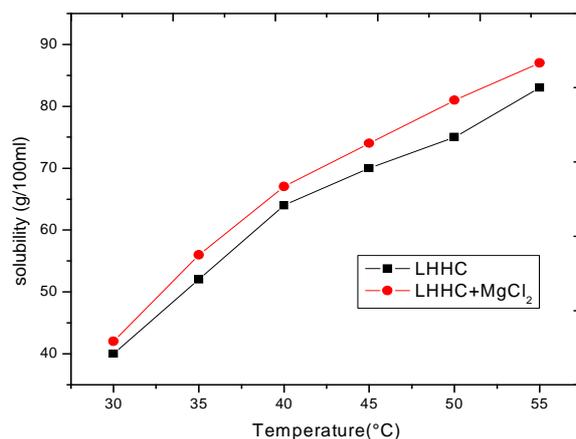


Fig.1. Solubility curves for undoped and  $\text{MgCl}_2$  doped LHHC samples

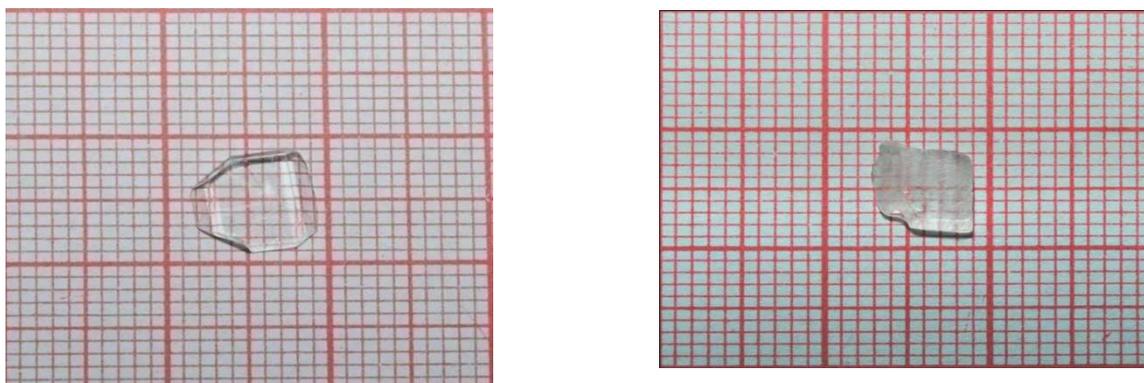


Fig.2. Photograph of undoped and  $\text{MgCl}_2$  doped LHHC crystals

### 2.3. Growth of crystals

Saturated solution of LHHC sample was prepared using the solubility data and it was stirred using a magnetic stirrer at room temperature for about 5 hours to get homogeneity and the solution was filtered twice using whatmann filter paper and filtered solution was kept in a borosil beaker covered with a porous paper. Colorless and transparent

crystals were harvested after a period of 27 days. To grow the  $\text{MgCl}_2$  doped single crystals, saturated solution was prepared using the  $\text{MgCl}_2$  doped sample and deionized water. The grown crystals were found to be transparent, free from visible inclusions and non-hygroscopic in nature. Fig. 2 shows the photograph of the undoped and  $\text{MgCl}_2$  doped LHC crystals.

#### 2.4. Instrument details for characterization

In order to ascertain the structure, purity and identification of the grown crystal, single crystal X-ray diffraction data were collected using a Bruker-Nonius MACH3/ CAD4 X-ray diffractometer with  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71069 \text{ \AA}$ ) powder X-ray diffraction pattern of the sample was obtained using a powder X-ray diffractometer (XPRT – PRO Model, Nickel filtered  $\text{CuK}\alpha$  radiations ( $\lambda = 1.540 \text{ \AA}$ ) at 40 kV, 30 mA. The FT-IR spectrum of the sample was recorded using a Perkin-Elmer FT-IR spectrometer model FT-IR 8400s by the KBr pellet technique in the range  $4000\text{--}400 \text{ cm}^{-1}$ . The optical absorption spectrum of the crystal was carried out using a Lambda 35 model Perkin Elmer double beam UV-Vis-NIR spectrophotometer. The Thermo Gravimetric Analysis (TGA) and Differential Thermal Analysis (DTA) were carried out for undoped and  $\text{MgCl}_2$  doped LHC samples using a SDT Q600 V 20.9 Build 20 thermal analyzer in Nitrogen atmosphere for the temperature range  $40^\circ\text{C}\text{--}1000^\circ\text{C}$  at a heating rate of  $20^\circ\text{C}/\text{min}$ . Mechanical property was studied by measuring microhardness of the grown undoped and magnesium chloride doped LHC crystals and it was carried out using Shimadzu hardness tester fitted with a diamond indenter. Second Harmonic Generation (SHG) test for the grown samples was performed by the powder technique of Kurtz and Perry using a pulsed Nd: YAG laser (Model: YG501C,  $\lambda = 1064 \text{ nm}$ ), pulse energy of  $4 \text{ mJ}$ /Pulse width of  $8 \text{ ns}$  and repetition rate of  $10 \text{ Hz}$  were used.

### RESULTS AND DISCUSSION

#### 3.1. Single crystal X-ray diffraction studies

Undoped and  $\text{MgCl}_2$  doped LHC crystals were analyzed by single crystal XRD method and it is observed that the grown crystals crystallize in orthorhombic structure with space group  $P2_12_12_1$ . The unit cell parameters of undoped and  $\text{MgCl}_2$  doped LHC crystals were shown in table 1. The diffraction data shows a very good match with data reported in the literature [10] and slight changes of lattice parameters have been noticed for the  $\text{MgCl}_2$  doped sample compared to undoped LHC crystal. The changes in the lattice parameters are due to incorporation of  $\text{MgCl}_2$  in the lattice of LHC crystal.

Table (1): XRD data of undoped and  $\text{MgCl}_2$  doped LHC crystals

Sample	Parameter ( $\text{\AA}$ )			Unit cell volume $\text{\AA}^3$	$\alpha^\circ$	$\beta^\circ$	$\gamma^\circ$
	a	b	c				
Undoped LHC crystal	6.827(2)	8.909(1)	15.282(3)	934.612(1)	90	90	90
$\text{MgCl}_2$ doped LHC crystal	6.813(2)	8.902(3)	15.264(1)	930.514(2)	90	90	90

Table 2. FT-IRs assignments of undoped  $\text{MgCl}_2$  doped LHC crystal  
(\*Vs- Very strong)

Wavenumber ( $\text{cm}^{-1}$ )		Assignments
Undoped	Doped	
3413.24	3412.78	O-H symmetric stretching of water
3100.9	3103.79	N-H symmetric stretching
3009.09	3014.67	C-H Stretching
2108.59(vs)	2615.28	$\text{CH}_2$ Asymmetric stretching
2613.48	----	$\text{NH}_2^+$ Asymmetric and Symmetric Stretching
1607.37	1607.94	$\text{H}_2\text{O}$ deformation
1495.59	1496.31	C-N stretching
1413.75	1412.45	N-H bending
1334.70	1335.10	$\text{CH}_2$ deformation
1172.59	1171.41	C-H in Plane bend & C-C Stretch
1141.34	1139.55	N-H bending
---	1064.54	C-H in plane bending
959.72	958.91	N-H bending
911.52	912.43	C-H out of plane bending
865.57	866.61	C-N deformation
820.71	821.58	Ring deformation
694.58	694.31	C=O deformation
625.22	625.43	Ring deformation
528.78	528.55	C-C deformation

#### 3.2. FT- IR Spectral Studies

FT-IR spectra of undoped and  $\text{MgCl}_2$  doped LHC are presented in fig. 3 and 4 respectively. The stretching vibrations of the water molecule are expected in  $3350\text{--}3700 \text{ cm}^{-1}$ . The broad vibrational band observed around

$3413.24\text{ cm}^{-1}$  and  $3412.78\text{ cm}^{-1}$  is attributed to symmetric stretching mode of water molecule. The medium broad band noticed around  $1607.37\text{ cm}^{-1}$  and  $1607.94\text{ cm}^{-1}$  is assigned to the bending vibration of water molecules. For the doped crystals significant difference could not be observed except for broadening and shifting of absorption peaks/bands in the FT-IR spectra. The assignments for peaks/bands are given in accordance with the data in the literature [11-14]. The FT-IR assignments for the absorption peaks/bands of the samples of this work are provided in the table.2.

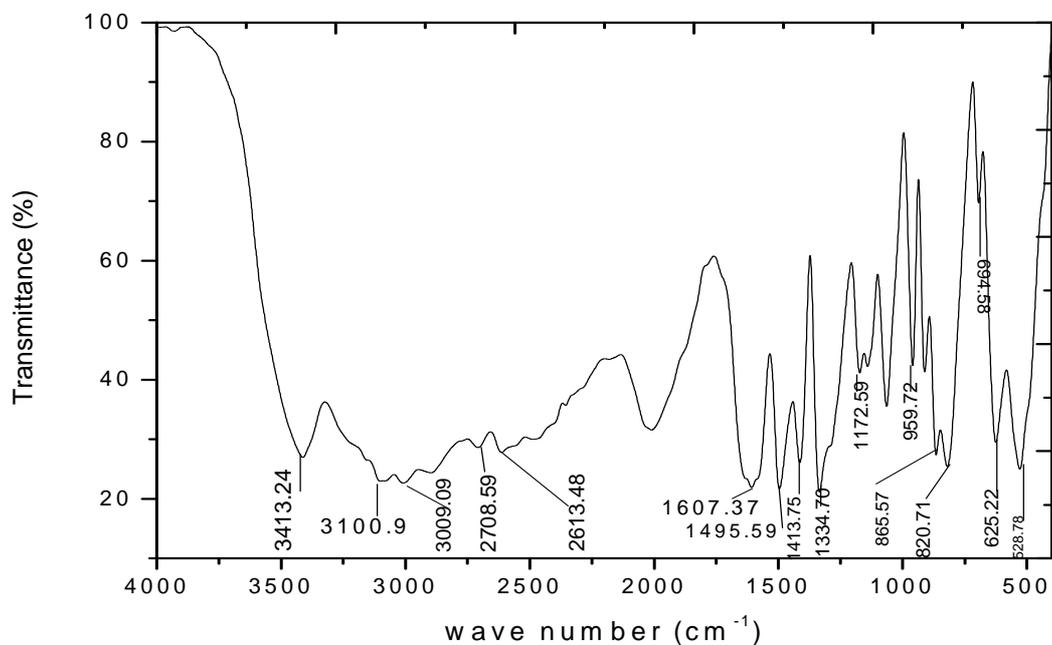


Fig.3. FT-IR Spectrum of undoped LHC crystal

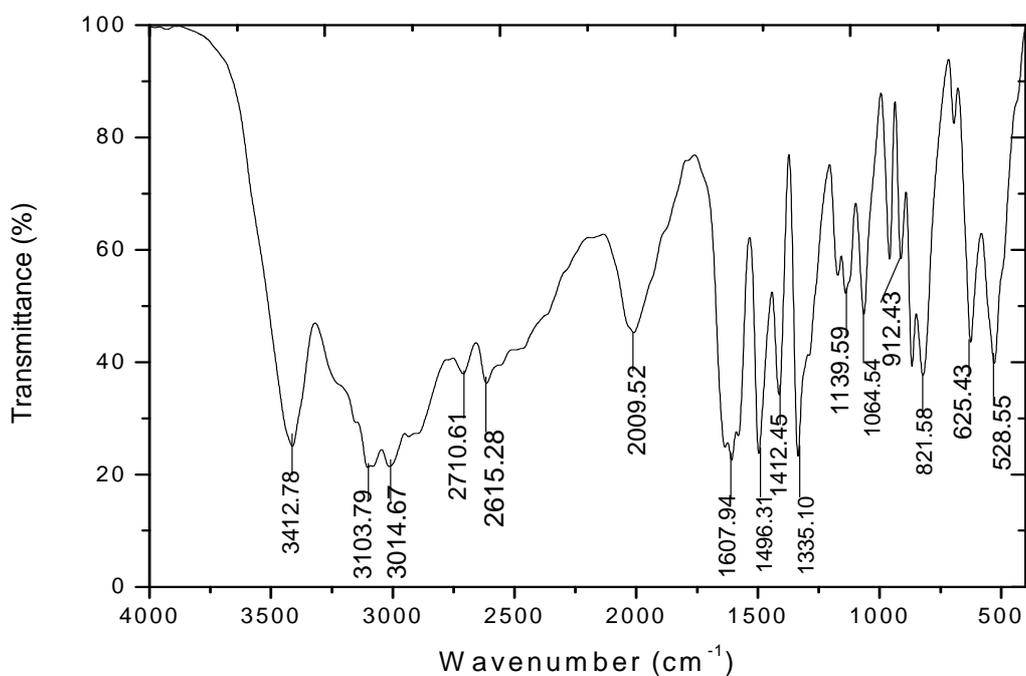


Fig.4. FT-IR Spectrum of  $\text{MgCl}_2$  doped LHC crystal

### 3.3. UV – Visible- NIR spectral studies

UV-Visible–NIR spectra of undoped and MgCl<sub>2</sub> doped LHC crystals are depicted in the fig.5. Optical transmission data were taken for the samples of thickness of about 3 mm. The material has a good optical transmittance in the entire visible region and the lower cut off wavelength ( $\lambda_{cut}$ ) is observed to be at 245 nm and 235 nm for undoped and MgCl<sub>2</sub> doped LHC crystals respectively and this is due to  $\pi$ - $\pi^*$  transition in the compounds. The band gap energy ( $E_g = \frac{hc}{\lambda}$ ) eV was found to be 5.06 and 5.27 eV for undoped and MgCl<sub>2</sub> doped LHC crystals respectively and thus ascertain the fact that the crystals are insulators and can be used for optoelectronic applications [15,16 ].

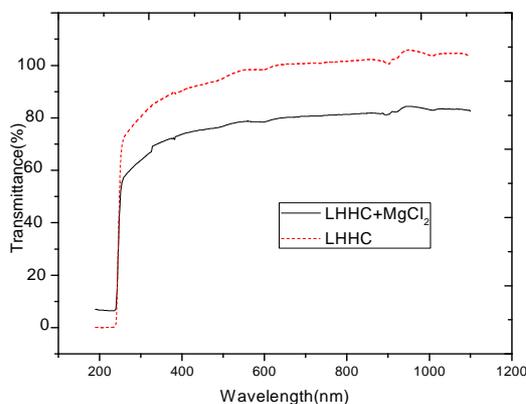


Fig.5. UV-Vis-NIR transmission spectrum of undoped and MgCl<sub>2</sub> doped LHC crystals

### 3.4. EDAX with CHN Analysis

Energy dispersive X –ray spectroscopy (EDAX) was used to identify the elements present in the undoped and MgCl<sub>2</sub> doped LHC crystal. The EDAX spectrum was recorded using Jeol 6390 LV model scanning electron microscope and it is shown the fig.6.and fig.7. From the results it is confirmed that the elements such as carbon, oxygen, and chlorine nitrogen are presented in the undoped LHC sample, in addition magnesium are presented in the MgCl<sub>2</sub> doped LHC sample. It is to be mentioned here that Hydrogen cannot be identified from the samples by EDAX method. The weight percentage of Hydrogen in the samples, from CHN analysis was carried out. The weight percentage of the different elements in the undoped and MgCl<sub>2</sub> doped LHC crystals is given in the table 3.

Table. 3. The elemental composition of the undoped and MgCl<sub>2</sub> doped LHC crystals

S.No	Sample	Element	Weight %
1.	Undoped LHC Crystal	Carbon	37.608
		Oxygen	16.69
		Nitrogen	21.92
		Chlorine	18.50
		Hydrogen	5.26
2.	MgCl <sub>2</sub> doped LHC crystal	Carbon	37.608
		Oxygen	16.69
		Nitrogen	21.92
		Hydrogen	5.26
		Magnesium	5.04
		Chlorine	13.664

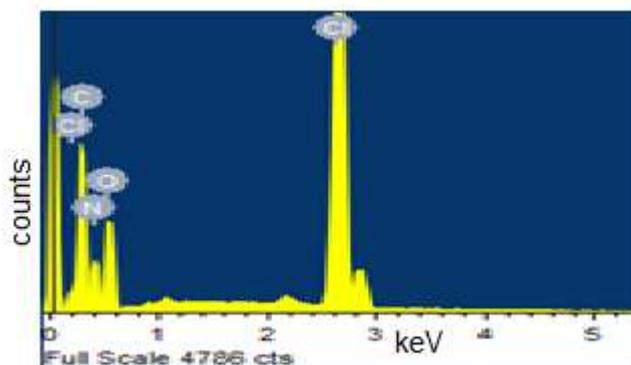
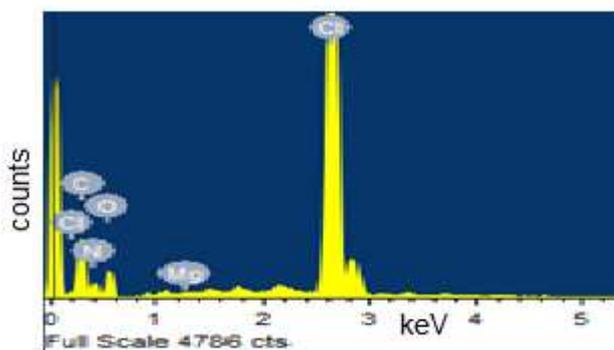


Fig.6. EDAX spectrum of undoped LHC crystal

Fig.7. EDAX spectrum of  $MgCl_2$  doped LHHC crystal

### 3.5. Thermal Analysis

The TG/DTA and DSC thermal traces for undoped and  $MgCl_2$  doped LHHC crystals are shown in the fig. 8 and 9. The fig.8 and 9 shows that the samples is thermally stable up to 168.70°C and 168.62°C, the weight loss starts above this temperature. The weight percentage about 70% and 68% observed at 183.29°C and 180.93°C may be attributed to the loss of lattice water [17]. From differential thermal analysis curve, it is observed that sample shows an endothermic peak at 268.44°C and 269.79°C which corresponds to the decomposition point of the samples. This endotherm closely matches with the major weight loss in TGA analysis. From the DSC curve in the fig.8 and.9, it is also confirmed that the undoped and  $MgCl_2$  doped LHHC crystals has water of crystallization and the decomposition point of the samples is at 168.70°C and 168.62°C.

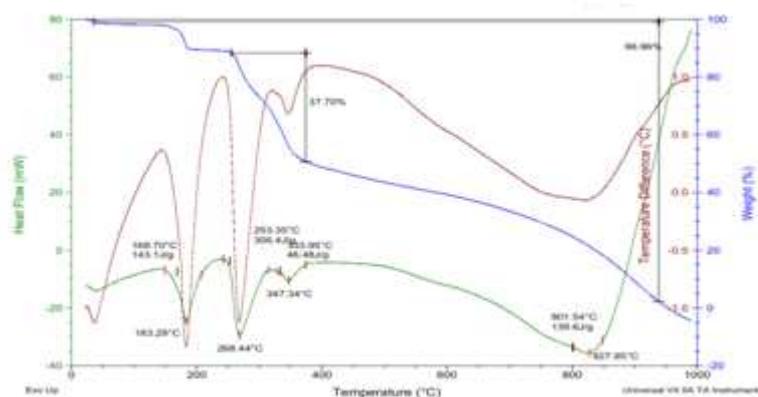
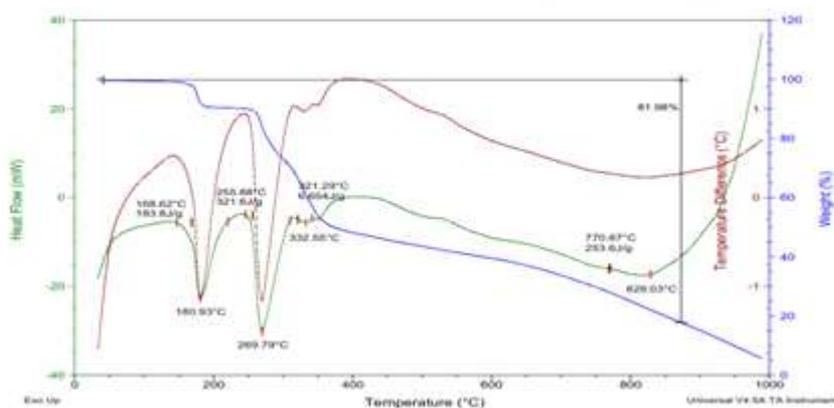


Fig.8. Thermal curves for undoped LHHC Crystal

Fig.9. Thermal curves for  $MgCl_2$  doped LHHC crystal

### 3.6. Vicker's Microhardness studies

Hardness is one of the important mechanical properties of solid material. It can be used as a suitable measure of the plastic properties and strength of the material. Microhardness testing is one of the best methods of understanding the mechanical properties of materials such as fracture behavior, yield strength, brittleness index and temperature of

cracking. Transparent crystals free from cracks were selected for microhardness measurements. Before indentations, the crystals were carefully lapped and washed to avoid surface effects. Microhardness analysis was carried out using Vicker's microhardness tester fitted with a diamond indenter. The well polished LHC crystal was placed on the platform of the Vickers microhardness tester and the loads of different magnitude were applied over a fixed interval of time. The indentation time was kept as 10 sec for all the loads. The hardness was calculated using the relation  $H_v = 1.8544 p/d^2$  in  $\text{kg/mm}^2$ , where  $p$  is the applied load in Kg and  $d$  is the diagonal length of the indentation impression in millimeter [18]. The relation between Vicker's hardness number ( $H_v$ ) and load ( $p$ ) for LHC crystal is shown in fig.10. The hardness increases gradually with the increase of load. The relation between load and size of the indentation is given by well known Meyer's law  $p=ad^n$ . Here 'a' and 'n' are constants depending upon the material. From fig.11. and 12 The value of the work hardening coefficient 'n' was found to be 2.20 for undoped LHC crystal and 2.045 for  $\text{MgCl}_2$  doped LHC crystals. According to onitsch,  $1.0 \leq n \leq 1.6$  for hard materials and  $n > 1.6$  for soft materials [19]. Hence it is concluded that undoped and  $\text{MgCl}_2$  doped LHC crystals belongs to the soft category material.

Other mechanical properties such as yield strength ( $\sigma_y$ ) and stiffness constant ( $C_{11}$ ) were calculated at different loads. The relations for determining yield strength ( $\sigma_y = (H_v/3) \text{ N/m}^2$ ) and the stiffness constant ( $C_{11} = (H_v)^{7/4} \text{ N/m}^2$ ) where  $H_v$  is the Vicker's microhardness number of the material [20]. The variations of yield strength and stiffness constant for undoped and  $\text{MgCl}_2$  doped LHC crystals with the applied loads are shown in the fig.13 and 14. It is observed from the results that the mechanical properties like hardness, yield strength and stiffness constant increase with increase in the applied load. As the values of hardness, yield strength and stiffness constant are found to be more for the  $\text{MgCl}_2$  doped LHC crystal than that of undoped one, it is concluded that the  $\text{MgCl}_2$  doped LHC crystal is more suitable for device fabrication.

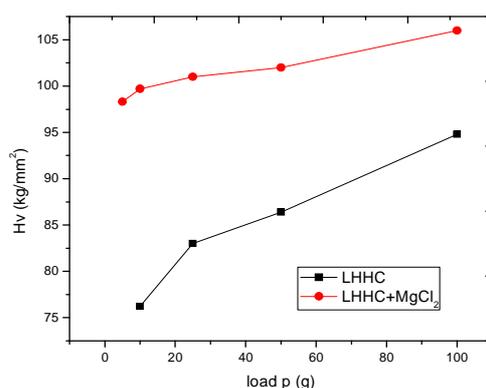


Fig.10. plot of Load versus Hv for undoped and  $\text{MgCl}_2$  doped LHC crystal

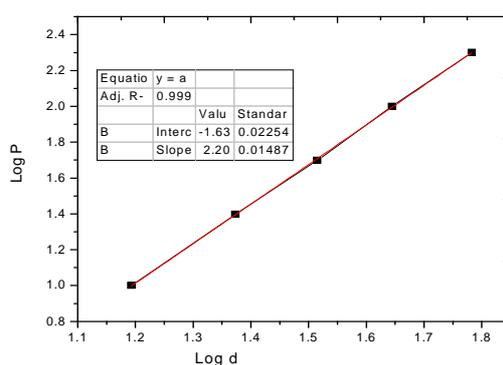


Fig.11. plot of Log d versus Log p for undoped LHC crystal

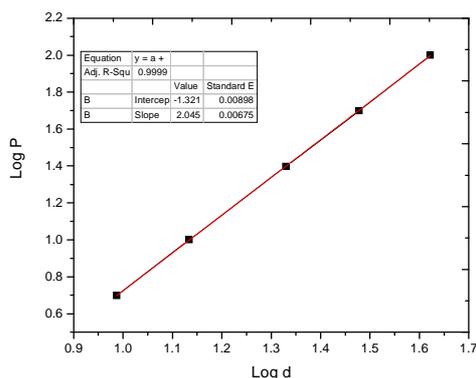


Fig.12. plot of Log d versus Log p for  $\text{MgCl}_2$  doped LHC crystal

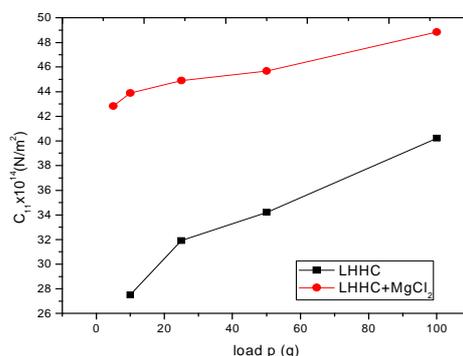


Fig.13. plot of Load versus Stiffness constant ( $C_{11}$ ) for undoped and  $\text{MgCl}_2$  doped LHC crystal

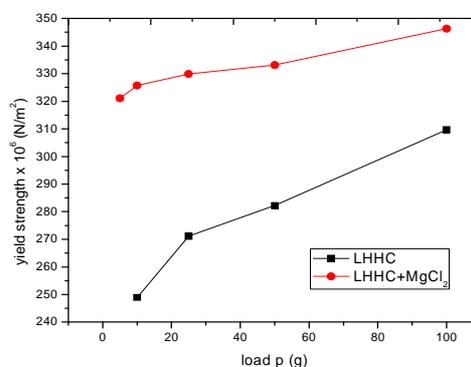


Fig.14. plot of Load versus yield strength ( $\sigma_y$ ) for undoped and  $\text{MgCl}_2$  doped LHC crystal

### 3.7. Measurement of SHG efficiency

Kurtz and Perry powder technique [21] was used to obtain the SHG efficiency for the grown crystalline samples. AQ - switched Nd: YAG laser ( $\lambda=1064\text{nm}$ ) was used as the source. SHG was confirmed by emission of green light ( $\lambda=532\text{nm}$ ). The SHG efficiencies of undoped and  $\text{MgCl}_2$  doped samples are found to be 3 and 3.2 times that of KDP [22]. Due to the presence of magnesium chloride in the crystal lattice, there is an increase in polarizability of the molecule, which tends to increase the SHG efficiency. Thus, the grown crystals are suitable for NLO active materials.

## CONCLUSION

Undoped and  $\text{MgCl}_2$  doped LHC crystals were grown successfully by slow evaporation method. Solubility was found to be more for  $\text{MgCl}_2$  doped LHC crystal than that of the undoped crystal. X - ray diffraction studies confirmed that the undoped and doped crystals crystallize in orthorhombic system with space group  $P2_12_12_1$ . The presence of functional groups were identified by FT-IR spectral studies. The UV-Vis-NIR spectral studies reveal that the transmittance is less for the  $\text{MgCl}_2$  doped sample compared to the undoped LHC sample and the Energy

gap ( $E_g$ ) values were determined. Various elements present in the samples have been identified by EDAX studies. The Vicker's microhardness study of the crystals was carried out the crystals is found to be soft material category and more suitable for device fabrication. The thermal stability is confirmed by the thermal analysis. SHG studies reveal that the suitability of the grown crystals for NLO applications.

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