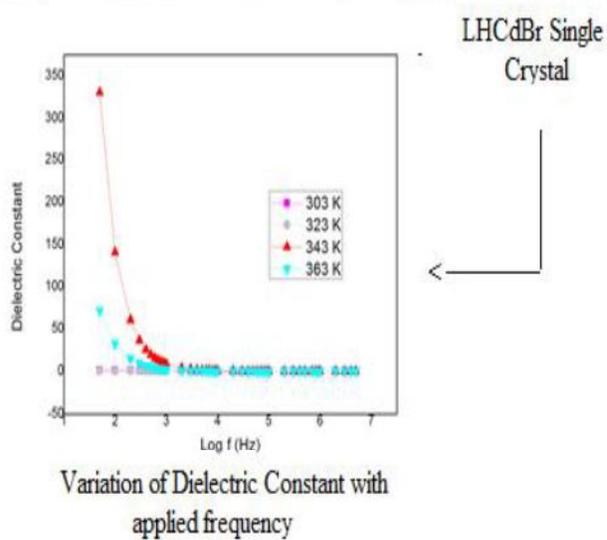# CHAPTER 8

GROWTH AND CHARACTERIZATION OF SINGLE CRYSTAL: L- HISTIDINE CADMIUM BROMIDE (LHCdBr)

8.1   GRAPHICAL ABSTRACT OF L – HISTIDINE CADMIUM BROMIDE

LHCdBr Single Crystal

Variation of Dielectric Constant with applied frequency

8.2 INTRODUCTION

Recent search for new frequency conversion materials is concentrated on semi organic materials due to their large nonlinearity, high resistance to laser induced damage and good mechanical hardness (Oliver 2007, Rosker et al. 1996). Semi organic crystals offer a variety of molecular structures by virtue of the changes brought out in selection of metals, ligand and coordination numbers. In semi organic materials the organic ligand is attached to the inorganic host by an ionic bond. Therefore semi organic crystals have higher chemical stability and mechanical strength compared to their inorganic counterparts. Second order nonlinear optics is widely used to convert the frequency of coherent laser source. Applications such as laser based imaging, communication; remote switching and counter measure systems require improved nonlinear optical materials to accomplish such conversions. A strong need continues to exist for lower cost, more efficient, higher average power materials for optical parametric amplifier operation and second harmonic generation throughout the blue-near-uv spectral region. L-Histidine and its family of crystals have been reported to be of very great interest for the nonlinear optical applications (Selvaraju et al. 2007, Nalini Jayanthi et al. Krishnakumar). Semi-organic materials have the potential for combining high optical nonlinearity and chemical flexibility of organics with the physical ruggedness of inorganic. Ligands like thiourea, allylthiourea, thiocyanate and thiosemicarbazide with S and N donors are capable to combine with metal to form stable complexes through coordinated bonds. These complexes show ligand to metal charge transfer by an electron movement form ligand to metal and metal to ligand in addition to $\pi- \pi^*$ conjugation(Abu El-Fadl et al. 2007).

In this present work Cadmium Bromide is combined with L-Histidine to form a new semiorganic nonlinear optical material. This

chapterreports the synthesis, crystal growth and characterization studies of LHCdBr single crystal grown by solution growth method. The title compound was subjected to X-ray diffraction, Powder X-ray diffraction, NLO studies, thermal analysis, FTIR, Micro hardness, Dielectric studies, FE-SEM Analysis.

8.3 EXPERIMENTAL PROCEDURE

8.3.1 Materials and Crystal Growth

The materials were synthesized by taking L-Histidine (AR grade) and Cadmium Bromide (AR grade) in a 1:1 stoichiometric ratio. The calculated amount of Cadmium Bromide was first dissolved in deionized water. L-Histidine was then added to the solution. The solution was agitated with a magnetic stirring device for 8h continuously and filtered after complete dissolution of the starting materials. The prepared solution was allowed to dry at room temperature and the crystals were obtained by slow evaporation technique. The purity of the synthesized crystal was further improved by successive recrystallization process; thereby good optical qualities of single crystals were obtained in 2 weeks which is shown in Figure8.1.
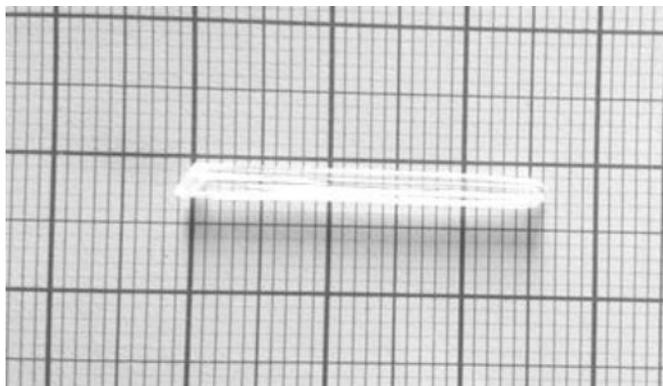

Figure8.1 Grown crystal of LHCdBr Crystal

8.4   RESULTS AND DISCUSSION

8.4.1   Single crystal X-ray Diffraction

The grown crystals were subjected to single crystal x-ray diffraction analysis using an ENRAF NONIUS CAD-4 for grown crystalto determine the lattice parameters. The calculated lattice parameters are a = 14.62 Å, b= 5.43 Å, c = 11.09 Å and V= 867 Å^3. The crystal belongs to triclinic crystal system.

8.4.2   Powder X-ray diffraction

Powder X-ray diffraction study was used for the identification of crystallinity of the grown crystal. The Kα radiations (λ = 1.5418 Å) from a copper target were used. The sample was scanned in the range between 10 and 100°C. Figure8.2 represents the indexed powder diffractogram for the grown crystal of L – Histidine Cadmium Bromide. The sharp intensity peaks found in spectra shows good crystalline nature and purity of the grown crystal.
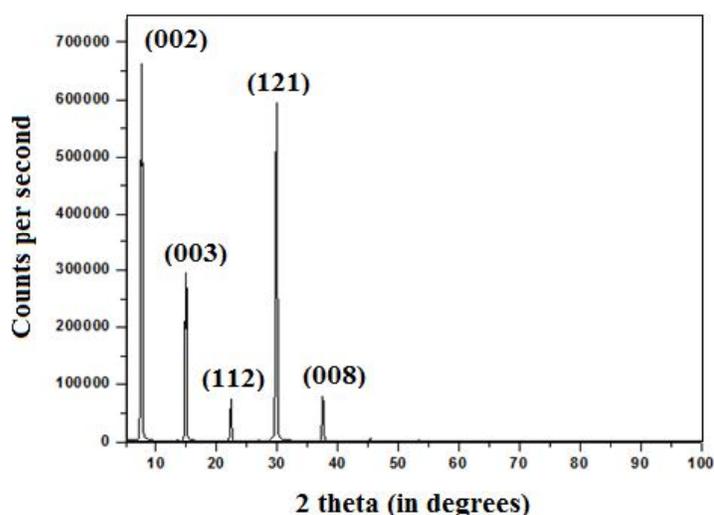

Figure8.2 PXRD graph of LHCdBr

8.4.3   FTIR Analysis

The infrared spectral analysis was carried out to understand the chemical bonding and it provides useful information about the molecular structure of the compound. Each and every one chemical compounds have their own typical IR spectrum. The FTIR spectrum ofL–Histidine Cadmium Bromide was recorded in the wavelength range of 450-4000 cm^{-1} using Perkin Elmer spectrometer by KBr pellet technique. The assignments are discussed in three different regions namely high wave number region (3500-2000 cm^{-1}) a medium wave number region (2000-1000 cm^{-1}) and a low wave number region (below 1000 cm^{-1}).
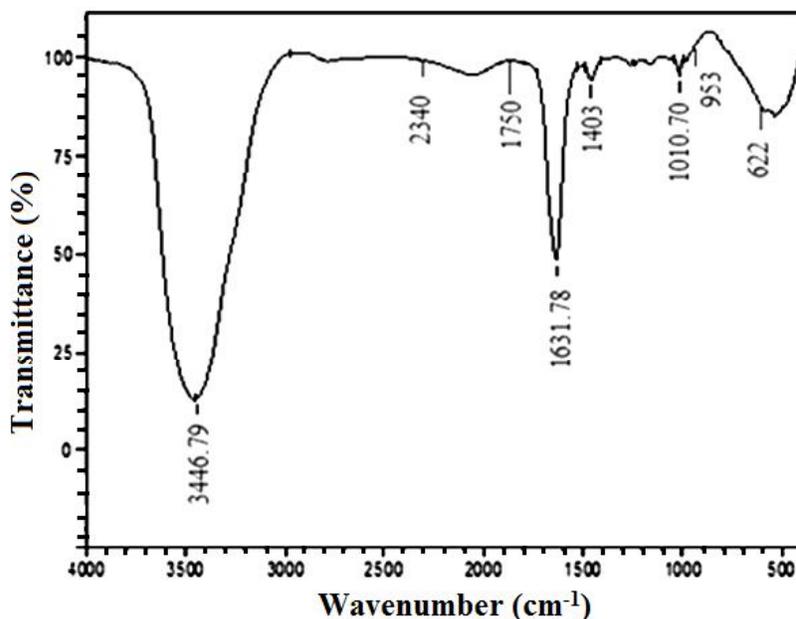

Figure 8.3 FTIR Analysis of LHCdBr

The resulting spectrum is presented in Figure 8.3. The C = O stretching vibration is found to be around 1750 cm^{-1}. The peak 2805 cm^{-1} indicates C – H stretching vibrations. The peaks at 1403 and 1010 cm^{-1} represents the asymmetric and symmetric vibrations ofN – C – N respectively.

The C = C stretching vibration peak shows around 2340 cm^{-1}. The C – H deformation appear at 622 cm^{-1} is due to out of plane bending vibrations. The symmetrical C – C stretching is found to be at 953 cm^{-1}.

8.4.4   Linear Optical Property

The crystal LHCdBr is well polished and the sample is dissolved in water to measure the absorption and transmission spectrum in the spectral region shown in Figure8.4 using LAMBDA-35 UV–Vis spectrometer 190 – 1100 nm with data interval 1.0000nm and Scan Speed 960.00nm/min. For optical fabrication, the crystal should be highly transparent over a considerable region of wavelength (Jaganathan et al. 2007, Pattanaboonmee et al. 2010). In the UV Vis spectrometer the lower cut off wavelength as recorded from the absorption spectrum is 315.96 nm. From the absorption spectrum the crystal is transparent in the range 381nm-1100nm without any absorption peak, which is an essential parameter of NLO crystals. Absence of absorption in the region400–1100 nm is an advantage and it is the key requirement for materials exhibiting NLO property.

Using the relation,

$$Eg = 1240/\lambda \tag{8.1}$$

The band gap energy was found to be 3.92 eV. The optical absorption spectrum shows that absorption was very less in the entire visible region and part of IR region.

Transmission spectra are very important for any NLO material because a nonlinear optical material can be of practical use only if it has wide transparency window. The optical transmission spectrum for the wavelengths

between 190 and 1100 nm were recorded. From the Figure8.5 the transmittance spectra, it is observed that the grown crystal have high transmittance in the entire visible and near IR region (Webster et al. 1999).

The UV cut-off wavelength of the crystal is found to be at 198 nm. It is found that the maximum transmittance of the grown L – Histidine Cadmium Bromide single crystal is 52% and it has almost more than 45% transmittance from 316 to 1100 nm. The advantage of using amino acids shows the absence of strongly conjugated bonds leads to wide transparency range in the visible and UV spectral regions. The transparency is an added advantage for this crystal to be utilized in the field of optoelectronic devices.
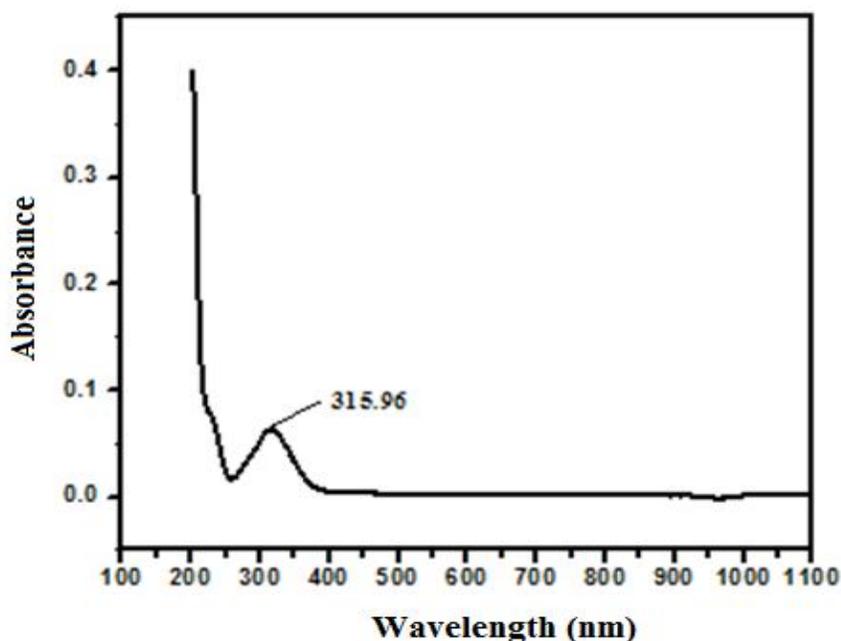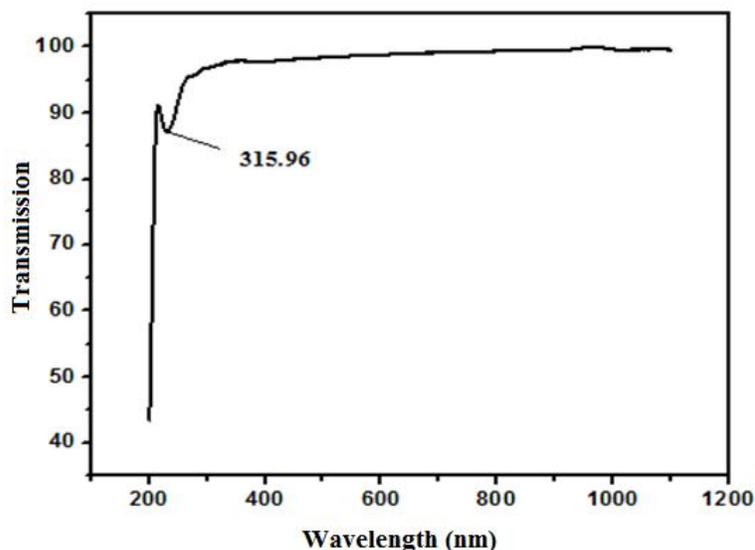

Figure 8.4 Absorption spectrum of LHCdBr

Figure8.5 Transmission spectrum of LHCdBr

8.4.5   Thermal Analysis

The thermo gravimetric analysis of L–Histidine Cadmium Bromide crystal was carried out for the sample between 50 and 800 ˚C at a heating rate of 20 K min^{-1} in nitrogen atmosphere using NETZSCHSTA 409 C/CD thermal analyzer and the resultant spectrum is shown in the   Figure8.6. The TGA illustrates that there is no loss below 212º C illustrating the absence of water in the crystal lattice (Nagalakshmi 2015). The sharp weight loss starts at 212º C to 298˚C without any intermediate stages, is assigned as melting point of the crystal. After that above 212º C the crystal sharply starts to decompose at 298˚C. The sharpness of this peak shows the good degree of crystallinity and purity of the sample. Thus from the thermal studies, the crystal can retain its texture upto 212º C.
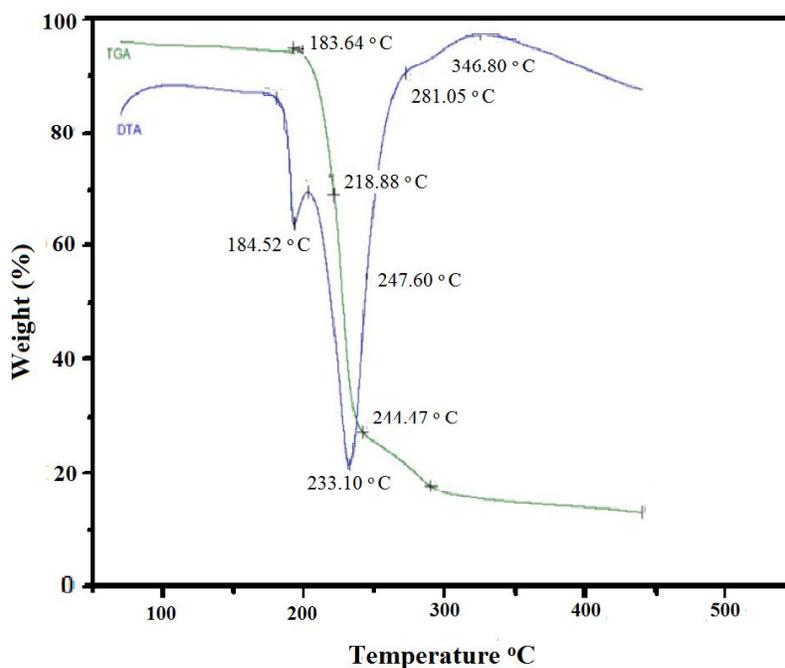
Figure 8.6 Thermal Analysis of LHCdBr

8.4.6 Micro Hardness Analysis

One of the methods to determine the mechanical behaviour of the grown crystal is micro hardness test. It is correlated with other mechanical properties like elastic constants, yield strength, brittleness index and temperature of cracking (Senthilet al. 2009). The indentation marks were made on the surface of TSMnAc single crystal at room temperature by applying load of 25, 50 and 100 g. The Hv is found to increase with increase in the load from 25 to 100 g and crack occurs at higher loads. Mechanical properties of the grown TSMnAc crystal were studied using MH–5 hardness testers. The diagonal lengths of the indented impression were measured using calibrated micrometer attached to the eyepiece of the microscope.

The Vickers micro hardness values were calculated from the standard formula (Marcy et al. 1992)

$$Hv = 1.8544 \ (P/d^2) \ kg/mm^2 \qquad\qquad (8.2)$$

Where, P is the applied load and d is the mean diagonal length of the indentation. The corresponding trace is shown in the Figure8.7, from which it is observed that the hardness increases with the increase of load up to 100g and crack occurs at that load. The micro hardness value was taken as the average of the several impressions made.
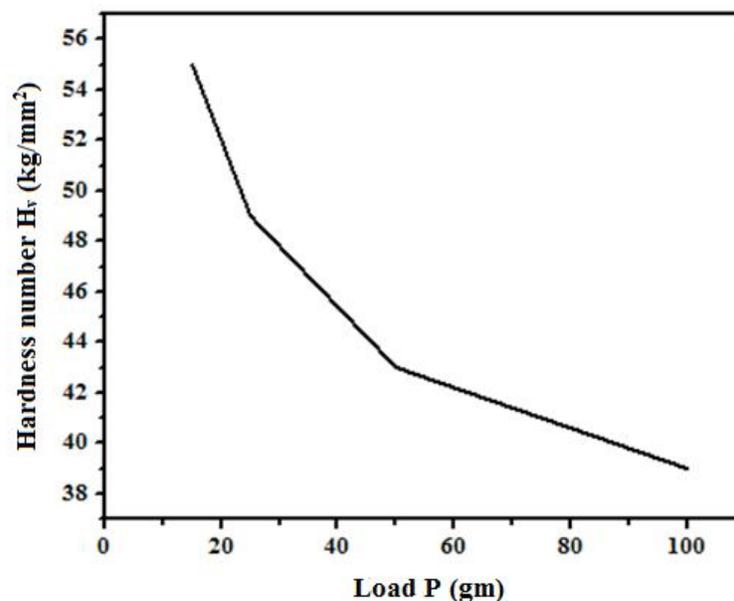

Figure 8.7 Relation between Vickers hardness number vs load

According to the normal Indentation size effect (ISE), micro hardness of crystal decreases with increasing load and in Reverse indentation size effect (RISE) hardness increases with applied load. In our case, Hv increases with applied load (Krishnakumar &Nagalakshmi 2005).

8.4.7 Dielectric Studies

Dielectric studies were measured using HIOKI 3532-50 LCR HITESTER. The selected samples were cut using a diamond saw and

polished using paraffin oil. Silver paint was applied on the both faces to make a capacitor with the crystal as a dielectric material. The dielectric constant is calculated using the relation

$$\varepsilon^{'} = \frac{Cd}{\varepsilon_0 \, A} \qquad (8.2)$$

Where, C is the capacitance, d is the thickness, A is the area and ε_0 is the absolute permittivity of the free space (8.854×10^{-12} F/m). The variation of dielectric constant ($\varepsilon^{'}$) was studied as a function of frequency for the grown crystal at various temperatures and is shown in Figure 8.8. The dielectric constant is one of the basic electrical properties of solids. The dielectric constant is the measure of how easily a material is polarized in an external electric field (Bright & Freeda 2010). The dielectric constant of the crystal was measured in the frequency range of 50 Hz to 2 MHz.
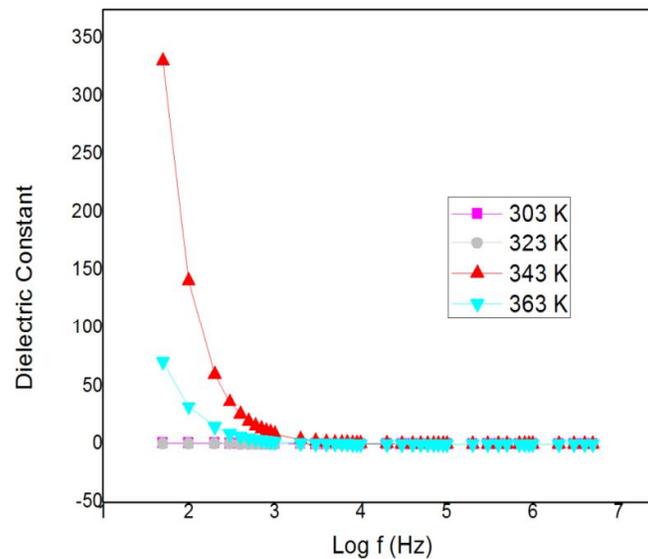

Figure 8.8 Variation of dielectric constant ($\varepsilon^{'}$) with applied frequency

It is observed that at low frequencies the higher the temperature, the larger is the dielectric constant. Due to the impedance to the motion of charge

carriers at the electrodes, space charge and macroscopic distortion results, which might cause larger values of dielectric constant at lower frequencies. As the frequency increases, the dielectric constant values are found to decrease exponentially and attain lower values. In accordance with the Miller rule, the lower values of dielectric constant are a suitable parameter for the enhancement of SHG coefficient (Kurtz & Perry 1968).

8.4.8 FE-SEM Analysis

The Field Emission Scanning Electron Microscopy (FE-SEM) has been carried out for the grown crystals to study the nature and surface morphology of L-histidine Cadmium Bromide. The transparent regions of the crystals were cut into few mm for examining the surface morphology. The FE-SEM micrograph of LHCdBr crystal is shown in Figure8.9. It gives information about surface morphology and the presence of imperfections in the crystals. Figure8.9 clearly shows the grain distribution over the surface and a few microcrystals present on the surface of the grown crystal.
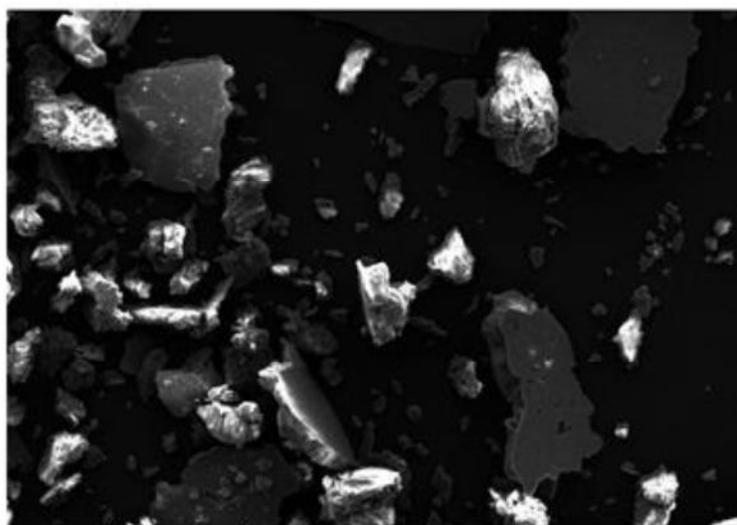

Figure 8.9 FE-SEM Analysis of LHCdBr

8.4.9 NLO Studies

The second harmonic generation efficiency measurement was carried out on the grown crystal using the Kurtz–Perry powder technique. The crystal was grounded into a homogenous powder of particles and densely packed between two transparent glass slides. The powder sample with average particle size 100–115µ was illuminated using Q-switched Nd:YAG laser emitting a fundamental wavelength of 1064nm with the pulse width of 8 ns. The output power is found to be 0.9 times greater than that of KDP.

8.5 CONCLUSION

L − Histidine Cadmium Bromide optical quality single crystal have been grown by slow evaporation technique. The grown crystals are colorless and transparent in appearance. Single crystal X-ray diffraction study of the crystal revealed that the crystal belongs to triclinic system with space group P and crystalline nature was confirmed by powder X-ray diffraction study. Its thermal behaviour was examined by TG/DTA. The optical transmission study confirms that the LHCdBr had good transparency in the entire visible region and there was no absorption of light to any appreciable extent in the visible range and the lower cut-off wavelength was found to be 315.96 nm. Vickers micro hardness was calculated in order to understand the mechanical stability of the grown crystals. Dielectric measurements indicate that the dielectric constant of the crystal decreases with increasing frequency significantly to make the crystal a more interesting material in the microelectronics industry. The Field Emission Scanning Electron Microscopy (FE-SEM) has been carried out for the grown crystals to study the nature and surface morphology of L-histidine Cadmium Bromide. The second harmonic generation was confirmed by Kurtz powder method and it is found to be 0.9 times more than that of KDP crystal. Hence LHCdBr crystal is found to be more beneficial from an application point of view.