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RESEARCH ARTICLE

INVESTIGATION ON THE STRUCTURAL, OPTICAL, ELECTRICAL AND MECHANICAL PROPERTIES OF A NEW RHODAMINE-B DOPED L-HISTIDINE HYDROCHLORIDE NLO CRYSTAL

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ABSTRACT

Rhodamine-B doped L- Histidine Hydrochloride was grown by solution method with slow evaporation technique at room temperature. The grown crystals were observed to be slightly pink in colour. The lattice constants of the grown crystals were determined by X-ray diffraction technique. The presence of the functional groups in the crystal was confirmed by Fourier Transform Infrared (FT-IR) spectral analysis. The optical transmittance of the sample was found by UV-Vis-NIR spectral studies. The fluorescence spectrum was recorded to understand the luminescence properties. The refractive index of the grown crystal was determined by Brewster's angle method. The microhardness, yield strength and stiffness constant of the samples was found by Vicker's microhardness studies. The dielectric constant, dielectric loss and AC conductivity of the crystal was studied as function of frequency and the results are discussed. The SHG efficiency of the crystal was found by Kurtz and Perry technique.

Key Words: XRD; Fluorescence; Refractive Index; Hardness; NLO.

INTRODUCTION

Amino acids and their complexes belong to the family of organic and semi-organic non linear optical (NLO) crystals which have potential applications in optical storage, optical communication, photonics, optical computing, optical parametric amplification, etc, (Misoguti et al., 1996; Theresita Shanthi et al., 2009; Albrecht and Corey, 1939; Eimerl et al., 1989). The importance of amino acid for NLO applications lies on the fact that almost all the amino acids except contain an asymmetric carbon atom and crystallize in non-centrosymmetric space group. Amino acids are organic materials and when they are combined with inorganic materials, new kind of materials called semi-organics are formed. The need for materials which combine large nonlinear optical characteristics with resistance to physical and chemical attack has led to the investigation of semiorganics (Meera et al., 2004; Anandha et al., 2009; Dhanuskodi and Mary, 2003; Uma Devi et al., 2008). Semiorganic compounds illustrate the features like dipolar structure composed of an electron donating and electron accepting group, the contribution from the delocalized π electrons belonging to organic ligand results in high nonlinear optic and electro-optic coefficients in the semiorganic crystals, the organic ligand is ionically bonded to metal ion to impart improved mechanical and thermal properties. L-Histidine Hydrochloride (LHHC) crystal is a semi-organic NLO material and some work has been done already on the growth and characterization of LHHC crystals by us. In this work, Rhodamine-B has been added as the dopant into LHHC crystal to improve the various properties.

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Rhodamine-B is a chemical compound and a dye, it is used extensively in biotechnology applications such as fluorescence microscopy, flow cytometry, fluorescence correlation spectroscopy and ELISA. In optical fields it is used a laser dye (Kubin, 1983). When Rhodamine-B is introduced as the dopant, the appearance of the grown crystals is observed to be pink in colour and they are subjected to different studies and the results are presented.

Experimental Method

Synthesis and Crystal growth

L-Histidine and Hydrochloric acid were taken in the molar ratio of 1:1 for the synthesis of L-Histidine Hydrochloride (LHHC) salt. The calculated amounts of L-Histidine and Hydrochloric acid were dissolved in double distilled water and stirred well using a magnetic stirrer for about 3 hours. The solution was heated until the synthesized salt of L-Histidine Hydrochloride salt was obtained. 5 wt% of Rhodamine-B was added to the solution of LHHC to obtain the Rhodamine-B doped LHHC sample. For the synthesis of the salts, the solutions were heated and stirred at 50 ^{o}C using a hot plate magnetic stirrer. Rhodamine-B doped L-Histidine Hydrochloride (RLHHC) crystals were grown by solution method with slow solvent evaporation technique. Saturated solution of the synthesized salt of RLHHC was prepared and the solution was constantly stirred for about 3 hours using a magnetic stirrer and it was filtered using a filter paper. Then the filtered solution was kept in a growth vessel covered with a porous paper for the growth of the crystals. The crystals were harvested after a period of about 36 days.

The photograph of the grown crystal is shown in the Figure.1. The grown crystal is observed to transparent and slightly pink in colour.

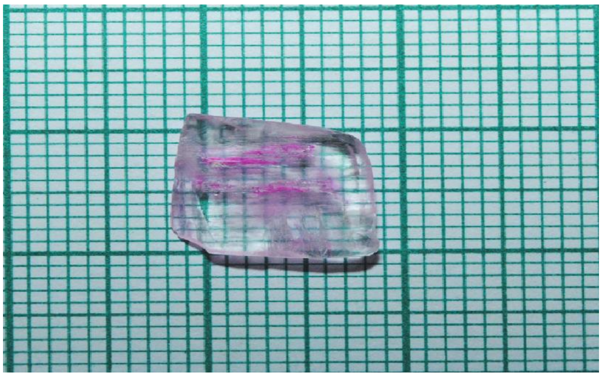

Figure.1. As grown crystal of Rhodamine-B doped L-Histidine Hvdrochloride

RESULTS AND DISCUSSION

Single and Powder XRD studies

The grown crystals of Rhodamine-B doped L-Histidine Hydrochloride (RLHHC) were characterized by both powder and single crystal XRD studies. The single crystal X-ray diffraction data were collected using Bruker Kappa Apex II X-ray diffractrometer with MoKα radiation (λ= 0.71069Å). The grown crystals were crushed into fine powder and powder X-ray diffraction analysis has been carried out using XPERT-PRO powder X-ray diffractometer Nickel filtered CuKα radiations (λ=1.540Å). The recorded pattern is shown in Figure. 2.

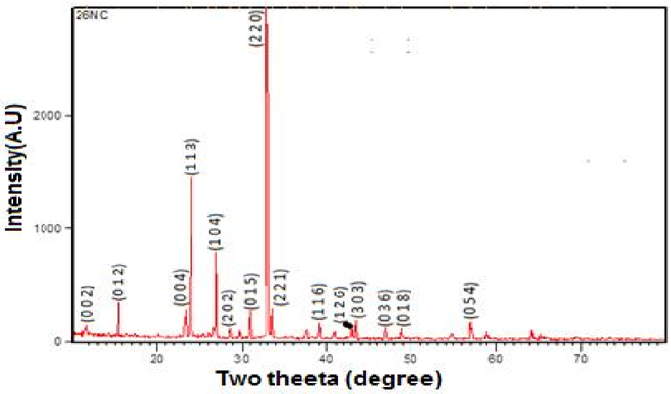

Figure 2. Powder XRD pattern of RLHHC crystal

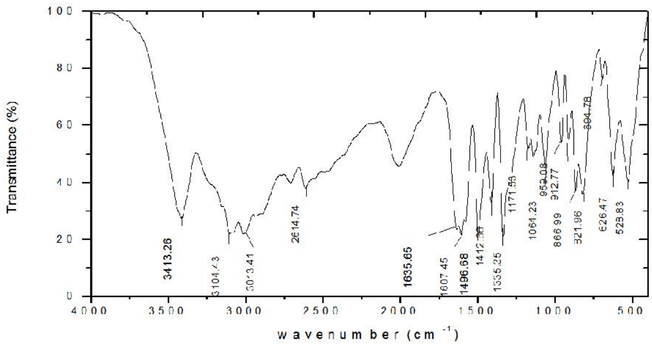

Figure 3. FT-IR spectrum of RLHHC crystal

The diffraction pattern was indexed and unit cell parameters were obtained using INDEXING and UNITCELL software packages. The crystal constants obtained by single crystal XRD and powder XRD analyses are found to be almost the same and the lattice parameters are given in the table.1. The data indicates that the Rhodamine-B doped LHHC crystal crystallizes in orthorhombic structure with space group $P2_12_12_1$ and the obtained data are observed to be almost the same as those of pure L-Histidine Hydrochloride crystal (Madhavan et al., 2007).

Table.1. Lattice constants Rhodamine-B doped L-Histidine Hydrochloride crystal

Sample	Lattice constants
Rhodamine-B doped L-Histidine Hydrochloride crystal	a = 6.795(3) Å b = 8.914(2) Å c =15.302(1) Å α = 90 ° β= 90(2) ° γ=90(2)°
Space group	$P2_12_12_1$
Cell volume	937.513(3)

FT-IR spectral studies

The FT-IR spectrum of the sample was recorded using a Perkin-Elmer FT-IR spectrometer model Spectrum RX1 using KBr pellet technique in the range 4000-400cm^{-1}. The observed FT-IR spectrum of RLHHB is as shown in Fig.3.The stretching vibrations of the water molecule are expected in 3413.26 cm^{-1}. The broad vibrational band observed around 3413.26 cm^{-1} is attributed to symmetric stretching mode of water molecule (Bellamy, 1995). The complete assignments to the vibrational frequencies of RLHHC crystal are provided in the Table.2.

Table.2. Vibrational frequencies and their assignments for RLHHC crystal

Wave number (cm^{-1})	Assignments
3413.26	O-H symmetric stretching of water
3104.43	N-H symmetric stretching
3013.41	NH_2^+ Asymmetric and Symmetric Stretching
2614.74	C-H Stretching
1635.65	C=O stretching
1607.45	H_2O deformation
1496.68	C-N stretching
1412.66	N-H bending
1335.35	CH_2 deformation
1171.53	C-H in Plane bend & C-C Stretch
1064.23	C-H Plane bending
959.08	N-H bending
912.77	C-H out of plane bending
866.99	C-N deformation
821.96	Ring deformation
694.78	C=O deformation
626.47	Ring deformation
528.83	C-C deformation

UV–Vis-NIR spectral studies

The optical transmittance spectrum of RLHHC crystal was recorded using Lambda 35 model Perkin-Elmer double beam spectrophotometer in the wavelength range of 190-1100 nm is shown in Figure.4. The lower cut-off wavelength for RLHHC crystal is found be around at 240 nm combined with the good transparency, makes the usefulness of this material for optoelectronic applications. The band gap energy (Eg) of RLHHC crystal is found to be 5.16 eV (Jiang and Fang, 1999).

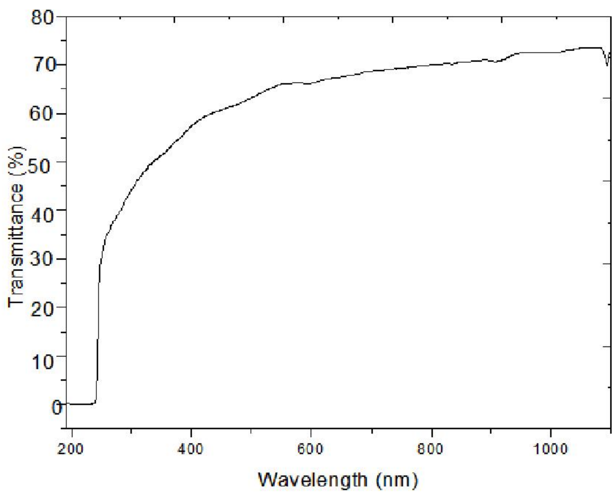

Figure.4. UV–Vis-NIR transmittance spectrum of RLHHC crystal

Fluorescence studies

Fluorescence is the phenomenon in which electronic states of solids are excited by light of particular energy and the excitation energy is released as light. The photon energies reflect the variety of energy states that are present in the materials (Paul et al., 2013). The Fluorescence spectrum of RLHHC crystal was recorded in the range 300-550 nm using Perkin-Elmer fluorescence spectrometer (Model: LS45), an excitation wavelength of 348.53 nm (Figure.5). The spectrum shows the strong emission of Blueish green at 485.64 nm.

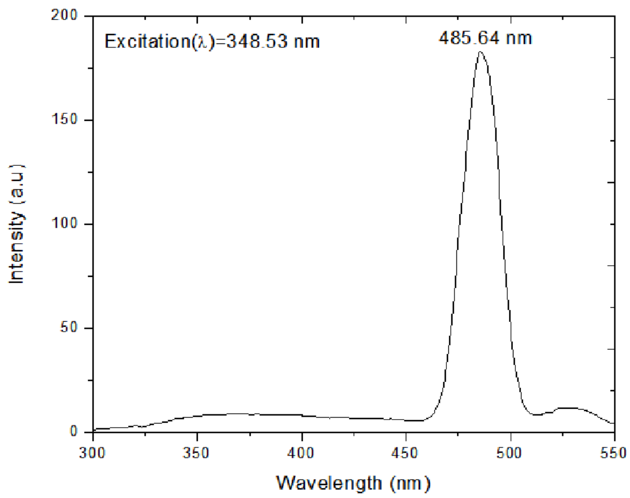

Figure 5. Fluorescence spectrum of RLHHC crystal

Refractive Index Measurement

The refractive index of the RLHHC crystal was determined by Brewster's angle method. A polished single crystal of RLHHC with 1mm thickness was mounted on a rotating mount at an angle varying from 0^0 to 90^0. The laser was made to fall on the crystal placed in a rotary stage.

The initial angular reading, when the crystal was perfectly perpendicular to the intra - cavity beam was noted. The transmitted light travelling through the crystal gets polarized when the crystal has zero reflection. The angle at which the crystal has zero reflection is called the Brewster's angle or polarizing angle (θ_p).

Thus, the crystal was rotated until the reflection of laser beam vanishes and the final angle was noted (Prabitha and Dhanasekaran, 2013). Brewster's angle for RLHHC was measured to be 54.5^0. A He-Ne Laser of wavelength 632.8 nm was used as the source. The refractive index was calculated as 1.401 using the formula $\mu=\tan\theta_p$.

Dielectric studies

A study of dielectric response in crystals is one of the basic electrical properties which give the information about the electric field distribution within the solid. The silver coating on the opposite faces of the polished sample crystal was placed between the two copper electrodes to form a parallel plate capacitor, using an LCRZ meter at various frequencies in the range 50 Hz - 200 KHz at room temperature. The dielectric constant (ε_r) is calculated using the relation $\varepsilon_r=\frac{Cd}{A\varepsilon_o}$, where C is the capacitance, d is the thickness of the sample, A is the area of the electrode contact and ε_o is the absolute permittivity of the free space. Figure.6. shows the variation of dielectric constant with applied frequency at room temperature. It is seen from the plot that the dielectric constant is relatively high in the lower frequency region and then decreases with the applied frequency. The high values of dielectric constant at low frequencies may be due to the presence of combinations of all four polarizations namely space charge, orientation, electronic and ionic polarization. The low value of dielectric constant at high frequencies occurs due to the loss of these polarizations at low temperature (Balarew and Dashlew, 1984; Sher Gill Kalainathan, 2011).

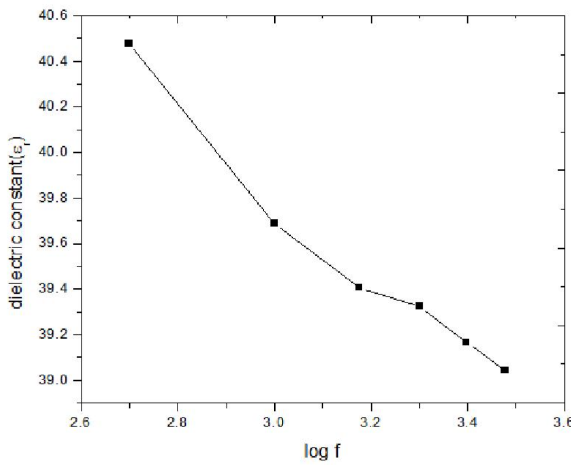

Figure 6. variation of dielectric constant with log frequency for RLHHC crystal

The dielectric loss (tan δ) studied as a function of frequency at room temperature is shown in Figure.7.These curves suggest that dielectric loss is also strongly dependent on the frequency of the applied field. The higher values of dielectric loss at low frequencies originate from space charge polarization mechanism dipoles. The characteristic of low dielectric loss at high frequencies classifies that the enhanced optical quality nature of the grown sample with lesser defects (Ginson et al., 2007; Mukerji et al., 1999). The AC conductivity (σ_{ac}) is calculated using the relation $\sigma_{ac} = 2\pi f\varepsilon_o\varepsilon_r \tan\delta$, where f is the frequency of the AC supply, ε_o is the permittivity of free space or vacuum (8.852×10^{-12} F/m), ϵ_r is the relative permittivity of dielectric constant and $\tan\delta$ is the dissipation factor or dielectric loss.

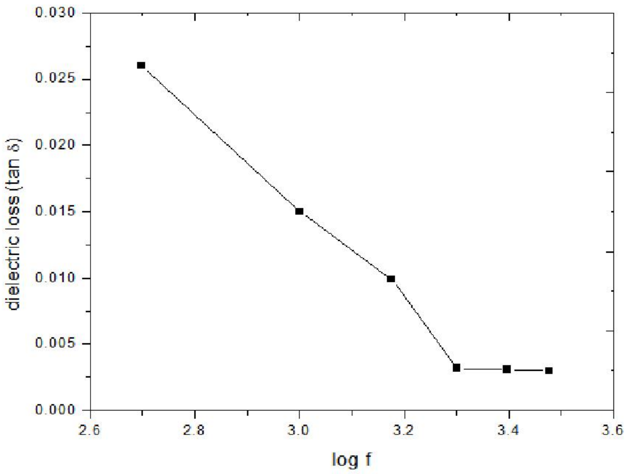

Figure 7. variation of dielectric loss with log frequency for RLHHC crystal

The variation of AC conductivity with frequency for RLHHC crystal is depicted in the Figure .8. The values of AC conductivity of the sample have been determined using the values of dielectric constant (ϵ_r) and dielectric loss (tanδ) in the frequency range 50 Hz to 2 KHZ. The increased AC conductivity increases with frequency (Selvarajan, 2011). The increased AC conductivity could be due to reduction in space charge polarization at higher frequencies.

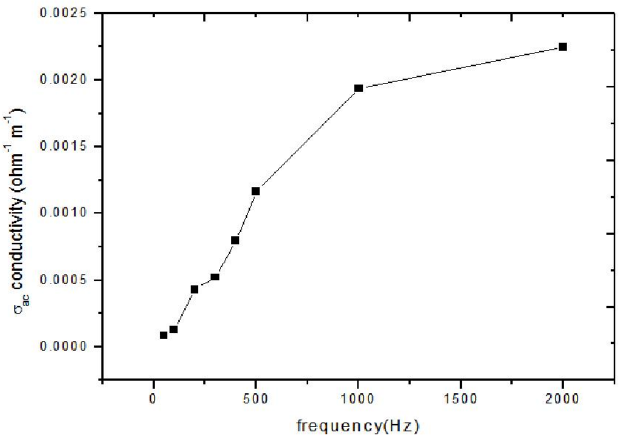

Figure 8. Variation of A.C. Conductivity with frequency for RLHHC Crystal

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 Shimadzu Vicker's microhardness tester fitted with a diamond indenter attached to an incident light Microscope. The well polished RLHHC crystal was placed on the platform of the Vicker's 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 Kg/mm^2, where p is the applied load in Kg and d is the diagonal length of the indentation impression in millimeter (Luciarose et al., 2011). The relation between Hardness number (H_v) and load (p) for RLHHC crystal is shown in Figure.9.

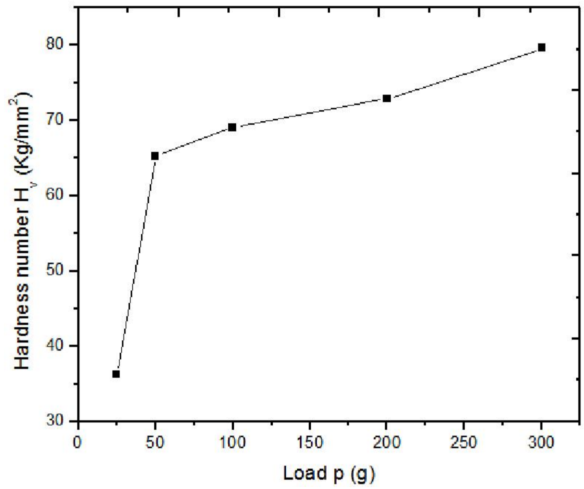

Figure 9.Variation of microhardness with applied load for RLHHC crystal

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. The value of the work hardening coefficient n was found to be 2.6196 from the figure.10. According to Onitsch, $1.0 \leq n \geq 1.6$ for hard materials and n >1.6 for soft materials (Onitsch, 1950). Hence, it is concluded that RLHHC belongs to the soft category materials.

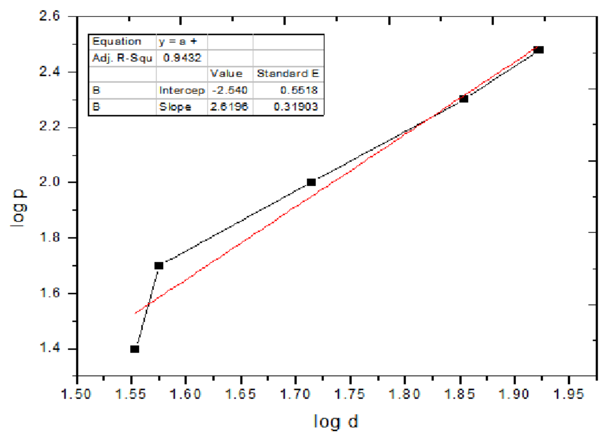

Figure 10. Plot of log d versus log p for RLHHC crystal

Other Mechanical properties such as yield strength (σ_y) and stiffness constant (C_{11}) were calculated at different loads using wooster's empirical formula. The relations for determining yield strength (σ_y= (Hv/3)N/m^2) and the stiffness constant (C_{11}=(Hv)$^{7/4}$ N/m^2) where H_v is the Vicker's Microhardness number of the material (Wooster, 1953). The variations of yield strength and stiffness constant for RLHHC crystal with the applied loads are shown in the Figure.11 and12.

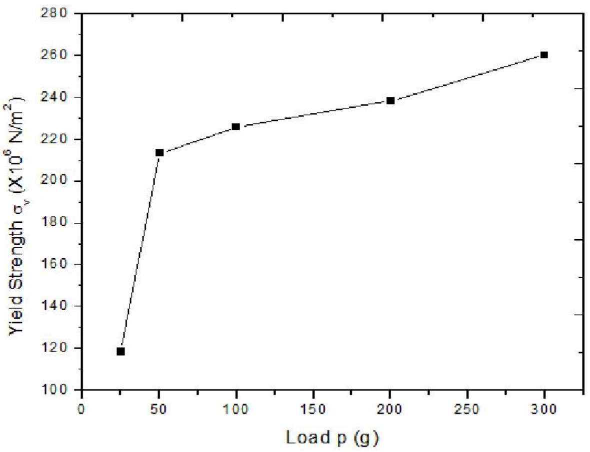

Figure 11.Plot of yield strength versus the applied load for RLHHC crystal

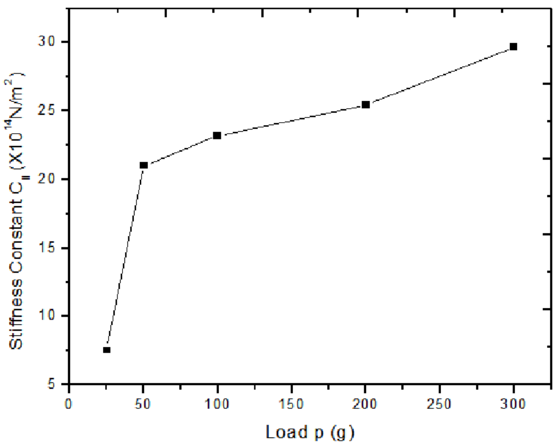

Figure 12. Plot of stiffness constant versus the applied load for RLHHC crystal

It is observed from the results that the mechanical properties like hardness, yield strength and stiffness constant increase with increase in the applied load.

SHG Efficiency Studies

The NLO behavior of the RLHHC crystal was evaluated by Kurtz and Perry method using a pulsed Nd: YAG laser (λ= 1064 nm), pulse energy of 4m J, Pulse width of 8 ns and repetition rate of 10 Hz were used (Kurtz, 1968). The emission of green light from the powdered sample, confirmed the second harmonic generation (λ=532 nm). The powder SHG efficiency was found to be 2.81 times that of KDP (Rajendran et al., 2003).

Conclusion

Rhodamine-B doped L-Histidine Hydrochloride (RLHHC) crystals were grown and the samples are observed to be pink in colour. Grown crystals were characterized by single crystal and powder XRD studies and it is confirmed that the grown crystals belong to orthorhombic structure with Space group $P2_12_12_1$. The Functional groups have been identified by FT-IR studies. The UV-Vis-NIR spectral studies confirm that the grown crystal have good transparency in the visible region. The good transparency shows that RLHHC crystal can be used for opto-electronic applications. The mechanical parameters such as microhardness, yield strength and stiffness constant have been evaluated by Vicker's Microhardness Studies. Fluorescence studies shows that the grown crystal gives out Blueish Green light when it is excited with the wavelength of 348.53 nm. The refractive index value was determined to be 1.401, this value shows that the grown crystal is suitable for optical applications. The dielectric constant and dielectric loss of the crystal decreases with increase in frequency and these low values at high frequencies reveals the desirable property of the crystal for NLO device applications. NLO studies reveal that the suitability of the grown crystal for NLO applications.

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