



GROWTH AND CHARACTERIZATION OF SEMIORGANIC NONLINEAR OPTICAL CRYSTAL: L-TYROSINE HYDROBROMIDE

S. Vanitha*, P. Koteeswari** & T. Kavitha**

* Department of Physics, Jeppiaar Institute of Technology, Kunnam, Sunguvachatram,
Chennai, Tamilnadu

** Department of Physics, Shrimathi Devkunvar Nanalal Bhatt Vaishnav College for
Women, Chennai, Tamilnadu

Cite This Article: S. Vanitha, P. Koteeswari & T. Kavitha, "Growth and Characterization of Semiorganic Nonlinear Optical Crystal: L-Tyrosine Hydrobromide", *International Journal of Advanced Trends in Engineering and Technology*, Volume 3, Issue 1, Page Number 119-125, 2018.

Abstract:

Single crystals of L-tyrosine hydrobromide (LTHB) single crystals have been grown by slow evaporation technique. From single-crystal XRD analysis, it is found that the crystal belongs to monoclinic system. Optical absorption studies were found to be absent in the UV, visible and near IR regions indicating that the crystal is completely transparent in the entire range of 280 nm to 1200 nm. The band gap, refractive index, reflectance, extinction coefficient and electrical susceptibility were calculated to analyze the optical property. The microhardness study shows that the Vickers hardness number of the crystal increases with the increase in applied load. The dielectric constant and dielectric loss measurements were carried out for different temperatures and frequencies. The photoconductivity studies confirm that the grown crystal has negative photoconductivity nature. The etching studies were carried out to study the formation of etches pits.

Key Words: Solution Growth, Single XRD, UV Analysis, Dielectric Constant And Dielectric Loss & Etching Studies

1. Introduction:

Single crystal growth has a prominent role in the present era of rapid scientific and technical advancement, whereas the application of crystals has unbounded limits. New materials are the lifeblood of solid state research and device technology. Nonlinear optical (NLO) crystals have come upon the materials science scene and are being studied by many research groups around the world. These materials operate on light in a way very analogous to the way of semiconductors which operate on electrons to produce very fast electronic switching and computing circuits. The search for new semiorganic nonlinear optical single crystals is very essential in order to develop materials to meet the growing industrial needs. While developing new materials several parameters are taken into consideration to achieve better properties. In the recent years, there has been a growing interest in nonlinear optical materials due to their effective usage in the field of electro-optical devices, data storage technology and optical signal processing [1]. However, semi-organic single crystals are attracting great attention in the field of nonlinear optics because of their high optical nonlinearity, chemical flexibility of ions, thermal stability and excellent transmittance in the UV-visible region [2, 3].

In the present investigation, the growth aspects of the L-tyrosine hydrobromide (LTHB) single crystals have been carried out by slow evaporation technique. The grown crystal was subjected to different characterizations such as single crystal X-ray analysis, optical analysis, micro hardness, dielectric, photo conductivity measurements and etching studies. The results of these studies have been discussed in this in detail manner.

2. Experimental Procedures:

Single crystals of L-tyrosine hydrobromide (LTHB) were grown, from aqueous solution by slow evaporation technique. The solution was prepared by dissolving equimolar amounts of L-tyrosine and hydrobromic acid in deionized water at room temperature and stirred well to yield a homogenous mixture of solution. The solution was then filtered. The filtered solution was taken in a beaker which was closed with a tissue paper and few pin holes were made on the tissue paper. The solution was then allowed to evaporate slowly which resulted gradually in supersaturation. LTHB crystal was harvested in a growth period of twenty five days by slow evaporation of the solvent.

3. Results and Discussion:

3.1 Single-Crystal X-Ray Diffraction Analysis:

Single crystal X-ray diffraction analysis for the grown crystals has been carried out to identify the cell parameters using an ENRAF NONIUS CAD 4 automatic X-ray Diffractometer. Single crystal XRD data confirms that the crystal belongs to monoclinic crystal system and the calculated lattice parameters are $a = 11.383 \text{ \AA}$, $b = 9.108 \text{ \AA}$, $c = 5.168 \text{ \AA}$, $\alpha = \gamma = 90^\circ$ and $\beta = 108.40^\circ$ and which agree well with the available reported literature values [4]

3.2 UV-Vis-NIR Spectral Analysis:

The UV-Vis-NIR spectrum gives valuable information about the absorption of UV and visible light, which involves promotion of electrons in σ and π orbital from the ground state to higher energy state. The

optical behavior of the material basically includes the interaction of light radiation over the range of the electromagnetic spectrum. The ultraviolet light absorbed by the sample gives information about the transparency window which is very essential in many optoelectronic applications. It is also helpful in asserting the activation energy due to electronic excitation as well as to ascertain the basic bonding present in the material. The optical transmittance spectrum of LTHB was recorded in the range 200 – 1200 nm with a crystal of thickness 2 mm. The Fig.1 shows that the crystal has a wide transmission of above 70% in the entire range without any absorption peak. The lower cutoff wavelength of LTHB was found to be at 280 nm. The crystal has good optical transmission in the visible region. The transparency in the visible region for this crystal suggests its suitability for second harmonic generation. The measured transmittance (T) was used to calculate the absorption coefficient (α) using the formula

$$\alpha = \frac{2.3026 \log\left(\frac{1}{T}\right)}{t} \quad (1)$$

Where t is the thickness of the sample. The optical band gap (E_g) is related to optical absorption coefficient (α) and energy ($h\nu$) of the incident photon as given by [5]

$$\alpha = \frac{A(h\nu - E_g)^{1/2}}{h\nu} \quad (2)$$

Where A is a constant, h is the Planck constant and ν is the frequency of the incident photons. The band gap of LTHB crystal was estimated by plotting $(\alpha h\nu)^2$ versus $h\nu$ as shown in Fig.2. From the figure, the value of band gap was found to be 4.80 eV. The extinction coefficient (K) can be obtained from the following equation,

$$K = \frac{\lambda \alpha}{4\pi} \quad (3)$$

The transmittance (T) is given by

$$T = \frac{(1-R)^2 \exp(-\alpha t)}{1 - R^2 \exp(-2\alpha t)} \quad (4)$$

Reflectance (R) in terms of absorption coefficient can be obtained from the above equation. The moderate value of refractive index and optical band gap suggest that the material has sufficient transmission range for NLO applications.

Hence,

$$R = \frac{1 \pm \sqrt{1 - \exp(-\alpha t + \exp(\alpha t))}}{1 + \exp(-\alpha t)} \quad (5)$$

Refractive index (n) can be determined from reflectance data using the following equation,

$$n = -\frac{(R+1) \pm \sqrt{3R^2 + 10R - 3}}{2(R-1)} \quad (6)$$

The refractive index (n) was found to be 1.81 at $\lambda = 1200$ nm. From the optical constants, electric susceptibility (χ_c) can be calculated according to the following relation [6]

$$\epsilon_r = \epsilon_0 + 4\pi\chi_c = n^2 - k^2 \quad (7)$$

Hence,

$$\chi_c = \frac{n^2 - k^2 - \epsilon_0}{4\pi} \quad (8)$$

Where ϵ_0 is the permittivity of free space. The value of electric susceptibility χ_c is 0.193 at $\lambda = 1200$ nm. The real part dielectric constant ϵ_r and imaginary part dielectric constant ϵ_i can be calculated from the following relations [7]

$$\begin{aligned} \epsilon_r &= n^2 - k^2 \\ \epsilon_i &= 2nk \end{aligned} \quad (9)$$

The value of real ϵ_r and ϵ_i imaginary dielectric constants at $\lambda = 1200$ nm were estimated at 1.752 and 6.912×10^{-5} , respectively. The moderate values of refractive index and optical band gap suggest that the material has the required transmission range for NLO application. The lower value of dielectric constant and the positive value of the material are capable of producing induced polarization due to intense incident light radiation.

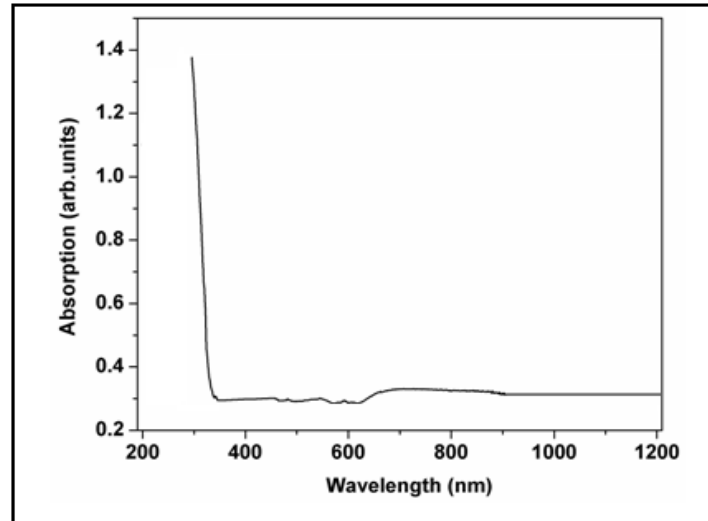


Figure 1: Absorption spectrum of LTHB crystal

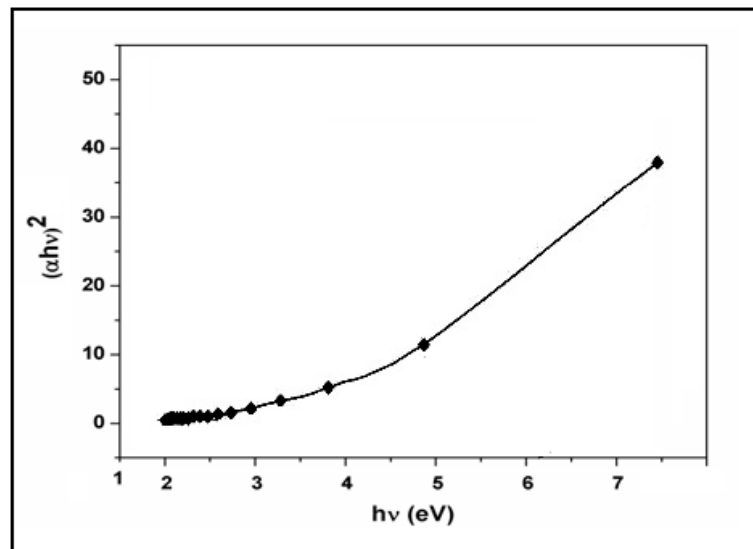


Figure 2: Plot of $(\alpha h\nu)^2$ Vs photon energy

From the observed spectrum, the lower cut-off wavelength is found to be 280 nm and there is no absorption peak in the visible region and near the infrared region which indicates the absence of overtones. Hence, UV absorption studies reveal that the grown LTHB crystal is one of the suitable materials for exhibiting second harmonic generation in the entire visible and near infrared region. Using Tauc's plot, the band gap of the LTHB crystal was found to be 4.80. This high value of bandgap indicates that the grown crystal possesses dielectric behavior to induce polarization when powerful radiation is incident on the material.

3.3 Micro Hardness Studies:

The hardness of the material depends on different parameters such as lattice energy, Debye temperature, heat of information and interatomic spacing. According to Gong, during an indentation process, the external work applied by the indenter is converted to a strain energy component which is proportional to the volume of the resultant impression and surface energy component proportional to the area of the result impression. The hardness number was measured by using Shimadzu HVM – 2000 Microhardness tester. To find surface hardness of the as-grown LTHB crystal, the applied load was varied from 25 to 100 g for a constant indentation period of 10 s. The Vicker's hardness number H_v is calculated using the following relation,

$$H_v = 1.8544 \left(\frac{P}{d^2} \right) \text{kg/mm}^2 \quad (10)$$

Where P is the indenter load in kg and d is the diagonal length of the impression in mm . The variation of H_v with applied load is shown in Fig.3. It is evident from the plot that the microhardness of the crystal increases with increasing loads. The increases in the microhardness values of LTHB with increasing load are in agreement with the reverse indentation size effect (ISE). The work hardening coefficient(n) was found to be 3.52 by taking

slope in the straight line portion of the graph drawn between $\log P$ and $\log d$ (Fig.4). According to Onitsch, if 'n' is greater than 2 the microhardness will increase with an increase in the load. If 'n' are less than 2 the microhardness will decrease with an increase in the load. The work hardening coefficient (n) for LTHB crystal is greater than 2 which confirm that the hardness increases with the increase of the load.

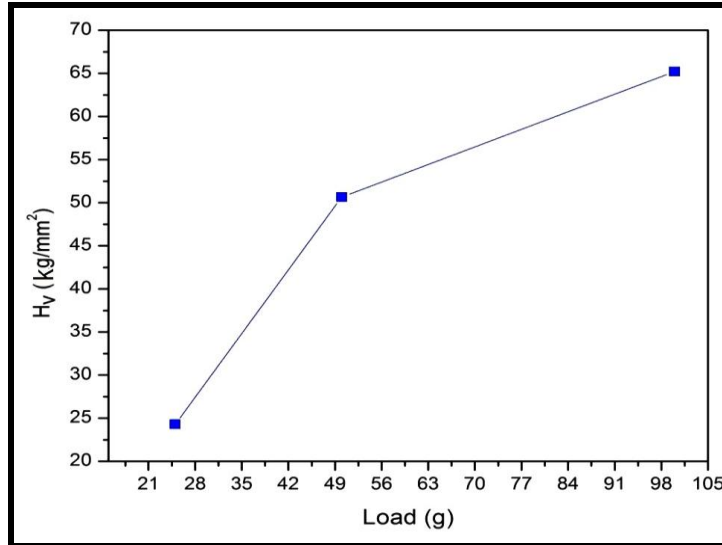


Figure 3: Vickers hardness profile of LTHB as a function of applied load

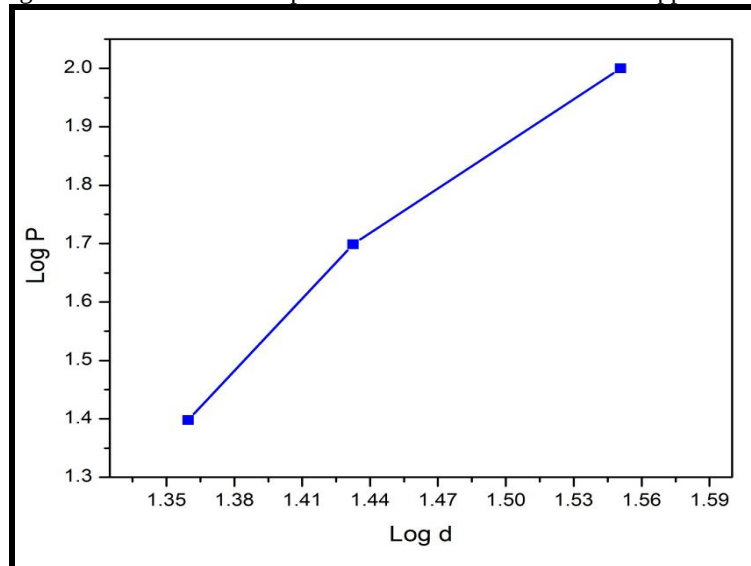


Figure 4: $\log P$ versus $\log d$ for LVP

The material LTHB is confirmed with large amount of mechanical strength which is better for device fabrications. Figure shows that the hardness increases with increase of load up to 100 g. It shows that the grown crystal can be used for devices which can withstand thermal local stresses. From the hardness study, the grown LTHB crystal is found to be relatively soft material.

3.4 Dielectric Studies:

Dielectric properties are related with the electric field distribution within solid materials. This is a normal dielectrics behavior that both dielectric constant and dielectric loss decreases with increase in frequency. The dielectric constant and the dielectric loss of the LTHB crystals were studied at different temperatures using a HIOKI 3532 LCR HITESTER in the frequency region from 50 Hz to 5 MHz. The dielectric constant (ϵ_r) and dielectric loss have been calculated using eqs. (11) & (12)

$$\epsilon_r = \frac{Cd}{\epsilon_0 A} \quad (11)$$

$$\epsilon_i = \epsilon_r \tan \delta \quad (12)$$

$$\tan \delta = \frac{\epsilon_i}{\epsilon_r}$$

$$= 1/\omega RC$$

Where d is the thickness of the sample, A is the area of the sample, C is the capacitance and ϵ_0 is permittivity of free space. Fig.5 shows the plot of dielectric constant versus log of frequency. The high value of dielectric constant at low frequencies may be due to the presence of all the four polarizations, namely, space charge, orientation, electronic and ionic polarization and its low value at higher frequencies may be due to the loss of these significant polarizations gradually [8]. From the plot, it is also observed that dielectric constant increases with an increase in temperature. The variation of dielectric loss with frequency is shown in Fig.6. The characteristics of low dielectric loss with high frequency for the sample suggest that it possesses enhanced optical quality with lesser defects and this parameter is imperative for nonlinear optical applications [9].

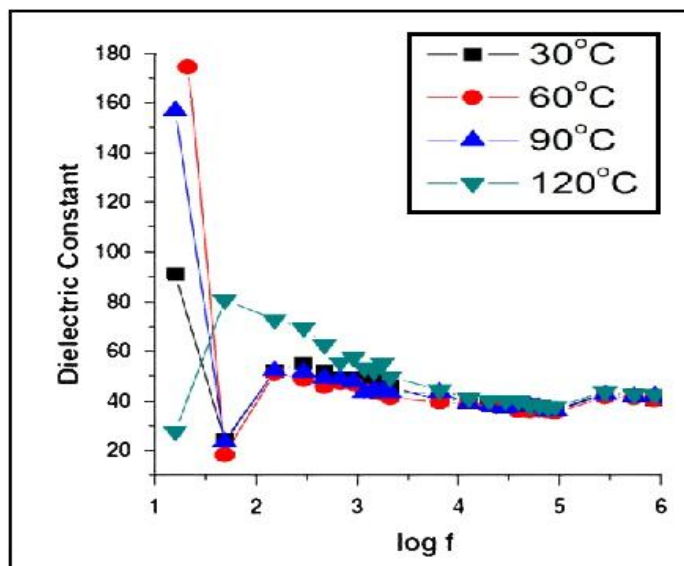


Figure 5: Plot of dielectric constant Vs log f

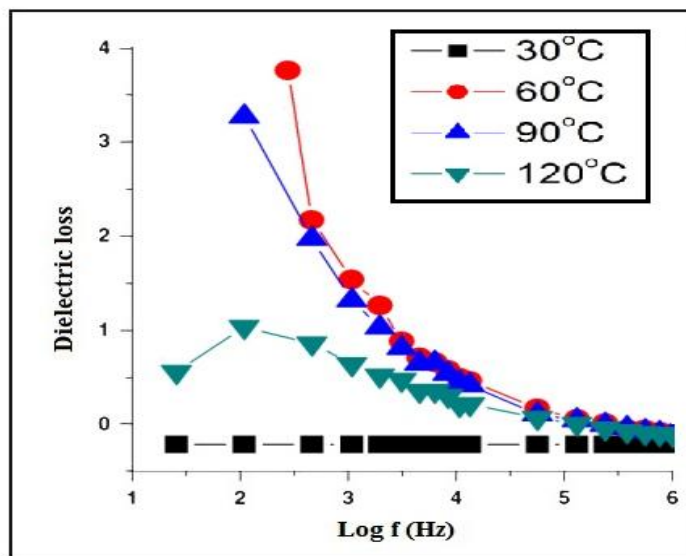


Figure 6: Plot of dielectric loss Vs log f

According to Miller rule, the low value of dielectric constant in the higher frequency region can enhance the SHG efficiency of the grown crystal. The lower value of dielectric loss at high frequencies will ensure that the grown crystal is free from major defects. Dielectric measurements reveal that replacement of other materials in microelectronic industry may be possible with LTHB crystals because of lower dielectric constant values at high frequencies. The variation at low temperature is mainly due to the crystal expansion and electronic and ionic polarizations. The variation at high temperatures is mainly attributed to thermally generated charge carriers and impurity dipoles. At higher frequencies no appreciable variation is found in the values of dielectric constant and dielectric loss when the temperature is increased. This behaviour is useful for the fabrication of microelectronic and nonlinear optical devices.

3.5 Photoconductivity Studies:

Photoconductivity measurements were carried out on a cut and polished sample of the grown single crystal by fixing it onto a microscope slide. The sample was connected in series with a DC power supply and KEITHLEY 485 Picoammeter. The sample was covered with a black cloth and the voltage applied was increased from 0 to 3000 V in steps of 500 V and the dark current was recorded. The sample was then exposed to light radiation and the photocurrent was recorded for the same values of the applied voltage. The field dependence of dark and photo currents of grown crystal is shown in Fig.7. The photocurrent is found to be less than the dark current at every applied electric field. This phenomenon is known as negative photoconductivity. Generally, this may be attributed to the loss of water molecules in the crystal [10]. However, the negative photoconductivity in this case may be due to the reduction in the number of charge carriers or their lifetime in the presence of radiation [11]. The decrease in lifetime with illumination could be due to the trapping process and increase in carrier velocity according to the relation,

$$\tau = (vsN)^{-1} \quad (13)$$

Where v is the thermal velocity of the carriers, s is the capture cross-section of the recombination centers and N is the carrier concentration. As intense light falls on the sample, the lifetime of the characterization decreases. In the Stockmann model, a two level scheme is proposed to explain negative photoconductivity [12]. As a result, the recombination of electrons and holes takes place resulting in decrease in the number of mobile charge carriers, giving rise to negative photoconductivity.

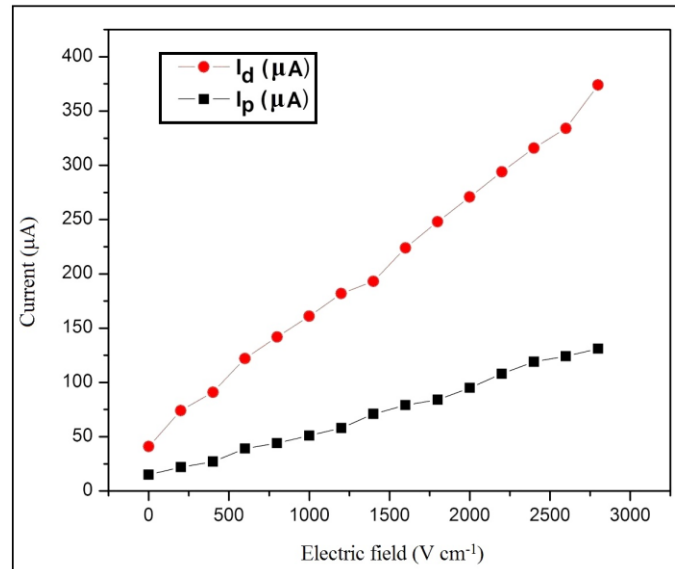


Figure 7: Field dependent photoconductivity of grown single crystal

3.6 Etching Studies:

The crystals with defects may destroy the mechanical and electrical properties, which affect the usefulness of the crystals. The nonlinear optical properties such as SHG efficiency, damage threshold etc, depend on the crystalline perfection. Chemical etching is a very simple and elegant technique to reveal the crystal defects and the crystal growth mechanism, which is able to develop some features such as growth striations, etch spirals; rectangular etches pits, etc., on the crystal surface. Etching studies on LTHB crystals were carried out using water as etchant. Etch pits were observed when etched with water for 60 sec. The etching photographs of LTHB crystals are shown in Fig.8. From the Fig.8 it is evident that when the crystals were etched for 60sec, well defined etch pits were observed.

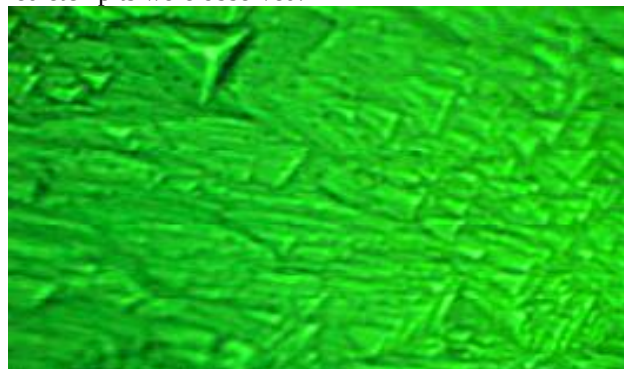


Figure 8: Etch pattern for LTHB crystal

4. Conclusion:

Single crystal of semi-organic L-tyrosine hydrobromide (LTHB) was grown from aqueous solution by slow evaporation technique. Single crystal X-ray diffraction studies confirm that the grown crystal belongs to monoclinic crystal system. The optical transmission analysis indicates that LTHB has a wide transparency window in the entire visible and near IR regions with a lower cutoff wavelength at 280 nm. The band gap was estimated to be 4.80 eV. Mechanical behaviour has been studied by Vickers microhardness test. The variation of dielectric constant and dielectric loss were studied as a function of frequency at different temperatures. The frequency dependence of dielectric constant and dielectric loss reveals the nature of polarization mechanism. The characteristics of low dielectric loss for the sample suggest that it possesses enhanced optical quality with lesser defects and this parameter is of vital significance for nonlinear optical applications. The Photoconductivity investigations reveal the negative photoconducting nature of material. Hence, the crystal LTHB is an excellent NLO material with more SHG efficiency required for the fabrication of optical devices. The growth pattern was analysed by etching studies.

5. References:

1. Shaokang Gao, Weijun Chen, Guimei Wang and Jianzhong Chen, Synthesis crystal growth and characterization of organic NLO material: N-(4-nitrophenyl)-N-methyl-2-aminoacetonitrile (NPAN), J.Cryst.Growth, 2006, 297, 361-365.
2. Pricilla Jeyakumari, A., Ramajothi, J. and Dhanuskodi, S., Structural and microhardness studies of a NLO material-bisthiourea cadmium chloride, J. Cryst. Growth, 2004, 269, 558-564.
3. Sun, H.Q., Yuan, D.R., Wang, X.Q., Cheng, X.F., Gong, C. R., Zhou, M., Xu, H.J., Wei, X.C., Luan, C.N., Pan, D.Y., Li, Z.F. and Shi, X.Z., A novel metal-organic coordination complex crystal: triallylthiourea zinc chloride (ATZC), Cryst. Res. Technol., 2005, 40, 882-886.
4. Anandan, P., Vetrivel, S., Jayavel, R., Vedhi, C., Ravi, G., Bhagavannarayana, G., (2012) Crystal growth, structural and photoluminescence studies of L-tyrosine hydrobromide semi organic single crystal. J. Phys. Chem. Solids. 73: 1296-1301
5. Ashour, A., El-Kadry, N. and Mahmoud, S.A., On the electrical and optical properties of CdS films thermally deposited by a modified source, Thin Solid Films, 1995, 269, 117-120.
6. Gupta, V. and Mansingh, A., Influence of post deposition annealing on the structural and optical properties of sputtered zinc oxide film, J. Appl. Phys., 1996, 80, 1063-1073.
7. Gaffar, M.A., Abu El-Fadl, A. and Bin Anooz, S., Influence of strontium doping on the indirect band gap and optical constants of ammonium zinc chloride crystals, Physica B., 2003, 327, 43-54.
8. Smyth, C.P., Dielectric Behavior and Structure, McGraw-Hill, New York, 1965.
9. Balarew, C. and Duhlew, R., Application of the hard and soft acids and bases concept to explain ligand coordination in double salt structures, J. Solid State Chem., 1984, 55, 1-6.
10. Bube, R.H., Photoconductivity of Solids, Wiley, New York, 1981.
11. Ashraf, M., Elshaik, H.A. and Badr, A.M., Photoconductivity in Tl_4S_3 layered single crystals, Cryst. Res. Technol., 2004, 39, 63-70.
12. Joshi, V.N., Photoconductivity, Marcel Dekker, New York, 1990.