Growth and Characterization of L-Threonine Lithium Chloride: A New Semiorganic Non Linear Optical single Crystal

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***Abstract*—A new novel semi organic nonlinear optical material L-Threonine Lithium chloride was synthesized and transparent single crystal were grown by slow evaporation solution growth technique at room temperature. The grown single crystal were characterized by Single crystal X-Ray Diffraction, Fourier transforms infrared spectroscopy, optical absorption spectrum. Single crystal X-ray diffraction analysis reveals that the crystal lattice of L-Threonine Lithium chloride is orthorhombic crystal structure with the non centrosymmetric space group of $P2_12_12_1$. The absorption range and the optical band gap were evaluated from UV-Vis-NIR spectral analysis. The dielectric response of the crystal with varying frequency was studied. The TG-DTA studies show that the crystal is thermally stable up to 236°C. The second harmonic generation efficiency of the crystal was studied and it found to be 1.76 times greater than standard KDP.**

***Keywords*—Single crystal growth, Characterization, Nonlinear optical materials.**

I. INTRODUCTION

Nonlinear optical materials have been plays an increasingly vital role in laser technology, even though profound efforts in the field of the light modulation, frequency conversions, second harmonic generation, optical switching and optical memory storage. In past few decades there has been extensive research in the growth of nonlinear optical materials, because of the wider application such as photonics and optoelectronics application [1]. Most of the organic NLO crystals have poor thermal and mechanical properties and are susceptible damage during processing. Moreover growth of large size bulk single crystal is difficult to grown for device fabrications. Inorganic crystals have excellent thermal and mechanical properties but possess relatively modest optical nonlinearity due to the lack of extended π-electron delocalization [2]. For the above reasons interests have been made on semiorganic NLO crystals, which have been combined the both properties of organic and inorganic crystals like chemical stability, high laser damage threshold, higher chemical strength and high transparency, which make them suitable for device fabrication. The semiorganic crystals possess positive aspects of both organic and inorganic material hence it is important to synthesis and growth of the novel semiorganic NLO crystals.

Amino acids are promising organic materials for NLO applications because they contain proton acceptor amino (NH_2) group and the donor carboxylic (COOH) group in them, which known as Zwitterions, it create hydrogen bonds. Due to its dipolar nature, amino acid compounds have physical properties which make ideal candidates for device fabrication and NLO applications. For the advantages of the properties of amino acid ligands, amino acids complexes were used as ligands, which used to synthesis a new heteronuclear complex. Complex of L-Threonine with lithium sulphate [3] and potassium iodide [4] has been reported for semiorganic nonlinear optical crystals. Many new complexes incorporating the amino acid L-Threonine have been crystallized and their various properties have been investigated [5-7]. The semiorganic NLO materials of L-Threonine lithium chloride (LTLC) was synthesized from aqueous solution by the slow evaporation technique. Highly transparent optically good quality single crystal of LTLC was obtained. The LTLC was characterized by Single crystal XRD to estimate the space group and cell parameters. The various functional groups were identified by FT-IR analyses. UV-Vis-NIR absorption spectral studies indicate that the grown crystal is transparent in the entire visible region with a lower cut off wavelength of 256nm. The TG-DTA studies show that the crystal is thermally stable up to 236°C. The results of dielectrics of this material are reported in this paper. Powder SHG results shows that LTLC is 1.76 times greater than standard reference KDP.

II. EXPERIMENT

Materials and methods

The single crystal growth of nonlinear optical crystal L-Threonine Lithium chloride (LTLC) has successfully synthesized by taking equimolar ratio quantity of L-Threonine and Lithium chloride mixing them thoroughly using deionised water. The crystal has grown by adopting the method of growing in a slow evaporation solution method using water as solvent at room temperature. The prepared solution was covered with a perforated cover and placed in an undisturbed condition, and it was inspected regularly over a period of a month. A single crystal has been harvested with dimensions of 27×4×3 mm^3 is shown in the Fig.1. The quality and the size of the crystal were improved by repeated crystallization process.

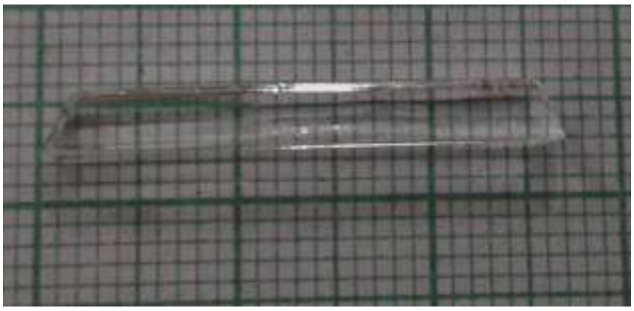

Figure 1 Photograph of the as grown LTLC crystal

III. RESULTS AND DISCUSSION

Single Crystal X-Ray Diffraction Analysis

Single crystal X-ray diffraction studies were carried out on the LTLC single crystal using a computer controlled ENRAF NONIUS CAD4 X- ray diffractometer to determine the lattice parameters and space group. The results obtained indicate that the crystal belongs to orthorhombic crystal system with space group $P2_12_12_1$ and the unit cell parameters are found to be a=5.137Å, b=7.723Å and c=13.593Å, $\alpha=\beta=\gamma=90^0$ and V=539Å^3. The slight variation of cell parameter of the grown LTLC single crystal from the pure L-Threonine crystal [8] confirms the incorporation of LiCl in the host lattice of L-Threonine. The space group suggests that the grown LTLC single crystal is non-centrosymmetric in nature which fulfils the fundamental criterion for the SHG activity of the material.

FT-IR spectroscopy - Functional group Analysis

The FT-IR spectroscopy was used to identify the presence of functional groups in the grown crystal. Fig. 2 shows the characteristic absorption peaks was recorded in the spectral region of 400 – 4000 cm^{-1} for the grown LTLC crystal. The band that appears at 3168 cm^{-1} with weak intensity shows CH_3 asymmetric stretching. The peak with strong intensity at 2049 cm^{-1} represents NH_3^+ asymmetric deformation. The medium intensity peak at 1639 cm^{-1} is due to the C=O asymmetric stretching. The O-H bending of COOH group is indicated due to the peak at 1249 cm^{-1}. The C-C-N symmetric stretching vibration is observed at 1112 cm^{-1}. The peak against 930 cm^{-1} shows C-C stretching vibration [9]. The peak observed at 704 cm^{-1} represents wagging vibration of CO_2 structure. NH_3 torsional mode is represented by the peak against 489 cm^{-1}. The transfer of hydrogen ions from carboxylic group ($COOH^-$) group to amino (NH_2^+) group provides the zwitterionic nature of the amino acid compounds. The zwitterionic nature of the materials clearly indicates that an imbalance of charge is provided to make the compound as non-centrosymmetric.

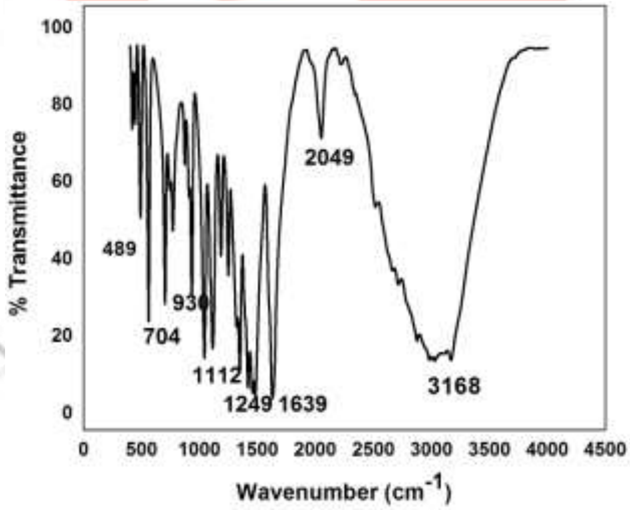

Figure 2. FT-IR spectrum of LTLC crystal.

UV-Vis-NIR absorption Spectral Studies

The optical absorption spectrum of LTLC crystal was recorded in the range of 200- 1100 nm using LAMBDA 35 UV-Vis-NIR spectrometer to evaluate the absorption range and optical band gap of the material. The lower cut-off wavelength for the crystal is found to be 256 nm with transparent range in the region of 250 -1100 nm is shown in the Fig. 3. The optical band gap of LTLC crystal is shown in Fig. 4. The Energy band gap of LTLC crystal is determined using the tauc's extrapolation method [10]. The optical band gap is found to be 4.8 eV which confirms the wide transparency nature (300nm-1100 nm) and dielectric behaviour of the material [11]. The wide optical band gap of the material shows that the material is dielectric in nature. The dielectric nature of the material really counts for the induced polarization in the material to exhibit NLO activity due to intense incident radiation on the material. This will result in the better conversion efficiency of the material LTLC for second harmonic generation.

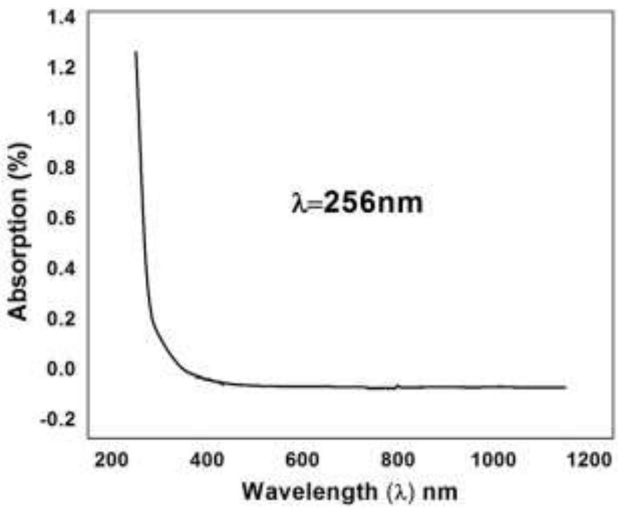

Figure 3. UV Absorption spectrum for LTLC crystal

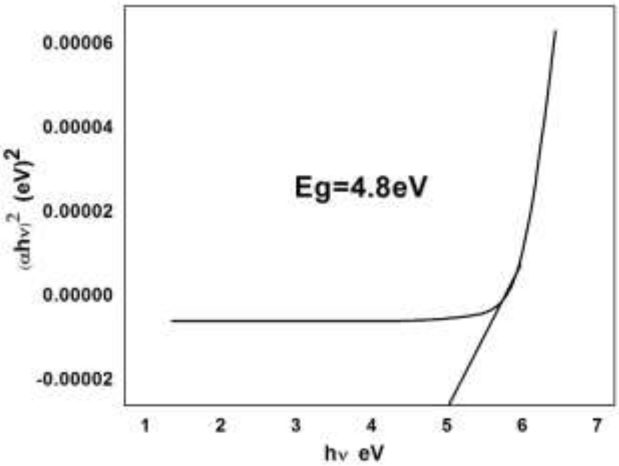

Figure 4. Energy band gap of LTLC single crystal.

Thermal stability study

The TG-DTA curves of LTLC crystal, recorded with heating rate 10°C/min in nitrogen gas environment, are shown in Fig. 5. The TGA curve shows a weight loss starting at around 236°C and ending at a temperature 283°C which result in maximum weight loss. In the DTA curve also, an endothermic peak starts at around 236°C and ends at 283°C. This endothermic peak and weight loss around 236°C corresponds to the decomposition of the material. Continuous heating results into slight weight loss, which confirms the maximum decomposition of material takes place only around at 283°C. This TG-DTA study confirms the LTLC crystal is stable up to 236◦C can be used in the NLO applications with high power lasers up to this temperature.

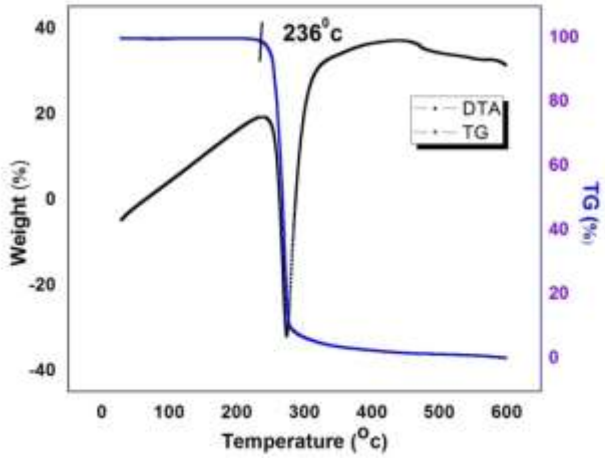

Figure 5. TG/DTA spectrum of LTLC crystals

Dielectric Measurements.

The dielectric measurements are one of the basic electrical properties of solids [12]. The study of dielectric constant and dielectric loss of a material gives an introduction about the nature of atoms in the solids, ionic nature and corresponding bonding in the material. The dielectric constant (ε_r) and dielectric loss (tanδ) values obtained for LTLC crystal are shown in Fig. 6 and Fig. 7 respectively. The increase in ε_r at low frequency may attributed to electric, ionic, orientation and space charge polarization and it decrease at high frequencies due to the loss of significance of these polarization gradually [13]. It has been found that the dielectric parameters (ε_r and tanδ) values are found to decrease with the increase in frequency. This is a normal dielectric behaviour and it indicates that it can be used for NLO applications.

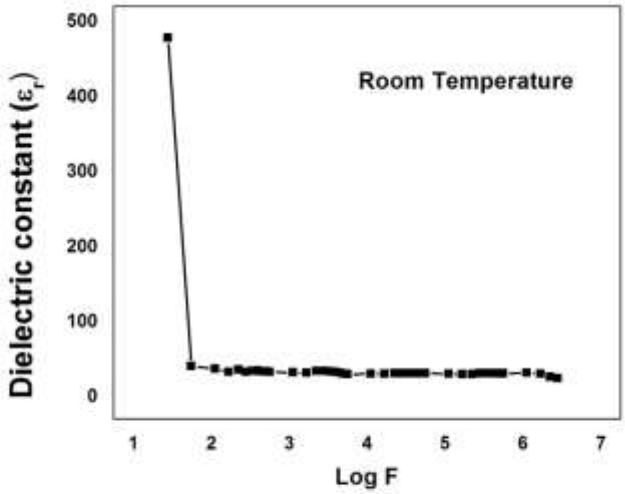

Figure 6. Dielectric Constant of LTLC Single crystal

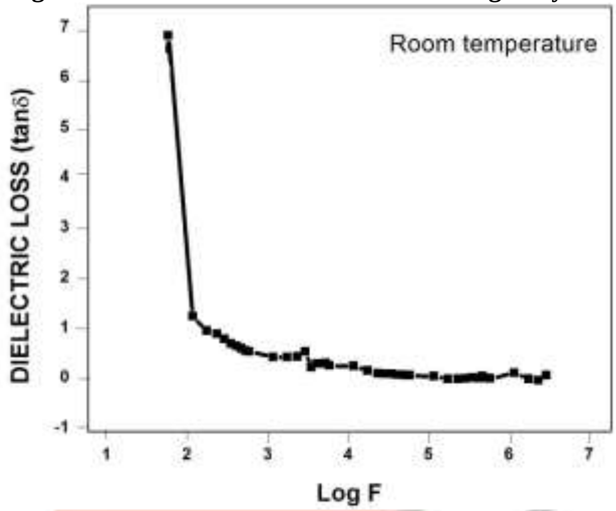

Figure 7. Dielectric Loss of LTLC Single crystal

Non Linear Optical Property

Kurtz and Perry powder technique was used to confirm the nonlinear optical (NLO) property of LTLC single crystal. A Q - switched Nd : YAG laser source emitting a wavelength of 1064 nm with pulse width 8 ns was used to illuminate the sample. The emission of green radiation of confirms the second harmonic generation by the crystal which is the characteristic of the nonlinear behaviour of the material. The input energy incident on the sample was 0.681 mJ / pulse and the corresponding output was measured as 15.68 mJ. This output was compared with the output (8.91mJ) obtained for the standard material KDP. The SHG efficiency of LTLC is found to be 1.76 times that of KDP and 1.2 times greater than the pure L-Threonine crystal [14]. The result shows that the doping of LiCl increases the second harmonic generation efficiency of L-Threonine and it concluded that LTLC is a most promising NLO material due to better linear and nonlinear optical properties of the material.

IV. CONCLUSION

The L-Threonine Lithium Chloride (LTLC) single crystals have been grown by slow evaporation method at room temperature. The single crystal XRD confirmed the orthorhombic crystal system with space group $P2_12_12_1$ of LTLC crystals. The high transparency and lower cut-off wavelength (256 nm) of LTLC crystal indicates the prominent potential for NLO device fabrications. The dielectric property studied at room temperature indicates that dielectric constant and dielectric loss decreases with the increase in frequency. The characteristics of low dielectric loss with high frequency for LTLC crystal indicates that the crystal possesses high optical quality with lesser defects and this parameter is vital for various applications of NLO materials. TG/DTA analysis show thermal stability of the materials up to 236°C which is ambient temperature for NLO application. The SHG efficiency of LTLC is found to be 1.76 times that of KDP which is greater than the pure L-Threonine single crystal.

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