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Synthesis, growth and optical properties of L-threoninium chloride for opto electronic applications

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Abstract - *The complex of amino acids and their salts are promising materials for optoelectronic applications. Organic systems were investigated as an alternative to inorganic species because of their low cost, fast and large nonlinear response over a broad range. A new charge transfer complex of organic crystal, L-threoninium chloride has been successfully synthesized by conventional slow evaporation method from aqueous solution. The grown crystal is structurally characterized by powder X-ray diffraction. The various functional groups present in the crystals are identified and the formation of molecular structure is confirmed by FTIR analysis. The UV-Vis-NIRanalysis revealed the transparency of the grown crystal is about 80% in the entire visible region. The NLO property was measured using Kurtz-Perry powder technique and SHG efficiency of the crystal is 50% times that of KDP.*

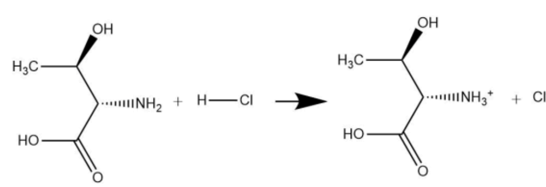
Key Words: L-Threonine, Slow evaporation, Charge transfer complex, Single crystal, NLO crystals.

1. Introduction

In recent years the nonlinear optical materials increased tremendously due to the reason of photonic applications. The organic compounds have the important role in nonlinear optics, because they have the high charge transfer mobility, high laser damage threshold and high optical responsibility [1].Materials with NLO activity find useas electro-optic switching elements for telecommunication andoptical information processing. The proton donor carboxyl group and proton acceptor amino groups contributes physicochemical properties of the material [2].L-threonine derivatives have the much contribution in the NLO materials such asL-threonine, L-threonine picrate and L-threoninium acetate, etc [3][4][5].Motivated by the above specifies, the L-threoninium chloride (LTC) organic charge transfer single crystal is synthesized. The grown crystal is characterized properly such as X-ray diffraction, Fourier transfer infrared spectrometry, UV-Vis-NIRanalysis and SHG studies.

2. Materials and methods

L-threoninium chloride (LTC) crystal was synthesized from equimolar amounts of L-threonine (SRS Chem.) and Hydrochloric acid (35 % Rankem Chem.). The calculated amount of L-threonine was first dissolved in double distilled water. To this solution an equivalent molar amount of the acid was slowly added accompanied good stirring by a temperature controlled magnetic stirrer to yield a homogeneous mixture of solution. The acid necessarily protonates the amino group of L-threonine resulting in the formation of L-threoninium chloride. The reaction scheme of LTC is shown in figure 1. The synthesized salt solution was left for crystallization by slow evaporation from a saturated aqueous solution, in a crystallizing vessel. After a period of 20 days the optically transparent and well-shaped single crystal of L-threoninium chloride of size ~ 15 x 3 x 2 mm^3 was harvested in 20 days period and is shown in insert of figure 2.



Fig– 1: The reaction scheme of LTC

3. Powder X-ray diffraction analysis

The powder X-ray diffraction analysis has been carried out to confirm the crystallinity of grown crystal using Rigaku Miniflex- II diffractometer with CuKα (1.5406 Å) radiation. The powdered sample scanned between the range of 5-80° with scanning rate of 2°/min. The narrow and sharpness of the peaks confirms the purity and single crystalline nature of the sample. The prominent intensity peaks were indexed with TREOR program [6].

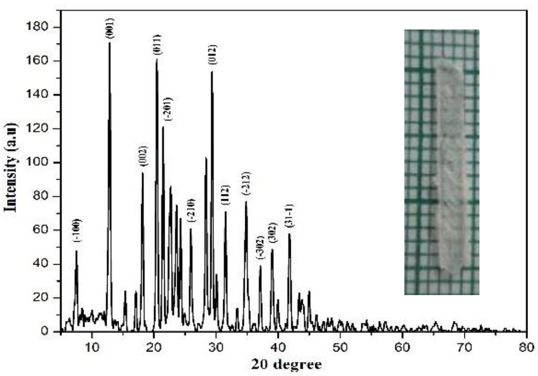


Fig – 2: Powder XRD pattern of LTC and as grown LTC crystal (insert)

4. FTIR analysis

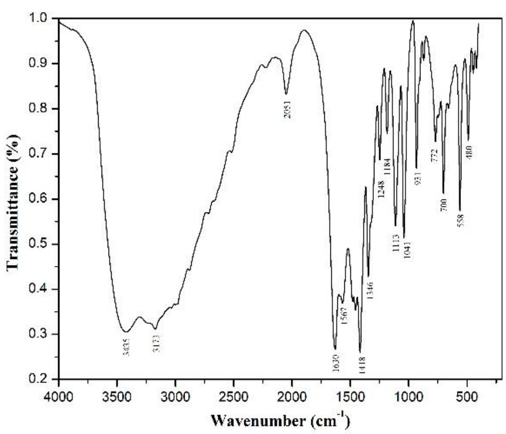
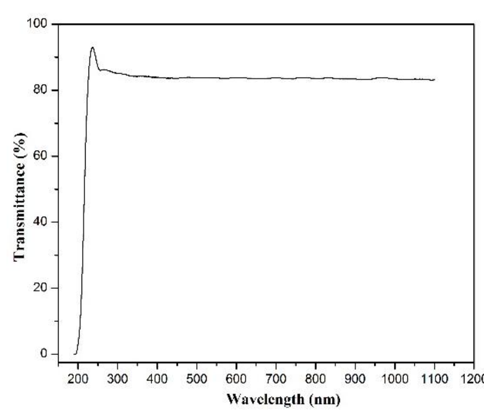


Fig - 3. FTIR assignments of LTC

The functional group assignments of the crystal areconfirmed by FTIR analysis. The FTIR spectrum of L-Threoninum chloride crystal is carried out using Bruker Tensor 27 FTIR spectrometer in the spectral range 4000-400 cm^{-1} by KBr pellet method shown in figure3. In L-threoninium chloride alcoholic hydroxyl groups form a weak hydrogen bond with chloride ion O–H⋯Cl therefore O–H stretching vibration is slightly shifted towards low frequencies which is observed at 3435 cm^{-1} [2]. N–H stretching vibration of protonated amino group is observed at 3173 cm^{-1}. Carboxyl group has characteristic stretching vibration of C=O bond which is observed as a very strong absorption band at 1630 cm^{-1} for *L*-threoninium chloride. In-plane deformation vibration of carboxylic OH group is coupled with stretching vibration of carboxylic C–OH bond and observed as a band at 1346 cm^{-1}. The NH_3^+group makes two bending vibrations, asymmetric and symmetric, which are presented at 1567cm^{-1} and 1418 cm^{-1} respectively. Rocking vibrations of $NH_3^+$and CH_3 groups are observed in the region 1150-1000 cm^{-1}. The stretching vibrations of C–N and C–C bonds absorbed the frequencies around 1050 - 900 cm^{-1}. The deformation vibration of carboxyl group, torsion oscillations of OH, $NH_3^+$and CH_3 groups are found in the lower region.

5. Optical studies

The optical transmission and cut of wavelength of the single crystal are more significant parameters for nonlinear optical applications. The UV-Vis-NIR spectrum of LTC is shown in figure4. The lower cut off wavelength of the crystal is 235 nm and hence the crystal is well suitable for second harmonic application for working in ultraviolet to mid infrared spectral region. The transmission window of thecrystal is 235-1100 nm and this large transmission in the entire visible region enables it to be a good candidate for optoelectronic applications.



Fig– 4: UV-Vis-NIR transmission curve of LTC

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6. Second harmonic generation efficiency

The second harmonic generation efficiency of grown crystal is analyzed by Kurtz-Perry powder technique[7].A Q-switched Nd-YAG laser of wavelength 1064 nm has an input energy of 1.2 mJ/pulse with a pulse width of 10 ns and repetition rate of 10 Hz was used an optical source.

The output SHG signal of LTC crystal is 20 mV for an input energy of 1.2 mJ/pulse, whereas, the KDP crystal hasthe output signal of 40 mV for the same input energy. The relative measurement from the crystal with respect to KDP crystal, the LTC second harmonic efficiency is 0.5 times that of standard KDP.

7. Conclusions

The organic single crystal of L-threoninium chloride have been grown from slow evaporation technique.The good crystallinity of the sample is confirmed by powder XRD analysis. The vibrational frequencies are assigned from FT-IR analysis, which confirm the functional group present in the L-threoninium crystal. The LTC crystal is high transmittance in the entire visible region, and cut- off wavelength was observed at 235 nm. The NLO efficiency of the sample is 0.5 times that of standard KDP. All the results confirm, the L-threoninium chloride is the potential candidate for optoelectronic applications

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