GROWTH AND INVESTIGATION OF A NON LINEAR OPTICAL CRYSTAL L-THREONINE TRIFORMATE (LTTF)

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ABSTRACT

Single crystals of L-threonine Triformate have been grown by slow evaporation technique. The powder X-ray diffraction studies confirmed the monoclinic structure of grown crystals. The presence of varioue functional groups were identified by FTIR STUDIES. The crystal is found to be transparent in the region 400–800 nm. Tharmal studies showed that the crystal up to 231^0 C without undergoing any sublimation.The SHG efficiency of L-threonine Triformate crystal was found to be 0.85 times higher than that of KDP.

Key words: Crystal Growth, L-Threonine Triformate,SHG Studies

1. INTRODUCTION

Nonlinear optical (NLO) frequency conversion materials have a significant impact on laser technology, optical communication and optical storage technology. The search for new frequency conversion materials over the past decade has led to the discovery of many organic NLO materials with high nonlinear susceptibilities. However, their often-inadequate transparency, poor optical quality,and lack of robustness, low laser damage threshold, and inability to grow to large size have impeded the use of single crystal organic materials in practical device applications. Hence, recent search is concentrated on semiorganic materials due to their large nonlinearity, high resistance to laser induced damage, low angular sensitivity and good mechanical hardness [1–3]. Particularly, amino acid family crystals are of great interest due to their attractive nonlinear optical properties [4-6].When the organic acid mixed with amino acid, NLO property has been increased due to the zwitter ionic nature and high transparency range [7-10]. L-threonine is one such amino acid with higher SHG efficiency. Formic acid forms crystalline formates with amino acids like L- arginine, L-alanine and L- glycine [11-12] Crystals like L-arginine formate, L- alanine formate, and L- glycine formate found to exhibit non-linear optical property.

In the present work, the growth of L-threonine Triformate by slow evaporation technique and the characterisation of grown crystals by X-ray diffraction, Fourier transform infrared spectroscopic analysis, optical absorption, thermal and second harmonic generation efficiency were discussed.

2. EXPERIMENTAL

The L-threonine Triformate (LTTF) was synthesized from L-threonine and formic acid in the stoichiometric ratio of 1:3 by slow evaporation technique as per the following reaction.

The growth rate of a crystal depends on the solvent, temperature, and degree of super saturation of the solution. The calculated amount of L-threonine and formic acid were dissolved in a mixed solvent of acetone and water. The reactants were stirred well for two hours using a temperature-controlled magnetic stirrer to yield a homogenous mixture of the solution. The solution was transferred to a clean petri dish and allowed to evaporate under room temperature. The product was re-crystallized twice to remove the impurities. The transparent crystals were harvested in a period of 15 days. The photograph of the grown crystals is shown in Figure 3.1.

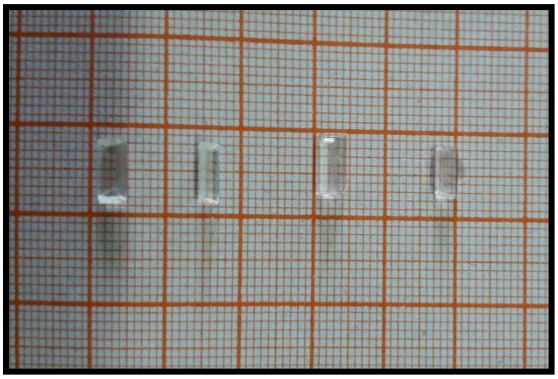

Figure 3.1 As-grown crystals of LTTF

3 RESULTS AND DISCUSSION

3.1 Single crystal X-ray diffraction

Single crystal X- ray diffraction studies of LTDF were carried out using CAD ENTRAF NONIUS X- ray diffractometer with MoK_α (λ = 0.7107 Å). The Crystal belongs to monoclinic system. The cell parameters are a=5.15 Å, b=7.74 Å, c=13.65 Å, and volume V =544 $Å^3$.

3.2 Powder X- ray diffraction

Powder X-ray diffraction analysis has been carried out using Rich Seifert X-ray diffractometer with CuK_α (λ = 1.5418 Å) line radiation and the recorded XRD pattern is shown in Figure 3.2. The X– ray diffraction peaks were indexed for the lattice parameters. The prominent peaks in the powder X-ray diffraction confirm the crystalline nature of the grown crystals. The peak corresponding to (0 1 1) has maximum intensity per second.

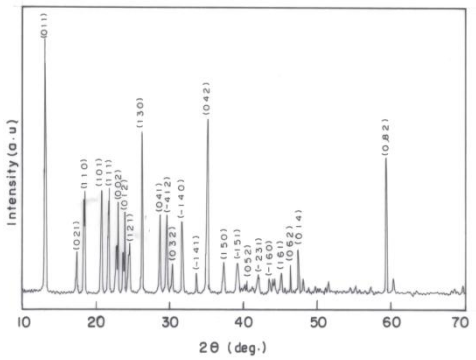

Figure 3.2 X-ray diffraction pattern of LTDF

3.3 FTIR Analysis

The FTIR analysis of LTDF crystal was recorded using BRUKER IFS 66v model spectrophotometer by KBr pellet method in the wave number range from 4000 to 500 cm^{-1} and the recorded spectrum is shown in Figure 3.3.

The absorption peaks due to the vibrations of various functional groups present in the material was interpreted. The peak at 3116 cm^{-1} is assigned to N–H symmetric stretching vibration. The C–H symmetric stretching is observed at 2873 cm^{-1}.

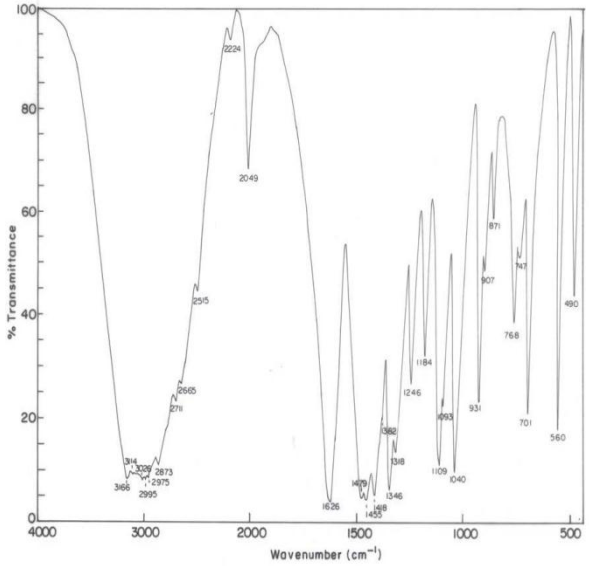

Figure 3.3 FTIR Spectrum of LTTF

The C-N stretching vibration appears as a very sharp peak at 2049 cm^{-1}. The peak at 1626 cm^{-1} is assigned to N-H bending. The peaks at 1346 cm^{-1}, 1246 cm^{-1}, 1184 cm^{-1} 1109 cm^{-1} and 1049 cm^{-1} are attributed to C-N stretching. The peak at 931 cm^{-1}, 871 cm^{-1} and 768 cm^{-1} corresponds to C-H bending. The peak at 701 cm^{-1} corresponds to N-H wagging. The C-N out of plane bending appears at 560 cm^{-1}.

3.4 UV-VIS-NIR Absorption Spectrum

Absorption spectrum is very important for any NLO material because a nonlinear optical material can be of practical use only if it has wide transparency window. Hence, to assess its suitability for NLO applications, the grown single crystal with a thickness of about 1 mm was subjected to UV-vis-NIR studies at room temperature in the wavelength range from 200 to 1000 nm using a Shimadzu UV–vis spectrophotometer and the recorded spectrum is shown in Figure 3.4. From the absorption spectrum, it was found that the lower cut-off wavelength is 340 nm. The crystal is found to be transparent in the region of 400–800 nm which is an essential parameter for frequency doubling applications [13]

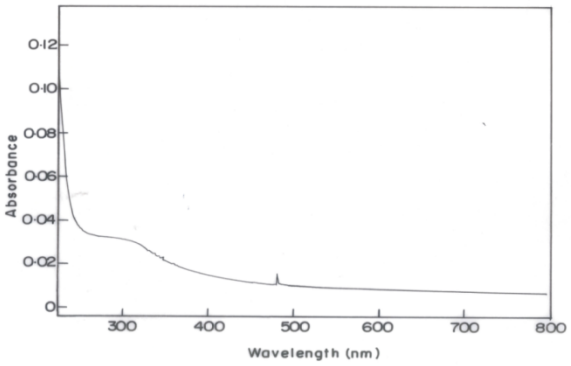

Figure 3.4 UV-Vis-NIR absorption spectrum of LTTF

3.5 Thermal Behavior

The thermal behavior of LTTF was studied using ZETZSCH – Geratebau GmbH thermal analyzer and the thermogram in Figure 3.5 of the LTDF crystal shows that the crystal is stable upto 248.99º C and undergoes complete decomposition in single stage from 248.99º C to 329º C.However DTA plot indicates that the decomposition is not taking place in single stage. The sample is not preheated for thermal analysis. The first peak of DTA indicates the loss of water molecule adhered to the crystal (4.6% of H_2O which is removed on heating to 104.77^0 C. The decomposition of the crystal is taking place between 231.25^0 C to 262.5^0 C & 262.5^0 C to 329^0 C by endothermic followed by exothermic reaction which is not the characteristics of sublimation. Crystal is stable at room temperature to 231^0 C without undergoing sublimation. As threonine contains nitrogen the oxides of nitrogen is removed as vapour is the range of $475\text{-}540^0$ C without leaving any residue.

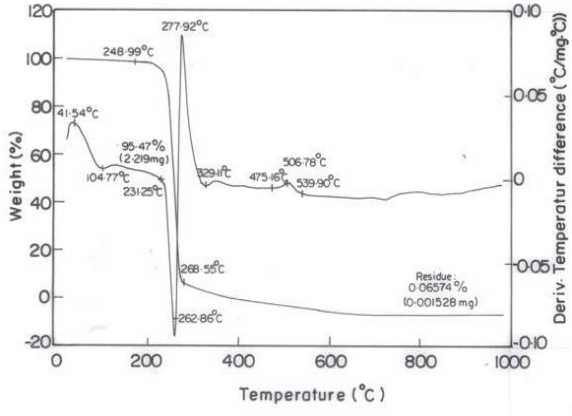

Figure 3.5 TGA and DTA of LTTF single crystal

3.6 NLO Studies

The NLO property of the powder sample was confirmed by the Kurtz and Perry powder technique [14]. A Q-switched Nd-YAG laser beam of wavelength 1064 nm was used with an input power of 2.0 mJ and pulse width of 10 ns, the repetition rate being 10 Hz. The SHG behavior is confirmed from the output of the laser beam having the bright green emission (λ=532 nm) from the crystal. The SHG relative efficiency of L-threonine Triformate crystal was found to be 0.85 times higher than that of KDP.

4.CONCLUSION

Single crystal of L-threonine Triformate was synthesized and grown by slow evaporation technique. The X-ray diffraction studies revealed that the crystal belongs to monoclinic system. FTIR spectroscopic studies were used to identify the functional groups present in the compound. Absorption spectrum shows lower wavelength cut off at 340 nm. Thermal behavior shows that the material is thermally stable up to 248.9º C. The SHG efficiency of the powdered sample of the crystal is 0.85 times higher than that of KDP.

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