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INVESTIGATIONS ON GROWTH KINETICS AND CHARACTERIZATIONS OF NONLINEAR OPTICAL MATERIAL: L-THREONINE SUCCINATE (LTS)

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ABSTRACT

L-threonine succinate (LTS), a new and efficient organic nonlinear optical (NLO) crystal, was successfully grown by slow evaporation technique. The grown crystal was then characterized using XRD and SEM-EDAX analyses, UV–vis–NIR, FTIR, and FT-NMR spectral studies, thermal, microhardness and NLO studies. From the XRD data, it is understood that the crystal LTS belongs to triclinic system with space group 'P_1'. From the UV-vis-NIR absorption study, it is found that the grown crystal shows transparent nature from 240nm onwards and extends beyond NIR region. The optical band gap was evaluated as 5.88eV from Tauc's plot. The functional groups, molecular structure, compositions, thermal and mechanical stabilities of the grown crystal were analysed. Finally, the nonlinear optical property was studied and the Second Harmonic Generation (SHG) efficiency of the grown material was found to be 1.20 times larger than that of KDP.

KEYWORDS: Optical material; Crystal growth; Nuclear Magnetic Resonance (NMR); Mechanical property

INTRODUCTION

The research field of nonlinear optics (NLO) investigates new materials which can be used to fabricate optical devices like optical modulators, optical data storage, and optical switching [1,2]. In recent years, various growth methods and apparatus designs have been continuously developed to improve the crystal quality and growth rate [3,4,5]. One of the obvious requirements for a nonlinear optical crystal is that it should have excellent optical quality with non-centrosymmetric space group. In the field of nonlinear optical crystal growth, amino acids play a vital role. Amino acids exhibit natural chiral properties and crystallize in non-centrosymmentric space group, which is an essential criterion for NLO applications. In addition, amino acids possess special features such as weak van der Waals and hydrogen bonds, and zwitterionic nature of the molecules. L-threonine is an extremely interesting and optically active amino acid in addition to its biological properties. It acts as a proton donor, proton acceptor and a nucleophilic reagent, and therefore, it shows higher SHG efficiency than other amino acids [6].

In this paper, we report growth and optimized growth condition and characterization of L-threonine succinate (LTS), a new nonlinear optical crystal, for the first time. LTS belongs to triclinic system and crystallizes in non-centrosymmetric space group 'P_1' with cell parameters a= 5.69 Å, b= 6.50 Å, c= 6.68 Å. In the present investigation, good quality and highly transparent single crystals of LTS have been grown from aqueous solution by slow evaporation technique. The grown crystals have been characterized using single crystal X-ray diffraction (XRD) analysis, SEM-EDAX analysis, UV-vis-NIR, Fourier Transform Infrared (FTIR) and FT-NMR spectral studies, thermal, microhardness and NLO studies.

SYNTHESIS AND GROWTH CONDITIONS

Synthesis

L-threonine (Merck-Germany) and succinic acid were taken with stoichiometric ratio 1:1 and dissolved in millipore water. The solution was constantly stirred using a magnetic stirrer for homogenization and then filtered using a whatmann filter paper. Usually, fungi and microorganisms attack amino acid solution. To avoid this problem and keep the crystals growing without any problem sodium azide was added to the amino acid solution. The solution was allowed to evaporate gradually which led to supersaturation for the formation of tiny crystal nuclei. Transparent, colourless LTS single crystals were harvested within a period of 18 days. Fig.1 shows the photograph of the as-grown LTS crystal with dimensions of 24 × 6 × 4 mm^3.

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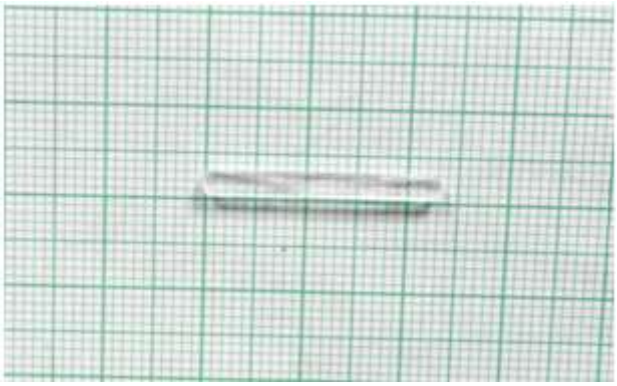

Fig.1.Photograph of the as-grown LTS single crystal

Growth condition

The growth condition was optimized using the critical supersaturation in order to improve the quality of the crystal. The nucleation rate, based on Arrhenius type of reaction, is given as

$$J = Aexp\left[\frac{-\Delta G^*}{kT}\right] \quad (1)$$

where A is the pre-exponential factor, ΔG* is the critical free energy change for the formation of critical nucleus, k is the Boltzmann constant and T is the constant temperature of the solution.

$$lnJ = lnA - \frac{\Delta G^*}{kT} \quad (2)$$

When J=1, the nucleation rate is reasonable to control the evaporation rate.

Hence $lnA = \frac{\Delta G*}{kT}$ (3)

But $\Delta G^* = \frac{16\pi\sigma_0^3}{3\Delta G_v^2}$ (4)

$$\therefore lnA = \frac{16\pi\sigma_\circ^3}{3kT\Delta G_v^2} \quad (5)$$

where $\Delta G_v = -\frac{kT}{v} lnS_c$ (6)

σ_0 is the surface energy per unit area, v is the specific volume and S_c is the critical supersaturation.

$$\therefore lnA = \frac{16\pi v^2\sigma_0^3}{3k^3T^3\,(lnS_c\,)^2} \quad (7)$$

$$\ln(S_c)^2 = \frac{16\pi v^2\sigma_0^3}{3lnAk^3T^3} \quad (8)$$

From the equation (8), the critical supersaturation was computed as 1.376. This is the maximum limit of supersaturation of the solution at a particular temperature. If the supersaturation is just within the critical supersaturation, the evaporation rate is controlled and thereby the nucleation rate is controlled in order to obtain good quality crystal with more transparency. The supersaturation at the time of harvesting the crystal was measured and it was found to be 1.30 which is below the predicted critical supersaturation value 1.376.

RESULTS AND DISCUSSION

Single crystal XRD Analysis

Single crystal X-ray diffraction analysis for the grown crystal has been carried out to identify the lattice parameters using an ENRAF NONIUS CAD4 automatic X-ray diffractometer. The lattice parameters of the grown crystal were found to be a = 5.69Å, b = 6.50 Å, c = 6.68 Å and volume V = 247 Å^3. From the XRD data it is observed that the grown crystal LTS belongs to triclinic system with the space group P_1.

SEM and EDAX Analysis

Figs. 2(a) and (b) show the recorded SEM images of LTS crystal with resolution 2µm and 10µm respectively. Both the Figs. 2(a) and (b) show layers of atoms of different sizes. It is observed from Fig.2a that the crystal surface contains traces of few lines showing some interstitial sites. With higher magnification (10µm), Fig.2b shows atoms of

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different radii with more clarity. Hence it is concluded that the grown crystal is more transparent containing different components.

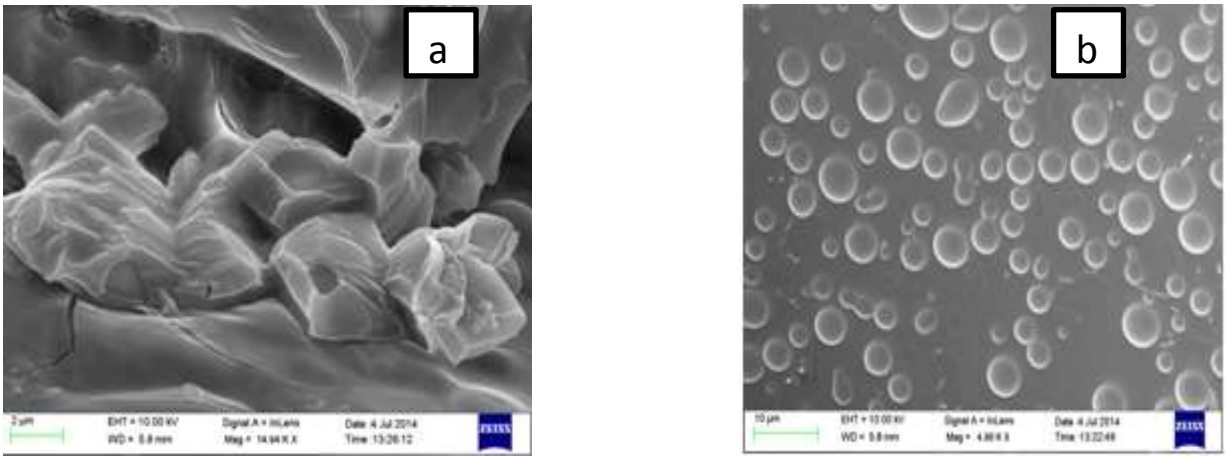

Fig.2.SEM micrograph of LTS crystal

Fig.3 shows EDAX spectra of LTS crystal which confirm the presence of various elements present in the grown crystal. Table 1 presents the compositional analysis of the elements Carbon, Nitrogen and Oxygen present in various proportions in the grown crystal.

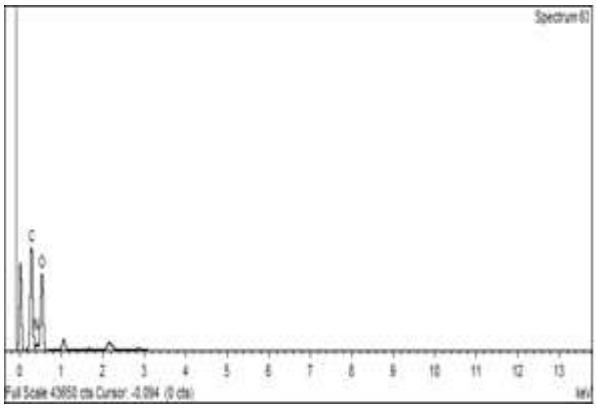

Fig.3. EDAX analysis of LTS crystal

Table 1Compositional analysis of LTS crystal from EDAX spectra

Element	Weight%	Atomic%
C K	38.4	44.75
N K	10.83	10.83
O K	50.77	44.42
Totals	100	100

UV- vis - NIR Spectral Study

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The optical properties of materials are important as they provide information about the transmission range, optical band gap and the dielectric nature of the grown material. The desired lower cut off wavelength in the transmittance analysis should be between 200 and 400nm for effective application of the NLO materials for Second Harmonic Generation [7]. The UV-vis-NIR spectrum(Fig.4) was recorded with the help of Perkin-Elmer Lambda 35 spectrometer for the LTS single crystal of 1mm thickness in the range of 200-1400nm. The material shows the transparent nature from 240nm onwards extending beyond 1400nm, the lower cut off wavelength being 240nm. It is observed that the crystal has wide transmission range covering the UV, visible and NIR region which is suitable range for Second Harmonic Generation SHG).

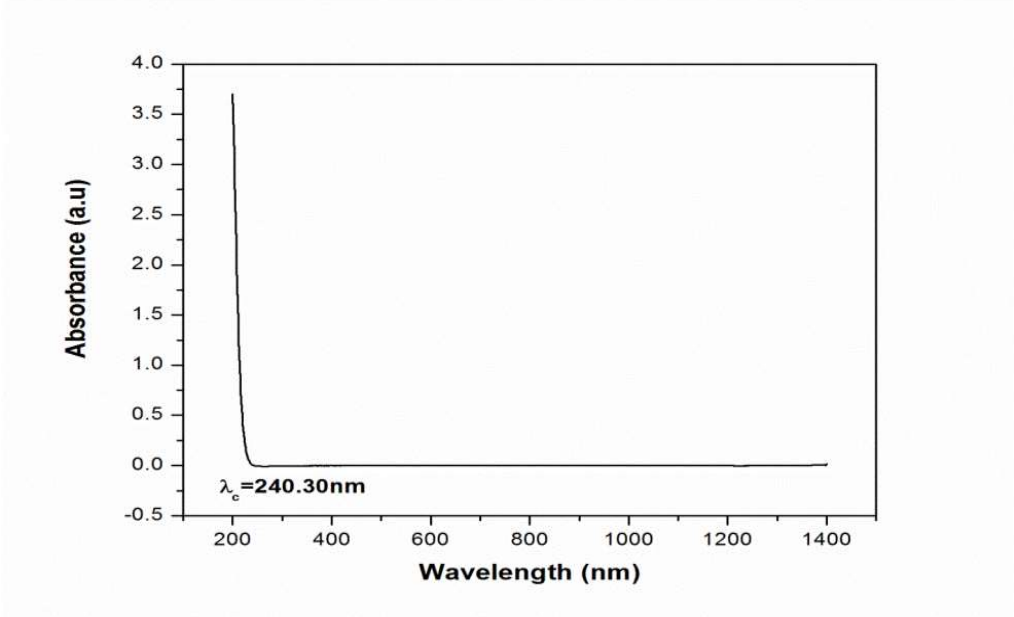

Fig.4.UV-vis-NIR absorption spectrum of LTS crystal

The optical band gap of the material has been estimated using the Tauc's [8] relation given by

$$\alpha = \frac{(h\nu - E_g)^{1/2}}{h\nu} \qquad (9)$$

where α is the absorption coefficient, hν is the photon energy (eV). The optical band gap was calculated from the plot of $(\alpha h\nu)^2$ versus hν as shown in Fig. 5. The calculated optical band gap of LTS crystal was found to be 5.88eV. From the larger value of optical band gap, it is concluded that LTS is a dielectric material suitable for inducing polarization when an intense radiation is incident on the material. Therefore, the material can be used for fabricating NLO devices.

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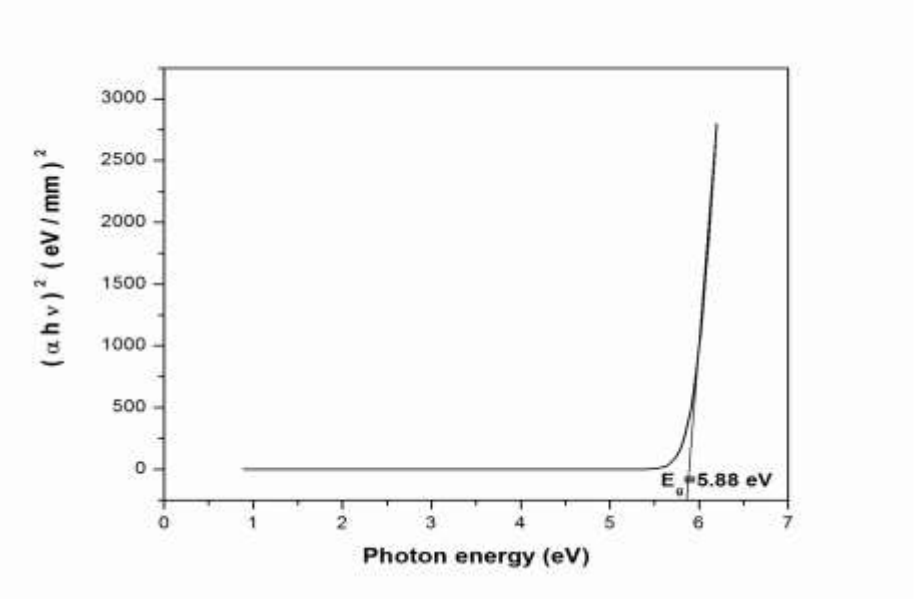

Fig.5.Plot of (αhv)2 versus photon energy for LTS crystal

Fourier Transform Infrared (FTIR) Analysis

FTIR spectrum of LTS crystal recorded in the region 400-4000cm^{-1} is shown in Fig.6. The broad absorption peak at 3168cm^{-1} with medium intensity has been assigned due to NH_3 asymmetric stretching vibration. The medium absorption peak at 2711cm^{-1} and weak absorption peak at 2049cm^{-1} are due to NH_3^+symmetric stretching vibration. The asymmetric stretching of $COO^-$is positioned at 1626 cm^{-1}.The peak observed at 2515cm^{-1} indicates the CH stretching vibration.

The asymmetric bending of NH_3 has been observed corresponding to the peak at 1479cm^{-1} .The peak at 1318cm^{-1}shows bending vibration of CH group. The two peaks observed at 1184cm^{-1} and 1110cm^{-1} are attributed to rocking mode of NH_3. The existence of stretching vibration involving carbon and nitrogen of the amino group is confirmed due to absorption at 1040cm^{-1}.The peaks observed at 908cm^{-1}corresponds to O-H out of the plane. The bending of CO_2^- is observed at 768cm^{-1} .The peaks at 701cm^{-1} can be assigned to the in plane deformation of CO_2 . The C-C-N deformation vibration is assigned due to the peak at 560cm^{-1}.The peak at 490cm^{-1}is associated with the torsional mode of NH_3. The presence of carboxyl group COO^- and NH_3^+ is thus confirmed from the FTIR spectral analysis [9].Based on the available data of vibrational frequencies of the characteristics of amino acids, the various functional groups of the grown compound (LTS) have been identified.

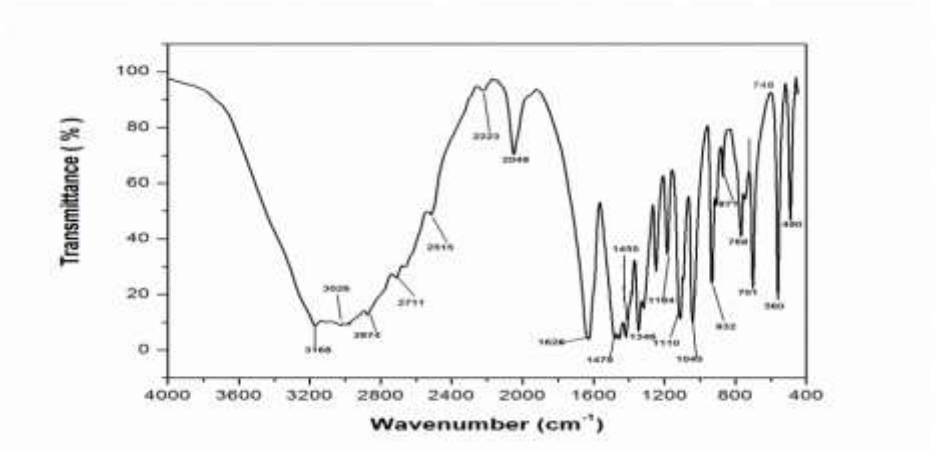

Fig.6.FTIR spectrum of LTS crystal

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FT-NMR Spectral Studies

The ^{1}H NMR and ^{13}C NMR spectral studies are very important to analyse the molecular structure of the grown compound LTS. Fig.7 shows the recorded ^{1}H NMR spectrum of LTS crystal. From the observed spectrum, the peaks corresponding to δ = 1.238ppm and δ = 1.252ppm are attributed to C-H protons present in the crystal. The signals observed at δ = 3.498ppm and δ = 3.508ppm are due to the presence of OH protons in the nearby region of $CHNH_2$ and C=O respectively. The peaks in the region of δ = 4.147ppm to δ = 4.197ppm are due to the protons associated with CH_2 group. The presence of various types of protons gives rise to dipolar characteristic of the grown crystal.

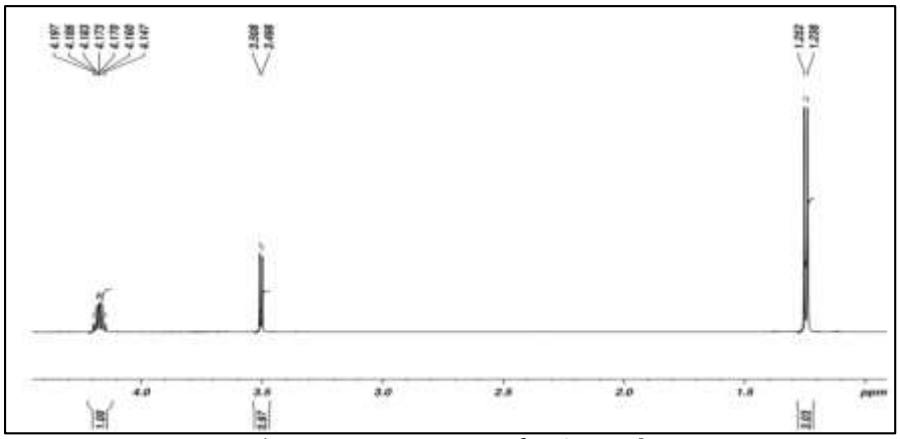

Fig.7. 1H NMR spectrum of LTS crystal

From Fig.8 the ^{13}C NMR spectrum of LTS crystal reveals four signals with respect to four carbon atoms of different chemical environments. From the spectrum, the peak at δ = 19.420ppm is due to the presence of $CH\text{-}NH_2$ group, and the peaks corresponding to δ = 60.411ppm and δ = 65.871ppm are due to the presence of CH_2 environmental carbons in amino acid. The signal observed at δ = 172.760ppm is due to CO group. From the ^{1}H NMR and ^{13}C NMR spectra, we are able to present the molecular structure of the grown compound.

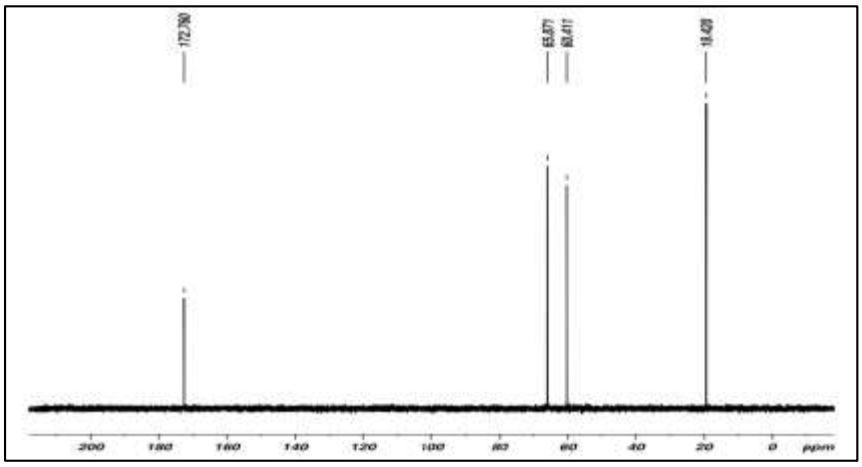

Fig.8. 13C NMR spectrum of LTS crystal

Thermal Analysis

The thermal behaviour of LTS has been analysed using the thermo gravimetric (TG) and differential thermogram (DT) analyses (Fig.9) in the temperature range of 0 - 500℃. From the thermal analysis, it is inferred that there is no weight loss below 235℃ and beyond this temperature there is a sudden weight loss

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due to decomposition of the compound. The decomposition is almost completed at 270℃.
In the DTA curve (Fig.9) an endotherm at 245℃ and an exotherm at 270℃ are observed. These peaks confirm the major decomposition of the compound between 235℃ and 270℃ as predicted by TGA curve. Therefore, it is established that this material can withstand the localized thermal stresses up to 235℃.

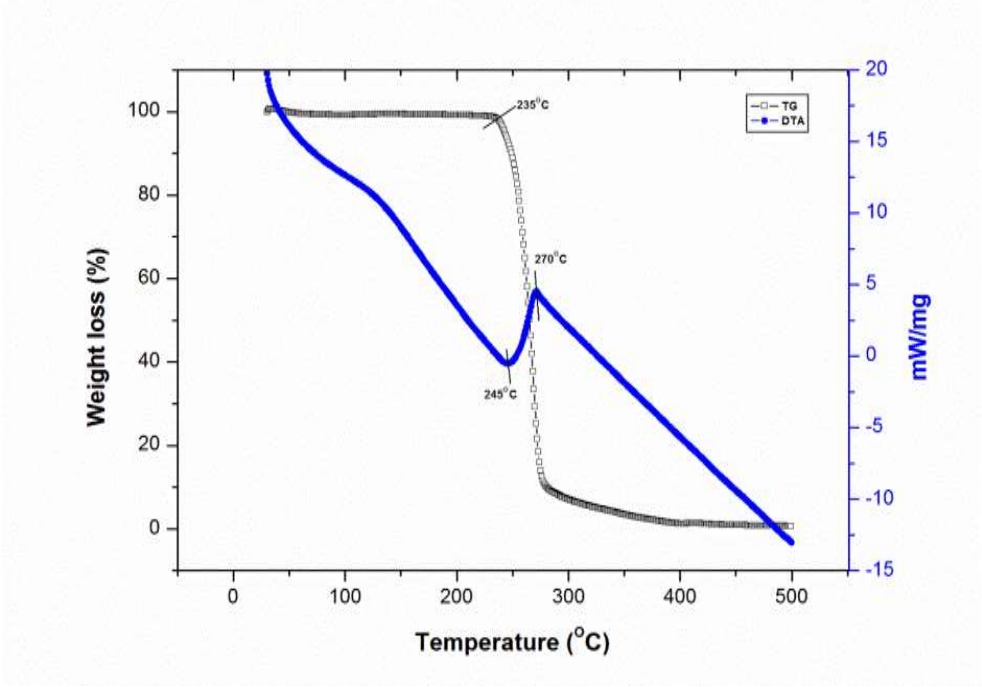

Fig.9.TGA and DTA curves of LTS crystal

Fig.10 shows the DSC trace of the grown crystal. The peak observed at 274℃ clearly confirms the completion process of the decomposition of the compound as predicted by TGA and DTA curves. Hence, it is understood that the grown material has higher thermal stability up to 235℃.

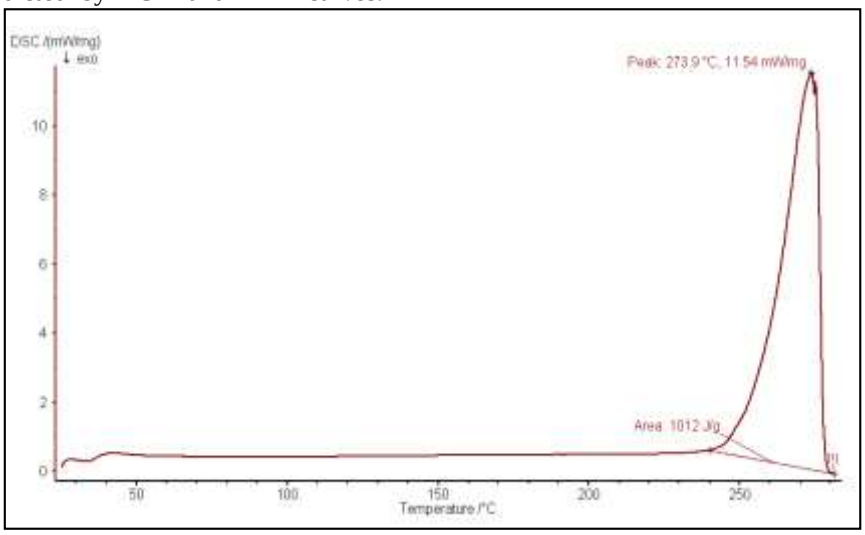

Fig.10.DSC curve of LTS crystal

Microhardness Measurement

Microhardness is the inherent property of the crystal to resist indentation. It is an important mechanical property required for the fabrication of electronic and optical devices. It is a measure of its resistance to local deformation [10]. The microhardness studies have

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been carried out on [111] plane of the grown LTS single crystal using the microhardness tester fitted with a Vickers diamond pyramid indenter. The mean diagonal length was estimated for various loads.
The Vickers hardness number was calculated using the below expression [11].

$$H_v = 1.8544(P/d^2)\ Kg/mm^2 \quad (10)$$

where P is the applied load in Kg and d is the average diagonal length of the indentation mark in mm. Fig.11shows the plot of hardness number against load.

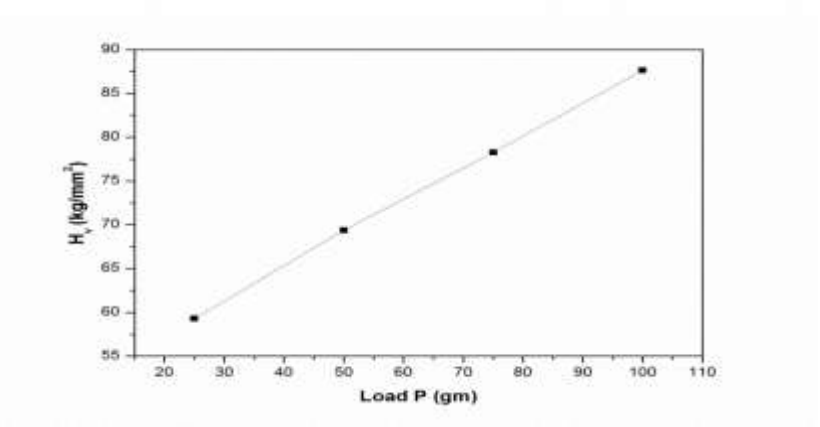

Fig.11.Plot of hardness number versus Load P for LTS crystal

From the graph, it is observed that the hardness value increases from 25-100g.The increase in the hardness number can be attributed to the electrostatic attraction between the zwitterions present in the molecule. This behaviour favours the material to have good mechanical strength. Therefore the grown crystal is found to possess sufficient mechanical strength to resist the internal stress developed when the material is used in devices

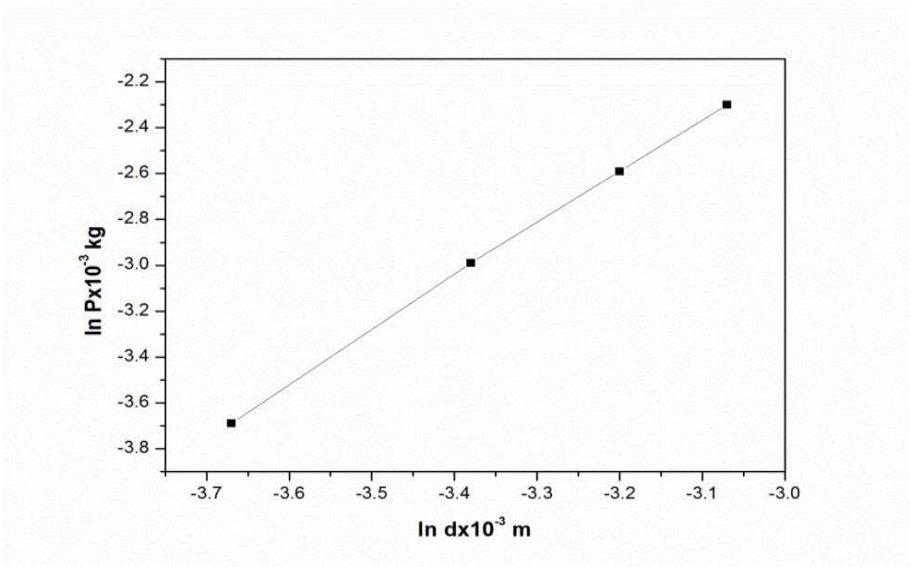

Fig.12.Plot of ln P versus ln d of LTS crystal

A plot of ln P against ln d for LTS crystal is shown in Fig.12.The slope of the straight line of the plot gives the work hardening coefficient (n). The work hardening coefficient (n) for LTS crystal is found to be 2.23.It is known that if n lies between 1 and 1.6, the material is soft one and if n is more than 1.6, the material is hard one.

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Moreover, according to Onitsch [12], if n is greater than 1.6, the microhardness number will increase with increase in load. From the experimental observations recorded for a particular plane of the grown crystal, it is concluded that the material is having sufficient mechanical strength due to higher value of n.

NLO Studies

The SHG efficiency of LTS was measured by Kurtz and Perry powder technique [13].The crystal was ground into fine powder and the powder was placed in a quartz cell. A fundamental wave with a pulse width of 9ns, and beam diameter of 1mm at repetition frequency of 10 Hz from Nd-YAG laser source was allowed to focus on the sample. As the wavelength of incident beam is 1064nm, emission of green light at 532nm appeared from the sample confirms the NLO behaviour of the LTS crystal. The NLO efficiency was measured as 1.20 times higher than that of KDP. Hence the grown material is one of the promising NLO materials to find wide applications in the fields of optoelectronics and photonics.

CONCLUSION

L-threonine succinate is one of the excellent nonlinear optical materials with more SHG efficiency. The crystal was grown successfully using the stabilized condition under slow evaporation method at isothermal condition. From XRD data, it is confirmed that the crystal belongs to triclinic system with non-centrosymmetric space group P1. The microstructure and compositions of the material were analysed using SEM-EDAX studies. The material shows wide transparent nature with optical band gap 5.88eV which confirms dielectric characteristic of the crystal. The functional groups identified from FTIR spectral study ascertains the amino acid characteristic of the material. The molecular structure of the grown crystal is established from the NMR spectral study. The thermal stability of the material is found to be sufficiently larger to withstand the localized thermal stresses. From the microhardness studies, it is established that the grown crystal is having sufficient mechanical strength. Finally, the material has been tested for NLO behaviour to confirm Second Harmonic Generation (SHG) in the material. The material is found to possess SHG efficiency 1.20 times higher than that of KDP. Hence, the new grown material LTS can be used in the optoelectronic and photonic devices with more efficiency.

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