Available online at www.scholarsresearchlibrary.com

Scholars Research Library

Archives of Physics Research, 2013, 4 (2):14-21
(http://scholarsresearchlibrary.com/archive.html)

Archives of Physics Research
Scholars Research Library
ISSN : 0976-0970
CODEN (USA): APRRC7

A study on optical, thermal, mechanical properties and particle size determination of non-linear optical L-threonine single crystals

D. Subashini[a], A. R. Prabhakaran[b], S. Nalini Jayanthi[c] and K. Thamizharasan[d]

[a]Department of Physics, Dr. Ambedkar Govt. Arts College, Chennai, India
[b]Department of Physics, Pachaiyappa's College, Chennai, India
[c]Department of Physics, AIHT, Kazhipattur, Chennai, India
[d]Department of Physics, Sir Theagaraya College, Chennai, India

---

ABSTRACT

L- threonine single crystals were grown successfully by slow-evaporation technique. To identify the morphology and structure , the as grown crystals were subjected to characterization like powder and single XRD analysis. UV-Vis-NIR spectrum and second harmonic generation were investigated to study the linear and nonlinear optical properties. In order to ascertain the thermal stability of the crystal, thermo-gravimetric analysis (TGA) , differential thermo-gravimetric analysis (DTA) and differential scanning calorimetry (DSC) were also carried out. The second harmonic generation conversion efficiency of the grown crystal shows the suitability for frequency conversion applications. The mechanical behaviour has been assessed by Vickers microhardness measurements. Structural parameters of the as grown crystals were also calculated.

INTRODUCTION

Non-linear optical materials has wide application in various fields like optical data storage, photorefractive crystals, frequency multipliers, fiber optics, optical switches etc. Nonlinear optics has been a rapidly growing field in recent decades. It is based on the study of effects and phenomena related to the interaction of intense coherent light radiation with matter. For the last several years, scientists working on non-linear optical (NLO) materials are making an intense search for new NLO materials which combine the high optical non-linearity and chemical flexibility of organics with the high mechanical strength of inorganics [1-3]. L-thr crystallizes with four zwitterionic molecules per unit cell [4] linked by a three dimensional network of N-H…O and O-H…) bonds. L-thr is one of the essential amino acid bearing an alcohol group. Also, optically active amino acids contain many highly efficient optical second-harmonic generators and are promising candidates for a great number of applications . By the physical point of view the L- threonine investigation is relevant both owing to the possibility to observe the behavior of a system where the hydrogen bond plays a fundamental role [5-6] and the technological importance of a material which shows a second-harmonic conversion efficiency greater than 1 relative to potassium dihydrogen phosphate [1]. Efforts are taken to study the growth and characterization of L-thr single crystals.

MATERIALS AND METHODS

SYNTHESIS AND CRYSTAL GROWTH

L-thr was synthesized by dissolving in deionised double distilled water. Recrystallization is one of the best method to improve the purity of the crystal. In the present study commercially available L-threonine was dissolved in water and by repeated recrystallisation process the material was used to prepare the saturated solution. The resulting solution was filtered and allowed to evaporate under optimized condition. Thus an optically good quality transparent crystals with dimensions 2 x 2 x 21mm^3 was harvested after a period of 30 days. The photograph of as grown crystal is shown in **figure 1.**

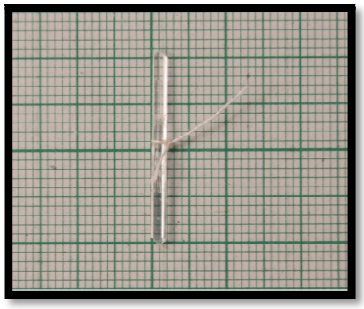

Figure 1. Photograph of as grown crystal of L-thr

RESULTS AND DISCUSSION

POWDER AND SINGLE CRYSTAL XRD STUDIES

The grown crystals were crushed into fine powder and subjected to **X-ray diffractometer** with CuK_α (1.5405Å) radiation . The sample was scanned for a 2θ range from 10° to 70° at a scan rate of 1°/min. **Figure 2.** shows the powder XRD pattern of L-thr single crystals.

In order to confirm the crystallinity and also to find the lattice parameters of the grown crystals single crystal X-ray diffraction analysis was carried out using **Enraf Nonius Cad 4-F** single crystal X-ray diffractometer with MoK_α (λ=0.71073 Å) radiation. The single crystal data are tabulated in table 1.

Table 1. Crystal data of L-thr crystal

Lattice parameters	L-threonine
a(Å)	5.139
b(Å)	7.723
c(Å)	13.579
α°	90
β°	90
γ°	90
crystal system	orthorhombic
cell volume	538.9Å^3

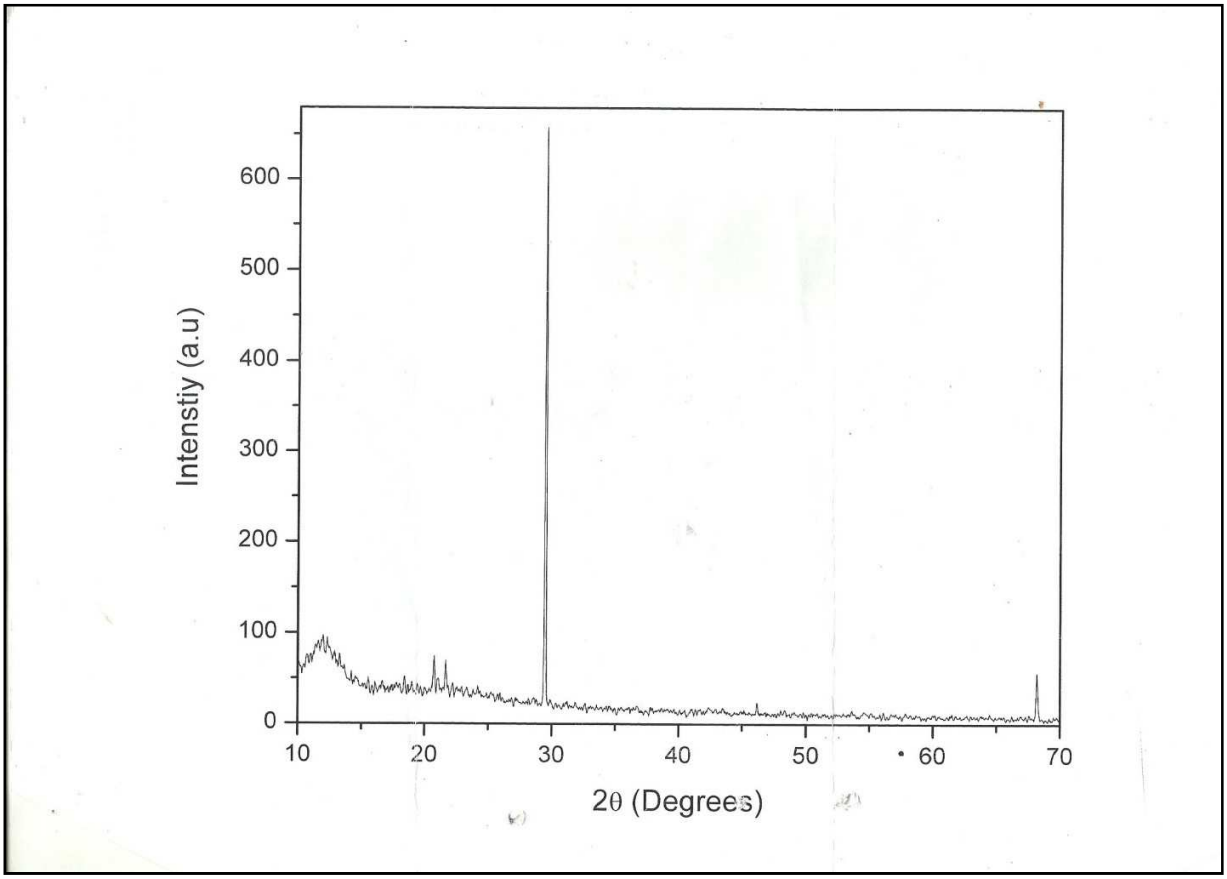

Figure 2. Powder XRD pattern of L-thr crystal

OPTICAL STUDIES

The UV-Vis-NIR spectrum was recorded in the wavelength range 100 to 1000n m using **Varian Cary 5E** model dual beam spectrometer. The spectrum of as grown crystals of L-thr was shown in **figure 3**. Using the formula $E_g = hc/\lambda$, the energy band gap was found to be 4.96 eV.

There are three types of electronic transitions,
a) Transition involving π, σ and n electrons
b) Transition involving charge-transfer electrons
c) Transition involving d,f electrons

The lower cut-off wavelength of the crystal observed around 250nm is due to the $\pi \rightarrow \pi^*$ transition in this material. Also lower cut-off is a desirous property for NLO applications [8]. Most absorption spectroscopy of organic compounds is based on transitions of n or π electrons to the π^* excited state. This is because the absorption peaks for these transitions fall in an experimentally convenient region of the spectrum (200-700nm).

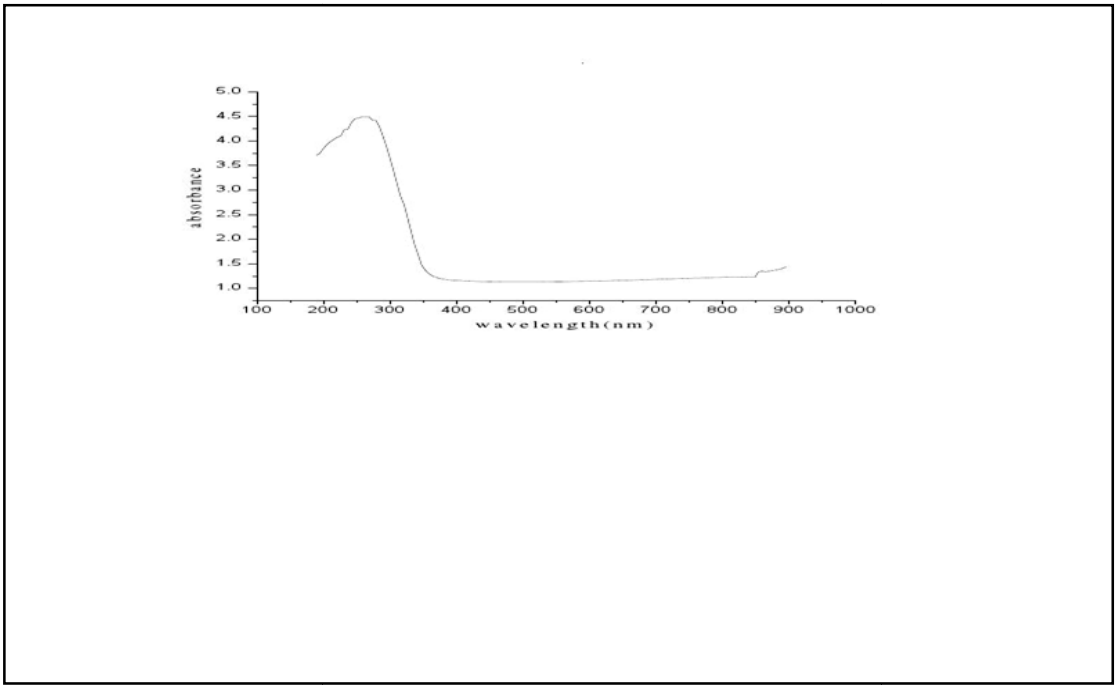

Figure 3. UV-VIS-NIR spectrum of L-thr crystal

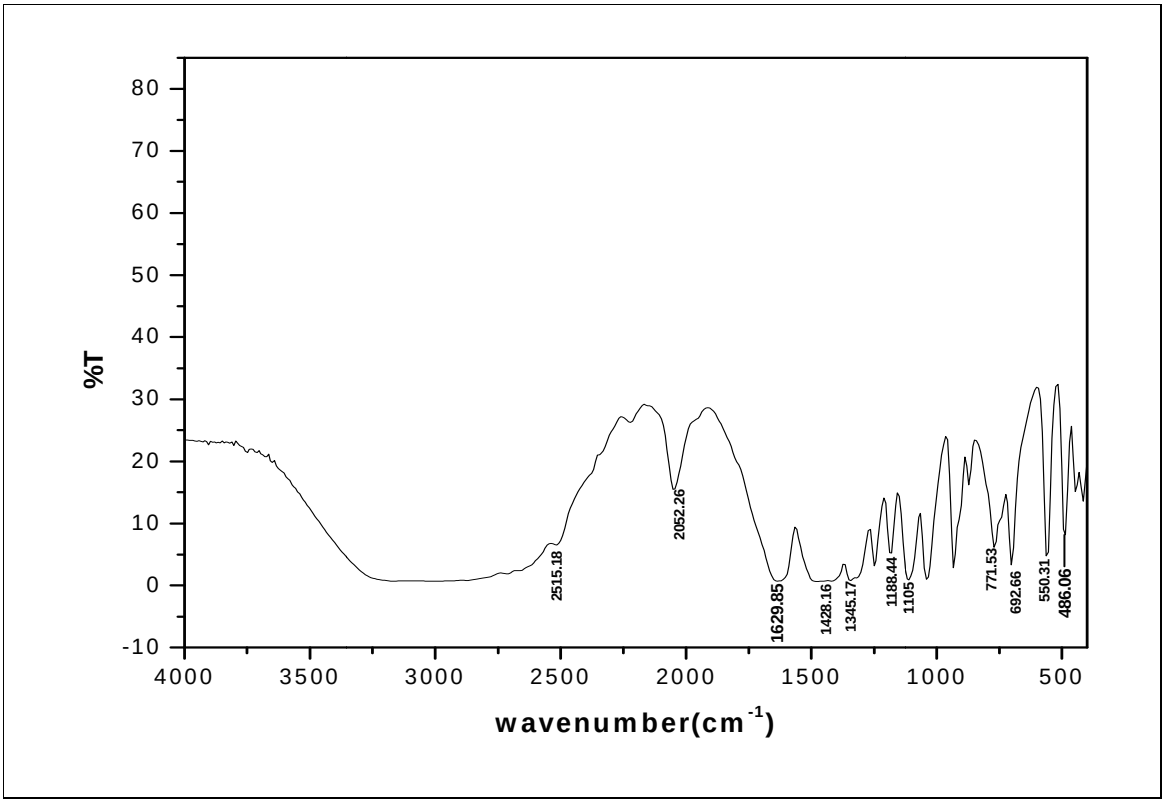

Figure 4. FT-IR spectrum of L-thr crystal

VIBRATIONAL BAND ANALYSIS

To quantitatively analyse the presence of functional groups in L-Thr, FT-IR spectrum of as grown crystals were recorded in the range 400-4000cm^{-1} using **Schimadzu FT-IR spectrometer**. The spectrum of as grown crystals are shown in **figure 4.** The band observed at 486.06 cm^{-1} is assigned to torsional mode of NH_3. The rocking of CO_2^- is assigned to the band observed at 563.21 cm^{-1}. The bending of CO_2^- is observed around 771.53 cm^{-1}. The sharp band at 871.82 cm^{-1} is related to stretching of CCN structure. The rocking of NH_3 structure is observed at wave numbers 1111 cm^{-1} and 1180.44 cm^{-1}. Bending vibrations of CH group was found in L-Thr with peak at 1342.46 cm^{-1}. The symmetric stretching of CO_2^- is observed at 1419.61 cm^{-1} in the IR spectrum [9].

THERMAL ANALYSIS

TG/DTA

The TG/DTA traces of L-thr were obtained by subjecting the crystal in nitrogen atmosphere at a heating rate of 10K/min using **NETZSCH STA 409°C/CD** instrument. **Figure 5**. shows the TG/DTA traces of L-thr single crystal. In thermogravimetric analysis(TGA) a sharp weight loss starts around 230 °C [10]. The endothermic peaks of the differential thermogravimetric (DT) trace coincide with the decomposition in the TGA trace. The sharpness of the endothermic peak shows good degree of crystallinity of the as grown crystal.

DIFFERENTIAL SCANNING CALORIMETRY(DSC)

Thermal techniques are the means to study the physical and chemical changes. DSC analysis was carried out using **NETZSCH DSC 204** and it is shown in **figure 6**. It was used to identify the purity and melting point of the as grown crystal. In the thermogram only one endothermic stage was found. The initial temperature of the endothermic peak was around 245°C and heat of transition was 995.5J/g. This thermogram indicates that L-thr melted completely at 281.9°C[11].

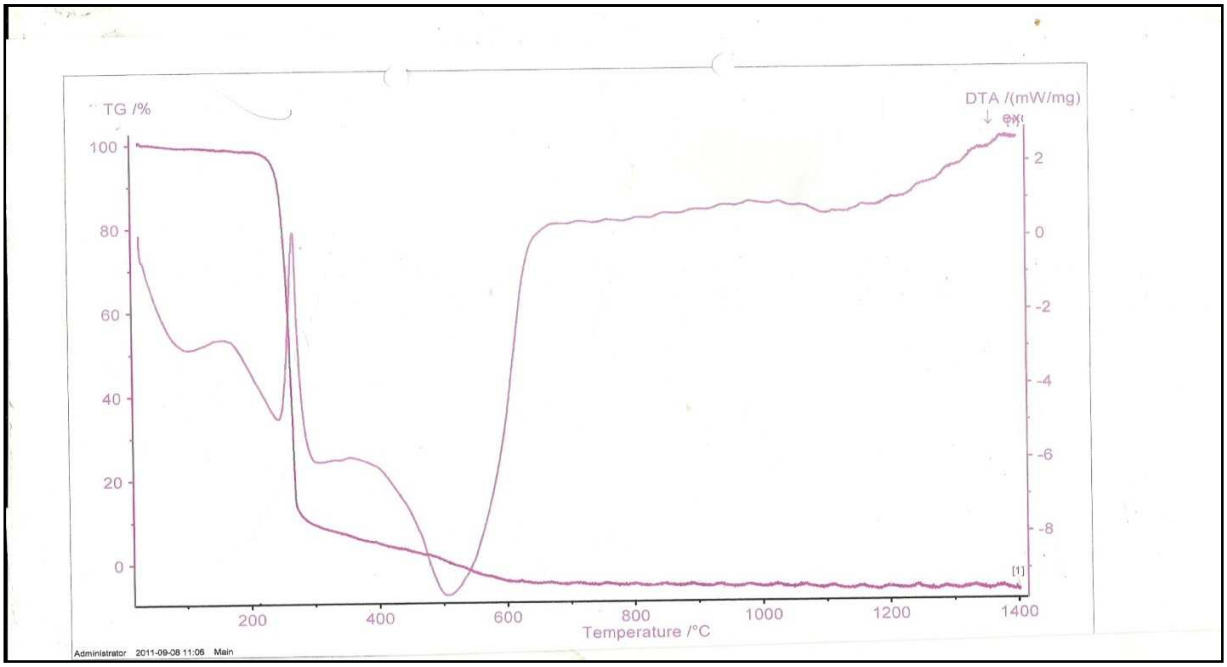

Figure 5. TG/DTA traces of L-thr single crystal

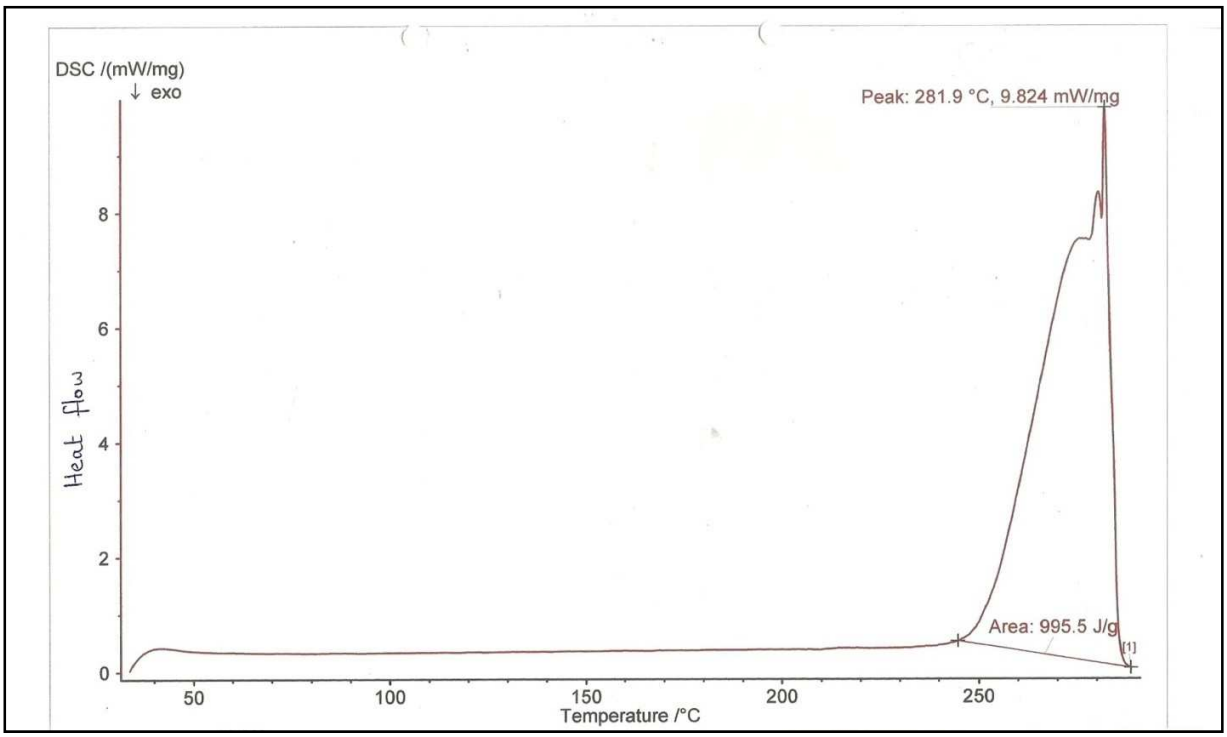

Figure 6. DSC trace of L-thr single crystal

SECOND HARMONIC GENERATION EFFICIENCY

Kurtz and Perry technique was extremely useful for the initial testing of materials for second harmonic generation[12]. The fundamental beam of wavelength 1064nm, from a Q-switched mode locked Nd:YAG laser was used to test the SHG property of the as grown crystals of L-thr with an input power of 0.68J. The emission of green radiation from the crystal confirmed the second harmonic signal generation in the crystal. The output power of the sample was 3.72J.

MECHANICAL PROPERTIES

There are different types of hardness tests available viz., static indentation test, dynamic indentation test, scratch test, rebound test, pendulum recoil test, in which Vicker's Microhardness test has been used for the present study. The mechanical property of the grown crystals has been studied using a LEITZ microhardness tester fitted with a Vickers diamond pyramidal indenter. A well-polished L-thr crystal was placed on the platform of Vickers microhardness tester and the loads of different magnitudes were applied over a fixed interval of time. The indentation time was kept (5s) for all the loads. The hardness number was calculated using the relation, **$Hv= 1.8544 \times P/d^2$ Kg/mm^2**

Where Hv is the Vickers microhardness number, P is the applied load in kg and d is the diagonal length of the indentation impression in the micrometer. A plot of hardness number (Hv) and applied load (P) is shown in **figure 7**. The hardness decreased gradually with the increase of load and above 50 g cracks developed on the smooth surface of the crystal due to the release of internal stresses generated locally by indentation[13]. Hence it may be suggested that the material may be used for the device fabrication below the applied load of 50g.

PARTICLE SIZE, DISLOCATION DENSITY AND STRAIN VALUES

Crystallite size analysis is used for quality control and to study the effects of processing on grain growth. Micro strain is the degree to which crystallite are deformed relative to unstrained material. Particle size (D), dislocation density (δ) and strain values (ε) for corresponding full width half maximum (FWHM) were calculated and listed in **Table 2.**

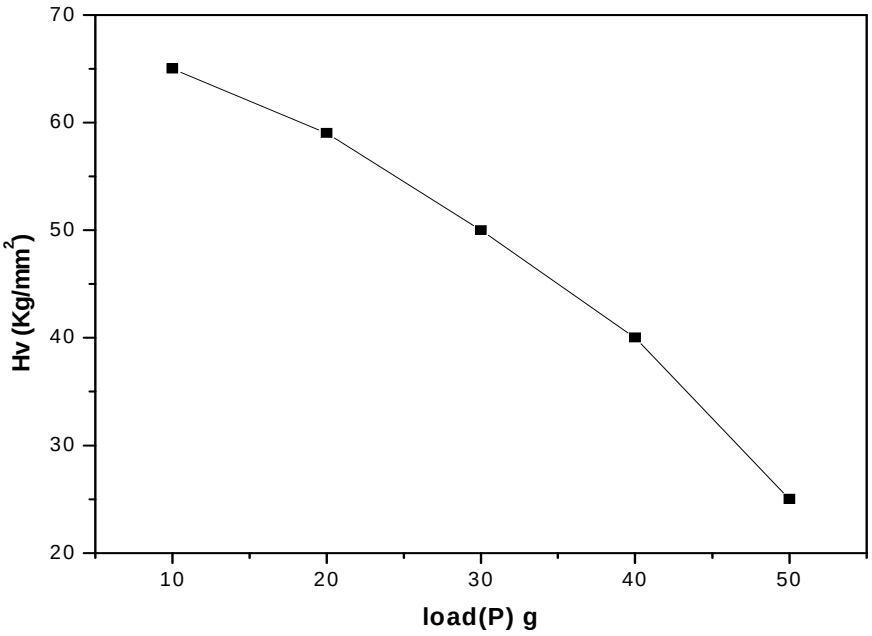

Figure 7. Variation of hardness with applied load

Table 2. Structural Parameters of L- Thr

FWHM deg	Particle size(D) nm	Dislocation density(δ) Kg/m^3	Strain(ε) lin^{-2}m^{-4}
0.12	1.2229	6.6871	0.0296
0.08	1.8422	2.9466	0.0196

It has been found that the crystalline size values increases which may be due to decrease in strain values. The decrease in the dislocation density indicates the formation of high quality crystals. The increase in particle size directly shows the decrease in dislocation density which is more appreciable.

The structural parameters has been reported for the first time.

CONCLUSION

L-threonine single crystals were grown by slow evaporation technique. Powder and single XRD confirms the structure of the crystal and the cell parameters are determined. FT-IR analysis confirms the presence of functional groups present in the crystal. The optical transmittance of the crystal was found to be around 250nm. TG/DTA confirms the stability of the crystal and also its suitability in the field of laser applications. DSC thermogram confirms the stability of the crystal. SHG efficiency shows that the crystal has a higher efficiency than KDP. Microhardness study estimates the mechanical strength of the crystal. Quality control analysis was also made.

REFERENCES

[1] K. E. Reickhoff, W. L. Peticolas, *Science* 147, 610 (**1965**).
[2] D. P. Shoemaker, J. Donohye, V. Shoemaker and R. B. Corey, *J. Am. Chem. Soc*. 72, 2328 (**1950**).
[3] A. Lautié and A. Novak, *Chem. Phys. Letters* 71, 290 (**1980**).
[4] D P Shoemaker, J Donohye, V Shoemaker and R B Corey **1950** *J.Am.Chem.Soc*.72 2328.

[5] V. A. Savel'ev and N. D. Sokolov, *Chem. Phys. Letters* 34, 281 (**1975**).
[6] M. Falk, *J. Raman Spectrosc*. 21, 563 (**1990**).
[7] G.Ramesh Kumar, S.Gokul Raj, R.Mohan, R.Jayavel, *J. crystal growth*, vol.275, issues 1-2.
[8] M.Senthil Pandian, P.Ramasamy, *J. crystal growth*,312(**2010**) 413-419.
[9] B.L. Silva, P.T.C. Freire, F.E.A. Melo, I. Guedes, M.A. Araújo Silva, J. Mendes Filho, A.J.D. Moreno, Braz. J.Phys.Vol.28.n.1 Sao Paulo Mar (**1998**).
[10] G.Ramesh Kumar, S.Gokul Raj, *Advances in materials science and Engineering* (**2009**).
[11] G.Ramesh Kumar, S.Gokul Raj, R.Mohan, R.Jayavel, *J. crystal growth*, vol.275, issues 1-2.
[12] S.K.Kurtz, T.T.Perry, *J.Appl. Phy*.39 (**1968**) 3798.
[13] J. Mary Linet, S. Jerome Das, Physica B: *Condensed matter*, vol.405, issue 18.