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Spectral, thermal investigations and particle size determination of L-threonine single crystals

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ABSTRACT

Single crystals of L- threonine (L-thr) were grown successfully by slow-evaporation technique. The as grown crystals were subjected to various characterization like powder XRD, FT-IR recordings. The structure of the crystal was confirmed by single crystal X-ray diffraction analysis. The 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) were also carried out. The second harmonic generation conversion efficiency of the grown crystal shows the suitability for frequency conversion applications. Structural parameters were also calculated which has been reported for the first time.

INTRODUCTION

Amino acids are favorable materials for NLO applications as they contain a proton donor carboxyl acid (COOH) group and proton acceptor amine group [1] . 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 [2-4]. Among NLO materials, organic NLO materials are generally preferred to be more efficient than their inorganic counterparts due to their favorable nonlinear response [5]. Organic non-linear optical materials are often formed by weak Vanderwalls and hydrogen bonds and hence possess high degree of delocalization [6].

L-thr crystallizes with four zwitterionic molecules per unit cell 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 [7,8] and the technological importance of a material which shows a second-harmonic conversion efficiency greater than 1 relative to potassium dihydrogen phosphate . Efforts are taken to study the growth and characterization of L-thr single crystals.

MATERIALS AND METHODS

2.1. Synthesis and crystal growth

Analytical reagent grade L-thr was dissolved in deionised double distilled 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 a transparent crystal 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.**

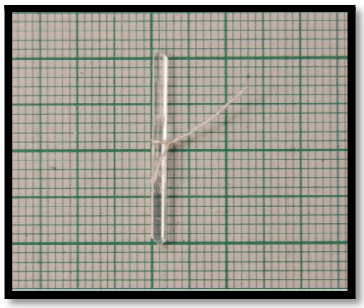

Figure 1. Photograph of as grown crystal of L-thr

RESULTS AND DISCUSSION

3.1. Powder and single X-ray diffraction studies

Using X-ray diffractometer with CuK$_\alpha$ (1.5405Å) radiation powder x-ray diffractometer studies of as grown crystals were carried out. The sample was scanned for 2θ values from 10° to 70°. **Figure 2.** shows the powder XRD pattern of L-thr single crystals. Single crystal X-ray diffraction analysis was carried out using Enraf Nonius Cad 4-F single crystal X-ray diffractometer with MoK$_\alpha$ (λ=0.71073 Å) radiation. The single crystal analysis data indicates that the crystal system belongs to orthorhombic and lattice parameters was found to be a=5.139 Å, b=7.723 Å, c=13.579 Å, α= β = γ= 90° and cell volume = 538.9 Å^3 [9] .

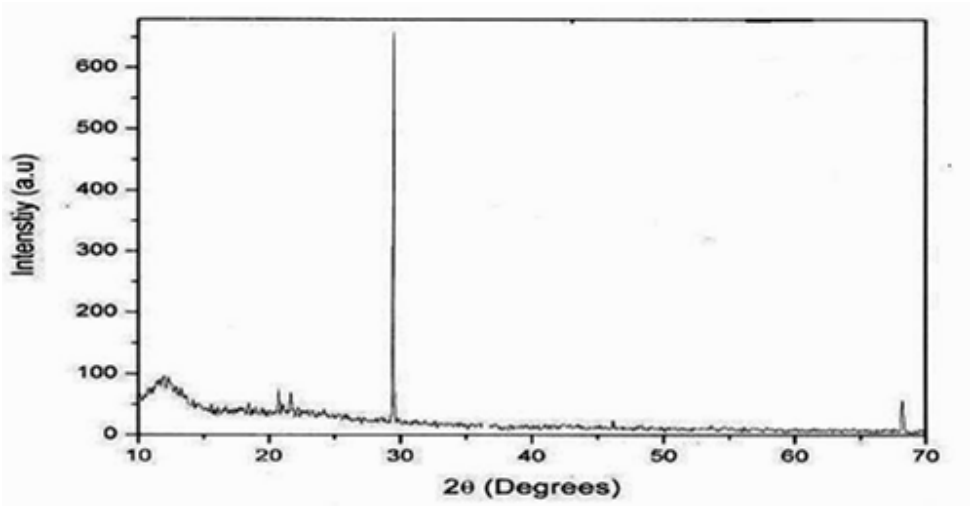

Figure 2. Powder XRD of L-thr crystal

3.2. UV-Vis-NIR

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

Electronic transitions:
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 [10]. 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).

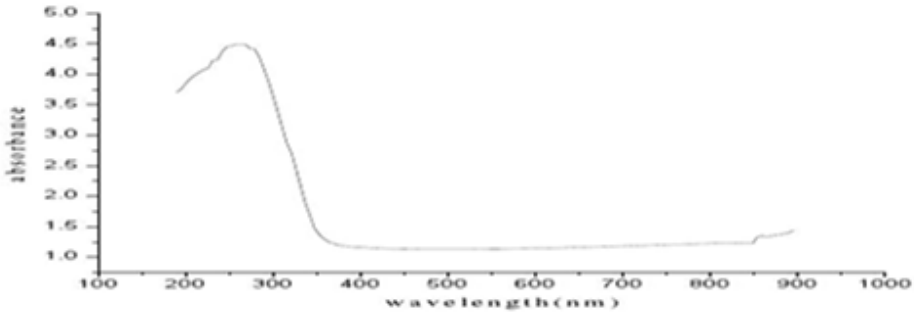

Figure 3. UV-VIS-NIR of L-thr crystal

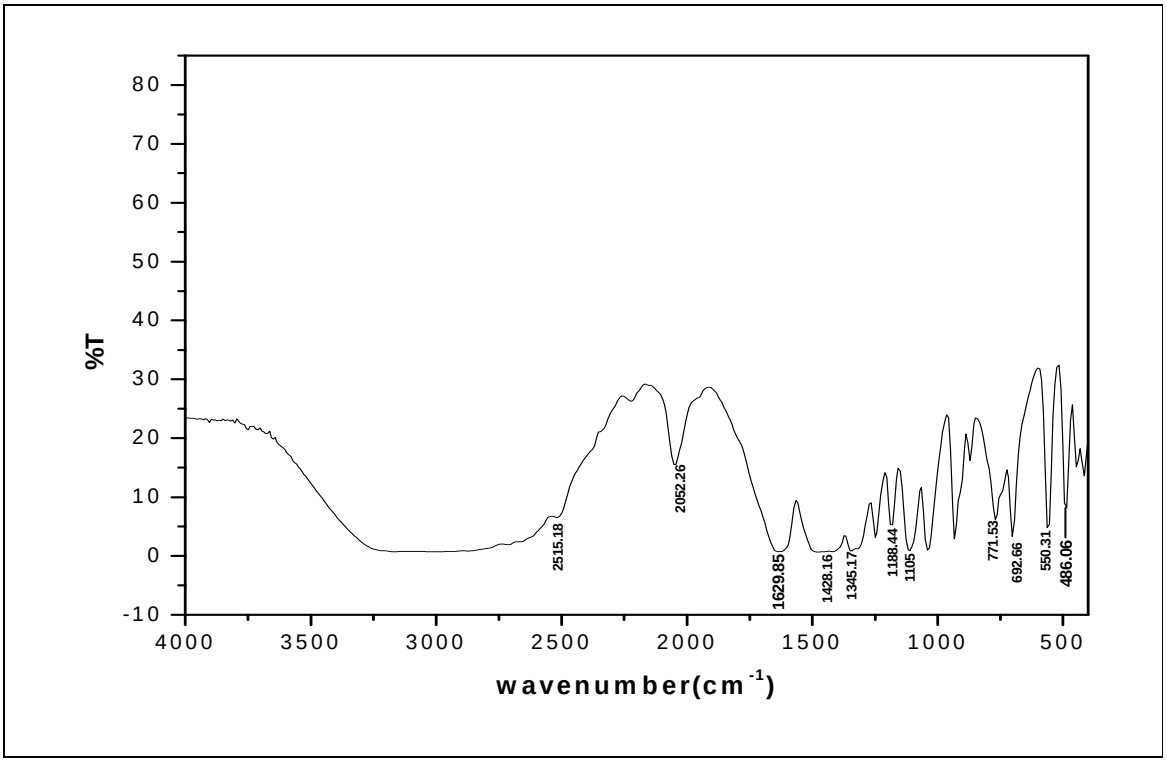

Figure 4. FT-IR spectrum of L-thr crystal

3.3. Vibrational band analysis

In order 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 [11].

3.4. TG/DTA analysis

Single crystal of L-thr were subjected to thermogravimetric analysis(TGA) and differential thermal analysis(DTA) simultaneously in nitrogen atmosphere at a heating rate of 10K/min using NETZSCH STA 409°C/CD instrument. **Figure 5.** shows the traces of L-thr crystal. In TG analysis a sharp weight loss starts around 230 °C [12]. The endothermic peaks of the DTA 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.

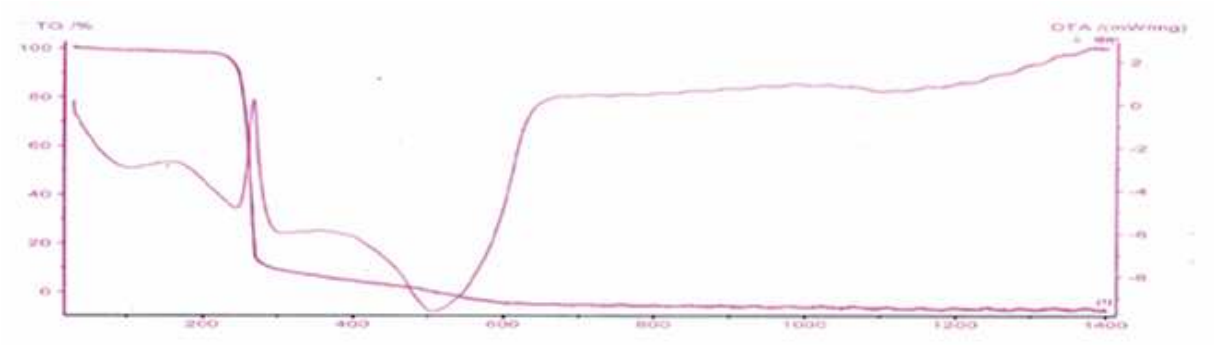

Figure 5. TG/DTA traces of L-thr crystal

4. Measurement of Second harmonic efficiency

The as grown crystals of L-thr was subjected to Kurtz second harmonic generation (SHG) test using Nd:YAG Q- switched laser beam for non-linear optical (NLO) property [13]. The sample was illuminated using using

Q-switched mode locked Nd:YAG laser (1064nm, Quanta series) Molectron power meter, USA with 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.

5. Particle size, dislocation density and strain values

The smallest diffracting domain in any specimen is called a crystallite. 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 1.**

Table 1. 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

Single crystals of L-threonine 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. SHG efficiency shows that the crystal has a higher efficiency than KDP. Quality control analysis was also made.

REFERENCES

[1] Yogam F, Vetha Pother I, Cyrac Peter A, Tamilselvan S, Leo Rajesh A, Vimalan M and Sagayaraj P, *Advances of Applied Science Research*, **2011**, 2(1):261-268.
[2] Reickhoff K. E, Peticolas W. L, *Science* **1965**, 610, 147.
[3] Shoemaker D.P, Donohye J, Shoemaker V and Corey R.B, *J Am Chem Soc* **1950**, 2328, 72 .
[4] Lautié A and Novak A, *Chem Phys Letters* **1980**, 290, 71.
[5] Ruby A and Alfred Cecil Raj S, *Advances of Applied Science Research*, **2012**, 3(3):1677-1685.
[6] Ramesh R, Aravinthraj M, Selvam M and Rajkumar D, *Advances of Applied Science Research*, **2011**, 2(5):136-142.
[7] Savel'ev V.A and Sokolov N.D, *Chem Phys Letters* **1975**, 281, 34.
[8] Falk M, *J Raman Spectrosc* **1990**, 563, 21.
[9] Ramesh Kumar G, GokulRaj S,Mohan R, Jayavel R, *J crystal growth*, **2005**, no.1-2, pp.e1947-e1951.
[10] Senthil Pandian M, Ramasamy P, *J crystal growth*, **2010**, pp.413-419.
[11] Silva B.L , Freire P.T.C, Melo F.E.A , Guedes I , Araújo Silva M.A, Mendes Filho J , Moreno A.J.D, *Braz. J. Phys*. **1998**,Vol.28, n.1.
[12] Ramesh Kumar G, Gokul Raj S, *Advances in materials science and Engineering* **2009**,2009.
[13] Kurtz S.K, Perry T.T, *J.Appl. Phy*. **1968**, 3798, 39.