Growth, Optical, Thermal and Mechanical Studies of Picric Acid Doped L-Threonine Single Crystals

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Abstract - *L-threonine and picric acid are organic compounds with nonlinear optical property. They were mixed in 1:0.2 molar ratio and single crystals were grown by slow evaporation solution growth technique. The powder XRD studies showed the crystallinity of the sample. From the uv-vis spectral analysis the wide transparency window and large band gap energy (5eV) of picric acid doped L-threonine were observed. TG-DTA studies and micro hardness studies indicated that the doped sample were thermally and mechanically stable than the pure one. An enhancement in the SHG efficiency (3.26 times) and laser damage threshold (1.78 times) was found on doping. Hence the picric acid doped L-threonine single crystal can be used for opto-electronic device fabrications.*

Key Words: *Nonlinear optics, crystal growth, single crystal, second harmonic generation*

1. INTRODUCTION

The synthesis and growth of new nonlinear optical (NLO) single crystals are of great requisite nowadays, as the field of optoelectronics focus on the fabrication of novel devices using them. They can be used, in frequency converters, high speed informatics, optical switch and optical modulators [1-3], depending up on their specific properties. The researchers are much interested on the NLO studies of organic molecules, because of their wide transparency range, large band gap, low mobility, high laser damage threshold and ease for molecular engineering [4]. Among organic molecules, amino acids are well known for their NLO behavior. The presence of donor and acceptor groups within the amino compound causes intermolecular charge transfer. Along with this, the presence of chiral carbon atoms, non-Centro symmetry in the structure etc. make them good competitor for the NLO applications.

The present work is targeted to study the thermal, mechanical and optical behavior of L-threonine (LTH) when it is doped with picric acid in 1:0.2 molar ratio. There are certain literatures on the growth and study of pure LTH[5,6]. It has got Second Harmonic Generation (SHG) efficiency 1.15 times that of KDP. Doping can alter the nonlinear behavior of a material and can make them suitable for different applications in the field of electro-optics.

2. CRYSTAL GROWTH

Picric acid is added to the supersaturated solution of L-threonine (AR grade) in 1:0.2 molar ratio. Then the doped

solution is stirred continuously for 10 hours at room temperature to ensure homogeneous mixing. The solution is then filtered and transferred to a crystal growth vessel. Its mouth is covered with porous polythene sheet to control the rate of evaporation. By successive recrystallisation good quality picric acid doped L-threonine (PA:LTH) single crystals are obtained within 10 days with 7x1x1mm3 dimension. Pure L-threonine (LTH) single crystals are also grown by slow evaporation solution growth technique (Fig.1 and Fig.2).

Fig-1: Pure LTH single crystal

Fig-2: PA:LTH single crystal

3. RESULTS AND DISCUSSION

3.1. XRD analysis

Fig.3 and Fig.4 show the powder XRD spectrum of the pure LTH and the PA:LTH single crystals. All the peaks present in Fig.3 are present in Fig.4 also. They are almost similar. But the intensity of XRD spectrum of doped sample is comparatively higher. The sharp and discrete peaks in the spectrum indicate the crystalline nature of the sample. It's found that, the unit cell parameters of PA:LTH show a very slight difference from that of pure LTH because of the effective strain produced in the lattices of LTH due to the

entering of dopant in to the lattice (a = 13.823A°, b = 8.011 A°, c = 5.325 A°).
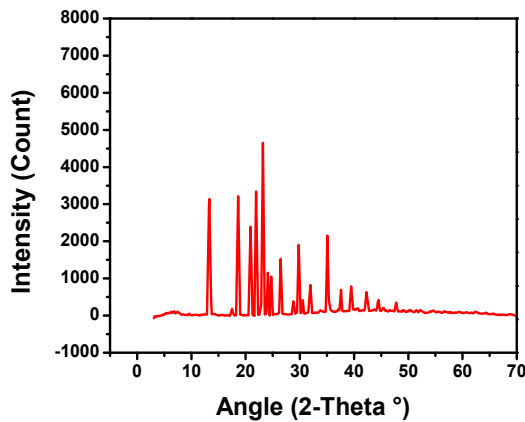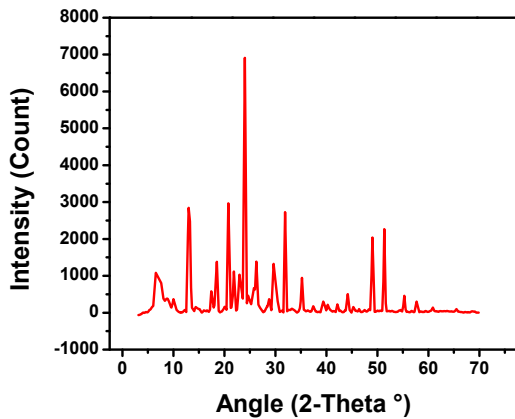

Fig.3. Powder XRD spectrum of LTH

Fig.4. Powder XRD spectrum of pure PA:LTH

3.2. UV-VIS-NIR spectrum

The UV-VIS spectral analysis reveals that, both the pure and doped LTH crystals are transparent in the entire visible region (Fig.5 and Fig.6). So they can be used in electro-optic device fabrication. An additional peak is visible in the absorption spectra of PA:LTH at 350nm.
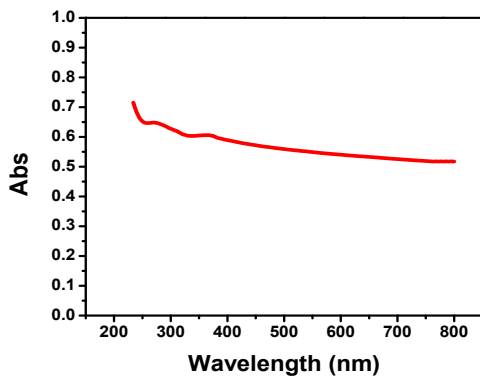

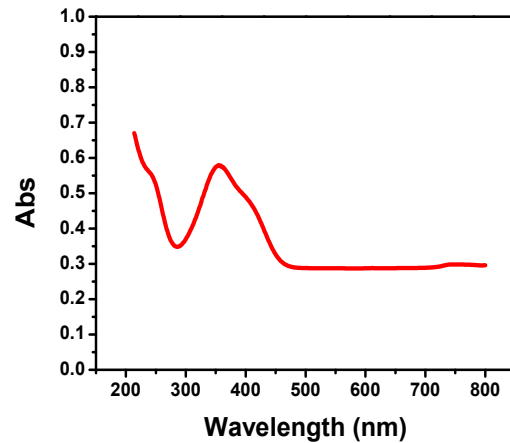**Fig.5.** UV-Visible spectrum of LTH

Fig.6. UV-Visible spectrum of purePA: LTH

Garces et.al. [7] Reported that, in doped systems, the impurities entering the lattices of the crystal during the growth process creates a local lattice stress and distortion in the crystal structure. These impurities absorb the electrons and protons produced during the laser irradiation and hence make the system more stable. The absorption by dopants are responsible for the additional peak in the PA: LTH absorption spectra. So doping of picric acid in L-threonine could bring notable changes in the optical behavior of the crystal.
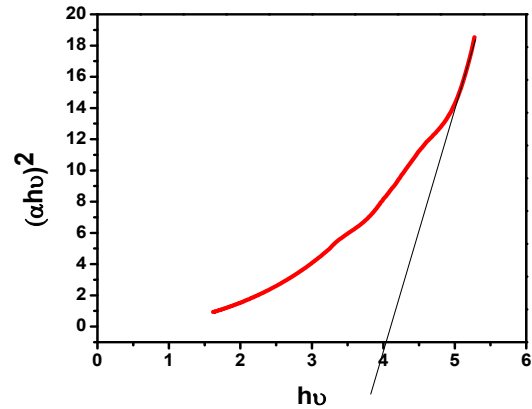

Fig.7. (hv) VS (αhv)^2 plot of LTH

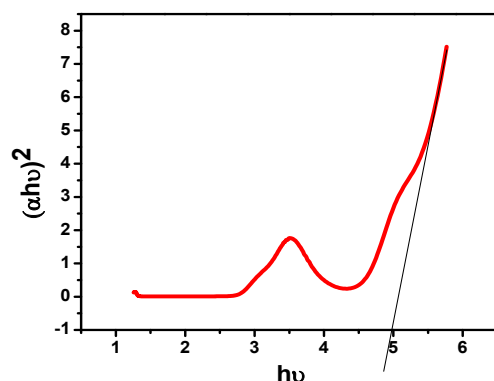**Fig.8.** (hv) VS (αhv)^2 plot of PA:LTH

The graph between (hv) and (αhv)^2 is shown in Fig.7 and Fig.8. where α is the absorption coefficient, h is the Planks constant and hv is the photon energy. The band gap energy of LTH and PA: LTH are obtained by extrapolating the linear section of the graph. It's found to be 4eV for pure LTH and 5eV for PA: LTH. The higher band gap value of PA: LTH indicates that it has got a very good dielectric behavior. So when the crystal is exposed to influential radiation it can induce polarization.

3.3. Thermal analysis

Thermal studies are performed to understand, the variation in energy and the weight loss of the sample with respect to temperature. TG-DTA spectrum of the LTH and PA: LTH are depicted in Fig.9 and Fig.10.

Fig.9. TG-DTA of LTH

Fig.10. TG-DTA of PA; LTH

Thermal studies are performed to understand, the variation in energy and the weight loss of the sample with respect to temperature. TG-DTA spectrum of the LTH a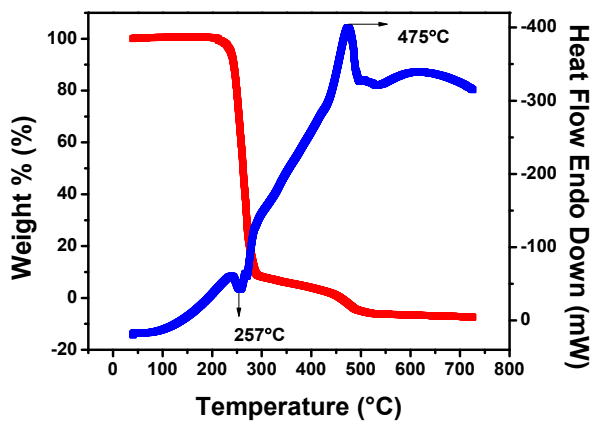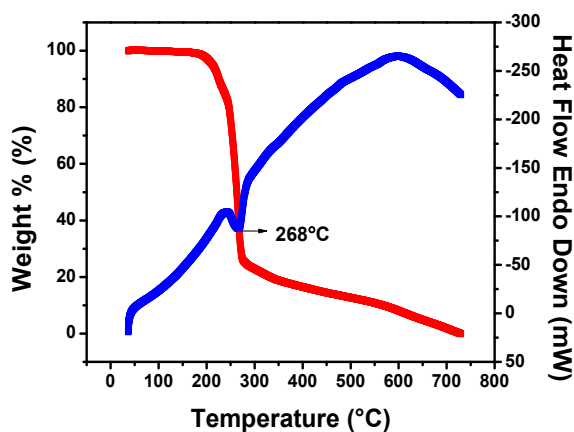nd PA: LTH are depicted in Fig.9 and Fig.10. As there is no weight loss up to 250℃ it can be concluded that, the samples are stable up to 250℃ and there is no solvent incorporation within the crystal lattice. Melting point of LTH is 257℃ and that of PA: LTH is 268℃. On doping melting point of LTH increases. Decomposition of both the samples occurs at 268℃. LTH melts just before the decomposition but PA: LTH melts while decomposing. The phase change present at 475℃ in the LTH single crystal is not visible in PA: LTH. So PA: LTH is thermally more stable than the pure LTH and hence is suitable for any application within 250℃ temperature range. A comparison between the melting points of some compounds are given in Table.1

Table.1. Comparison of melting points of some compounds

Compound name	Melting Point(℃)	References
PA:LTH	268	Present work
LTH	257	Present work
Sulphamic acid	219	[8]
L-serine phosphate	204	[9]
L-Histidine hydrochloride	171	[10]

3.4. Vickers Micro hardness Test

The hardness number of a material can be defined as a measure of its capacity to withstand local deformations [11, 12]. It can be calculated using the formula $H_v = 1.854\, P/d^2$ kg/mm^2 where P is the applied load in gram and d is the diagonal length of indentation in mm [13]. Indentations were made on the polished surfaces of pure and doped samples. Fig.11. depicts the Vickers hardness number (VHN) versus load graph. Pure LTH has got a maximum VHN, 51.94kg/mm^2 for a load of 25g and PA: LTH has got maximum VH N, 53.96kg/mm^2 for a load of 100g. Small micro cracks were observed on the LTH crystals for 50g load. But doped sample cracked at 200g load only. This means PA: LTH is having better mechanical strength and crystalline perfection than the pure LTH. Materials with good mechanical strength are useful in the device fabrication works. The hardness numbers of certain crystals are shown in Table.2
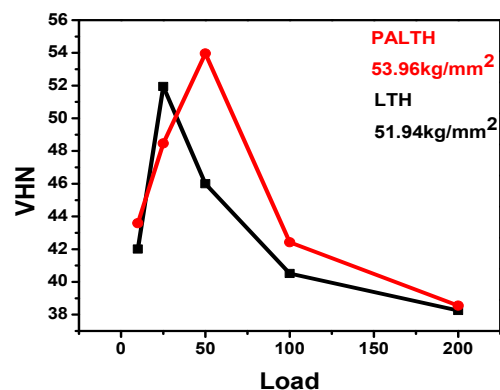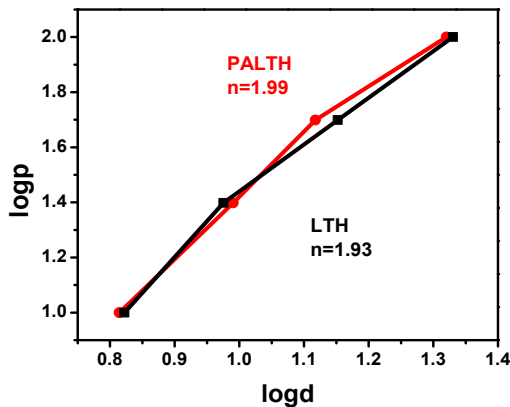

Fig.11. VHN versus load graph

Fig.12. logP versus logd graph

Fig.12. is the Mayer's plot. Slope of the graph gives the Mayer's index or work hardening coefficient (n). According to Onistch and Haneman if n>1.6 for a material, then it belong to softer material category [14]. Here, both the crystals LTH and PA: LTH are softer materials as their n values are 1.93 and 1.99 respectively.

Table.2. Comparison of hardness number of some compounds

Compound name	Hardness number(kg/mm^2)	References
PA:LTH	53.96	Present work
LTH	51.94	Present work
HLP	42	[15]
Stilbazolium derivatives	30	[16]
Guanidium p-nitrophenolate	29	[17]

3.5. SEM images

Morphology of the crystals are shown in the scanning electron microscopic images (Fig.13 and Fig.14)
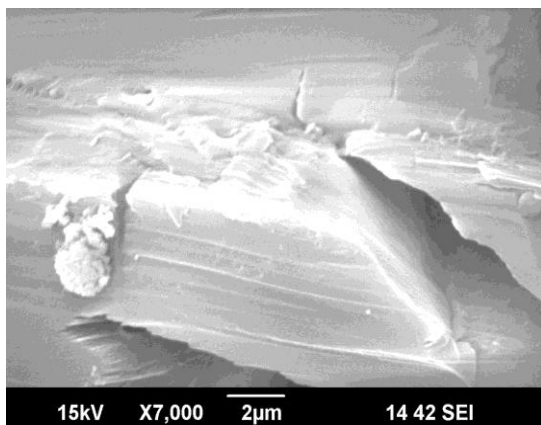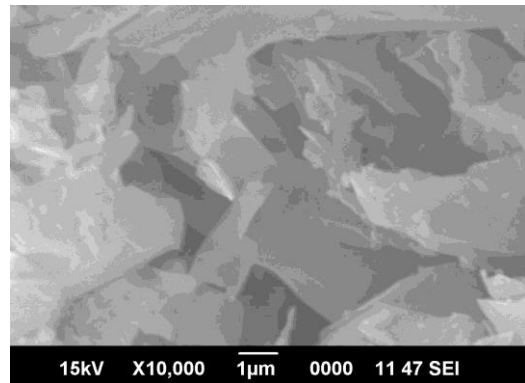

Fig.13. SEM image of LTH

Fig.14. SEM images of PA: LTH

3.6. SHG measurement

Second harmonic generation efficiency of the samples were analyzed by Kurtz and Perry Powder technique [18]. Q-switched Nd: YAG laser beam with the wavelength 1064nm and pulse width 10ns were allowed to fall on the powder samples taken in the capillary tube. It was found that LTH has an SHG efficiency 1.15 times greater than that of standard KDP whereas PA: LTH has an SHG efficiency 3.75 times greater than that of standard KDP. Hence when L-threonine is doped with picric acid, its SHG efficiency is increased by 3.26 times. SHG efficiency of some samples is listed in the Table.3.

Table.3. Comparison of SHG efficiencies of some compounds

Compound name	SHG efficiency(wrt KDP)	References
PA:LTH	3.75	Present work
LTH	1.15	Present work
2-Amino 5-Nitropyridinium Chloride	2.98	[19]
4-chloroanilinium-L-tartrate monohydrate	1.5	[20]
L-Phenylalaninium Methanesulfonate	1.2	[21]

3.7. Laser Damage Threshold

When the optical crystals are exposed to the laser beam there is a chance for them to absorb the laser energy. This may cause decomposition or melting of the crystal due to the increase in temperature. Hence the laser exposure can damage the crystal. So it is necessary to study the laser withstanding capacity of the crystal before choosing it for different applications. The laser damage threshold (LDT) studies were done on the smoother surfaces of LTH and PA: LTH. Shattering damages were observed at an energy level

257mJ and 352mJ with spot size 712µm and 624µm for LTH and PA: LTH respectively. The following relation is used for finding laser damage threshold.

Power density, $P_d = \dfrac{E}{\tau \pi r^2}$

Where E is the input energy density in mJ, τ is the pulse width in ns and r is the radius of the circular spot on the crystal in mm[22-24]. The LDT value for LTH is 3.23GW/cm^2 and that for PA: LTH is 5.76GW/cm^2. The higher LDT value of PA: LTH shows that it is more stable than the pure one. Table.4. shows the LDT value of some crystals.

Table.4. Comparison of LDT values of some compounds

Compound name	LDT values (GW/cm^2)	References
PA:LTH	5.76	Present work
LTH	3.23	Present work
Ammonium p-toluenesulfonate	3.18	[25]
l-serine	2.1	[26]

3.8. Structure-property relationship

The amino acids generally show good NLO nature. It is due to the presence of donor NH$_2$ group and acceptor COOH group within them. Picric acid contains a benzene ring, an OH group and three NO$_2$ groups. Usually, presence of delocalized π electrons, hydrogen bonds, heterocyclic aromatic rings etc. enhances NLO property of molecules. Here when L-threonine is doped with picric acid, a notable increase in SHG efficiency is observed (3.26 times that of pure LTH). This may be due to the delocalized π electrons within the benzene ring of the piric acid and the N-H...O and O-H...O hydrogen bonds formed between certain L-threonine and picric acid molecules [27].

4. CONCLUSION

Good quality single crystals of picric acid doped L- threonine were grown by slow evaporation solution growth technique. The PA: LTH single crystals were having good crystalline nature, transparency in the visible region. The crystal is thermally stable up to 268°C and mechanically strong with a hardness number 53.96kg/mm^2. It belongs to softer material category with Mayor Index 1.99. SHG efficiency of the doped sample is found to be 3.26 times greater than that of the pure LTH and LDT value is found to be 1.78 times greater than that of the pure LTH single crystal. The improved nonlinear behavior is attributed to the hydrogen bonds formed between the L-threonine and doped picric acid molecules. Hence the improved quality of PA: LTH single crystals makes them useful in the opto electronic device fabrication.

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