Synthesis, Growth, Structural, Spectroscopic, Thermal and Optical Properties of NLO Single Crystal: L-Threonine Zinc Acetate

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Abstract

Synthesis and single crystal growth of nonlinear optical crystal l-threonine zinc acetate (LTZA) is reported and compared with the pure l-threonine in this paper. L-threonine and LTZA crystals are characterized with single crystal and powder XRD, FTIR, UV-Vis-NIR, TG/DTA analyses and SHG test. Single crystals with optically desirable transparency were grown in solution by slow evaporation technique at 35^{o}C using a constant temperature bath (CTB) with an accuracy of ±0.01^{o}C. Single crystal XRD was carried out to examine the crystal system and unit cell parameters. Powder XRD pattern confirms that there is change in the basic structure of materials. The presence of functional groups in the crystal lattice was qualitatively analyzed by FTIR spectrum. Thermal property of grown crystals was reported in the TGA/DTA analyses. Thermal studies revealed that grown crystal LTZA is thermally stable upto 92^{o}C. Optical property of the crystals examined by UV-Vis-NIR studies showed that l-threonine and LTZA crystals are transparent in the range of 200-1100 nm. The second harmonic generation (SHG) efficiency of the LTZA crystal was studied by Kurtz powder method and the efficiency was 3.3 times greater than that of pure KDP and when compared with the parent compound, it was found that efficiency is three times greater than that of l-threonine.

Keywords

Zinc Acetate; l-threonine; Crystal Growth

introduction

Nonlinear optical (NLO) materials play a major role in nonlinear optics and in particular they have a great impact on laser technology and industrial applications. In the last decade, this effort has also brought its fruits in applied aspects of nonlinear optics, which essentially boosted the improvement on the performances of the NLO materials. The understanding of the nonlinear polarization mechanisms and their relation to the structural characteristics of the materials has been considerably improved. The new methods for the fabrication and growth of artificial materials have contributed to this evolution with the purpose to develop materials presenting large nonlinearities and satisfying at the same time all the technological requirements for applications such as wide transparency range, fast response, and high damage threshold. NLO scientist are working with the aims of discovery of new NLO materials, growth of promising NLO crystals and improving the characteristics of NLO crystals. The organic NLO materials have large nonlinear optical coefficients compared to the inorganic materials, but their use is impeded by their poor mechanical and thermal properties and low laser damage threshold. Inorganic NLO materials exhibit excellent mechanical and thermal properties but possess relatively modest optical nonlinearities because of the lack of extended π-electron delocalization. Recently, the approach of combining the high nonlinear optical coefficients of the organic molecules with the excellent physical properties of the inorganic has been found to be overwhelmingly effective. The semi-organic materials share the properties of both organic and inorganic materials. Recent interest is concentrated on metal complexes of organic compounds owing to their large non-linearity. In the case of metal–organic coordination complexes, the organic ligand is usually more dominant in the NLO effect. Since metal compounds (such as Zn, Cd, and Hg) have high transparency in the UV region. The metal-organic coordination complexes can also provide the following advantages: i) enhancement on the physico-chemical stability. ii) the breaking up of the centro-symmetry of the ligand in the crystal, and iii) an increase in NLO intensity, via metal-ligand bridging interactions.

Zinc acetate, a chemical compound with wide applications in many industries, as one of the important fertilizers for plants and well known in chemical industries, has been used as a raw material for manufacturing various chemicals. Zinc acetate dihydrate crystallizes in monoclinic system with the space group C2/c. The lattice parameter values of zinc acetate dihydrate are a=14.50 Å, b=5.32 Å and c=11.02 Å and β=100.00^{o} and cell volume V=850.0828 Å^{3}. The

optical absorption spectrum of Co^{2+} doped single crystal of zinc acetate dihydrate has been studied under polarization by P. A. Narayana et al. In recent times, one has witnessed a growing interest in the study of amino acid crystals. The complexes of amino acids and salts are promising materials for optical second harmonic generation (SHG) as they tend to combine the advantages of organic amino acids with those of the inorganic salts. Amino acids are interesting materials for second order Nonlinear Optical (NLO) applications as they contain a proton donor carboxylic acid group and the proton acceptor amine group in them. Scientsts are always in the search of new materials and their single crystal growth. From the stand-point of the search for newer NLO materials, amino acids offer a rich choice for researchers. Amino acids are bifunctional organic molecules that contain a carboxyl group (–COOH) as well as an amine group ($–NH_2$). In the solid state, amino acids have a protonated amino group ($NH3^+$) and de-protonated carboxylic acid group (COO^-). The zwitterionic nature exhibits peculiar physical and chemical properties in amino acid which makes them an ideal candidate for NLO application. Amino acids are also very interesting system for fundamental research as in the crystalline state they are present as zwitterions. The aliphatic amino acids valine and leucine contain two prochiral methyl groups, while isoleucine, but threonine, has two chiral centres. L-threonine occurs as white crystalline powder, and it is freely soluble in formic acid, soluble in water and practically insoluble in ethanol. By using l-threonine as dopant, enhancement in nonlinear and ferroelectric properties was reported by D. J. Dave and K. Meera. Lattice parameters of L-threonine are reported by F. D. Nunes et al with a=13.61 Å, b=7.74 Å and c=5.14 Å and volume V=537.98 $Å^3$ and l-threonine crystallizes in orthorhombic system with the space group $P2_12_12_1$. In this paper, highly transparent single crystals of L-Threonine Zinc Acetate (LTZA) have been grown successfully by using slow evaporation method and structural, thermal and optical properties are compared with pure l-threonine.

Experimental Procedure

Single crystals can be grown from the transport of crystal constituents in the solid, liquid or vapour phase. Materials, which have high solubility and variation in solubility with temperature can be grown easily by solution method. Of all the methods of crystal growth, solution growth is perhaps the most widely practiced next to melt growth. In this method crystals are prepared from a solution at a temperature well below its melting point. The constituents of the material to be dissolved in a suitable solvent and crystallization occur when the solution becomes critically supersaturated. To achieve supersaturation, the temperature is fixed constant and provision is made for evaporation. Non-toxic solvents allow the evaporation into the atmosphere. The evaporation techniques of crystal growth have the advantage that the crystals grow at a fixed temperature. However, inadequacies of the temperature control system still have a major effect on the growth rate. This method is the only one, which can be used with materials having very small temperature coefficient of stability. To obtain the single crystals of l-threonine, the AR grade chemical was dissolved in water at room temperature. L-Threonine Zinc Acetate (LTZA) was synthesized from l-threonine (AR grade) and zinc acetate dihydrate (AR grade), taken in the equimolar ratio (1:1). Zinc acetate dihydrate and l-threonine were dissolved separately in double distilled water. These solutions were mixed and stirred vigorously for two hours using temperature-controlled magnetic stirrer at 40°C. The solution was allowed to evaporate at room temperature, which gives white crystalline salt of l- threonine zinc acetate (LTZA). Purification of l-threonine and LTZA was carried out by successive recrystallization. To obtain single crystals of high quality, saturated solution of l-threonine and LTZA was prepared and filtered using Whatmann filter papers and kept in a constant temperature bath with an accuracy of ± 0.01°C at a temperature 35°C for slow evaporation. The period of growth for l-threonine and LTZA crystals was 55-60 days. Crystals with well optical transparency of l-threonine and LTZA were grown with the dimensions of 2×2×8 mm^3 and 4×3×14 mm^3 respectively. Fig. 1(a&b) shows photograph of grown crystals of l-threonine and LTZA.

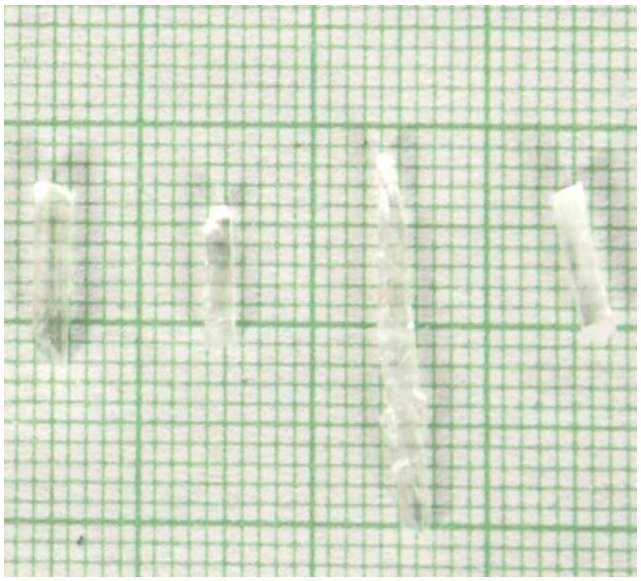


Fig. 1a Photograph of l-threonine.

Fig.1b Photograph of LTZA

Characterization

The grown crystals of l-threonine and LTZA were subjected to various characterizations viz. powder and single crystal X-ray diffraction, FTIR analysis, UV-Vis-NIR spectral study, TGA/DTA analysis, and SHG test.

A. Structural Analysis

The grown crystals of l-threonine and LTZA were subjected to single crystal X-ray diffraction and powder X-ray diffraction studies to find the lattice parameters. Single crystal XRD study carried out using Nonius CAD4/MACH 3 single crystal X-ray diffractometer with MoK_α (λ = 0.71069 Å) radiation revealed that pure l-threonine crystallized in orthorhombic system and that LTZA crystallizes in monoclinic system with lattice parameters a=21.1350 Å, b=6.0372 Å, c=9.4592 Å, β=101.43° and cell volume V=1206.958 Å^3.. The unit cell parameters were determined as a=5.1462 Å, b=7.6982 Å, c=13.5697 Å, and cell volume is 537.58 Å^{3}Comparison of unit cell parameters of grown crystals along with zinc acetate dihydrate is shown in table Ⅰ.

TABLE Ⅰ COMPARISON OF UNIT CELL PARAMETERS OF L-THREONINE AND LTZA CRYSTALS

Parameters	l-threonine [present work]	LTZA [present work]	Zinc acetate dihydrate [V. Ananthanarayanan]
a (Å)	5.1462	21.1350	14.50
b (Å)	7.6982	6.0372	5.32
c (Å)	13.5697	9.4592	11.02
α (°)	90.00	90.00	90.00
β (°)	90.00	101.43	100.00
γ (°)	90.00	90.00	90.00
Cell volume (Å^3)	537.58	1206.958	850.0828

Powder X-ray diffraction patterns recorded for grown crystals by an X-ray diffractometer (Model JDX 8030) with CuK_α (λ = 1.5408 Å) radiation are shown in Fig.2(a&b). Fig.2c shows powder XRD pattern of zinc acetate dihydrate. Sharp peaks of XRD pattern indicate high degree of crystalline structure of grown crystals. When compared with XRD pattern of pure l-threonine and zinc acetate, it is seen that LTZA has different pattern. Miller indices estimated by powder V1.0 software along with 2θ values of l-threonine and LTZA crystals is given in table Ⅱ. Powder XRD pattern of grown crystals was used to calculate lattice parameters using unit cell software and the values are found to be in good agreement with single crystal XRD values and they are shown in table Ⅲ for LTZA crystal.

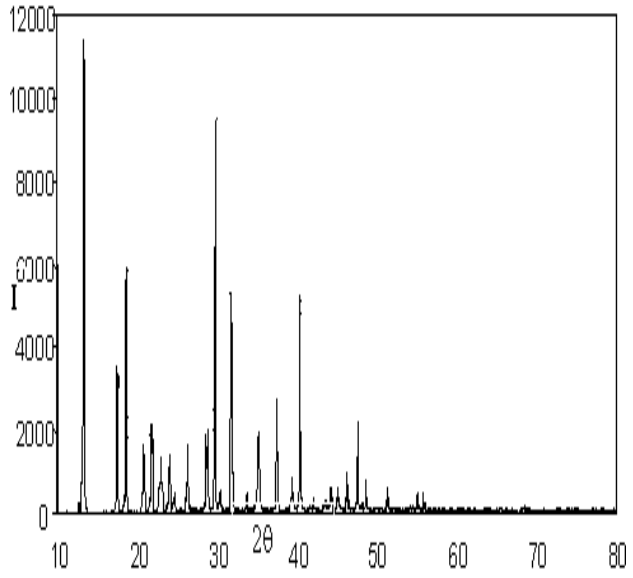


Fig. 2a Powder XRD pattern of l-threonine

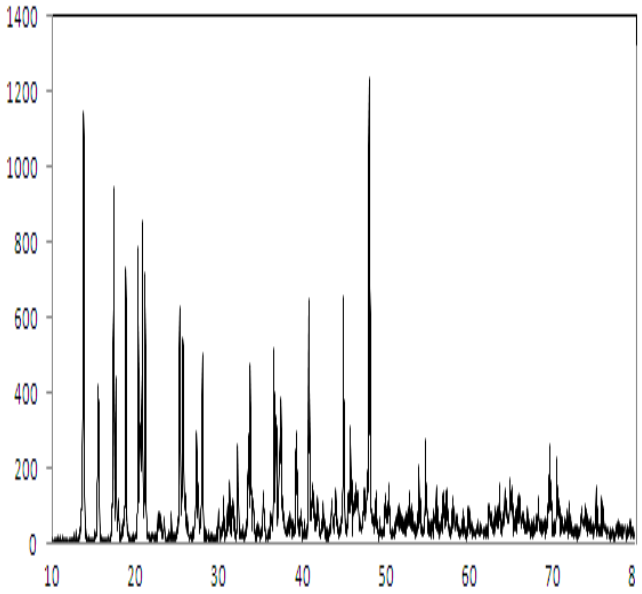


Fig. 2b Powder XRD pattern of LTZA

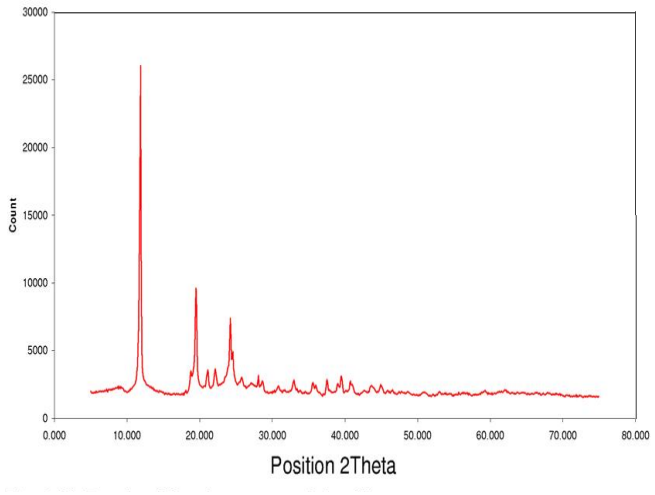


Fig. 2c Powder XRD pattern of zinc acetate.

TABLE Ⅱ POWDER XRD DATA OF L-THREONINE AND LTZA CRYSTALS

l-threonine		LTZA	
2 theta	hkl	2 theta	hkl
12.720	0 1 0	13.180	3 0 0
13.320	0 1 1	15.480	1 1 0
17.540	0 1 2	17.380	4 0 0
18.600	1 0 1	17.640	0 1 1
20.800	1 1 0	17.940	-4 0 1
21.860	1 1 1	18.820	-2 1 1
22.960	0 1 3	20.320	2 1 1
24.080	0 2 1	20.800	-3 0 2
24.680	1 1 2	21.160	4 0 1
26.280	1 0 3	25.300	1 1 2
28.600	1 1 3	25.720	6 0 0
29.760	1 2 1	27.340	2 1 2
30.360	0 2 3	27.540	-4 1 2
31.720	1 2 2	28.020	4 0 2
33.700	1 1 4	31.300	-1 2 1
34.680	2 0 0	31.640	5 0 2
35.220	0 2 4	32.300	3 2 0
37.480	0 3 2	33.540	7 0 1
39.360	1 1 5	33.780	7 1 0
40.280	2 0 3	34.120	-4 1 3
42.120	2 2 0	36.620	4 0 3
43.400	1 0 6	36.880	5 2 0
43.720	2 0 4	37.440	2 2 2
44.340	2 2 2	39.340	-9 0 1
45.220	1 1 6	40.780	-9 1 1
45.780	2 1 4	41.180	-3 1 4
46.320	0 2 6	44.920	9 1 1
47.680	0 4 1	45.540	6 1 3
48.360	0 1 7	45.800	8 1 2
48.700	2 0 5	46.460	7 0 3
51.420	0 4 3	46.700	6 2 2
52.140	1 3 5	47.480	4 2 3
52.800	0 2 7	48.000	-2 0 5
54.220	2 3 3	48.740	-4 0 5
55.960	1 2 7	49.960	-9 0 4
58.460	1 1 8	50.360	5 3 0
64.140	3 0 5	54.020	-1 3 3
68.560	3 0 6	54.780	7 0 4
75.160	4 1 1	57.360	7 3 1
-	-	58.040	4 1 5
-	-	63.660	-8 0 6
-	-	64.360	3 4 1
-	-	64.940	0 4 2
-	-	65.920	-5 4 1
-	-	69.680	8 1 5
-	-	69.880	1 4 3
-	-	70.580	2 2 6

TABLE Ⅲ LATTICE PARAMETERS OF LTZA CRYSTAL

	a(Å)	b(Å)	c(Å)	α (°)	β (°)	γ (°)	Cell volume ($Å^3$)
Powder XRD	21.1349	6.0472	9.4581	90	101.42	90	1208.8
Single crystal XRD	21.1350	6.0372	9.4592	90	101.43	90	1206.9

B. Functional Group Analysis

The identification of functional groups was performed by infra-red spectroscopy. The infra-red spectra are vibrational-rotational spectra. FTIR spectrum of a compound provides more information than normally available electronic spectra. The presence or absence of absorption bands helps in predicting the presence of certain functional groups in the compound. To analyze the FTIR spectrum, accurate information about structure of l-threonine and zinc acetate dihydrate is much essential. From the R. S. Krishnan and V. Koleva studies, molecular structure of l-threonine and zinc acetate dihydrate are given in the Fig.3(a&b). The structure of l-threonine comprises two CH groups and carboxylic group (COO), amine (NH_3), C=O, CH_3 and two CH groups as shown in Fig.3a. In zinc acetate dihydrate, zinc ion coordinated with two oxygen atom of COO as shown in Fig.3b. In FTIR spectrum, functional groups of CH_3, C=O and H_2O of zinc acetate dihydrate are expected. The FTIR spectra of the l-threonine and LTZA crystals recorded by Perkin Elmer spectrometer in the frequency region of 400-4000 cm^{-1} using KBr pellet technique are shown in Fig.4 (a&b).

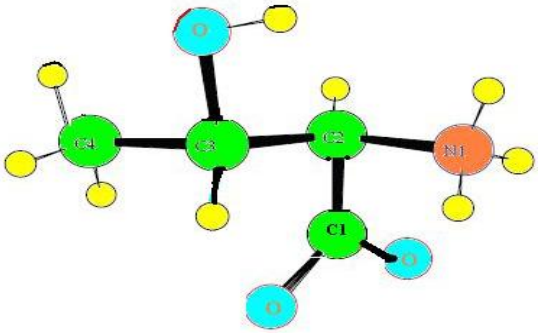


Fig. 3a Molecular structure of l-threonine crystal

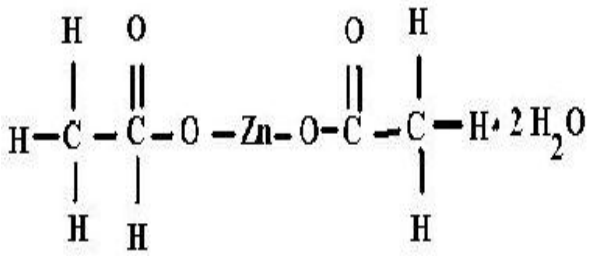


Fig. 3b Molecular structure of zinc acetate dehydrate

In order to do assignment, frequencies of l-threonine and zinc acetate are used and compared below. The peak observed at 459 cm^{-1} is attributed to OCO rocking, which is observed in zinc acetate at 477 cm^{-1}. OCO rocking vibration (622 cm^{-1}) of zinc acetate appears as shoulder at 620 cm^{-1} in LTZA crystal. Sharp peaks at 678 and 950 cm^{-1} are assigned to OCO symmetric bending and C-C stretching vibration respectively. The same peaks are observed at 695 and 954 cm^{-1} in pure zinc acetate. CH_3 rocking and bending vibrations are found at 1005, 1087, 1351 and 1416 cm^{-1}. The NH_3 torsion mode of l-threonine molecule shifted from 480 cm^{-1} to 498 cm^{-1} when compared to pure l-threonine. Peaks observed with wavenumbers of 575 and 789 cm^{-1} in grown crystals are tentatively assigned as rocking and torsion of COO of LTZA respectively. This is because in l-threonine, same frequencies are observed at 558 and 767 cm^{-1}. The peaks found at 908 and 1047 cm^{-1} are due to stretching vibrations of C-C and C-N (l-threonine). The stretching vibrations of the water molecule of zinc acetate dihydrate are expected in the region 3000-3600 cm^{-1}. The broad vibrational band observed at 3333 cm^{-1} is assigned to the symmetric stretching mode (O-H) of the water molecule. The tentative assignments are given in table IV. In the valine zinc complex, central zinc ion has a penta-coordinate distorted square-planar geometry where the two valine molecules in the basal positions are coordinated to the metal via their N (amine) and O (carboxylate) atoms, and the fifth coordination in the apical position is by an oxygen atom in water (solvent) molecule. Hence, it is presumed that in the grown crystal, the l-threonine molecule would be coordinated with zinc ion through its carboxyl and amine group. The major variation of frequencies of carboxylic group and NH_3, clearly confirms the above discussion.

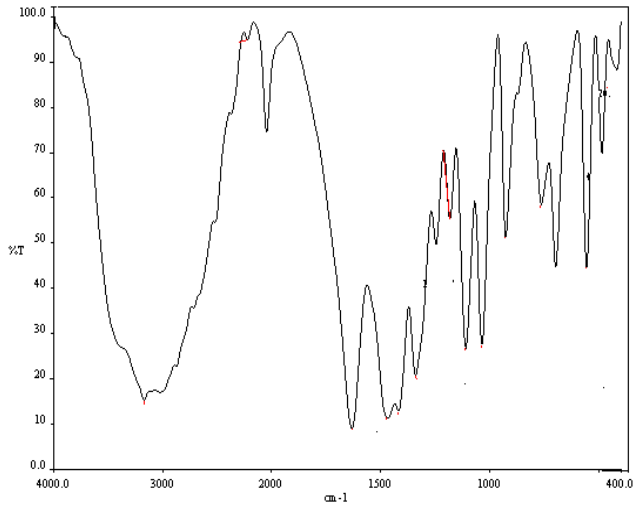


Fig. 4a FTIR spectrum of l-threonine crystal

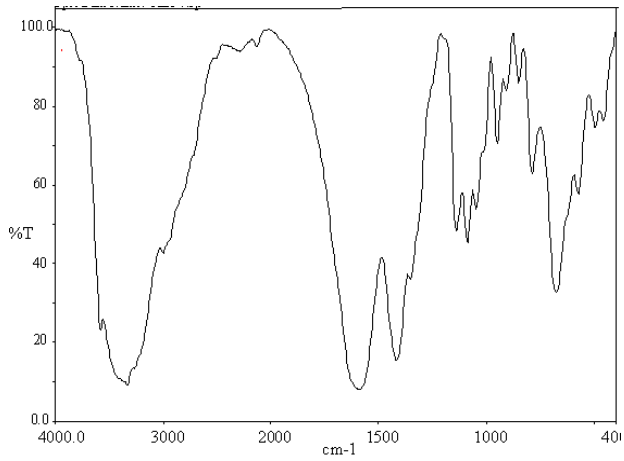


Fig. 4b FTIR spectrum of LTZA crystal

TABLE IV FUNCTIONAL GROUP ASSIGNMENTS OF LTZA

LTZA	l-threonine	Zinc acetate [V. Koleva et al]	Assignment
459	-	477	In plane OCO rocking
498	480	-	Torsion mode of NH_3
575	558	-	COO rocking
620 (sh)	-	622	Out of plane OCO rocking
678	-	695	OCO symmetric bending
789	767	-	Torsion of COO
851	850	-	Stretching of CCN
908	928	-	C-C stretching
950	-	954	C-C stretching
1005(sh)	-	1020	In plane CH_3 rocking
1047	1037	-	Stretching of CN
1087	-	1057	Out of plane CH_3 rocking
1139	1111	-	Rocking of NH_3
1184(sh)	1184	-	Rocking of NH_3
1351	1346	1350	CH_3 symmetric bending
1416	1417	1415	CH_3 asymmetric bending
1589	-	1558	CH_3 asymmetric stretching.
3001		2960	CH asymmetric stretching
3333	-	3100-3400	OH stretching vibration of H_2O

C. Optical Absorption Studies

When the molecule absorbs ultraviolet or visible light, its electrons get promoted from the ground state to the higher energy state. The optical transmittance spectra of l-threonine and LTZA recorded in the range 190-1100 nm using Lambda 35 spectrometer are shown in Fig.5 (a&b). Optical transmittance study reveals that there is no absorption peak in the range of 200 nm to 1100 nm. It can be seen from the transmission curve that below 350nm the transmittance of the grown crystal LTZA slightly decreases. Variation in the transmittance may be due to the presence of zinc acetate. Very low absorbance in the entire visible region would be attributed to the delocalization of electronic cloud through charge transfer. The absence of absorption in

the visible region clearly indicates that the grown crystal can be used for optoelectronic applications.

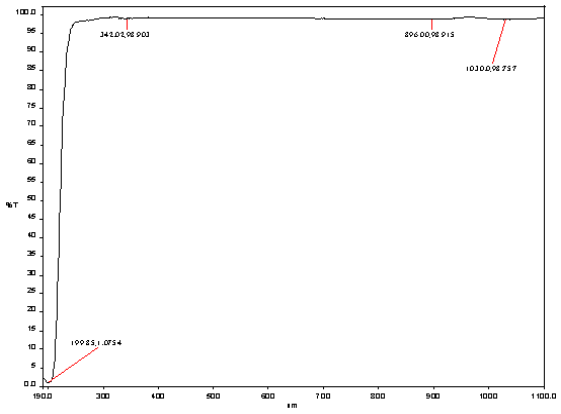


Fig. 5a UV-Vis-Nir spectrum of l-threonine crystal

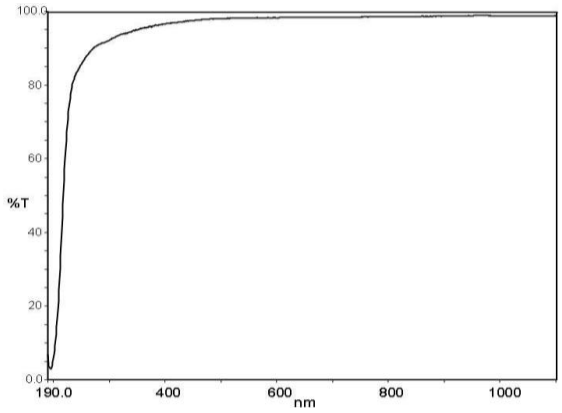


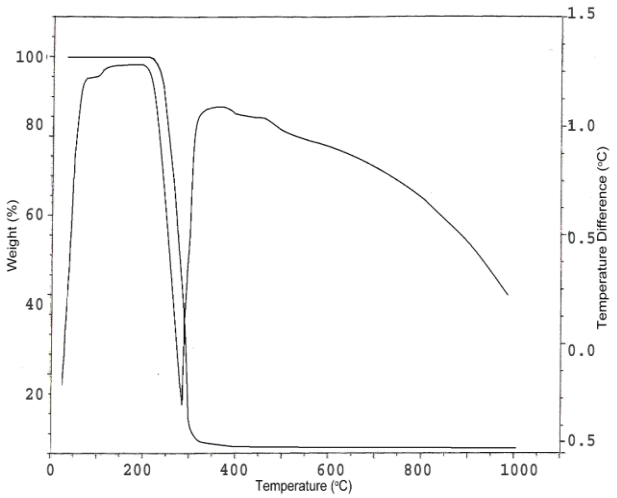
Fig. 5b UV-Vis-Nir spectrum of LTZA crystal

D. Thermal Studies

To investigate the thermal properties of the sample, l-threonine and LTZA were subjected to TGA/DTA studies. Thermo Gravimetric Analysis (TGA) provides quantitative measurement of any weight change associated with a transition of the sample. It can directly record the loss in weight with the time or temperature due to dehydration and decomposition. Differential Thermal Analysis (DTA) is a thermo analytical technique to record the difference in temperature between substance and a reference when they are subjected to identical heating at controlled rate. The record obtained is known as DTA cure, this series of peaks whose positions are determined by the composition and crystal structure of the sample. These experiments were performed in nitrogen atmosphere in the temperature range of 200-1100°C with the heating rate of 20°C/min using the instrument SDR Q600 V8 Build 101. TGA/DTA traces of l-threonine and LTZA are shown in Fig.6(a&b). Thermal property discussion of the l-threonine is as follows: There is no change in TGA curve upto 214°C showing thermal stability of l-threonine crystal and confirming the absence of water molecule within the crystal lattice. In the initial weight loss, more than 90% weight lost in the temperature range 214 to 272°C is due to decomposition of l-threonine. In DTA trace, the sharp peak at 267.9°C is melting point of the crystal which is higher than many organic compounds. This shows that melting and decomposition takes place simultaneously. Near 1000°C, the compound decomposed completely with mass left out of initial mass is only 2.65%. In the LTZA crystal, the TGA curve shows that initial weight loss (11%) of sample occurred between 92 °C and 124°C. Loss of weight near 100°C is due to the loss of water molecule of zinc acetate dihydrate. The same weight loss 16.2% is occured for pure zinc acetate dehydrate as reported by Tadashi Arii et al. The decrease in the percentage of loss of weight for dehydration of LTZA crystal is due to addition of mass of l-threonine. The DTA curve also shows an endothermic peak at 115°C. In this stage, sample would change into anhydrate product. In the next step another 34% of weight loss occurred from 218°C to 378°C corresponding to decomposition of l-threonine and zinc acetate which is inferred from the DTA peaks at 205°C and 256°C. McAdie concluded that anhydrous zinc acetate was decomposed through the following equation

$$4Zn(CH_3COO)_2 \rightarrow Zn_4O(CH_3COO)_6 + (CH_3CO)_2O$$
$$\rightarrow Zn_4O(CH_3COO)_6 \rightarrow 4ZnO + 3CH_3COCH_3 + 3CO_2$$

The above equation shows that zinc acetate decomposes in several steps. Part of weight loss observed from 208°C to 378°C is due to the liberation of $(CH_3CO)_2O$ that is inferred from the endothermic peak observed at 258°C. This is followed by the liberation of CH_3COCH_3 and CO_2 in the temperature range 378-705°C. The residue (28.62%) after decomposition may be zinc oxide.



. Fig. 6a TG/DTA traces of l-threonine.

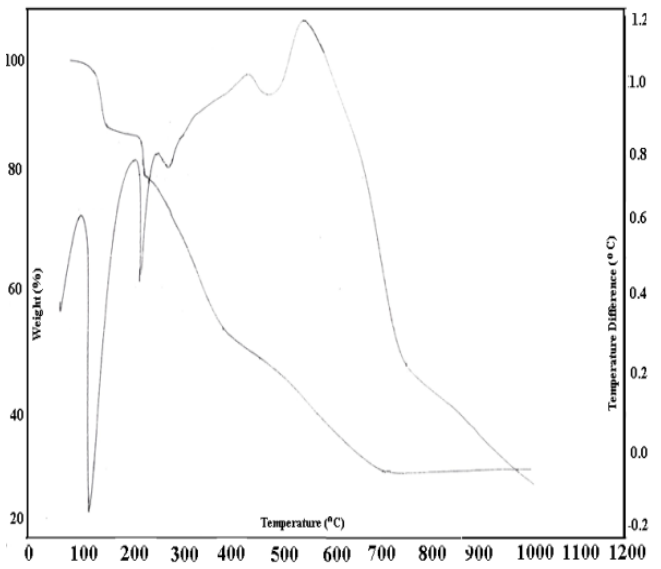


Fig. 6b TG/DTA traces of LTZA

E. Non Linear Optical Studies

Kurtz and Perry powder method is an important tool to evaluate NLO efficiency of the crystal. The LTZA crystal was powdered with uniform particle size, was and then packed densely in capillaries of uniform bore. An actively Q switched non linear mirror mode locked Nd:YAG laser (1064 nm) with an input power 2.9 mJ, pulse width of 10 ns and the repetition rate 10 Hz was used as the input beam for this experiment. The crystalline compound was illuminated by input beam. A photomultiplier tube (PMT) was used as detector and output was displayed on the oscilloscope (CRO). The optical signal, incident on the PMT converted into voltage and the output voltage for l-threonine and LTZA was 12 mV and 36 mV respectively. KDP crystal was also powdered and used as a reference material in this experiment. SHG output for KDP is 11 mV. It was found that the efficiency of the title compound is 3.3 times greater than that of KDP crystals. For pure l-threonine, SHG efficiency is 1.1 times of standard KDP crystal, which is in good agreement with the value reported by S. Natarajan et al. Formation of hydrogen bonds with the zinc may be the reason for the NLO efficiency enhancement. Ramesh kumar et al reported SHG conversion of l-threonine efficiency increases with the increment in wavelength. At lower wavelengths, the efficiency of l-threonine possesses higher values than l-alanine. L-threonine and l-alanine show the same SHG efficiency for the 732 nm wave length. The SHG efficiency comparison of l-threonine and many amino acid family is shown in table V. High SHG efficiency of LTZA recommends the crystal for NLO applications.

TABLE V. COMPARISON OF SHG EFFICIENCY OF VARIOUS AMINO ACID COMPOUNDS RELATIVE TO PURE KDP CRYSTAL

Compound	SHG efficiency compared with KDP
L-threonine [present work]	1.1
L-threonine zinc acetate [present work]	3.3
L-threonine acetate	1.14
L-alanine	0.2
L-alanine acetate	0.3
L-alaninium Oxalate	1.2
Glycine lithium sulphate	0.75
Bis-glycine maleate	0.84
Glycine potassium chloride	1.5

CONCLUSIONS

Good quality single crystals of l-threonine and l-threonine zinc acetate (LTZA) were grown by solution growth technique. Structural characterization of the grown crystals was carried out by single crystal and powder X-ray diffraction studies, and the lattice parameters have been evaluated. XRD studies revealed that l-threonine and LTZA are crystallized in orthorhombic and monoclinic system respectively. The functional groups present in l-threonine were ascertained using FTIR spectral analysis. The presence of functional groups of LTZA was assigned with the help of l-threonine and zinc acetate dihydrate. The UV-V is spectrum showing that grown crystals hold good optical transmittance in the entire visible region. Thermal properties have been reported by TGA/DTA analyses. In DTA trace of l-threonine, a sharp endothermic peak at 269^{o}C divulges that l-threonine melts at this temperature. The weight loss at initial stage, confirms the presence of water molecule in LTZA crystal due to hydrate of zinc acetate dihydrate. SHG efficiency of LTZA crystal is 3.3 times greater than that of KDP crystal.

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