

# Growth and Characterization of Lithium Threonate single crystal

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**Abstract - Single crystals of Lithium substituted L-Threonine were successfully grown by slow evaporation method at room temperature. The effect of lithium dopant on crystal properties has been studied. The crystals were characterized by Powder XRD and Single crystal XRD analysis, FTIR and NMR Techniques. Single crystal and Powder XRD analysis gave the lattice parameters of the crystal and h k l values of reflection planes. FTIR analysis identified the presence of functional groups in the grown crystals. From IR spectrum most of the bond vibrations were found to be coupled vibrations and zwitter ion of the amino acid was also found in the grown crystal. NMR analysis gave detail information about the different types of protons present in the single crystal of Lithium Threonate.**

**Key words—FTIR, L-Threonine, NMR, Single crystal XRD, Slow evaporation method, Zwitter ion.**

## I. INTRODUCTION

Amino acid consists of acid (COOH) and Amine (NH) group. Mostly the dominating atoms in the amino acids are C, N, H and O. Normally the C-C, C=C, C-N, C-H, C-O, C=O, C-OH bonds are found in the doped crystals. In these entire bonds hydrogen atom dominates, because they bonded with all the other atoms both in amino acids as well as the doped compounds [1].

L-threonine is found in protein which is alpha-amino-beta-oxybutyric acid that has an asymmetric hydroxyl group at the beta-position. Threonine is one of two amino acids out of the twenty with two chiral centers and four optic isomers are possible. As it has an alcoholic hydroxyl group, it can undergo both alkylation and acylation [2]. This hydrophilic amino acid with metal salt can grow as efficient single crystals and have various applications [3-5]. Hydrogen bonding between the molecules in amino acids is responsible for the many of specific characteristics of its crystals. H-bonding is the reason for the peculiar properties of water such as its high boiling point, melting point, vaporization temperature, high dielectric constant etc. [6]. The stability of the DNA double helix structure is mainly caused by the H-bonding between amino acids [7]. Hydrogen bonding is also useful in performing certain chemical reactions to make new products [8]. The study of hydrogen bond leads to molecular recognition properties of

organic materials [9]. The electronic and the optical properties of hybrid organic-inorganic materials can be tune by stabilizing those materials using hydrogen bonds [10]. Hydrogen bonding also influences the NLO properties of semi-organic materials. Most of the amino acid compound crystals have good NLO properties because of their molecular chirality, zwitter ion and nature of ligand formation [11].

In this work attempts were made to grow lithium doped L-threonine single crystals. The grown crystals were characterized using FTIR, NMR, PXRD and SXRD analysis and the influence of hydrogen bonding in the structure of grown crystal were discussed.

## II. EXPERIMENTAL METHOD

Single crystals of Lithium threonate were grown at room temperature (30° C) from an aqueous solution by slow evaporation method. AR grade L-Threonine and Lithium sulphate were dissolved in deionized water according to their stoichiometric ratio 1:1. The resulting solution was stirred with magnetic stirrer to get the homogeneous solution and then filtered using high quality Whatmann filter paper to remove dust particles. The filtered solution was taken in a beaker and covered by perforated thin paper and then allowed to evaporate under local atmospheric conditions. Good quality crystals of dimension 5mm X

1mm X 1mm, were obtained after 10 days. Photograph of the as grown single crystal was shown in figure 1.

The grown crystals were characterized by single crystal XRD, powder XRD, FTIR, and NMR techniques. A suitable Lithium threonate crystal was subjected to single crystal X-ray diffraction on Bruker Kappa Apex II Diffractometer with Molybdenum  $K\alpha$  radiation ( $\lambda=0.71073 \text{ \AA}$ ). The Powder X-Ray diffraction patterns was recorded on Bruker AXS D8 Advance X-ray diffractometer (Cu  $K\alpha$  radiation,  $\lambda=1.5406 \text{ \AA}$ ). Fourier Transformed-Infra Red (FT-IR) spectrum was recorded using Thermo Nicolet, Avatar370 spectrophotometer in the region  $400\text{-}4000 \text{ cm}^{-1}$ . Nuclear Magnetic Resonance spectrum was recorded on Bruker Advance 111 Spectrometer.

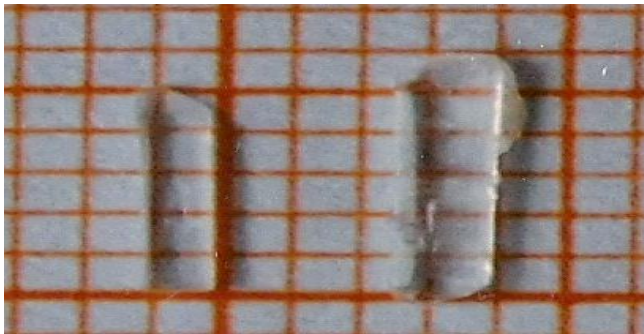


Fig. 1. Single crystals of Lithium Threonate

### III. RESULTS AND DISCUSSIONS

#### A. X-Ray Diffraction Studies

Single crystal XRD data showed that the unit cell parameters are  $a=5.1486 \text{ \AA}$ ,  $b=7.7367 \text{ \AA}$ ,  $c=13.6062 \text{ \AA}$ ,  $\alpha = 90 \text{ deg.}$ ,  $\beta = 90 \text{ deg.}$ ,  $\gamma = 90 \text{ deg.}$  and volume of the unit cell is  $541.98 \text{ \AA}^3$ . This confirms that the doped crystal belonged to the orthorhombic system with a space group  $P2_12_12_1$ .

Powder XRD pattern was recorded using Bruker AXS D8 advance diffractometer fitted with  $\text{CuK}\alpha$  radiation of wavelength  $1.5406 \text{ \AA}$ . Figure 2. shows the X-ray diffraction pattern of Lithium threonate.

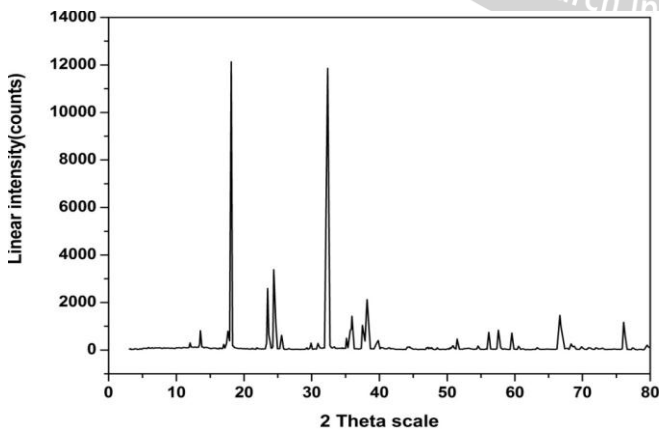


Fig. 2. Powder XRD Pattern of Lithium Threonate crystal.

Using unit cell parameters and d-spacing, the miller indices of reflecting planes were determined. High intense peaks

observed at  $18.10 \text{ deg.}$  and  $32.38 \text{ deg.}$  corresponding to 011 and 221 planes respectively. Two thetas and their corresponding miller indices are listed in Table. 1.

Table 1. Two Theta and ( h k l ) values of Lithium Threonate.

2 $\theta$	h k l
13.55	0 2 0
18.10	0 1 1
23.49	2 1 0
24.42	1 2 1
25.58	0 3 1
29.89	2 1 1
30.98	2 3 0
32.38	2 2 1
35.14	2 4 0
35.88	3 1 0
38.17	1 2 2
39.81	3 1 1
51.51	4 3 0
66.88	6 1 0

#### B. FTIR studies

FTIR spectrum recorded for Lithium Threonate from the region  $4000 \text{ to } 400 \text{ cm}^{-1}$  is shown in figure 3.

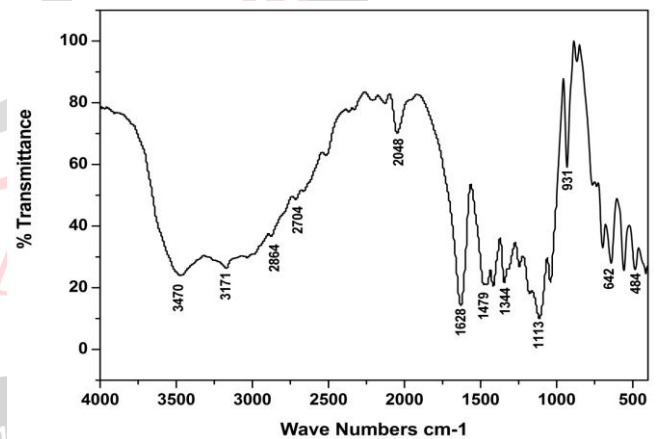


Fig. 3. FTIR spectrum of Lithium threonate crystals.

Most of the peaks in the spectrum are observed as broad bands which show that most of the vibrations are coupled vibrations. The peak positions and their assignments are listed in Table 2.

Table 2. Assignments on IR bands of Lithium Threonate

Absorption frequency in $\text{cm}^{-1}$	Assignments
3470	Symmetric O-H stretching
3171	Asymmetric N-H stretching
2864, 2704	Asymmetric and Symmetric C-H stretching

2048	combinational vibrations of zwitter ion
1628	C=O stretching
1479,1417	C-O stretching
1344	C-C-H in plane deformation
1113	C-N stretching
931	C-C stretching
698, 642	C-H out of plane bending
484	N-H torsional vibration

The strong absorption in the region  $3500\text{ cm}^{-1} - 2500\text{ cm}^{-1}$  corresponds to asymmetric N-H stretching vibration combined with symmetric and asymmetric stretching vibrations of C-H bond and symmetric O-H stretching vibrations. Intramolecular hydrogen bonding in O-H and N-H bonds broadens the absorbed peaks in the region  $3500\text{ cm}^{-1}$  to  $2900\text{ cm}^{-1}$ . The combinational vibrations of zwitter ion in amino acid are observed at  $2048\text{ cm}^{-1}$ . All amino acid has this characteristic peak around this region. The peak around  $1628\text{ cm}^{-1}$  corresponds to bending vibrations of N-H bond and stretching vibration of C=O bond. Because of mesomeric effect C=O stretching frequency is shifted from their original fundamental frequency (around  $1750\text{ cm}^{-1}$ ) to lower frequency (around  $1600\text{ cm}^{-1}$ ). N-H bending vibration around  $1600\text{ cm}^{-1}$  gives rise to overtone around  $3200\text{ cm}^{-1}$ . Because of Fermi resonance with an overtone of N-H bending, the N-H stretching vibrations observed as broad band in the region  $3500\text{ cm}^{-1}$  to  $3200\text{ cm}^{-1}$ [12]. The peaks  $1479\text{ cm}^{-1}$  and  $1417\text{ cm}^{-1}$  correspond to stretching vibrations of C-O bond in acids.  $1113\text{ cm}^{-1}$  is due to C-N stretching vibration. The peak  $931\text{ cm}^{-1}$  corresponds to C-H bending vibration. The peaks at  $698\text{ cm}^{-1}$  and  $642\text{ cm}^{-1}$  are corresponding to out of plane bending vibrations of C-H bond. Peaks at  $484\text{ cm}^{-1}$  is due to the torsional mode of vibrations of N-H bond in the single crystal.

### C. NMR study

NMR spectrum is a graph of intensity of absorption of radio waves versus magnetic field strength as chemical shift in terms of ppm (parts per million). The NMR spectrum of Lithium threonate is given in figure.4. The high intense peak around  $4.8\delta$  is due to the solvent  $\text{D}_2\text{O}$ . There are three signals are observed as multiplet, which showed the coupling effect of different protons in the crystal. The doublet centered at  $1.34\delta$  corresponding to the protons of methyl group ( $\text{CH}_3$ ) in the threonine molecule. The peak centered at  $3.62\delta$  observed as doublet is corresponding to the -CH- proton in which the amine group is attached. The octet centered at  $4.26\delta$  is corresponding to the -CH- proton in which the hydroxyl side chain is attached. Hydrogen bonding in amine group deshields the concerned proton and shifts its absorption to higher  $\delta$  values.

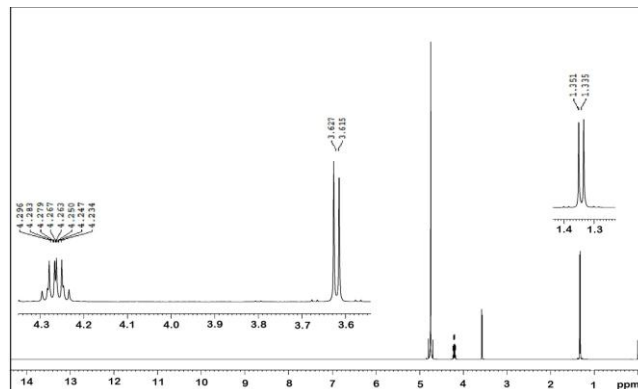


Fig. 4. NMR spectrum of Lithium threonate.

## IV. CONCLUSIONS

Substitution of the metallic element Lithium with an organic substance L-Threonine produced successfully single crystal of Lithium Threonate. The SXRD studies confirmed that the crystals of Lithium threonate crystallizes in the primitive orthorhombic structure with a space group  $P2_12_12_1$ . From powder XRD, it was found that most of the diffractions occurs at 0 0 1 and 2 2 1 planes of the crystal. The presence of zwitter ion and OH side chain of L-Threonine were confirmed by the FTIR spectrum. It also confirmed the variation in absorption frequencies of functional groups NH, CH and OH from their standard values on the influence of hydrogen bonding in the molecules of crystal. Again, NMR spectrum also confirmed the presence of methyl, hydroxyl and amino group in the grown crystal. All the above studies shows structural confirmation of Lithium threonate single crystal and it suggests that the grown crystal is non-centrosymmetric in nature which is necessary for the SHG activity of the material.

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