

Growth and Characterization of a New Semi-Organic Material : L-Threonine Doped Sodium Nitrate Crystal

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ABSTRACT

L-Threonine doped sodium nitrate single crystal was grown by solution growth slow evaporation technique successfully. LTSN, the as grown crystal were subjected to the following characterization studies such as UV-Vis-NIR, FTIR, TGA-DSC, Powder XRD and NLO etc., The investigation of optical linearity and nonlinearity was done from the UV-Vis-NIR and NLO studies. Thermal stability of the grown crystal was carried out using TGA and DSC spectral analysis. Conversion efficiency of the grown LTSN crystals to second harmonic generation confirms the suitability for fabricating devices used in the applications of frequency conversion.

1. Introduction

Aminoacids attract the attention of scientists and researchers for their special nonlinear optical behavior. The highlighted second harmonic generation of the amino acids is due to the following properties such as high thermal stability, solubility in water, non-volatile crystalline nature and so on. Because of the flexibility in fabrication, a number of new crystals were grown with a variety of properties on the inclusion of dopants(1-4). Devices in optoelectronics, a field such as switching, mixing and amplification requires day to day invention of new crystals with good optical behaviours for the advancement of technology(5-7).

Amino acid crystallization and their derivatives are one of the approaches to search a new NLO potential material. Source previously reported work shows that NaNO₃ and L-Threonine are having good NLO behaviour which induced to grow a new crystal on the above two combinations.

Quality crystals of NaNO₃ doped with L-Threonine were synthesized from solution growth technique adopting slow evaporation method at room temperature. Characterization techniques such as UV-Vis-NIR, XRD, FTIR, SHG, TG-DSC, and dielectrics were used to identify the grown crystal.

2. Experimental Procedure

The 9.2g of NaNO₃ was mixed with 0.1g of L-Threonine in 20ml distilled water and was stirred with the help of magnetic stirrer for about one hour. The above mixture was then filtered and collected in a beaker after making a proper stirring with a magnetic stirrer. The prepared solution was properly filtered with Whatman filter paper and made to expose to open aeration by covering it with a pin-holed paper. The entire setup is kept in a vibration free environment. The grown crystal is harvested within 28 days.



Figure 1: Photograph of L-Threonine doped Sodium Nitrate crystal

3. Results and Discussions

3.1. Powder XRD Studies

Figure 2 shows the powder XRD pattern which gives the confirmation about the grown L-Threonine doped sodium nitrate (LTSN) crystal structure by the computer program.

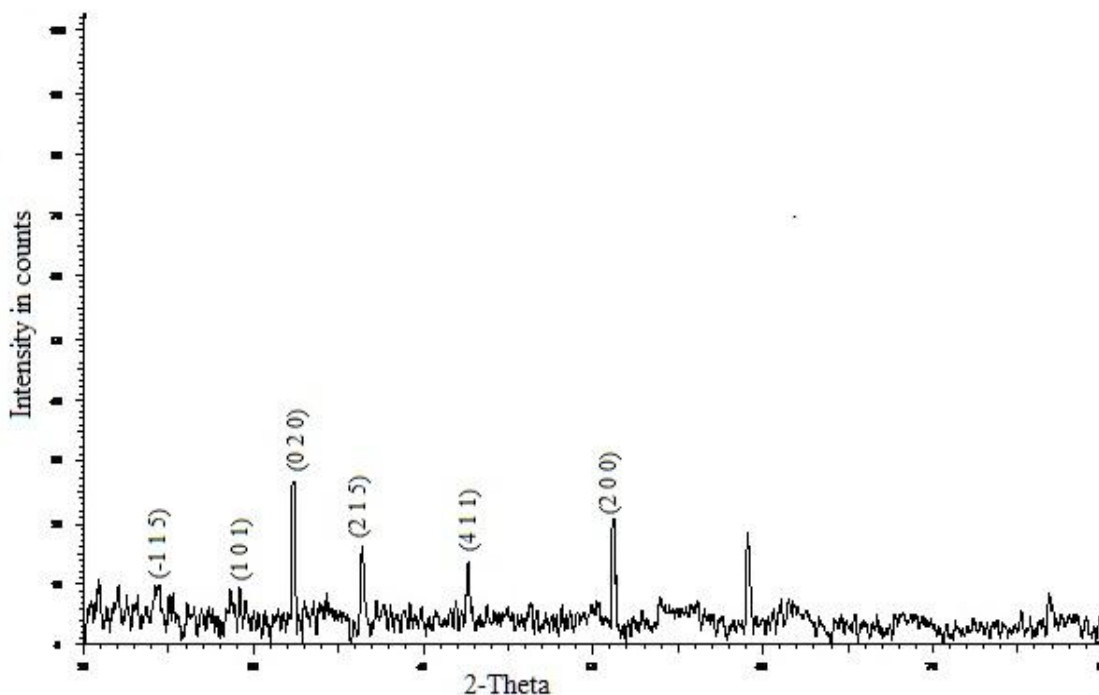


Figure 2: Powder XRD spectrum of LTSN Crystal

Using two theta values the lattice parameters were calculated and found to be matched with the previous standard data. The crystalline nature, purity, and identity were determined using the recorded values are tabulated in the below table 1.

Position 2θ	hkl
23.510	-115
30.000	101
32.064	020
36.641	215

42.860	411
51.158	200

Table 1: LTSN crystal powder XRD analysis

3.2. UV-Vis-NIR Analysis:

The L-Threonine doped sodium nitrate crystal plates with thickness 0.6cm without any antireflection coating were cut and used for optical measurements. The UV-Visible near-infrared transmission spectrum was recorded using Perkin-Elmer Lambda 35 UV-visible spectrometer in the range of 190-1100 nm. The transparency cutoff wavelength and optical transmission are shown in figure 3.

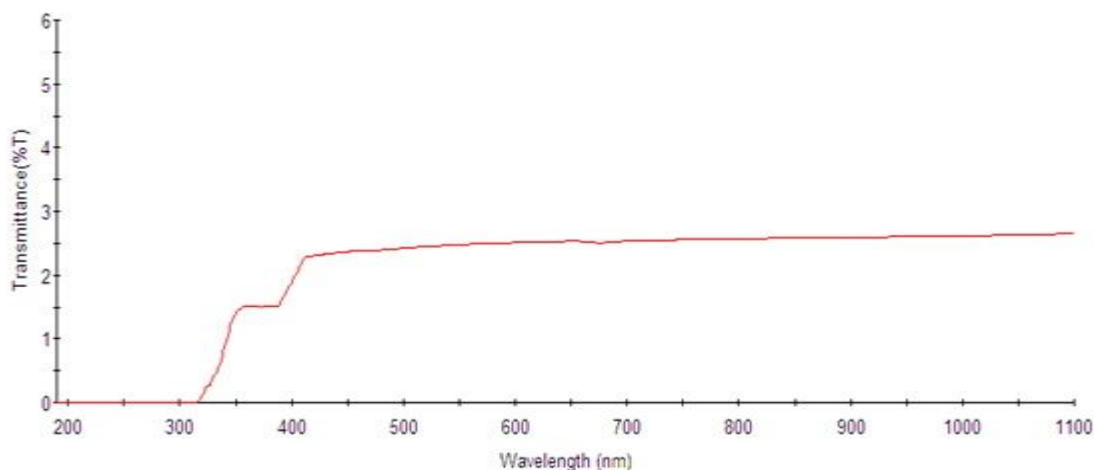


Figure 3: UV-Vis-NIR transmission spectrum of LTSN

It is seen that the grown L-Threonine doped sodium nitrate (LTSN) is transparent between the wavelength range 380-

1100nm. At 380nm it was observed that the UV transparency cutoff wavelength occurred. The complex forms of L-Threonine

with sodium nitrate have progressively improved the optical quality of the crystal with higher transparency. It could be concluded that the L-Threonine doping plays a key role in improving the optical quality of sodium nitrate crystals. This is the most desirable property of materials possessing non-linear optical activity.

3.3. FT-IR Spectral Analysis:

The FTIR spectrometry measurement was done with a Perkin Elmer spectrophotometer in the range of 400 to 4000 cm^{-1} to analyze the incorporation of different functional groups in the L-Threonine doped sodium nitrate crystal. The recorded FTIR spectrum is shown in figure 4.

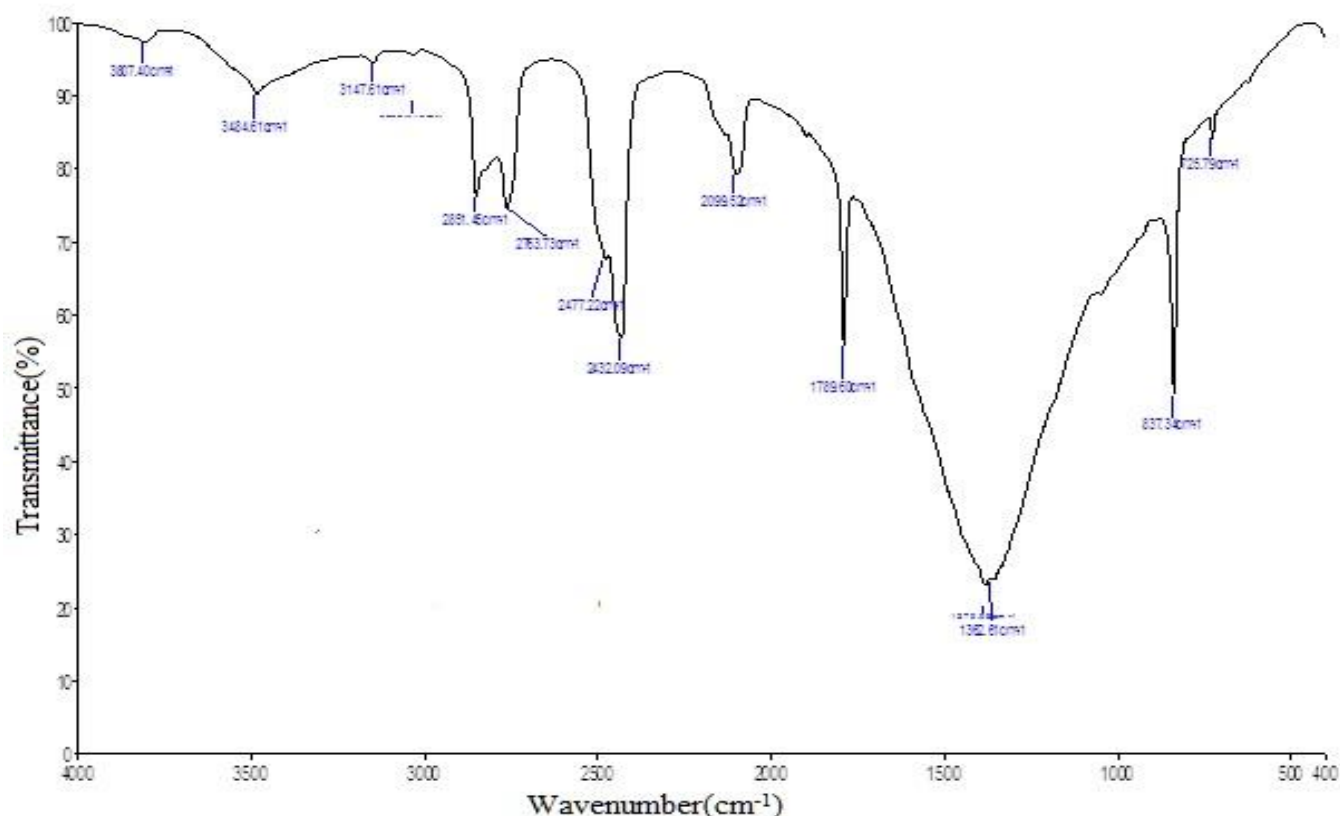


Figure 4: FT-IR of LTSN crystal

The observed FTIR frequencies and assignments of L-Threonine doped Sodium Nitrate crystal is tabulated in the below table 2.

The observed FTIR frequencies	Assignments
3807	Free O-H stretching hydrogen bonded threonine
3484	O-H stretching
3147	NH ₂ asymmetric
3030	NH ₂ asymmetric
2851	C-H asymmetric
2763	C-H symmetric stretching
1789	C=O stretching
1379	NH ₂ bending
837	COO ⁻ stretching

Table:2. LTSN crystals FTIR frequencies and assignments

The peak corresponding to the region 837 cm^{-1} confirms the presence of a carboxylic acid group (COO⁻). The strong peak at 1379 cm^{-1} is assigned to NH₂ bending vibration. The C=O stretching mode is observed at 1789 cm^{-1} . The peak at 2763 cm^{-1} is due to the C-H symmetric stretching and 2851 cm^{-1} is due to the asymmetric stretching of C-H. The band observed at 3030 cm^{-1} is due to the symmetric stretching vibration of NH₂. The asymmetric stretching vibration of NH₂ is observed at 3147 cm^{-1} . The O-H stretching mode is observed at

3484 cm^{-1} . The peak at 3807 cm^{-1} is due to the free O-H stretching hydrogen bonded threonine. The presence of COO⁻ and NH₂ indicates the characteristics of amino acid group material. The functional groups are found to be in good agreement with the available report(8-9).

3.4. Dielectric Studies:

The dielectric constant (ϵ_r) and dielectric loss ($\tan\delta$) of the L- threonine doped sodium nitrate (LTSN) crystal is measured using HIOKI 352-50 LCRHITESTER instrument by a conventional parallel plate capacitor method. Silver coating was applied on the opposite faces of the crystal which was then placed between two copper electrodes. The capacitance was measured for various frequencies in the range of 50 Hz to

200 KHz at room temperature. Further, the value of the dielectric constant was calculated using the relation:

$$\epsilon_r = \frac{Ct}{\epsilon_0 A}$$

Where C is a capacitance, t is a thickness of the sample, ϵ_0 is the permittivity of free space a and A is the area of cross-section. The variation of ϵ_r with applied frequency is shown in figure 5.

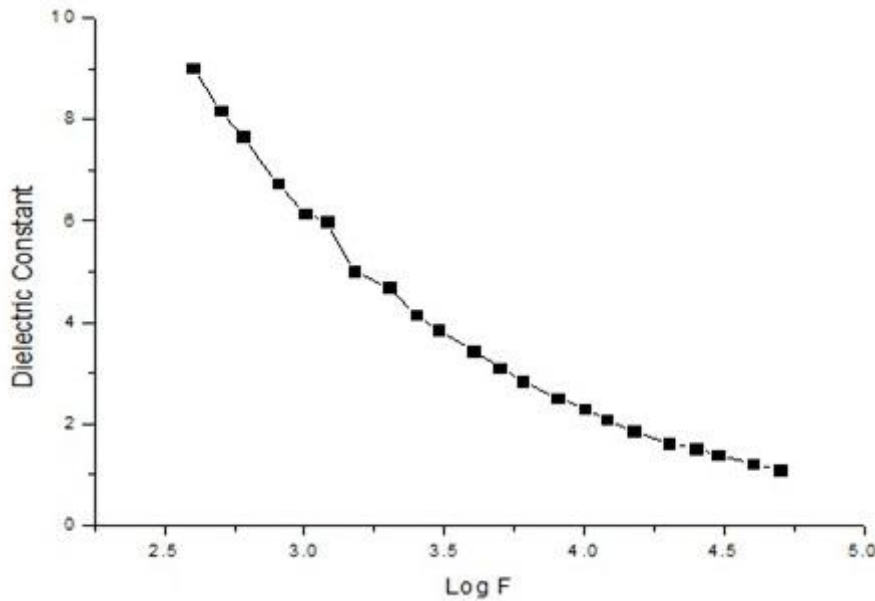


Figure 5: Dielectric constant Vs Log F graph

It is seen that the dielectric constant is high at low frequencies due to the predominance of electronic, ionic, dipolar and space charge polarization(10). However, the dielectric constant value decreases with an increase in frequency and attains a constant value at high-frequency region. This constant value being independent of frequency is

due to the fact that on the increasing frequency the polarisation mechanism is deactivated one after the other as they are unable to act in accordance with the change in electric field. At higher frequencies (Hz) electronic or interfacial polarization has a significant contribution. Further, figure 6 shows a dependence of dielectric loss on frequency.

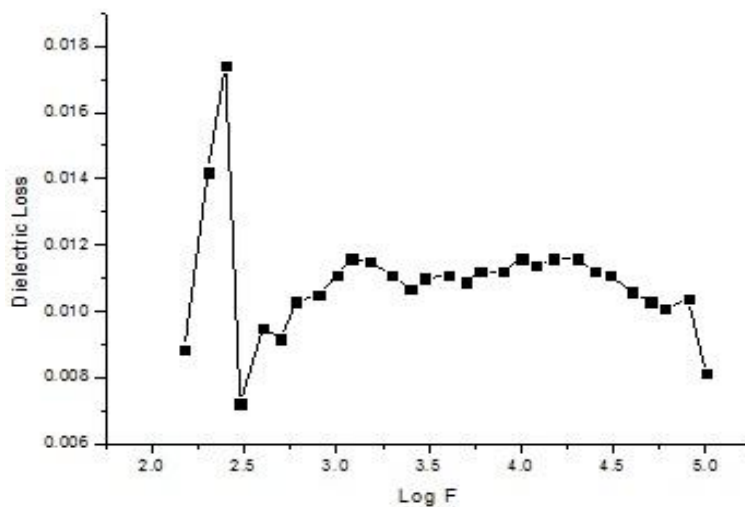


Figure 6: Dielectric loss Vs Log F

It is clear that dielectric loss also decreases with an increasing frequency similar to dielectric constant. The property of lower dielectric loss at higher frequency suggests that the grown crystal has a good optical quality with fewer defects. This parameter is of vital importance for NLO materials in their applications. The nature of decreasing of

dielectric constant and dielectric loss with frequency suggests that the grown crystal seems to contain dipoles of continuously varying relaxation times. As the dipoles of large relaxation times are not able to respond to the higher frequencies, the dielectric constant and dielectric loss are low. The materials which have lower dielectric constant and dielectric loss at

higher frequencies find important applications in the construction of electro-optic devices.

The σ_{AC} conductivity as a function of applied frequency was also measured using the relation:

$$\sigma_{AC} = \epsilon_r \epsilon_0 \omega \tan \delta$$

Where ϵ_0 and ω are permittivity of free space and the angular frequency ($\omega = 2\pi\nu$) of the applied field, respectively. The observed variation is shown in figure 7.

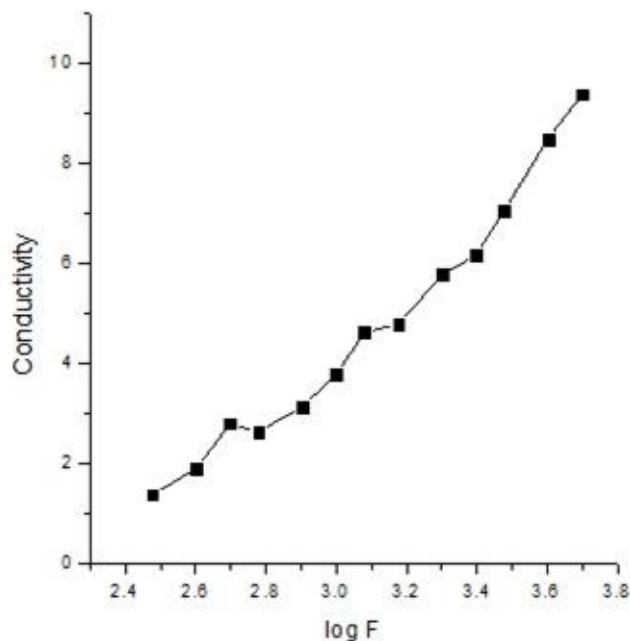


Figure 7: Conductivity Vs Log F graph

It is seen that the conductivity increases with increase in frequency. This nature is attributed to the reduction in the interfacial polarization at higher frequencies.

3.5. TGA-DSC Analysis:

In order to reveal the thermal properties of the L-Threonine doped Sodium Nitrate crystal TG analysis was carried out using a Perkin Elmer instrument. The TGA traces of L-Theronine doped sodium nitrate crystal is shown in figure 4.8.

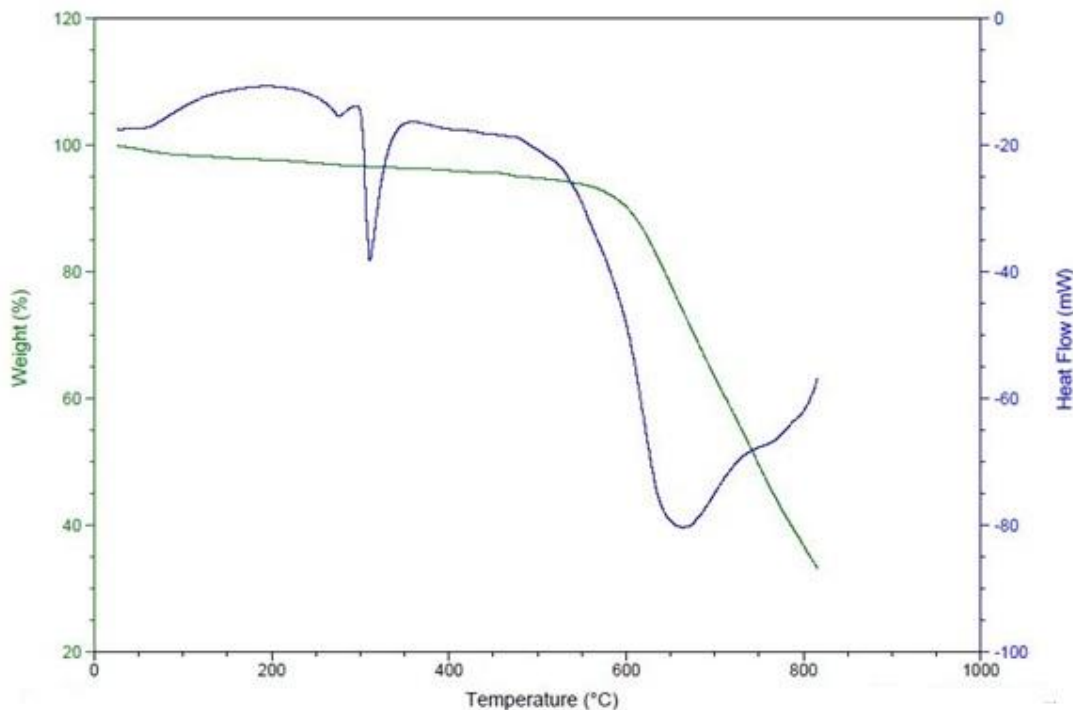


Figure 8: DSC-TGA Spectrum of LTSN crystal

The initial mass of the sample taken to carry out the experiment was 2.3930mg. Initially, 6% weight loss alone

occurred up to 550°C and the material starts to dissociate at 550°C - 600°C. The DSC spectrum shows that the crystal

starts to melt at 290°C and ends up to 325°C. From the Thermogravimetry it is confirmed that the melting point of NaNO₃ increased from 308°C to 550°C due to the inclusion of L-Threonine.

4. Conclusion

A new crystal of NaNO₃ doped with L-Threonine has been conventionally synthesized using slow evaporation technique by solution growth method. Functional groups identification of

the grown crystal is confirmed by FTIR analysis. Using Reitveld software along with the XRD measurements gives a clear cut view about the grown L-Threonine doped Sodium Nitrate crystals. The good optical quality of the grown crystal is confirmed by the observed transparency within the range 380-1100nm using UV-Vis-NIR spectrum. Thermal stability of the grown crystal confirms that the operating temperature of the grown crystal extended up to 600°C for device fabrications.

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