

Effect of L-threonine on the growth of sodium chloride crystals

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ABSTRACT

A new crystal with NLO behavior sodium chloride doped with L-Threonine is reported by growth and synthesis is reported. Characterization studies such as SHG, FTIR, Powder XRD, TGA-DSC, and UV-Vis-NIR are used to confirm the inclusion of L-Threonine. Optically transparent crystals were harvested by adopting solution growth slow evaporation technique. XRD pattern shows the occurred change in structure due to the dopant. Functional groups confirmation was done by FT-IR analysis. From the TGA-DSC studies, it was observed that the grown crystal thermal stability seems to be doubled on the inclusion of L-Threonine. Optical response of the grown material was confirmed using the UV spectra. Optical quality enhancement was confirmed with the dielectric studies.

1. Introduction

Non-Centro symmetric crystals find applications in non-linear optics (NLO), hence many research groups are currently involved in the growth of these new crystals and are exploring their behavior through various characterization techniques. The employability of organic single crystals in practical device applications has been impeded by their often inadequate transparency, poor optical quality, and low laser damage threshold. Hence, new frequency conversion materials primarily concentrated on organic NLO materials with high nonlinear susceptibilities are to be explored. Amino acids containing an amino (-NH₂) and the carboxylic acid (-COOH) functional group possess remarkable reactivity characteristics, due to which they can form several compounds in combination with inorganic and organic reagents. These crystalline materials possess excellent NLO properties(1-3). Wide transparency in the visible and UV region along with molecular chirality, zwitterionic nature of the molecules and high damage thresholds create an interest in nonlinear amino acids. L-threonine (C₄H₉NO₃), a promising polar amino acid with orthorhombic structure shows higher second harmonic generation (SHG) efficiency than other amino acids. Generating second harmonic frequency by means of NLO materials have a significant impact on laser technology, optical communication optical storage technology, and electro-optic modulation(4-6).

2. Experimental procedure

The 7.18g of NaCl was mixed with 0.2g 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 25 days with morphology 17 X 7 X 3 mm as shown in the figure. 1.



Figure.1: Photograph of L-Threonine doped Sodium Chloride crystal

3. Results and Discussion

3.1. X-ray diffraction studies

The Figure3.1 shows the powder X-rd pattern which gives the conformation about the grown L-Threonine doped sodium chloride crystal structure by the computer program.

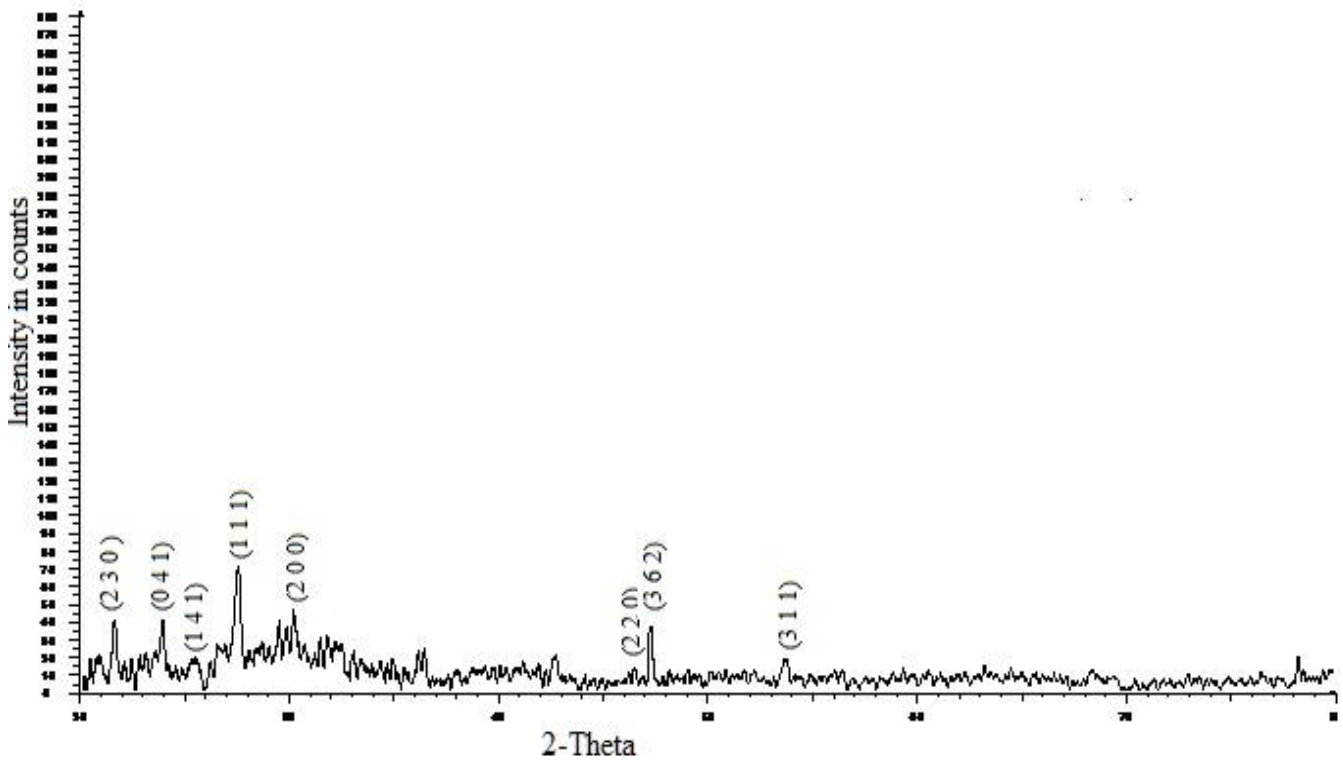


Figure.2 : Powder XRD spectrum

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.

47.677	362
54.077	311

Table.1: Powder XRD analysis

Position 2 θ	hkl
21.721	230
23.884	041
25.204	141
27.466	111
31.820	200
45.620	220

3.2. UV-Vis-NIR Spectral studies

The L-Threonine doped sodium chloride crystal plates with thickness 0.3cm 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.

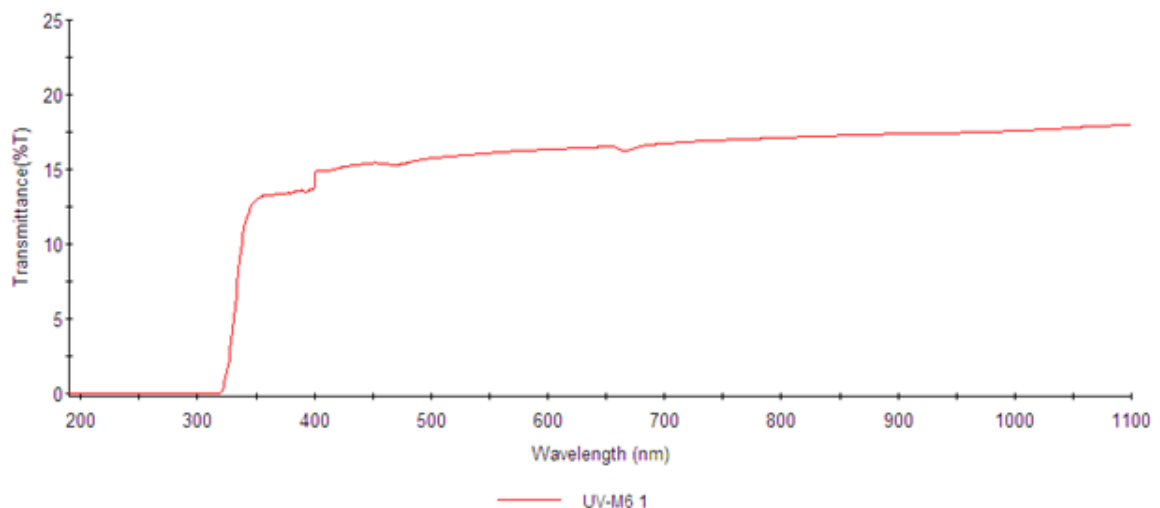


Figure .3: UV-Vis-NIR spectrum of L-Theronine doped sodium chloride crystal

It is seen that the grown L-Threonine doped sodium chloride is transparent between the wavelength range 390-1100nm. At 390nm it was observed that the UV transparency cutoff wavelength occurred. The complex forms of L-Threonine with sodium chloride 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 chloride crystals. This is

the most desirable property of materials possessing non-linear optical activity.

3.3. FTIR Spectral analysis

In order to qualitatively analyze the presence of functional groups in L-Threonine doped sodium chloride crystals, Fourier Transform Infrared Analysis (FTIR) spectrum is recorded in the range 400 to 4000 cm^{-1} using the Perkin Elmer spectrometer. The characteristic absorption peaks are shown in figure.4.

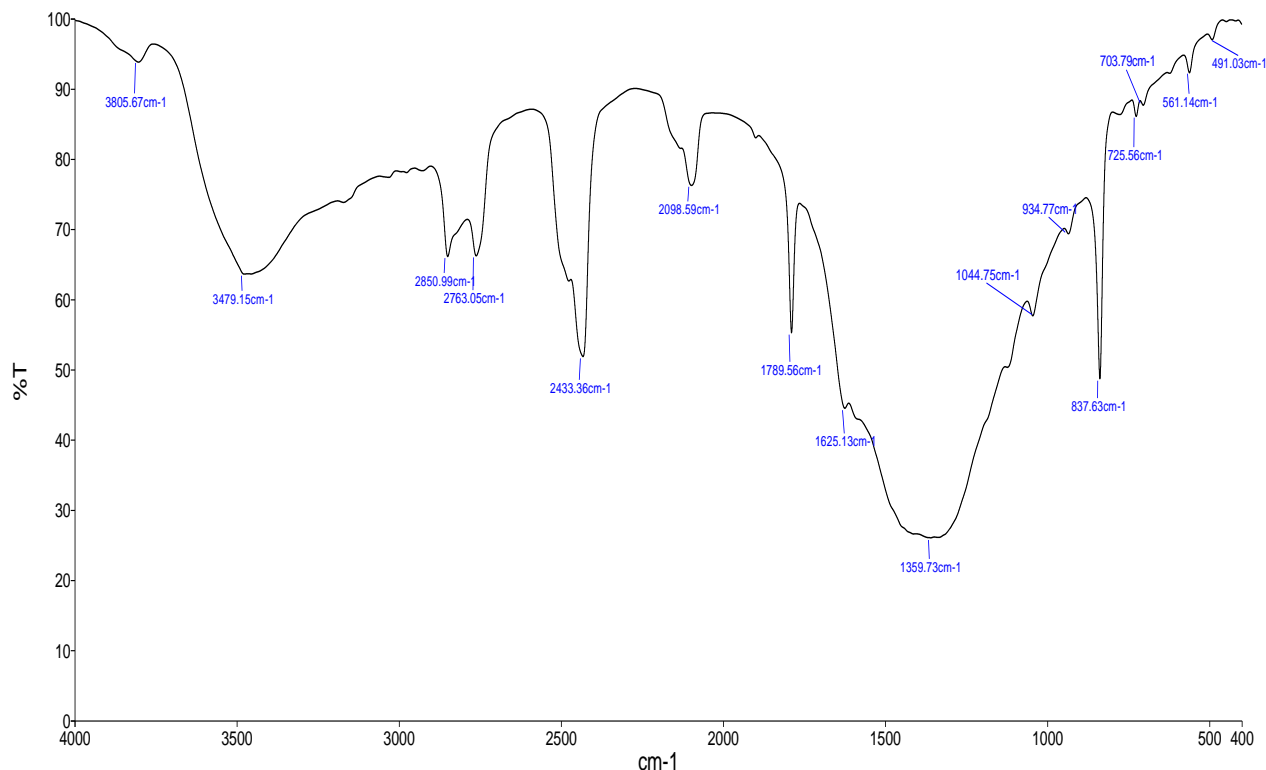


Figure.4 : FTIR spectrum for L-Theronine doped sodium chloride crystal

The observed FTIR frequencies	Assignments
3805	Asymmetric stretching of OH
3479	Symmetric stretching of OH
2850	C-H symmetric stretching
2763	C-H stretching
2433	COO ⁻ stretching
1789	C=O stretching
1625	C=O stretching
1359	NH ₃ bending

Table.2: FTIR frequencies and assignments

The peak at 3805cm^{-1} is due to the asymmetric stretching of OH. The symmetric stretching of OH is observed at 3479cm^{-1} . The peak at 2850cm^{-1} is due to the C-H symmetric stretching and 2763cm^{-1} is due to the C-H stretching. The peak corresponding to the region 2433cm^{-1} confirms the carboxylic acid group (COO⁻). The C=O stretching is observed at two bands is 1789 and 1625cm^{-1} . The strong peak at 1359cm^{-1} is assigned to NH₃ bending vibration. The presence of COO⁻ and NH₃ indicates the characteristics of amino acid group material(7-8). The predicted functional groups are found to be in good agreement with the available report.

3.4. Thermal analysis

In order to reveal the thermal properties of the L-Theronine doped Sodium Chloride crystal, TG analysis was carried out using a Perkin Elmer instrument. The TGA traces of L-Theronine doped sodium chloride crystal is shown in figure.5. The initial mass of the sample taken to carry out the experiment was 2.3930 mg. Initially, 8% weight loss has occurred at 92°C and the material starts to dissociate at 599°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 NaCl increased from 308°C to 550°C due to the inclusion of L-Theronine.

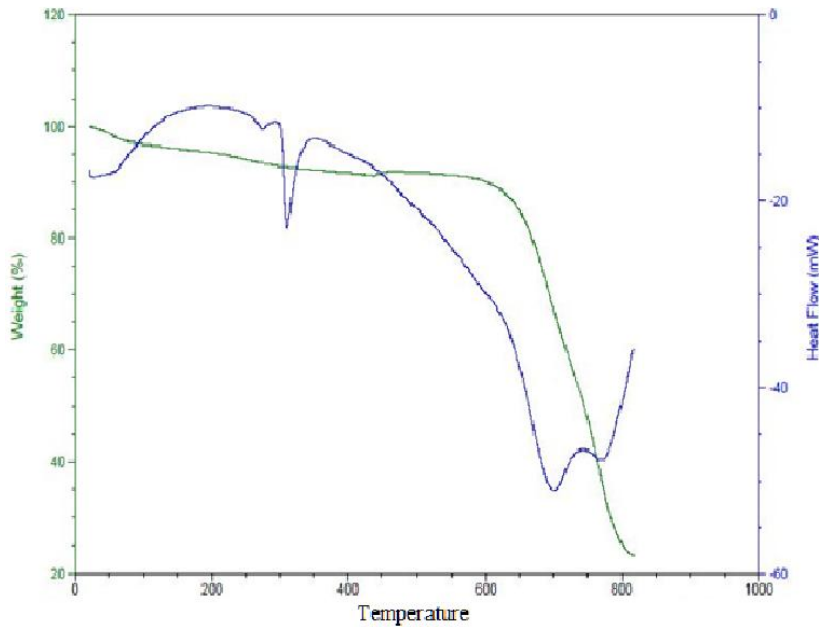


Figure.5: DSC-TGA Spectrum

3.5. Dielectric studies

The dielectric study on L- Theronine doped sodium chloride single crystal is carried out using HIOKI 3532 LCR HESTER. A sample with 0.3cm thickness having a silver coating on opposite faces is placed between the two copper electrodes and thus a parallel plate capacitor is formed. The capacitance of the sample was measured by varying the frequency from 50HZ to 200KHZ for room temperatures. The very high value of dielectric constant at low frequency may be attributed to space charge polarization. At the lower range of frequencies, dielectric constant decreases drastically with frequency, becoming a constant at of frequencies. The polarization occurs due to the local displacement of the electron, which is the electro of the electronic of the exchange of the number of ions in the crystal. As frequency increases the

electron exchange cannot follow the electric field and polarization becomes less dependent on frequency. Dielectric constant variation with temperature is generally attributed to the crystal expansion, orientation polarization, crystal defects and the presence of impurities. When temperature increases the dielectric constant decreases as evident from the figure. The thermal energy disrupts the ion-dipole interaction which is responsible for polarization at higher temperatures, causing the relaxation of polarization. Also, the dielectric loss is plotted against frequency and is shown in the figure. These curves suggest that the dielectric loss is strongly dependent on the frequency of the applied field, similar to that of dielectric loss is strongly dependent on the applied field frequency similar to that of dielectric constant(9-10). This behavior is common in the case of the ionic system.

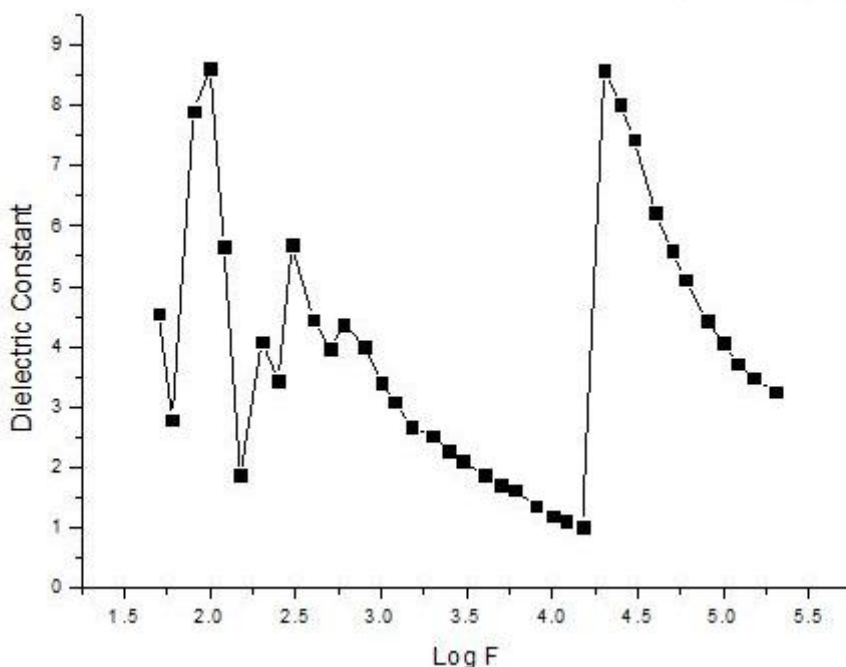


Figure .6: Dielectric constant vs Log F graph

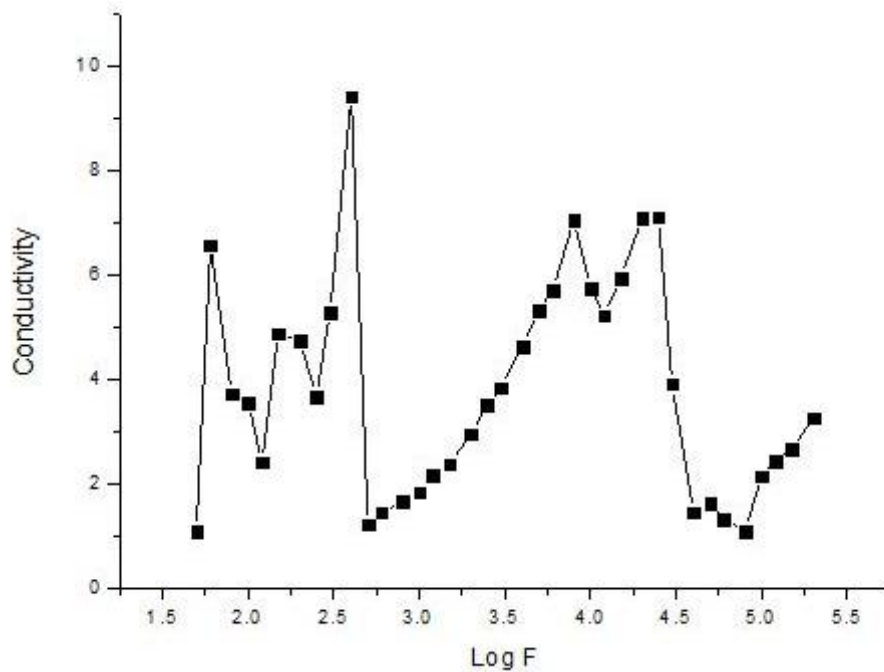


Figure .7: Conductivity vs Log F graph

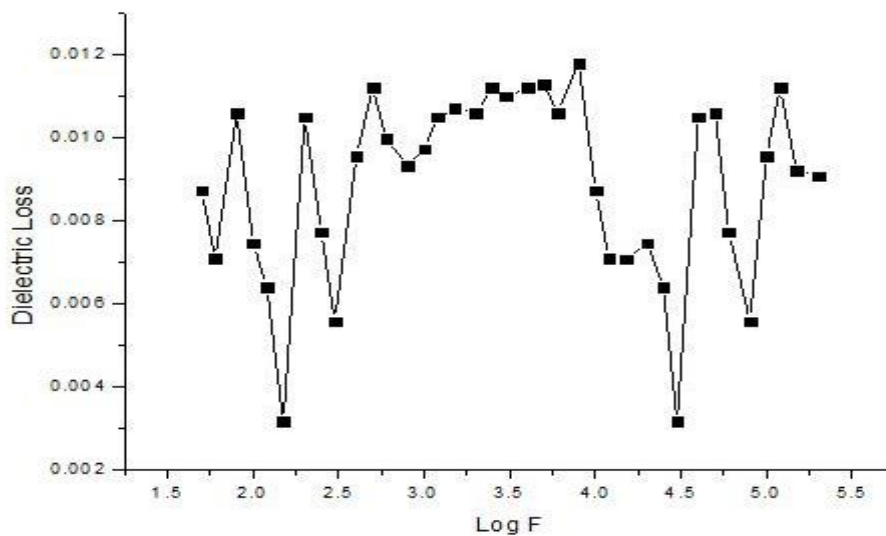


Figure .8: Dielectric Loss vs Log F graph

4. Conclusion

A new crystal of NaCl doped with L-Theronine 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-Theronine doped Sodium chloride crystals. The good optical quality of the grown crystal is

confirmed by the observed transparency within the range 390-1100nm 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. Optical quality enhancement of the grown crystal was confirmed due to the observed low dielectric constant at high-frequency region.

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