

Synthesis and characterization of Sodium salt of L-Cystine

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ABSTRACT

Nonlinear optical single crystals of sodium salt of L-Cystine have been grown by slow evaporation technique. Powder X-ray diffraction analysis has been carried out and the diffraction patterns have been indexed. Fourier transform infrared (FT-IR) analysis confirms the various functional groups present in the grown crystal. The thermal behavior of the grown crystal was investigated by DSC and TGA analysis. The optical properties of the crystal were determined by UV-Visible transmittance spectrum.

1. Introduction

In the last decade, extensive studies have been made on the synthesis and crystal growth of NLO materials because of their potential applications in the field of telecommunication, optical signal processing, laser fusion reactions, color display, etc[1-3]. These applications depend upon the various properties of materials such as transparency, refractive index, birefringence, dielectric constant, thermal, photochemical and chemical stability. Organic chemicals have large nonlinear susceptibilities compared to inorganic crystals. However these crystals have certain limitations such as increased optical absorption, narrow transparency window and poor mechanical and thermal studies [4, 5]. Inorganic materials have excellent mechanical and thermal properties but these materials have lack of π electron delocalization [6-8]. Combining the high optical nonlinearity and chemical flexibility of organics with thermal stability of in organics, semi organic materials have been proposed and attracting great deal of attention in the field of nonlinear optics [9]. Amino acids are the interesting materials for NLO application as they contain proton donor carboxyl acid (COOH) group and the proton acceptor amino (NH₂) group. Crystals of amino acids and their complexes are considered to be high potential for NLO application [10-13].

L- cystine is a sulphur containing amino acid. Functional groups such as NH₂ and COOH have a strong tendency to coordinate with inorganic cations and metals [14-16].

2. Experimental

2.1. Synthesis

Sodium salt of L-cystine is synthesized using L-Cystine and hydrochloric acid (AR Merck grade) which are mixed in the stoichiometric ratio of 1:1 in deionised water. The calculated amount of L-cystine was dissolved in deionised water. The mixture of the solution is cloudy and hydrochloric acid solution was added and stirred well for 12 hours till a clear solution was obtained. To the clear solution sodium chloride was added and

stirred well to get the homogenous solution. Then the clear solution was filtered using Whatmann filter paper in clean vessels containing the solution were closed with polythene sheets and maintained in the constant temperature bath 30°C. Optically transparent single crystals were obtained after 25 days and the harvested crystals are shown in **Fig.1**.



Fig. 1 Morphology of sodium salt of L-cystine

2.2. Measurements

Powder X-ray diffraction studies of L-cystine hydrochloride and sodium salt of L-cystine crystal were carried out on a Siemens D500 X-ray diffractometer with Cu K α ($k=1.5418$ Å) radiation. The samples were scanned for 2θ values from 10 to 60° at a rate of 2°min⁻¹. The infrared spectra of L-cystine hydrochloride and sodium salt of L-cystine crystal were obtained from potassium bromide pellets technique using MAKE-BRUKER Optic GmbH MODEL No-TENSOR 27 SOFTWARE-OPUS version 6.5 Spectrophotometer in the range of 4,000-400

cm^{-1} . The UV-Vis-NIR spectra were recorded on a Jasco spectrophotometer in the range of 200-00 nm with scanning speed of 400nm min^{-1} . Differential Scanning Calorimetric analysis (DSC) and Thermo Gravimetric Analysis (TGA) were carried out simultaneously on a thermal analysis instruments SDTQ600 v 20.9 Build 20. A small piece of crystals weighing 4.5020mg of L-Cystine hydrochloride and 3.8220mg of sodium salt of L-Cystine used for this investigation. The samples were heated at a rate of $10^\circ\text{C min}^{-1}$ in protected inert nitrogen atmosphere.

3. Results and Discussion

3.1. Fourier Transform Infrared Analysis (FT-IR)

The functional groups in the grown crystals have been identified by means of FT-IR spectral analysis using

spectrometer. The FT-IR spectrum of single crystals of L-cystine hydrochloride [5] and Sodium salt of L-cystine was recorded in the range of $400\text{-}4000\text{cm}^{-1}$ and the recorded spectrum is shown in Fig.2. The NH_3^+ stretching vibration of sodium salt of L-Cystine assigned at 3385.94cm^{-1} . The bands located at 2884.58 and 2887.83cm^{-1} were attributed to $-\text{CH}$ stretching of methyl group in sodium salt of L-cystine and L-cystine hydrochloride. The sharp and strong band at 1725.65cm^{-1} and 1774.82 indicates the $>\text{C}=\text{O}$ stretching of sodium salt of L-cystine and L-cystine hydrochloride. The increase in wave number of sodium salt of L-cystine indicates the inclusion of sodium in the crystal. The added sodium ion in L-Cystine enhance the polarity of $>\text{COO}^-$ and hence greater energy required for the stretching of $>\text{C}=\text{O}$ group. The C-C stretching vibration appears between 1136.71cm^{-1} . The $-\text{CN}$ and $>\text{COO}^-$ the stretching of sodium salt of L-cystine is observed at 1041.65cm^{-1} and 1433.39cm^{-1} .

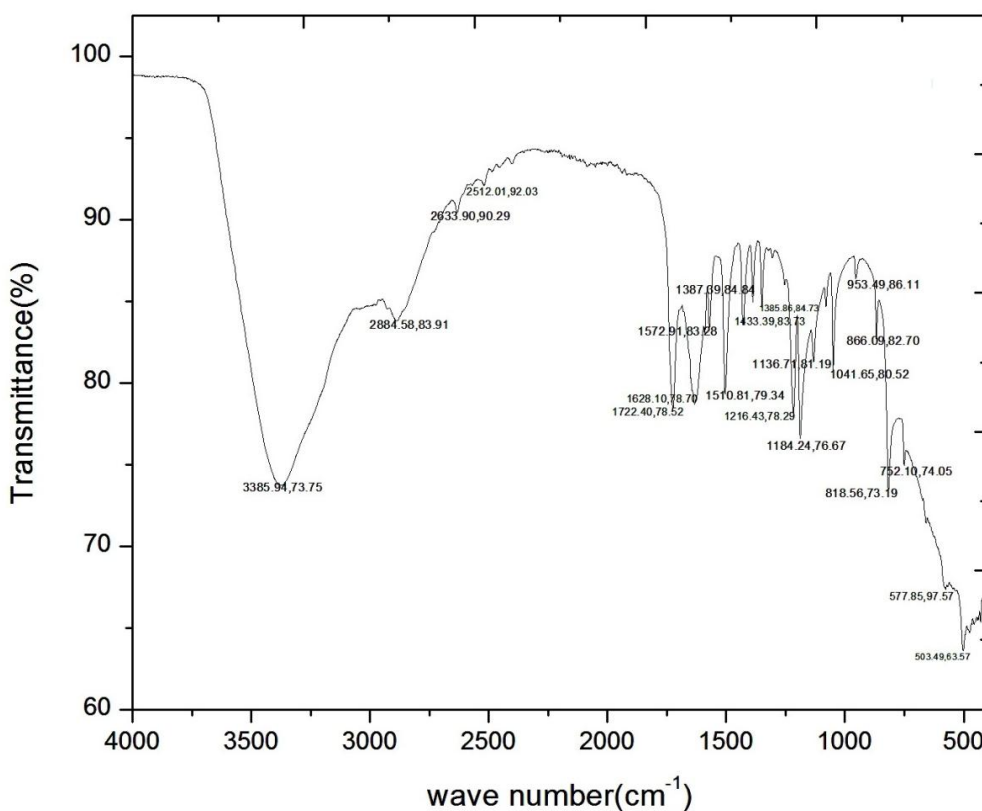


Fig. 2 FTIR spectrum of sodium salt of L-cystine

3.2. Thermal Studies

The TGA and DSC analysis of L-Cystine hydrochloride and sodium salt of L-Cystine are carried out between 0°C and 1000°C in the nitrogen atmosphere with a heating rate of 10°C per minute using Perkin Elmer, US, TGA Analyzer. The TG-DSC curve is shown in Fig.4. A small piece of crystals weighing 4.5020mg of L-Cystine hydrochloride and 3.8220mg of sodium salt of L-cystine used for this investigation. There are two sharp and one broad endothermic peak at 250°C , 350°C which corresponds to the major weight loss of sodium salt of L-Cystine (97.5%). The sharpness of these endothermic peaks shows good degree of crystalline of the grown crystal. This

endothermic peak indicates the complete decomposition of the entire compound in this temperature range 0°C and 1000°C . From the TG curve it is inferred that the decomposition of L-cystine hydrochloride and sodium salt of L-cystine starts at 225°C . The weight loss pattern of sodium salt of L-cystine is slightly different from the parent compound. The decomposition of sodium salt of L-cystine ends 1000°C and L-cystine hydrochloride ends at 846°C . There are endothermic peaks in sodium salt of L-cystine but in the case of L-cystine hydrochloride is only two. This indicates the incorporation of sodium in the crystal structure of L-cystine. **Fig.3**

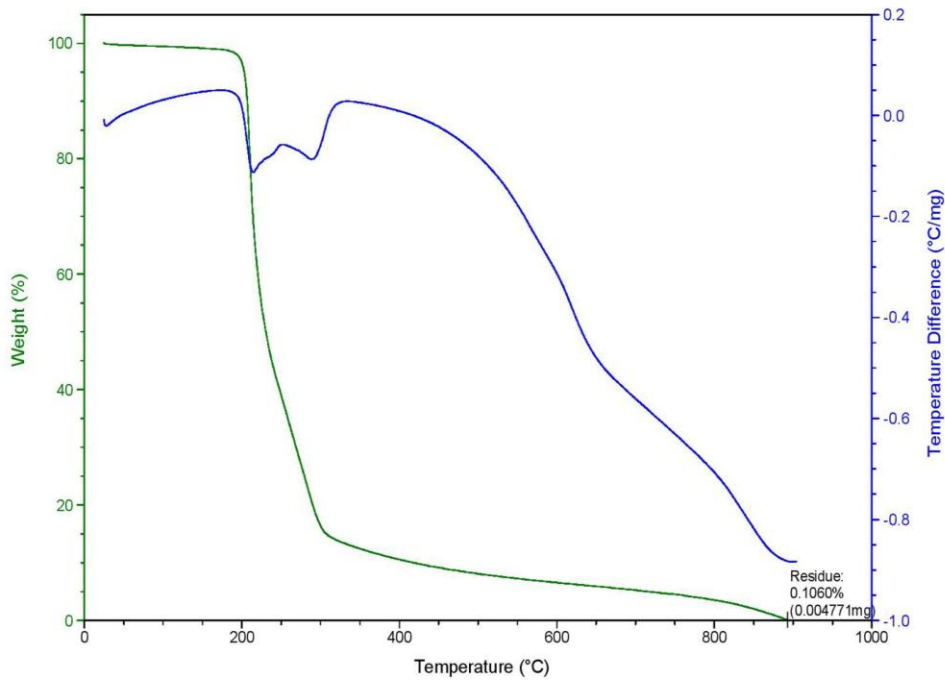


Fig. 3 TG-DSC of sodium salt of L-cystine

3.3 XRD analysis

The grown crystal was subjected to powder X-ray diffraction studies to analyze the crystalline nature. The lattice parameters are evaluated as $a=b=c=5.62\text{\AA}$ and $\alpha=\beta=\gamma=90$. Two peaks 22.624 and 24.261 does not match with the reported values. (111),(200),(222),(400) and (420) peaks confirms the inclusion of sodium. Fig.4

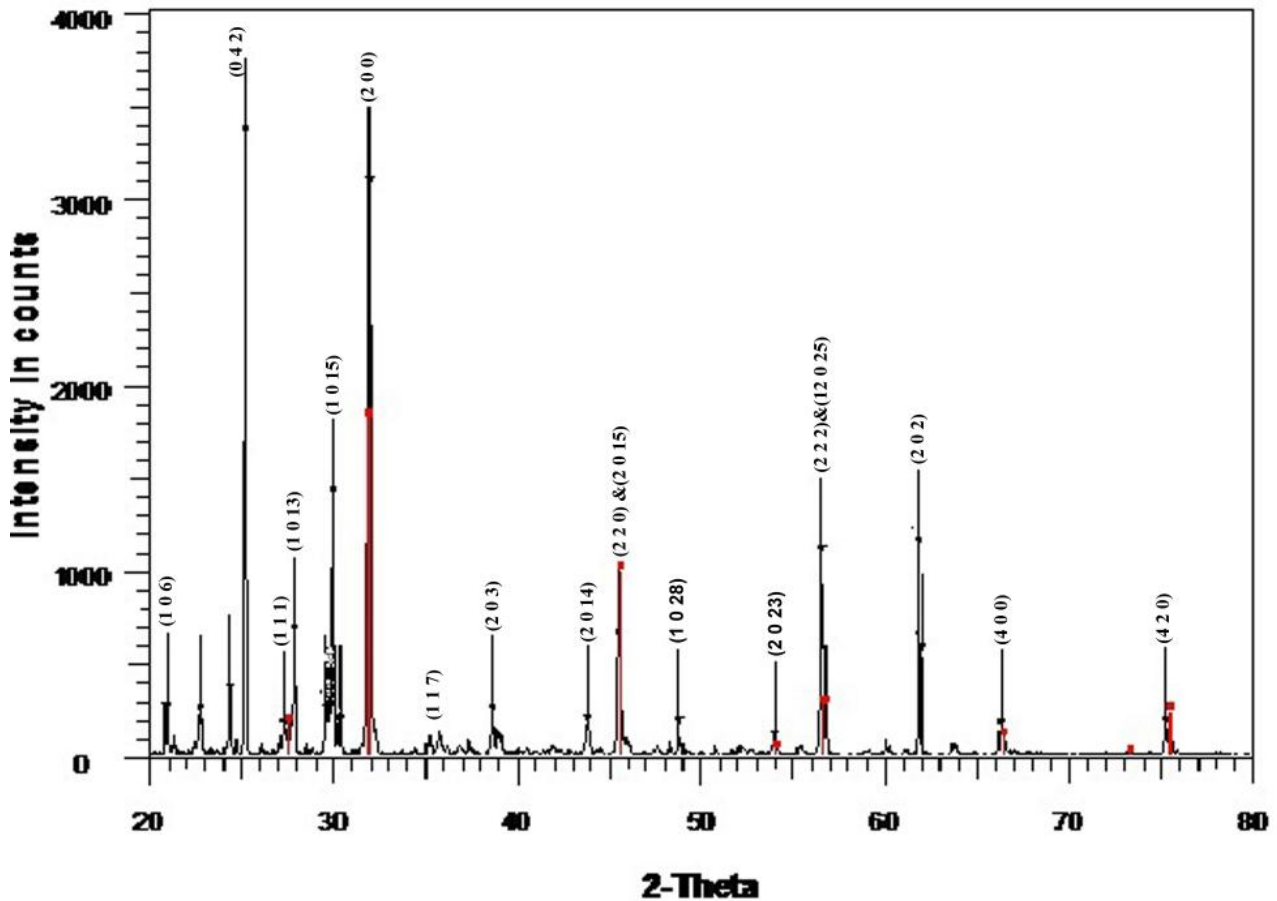


Fig. 4 X-ray diffraction pattern of sodium salt of L-cystine

3.4 UV Spectral Analysis

Confirmation of optical activeness of the grown crystal was determined by using the UV-Visible spectral analysis. From the figure it was found to be noted that the lower cut-off wavelength of the sodium salt of L-cystine is 206.14nm. This absorption

maximum at 206.14nm belongs to the π - π^* electronic transition shows the presence of resonance hybrid of carboxyl group. It is observed from the spectrum that the grown crystal is transparent in the entire visible region and the absorption takes place in the UV region ranges between 150-400nm. **Fig.5**

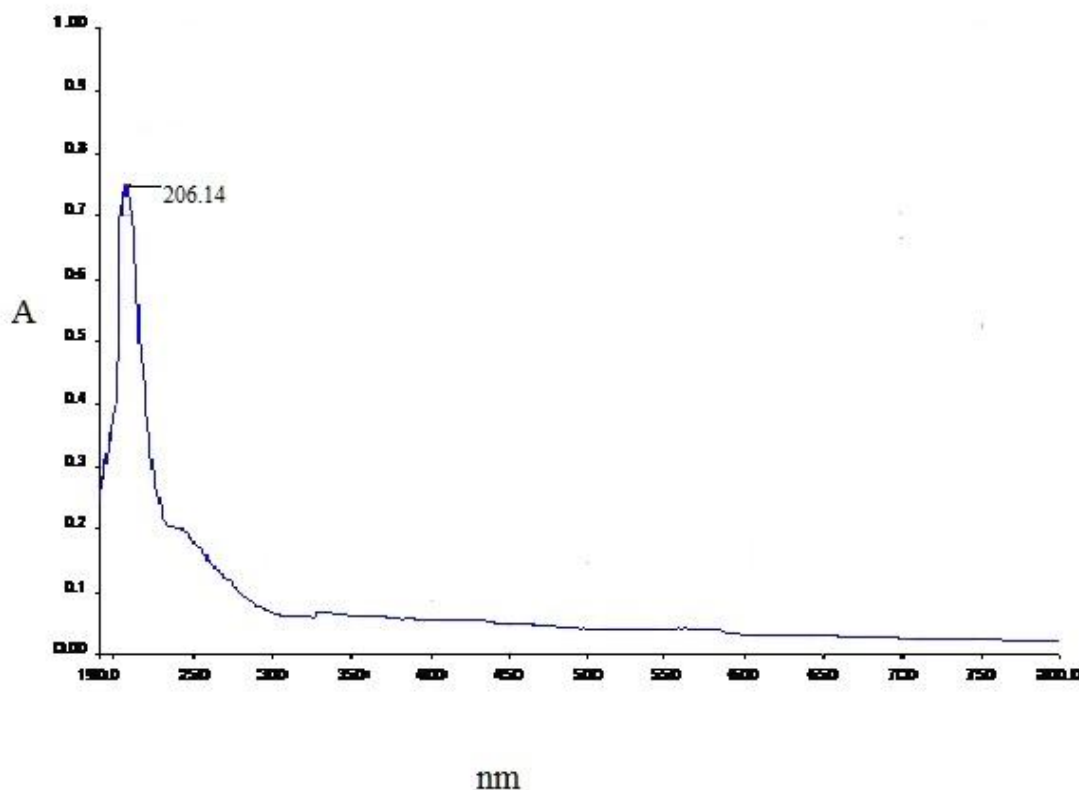


Fig. 5 UV-Visible spectrum of sodium salt of L-cystine

3.5 NLO Studies

The study of NLO efficiency was carried out using the modified experimental set up of Kurtz and Perry [17]. A Q-switched Nd:YAG laser beam of wavelength 1064 with input power of 2.8mj and pulse width of 8 ns with repetition rate of 10Hz was used. The SHG generated by the randomly oriented micro crystals was focused by a lens and detected by a photomultiplier tube. The generation of the SHG was confirmed by a strong bright green emission emerging from the powdered crystal. A KDP crystal was used as a reference material in the measurement. It is observed that the conversion efficiency of sodium salt of L-cystine is greater than that of L-cystine hydrochloride.

4. Conclusion

Bulk sized sodium salt of L-cystine single crystals were grown by slow evaporation technique. Powder XRD confirms the lattice parameter. UV-Vis-NIR and FT-IR studies revealed the transmittance range and the functional groups for the given material. The TG-DSC analysis depicted that the crystal is thermally stable up to 200°C. The NLO property of the grown crystal of sodium salt of L-cystine was examined by performing Kurtz Powder test using Nd:YAG laser. The SHG efficiency of sodium salt of L-cystine is greater than that of L-cystine.

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