J Therm Anal Calorim (2011) 104:875–878
DOI 10.1007/s10973-011-1300-8

Growth and characterization of cinnamic acid–urea single crystal

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CTAS2010 Conference Special Chapter

Abstract A single crystal of cinnamic acid–urea was grown by slow evaporation of methanol solution at room temperature. In this research, many analytical methods such as FTIR, second harmonic generation, NMR, and TG–DTA were used. The presence of title compound in the crystal lattice has been qualitatively determined by FTIR analysis. Thermal stability of the grown crystals was evaluated by TG-DTA. Incorporation of urea increases the thermal stability insuring the suitability of material for possible non-linear optical application up to 180 °C.

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Keywords Cinnamic acid-urea single crystal · FTIR · TG · DTA · SHG · NMR

Introduction

Thermal and spectral analyses are very useful techniques for materials characterization. Therefore, many investigators have used these techniques for various materials characterization [1–14]. Cinnamic acid (3-phenyl-2-propeonic acid), a derivative of phenyl alanine, composes a relatively large family of organic isomers [15–18]. Derivatives of cinnamic acid are important pharmaceutics for high blood pressure and stroke prevention and possess antitumour activity [19]. In nature, cinnamic acid derivatives are important metabolic building blocks in the production of lignins for higher plants. Cinnamic acid possesses antibacterial, antifungal, and parasite fighting abilities. Cinnamic acid derivatives and flavonoids in wine create pigments and tannin agents that give each vintage its characteristic bouquet and color. Cinnamic acid extensively studies not only due to its important biological activity but also because of its specific structure. The carboxylic group is separated from the aromatic ring by a double bond in the spectrum of cinnamic acid. It causes conjugation between the C=C and the π electron system. It is very interesting to compare the electronic structures of cinnamic acid and the structures of cinnamic acid-urea single crystal.

Experimental

Synthesis

The cinnamic acid–urea single crystals were prepared by digesting appropriate weighed amount of cinnamic acid in methanol of urea in stoichiometric ratio of 2:1. Then methanol was evaporated in a dryer.

Measurements

The FT–IR spectra were recorded with a Bruker IFS spectrometer in the range of 400–4000 cm^{-1}. Samples in the solid state were measured in KBr matrix pellets which were obtained with hydraulic press under 739 MPa. Powder diffraction of the crystal was done on a Brukker AXS D8 advance X-ray diffractometer. For this, well developed crystals devoid of major inclusions were ground to fine powder and were scanned in the 2θ range of 10°–180° under Cu-Kα radiations. The proton NMR spectrum was recorded for the crystal using JOEL/GSX 400 NB FT/NMR spectrometer, 500 MHz. Thermograms were traced simultaneously on a Perkin Elmer Pyres Diamond TG-DTA analyzer. A sample of 15 mg was used initially and thermal analysis was carried out from room temperature to 1300 °C at a heating rate of 10 K/min in the atmosphere of nitrogen gas.

Results and discussion

Sample preparation

The metal compounds were prepared by digesting appropriate weighed amount of cinnamic acid in methanol of cinnamic acid-urea in stoichiometric ratio of 2:1. Then methanol was evaporated in a dryer. The results of elemental analysis are as follows; for cinnamic acid-urea C = 70% and H = 5%.

UV spectral analysis

The UV spectrum for cinnamic acid urea is shown in Fig. 1. In cinnamic acid urea single crystal, the $\pi - \pi^*$ absorption band shifted to lower wavelength compared to cinnamic acid [20]. This is because of the formation of covalent bond between cinnamic acid with urea, thus greater energy required for this transition and hence the absorption shows the blue end of the spectrum.

FTIR spectral characterization

The FTIR spectrum recorded for the crystal is presented in Fig. 2. Spectral bands are interpreted and compared with known data for related compounds in literature [21]. Table 1 indicates the frequencies assigned to various vibrations of the title compound. It is obvious that the band assignments are in conformity with the structure of the proposed compound. The symmetric stretching of –OH group is revealed by the broad band centered around 3,451 cm^{-1}. Bands at wave numbers 1554.11 and 1413.96 cm^{-1} are attributed to antisymmetric and symmetric stretching modes, respectively of carboxylate group. Stretching of the carboxyl groups (cinnamic acid and urea) is revealed by the bands at 1810.22 and 1630.80 cm^{-1}. The band observed with wave number of 1073.53 cm^{-1} in the IR spectrum is due to N–C–N stretching vibration of urea and cinnamic acid–urea single crystal. The C–H group δ (C–H) (δ bending) band was found in cinnamic acid–urea mixed crystal with wave numbers 1216.31 and 1312.08 cm^{-1} in the IR spectrum. In high wave number region, the stretching vibrations of NH_3 and C–H structures were observed at wave numbers 2360.79 and 252622 cm^{-1} in the IR spectra. From the above functional group analysis of FTIR, the compound cinnamic acid–urea single crystal was identified.

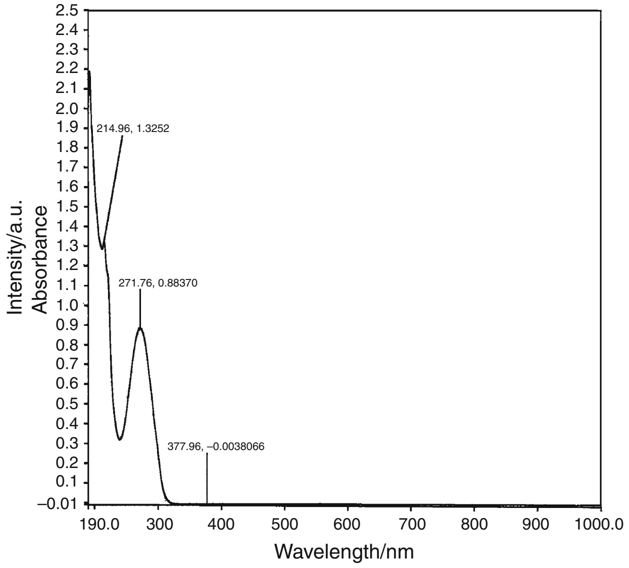

Fig. 1 UV spectrum of cinnamic acid–urea single crystal

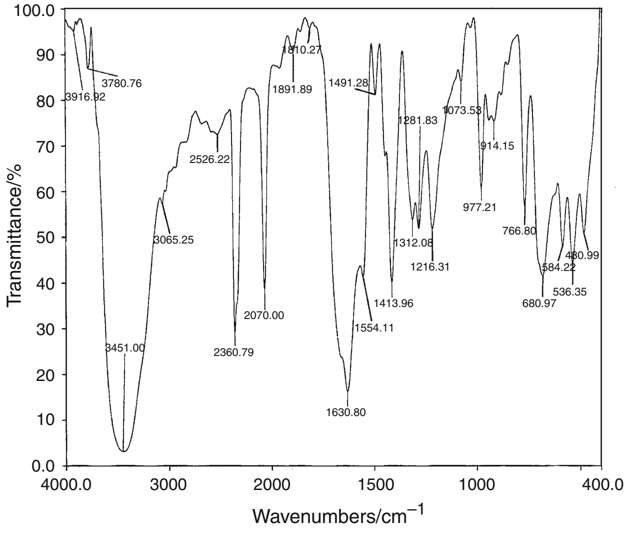

Fig. 2 FTIR spectrum of cinnamic acid–urea single crystal

Table 1 Spectral assignment of the FTIR peaks

Wave number/cm^{-1}	Assignment
3451.10	γ_{s}OH
2526.24	γ_{s}CH
2360.79	γ_{s}NH
1810.22	γ_{as}CO
1630.80	γ_{s}CO
1544.11	γ_{as}COO
1413.96	γ_{s}COO
1312.08	δCH
1216.31	δCH
1073.53	γ_{s}N–C–N

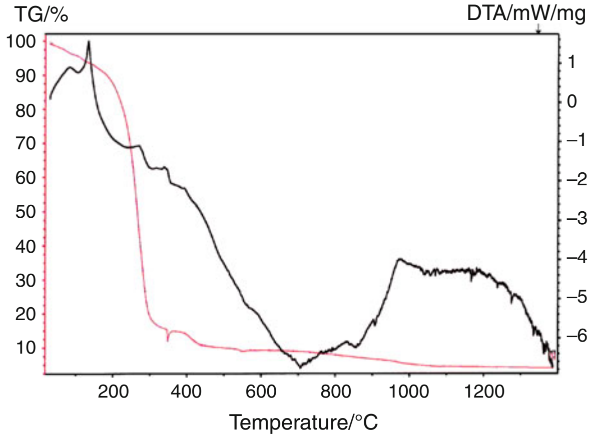

Fig. 3 TG–DTA curves of cinnamic acid–urea single crystal

Thermal analysis

The single crystal of cinnamic acid–urea was subjected to simultaneous thermogravimetric analysis–differential thermal analysis on a Netzsch STA 409C thermal analyzer in the nitrogen atmosphere. The samples were heated between 30 and 1300 °C at a heating rate of 10°K/min to study the mass loss and thermal stability.

The TG and DTA curves for cinnamic acid–urea crystal are shown in Fig. 3. The TG and DTA curves of that complex indicate three mass loss steps between 100–300 °C, 300–600 °C, and 600–1000 °C.

The DTA curve of grown crystal (Fig. 3) displays three exothermic peaks maximized at 140, 350, and 950 °C corresponding to the three mass loss steps, respectively. The thermal analysis results indicate that incorporation of urea increase the thermal stability insuring the suitability of material for possible non-linear optical (NLO) application up to 180 °C.

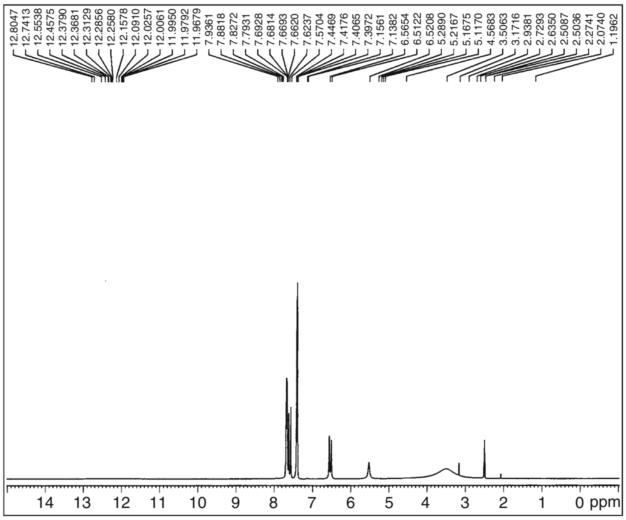

Fig. 4 NMR spectrum of Cinnamic acid–urea single crystal

NMR studies

The proton NMR spectrum or as the recorded for the crystal dissolved in deutrated (D_2O) using JOEL/GSX 400 NB FT/NMR spectrometer, 500 MHz. The C–H carbon adjacent to phenyl group shows its signal at 6.5654 ppm. The multiplet at 7.66–7.69 ppm is assigned to phenyl group. The signal at 5.5 ppm is assigned to =CH in cinnamic acid. The carboxyl proton signal is not shown in the spectrum because COOH exchanges its proton with solvent (Fig. 4).

X-ray diffraction

Single crystal X-ray diffraction (XRD) analysis for the grown crystals has been carried out to confirm the crystallinity and also to identify the lattice parameters using Enraf-Nonius CAD4 automatic X-ray diffractometer. The calculated lattice parameter values are $a = 7.9746$, $b = 8.9361$, and $c = 5.7140$ and the crystal belongs to orthorhombic structure. The XRD results are in good agreement with the repeated values and thus confirm the grown crystal [12].

Second harmonic generation (SHG) efficiency

An Nd:YAG laser with modulated radiation of 1064 nm was used as the optical source and directed on the powder sample through a filter. The doubling frequency was confirmed by the green radiation of 532 nm. Input radiation is 5.35 mj/pulse. Interestingly second harmonic generation gives an indication of NLO efficiency of the material. Nonlinearity is facilitated in the presence of urea. The dopant has catalytic effect on the NLO properties of cinnamic acid crystals. It is interesting to observe that the SHG efficiency is more pronounced in the presence of urea in the growth medium. It appears that the attainment of second order effects requiring favorable alignment of the molecule within the crystal structure is well facilitated in the presence of urea.

Conclusions

Optical quality single crystals of cinnamic acid-urea were grown by slow evaporation technique at room temperature. The solubility of cinnamic acid–urea single crystal has been determined in methanol. Functional groups present in cinnamic acid–urea crystals are confirmed by FTIR analysis. These crystals are thermally stable up to 180 °C. The powder XRD pattern reveals the strong crystalline nature of the sample. X-ray analysis for the exact determination of the structure is in progress.

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