

# Growth and characterization of mercury cinnamate single crystal

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**Abstract** Single crystals of mercury cinnamate were grown by slow evaporation of methanol solution at room temperature. The effect of mercury on the electronic structure of cinnamic acid was studied. The grown mercury cinnamate single crystals were characterized by UV, FTIR and TG-DTA. TG curve of mercury cinnamate exhibits higher thermal stability compared with cinnamic acid which was also confirmed by DTA curve. The spectroscopic studies give evidences of the distribution of the electronic charge in molecule, the delocalisation of  $\pi$  electrons and the reactivity of metal complexes. The Second harmonic generation efficiency is more pronounced in the presence of mercury dopant in the growth medium.

**Keywords** Solution growth · Mercury cinnamate single crystal · TG-DTA · UV · FTIR

## Introduction

Cinnamic acid (Fig. 1), a derivative of phenyl alanine, is part of a relatively large family of organic isomers [1–4]. Thermal and spectral analyses are very useful techniques for materials characterization. Therefore, many authors have used these techniques for various materials characterization [5–18]. Cinnamic acid has been extensively studied 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 structure of cinnamic acid. It causes conjugation between the C=C and the  $\pi$  electron system. It is very interesting to compare the electronic structures of cinnamic acid and the structures of mercury cinnamate single crystal. Literature survey shows that benzoic-cinnamic acid, ortho-ethoxy-trans-cinnamic acid, 3-bromo-trans-cinnamic acid and cinnamic acid and alkali metal cinnamate compounds have been studied but there is no reference in literature regarding the study of mercury cinnamate. This article reports the synthesis and characterization of mercury cinnamate using UV and FTIR spectral and TG and DTA studies. A detailed structural analysis of the compound is under progress.

## Experimental

### Synthesis

The metal compound was prepared by digesting appropriate weighed amount of cinnamic acid in methanol of mercuric

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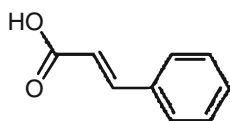
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**Fig. 1** Cinnamic acid (3-phenyl-2-propenoic acid)



chloride in stoichiometric ratio of 1:1. Then methanol was evaporated in a dryer. The results of elemental analysis are in good agreement with theoretical expectation.

### Measurements

The IR spectra were recorded with a Bruker IFS spectrometer in the range of 400–4000  $\text{cm}^{-1}$ . Samples in the solid state were measured in KBr matrix pellets which were obtained with hydraulic press under 739 MPa. The UV absorption spectra were recorded using double beam UV spectrometer in the spectral range 100–400 nm.

The thermogravimetric and differential thermal analyses were carried out on a Netzsch STA 409C thermal analyser in the nitrogen atmosphere. The sample was heated between 30 and 800  $^{\circ}\text{C}$  at a heating rate of 10  $^{\circ}\text{C}/\text{minute}$ .

## Results and discussion

### FTIR spectral studies

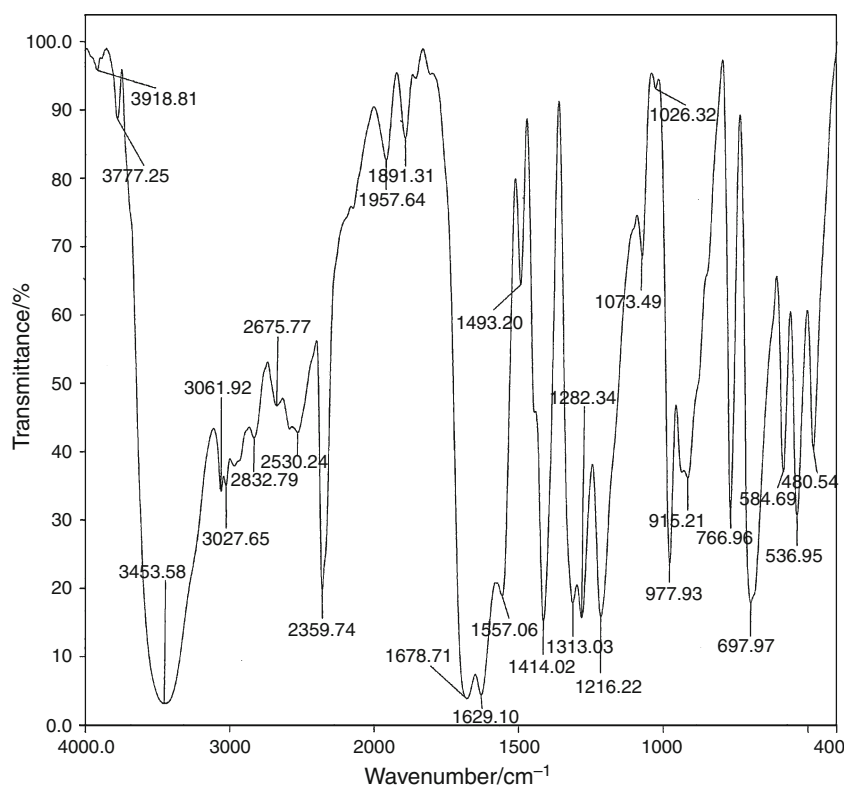
The FTIR spectra of cinnamic acid and mercury cinnamate are presented in Figs. 2 and 3. In the region of  $-\text{OH}$

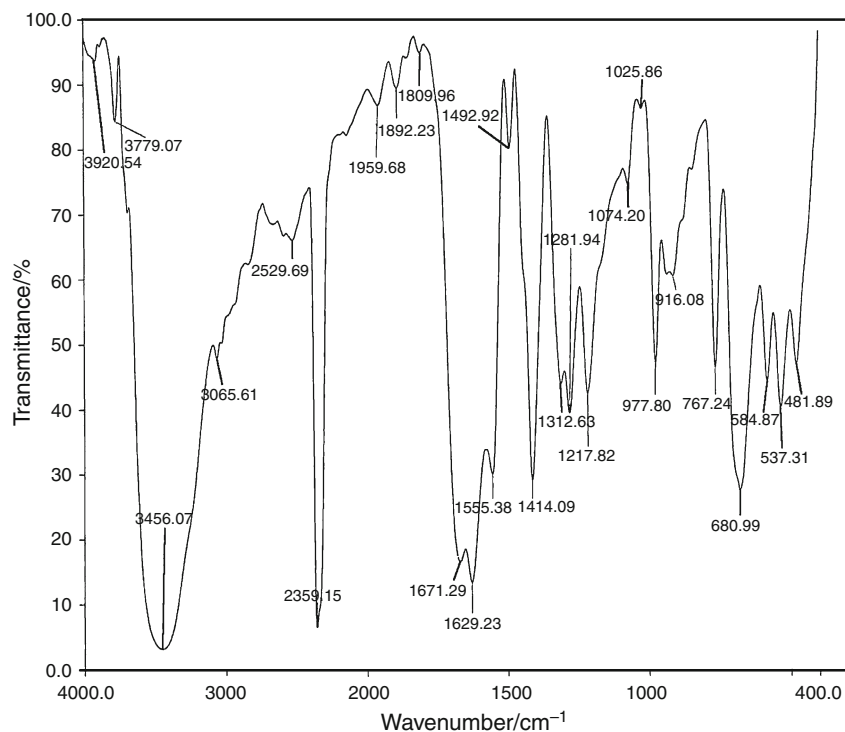
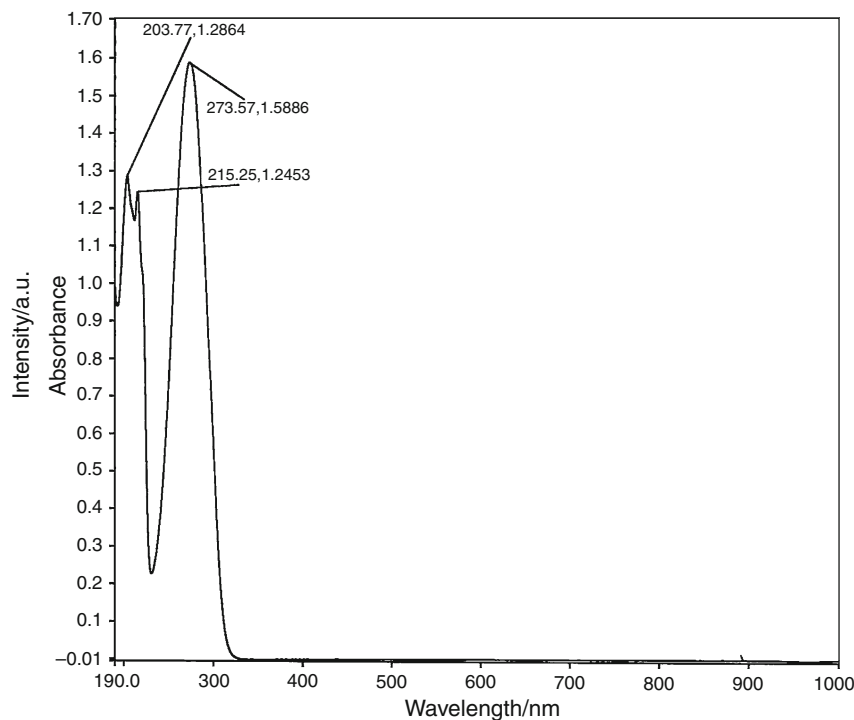
stretching vibrations there is an intense band occurs at 3456.07  $\text{cm}^{-1}$  in mercury cinnamate and broad bands in the range 2359–2529  $\text{cm}^{-1}$  assigned to the  $-\text{OH}$  stretching vibrations of acid dimers. In this range there are as well as the bands of the  $-\text{CH}$  stretching vibrations, what is seen in Figs. 2 and 3. In the infrared spectra of mercury cinnamate there are splitting bands assigned to the stretching vibrations of the  $\text{C}=\text{O}$  group (i.e., 1892.23, 1671.29 and 1629.23, 1809.96  $\text{cm}^{-1}$ ). This indicates the existence of different types of molecular packing and cinnamic acid with the intermolecular packing and associates cinnamic acid with intermolecular hydrogen bonds  $\text{C}=\text{O}\cdots\text{H}-\text{O}$ . Replacement of the carboxylic group hydrogen with a metal ion causes a break down of the intermolecular hydrogen bonding and the characteristic changes in the IR spectra of acid appeared. Namely the disappearance of bands which originate from stretching  $\nu_{\text{OH}}$  vibration an appearance of bands of the asymmetric and symmetric vibration of the carboxylate anion  $\nu_{\text{as}}(\text{COO}^-)$  shifted towards wave numbers along the series (cinnamic acid  $\rightarrow$  mercury cinnamate) in IR spectra. This indicates the formation of mercury cinnamate.

### UV spectral analysis

The UV spectra for cinnamic acid and mercury cinnamate are shown in Figs. 4 and 5.

**Fig. 2** FTIR spectrum of cinnamic acid



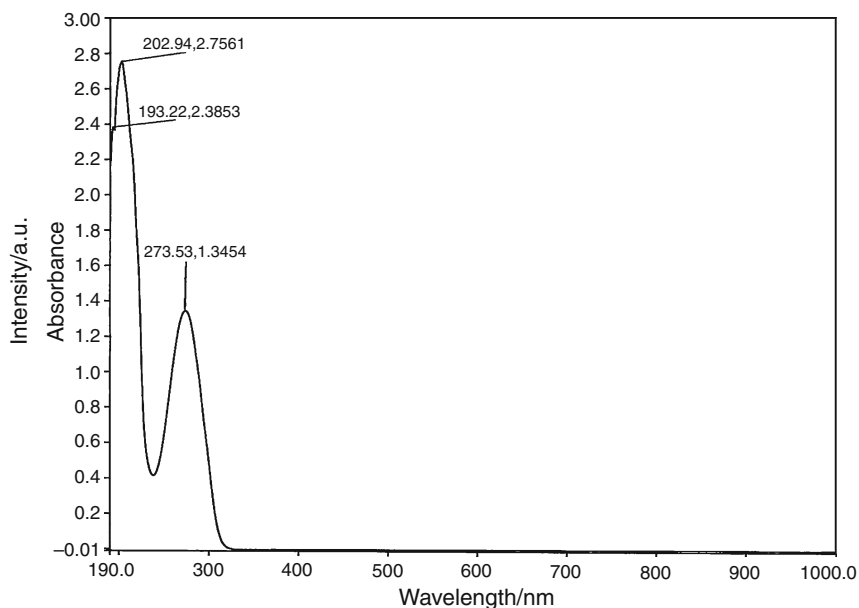
**Fig. 3** FTIR spectrum of mercury cinnamate**Fig. 4** UV spectrum of cinnamic acid

In mercury cinnamate, the  $\pi-\pi^*$  absorption band shifted to lower wavelength compared to cinnamic acid. This is because of the formation of co-ordinate bond between metal with cinnamic acid, thus greater energy required for this transition and hence the absorption shows the blue end of the spectrum.

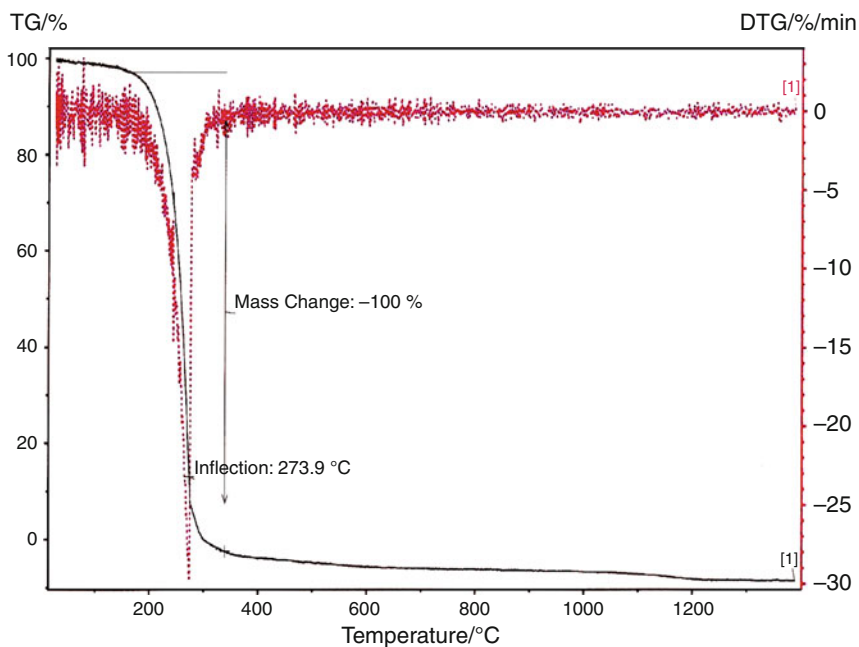
Second harmonic generation (SHG) efficiency

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

**Fig. 5** UV spectrum of mercury cinnamate



**Fig. 6** TG-DTG of cinnamic acid



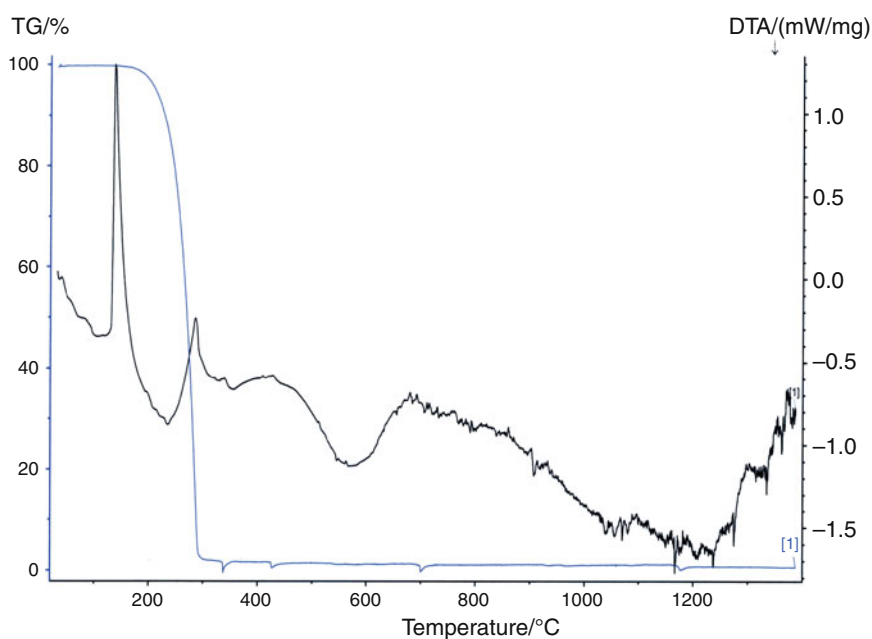
by the green radiation of 532 nm. Input radiation is 5.35 mJ/pulse. Interesting of second harmonic generation gives an indication of NLO efficiency of the material. Non-linearity is facilitated in the presence of dopant. The dopant has catalytic effect on the NLO properties of cinnamic acid crystals. It is interesting to observe that the SHG efficiency is more pronounced in the presence of mercury dopant in the growth medium. It appears that the attainment of second order effects requiring favourable alignment of the molecule within the crystal structure is well facilitated in the presence of inorganic dopant mercury.

#### Thermal analysis

The TG-DTG curves of cinnamic acid are given in Fig. 6 and TG-DTA curves of mercury cinnamate are shown in Fig. 7.

The thermal analysis showed that cinnamic acid and mercury cinnamate are relatively thermally stable. The TG and DTG curves of cinnamic acid indicate that it is thermally stable up to 200 °C, where the decomposition process commences with corresponding DTG peak at 273 °C.

**Fig. 7** TG-DTA curves of mercury cinnamate



The TG curve of mercury cinnamate confirmed that it is thermally stable up to 286.8 °C which was on a higher side compared to cinnamic acid. Such change was also confirmed by DTA curve shown in Fig. 7. This indicates that incorporation of mercury increase the thermal stability ensuring the suitability of material for possible nonlinear optical (NLO) application up to 286.8 °C.

## Conclusions

The transparency of optical quality single crystals of mercury cinnamate grown by slow evaporation technique at room temperature was confirmed by UV absorption spectrum. FTIR spectral analysis was carried out to study the molecular vibration and functional groups of the grown crystals. Mercury cinnamate it is thermally more stable compared to cinnamic acid. It can be seen from the thermal analysis that the crystals were retaining its texture up to 286.8 °C. The dopant has catalytic effect on the NLO properties of the studied crystals. The attainment of second order effects requiring favourable alignment of the molecule within the crystal structure is well served in the presence of dopant mercury.

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