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Thermal, UV and FTIR spectral studies in alkali metal cinnamates

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Abstract A single crystal of sodium and potassium cinnamates was grown by slow evaporation of methanol solution at room temperature. The effect of metals sodium and potassium on the electronic structure of cinnamic acid was studied. In this research many analytical methods such as FTIR, UV, second harmonic generation (SHG) and TG–DTA were used: The spectroscopic studies lead to conclusions containing the distribution of the electronic charge in molecule, the delocalisation of π electrons and the reactivity of metal complexes. The SHG efficiency is more pronounced in the presence of sodium and potassium dopant in the growth medium. Incorporation of sodium and potassium increase the thermal stability ensuring the suitability of material for possible non-linear optical (NLO) application up to 180 °C.

Keywords Solution growth · Sodium and potassium cinnamate · Single crystal · TG–DTA · UV · FTIR

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Introduction

Cinnamic acid (3-phenyl-2-propeonic acid), a derivative of phenyl alanine, composes a relatively large family of organic isomers [1–4]. Thermal and spectral analyses are very useful techniques for materials characterisation. Therefore, many investigators have used these techniques for many materials characterisation [2, 5–24]. 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. Derivatives of cinnamic acid are important pharmaceutics for high blood pressure and stroke prevention and possess antitumour activity. Cinnamic acid derivatives and flavonoids in wine create pigments and tannin agents that give each vintage its characteristic bouquet and colour. Cinnamic acid extensively studies not only due to its important biological activity, but also because of its specific structure. In the spectrum of cinnamic acid the carboxylic group is separated from the aromatic ring by a double bond. 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 metal cinnamates.

Experimental

Sample preparation

The metal compounds were prepared by digesting appropriate weighed amount of cinnamic acid in methanol of alkali metal thiocyanides in stechiometric ratio of 1:1. Then methanol was evaporated in a dryer. The results of elemental analysis are as follows; for sodium cinnamate

C = 64% and H = 5%; for potassium cinnamate C = 59% and H = 4%.

Measurements

The FTIR 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.

The UV absorption spectra were recorded using a 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 °C at a heating rate of 10 °C per minute.

Results and discussion

FTIR spectral studies

The FTIR spectra of cinnamic acid, sodium and potassium cinnamates, recorded in KBr pellet technique and in organic matrix are presented in Figs. 1, 2 and 3. There is an intensive band at 3445.72 cm^{-1} in sodium cinnamate, 3441.31 cm^{-1} in potassium cinnamate and broad bands in the range 2359–2528 cm^{-1} assigned to the –OH stretching vibrations of acid dimmers [25–27]. In this range there are also the bands of the –CH stretching vibrations what is seen in the Figs. 1, 2 and 3.

There are splitting bands assigned to the stretching vibrations of the C=O group (i.e. 1891.28, 1667.56 and 1892.16, 1819.85 cm^{-1}, respectively) in the infrared spectra of sodium and potassium cinnamates. 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 C=O···H–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 γOH vibration, an appearance of bands of the unsymmetric and symmetric vibration of the carboxylate anion $\gamma_{as}(\mathrm{COO}^-)$ shifted towards wave numbers along the series (Na → K) in FTIR spectra. Moreover, band wave numbers of $\beta_S(\mathrm{COO}^-)$ decrease along the metal series (Na → K). This indicates the formation of sodium and potassium cinnamates.

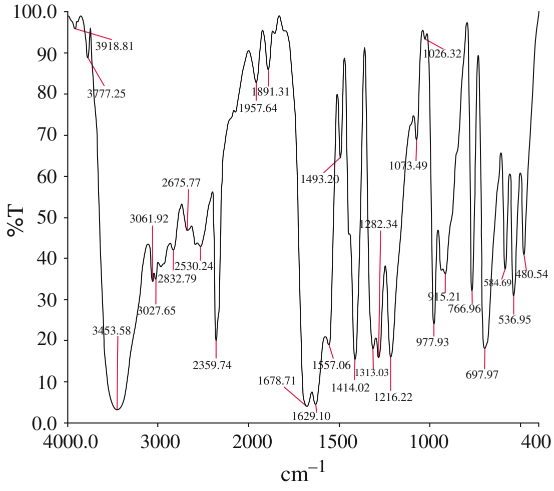

Fig. 1 FTIR spectrum of cinnamic acid

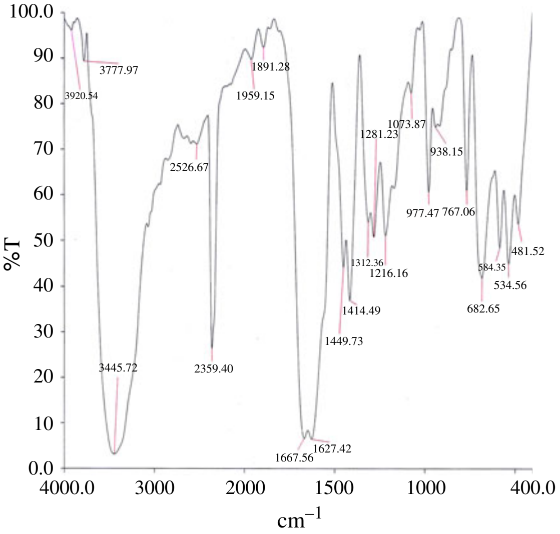

Fig. 2 FTIR spectrum of sodium cinnamate

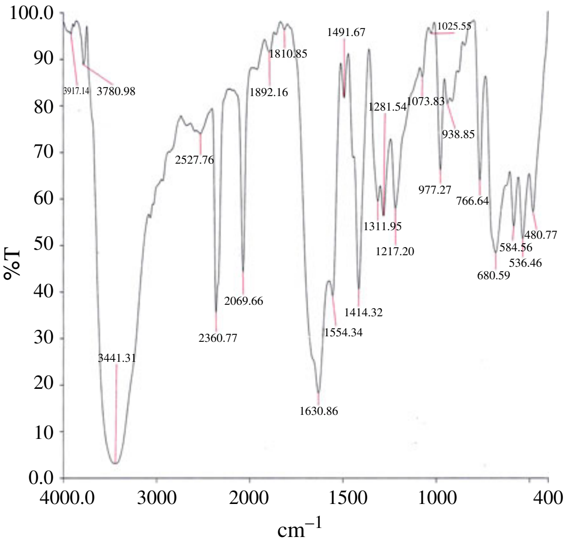

Fig. 3 FTIR spectrum of potassium cinnamate

UV spectral analysis

The UV spectra for cinnamic acid and alkali metal cinnamates are shown in Figs. 4, 5 and 6. In alkali metal cinnamates, the π–π^* absorption band shifted to lower wavelength compared to cinnamic acid. This is because of the formation of co-ordinated bond between metal with cinnamic acid, thus greater energy required for this transition and hence the absorption shows the blue end of the spectrum.

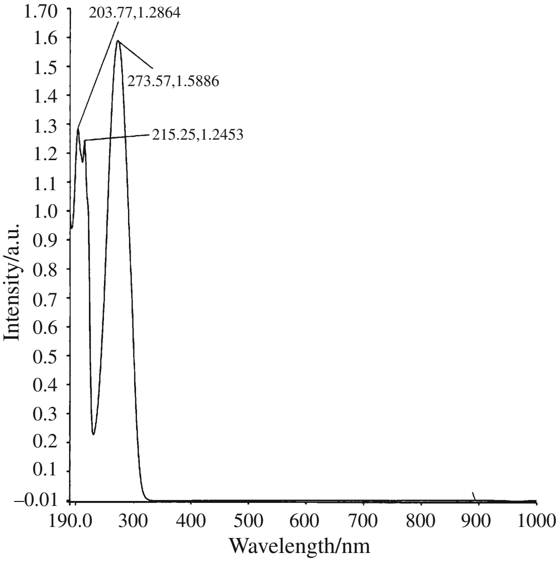

Fig. 4 UV spectrum of cinnamic acid

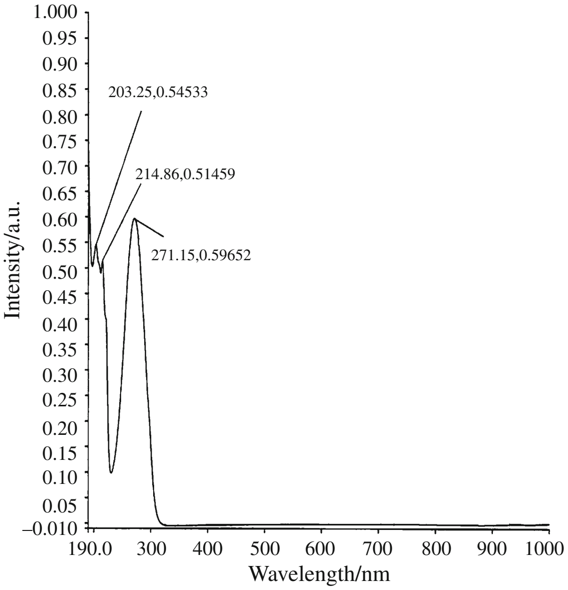

Fig. 5 UV spectrum of sodium cinnamate

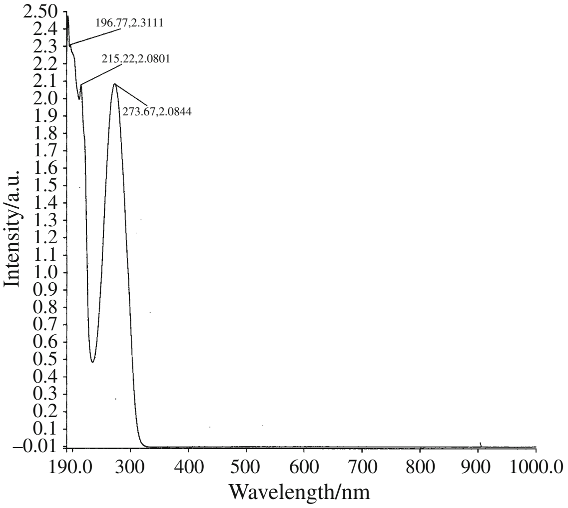

Fig. 6 UV spectrum of potassium cinnamate

Second harmonic generation 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 (SHG) gives an indication of NLO efficiency of the material [28]. Nonlinearity 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 sodium and potassium 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 sodium and potassium.

Thermal analysis

The single crystal of sodium and potassium doped cinnamic acid was subjected to simultaneous thermogravimetric analysis–differential thermal analysis using a Netzsch STA 409C thermal analyser in the nitrogen atmosphere. The samples were heated between 30 and 800 °C at a heating rate of 10 °C per minute to study the mass loss and thermal stability. The TG–DTA curves of grown crystals were shown in Figs. 7, 8 and 9. The TG curves reveal that the major mass loss took place at 253.2 °C in sodium cinnamate and 275 °C in potassium cinnamate, respectively. Such change was also observed by DTA. This indicates that incorporation of sodium and potassium increase the thermal stability ensuring the suitability of material for possible NLO application up to 180 °C.

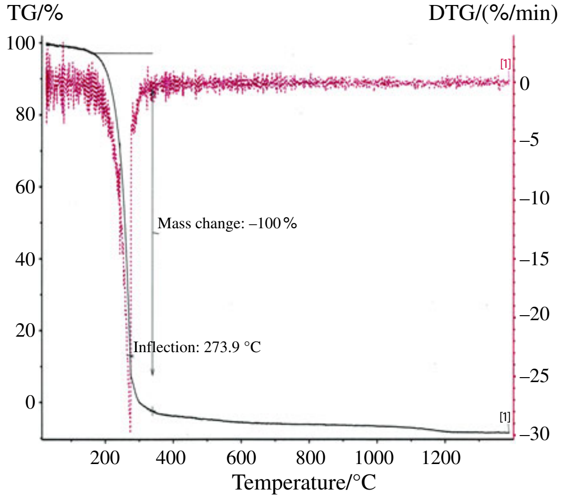

Fig. 7 TG–DTA of cinnamic acid

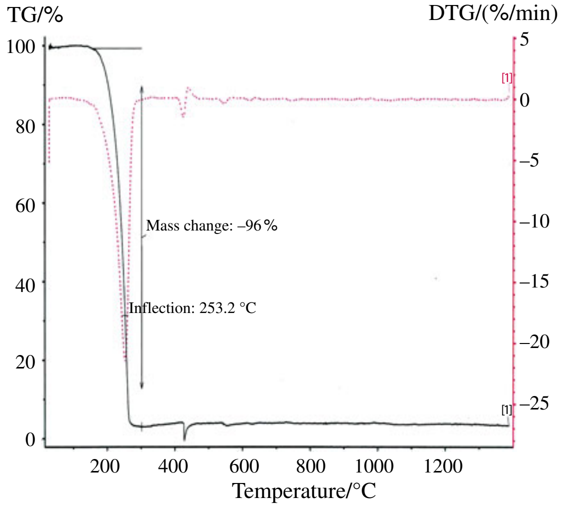

Fig. 8 TG–DTA of sodium cinnamate

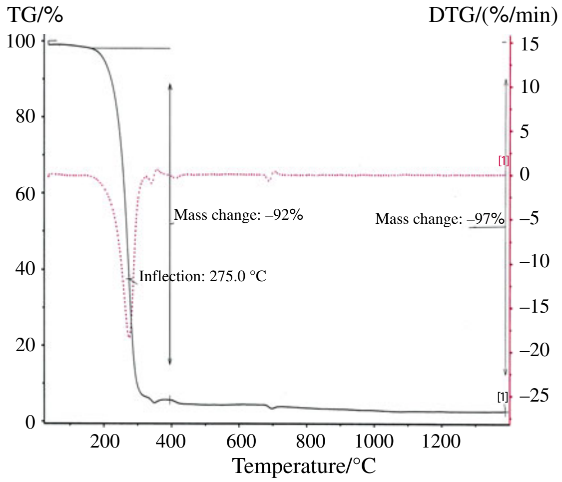

Fig. 9 TG–DTA of potassium cinnamate

Conclusions

Optical quality single crystals of sodium and potassium cinnamates were grown by slow evaporation technique at room temperature. UV absorption spectra confirm the transparency of the crystals. The molecular vibration and functional groups of the grown crystals were studied by FTIR spectral analysis. Thermal analyses showed that the crystals retain its texture up to 253.2 °C. The dopants have catalytic effect on the NLO properties of cinnamic acid crystals.

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