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Synthesis and characterization of semicarbazone of p-hydroxy-3-methoxy acetophenone (SPH3MA) single crystal

S. Janarthanan^a, Y.C. Rajan^b, P.R. Umarani^a, S. Selvakumar^c, S. Pandi^{a,*}

^a Department of Physics, Presidency College, Chennai, Tamilnadu, India

^b Department of Materials Science, National Chiao Tung University, Taiwan, ROC

^c Department of Physics, L.N.G. College, Ponneri, Tamilnadu, India

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ABSTRACT

Single crystals of semicarbazone of p-hydroxy-3-methoxy acetophenone (SPH3MA) were grown by a slow evaporation solution growth technique at room temperature. This is the first report in the literature on the crystallization of SPH3MA. The cell parameters of the grown crystals were estimated by single crystal X-ray diffraction analysis. The various planes of reflection were identified from the XRD powder pattern. The presence of functional groups was identified from FTIR and ¹H NMR. The results were found to be in accordance with the structure of the crystal. The formation of charge transfer complex was confirmed by UV–vis–NIR spectroscopy. The thermal stability of the grown crystal was studied by thermal analysis.

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1. Introduction

Optical nonlinear conjugated organic systems have been widely studied in view of their potential application as active components in photonic and electro–optic devices [1,2]. Research in this area is focused on finding materials exhibiting large nonlinearity, fast response time, low transmission loss, and high thermal stability. Research in the field of organic NLO materials has gained momentum in the recent past on account of the interesting applications of the materials such as optical parametric amplifiers, optical parametric oscillators, Q-switched optical applications, etc. [3–7]. However, most of the organic NLO crystals are associated with poor mechanical strength and thermal stability [8,9]. An organic molecule should have high second order hyperpolarizability (β) to exhibit large NLO properties. The hyperpolarizability can be enhanced by increasing intramolecular charge transfer interaction by extending the π -conjugated system [10]. The increase in conjugation length decreases the energy gap and narrows down the optical transparency window. Basically, semicarbazone family crystals exhibit nonlinear optical behaviour [11,12].

A thorough literature study on semicarbazone crystals and their applications due to the NLO property reveals that there is no systematic study on the synthesis and characterization of acetophenone based semicarbazone derivatives. In this paper,

we report the synthesis, growth and characterization of a new organic crystal viz. semicarbazone of p-hydroxy-3-methoxy acetophenone (SPH3MA) by a slow evaporation technique. The low temperature solution growth technique can be applied to a wide range of compounds for producing high quality crystals [13–15].

2. Experimental

Single crystals of semicarbazone of p-hydroxy-3-methoxy acetophenone were grown by a slow evaporation method from semicarbazide hydrochloride and p-hydroxy-3-methoxy acetophenone using sodium acetate as a catalyst. Alcoholic solvents like ethanol and methanol were used for growing semicarbazone crystals. Semicarbazide hydrochloride, sodium acetate, and p-hydroxy-3-methoxy acetophenone were mixed in the mole ratio 2:4:1, respectively. The prepared solution was found to be turbid. Hence, ethanol was added and stirred well, and the solution was gently warmed till a clear solution was obtained [16].

The obtained product was purified by repeated recrystallization before it was used for crystal growth. The growth experiment was performed in a constant temperature bath at 32 °C. Good quality single crystals (Fig. 1) were harvested after 15–20 days. The reaction and molecular structure of the grown crystal is shown in Scheme 1. The grown crystal was subjected to powder X-ray diffraction analysis to confirm the crystallinity and also to estimate the lattice parameters. Powder X-ray diffraction pattern

* Corresponding author. Tel.: +91 9444018924.

E-mail addresses: srijana26@gmail.com, drspandi@gmail.com (S. Pandi).

was recorded using a Rich Seifert diffractometer with $\text{CuK}\alpha$ ($\lambda=1.5418 \text{ \AA}$) radiation by crushing the SPH3MA crystal into a fine powder. FTIR spectrum was recorded for SPH3MA on a BRUKER 66 V FTIR spectrometer by the KBr pellet technique in the range $400\text{--}4000 \text{ cm}^{-1}$ for the identification of the functional groups. ^1H NMR spectrum was recorded in a BRUCKER spectrometer of frequency 300 MHz using DMSO-d_6 as a solvent (Aldrich) and TMS (0.03%) as an internal standard. The optical absorption spectrum of SPH3MA was recorded in a VARIAN CARY 5E spectrophotometer. Thermal analyses were carried out simultaneously in a NETZSCH STA 409C thermal analyser from 28 to $1200 \text{ }^\circ\text{C}$ at a heating rate of $20 \text{ }^\circ\text{C}$ per min in nitrogen atmosphere. The results of these analyses are presented in detail in the following sections.

3. Results and discussion

The inner arrangement of atoms or molecules in a crystalline material was revealed using the X-ray diffraction technique. The powder X-ray diffraction analysis (Fig. 2) carried out confirmed the crystallinity and provided the lattice parameters (Table 1). The sample was scanned over the range $10\text{--}70 \text{ }^\circ\text{C}$ at a heating rate of $1 \text{ }^\circ\text{C}$ per min. The lattice parameters and the cell volume were calculated using the PROSZKI software package. The peak obtained corresponds to (0 2 0), having a maximum count of 268 cps. This was the strongest diffraction peak for the SPH3MA crystal. The SPH3MA crystal was found to be a monoclinic crystal system.

The phenolic OH stretching in the FTIR spectrum (Fig. 3) gave sharp as well as broad peaks illustrating the presence of free OH grouping without intermolecular bonding and intensely hydrogen bonded OH groupings. The broad peak due to hydrogen bonded OH groupings had the peak maximum at 3210 and 3350 cm^{-1} . There was an intense sharp peak at 3461 cm^{-1} , assigned to the

free N–H stretch. The broad envelope between 2780 and 3368 cm^{-1} was due to overlapping of peaks of hydrogen bonded N–H and aromatic C–H stretching modes. The considerable

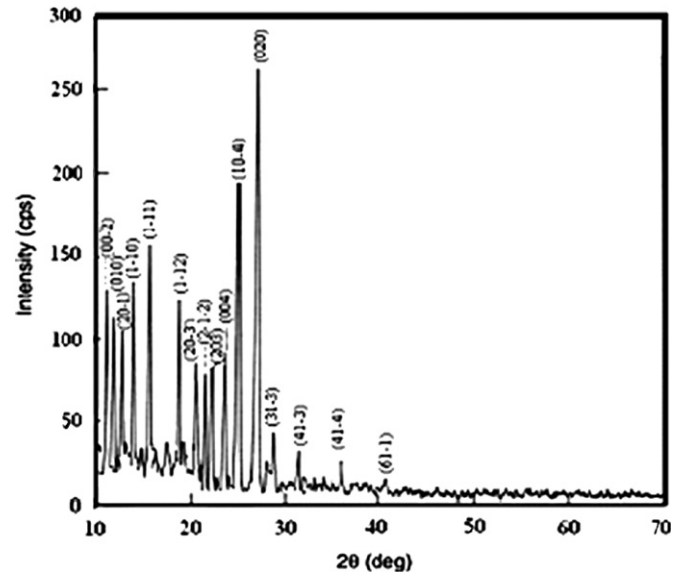


Fig. 2. PXRD data of SPH3MA crystal.

Table 1

Crystallographic data of SPAS crystal.

<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	α	β	γ	<i>V</i> (Å) ³	Crystal system
15.30	6.91	14.17	90°	92.28°	90°	1497.67	Monoclinic

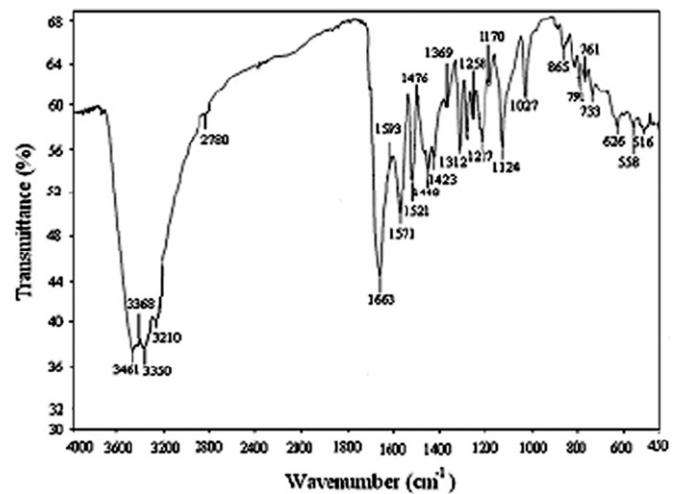


Fig. 3. FTIR spectrum of SPH3MA crystal.

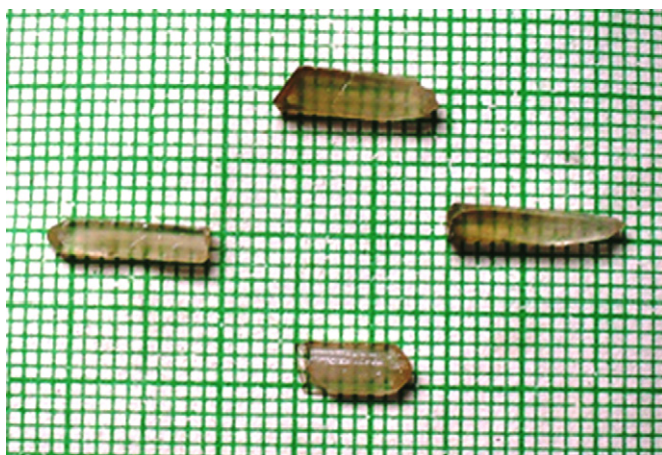
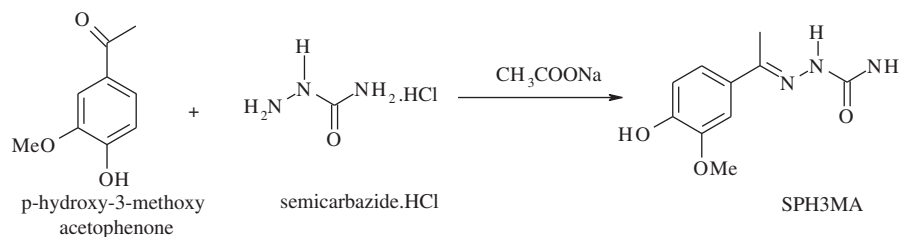


Fig. 1. Grown SPH3MA crystal.



Scheme 1. Synthesis of SPH3MA.

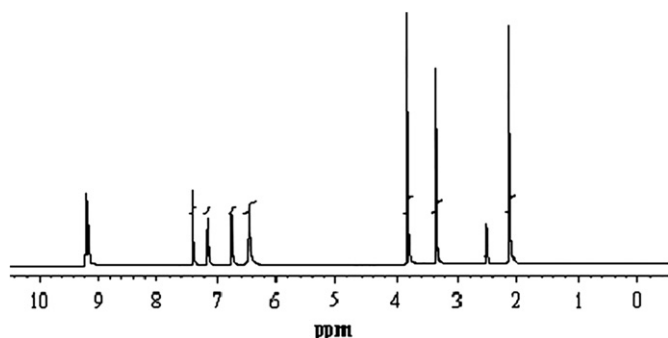


Fig. 4. ^1H NMR spectrum of SPH3MA crystal.

broadening revealed that the packing of the molecules in the crystal was largely through intermolecular hydrogen bonding of these N–H groups. The symmetric and asymmetric C–H stretching modes of $-\text{CH}_3$ group appear as a shoulder just below 3000 cm^{-1} in the broad envelope. The C=O stretch of the semicarbazide moiety was observed at 1663 cm^{-1} . The aromatic ring skeletal vibrations were observed at 1593 and 1476 cm^{-1} . The $-\text{CH}_3$ bending modes were positioned at 1423 and 1312 cm^{-1} . The $-\text{HN}-\text{C}=\text{O}$ stretch was seen at 1124 cm^{-1} . The out-of-plane aromatic C–H bond was observed at 761 cm^{-1} . The peak at 1571 cm^{-1} was assigned to the C=N stretching vibration. The N–H bending vibration gave a peak at 1521 cm^{-1} . The CH_2 bending modes were observed at 1448 cm^{-1} . The bands obtained between 1170 and 1258 cm^{-1} were due to ether stretching vibration [17]. From the FTIR spectrum it was well understood that the coupling between carbonyl group of substituted acetophenone and amine group of semicarbazide had well gone through without leaving any trace of starting materials.

The typical ^1H NMR spectrum (Fig. 4) of SPH3MA had a sharp singlet at 2.11 ppm due to the presence of the OCH_3 group attached to the aromatic group. The peak observed at 3.80 ppm could be attributed to the $\text{H}_3\text{C}-$ group attached to the semicarbazone group. The NH_2 and NH groups of the semicarbazone moieties were observed at 9.1 and 6.4 ppm, respectively. The appearance of two sharp doublets at 6.7 and 7.1 ppm corresponded to two protons present at ortho and meta to the phenolic $-\text{OH}$ attached to the aromatic rings. However the sharp singlet at 7.3 ppm was due to the presence of single proton ortho to the $-\text{OCH}_3$ group in the aromatic ring.

Optical absorption measurements were carried out to characterize the optical properties of SPH3MA. A crystal of 2 mm thickness was used to record the spectrum. Wavelength versus absorbance was plotted for the sample (Fig. 5). The absorbance was found to be very low in the entire visible and near IR region, which was the most desired property for NLO materials. The large transmission window in the visible region enabled it to be a potential candidate for optoelectronic applications [18]. From the obtained spectrum, the UV cut-off wavelength was found to be 250 nm.

The thermograms provide information about decomposition pattern of materials and weight loss. Hence, the thermogravimetric methods are limited to decomposition and oxidation reactions. The thermal stability of SPH3MA was identified by thermogravimetric (TG) and differential thermal analyses (DTA) (Fig. 6). The SPH3MA sample weighing 6.978 mg was taken for the analysis. The material was found to be stable upto 230°C and decomposed slightly at this temperature. The DTA revealed exactly the same changes shown by TGA. The major weight loss that occurred in the low temperature region began at 230°C and ended at around 260°C .

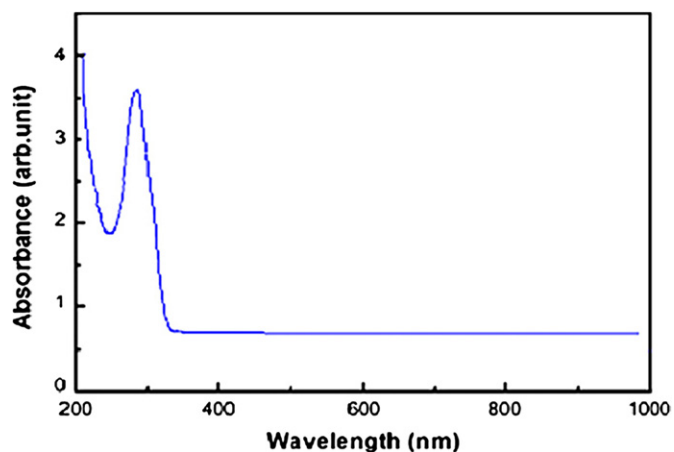


Fig. 5. UV-vis-NIR spectrum of SPH3MA crystal.

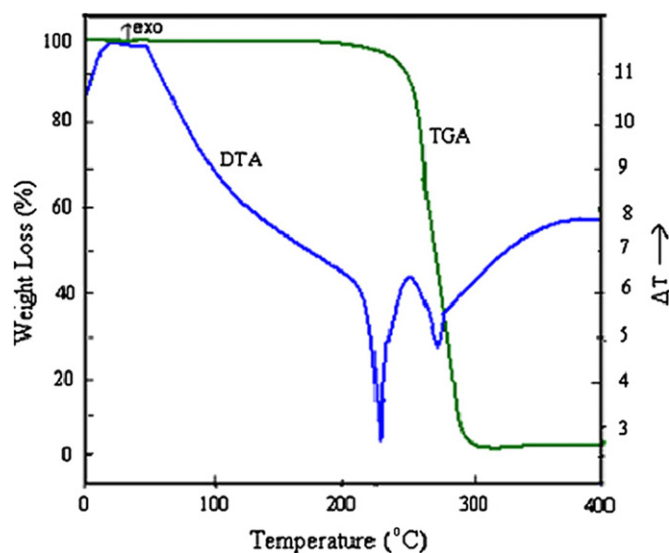


Fig. 6. TGA/DTA curve of SPH3MA crystal.

4. Conclusion

The SPH3MA single crystal was grown by the slow evaporation method. Powder XRD, FTIR, ^1H NMR, and UV absorption studies were carried out for characterization of the synthesized crystal. Powder XRD confirmed the crystal structure. The spectral study revealed the C=O stretch, which in turn confirmed the structure of SPH3MA. Optical studies showed that the crystal had a wide transparency window in the entire visible region, making it an ideal candidate for NLO device applications. The decomposition temperature and percentage weight loss of the material were found out from the TG/DTA analysis. The degree of crystallinity and purity was also confirmed from a sharp endothermic peak in the DTA.

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