

# Growth, spectral, and thermal characterization of semicarbazone of *p*-hydroxy acetophenone (SPHA)

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**Abstract** A new organic nonlinear optical material semicarbazone of *p*-hydroxy acetophenone (SPHA) was synthesized. Good quality single crystal of SPHA was successfully grown by slow evaporation method at room temperature. The crystal system was identified and lattice dimensions were measured from the single crystal X-ray diffraction (XRD) analysis. The various planes of reflection were identified from the powder XRD pattern. The presence of functional groups was qualitatively found by Fourier transform infrared (FTIR) spectral analysis. The proton and carbon nuclear magnetic resonance ( $^1\text{H}$ NMR and  $^{13}\text{C}$ NMR) spectral studies confirmed the presence of hydrogen and carbon bonded network in the grown crystal. The UV–Visible absorption spectrum was recorded to study the optical transmittance in the range from 200 to 800 nm. The thermal stability of compound was determined by thermogravimetric and differential thermal analysis (TG-DTA) traces. The existence of second harmonic generation (SHG) signal was observed using Nd:YAG laser with fundamental wavelength of 1064 nm.

**Keywords** Semicarbazone of *p*-hydroxy acetophenone · Solution technique · Spectral analysis · Thermal studies

## Introduction

In recent years, considerable research efforts have been made in exploring novel organic materials for their potential use in a variety of devices. The materials which could produce green/blue laser light and could withstand high energy light radiation are of vital importance for their uses in devices. The basic understanding of organic nonlinear optical materials has been well established [1, 2] and extensive studies have been motivated by their wide range of potential applications [3]. These organic materials are attracting a great deal of attention as they have large optical susceptibilities, inherent ultra fast response times, and high optical thresholds for laser power over the inorganic materials [4–7]. Organic materials have been known for their applications in semiconductors, superconductors, and nonlinear optical devices [8–13]. Production of carbonyl compounds as semicarbazones is of great interest to organic chemists as they are readily prepared and highly stable [14]. The semicarbazones are extensively used for purification and characterization of carbonyl compounds [15]. Basically, semicarbazone family crystals have attractive nonlinear optical behavior [16–18]. SPHA is one of the NLO materials which find applications in optical communication and storage devices. Since, the organic nonlinear optical materials are often formed by weak Vander walls and hydrogen bonds; they possess high degree of delocalization. Hence, these organic materials offer unique opportunities for fundamental research as well as technological applications.

The SPHA belongs to the ketone group of compounds. This investigation involves synthesis of SPHA and the crystal growth by slow evaporation solution growth technique [19–21] and characterization by XRD studies,

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spectral and thermal analysis, and NLO property studies by Kurtz–Perry powder technique [22].

## Experimental

### Synthesis and growth

Semicarbazide hydrochloride and *p*-hydroxy acetophenone were used as the starting materials for growing SPHA single crystals. Sodium acetate was used as a catalyst and methanol was used for growing semicarbazone crystals. Semicarbazide hydrochloride, sodium acetate, and *p*-hydroxy acetophenone were mixed in the mole ratio of 1:1:0.5, respectively. Since the prepared solution was turbid methanol was added and stirred well and warmed gently in a temperature bath until a clear solution was obtained. The solution was taken in a closed container and placed in a constant temperature bath at 35 °C. After few hours, spontaneous nucleation was observed in the solution. Needle-shaped good transparent single crystals of SPHA (Fig. 1) were obtained in a fortnight. A large-sized single crystal can be obtained by taking a large quantity of reactants. The chemical reaction and molecular structure of SPHA are shown in Scheme 1.

## Results and discussion

### Powder and single crystal XRD studies

The powdered sample of SPHA was scanned between the  $2\theta$  ranges from 10° to 50° at a rate of 1° min<sup>-1</sup> using a Rich Seifert Powder X-ray diffractometer with CuK<sub>α</sub> (1.54289 Å) radiation. The obtained XRD pattern was



**Fig. 1** As grown crystal of SPHA

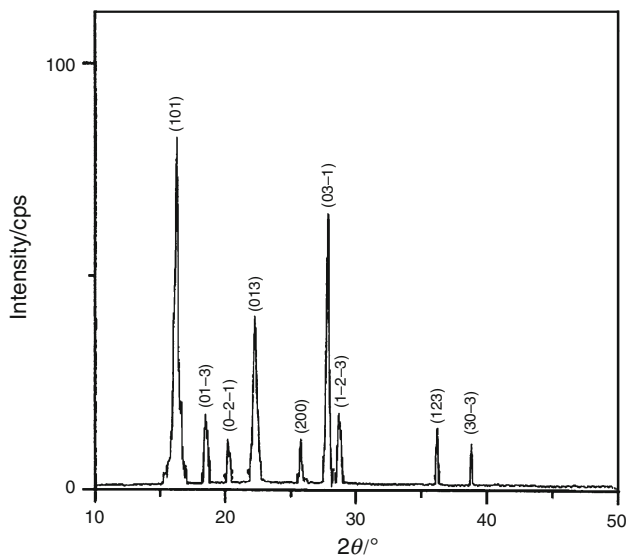
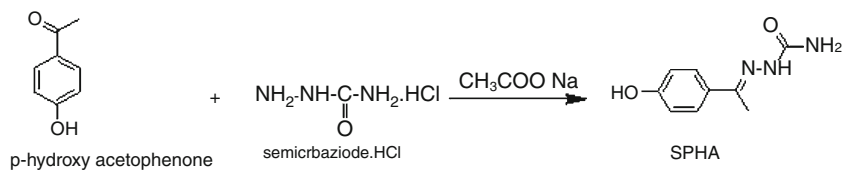
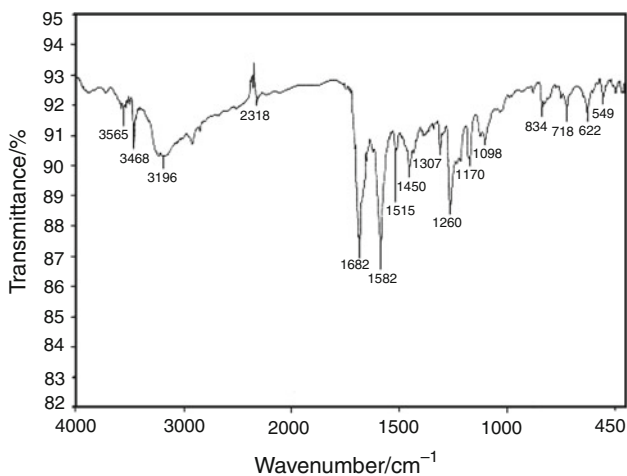
analyzed using PROSZKI software package [23] and the diffraction peaks are indexed (Fig. 2). The grown single crystal of SPHA was also confirmed by single crystal XRD analysis. The obtained lattice parameters revealed that the SPHA crystal belonged to triclinic system with  $a = 7.19$  Å,  $b = 10.00$  Å,  $c = 15.16$  Å and  $\alpha = 102.53^\circ$ ,  $\beta = 102.16^\circ$ ,  $\gamma = 102.58^\circ$  and cell volume  $V = 998$  Å<sup>3</sup>.

### FTIR spectral analysis

In order to absorb infrared radiation, a molecule must undergo a net change in dipole moment, as a consequence to its vibrational motion. The Fourier transform infrared (FTIR) spectrum (Fig. 3) was recorded using BRUKER IFS 66 V FTIR spectrometer in the region between 4000 and 400 cm<sup>-1</sup>. The higher wavenumber region gives interesting information with regard to bonding of the groups in the crystal. The phenolic OH stretching provides sharp as well as broad peaks illustrating the presence of free OH grouping without intermolecular bonding and intensely hydrogen bonded OH grouping. The former free OH groupings provide the stretching patterns at 3565, 3468, and 3196 cm<sup>-1</sup>. The broad peak due to hydrogen bonded OH grouping has its peak maximum at 3210 and 3350 cm<sup>-1</sup>. The spectrum reveals the characteristic N–H vibrations in the higher energy region at 3468 and 3196 cm<sup>-1</sup> as very intense peaks. The sharpness of the peak at 3468 cm<sup>-1</sup> may be due to interaction free nature among the neighboring molecules and it is assigned to N–H stretching of the –HN–C=O group. The broadness at 3196 cm<sup>-1</sup> is due to hydrogen bonded N–H stretching of amide NH<sub>2</sub> group. The C=O stretching of semicarbazide moiety is observed at 1682 cm<sup>-1</sup> and the peak at 1582 cm<sup>-1</sup> is assigned to C=N stretching vibration. The N–H bending vibration gives a peak at 1515 cm<sup>-1</sup>. The CH<sub>2</sub> bending modes are observed at 1450 and 1307 cm<sup>-1</sup>. The –HN–C=O stretch is seen at 1098 cm<sup>-1</sup> and the out of plane aromatic C–H bond is observed at 718 cm<sup>-1</sup>. The bands obtained between 1170 and 1260 cm<sup>-1</sup> are due to C=N stretching vibration [24].

### <sup>1</sup>HNMR and <sup>13</sup>CNMR spectral studies

The NMR technique is used to detect the presence of particular nuclei in a compound for a given nuclear species. It is also an important tool for the identification of molecules and the examination of their electronic structure [25]. To determine the molecular structure by studying the hydrogen and carbon network of SPHA, the <sup>1</sup>HNMR and <sup>13</sup>CNMR spectra (Figs. 4, 5) were recorded using a JEOL: GSX 500 instrument in DMSO-d<sub>6</sub> solvent. The four aromatic ring protons produce characteristic signals between 6.72 and 7.67 ppm. The –NH<sub>2</sub> protons appear as a broad

**Scheme 1** Reaction mechanism and molecular structure of SPHA**Fig. 2** Powder XRD pattern of SPHA**Fig. 3** FTIR spectrum of SPHA

signal at 3.42 ppm and the amide NH proton gives its characteristic signal at 9.2 ppm. From the  $^1\text{H}$ NMR spectral data, it was observed that the prepared compound was analytically pure and free from any other impurity. In the  $^{13}\text{C}$ NMR spectrum, the three prominent peaks confirm the predicted molecular structure of SPHA. The signal at 158.65 ppm represents the carbonyl carbon (C=O). The signals ranging from 129.89 to 128.12 ppm are due to aromatic carbons. The signal at 13.89 ppm represents  $\text{CH}_3$

group attached to azomethine carbon. Thus, the molecular structure of SPHA is confirmed by  $^1\text{H}$ NMR and  $^{13}\text{C}$ NMR spectral studies.

#### UV-Visible spectral analysis

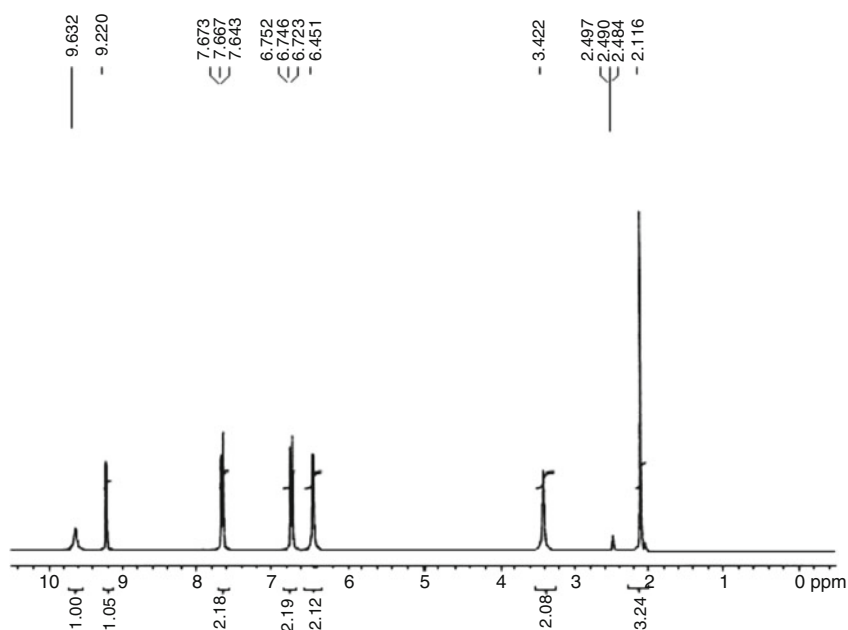
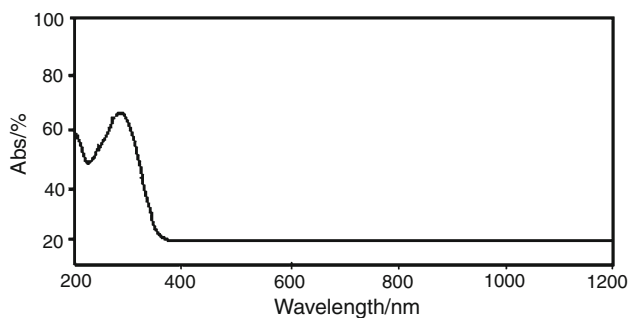
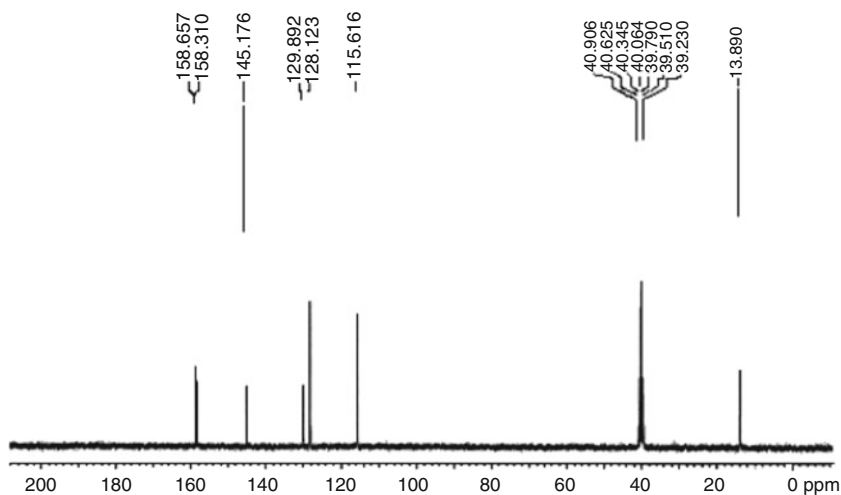
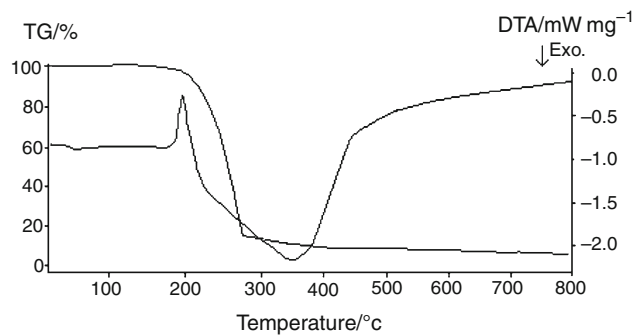
Since, single crystal is mainly used in optical applications; its optical transmission range and the transparency cut-off wavelength are essential data. The optical behavior of SPHA was measured by VARIAN CARRY 5E UV-Vis-NIR spectrophotometer between 200 and 1200 nm. The UV-Visible spectrum of SPHA (Fig. 6) had no absorption band between 340 and 1200 nm. Hence, the crystal of SPHA is expected to be transparent to all the UV-Visible radiations in between these two wavelengths [26]. The characteristic absorption band is observed only at 290 nm.

#### Thermal analysis

Thermogravimetric and differential thermal analyses (TG-DTA) give information regarding phase transition and different stages of decomposition of the crystal system. The thermogravimetric analysis of SPHA crystal is carried out between 50 and 400 °C in the nitrogen atmosphere at a heating rate of 10 °C  $\text{min}^{-1}$  using NETZSCH STA 409C thermal analyzer. The TGA curve of SPHA (Fig. 7) indicates that the sample is stable up to 200 °C. The DTA analysis was also carried out in the same atmospheric condition. The exothermic peak at 203 °C is due to the melting of the sample. The sharp exothermic peak shows the good crystalline perfection quality of the sample. There are no endothermic or exothermic peaks observed before 203 °C. It shows that this crystal is stable up to the melting point without any phase transition and after that it immediately starts to decompose. Hence, it may be useful for making the NLO devices below its melting point.

#### NLO test

The second harmonic generation (SHG) of SPHA was confirmed by Kurtz-Perry powder technique. The powdered sample of SPHA was illuminated using a Q-switched Nd:YAG laser emitting a fundamental wavelength ( $\lambda$ ) at 1064 nm. The pulse energy used was 300  $\text{mJ s}^{-1}$  with a

**Fig. 4**  $^1\text{H}$ NMR spectrum of SPHA**Fig. 5**  $^{13}\text{C}$ NMR spectrum of SPHA**Fig. 6** UV-Visible spectrum of SPHA**Fig. 7** TG-DTA curves of SPHA

pulse width was about 10 ns. The output from the Q-switched laser was focused on the sample of SPHA. The output could be seen as a bright green flash emission from the sample, which confirmed the SHG of SPHA.

## Conclusions

A good quality crystal of SPHA was successfully grown by the slow evaporation solution growth technique for the first

time. The powder XRD and single crystal XRD analysis confirmed the crystal structure of SPHA. The presence of functional groups of SPHA was confirmed by FTIR,  $^1\text{H}$ NMR, and  $^{13}\text{C}$ NMR spectral analysis. UV–Visible spectrum confirmed the transparency of the crystal between the wavelength 340 and 1200 nm. Thermal studies revealed that the sample was stable up to 200 °C. The second harmonic generation property was confirmed by using the Nd:YAG laser with the emission of green light by the SPHA sample.

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