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Spectral and thermal characterization of grown organic single crystal

Semicarbazone of *p*-hydroxy benzaldehyde (SPHB)

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Abstract The growth of semicarbazone of *p*-hydroxy benzaldehyde (SPHB) single crystal by slow evaporation solution growth technique is reported in this article. The grown crystal was subjected to powder XRD study to identify the crystalline nature. Single crystal XRD study was done to measure unit cell parameters and to confirm the crystal structure. In the presence of various functional groups of SPHB was identified by FTIR spectrum. Its optical behavior was examined by UV–Vis–NIR spectrum and the crystal was found to have transparency in the region between 245 and 1100 nm. Thermal properties of the crystal were investigated using thermogravimetric and differential thermal analysis (TG-DTA), which indicated that the melting of the material occurred before decomposition. The nonlinear optical (NLO) property was tested by Kurtz–Perry powder technique for second harmonic generations.

Keywords Crystal growth · X-ray diffraction · Optical material · Thermal studies

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Introduction

It is very essential to grow large size single crystals of new organic non-linear optical (NLO) materials with increased perfection due to rapid developments happening in the photonics technology. Many organic materials are identified to have higher NLO efficiency than inorganic substances [1, 2]. The organic inter-charge transfer compounds are experimentally and theoretically shown to exhibit anomalously large NLO effects [3]. In recent decades crystal growth and optical properties of organic single crystals have attracted attention of both chemists and physicists owing to their potential applications in frequency doublers. The organic NLO crystals are preferred to inorganic ones due to their potentially high nonlinearities and rapid responses in electro-optic devices. The microscopic origin of nonlinearity in the organic molecular NLO materials is due to the presence of delocalized π-electron systems connecting donor and acceptor groups, which enhance the necessary asymmetric polarizability [4]. The NLO materials play an important role in second harmonic generation, frequency mixing, electro-optic modulation, optical stability, etc. NLO is at the forefront of current research because of its importance for the emerging technologies in areas such as telecommunication, signal processing, and optical interconnections [5, 6]. Owing to their properties like, nonlinear optical properties and hyperpolarizabilities; these materials have become an area of extensive research. Lots of experimental [7, 8] and theoretical efforts [9, 10] are focused on bulk NLO properties and their dependence on the first hyperpolarizabilities of molecules. Semicarbazones are very common derivatives of aldehydes and ketones and are frequently used in the qualitative analysis of these carbonyl compounds [11, 12]. This has stimulated research work on crystal growth; since,

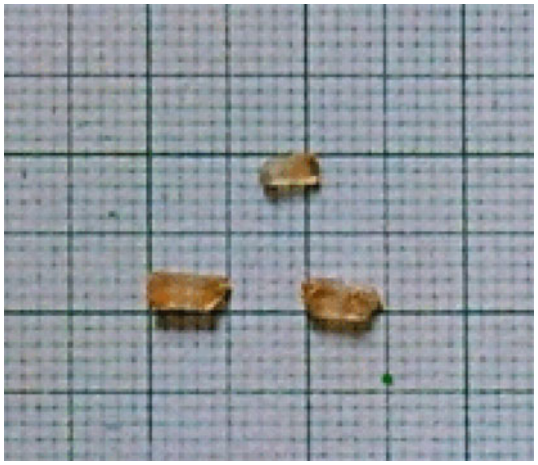


Fig. 1 Grown crystals of SPHB

optical quality materials are required for applications. There are only few reports in the literature dealing with the crystal structure of the semicarbazone compounds. The spectral and thermal analyses are very useful techniques for materials characterization. Therefore, many investigators have used these techniques for many materials characterization [13–21].

In this article the synthesis and growth of organic nonlinear SPHB single crystal by slow evaporation solution growth method is reported along with its characterization by powder and single crystal XRD studies, FTIR and UV–Vis–NIR spectral analysis and thermogravimetric and differential thermal analysis (TG-DTA). The NLO property of the compound was confirmed by Kurtz–Perry powder technique.

Materials and methods

Material synthesis and crystal growth

SPHB was synthesized from *p*-hydroxy benzaldehyde and semicarbazide hydrochloride using sodium acetate as a catalyst. The *p*-hydroxy benzaldehyde, semicarbazide hydrochloride, and sodium acetate were taken in the mole ratio 1:1.5:0.5, respectively. Semicarbazide hydrochloride and sodium acetate were dissolved in distilled water. Ethanol was used as a solvent for *p*-hydroxy benzaldehyde. Both the solutions were mixed. Since the prepared solution was turbid, ethanol was added and stirred well and the solution was gently warmed using water bath till a clear solution was obtained [22]. The solution was taken in a covered container for controlled evaporation and kept in a constant temperature bath (CTB) at 35 °C. After few hours spontaneous nucleation was observed in the solution. Good quality single crystals of semicarbazone of *p*-hydroxy benzaldehyde (Fig. 1) were harvested in a fortnight. A large-sized single crystal can be obtained by taking a large quantity of the reactants. The reaction mechanism and the molecular structure are given in Scheme 1.

Characterization

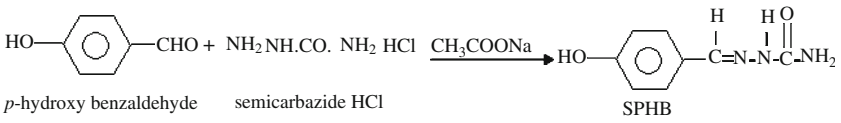
The grown SPHB single crystal was subjected to various characterization techniques like powder XRD analysis, single crystal XRD analysis, FTIR spectral studies, UV–Vis–NIR spectral studies, TG-DTA thermal analysis and Kurtz–Perry powder technique for nonlinear optical studies. The powder XRD analysis on the SPHB single crystal was carried out using Rich Seifert diffractometer with CuKα radiation ($\lambda = 1.5418$ Å) over the range from 10° to 70° at a scan rate of 0.02° s^{-1} to identify the crystalline nature. The single crystal XRD studies have been carried out using Enraf–Nonius CAD4 diffractometer with MoKα radiation ($\lambda = 0.7170$ Å) to determine the cell parameters. The coordination of *p*-hydroxy benzaldehyde with semicarbazide hydrochloride was confirmed by FTIR spectral studies by KBr pellet using BRUKER 66 V FTIR spectrometer in the range from 4000 to 450 cm^{-1}. To study the optical transparency of SPHB, UV–Vis–NIR spectrum was recorded in the region from 200 to 1100 nm using VARIEN CARY 5E UV–Vis–NIR spectrophotometer. Thermal characterization was done by TGA and DTA using NETZSCH STA 409C thermal analyzer in nitrogen atmosphere. The measurements were taken by varying the applied load from 10 to 50 g. The NLO property of the crystal was confirmed by Kurtz–Perry powder second harmonic generation (SHG) test [23].

Results and discussion

Powder XRD and single crystal XRD analysis

The powder XRD analysis confirmed the crystallinity of the grown SPHB crystal. In order to identify the lattice parameters of the SPHB, the single crystal XRD was taken

Scheme 1 Synthesis and molecular structure of SPHB



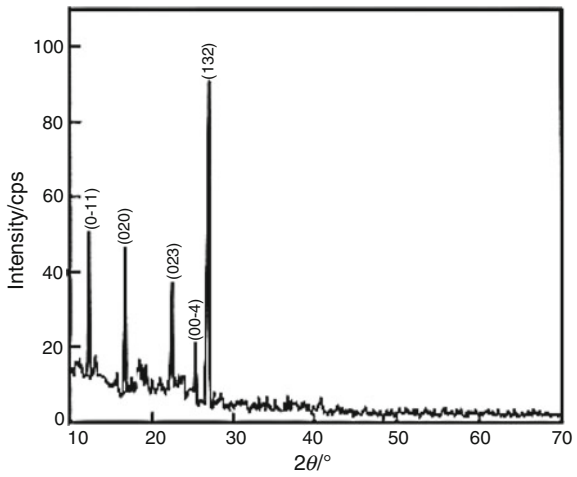


Fig. 2 Powder XRD pattern of SPHB

Table 1 Crystal data of SPHB

Empirical formula	a/Å	b/Å	c/Å	α	β	γ	Z	Crystal system
$C_8H_9N_3O_2$	20.88	5.60	14.58	90°	102°.71	90°	6	Monoclinic

(Fig. 2). The lattice parameter values were calculated from this XRD data using Celn software package. The calculated a, b, c, α, β, and γ values are tabulated (Table 1).

FTIR spectral studies

The FTIR spectrum (Fig. 3) of the grown SPHB single crystal shows a sharp peak at 3473 cm^{-1} due to the presence of free hydroxyl and free NH_2 groups in the molecular structure. Similarly a broad peak at 3263 cm^{-1} corresponds to N–H-stretching of semicarbazone group. An intense sharp peak at 1682 cm^{-1} is attributed to the presence of carbonyl functional group. The peak corresponding to semicarbazone C=N is observed at 1583 cm^{-1}. Appearance of peak at 1509 cm^{-1} corresponds to N–H bending of both free $–NH_2$ and N–H of semicarbazone group.

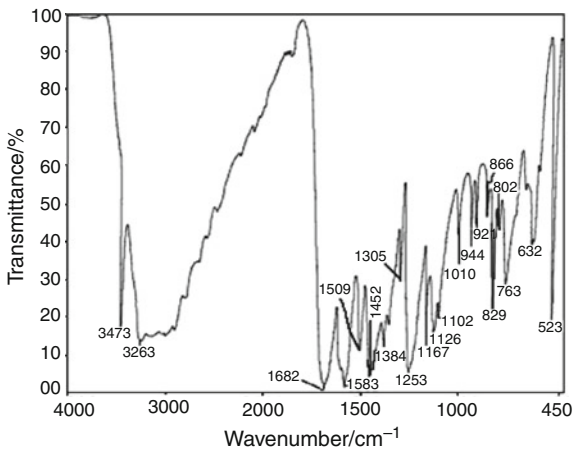


Fig. 3 FTIR spectrum of SPHB

UV–Vis–NIR spectral studies

The UV–Vis–NIR spectrum (Fig. 4) of the highly transparent SPHB crystal of thickness 3 mm shows the lower cut off of at 223 nm. The crystal is found to be transparent in the region between 280 and 1200 nm, which is an essential parameter for frequency doubling purposes.

Thermal analysis

Thermogravimetric and differential thermal analysis (TG-DTA) are very important characteristic techniques to study the thermal stability of the grown crystals. A ceramic crucible was used for heating the sample. In the TG-DTA curve (Fig. 5) of the SPHB crystal, it is found that there is a major weight loss starting at 224 °C. Hence, the compound decomposes at 224 °C. The endothermic peak of the DTA trace coincides with the decomposition in the TG trace.

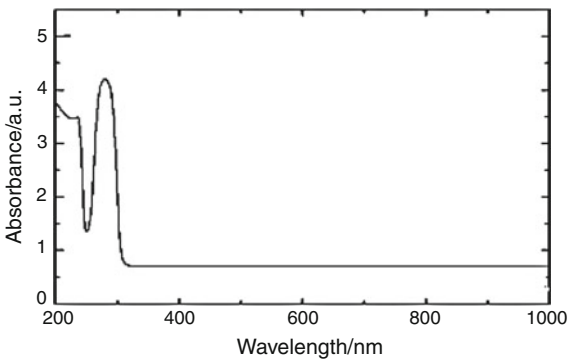


Fig. 4 UV–Vis–NIR spectrum of SPHB

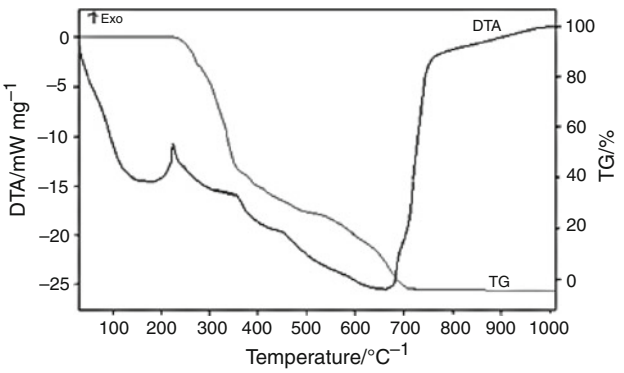


Fig. 5 TG-DTA curves of SPHB

NLO test

The powdered crystal was illuminated using Spectra Physics Quanta Ray S2. Nd: YAG laser using the first harmonics output of 1064 nm with pulse width of 8 ns at a repetition rate of 10 Hz. The second harmonic signal generated in the crystal was confirmed from the emission of green radiation by the crystal.

Conclusions

The novel SPHB material was synthesized and the single crystal was grown by slow evaporation technique. The powder XRD confirmed the crystallinity and the lattice parameters and crystal structure were obtained by the single crystal XRD analysis. The FTIR spectrum revealed the molecular groups present in SPHB. The optical transmission studies showed that the SPHB crystal was optically transparent in the entire visible region with a lower cut-off below 223 nm. Thermal studies revealed that SPHB melts before decomposing. It thus substantiates its suitability for NLO applications up to 224 °C. The second harmonic generation (SHG) of the sample was confirmed by the Kurtz–Perry technique. The SHG efficiency measurements and etching studies are in progress.

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