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Growth, spectral, and thermal characterization of the NLO crystal: semicarbazone of DL-camphor (SDLC)

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Abstract Semicarbazone of DL-camphor (SDLC) crystals were grown using methanol as a solvent by slow evaporation solution growth technique at room temperature. Formation of the product and the presence of various functional groups present in the grown crystal have been identified using FTIR spectra. Single crystal XRD study was conducted to obtain the crystal structure and lattice parameters. The grown crystal was subjected to ^{1}HNMR and ^{13}CNMR spectral studies and TG-DTA in order to confirm its structure, purity, and stability, respectively. The optical transparency of the crystal was tested using UV–Vis–NIR spectroscopy. The nonlinear optical (NLO) property of the grown crystal was confirmed from the second harmonic generation (SHG) by Kurtz–Perry powder test.

Keywords Characterization · X-ray diffraction · Nonlinear optical material · Organic compound

Introduction

The organic crystals are now-a-days highly recognized as the materials of the future because, their molecular nature combined with versatility of synthetic chemistry, which can alter their structure in order to maximize the nonlinear properties [1–3]. Optical second harmonic generation (SHG) is widely used as a noninvasive and noncontact probe of the electronic and structural properties of crystals [4].

The organic nonlinear optical (NLO) materials offer many advantages over the inorganic NLO materials in high optical nonlinearities, fast response times, facile modification of molecular properties through well-defined synthetic methods and high optical damage thresholds [5]. Nevertheless, the transfer of these materials into actual devices is not simple because of some of the demanding requirements such as noncentrosymmetric packing of NLO chromophores, low optical losses from either absorption or scattering and environmental and photochemical stabilities. The NLO chromophores need to be packed with an ideal orientation in the crystals for even to achieve noncentrosymmetry in order to attain a maximum efficiency with phase-matching conditions [6–9].

In organic NLO materials, the structure is decided mostly by the π-bond system extended over a large length scale of the molecule. This can be very easily manipulated by substitution of electron donating and electron withdrawing groups around the aromatic moieties, which in turn can increase optical nonlinearity [10, 11]. Apart from structural flexibility, which allows fine-tuning of chemical structures for the desired NLO properties, the organic materials are of great technological interest due to their low cost, ease of fabrication, handy integration into devices, low dielectric constant, high electro-optic coefficient value, and resistance to laser damages. Polar organic crystals, which form noncentrosymmetric crystal structures, are attracting much interest due to their potentially high nonlinearities and a rapid response in electro-optic effects that often surpass those on inorganic nonlinear optical materials.

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Due to chemical, biological, and environmental importance, many authors have investigated various organic compounds and examined their various properties [12–22]. We have synthesized a compound called semicarbazone of DL-camphor (SDLC) and grown a large single crystal of this compound by solution growth method. The results of the standard characterization such as spectral, thermal, and NLO property studies show that SDLC is one of the new organic nonlinear optical crystals.

Experimental results and discussion

Synthesis

SDLC was synthesized from raw materials of high purity (99.9% of Merck). The semicarbazide hydrochloride, sodium acetate, and DL-camphor were taken in mole ratio 3.41:2.15:3, respectively [23]. Since, initially 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. The chemical reaction for the preparation of SDLC and its molecular structure are given in Scheme 1.

Crystal growth

Crystal growth experiments were performed by slow evaporation method. Saturated solution of SDLC was prepared at 35 °C. The solution was heated 5 °C above their saturation temperature in order to remove un-dissolved crystallites. The crystallizer was then placed in a constant temperature bath and cooled to the predefined saturation temperature of 35 °C. Few perforations were made on the covering sheet of the container for the evaporation of solvent. The nucleation was noticed on the 6th day and it was allowed to grow for a period of 30 days. The photographs of the harvested crystals are shown in Fig. 1.

X-ray diffraction studies

Single crystal X-ray diffraction analysis was performed for SDLC crystal using CAB4 Enraf-Nonius 4-circle automatic diffractometer. From this, it is found that the SDLC crystal is orthorhombic and the lattice parameter values are presented in Table 1. The obtained cell parameters values of SDLC are in good agreement with the reported data [24].

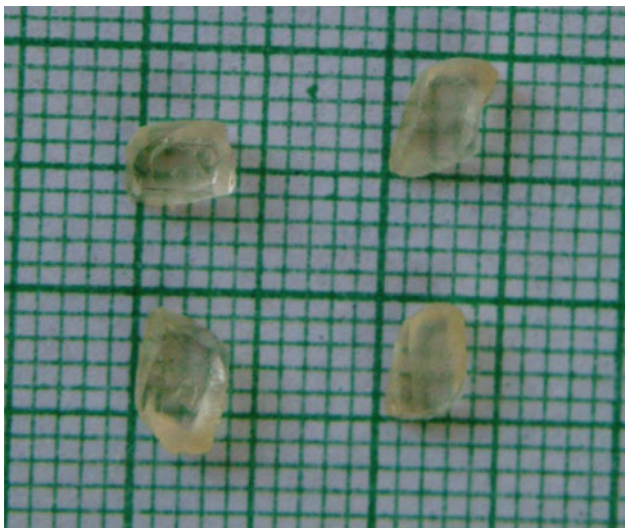


Fig. 1 As grown crystals of SDLC

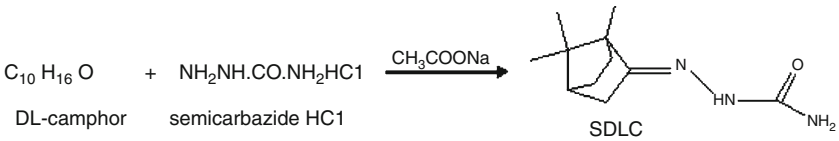
Table 1 Experimental details of single crystal X-ray diffraction

Item	Present compound	From Ref. [24]
Molecular formula	$C_{11}H_{19}N_3O$	$C_{11}H_{19}N_3O$
Formula weight	209.29 g mol^{-1}	209.29 g mol^{-1}
Space group	$P2_12_12_1$	$P2_12_12_1$
Unit cell parameters	$a = 11.302$ Å	$a = 11.203$ Å
	$b = 14.216$ Å	$b = 14.206$ Å
	$c = 7.392$ Å	$c = 7.410$ Å
	$\alpha = \beta = \gamma = 90°$	$\alpha = \beta = \gamma = 90°$
Volume	1187.7 $Å^3$	1179.4 $Å^3$
Crystal system	Orthorhombic	Orthorhombic

FTIR analysis

The absorption of IR radiation causes the various bonds in a molecule to stretch and bend with respect to one another. For the study of organic compounds, from 4,000 to 650 cm^{-1} range is of prime importance for spectral analysis [25]. The FTIR spectrum was recorded in the range between 4,000 and 450 cm^{-1} for SDLC sample on an AVATAR330 FTIR spectrophotometer using KBr pellet technique. The FTIR spectrum of compound SDLC (Fig. 2) shows sharp signals at 3,520 and 1,550 cm^{-1} which are assigned to –NH stretching and bending vibrations of semicarbazone group, respectively. An intense peak at 2,926 cm^{-1} is due to presence of alkyl groups in the camphor moiety. The intense signals of 1,691 and

Scheme 1 Preparation and molecular structure of SDLC



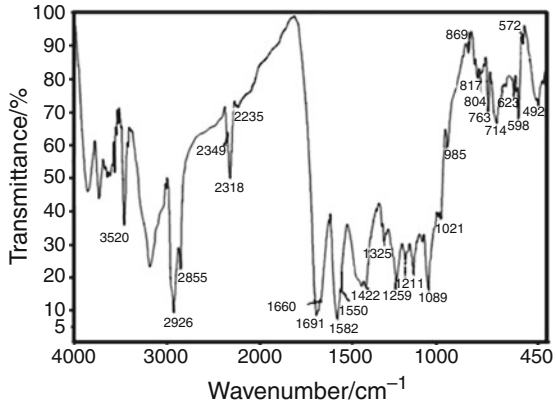


Fig. 2 FTIR spectrum of SDLC

1,582 cm^{-1} are due to presence of carbonyl group and C=N stretching frequencies, respectively.

^{1}HNMR spectral analysis

The ^{1}HNMR spectra of SDLC, was recorded on a Varian XL-200 spectrometer operating at 200 MHz using $CDC1_3$ as solvent. The recorded ^{1}HNMR spectrum of SDLC (Fig. 3) shows well resolved and distinct signals for various types of aliphatic protons present in the structure. Appearance of two signals at 0.52 and 0.78 ppm corresponds to the presence of two types of methyl groups in the molecular structure. A multiplet between 1.02 and 0.92 ppm can be attributed to the presence of two types of HC and $–CH_2$ groups. Existence of two sharp quartets between 1.21 and 1.43 ppm is due to presence of bicyclic $–CH_2$ groups. Presence of one quartet at 2.11 ppm and one doublet at 2.32 ppm correspond to –CH and $–CH_2$ protons, respectively. Semicarbazone–NH and carbonyl amide (O=C–NH_2) appear as broad signals at 3.22 and 4.52 ppm, respectively.

^{13}CNMR spectral analysis

^{13}CNMR spectrum of SDLC (Fig. 4) shows well-separated and clear signals. From this it is understood that the product formed is free from solvent and reactant impurity. The sharp signals at 15 and 22 ppm correspond to two types of methyl groups present in the compounds. The signals appeared between 25 and 60 ppm correspond to 8 types of carbons present in the compound. The appearance of peaks at 160 and 168 ppm can be attributed to the presence of semicarbazone (–C=N) and semicarbazone carbonyl group (O=C–NH_2), respectively.

UV–Vis–NIR analysis

The SDLC was subjected to UV–Vis–NIR spectral studies to determine its transparency which is an important requirement for NLO applications. The UV–Vis–NIR spectrum was taken between 200 and 1,000 nm using Shimadzu UV 240 spectrometer. In the absorption spectrum of SDLC (Fig. 5), the characteristic absorption is found between 300 and 400 nm which is assigned to the presence of π–π^* carbonyl group in the semicarbazone moiety. The spectrum also shows clearly that it is completely transparent between 400 and 800 nm which indeed prove that it can be conveniently used for modulation purposes.

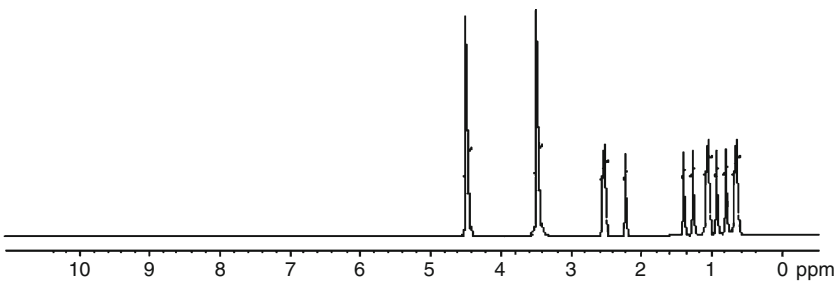


Fig. 3 ^{1}HNMR spectrum of SDLC

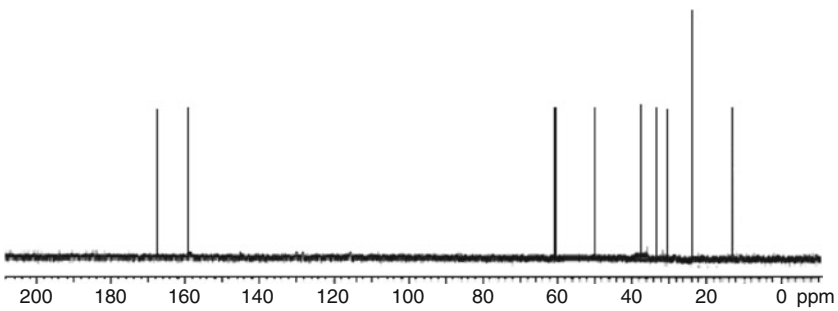


Fig. 4 ^{13}CNMR spectrum of SDLC

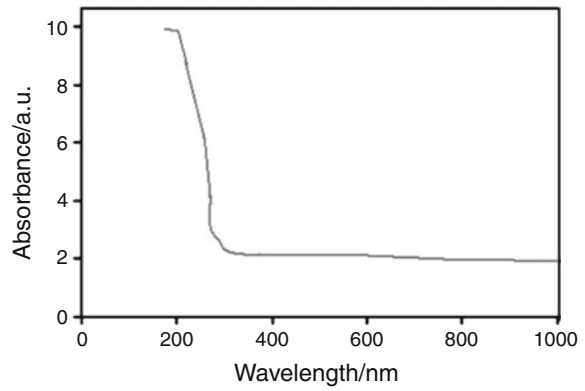


Fig. 5 UV–Vis–NIR absorption spectrum of SDLC

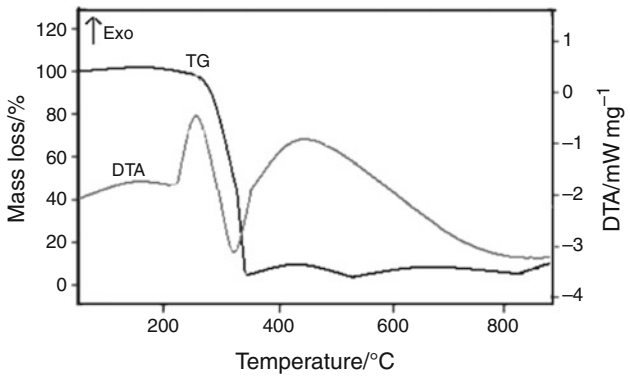


Fig. 6 TG-DTA curves of SDLC

Thermal studies

The thermogravimetric and differential thermal analysis (TG-DTA) was carried out using Netzsch STA 409 instrument simultaneously using alumina crucible in nitrogen atmosphere at a heating rate of 10 °C min^{-1} in the temperature range between 28 and 800 °C. The TGA-DTA curves of the SDLC are shown in Fig. 6. The TGA curve indicates that the synthesized compound is thermally stable up to 234 °C. This thermal analysis confirms the purity and single crystalline nature of solution grown SDLC crystal. The main SDLC decomposition in TG curve corresponds to the exothermic peak at 234 °C in DTA curve.

NLO test

The SHG property of the grown SDLC crystal was tested by the Kurtz–Perry powder method [26]. The fundamental beam of wavelength 1,064 nm from a Q-switched Nd:YAG laser with a pulse energy 3 mJ per pulse with a pulse width 8 ns at a repetition rate of 10 Hz was used. A photo multiplier tube (Hamahatsu R2059) was used as a detector and the 90° geometry was employed. The green light (532 nm) emitted from the sample, which is the fundamental SHG, detected by the detector confirmed the NLO property of the SDLC crystal.

Conclusions

Good quality SDLC crystals were grown by solution growth technique using slow evaporation method. A grown crystal was subjected to single crystal XRD analysis, FTIR, ^{1}HNMR, ^{13}CNMR, and UV–Vis–NIR spectral analysis and TG-DTA. The XRD results confirmed the single crystalline nature of the solution grown SDLC. The presence of semicarbazone functional group and alkys groups were supported by FTIR spectral analysis. The ^{1}HNMR and ^{13}CNMR spectral studies confirmed the presence of the functional groups and purity of the grown crystals. The UV–Vis–NIR spectral studies revealed its transparency. It was found that the grown crystal has been transparent for a wide range which is characteristic property for a NLO material. Thermal studies confirmed the purity and single crystalline nature of the solution grown SDLC and also found it was thermally stable up to 234 °C. The NLO behavior of the SDLC crystals was observed by Kurtz–Perry powder technique. Hence, it is concluded that the grown crystal is a potential candidate for optoelectronic applications.

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