RESEARCH ARTICLE

DOI: 10.34256/bsr2112

BULLETIN OF SCIENTIFIC RESEARCH

Growth, optical, spectral, thermal and mechanical investigations of organic NLO crystal *cis*-2, 6-bis(4-chlorophenyl)-3, 3-dimethylpiperidin-4-one

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Received: 01-11-2020
Accepted: 02-01-2021

Abstract: The single crystal of *cis*-2,6-bis(4-chlorophenyl)-3,3-dimethylpiperidin-4-one (4C3DMPO) has been grown using a slow evaporation technique. 4C3DMPO is a non-centrosymmetric crystal which crystallizes in the orthorhombic system with space group $Pna2_1$. Benzene is used as a solvent for the crystal growth based on solubility studies. The mechanical studies, using microhardness methods, have also been carried out. The compound is characterised using UV, FT-IR and NMR spectral studies. Furthermore, the thermal stability of the crystal is established by TG/DTA. The nonlinear optical studies (SHG) of the crystal have been determined using the Kurtz and Perry powder technique and the activity observed is 2.5 times greater than that of KDP.

Keywords: Crystal growth, Solubility, Microhardness, Thermal properties.

1. Introduction

Organic crystals have been extensively studied due to their nonlinear optical (NLO) coefficients often being larger than those of inorganic materials. Many new organic crystals have been grown based on the predictive molecular engineering approach and have been shown to contain potential applications in nonlinear optics. Some interest has been shown in the search for ultraviolet laser materials [1-4]. Crystal growth from a solution is a very important process is used in many applications from the laboratory to the industrial scale. An innumerable number of organic and inorganic crystals is grown in this fashion [5-7]. In the last decade, organic nonlinear optical (NLO) crystals with aromatic rings have attracted much attention because of their high nonlinearity, fast response and tailor made flexibility [1-10].

The search and design of highly efficient nonlinear optical (NLO) crystals for visible and ultraviolet (UV) regions are essential for laser processing. High-quality organic NLO crystals must possess a sufficiently large NLO coefficient, transparent in the UV region, high laser damage threshold power, and easy growth with large dimensions [9-11].

In this paper, the single crystal of *cis*-2,6-bis(4-chlorophenyl)-3,3-dimethylpiperidin-

one (4C3DMPO) is grown by a slow evaporation method using benzene as a solvent. 4C3DMPO is a non-centrosymmetric crystal that crystallizes in the orthorhombic system with space group $Pna2_1$ [12]. The grown single crystal of 4C3DMPO has been subjected to various characterization techniques *viz*., UV-VIS, FT-IR, ^1H & ^{13}C NMR spectroscopy, thermal studies, microhardness test and SHG studies.

2. Experimental

2.1 Preparation and Crystal growth

To a solution of ammonium acetate (0.05 mol) in absolute ethanol (60 ml), 4-chloro-benzaldehyde (0.1 mol) and 2-methylbutanone (0.05 mol) were added and the resultant contents were taken in a round bottom flask fitted with a water condenser. The contents were heated for 30 minutes and kept at room temperature overnight [13]. The separated crystals were washed well with absolute alcohol and purified by recrystallisation from benzene (Fig.1). The melting point is found to be 128-30 ^{0}C at RT.

A slow evaporation technique is used to obtain large crystals. The saturated solution of benzene is prepared at 45 ^{0}C based on the solubility studies and it is covered with a perforated sheet for slow evaporation. The solution is kept in dust free environment for crystallization. Under the experimental condition, bright, transparent and colorless crystals of 4C3DMPO are obtained within 7 days. The grown crystals are collected from the mother liquor by using well cleaned forceps. The photograph of the 4C3DMPO crystal is shown in Fig.2.

2.2 Solubility

The solubility of 4C3DMPO is determined at various temperatures using a recrystallized compound. The solubility of 4C3DMPO is tested with benzene and pet-ether at 25, 35, 45 and 55 ^{0}C by gravimetric method [14].

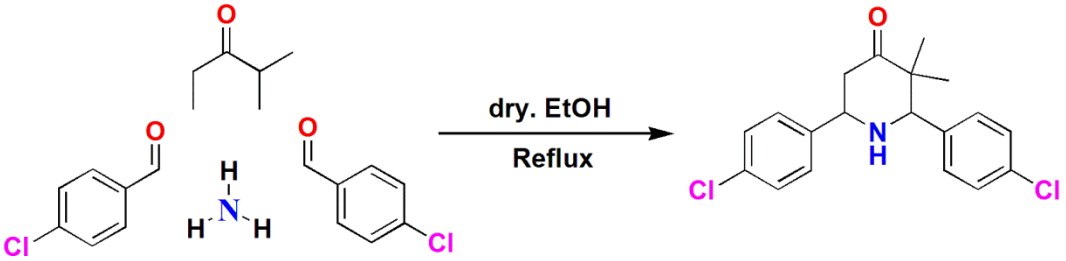

Figure 1. Synthesis of *r*-2,*c*-6-bis(4-chlorophenyl)-*c*-3,*t*-3-dimethyl piperidin-4-one (4C3DMPO).

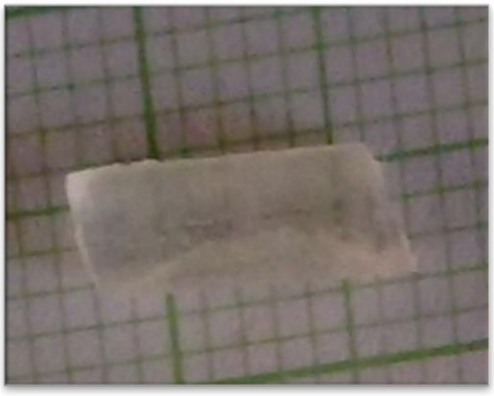

Figure 2. As grown crystals of 4C3DMPO

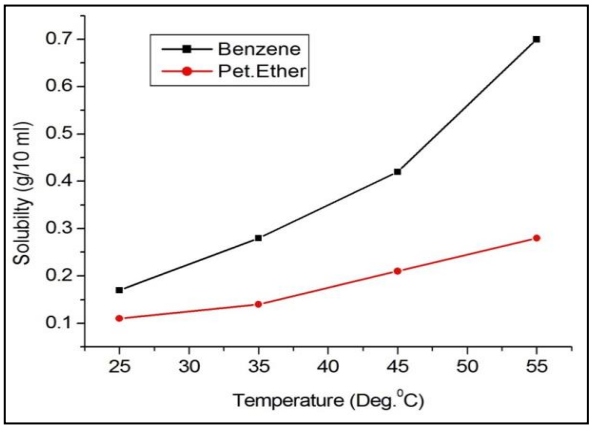

Figure 3. Solubility test for 4C3DMPO

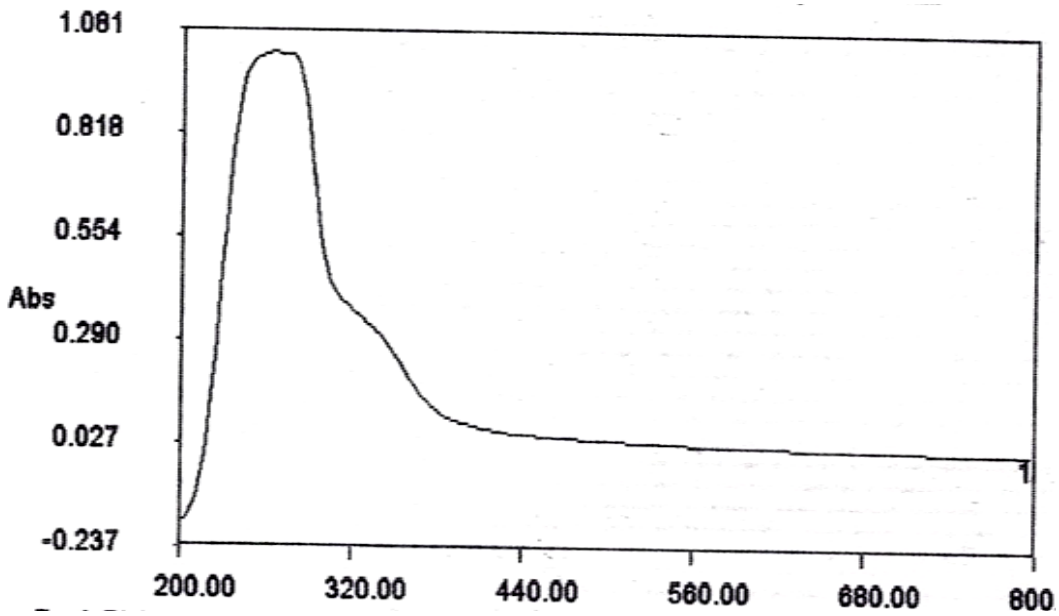

Figure 4 UV-Vis absorption spectrum of 4C3DMPO.

The selected solvent and excess 4C3DMPO are added to a 250 ml airtight glass container. The solution is gently stirred for an optimum period to attain saturation. After attaining saturation, the equilibrium concentration of the solute is analyzed gravimetrically. From the solubility curve shown in Fig. 3., benzene is found to be the most suitable solvent.

3. Characterization

3.1 Analysis of UV-VIS Spectrum

To determine the transmission range as well as to know the suitability of the 4C3DMPO crystals for the optical applications, the UV-Visible absorption spectrum of 4C3DMPO is recorded and reproduced in Fig. 4. The Electronic absorption spectrum of the compound is recorded in ethanol by employing Systronics make Double Beam UV-Vis spectrometer Model 2202 in the range of 200 nm to 800 nm. The spectrum exhibits strong absorption bands due to π-π* and n-π* transitions in the near UV-region of the spectrum. The crystal does not exhibit any absorption band in the entire visible region up to 800 nm and shows a wide transparency window. A very good optical transparency strongly suggests that the grown crystals of the title material are suitable for various optical and NLO applications.

3.2 FT-IR studies

The FT-IR spectrum of the grown crystal is recorded by employing the Perkin Elmer IR spectrophotometer in the region 4000-400 cm^{-1} using KBr pellet technique. The vital application of infrared spectroscopy to organic compounds is to identify the presence of various functional groups, which in turn supports the determination of the molecular structure. The FT-IR spectrum of 4C3DMPO is depicted in Fig.5. The sharp band appearing at 3302 cm^{-1} is ascribed to the stretching vibration of the N–H group. The aromatic C–H symmetric stretching vibration is observed at 3000-27 cm^{-1}. The bunch of frequencies appearing around 2900-3000 cm^{-1} has been assigned to the C–H asymmetric and symmetric stretching vibrations of methyl and methylene groups in the molecule. The strong and sharp band appearing at 1702 cm^{-1} is assigned to the carbonyl (>C=O) stretching vibration.

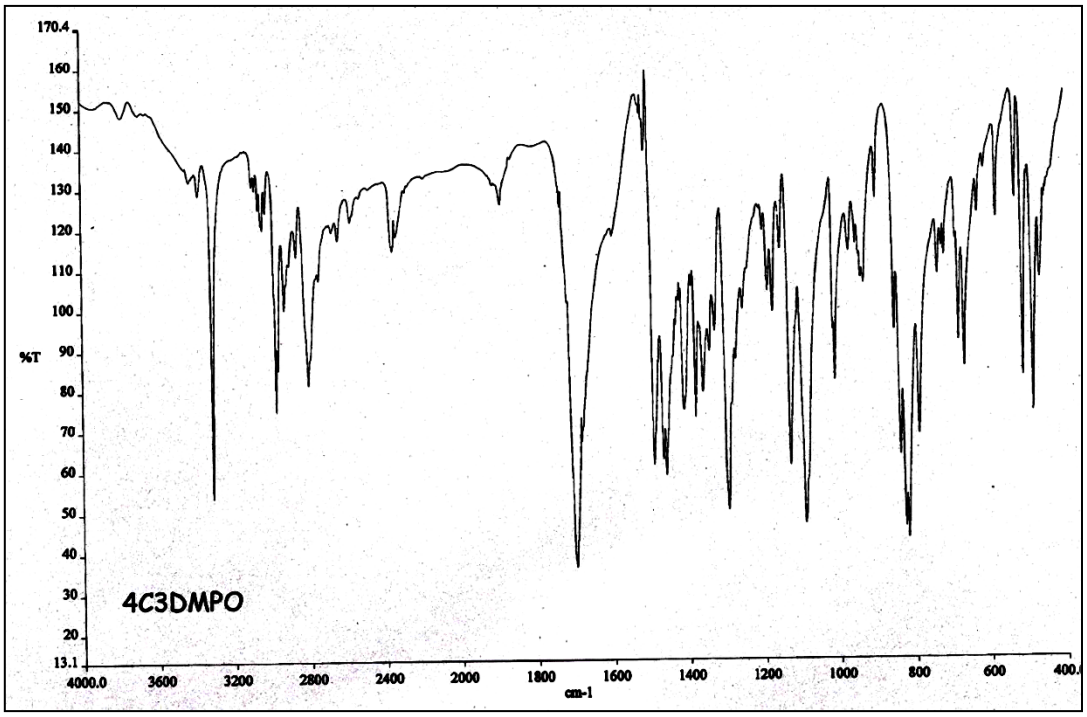

Figure 5. FT-IR spectrum of 4C3DMPO.

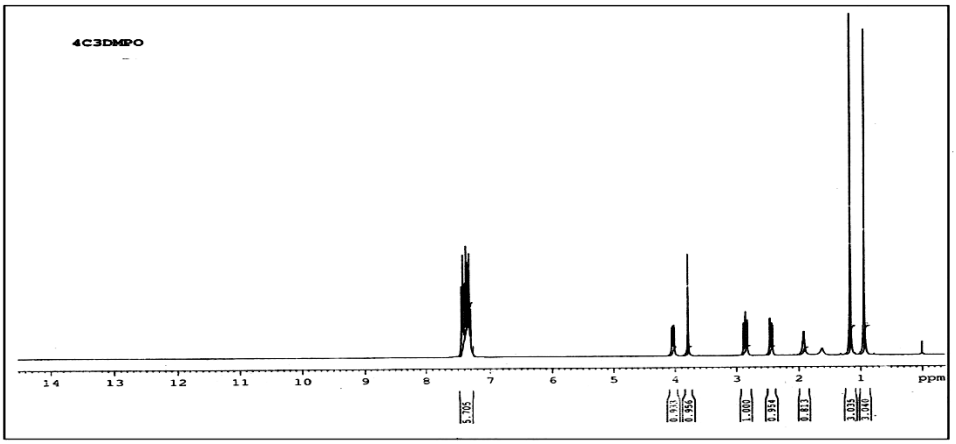

Figure 6 ^{1}H-NMR spectrum of 4C3DMPO.

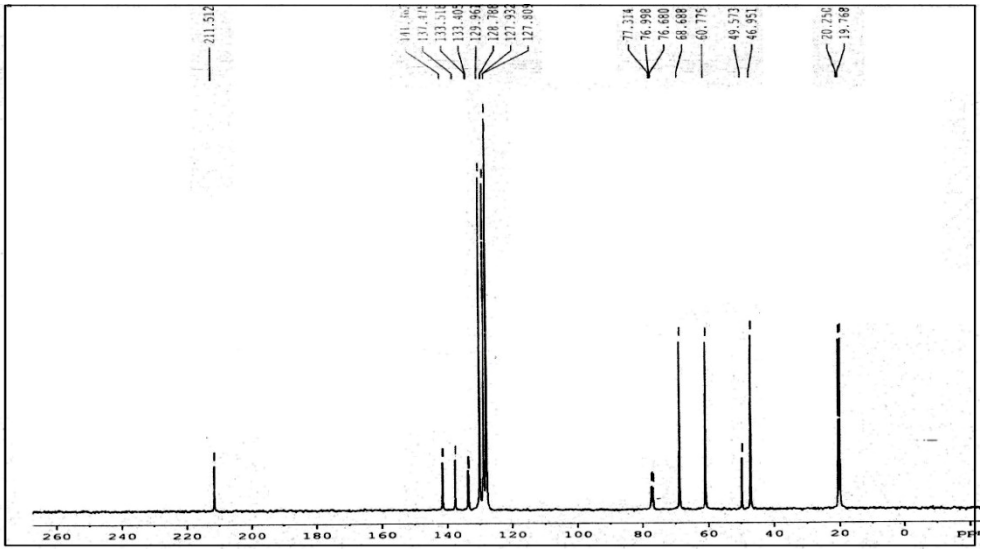

Figure 7 ^{13}C-NMR spectrum of 4C3DMPO.

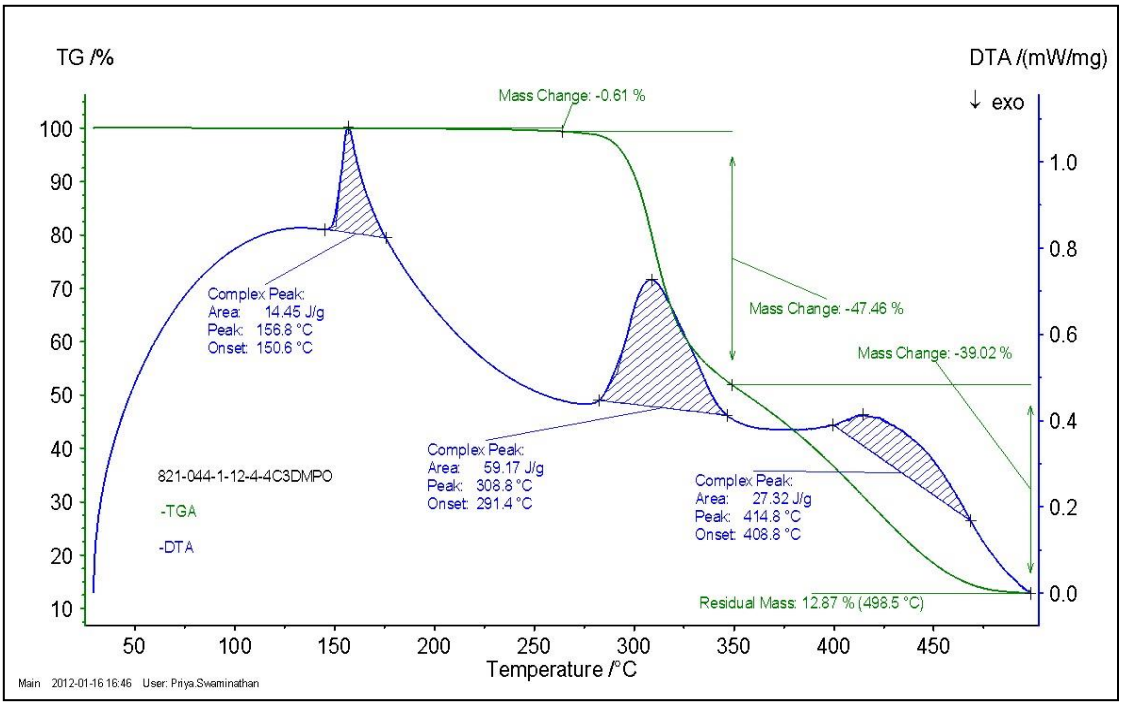

Figure 8 TG/DT Analysis of 4C3DMPO.

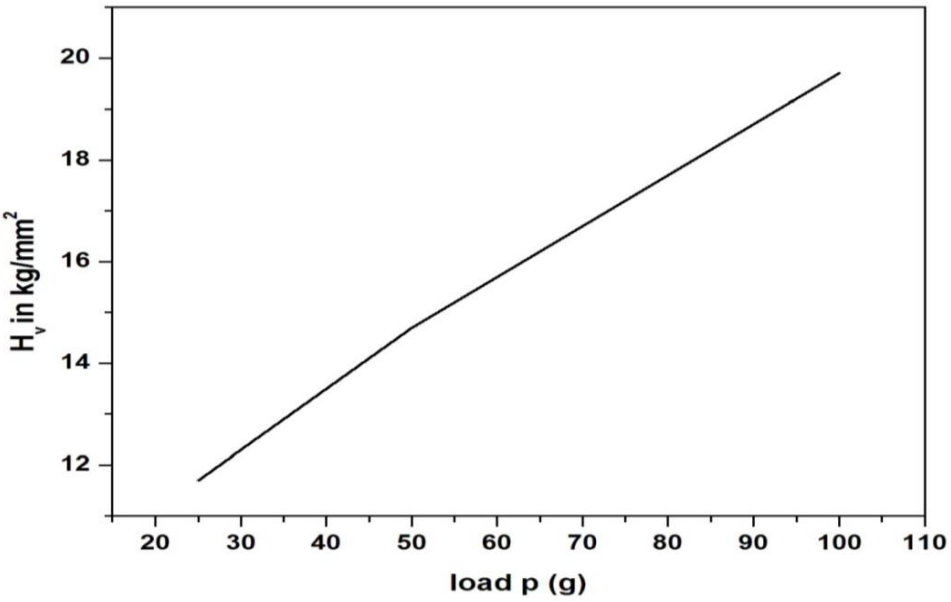

Figure 9 Vicker's micro hardness test for 4C3DMPO

3.3 Analysis of ^{1}H & ^{13}C NMR spectrum

The ^{1}H NMR spectrum of 4C3DMPO (δ ppm) is recorded in a Bruker-500 MHz NMR spectrometer in $CDCl_3$ (Fig.6). The protons of two methyl groups appear at 0.93 (s, 3H, CH_3 at C3a) and 1.16 (s, 3H, CH_3 at C-3e). The NH proton appearing at 1.91 has been confirmed by the D_2O exchange experiment. The equatorial and axial protons at C5 appear at 2.44 (dd, 1H, $J_{5a,\ 5e}$ = 12 Hz and $J_{5e,6a=}$ 3.2 Hz, H-5e) & 2.85 (dd, 1H, $J_{5a,\ 5e}$ = 12 Hz and $J_{5a,\ 6a}$ = 12 Hz, H-5a). The benzylic protons at C2 & C6 appear at 3.79 (s, 1H, H-2a) and 4.03 (dd, 1H, $J_{5a,\ 6a}$ = 12 Hz and $J_{5e,6a=}$ 3.2 Hz, H-6a). The signals appear in the aromatic region accounting for 8 protons observed as a multiplet between 7.26 and 7.43.

The ^{13}C NMR spectrum of 4C3DMPO (δ ppm) is given in Fig.7. The carbons of two methyl groups at C3 appear at 19.76 and 20.25. The intense signal appearing at 46.95 is due to C5 carbon and a less intense signal at 49.57 is assigned to the C3 carbon. The benzylic carbon signals at C2 & C6 appear at 68.68 & 60.77, respectively. The aromatic carbon signals appear in the region 127.8-129.7 and the *ipso* carbons are responsible for the weak signals at 133.4-141.4. Further, the carbonyl carbon appears at 211.51.

3.4 Thermal Analysis

The thermal analysis provides information about the thermal stability, thermal decomposition and products formed on decomposition. Fig. 8 shows the TGA and DTA curve of 4C3DMPO performed on a thermal analyser, NETZSCH STA 449F3, recorded in multiples of -10 ºC/min up to 500 ºC.

A thermal analyzer is used at a heating rate of 10 ºC/min under nitrogen for the compound 4C3DMPO between a temperature range of 25 ºC and 500 ºC. Absence of physically adsorbed and lattice water is accounted for an extended temperature of up to 230 ºC since weight loss occurred beyond 230 ºC. A steep decrease of weight loss (47.46 %) in the temperature range from 230 ºC to 348 ºC of the TG curve ensured the partial breakdown of the compound. A further gradual decrease in the change in weight loss (≈ 39.02 %) between 348 and 498 ºC is due to the complete rupture of the compound. From DTA curve, it is observed that material attains a solid–liquid transition temperature at 156 ºC indicative of the melting point of the substance exhibiting a stable condition up to 156 ºC. From the DTA curve above 156 ºC, it is seen that the material begins to attain an endothermic transition and decompose. The sharpness of this endothermic peak shows a good degree of crystalline nature of the sample as well as its stability. From the observation of TG/DTA, the ideal property for the choice of an NLO crystal is ensured.

3.5 Vickers microhardness studies

Vickers microhardness measurement studies are carried by using Shimadzu hardness tester at room temperature. The Vickers microhardness number, Hv, is calculated using the relation, $Hv=1.8544(P/d^2)$ kg/mm^2, where P is applied load (g) and d is the diagonal length (μm) of the indentation. The variation of Hv as a function of applied load ranges from 25 to 100 g on 4C3DMPO crystal (Fig. 9). It is very clear from the figure that H_v increases with an increase in the load. The phenomenon of the dependence of microhardness of a solid on the applied load is known as the indentation size effect (ISE). Mayer's law relates the load and size of indentation as $P=k_1d^n$, where k_1 is the material constant and 'n' Mayer's index. The slope of the graph of log P against log d gives the value of 'n' and it is found to be 2.00. Hence, 4C3DMPO crystal belongs to the softer material category [15].

3.6. SHG measurements

SHG conversion efficiency of the grown 4C3DMPO crystals is measured by Kurtz and Perry technique [16]. A Q-switched Nd: YAG laser is used as a light source. A laser beam of fundamental wavelength 1064, 8 ns pulse width, with a 10 Hz pulse rate is made to fall normally on the sample cell. Potassium dihydrogen orthophosphate (KDP) crystal is powdered and is used as reference material in the SHG measurement. The input laser energy incident light is 2.5 mj/pulse. The SHG is confirmed by the emission of bright green radiation. The 4C3DMPO second harmonic signal of 45 mv is obtained while the KDP gives an SHG signal of 18mv for the same input beam energy. Thus SHG relative efficiency of 4C3DMPO is found to 2.5 times higher than that of KDP crystal.

4. Conclusion

The single crystals of 4C3DMPO material with good optical quality have been grown from benzene solution by slow evaporation technique at ambient temperature. The characterization of the crystal has been carried out using UV-Visible, FT-IR & ^{1}H, ^{13}C NMR spectra and thermal & NLO studies. Vickers microhardness measurement studies show that the crystal belongs to the softer material category. Further, the SHG efficiency was found to be 2.5 times higher than that of standard KDP, which suggests that 4C3DMPO is a much useful material for the NLO applications.

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Acknowledgement

The authors thank **Dr. N. Velmani** for his help in the discussion on thermal analysis.

Funding

This study was not funded by any grant

Authors Contribution

Methodology, Manuscript preparation, review and editing; **V. Mohanraj**, Manuscript preparation, review and editing; **S.S. Ilango**, Study conceptualization, supervision, manuscript review and editing, **S. Ponnuswamy**. All authors have read and approved the manuscript.

Conflict of interest

None of the authors have any conflicts of interest to declare.

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