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Growth and characterization of a new organic nonlinear optical 2-methoxy-1-naphthaldehyde (2MN) single crystal

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ABSTRACT

2-methoxy-1-naphthaldehyde (2MN) an intriguing new organic material for frequency conversion has been grown by slow evaporation solution growth technique at room temperature. Their structural, optical and physicochemical properties were characterized by X-ray powder diffraction, FTIR and UV-Vis spectra. The crystal belongs to monoclinic system with point group m and space group C_s. The material has a wide transparency in the entire visible region. It is found that the cutoff wavelength lies in the UV region. The mechanical response of the crystal has been studied using Vickers microhardness technique. The SHG relative efficiency of 2MN crystal was found to be 12 times higher than that of KDP and 1.6 times higher than that of Urea.

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Introduction

The development of organic materials for use in nonlinear optical (NLO) devices is of interest because their optical nonlinearities are orders of magnitude larger than those of conventional inorganic materials such as lithium niobate ($LiNbO_3$) and potassium dihydrogen phosphate (KDP). Moreover, organic materials offer flexibility of molecular design, virtually an unlimited number of crystalline structures, purification by conventional methods, and a high damage resistance to optical radiation. The current interest in finding organic nonlinear optical (NLO) materials is a result of the promising potential applications in optical information processing, telecommunications, and integrated optics [1], as well as the much larger nonlinear response, extremely fast switching time, and higher laser damage threshold compared to the currently studied inorganic materials. To have useful second-order nonlinear optical properties, the compound must possess a large second-order molecular nonlinearity and also be crystallized in a noncentrosymmetric structure to have a nonzero $x^{(2)}$. Since optical nonlinear response of organic materials is related to both the magnitude of the molecular hyperpolarizability and the alignment of the molecules in the medium [2], the magnitude of the molecular second-order hyperpolarizability β should first be enhanced in order to increase the macroscopic nonlinearities of NLO materials. That is to say, the molecular hyperpolarizability β plays an important role in the NLO properties and a systematical study on β should be carried out. Generally, β increases when strong donor and acceptor groups are attached and π-conjugation is elongated [3,4]. But very strong donor or acceptor groups and large-conjugated system usually cause redshift of the first electronic absorption peak [5] and therefore the transparency of the NLO materials will decrease, which is unexpected in application fields. However, it seemed that the small conjugated system is more suitable for the useful NLO materials, especially for the transparency. The growth of high quality crystals is required for the use of organic materials in nonlinear optical devices. One reason for this requirement is that inhomogeneities in optical materials give rise to variations in the refractive index or absorption, which results in distortion of the optical beam to be processed [6]. In optical devices these distortions give rise to a low signal-to-noise ratio. As a rule, the problem of inhomogeneties becomes more serious as the nonlinearities of materials become larger. This work elucidate the intermolecular interactions in 2-methoxy-1-naphthaldehyde (2MN), by investigation of its molecular structure and IR spectra and the optical studies. From this technological point of view, 2MN having superior non-linear optical properties has been exploited for variety of applications.

Experimental Techniques

Synthesis and Crystal Growth

The low-temperature solution growth technique is widely used for the growth of organic and inorganic single crystals to get more transparent single crystals. The single crystals of 2-methoxy-1-naphthaldehyde have been successfully grown from slow evaporation solution growth technique at room temperature using acetone as solvent. The commercially available 2-methoxy-1-naphthaldehyde (LOBA Chemie make) is purified by repeated recrystallization process. The repeated recrystallized materials have been used for growth as charge material. Since 2-methoxy-1-naphthaldehyde is insoluble in water, we have chosen acetone as solvent for our growth. The growth process and the quality of crystals significantly depend on supersaturation. The saturated solution of 2-methoxy-1-naphthaldehyde was obtained by dissolving the charge material into the acetone solvent with continuous stirring of the solution using a magnetic stirrer at room temperature (32°C). On reaching saturation, the equilibrium concentration of the solute was determined by gravimetry. The beaker containing the solution was optimally closed for controlled evaporation. Transparent bright yellow single crystals were obtained from the mother solution after a week. The molecular structure of the grown crystal is given below:

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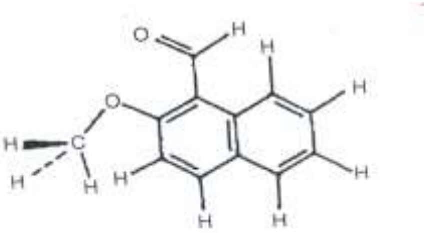

Solubility

The solubility of 2-methoxy-1-naphthaldehyde was measured in the temperature range from room temperature to 52°C. A volume of 150 ml of acetone was taken in an airtight container and recrystallized salt was added. Once the saturation was reached, the equilibrium concentration of the solute was analyzed gravimetrically.Single crystals of the title compound have been grown from saturated solution at a pH of 3.5 by slow evaporation solution growth technique at 35°C using constant temperature bath having controlled accuracy of 0.01°C. The growth of the title compound needed a week, single crystals with good optical quality having rectangular shape and dimensions of 12 x 9 x 5 mm^3 have been obtained. The experiment was carried out for various temperatures from room temperature to 52°C in steps of 10°C and the solubility curves were drawn in Fig.1.The photograph of the grown crystals is depicted in Fig.2.

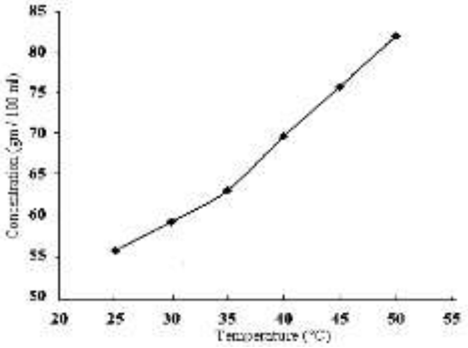

Fig 1. Solubility curve of 2MN

Fig 2. Photograph of the 2MN crystal grown in methanol

Recording of Spectra

X-Ray Diffraction Studies

Powder X-ray diffraction analysis has been carried out to confirm the crystallinity and also to identify the lattice parameters. Powder X-ray diffraction pattern was recorded using a Rich Seifert diffractometer with CuKα (λ = 1.5406 Å) radiation. The crystal belongs to monoclinic system with point group *m* and space group C_s. There are 12 molecules in a unit cell. The X-ray diffraction pattern for the sample of 2MN is shown in Fig.3. The lattice parameter values are a =11.985 Å, b=5.484 Å, c= 12.963 Å, α=β=90° and γ=102.27°. The crystallographic data of 2MN is given in Table.1.

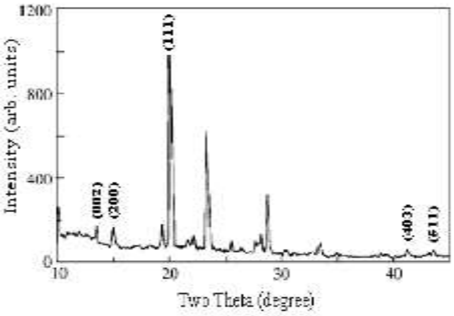

Fig 3. The indexed X-ray diffraction pattern of 2MN

Table 1.
Crystallographic data of 2MN

Identification code	2MN
Empirical formula	$C_{12}H_{10}O_2$
Formula weight	186.2102
Crystal structure	Monoclinic
Space group	C_s
Cell parameters	
a(Å)	11.985
b(Å)	5.484
c(Å)	12.963
α(°)	90
β(°)	90
γ(°)	102.27
Volume (Å)^3	852.00277
Z	12
Point group symmetry	*m*
Crystal size	12 x 9 x 5 mm^3

FT IR Measurements

The Fourier transform infrared spectrum of the title crystal was recorded in the region 400 – 4000 cm^{-1} using Perkin Elmer Spectrum RX1 spectrophotometer. The experimental spectrum is shown in Fig.4.

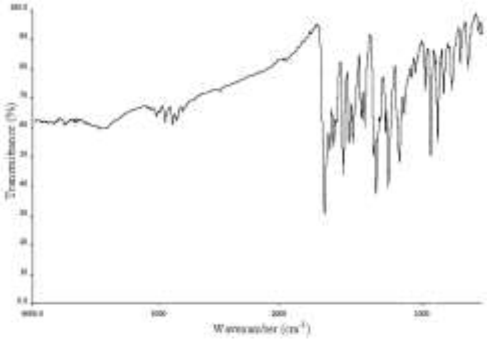

Fig 4. Experimental FT IR spectrum of 2MN

Results and Discussions

Vibrational Spectral Analysis

Vibrational spectroscopy is an important tool in understanding the chemical bonding and provides useful information in studying the microscopic mechanism of the NLO properties of new materials.

Carbon-Hydrogen Vibration

The substituted benzene gives rise to C-H stretching, C-H in-plane and C-H out-of-plane bending vibrations. Aromatic compounds commonly exhibit multiple weak bands in the region 3100-3000 cm^{-1} due to aromatic C-H stretching vibrations. The bands due to C-H in-plane bending vibrations interact with C-C stretching vibrations and observed as a number of bands in the region 1300-1000 cm^{-1}. The C-H out-of-plane bending vibrations occur in the region 900-667 cm^{-1}[7]. In this region the bands are not affected appreciably by the nature of the substituents. Hence, in the present investigation the infrared bands identified at 3083-2943 cm^{-1} are assigned to C-H stretching vibrations. The FT IR band at 1271 cm^{-1} were assigned to C-H in-plane bending vibration, this mode between carbon and hydrogen atoms are identified at 1369, 1265, 1250, 1175 and 1147 cm^{-1}. The out-of-plane bending vibrations of C-H of the title compounds were well identified in the recorded spectra within their characteristic region.

Methyl Group Vibration

The title compound consists of one CH_3 group. For the assignments of CH_3 group frequencies one can expect that nine fundamentals can be associated to CH_3 group, namely the symmetrical (CH_3 ips) and asymmetrical (CH_3 ops), in-plane stretching modes (i.e. in-plane hydrogen stretching mode), the symmetrical (CH_3 ss), and asymmetrical (CH_3 ips), deformation modes, the in-plane rocking (CH_3 ipr) out-of-plane rocking (CH_3 opr) and twisting (τ CH_3) bending modes. In addition to that the asymmetric stretching (CH_3 ops) and asymmetric deformation (CH_3 opb) modes of the CH_3 group are expected to be depolarised for A" symmetry species. The infrared band found at 2803cm^{-1} and 2883, 2841cm^{-1} represent symmetric and asymmetric CH_3 stretching vibrations of the methyl group in 2MN.

The fundamental vibrations arising from symmetric, asymmetric in-plane and out-of-plane deformations, rocking and twisting modes of CH_3 group are observed in their respective characteristic regions and they are listed in Table.2 respectively.

Table 2.
Observed IR wavenumbers (in cm^{-1}) of 2MN and its vibrational assignments

Wavenumber FTIR	Assignments
3083 ms	ν(CH)
3059 s	ν(CH)
3012 ms	ν(CH)
2988 ms	ν(CH)
2943 ms	ν(CH)
2883 w	$\nu_{in\ plane}(CH_3)$
2841 w	$\nu_{out\ of\ plane}(CH_3)$
2803 w	$\nu_{sym}CH_3$
2791 vw	ν(CH)
1664 vs	ν(C-C), ν(CO)
1369 ms	b(CH), ν(C=C)
1271 w	b(CH), ν(C=C),ν(CO)
1265 ms	b(CH), ν(C=C)
1250 s	b(CH), ν(C=C)
1175 ms	b(CH), ν(C=C)
1147 s	b(CH), ν(C=C)
858 ms	$\varphi_{in\ plane\ stretching}$,b(CH), ν(C=C)
850 w	$\varphi_{in\ plane\ stretching}$,b(CH), ν(C=C)
790 w	$\varphi_{in\ plane\ stretching}$,b(CH), ν(C=C)
776 ms	$\varphi_{in\ plane\ stretching}$
525 w	$\varphi_{out\ of\ plane\ stretching}$
509 ms	ω(CH), ω(C=C)
418 w	b(C=C)
405 w	b(C=C)

ν, stretching; φ, ring; ω, torsion; b, bending;
w, weak; m, medium; ms, medium strong; s, strong;

Aldehyde Group Vibration

The carbonyl (C=O) stretching in aldehydes generally occurs in the region 1740-1720 cm^{-1}[7]. The introduction of a methyl group in conjugation with the carbonyl (aldehyde) group results in 40-60 cm^{-1} shift to lower frequency and consequently the band will appear at 1664cm^{-1}.

The C-H stretching absorption in aldehydes generally appears as weak intensity doublet in the region 2030-2795 cm^{-1}. Accordingly in the present investigation, the aldehyde C-H stretching vibrations for the title compound were observed at 2791 cm^{-1} respectively. The other aldehyde group vibrations obtained and assigned in this study were found in agreement with literature[8-11].

Ring Vibrations

In the present study the bands at 858, 850, 790, 776, 418, 405 cm^{-1} and 525, 509 cm^{-1} have been designated to ring in-plane and out-of-plane bending modes respectively by careful consideration of their quantitative descriptions. A small changes in frequency observed for these modes are due to addition of methoxy group to naphthaldehyde and from different extents of mixing between the ring and substituent group vibrations.

Optical Characterization

Transparency Range

The transparency of 2MN crystal was measured using Perkin Elmer Lambda 35 UV visible spectrophotometer in the range 190 to 1100 nm and the transmittance spectrum of the pure crystal is shown in the Fig.5(a). Allowing for orbit hybridization, the ultraviolet cutoff wavelength of organic crystals depends on π - π* transitions of aromatic rings. The title crystal possesses good stability and do not show any hygroscopic effect for a long time. The absorption near the Nd:YAG laser fundamental (1064 nm) and second harmonic wavelengths (532 nm) is reduced which contributes the resistance of the material to laser damage threshold. The useful transmission range makes it valuable for applications that require blue green light. This made us to come to a tangible conclusion that the material is better entrant for nonlinear optical applications. Fig.5(b) shows the plot of $(\alpha h\nu)^2$ against photon energy $h\nu$ for the 2MN crystal. The bandgap for the crystal is calculated as 5.33154eV. The energy gap of semiconductors is much smaller than those of the organic crystals. This results in the shortening of UV absorption edge below 200 nm in the recorded spectrum of 2MN.

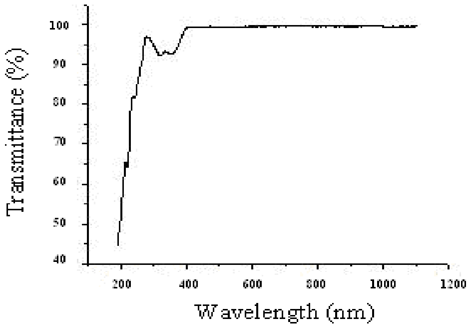

Fig. 5(a) Optical transmission spectrum of 2MN

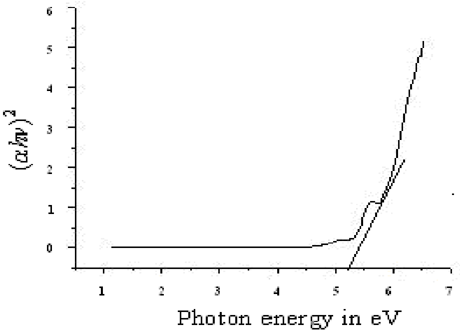

Fig. 5(b) Plot of $(\alpha h\nu)^2$ versus photon energy *h*

Second Harmonic Generation Studies

A quantitative measurement of the conversion efficiency of 2MN crystal was determined by the modified version of powder technique developed by Kurtz and Perry.The SHG relative efficiency of 2MN crystal was found to be 12 times higher than that of KDP and 1.6 times higher than that of Urea.

Mechanical Behaviour

In order to study the mechanical properties, microhardness measurements were carried out on 2-methoxy-1-naphthaldehyde single crystals. The variation of Vickers hardness number with applied load for 2MN is shown in Fig.6. Indentations were made using a Vickers indenter for various loads from 5 to 25 g. It is observed that the Vickers hardness value increases with applied load. According to Onitsch if n > 2, the microhardness number Hv increases with increasing load. Test load above 25g develop multiple cracks on the crystal surface due to the release of internal stress generated locally by indentation. The work hardening coefficient 'n' is found to be 3.94, which proves the high mechanical strength of the grown 2MN crystal.

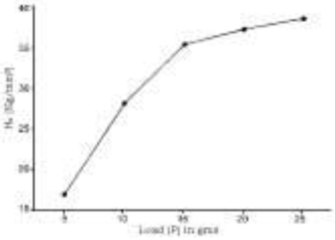

Fig. 6 Plot of H_v versus Load of 2MN

Conclusion

A single crystal of 2-methoxy-1-naphthaldehyde was grown from the acetone by slow evaporation method. FTIR confirmed the various molecular group vibrations and protonation of benzene in the grown crystals. As there is no change in transmittance in the entire visible range upto 200nm, these materials can find application as window in spectral instruments in that region. The SHG relative efficiency of 2MN crystal was found to be 12 times higher than that of KDP and 1.6 times higher than that of Urea. The vibrational spectral analysis also justifies the presence of methyl group and aldehyde group. Hence the 2-methoxy-1-naphthaldehyde have nonlinear polarizability and exhibit SHG property. Vickers hardness was carried out and found that the present material obeys the Indentation Size Effect. Based on these facts it could be concluded that the present material has good propensity for nonlinear optical activity.

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