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Synthesis, growth, structural, optical, spectral, thermal and mechanical studies of 4-methoxy 4-nitrostilbene (MONS): A new organic nonlinear optical single crystal

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HIGHLIGHTS

G R A P H I C A L A B S T R A C T

- ► 4-Methoxy 4-nitrostilbene (MONS) crystal was grown by slow evaporation method.
- Lattice parameters of the crystal were determined by single crystal XRD.
- Crystalline perfection was studied using high resolution X-ray diffraction.
- ¹H NMR confirms the structure of the MONS crystal.
- SHG efficiency of the MONS was found to be 1.55 times greater than that of KDP.

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ABSTRACT

4-Methoxy 4-nitrostilbene (MONS), a new organic nonlinear optical material has been synthesized. Based on the solubility data good quality single crystal with dimensions up to $38 \times 11 \times 3 \text{ mm}^3$ has been grown by slow evaporation method using ethyl methyl ketone (MEK) as a solvent. Powder XRD confirms the crystalline property and also the diffraction planes have been indexed. The lattice parameters for the grown MONS crystals were determined by using single crystal X-ray diffraction analysis and it reveals that the crystal lattice system is triclinic. The crystalline perfection of the grown crystals has been analysed by high resolution X-ray diffraction (HRXRD) rocking curve measurements. Fourier transform infrared (FTIR) spectrum for powdered MONS sample confirms the functional groups present in the grown crystal. The UV-vis absorption spectrum has been recorded in the range of 190–1100 nm and the cut off wavelength 499 nm has been determined. The optical constants of MONS have been determined through UV-vis-NIR spectroscopy. The MONS crystals were further subjected to other characterizations. i.e., ¹H NMR, TG/DTA, photoluminescence and microhardness test. The Kurtz and Perry powder technique confirms the NLO property of the grown crystal and the SHG efficiency of MONS was found to be 1.55× greater than that of KDP crystal.

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SPECTROCHIMICA ACTA

Introduction

In the past decades significant research attention has been paid to organic NLO materials due to their large advanced applications in fast developing fields such as photonics and optoelectronics [1]. 3-Methyl 4-methoxy 4-nitrostilbene (MMONS) was found to be significantly more efficient (1250× greater than Urea) for second harmonic generation. Optimization of MMONS can be done in order to get new derivatives that possess higher order optical nonlinearities and better characteristics with high optical quality single crystals for various optoelectronic applications using different crystal growth techniques [2] Shoukui et al. [3] reported that 3-methoxy 4-methoxy 4-nitrostilbene (MOMONS) crystal has been

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grown by melt growth technique with SHG efficiency $0.2-3\times$ greater than that of KDP, which was measured by the powder technique. The MONS crystals composed of aromatic molecules with π electron donor and acceptor substitutions normally exhibits intermolecular charge transfer that leads to the non centrosymmetric property which makes them as a good frequency conversion material [4]. The identification, design, synthesis of new molecules and tailoring of molecular structure has been utilized to promote crystallization of potentially useful molecules in non centrosymmetric crystal structures [5]. Interestingly, only powder SHG studies were carried out on this material using different solvents [6]. To the best of our knowledge, no other report is available on MONS crystal till date. In this communication, we report the novel MONS crystal, which is a derivative of Stilbene family with NLO property and it was grown by the slow evaporation method. The grown crystals were subjected to the characterizations like X-ray diffraction analyses, high resolution XRD, FTIR, ¹HNMR, TG/DTA, UV-vis absorption spectrum, photoluminescence and SHG test.

Experimental procedure

Material synthesis

The title compound was synthesized by the addition of diethyl p-nitrobenzyl phosphonate ($C_{11}H_{16}NO_5P$) and p-anisaldehyde ($C_8H_8O_2$) in the presence of sodium ethoxide as catalyst. The mixture was taken in ethanol 35 ml. The mixture was stirred well for about 12 h at 0 °C and refluxed for 2 h and then the yellowish precipitate MONS ($C_{15}H_{13}NO_3$) product was filtered. The synthesized and dried MONS was collected [7]. The MONS material was purified by repeated recrystallization using ethyl methyl ketone (EMK) as solvent. The chemical reaction as follows:

$$C_{11}H_{16}NO_4P+C_8H_8O_2 \overset{C_2H_5ONa}{\underset{Strring \ 0^{\circ}C}{\longrightarrow}} C_{15}H_{13}NO_3$$

Solubility and crystal growth

The solubility of MONS was determined for five different temperatures such as 25, 30, 35, 40 and 45 °C by using a constant temperature ultracryostat water bath with magnetic stirrer rotation facility. The measurements were performed dissolving the MONS



material in ethyl methyl ketone solvent in an airtight container for each temperature. The solution was stirred for 2 h for homogenization. The solubility of MONS is shown in Fig. 1. Good quality crystal of size $10 \times 6 \times 3 \text{ mm}^3$ (Fig. 2) were obtained after three days by slow evaporation method at room temperature (see Fig. 3).

Results and discussion

Single crystal X-ray diffraction

The single crystal X-ray diffraction analysis was carried out using a Nonius CAD-4/MACH3 diffractometer to determine unit cell parameters and space group of the grown MONS crystal. We found that the crystal system is triclinic with cell parameters a = 11.716 (4) (Å); b = 12.002 (4) (Å); c = 14.949 (5) (Å), $\alpha = 110.33(3)$ Å, $\beta = 103.59$ (4) Å, $\gamma = 91.21(3)$ Å, and volume = 1904(1) Å³ and the space group is 'P1'.

Powder X-ray diffraction

A powder X-ray diffraction study was carried out using BRUKER X-ray diffractometer with the CuK α radiation (λ = 1.5406 Å) in the range of 10°–35°, in steps of 0.02°. Powder XRD pattern is shown in Fig. 4. It reflects good crystallinity of the grown crystals. The lattice parameters were calculated using the TREOR programs which coincide with the single crystal XRD results and the peaks were indexed using APPLEMAN program from the observed 2 θ values.

HR X-ray diffractometry

High resolution X-ray diffraction analysis was carried out to evaluate the crystalline perfection of the grown MONS crystal. The obtained beam with well collimated and monochromated MoKa1 from three monochromator Si crystals set in dispersive (+,-,-) configuration has been used in exploring the X-ray beam. The specimen crystal with good optical quality is rotated about a vertical axis, which is perpendicular to the plane of diffraction with 0.4 arc s angular intervals [8]. In identical experimental conditions, rocking curves (RC) were recorded for the MONS specimen crystal using (111) diffracting planes in symmetrical Bragg geometry. Using Lorentzian fit, the solid line follows the experimental points which represent the convoluted curve of two peaks. The additional peak has the tilt angle of 212 arcs from its adjoining region and shows an internal structural low angle boundary [9]. The low angle boundary and the FWHM (full width at half maximum) of the main peak are 72 and 110 arc s respectively. The crystal contains a low



Fig. 2. Grown crystals of MONS.



Fig. 3. Morphology of the grown crystal.



Fig. 4. Powder X-ray diffraction pattern.

angle boundary with a low angular spread of 500 arc s of the Rocking Curve (RC) which indicates that the quality of the crystal is fairly good. The recorded rocking curve (RC) is shown in Fig. 5.

Fourier transform infrared spectroscopic studies

The Fourier transform infrared spectrum was recorded using SHIMADZU IRAFFINITY instrument for the powder sample of the crystals using the KBr pellet technique in the range of 4000–400 cm⁻¹. The FTIR spectrum of MONS is shown in Fig. 6. The peaks around 686.66–970.19 cm⁻¹ corresponds to aromatic C–H bending vibrations. The peak at 3021 cm⁻¹ corresponds to C–H stretching alkenes. The peaks at 1510.26 and 1336.67 cm⁻¹ corresponds to NO₂ asymmetric and symmetric stretching vibrations respectively. The peak at 3072.60 cm⁻¹ corresponds to aromatic C–H stretching vibration. The peaks observed at 2962.66 and 1587.42 cm⁻¹ corresponds to =C–H stretching and C–C stretching of the olefinic double bond [10].



Fig. 5. Rocking curve recorded for a typical MONS single crystal for (111) diffracting planes by employing the multicrystal X-ray diffractometer with $MoK\alpha_1$ radiation.

¹H NMR spectrum

The proton NMR spectrum (1 H NMR) of MONS crystal was recorded using BRUKER Spect instrument operating at 400 MHz with CDCl₃ solvent as shown in Fig. 7. The singlet peak lies at 3.833 ppm (3H, S, OCH₃) is due to three protons in the methoxy group. The aromatic protons produce signals around 6.896 and 8.160 ppm (8H, multiplet). The doublet peak lies at 8.165 and 8.178 ppm to confirm the vinylic protons in the structure. Thus the structure of the title compound is confirmed by the proton NMR [11].

Optical studies

The optical absorption spectrum of MONS crystal was recorded at room temperature using Elico SL218 Double beam UV–vis spectrophotometer in the wavelength range 190–1100 nm, which covers the entire near-UV, visible and NIR regions. The recorded spectrum is shown in Fig. 8. The thickness of the sample used for measurement was 1.5 mm. The absorbance was reduced drastically between the wavelength of 438 and 1100 nm due to its good optical behaviour [12]. The crystal has sufficient transmission in the UV region and enables good optical transmission of the second harmonic frequencies of Nd:YAG laser.

Determination of optical band gap and optical constants

The absorption coefficient (α) was calculated from the transmittance data (*T*) using the relation [13]

$$\alpha = \frac{2.303 \log(1/T)}{t}$$
(1)

where *T* is the transmittance and *t* is the thickness of the sample. The optical band gap (E_g) has been estimated from the transmission spectra and the optical absorption coefficient (α) near the absorption edge is given by

$$\alpha h \nu = A (h \nu - E_g)^{1/2} \tag{2}$$

where *A* is a constant, E_g is the optical band gap, *h* is the plank's constant and *v* is the frequency of incident photons. The optical band gap was evaluated by plotting $(\alpha hv)^2$ vs. *hv* as shown in Fig. 9 and extrapolating the linear portion of $(\alpha hv)^2$ in the photon energy axis gives the optical band gap of the crystal. The optical band gap of the MONS is 3.28 eV.The Extinction coefficient (*k*) can be obtained from the following equation

$$K = \frac{\lambda \alpha}{4\pi} \tag{3}$$



Fig. 7. ¹H NMR spectrum of MONS.

The extinction coefficient is the fraction of electromagnetic energy lost due to absorption and scattering per unit distance in a sample medium. The extinction coefficient (k) vs. wavelength (λ) is shown in Fig. 10. The extinction coefficient decreases with increase of wavelength and it shows the light loss steeply decreases from 438 to 515 nm and nullified for higher wavelengths.

The reflectance (R) in terms of the absorption coefficient can be obtained from the equation [14]

$$R = \frac{1 \pm \sqrt{(1 - \exp(-\alpha t) + \exp(\alpha t))}}{(1 + \exp(-\alpha))}$$
(4)

The wavelength dependent reflectance of MONS shown is in Fig. 11 in the range of 375-1100 nm. The reflectance decreases with increase of wavelength, then becomes constant. The low reflectance value shows higher transmittance of the grown MONS crystal.The refractive index (*n*) can be calculated from reflectance data using the following equation [15]

$$n = \frac{-(R+1) \pm \sqrt{(-3R^2 + 10R - 3)^2}}{2(R-1)}$$
(5)

The optical conductivity ($\sigma_{\rm op}$) of MONS crystal was calculated using the following relations [16]

$$\sigma = \frac{\alpha nc}{4\pi} \tag{6}$$

where *c* is the velocity of light. The optical conductivity against absorption coefficient was plotted and shown in Fig. 12. From the spectrum it is evident that the optical conductance increases with increase of photon energy. The optical conductivity of the material depends on the absorption coefficient (α) and refractive index (*n*) and also it is clearly observed from the graph. The optical conductivity increases from the photon energy 1.97–2.20 eV and small variations obtained for higher photon energies.





Fig. 10. Plot of wavelength (λ) vs. Extinction coefficient (k).

1000

2.4

MONS crystal was identified by thermograviometric (TG) and dif-

ferential thermal analysis (DTA). The analyses were carried out using a TA Instruments SBT Q600 apparatus thermally analyzed in a nitrogen atmosphere. The different stages of mass losses are

shown in Fig. 13. In DTA curve, only one sharp endothermic peak was observed at 135.97 °C which corresponds to the melting point of the material. The sharpness shows the good crystalline nature

and purity of the grown crystal. Two sharp and broadened exothermic peaks were observed at 376 and 645.24 °C. TGA curve shows

that the material is stable upto 201.65 °C and there is no phase transition occurred before the melting point. After the occurrence of steep weight loss at 387.95 °C, the weight loss gradually de-

The photoluminescence (PL) measurement of MONS was car-

ried out at room temperature using the Jobin Yvon-Spex spectro-

fluorometer (Fluorolog version-3; Model FL3-11), 450 W high

pressure xenon lamp was used as an excitation source. The spec-

creased and remained as residue at 716.04 °C [17].

Photoluminescence study

2.6



Fig. 13. TG/DTA spectra of MONS.







Fig. 15. Vickers hardness analysis.

trum was recorded (Fig. 14) for a spectral resolution of 0.2 nm and excitation wavelength of 350 nm. A broad band observed in the range of 540–650 nm and also the maximum intensity was found at 564 nm. The result indicates that the MONS crystals have a bright emission in the visible region [18].

Microhardness studies

The microhardness study was carried out using Mututoyo MH112, Japan hardness tester with Vickers indenter. Microhardness testing is the versatile method to understand the mechanical properties of the crystal [19]. The crystal plane (111) was gently indented by diagonal pyramid shaped Vickers indenter for different loads (10, 25, 50 and 100 g) with dwell time of 10 s. The Vickers hardness number was calculated using the expression

$H_V = 1.8544 (P/d^2) kg/mm^2$

where H_V is the hardness number in kg/mm², *P* is the applied load in g. 1.8544 is a constant geometric factor for diagonal pyramid and d is the diagonal length of the indentation. The variation of HV as a function of applied load ranging from 10 to 100g for the MONS crystal is shown in Fig. 15. The graph shows that the hardness value (HV) increases with the increase of load. This is known as load dependent hardness.

SHG studies

SHG conversion efficiency of the powdered sample of MONS was measured by the Kurtz and Perry technique with 1064 nm laser radiations. A Quanta Ray Spectra Physics Nd:YAG laser producing pulses with a width of 8 ns and a repetition rate of 10 Hz was used. The SHG efficiency is confirmed by bright green light emission which is collected by a photomultiplier tube (PMT) (Philips photonics 8563) after being monochromated (Coherent Molectron USA 2000). The incident optical signal in PMT was converted into voltage output at the CRO (Tektronix TDS 3052B) [20]. The second harmonic signal of 33.7 mV was obtained for an input energy of 2.4 mJ/pulse, while the reference material Potassium dihydrogen orthophosphate (KDP) sample gives a SHG signal of 21.7 mV for the same input energy. The SHG relative efficiency of MONS with that of KDP has been calculated. It is found that the efficiency of the title crystal is 1.55× greater than that of KDP [3].

Conclusion

Organic material MONS has been synthesized and the good optical quality single crystals have been grown from ethyl methyl ketone (EMK) by slow evaporation technique. The structure of the grown MONS crystal was confirmed by single crystal XRD. From the Fourier transform infrared spectrum, functional groups have been confirmed. Proton NMR spectroscopic analysis confirms the molecular structure of the grown crystal. The optical absorption study reveals the transparency of the crystal with a UV cut-off at 499 nm. The optical band gaps (E_g) , extinction coefficient (k), reflectance (*R*) have been calculated as a function of wavelength. The optical conductivity of the grown crystal was determined. The thermal analysis reveals that the grown MONS crystal is stable up to 201.65 °C. The photoluminescence measurement shows that the MONS material can be a good scintillator. Microhardness testing shows the load dependent hardness of the crystal. The SHG test confirms that the NLO efficiency of the grown crystal is $1.55 \times$ greater than that of KDP.

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References

- R.W. Munn, E.N. Ironside, Principles and Applications of Nonlinear Optical Materials, Chapman & Hall, London, 1993. p. 2.
- [2] K.H. Hyung, W.P. Jae, S.L. Kwang, S.Y. Choon, J. Cryst. Growth. 277 (2005) 509-517.
- [3] P. Shoukui, G. Minmin, C. Mingin, J. Cryst. Growth. 153 (1995) 55–59.
- [4] G. Anandha babu, G. Bhagavannarayana, P. Ramasamy, J.Cryst.Growth. 310 (2008) 1228–1238.
- [5] S.G. Amirdha, S. Kalainathan, G. Bhagavannarayana, Mater. Lett. 64 (2010) 1989–1991.

- [6] Y. Wang, W. Tam, S.H. Stevenson, R.A. Clement, J. Calabrese, Chem. Phys. Lett. 148 (1988) 136–141.
- [7] T. Wilson, G. Brigitte, C.C. Joseph, H.S. Sylvia, Chem. Phys. Lett. 154 (1989) 93– 96.
- [8] K. Jagannathan, S. Kalainathan, T. Gnansekaran, N. Vijayan, G. Bhagavannarayana, Cryst. Res. Techno. 42 (2007) 483–487.
- [9] G. Bhagavannarayana, R.V. Ananathamurthy, G.C. Budakoti, b. Kumar, K.D. Bartwal, J. Appl. Cryst. 38 (2005) 768–771.
- [10] K. Jagannathan, S. Kalainathan, Mat. Res. Bull. 42 (2007) 1881-1887.
- [11] K. Jagannathan, S. Kalainathan, G. Bhagavannarayana, Spectrochim. Acta A: Mol. Biomol Spectrosc. 73 (2009) 79–83.
- [12] T. Sudhan, N.P. Rajesh, P.V. Dhanaraj, C.K. Mahadevan, Spectrochim. Acta A: Mol.biomol Spectrosc. 75 (2010) 69–73.
- [13] A. Ashour, N. El-kadry, S.A. Mahmud, Thin Solid Films 269 (1995) 117-120.
- [14] K. Russel Raj, P. Murugakoothan, Optik. 123 (2012) 1082-1086.
- [15] R. Hanumantharao, S. Kalainathan, G. Bhagannarayana, Spectrochim. Acta A: Mol.biomol Spectrosc. 91 (2012) 345–351.
- [16] E.I. Vgwu, A.S. Olayinka, F.I. Olabode, J. Eng. Apply. Sci 4 (2009) 126-131.
- [17] Amirdha sher gill, S. Kalainathan, J. Phys. Chem. Solids 72 (2011) 961–967.
- [18] T. Kanagasekaran, P. Mythili, P. Srinivasan, Shailesh N. Sharma, R. Gopalakrishnan, Mater. Lett. 62 (2008) 2486–2489.
- [19] Amirdha sher gill, S. Kalainathan, Matt.Lett. 65 (2011) 53-55.
- [20] S.K. Kurtz, T.T. Perry, J. Appl. Phys. 39 (1698) 3798–3813.