

Crystal growth and characterization of a new NLO material: 4-Methoxyaniline

M. Suresh¹, S. Asath Bahadur² and S. Athimoolam^{3*}

¹Department of Physics, Er. Perumal Manimekalai College of Engineering, Hosur, Tamil Nadu, India

²Department of Physics, Kalasalingam University, Krishnakoil, Tamil Nadu, India

³Department of Physics, University College of Engineering Nagercoil, Nagercoil, Tamil Nadu, India

ABSTRACT

Single crystals of 4- Methoxyaniline (4MAL), an organic nonlinear optical (NLO) material, have been grown slow evaporation method at room temperature from the ethanol – Water solution. The crystal system has been confirmed from the single crystal X-ray diffraction analysis. The functional groups were identified using FTIR spectroscopy. UV–Vis–NIR spectrum showed the absence of absorption in the wavelength region of 340–800 nm and UV cut-off wavelength of 4MAL occurs at 340 nm. The SHG efficiency of 4MAL was measured by employing Kurtz and Perry powder technique using a Q-switched mode locked Nd: YAG laser emitting 1064 nm for the first time. Intensity of the bright emission was found to be 1.66 times of standard KDP. Its thermal, mechanical properties were examined by TG/DTA, Vickers microhardness tester respectively.

Keywords: X-ray diffraction; Growth from solution; Organic compound; Nonlinear optical materials

INTRODUCTION

Materials with large nonlinear optical susceptibilities are of current interest in the area of harmonic generation and optical modulation. In recent years, some polar organic crystals, which form a non-centro symmetric structure exhibit second-order nonlinear optical properties that far surpassed those of the conventional materials has led to the synthesis and evaluation of a wide range of potentially useful solids [1]. Materials showing high optical non linearity have potential applications in signal transmission, data storage, optical switching, laser printing, displays, inflorescence, photolithography, remote sensing, chemical and biological species detection, high resolution spectroscopy, medical diagnosis and underwater monitoring & communication [2]. Different types of molecular and bulk materials have been examined for nonlinear optical properties. Organic nonlinear materials are attracting a great deal of attention, as they have large optical susceptibilities, inherent ultra-fast response times and high optical thresholds for laser power as compared with inorganic materials [3,4]. Organic molecules with significant nonlinear optical activity generally consist of a π – electron conjugated structure[5]. The conjugation π -electron moiety provides a pathway for the entire length of conjugation under the perturbation of an external electric field. Fictionalization of both ends of the π bond systems with appropriate electron donor and acceptor group can increase the asymmetric electronic distribution in either or both the ground and excited states, thus leading to an increased optical nonlinearity [6, 7, 8,9]. In the present investigation we report the SHG efficiency of 4- Methoxyaniline (4MAL) for the first time. The grown crystals have been subjected to the characterizations like XRD, FTIR, UV-vis, thermal analysis, powder SHG and micro-hardness studies.

MATERIALS AND METHODS

2.1 crystal growth

Single crystals of 4MAL were grown from ethanol and water mixer from the commercially available 4-Methoxyaniline by slow evaporation method. The solution was stirred continuously using magnetic stirrer for 3 hrs. The solution was then filtered to remove suspended impurities and allowed to crystallize. Seed crystals were formed due to spontaneous nucleation. Optically transparent good quality seed crystals were used for growth experiments. Good quality crystals of characteristic shape and size of $11 \times 6 \times 2 \text{ mm}^3$ were obtained within 10 days. Fig. 1 shows the photograph of the grown crystal of 4MAL.



Fig.1 Photograph of as grown crystal of 4MAL

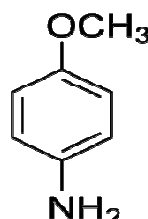


Fig.2 Molecular formula of 4MAL

2.2. characterization

In order to confirm the grown crystal, single crystal X-ray diffraction studies were carried out using ENRAF NONIUS CAD4-F single X-ray diffractometer with $\text{MoK}\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation. The FT-IR spectrum of the sample was recorded in the range $4000 - 450 \text{ cm}^{-1}$ using Jasco Spectrometer (FTIR, model 410) by KBr pellet technique. The UV-Vis-NIR analysis was carried out between 200 and 800 nm, covering the entire near ultra violet, visible and near infrared regions using the UV -1700 Shimadzu spectrometer. Vicker's microhardness tester was used to assess the mechanical properties of the grown crystal for various loads ranging from 25 to 100 g. The thermal behavior of the grown crystal was studied using Simultaneous TG/DTA, SEIKO, Japan TG/DTA6200 analyzer in nitrogen atmosphere at a heating rate of $20 \text{ }^\circ\text{C}/\text{min}$ in the temperature range of $20 \text{ }^\circ\text{C} - 600 \text{ }^\circ\text{C}$. The SHG efficiency was measured by employing Kurtz and Perry powder technique using a Q-switched mode locked Nd: YAG laser emitting 1064 nm.

RESULTS AND DISCUSSION

3.1 Single-crystal X-ray diffraction

Nonius CAD-4/MACH 3 Diffractometer with Mo Ka (0.71073 \AA) radiation was used to obtain the accurate cell parameters of the grown crystals at room temperature, by the least-squares refinement of the setting angles of 25 reflections. The XRD study reveals that the crystal belongs to orthorhombic system with lattice parameters $a = 14.545 \text{ \AA}$, $b = 7.516 \text{ \AA}$ and $c = 6.150 \text{ \AA}$, $Z = 4$ and space group is $\text{Pca}2_1$, which is in agreement with those of reported values [10].

3.2 Measurement of Density

The measurement of density is one of the important methods to study the purity of crystals. The most sensitive method to find the density of the crystal, namely, the swim or sink method [11] is used in the present study. In this analysis, theoretical density value is found using the formula, $\text{density} = (MZ)/(NV)$; where M is the molecular weight, Z is the number of molecules per unit cell, N is the Avogadro number, and V is the volume of the unit cell. The density values are experimental: 1.08 g/cm^3 ; and theoretical: 1.06 g/cm^3 .

3.3 FTIR analysis

The FTIR spectra of the crystal were recorded in the KBr phase in the frequency region of $400-4000 \text{ cm}^{-1}$ using a Jasco Spectrometer (FTIR, model 410) at a resolution of 4 cm^{-1} and with a scanning speed of 2 mm/s shown in Fig. 3. The recorded FTIR spectra were compared with the standard spectra of the functional groups [12]. The medium

peaks at 3452 cm^{-1} and 3344 cm^{-1} were observed and is assigned to the NH anti symmetric stretching and symmetric stretching respectively. Weak peak at 3071 cm^{-1} , 3037 cm^{-1} and 3008 cm^{-1} are assigned to the CH stretching mode. The strong peak at 2838 cm^{-1} is been assigned to Methoxy C-H stretch (CH₃-O-). The medium variable peak in the range 1634 cm^{-1} is been conforms the presence of Aromatic ring stretching vibration. The strong variable peak at 1506 cm^{-1} and the medium variable peak at 1457 cm^{-1} are further conforms the presence of aromatic ring stretching mode vibration. The medium peak at 1333 cm^{-1} and strong peak at 1330 cm^{-1} were exposes the CH stretching vibration mode. The strong peak at 1235 cm^{-1} is also assigned to CN stretching vibration. The weak peak at 1179 cm^{-1} is assigned to CN stretching mode. The strong peak at 1031 cm^{-1} conforms the C-O-C symmetric stretching mode vibration. The weak peak around 990 cm^{-1} is assigned to CH – in plane H bending. The strong peak at 832 cm^{-1} is been assigned as NH wagging broad peak.

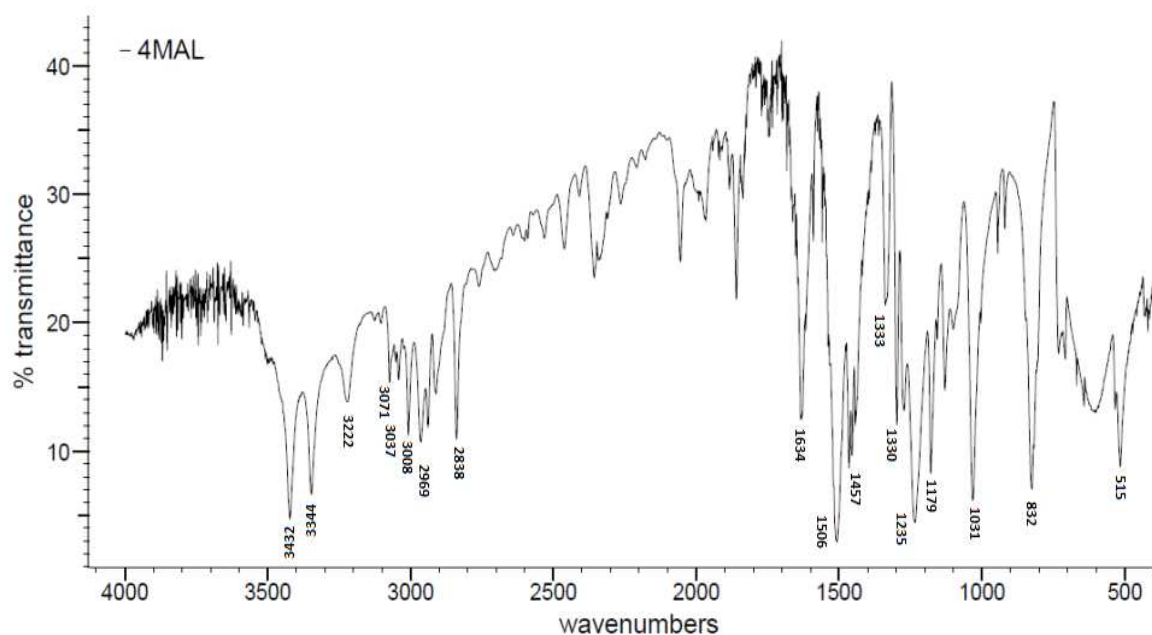


Fig. 3 FTIR spectrum of 4MAL

3.4 UV- VIS- NIR spectral analysis

In general, for optical applications, especially for second harmonic generations, the material considered must be transparent in the wavelength region of interest. Fig.4. shows the transmittance spectrum of 4MAL. The optical transmittance study shows that the UV cut-off wavelength of 4MAL occurs at 340 nm. It is well known that the efficient NLO crystal has an optical transparency at lower cut-off wavelength between 200 and 400 nm [13]. The wide transmission range in the entire visible region reveals that it can find applications in the optoelectronic devices. 4MAL has no absorption around 532 nm, which in turn signifies the resistance of the grown crystal to laser induced damage [14].

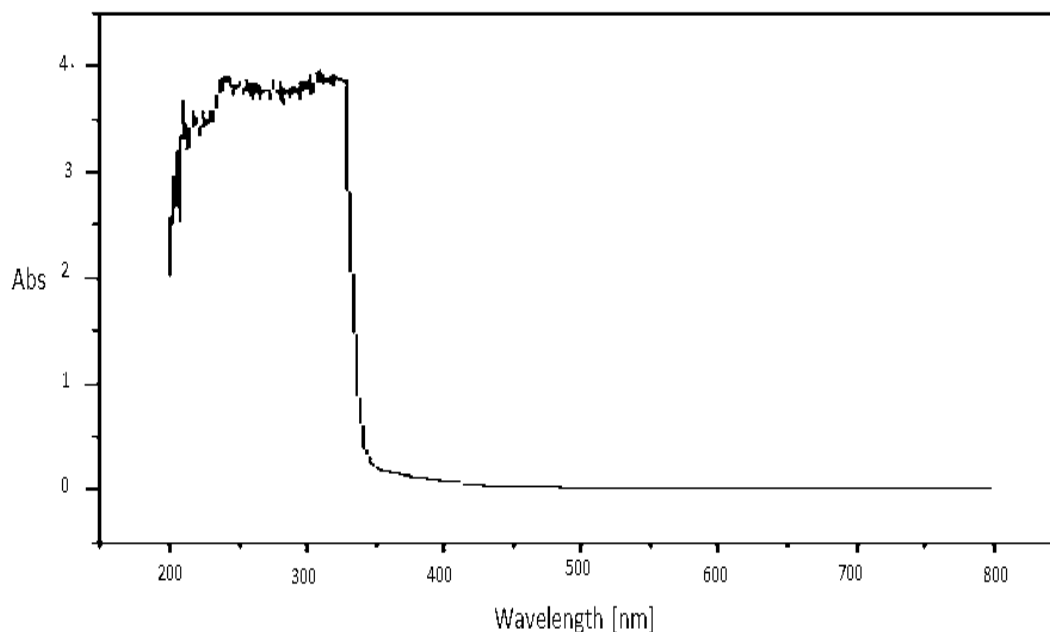


Fig. 4 UV- vis - NIR spectrum of 4MAL

3.5 Mechanical properties

Hardness is one of the important mechanical properties to determine the plastic nature and strength of a material. The well polished 4MAL crystal was placed on the platform of the Vicker's micro hardness tester and the loads of different magnitudes were applied over a fixed interval of time. The hardness number was calculated using the relation $H_v = (1.8544P)/(d^2)$ kg/mm², where P is the applied load in kg and d is the diagonal length of the indentation in micrometer. The relation between hardness number (H_v) and load (P) for 4MAL is shown in Fig. 5. The hardness increases gradually with the increase in load and above 100 g cracks were developed on the plane of the crystal due to the release of internal stresses generated locally by indentation. Meyer's index n was calculated from the graph (Fig. 6) plotted against log P vs log d. The slope of the line obtained from graph predicts that the value of n is greater than 2. H_v should increase with the increase of P if $n > 2$ and decrease if $n < 2$ [15]. Thus the n value satisfies the observed result.

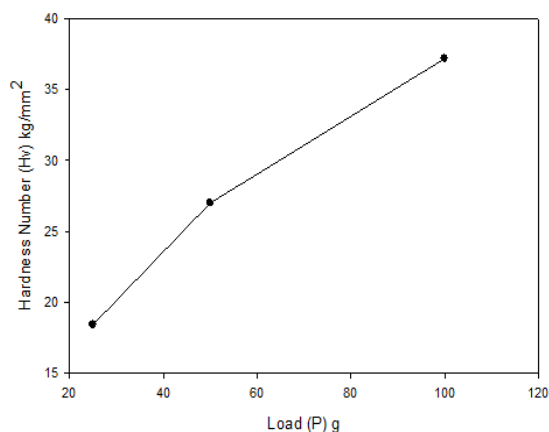


Fig. 5 Plot of hardness vs. load

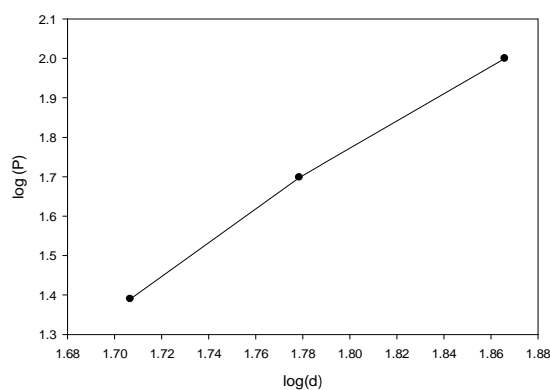


Fig. 6 Plot of log P vs. log d

3.6 Thermal analysis

Differential thermal analysis (DTA) response curves for the powder sample of 4MAL are shown in Fig. 7. The DTA curve of 4MAL indicates that the material has two sharp exothermic peaks, one at 61° C and the other at 177° C, which represent the melting and decomposition points, respectively. The TGA curve of 4MAL indicates that the sample is stable from ambient up to 100° C. The major weight loss between 100 and 175° C is due to the

decomposition. The total weight loss of the sample is 90% at 175 °C. Based on this study it can be said that the crystal can be subjected to NLO applications up to 100 °C since the material started to decompose at 100 °C.

3.7 Second harmonic generation

Since 4MAL has crystallized in a non-centrosymmetric space group, a preliminary study of the powder SHG conversion efficiency was carried out with Nd: YAG laser beam of wavelength 1064 nm, using the Kurtz and Perry method [16]. A Q-switched Nd: YAG laser beam of wavelength 1064 nm was used with an input power of 2 mJ pulse⁻¹, pulse width of 10 ns, the repetition rate being 10 Hz. The crystals of 4MAL were ground to a uniform particle size of about 125–150µm and then packed in capillaries of uniform bore and exposed to the laser radiation. A powder of KDP, with the same particle size, was used as the reference. The output from the sample was monochromated to collect only the second harmonic ($\lambda = 532$ nm) eliminating the fundamental, and the intensity was measured using a photomultiplier tube. Second harmonic signal of 30 mV was obtained. The standard KDP crystals gave a SHG signal of 18mV for the same input energy. Intensity of the bright emission was found to be 1.66 times of standard KDP.

CONCLUSION

Single crystals of 4-Methoxyaniline (4MAL) were grown from ethanol- Water solution by slow evaporation of the solvent at room temperature. The crystal system has been confirmed from the single crystal X-ray diffraction analysis. The functional groups of the compound have been determined from FTIR spectrums. Optical absorption studies show that the sample is optically transparent over a wide wavelength region and minimum absorption is observed in the entire visible region. The melting point is found to be 61°C from the DTA curve. The SHG efficiency of 4MAL is found to be very high when compared with KDP. Vicker's microhardness test shows that the crystal is stable up to 100g.

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