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Bulk Crystal growth and Characterization of Organic Nonlinear Optical Crystal: 2-(2,4-dimethoxybenzylidene) malononitrile (DMM)

A. Priyadharshini¹, S.Kalainathan^{1, a}

¹ – Centre for Crystal Growth, School of Advanced Sciences, VIT University, Vellore –632 014, India

a – kalainathan@yahoo.com



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Keywords: DMM crystal, bulk crystal growth, single crystal XRD, FT-IR, UV-Vis-NIR spectral analysis, Z-scan technique.

ABSTRACT. Bulk organic nonlinear optical single crystal of 2-(2,4-dimethoxybenzylidene) malononitrile (DMM) with size up to 24×18×13 mm² was successfully grown by slow evaporation solution growth technique. The single crystal X-ray diffraction studies of the grown crystal exhibit that the crystal belongs to a monoclinic system with P2₁/n space group. The FT-IR spectrum confirms the various functional groups present in the grown crystal. The optical properties of the grown crystals were analyzed by UV-Vis-NIR spectral analysis. Third-order nonlinear optical behaviour of the title crystal was studied by Z-scan technique. All the finding results in the present work indicate that DMM has a potential application as a useful NLO candidate.

Introduction. In recent years, organic non-linear optical (NLO) crystals have gained considerable attention due to their relatively high nonlinearity and fast response. Particularly, third order nonlinear optical (TONLO) organic materials have gained much consideration because of their promising applications in optical switching, optical data processing, optical limiting, signal processing and ultra-fast optical communications, etc [1,2]. The centrosymmetric organic crystals with good stability lead to third order susceptibility ($\chi^{(3)}$) and higher nonlinear absorption co-efficient (β) and fast response time for nonlinear optical properties. However, only very few organic materials could so far be crystallized in reasonable crystal size and optical grade to realize various applications. For the first time, we present here investigations on the bulk growth of DMM organic crystals and its different characterizations.

Material synthesis and crystal growth. The title material of 2-(2,4-dimethoxybenzylidene) malononitrile (DMM) was synthesized by Knoevenagel condensation reaction method by using 2,4-dimethoxybenzaldehyde and malononitrile stoichiometric ratio and dissolved in ethanol (25 ml). The above mixture solution was taken in the 100 ml round bottom flask (RBF) and 5 drops piperidine was added as a catalyst. The solution was refluxed at 65 °C for 3h. The reaction mixture was cooled to ambient temperature. Yellowish salt was collected by filtration, washed with diethyl ether several times and then dried in an oven. The chemical reaction is shown in Fig. 1.

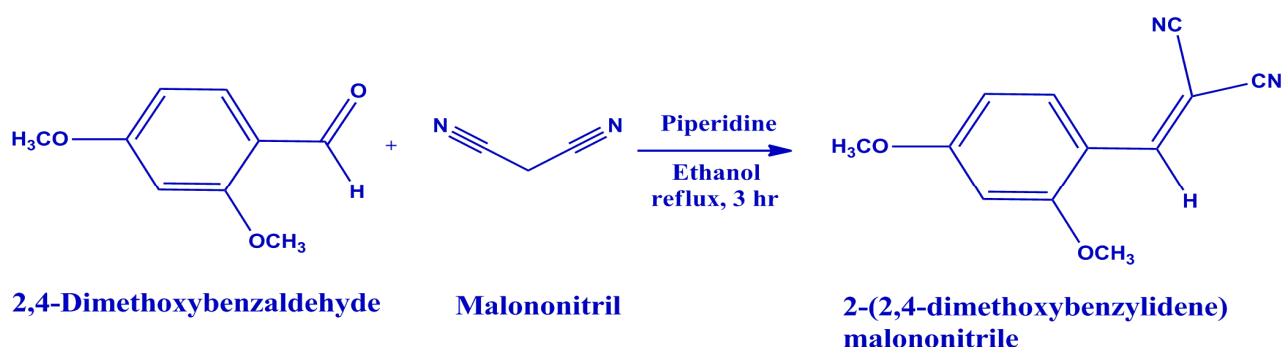


Fig. 1. Chemical reaction.

The dried product of DMM was dissolved in acetone at 35 °C to form a saturated solution, and the solution was stirred using a motorized magnetic stirring device for 12 h to obtain a homogeneous solution. The solution was filtered into a 150 ml beaker using high-quality Whatman filter paper. The solvent was allowed to slowly evaporate at 35 °C in a constant temperature water bath (accuracy of ± 0.01 °C). Optical quality DMM crystals were harvested with dimensions $24 \times 18 \times 13$ mm² after a period of 22 days by slow evaporation solution growth technique. The grown DMM crystal is shown in Fig. 2.

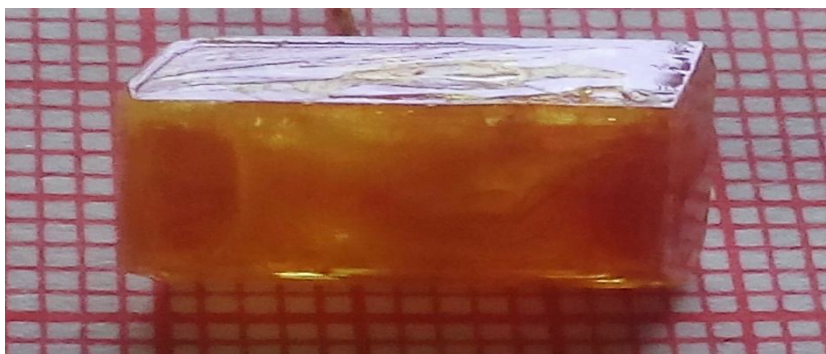


Fig. 2. Photograph of as-grown DMM crystal.

Results and discussions.

Single crystal X-Ray diffraction analysis (SXRD). The single-crystal X-ray diffraction analysis of the grown crystal have been carried out to identify the structure and to estimate the lattice parameters. It reveals that the DMM crystal has crystallized in the monoclinic crystallographic system with centrosymmetric space group $P2_1/n$. The calculated unit cell parameters of the DMM crystal are $a = 8.394$ (8) Å ; $b = 7.525$ (2) Å ; $c = 17.152$ (8) Å. The volume of the crystal is 1080.6 (2) Å³. The obtained lattice parameter values are good agreement with the reported values [3] and thus confirmed the grown title compound.

FT-IR spectral analysis. The FT-IR analysis of DMM was carried out to investigate the presence of functional groups and their vibrational modes. The sample was prepared by mixing DMM with KBr pellet. The spectrum was recorded in the wavenumber range 400- 4000 cm⁻¹ using a BRUKER 66V FT-IR spectrometer and the spectrum is shown in Fig. 3. The broad envelope positioned between 3089 and 2976 cm⁻¹ corresponds to the symmetric C-H stretching vibration. The strong absorption at 2220 cm⁻¹ indicates the existence of C≡N stretching mode of nitrile group. The peak at 1467 and 1354 cm⁻¹ indicate the existence O-CH₃ methyl group. The FT-IR spectrum confirms the formation of DMM crystal.

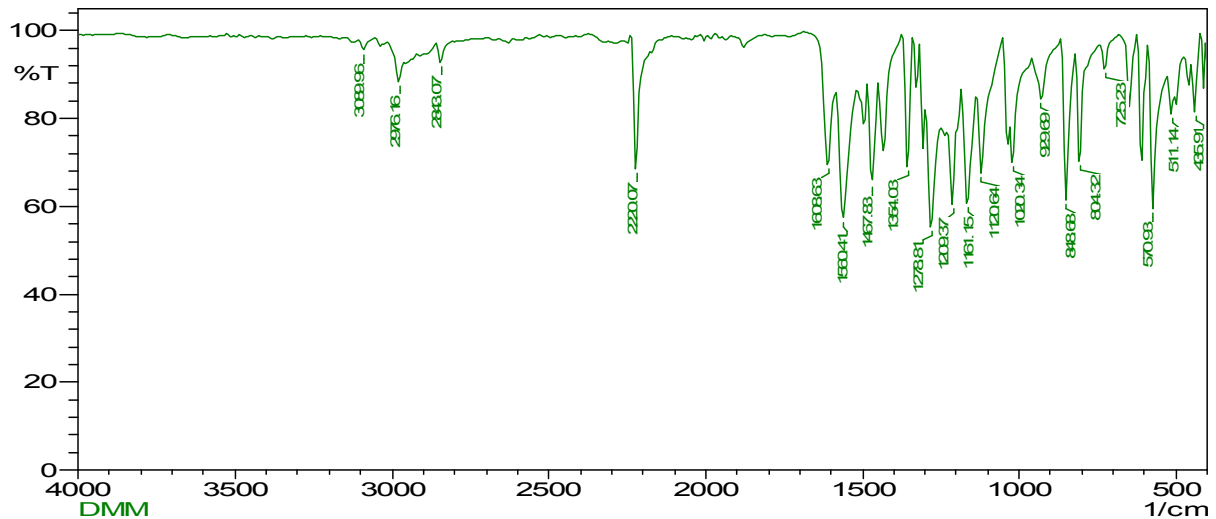


Fig. 3. FT-IR spectra of DMM.

UV-Vis-NIR spectral analysis. The optical absorbance spectrum (AS) of DMM crystal was recorded between the wavelength range 400 and 1000 nm using a ELICO SL 218 double beam UV-Vis-NIR spectrometer. For this study, the an optically polished single crystal of thickness (t) 1.3 mm was used and the recorded absorption spectrum is shown in Fig 3. The lower cut-off wavelength is found to be 483 nm, and the crystals show good transmittance percentage in the range of 490–1000 nm. The transmittance nature in the entire visible and near IR region is the desired criteria for NLO applications [4].

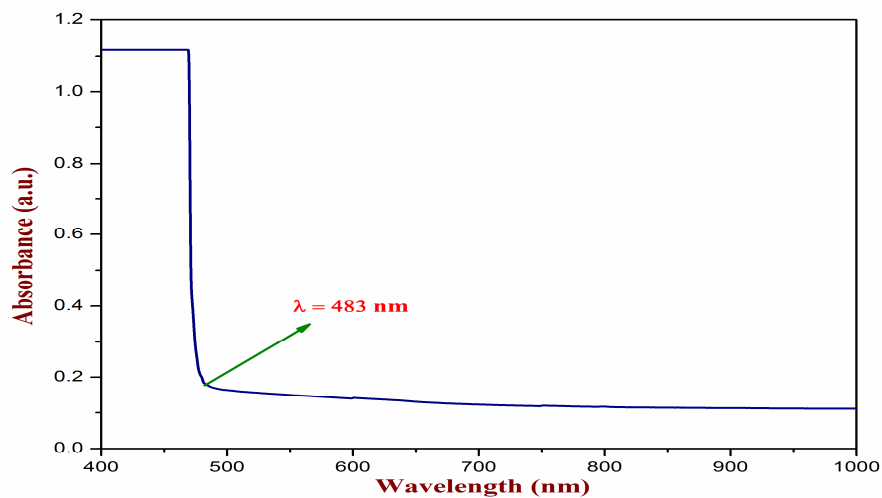


Fig. 4. UV-Vis-NIR spectra of DMM crystal.

Z-Scan measurement. Single-beam Z-scan technique was employed to measure the third-order optical nonlinearities of the DMM crystal. The experiments were performed using a continuous He-Ne laser of the wavelength of 632.8 nm, which was focused by a 30 mm focal length lens. The laser beam waist at the focus is measured to be 12.05 μm and the Rayleigh length is 0.72 mm. The sample was mounted on a translation stage (-Z to +Z) that was controlled by the computer to move along the Z-axis with respect to the focal point. An aperture 2 mm radius was placed in front of the transmission detector, and the transmittance was recorded as a function of the sample position on the Z-axis i.e., closed aperture (CA) Z-scan. For measuring the NLO absorption, the Z-dependent sample transmittance was taken without the aperture i.e., open aperture (OA) Z-scan. Actually, the nonlinear absorption coefficient (β) and nonlinear refractive index (n_2) could be assessed by OA and CA Z-

scan. The obtained results of the Z-scan curves in open and closed aperture modes are shown in Fig. 5 (a - b).

The nonlinear refractive index (n_2) can be obtained by the relation, given below:

$$n_2 = \frac{\Delta\Phi_o}{KI_oL_{eff}} \quad (1)$$

where K is the wave number ($K= 9.924 \times 10^6 \text{ m}^{-1}$), I_o is the intensity of the laser beam at the focal point ($I_o = 26.50 \text{ MW /m}^2$), and L_{eff} is effective thickness of the grown crystal can be estimated as $L_{eff} = [1 - \exp(-\alpha L)]/\alpha$, where L is the thickness of the crystal and α is the linear absorption coefficient.

From the OA curve line, the nonlinear absorption coefficient (β) was estimated by,

$$\beta = \frac{2\sqrt{2}\Delta T}{I_oL_{eff}} \quad (2)$$

where ΔT is the valley value at the OA data. The absolute value of the third-order nonlinear optical susceptibility ($\chi^{(3)}$) was calculated by using the equation [5],

$$|\chi^{(3)}| = \left[(\text{Re}(\chi^{(3)}))^2 + (\text{Im}(\chi^{(3)}))^2 \right]^{1/2} \quad (3)$$

where Re and Im are the real and imaginary part of the optical susceptibility. From the Z-scan data, the calculated value of $\chi^{(3)}$ is $4.30 \times 10^{-5} \text{ esu}$; n_2 is $1.876 \times 10^{-11} \text{ m}^2/\text{W}$, and β is $2.537 \times 10^{-5} \text{ m/W}$. Thus, the overall experimental results indicate that DMM crystal has better NLO properties.

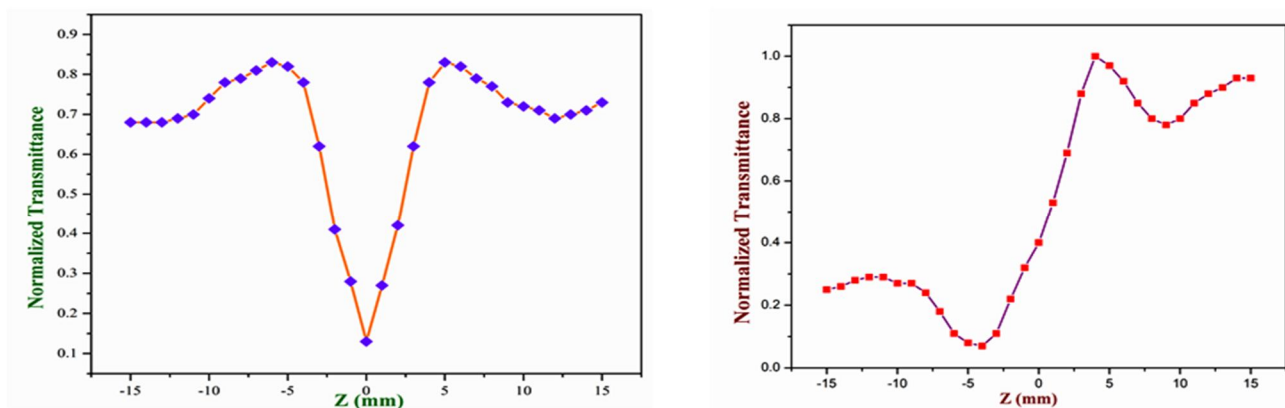


Fig. 5. (a) Open aperture Z-scan plot of DMM. (b) Closed aperture Z-scan plot of DMM.

Summary. A bulk single crystal of DMM has been synthesized and grown by the slow evaporation method. The lattice parameter was confirmed by SXRD analysis. FT-IR study confirmed the formation of the desired material. UV-Vis-NIR spectral study showed that the grown crystal is

transparent in the entire visible region ranging from 490 nm to 1000 nm. A third-order nonlinear optical study of the DMM crystal reveals that a reverse saturation absorption (RSA) and a positive sign of nonlinear refractive index (n_2), which are required for optical limiting applications. From the present investigation, we conclude that DMM is a new candidate for NLO device applications.

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