Crystal growth and optical characterization of an organic single crystal for frequency conversion applications

M. Divya Bharathi\textsuperscript{a}, G. Ahila\textsuperscript{a}, J. Mohana\textsuperscript{a}, R. Bhuvaneswaria, G. Anbalagan\textsuperscript{b}\textsuperscript{*}

\textsuperscript{a}Department of Physics, Presidency College, Chennai-600005, Tamil Nadu, India
\textsuperscript{b}Department of Nuclear Physics, University of Madras, Chennai-600025, Tamil Nadu, India
\textsuperscript{*}anbu24663@yahoo.co.in

**Abstract.** Organic nonlinear optical 2-methylquinolinium L-malate single crystals have been grown by slow evaporation solution growth technique from a mixture of 2-methylquinoline and L-malic acid in ethanol solution at ambient temperature. Single crystal X-ray diffraction analysis reveals that grown crystal in monoclinic system with non-centrosymmetric space group P2\(_1\) and the lattice parameters are \(a = 7.35 \text{ Å}, b = 26.51 \text{ Å}, c = 10.83 \text{ Å},\) \(\alpha = \gamma = 90^\circ,\) \(\beta = 102.95^\circ\) and \(V = 2057.4 \text{ Å}^3.\) UV-vis spectrum indicates that the crystal is transparent (75\%) in the entire visible region with a cut-off wavelength of 437 nm and optical energy band gap \(E_g\) is found to be 2.71 eV. Microhardness measurement reveals the mechanical strength of the grown crystal. The photoluminescence spectrum shows the blue emission of the crystal. Laser damage threshold studies was carried out to ascertain the suitability of grown crystal for laser applications. The relative second harmonic generation efficiency of 2-methlquinolinium L-malate crystal was found to be two times greater than that of KDP.

**Keywords:** Crystal growth, Photoluminescence, Optical band gap, Laser damage threshold, SHG studies.

1. Introduction

Nonlinear optics (NLO) has emerged in a grand manner with the evolution of material science in the growth of optimistic organic and inorganic single crystals [1]. Second-order NLO materials have evoked much attention because of their application in frequency shifting, optical modulation, signal processing and telecommunications [2]. Organic molecular materials are appealing in controlling a light beam by an electric field because they offer many possibilities to tune their optical properties and obtain large electro-optic effects [3]. Currently, much attention has been given to hybrid organic–inorganic crystals because of their large hyperpolarizabilities and high laser damage resistance compared to inorganic materials [4, 5]. The main advantage of organic materials is that their structures can be easily altered to get the craved optical properties [6, 7]. The hydroxyl groups of carboxylic acids and heterocyclic nitrogen atoms has been proved to be a useful and powerful organizing force for the formation of supramolecules due to its strong hydrogen bonding. It is evident that these structures are normally held together by hydrogen-bonding, and in this contemplate, the most frequently used moieties with hydrogen bonding capability are pyridyl and carboxyl. As a pyridyl derivative, besides the methyl group, 2-methylquinoline bears more aromatic \(\pi\)-electrons which can be a better group in creating aromatic stacking interactions. Many of the dicarboxylic salts are delineated to be active in second-harmonic generation (SHG) and it may...
be useful to review complexes with carboxylic acids and their properties. The intramolecular hydrogen bond in malic acid is very strong, also malic acid forms crystalline malate of various organic molecules through hydrogen bonding and π–π interactions. It is popular that malic acid acts not only as an acceptor to form various π-stacking complexes with other aromatic molecules but also as an acidic ligand to form salts through determined electrostatic or hydrogen bond interactions. 2-methylquinolinium L-malate (MLM) is one such π donor–acceptor molecular compound in which L-malic acid fetches one of its proton to the 2-methylquinoline, hence the asymmetric unit consists of 2-methylquinoline molecules in protonated form and a L-malic acid in monoionized state. The structure of 2-methylquinolinium L-malate crystal was illustrated by Jing Zhang [8]. In the contemporary work, we report the crystal growth and optical characterization of an organic single crystal for frequency conversion applications.

2. Experimental Procedure

2.1. Material Synthesis

The 2-methylquinolinium L-malate has been synthesized from a solution of ethanol containing 2-methylquinoline (SRL) and L-malic acid (Merck) in 2:1 molar ratio by slow evaporation technique at room temperature. The reaction scheme is shown in Fig.1. The calculated amount of 2-methylquinoline was dissolved separately in the ethanol. L-malic acid was added slowly to the 2-methylquinoline solution with continuous stirring. The prepared mixture was stirred well for 5 h and clear solution was obtained. The solution was filtered off to remove insoluble impurities. Then the solution was allowed to evaporate at room temperature. Optically good quality single crystals were harvested from the mother solution in a growth period of 20 days and the photograph of the grown crystal is given in Fig. 2.

![Figure 1. Reaction scheme of MLM crystal](image-url)
3. Result and Discussion

3.1. Single Crystal X-Ray Diffraction Analysis

Single crystal X-ray diffraction was analyzed using Bruker AXS Kappa Apex II CCD diffractometer with MoKα radiation (λ=0.71073 Å; graphite monochromator). Single crystal X-ray diffraction analysis reveals that MLM crystal belongs to the monoclinic system with non-centrosymmetric space group P2₁. The obtained lattice parameters are presented in Table 1. These values are in good agreement with the literature [8].

| Parameter | Presented study | Reported values [1] |
|-----------|-----------------|---------------------|
| a         | 7.3530 Å        | 7.3530(6) Å         |
| b         | 26.5102 Å       | 26.5100(2) Å        |
| c         | 10.8307 Å       | 10.8301 (9)Å        |
| α         | 90 °            | 90 °                |
| β         | 102.950°        | 102.951(2)°         |
| γ         | 90 °            | 90 °                |
| V         | 2057.4 Å³       | 2057.4(3)Å³         |
| System    | Monoclinic      | Monoclinic          |
| Space group | P2₁            | P2₁                |

3.2. UV-Vis Spectral Studies

UV-vis transmission spectrum of MLM crystal was recorded in the range of 190-900 nm using T-90+ UV-vis Spectrophotometer with sample thickness 1.2 mm. The dependence of optical absorption coefficient with the photon energy helps to understand the band structure and the type of transitions of electrons [9-11]. Fig. 3(a) shows the transmittance spectrum of MLM crystal. It has good transparency of about 75% with cut-off wavelength of 437 nm. This crystal is active in the entire visible region and hence MLM material could be viable alternative for optical materials in the entire visible region and there is no significant absorption between 438 - 900 nm, which enables it to be a potential candidate for optoelectronic and frequency conversion applications.
\[
\alpha = \frac{2.303 \log \left( \frac{1}{T} \right)}{t}
\]

where \( T \) is the transmittance, \( t \) is the thickness of the crystal. The quantity \( \alpha \) can be displayed in a number of ways as described by the Tauc’s relation [12, 13],

\[
(\alpha h \nu)^2 = A(E_g - h \nu)
\]

where \( \alpha \) is the absorption coefficient, \( h \) is Planck constant, \( \nu \) is the frequency of the incident radiation, \( A \) is a constant and \( E_g \) represents the optical band gap. A plot of \((\alpha h \nu)^2\) versus \( h \nu \) was drawn by extrapolating the linear part of the plot to the axis \((h \nu)\) as shown in Fig. 3(b) and the optical band gap was found to be 2.71 eV. As a significance of a wide band gap, the grown crystal has a large transmittance in the visible region.

![Figure 3(a). UV-Vis transmittance spectrum (b) Tauc’s Plot of MLM crystal](image)

### 3.3. Photoluminescence Studies

Photoluminescence (PL) spectroscopy is one of the effective tools to provide relatively direct information about the physical properties of materials at the molecular level, including shallow and deep level defects and band gap states. The photoluminescence (PL) spectrum of MLM recorded in the range between 400-650 nm with excitation wavelength of 437 nm at room temperature is shown in Fig. 4. The broad emission spectrum showed a single peak centered at about 2.62 eV (473 nm) and no other visible emission was observed. The enhanced PL emission is due the presence of electron donating group COOH and electron-withdrawing group NH. It also revealed that MLM crystals had blue fluorescence emission.
The maximum intensity peak at 473 nm is due to the protonation of carboxyl group from L-malic acid to 2-methylquinoline of nitrogen group. As the energy of emission peak is lower than the band gap energy, the observed PL is not related to a direct electronic transition between the valence and conduction bands and hence it could be associated with the radiative recombination involving trapped electrons and holes which occur between localized states situated in the band gap [14]. The intensity and broadness of peak reveal the crystalline nature.

![PL emission spectrum of MLM crystal excited at 437 nm](image)

**Figure 4.** PL emission spectrum of MLM crystal excited at 437 nm

### 3.4. Mechanical Studies

Hardness is a measure of the resistance offered by a material to the localized plastic deformation caused by scratching [15]. A microhardness study was carried out on the smooth and flat surface of the MLM crystal for various loads ranging from 10 – 100 g with a constant time of indentation (10 s) using Leitz - Wetzlar Vickers microhardness tester fitted with diamond pyramidal indenter attached to an optical microscope. The Vickers microhardness number $H_V$ was calculated using the relation

$$H_V = 1.8544 \left( \frac{P}{d^2} \right) \text{kg/mm}^2$$

where ‘$P$’ is applied load in g and ‘$d$’ is the diagonal length of impression in µm. For an applied load above 100 g, the crystal gets crack initiation and materials starts breaking. The variation of microhardness ($H_V$) with applied load ($P$) is shown in Fig.5. From the plot it is observed that the hardness number increases with increase of applied load, which reveals that the MLM crystal exhibits reverse indentation size effect (RISE). For load above 100 g crack started developing around the impression mark, which may be due to the release of internal stress [16].
**Figure 5.** Variation of microhardness number with applied load for MLM crystal

**Figure 6.** log P with log d of MLM crystal
The size of indentation and load are related through Meyer’s law [17]. \( P = k_1d^n \) where ‘\( k_1 \)’ is standard hardness constant and ‘\( n \)’ is Meyer’s index or work hardening coefficient. A plot of \( \log P \) versus \( \log d \) before cracking gives a straight line Fig.6 which is in good agreement with Meyer’s law. The slope of the plot is found to be 2.26. According to Onitsch and Hanneman ‘\( n \)’ should lie between 1 and 1.6 for harder materials and above 1.6 softer materials [18, 19]. Hence the grown MLM crystal belongs to the soft material category.

3.5. Laser Damage Threshold Studies
LDT depends on many external factors like repetition rate, spot size, pulse duration, beam size, location of beam, irradiance and experimental geometry. A well polished good quality MLM crystal surface was treated with high power laser and its laser damage resistance values was calculated. In the present study, an actively Q-switched high energy Nd: YAG laser input pulse width of 6 ns at 1064 nm in the repetition rate of 10 Hz. The output intensity of the laser was controlled with a variable attenuator and delivered to the test sample located at the near focus of the converging lens. The energy density of the laser beam was recorded using a power meter which the crystal gets damaged. The surface damage threshold of the MLM crystal was calculated by using the following relation,

\[
\text{Power density } P(d) = \frac{E}{\tau \pi r^2}
\]

where \( E \) is the input energy (mJ), \( \tau \) is the pulse width (ns) and \( r \) is the radius of the circular spot size (cm\(^2\)). The measured multiple shot laser damage threshold value is 5.58 GW/cm\(^2\) which is higher than that of KDP and Urea [20]. The surface damage of the crystal using high power laser limits the performance of the NLO applications of the materials.

3.6. Second Harmonic Generation Measurement
The polarizability of MLM and KDP were calculated using Clausius –Mosotti relation:

\[
\alpha = \frac{3M}{4\pi \rho N_A} \left( \frac{\varepsilon_r - 1}{\varepsilon_r + 2} \right)
\]

where \( M \) is the molecular weight, \( N_A \) is Avogadro number, \( \rho \) is the density and \( \varepsilon_r \) is the dielectric constant. The calculated values for polarizability for both MLM and KDP are given as 5.0591 \( \times 10^{-23} \) C m\(^3\) and 2.1499 \( \times 10^{-23} \) C m\(^3\) respectively. Since the polarizability of MLM is found to be higher than that KDP, the SHG of MLM is theoretically interpreted as higher than that of KDP.

The second harmonic generation efficiency of MLM crystal has been measured by Kurtz–Perry technique [22]. The grown single crystal of MLM is powdered with a uniform particle size and then packed in a micro-capillary tube of uniform bore and exposed to laser radiation. A high intense beam from the Q-switched Nd: YAG laser with the wavelength of about 1064 nm with an input power of 1.2 mJ, and repetition rate of 10 Hz with a pulse of width 8 ns is allowed to be incident on the sample. The fundamental beam was filtered by using an IR filter. A photo-multiplier tube was used as detector. The output from the sample was monochromator to collect the intensity of 532 nm component and to eliminate the fundamental radiation. The efficiency of energy (frequency) conversion is confirmed by the emission of green light from the powder sample. The SHG output for MLM and KDP samples were found to be 200 mV and 100 mV, respectively. Thus, it is observed that SHG efficiency of MLM crystal was found to be two times higher than that of KDP. Hence, the experimental
result is found to be good agreement with the theoretically predicted value from the polarizability values.

4. Conclusion
Good quality of single crystals 2-methylquinolinium L-malate were grown by the slow evaporation solution growth technique in ethanol as solvent at room temperature. Grown crystals were characterized by single crystal XRD and confirmed that the crystal belongs to monoclinic system with space group P21. UV-vis study revealed that the crystal possesses good optical transmittance (75%) in the visible region. The optical cut-off wavelength and band gap energy of MLM crystal were found to be 437 nm and 2.71 eV, respectively. The photoluminescence spectrum shows the blue emission for the crystal. Vickers microhardness studies showed that MLM crystal belongs to soft material (n= 2.26) category. The laser damage threshold value for MLM crystal was found to be 5.58 GW/cm² and is higher than that of KDP. The relative second harmonic generation efficiency of the MLM crystal was found to be two times greater than that of KDP. Thus, MLM crystal seems to be a promising material for frequency conversion applications.

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