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# Growth, optical, mechanical, dielectric and theoretical properties of picolinium maleate NLO single crystal

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ABSTRACT

Nonlinear optical single crystals of picolinium maleate (PM) were grown by slow evaporation method. The grown crystal was subjected to single crystal X-ray diffraction analysis to confirm that the crystal belongs to the monoclinic crystal structure with space group $P2_1/c$. The optical transmission range of the grown crystal was measured by UV–Vis–NIR region with the lower cut-off wavelength as 330 nm. The optical bandgap is found to be 3.75 eV. Mechanical strength of the grown crystal was analyzed using Vickers microhardness tester. Dielectric constant and dielectric loss of picolinium maleate are measured in the frequency range from 50 Hz to 5 MHz at different temperatures. Further, electronic properties, such as valence electron plasma energy, Penn gap, Fermi energy and electronic polarizability of the grown crystal have been estimated.



## 1. Introduction

In recent years very much focused was invested to materials with high second order nonlinearities outstanding to their potential use in numerous modern research fields such as nonlinear optics, electro-optic modulation, parametric light generation, optical data storage, high speed telecommunications and terahertz wave generation and detection [1–9]. Electron donor–acceptor or charge transfer complexes have been gaining importance due to their wide applications as potential high efficiency nonlinear optical materials, metallic and semiconducting materials [10–12]. They also play an significant role in chemical reactivity because they constitute in many cases the very former interaction between two substrates and their physical properties such as nonlinear optical effects and electrical conductivity are strongly depend on degree and nature of the charge transfer interaction [13,14]. In this way, Pandi et al. have reported synthesis, growth, structural, thermal and nonlinear studies of picolinium maleate [15]. Hence, in the present investigation, we report the synthesis and characterization of the title compound for NLO applications. The grown crystal was characterized using the studies of single crystal XRD, UV–Vis–NIR spectral analysis, microhardness and dielectric studies. The lattice parameters and crystal structure of the grown crystal were confirmed using single crystal X-ray diffraction analysis. The optical transmission study reveals the transparency of the crystal in the entire visible region and the cut off wavelength has been found to be 330 nm. Vicker's microhardness test enumerating the mechanical strength of the crystal has been determined. Dielectric constant and dielectric loss measurements were carried out at different temperatures and frequencies. Electronic properties, such as valance electron plasma energy, Penn gap, Fermi energy and electronic polarizability of the grown crystal were calculated.

## 2. Experimental details

Picolinium maleate single crystals were synthesized by dissolving picolinic acid and maleic acid in the molar ratio 1:1 in distilled water. The solution has been stirred continuously using magnetic stirrer. The prepared solution was filtered and kept undisturbed at room temperature. Tiny seed crystals with good transparency have been obtained due to the spontaneous nucleation. Among them, defect free seed crystal was suspended in the mother solution, which was allowed to evaporate at room temperature. Large size single crystals have been obtained due to collection of monomers at the seed crystal sites from the mother solution. Fig. 1 shows the photograph of as grown picolinium maleate single crystal.

## 3. Results and discussion

### 3.1. Single crystal XRD

Single crystal X-ray diffraction analysis for the grown crystals has been carried out to identify the cell parameters using an ENRAF NONIUS CAD 4 automatic X-ray diffractometer. Single crystal XRD data confirms that the crystal belongs to monoclinic crystal

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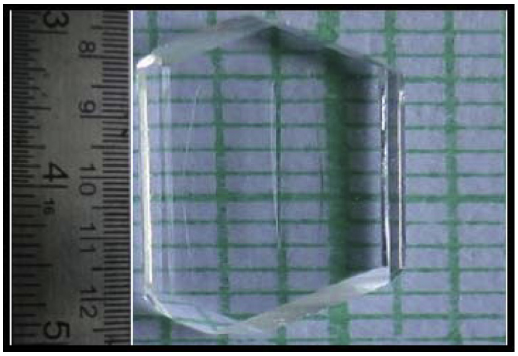

**Fig. 1.** As-grown single crystal of picolinium maleate.

system with space group $P2_1/c$. The calculated lattice parameters are; $a = 14.656$ Å, $b = 10.385$ Å, $c = 6.912$ Å, $\alpha = \gamma = 90^\circ$ and $\beta = 102.40^\circ$ and which agree well with the available reported literature values [15].

### 3.2. Optical transmission

Fig. 2 shows optical transmission spectrum of picolinium maleate single crystal recorded in the wavelength region ranging from 200 nm to 1100 nm. The UV cut off wavelength for the grown crystal was found to be 330 nm. The measured transmittance ($T$) was used to calculate the absorption coefficient ($\alpha$) using the relation,

$$\alpha = \frac{2.3026 \log\left(1/T\right)}{t} \tag{1}$$

where $T$ is the transmittance and $t$ is the thickness of the crystal. As a direct bandgap of the crystal below study has an absorption coefficient ($\alpha$) obeying the following relation,

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

where $E_g$ is the optical band gap of the crystal and $A$ is a constant. The plot of $(\alpha h\upsilon)^2$ versus $h\upsilon$ is shown in Fig. 3. $E_g$ was measured by the extrapolation of the linear part [16]. The bandgap value is found to be 3.75 eV. As a consequence of wide bandgap, the grown crystal has large transmittance in the visible region [17].

### 3.3. Vickers microhardness

Analysis of mechanical property of the grown crystal is also important for the fabrication of electronic and optical devices.

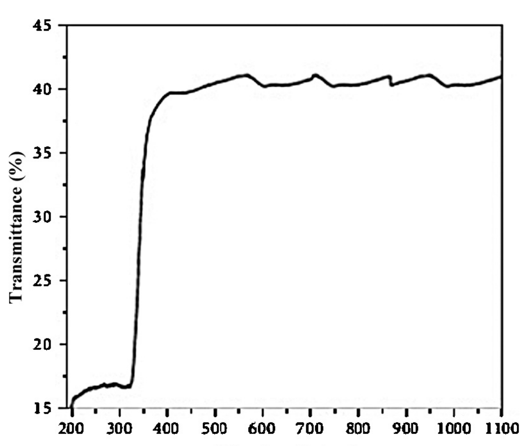


**Fig. 2.** UV–Vis–NIR transmission spectrum of picolinium maleate crystal.

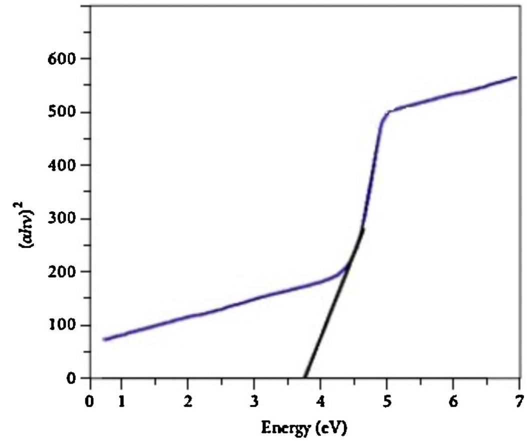


**Fig. 3.** $(\alpha h\upsilon)^2$ vs $h\upsilon$.

Microharness studies were carried out on a selected well transparent single crystal using microharness tester, fitted with a Vickers diamond pyramidal indenter [18]. To get exact results of hardness of the grown crystal indentations were made on the picolinium maleate crystals with applied load ranging from 10 g to 50 g. The time of indentation has been kept constant for 10 s. Five indentations were made on each surface under test for the same load and the mean diagonal length was measured. To deflect surface defects, the distance between consecutive indentations was kept more than five times the diagonal length of the indentation mark. The diagonal length of indentation mark has been assessed using a micrometer eyepiece. The values of Vicker's microhardness at different loads were calculated using the relation,

$$Hv = 1.8544 \times \frac{P}{d^2} \text{kg/mm}^2 \tag{3}$$

where, $P$ is the applied load and $d$ is the mean diagonal length of the indenter impression. Fig. 4 shows the variation of hardness with the applied load. It is observed that the hardness of picolinium maleate increases by increasing load up to 50 g which indicates the reverse indentation size effect [19,20]. The increasing trend of microhardness with the load up to 50 g is well understood from Mayer law and onitisch condition. According to Mayer law, the relationship between the load ($P$) and the size ($d$) of the indentation is given as

$$P = kd^n \tag{4}$$

where, $n$ is called Mayer index or work hardening index. Hence, the slope of the plot of log $d$ versus log $P$ will give the work hardening index. The slope of the plot for picolinium maleate (Fig. 5) is found to

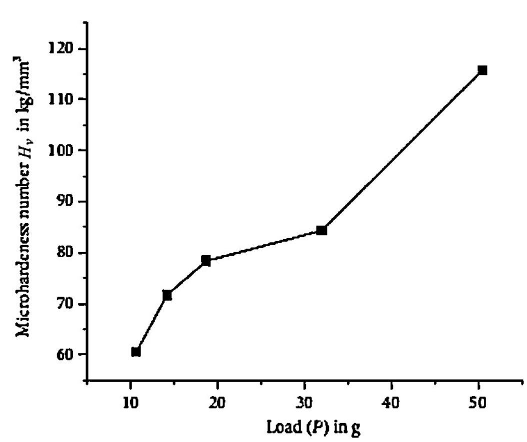


**Fig. 4.** Vickers microhardness of picolinium maleate single crystal.