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Growth and Characterization of Morpholium Cadmium Acetoperchlorate Single Crystal

D. Shyamala¹, R. Rathikha², K. Gomathi²

¹Department of Physics, D.G. Vaishnav College, Chennai 600 106, India ²Department of Physics, Presidency College, Chennai 600 005, India

ABSTRACT

In the search for novel crystal with promising nonlinear optical properties an attempt is made to grow morpholium cadmium aceto-perchlorate single crystals. The title compound is synthesized by slow evaporation technique at room temperature. The powder X-ray diffraction pattern has been recorded and the various planes of reflections are identified. The transmittance spectrum of the crystal in the UV–Vis region has been obtained. Using the FTIR spectrum, the vibrational modes of the crystal is analysed and the presence of cadmium in the crystal is confirmed. Thermogravimetric analysis and differential thermal analysis studies have been done to assess the thermal stability of the grown crystal. The dielectric measurement for the crystal is carried out in the range of 50 Hz to 5 MHz for three different temperatures 40°C, 80°C and 120°C to study the electrical nature of the grown crystal. The nonlinear optical property of the grown crystal is confirmed.

Keywords: Optical materials, Crystal growth, Thermogravimetric analysis (TGA), X-ray diffraction, Dielectric properties

I. Introduction

During the past decade, considerable interest has been shown in synthesizing and device development of many propitious metallo-organic nonlinear optical (NLO) crystals widely used in optical communication, laser medicine and signal processing [1]. It is reported that molecular ionic simple complex crystals like perchlorate with morpholine (of ratio 1:1) show NLO physical properties unique to the crystal structure [2,3]. The distinct features of molecular ionic crystal give empathizing correlation between the crystal packing and physical properties. This has initiated many researchers to synthesize and to grow newly designed molecular ionic crystals. Since metalloorganic crystals are promising NLO materials, it is attempted to synthesize morpholium cadmium aceto-perchlorate (MCAP) crystal and to establish and improvement in its characteristics.

II. Experimental Details

The title material MCAP is synthesized by the chemical reaction of morpholine with perchloric acid, taken in the ratio 1:1 by dissolving in the mixture of (1:1) ethanol and deionized water. Stoichiometrically calculated amounts of the materials are transferred into a beaker and dissolved in ethanol and deionized water which is stirred well with the help of a magnetic stirrer to make a homogeneous solution of the material at room temperature for a proper chemical reaction. Then cadmium acetate is added to the solution. The obtained MCAP solution is allowed to evaporate at room temperature. The well-defined single crystals of MCAP are harvested from mother solution after a growth period of 2 weeks. The as grown single crystals of MCAP are shown in Fig. 1.



Fig. 1: As grown single crystals of MCAP. CAP salt is synthesized according to the following reaction



III. Results and Discussion 3.1 Powder Crystal XRD Studies

Powder X-ray diffraction (XRD) is a rapid analytical technique primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions. The analyzed material is finely ground, homogenized, and average bulk composition is determined. The powdered form of the specimen is subjected to powder X-ray diffraction analysis and scanned between the range 10° and 70° . Fig. 2 shows the recorded spectrum. Crystalline nature of the crystal is quite clear from the occurrence of sharp peaks at specific Bragg's angles. The peaks observed in the XRD pattern have been indexed using the FULLPROF software shown in Fig. 3. The crystallite size is calculated using the Debye– Scherrer equation $D = \frac{0.9 \lambda}{\beta \cos \theta}$ where D is the crystallite size λ the usual path of CyVrs

crystallite size, λ the wavelength of CuK α radiation, β is the line width at half peak intensity and θ_{max} is the diffraction peak angle. Crystallite size calculated for all planes is given in Table 1. The average crystallite size is found to be 64 nm.



Fig. 2: Recorded powder pattern of MCAP.



Fig. 3: Indexed powder pattern of MCAP.

Table 1: Crystallite Size of the Crystalline Powder of MCAP							
Angle (2 θ_{abs})	$d_{\rm abs}({ m \AA})$	Peak width at half intensity	Peak intensity	Reflection plane	Crystallite size (nm)		
26	3.4212	0.16	4000	400	53.25		
32	2.8105	0.1306	2200	020	66.12		
35	2.5998	0.154	3100	220	56.52		
39	2.281	0.14	1000	600	62.9		
42	2.171	0.11	2000	420	80.83		

3.2 Fourier Transform Infrared Spectroscopy

Fourier transform infrared (FTIR) spectroscopy is an important technique in organic chemistry. It is an easy way to identify the presence of certain functional groups in a molecule [4,5]. Also, one can use the unique collection of absorption bands to confirm the identity of a pure compound or to detect the presence of specific impurities. The FTIR spectrum is recorded in the range 4000 to 400 cm⁻¹ by KBr pellet technique.

The recorded spectrum of MCAP single crystal is shown in Fig. 4. All the wave numbers are assigned in terms of fundamentals, overtones and combination bands. The observed wave numbers along with their relative intensities and assignment are presented in Table 2. The wave numbers are assigned on the basis of earlier assignments of cadmium acetate, benzene and morpholine, naphthalene molecules



Fig. 4: FTIR spectrum of MCAP.

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Observed wave number (cm ⁻¹)	Relative intensity	Spectral assignment
3413	St	N-H asymmetric stretching
3287	St	N-H symmetric stretching
3038	St	Asymmetric stretching
2444	W	Symmetric stretching
1091	VS	NH ₂ rocking
1562	М	C-C stretching vibration
1431	М	
1313	St	CH ₃ stretching
940	W	C-NH ₂ stretching
690	W	Carbon in plane bending vibration
636	St	NH ₂ out of plane wagging
626	St	Carbon in plane bending vibration
593	М	Carbon out of plane bending vibration
482	VW	
462	VW	Bending vibration

VS – very strong; St – strong; M – medium; W – weak, VW – very weak.

N–H Stretching. The molecule under consideration has only one NH_2 group and hence one N–H asymmetric and N–H symmetric stretching vibration is expected. In primary aromatic amines, the N–H stretching frequency occurs in the region 3300 to 3500 cm⁻¹. Hence the absorption bands observed at 3413 and 3287 cm⁻¹ is assigned to N–H asymmetric and symmetric stretching mode of the NH_2 group, respectively.

C-NH₂, C-CH₃ Group Vibrations. Shukla et al. [6] have reported that the bands observed at 975 and 979 cm^{-1} can be assigned to C-NH₂ stretching vibrations. The C-NH₂ in plane and out of plane bending vibrations occurs at 421 and 200 cm⁻¹, respectively. Similarly in the case of MCAP, the band seen at 940 and 462 cm^{-1} is assigned to C-NH₂ stretching and bending vibration, respectively. The NH₂ rocking mode is normally expected at 1050 cm^{-1} and the NH₂ out of plane wagging modes in the region 550 to 700 cm^{-1} . So, the modes observed at 1091, 626 and 593 cm^{-1} can be assigned as above. The C-CH₃ stretching modes at 1208 and 1223 cm⁻¹ are reported for toluene and o-xylene, respectively. Along similar lines, the peak at 1313 cm⁻¹ can be considered as due to this CH₃ stretching. It is observed that the wave number seems to have increased appreciably and this is probably due to the co-ordination of cadmium acetate with morpholinium perchlorate.

Carbon Vibrations. In benzene, bands between 1400 and 1650 cm⁻¹ have been assigned to C–C stretching modes. It has two double degenerate modes 1596 and 1485 cm⁻¹ and two nondegenerate modes 1310 and 995 cm⁻¹. So the prominent peaks observed in the spectrum at 1562 and 1431 cm⁻¹ are assigned to C–C stretching vibrations. The in plane carbon bending vibration are obtained at 1010 and 606 cm⁻¹ from the modes of benzene. The carbon out of plane bending vibrations is defined with reference to the nondegenerate 707 cm⁻¹ and degenerate 404 cm⁻¹ modes of benzene. Hence in the present work, the carbon in plane and out of plane bending vibrations are assigned to the bands 690, 626, 593 and 482 cm⁻¹, respectively.

C-H Vibration. The MCAP molecule gives rise to C–H stretching modes from the ring and also from cadmium acetate. Aromatic structures show the presence of C–H stretching vibration around 3000 cm⁻¹. In general, the methyl group has shown characteristic C–H stretching vibration at around 2962 and 2782 cm⁻¹. In our grown crystal, the recorded FTIR spectrum shows strong peaks at 3038 and 2444 cm⁻¹. The values are found to be slightly greater with respect to C–H vibration of morpholinium perchlorate and lesser in the case of C–H vibration of cadmium acetate. This change of value can be attributed to the coordination between morpholinium perchlorate and cadmium acetate.

3.3 UV–Vis Transmittance Spectrum

The UV–Vis-NIR spectral transmission is studied using a Perkin Elmer UV–Vis–NIR spectrophotometer in the range 100 to 900 nm. The recorded spectrum is shown in Fig. 5. The lower UV cut off of the MCAP crystal is at 250 nm, which makes it a very potential material for blue light emission. The crystal has a wider transparency range extending into the visible and IR region.



Fig. 5: UV–Vis spectrum of MCAP.

3.3.1 Determination of Band Gap Energy from UV–Vis Spectrum

The band gap energy and refractive index are the two fundamental physical quantities which characterize electronic and optical properties of the crystal. Optical band gap of MCAP is calculated from the transmittance spectrum. The measured transmittance (*T*) is used to calculate the absorption co-efficient (α) using the formula:

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

where t is the thickness of the sample. Optical band gap (E_g) is evaluated from the transmission spectrum and optical absorption coefficient (α) near the absorption edge using the formula [7]:

1

$$\alpha h\gamma = A(hv - E_g)^{\overline{2}}$$
(2)

where A is a constant, E_g the optical band gap, h Planck's constant and n the frequency of the incident photons. The band gap of MCAP crystal is estimated by plotting $(\alpha h\gamma)^{1/2}$ versus hv as shown in Fig. 6 and extrapolating the linear portion near the onset of absorption edge to the energy axis.



Fig. 6: A plot of $(\alpha hv)^{1/2}$ versus hv.

From Fig. 6, the value of band gap is found to be 4.9 eV. The band gap energy (E_g) calculated using the cut off wavelength that is obtained from the UV–Vis spectrum using the relation:

$$E_{g} = \frac{hc}{\lambda_{(cut)}} eV$$
(3)

where $E_{\rm g}$ is the band gap energy, $h = 6.626 \times 10^{-34}$ J s⁻¹, $C = 3 \times 10^8$ m s⁻¹ and $\lambda_{\rm (cut)}$ is the cut off wavelength which is 439 nm. The band gap energy is 4.72 eV. The calculated value is found to be similar to the value 4.9 eV obtained by Tauc's plot [8].

Reflectance (R) in terms of absorption coefficient can be obtained from the following equation:

$$R = \frac{\exp(-\alpha t) \pm \sqrt{\exp(-\alpha t)T - \exp(-3\alpha t)T + \exp(-2\alpha t)T^{2}}}{\exp(-\alpha t) + \exp(-2\alpha t)}$$
(4)

Refractive index (n) can be determined from reflectance data using the following equation:

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

For wavelength $\lambda = 211$ nm, the refractive index (*n*) is found to be 1.76.

3.4 Second Harmonic Generation

NLO plays a significant role in photonics and optoelectronics. The first and the most widely used technique for confirming the second harmonic generation (SHG) efficiency from prospective second-order NLO material is the Kurtz powder technique [9]. The NLO property of MCAP crystal is studied by Kurtz powder SHG test at B.S. Abdur Rehman University, Chennai. The crystal is illuminated using Spectra Physics Quanta Ray DCR 11 Nd:YAG laser using the first harmonic output of 1064 nm with pulse width of 8 ns and repetition rate of 10 Hz. The SHG in the crystal is confirmed by the emission of green radiation.

3.5 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) is a thermal analysis technique used to establish the melting point of variety of materials. The TGA data is obtained from Department of Chemistry, IIT, Chennai. The TGA of MCAP measured at three different heating rates 15°C min⁻¹, 20°C min⁻¹ and 25°C min⁻¹ is shown in Fig. 7A–C. From the graphs, it is seen that only one peak is observed which shows that thermal degradation occurs in only one stage. The TGA result shows that there is no weight loss up to 230°C and decomposition starts at this temperature which indicates that sample is stable from ambient up to 230°C making it suitable for device applications [10,11].



Fig. 7: TGA–DTA spectrum of MCAP crystal at 15°C min⁻¹ (A), 20°C min⁻¹ (B) and 25°C min⁻¹ (C).

3.6 Dielectric Studies

Dielectric constant and dielectric loss give an insight into the nature of bonding [12]. The dielectric measurements are carried out for crystal MCAP for three different temperatures 40°C, 80°C and 120°C. The dielectric constant is calculated using the formula:

$$\varepsilon' = \frac{Ct}{A\varepsilon_0} \tag{6}$$

where *C* is capacitance, *t* is thickness of the sample, ε_0 is the permittivity of free space (8.85 × 10⁻¹² F m⁻¹) and *A* is the area of the sample. The plot of frequency versus dielectric constant (ε') for various temperatures is shown in Fig. 8.



Fig. 8: Variation of dielectric constant with frequency.

It is seen from the Fig. 8 that at low frequencies the value of dielectric constant is high and as the frequency increases the dielectric constant attains a low value. The value of high dielectric constant at low frequency is due to space charge and ionic polarization. The value of dielectric constant increases with increase in space charge polarization due to a large concentration of defects at higher temperatures [13]. The dipolar polarization, which is present in the lower frequency region, is very important for applications in capacitive and insulating properties of crystals. It is understood that the contribution of all types of polarization will be more at lower frequencies. The low value of dielectric constant at higher frequencies are due to factors such as voids, grain boundaries, purity and other defects too, which are present in the sample. The electronic and ionic polarizations always exist at higher frequencies. The considerable low value of dielectric constants

observed for the grown crystals is important for extending the material applications towards photonic, electro-optic and NLO devices.

Dielectric or tangent loss (tan δ or ε'') is nothing but the wastage of energy. For a material to be a potential candidate for NLO applications, the dissipation factor must be kept as low as possible. A graph is plotted between frequency and dielectric loss/dissipation factor, shown in Fig. 9. It is seen from Fig. 9 that at low frequencies the value of dielectric loss is high and as the frequency increases the dielectric loss attains a low value. The low value of dielectric loss at high frequencies shows that the sample has enhanced optical quality with minimum defects. This parameter is of vital importance for NLO applications. These plots exemplify the fact that the dielectric constant and the dielectric loss are both inversely proportional to the frequency.



Fig. 9: Variation of dielectric loss with frequency.

The sudden increase of $\tan \delta$ in the hightemperature region could be associated with free charge carrier conductivity. Since the concentration of free charge carriers depends on temperature, the rate of loss is also high in the higher temperature region. As the loss factor is inversely proportional to frequency, it is related to disappearance of space charges at higher frequencies. According to Miller rule, lower the dissipation factor, higher will be the conversion efficiency. Thus MCAP single crystals could be expected to possess higher efficiency and hence they could be potential candidates for high speed optoelectronic applications like interlayer dielectric.

IV. Conclusion

Single crystal of MCAP is grown by slow evaporation at room temperature. From the XRD peak intensity it is concluded that in the present work crystalline nature of the grown crystal is very high. The peaks are indexed using FULLPROF software using the knowledge of atomic positions. The crystallite size of the powdered crystal is approximately 64 nm. The FTIR spectrum of the grown crystal helped to confirm the different functional groups present in it. It is observed that there is a significant shift in the peaks confirming the coordination of morpholinium perchloric acid with cadmium acetate. The UV-Vis transmittance spectrum of the grown crystal confirms that it is suitable for NLO applications because it is characterized by a wide transmission window. Using UV-Vis spectrum, the energy gap of the grown crystal is found from its cut off wavelength as 5.1 eV and from the theoretical data as 4.9 eV. The refractive index of the crystal is found to be 1.76 at 211 nm. The emission of the green light is confirmed by NLO studies. The thermal stability of the materials clearly indicates that it can be exploited for NLO applications up to 230°C. The higher values of dielectric loss (tan δ) and dielectric

constant observed at lower frequencies may be attributed to space charge polarization owing to charged lattice defects. The dielectric studies also confirm that the crystal has good optical quality. Hence the grown crystal from the characterization studies is established to be an efficient NLO material.

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