An insight on spectral, microstructural, electrical and mechanical characterization of ammonium oxalate monohydrate crystals

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Single crystals of ammonium oxalate monohydrate (AO) were grown using the slow evaporation solution growth technique. The cell parameters obtained from the single crystal diffraction experiments matched with those known earlier showed that the grown crystals were composed of AO. The variation of dielectric constant as a function of frequency shows that the dielectric constant is relatively high in low frequency region and low in the high frequency region. Microhardness study indicates that the grown AO crystal is of a soft nature. The TG and DTA studies reveal that the grown crystal has good thermal stability and can be exploited in various applications up to 100 °C. There is a change in morphology of etch pits on prolonged etching. A very low value of dielectric constant supports that the material can be exploited in photonic and electro-optic devices. Thermal stability of the grown crystal is good.

Keywords: etching; dielectric constant; microhardness study; single crystal

1. Introduction

Molecular engineering and chemical synthesis can be used to tailor the properties of organic compounds [1]. The spectacular success of molecular engineering in controlling NLO properties has led to the growth and characterization of a new variety of NLO materials [2]. Electronic devices like optical memories, color displays and so on, use organic crystals which are bulk in size, mechanically hard, chemically stable and transparent in blue green region. The aromatic nature of the π electron system and the donor and acceptor groups are the important factors that enhance the NLO effects in organic systems. This, in turn, has made the organic materials play a vital role in the research of nonlinear optics. Thus the search for new organic NLO crystals, which possess shorter cut off wavelength, good optical quality, sufficiently large nonlinear coefficient, transparency in UV region and high damage threshold became mandatory. The extensive study on the influence of hydrogen bonds in the radiation damage processes in solids revealed that the dicarboxylic acids and their salts are suitable for such studies. A profound fact about oxalic acid is that it is a parent compound for many derivatives and metal salts and the first member of a homologous series of dicarboxylic acids. This interest is enhanced by the fact that both chemical forms of oxalic acid (anhydrous and dehydrated) and many oxalate salts can be readily obtained as pure crystals of a known structure. Oxalate ions are of considerable importance due to their capacity to form stable complexes with various metal ions. Oxalates are used in numerous industrial, geological and biological systems and as an ingredient in the manufacturing of explosives and metal polishing compounds.

Ammonium oxalate monohydrate (AO) is an organic, noncentrosymmetric and efficient nonlinear optical crystal. Though many works [3–6] have been reported on the characteristic changes due to inclusion of impurities in AO crystals, the literature survey revealed that various properties of AO crystals have to be probed yet. Optical quality single crystals of AO were grown by slow
evaporation solution growth technique. Their optical, electrical, spectral, mechanical and thermal properties were studied to explore the suitability of the crystal for nonlinear applications and electro-optic device fabrication. This paper presents the detailed results obtained during the studies.

2. Growth of ammonium oxalate monohydrate single crystals

2.1. Solubility

Solubility is an essential prerequisite for the solution growth method. It plays a key role to select the best solvent and temperature to grow good quality single crystals. Commercially available ammonium oxalate (AO) (98 % purity form Merck Company) was purified by repeated recrystallization in deionized water. The recrystallized salt was added in small quantity into a beaker containing 100 mL of water at 30 °C. The solution was stirred continuously and the saturation level of AO at 30 °C was estimated. The experiment was repeated and the solubility as a function of temperature (30 °C to 50 °C) in deionized water was assessed and plotted. It is noted from Fig. 1 that the solubility of AO increases with increasing temperature, thus revealing a positive gradient of solubility.

2.2. Crystal growth

The solution growth technique is suitable for the growth of organic crystals because the crystals with good morphology can be obtained by this method [7]. Also, the low temperature involved in the growth from solution makes it easier to obtain less defective crystals than in high temperature growth methods [8]. Hence, slow evaporation solution growth technique was employed to grow single crystals of AO. Recrystallized salt of AO was used to prepare the saturated solution at 40 °C and the solution was kept at a constant temperature water bath (CTB) with an accuracy of ±0.01 °C. Controlled slow evaporation of the solvent yielded excellent seed crystals. A good quality seed crystal was selected and suspended in the original solution and then left for about 90 days without disturbing. The optically transparent as-grown single crystals are shown in Fig. 2.

3. Characterization studies

3.1. Structural studies

3.1.1. Single crystal X-ray diffraction studies

Single crystal X-ray diffraction analysis using ENRAF NONIUS CAD4 X-ray diffractometer was employed to determine the cell dimensions of AO crystals. A crystal of dimensions 0.5 mm × 0.6 mm × 0.6 mm obtained from the grown AO was used as a specimen for the analysis. It was found from the single crystal X-ray diffraction study that AO crystallizes in an orthorhombic system with the space group P2₁2₁2 and its cell parameters are a = 8.49 Å, b = 10.37 Å.
and $c = 3.82 \text{ Å}$ which is in a good agreement with the values reported in the literature [9].

### 3.1.2. Powder X-ray diffraction studies

The powder X-ray diffraction pattern was recorded for AO using a Rich Seifert X-ray diffractometer with CuKα ($\lambda = 1.5418 \text{ Å}$) radiation over the range of 10° to 70° at a scanning rate of 10°/min and it is shown in Fig. 3. The peaks were indexed by using the PROZSKI software package. The calculated lattice parameters are in accordance with those reported in the literature.

![Powder X-ray diffraction pattern of AO.](image)

### 3.2. Spectral analysis

#### 3.2.1. Factor group analysis

Information about the charge transfer interaction between donor and acceptor groups through $\pi$ electron cloud which makes the molecule highly polarized are provided by vibrational spectral studies. This intermolecular charge transfer interaction is highly responsible for the NLO properties of the grown crystal.

AO belongs to the orthorhombic crystal system and the unit cell contains two formula units. The space group of the crystal is $P_{2_1}2_12$, the site symmetry is $C_1(2)$. The unit cell contains 19 atoms giving rise to a total of 114 vibrational modes. These modes are classified according to the irreducible representations of the point group. The site correlation method of factor group analysis was applied to classify the vibrational modes of AO. The symmetries of zone center normal modes and their IR and Raman active species were derived using the method outlined by Rousseau et al. [10]. The representation $\Gamma_{\text{total}}$ of all the vibrations decomposes according to irreducible representation of the point group such as $(29 A + 29 B_1 + 28 B_2 + 28 B_3)$ among which three acoustic modes $\Gamma_{\text{acoustic}} = (1B_1 + 1B_2 + 1B_3)$ corresponding to the block translations of the crystal are included. The remaining $(1 1 1)$ vibrations are optical modes. According to the group theoretical considerations, these $(1 1 1)$ optical modes can be divided into 9 external and 102 internal modes which in turn can be decomposed into $(26 A + 26 B_1 + 25 B_2 + 25 B_3)$. The translational lattice modes decompose as $\Gamma_{\text{trans}} = (1 B_1 + 1 B_2 + 1 B_3)$ and rotational lattice modes decompose into $\Gamma_{\text{rot}} = (2B_1 + 2 B_2 + 2 B_3)$. The summary of the factor group analysis is presented in Table 1.

#### 3.2.2. Internal vibrations

**N–H bond**

The presence of hydrogen bond, besides Columbic interactions between the ionic species, helps in building stable structures, and it is also one of the favorable factors that help to increase the melting point and to grow single crystals with ease. Infinite ion-pair arrays are usually formed by the hydrogen bonding network. Nagalakshmi et al. [11] has mentioned in their work that in many cases, specific intermolecular hydrogen bonding networks act as the driving force to form noncentrosymmetric crystal structure. The bonds due to N–H stretching vibrations are sharper in general [12]. The N–H stretch occurs at 3201 cm$^{-1}$. The asymmetric NH$_4^+$ bending vibrations occur at 1642 cm$^{-1}$ and the symmetric vibrations appear at 1402 cm$^{-1}$.

**C–O–O bond**

The carboxylate group gives symmetric and asymmetric vibrations at 1402 cm$^{-1}$ and 1642 cm$^{-1}$. The group of peaks between 517 cm$^{-1}$ and 810 cm$^{-1}$ are due to C–O–O bending modes.
Table 1. Factor group analysis summary.

| Factor group species | Site symmetry (C1[4]) | N | H | C | O | Optical modes | Acoustic modes | Total |
|----------------------|----------------------|---|---|---|---|---------------|----------------|-------|
| A                    | 26                   | – | 3 | 15| 7.5| 29            | 0              | 29    |
| B_1                  | 26                   | 1T, 2R | 3 | 15| 7.5| 29            | 1              | 28    |
| B_2                  | 25                   | 1T, 2R | 3 | 15| 7.5| 28            | 1              | 27    |
| B_3                  | 25                   | 1T, 2R | 3 | 15| 7.5| 28            | 1              | 27    |
| Total                | 102                  | 3T, 6R | 12| 60| 12| 30           | 3              | 111   |

3.2.3. External vibrations

External vibrations are mainly due to the bonds observed below 500 cm\(^{-1}\) which are due to the rotational and translational modes of vibrations of AO ions. In Raman spectra the rotational modes are expected to have higher frequency and intensity than the translational modes. However, the translational modes are more intense in IR spectra [13]. AO is found to have 9 external modes and these vibrations can be achieved experimentally by polarized Raman measurements. The correlation scheme is given in Table 2.

Table 2. Correlation scheme for AO.

| Factor group symmetry | Activity |
|-----------------------|----------|
|                       | IR       | Raman   |
| A                     | –        | α\(_{xx}\), α\(_{yy}\), α\(_{zz}\) |
| B_1                   | Z        | α\(_{xy}\) |
| B_2                   | Y        | α\(_{xz}\) |
| B_3                   | X        | α\(_{yz}\) |

3.2.4. FT-IR analysis

Identification of the functional units, internal structure of molecules and chemical bonds of compounds can be effectively carried out using the FT-IR spectral analysis. This spectroscopy also provides information on the chemical bonding and the microscopic mechanism of the NLO properties of new materials. Strong absorption in the IR region arises due functional groups with a strong dipole. The FT-IR spectrum of the AO sample is shown in Fig. 4. In the spectrum there is a broad band between 3400 cm\(^{-1}\) and 3600 cm\(^{-1}\). It includes O–H stretching of H\(_2\)O at 3415 cm\(^{-1}\), N–H at 3201 cm\(^{-1}\) and fine structure due to H\(_2\) bonding at 2859 cm\(^{-1}\). The carboxylate group gives symmetric and asymmetric vibrations at 1402 and 1642 cm\(^{-1}\). Ammonium ions give peaks at 2154 cm\(^{-1}\) and 2360 cm\(^{-1}\). The asymmetric NH\(_4^+\) vibrations occur at 1642 cm\(^{-1}\) and the symmetric vibrations are seen at 1402 cm\(^{-1}\). The shoulder at about 1630 cm\(^{-1}\) in the lower energy portion group is due to O–H\(_2\) bending. The group of peaks between 517 cm\(^{-1}\) and 810 cm\(^{-1}\) are due to COO\(^-\) bending mode. The assignments made are shown in Table 3.

3.3. Etching studies

Etching studies were performed on the crystals etched for shorter and longer times
so that the dissolution layer obtained at shorter duration could preserve its micromorphology. Prolonged etching gives the macroscopic form different from the micromorphology. Both time and etchant are the etching parameters that control the micro and macro morphology of the crystal. As AO is water soluble, the dissolution patterns were obtained using water as etchant.

Fig. 5a shows the terracing of etch pits on the as-grown crystal surface. The tiny pores observed on the surface of the crystal may be due to the evaporation of ammonia. The roughness of the surface of a grown crystal can also be attributed to the acidic nature of oxalic acid. However, while reducing the acidic nature by reacting with the etchant (water) the surface roughness seems to disappear. On etching the surface for 5 s, the spike-like structures were formed (Fig. 5b). These spikes are due to the lower supersaturation region or dissolution of the crystal surface. The concentration of the spikes increases with increasing time. It is also to be mentioned that all the etching experiments were carried out on the same face. The change in morphology of the etch pits on prolonged etching can be attributed to the adsorption of inhibiting species and solvent molecules at the newly created surface. These observations can be associated with the decreasing undersaturation at the dislocation sites with increasing time.

The difference in the shape and density of the etch pits is due to the different arrangement of ions, atoms or molecules comprised on the crystal surface. The sites of origin of the etch pits are the points of dislocations developing on the surface resulting from dissolution leading to the localized etching action. The decrease in the density of the etch pits on increasing the etching time reveals that volume defects are localized at random positions in the crystal interior. This is the reason for the stacking type of etch pits. The striations formed are due to the volume and linear defects. Volume defects were confirmed further by the disappearance of the etch pits on successive etching. The etch pits formed for 10 s, 15 s, 20 s and 25 s etch time periods are shown in Fig. 5c, Fig. 5d, Fig. 5e and Fig. 5f.

### 3.4. Dielectric studies

The understanding of dielectric constant of a material is important to interpret the dynamics of that material. When the dielectric material is under the influence of an alternating electric field, the motion of the particles present in the material builds up an equilibrium polarization. Hence, the dielectric parameters depend on the frequency of AC voltage applied across the material. Also it is noted that with an increase in temperature the ionic and electronic polarizations decrease marginally.

In the present study, the AO single crystal was mounted between a pair of flat stainless steel electrodes. The variation of temperature for the dielectric study was made after enclosing the cell in a resistance heated muffle furnace and the temperature was controlled by the chromel-alumel thermocouple (±0.01 °C). The capacitance was also measured. The experiment was carried out for different frequencies ranging from 50 Hz to 5 MHz and at various temperatures of 35 °C to 95 °C.

![Fig. 6](unavailable)

Fig. 6 shows the variation of dielectric constant with frequency at different temperatures. From the curve it is observed that the dielectric constant decreases slowly with an increase in frequency and attains a saturated value at higher frequencies. This is attributed to the presence of all the four types of polarizations, such as electronic, ionic, dipolar and space charge polarization [14]. At low frequencies all the mechanisms of polarization contribute to the dielectric constant and with the increase

### Table 3. FT-IR assignments for AO crystal.

| Sl. No. | Wave number [cm⁻¹] | Assignments                  |
|--------|--------------------|-------------------------------|
| 1      | 3415               | OH-stretch of H₂O             |
| 2      | 3201               | NH-stretching                 |
| 3      | 2859               | Fine structure due to H₂ bonding |
| 4      | 2360 & 2154        | ammonium ions                |
| 5      | 1642               | asymmetric stretch of NH⁺⁺    |
| 6      | 1630               | OH₂ bend                      |
| 7      | 1402               | symmetric stretch of NH⁺⁺     |
| 8      | 810-517            | COO⁻ bending mode             |
in frequency the contributions from different polarizations start decreasing. This may also be due to the loosely bonded ions in the crystal. The very low value of dielectric constant at high frequency is important for extending the material applications towards photonic, electro-optic and NLO devices.

The variation of dielectric loss with frequency shown in Fig. 7 reveals that the dielectric loss strongly depends on the frequency of the applied field. Moreover, the low dielectric loss at high frequency reflects the good optical quality of the crystal with lesser defects. The low value of dielectric loss suggests that the crystal contains minimum defects.

The frequency dependence of AC conductivity with temperature is shown in Fig. 8. The observed high value of conductivity for higher frequencies at a given temperature confirms polaron hopping in the crystals. It is evident from the figure that conductivity increases as the temperature increases. This observed increase in the conductivity could be due to the reduction of the space charge polarization at higher frequencies [15]. The activation energy for AO was calculated from the plot.
of conductivity (log$$\sigma_{ac}$$) versus temperature ($$10^3/T$$), using the equation:

$$\sigma_{AC} = \sigma_o \exp\left[-E_a/k_BT\right]$$  \hspace{1cm} (1)

where $$E_a$$ is the activation energy, $$k_B$$ is the Boltzmann constant, $$\sigma_o$$ the pre-exponential factor. The calculated activation energies at different frequencies are tabulated in Table 4.

It is well understood from theoretical calculations that the high frequency dielectric constant explicitly depends on the valence electron plasmon energy, an average gap referred to as the Penn gap and the Fermi energy. The Penn gap can be established by fitting the dielectric constant with the plasmon energy. The Fermi energy value and polarizability was calculated using the procedure outlined by Ravindra [16]. The calculated theoretical energy values for AO crystals are listed in Table 5.

### 3.5. Theoretical calculation of first order hyperpolarizability \( \beta \)

The first order hyperpolarizability value of AO was calculated by using the GAUSSIAN 98 W and the computational details used for the calculation of $$\beta$$ were as described in our earlier
Table 5. Results of theoretical energy values.

| Parameters                              | Values          |
|-----------------------------------------|-----------------|
| Plasma energy [eV]                      | 17.468          |
| Penn gap [eV]                           | 0.1235          |
| Fermi energy [eV]                       | 13.36           |
| Polarizability: Penn analysis [cm$^3$]  | $3.6591 \times 10^{-23}$ |
| Polarizability: Clausius-Mossotti [cm$^3$] | $3.6643 \times 10^{-23}$ |

All the calculations were carried out by the density functional triply parameter hybrid model DFT/B3LYP using GAUSSIAN 98 W. The HF/3-21 G (d, p) basis set has been employed. The calculated first order hyperpolarizability of AO is $4.94 \times 10^{-31}$ esu. The calculated first order hyperpolarizability $\beta$ is presented in Table 6.

Table 6. First order hyperpolarizability $\beta$ of AO.

| $\beta_{xyx}$ | $-230.72$ |
| $\beta_{yxy}$ | $31.95$   |
| $\beta_{yxy}$ | $-34.76$  |
| $\beta_{yy}$  | $13.59$   |
| $\beta_{zx}$  | $-102.89$ |
| $\beta_{zy}$  | $19.33$   |
| $\beta_{zy}$  | $-28.84$  |
| $\beta_{xz}$  | $-88.64$  |
| $\beta_{yz}$  | $11.57$   |
| $\beta_{zz}$  | $-84.29$  |
| $\beta_{total}$ | $4.94 \times 10^{-31}$ |

$\beta=-2\omega; \omega, \omega$ in $10^{-31}$ esu.

Domination of particular components indicates substantial delocalization of charges in those directions. The highest value of hyperpolarizability corresponds to propagation along the dielectric axis having the smallest refractive index.

### 3.6. Thermal studies

The thermogravimetric and the differential thermal analyses presented in Fig. 9 show the mass variation recorded during heating between 30 °C to 100 °C at a heating rate of 20 °C/min in the nitrogen atmosphere. This analysis also gives information regarding the loss of water of crystallization and different stages of decomposition of the crystal system [18]. We see from the spectra two stages of weight loss between 100 °C and 300 °C. The first weight loss occurring at 100 °C is due to the loss of lattice water. It is followed by a major weight loss at about 200 °C. During the second stage of weight loss the material is observed to be completely decomposed without any residues. As there is no weight loss below 100 °C there is no surface adsorbed water on the crystal surface. The presence of lattice water is also evident from the IR as discussed earlier. The DTA was carried out under the similar conditions as that of TGA. The spectrum shown in Fig. 9 shows two major endotherms with the first one starting close to 100 °C and the second at 220 °C. These two endotherms exactly coincide with the two stages of weight loss in the TGA trace. Since there is no endotherm below 100 °C the crystal is thought to decompose without melting. Also as there is no endotherm in between those two major endotherms, the dehydrated AO seems to decompose without melting. Based on the above
Two analyses it can be said that the crystal can be used up to 100 °C for NLO applications.

### 3.7. Microhardness study

The resistance that a material withstands local deformation caused by scattering or by indentation is one of the important properties of any device material and is represented by its hardness. In an ideal case the hardness values measured should be independent of the applied load [19]. However, in practice hardness is load dependent. Typically, the measured hardness increases with applied load. Microhardness measurements were carried out for applied loads varying from 5 g to 25 g. Several indentations were made for each load and the diagonal lengths (d) of the indented impressions were measured. Vickers hardness number was determined using the relation:

\[
H_V = 1.8554 \left( \frac{P}{d^2} \right)
\]  

(2)

where \( P \) is the applied load in kg and \( d \) is the diagonal length of the indentation impression in mm. The hardness profile as a function of applied load is depicted in Fig. 10.

The Meyer’s index number was calculated from the Meyer’s law, which relates the load and indentation diagonal length:

\[
P = kd^n
\]

(3)

\[
\log P = \log k + n \log d
\]

(4)

where \( k \) is a material constant and \( n \) is the Meyer’s index. In order to calculate the value of \( n \), the graph of \( \log P \) versus \( \log d \) was plotted (Fig. 11). It is a straight line and the slope of the straight line gives the value of \( n \).

![Fig. 11. Plot of logP vs. logd for AO crystal.](image)

The calculated value of \( n \) for AO is 2.9. According to Onitsch [20] \( n \) should lie between 1 and 1.6 for hard materials and above 1.6 for soft materials. Hence, the calculated value of \( n \) (2.9) suggests that AO is a soft material.

### 4. Conclusions

Good quality single crystals of AO were grown by slow evaporation solution growth technique. The single crystal X-ray diffraction studies confirm that the grown crystal belongs to the orthorhombic crystal system and the powder X-ray diffraction analysis supports the good crystalline perfection.
of the grown crystals. The factor group analysis predicts 114 total vibrational optical modes that decompose into $\Gamma_{114} = (29 A + 29 B_1 + 28 B_2 + 28 B_3)$ modes apart from 3 acoustic modes. The functional groups are confirmed by the FT-IR analysis. The etching studies reveal the volume and linear defects. The variation of dielectric constant as a function of frequency suggests that the dielectric constant is relatively higher in low frequency region and lower in the high frequency region which substantiates that this material is a promising material for NLO applications. Conductivity measurements show that the conduction is high at higher frequencies, which is predominantly due to the polaron hopping. The first order hyperpolarizability value of the AO is found to be equal to $4.94 \times 10^{-31}$ esu. The TGA and DTA show the good thermal stability of the material. From the hardness measurement it is found that the grown crystal is a soft material.

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