

A novel approach to the synthesis of semiorganic ammonium hydrogen oxalate oxalic acid dihydrate single crystal and its characterization

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Abstract

A different approach used in the synthesis of ammonium hydrogen oxalate oxalic acid dihydrate ($NH_4H_3(C_4O_8) \cdot 2H_2O$) single crystals is presented. The crystals are synthesized using solvent evaporation technique. The analysis of the synthesized $NH_4H_3(C_4O_8) \cdot 2H_2O$ single crystals has been carried out through measurements such as single-crystal X-ray diffraction (SCXRD), powder XRD, UV–Vis and photoluminescence spectroscopy, Fourier transform infrared spectroscopy, thermogravimetric and differential thermal analysis (TG–DTA), Vickers microhardness measurements and current versus voltage (*I–V*) characteristics. The evaluation of the molecular structure of the crystals using SCXRD shows that they belong to the triclinic crystal system with space group P-1. The structural properties of the crystals are also evaluated using powder XRD measurements on their finely crushed powder. These measurements corroborate the results of SCXRD and confirm the triclinic system of the crystals. The optical properties like absorbance and emission of these crystals are determined using UV–Vis and photoluminescence spectroscopy, respectively. These measurements show that the crystals exhibit substantial emission in the blue region. The thermal stability and the decomposition mechanism of the crystals is studied using TG–DTA analysis. The mechanical strength of the crystals is determined using Vickers microhardness technique. The photoresponse of the $NH_4H_3(C_4O_8)\cdot 2H_2O$ crystals is analyzed from light-dependent *I–V* characteristics, and it is observed that the crystals exhibit photoresistive behavior.

Keywords Ammonium hydrogen oxalate oxalic acid dihydrate · Synthesis · Single-crystal X-ray diffraction · Negative photoconductivity

Introduction

Optoelectronic devices and their applications in high-speed information processing, optical communication, optical data storage, etc., have pervaded our everyday lives to an enormous extent [1–7]. The key enabling technology which provides a basis for innovation in these applications is a prominent field in photonics called nonlinear optics (NLO) [1, 8, 9]. Various materials exhibit nonlinear optical behavior, and

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² Department of Post Graduate Studies and Research in Physics, St Aloysius College (Autonomous), Mangalore, Karnataka 575003, India over the decades, a lot of effort has been made by researchers to design such highly efficient materials used in these devices [10-13]. Organic and inorganic crystals are important classes of optoelectronic materials, which are widely used in these applications due to their availability in abundance [14, 15]. However, they possess their own merits and demerits [16]. Organic materials exhibit excellent optical properties, but are brittle in nature. Certain applications require a smooth surface of these materials, which can be achieved by polishing them [17]. Nevertheless, polishing organic materials is extremely challenging since they are soft materials having weak hydrogen bonds [18, 19]. Moreover, they also require extreme care during device fabrication due to their poor thermal and mechanical stability. On the other hand, inorganic materials possess excellent mechanical and thermal stabilities, but moderate optical properties. These drawbacks can be overcome by developing an alternate class of materials known as metal-organic or semiorganic. They

possess excellent optical properties as in the case of organic materials, and good mechanical and thermal stabilities of inorganic materials [20–23].

Recently, Stash et al. have reported the synthesis of semiorganic ammonium oxalate oxalic acid dihydrate $(NH_4H_3(C_4O_8)\cdot 2H_2O)$ single crystal and its single crystal XRD characterization [9]. The standard method they used for synthesis is as follows:

Ammonium 2,3,5,6-tetraoxo-4-nitropyridinate aqueous solutions were boiled for a long time to obtain $NH_4^+ \cdot C_2HO_4^- \cdot C_2H_2O_4 \cdot 2H_2O_4$. Minimum quantity of water was taken to dissolve ammonium 2,3,5,6-tetraoxo-4-nitropyridinate single crystals. This solution was maintained in a boiling water bath for a time duration of 30 min and then kept at room temperature for evaporation. Finally, dark red colored ammonium 2,3,5,6-tetraoxo-4-nitropyridinate single crystals and colorless prismatic single crystals of ammonium oxalate oxalic acid dihydrate were isolated. However, to the best of our knowledge, there are no reports till date on the structural, optical, thermal and electrical properties of $NH_4H_3(C_4O_8) \cdot 2H_2O$ single crystals. We report a different approach and relatively simple method to synthesize ammonium oxalate oxalic acid dihydrate $(NH_4H_3(C_4O_8)\cdot 2H_2O)$ single crystal. We also present a detailed experimental investigation of the synthesized crystals.

In the present work, we report the synthesis of $NH_4H_3(C_4O_8)\cdot 2H_2O$ single crystal using oxalic acid dihydrate and ammonium dihydrogen phosphate, and the crystal structure is solved to the *R* value of 0.0409. The synthesized crystal is subjected to further characterization using powder XRD, UV–Vis and photoluminescence spectroscopy, thermogravimetric and differential thermal analysis (TG–DTA), Fourier transform infrared spectroscopy (FTIR), Vickers microhardness measurements and *I–V* studies.

Material synthesis

Salts of oxalic acid dihydrate and ammonium dihydrogen phosphate obtained from M/s. Merck were taken in 1:1 molar concentration and mixed in double distilled water. The mixture was stirred for 4 h using a magnetic stirrer to obtain clear saturated solution. This solution was then filtered and kept for slow evaporation at room temperature. Colorless and transparent crystals were harvested after 3 weeks, and these crystals were purified by multiple crystallization process to enhance their quality.

Characterization techniques

Single-crystal X-ray diffraction analysis using Apex II duo Bruker diffractometer coupled with CCD detector was used to study the molecular structure of the crystal. The X-ray

source is a monochromatic wavelength 0.7107 Å of molybdenum Ka radiation, and data were collected at ambient temperature (296 K). The molecular structure was solved using direct method and further refinement of the structure was performed using SHELXL-2007/2014 software by means of full matrix least square technique. Powder X-ray diffractometer (PXRD) (Rigaku 600) with an X-ray source of wavelength 1.5405 Å (CuK α) and scan range 10° to 50° with a scanning speed of 2° per minute was used for the structural characterization of the synthesized crystal. Absorbance spectrum over a spectral range of 200 nm to 900 nm was recorded using Ocean Optics USB 4000 UV-Vis spectrometer. Fundamental molecular vibrations were studied by recording IR spectrum using Shimadzu FTIR Spectrometer employing ATR method. Thermal studies of the synthesized single crystals were carried out using PerkinElmer thermal analyzer in nitrogen-inert atmosphere over a temperature range of 30 °C to 800 °C with a heating rate of 10 °C per minute. Photoluminescence spectra was recorded using Horiba Scientific-Fluromax-4 spectrophotometer with excitation wavelength 280 nm. Vickers microhardness technique was employed to examine the mechanical strength of the single crystals. Varying indenter load of masses 10 g, 25 g, 50 g, 100 g and 200 g was applied for a dwell time of 15 s on the (1 0 0) plane of $NH_4H_3(C_4O_8)\cdot 2H_2O$ crystals. Lightdependent I-V studies were carried out using Keithley-2410-C source meter. In these measurements, a customized setup was used in order to characterize the crystal sample in dark and illuminated conditions. The crystal sample was polished at both the sides and placed in between a two-probe sample holder. A 50 W halogen dichroic lamp was used as white light source. An input voltage ranging from -5 V to + 5 V was applied to the sample and the resulting current was measured.

Results and discussions

Single-crystal XRD (SCXRD) analysis

An asymmetric unit of $NH_4H_3(C_4O_8)\cdot 2H_2O$ crystal consists of one molecule of oxalic acid, one molecule of hemi oxalate and two molecules of water. Ammonium transition in this crystallographic unit forms a cyclic tetramer unit (Fig. 1) with oxalic acid and two molecules of water via N–H–O (bond length 2.944 Å) and O–H–O hydrogen bonds (bond lengths 2.834 Å and 2.901 Å). This interaction further continues, resulting in a linear 1D chain structure of $NH_4H_3(C_4O_8)\cdot 2H_2O$. The 1D structure further converts to a 2D structure due to O–H–O hydrogen bond (O–H–O of oxalic acid and oxygen of water molecule) and N–H–O hydrogen bond. The packing view and 3D representation of the $NH_4H_3(C_4O_8)\cdot 2H_2O$ crystal are shown in Figs. 2 and 3,



Fig. 1 Asymmetric unit of NH₄H₃(C₄O₈)·2H₂O single crystal



Fig. 2 Packing view of NH₄H₃(C₄O₈)·2H₂O single crystal



respectively. Complete information about the crystal structure obtained from the SCXRD analysis is shown in Table 1. It can be seen from the table that the crystal belongs to centrosymmetric space group P-1 with triclinic crystal system. The photograph of the synthesized $NH_4H_3(C_4O_8)\cdot 2H_2O$ single crystal is shown in Fig. 4.

Powder XRD analysis

Powder XRD analysis was carried out on the fine powder obtained by crushing the synthesized single crystals using motor and pestle. Sharp peaks are observed in the XRD pattern as shown in Fig. 5, indicating crystalline nature of the sample. The SCXRD data are first analyzed using Mercury software, and the Miller indices obtained are used to index the crystals. X-pert HighScore software is then used for the analysis of powder XRD data. It is found that the crystals belong to triclinic crystal system, which is in good agreement with the results obtained from single crystal XRD data. The obtained XRD patterns are further refined using Xpert Highscore Plus software to obtain unit cell parameters and shown in Table 2.

UV–Vis analysis

UV–Vis spectroscopy in the range 200–900 nm was used to obtain the absorption spectrum of the crystals. In the UV region, the crystals show strong absorbance, whereas in the visible region they show no absorbance, as observed in Fig. 6a. The absorption peak of the crystals is observed around 290 nm, corresponding to the UV region of the electromagnetic spectrum.

The optical bandgap (E_g) of the crystals is associated with the incident photon energy as shown in the equation $(\alpha h\nu)^2 = A(h\nu - E_g)$ [24], where A is a constant, α is the optical absorption coefficient and $h\nu$ is the photon energy. This



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 Table 1
 Crystal information, data collection and refinement details

NH ₄ H ₃ (C ₄ O ₈)·2H ₂ C		
1,547,828		
C ₄ H ₁₁ N O ₁₀		
466.28		
Triclinic		
ΡĪ		
6.3409 (10)		
7.2278 (9)		
10.5586 (18)		
94.143 (6)		
100.248 (6)		
97.779 (5)		
469.50 (12)		
1		
1.649		
0.169		
296 (2)		
2340		
1748		
164		
0.0409		
0.1053		
0.732		



Fig. 4 Photograph of NH₄H₃(C₄O₈)·2H₂O single crystal

relation is known as the Tauc relation and a graph of $(\alpha h\nu)^2$ versus photon energy $(h\nu)$ gives the Tauc plot (Fig. 6b). The optical bandgap can be estimated by extrapolating the linear portion of this graph. As seen in Fig. 6b, the optical bandgap value for NH₄H₃(C₄O₈)·2H₂O single crystals is found to be 4.03 eV. The bandgap energy is very close to the bandgap values (4.09 eV–5.01 eV) for other oxalate crystals reported in literature [25–29]. This makes them suitable for wide bandgap applications. Moreover, the high transmittance (low



Fig. 5 Powder XRD pattern

Table 2 The refined unit cell parameters of the $NH_4H_3(C_4O_8){\cdot}2H_2O$ single crystals

Crystal structure details	AHOOD		
Compound	Ammonium hydrogen oxalate oxalic acid dihydrate		
Formula	$NH_4H_3(C_4O_8)\cdot 2H_2O$		
Space group	P-1		
Density	1.63 g/cc		
a/Å	6.2382		
b/Å	7.2056		
c/Å	10.5095		
α	94.6059°		
β	100.0921°		
γ	97.0821°		
Volume/Å ³	461.46		
Crystal system	Triclinic		

absorbance) of the crystals in the visible region favors their use in optoelectronic industry applications.

FTIR analysis

Figure 7 shows the FTIR spectrum used to study the fundamental molecular vibrations of the synthesized $NH_4H_3(C_4O_8)\cdot 2H_2O$ single crystals. The absorption in the plot of FTIR spectrum at 3437 cm⁻¹ represents the stretching frequency which can be assigned to O–H stretching and confirms the water molecules in the structure of $NH_4H_3(C_4O_8)\cdot 2H_2O$ [26, 30, 31]. The absorption at 3137 cm⁻¹ can be assigned to NH stretching vibration [31]. Asymmetric and symmetric stretching vibration of C=O is represented by the absorption at 1706 cm⁻¹ and 1278 cm⁻¹,





Fig. 7 FTIR spectrum of NH₄H₃(C₄O₈)·2H₂O single crystal

respectively [26, 32]. Likewise, absorption at 1624 cm⁻¹ corresponds to the asymmetric stretching of NH₃ and COO bending [33–35]. NH₄ stretching and COO bending leads to absorption at 1402 cm⁻¹ [33–38], whereas the C–C vibrations [33, 35] and O–C–O stretching [30, 36, 37] leads to absorption at 1105 cm⁻¹ and 732 cm⁻¹, respectively. All the assignments in the FTIR spectra are given in Table 3.

Thermal analysis

Thermal analysis of a crystal is extremely crucial to investigate its viability in several technological applications. Thermogravimetric and thermal decomposition analysis measurements of different oxalates of strontium, uranium, uranyl, barium, thorium, etc., and their composites have been performed intensively by researchers due to their potential applications in nuclear industry and medicine [39–41].

Table 3 FTIR assignments of $NH_4H_3(C_4O_8) \cdot 2H_2O$ single crystal

Wave number/cm ⁻¹	Assignment		
3137	NH stretch		
1706	C = O asymmetric stretch		
1624	NH_3 asymmetric stretch + COO ⁻ bending		
1402	NH_4 Stretch + COO ⁻ bending		
1278	C = O symmetric stretch		
1105	C–C stretch		
732	O–C–O stretch		

In the present work, thermal analysis was carried out on $NH_4H_3(C_4O_8)\cdot 2H_2O$ single crystals using TG and DTA in order to determine their melting point, decomposition temperature, purity and crystallinity. The characterization was performed in nitrogen atmosphere on the crystal compound of 6 mg. Figure 8 shows the TG and DTA plots of the synthesized crystals. It is observed that $NH_4H_3(C_4O_8)\cdot 2H_2O$ has a 4.5% loss in mass starting at 71 °C, indicating the diffusion of adsorbed water molecules through the crystal [26, 42]. The process of dehydration continues till anhydrous $NH_4H_3(C_4O_8) \cdot 2H_2O$ compound is obtained and the mass loss is also observed in steps of 14% and 6% (Fig. 8). Major mass loss is witnessed beyond 156.4 °C due to the flash point of NH₄H₃(C₄O₈)·2H₂O crystal, with 76% mass loss occurring at 223.6 °C which is the melting point of the compound. The volatilization of gases confined in the material occurs at 167.9 °C and is in good agreement with the flash point of C₂H₅NO₄·1/2 H₂O [31]. At 223.6 °C, molecules of NH₃, CO, CO₂ and H₂O gases are obtained and the material decomposes. The amount of material remaining evaporates at 259.8 °C and the corresponding mass loss is 3.4%. The reactions occurring during the thermal characterization are shown in Eqs. 1 and 2.





Fig.9 Photoluminescence spectrum of $\rm NH_4H_3(\rm C_4O_8){\cdot}\rm 2H_2O$ single crystal

$$\mathrm{NH}_{4}\mathrm{H}_{3}\mathrm{C}_{4}\mathrm{O}_{8}\cdot 2\mathrm{H}_{2}\mathrm{O} \rightarrow \mathrm{NH}_{4}\mathrm{H}_{3}\mathrm{C}_{4}\mathrm{O}_{8} + 2\mathrm{H}_{2}\mathrm{O} \uparrow \tag{1}$$

$$\mathrm{NH}_{4}\mathrm{H}_{3}(\mathrm{C}_{2}\mathrm{O}_{4})_{2} \rightarrow 2\mathrm{CO}_{2}\uparrow + 2\mathrm{CO}\uparrow + \mathrm{NH}_{3}\uparrow + 2\mathrm{H}_{2}\mathrm{O}\uparrow$$
(2)

Photoluminescence spectrum

Photoluminescence spectrum of $NH_4H_3(C_4O_8) \cdot 2H_2O$ single crystals is shown in Fig. 9. It can be observed from the figure that the crystal has emission of substantial intensity in the blue region and the peak at 360 nm (UV region) corresponds to the deformation of O–C=O bond. These results corroborate with the UV–Vis measurements. Emission in blue region has also been reported by Dalal and Kumar in 2016 for lithium nitrate oxalate monohydrate single crystals [25].

Vickers microhardness measurements

Hardness of a material is the amount of resistance offered by the material to local deformation caused by indentation or scratching [43]. The mechanical strength of our crystals was tested using Vickers microhardness technique. The Vickers microhardness number is represented by H_v and is evaluated using the formula $H_v = 1.8544 P/d^2$ [44], where *P* is the applied indenter load in kg and *d* is the average diagonal length of the indent in mm. The computed microhardness values are given in Table 4. Figure 10 shows the graph of microhardness number (H_v) versus applied load (*P*) of the NH₄H₃(C₄O₈)·2H₂O single crystals. It can be observed from the figure that the microhardness value of the crystals decreases from 94.65 kg/ mm² to 72.12 kg/mm² as the load is increased from 10 g to 200 g. This can be attributed to the phenomenon of indentation

Sl. no.	Load P/g	Hardness H_v /kg mm ⁻²	Yield Strength $\sigma_y/\text{kg mm}^{-2}$	Elastic stiffness constant (C_{11})/Pa	Fracture toughness $K_c/g \ \mu m^{-3/2}$	Brittle- ness B_i / $\mu m^{-1/2}$
1	10	94.65	31.55	2872.18	_	_
2	25	79	26.33	2093.37	-	-
3	50	74	24.66	1867.04	-	-
4	100	72.3	24.1	1792.63	-	-
5	200	72.12	24.04	1784.83	0.04969	1453.41

Table 4Various parametersrelated to microhardness



size effect (ISE) [45], which is normally observed in single crystals. The hardness also depends on the elastic stiffness (C_{11}) parameter which provides information about the molecular bond strength in crystals. For different loads applied, C_{11} can be computed from Wooster's relation as follows [46].

$$C_{11} = H_{v}^{(7/4)} \tag{3}$$

The calculated C_{11} values are shown in Table 4.

The relation between size of indentation and the load applied is given by Meyer's law [47–50]

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

where *K* is the material constant and *n* is the Meyers index. The value of *n* computed from the slope of log *P* versus log *d* plot is 1.85, which confirms the normal indentation size effect (ISE) behavior observed in hard materials (n < 2) [45].

The yield strength values shown in Table 4 are computed using the following relation [51]

$$\sigma_{\rm y} = \frac{H_{\rm v}}{3} \tag{5}$$

Other microstructural parameters such as fracture toughness (K_c) and brittleness (B_i) of the crystal are also determined. The fracture toughness is calculated using the following expression [49, 52]

$$K_{\rm c} = \beta_0 C^{(3/2)} \tag{6}$$

where *C* is crack length (61 μ m) and β_0 is taken as 7 for Vickers indenter [53]

The relative measure of the material brittleness is obtained from the crack produced on the indented surface and is related to the hardness and fracture toughness as follows [54].

$$B_{\rm i} = \frac{H_{\rm v}}{K_{\rm c}} \tag{7}$$

The calculated values of K_c and B_i are tabulated in Table 4. From Table 4, it is observed that the values of all

the parameters decrease with increase in applied load, suggesting normal indentation size effect behavior in the synthesized $NH_4H_3(C_4O_8)\cdot 2H_2O$ single crystal. The crack formed during the indentation process is shown in Fig. 11.

Negative photoconductivity

I-V plots of NH₄H₃(C₄O₈)·2H₂O single crystals in the illuminated and dark conditions are shown in Fig. 12. A linear increment in the dark current and photocurrent with respect to the applied electric field is observed. At any particular value of applied electric field, the dark current is measured to be superior than the photocurrent. This phenomenon is termed as negative photoconductivity, and its occurrence in the crystals may be due to the decrease in the charge carrier numbers or their lifetime upon illumination [55]. When the sample is irradiated using white light, recombination of holes and electrons takes place, thereby decreasing the amount of mobile charge carriers and their lifetime, ultimately leading to negative photoconductivity. According to the well-known Stockmann model [56, 57], the forbidden gap of a material has two energy levels corresponding to two types of recombination centers. The position of one of these levels is located in between the conduction band and



Fig. 11 Indentation image at 200 g load



Fig. 12 *I–V* curve in dark and illuminated conditions

the Fermi level. Furthermore, the other level is present near the valence band or in between the valence band and the Fermi level. The capture cross section of the first type is high for electrons, implying that these centers, in the presence of light, create holes by accepting valence band electrons, but do not increase the number of free electrons. However, the capture cross section of the second type is high for both electrons and holes. This causes these centers to capture holes from the valence band and electrons from the conduction band to recombine in the material. Therefore, the net amount of mobile charge carriers reduces, in turn reducing the current, in the presence of light. Thus, the material exhibits negative photoconducting effect. This is affirmed by the conductivity values obtained in the dark and illuminated conditions as $6.05 \times 10^{-4} \Omega \text{ m}^{-1}$ and $5.45 \times 10^{-4} \Omega \text{ m}^{-1}$, respectively. This interesting observation indicates that the synthesized $NH_4H_3(C_4O_8)\cdot 2H_2O$ crystals can be used for photoresistive applications.

Conclusions

Single crystals of $NH_4H_3(C_4O_8)\cdot 2H_2O$ were synthesized using a novel and simple method called slow evaporation technique. Single-crystal XRD analysis was used to solve the crystal structure. It confirms that the crystals belong to centrosymmetric space group P-1 with triclinic crystal system, which is also evident from powder XRD analysis. Optical characterization of the $NH_4H_3(C_4O_8)\cdot 2H_2O$ crystals using UV–Vis spectroscopy shows that they absorb in the UV region and transmit excellently in the visible region, thereby proving the suitability of these crystals in optoelectronic applications. FTIR analysis was used to study the functional vibrations and to identify the vibrational modes present in the crystal. From the thermal studies on the synthesized crystals, the melting point of the crystal is found to be 223.6 °C. Photoluminescence spectroscopy was used to study the emission characteristics of the crystals, and it shows that the crystal has maximum emission at 360 nm along with substantial emission intensity in the blue region. The crystals show negative photoconductivity with values $6.05 \times 10^{-4} \Omega m^{-1}$ and $5.45 \times 10^{-4} \Omega m^{-1}$ in dark and illuminated conditions, respectively. The results obtained in the present work are in agreement with those reported in literature for other oxalates. The structural, optical, thermal and electrical properties of the NH₄H₃(C₄O₈)·2H₂O crystals synthesized using a different approach affirm their suitability as potential candidates in optoelectronics.

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