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Investigations on the growth and characterisation of an isomorphous ammonium tetroxalate dihydrate superacid crystal

Eunice Jerusha [a,d], R. Infant Shyam Kumar [b], S. Shahil Kirupavathy [c,*], R. Gopalakrishnan [d]

[a] Department of Physics, R.M.D. Engineering College, Kavaraipettai 601206, India
[b] Department of Physics, Rajalakshmi Engineering College, Chennai, India
[c] Department of Physics, Velammal Engineering College, Chennai 600066, India
[d] Crystal Research Lab, Department of Physics, Anna University, Chennai 600025, India

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ABSTRACT

Single crystals of ammonium tetroxalate dihydrate (ATOXAL) were grown by the slow evaporation solution growth technique. The crystal structure was confirmed by single crystal XRD analysis. The functional groups present were explored and ammonium ion reveals its group frequency at 1404 cm^{-1} and 1489 cm^{-1} respectively from the recorded FT-IR and FT-Raman spectra. Microhardness studies were carried out with the Vicker's microhardness tester. The TG, DTA and DSC studies divulged information about thermal behaviour. The HOPM studies supported the thermal anomalies in the crystal. The density was evaluated to be 1.639 g/cc. The optical behaviour was examined with DRS, UV–vis, photoluminescence and photoconductivity studies. The optical band gap was assessed to be 3.963 eV. Negative photoconductivity was exhibited. SEM micrographs showed the purity and crystalline nature of the grown crystals. Dielectric anomalies are seen in the variation of the dielectric constant with temperature suggesting the ferroelectric nature of the crystal.

1. Introduction

New materials are the basis of solid state research and device technology. Semiconductors, piezoelectric, ferroelectric and infrared sensitive crystals are part of several solid state devices in use today. The current trend is to design organoelectronics for which the development of organic ferroelectrics is mandatory. Charge based speed and efficient non-volatile memories with switching mechanism of the spontaneous polarisation by the external electric field, based on the ferroelectric property of crystals are currently developed for a variety of applications [1]. Ferroelectric material is a sub-group of the pyroelectric materials whose characteristics are the electric analogue of the properties of ferromagnetic materials. Strong electromechanical coupling is a fundamental behaviour of these materials. Spontaneous polarisation is exhibited below the Curie temperature when the material is polar. A first order phase transition is observed with change in symmetry. Many practical devices using ferroelectrics require a phase transition temperature above or closer to the room temperature. When the phase transition temperature shifts towards the room temperature the utility of these single crystals increases in the fabrication of devices.

Different crystalline forms of oxalic acid and oxalates are known to exist [2]; and interest was shown in the study of tetroxalates, i.e. the superacid salts of general formula $MH_3(C_2O_4)_2{\cdot}2H_2O$, with M = NH_4, K, Rb, Cs, or Tl, which are isomorphous in the triclinic crystal system. In the title crystal ammonium tetroxalate dihydrate (ATOXAL), ferroelectricity appears due to proton ordering in the interoxalate hydrogen bonds. The structure of ATOXAL has infinite chains of hydrogen-bonded oxalate anions which are directed along an axis to which the ammonium ions are attached by strong hydrogen bonds. Hence, a large isotopic effect can be expected by isotopic substitution for hydrogen in the ATOXAL crystal which drastically increases the phase transition temperature above the room temperature. The molecular structure is shown in Fig. 1.

Previous investigations on this material include crystal structure determination by neutron diffraction [3], EPR studies [4], X-ray studies [5] and anisotropic elastic properties [6]. In addition to the work reported in literature, present investigation has been made due to two reasons: first, the tetroxalate structure exhibits interesting variety of hydrogen bonds and secondly, various properties exhibited by it are still unearthed by none. The present article discusses the results of the structure confirmation and the various characterisation studies on the grown crystals for the first time.

* Corresponding author. Tel.: +91 98403 08986.
E-mail address: shahilkirupavathy@yahoo.co.in (S.S. Kirupavathy).

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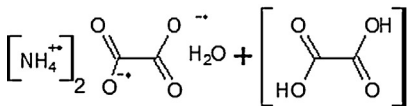
2. Crystal growth

The salt of ATOXAL was synthesised using different starting reagents described as Route 1 and Route 2. Since the starting reagents for Route 2 are readily available, it was adopted for further crystal growth.



2.1. Route 1

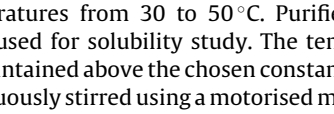
The starting reagents of L-asparagine monohydrate (L-Asp) ($C_4H_{10}N_2O_4$) and oxalic acid dihydrate ($H_2C_2O_4{\cdot}2H_2O$) were purified by repeated recrystallisation process and these were used for synthesis and crystal growth. Colourless salt of ATOXAL was obtained at room temperature by vacuum filtration from the aqueous solution of L-Asp:$H_2C_2O_4{\cdot}2H_2O$. The synthesised salt was dissolved in water and the aqueous solution was slightly heated and kept in an undisturbed condition for slow evaporation in a constant temperature bath. Transparent crystals were obtained after 4 weeks as seen in Fig. 2.

Though the starting reagents are expected to yield L-asparagine oxalate, the obtained product was ATOXAL standing as an exceptional result. This can be due to the difficulties in the solubility of the phases during synthesis and crystal growth of amino acid compounds as described by Fleck and Petrosyan [7].

Solubility studies for the title compound were performed at different temperatures from 30 to 50 °C. Purified recrystallised materials were used for solubility study. The temperature of the solution was maintained above the chosen constant temperature of 35 °C and continuously stirred using a motorised magnetic stirrer to ensure homogeneous temperature and concentration throughout the entire volume of the solution. The solubility of the title compound was found to linearly increase with increasing temperature in water which was chosen as the solvent.

2.2. Route 2

Ammonium oxalate monohydrate ($(NH_4)_2C_2O_4{\cdot}H_2O$) and Oxalic acid dihydrate ($C_2O_4H_2{\cdot}2H_2O$) were taken in 1:1 molar ratio and dissolved in water. The aqueous solution was stirred continuously for 6 h and filtered to remove any impurities. Also care was taken to avoid thermal and mechanical disturbances in the filtered solution as it was allowed to undergo slow evaporation. Colourless ATOXAL crystals of size $13 \times 10 \times 4\ mm^3$ were obtained over a time span of 4 weeks. The reaction mechanism is given below.



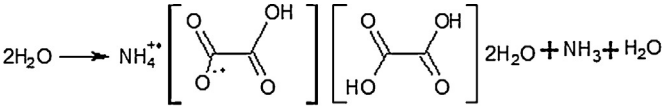


Fig. 1. Molecular structure of ATOXAL.

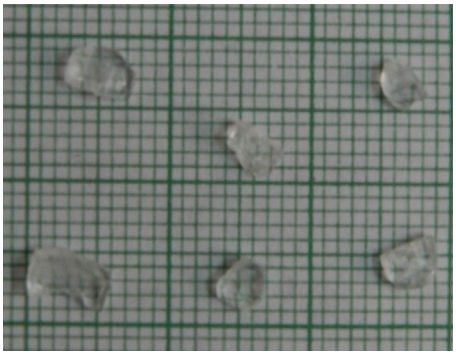


Fig. 2. As grown ATOXAL crystals.

3. Characterisation studies

Confirmation of the chemical composition of the synthesised compound was carried out using Perkin-Elmer 2400 Series CHNS/O Analyser. The single crystal X-ray diffraction analysis of ATOXAL crystal was performed using ENRAF NONIUS CAD4 X-ray diffractometer and the lattice parameters of the grown crystal were verified. The samples were then subjected to powder X-ray diffraction (XRD) analysis using PANalytical X-ray diffractometer with Cu K_α radiation ($\lambda = 1.5406$ Å) in the 2θ range of 10–60° at a scanning rate of 0.05°/min. FT-IR spectrum was recorded by the KBr pellet technique using a BRUKER 66V FT-IR spectrometer to confirm the functional groups present in the title compound in the range of 400–4000 cm^{-1}. Perkin Elmer GX2000 FT-Raman spectrometer in the wave- number range 100–3500 cm^{-1} with 4 cm^{-1} resolution was employed to carry out the vibrational studies of the grown crystal. The hardness of the grown crystal was found for a load ranging from 1 to 200 g using the Vicker's hardness tester (SHIMADZU HMV-FA) fitted with a diamond pyramidal indenter attached to an optical microscope. The thermal behaviour was studied by thermo gravimetric analysis using a NETZSCH STA 409 PC/PG thermal analyser in the nitrogen atmosphere and the NETZSCH DSC 200F3 was used to study the phase transition that occurred in the crystal. Hot stage optical polarised microscopy (HOPM) studies were performed using Euromax polarising optical microscope equipped with a Linkem HFS-91 heating stage and a TP-93 temperature programmer and the microstructure at different temperatures were photographed using a Canon EOS 1000D camera. Optical absorption was studied using CARY 5E UV–vis–NIR diffuse reflectance mode spectrophotometer and the photoconducting property was studied by connecting the sample in series with a dc power supply and a Pico ammeter (Keithley 480) at room temperature. The VEGA-3 TESCAN instrument was used to examine surface morphology of the grown crystal. The HIOKI 3532-50 LCR HITESTER was used to analyse the crystal sample for its dielectric behaviour.

4. Results and discussion

4.1. CHN analysis

The CHN analysis carried out confirmed quantitatively the elemental composition of the grown crystal. The empirical formula for the title compound is $C_4H_{11}NO_{10}$. The experimental and calculated values of C, H and N presented in Table 1 are similar, confirming the formation of ATOXAL crystal.

Table 1
Elemental analysis.

Measurement	%C	%H	%N
Experimental	20.92	4.92	6.32
Theoretical	20.60	4.75	6.00