INTERNATIONAL JOURNAL OF CURRENT RESEARCH IN CHEMISTRY AND PHARMACEUTICAL SCIENCES
(p-ISSN: 2348-5213: e-ISSN: 2348-5221)
www.ijcrcps.com
(A Peer Reviewed, Referred, Indexed and Open Access Journal)
DOI: 10.22192/ijcrcps Coden: IJCROO(USA) Volume 12, Issue 1- 2025

Research Article

DOI: http://dx.doi.org/10.22192/ijcrcps.2025.12.01.001

Thermal, Spectral and Nonlinear Optical Properties Of Dianilinium Tetrachloroferrate (Ii) Dihydrate Crystal For Optoelectronic Applications

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Abstract

A semiorganic crystal, dianilinium tetrachloroferrate (II) dihydrate was prepared and crystallised by slow evaporation solution growth method at room temperature. The synthesized crystal was characterized through elemental analysis, powder X-ray diffraction (XRD), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), Fourier transform infrared (FTIR), nuclear magnetic resonance (NMR) and non linear optical studies. The elemental analysis and thermal studies confirm the stoichiometry of the crystal. The sharp and well defined Bragg peaks observed in the powder XRD pattern confirm its crystallinity. The low temperature DSC of the crystal result indicates that the there is no phase transitions in the cooling cycle. The FTIR spectrum of the crystal characterizes the various

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chemical bondings and water molecule in the crystal. The presence of aromatic protons in the crystal is confirmed by NMR spectroscopy. The SHG efficiency of the crystal was confirmed by NLO study.

Keywords: Crystal growth, Thermogravimetric analysis, Phase transitions, Phase transition, FTIR, SHG efficiency

1. Introduction

In recent years A2BX4 type crystals (where A = univalent cation, B = bivalent transition metal cation and X = halogen) are widely synthesized and investigated by various experimental methods. These crystals represent the largest known groups of insulating crystals with structurally incommensurate phase [1-2]. There are two groups of A2BX4 type crystals with two different structures. One is the group of crystals having the orthorhombic β-K2SO4 type with space group: Pmcn and the other is that having the monoclinic Sr2GeS4 type structure with space group P21/m, at room temperature [3]. Most of this family show commensurate-incommensurate phase transitions and ferroelectric behaviour in a narrow temperature range in the commensurate phase [4-6]. In the incommensurate phase, modulated polarization turns up with a period irrational to the period of the crystal lattice and in the commensurate phase some of the A2BX4 crystals have ferroelectricity or ferroelasticity [7]. Hydrated A2BX4 crystals form another interesting class of crystals. Bansal et al. [8] have reported Raman scattering study of [NH4]2CuCl4.2H2O crystals at 300K, 205K and 100K. They concluded that there is parallel ordering of NH4 tetrahedra at low temperature in this crystal. Narsimlu et al. [9] have studied single crystal XRD of [NH4]2CuCl4.2H2O crystal and found it has a tetragonal structure with the unit cell dimensions of a = 7.58 Å, c = 7.95 Å, Z = 2, β = 90 and two water molecules in the unit cell. Many authors have reported successive phase transitions and ferroelectricity at low temperatures for copper compounds like [N(CH3)4]2CuCl4, [N(CH3)4]2CuBr4 and [N(C2H5)4]2CuBr4 [10,11]. The dielectric measurements that the phase transitions in [N(C2H5)4]2CuCl4 at 259K is of first order [12]. Another interesting subclass in this series is the dihydrated crystals. [13,14].

Hydrated crystals of the type A2BX4.2H_2O and A3BX5 .2H_2O are also interesting class of compounds as they show a number of successive phase transitions at low temperatures. The phase transitions occurring in (NH4)3 BaCl5 .2H_2O is due to the stepwise dehydration of the two water molecules of crystallization [15]. Nonlinear optical (NLO) materials are attracting a great deal of attention because of their use in optical devices, such as optical switches, optical modulators, optical bistable devices and electrooptical devices. Organic materials have been of particular interest because the nonlinear optical responses in this broad class of materials are microscopic in origin, offering an opportunity to use theoretical modeling coupled with synthetic flexibility to design and produce novel materials [16]. Most of the organic NLO crystals are constituted by weak van der Waals and hydrogen bonds. So they are soft in nature and it is difficult to cut and polish the crystal due to its softness [17]. In some case centre symmetric of the crystal possess optical property, which may be due to internal molecule arrangement and intermolecular hydrogen bonding.

In this paper we reported thermal, spectral and nonlinear optical properties of dianilinium tetrachloroferrate (II) dihydrate crystals (hereafter abbreviated as DATC-Fe) through elemental analysis, Powder XRD, TG-DTA, DSC, FTIR, NMR and Nonlinear optical studies.

2. Experimental details

Single crystals of dianilinium tetrachloroferrate (II) dihydrate crystals (DATC-Fe) were grown by slow evaporation method at room temperature.

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The crystals, anilinium chloride (E-Merck, Germany) and ferrous chloride (AR grade) were separately dissolved in triply dissolved water in 2:1 ratio respectively. The two solutions were thoroughly mixed and allowed to evaporate at room temperature. The DATC-Fe crystals are formed according to following equation:

$$2C_6H_5NH_3Cl + FeCl_2.2H_2O \xrightarrow[H_2O]{\text{Solvent}} [C_6H_5NH_3]_2FeCl_4.2H_2O$$

DATC-Fe

The grown DATC-Fe crystals are bright, transparent and golden brown coloured. Crystallization took place within 15-20 days under the experimental conditions with average dimension of 0.6 cm × 0.5 cm × 0.2 cm. The grown crystals were collected from the mother liquid by using well cleaned forceps. The crystallization process was repeated to get a good quality of the crystals.

2.2 Physio-Chemical characterization techniques

A VARIO EL III model analyzer was used to analyze the C, H N S in the crystal. The powder X-ray diffraction pattern of the sample was obtained using BRUKER AXS D8 Advance instrument. The TG/DTA thermograms were obtained using a PERKIN ELMER DIAMOND thermal analyzer under nitrogen atmosphere heated from room temperature to 900°C at a heating rate of 15°C per minute. The low temperature differential scanning calorimetry of the sample was obtained using a METTLER TOLEDO DSC 822e instrument under nitrogen atmosphere at the cooling rate of 15°C per minute from 20°C to -140°C. The FTIR spectrum of the crystal was recorded at room temperature on a THERMO NICOLET AVTAR 370 DT GS spectrometers using KBr pellet technique. The NMR spectrum of the crystal recorded using BRUKER AV II 500MHz FT-NMR instrument. The second harmonic generation efficiencies of the complexes were carried out by modified Kurtz-Perry powder technique using Nd: YAG laser.

3. Results and Discussion

3.1 C H N S analysis

The elemental analysis data obtained for DATC-Fe crystals is given as following C-40.53% (40.12%), H-4.76% (4.74%) and N-8.01% (7.98%). The experimental values of carbon, nitrogen and hydrogen are very close to the theoretical values (Given in bracket). Thus, the stoichiometry of the crystal is confirmed.

3.2 Powder X-ray diffraction pattern method

The powder XRD pattern of DATC-Fe crystals is shown in figure 1**.** The sharp and well defined Bragg' peaks specific 2θ values in the powder XRD pattern confirm the crystalline nature of the crystal. The Bragg' peak at 2θ value at 20 indicates crystalline nature of the title crystal.

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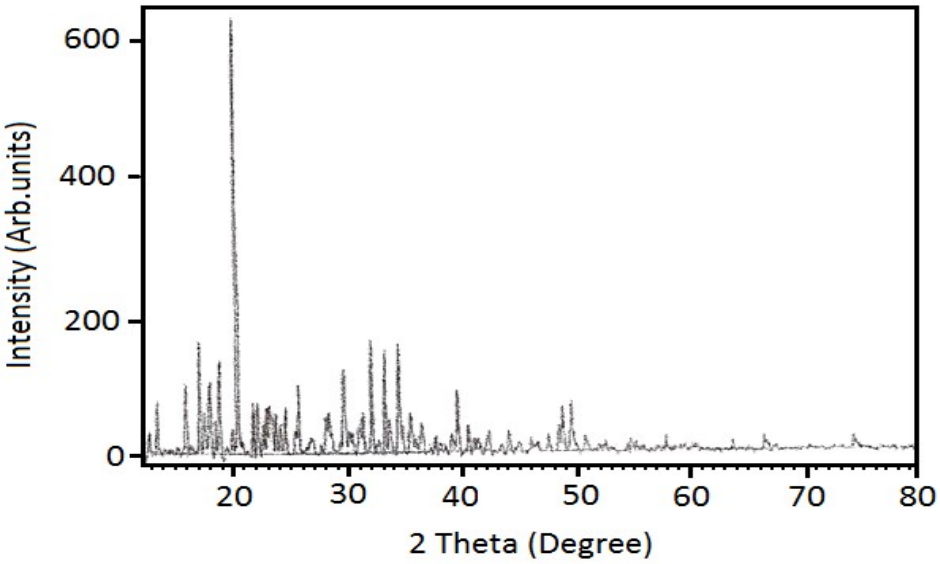

Figure 1 Powder XRD pattern of DATC-Fe crystals.

3.3 Thermal studies

3.3.1 Thermogravimetric analysis

The TGA of DATC-Fe crystal is shown in figure 2. The crystal is subjected to uniform heating at a rate of 15°C per minute under nitrogen atmosphere. Two step weight loss occurs between room temperature and 900°C. In the first stage, 6.5% weight loss occurs between 55 and 122°C. This is reasonably accounted by the loss of water molecules of crystallization. The formulated weight loss is 8.5%. The difference in the weight losses between the experimental and the formulated value is very small. In the second stage, 65% weight loss occurs between 122 and 368°C. This is due to the loss of some hydrocarbon having a total formula of $C_{10}H_{12}$, two molecules of ammonia and one molecule of chlorine from $[C_6H_5NH_3]_2FeCl_4$. The ferrous chloride formed in this step slowly vapourises up to 900°C. The experimental weight loss in this step is 61.5%. The difference between the experimental and theoretical weight losses is very small.

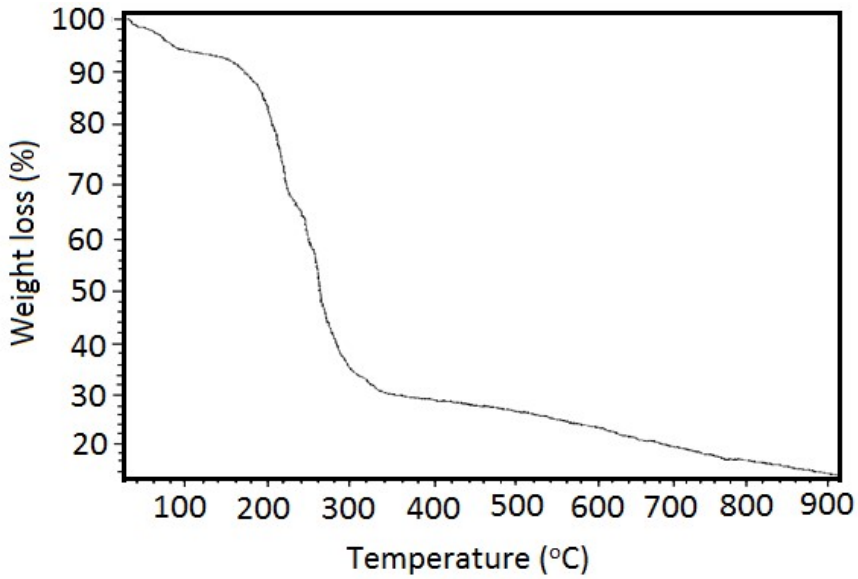

Figure 2 TG curve of DATC-Fe crystals.

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The following decomposition pattern has been formulated to account for the weight losses observed.

Step 1

$$[C_6H_5NH_3]_2FeCl_4.2H_2O \xrightarrow{55°C \text{ to } 122°C} [C_6H_5NH_3]_2FeCl_4 + 2H_2O \uparrow$$

(Molecular mass: 385) (36)

Weight loss: 8.5%

Step 2

$$[C_6H_5NH_3]_2FeCl_4 \xrightarrow{122°C \text{ to } 370°C} C_{10}H_{12} \uparrow + 2NH_3 \uparrow + Cl_2 \uparrow + FeCl_2$$

Weight loss: 61.5%

Thus, TG study confirms the formation of the crystal in the stoichiometric ratio. The presence of water molecule of crystallization in the crystal along with the adsorbed moisture is also confirme

3.3.2 Differential thermal analysis

The DTA curve of the crystal DATC-Fe is shown in the figure 3. There are three exothermic peaks. The first peak at 130°C is due to the removal of the water molecules. The next two endothermic peaks at 180°C and 260°C are due to the second stage decomposition of the crystal. The broad band at 260°C indicates decomposition of $FeCl_2$. The DTA thus confirms the TG analysis.

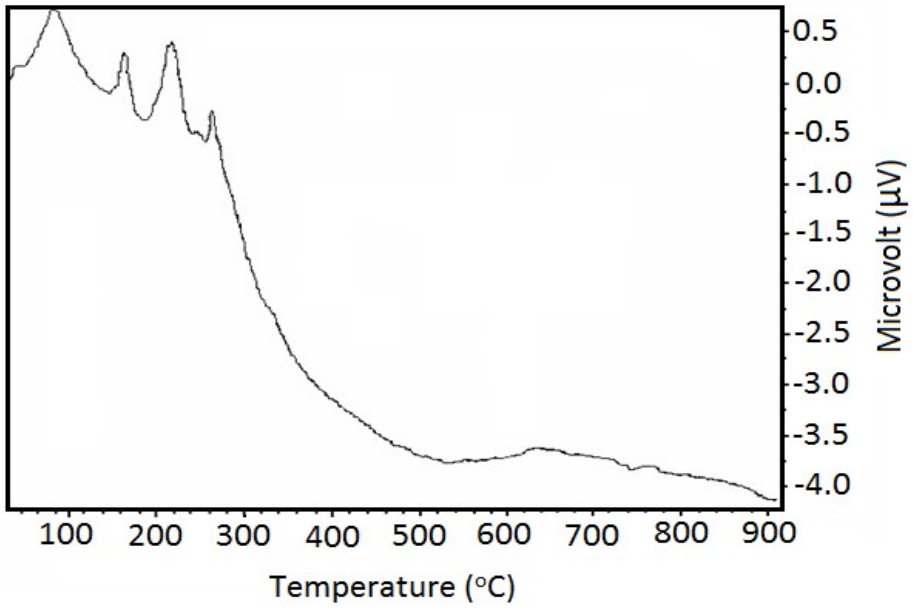

Figure 3 DTA curve of DATC-Fe crystals.

3.3.3 Differential scanning calorimetric analysis

The DSC curve of DATC-Fe crystals is shown in the figure 4. DSC curve shows no phase thermal anomaly, which confirms that there is no phase transition in this crystal between 20°C and -140°C.

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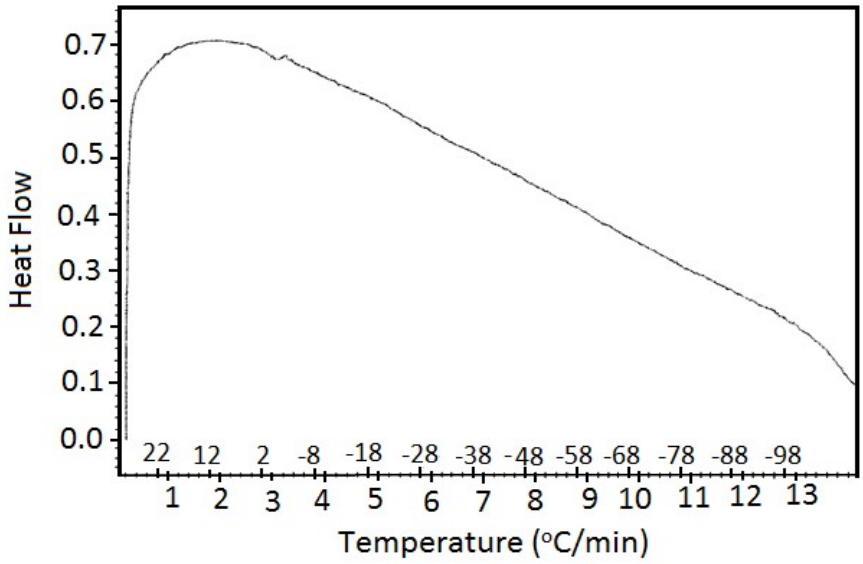

Figure 4 DSC curve of DATC-Fe crystals

3.4 FTIR spectral study

The FT-IR spectrum of the grown DATC-Fe crystals is shown in figure 5. The O-H stretching frequencies and intermolecular hydrogen bonding in the water molecules observed at 3431 cm^{-1}. The aromatic C-H stretching vibration is observed at 3005 cm^{-1}. The peak observed at 2685 cm^{-1} is due to the multiple combination band of NH_3^+ vibrations. The N-H bending vibration (scissoring) is observed at 1636 cm^{-1}. The absorption peak at 1405 cm^{-1} is due to the C-N stretching vibration. The weak C-H stretching vibration is observed at 1387 cm^{-1}. The peak observed at 1113 cm^{-1} represents the in-plane C-H bending vibration. The out-of-plane C-H bending vibration observed at 990 cm^{-1}. The absorption peak at 744 cm^{-1} is characteristics of C-H bending and N-H wagging vibration. The out-of-plane ring C=C stretching bending vibration is observed at 682 cm^{-1}. The absorption peak at 475 cm^{-1} is due to the internal vibration of $FeCl_4^{2-}$ [16].

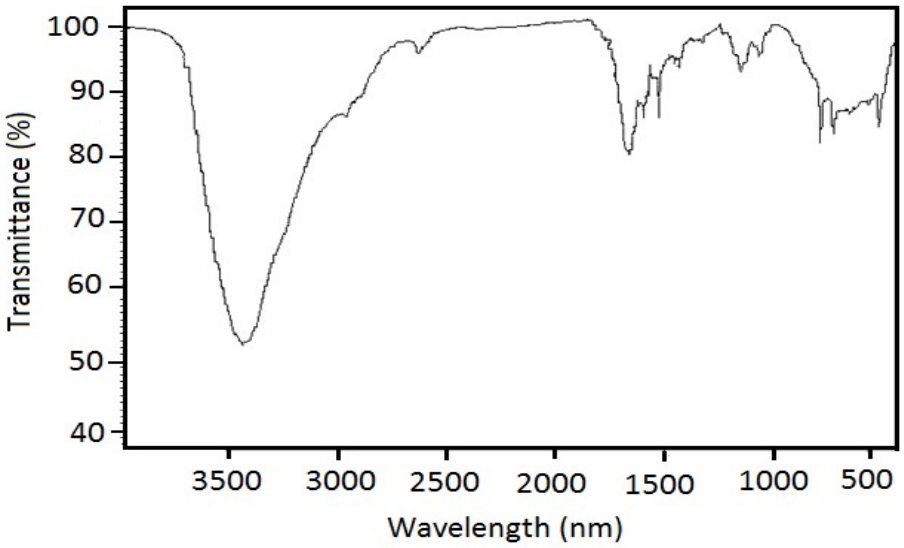

Figure 5 FTIR spectrum of DATC-Fe crystals

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3.5 1H NMR spectral analysis

The NMR spectrum of DATC-Fe crystals is shown in figure 6. The multiplet at 7 to 8 ppm is due to the aromatic protons present in the anilinium chloride moiety. The peak between 4 and 5 ppm is the solvent peak.

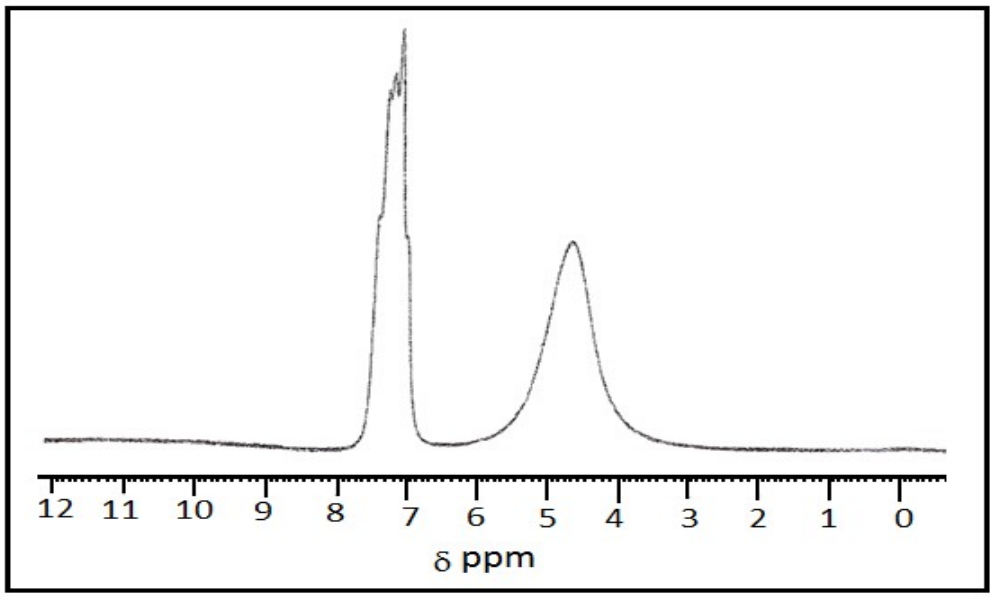

Figure 6 H^1 NMR spectrum of DATC-Fe crystals

3.6 Non linear optical Study

Kurtz-Perry test was performed to find the NLO property of the BTMA crystals. Kurtz technique is used as a screening technique to identify the materials with the capacity for phase matching in addition to indentifying the materials with non-Centro symmetric crystal structures. The crystals were ground into powder and densely packed in between two glass slides. An Nd:YAG laser beam of pulse width 10ns at a wavelength of 1064 nm and 10Hz fundamental radiation was made to fall normally on the sample cell. The emission of green light confirms by the crystal, it indicates the grown crystal possesses SHG efficiency. The SHG efficiency of the compound may be due to the presence of intermolecular hydrogen bonding in the crystal lattice of the title compound.

4.Conclusion

Dianilinium tetrachloroferrate (II) dihydrate crystal was prepared by slow evaporation solution growth method at room temperature. The grown crystals were bright, transparent and brown coloured. The crystalline nature of the crystal was confirmed by sharp and well defined Bragg peaks observed in the powder XRD pattern. The C H N S and TG-DTA studies confirm the formation of the crystal in the stoichiometric ratio. The study also indicates the presence of water molecules of crystallization in the crystal. DSC thermal analysis shows that the no thermal anomalies observed in DSC curve between 20°C and 140°C in the cooling cycle indicate a no phase transition observed in the crystal. The FTIR spectrum of the crystal characterizes the various chemical bonding and characteristic vibration of $FeCl_4^{2-}$. The presence of water molecules in the crystals is also confirmed by FTIR spectrum. The aromatic protons present in the crystal were confirmed by NMR spectroscopic technique. The emission of green light confirms by the crystal, it indicates the grown crystal possesses SHG efficiency.

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How to cite this article:
T. Dhanabal, M. Thangarasu, K. Kanagavalli, V.Ravi, D. M. Muniraj. (2025). Thermal, Spectral and Nonlinear Optical Properties Of Dianilinium Tetrachloroferrate (Ii) Dihydrate Crystal For Optoelectronic Applications. Int. J. Curr. Res. Chem. Pharm. Sci. 12(1): 1-8.
DOI: http://dx.doi.org/10.22192/ijcrcps.2025.12.01.001

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