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**Thermal, Spectral and Phase Transition
Characterization of Dianilinium
Tetrachloroferrate(II) Dihydrate Single Crystal**

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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 (TG-DTA), differential scanning calorimetry (DSC), Fourier transform infrared (FTIR) and nuclear magnetic resonance (NMR) 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 decomposition pattern and thermal stability of the crystal were ascertained by TG-DTA analyses. The low temperature DSC of the crystal result shows that there is no phase transitions in the cooling cycle. The FTIR spectrum of the crystal characterizes the various chemical bondings and water molecule in the crystal. The presence of aromatic protons in the crystal is confirmed by NMR spectroscopy.

Keywords: Crystal growth, Single crystal, Thermogravimetric analysis, Phase transitions, FTIR

1. Introduction

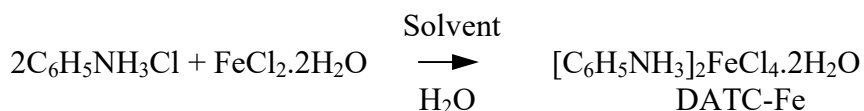
In recent years A_2BX_4 type crystals (where A = univalent cation, B = bivalent transition metal cation and X = halogen) are widely synthesized and investigated by various experimental methods. These crystals represent the largest known groups of insulating crystals with structurally incommensurate phase [1-2]. There are two groups of A_2BX_4 type crystals with two different structures. One is the group of crystals having the orthorhombic β - K_2SO_4 type with space group: $Pmcn$ and the other is that having the monoclinic Sr_2GeS_4 type structure with space group $P2_1/m$, 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 A_2BX_4 crystals have ferroelectricity or ferroelasticity [7]. Hydrated A_2BX_4 crystals form another interesting class of crystals. Bansal et al. [8] have reported Raman scattering study of $[NH_4]_2CuCl_4 \cdot 2H_2O$ crystals at 300K, 205K and 100K. They concluded that there is parallel ordering of NH_4 tetrahedra at low temperature in this crystal. Narsimlu et al. [9] have studied single crystal XRD of $[NH_4]_2CuCl_4 \cdot 2H_2O$ crystal and found it has a tetragonal structure with the unit cell dimensions of $a = 7.58 \text{ \AA}$, $c = 7.95 \text{ \AA}$, $Z = 2$, $\beta = 90$ and two water molecules in the unit cell. Many

authors have reported successive phase transitions and ferroelectricity at low temperatures for copper compounds like $[N(CH_3)_4]_2CuCl_4$, $[N(CH_3)_4]_2CuBr_4$ and $[N(C_2H_5)_4]_2CuBr_4$ [10,11]. The dielectric measurements that the phase transitions in $[N(C_2H_5)_4]_2CuCl_4$ at 259K is of first order [12]. Another interesting subclass in this series is the dihydrated crystals. [13,14]. Hydrated crystals of the type $A_2BX_4 \cdot 2H_2O$ and $A_3BX_5 \cdot 2H_2O$ are also interesting class of compounds as they show a number of successive phase transitions at low temperatures. The phase transitions occurring in $(NH_4)_3BaCl_5 \cdot 2H_2O$ 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 phase transitions characterization of dianilinium tetrachloroferrate(II) dihydrate crystals (hereafter abbreviated as DATC-Fe) through elemental analysis, Powder XRD, TG-DTA, DSC, FTIR and NMR studies.

2. Materials and Methods

Single crystals of dianilinium tetrachloroferrate (II) dihydrate crystals (DATC-Fe) were grown by



The grown DATC-Fe crystals are bright, transparent and golden brown coloured. The grown crystals were repeatedly recrystallized. The crystals were characterized as follows: A VARIO EL III model analyzer was used to analyze the C, H and N 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 crystal was carried out using Bruker AVIII 500 MHz NMR instrument model at IIT, Madras.

slow evaporation method at room temperature. The crystals, anilinium chloride (E-Merck, Germany) and ferrous chloride (AR grade) were separately dissolved in triply distilled 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:

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 crystal is shown in figure 1. The sharp and well defined Bragg's peaks at specific 2θ values in the powder XRD pattern confirm its crystallinity. The peak at specific 2θ value 21 indicates that the grown crystal possesses good crystalline nature.

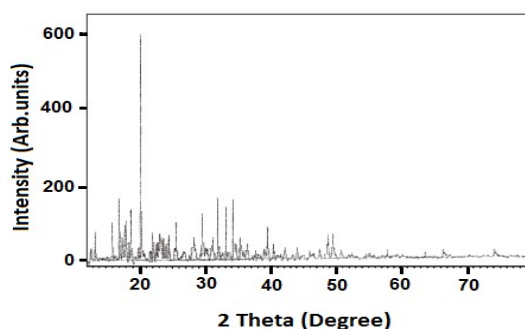


Figure 1. Powder XRD pattern of DATC-Fe crystals.

3.3 Thermal studies

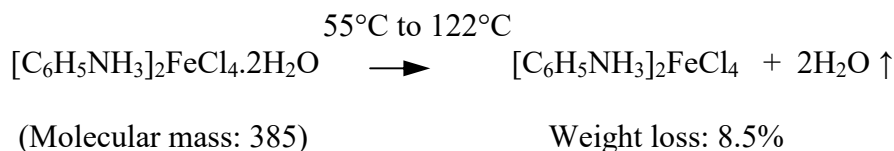
3.3.1 Thermogravimetric analysis

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

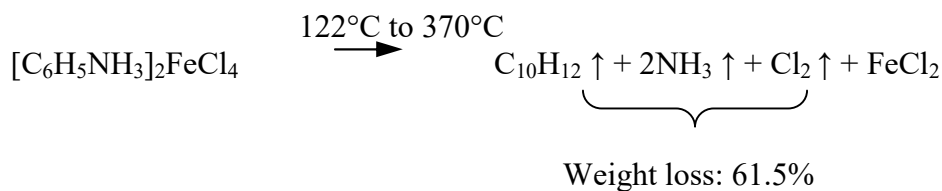
stage, 65% weight loss occurs between 122 and 368°C. This is due to the loss of some hydrocarbon having a total formula of C₁₀H₁₂, two molecules of ammonia and one molecule of chlorine from [C₆H₅NH₃]₂FeCl₄. The ferrous chloride formed in this step slowly vapourises up to 900°C. The experimental weight loss in this step is 61.5%. The difference between the experimental and theoretical weight losses is very small.

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

Step 1



Step 2



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 confirmed.

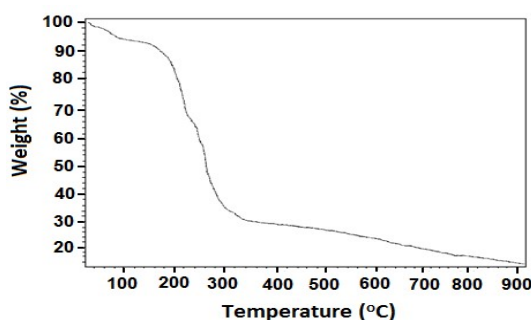


Figure 2. TG thermogram of DATC-Fe crystals.

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.

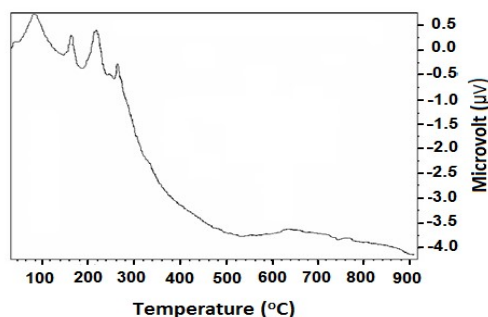


Figure 3. DTA thermogram of DATC-Fe crystals.

3.3.3 Differential scanning calorimetric analysis

The DSC curve of DATC-Fe crystal 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.

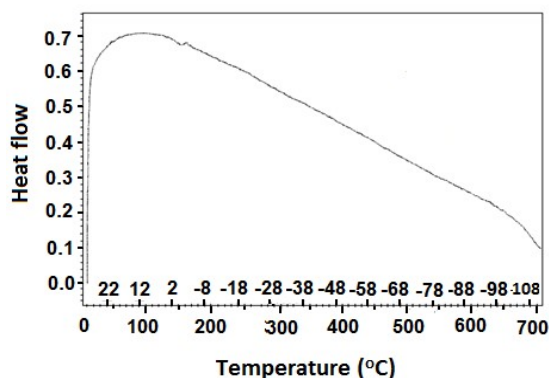


Figure 4. DSC curve of DATC-Fe crystals

3.4 FTIR spectral study

The FTIR spectrum of the grown DATC-Fe crystal 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^+ ions. 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 gives 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 gives at 682 cm^{-1} . The absorption peak at 475 cm^{-1} is due to the internal vibration of FeCl_4^{2-} [18].

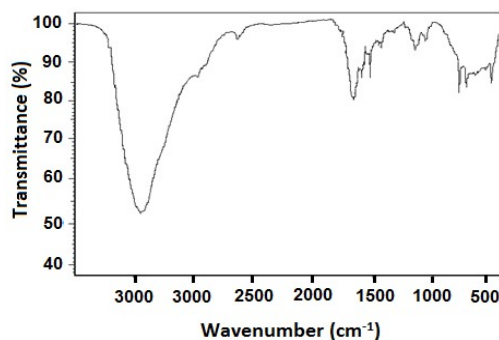


Figure 5. FTIR spectrum of DATC-Fe crystals

3.5 NMR spectral analysis

The NMR spectrum of DATC-Fe crystal is shown in figure 6. The multiplet at 7 to 8 ppm is

assigned to the aromatic protons present in the anilinium chloride moiety. The peak between 4 and 5 ppm is the solvent peak.

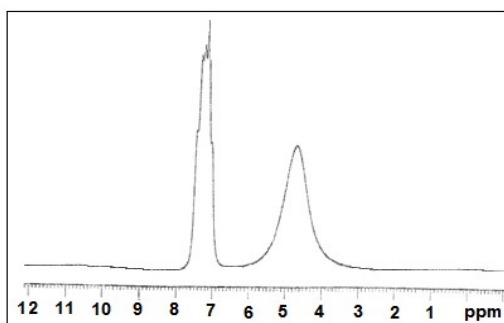


Figure 6. ^1H NMR spectrum of DATC-Fe crystals

4. Conclusions

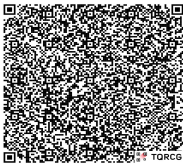
Dianilinium tetrachloroferrate(II) dihydrate crystal was prepared by slow evaporation solution growth method at room temperature. The bright, transparent and brown coloured crystals were obtained. The C H N S and TG-DTA studies confirm the formation of the crystal in the stoichiometric ratio. The crystalline nature of the crystal was confirmed by sharp and well defined Bragg peaks observed in the powder XRD pattern. These studies also confirm the presence of water molecules of crystallization in the crystal. No thermal anomalies observed in DSC curve between 20°C and 140°C in the cooling cycle indicate a no phase transition in the crystal. The FTIR spectrum of the crystal characterizes the various chemical bonding and shows characteristic vibration of FeCl_4^{2-} . The presence

of water molecules in the crystals is also confirmed by FTIR spectrum. The aromatic protons and carbons present in the grown crystal were confirmed by NMR spectroscopy.

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