



THE IRON-TARTRATE CRYSTALS GROWN IN AGAR-AGAR GEL

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Abstract: The crystals of pure Iron-Tartrate [Fe-Ta] grown in the 1% agar-agar gel in aqueous medium found pale-yellow shiny crystals look like canary diamond. The crystallization achieved by the 1M FeCl₃, 1M Disodium Tartrate. The growth of crystal is controlled by 4M NH₄Cl as an additive. The crystals are characterized by the FTIR, Powder XRD, and the thermal decomposition of the grown crystals studied by TGA and DTA analysis and observed that on heating the hydrated crystals became anhydrous and then converted into oxides.

Index Terms - Iron tartrate crystals; crystal growth; agar-agar gel; solution-gel technique

1. INTRODUCTION:

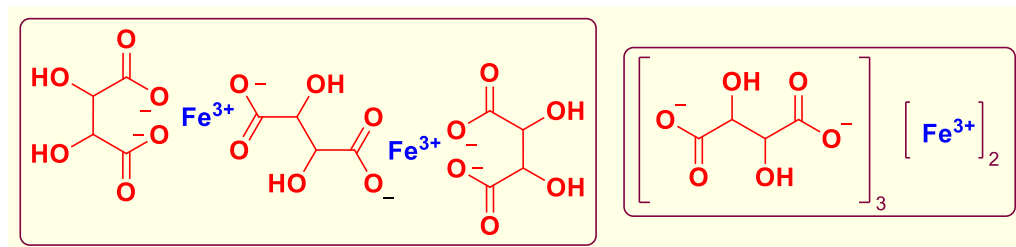
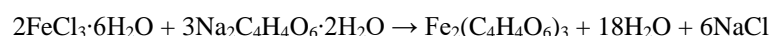
Crystals are very important in the materials; they are having the several applications due unique shape, geometry and its fascinating properties. The crystal growth always well connected with the molecular structure, symmetry, and purity with the suitable physicochemical environment for their formation. These features provide unique physical and chemical properties, which are useful to electronic devices and other related industrial applications [1].

The Metal-tartrate crystals are the most interesting area for the scientific community due to its properties like magnetic [2], ferroelectric [3, 4], laser emission and modification for the laser radiation [5, 6]. The Fe-Tartrate crystals plays a vital role in the prevention of anemia in animals, as a catalyst in the manufacturing process of Champagne, tanning action on tan skin [7, 8].

In the present investigation crystals of iron-tartrate was grown by the single diffusion gel growth technique and characterize by several advanced analytical methods. To the best of our knowledge this is the first report to have the Fe-Tartrate crystals are grown in agar-agar gel.

2. EXPERIMENTAL:

The growth of Fe-Tartrate crystals was carried out in Agar-agar gel. All the chemicals Ferric Chloride hexahydrate, Ammonium chloride and agar-agar Type-I of AR grade are used. The crystals were grown by the single diffusion gel growth technique. Glass test tubes of 25 mm diameter and 200 mm length were used as crystallization apparatus. The 1% Agar-agar gel was found suitable for the growth of crystals [1, 9, 10]. The following reaction is expected to take place in the gel medium:



The gel was prepared by dissolving 1% w/v of extra pure agar-agar powder in hot doubly deionized water. The hot solution of 1% agar-agar gel was added to the tube containing the solution of 10 mL of 1M FeCl₃·6H₂O. The tube was kept for 3 days to setting up the gel, after aging and setting of the gel 15 mL of 1M disodium tartrate solution was added over the set gel. An immediate and heavy nucleation was observed in the tube after 24 hrs in the form of powder. To overcome this problem to control the rate of nucleation during crystal growth, a 4M ammonium chloride (8.0 mL, 8.5 mL, and 9.0 mL) as an additive along with ferric chloride and agar-agar gel is used. Then 15 mL of 1M Disodium Tartrate solution was poured over the set gel. Seven to eight translucent pale-yellow crystals look like canary diamond were grown at the interstitial layer of the glass tube, containing 8.5 mL 4 M NH₄Cl solution as shown in Figure 1(a). Some good quality crystals of Iron-tartrate are shown in Figures 1(b). The largest crystal having the weight about 0.089 g and size 11 mm x 6 mm x 6 mm.

Table-1: Summary of the optimum conditions

Conditions	Single diffusion
% of agar-agar gel	1.0
Concentration of Ferric chloride	1 M
Concentration of disodium tartrate	1 M
Concentration of NH ₄ Cl additive	4 M
Volume of NH ₄ Cl additive	8.5 mL
Gel setting period	3 days
Gel aging period	1 day
Period of growth	30 days
Temperature	Room temperature
Quality	Large Size, Looks like canary diamond
Size	10 x 6 x 6 mm

**Figure 1:** (a) Crystals of Iron-tartrate, (b) Translucent pale-yellow crystals

3. RESULTS AND DISCUSSION:

The optimum conditions of growing crystals for single diffusion are given in Table 1. The mechanism of nucleation, mass transfer, and growth process are the main aspects in the crystal growth. Different parameters such as gel density, gel setting time, gel aging time, concentration of reactant, and addition of impurities in gel have a considerable effect on rate of crystal growth [11].

In a conventional single diffusion method, initially a thin precipitate layer was formed on the surface of the gel. The pale-yellow precipitate band grows gradually as the diffusion proceeds into the gel. This is due to the ferric ions inside the gel accumulating in greater numbers by diffusion near interstitial of the gel throughout the gel setting and ageing processes. The supernatant was poured on the top of the set gel and the tartrate ions present in the gel reacted with ferric ions, as a result spurious nucleation, which in turns into a precipitation band and observed the heavy nucleation inside the gel. To overcome this problem added NH₄Cl as an additive impurity toward the crystal growth control [12]. The best results in the form of fine crystal growth were obtained in the glass tube having 8.5 mL of 4M NH₄Cl solution. The crystal grown in this system are good quality, transparent, type of dodecahedron, and pale-yellow look like canary diamond shaped crystals. Deliberate addition of NH₄Cl solution may dissolve extra nuclei until the process of dissolving iron tartrate in NH₄Cl reaches equilibrium and favouring the formation of nuclei to grow quality crystals.

4. CHARACTERIZATION

4.1 FTIR SPECTRAL ANALYSIS:

In the present IR study Attenuated Total Reflection (ATR) method was used. IR deals with the interaction between a molecule and radiation from the electromagnetic region and very helpful for identification of a compound [13]. The Infra-Red analysis done on Agilent Cary 630 FTIR Spectrometer. The spectrum was recorded in the range 4000-400 cm^{-1} at room temperature. In this analysis, the infrared radiations induce transitions in a molecule between rotational and vibrational energy levels of the ground electronic energy state.

It can be observed from the spectrum that the band at 3233.5 cm^{-1} due to -O-H stretching and water of crystallization. The absorption band at 1718.3 and 1545.0 cm^{-1} due to $>\text{C}=\text{O}$ stretching vibrations. The absorption band at 1388.4, 1299.0 and 1259.8 cm^{-1} are due to -C-O stretching vibrations, also the absorption band at 1131.0 cm^{-1} is due to -C-H stretching vibrations. The absorptions bands found at 672 cm^{-1} due to the metal-oxygen bonding vibrations [13, 14, 15].

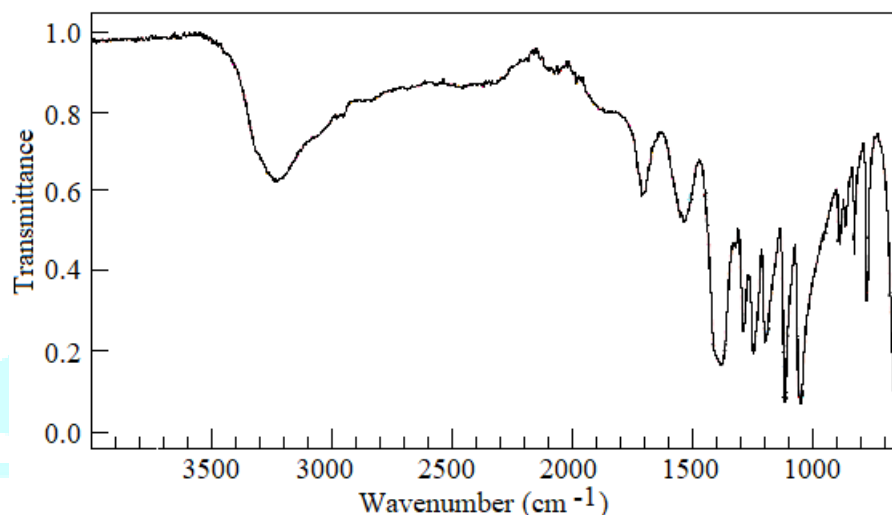


Figure 2: FTIR spectrum for Fe-Ta crystal

4.2 POWDER XRD ANALYSIS:

The powder XRD studies were carried out using Small Angle X-ray Scattering, ANTON PAAR, (SAXSPACE) with $\text{CuK}\alpha$ radiation ($\lambda=1.54056 \text{ \AA}$). The samples were scanned over the range of 2θ values (200 to 800). The powder XRD pattern of Fe-Tartrate is shown in Figure 3. It was indexed using Rietveld refinement method to identify the reflecting planes. The XRD data was analysed using FullProf Suite software and Crystallography Open Database (COD) CIF file (space group: P-63m) [16, 17]. The sharp and well-defined peaks at specific 2θ values testify the excellent crystalline nature and purity of the grown crystal. The 2θ values, d values and the indices of major peaks observed in the spectra of the Fe-Tartrate are given in Table 2. The indices of the major peaks for Fe-Tartrate in decreasing order of intensity are (112), (113), (121), (214), (130). Calculation of cell parameters reveals that Fe-Tartrate crystal belong to hexagonal crystal system having space group P-63m. The cell parameters of crystal are worked out using FullProf software and are $a=2.4906 \text{ \AA}$, $b=2.4906 \text{ \AA}$, $c=3.8504 \text{ \AA}$, $\alpha=90.0^\circ$, $\beta=90.0^\circ$, $\gamma=120.0^\circ$ and unit cell volume 20.68 \AA^3 . The experimental d-values are in conformity with the calculated ones using the above cell parameters for crystals.

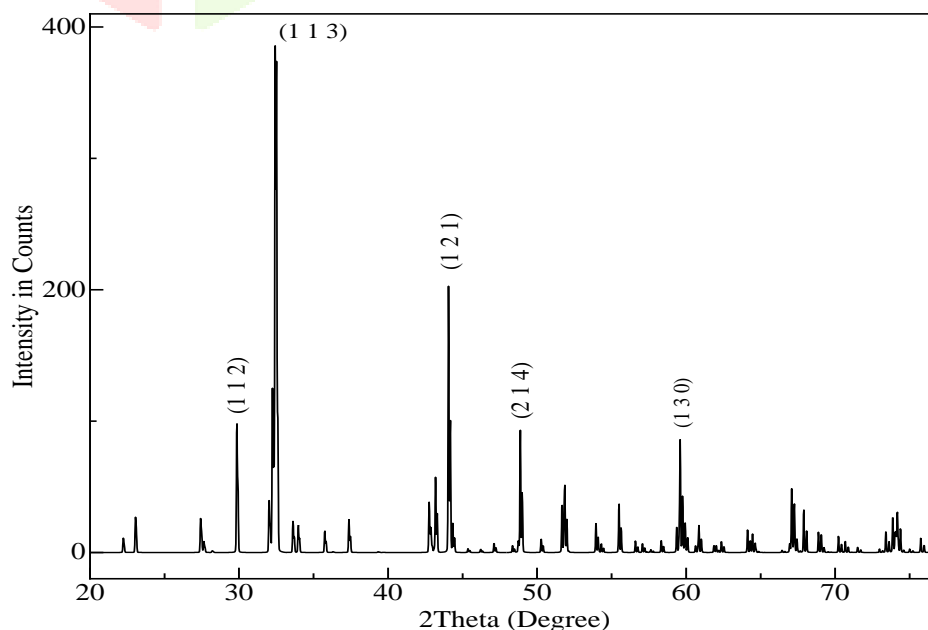


Figure 3: Powder XRD pattern for FeTa crystal

Table 3: Fe-Ta XRD data

2θ	$d \text{ \AA}$	Relative Intensity (cts)	Indices
29.8517	2.9896	97.9	(112)
32.4263	2.7586	385.65	(113)
44.06	2.0537	202.61	(121)
48.873	1.8622	83.37	(214)
59.6297	1.5493	63.23	(130)

4.3 THERMAL ANALYSIS (TGA AND DTA):

The thermal analysis studies were carried out using TGA 55 from TA Instruments United States. The initial mass of the material taken in the form of powder was 3.809 mg and the final mass left after the experiment was 0.045 mg at 600 °C and found the total weight loss is 98.83%. From the graph (Figure 4) it was seen that Fe-Tartrate crystals are stable up to 180 °C. The horizontal portion 30-180 °C shows the thermal stability of the Fe-Tartrate crystal. The well-defined sharp peaks from 180-240 °C attribute to major weight loss. The heating above 240 °C the crystal exhibited thermal stability in the oxide state at 500 °C [12,18]. The measured weight loss up to 500 °C was about 98.83%. In the differential thermal analysis, temperature changes in the sample were due to the reactions caused by phase changes, decomposition, oxidation, reduction, or other chemical reactions [19].

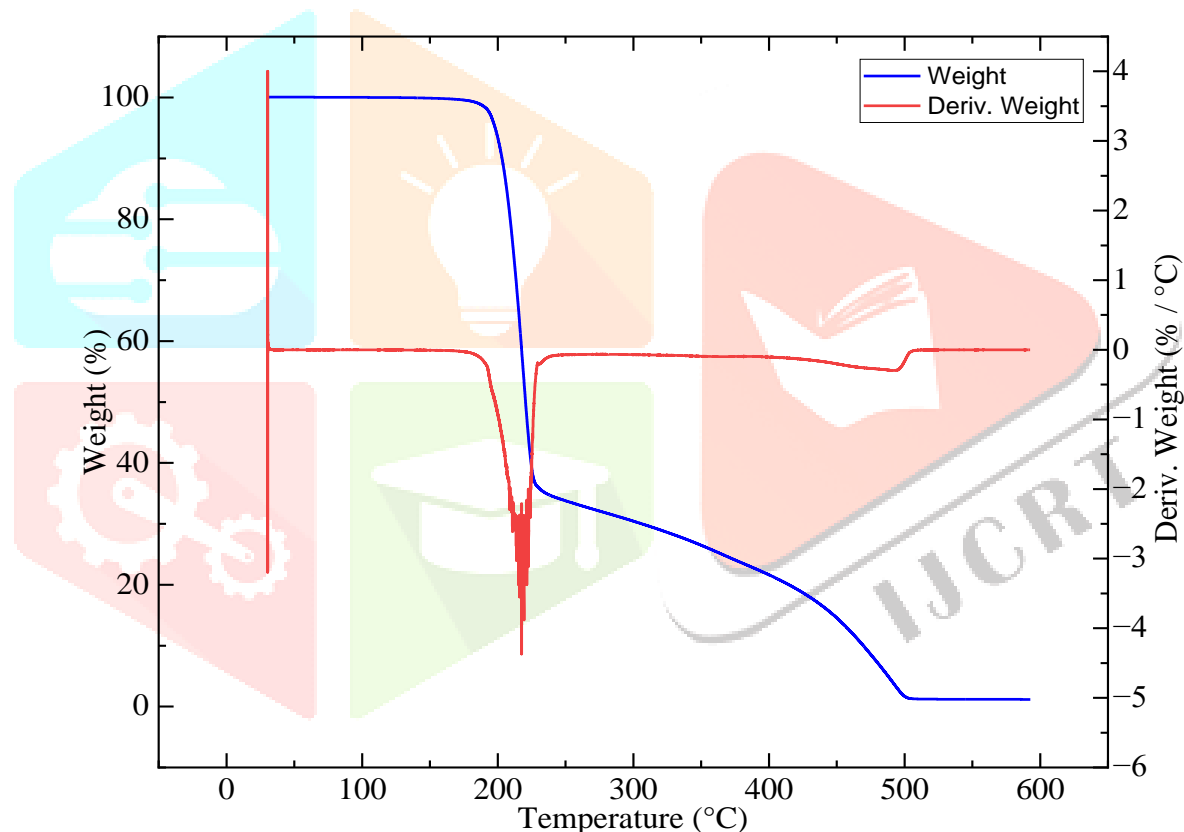


Figure 4: TGA and DTA for Fe-Ta crystal

5. CONCLUSIONS:

- Fe-tartrate crystals can be grown in agar-agar gel medium, using tartaric acid as upper reactant and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ as lower reactant. Deliberate addition of NH_4Cl solution favouring the formation of critical sized nuclei. The growth parameters are tuned to obtain a reasonably good size, quality and morphology of the crystals.
- FTIR spectrum shows the presence of tartrate ligands and establishes that one of the tartrate ions was singly ionized.
- X-ray powder diffraction studies reveal the degree of crystallinity of the grown material. XRD results shows that the crystals belong to hexagonal system with cell parameters $a = 2.4906 \text{ \AA}$, $b = 2.4906 \text{ \AA}$, $c = 3.8504 \text{ \AA}$, $\alpha = 90.0^\circ$, $\beta = 90.0^\circ$, $\gamma = 120.0^\circ$ and unit cell volume 20.68 \AA^3 bearing a non-centrosymmetric space group P-63m.
- Thermogravimetric analysis reveals that the material is thermally stable up to 200 °C and decomposed above 500 °C into oxide.

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