

XRD, FE-SEM, FT-IR and ESR studies of cation deficient potassium tris(oxalato)ferrate(III)trihydrate

M. Narsimhulu and K.A. Hussain

Department of Physics, Kakatiya University, Warangal-506009, India

Corresponding author Email: narsimhulu257@gmail.com

Abstract. Cation deficient potassium tris(oxalato)ferrate(III)trihydrate $\{K_{2.72}[Fe(C_2O_4)_3] \cdot 3.17H_2O\}$ (CDPIOX) crystals were characterized by X-ray powder diffractogram, Fourier Transform Infrared Spectroscopy (FT-IR), quantitative elemental analysis of EDAX, Field Emission Scanning Electron Microscope (FE-SEM), Electron Spin Resonance Spectroscopy (ESR) and Thermogravimetry and Differential thermal analysis (TG-DTA). This compound crystallizes in the monoclinic system with $P2_1/c$ space group and shows three-dimensional (3D) chain structure. The elements present in the grown crystal were confirmed by the energy dispersive X-ray analysis (EDAX). The microstructural features on the surface of the single crystals were determined using FE-SEM. Powder X-ray diffraction results indicate the polycrystalline nature of the material. Infrared spectroscopy was used to study the vibrational modes of the compound. The room temperature crystalline ESR spectra indicate the high-spin ($S = 5/2$) of Fe(III) ion. Thermal behaviour of the compound has been studied using thermogravimetry and differential thermal analysis.

Keywords: Inorganic material, morphology, elemental analysis, FT-IR spectroscopy, ESR.

1. Introduction

The salts of metal oxalate complexes are interesting materials, which have technological applications as precursors to nanocrystalline metallic oxides [1, 2] and to molecular-based magnetic materials [3–6]. The interest in using metals with oxalate ions is due to the flexible bonding mode of oxalate ions with metal ions. The negative charge, planar shape and good donor capability due to the existence of four oxygen donors, make oxalate ligand very suitable to build coordination polymers in its interaction with metal ions [7]. The tris(oxalato)ferrate anion is an interesting “building block” due to its magnetic properties and possibility of different dimensional network formations [8].



The structural versatility of metal oxalate complexes is potential to engineering of multifunctional materials mainly in the field of molecular based magnetism and photophysics [9]. In this regard here, we report the results on XRD, FE-SEM, FT-IR, ESR and TG-DTA studies of CDPIOX.

2. Experimental Details

Energy dispersive analysis of X-rays was obtained from X-ray energy analyzer OXFORD INSTRUMENTES (MODEL: Inca Penta FET x3) attached to Carl Zeiss SEM (MODEL: EVO MA 15). The FE-SEM images of the compound were recorded using Carl Zeiss Ultra 55 model. The powder X-ray diffraction patterns were recorded using JEOL-JDX-8P X-ray diffractometer fitted with a scintillation counter and nickel filtered $\text{CuK}\alpha$ radiation ($\lambda=1.5406 \text{ \AA}$). The infrared spectrum was recorded at room temperature using Nicolet NEXUS Spectrometer in the range of $400\text{--}4000 \text{ cm}^{-1}$ using KBr matrix. ESR measurements were performed with a JEOL JES-FA200 spectrometer on a single crystal at room temperature. The TG-DTA measurements were performed using a Mettler Toledo instrument in the temperature range of room temperature to $1000 \text{ }^\circ\text{C}$ at a heating rate of $10 \text{ }^\circ\text{C/min}$.

3. Results and discussion

All the chemicals were of reagent grade and used without further purification. CDPIOX single crystals were grown by slow evaporation of mixture of solutions obtained from adding potassium oxalate monohydrate ($\text{K}_2\text{C}_2\text{O}_4\cdot\text{H}_2\text{O}$), ammonium oxalate monohydrate $[(\text{NH}_4)_2\text{C}_2\text{O}_4\cdot\text{H}_2\text{O}]$ and ferrous sulphate heptahydrate ($\text{FeSO}_4\cdot 7\text{H}_2\text{O}$) in 100 ml distilled water in equimolar ratio with constant stirring. This aqueous solution was bioled about 30 minutes and filtered at cold condition to remove any unreacted residue. This green colour solution was kept for crystallization. The as grown good quality single crystals are shown in Figure 1. Single crystal X-ray diffraction data reveals that the crystals are $\text{K}_{2.72}[\text{Fe}(\text{C}_2\text{O}_4)_3]\cdot 3.17\text{H}_2\text{O}$, crystallizes in the monoclinic system with $\text{P2}_1/\text{c}$ space group. The unit cell dimensions are $a = 7.7573(4) \text{ \AA}$, $b = 19.8655(3) \text{ \AA}$, $c = 10.3489(6) \text{ \AA}$, $\alpha = \gamma = 90^\circ$, $\beta = 107.946(6)^\circ$ and $Z = 4$. This compound is isostructutral with its parent potassium tris(oxalato)ferrate(III)trihydrate $\{\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3]\cdot 3\text{H}_2\text{O}\}$ [10]

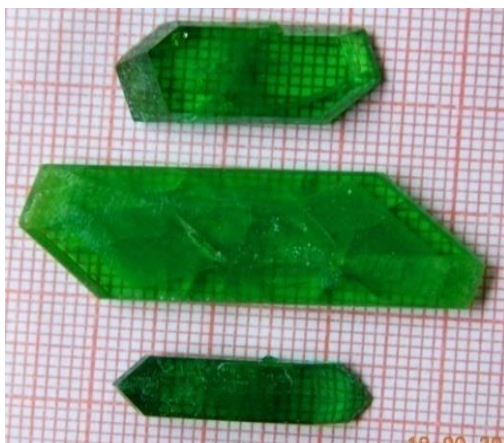


Figure 1. Photograph of CDPIOX crystals.

The elemental analysis of CDPIOX shows the compound contains 14.95% (calc.14.90%) of carbon and 1.283% (calc.1.284%) of oxygen and it confirmed the presence of hydrogen in the crystal lattice. In order to confirm the presence of iron, potassium and oxygen, quantitative elemental analysis were performed on the application of EDAX. The EDAX spectrum (Figure 2) reveals the presence of chemical elements Fe, K and O in the crystal.

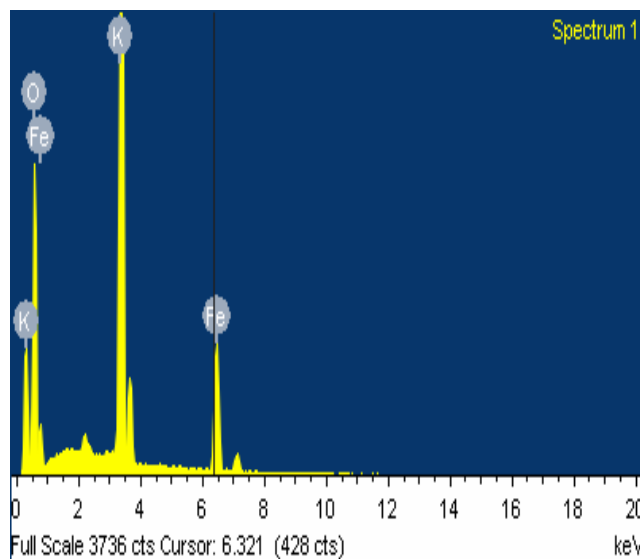


Figure 2. EDAX analysis for CDPIOX.

Field emission scanning electron micrographs of CDPIOX are presented in Figure 3. The FE-SEM images indicate that the compound has layered like and rod like morphology with irregular shapes.

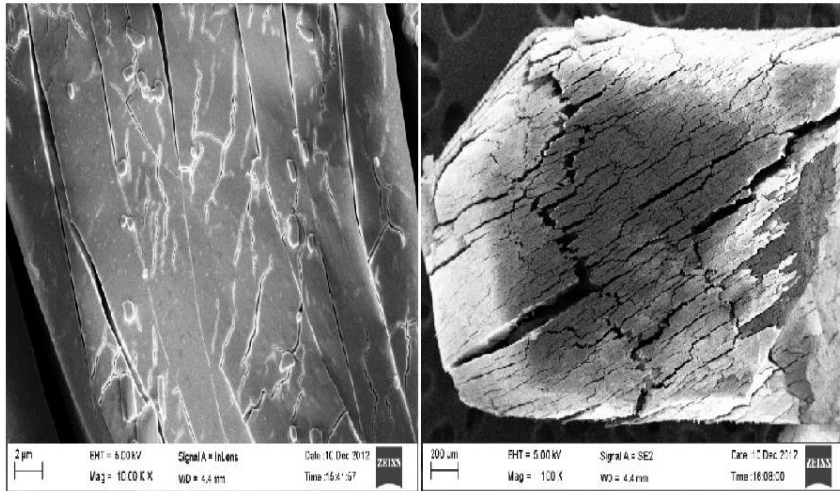


Figure 3. FE-SEM images of CDPIOX.

Figure 4 shows the powder X-ray diffraction pattern of CDPIOX. The diffraction peaks were indexed using powderX program [11]. The experimental and calculated interplanar spacings (d) and corresponding miller indices ($h k l$) are shown in Table 1. The average particle size of powder crystallites (t) of the compound has been calculated by Debye-Scherrer equation:

$$t = \frac{K\lambda}{\beta \cos \theta}$$

Where β is the integrated breadth of reflections located at 2θ (in radians), θ is the diffraction angle in radians and λ is the wave length of X-rays (1.5406\AA for Cu $K\alpha$). Crystallite size of powder for the compound has been estimated as 37 nm.

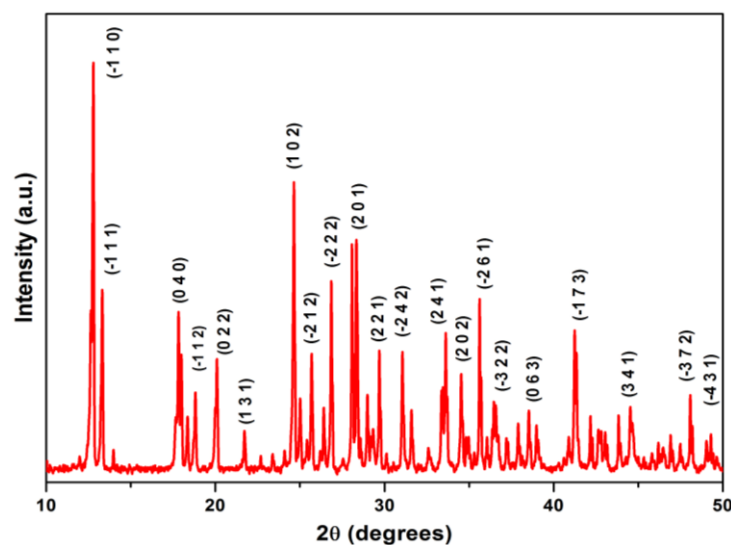


Figure 4. Powder XRD pattern for CDPIOX.

Table 1: d-spacing's and 2θ values for CDPIOX.

h	k	l	$2\theta_{\text{exp}}$	$2\theta_{\text{cal}}$	$2\theta_{\text{diff}}$	d_{exp}	d_{cal}
-1	1	0	12.784	12.786	0.002	6.918	6.917
-1	1	1	13.311	13.338	0.027	6.646	6.632
0	4	0	17.823	17.846	0.023	4.972	4.966
-1	1	2	18.814	18.851	0.037	4.712	4.703
0	2	2	20.088	20.116	0.028	4.416	4.410
1	3	1	21.721	21.746	0.024	4.088	4.083
1	0	2	24.635	24.618	0.018	3.610	3.613
-2	1	2	25.688	25.694	0.006	3.465	3.464
-2	2	2	26.853	26.861	0.009	3.317	3.316
2	0	1	28.347	28.301	0.046	3.145	3.150
2	2	1	29.699	29.722	0.023	3.005	3.003
-2	4	2	31.062	31.128	0.066	2.876	2.870
2	4	1	33.621	33.659	0.037	2.677	2.680
2	0	2	34.536	34.552	0.016	2.594	2.593
-2	6	1	35.622	35.662	0.040	2.518	2.515
-3	2	2	36.577	36.555	0.022	2.454	2.456
0	6	3	38.532	38.597	0.064	2.334	2.330
-1	7	3	41.241	41.334	0.093	2.187	2.182
3	4	1	44.534	44.493	0.041	2.032	2.034
-4	3	1	49.303	49.283	0.020	1.846	1.847

The FT-IR spectrum of CDPIOX is shown in Figure 5. The band assignments are made based on earlier IR studies of similar metal oxalate complexes [12–14]. The bands observed at 498 and 530 cm^{-1} are assigned to $\nu(\text{Fe-O})$. The (C-C) symmetric stretching mode of oxalate ion and (O-C-O) deformational mode are observed at 889 cm^{-1} and 806 cm^{-1} respectively. The stretching oxalate modes were exhibited at 1250, 1270, 1390 and 1682 cm^{-1} respectively. The $\nu(\text{O-H})$ mode at 3430 cm^{-1} shows the presence of lattice water molecules.

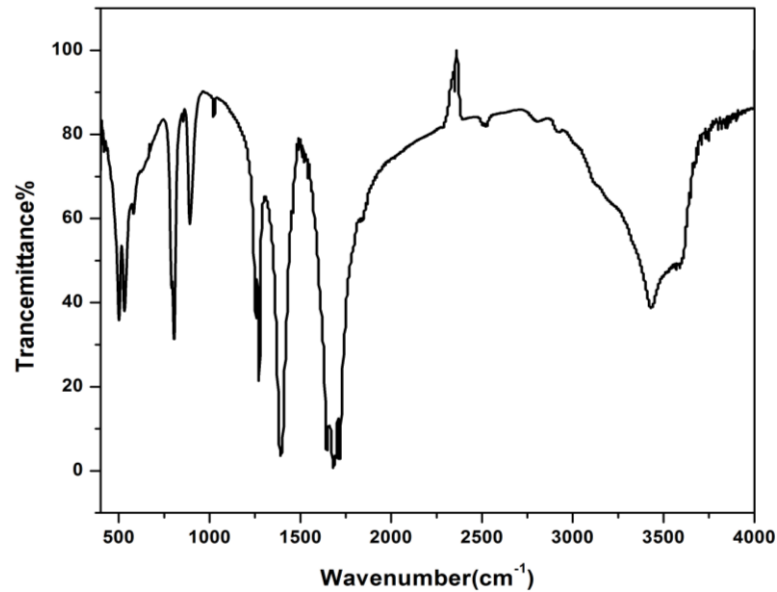


Figure 5. FT-IR spectrum of CDPIOX.

Figure 6 shows the room temperature X-band (9.45 GHz) ESR spectra of CDPIOX. It shows one broad intense resonance signal with $g = 6.06$ with both peak to peak line width of 51.89 mT, and two weak resonance signals with $g = 2.07$ and $g = 1.13$ respectively. The features of the ESR spectrum are very similar to those reported by Collision and Powell [15].

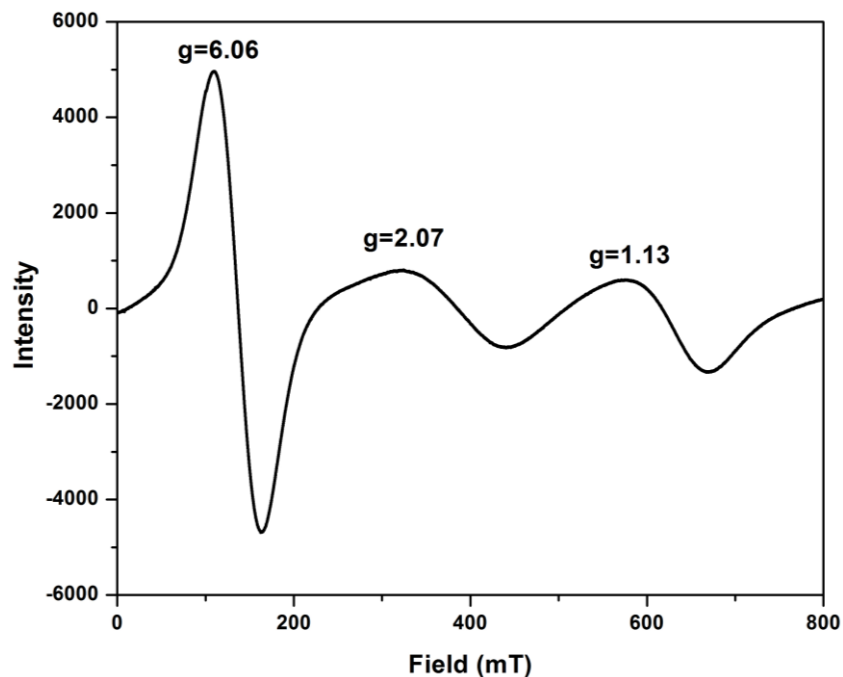


Figure 6. X-band ESR spectrum of CDPIOX.

Figure 7 shows the TG-DTA curves for CDPIOX. TG-DTA curves show five separate decomposition stages. An initial weight loss of 10% (calc. 10.6%) around 104 °C indicates the loss of three water molecules. The resulting anhydrous compound undergoes continuous decompositions as shown by the TG curve from 110 °C to 590 °C. The compound is stable up to 220 °C, above this temperature it starts to decompose in the temperature range 220-250 °C (exp. 4.4%, calc. 4.6%) with the release of half-a-mole of CO₂, resulting formation of mixture of potassium iron oxalate and potassium oxalate. The exothermic peak at 228 °C in the DTA curve shows this process.

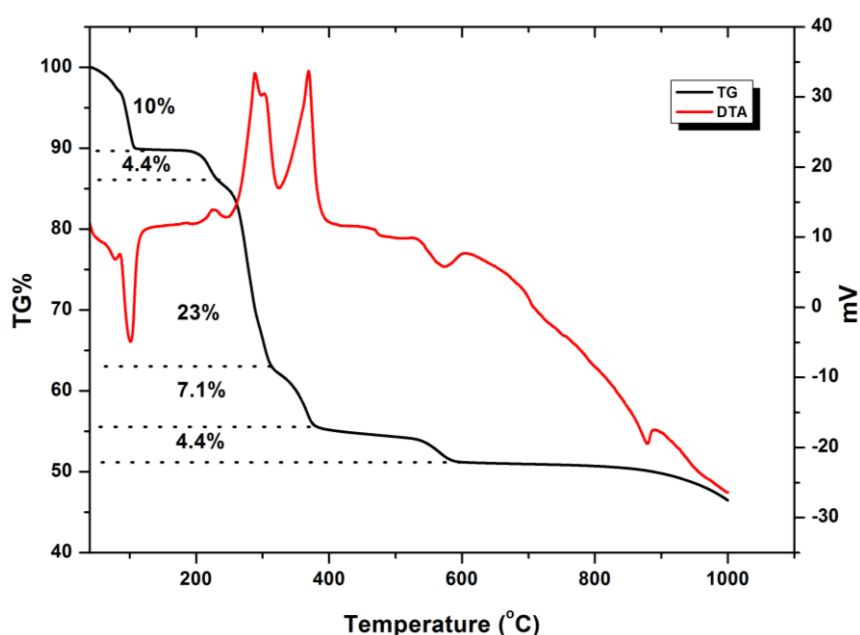


Figure7. TG-DTA curves for CDPIOX.

In the temperature range of 270-295 °C, the loss of one mole of CO₂ and two moles of CO corresponds (exp. 23%, calc. 23.97%) to the decomposition of potassium iron oxalate to potassium oxalate and iron oxide and the corresponding exothermic peak in DTA curve occurred at around 287 °C. The exothermic peak at 370 °C corresponds to formation of mixture of iron oxides with the loss of half-a-mole of CO₂ and half-a-mole of CO. The peak at 570 °C in DTA curve corresponds to decomposition of potassium oxalate to potassium carbonate. The endothermic peak at around 325 °C does not involve any weight loss and corresponds to the characteristic phase transition of K₂C₂O₄ [16]. A small endothermic peak at 887 °C corresponds to the melting point of K₂CO₃ formed. These observations indicate that this compound could be a potential for precursor to nano crystalline iron oxide.

4. Conclusion

The synthesized single crystals of CDPIOX were grown from solutions on slow evaporation. The crystallographic data indicates the compound crystallizes in the monoclinic system with space group $P2_1/c$. FE-SEM studies reveal that the crystals have layered and rod like morphology. FT-IR spectrum confirms the functional groups associated with the oxalate ions. ESR spectra confirm the state of Fe(III) ion in the compound is high-spin ($S=5/2$). The thermal analysis results show that the compound first decomposes to anhydrous potassium iron oxalate and then to the final mixture of oxides through formation of potassium carbonate and iron oxide as intermediates. Thermal decomposition of this material suggests that it may have potential application as a precursor for synthesis of iron oxide nano particles.

Acknowledgments

The authors are thankful to University Grants Commission, New Delhi, India for providing financial support under DRS-SAP programme to carry out this work.

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