

Synthesis, Structure, Optical, Thermal, Dielectric And Magnetic Properties Of Cation Deficient $K_{2.72}[Fe(C_2O_4)_3] \cdot 3.17H_2O$ Crystals

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ABSTRACT: In this study, we investigated the crystal structure, optical, thermal, dielectric and magnetic properties of cation deficient potassium tris(oxalato)ferrate(III) trihydrate $\{K_{2.72}[Fe(C_2O_4)_3] \cdot 3.17H_2O\}$ crystals. Single crystal X-ray analysis reveals that the compound crystallized in the monoclinic system with $P2_1/c$ space group and exhibits a three-dimensional (3D) chain structure. The structure of the complex consists of infinite anionic $[Fe(C_2O_4)_3]^{3-}$ units with Fe(III) metal center possesses a distorted octahedral environment surrounded by six oxygen atoms from three bidentate oxalate ligands. Raman spectroscopy was used to study the vibrational modes of the compound. The two broad absorption bands at 676 and 972 nm from UV–vis absorbance spectra were attributed to a ligand to-metal charge transfer. The thermal studies of the compound confirm the presence of water molecule. The magnetic susceptibility and field dependent magnetization measurements revealed a paramagnetic behavior above 2.5 K and antiferromagnetic ordering at low temperatures.

KEYWORDS: Inorganic materials, Crystal structure, Raman spectra, UV-vis spectroscopy, Magnetic property.

I. INTRODUCTION

Cation deficient (CD) one-dimensional metallic complexes for platinum with oxalate as ligand i.e. $Rb_{1.67}[Pt(C_2O_4)_2] \cdot 1.5H_2O$ and a series of divalent CD bis(oxalato)platinum salts, $M_{0.8}[Pt(C_2O_4)_2] \cdot 6H_2O$ (where $M=Mg^{2+}$, Co^{2+} , Ni^{2+} and Zn^{2+}) which are found to be isostructural at room temperature had been reviewed [1]. The salts based on oxalate complexes are interesting materials, which have technological applications as precursors to nanocrystalline metallic oxides [2,3], and to molecular-based magnetic materials [4-7]. The charge-transfer salts of tris(oxalato)metalate(III) anions are suitable for building multifunctional properties in a molecular lattice [8-10]. The flexible bonding mode of oxalato ion with metal ions and its capability to transmit electronic effects when acting as bridges between paramagnetic centres and also synthetic control over the lattice dimensionality enables to design two- and three-dimensional multifunctional magnets [11]. The tris(oxalato)ferrate anion is an interesting “building block” due to its magnetic properties and possibility of different dimensional network formations [12]. The synthesis of potassium tris(oxalato)ferrate(III) trihydrate was reported for the first time by Blair and Jones in 1939 [13] and it belongs to monoclinic system with $P2_1/c$ space group [14,15]. This material was extensively investigated owing to its wide applications in photochemical studies, actinometry, sensors, magnetic materials, etc [16,17]. We have synthesized $K_{2.72}[Fe(C_2O_4)_3] \cdot 3.17H_2O$ compound by a modified method. Herein, we report the results on synthesis, crystal structure, thermal, optical, dielectric and magnetic properties of $K_{2.72}[Fe(C_2O_4)_3] \cdot 3.17H_2O$ compound.

II. MATERIALS AND METHODS

All the chemicals were reagent grade and used without further purification. Single crystals of $K_{2.72}[Fe(C_2O_4)_3] \cdot 3.17H_2O$ were grown by slow evaporation of a mixture of solutions obtained from adding potassium oxalate monohydrate ($K_2C_2O_4 \cdot H_2O$), ammonium oxalate monohydrate $[(NH_4)_2C_2O_4 \cdot H_2O]$ and ferrous sulphate heptahydrate ($FeSO_4 \cdot 7H_2O$)

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 4, Issue 8, August 2015

in 100 ml distilled water in equimolar ratio with constant stirring. This solution was boiled about 30 min and filtered at cold condition to remove any unreacted residue. After filtration the green colour solution was kept for slow evaporation at room temperature for crystallization. The as grown crystals are shown in Fig.1(a). The morphology of as grown crystals is shown in Fig. 1(b).

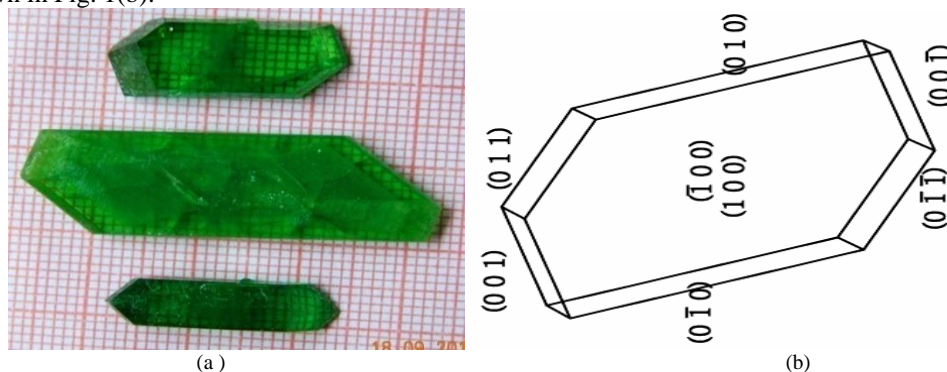


Fig. 1 (a) Photograph (b) morphology of $K_{2.72}[Fe(C_2O_4)_3] \cdot 3.17H_2O$ crystals.

Single-crystal XRD data was collected on Oxford X Calibur Gemini diffractometer equipped with EOS CCD detector at 293 K. Monochromatic $Mo-K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) was used for the measurements. Data were collected and reduced by using the ‘‘CrysAlispro’’ program [18]. An empirical absorption correction using spherical harmonics was implemented in ‘‘SCALE3 ABSPACK’’ scaling algorithm. The crystal structure was solved by direct methods using SHELXS-97 [19] and the refinement was carried out against F^2 using SHELXL-97. Elemental analysis was performed with an Elementar Vario Micro cube CHN analyzer, UV–vis spectra were obtained from JASCO V-570 spectrophotometer. The Raman spectra were recorded at room temperature using a micro-Raman spectrometer (LABRAM-HR) with a laser excitation of 514.5 nm. The thermal stability of the compound is tested by using TA Q20 differential scanning calorimeter under a nitrogen atmosphere with a heating rate of $10^\circ C/min$. Dielectric measurements were made using HIOKI 3532-50 LCR meter and Magnetic measurements were performed on polycrystalline samples of the compound with a commercial Quantum Design 9 T PPMS-VSM over the range from 2.5 to 300K.

III. RESULTS AND DISCUSSIONS

The elemental analysis of the crystal reveals that it contains 14.95% (cal.14.90%) of carbon and 1.283% (cal.1.284%) of oxygen and it confirmed the presence of hydrogen in the crystal lattice. The single crystal X-ray data revealed that the crystals are $K_{2.72}[Fe(C_2O_4)_3] \cdot 3.17H_2O$ and they belong to monoclinic structure with centrosymmetric space group $P2_1/c$. The structural data of the compound are consistent with an earlier report [14]. The standard ORTEP diagram with the atom numbering scheme is shown in Fig. 2 (a). The basic unit of the complex is shown in Fig.2(b).

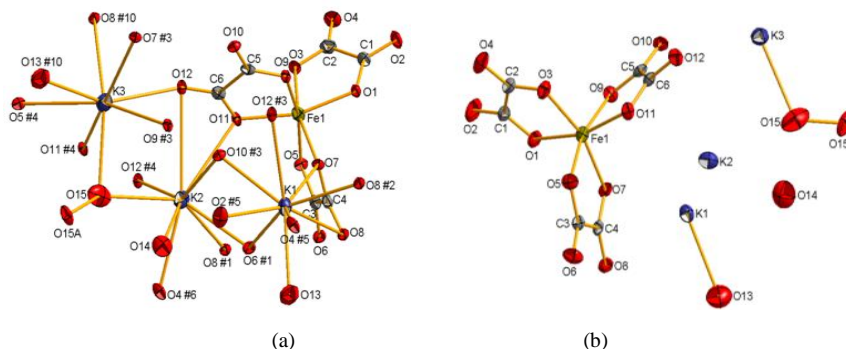


Fig. 2 (a) ORTEP diagram and 50% thermal ellipsoid (b) basic unit of $K_{2.72}[Fe(C_2O_4)_3] \cdot 3.17H_2O$.

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 4, Issue 8, August 2015

The basic unit consists of one half of $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$, three potassium cations and oxygen atoms of water molecules. The atomic coordinates and equivalent isotropic displacement parameters are listed in Table 1.

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{K}_{2.72}[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 3.17\text{H}_2\text{O}$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	x	y	z	U(eq)
C(1)	1273(5)	7629(2)	2897(3)	35(1)
C(2)	2589(5)	7707(2)	2063(3)	32(1)
C(3)	4718(4)	5882(2)	4991(3)	25(1)
C(4)	2850(4)	5553(1)	4879(3)	24(1)
C(5)	246(4)	5778(1)	10(3)	23(1)
C(6)	2228(4)	5591(1)	128(3)	22(1)
O(1)	1058(3)	7019(1)	3222(2)	36(1)
O(2)	531(5)	8117(1)	3186(3)	64(1)
O(3)	3158(3)	7146(1)	1738(2)	33(1)
O(4)	3007(4)	8264(1)	1772(3)	54(1)
O(5)	4701(3)	6240(1)	3956(2)	32(1)
O(6)	6015(3)	5782(1)	5978(2)	38(1)
O(7)	1636(3)	5652(1)	3735(2)	27(1)
O(8)	2659(3)	5229(1)	5821(2)	33(1)
O(9)	71(3)	6100(1)	1027(2)	26(1)
O(10)	-985(3)	5612(1)	-998(2)	29(1)
O(11)	3372(3)	5742(1)	1280(2)	27(1)
O(12)	2583(3)	5308(1)	-808(2)	32(1)
O(13)	1188(5)	3316(2)	5267(4)	80(1)
O(14)	2935(5)	2888(2)	1631(4)	81(1)
O(15)	4091(7)	3128(3)	-573(6)	115(3)
K(1)	240(1)	4273(1)	3379(1)	33(1)
K(2)	4615(1)	4233(1)	1632(1)	38(1)
K(3)	2587(1)	4131(1)	-2435(1)	41(1)
Fe(01)	2348(1)	6312(1)	2493(1)	21(1)
O(15A)	3692(17)	2344(5)	-1101(14)	54(5)

The compound exhibits 3D chain structure in which $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ complex anions, three K^+ cations are present. The Fe(III) metal center (Fig. 3) possesses distorted octahedral environment with six oxygen atoms from three bidentate oxalate ligands. The K1, K2 ions are coordinated by nine oxygen atoms with double trigonal prismatic geometry and The geometry of K3 ion is dodecahedral with eight coordinated oxygens.

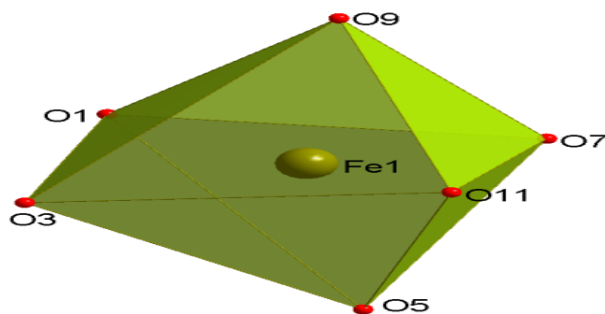


Fig. 3 Distorted coordination environment around Fe ion in $\text{K}_{2.72}[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 3.17\text{H}_2\text{O}$.

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 4, Issue 8, August 2015

The UV-vis absorption spectrum of $K_{2.72}[Fe(C_2O_4)_3] \cdot 3.17H_2O$ (Fig. 4(a)) exhibits two absorption bands at 676 and 972 nm attributed to ${}^6A_{1g} \rightarrow {}^4T_{2g}$ and ${}^6A_{1g} \rightarrow {}^4T_{1g}$ ligand-to-metal charge transfer in distorted octahedral Fe(III) complex with high spin state [20, 21]. The energy band gap (E_g) was calculated as 2.60 eV from the plot of $h\nu$ (h = Planck's constant and ν = frequency of light) versus $(\alpha h\nu)^2$ (α = absorption coefficient of the material) is shown in Fig. 4(b).

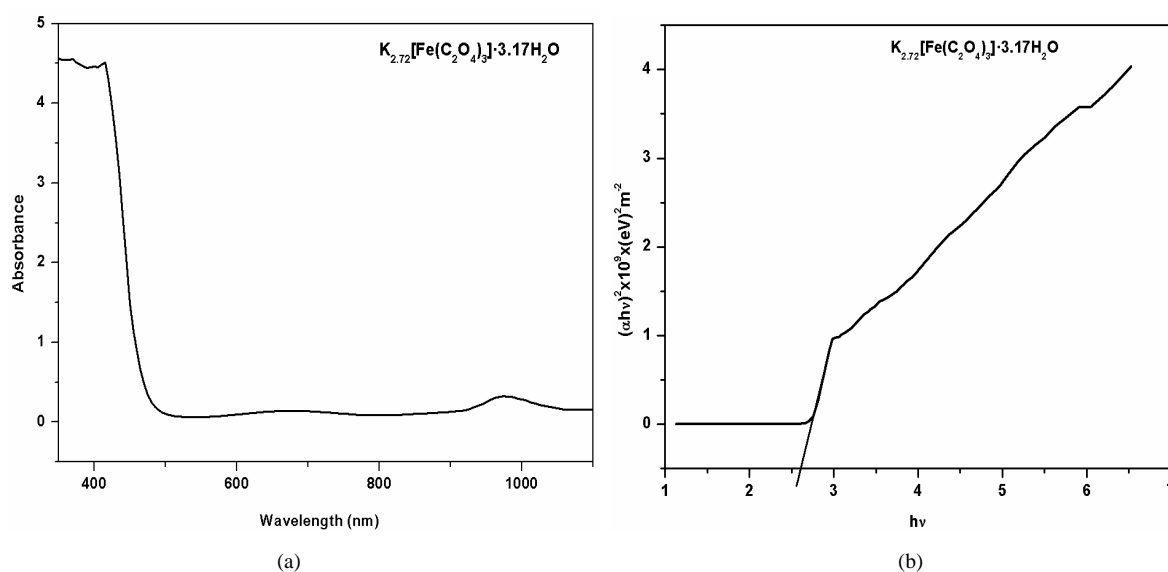


Fig. 4 (a) UV-visible absorption spectrum of (b) Plot of $(\alpha h\nu)^2$ versus photon energy ($h\nu$) of $K_{2.72}[Fe(C_2O_4)_3] \cdot 3.17H_2O$.

The Raman spectrum of $K_{2.72}[Fe(C_2O_4)_3] \cdot 3.17H_2O$ is shown in Fig. 5. The band assignments are made based on earlier Raman studies of similar metal oxalate complexes [22-24]. The bands observed at 136, 257, 370 and 558 cm^{-1} are assigned to $\nu(Fe-O)$. The $\delta(O-C-O)$ mode of oxalate ion is observed at 782. The band observed at 898 cm^{-1} has been assigned to $\nu(C-C)$. The stretching oxalate modes are exhibited at 1252, 1451, and 1720 cm^{-1} .

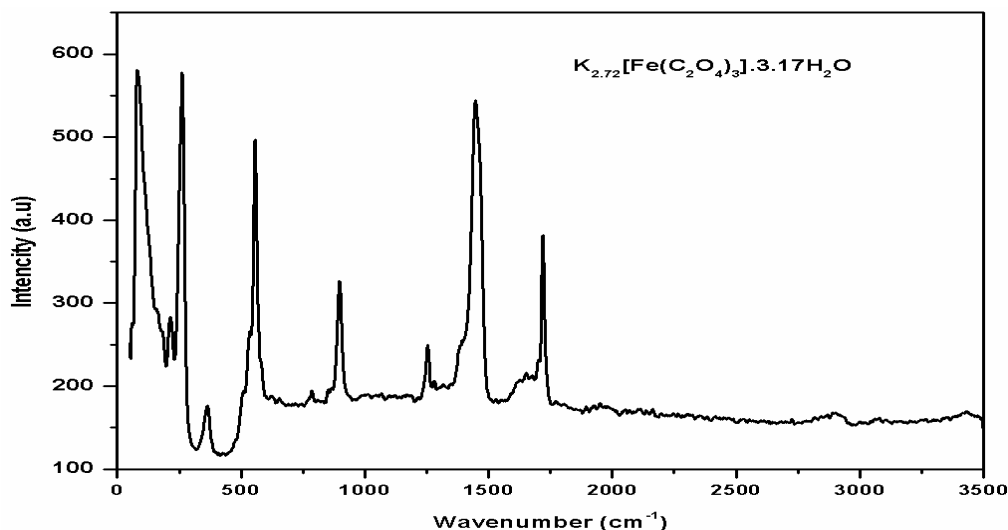


Fig. 5 Raman spectrum of $K_{2.72}[Fe(C_2O_4)_3] \cdot 3.17H_2O$.

The DSC thermogram of $K_{2.72}[Fe(C_2O_4)_3] \cdot 3.17H_2O$ is shown in Fig.6. The endothermic peak around 100°C confirms the presence of water molecule in the compound. The two endothermic peaks around 250°C and 420°C correspond to

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 4, Issue 8, August 2015

the decomposition of anhydrous potassium iron oxalate to potassium oxalate, iron oxide and iron oxide, potassium carbonate respectively [25].

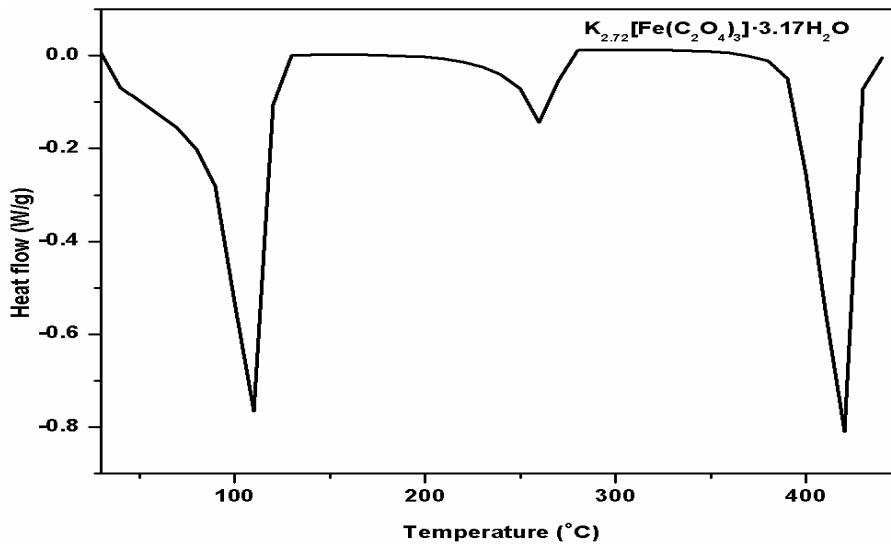


Fig.6 DSC curve of $K_{2.72}[Fe(C_2O_4)_3] \cdot 3.17H_2O$.

The variation of dielectric constant (ϵ) of $K_{2.72}[Fe(C_2O_4)_3] \cdot 3.17H_2O$ as a function of frequency at room temperature is shown in Fig. 7. The dielectric constant decreased gradually with the increase of frequency.

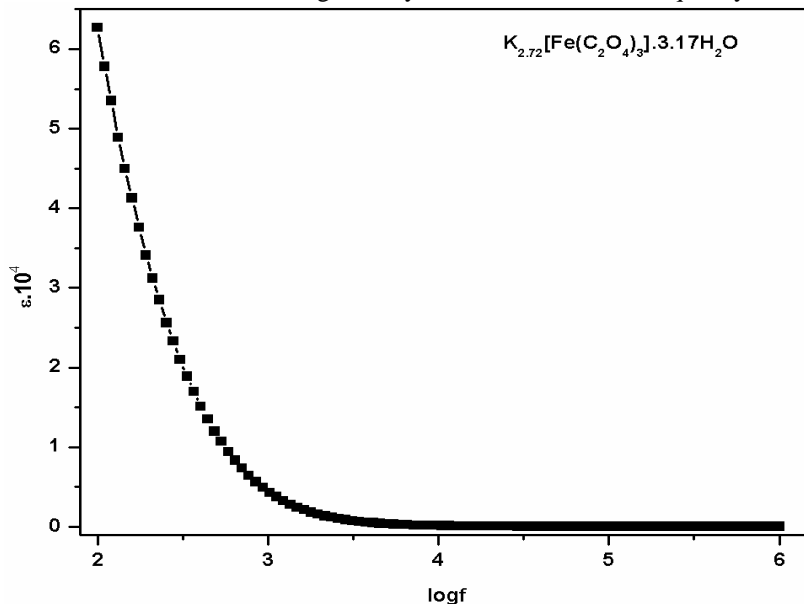


Fig.7 Variation of dielectric constant with frequency at room temperature.

The high value of ϵ at low frequency may be due to the presence of all polarizations and its low value at higher frequencies may be due to the significant loss of all polarisations. The variation of dielectric loss ($\tan \delta$) as a function of frequency at room temperature is shown in Fig. 8.

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 4, Issue 8, August 2015

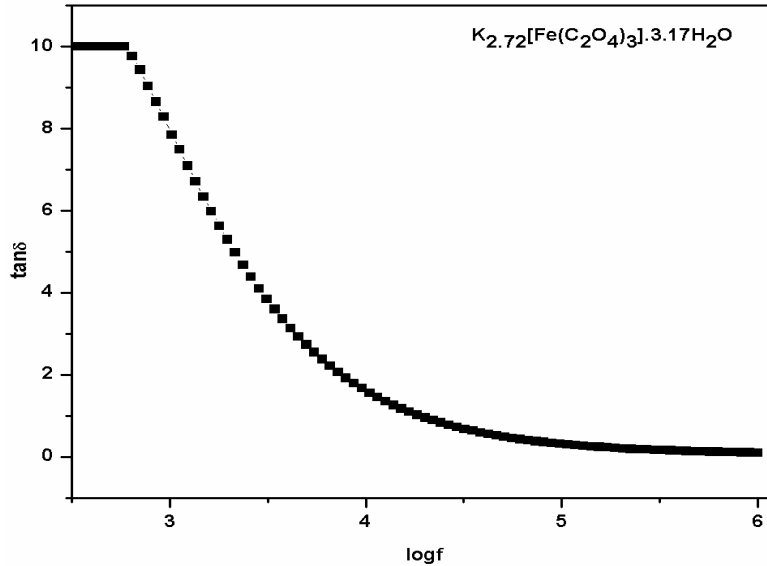


Fig.8 Variation of dielectric loss with frequency at room temperature.

The dielectric loss is decreased gradually with the increase of frequency. The observed lower values of dielectric loss at higher frequency suggest that the grown crystal contains less number of defects with high optical quality [26].

The temperature dependence of the magnetic susceptibility for $K_{2.72}[Fe(C_2O_4)_3] \cdot 3.17H_2O$ measured under field cooling (FC) and zero field cooling (ZFC) conditions at an applied field of 100 Oe is shown in Fig 9. The magnetic susceptibility increases gradually with decreasing temperature and increased quickly below 50 K. The temperature dependence of the inverse susceptibility is linear above 10 K and obeys the Curie-Weiss law with a Curie constant $C = 0.918 \times 10^{-2}$ emu K/gOe and a Weiss constant $\theta = -12.19$ K, which is greater than the earlier reported value i.e. $\theta = -3.0(1)$ of $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$ [15].

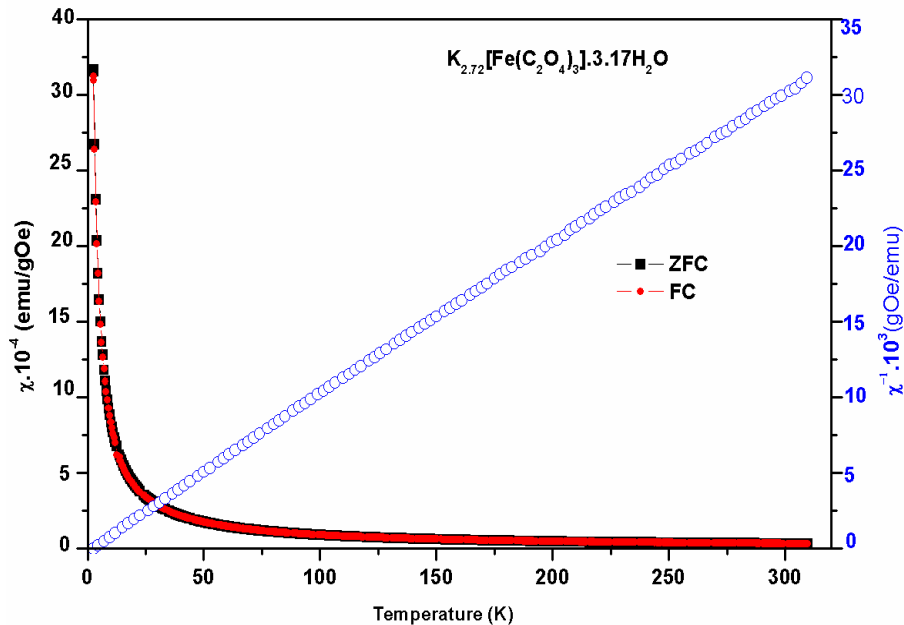


Fig. 9 Magnetic susceptibility and inverse susceptibility as a function of temperature.

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 4, Issue 8, August 2015

The higher value of θ of $K_{2.72}[Fe(C_2O_4)_3] \cdot 3.17H_2O$, may be attributed to charge distribution in Fe ion. This negative θ value indicates very strong antiferromagnetic interactions between Fe localized moments in the complex. The calculated effective magnetic moment for the $K_{2.72}[Fe(C_2O_4)_3] \cdot 3.17H_2O$ complex is 5.91 BM, which is close to the spin-only value of 5.9 BM for spin of $S=5/2$ (Fe^{3+}). In order to check the possible magnetic behavior at low temperatures, we have also carried out field dependent magnetization studies at different temperatures.

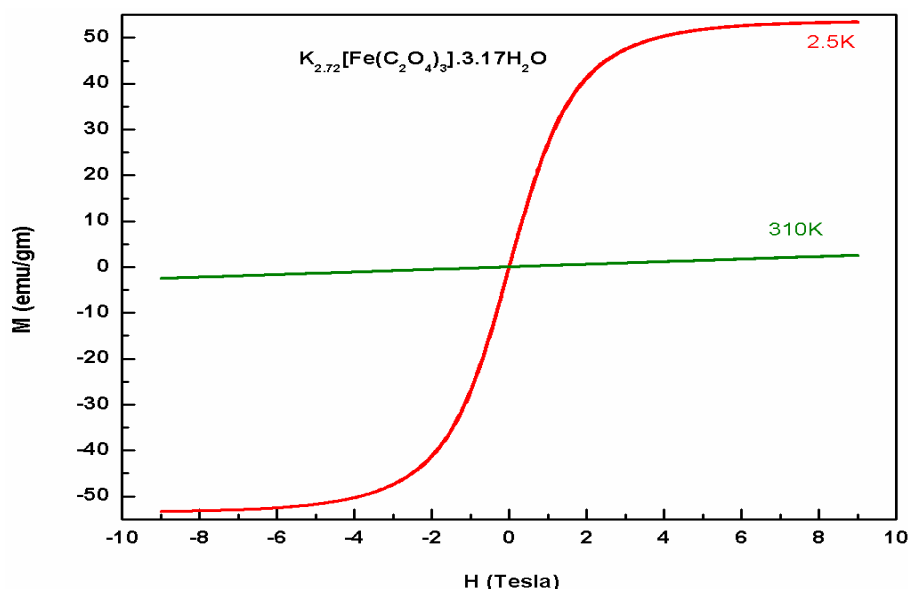


Fig. 10 M - H curves for $K_{2.72}[Fe(C_2O_4)_3] \cdot 3.17H_2O$ at 310 and 2.5 K respectively.

The $M(H)$ curves at 310 and 2.5 K are shown in Fig. 10 respectively. The complex shows a paramagnetic behavior at 310, however at around 2.5 K the non-saturating behavior of the $M(H)$ indicates an antiferromagnetic state of the complex.

IV. CONCLUSIONS

In summary, we have synthesized and grown good quality $K_{2.72}[Fe(C_2O_4)_3] \cdot 3.17H_2O$ crystals using the slow evaporation method. The CHNS analysis confirmed the presence of hydrogen in the crystal lattice. In the crystal structure, the central Fe(III) is in distorted octahedral environment and is coordinated with six oxygen atoms from three bidentate oxalate ligands. The observed UV emission from this material suggests that it may have potential applications in optoelectronic emitters, photo diodes, sensors, and renewable energy. The magnetic measurements indicate paramagnetic behavior above 2.5 K and antiferromagnetic ordering at low temperatures.

ACKNOWLEDGEMENT

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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International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 4, Issue 8, August 2015

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