

Characterization of pure and copper-doped iron tartrate crystals grown in silica gel

V MATHIVANAN^{1,2} and M HARIS^{1,*}

¹Department of Physics, Karunya University, Karunya Nagar, Coimbatore 641 114, India

²Department of Physics, United Institute of Technology, Coimbatore 641 020, India

*Corresponding author. E-mail: harismuthiah@gmail.com

MS received 22 January 2013; revised 11 March 2013; accepted 12 March 2013

Abstract. Single crystal growth of pure and copper-doped iron tartrate crystals bearing composition $\text{Cu}_x\text{Fe}_{(1-x)}\text{C}_4\text{H}_4\text{O}_6 \cdot n\text{H}_2\text{O}$, where $x = 0, 0.07, 0.06, 0.05, 0.04, 0.03$, is achieved using gel technique. The elemental analysis has been done using energy-dispersive X-ray analysis (EDAX) spectrum. The characterization studies such as Fourier transform infrared spectroscopy (FTIR), powder X-ray diffraction (XRD), magnetic analysis and thermal analysis have been done for crystals with $x = 0$ for pure iron tartrate and with $x = 0.05$ for copper-mixed iron tartrate crystals. A detailed comparison has been made between pure and doped crystals.

Keywords. Gel growth; copper-doped iron tartrate; energy-dispersive X-ray analysis; Fourier transform infrared spectroscopy; X-ray diffraction; magnetic moment; thermal studies.

PACS Nos 61; 61.05.cp; 61.05.–a

1. Introduction

Many of the tartrate compounds find applications in medical, pharmaceutical and industrial fields due to their special properties. For example, injections of Na–Cr tartrate increase the susceptibility of the transplanted sarcoma to the effect of X-rays, calciphylic responses of various ferrous tartrate compounds prevent anemia in animals, ferrous tartrate is used as a catalyst in the manufacture of champagne, ferrous tartrate is used to tan skin and manganese tartrate crystals are used as chemical temperature indicators.

Good single crystals can be grown in substances that are normally classified as gels. It has been observed that gels, particularly silica gel, are the best and the most versatile growth media. Crystal growth using gel method is useful for substances having low solubilities and low dissociation temperature. A series of pure and mixed crystals have been grown by several researchers with the aim of identifying new materials for practical and industrial purposes [1–5]. Compounds of tartaric acid find several practical applications in science and technology because of their interesting physical properties such

as dielectric, ferroelectric, piezoelectric and non-linear optical properties [6–10]. Many of the tartrate compounds are insoluble in water and decompose before melting. Hence, single crystals of such compounds cannot be grown by either slow evaporation or melt technique. Mixed crystals of tartrate have several applications in medicine, optics, etc. Hence, it was thought worthwhile to undertake an investigation on growth of crystals of mixed tartrate and their characterization by different methods.

The present work describes the growth of pure and mixed crystals of copper–iron tartrate in silica gel. The characterization of these mixed crystals are done for the first time.

2. Experimental method

The test tube single diffusion method was employed to grow pure and copper-doped iron tartrate single crystals in gel medium. 0.5 M sodium metasilicate ($\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$) was titrated with 0.5 M tartaric acid till the mixture attained the pH of 4.5. This gelling mixture was allowed to set in glass tubes of 200 mm length and 25 mm diameter. The gel was set in about 24 h. The gel setting was found to be strongly dependent on pH, i.e., gel with higher pH value takes lower time to set than gel with lower pH value. After

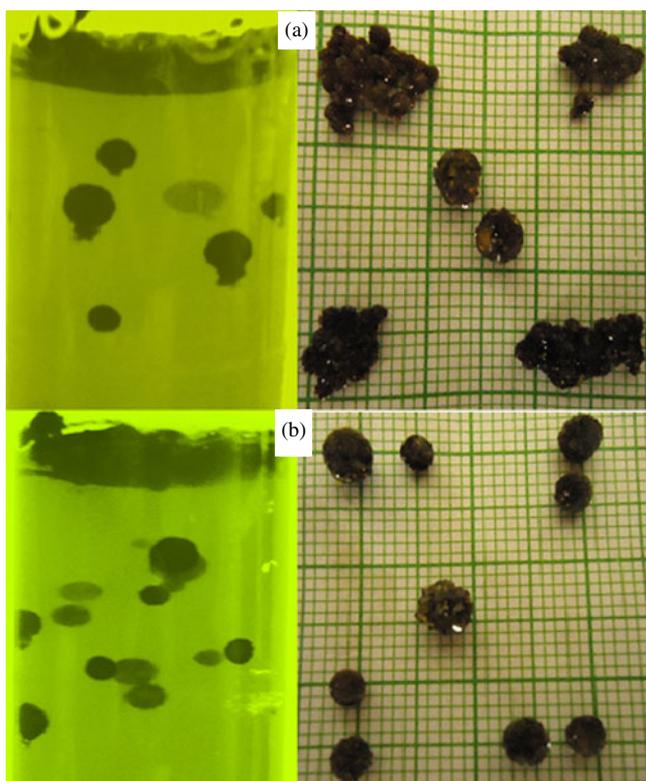
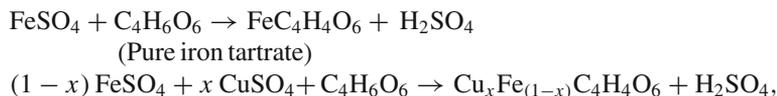


Figure 1. Crystals of (a) pure iron tartrate and (b) copper-doped iron tartrate.

confirming the gel setting, an aqueous solution of iron sulphate of required concentration was poured slowly along the sides of the test tubes, to avoid breaking of the gel surface. Similarly, for growing copper-doped iron tartrate crystals, an aqueous solution of FeSO_4 and CuSO_4 of required concentration has been used. Slow diffusion of the upper reactant ions through the narrow pores of the silica gel leads to reaction between these ions and the ions present in the gel which acts as lower reactant.

The following reaction was expected to occur:



where $x = 0.07, 0.06, 0.05, 0.04, 0.03$ (copper-doped iron tartrate).

The crystals of pure and copper-doped iron tartrate crystals are shown in figure 1. Spherulitic crystals of pure and Cu-Fe tartrate crystals exhibit slight variation in colour.

3. Results and discussion

3.1 Energy-dispersive X-ray (EDAX) analysis

The elemental analysis of copper-doped iron tartrate crystals are shown in figure 2. Table 1 gives the observed and calculated atomic/weight% of pure and copper-doped iron tartrate crystals. From figure 2 and table 1, it is confirmed that copper has entered into the lattices of iron tartrate crystals.

3.2 Fourier transform infrared (FTIR) spectroscopy

In the present investigation, KBr pellet method was used. The instrument used was Thermo Nicolet Avatar 370. The spectrum was recorded in the region $4000\text{--}400\text{ cm}^{-1}$ at room temperature. The infrared radiations promote transitions in a molecule between rotational and vibrational energy levels of the ground electronic energy state.

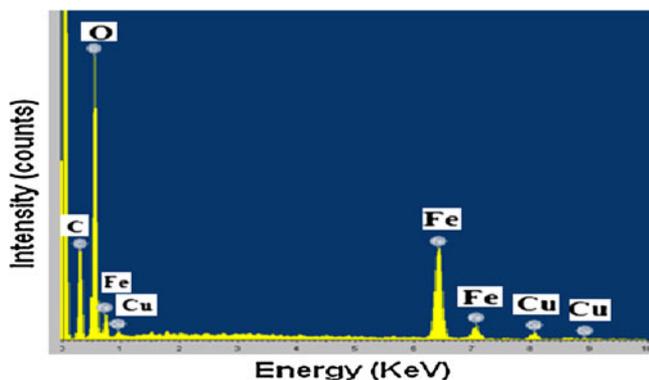


Figure 2. EDAX spectrum of copper-doped iron tartrate.

Table 1. Elemental analysis of pure and copper-doped iron tartrate crystals.

Element	Calculated		Observed	
	Atomic %	Weight %	Atomic %	Weight %
FeC ₄ H ₄ O ₆	Fe 100	100	100	100
Cu _{0.07} Fe _{0.93} C ₄ H ₄ O ₆	Fe 94	85.08	93	86.09
	Cu 6	14.92	7	13.91
Cu _{0.06} Fe _{0.94} C ₄ H ₄ O ₆	Fe 95	86.88	94	87.95
	Cu 5	13.12	6	12.05
Cu _{0.05} Fe _{0.95} C ₄ H ₄ O ₆	Fe 96	87.99	95	89.85
	Cu 4	12.01	5	10.15
Cu _{0.04} Fe _{0.96} C ₄ H ₄ O ₆	Fe 97	90.12	96	91.80
	Cu 3	9.88	4	8.20
Cu _{0.03} Fe _{0.97} C ₄ H ₄ O ₆	Fe 98	92.66	97	93.78
	Cu 2	7.34	3	6.22

The FTIR spectra of pure and copper-doped iron tartrate crystals are shown in figure 3. The observed bands with intensity and their vibrational assignments are given in table 2. Several authors have reported the vibrational spectra of metal tartrate crystals [11–13]. It is observed that the transmittance percentage of copper-doped iron tartrate is more than that of the pure iron tartrate crystals. The variation in FTIR transmittance for pure and copper-doped iron tartrate crystals is due to the different atomic masses of iron and copper, 55.85 for iron and 63.55 for copper, giving rise to a small change in molecular geometry and mechanical vibrations [11]. Due to this, the transmittance percentage of copper-doped iron tartrate crystals is more when compared to pure iron tartrate crystals with slight shift in bands.

The peaks observed at 3356.90 and 3453.07 cm⁻¹ are due to the OH stretching mode. The band at 2360.68 cm⁻¹ is attributed to the CH stretching mode of tartaric acid. The strong peaks at 1612.01 and 1610.91 cm⁻¹ are due to C=O stretching mode of vibration. The bands at 1373.78 and 1378.08 cm⁻¹ are attributed to λ (C=O) + δ (O–C=O). The absorption peaks at 1237.63 and 1286.78 cm⁻¹ are assigned to OH plane bending. The strong peaks at 1119.65 and 1119.11 cm⁻¹ are attributed to δ (C–H) + π (C–H) modes of vibration. The bands at 1081.94 and 1082.38 cm⁻¹ are assigned to γ C(OH) mode. The absorption peaks at 1049.96 and 1047.24 cm⁻¹ are attributed to C–O stretching. The bands at 930.49 and 931.33 cm⁻¹ are due to stretching modes of carbonyl group γ CC. The bands observed at 628.08 and 628.39 cm⁻¹ are attributed for CO₂ deformation. Absorption wave numbers below 500 cm⁻¹ are assigned for Fe–Cu–O mode or metal–oxygen stretching.

3.3 Powder X-ray diffraction (XRD)

The grown crystals were characterized by powder X-ray diffraction using a Bruker D8 Advance, Germany instrument with CuK α radiation (1.5406 Å). The sample was scanned

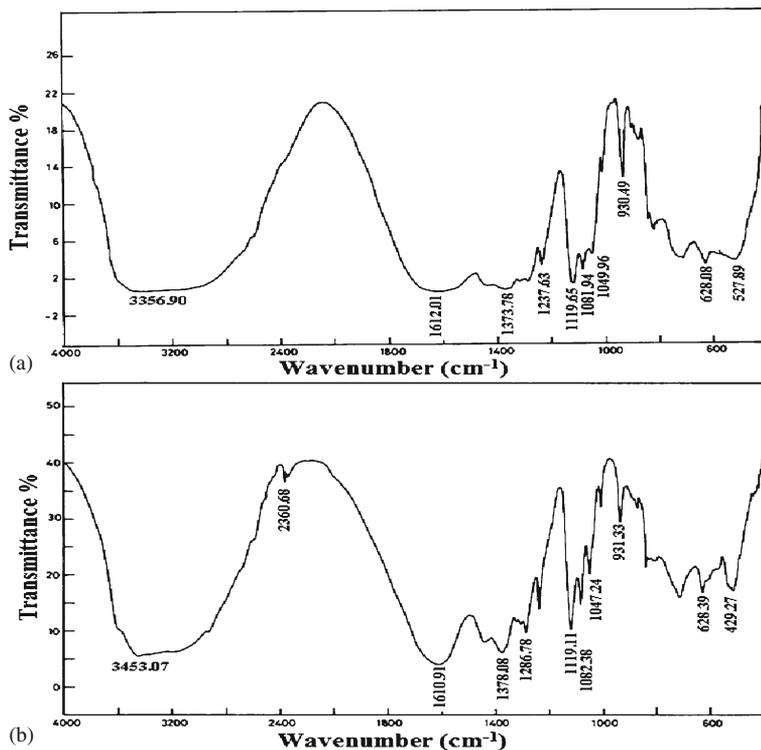


Figure 3. FTIR spectra of (a) pure and (b) copper-doped iron tartrate crystals.

in the range 5° to 70° at the scan rate of $1^{\circ} \text{ min}^{-1}$. The powder XRD patterns of pure and copper-doped iron tartrate crystals are given in figure 4. There are slight variations between the pure and doped crystals [14]. The indexed XRD of the pure and doped

Table 2. FTIR assignments for pure and copper-doped iron tartrate crystals.

Absorption in wave number (cm^{-1})		Assignments
Pure iron tartrate	Copper-doped iron tartrate	
3356.90	3453.07	OH stretching
–	2360.68	CH stretch
1612.01	1610.91	C=O stretch
1373.78	1378.08	λ (C=O) + δ (O–C=O)
1237.63	1286.78	OH plane bending
1119.65	1119.11	δ (C–H) + π (C–H)
1081.94	1082.38	γ C(OH)
1049.96	1047.24	C–O stretching
930.49	931.33	γ CC
628.08	628.39	CO ₂ deformation
Below 500	Below 500	Metal–oxygen stretching

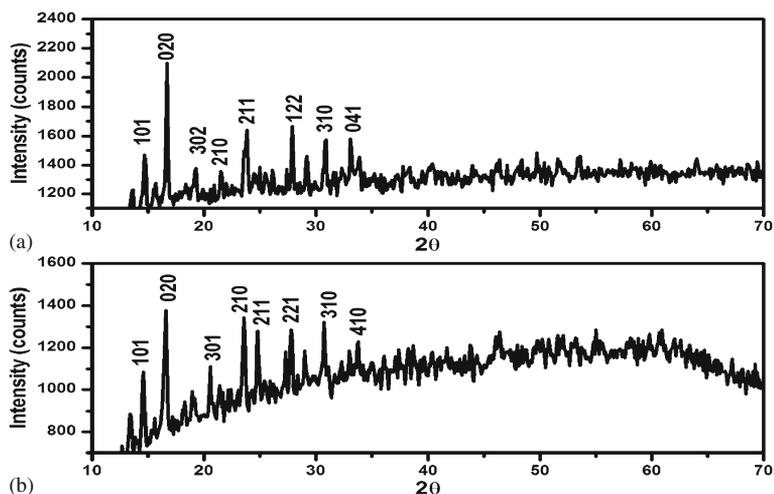


Figure 4. Powder XRD spectrum of (a) pure iron tartrate and (b) copper-doped iron tartrate.

crystals are given table 3. The data observed from powder diffraction are well correlated with the data available in the JCPDS file No. 01-0539. The peaks observed from the X-ray diffraction spectrum were analysed and the lattice parameters were calculated by the unit cell software program. The calculated lattice parameter and unit cell volume are shown in table 4. Hence, the grown crystals have orthorhombic structure with $\alpha = \beta = \gamma = 90^\circ$ and $a \neq b \neq c$.

3.4 Magnetic susceptibility and magnetic moment

The pure and doped $\text{FeC}_4\text{H}_4\text{O}_6$ crystals were finely ground, crushed and the resulting powders were packed in a Gouy tube of known magnetic susceptibility. These experiments were repeated five times and the change in weight was calculated for the given

Table 3. Indexed XRD data for pure and copper-doped iron tartrate.

Pure iron tartrate		Copper-doped iron tartrate	
<i>hkl</i>	$2\theta^\circ$	<i>hkl</i>	$2\theta^\circ$
101	14.6812	101	14.5645
020	16.6812	020	16.5313
302	19.2044	301	21.0462
210	21.7523	210	22.5973
211	24.8927	211	24.8135
122	27.1510	221	27.2666
310	31.8022	310	30.6904
041	33.1231	410	33.7141

Table 4. Comparative powder XRD data for pure and copper-doped iron tartrate crystals.

Chemical formula	Interaxial angle	Unit cell dimensions (Å)	Unit cell volume (Å ³)
Pure FeC ₄ H ₄ O ₆	$\alpha = \beta = \gamma = 90^\circ$	$a = 9.8845, b = 7.4420, c = 8.8480$	650.96
Cu _{0.05} Fe _{0.95} C ₄ H ₄ O ₆	$\alpha = \beta = \gamma = 90^\circ$	$a = 9.9832, b = 8.9142, c = 7.8892$	702.07

magnetic field. The readings of Gouy balance were recorded when the values became steady. These values are given in table 5. The magnetic susceptibility of the samples were found out by using the equation $mg = (A/2)\chi H^2$, where m is the mass of the substance, A is the area of cross-section of the glass tube, H is the magnetic field between the pole-pieces and χ is the magnetic susceptibility of the substance. A graph is drawn between m and H^2 and the slope gives $A\chi/2g$. Hence the susceptibility χ is calculated. This is shown in figure 5. The slope was found at the linear region of the graph. The magnetic moment μ of the pure and doped FeC₄H₄O₆ crystals were calculated using the formula $\mu = 2.828(\chi \times T)^{1/2}$ BM, where T is the room temperature in Kelvin. The susceptibility and magnetic moment of the pure and doped crystals are given in table 6. In the Guoy method, a long sample was placed such that part of the sample was in the field and part, outside the field ($H = 0$). The magnetic field gradient was obtained by using mass (m) and applied magnetic field (H). Thus, the induced magnetic moment translates to a change in weight of the object in the presence of an external magnetic field. This induced moment may have two orientations: parallel to the external magnetic field or perpendicular to the external magnetic field. The former is known as paramagnetism and the latter is known as diamagnetism. The paramagnetism causes an attraction to the source of magnetic field (increase in weight when measured by Guoy balance) and the diamagnetism causes a repulsion from the source of magnetic field (decrease in weight when measured by a Guoy balance). Thus, pure iron tartrate crystals, due to a decrease in mass with respect to the applied magnetic field, is said to exhibit diamagnetism and copper-doped

Table 5. Change in mass with respect to the applied magnetic field for pure FeC₄H₄O₆ and copper-doped FeHC₄H₄O₆.

Name of the crystal	Magnetic field (kG)	Mass (kg)
Pure FeC ₄ H ₄ O ₆	1	0.0690
	2	0.0688
	3	0.0685
	4	0.0681
	5	0.0677
Copper-doped FeC ₄ H ₄ O ₆	1	0.0395
	2	0.0397
	3	0.0399
	4	0.0401
	5	0.0403

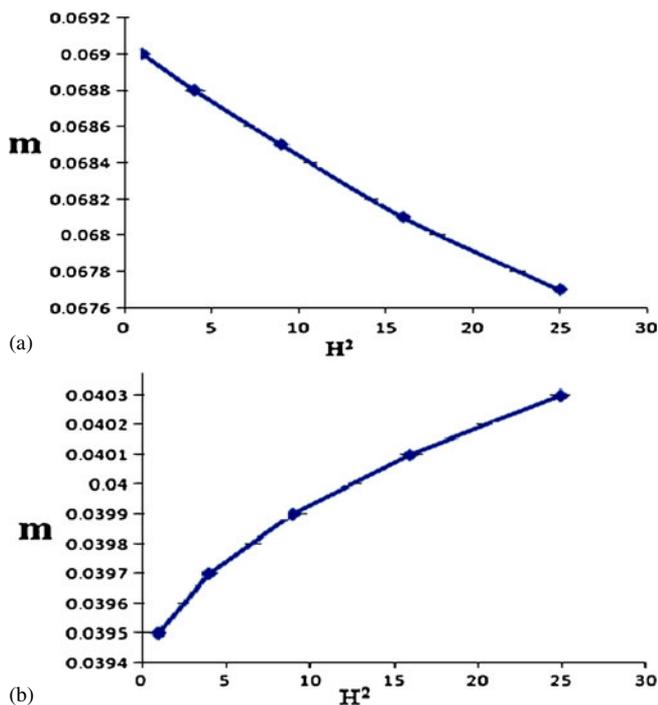


Figure 5. Graph between m and H^2 for (a) pure iron tartrate and (b) copper-doped iron tartrate crystals.

iron tartrate crystals, due to increase in mass with respect to the applied magnetic field, said to exhibit paramagnetism.

3.5 Thermal analysis

The TGA analysis of pure and copper-doped iron tartrate crystals are shown in figure 6. The TGA analysis was done between 40 and 500°C at a heating rate of 20°C min⁻¹ in nitrogen atmosphere. In the case of pure iron tartrate crystals as shown in figure 6a, the first stage of decomposition is due to water of hydration. This starts at 50.42°C and continues up to 325.5°C with an observed weight loss of about 25%. The second stage of decomposition starts from 325.56°C and continues up to 368.45°C with an observed

Table 6. Susceptibility χ and magnetic moment μ for pure and doped FeC₄H₄O₆ crystal.

Name of the crystal	Magnetic susceptibility $\chi \times 10^{-6}$ emu	Magnetic moment (μ BM)
Pure FeC ₄ H ₄ O ₆	27.59	2.572
Copper-doped FeC ₄ H ₄ O ₆	16.98	2.01

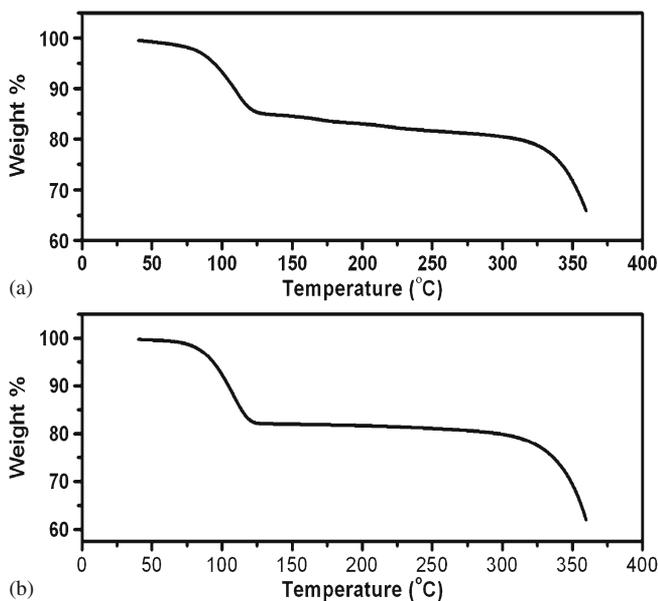


Figure 6. TGA results of (a) pure and (b) copper-doped iron tartrate crystals.

weight loss of about 14.95%. The comparison of the observed and calculated percentage weight losses suggests that the chemical formula for the given crystal is $\text{FeC}_4\text{H}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$. Similarly, in the copper-doped iron tartrate crystal shown in figure 6b, the first stage of decomposition starts from 50.45°C and continues up to 123.45°C with a weight loss of about 20%. The second stage of decomposition starts from 320.05°C and continues up to 360°C with a weight loss of about 22%. The comparison of the observed and calculated percentage weight losses suggests that the chemical formula for the given crystal is $\text{Fe}_{0.95}\text{Cu}_{0.05}\text{C}_4\text{H}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$. The TGA results of pure and copper-doped iron tartrate crystals are shown in table 7.

DSC is a thermoanalytical technique in which the difference in the amount of heat required to increase the temperature of a sample and the reference material is measured

Table 7. TGA results of pure and copper-doped iron tartrate crystals.

Name of the the crystal	Stage	Temperature range (°C)	Weight loss%		Reaction
			Observed	Calculated	
Pure iron tartrate	I	50.42–325.56	25	24.5	$\text{FeC}_4\text{H}_4\text{O}_6 \cdot 2\text{H}_2\text{O} \rightarrow \text{FeC}_2\text{H}_4\text{O}_2$
	II	325.56–368.45	14.95	15.08	$\text{FeC}_2\text{H}_4\text{O}_2 \rightarrow \text{FeO}$
Copper-doped iron tartrate	I	50.45–123.45	20	19.58	$\text{Fe}_{0.95}\text{Cu}_{0.05}\text{C}_4\text{H}_4\text{O}_6 \cdot 2\text{H}_2\text{O} \rightarrow \text{Fe}_{0.95}\text{Cu}_{0.05}\text{C}_2\text{H}_4\text{O}_2$
	II	320.05–360	22	22.05	$\text{Fe}_{0.95}\text{Cu}_{0.05}\text{C}_2\text{H}_4\text{O}_2 \rightarrow \text{Fe}_{0.95}\text{Cu}_{0.05}\text{O}$

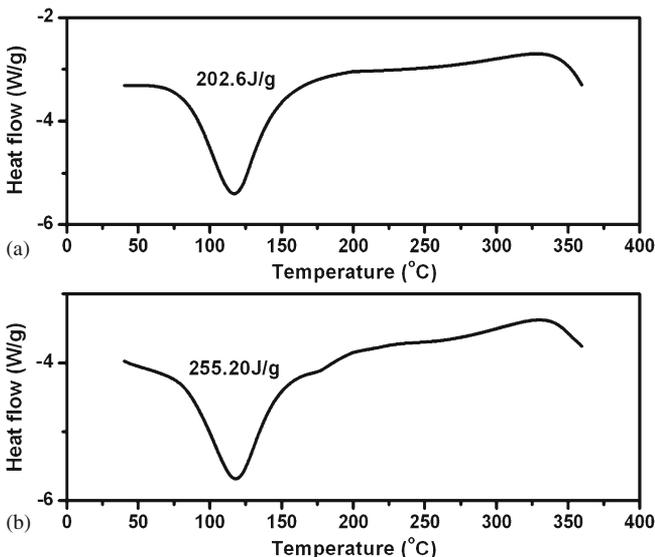


Figure 7. DSC curves of (a) pure and (b) copper-doped iron tartrate crystals.

as a function of temperature. Both the sample and the reference material are maintained at nearly the same temperature throughout the experiment.

The result of the DSC experiment is a curve of heat flux vs. temperature. These curves may be exothermic or endothermic which are used to calculate enthalpies of transition. The DSC curves for pure and copper-doped iron tartrate crystals are shown in figure 7. The endothermic peaks at 118.95°C and 120.45°C show the decomposition temperature for pure and copper-doped iron tartrate crystals respectively.

4. Conclusions

Single crystal of pure and copper-doped iron tartrate were grown successfully by single diffusion method from the gel. The EDAX analysis confirmed that the dopant Cu^{2+} had entered into the lattice of the iron tartrate crystals. The presence of O–H, C=O, C–O, C–H and metal–oxygen bonds were confirmed by FTIR spectroscopy. From XRD studies the unit cell volume of pure iron tartrate was found to be 650.86 \AA^3 and that of copper-doped iron tartrate was found to be 702.07 \AA^3 . The magnetic moment of pure and copper-doped iron tartrate crystals were found to be 2.572 BM and 2.01 BM respectively. The thermal analysis of the samples revealed that there are water of hydration for both samples and the chemical formula for the given samples are $\text{FeC}_4\text{H}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$ and $\text{Fe}_{0.95}\text{Cu}_{0.05}\text{C}_4\text{H}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$ respectively.

Acknowledgements

Special thanks are due to Dr M Sekar, Department of Chemistry, Sri Ramakrishna Mission Vidyalaya College of Arts and Science, Coimbatore, India for the timely help during the

course of this work. The authors are thankful to Karunya University, Coimbatore for the research facilities provided during the course of this work. The authors also wish to thank Mr Raja, Karunya University, Coimbatore for taking the EDAX and powder XRD spectrum of the samples. The corresponding author wishes to thank T V Manimaran, Head, Marketing, Pricol Castings Ltd., Coimbatore for the support during the course of the work.

References

- [1] P Shenoy, K V Bangera and G K Shivakumar, *Cryst. Res. Technol.* **45(8)**, 825 (2010)
- [2] Sushama Bhat and P N Kotru, *Mater. Chem. Phys.* **39**, 118 (1994)
- [3] M V John and M A Ittyachen, *Cryst. Res. Technol.* **36(2)**,141 (2001)
- [4] B B Parekh, R M Vyas, Sonal R Vasant and M J Joshi, *Bull. Mater. Sci.* **31**, 143 (2008)
- [5] Pan Gao, Mu Gu and Xiao Lin-Liu, *Cryst. Res. Technol.* **43(5)**, 496 (2008)
- [6] M E Toress, T Lopez, J Peraza, J Stockel, A C Yanes, C Gonzalez-Silgo, C Ruiz-Perez and P A Lorenzo-Luis, *J. Appl. Phys.* **84**, 5729 (1998)
- [7] M E Toress, T Lopez, J F Peraza, J Stockel and A C Yanes, *J. Crystal Growth* **156**, 421 (1995)
- [8] M E Toress, T Lopez, J Peraza, J Stockel, A C Yanes, C Gonzalez-Silgo, X Solan, M Garcia-Vallés and E Rodriguez-Castellon, *J. Solid State Chem.* **163**, 491 (2002)
- [9] F Fousek, L E Cross and K Seely, *Ferroelectrics* **1**, 63 (1970)
- [10] N R Ivano, *Ferroelectr. Lett.* **27**, 45 (1984)
- [11] I Quasim, A Firdous, N Sahni, S K Khosa and P N Kotru, *Cryst. Res. Technol.* **44**, 539 (2009)
- [12] S K Arora, A Kothari, B Amin and B Chudasama, *Cryst. Res. Technol.* **42**, 589 (2007)
- [13] A Firdous, I Quasim, M M Ahmad and P N Kotru, *J. Crystal Growth* **311**, 3855 (2009)
- [14] S J Joshi, *Growth and characterization of iron–manganese mixed tartrate crystals and the derivative compounds*, Ph.D. Thesis (Saurashtra University, Rajkot, India, 2008)