

PREPARATION OF FERRITES FROM THE THERMAL DECOMPOSITION OF MAGNESIUM AND CALCIUM *tris*(SUCCINATO)FERRATES(III) PRECURSORS

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Thermal analysis of alkaline earth metal ferrisuccinate precursors, $M_3[Fe(C_4H_4O_4)_3]_2 \cdot xH_2O$ ($M=Mg, Ca$) has been studied isothermally and non-isothermally employing simultaneous TG-DTG-DSC, XRD, IR and Mössbauer spectroscopy to characterize the intermediates/end products. After dehydration, the anhydrous complexes decompose to yield an iron(II) oxalate intermediate, $Fe^{(II)}C_2O_4$ in the temperature range 180–250°C. Decomposition of this iron(II) species leads to the formation of α - Fe_2O_3 and respective alkaline earth metal oxide/carbonate in the temperature range 250–300°C. Finally, ferrites of the stoichiometry, $MgFe_2O_4$ and $Ca_2Fe_2O_5$ are formed as a result of solid-state reaction between α - Fe_2O_3 and MO/MCO_3 . A special feature of the precursor method, adopted by us, is that the formation of ferrites occurs at much lower temperature than that of conventional ceramic method.

Keywords: ferrisuccinates, ferrites, Mössbauer spectra, SEM, thermal decomposition, XRD

Introduction

Apart from the academic interest involved in studying the mode of thermal decomposition of metal ferriccarboxylates, these studies are of technical importance as ferrites find an extensive application in radio, television, microwave and satellite communication, bubble devices, audio-video and digital recording and as permanent magnets [1]. Magnesium ferrite is especially used in transformer cores, magnetic recording devices and various microwave appliances [2, 3]. Magnesium ferrite nanoparticles are also used as ferrofluids and contrast agents for magnetic resonance imaging [4]. Since the preparation of ferrites by the conventional ceramic method has several disadvantages [5, 6], viz. non-homogeneity, high temperature sintering, large particle size and low surface area, the precursor technique has been applied to obtain ferrites at lower temperature and in shorter time from the thermolysis of their respective ferrioxalate/malonate/maleate/citrate precursors [7–14]. In continuation of this study, preparation of magnesium and calcium ferrites from their succinate precursors has been undertaken.

Experimental

Alkaline earth metal *tris*(succinato)ferrates(III), $M_3[Fe(C_4H_4O_4)_3]_2 \cdot xH_2O$ ($M=Mg, Ca$) were prepared by mixing stoichiometric quantities of aqueous solutions of ferric nitrate nanohydrate, respective alkaline earth metal succinate and succinic acid. The reaction mixture was stirred vigorously and then concentrated on water bath until a brown product formed. The product was filtered, washed with cold water, dried and stored in vacuum desiccator. Analytical data are given in Table 1. Iron was determined spectrophotometrically using 1,10-phenanthroline [15] while magnesium and calcium contents were determined by atomic absorption spectroscopy.

Infrared (IR) spectra of the complexes and thermolysis products were recorded on Pye-Unicam SP3-300 IR spectrophotometer in the range 4000–400 cm^{-1} using KBr matrix. Simultaneous TG-DTG-DSC curves were recorded on a Pyris Diamond Model [Perkin Elmer] at a heating rate of 5°C min^{-1} . The room temperature X-ray diffraction (XRD) data were recorded at Soils Department, P.A.U., Ludhiana using nickel filtered CuK_{α} radiation. SEM micrographs were recorded by

Table 1 Composition of the complexes

Complex		C/%	H/%	Fe/%	M/%
$M_3[Fe(C_4H_4O_4)_3]_2 \cdot 6H_2O$	Obsd.	30.90	3.68	11.95	7.34
	Calc.	31.44	3.93	12.22	7.86
$Ca_3[Fe(C_4H_4O_4)_3]_2 \cdot 12H_2O$	Obsd.	24.95	4.12	9.62	10.25
	Calc.	25.17	4.19	9.79	10.48

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using JEOL-6100 (Tokyo, Japan) microscope at RSIC, Panjab University, Chandigarh. Mössbauer spectra were recorded at Technical University of Braunschweig (Germany) using a conventional transmission spectrometer in a constant acceleration mode. A $^{57}\text{Co}/\text{Rh}$ source was employed and the isomer shift values are reported relative to pure iron absorber. For the identification of intermediates and products, the complexes were also calcined isothermally in nickel crucibles. The variation in temperature was kept $\pm 5^\circ\text{C}$ during isothermal calcination.

Results and discussion

IR spectrum of magnesium *tris*(succinato)ferrate(III) hexahydrate shows a broad band centered at about 3310 cm^{-1} due to $\nu_{\text{O-H}}$ of lattice water and a small but distinct shoulder at 2900 cm^{-1} due to $\nu_{\text{C-H}}$ of the succinate group. A broad band centered around 1630 cm^{-1} and a strong band at 1380 cm^{-1} is attributed to $\nu_{\text{asy(C=O)}}$ and $\nu_{\text{sym(C=O)}}$ of the coordinated carboxylate groups respectively [16]. A small but distinct band at 580 cm^{-1} due to $\nu_{\text{Fe-O}}$ suggests the presence of Fe–O(carboxylate) bonding [17]. Calcium *tris*(succinato)ferrate(III)dodecahydrate showed a similar IR spectrum.

Mössbauer spectra of the precursors exhibit a doublet (Fig. 1) with isomer shift (δ) and quadrupole splitting (Δ) values of $0.36, 0.54\text{ mm s}^{-1}$, respectively for magnesium and $0.38, 0.63\text{ mm s}^{-1}$ for calcium ferrisuccinate, respectively. These parameters are in close agreement to those reported for high spin Fe(III) complexes with octahedral geometry [18]. The coordination number of six for iron is satisfied by three succinate ligands that bind to iron through oxygen atoms of the carboxylate groups. The outer cation ($\text{Mg}^{2+}, \text{Ca}^{2+}$) and water molecules seem to be responsible for linking together the complex ion, $[\text{Fe}(\text{suc})_3]^{3-}$. The high spin nature of iron(III) in these complexes has also been confirmed by their magnetic susceptibility values of 5.87 and $5.90\ \mu_{\text{B}}$ respectively.

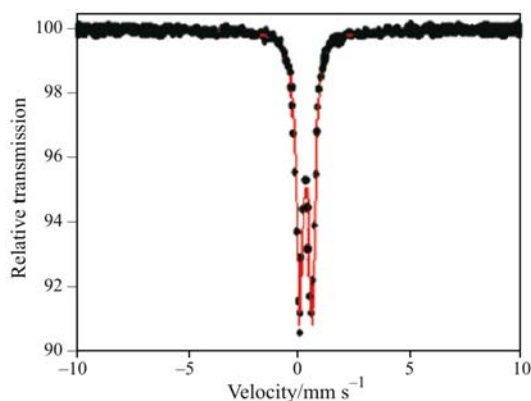


Fig. 1 Mössbauer spectrum of magnesium ferrisuccinate hexahydrate

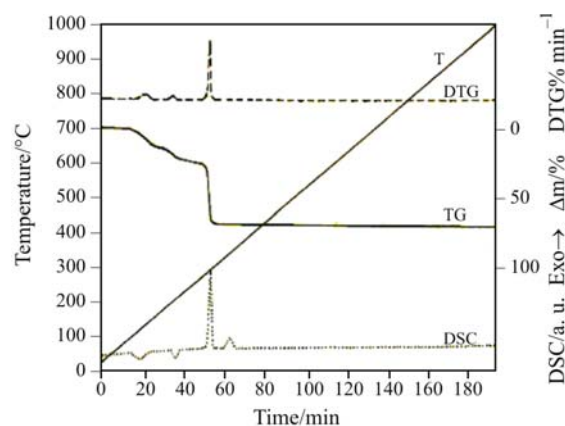


Fig. 2 Simultaneous TG-DTG-DSC curves of magnesium ferrisuccinate hexahydrate

Figure 2 shows the simultaneous TG-DTG-DSC curves of magnesium *tris*(succinato)ferrate(III)-hexahydrate in flowing air atmosphere at a heating rate of 5°C min^{-1} . The dehydration commences at 90°C and completes at 140°C as shown by a mass loss of 13%. This dehydration step is accompanied by an endotherm in DSC at 112°C and a small DTG peak at 117°C . The anhydrous complex gets decomposed into magnesium oxalate and iron(II)oxalate intermediates till a mass loss of 31.5% is reached at 265°C (calc. loss=32%). The respective DTG and DSC (endo) peaks lie at 180 and 185°C respectively. DSC displays an enthalpy change (ΔH) of $-77.49\text{ kJ mol}^{-1}$ for this endothermic decomposition step. The presence of iron(II)oxalate has been confirmed by recording Mössbauer spectrum of the residue obtained by isothermal calcination of the parent complex at 250°C for 30 min. The Mössbauer spectrum (Fig. 3) consists of a quadrupole doublet having isomer shift and quadrupole splitting values of 1.32 and 1.80 mm s^{-1} respectively, which are in close agreement to those reported for ferrous oxalate [19]. As heating continues, the intermediates species undergo an abrupt oxidative decomposition process to yield Fe_2O_3 and magnesium

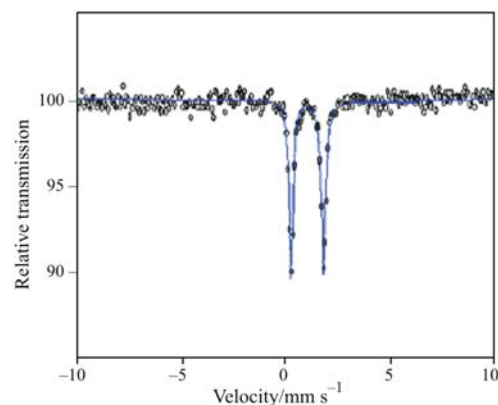


Fig. 3 Mössbauer spectrum of the residue obtained by calcining the parent complex at 250°C for 30 min

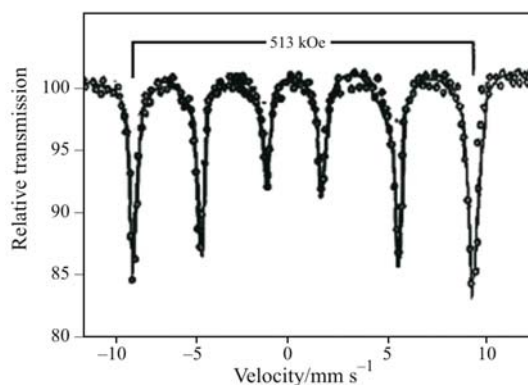


Fig. 4 Mössbauer spectrum of magnesium ferrisuccinate hexahydrate calcined at 300°C for 30 min

oxide as supported by a mass loss of 69% at 300°C (calc. loss=69.4%). This step is accompanied by sharp signals in DSC (exo) and DTG at 285 and 280°C, respectively. The presence of Fe₂O₃ has been confirmed by recording Mössbauer spectrum of the residue obtained by calcining the parent complex at 300°C for 30 min (Fig. 4). It displayed a symmetrical sextet due to magnetic hyperfine interactions with an isomer shift and internal magnetic field values of 0.42 mm s⁻¹ and 513 kOe respectively. These parameters are in close agreement to those reported for bulk α-Fe₂O₃ [20]. Finally, a solid-state reaction occurs between α-Fe₂O₃ and MgO at 350°C to yield magnesium ferrite, MgFe₂O₄, as reflected by an exotherm in DSC at 320°C. The unreacted MgO, present in the final thermolysis residue, was removed to obtain pure ferrite, MgFe₂O₄, by treating it with 2 N HNO₃, followed by repeated washings with distilled water. The identity of the ferrite has been confirmed by recording Mössbauer spectrum and XRD powder data of the end product that exhibits only single phase (Table 2). A computer analysis of Mössbauer spectrum (Fig. 5) shows that there are two cationic sites, i.e., octahedral and tetrahedral with cationic (Fe³⁺) distribution of 57.20 and 42.80%, respectively, (Table 3). The Mössbauer parameters are in close agreement to those reported for the ferrimagnetic inverse spinel, MgFe₂O₄ [21–23]. SEM micrograph reveals the formation of MgFe₂O₄ with the average particle size of 75 nm.

Based on the above discussion, the following pathway for the thermal decomposition of magnesium tris(succinato)ferrate(III)hexahydrate is proposed:

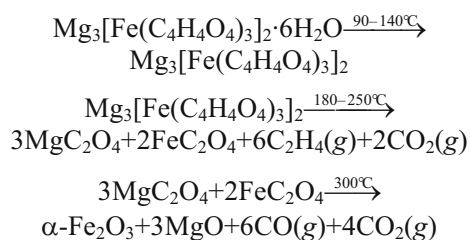


Table 2 Room temperature XRD powder data of the final thermolysis product of magnesium tris(succinato)ferrate(III)hexahydrate

Experimental			ASTM data*	
<i>d</i> /Å	<i>I</i> _{rel}	<i>hkl</i>	<i>d</i> /Å	<i>I</i> _{rel}
2.962	38	220	2.960	40
2.520	100	311	2.525	100
2.092	26	400	2.094	25
1.715	16	422	1.709	14
1.615	28	333	1.612	30
1.484	34	440	1.481	35
1.094	12	553	1.090	12
0.858	10	844	0.855	10

*ASTM Card Number 17-464

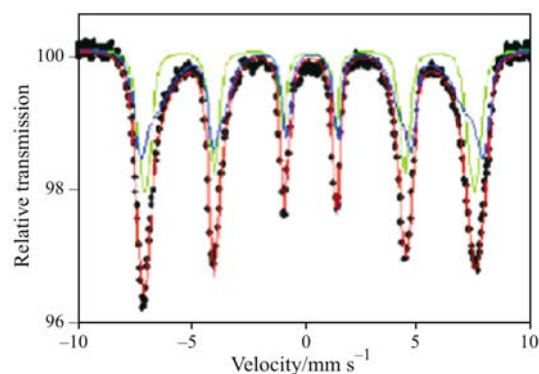


Fig. 5 Mössbauer spectrum of the final thermolysis residue of magnesium ferrisuccinate hexahydrate

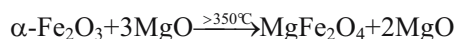


Figure 6 shows the simultaneous TG-DTG-DSC curves of calcium tris(succinato)ferrate(III)dodecahydrate in flowing air atmosphere at a heating rate of 5°C min⁻¹. The complex undergoes simultaneous dehydration and decomposition processes till a mass loss of 43% is reached at 205°C, as shown by the slope of TG curve, indicating the formation of calcium oxalate and iron(II)oxalate intermediate species (calc. loss=43.2%). There exists a respective endotherm (doublet) with peak maxima at 170 and 190°C for this decomposition step. DTG also shows a broad doublet with peak maxima at 175 and 188°C corresponding to this mass loss, indicating that decomposition and dehydration steps are clubbed together. The presence of iron(II) oxalate has been confirmed by recording the Mössbauer spectrum of the residue obtained by isothermal calcination of the parent complex at 200°C for 30 min. The Mössbauer parameters listed in Table 3 confirm the presence of Fe(II) oxalate. As heating continues, iron(II) oxalate and calcium oxalate undergo an oxidative decomposition

Table 3 Mössbauer parameters for thermolysis products of $M_3[Fe(C_4H_4O_4)_3]_2 \cdot xH_2O$ at 300 K

<i>M</i>	Temperature of calcination/ $^{\circ}C$	$\delta^{\#}/mm\ s^{-1}$	$\Delta/mm\ s^{-1}$	B^*/kOe	Cationic (Fe^{3+}) distribution/%	Assignment
Mg	250	1.32	1.80	–	–	$Fe^{(II)}C_2O_4$
	300	0.42	–	513	–	$\alpha-Fe_2O_3$
	450	0.24	0.01	485	57.2(oct)	$MgFe_2O_4$
		0.13	0.05	450	42.8(tet)	
Ca	200	1.28	1.85	–	–	$Fe^{(II)}C_2O_4$
	300	0.46	–	542	–	$\alpha-Fe_2O_3$
	750	0.34	0.55	510(S)	44.1(oct)	$Ca_2Fe_2O_5$
		0.16	0.72	425(S)	48.5(tet)	
		0.28	0.85	–(CD)	7.4	

[#]w.r.t pure iron absorber, ^{*}Internal magnetic field, S=sextet, CD=Central doublet

into Fe_2O_3 and calcium carbonate as supported by a mass loss of 59.6% (calc. loss=59.7%) at 300 $^{\circ}C$. A very sharp exotherm in DSC at 280 $^{\circ}C$ with $\Delta H = -1311\ kJ\ mol^{-1}$ confirmed this oxidative decomposition step. A corresponding sharp signal also appeared at 275 $^{\circ}C$ in DTG. The presence of Fe_2O_3 has been confirmed by recording Mössbauer spectrum of the residue obtained by firing the parent complex at 300 $^{\circ}C$ for 30 min. A symmetrical sextet displayed in the spectrum (Fig. 7) shows an isomer shift and

internal magnetic field values of 0.46 $mm\ s^{-1}$ and 542 kOe respectively. These parameters are in good agreement to those reported for bulk $\alpha-Fe_2O_3$ [20]. IR spectrum of the residue showed a characteristic band at 1450 cm^{-1} indicating the presence of $CaCO_3$. After remaining stable up to 600 $^{\circ}C$, calcium carbonate undergoes an endothermic decomposition process to yield calcium oxide with a mass loss of 71% (calc. loss=71.3%). DSC shows a corresponding characteristic endothermic peak at 650 $^{\circ}C$ due to the evolution of CO_2 . The decomposition of calcium carbonate present in the reaction mixture at a lower temperature than that of the pure calcium carbonate (900 $^{\circ}C$) may be attributed to the catalytic effect of $\alpha-Fe_2O_3$ present. At higher temperature, a solid-state reaction occurs between oxides i.e. $\alpha-Fe_2O_3$ and calcium oxide to yield calcium ferrite, $Ca_2Fe_2O_5$, as supported by an exotherm at 680 $^{\circ}C$. The unreacted CaO present in the final thermolysis residue was removed to get the pure ferrite, $Ca_2Fe_2O_5$, by treating it with 2 N HNO_3 , followed by repeated washings with distilled water. Formation of single phase ferrite, $Ca_2Fe_2O_5$ has been confirmed by XRD powder data (Table 4) and Mössbauer spectrum (Fig. 8) of the final thermolysis residue. Mössbauer spectrum of the

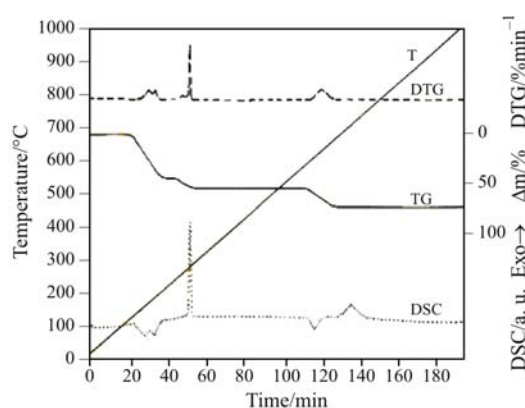
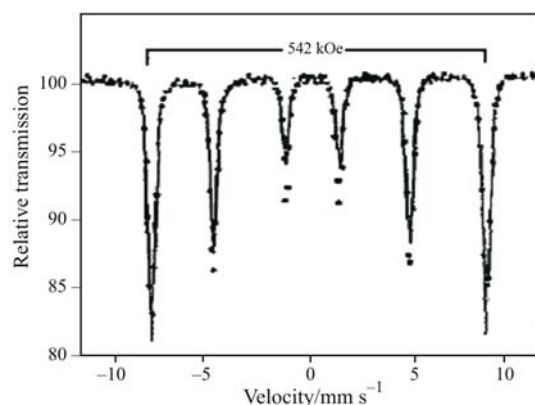
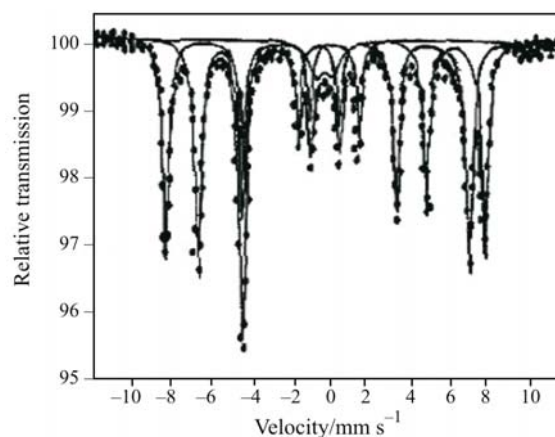

Fig. 6 Simultaneous TG-DTG-DSC curves of calcium ferrisuccinate dodecahydrate

Fig. 7 Mössbauer spectrum of calcium ferrisuccinate dodecahydrate calcined at 300 $^{\circ}C$ for 30 min

Fig. 8 Mössbauer spectrum of the final thermolysis residue of calcium ferrisuccinate dodecahydrate

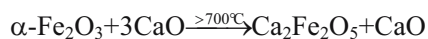
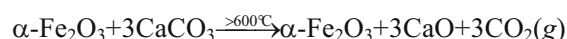
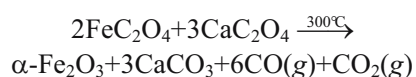
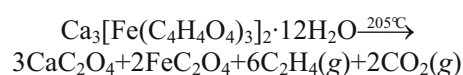
Table 4 Room temperature XRD powder data of the final thermolysis product of calcium tris(succinato)ferrate(III)dodecahydrate

Experimental			ASTM data*	
<i>d</i> /Å	<i>I</i> _{rel}	<i>hkl</i>	<i>d</i> /Å	<i>I</i> _{rel}
7.372	38	020	7.370	40
5.234	10	111	5.230	10
3.685	18	040	3.690	20
2.805	72	200	2.803	70
2.720	70	002	2.717	70
2.684	100	440	2.685	100
2.615	20	220	2.613	20
1.945	70	202	1.950	70

*ASTM Card Number 19–222

final residue exhibits a complex Zeeman pattern displaying two overlapping sextets along with a central doublet, the parameters for which (Table 3) suggest the formation of calcium ferrite, Ca₂Fe₂O₅ of mixed particle size [24]. The presence of a central doublet in addition to the sextets suggests the coexistence of ferrimagnetic and superparamagnetic phases of ferrite particles. A computer analysis shows that there are two cationic sites, i.e., octahedral and tetrahedral with cationic (Fe³⁺) distribution of 44.1 and 48.5%, respectively, (Table 3). SEM micrograph reveals the formation of Ca₂Fe₂O₅ with an average grain size of 90 nm.

In view of the above results, the following decomposition scheme is suggested:



Conclusions

Because of their different electrostatic properties (polarizability, cationic size, etc.), magnesium and calcium ferrisuccinates yield different products i.e., MgFe₂O₄ and Ca₂Fe₂O₅ during pyrolysis. Both precursors yield ferrites at lower temperature and in shorter time interval as compared to the conventional ceramic method [25]. An advantage of the method used is that nano-ferrites with an average particle size of 75–90 nm have been obtained. The room temperature saturation magnetization and Curie temperature values for ferrimagnetic MgFe₂O₄ are 1675 G and 685 K,

respectively. A comparatively lower magnitude of Curie temperature as compared to the reported [1] value for bulk ferrite (710 K) may be attributed to smaller particle size of the ferrite obtained.

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