JOURNAL OF
Materials
CHEMISTRY

Preparation of ferrites from the thermolysis of transition metal ferrioxalate precursors

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Received 9th May 2000, Accepted 7th September 2000
First published as an Advance Article on the web 30th October 2000

The thermolysis of some transition metal ferrioxalate precursors, $M_3[Fe(ox)_3]_2{\cdot}xH_2O$ (M = Mn, Co, Ni, Cu) has been studied in a static air atmosphere from ambient to 600 °C. Various physicochemical techniques *e.g.* TG, DTG, DTA, XRD, IR, Mössbauer *etc.* have been employed to characterize the intermediates and products. After dehydration the anhydrous precursors undergo decomposition to yield an iron(II) intermediate, $M[Fe^{II}(ox)_2]$ (M = Mn, Co, Ni) in the temperature range 175–290 °C. A subsequent oxidative decomposition of the iron(II) species leads to the formation of α-Fe_2O_3 and MO in successive stages. Finally a solid state reaction occurs between the oxides above 400 °C resulting in the formation of transition metal ferrites, MFe_2O_4. The ferrites have been obtained at much lower temperature and in less time than in the conventional ceramic method.

Introduction

The precursor method has achieved great importance in synthesizing stoichiometric, pure and single phase fine particles of ferrites. Ferrites have an extensive application in radio, television, microwave and satellite communication, bubble devices, audio-video and digital recording and as permanent magnets.[1] Although a detailed investigation has been made of the thermal decomposition of transition metal oxalates,[2] a similar interest in complex ferrioxalates is lacking. Another reason for undertaking these investigations is to obtain ferrite at a lower temperature and in less time than possible by the conventional ceramic method. Because of their complexing ability and sensitivity towards oxidation state, metal ferricarboxylates have proven to be the most suitable precursors for the preparation of ferrites.

Experimental

Ferrioxalate precursors *i.e.* $M_3[Fe(ox)_3]_2{\cdot}xH_2O$ (M = Mn, Co, Ni, Cu) were prepared by mixing equimolar quantities of aqueous solutions of ferric chloride, oxalic acid and the respective transition metal oxalate with vigorous stirring. The reaction mixture was heated on a water bath to ~80 °C and allowed to cool slowly with constant stirring. Yellowish-green crystals began to appear at ~60 °C. After cooling to room temperature the crystals were filtered and washed with distilled water. The product was dried and stored in the dark to avoid any chemical change. The identities of the precursors were established by chemical analysis (Table 1). The iron content in various complexes was determined spectrophotometrically using 1,10-phenanthroline.[3] The transition metal (Co, Ni, Cu) content was determined electrogravimetrically after removing the iron through complexation with 1,10-phenanthroline and precipitation by addition of excess ethanol. The red precipitates were filtered out and the filtrate was subjected to electrogravimetric analysis[4] using a platinum electrode. Manganese content in the manganese complex was estimated titrimetrically using EDTA (ref. 3, p. 434).

Table 1 Microanalytical data of transition metal ferrioxalates $M_3[Fe(ox)_3]_2{\cdot}xH_2O$

Complex (precursor)		%C	%H	%Fe	%M
$Mn_3[Fe(ox)_3]_2{\cdot}8H_2O$	obs.	14.95	1.59	11.7	17.0
	calc.	15.17	1.68	11.8	17.4
$Co_3[Fe(ox)_3]_2{\cdot}8H_2O$	obs.	15.02	1.59	11.2	17.9
	calc.	14.98	1.66	11.6	18.4
$Ni_3[Fe(ox)_3]_2{\cdot}8H_2O$	obs.	14.51	1.51	11.3	18.0
	calc.	14.98	1.66	11.6	18.4
$Cu_3[Fe(ox)_3]_2{\cdot}3H_2O$	obs.	16.40	0.80	12.4	21.2
	calc.	16.27	0.68	12.6	21.5

Mössbauer studies were performed at laboratoire de Physique de L'Etat condense UPRES, CNRS, Universite du Maine, France using a conventional transmission spectrometer with a constant acceleration drive. A 25 mCi ^{57}Co(Rh) source was employed. All Mössbauer spectra were recorded at 300 K and fitted to a Lorentzian lineshape. The isomer shift values are reported with respect to a pure iron absorber. IR spectra of the precursors and their thermolysis products were recorded in the 4000–200 cm^{-1} range on a SP3-300 (Pye-Unichem. Ltd., England) spectrophotometer in a KBr matrix. Powder XRD patterns were recorded at USIC, UOR, Roorkee (India) using Ni filtered Cu-K$_\alpha$ radiation. Simultaneous non-isothermal thermograms (TG, DTG, DTA) were recorded on a Stanton Redcroft Model (STA-780) at a heating rate of 10 °C min^{-1}. For indentification of the intermediates and products, the precursors were also calcined isothermally in silica crucibles in a muffle furnace at different temperatures for different time

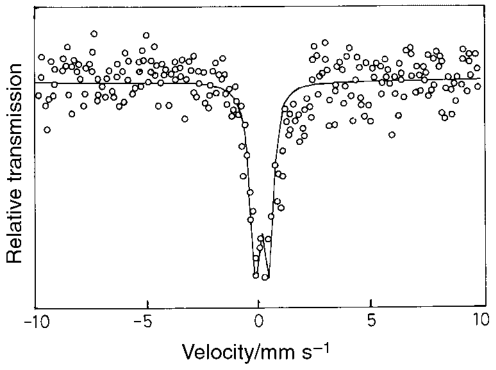

Fig. 1 Mössbauer spectrum of nickel tris(oxalato)ferrate(III).

DOI: 10.1039/b003690k

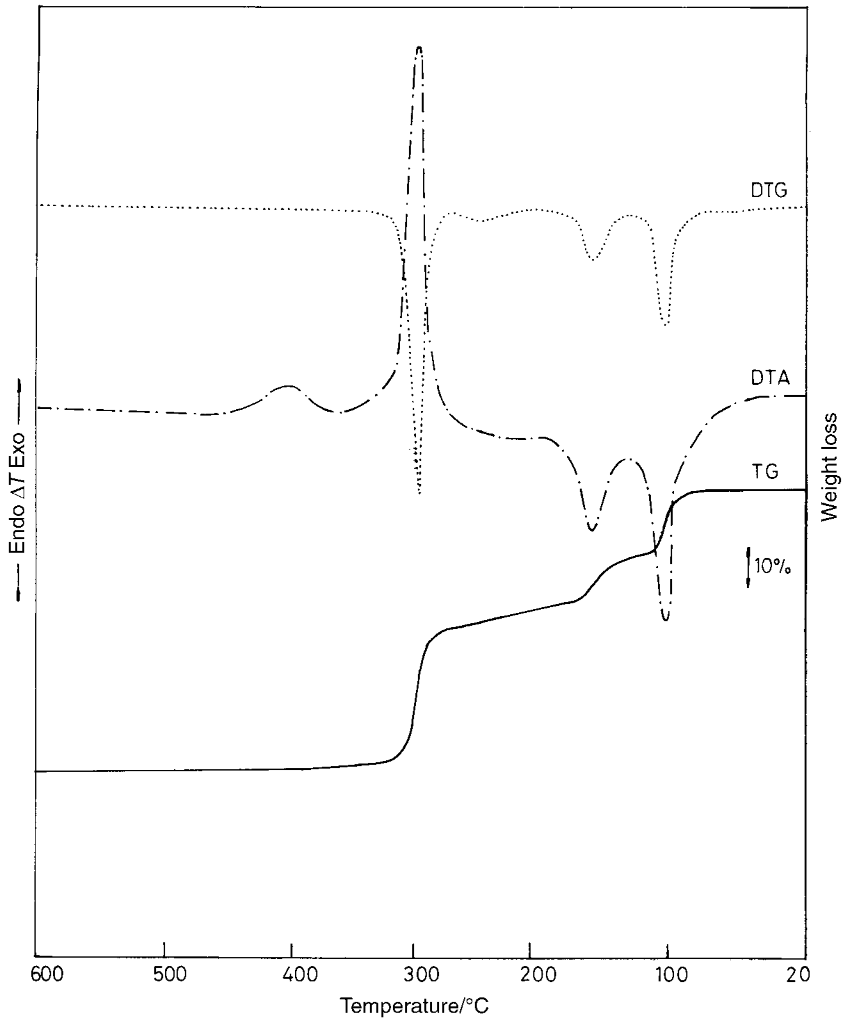

Fig. 2 Simultaneous TG–DTG–DTA thermograms of manganese tris(oxalato)ferrate(III) octahydrate.

intervals. The variation in temperature was kept within ±5 °C during isothermal calcination.

Results and discussion

Infrared spectra of transition metal tris(oxalato)ferrates(III) show a broad band centred at about 3260 cm^{-1} due to ν(OH) of lattice water molecules. Intense bands in the range 1640–1660 cm^{-1} correspond to ν_{asym}(C=O) and bands at 1250–1410 cm^{-1} are attributed to ν_{sym}(C=O) of the coordinated oxalate group.[5] Bands lying in the range 500–300 cm^{-1} are characteristic for the presence of ν(Fe–O) and ν(M–O).

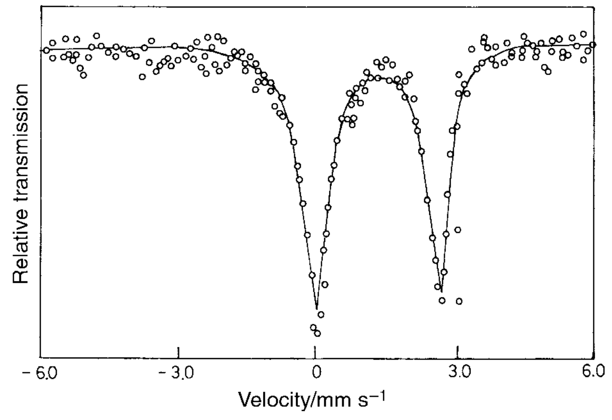

Fig. 3 Mössbauer spectrum of manganese ferrioxalate heated at 175 °C.

Mössbauer spectra of transition metal tris(oxalato)ferrates(III) at 25±2 °C exhibit a doublet (Fig. 1). The magnitudes of the isomer shift and quadrupole splitting lie in the ranges 0.30–0.36 and 0.51–0.63 mm s^{-1}, respectively. These parameters are in agreement with those reported for high spin iron(III) complexes with octahedral geometry.[6] The six coordination of iron is satisfied by three carboxylate ligands which are bound through the oxygen atoms of the oxalate groups. The transition metal and water molecules seem to be responsible for linking together the complex ion,[7] $[Fe(ox)_3]^{3-}$.

The decomposition behaviour of each complex will be discussed separately.

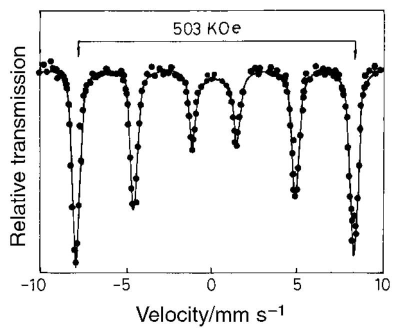

Fig. 4 Mössbauer spectrum of manganese ferrioxalate heated at 320 °C.

Table 2 Mössbauer parameters of the thermolysis products of $M_3[Fe(ox)_3]_2{\cdot}xH_2O$ at 300 K

M	Calcining temp./°C	δ^a/mm s^{-1}	ΔE_Q/mm s^{-1}	$H_i{}^b$/kOe	Fe^{3+} distribution	Assignment
Mn	175	1.28	2.65	—	—	$Mn[Fe^{II}(ox)_2]$
	320	0.35	—	503	—	α-Fe_2O_3
	500	0.38	—	508(S)	31%	α-Fe_2O_3
		0.37	0.91	— (CD)	42% (oct)	$MnFe_2O_4$
		0.30	0.45	—	27% (tet)	
Co	250	1.25	2.68	—	—	$Co[Fe^{II}(ox)_2]$
	340	0.36	—	507	—	α-Fe_2O_3
	500	0.34	−0.18	498(S)	21% (oct)	$CoFe_2O_4$
		0.26	0.01	472(S)	30% (tet)	
		0.30	0.55	— (CD)	49%	
Ni	290	1.22	2.75	—	—	$Ni[Fe^{II}(ox)_2]$
	400	0.40	—	512	—	α-Fe_2O_3
	500	0.36	—	522 (S)	49% (oct)	$NiFe_2O_4$
		0.24	—	478 (S)	41% (tet)	
		0.33	0.81	— (CD)	10%	
Cu	300	0.33	—	501	—	α-Fe_2O_3
	500	0.36	0.89	—	51% (oct)	$CuFe_2O_4$
		0.27	0.51	—	49% (tet)	

[a]The isomer shift is quoted with respect to a pure iron absorber. [b]H_i = Internal magnetic field, S = sextet, CD = central doublet.

Manganese tris(oxalato)ferrate(III) octahydrate, $Mn_3[Fe(C_2O_4)_3]_2{\cdot}8H_2O$

Fig. 2 shows the simultaneous (TG, DTG and DTA) thermograms of manganese tris(oxalato)ferrate(III) octahydrate at a heating rate of 10 °C min^{-1}. TG shows three steps for thermal decomposition of the precursor, the first corresponding to dehydration followed by another two steps associated with decomposition of the anhydrous complex. The dehydration is complete at 115 °C as shown by a stable plateau at a mass loss of 15% (calc. loss = 15.1%). The corresponding DTG peak lies at 95 °C which is endo in DTA. The anhydrous complex remains stable up to 136 °C and starts decomposing until a mass loss of 24% is reached suggesting the formation of iron(II) species and manganese oxalate (calc. loss = 24.4%) with respective DTG and DTA peak temperatures of 157 °C each. The identity of the iron(II) intermediate has been revealed by a Mössbauer spectrum of the residue obtained by calcining the parent complex isothermally at 175 °C for 15 min. The parameters of the doublet displayed in the Mössbauer spectrum (Fig. 3) are comparable to those reported[8] for $[Fe(C_2O_4)_2]^{2-}$. The shape of the DTG curve and the slant in the TG up to a mass loss of 28% indicate a gradual decomposition of manganese oxalate into carbonate (calc. loss = 27.4%). However, the iron(II) intermediate remains stable up to 280 °C. A further steep rise in mass loss up to 61% suggests the oxidative decomposition of these intermediate products into their respective oxides as shown by a sharp DTG peak at 295 °C which is exo in DTA. The presence of Fe_2O_3 has been confirmed by Mössbauer spectroscopy (Fig. 4) of the residue obtained by calcining the parent complex isothermally at 320 °C for 15 min. The Mössbauer parameters of the sextet, listed in Table 2, agree with those reported[9] for α-Fe_2O_3. As heating continues a solid state reaction occurs between Fe_2O_3 and manganese oxide (as suported by an exotherm at 415 °C) to yield manganese ferrite, $MnFe_2O_4$. The formation of manganese ferrite $MnFe_2O_4$ has been confirmed by Mössbauer spectroscopy of the final thermolysis residue which exhibits a six line pattern along with a central doublet (Fig. 5). The central doublet has been resolved into two sites (octahedral and tetrahedral) with Mössbauer parameters (Table 2) consistent with those reported for ultrafine manganese ferrite,[10] which is an inverse spinel. Formation of manganese ferrite as the

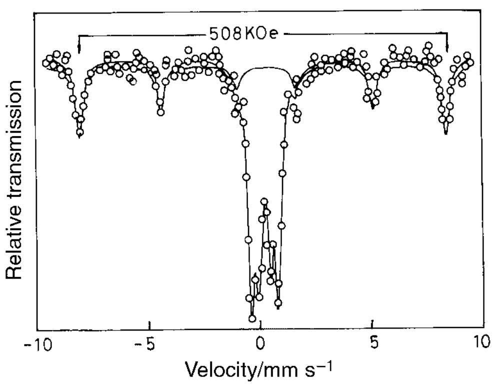

Fig. 5 Mössbauer spectrum of the final thermolysis product of manganese ferrioxalate at 25 ± 2 °C.

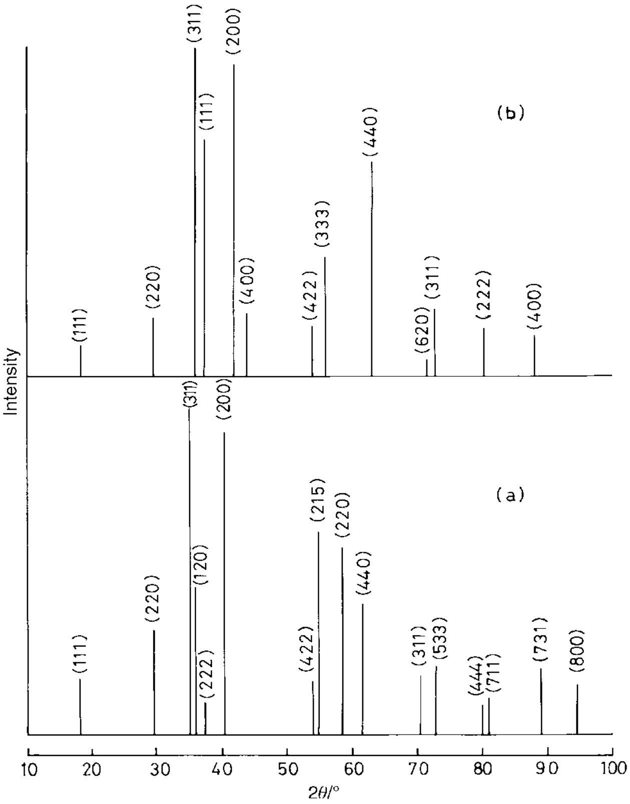

Fig. 6 Powder XRD patterns of the final thermolysis products of (a) manganese ferrioxalate and (b) cobalt ferrioxalate.

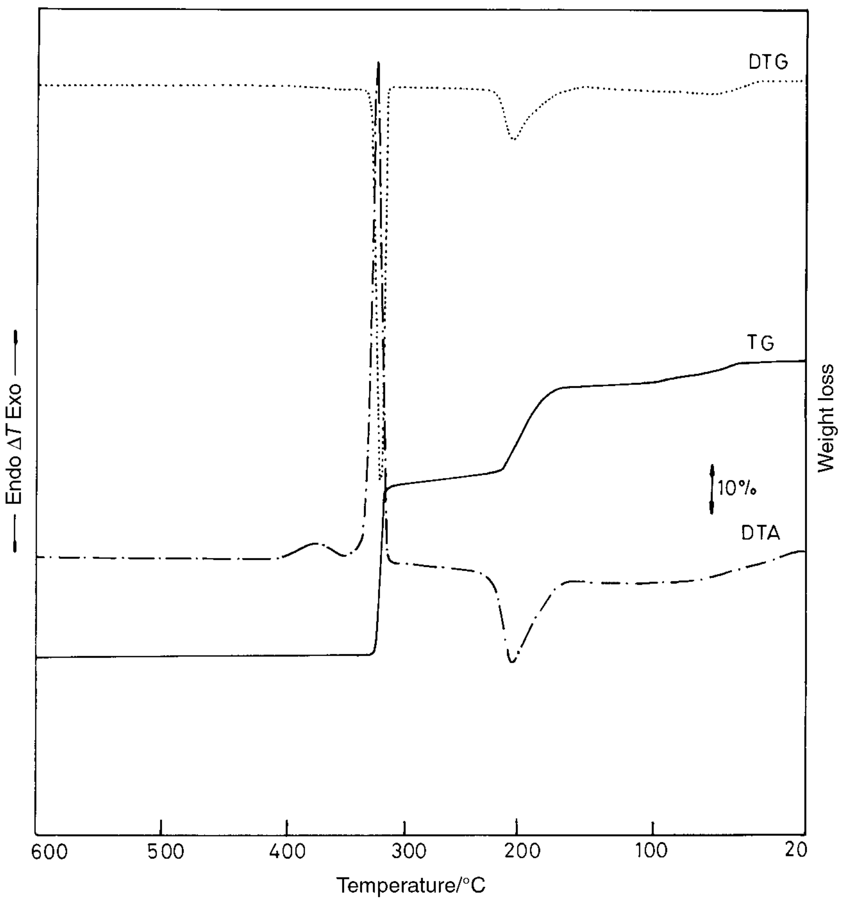

Fig. 7 Simultaneous TG–DTG–DTA thermograms of cobalt tris(oxalato)ferrate(III) octahydrate.

ultimate product has been further confirmed by the powder XRD pattern (Fig. 6a).

Cobalt tris(oxalato)ferrate(III) octahydrate, $Co_3[Fe(C_2O_4)_3]_2{\cdot}8H_2O$

Fig. 7 shows the simultaneous (TG, DTA and DTG) thermograms of cobalt tris(oxalato)ferrate(III) octahydrate at a heating rate of 10 °C min^{-1}. The dehydration of the complex occurs in two steps, initially there is a gradual elimination of three water molecules up to a mass loss of 6% (calc. loss = 5.6%) as indicated by the shape of the various thermograms. Beyond 170 °C, there is a rapid change in mass loss up to 24% suggesting the removal of the remaining five water molecules and subsequent decomposition of the anhydrous complex into iron(II) species and cobalt oxalate. These thermal changes are accompanied by a DTG peak at 204 °C which is endo in DTA. TG shows a stable plateau for the iron(II) species, the composition of which has been confirmed by Mössbauer spectroscopy of the residue obtained by calcining the parent complex isothermally at 250 °C for 15 min, displaying a doublet with parameters similar to those obtained for the iron(II) moiety in the manganese precursor. The intermediate products remain stable up to 310 °C and then undergo an abrupt change in mass loss up to 60% due to oxidative decomposition to their respective oxides at 335 °C. The corresponding sharp exotherm and DTG peak lie at 320 and 317 °C, respectively. The existence of the Fe(III) oxide as α-Fe_2O_3 has been confirmed by the Mössbauer parameters of the residue (Table 2). Cobalt oxalate is reported to decompose directly into oxide without forming the carbonate phase.^{2} The existence of an exotherm at higher temperature suggests a solid state reaction between α-Fe_2O_3 and cobalt oxide to yield cobalt ferrite, $CoFe_2O_4$. The identity of the ferrite has been confirmed

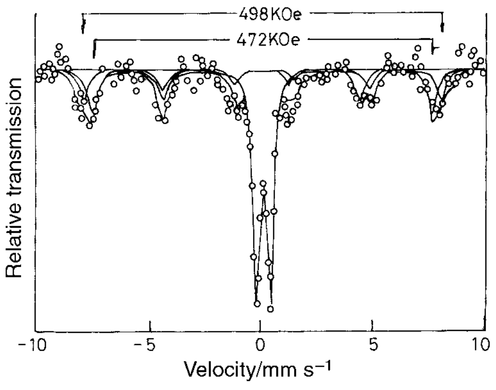

Fig. 8 Mössbauer spectrum of the final thermolysis product of cobalt ferrioxalate at 25 ± 2 °C.

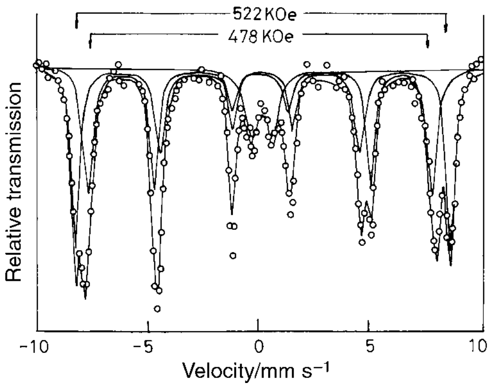

Fig. 9 Mössbauer spectrum of the final thermolysis product of nickel ferrioxalate at 25 ± 2 °C.

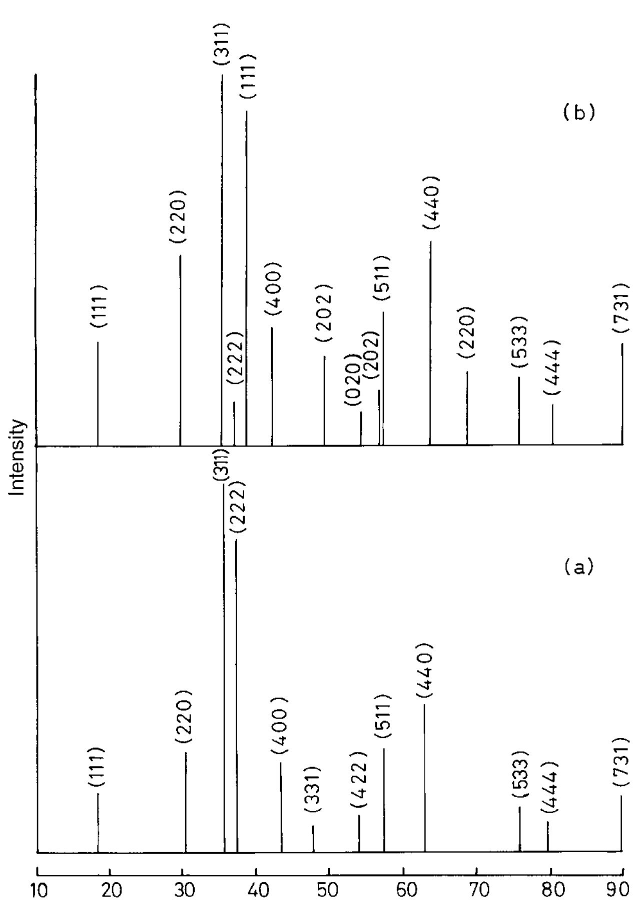

Fig. 10 Powder XRD patterns of the final thermolysis products of (a) nickel ferrioxalate and (b) copper ferrioxalate.

by Mössbauer spectroscopy of the final thermolysis product (Fig. 8). This type of Mössbauer spectrum has been reported in the literature for a cobalt ferrite having a particle size of 7.48 nm.[11] The existence of cobalt ferrite has been reaffirmed by a powder XRD pattern of the final thermolysis product (Fig. 6b).

Nickel tris(oxalato)ferrate(III) octahydrate, $Ni_3[Fe(C_2O_4)_3]_2 \cdot 8H_2O$

The mode of decomposition of the precursor is quite similar to that of cobalt tris(oxalato)ferrate(III) octahydrate. The Mössbauer spectrum of the final thermolysis residue shows a complex Zeeman pattern consisting of two sextets along with a central doublet (Fig. 9). Thus a combination of ferrimagnetism (sextets) and super paramagnetism (doublet) co-exist in the resulting ferrite.[12,13] The Mössbauer parameters of the thermolysis products are summarised in Table 2.

The identity of the nickel ferrite has been further confirmed by a powder XRD pattern of the ultimate product (Fig. 10a).

Copper tris(oxalato)ferrate(III) trihydrate, $Cu_3[Fe(C_2O_4)_3]_2 \cdot 3H_2O$

The simultaneous TG, DTA and DTG thermograms of copper tris(oxalato)ferrate(III) trihydrate are displayed in Fig. 11. Various thermograms show that the thermolysis occurs in two steps *i.e.* dehydration and subsequent decomposition of the anhydrous complex. The dehydration follows a gradual path as indicated by the shapes of DTG and DTA (endo) curves and is complete at 200 °C with a mass loss of 6% (calc. loss = 6.1%). The anhydrous precursor undergoes a steep rise in mass loss up to 55% accompanied by an intense DTG peak at 270 °C which is exo in the DTA. This mass loss corresponds to the formation of copper- and iron(III) oxides (calc. loss = 54.9%). The Fe(III) oxide has been identified as α-Fe_2O_3 from the Mössbauer

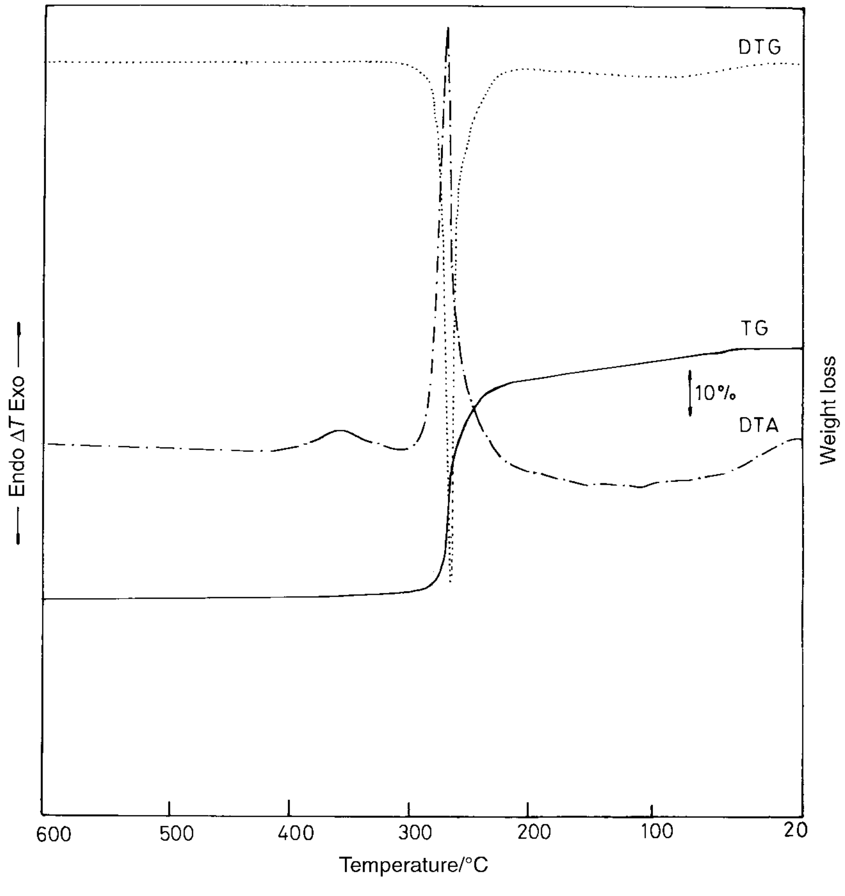

Fig. 11 Simultaneous TG–DTG–DTA thermograms of copper tris(oxalato)ferrate(III) trihydrate.

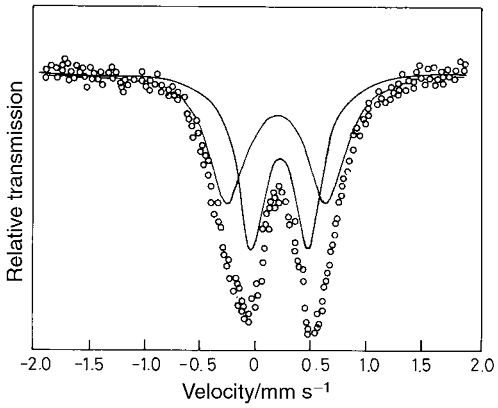

Fig. 12 Mössbauer spectrum of the final thermolysis product of copper ferrioxalate at 25±2° C.

Table 3 Magnetic parameters of the ferrites obtained from thermolysis of $M_3[Fe(ox)_3]_2 \cdot xH_2O$

MFe_2O_4	Density/ g cm^{-3}	Specific magnetization/ G cm^{-3}	Saturation magnetization/ G	Curie temp./ °C
$MnFe_2O_4$	4.65	250	1163	305
$CoFe_2O_4$	3.54	210	744	500
$NiFe_2O_4$	4.75	517	2455	580
$CuFe_2O_4$	4.22	169	715	436

parameters of the residue obtained by isothermal heating of the parent complex at 300 °C for 15 min. Copper oxalate is reported[2] to decompose directly into its oxide without the intermediate formation of carbonate. The presence of another exotherm at higher temperature suggests a solid state reaction between the oxides to yield copper ferrite, $CuFe_2O_4$. The identity of the ultrafine copper ferrite has been confirmed by Mössbauer spectroscopy of the final thermolysis residue which exhibits two overlapping doublets showing the presence of two sites (Fig. 12), the parameters for which are listed in Table 2. Formation of copper ferrite has been further confirmed by the powder XRD pattern of the final thermolysis residue (Fig. 10b).

Various physicochemical studies performed during the aerial thermolysis of transition metal tris(oxalato)ferrates(III) suggest that the decomposition occurs in three major consecutive steps:

(1) Dehydration of the complex.
(2) Reduction of the anhydrous complex to the iron(II) state.
(3) Reoxidation of the iron(II) species to an iron(III) oxide followed by its solid state reaction with a transition metal oxide to yield ferrite.

However, copper ferrioxalate decomposes directly to give iron(III) oxide without intermediate reduction to the iron(II) state.

The intrinsic magnetic properties (saturation magnetization, Curie temperature *etc.*) possessed by ferrites play a key role in establishing their supremacy over the metallic magnetic meterials which cannot be used at microwave frequencies. Various magnetic properties of the ferrites are listed in Table 3. Both saturation magnetization and Curie temperature are particle size dependent. A decrease in particle size lowers the magnitude of these magnetic parameters.[14] The lower values of these parameters observed for manganese, cobalt and copper ferrites are attributed to the ultrafine particle nature of these materials as revealed by the presence of a doublet in their respective Mössbauer spectra. The bulky nickel ferrite shows a Curie temperature in agreement with the reported value.[1]

Conclusion

Ferrites have been obtained from the thermolysis of transition metal ferrioxalates at a temperature (350–500 °C) much lower than that of alkali/alkaline earth ferrioxalates (550–800 °C). This is due to the direct decomposition of the former into the oxide phase. These temperatures of ferrite formation are also notably lower than for the ceramic method.[15–17] Another attractive feature of this method, compared to the ceramic method, is that it does not involve milling of the precursor which introduces defects and strains into the ferrite and hence affects the permanent magnetic properties of the material.

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