

## Development of pure and doped gamma ferric oxide

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**Abstract.** Optimum conditions and experimental details for the formation of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> from goethite have been worked out. In another method, a cheap complexing medium of starch was employed for precipitating acicular ferrous oxalate, which on decomposition in nitrogen and subsequent oxidation yielded acicular  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>. On the basis of thermal decomposition in dry and moist nitrogen, DTA, XRD, GC and thermodynamic arguments, the mechanism of decomposition was elucidated. New materials obtained by doping  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> with 1–16 atomic percent magnesium, cobalt, nickel and copper, were synthesised and characterized.

**Keywords.** Magnetic recording materials; gamma ferric oxide; thermal decomposition.

### 1. Introduction

The potential of gamma ferric oxide ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>) as a magnetic tape recording material has provoked a great deal of investigations over the past several years (Smit 1971; Venkatesh Rao *et al* 1974; Seshan *et al* 1981b; Anantharaman *et al* 1981). It can be prepared commercially with the required parameters from synthetic goethite. However the present annual demand of our country ( $\sim 25$  MT) is met mainly through import (Patil 1977). Since most of the literature on this method is patented and/or vaguely known, the first step in the indigenization process involves working out the optimum conditions and experimental details of each step of synthesis on a laboratory scale, before it is taken up on a pilot-plant scale. These have been reported in the present communication. Another preparative method involves thermal decomposition of ferrous oxalate dihydrate in an inert atmosphere to magnetite, followed by careful oxidation to  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> (Seshan *et al* 1981a). However, this method involves a costly glycerol medium, which is required to retain acicularity. With a view to economizing the process, a cheap complexing medium of starch has been employed for precipitating acicular ferrous oxalate, almost without loss of quality. Further, the mechanism of thermal decomposition of the oxalate has been reported to involve the existence of FeO and H<sub>2</sub> (Dollimore *et al* 1963; Bevan and Brown 1966; Venkatesh Rao *et al* 1974). Experimental evidences, in conjunction with thermodynamic arguments, are being presented to unequivocally elucidate the mechanism. Finally, since  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, a vacancy-ordered spinel, is thermodynamically unstable with respect to  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> at ambient temperatures, efforts were made to stabilize the structure and to develop new materials, by doping with small amounts of magnesium, cobalt, nickel and copper in the atomic percent range 1–16.

## 2. Experimental

Apart from the conventional solution chemistry precipitation technique, various instrumental methods such as x-ray powder diffraction (XRD), differential thermal analysis (DTA), thermogravimetry (TG), gas chromatography (GC), magnetic hysteresis loop tracing (HLT), initial susceptibility ( $\chi_i$ ) and transmission electron microscopy (TEM) were employed to characterize the intermediates at each stage of the reaction process. DTA/TG curves were recorded in air and also in oxygen-free moist and dry nitrogen, using 10 mg of the sample at a heating rate of 5°C/min and a gas flow rate of 150 ml/min. The XRD of the samples were carried out in a Philips x-ray diffractometer (PW1140) using  $\text{FeK}_\alpha$  radiation. The evolution of hydrogen was detected in an on-line gas-chromatograph (AIMIL-NCL Dual Column gas chromatograph Mk II) using molecular sieve 13  $\times$  column in a carrier gas atmosphere of oxygen-free nitrogen. The magnetic properties were measured on a hysteresis loop tracer and initial susceptibility unit (Likhite *et al* 1965; Radhakrishnamurty and Sahasrabudhe 1965). The shape and size of the particles were determined from transmission electron micrographs taken on a Philips electron microscope (EM301).

### 2.1 Synthesis of goethite

Goethite was synthesized from a solution of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (Camras 1954) and scrap iron containing a seed solution of  $\alpha\text{-FeOOH}$  aided by constant aeration (Camras 1954) for several hours.

### 2.2 Synthesis of ferrous oxalate

It is well-known that the aqueous medium is unsuitable for the precipitation of  $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  (FOD), as it yields only spherical particles (Seshan *et al* 1981a). Literature reports (Berkowitz and Schuele 1968; Seshan 1981b) show employment of the costly glycerol as the complexing medium to precipitate acicular FOD. After trying several media, it has been found that a saturated solution of starch and water could be employed to obtain acicular crystals.

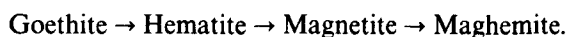
### 2.3 Synthesis of mixed oxalates

The starting materials for the synthesis of doped gamma ferric oxide were mixed oxalates of iron and the dopant (Mg/Co/Ni/Cu), which was co-precipitated from a solution of the corresponding sulphates in required proportions, using oxalic acid. The medium for precipitation was starch and water in order to yield needle-like crystals of the mixed oxalate. The dopant concentration was varied between 1 and 16 atomic percent.

## 3. Results and discussion

### 3.1 Formation of maghemite from synthetic goethite

It is well-known that the preparation of synthetic goethite ( $\alpha\text{-FeOOH}$ ) follows the sequence



Analysis of the XRD pattern showed 3 principal  $d_{hkl}$  lines viz., 4.179 Å, 2.440 Å and 2.684 Å corresponding to 100, 72 and 45  $I/I_0$  respectively. These are in good agreement with the reported ASTM data (1966). DTA of these samples exhibited an endothermic peak at 250°C, with a corresponding mass loss of 10.3% (from TG) associated with the formation of  $\text{Fe}_2\text{O}_3$ . Therefore, dehydration of goethite was carried out isothermally at 250°C for a sufficient length of time (30 min) to yield  $\alpha\text{-Fe}_2\text{O}_3$ . The XRD pattern of these samples on analysis indicated the presence of 3 principal  $d_{hkl}$  lines, viz., 2.69, 1.69 and 2.51 Å corresponding to 76, 38 and 100  $I/I_0$  respectively. These are in good conformity with the reported ASTM data (1966).

Further, both  $\alpha\text{-FeOOH}$  and  $\gamma\text{-Fe}_2\text{O}_3$  were found to be acicular (length/breadth  $\approx 10$ ) from TEM micrographs (cf figure 1). It has been reported (Camras 1954) that reduction of  $\alpha\text{-Fe}_2\text{O}_3$  at about 400°C yields  $\text{Fe}_3\text{O}_4$ . Therefore,  $\alpha\text{-Fe}_2\text{O}_3$  was isothermally reduced at 350°, 370° and 400°C respectively with hydrogen for 45 min. It was found that at 370°C, quantitative reduction to black, acicular  $\text{Fe}_3\text{O}_4$  takes place. The experimentally observed lattice constant ( $a = 8.36$  Å) agreed favourably with the reported ASTM value of 8.396 Å (1966). Further, the magnetization value of 85 emu/gm was in excellent agreement with the expected one (90 emu/gm).

The oxidation of  $\text{Fe}_3\text{O}_4$  to  $\gamma\text{-Fe}_2\text{O}_3$  is generally carried out in air containing water vapour with  $P_{\text{H}_2\text{O}} \approx 30$  torr (David and Welch 1956). To find the optimum conditions, DTA and TG of  $\text{Fe}_3\text{O}_4$  were carried out in a current of moist air ( $P_{\text{H}_2\text{O}} \approx 28$  torr) which

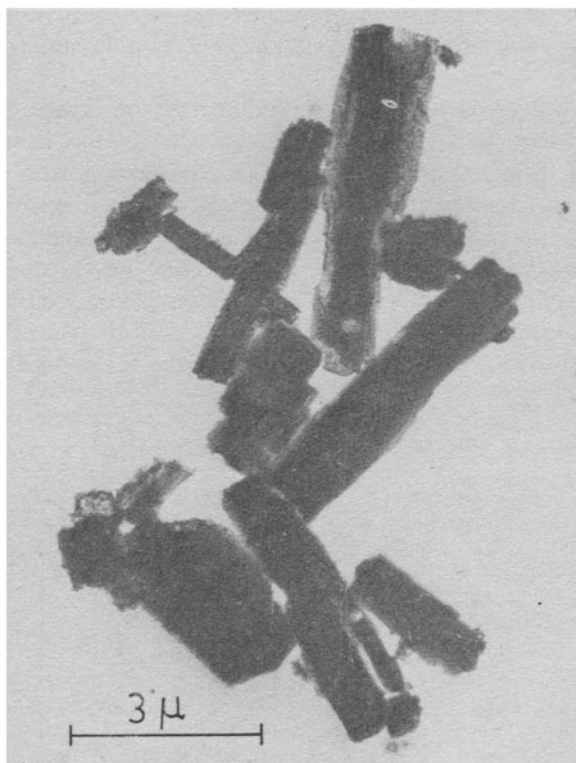
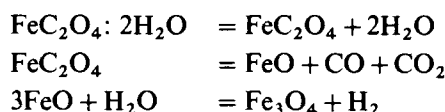


Figure 1. TEM photograph of acicular  $\gamma\text{-Fe}_2\text{O}_3$ .

indicated an exothermic peak at 250°C, accompanied by a gain in mass of 3.2% corresponding to the formation of  $\text{Fe}_2\text{O}_3$ . Therefore the oxidation process was isothermally carried out in moist air. ( $P_{\text{H}_2\text{O}} \approx 28$  torr) at 150°, 180°, 210° and 250°C respectively for 30 min each. At a minimum temperature of 180°C,  $\gamma\text{-Fe}_2\text{O}_3$  ( $a = 8.34$  Å) with required properties (magnetization = 74 emu/gm; coercive field = 290 Oe) was formed.

### 3.2 Mechanism of thermal decomposition of ferrous oxalate dihydrate under nitrogen atmosphere

There have been several reports in the literature about the thermal decomposition of FOD in inert-mainly nitrogen atmosphere (Bevan and Brown 1966; Venkatesh Rao *et al* 1974; Seshan *et al* 1981a). The accepted mechanism of decomposition has been



This, however, raises a few questions:

(i) Has the existence of intermediate FeO been experimentally established? FeO has been known to be thermodynamically unstable below 575°C and disproportionates according to



(ii) Does the presence or absence of moisture have any effect on the stability of FeO, if at all formed?

(iii) Has the evolution of hydrogen gas been experimentally observed?

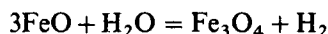
In an attempt to prove the existence of FeO at 710 K—the temperature of decomposition inferred from DTA/TG studies—iso-thermal decomposition of ferrous oxalate dihydrate was carried out in dry as well as in moist oxygen free, ultra high pure nitrogen. The decomposition products were analysed using XRD, GC and magnetization measurements. These analyses confirmed the formation of  $\text{Fe}_3\text{O}_4$  during the decomposition under moist nitrogen atmospheres. The decomposition products obtained under dry conditions were highly reactive and to inhibit oxidation of the products, they were quickly transferred to molten wax. X-ray analysis of the above products showed

**Table 1.** Products of decomposition of  $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ .

In dry nitrogen				In nitrogen containing water vapour			
$d(\text{\AA})$	$I/I_0$	$hkl$	Phase	$d(\text{\AA})$	$I/I_0$	$hkl$	Phase
3.742	44	210	$\text{Fe}_2\text{O}_3$	4.833	8	111	$\text{Fe}_3\text{O}_4$
2.975	3	220	$\text{Fe}_3\text{O}_4$	2.960	26	220	$\text{Fe}_3\text{O}_4$
2.525	7	311	$\text{Fe}_3\text{O}_4$	2.529	100	311	$\text{Fe}_3\text{O}_4$
2.489	2	111	FeO	2.410	5	222	$\text{Fe}_3\text{O}_4$
2.234	8	321	$\text{Fe}_2\text{O}_3$	2.098	23	400	$\text{Fe}_3\text{O}_4$
2.141	4	200	FeO	1.710	5	422	$\text{Fe}_3\text{O}_4$
1.513	5	220	FeO	1.615	23	511	$\text{Fe}_3\text{O}_4$
1.482	22	440	$\text{Fe}_2\text{O}_3$				

the presence of FeO lines along with those of  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_2\text{O}_3$ . This confirmed the formation of FeO during the course of reaction. The details of the xRD findings are reproduced in table 1 as reported by Anantharaman *et al* (1982). Further, on line GC studies conducted for the isothermal decomposition of ferrous oxalate dihydrate indicated the liberation of hydrogen as required by the suggested mechanism.

Since the standard free energy change for the reaction  $\text{Fe} + \text{H}_2\text{O} = \text{FeO} + \text{H}_2$  is negative ( $\sim -2.2$  kcal/mol) at 710 K, it is probable that, in the presence of moisture, iron metal resulting from the disproportionation reaction,  $4\text{FeO} = \text{Fe}_3\text{O}_4 + \text{Fe}$ , will get oxidised to FeO. A combination of these two reactions gives



thus it appears that, in the absence of moisture, 1 mol of  $\text{Fe}_3\text{O}_4$  is produced from 4 moles of FeO, while in the presence of moisture, only 3 moles are required to yield the same quantity of  $\text{Fe}_3\text{O}_4$ . Therefore, the presence of moisture increases the yield of magnetite—a fact recognized empirically several years ago by David and Welch (1956).

### 3.3 Synthesis of doped maghemite

DTA of all the mixed oxalates in moist nitrogen ( $P_{\text{H}_2\text{O}} \simeq 35$  torr) showed two characteristic endothermic peaks, corresponding to dehydration ( $\sim 495$  K) and decomposition ( $\sim 710$  K) respectively. Accordingly, the mixed oxalates were decomposed around 710 K for 30 min, followed by oxidation at 475 K in a stream of air. All the compositions were found to be monophasic cubic spinels, with practically no change in lattice parameter from that of pure maghemite. The magnetic properties of the doped compositions have been reported recently by Anantharaman *et al* (1982) and are reproduced in table 2. Indications are that only cobalt-doped  $\gamma\text{-Fe}_2\text{O}_3$  has high  $\sigma_s$  and  $H_c$  values and, therefore potentially useful in applications.

### 3.4 Thermal stability of doped maghemite

It is well-known that  $\gamma\text{-Fe}_2\text{O}_3$  has a defect spinel structure  $\text{Fe}^{3+} [\text{Fe}_{5/3}^{3+} \square 1/3] \text{O}_4^{2-}$  where the vacancies are concentrated at the octahedral sites. The structure is unstable and converts irreversibly to rhombohedral  $\alpha\text{-Fe}_2\text{O}_3$  around  $400^\circ\text{C}$ . Thus it may be worthwhile to assess the effect of dopants on the thermal stability of  $\gamma\text{-Fe}_2\text{O}_3$  structure.

Table 2. Magnetic properties of doped  $\gamma\text{-Fe}_2\text{O}_3$ .

Dopant (atomic %)	Cobalt		Nickel		Magnesium		Copper	
	$\sigma_s$ (emu/g)	$H_c$ (Oe)	$\sigma_s$ (emu/g)	$H_c$ (Oe)	$\sigma_s$ (emu/g)	$H_c$ (Oe)	$\sigma_s$ (emu/g)	$H_c$ (Oe)
1	94	270	83	225	89	320	76	300
2	71	382	86	270	100	270	80	270
4	74	371	78	250	76	230	94	320
6	72	562	75	230	91	270	80	250
8	90	810	73	230	81	210	77	250
10	93	675	81	250	80	200	69*	230
16	81	675	74	250	86	200	55*	250

\*Unsaturated

The dopant ions may occupy A or B sites depending on their site preference, details of heat treatment etc.

DTA studies did not provide fruitful results, presumably due to very small energy change associated with the  $\gamma \rightarrow \alpha$  conversion process. Since the  $\gamma$ -phase is ferrimagnetic and the  $\alpha$ -phase antiferromagnetic, initial susceptibility ( $x_i$ ) measurements were employed to serve as a tool for distinguishing between the magnetic (ferrimagnetic) and non-magnetic (antiferromagnetic) state of samples. The onset of  $\gamma \rightarrow \alpha$  transition was expected to be accompanied by a rapid decrease in  $x_i$  value which subsequently should reduce to zero.

While pure  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> showed a transition beginning around 275°C, the doped samples consistently showed a higher conversion temperature ( $\geq 300^\circ\text{C}$ ) indicating greater thermal stability. The stability thus achieved could have been partly due to increased potential energy determined by the valence states of the dopant and the host Fe<sup>3+</sup> ions. To check the microstructural changes thus introduced, preliminary Mössbauer spectra were recorded with a Fe<sup>57</sup> source at room temperature. Hyperfine fields, isomer shifts and quadrupole splittings were calculated. The values of hyperfine fields in these samples did not differ from that of pure  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> ( $505 \pm 20$  kOe) indicating that the dopant concentrations were too low to introduce discernible variations in the magnetic field. The hyperfine pattern of the Mössbauer spectra was characteristic of a single magnetic field, since the effective magnetic field was found to be the same for both A and B sites. The isomer shifts also remained unaffected with doping suggesting that Fe<sup>3+</sup> ions do not change their valence state.

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