

A new combustion route to $g\text{-Fe}_2\text{O}_3$ synthesis

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MS received 2 April 2001

Abstract. A new combustion route for the synthesis of $g\text{-Fe}_2\text{O}_3$ is reported by employing purified $\alpha\text{-Fe}_2\text{O}_3$ as a precursor in the present investigation. This synthesis which is similar to a self propagation combustion reaction, involves fewer steps, a shorter overall processing time, is a low energy reaction without the need of any explosives, and also the reaction is completed in a single step yielding magnetic iron oxide i.e. $g\text{-Fe}_2\text{O}_3$. The as synthesized $g\text{-Fe}_2\text{O}_3$ is characterized employing thermal, XRD, SEM, magnetic hysteresis, and density measurements. The effect of ball-milling on magnetic properties is also presented.

Keywords. $g\text{-Fe}_2\text{O}_3$; combustion synthesis; thermal; ball-milling; magnetic hysteresis.

1. Introduction

Fine metal particles of ferrites are receiving increased attention due to their applications in preparation of high density ferrite cores, as suspension materials in ferro-magnetic liquids, as catalysts, adsorbents and sensors to name a few. Iron oxides are technologically important as pigments, semiconductors, recording materials and memory devices. The high stability and semiconducting property of $\alpha\text{-Fe}_2\text{O}_3$ allows its use as photocatalyst (Yang and Kung 1982), while maghemite i.e. $g\text{-Fe}_2\text{O}_3$, is a commercially important magnetic recording material (Cullity 1972; Ziolo *et al* 1992). $g\text{-Fe}_2\text{O}_3$ is usually synthesized from α -goethite (Eberhard and Thomas 1998). The process of transformation of α -goethite to $g\text{-Fe}_2\text{O}_3$ is represented as $\alpha\text{-FeOOH} \rightarrow \alpha\text{-Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 \rightarrow g\text{-Fe}_2\text{O}_3$. Recently, the study of nanoparticle synthesis of this compound and its composites has received greater attention (Guerrero *et al* 1997). The ultra fine particles of ferrites are found to alter the electrical, magnetic, electro-optical and chemical properties (Gotic *et al* 1994; Sale 1994). New synthetic routes for the preparation of ultra fine $g\text{-Fe}_2\text{O}_3$ are being continuously investigated. Gautam and Madan Rao (1982) have reported that when lepidrocite [$g\text{-FeO(OH)}$] is treated with pyridine and carefully oxidized for long hours a complete conversion to $g\text{-Fe}_2\text{O}_3$ with nanosized particles takes place. These powders are reported to have applications for magnetic recording purpose. Other reports for the synthesis of $g\text{-Fe}_2\text{O}_3$ include, the ion exchange reaction in $\alpha\text{-NaFeO}_2$ with benzoic acid (Blesa *et al* 1986), decomposition of microemulsions (Ocana *et al* 1995), thermal decomposition of metal hydrazine carboxy-

lates (Moye *et al* 1990; Patil *et al* 1997; Rane and Verenkar 2001) microwave assisted synthesis of ferrites (Rao *et al* 1999) through a wet chemical synthesis of successive hydrolysis, oxidation and dehydration of ferrous chloride to obtain as small as 5 nm particles (Ennas *et al* 1999), and decomposition of metal carboxylates (Venkataraman 1993, 1996). Gopal Reddy *et al* (2000) have reported the synthesis of $g\text{-Fe}_2\text{O}_3$ for sensor application through a novel technique of combustion of ferric salts with hydrazine hydrate. They have reported that the $g\text{-Fe}_2\text{O}_3$ and the Pt dispersed $g\text{-Fe}_2\text{O}_3$ samples prepared through this process can be effectively used as materials for gas sensors. Recently, monodisperse, monophasic cobalt ferrite is synthesized by hydrolysis in polyol medium (Sounad *et al* 2001). Finely dispersed $g\text{-Fe}_2\text{O}_3$ in polymers is studied to understand the effect of transparency (Toshinobu *et al* 2000), dispersivity in microwave application (Philippe *et al* 1998) for the magnetic recording behaviour (Cullity 1972) and in the thermal stability in mullite matrix (Morales *et al* 2000). The synthesis of $g\text{-Fe}_2\text{O}_3$ and $g\text{-Fe}_2\text{O}_3/\text{SiO}_2$ composites are found as in Faraday rotators (Guerrero *et al* 1997). Many of these methods involved in the synthesis of $g\text{-Fe}_2\text{O}_3$ are tedious, some of them time consuming with many reaction steps and often in many cases a small quantity of the material could be synthesized. It is understood that if the synthesis of $g\text{-Fe}_2\text{O}_3$ could be taken through the conversion of a naturally occurring ore of iron ($\alpha\text{-Fe}_2\text{O}_3$, i.e. red oxide of iron), an economic route to the synthesis of this important ferrite could be achieved. However, no such reports in the literature could be found. Our interest was to see the feasibility for the conversion of $\alpha\text{-Fe}_2\text{O}_3$ to $g\text{-Fe}_2\text{O}_3$ through combustion process in a single step. In search of a suitable economic oxidant our trials with polyethylene glycol (hereafter represented as PEG) gave promising

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results in the synthesis of $g\text{-Fe}_2\text{O}_3$ (Vijay 2000; Mallikarjuna *et al* 2001). Some of the possible reasons for employing PEG in the present study are (i) PEG has a sharp melting point and decomposition temperature, which are widely separated, (ii) PEG is known to be a good surfactant and a dispersant, which when employed may aid in deagglomeration of the powders and (iii) PEG could act as a solvent for the precursor because of its high relative permeability and allows reactions to be carried out under atmospheric pressure and within a wide range of temperatures up to its boiling point and beyond ($\sim 200^\circ\text{C}$). It is also reported (Jeequel *et al* 1995; Palchik *et al* 2000) that some polyols appear as crystal growth medium of particular interest in the synthesis of some oxides.

In the present reaction, we have observed that when heat treatment is given to a mixture of $\alpha\text{-Fe}_2\text{O}_3$ and PEG, $\alpha\text{-Fe}_2\text{O}_3$ disperses in the liquid PEG phase forming possibly $\text{FeO}(\text{OH})$ and later on converts to $g\text{-Fe}_2\text{O}_3$, which is on expected lines of goethite to $g\text{-Fe}_2\text{O}_3$ transformation (Tatsuo and Katsuya 1972). The residue obtained after the heat treatment is found to be purely monophasic $g\text{-Fe}_2\text{O}_3$. The whole reaction is completed within a few minutes. The synthesis of $g\text{-Fe}_2\text{O}_3$ takes place without going through any of the highly exothermic reactions to achieve fine well-dispersed high dense particles.

This paper also discusses the conditions for optimization, by carrying out the reaction employing different weight ratios of $\alpha\text{-Fe}_2\text{O}_3$: PEG.

2. Experimental

2.1 Preparation

PEG with molecular weight 6000 obtained commercially was employed in the present study. The commercially available red oxide (marketed as equivalent to IS grade 445) is purified employing methyl isobutyl ketone through solvent extraction route (Akira and Osamura 1989), since iron oxide of high purity is needed in order to control magnetic properties and grain size of ferrites. This purified $\alpha\text{-Fe}_2\text{O}_3$ hereafter is called as VH_1 .

The VH_1 sample was mixed with PEG in four different weight ratios of 1 : 2, 1 : 3, 1 : 4, and 1 : 5, and was ground in a pestle and mortar. The resultant solids were placed in a alumina crucible and heated in air. It was observed that PEG melted and $\alpha\text{-Fe}_2\text{O}_3$ formed a dispersed phase in this melt. The solution initially boiled and immediately ignited to give fine particles of $g\text{-Fe}_2\text{O}_3$. The whole reaction was completed within three min. The $g\text{-Fe}_2\text{O}_3$ samples thus obtained are hereafter called as VH_2 , VH_3 , VH_4 and VH_5 , respectively. To observe the effect of ball-milling on the $g\text{-Fe}_2\text{O}_3$, the sample VH_5 (which was a monophasic $g\text{-Fe}_2\text{O}_3$) was subjected to wet ball-milling for 6 h. This wet ball-milled sample is now

called as VH_6 . The progress of this reaction resembled the strong combustion reaction for the preparation of SnO_2 (Pathak *et al* 1997) to a greater extent, and hence may be called a self propagating combustion process. The formation of the monophasic $g\text{-Fe}_2\text{O}_3$ was observed from the X-ray diffraction data for the weight ratio of 1 : 5.

2.2 X-ray diffraction

The X-ray powder diffraction patterns were recorded using Philips Model PW 1050/70 X-ray diffractometer using CuK_α radiation. The mean crystalline sizes of the samples were calculated using the Scherrer formulae (Mark 1996).

2.3 Thermal analysis

Thermogravimetric analysis and differential thermal analysis under nitrogen atmosphere were carried out employing Seiko instrument Model no. 320. The flow rate of nitrogen was 100 ml/min, and the heating rate was $10^\circ\text{C}/\text{min}$. The thermal traces under air (static) atmosphere were recorded employing Mettler Toledo Star Instruments.

2.4 Magnetic hysteresis

A vibrating sample magnetometer (VSM: EG & G Princeton, Applied Research Model 4500) was employed to determine the saturation magnetization (M_s), coercive force (H_c) and remanence ratio (M_r/M_s) of $g\text{-Fe}_2\text{O}_3$ samples at room and liquid nitrogen temperatures.

2.5 Density

2.5a Tap density: The as-prepared voluminous oxide samples (VH samples) were hand crushed in agate mortar using a pestle and a known amount of this powder was filled into a graduated cylinder of 5 ml capacity. The cylinder was tapped until the powder level remained unchanged. The volume occupied by the powder was noted. The ratio between the weight of the substance and the volume gave tap density (Kinsman 1978).

2.5b Powder density: The powder densities were measured using Archimedes principle (Culbertson and Dunber 1937) with a pycnometer and xylene as liquid medium. The pycnometer of volume 25 ml was used. The following weights were taken and used in the density calculation: Weight of the bottle = W_1 g; weight of the bottle + substance = W_2 g; weight of the bottle + substance + xylene = W_3 g; weight of the bottle + xylene = W_4 g; density of xylene = r_{sol} ; and density of sample = r_{sample} .

$$r_{\text{sample}} = \frac{(W2 - W1) \times r_{\text{sol}}}{(W4 - W3) + (W2 - W1)} \quad (1)$$

2.5c *Density evaluation from X-ray data:* The X-ray density of the samples have been computed from the values of lattice parameters using the formula (Smith and Wijn 1995)

$$D = \frac{8M}{Na^3},$$

where 8 represents the number of atoms/molecules in an unit cell of a spinel lattice, M the molecular weight of ferrite sample, N the Avagadro's number and a the lattice parameter of the ferrite.

The lattice constant a of the unit cell was calculated using standard equation.

2.6 Scanning electron microscopy

Leica Steroscan 440 Cambridge instrument was employed for the morphology study of the samples.

3. Results and discussion

Table 1 shows the conversion of $a\text{-Fe}_2\text{O}_3$ to $g\text{-Fe}_2\text{O}_3$ for the different weight ratios of $a\text{-Fe}_2\text{O}_3$ to polyethylene glycol. It is observed from this table that the proper weight ratio for the formation of the monophasic $g\text{-Fe}_2\text{O}_3$ (VH₅) is 1 : 5, whereas the other $g\text{-Fe}_2\text{O}_3$ samples (VH₂, VH₃ and VH₄) corresponding to other ratios showed a mixture of a - and g -phases. Hence the sample VH₅ was used for further study. The X-ray diffraction pattern of VH₅ sample is shown in figure 1. The lattice constant of this sample was found to be 8.34 Å and the crystallite size was calculated as 22.76 Å. It is understood that wet ball-milling is found to change some of the properties viz. mechanical strength, crystallite size, magnetic parameters, etc of the ferrite powders. Hence the VH₅ sample was subjected to wet ball-milling. The ball-milled sample is now called as VH₆. The X-ray diffraction of VH₆ sample reported in table 1 showed the presence of a monophasic $g\text{-Fe}_2\text{O}_3$ particles, having lattice constant of

8.33 Å and crystallite size of 16.93 Å. It is observed from this table that the lattice constant of VH₅ and VH₆ remained same while the crystallite size decreased from 22.76 to 16.93 Å. The decrease in crystallite size is also in agreement with that reported by other workers (Hideo and Mamoru 1978). The results of density and magnetic properties upon ball-milling are discussed later. Table 2 shows densities for the VH samples employing tap density, Archimedes principle and X-ray techniques. The $g\text{-Fe}_2\text{O}_3$ samples (VH₅ and VH₆) show higher densities when compared with $a\text{-Fe}_2\text{O}_3$ (VH₁) and other VH samples. The increase in density due to ball-milling was observed. The effect of ball-milling gives the densities of the $g\text{-Fe}_2\text{O}_3$ almost nearer to the calculated value.

The room temperature magnetization studies i.e. saturation magnetization, coercive force, and remanence ratio for the samples VH₂ to VH₆ are given in table 3. It is observed that the coercive force values remain less affected when compared to the changes observed in the saturation magnetization values. The saturation magnetization steadily changes from 8.35 to 33.11 from VH₂ to VH₅ samples, and upon ball-milling the value rises to 60.98 emu/g (VH₆ sample). The presence of antiferromagnetic material ($a\text{-Fe}_2\text{O}_3$) might have contributed to the lower saturation magnetization values, in the VH₂ to VH₄ samples. The increase in this value of the ball-milled sample (VH₆) could be due to the better chemical homogeneity and anisotropy of the sample.

Figures 2a and b show the thermal traces (TG/DTA) of the $a\text{-Fe}_2\text{O}_3$: PEG mixture in the weight ratio of 1 : 5. These traces were recorded to understand the behaviour of combustion process in the present study. Figure 2a shows the thermal trace under the static air atmosphere. This figure shows a well-defined endothermic peak in the temperature range 45–80°C. This endotherm is followed with a broad exothermic peak in the range from 290 to 370°C. The endothermic peak corresponded to the melting of the PEG and the exothermic reaction corresponded to the formation of $g\text{-Fe}_2\text{O}_3$. On the basis of the

Table 1. Crystallite sizes of VH samples from XRD data.

Sample	Weight ratio of $a\text{-Fe}_2\text{O}_3$: PEG	Phases present (XRD data)	Crystallite size of a - and $g\text{-Fe}_2\text{O}_3$ (Å)
VH ₁	–	a -	22.76
VH ₂	1 : 2	a/g -	22.76
VH ₃	1 : 3	a/g -	22.76
VH ₄	1 : 4	a/g -	22.76
VH ₅	1 : 5	g -	22.76
VH ₆ (wet ball-milled for 6 h)	1 : 5	g -	16.93

a - = $a\text{-Fe}_2\text{O}_3$ and g - = $g\text{-Fe}_2\text{O}_3$.

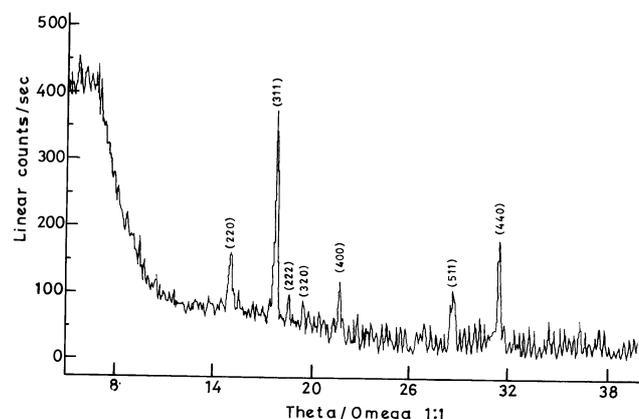


Figure 1. XRD pattern of $g\text{-Fe}_2\text{O}_3$ (VH₅) sample.

Table 2. Density values of VH samples.

Sample	Calculated density (kg/m ³)	X-ray density (kg/m ³)	Tap density (kg/m ³)	Bulk density (kg/m ³)
VH ₁	—	3975	3725	3975.5
VH ₂	4880	4404	4281	4506
VH ₃	4880	4426	4362	4626
VH ₄	4880	4423	4641	4721
VH ₅	4880	4523	4802	4796
VH ₆	—	4733	4831	4806

Table 3. Magnetic hysteresis of samples.

Sample	Phases present	Coercive force (H _c , Oe)	Saturation magnetization (M _s , emu/g)	Squareness ratio (M _r /M _s)
VH ₁	<i>a</i> -	—	—	—
VH ₂	<i>a</i> -/ <i>g</i> -	263.2	8.40	0.51
VH ₃	<i>a</i> -/ <i>g</i> -	301.7	9.11	0.48
VH ₄	<i>a</i> -/ <i>g</i> -	268.2	24.95	0.51
VH ₅	<i>g</i> -	307.0	33.10	0.45
VH ₆	<i>g</i> -	263.2	60.98	0.48
VH ₆ *	<i>g</i> -	265.0	66.64	0.49

*at liquid nitrogen temperature.

a- = *a*-Fe₂O₃ and *g*- = *g*-Fe₂O₃.

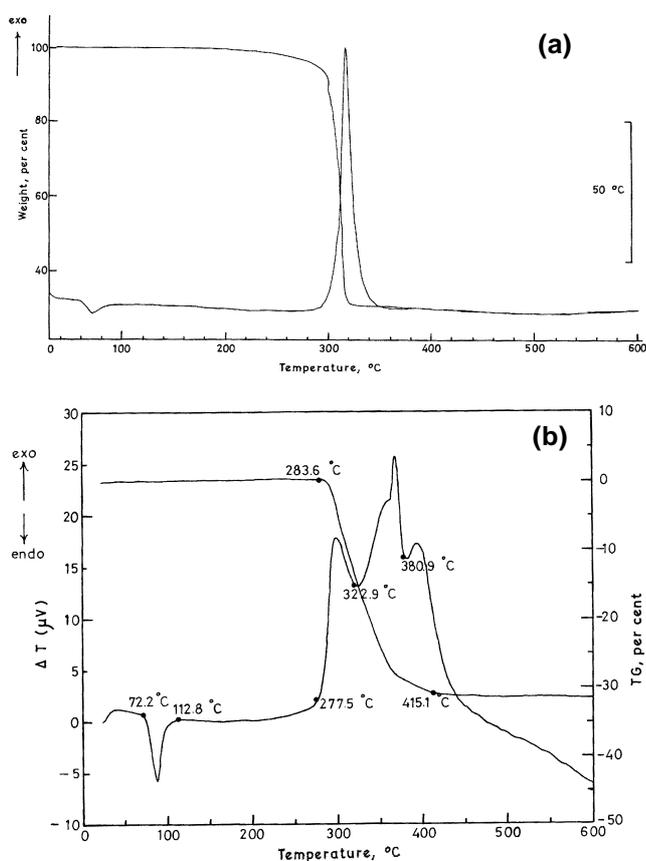


Figure 2. (a) TGA and DTA trace of a mixture of VH₁ with PEG (1 : 5), in static air atmosphere and (b). TGA and DTA trace of a mixture of VH₁ with PEG (1:5), in nitrogen atmosphere.

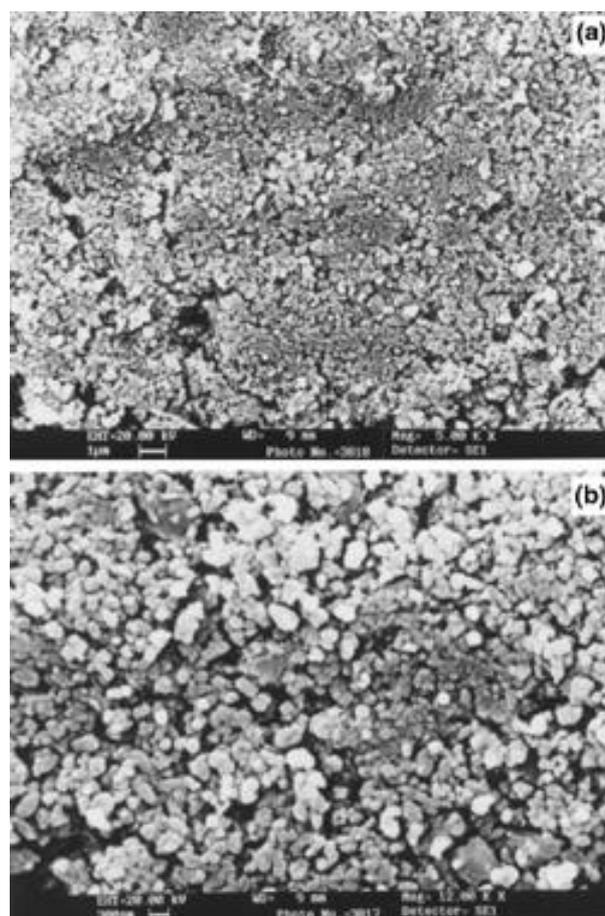


Figure 3. SEM of VH5 samples: (a) low magnification and (b) high magnification.

thermal trace, it may be suggested that the flame temperature of the mixture would be around 300–370°C, and the residue obtained was monophasic *g*-Fe₂O₃ (VH₅). A 70 wt% loss occurred on the TGA curve.

To understand the possible mechanism involved in the combustion process, a thermal study under a different atmosphere for the same mixture was undertaken, i.e. under the dynamic flow of nitrogen atmosphere.

Figure 2b shows the thermal trace of the mixture i.e. 1 : 5 weight ratio of *a*-Fe₂O₃ : PEG under the nitrogen atmosphere. The DTA trace shows three peaks in the temperature range 72.2–112.8°C, 277.5–322.9°C and 323–380°C, respectively. The TGA trace shows a slow weight loss of 32% from 280 to 515°C.

The endothermic peak in the range 72–112°C indicated the melting of PEG. The peak ranging from 277.5–322.9°C may be due to the transformation of *a*-Fe₂O₃ to Fe₃O₄ along with a partial decomposition of the PEG. The next endothermic peak from 322.9 to 380.9°C is due to the transformation of the Fe₃O₄ phase to *g*-Fe₂O₃ phase along with the further partial decomposition of the PEG. The formation of *g*-Fe₂O₃ was complete above 500°C and is found to be monophasic based on X-ray diffraction study. It is observed that under the nitrogen atmosphere some PEG is present till 500°C.

Figures 3a and b show the scanning electron micrographs of *g*-Fe₂O₃ at low and high magnifications, respectively for the VH5 sample. It is seen from these photographs that particles have spherical and ellipsoidal shape and many of these particles are within 300 nms. The particles also look highly dense.

4. Conclusions

It may be concluded from the present study that the reaction of PEG with *a*-Fe₂O₃ in a proper weight ratio yields monophasic ultra fine *g*-Fe₂O₃ through a self-propagating combustion process, and the whole reaction is completed within a few minutes.

The effect of wet ball-milling on *g*-Fe₂O₃ is found to be highly effective on the saturation magnetization values, raising the *M_s* value to that reported for the recording material.

The effect of temperature on *M_s* value is also quite noticeable. The wet ball-milling has also increased the density values close to the reported values.

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