

Hydrazine method of synthesis of γ -Fe₂O₃ useful in ferrites preparation. Part IV – preparation and characterization of magnesium ferrite, MgFe₂O₄ from γ -Fe₂O₃ obtained from hydrazinated iron oxyhydroxides and iron (II) carboxylato-hydrazinates

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Electro-magnetic properties and microstructural characterization of MgFe₂O₄ synthesized by a ceramic technique at ~ 1000 °C from iron oxides, consisting of mainly γ -Fe₂O₃ and traces of α -Fe₂O₃, prepared from iron ore rejects, are compared with the ferrite obtained from commercial α -Fe₂O₃. The sources of γ -Fe₂O₃ are hydrazinated iron (II) carboxylates and iron oxyhydroxides which autocatalytically decompose giving mainly γ -Fe₂O₃ of uniform particles of 10–30 nm (by scanning electron microscopy (SEM) studies) having high surface area. The ferrite synthesized from such nanoparticle size γ -Fe₂O₃ gave a porosity of $\sim 25\%$ with grains ranging from 0–3 μ m. On the other hand, MgFe₂O₄ obtained from commercial α -Fe₂O₃ grains (of 1–2 μ m size) gave particles of 0–6 μ m with a porosity $\sim 42\%$. Saturation magnetization values 922–1168 G are found for MgFe₂O₄ from γ -Fe₂O₃ source while the α -Fe₂O₃ source gave the lowest value, ~ 609 . The Curie temperature, T_c , from magnetic susceptibility, initial permeability and resistivity measurements indicated a highest T_c of ~ 737 K for MgFe₂O₄ from α -Fe₂O₃, while lower values are found for the ferrite prepared from γ -Fe₂O₃.

1. Introduction

Alpha iron oxide, α -Fe₂O₃ (hematite) is the major raw material amounting to more than 70% in the raw meal in the synthesis of ferrites (soft and hard). The other metals that are required for completing the desired ferrite are taken in the form of oxides, MO, or easily decomposable metal carbonates, hydroxides or nitrates. A homogeneous mixing of these raw materials needs a thorough grinding to uniform size. To initiate the solid state reactions a well programmed heat treatment with intermittent grinding and pelletizing is needed to finally produce a suitable sintering process at higher temperatures to achieve a single phase ferrite in the ceramic technique. However, there are a few reports in the literature that suggest the use of γ -Fe₂O₃ instead of α -Fe₂O₃ in ferrite synthesis. In one such study iron oxide consisting of a larger portion of gamma ferric oxide, γ -Fe₂O₃ (maghemite, spinel) is used [1] in the synthesis of ferrites, zinc and barium ferrite and it was found that the reaction rate between Fe₂O₃ and MO increases and the ferrites are formed at a much lower temperature than using the normal α -Fe₂O₃. In nickel–zinc ferrite preparation it has been noticed [2] that the magnetic performance parameters and resistivity values show that γ -Fe₂O₃ is a better precursor than α -Fe₂O₃.

In barium ferrite synthesis, natural magnetite, Fe₃O₄ (inverse spinel) is found to give better electromagnetic characteristics and large reserves of natural magnetites are, thus, used successfully for producing ferrite magnets in Vietnam [3]. The magnetite has a phase transition from Fe₃O₄ to Fe₂O₃ in the heating process and due to the high reactivity of the phase transformation, the ferritization occurs readily and is completed more rapidly using the iron oxide, Fe₂O₃.

Magnetite, as spinel iron sand found on the west coast of the North island of New Zealand, was used [4] in the synthesis of nickel ferrites and their properties compared with the ferrite prepared from hematite (α -Fe₂O₃) and pure synthetic magnetite (Fe₃O₄). All three starting materials form NiFe₂O₄ in air. The reaction in magnetite proceeds via an oxidation step at 220 °C. Inert atmospheres are also used in the synthesis of the ferrite and from Mössbauer studies the cation distributions are determined. The magnetic saturation moment of the ferrite derived from iron sand, both in air and nitrogen, is smaller than that obtained from pure iron oxides, as Ti⁴⁺ present in iron sand appeared on the octahedral sites of the ferrite.

In the hydrothermal method, barium hexaferrite has

been synthesized [5, 6] from $\gamma\text{-Fe}_2\text{O}_3$ and $\text{Ba}(\text{OH})_2$ in an alkaline solution at high temperatures and pressures in a closed batch reactor.

We are studying this aspect of using iron oxides (mainly $\gamma\text{-Fe}_2\text{O}_3$) in synthesizing $\text{MnZnFe}_2\text{O}_4$ and MgFe_2O_4 . The present paper deals with preliminary results on such studies carried out in the preparation of magnesium ferrite, MgFe_2O_4 . The $\gamma\text{-Fe}_2\text{O}_3$ samples used here are as prepared in part I [7] and part II [8]. Here, we are reporting our investigations carried out on microstructural aspects of the iron oxides and MgFe_2O_4 prepared, from these iron oxides and an attempt has been made to correlate some electro-magnetic characteristics of these ferrites with the ferrite synthesized using commercial grade $\alpha\text{-Fe}_2\text{O}_3$ (hematite).

MgFe_2O_4 is usually synthesized by routine solid state techniques [9–13] at high temperatures ($> 1100^\circ\text{C}$). Alternative methods for obtaining high quality materials use precursor techniques [14–16]. It has been observed that [12] microstructural characteristics of Mg-Fe spinel powders are affected by the preparative methods and parameters. High reactivity leading to a spinel with a uniform particle distribution is possible if the starting materials have submicrometer particles.

This study is significant in the sense that the $\gamma\text{-Fe}_2\text{O}_3$ samples that are used here are prepared from iron ore rejects. The detailed chemical beneficiation and preparation are described elsewhere [17]. We have the objective in our current research activities to make use of low grade iron ore rejects in the synthesis of $\gamma\text{-Fe}_2\text{O}_3$ by the hydrazine method to use in ferrite synthesis of technological importance.

2. Experimental

2.1. Preparation of $\gamma\text{-Fe}_2\text{O}_3$

$\gamma\text{-Fe}_2\text{O}_3$ is prepared using various precursors as mentioned in parts I and II [7, 8]. The $\gamma\text{-Fe}_2\text{O}_3$ samples used in the present studies are autocatalytically decomposed end products of

- I. Iron (II) carboxylato-hydrazinates:
 - a) Ferrous fumarato-hydrazinate (FFHA)
 - b) Ferrous succinato-hydrazinate (FSHA)
 - c) Ferrous malonato-hydrazinate (FMHA)
 - d) Ferrous tartrato-hydrazinate (FTHA)
- II. Hydrazinated iron (III) oxyhydroxides
 - a) Hydrazinated $\gamma\text{-FeOOH}$ (γFA)
 - b) Hydrazinated amorphous FeOOH (AmpFA)
 - c) Hydrazinated $\alpha\text{-FeOOH}$ (αFA)

2.2. Preparation of MgFe_2O_4 : ceramic technique

2.2.1. $\gamma\text{-Fe}_2\text{O}_3 + \text{MgCO}_3$

A requisite amount of pure MgCO_3 and $\gamma\text{-Fe}_2\text{O}_3$ (described in Section 2.1) were mixed, pelletized and preheated $\sim 800^\circ\text{C}/12\text{ h}$ in air and cooled. After grinding and pelletizing the samples were finally sintered at 1000°C for 24 h in air. The samples prepared were coded as below, depending upon their iron oxide source.

Iron oxide source	code name of magnesium ferrite
(1) FFHA	→ MgFFHA
(2) FSHA	→ MgFSHA
(3) FMHA	→ MgFMHA
(4) FTHA	→ MgFTHA
(5) γFA	→ Mg γFA
(6) AmpFA	→ MgAmpFA
(7) αFA	→ Mg αFA

2.2.2. Commercial $\alpha\text{-Fe}_2\text{O}_3 + \text{MgCO}_3$

For the comparison of the ferrites prepared from the above $\gamma\text{-Fe}_2\text{O}_3$ samples, a commercial grade hematite, $\alpha\text{-Fe}_2\text{O}_3$ (Baker Analysed, 99.9%), was used for MgFe_2O_4 preparation as in Section 2.2.1. It is coded as MgHEM.

2.3. Characterization

2.3.1. X-ray characterization

X-ray diffraction measurements of magnesium ferrite samples were carried out on a Rigaku D Max II X-ray diffractometer. The observed d values were compared with JCPDS files [18].

2.3.2. Micro-structural characterization

SEM of iron oxides and MgFe_2O_4 were taken on a Cambridge Stereoscan S 250 MK III.

2.3.3. Magnetic characterization

2.3.3.1. *Saturation magnetization.* Saturation magnetization values of the MgFe_2O_4 samples were measured on a high field hysteresis loop tracer, described by Likhite *et al.* [19].

2.3.3.2. *a.c. Susceptibility.* The domain structure and the Curie temperature were determined by the a.c. susceptibility method, developed by Likhite and Radhakrishnamurthy [20].

2.3.3.3. *Initial permeability.* The initial permeability as a function of temperature was measured at 1 kHz over the temperature range of 300 K to 800 K using a MIC 4060-D LCR meter.

2.3.4. Electrical characterization

2.3.4.1. *Resistivity.* Direct current (d.c.) electrical resistivity measurements of the MgFe_2O_4 samples were carried out from room temperature to 700°C by the usual two probe method.

3. Results and discussion

3.1. X-ray analysis

3.1.1. Thermal products of autocatalytically decomposed iron (II) carboxylato-hydrazinates

The autocatalytically decomposed end products of iron (II) carboxylato-hydrazinates: ferrous fumarato-hydrazinate (FFHA), ferrous succinato-hydrazinate (FSHA),

ferrous malonate-hydrazinate (FMHA) and ferrous tartrato-hydrazinate are magnetic in nature and their X-ray diffraction (XRD) patterns match with the pattern of standard gamma ferric oxide, $\gamma\text{-Fe}_2\text{O}_3$ and the d_{hkl} values of these compare well with the values of JCPDS files [21, 22] for $\gamma\text{-Fe}_2\text{O}_3$. An extra peak at $d=0.27$ nm is found in these as prepared end products which corresponds to the strongest line of $\alpha\text{-Fe}_2\text{O}_3$. The XRD patterns of these are shown in Fig. 1 and, for comparison, the pattern of standard $\gamma\text{-Fe}_2\text{O}_3$ is included. The traces of $\alpha\text{-Fe}_2\text{O}_3$ that are found due to the intense heating taking place during autocatalytic decomposition, converting a few particles of $\gamma\text{-Fe}_2\text{O}_3$ to $\alpha\text{-Fe}_2\text{O}_3$ magnetic studies carried out [7, 17] on these also show the presence of $\alpha\text{-Fe}_2\text{O}_3$.

3.1.2. Thermal products of autocatalytically decomposed hydrazinated iron oxyhydroxides

The autocatalytically decomposed end products of hydrazinated iron oxyhydroxides: $\gamma\text{-FeOOH}$ (γFA), $\alpha\text{-FeOOH}$ (αFA) and amorphous FeOOH (AmpFA) are magnetic in nature and their XRD patterns match with

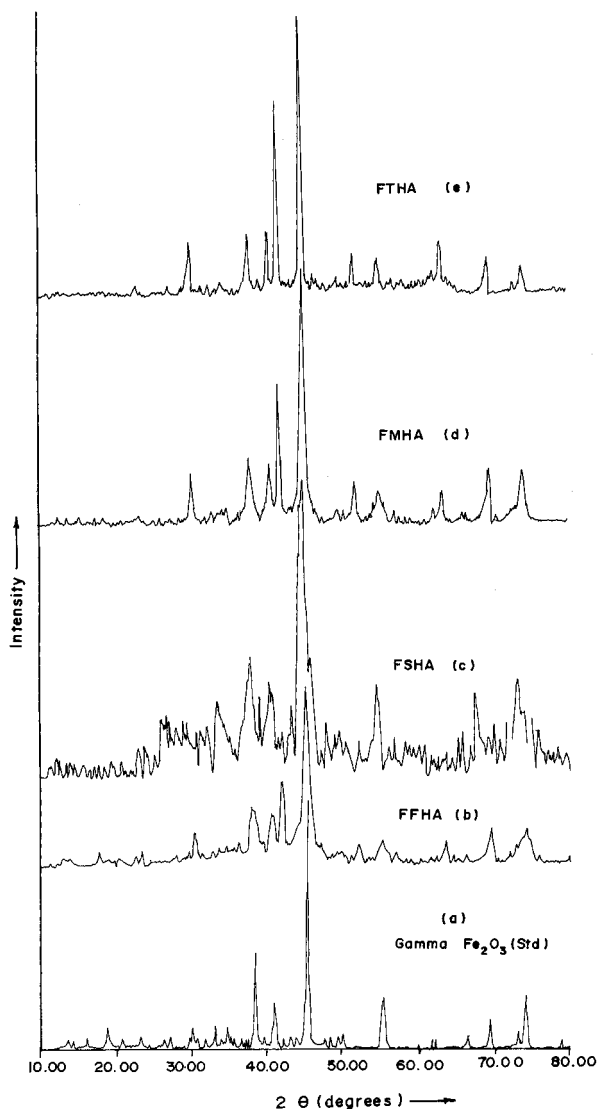


Figure 1 XRD pattern of decomposed end products of iron (II) carboxylato-hydrazinates and standard $\gamma\text{-Fe}_2\text{O}_3$.

the $\gamma\text{-Fe}_2\text{O}_3$, although a few traces of $\alpha\text{-Fe}_2\text{O}_3$ are also observed. However, the autocatalytically decomposed hydrazinated $\gamma\text{-FeOOH}$ shows no traces of $\alpha\text{-Fe}_2\text{O}_3$ and the $\gamma\text{-Fe}_2\text{O}_3$ obtained thus, is the best of the end products studied here. Magnetic studies above reveal that it has ~ 71.6 emul/g⁻¹ [8, 17] which is very close to the expected saturation magnetization value for $\gamma\text{-Fe}_2\text{O}_3$ [23]. In Table I, the XRD data are compiled along with the reported d values of different iron oxides.

3.1.3. Formation of MgFe_2O_4

The X-ray diffraction method is used to confirm the formation of magnesium ferrite from iron oxides (mainly $\gamma\text{-Fe}_2\text{O}_3$) that are obtained from various precursors as mentioned in Section 2.1. The XRD patterns of MgFe_2O_4 obtained from different iron oxide sources are presented in Fig. 2. For comparison, the XRD pattern of the MgFe_2O_4 (MgHEM) obtained from $\alpha\text{-Fe}_2\text{O}_3$ is also shown in the figure. Since the patterns of MgFe_2O_4 from different iron oxide sources are almost identical, only a representative sample pattern MgFMHA , is shown in the figure.

The calculated d values, considering the cubic structure for the ferrite, agree with the observed d values, as well as with the reported ones for MgFe_2O_4 [18] which confirms the single phase spinel formation. The sample MgHEM prepared from commercial $\alpha\text{-Fe}_2\text{O}_3$, however, shows some extra peaks and these match with $\alpha\text{-Fe}_2\text{O}_3$ suggesting that single phase MgFe_2O_4 is not achieved at a temperature of 1000°C . The lattice parameters of all the magnesium ferrite samples are given in Table II. They are found to be $0.839\text{--}0.841$ nm which are within the range of the reported values [16, 24–28].

The X-ray densities, d_x , of all the samples found in the range 4.45 to 4.49 g cm⁻³ are close to the reported value of 4.52 [29] and the actual density, d_a , measured enabled us to calculate porosity using the formula,

$$P(\%) = \frac{d_x - d_a}{d_x} \times 100$$

All the ferrite samples prepared from $\gamma\text{-Fe}_2\text{O}_3$ (mainly) show porosity of $\sim 25\%$ (Table II), whereas, the spinel synthesized from $\alpha\text{-Fe}_2\text{O}_3$ (MgHEM) indicates a high porosity of $\sim 42\%$. Porosities of 31% [30] and 27% [31] were found for MgFe_2O_4 obtained at 1100°C .

The literature survey reveals that the sintering temperature used by researchers for the preparation of MgFe_2O_4 by the ceramic method, is 1100°C and above [12, 26, 30, 32, 33]. In the present study, the sintering temperature of 1000°C was used for the preparation of impurity-free MgFe_2O_4 samples. This was possible as the raw material, iron-oxide, used here was mainly $\gamma\text{-Fe}_2\text{O}_3$ with or without traces of $\alpha\text{-Fe}_2\text{O}_3$, which was found to increase the rate of ferritization at lower temperatures [1, 2]. However, the MgFe_2O_4 sample prepared from commercial $\alpha\text{-Fe}_2\text{O}_3$ (MgHEM) shows an impurity peak of $\alpha\text{-Fe}_2\text{O}_3$, suggesting that the sintering temperature is not sufficient to form single phase MgFe_2O_4 .

TABLE I *d*-values of different iron oxide samples

Sample	<i>d</i> values										
γ -Fe ₂ O ₃ *	—	2.95	—	—	2.51	2.09	—	1.70	1.60	1.47	1.2
γ -Fe ₂ O ₃ *	—	2.95	2.78	—	2.52	2.08	—	1.70	1.61	1.48	1.27
Fe ₃ O ₄ *	—	2.97	—	—	2.53	2.09	—	1.71	1.61	1.48	1.28
α -Fe ₂ O ₃ *	3.66	—	—	2.70	2.51	2.20	1.83	1.69	—	1.45	—
FFHA	3.68	—	2.78	2.70	2.52	2.08	1.84	1.70	1.60	—	—
FSHA	—	2.95	2.78	—	2.51	2.09	—	1.71	1.61	—	—
FMHA	—	2.97	2.78	2.70	2.52	2.09	1.83	1.70	1.61	—	—
FTHA	—	2.95	2.78	2.70	2.52	2.09	1.84	1.70	1.61	—	—
γ FA	—	2.96	—	—	2.52	2.09	—	1.70	1.61	1.48	1.27
AmpFA	—	2.95	—	—	2.51	2.08	—	—	1.60	1.47	1.27
α FA	—	—	—	2.70	2.52	—	1.83	1.69	1.60	1.48	1.27

*Reported

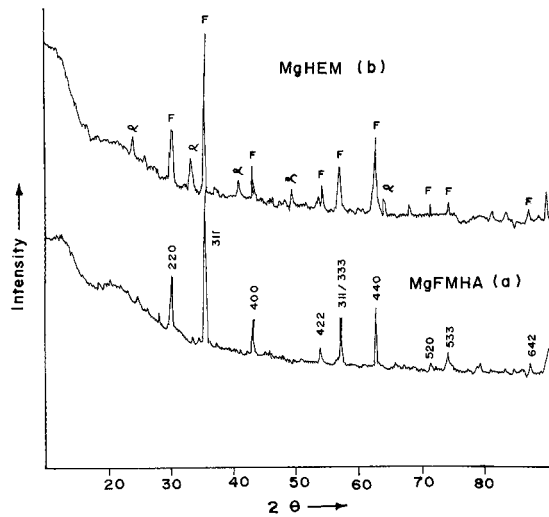


Figure 2 XRD pattern of MgFe₂O₄: (a) representative sample from γ -Fe₂O₃ source; (b) from commercial α -Fe₂O₃ (F = ferrite; α = α -Fe₂O₃).

3.2. Magnetic and electrical characterization

3.2.1. Saturation magnetization

Saturation magnetization, σ emu g⁻¹ values of all the MgFe₂O₄ samples fall in the range 22–28 emu g⁻¹ (Table II) except for the ferrite prepared from commercial α -Fe₂O₃ (MgHEM) which shows 17.2 emu g⁻¹. The saturation magnetization values, $4\pi M_s$ in G are also found to be in the range of 922–1168 except for MgHEM which shows the lowest value of 609.5 G (Table II). The magnetone number (n_B) calculated (Table II) shows the

lowest value of 0.62 for MgHEM, while the other samples are in the range 0.79–1.01, which are close to the reported values of 0.93–1.2 [9, 34].

3.2.2. a.c. susceptibility

The $\chi - T$ curves indicate multidomain (MD) grains for MgFTHA and predominantly single domain (SD) for the other samples. A sharp fall in the curves at Curie temperature for all samples indicates no impurity phase in the ferrites. The Curie temperatures for the ferrites in the present investigation fall in the range 642–700 K, while the spinel from commercial α -Fe₂O₃ shows the highest T_c of 730 K (Table II). The reported values show a wide range of T_c of 593–713 K [35].

3.2.3. Initial permeability

A sharp decrease in μ_i at the Curie temperature after the initial increase from room temperature suggests a single phase ferrite formation in the present investigations, except for MgHEM. The Curie temperatures, T_c , obtained from such studies are given in Table II. The T_c obtained by this method shows higher values than that observed from magnetic susceptibility measurements.

In general, the MgFe₂O₄ samples in the present investigations show lower values of saturation magnetization ($4\pi M_s$) and magnetone number than the reported one. This is due to the lower temperature (1000 °C) and comparatively shorter duration (24 h) used for sintering which results in higher porosity, thus, decreasing magnetic properties.

TABLE II Lattice parameter, porosity, magnetization data and Curie temperature of magnesium ferrite samples

Sample	Lattice parameter “ <i>a</i> ”	Porosity <i>P</i> (%)	Magnetization data				Curie temperature (K)	
			$4\pi M_s$ (G)	n_B	σ_s (emu g ⁻¹)	Magnetic susceptibility	Initial permeability	Resistivity
MgFFHA	8.3927	26.04	1082	0.93	25.96	658	689	672
MgFSHA	8.3912	29.58	967.2	0.87	24.36	670	—	672
MgFMHA	8.3877	26.24	922.3	0.79	22.15	642	667	658
MgFTHA	8.3999	21.31	1097	0.89	24.79	660	682	685
Mg α FA	8.4103	23.63	1110.2	0.93	25.96	700	725	712
Mg γ FA	8.4147	26.41	1042.6	0.91	25.34	680	712	699
MgAmpFA	8.4143	25.92	1168.4	1.01	28.2	680	717	698
MgHEM	8.4172	42.19	609.5	0.62	17.2	730	742	739

Grain size and porosity are the important factors which influence magnetic and electrical properties in ceramics. In all samples, except the one synthesized from $\alpha\text{-Fe}_2\text{O}_3$, many of the above magnetic characteristics show uniform behavior. X-ray characterization also reveals single phase MgFe_2O_4 formation in all samples except the one obtained from $\alpha\text{-Fe}_2\text{O}_3$. These results, therefore, suggest that the microstructure of all the samples, except MgHEM , should be similar compared to the one synthesized from $\alpha\text{-Fe}_2\text{O}_3$. Therefore, detailed microstructural studies were carried out.

3.2.4. Electrical resistivity

Direct current electrical resistivity measurements as a function of temperature show a transition from a ferrimagnetic to a paramagnetic region. The temperature at which this switching takes place is considered as the Curie temperature and is shown in Table II for all the ferrites studied here.

3.3. Microstructural studies by SEM

3.3.1. Particle size distribution of MgFe_2O_4

Scanning electron micrographs of all the MgFe_2O_4 samples prepared from $\gamma\text{-Fe}_2\text{O}_3$ show a particle size distribution (Fig. 3) up to $3\ \mu\text{m}$, except for the ferrite MgHEM in which a wide range in sizes up to $6\ \mu\text{m}$ is observed.

$\text{Mg}\gamma\text{FA}$, $\text{Mg}\alpha\text{FA}$ and MgAmpFA

The sample $\text{Mg}\gamma\text{FA}$, shows $\sim 72\%$ particles between $1\text{--}2\ \mu\text{m}$, 22% grains $< 1\ \mu\text{m}$ and 6% in the range of $2\text{--}3\ \mu\text{m}$. The samples $\text{Mg}\alpha\text{FA}$ ($\gamma\text{-Fe}_2\text{O}_3$ source from

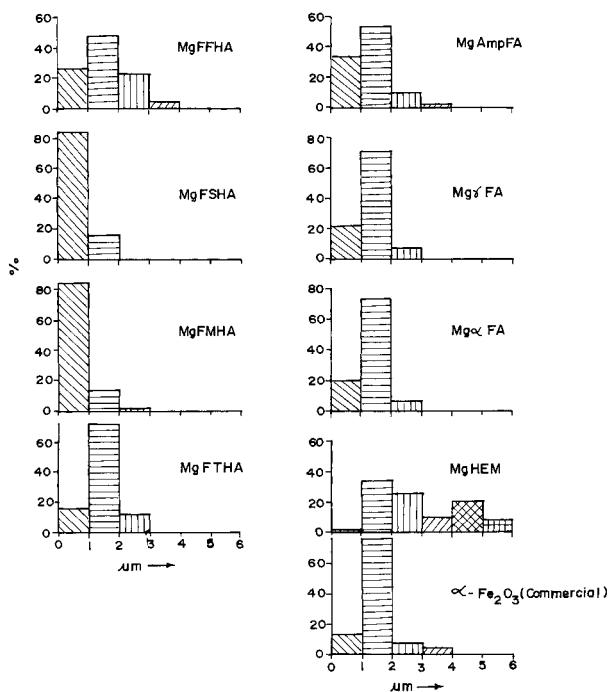
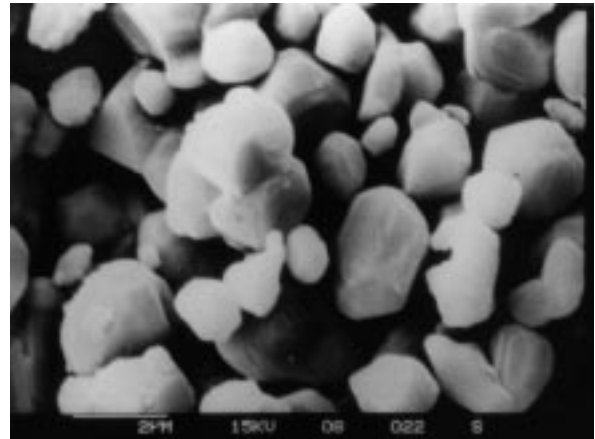
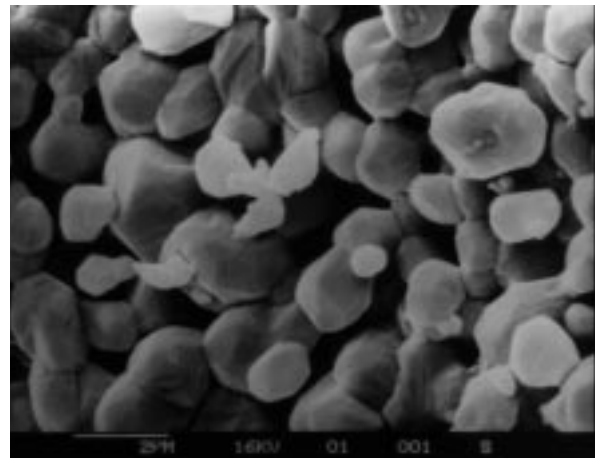


Figure 3 Particle size distribution of MgFe_2O_4 and commercial $\alpha\text{-Fe}_2\text{O}_3$.

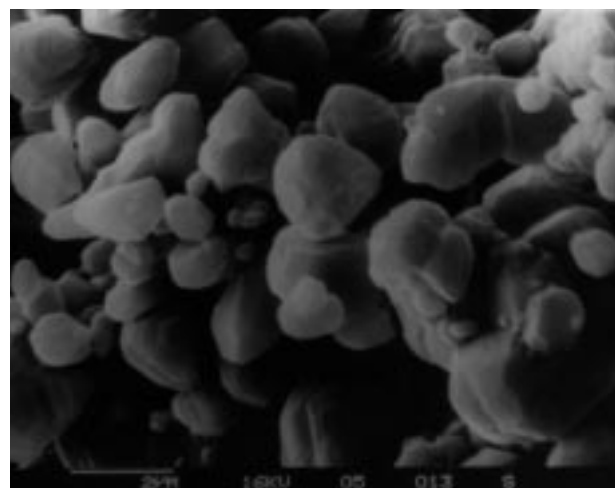
$\alpha\text{-FeOOH}$) and MgAmpFA ($\gamma\text{-Fe}_2\text{O}_3$ from amp. FeOOH) also show more or less similar grain size distribution to the $\text{Mg}\gamma\text{FA}$. The micrographs of these are shown in Fig. 4a ($\text{Mg}\gamma\text{FA}$), Fig. 4b ($\text{Mg}\alpha\text{FA}$) and Fig. 4c (MgAmpFA). There is a uniform grain size distribution in these samples. The measured porosity from X-ray density and actual density of these are similar: $23.63\text{--}26.41$ (Table II).



(a)



(b)



(c)

Figure 4 Scanning electron micrographs of MgFe_2O_4 : (a) $\text{Mg}\gamma\text{FA}$, (b) $\text{Mg}\alpha\text{FA}$ and (c) MgAmpFA .

MgFFHA, MgFSHA, MgFMHA and MgFTHA

The MgFe_2O_4 synthesized from $\gamma\text{-Fe}_2\text{O}_3$ obtained from iron (II) carboxylato-hydrazinates show a grain distribution of up to $3\ \mu\text{m}$. The MgFMHA and MgFSHA have $\sim 85\%$ grains $< 1\ \mu\text{m}$ and $\sim 14.4\%$ particles of $1\text{--}2\ \mu\text{m}$. A few particles of $2\text{--}3\ \mu\text{m}$ are also observed in MgFMHA. On the other hand, MgFFHA and MgFTHA show a majority of grains sized $1\text{--}2\ \mu\text{m}$. The SEM micrographs are shown in Fig. 5. The porosity of these range from 21–29%.

MgHEM

The MgFe_2O_4 prepared from commercial $\alpha\text{-Fe}_2\text{O}_3$ shows a wide range of grain size distribution (up to $6\ \mu\text{m}$). In Fig. 3 it can be seen clearly that 34% of particles are of $1\text{--}2\ \mu\text{m}$, 26% are $2\text{--}3\ \mu\text{m}$, 10% are $3\text{--}4\ \mu\text{m}$, 20% are $4\text{--}5\ \mu\text{m}$ and 8% are $5\text{--}6\ \mu\text{m}$ in size. Such a distribution of grains effectively makes these samples more porous (SEM micrograph Fig. 6) and the porosity observed from X-ray density and actual density is 42%.

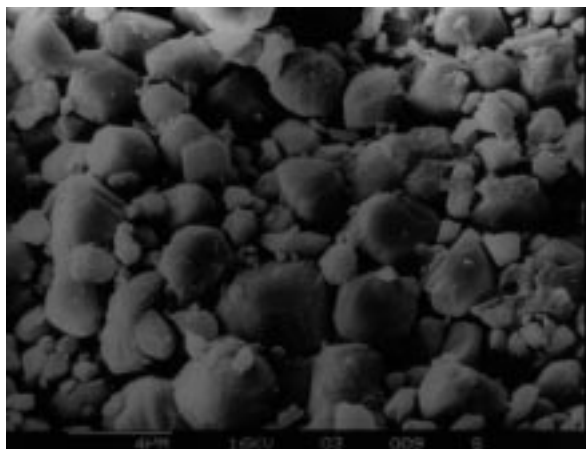
Thus, all samples, except MgHEM, show uniform microstructure. This leads to different magnetic characteristics, as observed in our studies.

3.3.2. Reactivity of iron oxides leading to MgFe_2O_4

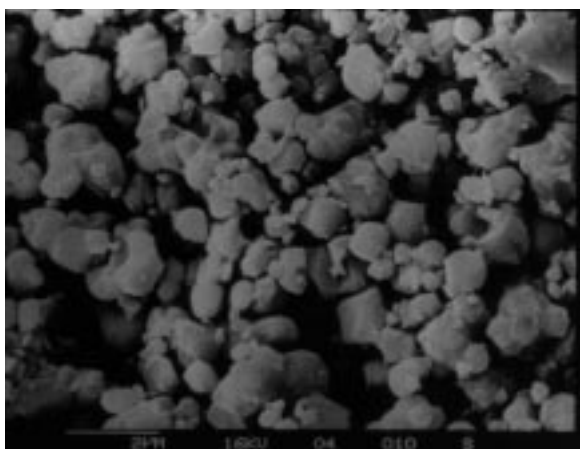
The MgFe_2O_4 synthesized from iron oxide (mainly $\gamma\text{-Fe}_2\text{O}_3$) obtained from different sources show similar micro-structural characteristics with a majority of grains sized $< 2\ \mu\text{m}$. The MgFe_2O_4 obtained from commercial $\alpha\text{-Fe}_2\text{O}_3$ (MgHEM), however, shows particles up to $6\ \mu\text{m}$ with different grain sizes. The iron oxide (mainly $\gamma\text{-Fe}_2\text{O}_3$) sources used for the synthesis of MgFe_2O_4 are from autocatalytically decomposed iron (II) carboxylato-hydrazinates and hydrazinated iron oxyhydroxides. The autocatalytic decomposition leads to oxides of uniform particle size with very high surface area.

The BET surface area of iron oxides (mainly $\gamma\text{-Fe}_2\text{O}_3$) measured by using volumetric adsorption of nitrogen at liquid nitrogen temperature on a few samples are shown to be $30\text{--}70\ \text{m}^2\ \text{g}^{-1}$ and SEM micrographs also indicated a uniform distribution of particles of $10\text{--}30\ \text{nm}$ size. Representative micrographs of FSHA and γFA are shown in Fig. 7a and b, respectively. These iron oxides then react with MgCO_3 and the samples sintered at $1000\ ^\circ\text{C}$ show $< 3\ \mu\text{m}$ size grains in the ferrite, as described above.

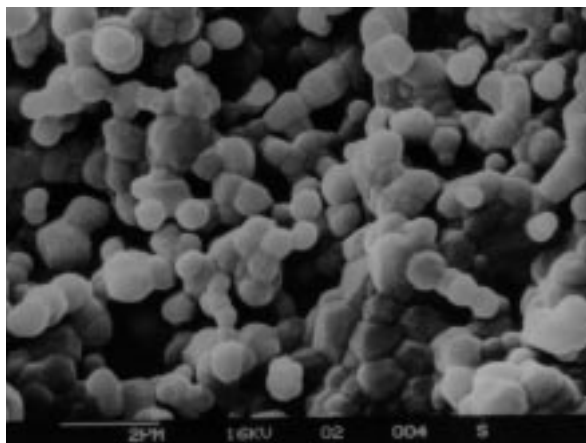
On the other hand, the wide distribution of particle size in MgFe_2O_4 (MgHEM) obtained from commer-



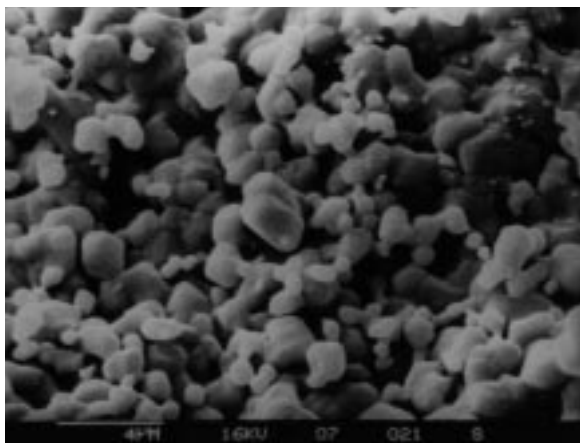
(a)



(b)

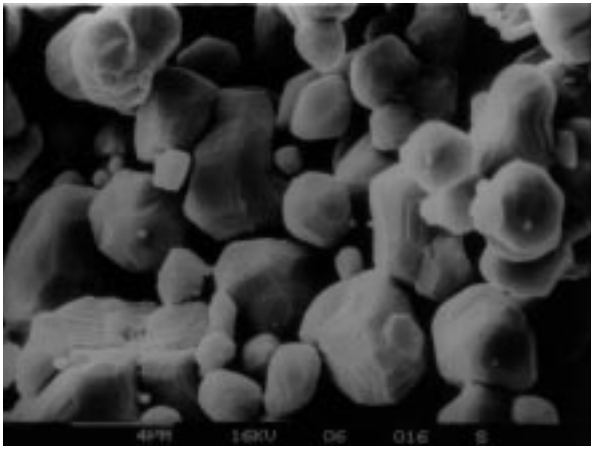


(c)

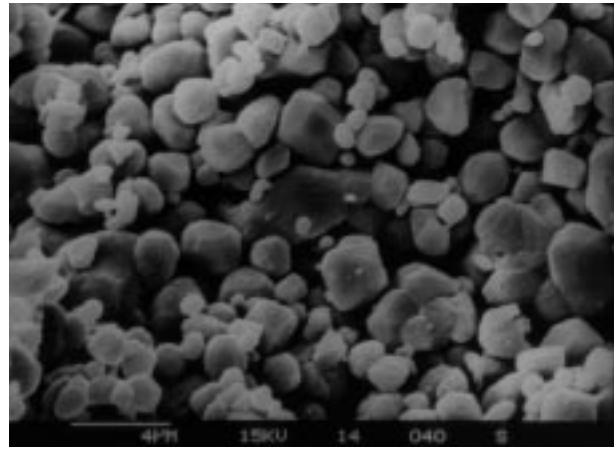


(d)

Figure 5 Scanning electron micrographs of MgFe_2O_4 : (a) MgFFHA, (b) MgFSHA, (c) MgFMHA and (d) MgFTHA.



(a)



(b)

Figure 6 Scanning electron micrographs of (a) MgFe_2O_4 : MgHEM (from commercial $\alpha\text{-Fe}_2\text{O}_3$) and (b) commercial $\alpha\text{-Fe}_2\text{O}_3$

cial $\alpha\text{-Fe}_2\text{O}_3$ may be due to the large grain size of 1–2 μm observed in this oxide. In Fig. 3 and Fig. 6b it can be clearly seen that $\alpha\text{-Fe}_2\text{O}_3$ (commercial) has 76% of grains 1–2 μm , 13% grains < 1 μm , 7% particles are in the range 2–3 μm , 4% are 3–4 μm . Such a large grain sized $\alpha\text{-Fe}_2\text{O}_3$ material compared to small sized $\gamma\text{-Fe}_2\text{O}_3$ is responsible for the wide range of particles in the ferrites with large porosity, as observed in MgHEM (Fig. 6a). The small grain $\gamma\text{-Fe}_2\text{O}_3$ samples, however, give uniform and smaller particles of ferrites with uniform porosity but less than MgHEM. These observations indicate that nanometer size particles give uniform 1–3 μm size ferrites at 1000 $^\circ\text{C}$ allowing further scope to increase the particle size by increasing the sintering temperature, giving better characteristics. However, non-uniform particles in MgHEM may further enhance non-uniform grains. Further studies on the influence of sintering temperature on grain size and magnetic characteristics are in progress.

4. Conclusion

1. Iron (II) carboxylato-hydrazinates and iron oxyhydroxides obtained from iron ore rejects decompose autocatalytically giving mainly $\gamma\text{-Fe}_2\text{O}_3$. A few traces of $\alpha\text{-Fe}_2\text{O}_3$ are found in some samples.

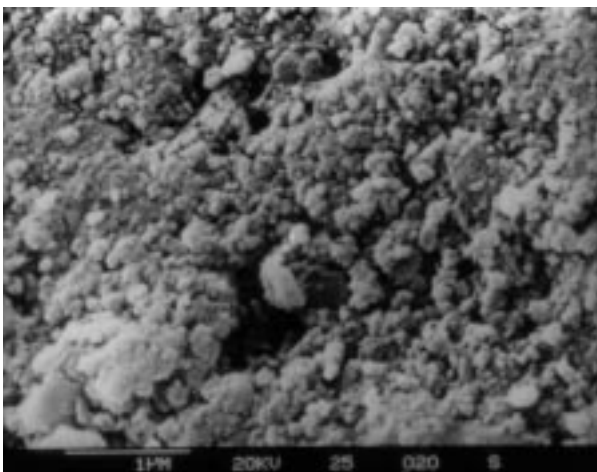
2. The iron oxides (mainly $\gamma\text{-Fe}_2\text{O}_3$) yield single phase MgFe_2O_4 when mixed with MgCO_3 and heated $\sim 1000^\circ\text{C}$.

3. Commercial $\alpha\text{-Fe}_2\text{O}_3$ (hematite) plus MgCO_3 at $\sim 1000^\circ\text{C}$ give mainly MgFe_2O_4 with a few traces of $\alpha\text{-Fe}_2\text{O}_3$, suggesting single phase spinel is not formed.

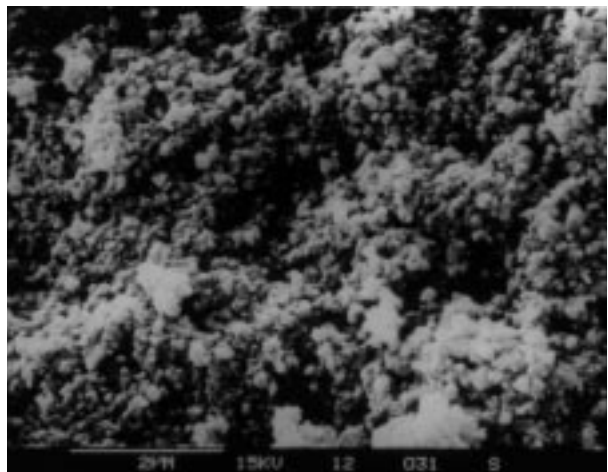
4. MgFe_2O_4 prepared from commercial $\alpha\text{-Fe}_2\text{O}_3$ shows high porosity of $\sim 42\%$, while $\gamma\text{-Fe}_2\text{O}_3$ sources result in ferrites of porosity $\sim 25\%$.

5. A low saturation magnetization value of 609 G is observed for MgFe_2O_4 prepared from $\alpha\text{-Fe}_2\text{O}_3$, whereas the ferrite obtained from all $\gamma\text{-Fe}_2\text{O}_3$ sources show values between 922–1168 G.

6. Curie temperatures T_c of 730, 742 and 739 K are observed for MgFe_2O_4 obtained from $\alpha\text{-Fe}_2\text{O}_3$ from the



(a)



(b)

Figure 7 Scanning electron micrographs of $\gamma\text{-Fe}_2\text{O}_3$ (a) FSHA and (b) γFA .

temperature variation of magnetic susceptibility, initial permeability and resistivity. All other samples showed T_c values lower than this, which are close to the reported values.

7. Uniform grain size in the range of 0–3 μm is observed for MgFe_2O_4 from nanometer size $\gamma\text{-Fe}_2\text{O}_3$ prepared from hydrazine precursors. A large distribution in particle size, 0–6 μm , is indicated by MgFe_2O_4 synthesized from commercial grade $\alpha\text{-Fe}_2\text{O}_3$ of mainly 1–2 μm size grains.

8. The uniform grain size distribution found in MgFe_2O_4 obtained from $\gamma\text{-Fe}_2\text{O}_3$ sources give further scope to increase sintering temperature to achieve better magnetic characteristics.

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