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Influence of dopants on the properties of maghemite

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Preparation of acicular maghemite containing dopants like Mg, Ni and Gd and their characterisation using different analytical techniques have been reported. These investigations reveal that the addition of dopants like Mg, Ni and Gd modifies the magnetic properties without effecting any structural changes. The optical bandgaps of these doped compositions have also been determined. Evidence is also available from spectroscopic investigations suggesting that maghemite prepared via the oxalate precursor route does not exhibit a hydrogen ferrite structure.

1 Introduction

Maghemite (γ-Fe_2O_3) and materials derived from γ-Fe_2O_3 in the acicular form find applications as a magnetic storage medium[1]. About 90 % of audio/video and computer diskettes employ these needle shaped gamma ferric oxides either in the particulate or thin film form[2]. The γ-Fe_2O_3 is a widely used material for recording media because it has the ideal combination of hysteresis loop parameters such as saturation magnetisation (Ms), coercivity (Hc) and squareness ratio (Mr/Ms). It is generally preferred in the form of acicular single domain particles[3]. The need for single domain particles is for obtaining optimum value of coercive force[4]. The acicular shape is for better alignment of particles while on recording which in turn is related to signal to noise ratio[5]. Gamma ferric oxide is also used as a potential catalyst in petrochemical industry[6]. Hence studies relating to gamma ferric oxide and gamma ferric oxide based materials are commercially very important. It has also been discovered recently that polymer nanocomposites containing gamma iron oxide exhibit novel properties like superparamagnetism and are potential materials for magnetic refrigeration[7,8].

Gamma ferric oxide is a vacancy ordered spinel having the structure $Fe^{3+}[(Fe^{3+})_{5/3}\square_{1/3}]O_4$ where the vacancies are exclusively concentrated on the octahedral sites[9]. These vacancies give scope for doping gamma ferric oxide with cations having octahedral site preferences, thereby leading to modification of magnetic properties without altering its basic structure. This will lead to thermal stability[10]. There are also reports stating that γ-Fe_2O_3 exhibits a structure similar to hydrogen ferrite having the formula $Fe_8[H_4Fe_{12}]O_{32}$ (Ref. 11). The addition of dopants into the γ-Fe_2O_3 lattice has been known to modify the magnetic properties[12]. Here in this study pure and doped acicular γ-Fe_2O_3 have been prepared using acicular ferrous oxalate dihydrate precursors[13]. Dopants like magnesium, nickel and gadolinium were incorporated in to the lattice. These were then characterised using XRD, UV-VIS-NIR, FTIR and magnetic measurements. Doping may effect changes in symmetry and also on the optical bandgap. Changes if any, introduced by doping can be detected by using spectroscopy as an analytical tool.

2 Experimental Details

2.1 Synthesis of gamma iron oxide containing dopants

Gamma ferric oxide containing dopants were prepared in the form of acicular particles by employing acicular oxalate precursors[14]. The oxalate precursors containing the appropriate dopants were decomposed in an inert atmosphere containing oxygen free nitrogen at around 400 °C to yield Fe_3O_4 which was then carefully oxidised to doped gamma ferric oxide at around 200 °C. The preparation scheme is depicted in the form of a flow chart (Fig. 1).

2.2 Characterisation

2.2.1 Structural studies — Powder diffractograms were recorded on a Philips PW1140 diffractometer using CuK_α radiation. The lattice parameters for pure and doped γ-Fe_2O_3 were evaluated assuming cubic symmetry.

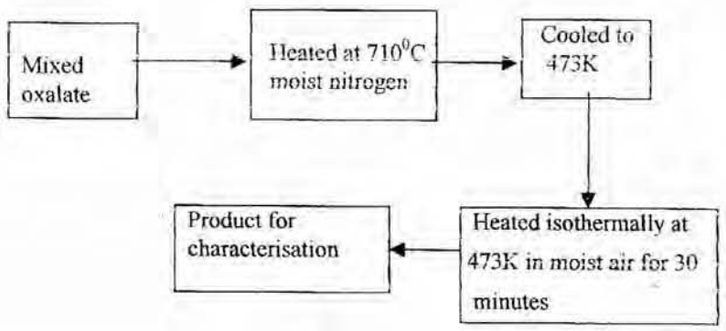

Fig. 1 — Preparation details of doped acicular gamma ferric oxide

2.2.2 Morphology studies — The optical micrographs and TEM of some representative samples were recorded by using optical microscope (Versamet 2) and TEM (Philips EM 301) respectively.

2.2.3 Magnetisation measurements — Magnetisation measurements on magnesium and nickel doped samples were carried out using hysteresis loop tracer (HLT) (Ref. 15). Magnetic properties such as saturation magnetisation, coercivity and squareness ratio were evaluated by using HLT.

2.2.4 Spectroscopic studies — UV-VIS-NIR absorption spectra of pure and doped γ-Fe_2O_3 samples were charted by using Hitachi UV-VIS-NIR spectrophotometer (model U3410). The optical band gap of these samples was evaluated from the spectra by noting the wavelength λ_g corresponding to the absorption edge. The energy corresponding to this wavelength was calculated using the formula

$$E_g = hc/\lambda_g$$

FTIR spectra of these samples were also recorded to find out different IR absorption bands. The spectrum was charted on a FTIR spectrophotometer (Schimadzu 8101) in the range 1500-400 cm^{-1}.

3 Results and Discussion

3.1 Structural studies

X-ray powder diffractograms were recorded for pure and doped compositions. Lattice parameters for pure and doped samples were calculated under the assumption that they crystallize in the spinel structure. The details are given in Tables 1, 2 and 3 for magnesium, nickel and gadolinium doped samples respectively. The lattice parameters were found to be 0.833nm, 0.830 nm and 0.832 nm for Mg, Gd and Ni doped samples. It can be seen that doping do not effect any notable change in lattice parameter. The absence of any increasing or

Table 1 — Lattice parameter, magnetisation data and optical bandgap for magnesium doped γ-Fe_2O_3 samples

Dopant concentration in atomic %	Lattice parameter in nm	Saturation magnetisation M_s in Am^2/kg	Coercivity H_c in A/m	Optical bandgap in eV
0	0.834	77	19900	1.84
1	0.833	89	25950	1.83
2	0.833	100	21492	1.83
4	0.833	76	18308	1.85
6	0.833	91	21492	1.81
8	0.834	81	16716	1.84
10	0.833	80	15920	1.84
16	0.833	86	15920	1.84

Table 2 — Lattice parameter, magnetisation data and optical bandgap for nickel doped γ-Fe_2O_3 samples

Dopant concentration in atomic %	Lattice parameter in nm	Saturation magnetisation M_s in Am^2/Kg	Coercivity H_c in A/m	Optical bandgap in eV
0	0.834	77	19900	1.84
1	0.832	83	17910	1.83
4	0.832	78	19900	1.72
8	0.832	73	18308	1.72
16	0.834	74	19900	1.83

decreasing trend in lattice parameter with increase in dopant concentration can be attributed to the following.

These cations have the right ionic radii to fill the octahedral voids of the spinel lattice. An ideal close packed structure consisting of rigid ions in the tetrahedral interstices should permit ions with maximum ionic radii of 0.04 nm and whereas the octahedral ones can have a maximum radius of 0.073 nm (Refs. 9,16). Since the ionic radii of nickel, magnesium and gadolinium are greater than 0.04 nm, it is right to assume that they occupy octahedral sites. Normally in order to accommodate larger sized ions the lattice should expand. Since we do not observe any increase in lattice parameter it is presumed that these ions occupy octahedral vacancies.

3.2 Morphological studies

The optical and TEM micrographs of some representative samples are shown in Figs 2(a) and 2(b). These micrographs confirm the acicular nature of the precursors as well as that of maghemite.

Table 3 — Lattice parameter and optical bandgap for gadolinium doped γ-Fe_2O_3 samples

Dopant concentration in atomic %	Lattice parameter in nm	Optical bandgap in eV
0	0.834	1.84
1	0.830	1.93
2	0.834	1.82
4	0.834	1.84
6	0.832	1.69
8	0.833	1.85

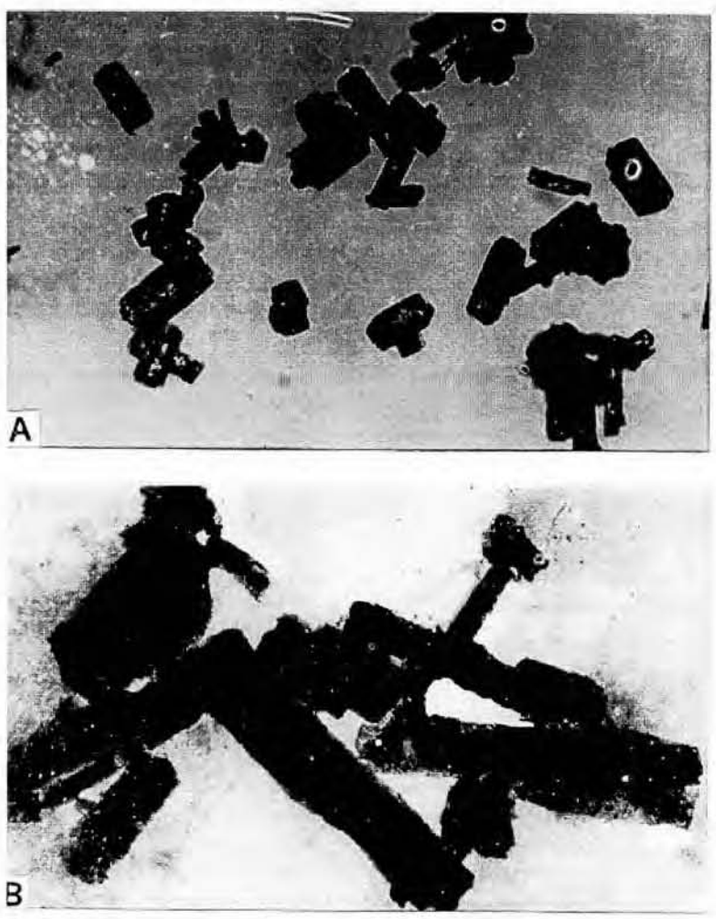

Fig. 2 — (a) Optical micrograph of acicular ferrous oxalate dihydrate precursors; (b) Transmission electron micrograph of γ-Fe_2O_3 prepared using precursors

3.3 Magnetic measurements

Saturation magnetisation (Ms) and coercivity (Hc) of pure as well as magnesium and nickel doped samples are listed in Tables 1 and 2 for magnesium and nickel doped samples respectively. Doped gamma ferric oxide exhibits higher saturation magnetisation than that of pure gamma ferric oxide. Theoretically one should expect a steady increase in Ms with increase in dopant concentration. The expected gradual increase in Ms is not observed probably because due weightage for particle size effects is not given. Moreover, the presence of superparamagnetic particles even in small quantities can bring down the saturation magnetisation value considerably. Since the particle size measurements have not been carried out it is hard to conclude that only superparamagnetic particles are responsible for reduction in saturation magnetisation. It is also possible that some amount of alpha iron oxide is present in these samples which is out of the detectable limits of XRD. These doped samples exhibit a relative increase in saturation magnetisation with respect to pure γ-Fe_2O_3. Since the dopant concentration is very small and a thorough chemical analysis is not performed on these samples, these inferences are only tentative. Coercivity (Hc) largely depends on magnetocrystalline anisotropy, and in this case it does not show any specific trend.

3.4 Spectroscopic studies

Absorption spectra were recorded to determine the influence of dopants on the bandgap of these materials. From the UV-VIS-NIR absorption spectra the optical bandgap for pure and doped γ-Fe_2O_3 were calculated and are listed in Tables 1,2 and 3 for magnesium, nickel and gadolinium doped samples respectively. The bandgap calculation employing the method of absorption edge involves an error of < 2 %. It is seen that pure γ-Fe_2O_3 exhibits a bandgap of 1.84 eV, while doped compositions except 6 % gadolinium and 4 and 8 % nickel doped samples have almost the same bandgap as that of pure γ-Fe_2O_3. This gives complementary evidence to the inference drawn from the structural characterisation that no significant structural changes are effected by doping. In the case of 6 % gadolinium and 4 and 8 % nickel doped samples the bandgap is found to be less than that of pure gamma ferric oxide. This may be due to the presence of alpha ferric oxide which may be present in the form of impurities.

Spectroscopy has been a valuable tool for detecting the fundamental vibrations of OH stretching[17]. This is especially true for determining the OH vibrations on oxide surfaces. Extensive investigations were carried out on γ-Al_2O_3 which resemble the structure of γ-Fe_2O_3. On alumina surfaces three bands are detected in the range 3700 to 3800 cm^{-1}. However at higher resolutions 5 bands can be observed. The five OH stretching bands which were observed during dehydroxylation of γ-Al_2O_3 surfaces were attributed to OH groups in distinct lateral surface environments. Thus the high wave number band at 3800 cm^{-1} was assumed to be characteristic for OH group with four oxide neighbours in the surfaces whereas the lowest band at 3700 cm^{-1} correspond to the OH group that has no oxide neighbours. The other OH groups which give rise to intermediate wave numbers at 3711, 3744 and 3780 cm^{-1} were assumed to be located at one, two and three nearest neighbour oxide ions respectively. If gamma ferric oxide crystallizes in the hydrogen ferrite structure as predicted by researchers[18], then bands due to OH should have been present in the spectra. We did not detect OH bands in the FTIR spectra. Our attempts to detect OH overtones in UV-VIS-NIR spectra was also in vain. Thus it may be noted that these conclusions drawn from the structural studies also points to the formation of a vacancy ordered spinel structure of gamma ferric oxide. This leads us to believe that gamma ferric oxide prepared via the oxalate precursor route has crystallised in the vacancy ordered spinel structure.

Normally compounds exhibiting spinel structure should possess four IR active modes leading to four IR bands in the spectra (Refs 19, 20). In the spinel lattice every oxygen anion is bonded to three octahedral and one tetrahedral cations as shown in Fig. 3. The three octahedral bonds are perpendicular to each other and hence provide an isotropic field. The tetrahedral cation

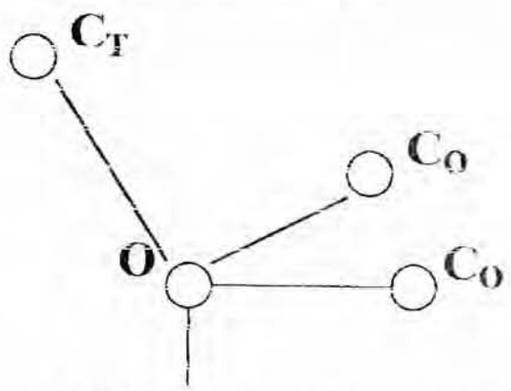

Fig. 3 — Bonding of the tetrahedral and octahedral cations with oxygen in the spinel lattice

C_T introduces a restoring force in a direction along C_T-O bond and this appears as stretching vibration of the tetrahedral group. Considering the vibration of oxygen atom at right angles with the preceding one this restoring force due to tetrahedral cation C_T will be negligible. This leads to ν_3 mode which can be considered as the stretching vibration of the octahedral group. Two other modes ν_3 and ν_4 are related to the displacement of cations in the lattice.

FTIR spectra of the pure as well as doped gamma ferric oxide were charted in the range 1500-400 cm^{-1} and a representative spectrum is shown in Fig. 4. Bands characteristics of these samples were obtained in the range 700-400 cm^{-1}. Peaks were obtained at around 636, 555 and 443 cm^{-1}. Bands at 636 and 555 cm^{-1} may be assigned to the stretching vibrations of tetrahedral and octahedral groups respectively. The bands related to ν_3 and ν_4 can be assigned to the motion of Fe^{3+} ions to the tetrahedral sites against those at the octahedral sites and the O-Fe-O bonding mode of the tetrahedral to octahedral mode respectively. These bands are reported to be at 268 and 178 cm^{-1} which could not be detected because of the instrument limitations. The band at around 440 cm^{-1} may be assigned to the alpha phase of iron oxide that may be present in the sample. However discrepancy exists in the 4 and 8 % nickel doped samples, which may be due to impurities present in minute amounts.

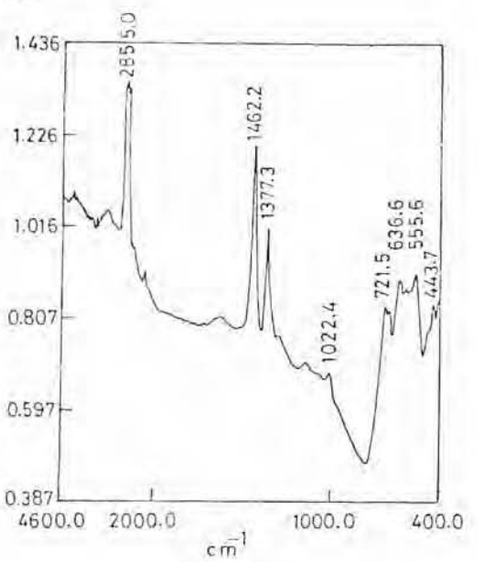

Fig. 4 — A representative FTIR spectrum (1 % Mg doped γ-Fe_2O_3)

4 Conclusion

The present studies conducted on doped gamma iron oxide indicate that saturation magnetisation (Ms) can be modified by an appropriate choice of cations. The advantage of employing oxalate precursor route is that doped oxides can be prepared in the acicular form. It can be concluded that spectroscopic studies can be used in conjunction with X-ray diffraction for evaluating the role of dopants and its effect, if any on the crystal structure. Though literature reports on the γ-Fe_2O_3 are varied our investigations indicate that it crystallises in the vacancy ordered spinel structure.

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