

Superparamagnetic behaviour of MgFe_2O_4 nano-ferrite

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ABSTRACT

In the present work, magnesium ferrite (MgFe_2O_4) nanostructures are fabricated by sol-gel method. Structural studies are carried out using X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). The XRD patterns of MgFe_2O_4 show single-phase formation of FCC spinel structure. The average particle size of samples sintered at different temperatures (300-800°C) is controlled in the nano-range i.e. ~ 10 nm. The crystallinity shows increment with increasing sintering temperature. Formation of spinel structure is confirmed using FTIR. The magnetic measurements are made from M-H hysteresis loops traced at room temperature using vibrating sample magnetometer (VSM). It is found that ferrites in the nanoregime are found to behave as single domain. The low temperature (300°C) sintered ferrite has almost zero coercivity and retentivity which shows superparamagnetic behaviour of the as-prepared ferrite.

Keywords: Ferrite; superparamagnetism; VSM.

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1. INTRODUCTION

Magnesium ferrite (MgFe_2O_4) belongs to the class of soft magnetic materials having spinel structure. This ferrite has low permeability, low saturation magnetization, high coercive forces and high electrical resistivity ($\rho \approx 10^2 \Omega\text{-m}$) [1]. It is one of the most important ferrites which has a cubic structure of normal spinel-type and is a soft magnetic n-type semiconducting material, and has a number of applications in heterogeneous catalysis, adsorption, sensors, and in magnetic technologies [2].

Superparamagnetic nanoparticles have attracted a lot of attention due to applications in ferrofluid technology, thermal sensing switches and magnetocaloric refrigeration. They also have been used in biomedicine and biotechnology as contrast agent in magnetic resonance imaging (MRI) and as drug carriers for magnetically guided drug delivery [3].

A number of methods have been developed to fabricate materials with nano structures such as: sol-gel method [4], ball milling (solid state reaction) route [5], wet chemical co-precipitation method [6], ceramic method [7], hydrothermal process [8], and citrate precursor method [9].

In this work, single phase, nanosized MgFe_2O_4 particles are synthesized by sol-gel method. The temperature dependent behaviours of the synthesized precursor are studied, and the

grain size, morphology as well as magnetic properties of the resultant nanocrystalline MgFe_2O_4 are also investigated.

2. EXPERIMENTAL PROCEDURE

2.1 SYNTHESIS METHOD

Nanosized magnesium ferrite (MgFe_2O_4) is synthesized using sol-gel method and then sintered at different sintering temperature. Chemicals required for synthesis of MgFe_2O_4 are: magnesium nitrate, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with molecular weight 256.41 (AR grade) and ferric nitrate $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ with molecular weight 404.00 (AR grade). Citric acid $\text{C}_6\text{H}_8\text{O}_7$ with molecular weight 192.13 (AR grade) is taken as catalyst. Aqueous solutions of metal nitrates are prepared separately in stoichiometric proportion by dissolving the salts in distilled water. Aqueous solution of citric acid is added to the salt solution with cation to citric acid molar ratio of 1:1. The solution is then heated at 80°C with continuous stirring for about 2 hours with the help of magnetic stirrer until a viscous gel is formed. The viscous gel is dried in an oven by overnight heating for about 20 hours at 120°C to form the dried precursor powder. This precursor is sintered at different temperatures ranging from 300-800°C for 1 hour in a furnace. Samples prepared after sintering are gently crushed with mortar and pestle to get powder for characterization.

2.2 CHARACTERIZATION TECHNIQUES

The X-ray diffraction (XRD) patterns of the samples are taken from PANALYTICAL instrument (X'pert pro) using Cu-K α ($\lambda= 1.54060 \text{ \AA}$) radiation. FTIR spectra are recorded in KBr medium in the range of 4000-375 cm^{-1} with a IR Prestige-21 FT-IR (Model SHIMADZU-8400S). Magnetization measurements are made through VSM (PAR 155 Model) at room temperature upto 8 KOe.

3. RESULTS AND DISCUSSIONS

3.1. XRD STUDY

X-ray diffraction patterns of MgFe_2O_4 ferrite yield promising results in the synthesis of fine nanoparticles at fairly low temperature. The sol-gel method facilitates the formation of well-crystalline single phase structure of MgFe_2O_4 crystallites. XRD patterns of MgFe_2O_4 samples prepared at different sintering temperatures i.e. at 300, 600, 800°C with pH less than 1, are shown in Fig. 1. It is clear that all the samples of the MgFe_2O_4 ferrites have FCC spinel structure due to the presence of (220), (311), (400), (422), (511), (440) and (533) reflection planes [10-12]. All the main peaks are indexed as the FCC spinel MgFe_2O_4 in the standard data files of Joint Committee on Powder Diffraction Standards, (JCPDS no. 88-1937). Well resolved peaks in XRD pattern clearly indicate the single phase and polycrystalline nature of the samples. It can be seen that no change in the crystal structure occurs when nanoparticles are prepared at different sintering temperatures

The lattice parameter 'a' is calculated using the formula [13] corresponding to prominent peak (311):

$a = d_{hkl} \sqrt{h^2 + k^2 + l^2}$ where 'a' is the lattice parameter of the unit cell, 'd_{hkl}' is the interplanar spacing and (h k l) are Miller indices of the plane. The required experimental values of interplanar distance d_{hkl} for prominent peak (311) of different samples, needed for the calculation, are shown in Table 1. The calculated values of lattice parameter of all samples are also given in Table1 which are in good agreement with the earlier reporters [14-15]. The lattice parameter 'a' which is determined as 8.386 Å matches well with JCPDS no. 88-1937. It is found that there is slight decrease in values of lattice constant with increase of sintering temperature. Similar trend was observed for copper zinc ferrites by P. Chand (2008) [16]. This behaviour may be related to normal-inverse spinel transitions, as a consequence of temperature increase.

The crystallite size (D) of the particle of synthesized powder is determined from XRD peak broadening of (311) peak using Scherrer's formula [13]:

$$D = \frac{0.9\lambda}{\beta \cos \theta}$$

where D is the average particle size, β is full width at half maximum (FWHM) in radians, λ is the wavelength, and θ is

the Braggs angle for the diffraction peak. The calculated values of particle size of the samples are given in Table 1. The required experimental values of peak position and FWHM for different samples, needed for the calculation, are also given in Table 1.

The bond length of tetrahedral (A-O) and octahedral (B-O) sites of cubic spinel structure have been estimated by using Standely's equations [17].

$$A - O = \left(u - \frac{1}{4}\right)a\sqrt{3}$$

$$B - O = \left(\frac{5}{8} - u\right)a$$

where 'a' is the lattice constant and 'u' is oxygen ion parameter ($u = 0.382$ for MgFe_2O_4). The calculated values of the bond lengths of tetrahedral (A-O) and octahedral (B-O) sites of cubic spinel structure of the samples are given in Table 1. The data shows complete relevance with the well known fact that bond length of octahedral site is greater than that of tetrahedral site.

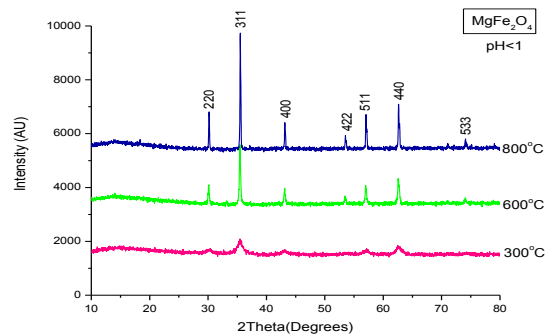


Fig.1: XRD patterns of MgFe_2O_4 ferrites sintered at different temperatures.

Slight variation observed in bond lengths is attributed to the respective values of lattice constant, higher values of lattice constant indicates decrease in covalent character .

It is found that that particle size remains almost constant as sintering temperature increases from 300°C to 800°C. This may be due to small pH value of the samples which is a controlling parameter of size for nanoparticles growth. It is observed that peaks get sharpen and intense with increasing sintering temperature, as expected for nanocrystalline materials. This is due to increase in crystallinity with increase in sintering temperature.

3.2. FTIR STUDY

FTIR spectrum is taken for the samples, prepared by grinding them with mortar and pestle into a mixture with KBr at approximately 1:10 mass ratio. The mixture is then pressed to make the thin pallets. The spectra of the samples are collected in the range of 4000-375 cm^{-1} with IR Prestige-21 FTIR (model-8400S) of Shimadzu Corporation.

TABLE 1: Peak position, d_{hkl} -spacing and FWHM of $MgFe_2O_4$ system sintered at different temperatures for (311) plane.

| Sintering Temperature(°C) | Position(°2Theta) | d_{311} - spacing(Å) | FWHM (°2Theta) | Particle size(nm) | Lattice-constant (Å) | Tetrahedral bond-length(Å) | Octahedral bond-length (Å) |
|---------------------------|-------------------|------------------------|----------------|-------------------|----------------------|----------------------------|----------------------------|
| 300 | 35.4141 | 2.53472 | 0.8029 | 10.382 | 8.406 | 1.922 | 2.043 |
| 600 | 35.4796 | 2.53020 | 0.8029 | 10.384 | 8.391 | 1.918 | 2.039 |
| 800 | 35.5035 | 2.52855 | 0.8029 | 10.385 | 8.386 | 1.917 | 2.038 |

Figure 2 presents the infrared spectra of ferrite system $MgFe_2O_4$ prepared at different sintering temperature. The FTIR spectra are found to exhibit two major bands in the range $375-600\text{ cm}^{-1}$. The high frequency band (ν_1) is in the range $560-580\text{ cm}^{-1}$ and the lower frequency band (ν_2) is in the range $390-410\text{ cm}^{-1}$. These bands are common characteristics of spinel structure. The vibration of unit cell of the cubic spinel can be constructed in the tetrahedral (A) site and octahedral (B) site. The absorption band (ν_1) is caused by stretching vibrations of the tetrahedral metal-oxygen bond and absorption band (ν_2) is caused by the metal-oxygen vibrations in octahedral sites [18]. The change in band position is expected because of the difference in the $Fe^{3+}-O^{2-}$ distances for tetrahedral and octahedral complexes. It is found that Fe–O distance of A-site (1.89 Å) is smaller than that of the B-site (1.99 Å). This can be interpreted by more covalent bonding of Fe^{3+} ions at A-sites than B-sites.

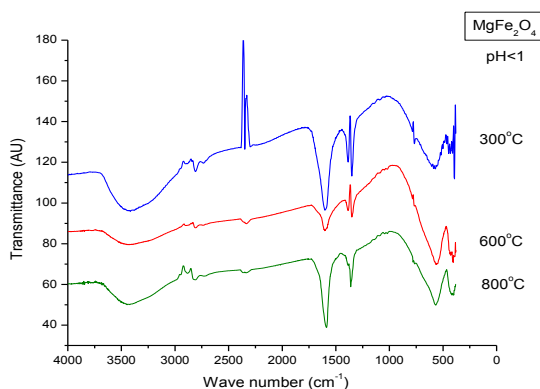


Fig. 2: FTIR patterns of $MgFe_2O_4$ ferrites sintered at different temperatures.

There is slight variation in band frequency positions of tetrahedral and octahedral sites (ν_1 , ν_2), for different samples. This is due to redistribution of cations among tetrahedral and octahedral sites, when samples are prepared as nanoparticles. More constructively, the increase in tetrahedral absorption frequency (ν_1) for some samples may be accounted to the transition from normal to inverse spinel. In an inverse spinel ferrite the tetrahedral site is occupied by Fe^{3+} ions and

octahedral site is occupied by Fe^{3+} and divalent ions. Due to charge imbalance the oxygen ion is likely to shift towards Fe^{3+} ions increasing the force constant between Fe and O. Hence we expect an increase in the tetrahedral band frequency (ν_1), as we go from normal to inverse spinel.

One more thing is observed in some samples that there is splitting of octahedral absorption band as shown in Figure 2, which may be due to presence of different cations at B-site; Mg^{2+} and Fe^{3+} ions, showing inverse or partial inverse spinel structure.

FTIR spectra of $MgFe_2O_4$ samples show some additional bands with strong absorption around $3600-3200\text{ cm}^{-1}$, $1650-1560\text{ cm}^{-1}$ and $1390-1340\text{ cm}^{-1}$ which correspond to the stretching modes of O–H group, bending vibration of N–H bond in amine ($-NH_2$) group and symmetrical stretching of N–O bond in nitro ($C-NO_2$) group respectively. Also small absorption at nearly 2808 cm^{-1} is due to $-CHO$ group. The presence of hydroxyl group is associated with water molecule, as water plays an important role in the formation of ferrites and their stabilization. No particular trend is observed in the absorption intensity due to functional groups in FTIR spectra of the samples. So, it appears that these groups are present in the samples during preparation of the spinel ferrites by sol-gel method and are not completely removed after sintering the samples at high temperature.

3.3. VSM STUDY

Magnetic Hysteresis loops of different $MgFe_2O_4$ ferrite samples are analyzed at room temperature up to the applied magnetic field 8 kOe using VSM (Model PAR 155, from Princeton Applied Research USA). $MgFe_2O_4$ nanoparticles show typical hysteresis behaviour. Hysteresis loops are plotted for the measurements of magnetic parameters, particularly saturation magnetization (M_s) and coercivity (H_c) of the nanoferrite.

Figure 3 shows the hysteresis loops of $MgFe_2O_4$ samples sintered at temperatures 300 and 800°C for 1 hour. The sample exhibits vanished hysteresis as the sintering temperature is lowered. First, smaller value of saturation magnetization is observed. Second, coercivity approaches to zero with decrease in sintering temperature.

TABLE 2: Particle size, saturation magnetization (M_s), coercivity (H_c) and remanent magnetization (M_r) of $MgFe_2O_4$ system sintered at different temperatures.

| Sintering Temperature (°C) | Particle size(nm) | Saturation Magnetization M_s (emu/g) | Coercivity H_c (Oe) | Remanent Magnetization M_r (emu/g) |
|----------------------------|-------------------|--|-----------------------|--------------------------------------|
| 300 | 10.382 | 7.40 | ≈ 0 | ≈ 0 |
| 800 | 10.384 | 37.10 | 18.66 | 1.10 |

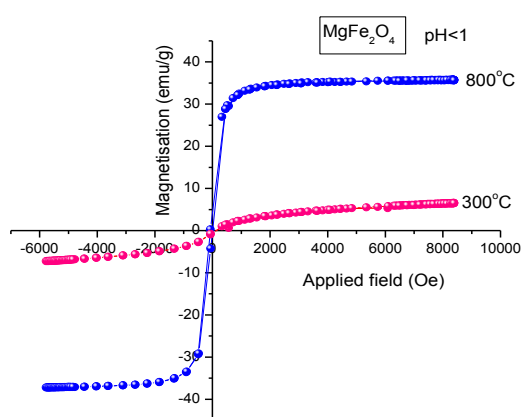


Fig. 3: Room temperature hysteresis loops of $MgFe_2O_4$ ferrites sintered at different temperatures.

The observed values of saturation magnetization and coercivity of $MgFe_2O_4$ ferrites sintered at 300 and 800°C are listed in Table 2. An appreciable decrease in the saturation magnetization (M_s) of the sample sintered at 300°C (≈ 7.40 emu/g) than one sintered at 800°C (≈ 37.40 emu/g) is found. It is found that the coercivity (H_c) decreases for the sample sintered at 300°C (≈ 0 Oe) as compared to sample sintered at 800°C (≈ 18.66 Oe).

The small value of coercivity may be attributed to the small size of the ferrite particle. Nanoparticles prepared are small enough that have reached single domain range and due to the randomizing effects of thermal energy, coercivity is very less.

A single domain particle of volume v has a uniform magnetization directed along the easy axis of magnetization. If v is small enough and the temperature is high enough that thermal energy will be sufficient to overcome the anisotropy energy causing a spontaneous reversal of magnetization. Coercivity (H_c) decreases due to thermal activation of magnetic spins below a critical volume and finally vanishes at superparamagnetic critical volume [19].

CONCLUSIONS

The investigation in the present work indicates that the sol-gel method is efficient for synthesizing $MgFe_2O_4$ nanoparticles possessing unique spinel structure, superparamagnetic properties and enhanced magnetic properties that occur when the material dimensions are reduced to nanoscale. Apart from size of the particles, the behaviour of nanoferrites also depends upon preparation parameters. The samples are resulting in comparatively smaller magnetizations and coercivities as the sintering temperature is lowered.

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