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EFFECT OF SINTERING TEMPERATURE ON THE STRUCTURAL AND MAGNETIC PROPERTIES OF COBALT FERRITE NANOPARTICLES

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Cobalt ferrite nanoparticles have been synthesized by the sol-gel method. The prepared sample was sintered at four different temperatures (300 ° C, 400 ° C, 500 ° C and 700 ° C) for four hours. The structural characterizations of all the prepared samples were done using XRD, TEM and FTIR. Crystallite size was found to increase with sintering temperature and this can be attributed to the grain growth of the particles. The particle size of each sample was determined using TEM. The FTIR spectra show two strong absorption bands in the range of 1000–400 cm^{-1}, characteristic of spinel ferrites. The room temperature magnetic measurements showed a strong influence of sintering temperature on saturation magnetization and coercivity.

Keywords: sol gel, ferrites, sintering temperature, magnetic properties.

1. Introduction

Nanosized spinel ferrite particles have attracted much attention in recent years because of their potential applications in high density magnetic recording, magnetic fluids, spintronics, data storage and gas sensors [1, 2]. Among the ferrite nanoparticles, cobalt ferrite has been widely studied due to its excellent chemical stability, mechanical hardness, reasonable saturation magnetization and high magneto-crystalline anisotropy [3]. These properties make it a promising candidate for many applications, such as magnetic data storage, magnetic drug targeting, biosensors and magnetic refrigeration [4].

Nano ferrites are simultaneously good magnetic and dielectric materials. These properties of the nano ferrites are affected by the preparation conditions, chemical composition, sintering temperature and the method of preparation [5]. Several chemical and physical methods such as spray pyrolysis, sol-gel, co-precipitation, combustion technique, high energy milling etc. have been used for the fabrication of stoichiometric and chemically pure nano ferrite materials [6]. Among the available chemical methods, the sol-gel technique is an excellent method to synthesize nanoparticles with maximum purity [7]. This method has the advantage of good stoichiometric control and the production of ultrafine particles with a narrow size distribution.

Mathew George et al [2] studied the effect of finite size on the structural and magnetic properties of nickel ferrite nanoparticles. They reported a decrease in saturation magnetization with decreased grain size. Chinnasamy et al [9] reported the synthesis of cobalt ferrite nanoparticles by co-precipitation method. They observed that the magnetic properties of cobalt ferrite nanoparticles are strongly dependent on their size. In spite of the development of a variety of synthesis routes, the production of cobalt ferrite nanoparticles with desirable size and magnetic properties is still a challenge. This would justify any effort to produce size tuned cobalt ferrite nanoparticles with size ranging from the superparamagnetic threshold of 10 nm to the critical single domain size of 70 nm [10, 11]. In

the present paper, the structural and magnetic properties of nanocrystalline cobalt ferrite in relation to sintering temperature were investigated.

2. Experimental

2.1. Synthesis

Nano particles of cobalt ferrite were synthesized by the sol-gel combustion method. A stoichiometric ratio of cobalt nitrate and ferric nitrate (AR grade MERCK) were dissolved in ethylene glycol using a magnetic stirrer. The solution was then heated at 60 ° C for 3 hours until a wet gel of the metal nitrates was obtained. The gel was then dried at 120 ° C. This resulted in the self ignition of the gel producing a highly voluminous and fluffy product. The combustion can be considered as a thermally induced redox reaction of the gel wherein ethylene glycol acts as the reducing agent and the nitrate ion acts as an oxidant. The nitrate ion provides an oxidizing environment for the decomposition of the organic component. The obtained powder was ground well and divided into four portions. They were sintered for four hours in a muffle furnace at four different temperatures 300, 400, 500 and 700 ° C.

2.2. Characterization

The cobalt ferrite samples were characterized by an X-ray powder diffractometer (XRD, Bruker AXS D8 Advance) using Cu-Kα radiation (λ = 1.5406Å) at 40 kV and 35 mA. Lattice parameter was calculated assuming cubic symmetry. The crystal structure, crystallite size and X-ray density were determined. The particle size was determined by subjecting the sample to Transmission Electron Microscopy (Philips, CM200). Wavelength Dispersive X-ray Fluorescence (WD-XRF) Spectrometer (Bruker S4-Pioneer) was used for elemental analysis. The Fourier transform infrared (FTIR) absorption spectra of the samples were recorded using FTIR spectrometer (Thermo Nicolet, Avatar 370) in the wave number range 4000–400 cm^{-1} with Potassium bromide (KBr) as binder. The Magnetic characterization was carried out using a vibrating sample magnetometer (VSM; Lakeshore 7410) at room temperature up to a maximum field of 20kOe.

3. Results and Discussion

3.1. Structural Analysis

The XRD patterns of $CoFe_2O_4$ nanoparticles sintered at 300, 400, 500 and 700 ° C are depicted in Fig. 1 and are typical of spinel structure.

Comparing the XRD pattern with the standard data (JCPDS PDF card No. 22-1086), the formation of cobalt ferrite nanoparticles was confirmed. The sample sintered at 700 ° C showed an extra peak, indicating the formation of hematite phase at this temperature. The diffraction peaks are broad because of the nanometer size of the crystallite. The crystallite size 'D' of the samples has been estimated from the broadening of XRD peaks using the Scherrer equation [7].

$$D = \frac{K\lambda}{\beta \cos\theta} \tag{1}$$

The lattice parameter 'a' is calculated for prominent peak (311) using Bragg's equation.

$$a = d_{hkl}\sqrt{h^2 + k^2 + l^2} \tag{2}$$

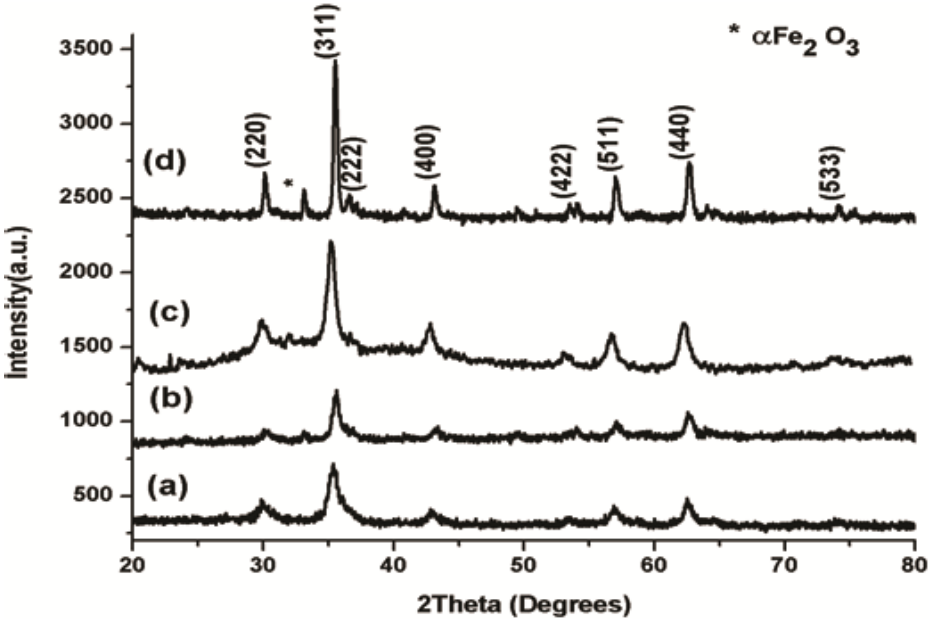

Fig. 1. XRD patterns of $CoFe_2O_4$ sintered at (a) 300 ° C, (b) 400 ° C, (c) 500 ° C, (d) 700 ° C

The actual X-ray density, ρ_x was calculated using the formula

$$\rho_x = \frac{8M}{Na^3} \tag{3}$$

where, 'M' is the molecular weight, 'N' is Avogadro's number and 'a' is the lattice parameter. Calculated values of lattice parameter, crystallite size and X-ray density of all the samples are listed in Table 1.

Table 1. Lattice parameter, crystallite size, X-ray density and vibrational frequency band positions of $CoFe_2O_4$

Sintering temperature (° C)	Lattice parameter (nm)	Crystallite size D (nm)	X-ray density (g/cc)	$\nu 1$ (cm^{-1})	$\nu 2$ (cm^{-1})
300	0.841	12.82	5.243	575	397
400	0.836	18.47	5.330	581	399
500	0.842	19.72	5.217	575	399
700	0.838	52.49	5.306	580	405

The crystallite size was observed to increase with higher sintering temperatures. It has been reported that the sintering process generally decreases lattice defects and strain, but this technique can cause the coalescence of smaller grains, resulting in an increased average grain size for the nanoparticles [12]. Calculated values of lattice parameter of cobalt ferrite samples were in close agreement with standard data [13].

3.2. WD-XRF Analysis

The stoichiometry of the powder samples were checked by WD-XRF analysis. The composition of the elements present in the sample sintered at 400 ° C is shown in Table 2.

From the table it is obvious that the samples show the expected stoichiometry. No trace of any impurity was found. This indicated the purity of the samples.

Table 2. Elemental analysis of $CoFe_2O_4$

Elements present	Expected (wt. %)	WD - XRF (wt. %)
Co	25.11	25.25
Fe	47.61	47.30
O	27.26	27.30

3.3. TEM Analysis

Fig. 2 shows the TEM image of $CoFe_2O_4$ sample sintered at 400 °C. In the figure most of the nanoparticles appear with an almost spherical shape and are agglomerated. The average particle size determined from TEM analysis was 28 nm, which was found to be in reasonable agreement with the figure obtained from XRD analysis.

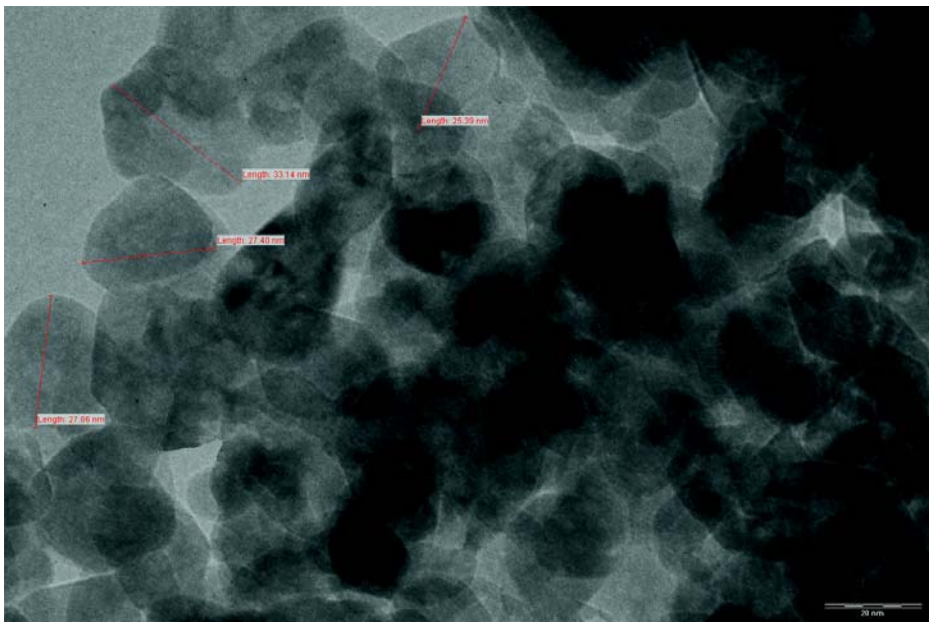

Fig. 2. TEM image of $CoFe_2O_4$ sintered at 400 °C

3.4. FTIR Analysis

Ferrite possesses the structure of mineral spinel $MgAl_2O_4$. It crystallizes in the cubic form with the space group Fd3m. Ferrite can be considered as a continuously bonded crystal with atoms bonded to all nearest neighbours by equivalent forces [14]. In the wave number range 1000–300 cm^{-1}, the infrared bands of solids are usually assigned to vibration of ions in the crystal lattice. FTIR spectra of the investigated samples are shown in Fig. 3.

Two main broad metal-oxygen bands are seen in the IR spectra of all spinels, and ferrites in particular. The highest one ($\nu 1$) generally observed in the range 600–550 cm^{-1}, corresponds to intrinsic stretching vibrations of the metal at the tetrahedral site, whereas the lowest band ($\nu 2$), usually observed in the range 450–385 cm^{-1}, is assigned octahedral-metal stretching [15]. The spectra showed prominent bands near 3400 and 1600 cm^{-1},

which were attributed to the stretching modes and H-O-H bending vibrations of the free or absorbed water. The vibrational frequencies of IR bands are listed in table 1, which are in agreement with the reported values.

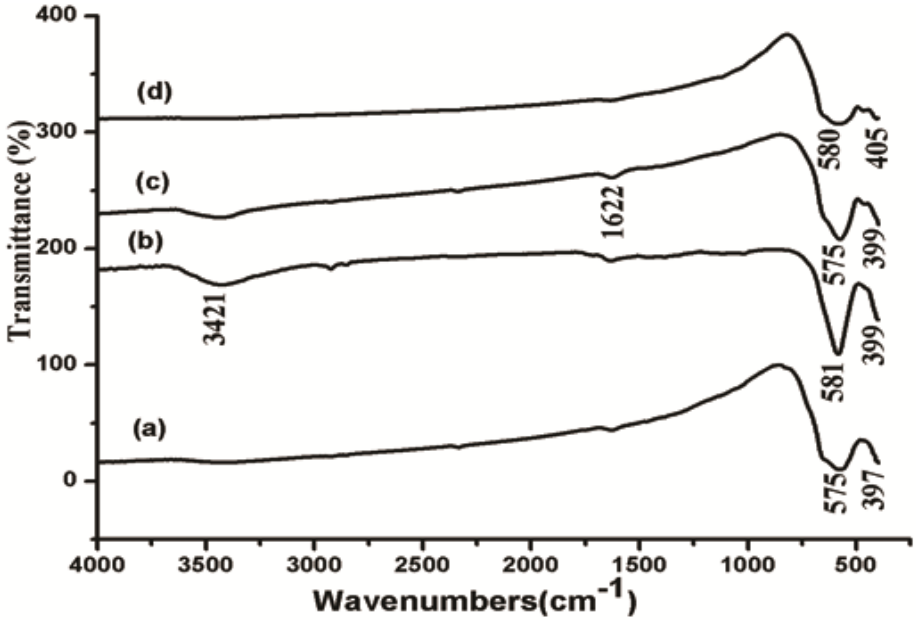

Fig. 3. FTIR spectra of $CoFe_2O_4$ sintered at (a) 300 ° C (b) 400 ° C (c) 500 ° C (d) 700 ° C

4. Magnetic Properties

Hysteresis loops were measured to determine magnetic parameters such as the saturation magnetization M_s, coercivity H_c and remnant ratio R for all the samples. Fig. 4 shows the typical magnetic hysteresis loops of $CoFe_2O_4$ sintered at 300, 400, 500 and 700 ° C.

The saturation magnetization values of the cobalt ferrite samples were found to be lower than the corresponding bulk value of 80.8 emu/g [1]. The low value of saturation magnetization compared with that of the bulk can be understood on the basis of the core- shell model, which explains that the finite size effects of the nanoparticles lead to canting or non-collinearity of spins on their surface, thereby reducing magnetization [16, 17]. The saturation magnetization increased linearly with the sintering temperature. The coercivity varied from 1379.2 to 1893.4 Oe. The coercivity values for cobalt ferrite samples synthesized by the sol gel method were higher than the figures obtained for the same compound produced by other synthesis methods [18, 19]. The changes in the magnetic properties of cobalt ferrite can be attributed to the modification of the particle sizes, which is dependent upon the sintering temperature. With an increase in the sintering temperature, the crystallite size of the cobalt ferrite nanoparticles changed from 12.82 (300 ° C) to 52.49 nm (700 ° C).

The decrease in saturation magnetization along with particle size can be attributed to the following: in the ferrimagnetic ferrite structure, the magnetization of tetrahedral sublattice is antiparallel to that of the octahedral sublattice, however, ultrafine ferrites have non-collinear magnetic structure on the surface layer. The reduction in particle size causes an increase in the proportion of non-collinear magnetic structure, in which the magnetic

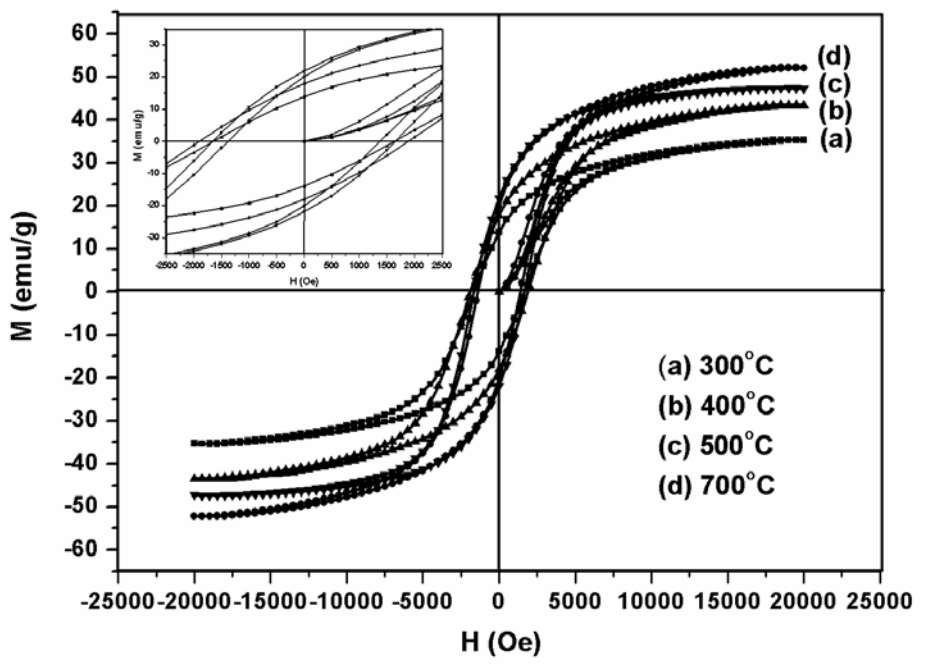

Fig. 4. Room temperature magnetic hysteresis of $CoFe_2O_4$

moments are not aligned with the direction of external magnetic field. This increase in the proportion of non-collinear structure decreases the saturation magnetization.

Table 3. Magnetic parameters of $CoFe_2O_4$ nanoparticles

Sintering temperature (°C)	M_S (emu/g)	M_R (emu/g)	H_C (Oe)	R
300	35.38	13.85	1640.3	0.3915
400	43.50	17.95	1893.4	0.4126
500	47.37	21.84	1652.9	0.4611
700	52.24	20.07	1379.2	0.3842

The coercivity first increased as the sintering temperature increased, reaching a maximum value of 1893 Oe at 400 °C , and then decreased for any further increase in temperature. It is reported that coercivity is affected by the factors such as magneto-crystallinity, micro strain, size distribution, anisotropy and the magnetic domain size [20–22]. In the multidomain regime, the coercivity is inversely proportional to the size of the nanoparticles [20]. The low value of coercivity at 300 °C may be due to the presence of superparamagnetic particles, particularly for values close to 10 nm. The saturation magnetization is related to coercivity through the Brown's relation;

$$H_C = \frac{2\,K_1}{\mu_0 M_s}, \tag{4}$$

where K_1 is the anisotropy constant and μ_0 is the permeability of free space. According to this relation, coercivity is inversely proportional to the saturation magnetization. The results of our experiments also lead to the above relation except for the sample sintered at 300 °C. As indicated earlier this deviation could be attributed to the presence of superparamagnetic particles. The variation of coercivity and saturation magnetization with

sintering temperature is shown in figure 5. The remnant ratio $R=M_r/M_s$ is an indication of the ease with which the direction of magnetization reorients to the nearest easy axis magnetization direction after the magnetic field is removed. The values of the remnant ratio of the prepared samples are in the range 0.38–0.46. The low value of R is an indication of the isotropic nature of the material [23].

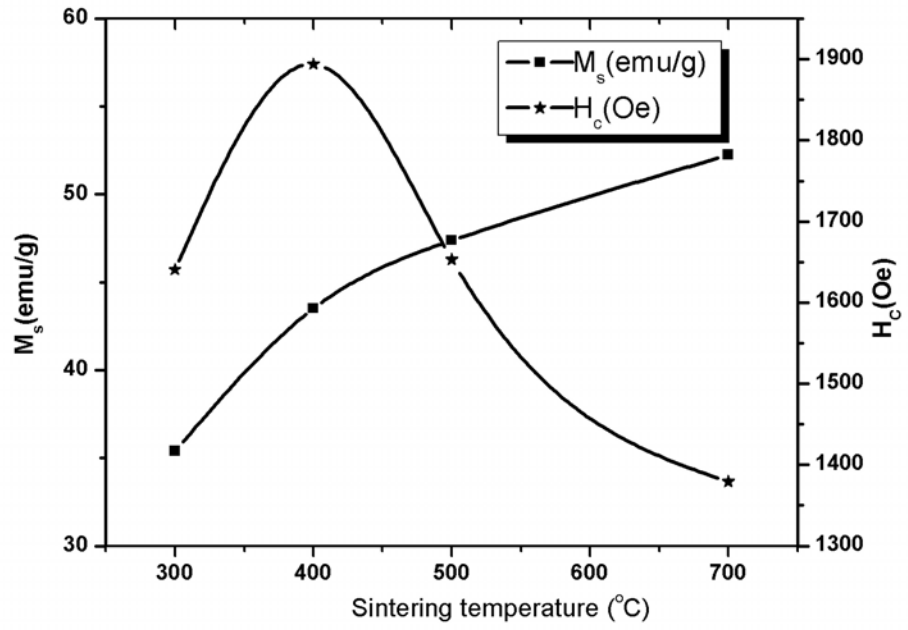

Fig. 5. Variation of saturation magnetization and coercivity as a function of sintering temperature

5. Conclusions

Nanocrystalline cobalt ferrite has been successfully synthesized by the sol-gel method. XRD results confirmed the formation of cubic spinel structure in all the samples. The crystallite size of the samples increased with the higher sintering temperatures. The crystallite size varied from 13 to 52 nm and was in reasonable agreement with the results obtained from TEM. The FTIR analysis corroborated the spinel structure of the samples. The expected stoichiometry of the samples was confirmed by the XRF elemental analysis. The saturation magnetization increased gradually with increasing sintering temperatures, while coercivity initially increased, attaining a maximum value and then decreased. These results have been explained based on the particle size and surface effects of the ultrafine materials and were in agreement with the Brown's relation.

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