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Original Research

Size Induced Structural and Magnetic Properties of Nanostructured Cobalt Ferrites Synthesized by Co-precipitation Technique

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Abstract

Cobalt ferrite ($CoFe_2O_4$), a well-known hard magnetic material. It is also one of the candidates for high frequency applications and high-density recording media. Due to their good chemical and thermal stability, high permeability, high electrical resistivity, high saturation magnetization and coercivity etc. they found wide technological applications. Size dependent properties of $CoFe_2O_4$ include catalytic properties, electrochemical properties, magnetic properties and optical properties. Thermally induced changes in nanocrystalline $CoFe_2O_4$ spinel ferrites were synthesized by co-precipitation technique. Unlike other techniques, co-precipitation is reported to be the most economical and successful technique for synthesizing ultrafine $CoFe_2O_4$ powders having narrow particle size distribution. Their structural and magnetic properties were investigated using X-ray diffraction (XRD), scanning electron microscopy (SEM) and vibrating sample magnetometer (VSM) measurements. The average crystallite size of $CoFe_2O_4$ was observed to increase from 23 to 65 nm as the annealing temperature was increased from 300 to 900°C. The lattice parameters were observed to increase due to increase in the crystallite size. The activation energy (*E*) of nanostructured $CoFe_2O_4$ was observed to be 11.6 kJ/mol. The annealing temperature has a prominent effect on the nanocrystallite growth. The saturation magnetization, coercivity and remanence were observed to increase with increasing crystallite size. In our future work, we plan to synthesize nanocrystalline $CoFe_2O_4$ using different techniques in order to understand the role of synthesis techniques on the structural and magnetic properties.

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INTRODUCTION

Nanocrystalline spinel ferrites are of great interest because of their novel properties and also in understanding the fundamental properties point of view. In fact, there are number of studies which explains the magnetic properties at the atomic level. In addition, the structural properties and the rich crystallography of spinel ferrites offer excellent opportunities for understanding and fine tuning the magnetic properties (Chen *et al.,* 1996). The cation distribution of spinel ferrites is influenced by the type of chemical environment, doping elements, synthesis techniques, crystallite size and the annealing process.

The magnetic properties of $CoFe_2O_4$ nanomaterials are determined by many factors like chemical composition, type of crystal lattice, shape, morphology and interactions of particles with surrounding matrix (Zhang *et al.,* 2004). By changing the crystallite size, shape, composition, and structure, one can control the magnetic properties. However, these factors cannot always be controlled during synthesis of nano materials. Therefore, the properties of nanomaterials even for the same type of ferrites are different. In the last few decades, $CoFe_2O_4$ materials have been widely investigated due to their high excellent chemical stability, high coercivity and saturation magnetization, mechanical hardness, and electromagnetic properties, which make this material a suitable candidate for the recording devices, magnetic cards and in electronic components (Alivisatos, 1996; Sugimoto, 1999 and Fan e*t al.*, 2009).

In this present work, we aimed to synthesize nanocrystalline cobalt ferrites using co-precipitation technique which is one of the most economical routes and consumes very less time over other synthesis techniques. The results of crystallite size dependent structural and magnetic properties of cobalt ferrites are presented in detail.

MATERIALS AND METHODS

Nanostructured $CoFe_2O_4$ were synthesized using co-precipitation technique (Raghavender *et al.,* 2011;

Berhanu *et al.,* 2014). The AR grade sodium hydroxide (NaOH), Cobalt (II) nitrate hydrate ($Co(NO_3)_2.6H_2O$), ferric (III) nitrate nonahydrate ($Fe(NO_3)_3.\ 9H_2O$) (98%) were used as starting materials. The metal nitrates were dissolved together in minimum amount of deionized water to get a clear solution. NaOH solution was added drop by drop to metal nitrates solution under vigorous stirring. The precipitation occurred immediately to change the reaction solution to dark brown. The entire reaction was carried out at 75 °C for 2 h. The pH of the solution was varied by NaOH. The resulting precipitates were washed with deionized water and ethanol several times. The resulting precipitates was dried at 200 °C for 3h. The structural characterization of precipitates powders was carried out using Philips (France) X-ray diffraction (XRD) system with Ni filter using Cu –Kα radiation (wave length λ = 1.54 A^o). The morphology was verified using FEI Quanta (USA) FEG 200 High Resolution Scanning Electron Microscope (HR-SEM). Room temperature magnetic properties were investigated using Lakeshore (USA) vibrating sample magnetometer (VSM 7410).

RESULTS AND DISCUSSIONS

Figure 1 shows the X-ray diffraction patterns of $CoFe_2O_4$ samples annealed at temperatures from 300 to 900 °C. The crystallite size was observed to increase from 23 to 65 nm due to increase in the annealing temperature as shown in Figure 2 and Table 1. The crystallite size was evaluated from the most intense (311) peak employing the Scherrer formula

$$D = \frac{0.9^{a}}{\cos^{-}} \qquad (1)$$

where β is the angular line width at half maximum intensity and θ is the Bragg angle for the actual peak.

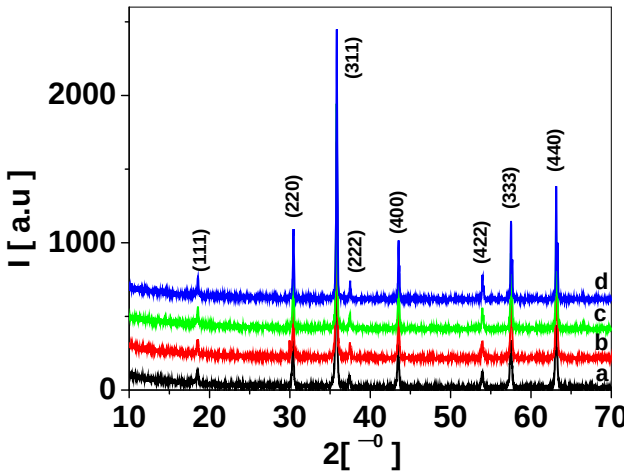

Figure 1: X-ray diffraction patterns of $CoFe_2O_4$ samples annealed at temperatures (a) 300 °C, (a) 500 °C, (a) 700 °C and (a) 900 °C

Table.1: Dependence of crystallite size (*D*), lattice constants (*a*), saturation magnetization (M_s), remanence magnetization (M_r), coercivity (H_c) and remanence ratio (M_r / M_s)

Temp. (°C)	D (nm)	a (Å)	M_s (emu/g)	M_r (emu/g)	H_c (Oe)	M_r / M_s
300	23	8.299	9.13	5.09	915	0.56
500	31	8.304	18.2	9.87	979	0.54
700	54	8.308	23.3	10.42	1386	0.44
900	65	8.314	27.4	13.86	1850	0.5

The increase in the crystallite size is due to increase in the volume of the grains. When the particles are in nanoregime, due to increase in the annealing temperature the grain growth takes place (Kumar *et al.,* 2008). As observed from Figure 1, the XRD lines are broad and the broadening of the peaks decreases with increasing annealing temperature. Further, the increase in the intensity of X-ray diffraction shows improved crystallinity and gradual increase in the crystallite sizes of $CoFe_2O_4$ as a function of heat treatment process.

The lattice constants were calculated from the most intense (311) peak of the XRD and the corresponding values are presented in Table. 1. The lattice constants were observed to be nearly equal to that of bulk $CoFe_2O_4$. The lattice constants were observed to increase from 8.299 Å to 8.314 Å with increasing annealing temperature from 300 to 900 °C as shown in Figure 2 and Table 1. The observed change in the lattice constants with annealing temperature is the evidence of structural changes taking place in $CoFe_2O_4$ (Singh *et al.,* 2004). This can be explained in terms of a meta-stable cation distribution in nanocrystallies. Since on increasing the annealing temperature the crystallite size *D* increases, the lattice constants *a* is expected to increase (Chen *et al.,* 1996, Oliver *et al.,* 2000).

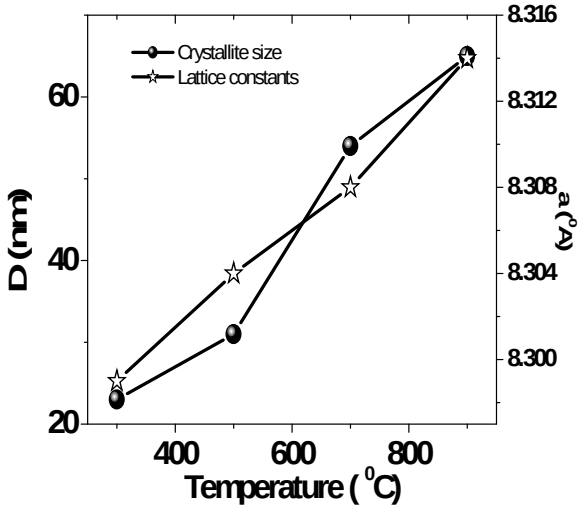

Figure 2: Dependence of crystallite size (*D*) and lattice constants (*a*) on the annealing temperatures of $CoFe_2O_4$ samples

The annealing temperature has prominent effect on the $CoFe_2O_4$ crystallite size. This is directly related to the crystallization of the nanocrystals. A straight line of ln (*d*) against 1/*T* (Figure 3) is plotted according to the Scott equation given below under the condition of homogeneous growth rate of nanocrystallite (Scott, 1983; Yang *et al.,* 2004). The Scott equation approximately describes the growth rate of nanocrystallites from thermal treatment of amorphous compound:

$$d = C\ exp\ (-E / RT) \qquad (1)$$

where *d* is the XRD crystallite size, *C* is a constant, *E* is the activation energy for grain growth, *R* is the ideal gas constant and *T* is the absolute temperature.

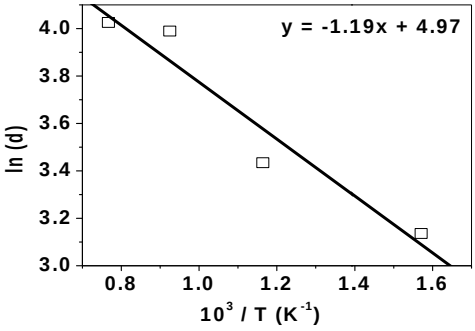

Figure 3: Plot of ln(*d*) against 1/T. Line presents a linear fit for ln(d) vs 1/T dependence

There exists a good linear relationship between ln*d* and 1/*T*. *E* values could be calculated from the slope of the straight line, presented in Figure 3 as *E* = 11.6 kJ/mol. It can be considered that the grain grows primarily by means of an interfacial reaction. It also shows that growth of Cobalt ferrite nanocrystals are easily effected by annealing temperature, which is confirmed from Figure 3. Our activation value *E* = 11.6 kJ/mol is much less than 18.5 kJ/mol for $CoFe_2O_4$ prepared by ball milling (Yang *et al.,* 2004).

Figure 4 presents the SEM images of $CoFe_2O_4$ samples annealed at 500 and 900 °C. The SEM images suggest that, there is slight agglomeration among the particles. The nanocrystals distinctly exhibit narrow particle size distribution and present mainly sphericity. The SEM image of the sample annealed at 500 °C (See Figure 4(a)) show the microstructure with fairly smaller grain size. As the annealing temperature was increased to 900 °C, a non-uniform grain growth with the presence of intragranular pores were observed (Figure 4(b)). Higher annealing temperature may lead to abnormal grain growth and closed pores. These kinds of pores were generally accounted for poor physico-mechanical properties and which may have significant affect on the structural and magnetic properties.

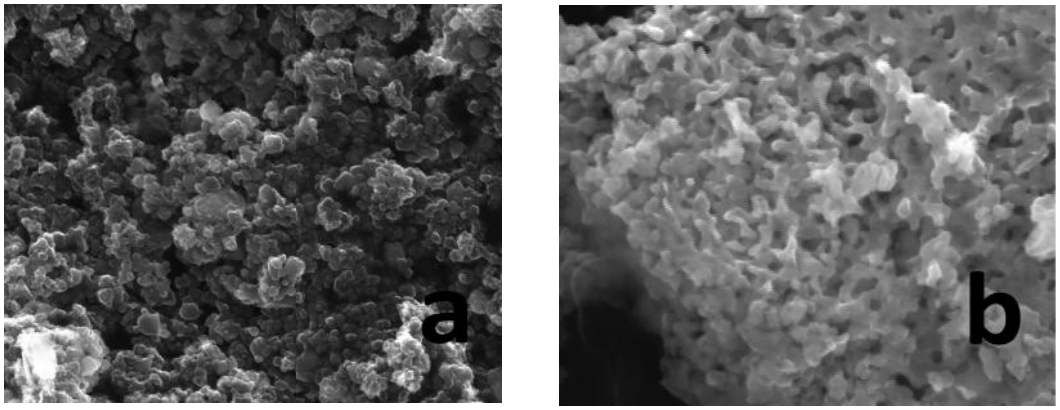

Figure 4: SEM images of $CoFe_2O_4$ samples annealed at temperatures (a) 500 °C and (b) 900 °C.

The room-temperature hysteresis loops for the samples annealed at temperatures from 300 to 900°C are shown in Figure 5. The derived parameters from the hysteresis loops are presented in Table. 1. The saturation magnetization (M_s) for the sample annealed at 300°C is observed to be 9.13 emu/g, which is very much smaller than the saturation magnetization of bulk $CoFe_2O_4$. As the annealing temperature increased to 900°C, the magnetization attains the value of 27.4 emu/g, which is comparable to the saturation magnetization value of $CoFe_2O_4$ synthesized from other techniques (Raghavender, 2013). The discrepancy in the observed magnetization in our case might be due to several facts such as, synthesis technique and conditions, chemical used, annealing temperature, grain / particle size, cluster size (Singh, 2013).

The saturation magnetization values for of $CoFe_2O_4$ samples was observed to increase with increase in crystallite size. This kind of behavior was observed for $CoFe_2O_4$ (Shafi *et al.,* 1998; Gharagozlou, 2009; Haneda *et al.,* 1988), $NiFe_2O_4$ (Zhang *et al.,* 2004; Sepelak *et al.,* 2007), and $MnFe_2O_4$ (Muroi *et al.,* 2001) synthesized by other techniques. When the crystallite size increases, the redistribution of cations in the lattice takes place and is reported to influence the magnetic properties of ferrites (Wang, 2006 and Kodama *et al.,* 1996). It is clearly observed that the saturation magnetization depends strongly on the crystallite size. The magnetization for ferromagnetic material usually increases with increasing crystallite size (Ahmed *et al.,* 2009). The same argument is valid for remanence magnetization also.

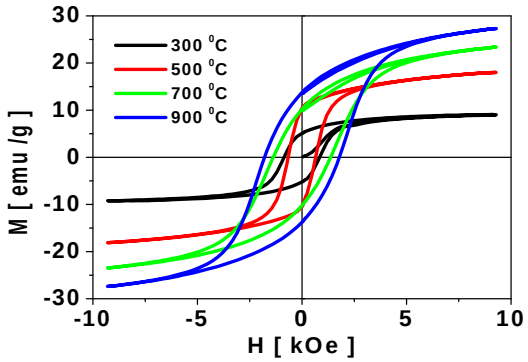

Figure 5: Room temperature magnetization measurements for $CoFe_2O_4$ samples annealed at different temperatures

Coercivity (H_c) was observed to increase from 915 to 1850 Oe as the crystallite size increased from 23 to 65 nm. The coercivity was observed to depend strongly on the crystallite size. The M_r / M_s ratio (remanent magnetization to saturation magnetization) decreased with increase in the crystallite size. The M_r / M_s , values indicates the fraction of superparamagnetic particles in the synthesized samples and the decrease in these values may be due to the existence of spin canting (Jiang

et al., 1999).. One of the possibilities of spin canting may be due to surface and interface effect (Ahmed *et al.,* 2009). The remanent ratio M_r / M_s, is a characteristic parameter of the material and is dependent on the anisotropy (Singh *et al.,* 2004), indicating the ease with which the magnetization direction is reoriented to the nearest easy axis magnetization direction after the magnetic field is removed. The lower the M_r / M_s ratio, the more isotropic the material will be. The values of M_r / M_s varied from 0.56 to 0.44 with increase in crystallite size except for the 65 nm particles. The observed variation in the coercivity field and remanence ratio with crystallite size can be explained on the basis of domain structure, critical size, and the anisotropy of the crystal (Qu *et al.,* 2006; Vasic *et al.,* 2006 and George *et al.,* 2006). It is worth mentioning that the magnetic properties of nanocrystalline $CoFe_2O_4$ depends on the synthesis technique and conditions.

CONCLUSIONS

Nanocrystalline $CoFe_2O_4$ were successfully synthesized using co-precipitation technique. The structural and magnetic properties were investigated using X-ray diffraction, scanning electron microscopy and magnetization measurements. The average crystallite size of $CoFe_2O_4$ was observed to increase from 23 to 65 nm as the annealing temperature was increased from 300 to 900°C. The lattice parameters were observed to increase with increasing crystallite size due to changes in the structural properties. The magnetic properties exhibit a strong dependence on the crystallite size. Magnetization was observed to increase from 9.13 to 27.4 emu/g. The coercivity was observed to increase from 915 to 1850 Oe.

Conflict of Interest

Authors declared no conflict of interest.

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