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# The effect of annealing on the structure, magnetic properties and AC heating of $CoFe_2O_4$ for biomedical applications

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ABSTRACT

Single and nanosized spinel $CoFe_2O_4$ phase has been prepared successfully by a simple combination of mechanical milling from a mixture of $Fe_2O_3$ and $Co_3O_4$ powder precursors followed by a subsequent annealing. X-ray diffraction analysis reveals that the estimated crystallite size of $CoFe_2O_4$ increases with increasing temperature but remains at the nanoscale, i.e. 85 nm at 900 °C. Moreover, magnetic measurements show that a great enhancement in the saturation magnetization was achieved whereas a large hysteresis loop was observed (i.e.72 emu/g at 900 °C). Evaluation and applicability of $CoFe_2O_4$ nanoparticles under high frequency AC magnetic field for heating in biomedical applications were examined. It was found that under fixed amplitude (516 Oe) and frequency (229 kHz), the prepared nanoparticles generate significant heat: after 5 s the temperature was around 97 °C for the as-milled powder and reached almost 178 °C for the powder annealed at 900 °C.



## 1. Introduction

Cubic spinel ferromagnetic oxides such as $CoFe_2O_4$ have attracted many researchers in recent years because of their potential technological importance due to their large magneto crystalline anisotropy [1]. Among the applications of $CoFe_2O_4$ in technology based on nanosize are high density recording, spintronics, magnetic resonance imaging, magneto refrigeration, ferrofluids, photonic crystals, drug-delivery technology, etc. [2–5]. Several techniques have been employed to synthesize this material at the nanoscale. These methods include sol–gel [3,6], micelle chemical control method (micro-emulsion) [7], citrate-gel method [8,9], hydrothermal process [10], polymerized complex method [11], mechanical alloying [8,12,13], mechanochmical method [14], and electrospinning [15].

Mechanical alloying as a solid state process is a powerful technique which offers many possibilities for chemical alloying and microstuctural modifications, as well as in the preparation of new materials at the nanoscale. In this work, the mechanical alloying of a mixture of oxides ($Fe_2O_3$ and $Co_3O_4$) followed by annealing at 600 °C, 750 °C, and 900 °C respectively was used to produce a single and pure nanoscale $CoFe_2O_4$ phase. Structure, microstructure and magnetic properties studies were carried out using X-ray diffraction and Vibrating Sample Magnetometer (VSM), respectively.

## 2. Experimental

High purity oxide reactants used in this work were provided by Aldrich: $Fe_2O_3$ (99.7%) and $Co_3O_4$ (99.0%). The mechanical milling was carried out using a Fritsch Pulverisette P6 unit under air for carefully weighed oxide powder precursors. It is known that milling intensity depends on several parameters like balls/powder ratio, balls diameter, milling speed, and duration. In this study, a balls/powder (BP) ratio of 20 was used, along with a speed of 300 rpm, and a milling time of 20 h for all samples. The milled mixture was then annealed at various temperatures for 1 h under air using a Thermoline furnace.

Powder X-ray diffraction (XRD) measurements were carried out using a Phillips diffractometer equipped with Cu α radiation (1.54 Å). The crystallite size (CS) and the microstrain (MS) were estimated using peak profile analysis with a software provided with the diffractometer, where the full width at half maximum (FWHM) is determined then used for the calculation by introducing a standard value for instrument contribution to the peak broadening. Peak broadening can be modeled or fitted using a pseudo-voight function taking into account the instrument parameters (which are determined by measuring Si standard sample) as well as crystallite size (Gaussian form) and micro-strain (Lorentzian form).

Magnetic measurements were performed at room temperature using PMC MicroMag 3900 model Vibrating Sample Magnetometer (VSM) having a 1 T magnet. The magnetic parameters, i.e. saturation magnetization (Ms), remanence magnetization (Mr), and coercivity (Hc) were determined from the M–H curves.

The solid nanocrystalline particles were exposed to a 516 Oe, 229 kHz magnetic field using a 4-turn coil [16] as part of a custom-built magnetic hyperthermia unit (Induction Atmospheres, Rochester, NY, USA) connected to a high voltage power

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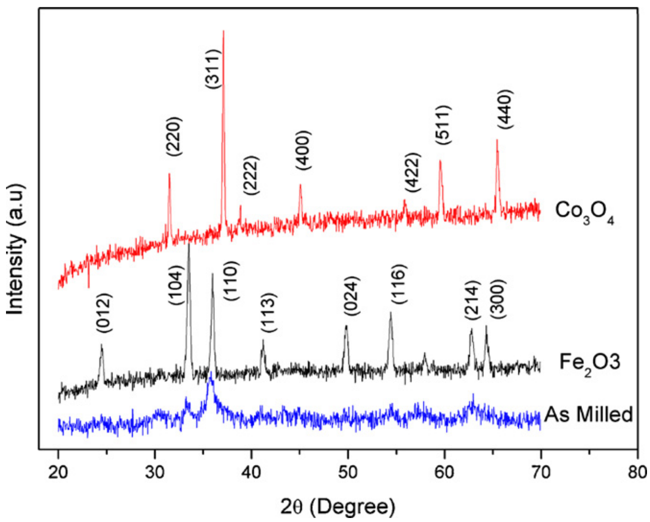


**Fig. 1.** XRD patterns of $Co_3O_4$, $Fe_2O_3$, and the as milled mixture.

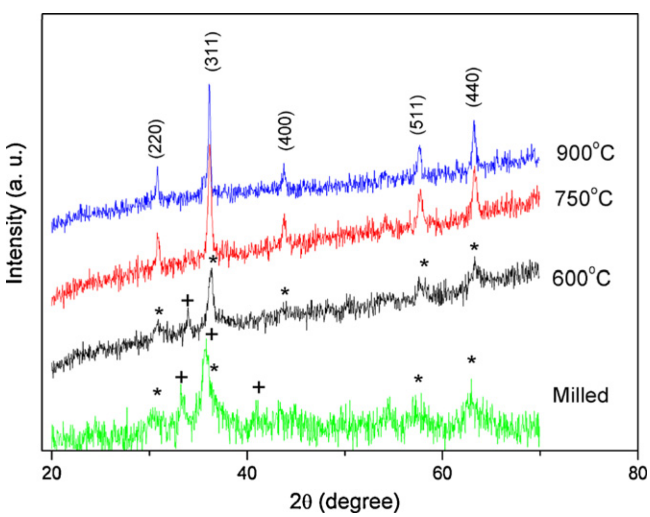


**Fig. 2.** XRD patterns of the as milled mixture and after annealing at 600 °C, 750 °C, and 900 °C (*): $CoFe_2O_4$; and (+): $Fe_2O_3$).

supply (NovaStar 5 kW RF Power supply, Ameritherm, Inc., Scottsville, NY, USA) and circulating chiller bath (Koolant Koolers, Kalamazoo, MI, USA). The temperature of the nanoparticles was monitored using an infrared camera (FLIR Thermacam SC2000, FLIR Systems, Boston, MA, USA). The temperature of the $CoFe_2O_4$ nanoparticles under various AC magnetic fields was measured by focusing on the centre of samples from above the magnetic-induction coils using the Thermacam.

## 3. Results and discussion

Fig. 1 shows the XRD patterns for $Co_3O_4$, $Fe_2O_3$, and the as milled mixture oxides. It is clear that after milling $Fe_2O_3$ peaks remain but broaden, and that their relative intensity decreases, an indication of particle size reduction and accumulation of microstrain. It is worth to note the existence of a halo around the major peaks of the as milled mixture of oxides, an indication of a partial amorphisation of the mixture. It is important also to note that the spinel phase $CoFe_2O_4$ peaks appear, which are indexed by "*" in the XRD pattern (Fig. 2). Rajath Varama et al. [8] used $Co_3O_4$ and $Fe_2O_3$ as starting oxides then ball milled the mixture for 24 h in a PVC container using zirconia balls and distilled water as medium. The final product remained mainly a mixture of $Co_3O_4$ and $Fe_2O_3$ with very small quantity of $CoFe_2O_4$. Even after annealing at 900 °C for 4 h, $Fe_3O_3$ remains as the major phase with a slight increase of the amount of $CoFe_2O_4$. Moreover, Ding et al. [12] mechanically alloyed a mixture of $Co_3O_4$ and $Fe_3O_4$ (instead of $Fe_2O_3$) for 24 h and a BP ration of 8:1 using a Spex 8000 mixer. The spinel phase was formed directly after milling with a crystallite size of 30 nm and 50 nm when annealed at 750 °C and 1000°C, respectively. Sani et al. [13] started with a mixture of $Fe_2O_3$ and Co metal powders using a Spex 8000 mixer and a BP ratio of 10:1 then the mixture was milled for various periods of time. An XRD pattern of the sample milled for 1 h did not show evidence of the formation of $CoFe_2O_4$ but Mö ssbauer spectra confirmed its existence. However, XRD patterns of the samples milled for 5, 15, 25, and 30 h clearly show the formation of the of $CoFe_2O_4$ phase, and that its amount increases with milling time at the expense of $Fe_2O_3$. Finally Shi et al. [14] prepared $CoFe_2O_4$ phase via a mechanochemical route by the combination of co-precipitation and mechanical alloying. The precursors obtained from the co-precipitation were then milled at 300 rpm for 62 h using a BP ratio of 10:1. The spinel phase was obtained directly after milling without any further annealing, with a crystallite size around 20 nm.

**Table 1**
Microstructural and magnetic parameters, for as milled mixture and after annealing at 600 °C, 750 °C, and 900 °C.

| Sample | CS (nm) | MS (%) | Ms (emu/g) | Mr (emu/g) | Hc (Oe) | Mr/Ms |
|---|---|---|---|---|---|---|
| As Milled | 12 | 1.08 | 27.6 | 6.9 | 935 | 0.25 |
| 600 °C | 20 | 0.68 | 35.5 | 11.6 | 917 | 0.33 |
| 750 °C | 34 | 0.45 | 59.3 | 23.4 | 1117 | 0.39 |
| 900 °C | 85 | 0.21 | 72.1 | 37.7 | 1517 | 0.52 |

In order to investigate the effect of annealing on the phase formation as well as the crystallization of $CoFe_2O_4$, the milled powder has been subjected to annealing. At 600 °C the halo disappeared leading to the enhancement of the formation/crystallization of the spinel phase with some residue of $Fe_2O_3$ (Fig. 2). Further annealing at 750 °C, results in the total disappearance of $Fe_2O_3$ phase with substantial increase of the relative intensity of $CoFe_2O_4$ peaks, indicating a higher crystallinity. Finally, at 900 °C a pure and a single $CoFe_2O_4$ phase is formed as shown in Fig. 2. The microstructural parameters, i.e. crystallite size and microstrain, were estimated from peak profile analysis and the results are reported in Table 1. As can be observed, the crystallite size increases with annealing, whereas the microstrain decreases, as expected due to the crystal growth and relaxation, respectively.

Fig. 3 illustrates the VSM measurements for the starting oxide powders ($Co_3O_4$ and $Fe_2O_4$) and the as milled mixture. It is clear that from M–H curve of the milled mixture, a solid state reaction

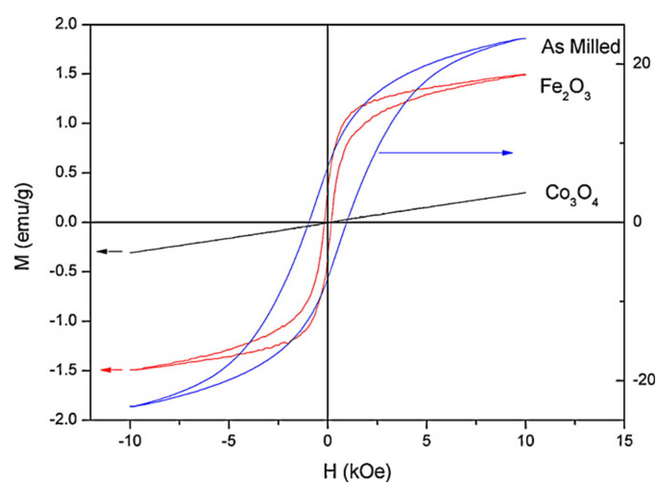


**Fig. 3.** VSM measurements of $Co_3O_4$, $Fe_2O_3$ and as milled mixture.

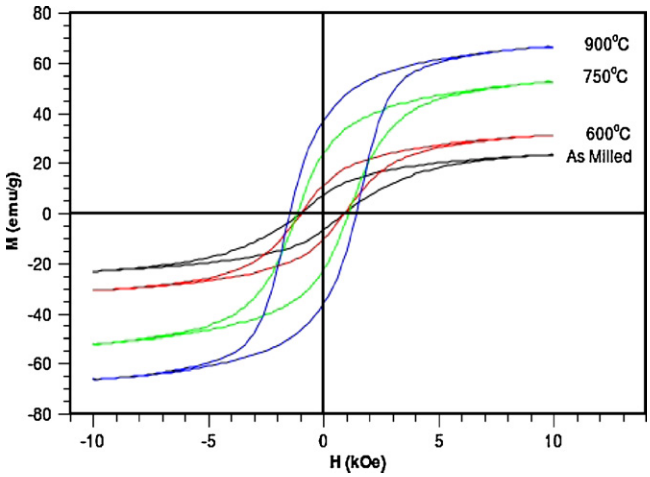


**Fig. 4.** VSM measurements of the as milled mixture and after annealing at 600 °C, 750 °C, and 900 °C.

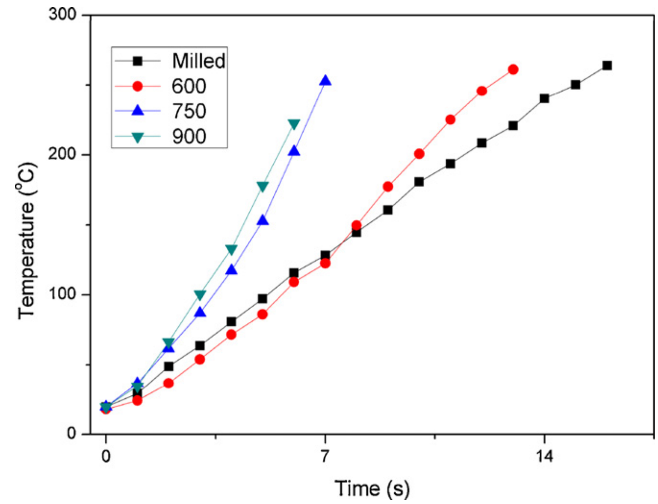


**Fig. 5.** The effect of AC magnetic heating as a function of time for the as milled mixture and after annealing at 600, 750, and 900 °C at a frequency of 229 kHz and a magnetic field of 516 Oe.

occurs between the starting oxide powders to form the spinel phase $CoFe_2O_4$, all magnetic parameters changed drastically, i.e. saturation magnetization (Ms) becomes 27.6 emu/g, which is very much higher than that of both oxides. It is important to note that this value is still smaller than that of pure $CoFe_2O_4$ as reported in the literature [8–15]. Therefore, milling resulted in a partial formation of $CoFe_2O_4$. The results of VSM measurements for the milled mixture as a function of the annealing temperature are illustrated in Fig. 4. M–H curves show a ferromagnetic behavior with a wide hysteresis loop. It is important to note that the width of the hysteresis loop increases with increasing the annealing temperature hence inducing a notable changes in the magnetic parameters, the values of Mr and Ms show the highest increase and to less extent for Hc (see Table 1): the percentage change of the magnetic parameters occurring between 600 °C and 900 °C are 225%, 103%, and 65% for Mr, Ms, and Hc respectively.

Both XRD and VSM analysis indicate that the milled mixture is represented by a ferromagnetic phase, which is typical of $CoFe_2O_4$ spinel phase. When the milled mixture is annealed at 600 °C, both saturation magnetization (Ms) and remanence magnetization (Mr) show an increase, while the coercivity (Hc) decreases very slightly. This is, however, due to the enhancement of the formation of the spinel phase from the remaining un-reacted starting oxides ($Co_3O_4$ and $Fe_2O_4$) as can be observed from the pattern of XRD in Fig. 2. As the milled mixture is further annealed at 750 °C, a considerable increase in all magnetic parameters such as Ms, Mr, and Hc is notable from Fig. 4 and Table 1. These drastic changes are attributed to enhancement of the crystallinity. Finally, at 900 °C a further increase in the magnetic parameters are obtained due to the increase in the crystallite size as observed in the XRD pattern (Fig. 2) and reported in Table 1. Rajath Varama et al. [8] report that Ms increases with increasing of the particle size, which is in good agreement with the results obtained in this work. Moreover, the crystallite were much larger i.e. 0.29–0.53 μm. Shi et al. [14] showed that Ms remains almost constant with increasing annealing temperature up to 500 °C then drastically decreases. However, Hc increases to reach a maximum value at 600 °C then decreases with further annealing. The discrepancy between our results with those of Shi et al. is due to several reasons: (1) in this study the precursors were $Fe_2O_3$ and $Co_3O_4$ oxides whereas Shi et al. used $FeCl_3$, $CoCl_2$ and NaOH pellets; and (2) Shi et al. report the presence of $\alpha$-$Fe_2O_3$ in their samples, which is a weak ferromagnetic oxide with low saturation magnetisation (~1.5 emu/g) whereas in this study, the amount of $\alpha$-$Fe_2O_3$ decreases with annealing leading to an increase of Ms. Ding et al. [12] report the variation of Ms versus annealing temperature: a slight increase below 450 °C then a sharp increase between 450 and 650 °C to reach saturation above 650 °C. Hc showed a similar behavior as Ms, however it reach a maximum value at 700 °C then drastically decreased with further annealing.

The heat generated by the $CoFe_2O_4$ nanoparticles was measured at 229 kHz and magnetic field of 516 Oe. It is noted from Fig. 5 that the nanoparticles heat appreciably in a matter of only few seconds and the temperature even exceeds the limit of the measurement scale. Thus it was impossible to reach saturation temperature, however, the figure clearly illustrates the existence of different heating rate: (1) a low heating rates for the as-milled mixture and after annealing at 600 °C where the spinel phase is not completely formed; and (2) a high heating rate for the samples annealed subsequently at 750 and 900 °C when the milled mixture is fully transformed into a pure spinel phase. Since the obtained self heating rates are very high for biomedical applications, further investigations on the effects of lower frequencies, lower applied magnetic field and the media (nanoparticles dispersed in different liquids such as water) are underway.

## 4. Conclusion

Mechanical milling of $Fe_2O_3$ and $Co_3O_4$ oxides mixture leads to the formation of the spinel phase $CoFe_2O_4$ with substantial particle size reduction to the nanoscale, i.e. 12 nm. As the milled mixture is annealed, the spinel phase is further enhanced, at 900 °C a pure single nano-size $CoFe_2O_4$ phase is obtained with a drastic increase in the crystallite size from 12 up to 85 nm. VSM measurements show a progressive increase in the magnetic parameters Ms, Mr, and Hc with annealing temperature: at 900 °C Ms = 72.1 emu/g, Mr = 37.7 emu/g, and Hc = 1517 Oe. AC heating measurements reveal a relatively high heating rate i.e. at 900 °C the heating rate is around 40 °C/s. Therefore, for biomedical applications only small amounts of nanoparticles will be required to generate the necessary heat for treatments in a relatively short time.

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