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Dependence of magnetic properties on crystallite size of CoFe_2O_4 nanoparticles synthesised by auto-combustion method

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Cobalt ferrite (CoFe_2O_4) nanoparticles were prepared through an auto-combustion method. The results of XRD show that the crystallite size of CoFe_2O_4 nanoparticles increases from 57 to 105 nm with a slight change in lattice constant as the annealing temperature increases from 300 to 1200°C. The magnetic measurements by vibrating sample magnetometer (VSM) show that M_s increases monotonously by increasing the annealing temperature from 300 to 1200°C and C_{HB} and M_s reached a maximum when annealing temperature is about 400°C due to the change of the grain size.

Keywords: nanoparticle; cobalt ferrite (CoFe_2O_4); auto-combustion; anneal; magnetic properties

1. Introduction

Cobalt ferrite (CoFe_2O_4), a kind of inverse-spinel oxide, which belongs to the square group O_h^7 (Fd3m), has been widely investigated because of its cubic magnetocrystalline anisotropy, relatively high H_c , moderate saturation magnetisation (M_s), good chemical stability [1,2] and broad prospect of applications in several technological fields, including electronic devices, ferrofluids and high-density information storage [3–6]. Various methods, including co-precipitation [7,8], hydrothermal synthesis [9,10], sol-gel techniques [11], microemulsion method [12,13], forced hydrolysis method [14] and sonochemical reaction [15], have been reported for preparing CoFe_2O_4 . Most of these methods suffer with troublesome post-treatment and cannot be applied to a large-scale and economic production. Some researches [16,17] have prepared nanoparticles of CoFe_2O_4 using auto-combustion method. It is noticed that this method stands out as an alternative and highly promising method for synthesis of CoFe_2O_4 . However, problems still exist. For instance, NH_4OH was added into the starting solution to adjust pH, which was thought to be a necessary step, but this step induces the existence of some byproducts, such as NH_4^+ and Co_2O_3 [17].

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In this article, single-phase CoFe_2O_4 nanoparticles with rare by-products were prepared by auto-combustion method without the addition of NH_4OH . The as-prepared powder of CoFe_2O_4 is relatively small, which is convenient for us to control the crystallite size by subsequent heat treatment. It is known that most of the physical properties of CoFe_2O_4 spinel depend strongly on the shape and size of the nanoparticles. Thus, the other purpose of this work is to investigate the dependence of magnetic properties on crystallite size of CoFe_2O_4 nanoparticles.

2. Experimental procedure

First, the analytical grade reagent of citric acid (CA 99.5%), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (98.5%) and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99%) were dissolved in distilled water. The initial ratio was $\text{Co}^{2+} : \text{Fe}^{3+} = 1 : 2$ and $\text{CA} : \text{metal ions} = 1 : 1$. The pH of the solution was about 2. The mixed solution was then heated on a high-power heating device. With the evaporation of H_2O , the solution became viscous gel and combusted finally. This combusting process just lasts for several seconds and at last black fleecy powder is formed. The as-burnt powders were then annealed at 300, 400, 600, 700, 900 and 1200°C , respectively.

X-ray fluorescence spectrometry (XFS S4 PIONEER) and X-ray photoelectron spectroscopy (XPS XSAM 800 Krato. Ltd) were used to determine the atomic percentage of the as-burnt powders and showed that the molar ratio of $\text{Co} : \text{Fe} : \text{O}$ is very close to $1 : 2 : 4$. The structure was determined from the X-ray diffraction (XRD D8-Advance $\text{Cu-K}\alpha$). The average crystallite sizes were calculated by using (311) peaks and Scherrer's formula. Fourier transform infrared (FT-IR) transmission spectra were taken on NICOLET 5700 Infrared Spectrometer from 4000 to 400 cm^{-1} . Raman spectra were carried out using RM 1000 Raman microscope. The microstructure and morphology of the powders annealed at 400°C were specified by transmission electron microscopy (TEM JEM2010). The magnetic hysteresis loops of all samples were collected at room temperature by using vibrating sample magnetometer (VSM).

3. Results and discussion

The typical FT-IR spectrum of the as-burnt powder is as shown in Figure 1. The intensive broad band at 3430 cm^{-1} is associated with the O–H stretching vibration. The band at 1623 cm^{-1} is due to the H–O–H bending vibration. This indicates the presence of residual water, which may be ascribed to the physical absorption of H_2O by the as-burnt powder. The band at 1100 cm^{-1} comes from the coupling of the O–H bending vibration and stretching vibration of C–O. This indicates the existence of $-\text{COOH}$. The bands at 1384 and 1452 cm^{-1} are associated with the bending vibration of C–H of $-\text{CH}_2$. The band at 2330 cm^{-1} is ascribed to the stretching vibration of C–C. The bands at 2860 and 2925 cm^{-1} are ascribed to the stretching vibration and anti-symmetric stretching vibration of C–H and $-\text{CH}_2$, respectively. It is clear that the as-prepared powder contains some organic products. The wide absorption band at 570 cm^{-1} corresponds to the character band of Fe–O stretching vibration mode in CoFe_2O_4 compounds. It indicates the formation of CoFe_2O_4 compound in the as-burnt powder. However, the band associated with Co–O stretching vibration in CoFe_2O_4 compounds, which is generally around 700 cm^{-1} ,

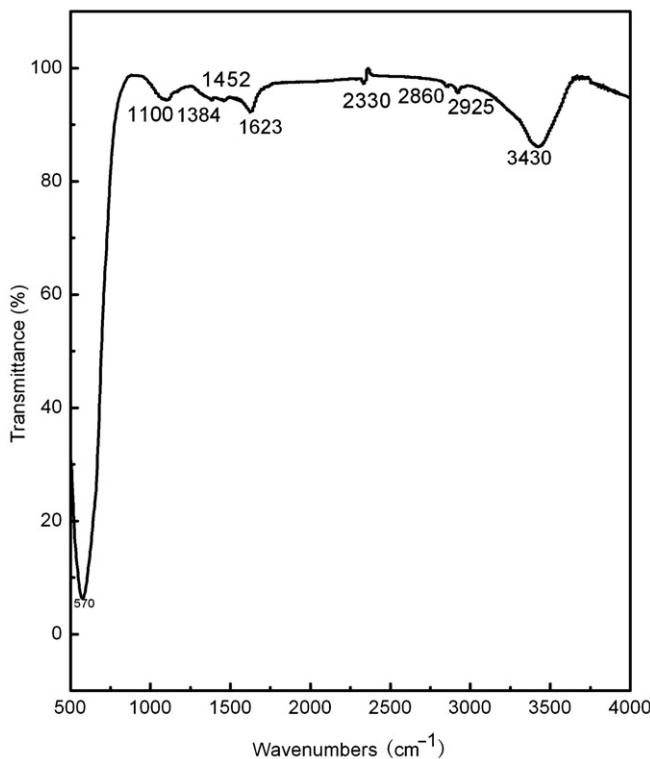


Figure 1. The FTIR spectrum of the as-burnt powder.

is undistinguished due to its weak absorption and usually being covered by the wide absorption of Fe–O stretching vibration.

Figure 2 shows the XPS core spectra of Fe and Co for the as-burnt powders. The peak of Fe 2p_{3/2} has an asymmetric shape with the maximum around 711.2 eV and a broaden shoulder at 713.4 eV. Both peaks have the characteristic of +3 value, and can be ascribed to Fe³⁺ ions in octahedral and tetrahedral sites, respectively. The XPS spectrum of Co 2p_{3/2} in CoFe₂O₄ also exhibits asymmetry due to the two sites of Co²⁺ ions, in octahedral and tetrahedral sites. It is noted that intense satellite structure is found on the high binding energy side of the Co 2p_{3/2} and Co 2p_{1/2}, which is believed to be a direct evidence of the band structure associated with octahedral Co²⁺ in the oxide lattice.

The XRD patterns of the as-burnt sample as well as the samples annealed at various temperatures are depicted in Figure 3(a). It is clear that all patterns are consistent very well consistent with the data of CoFe₂O₄ spinel (JCPDS cards No. 22-1086). The intensity of all peaks increases while the full-width at half maximum (FWHM) decreases with the increase of the annealing temperature. In order to evaluate the influence of annealing temperature, the lattice constants were calculated by least squares, and the average crystallite size were determined from the FWHM of the (311) peak using the Scherrer's formula. The results are shown in Figure 3(b). It is noted that the lattice constants show little change while the average crystallite size increases from 57 to 105 nm as the annealing temperature increases

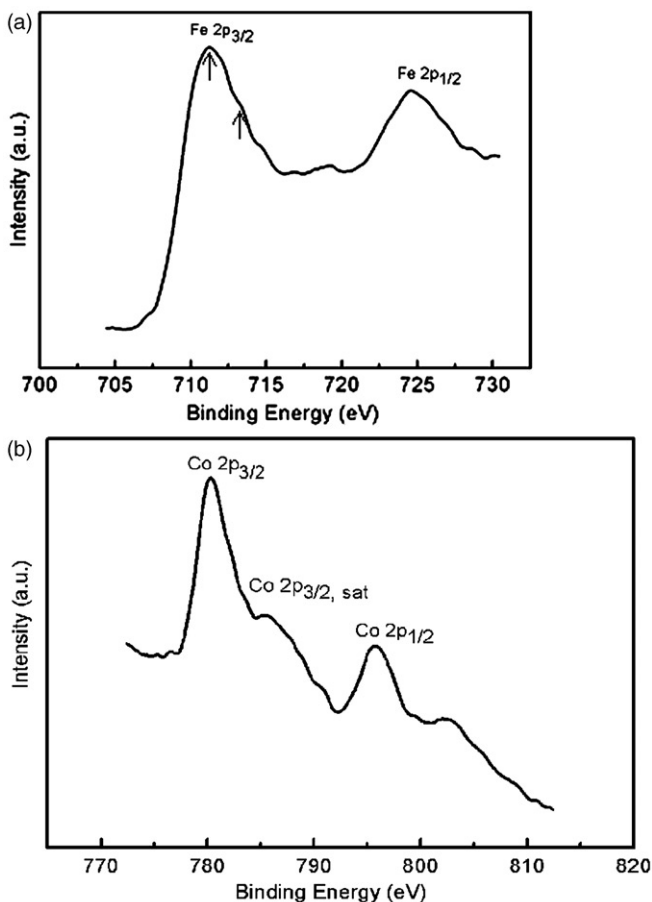


Figure 2. The XPS core spectra of (a) Fe and (b) Co.

from 300 to 1200°C. It indicates that the annealing temperature has little influence on the crystal structure but increases the crystallite size.

However, it is hard to conclude that all the samples are single-phase CoFe_2O_4 due to the similar spinel structure of CoFe_2O_4 and $\gamma\text{-Fe}_2\text{O}_3$ [18]. It is known that the Raman spectra of $\gamma\text{-Fe}_2\text{O}_3$ exhibit much stronger Raman peaks at 1378 and 1576 cm^{-1} than that of CoFe_2O_4 [19]. So the Raman spectra are introduced for further confirmation. The Raman spectra of the samples annealed at temperature from 300 to 1200°C were carried out and no peaks were observed above 1000 cm^{-1} . It suggests that the formation of $\gamma\text{-Fe}_2\text{O}_3$ is unlikely and the samples are at single CoFe_2O_4 phases.

CoFe_2O_4 has a cubic inverse-spinel structure and belongs to the square group O_h^7 (Fd3m) [20,21]. The factor group analysis predicts the following modes in spinel:

$$A_{1g} + E_g + F_{1g} + 3F_{2g} + 2E_{2g} + 2E_u + 2F_{1u} + 2F_{2u}.$$

As for CoFe_2O_4 , there are five Raman active modes ($A_g + E_g + 3F_{2g}$) and four infrared modes ($4F_{1u}$) [22,23]. Figure 4 shows the measured Raman spectra from 1000 to 100 cm^{-1} .

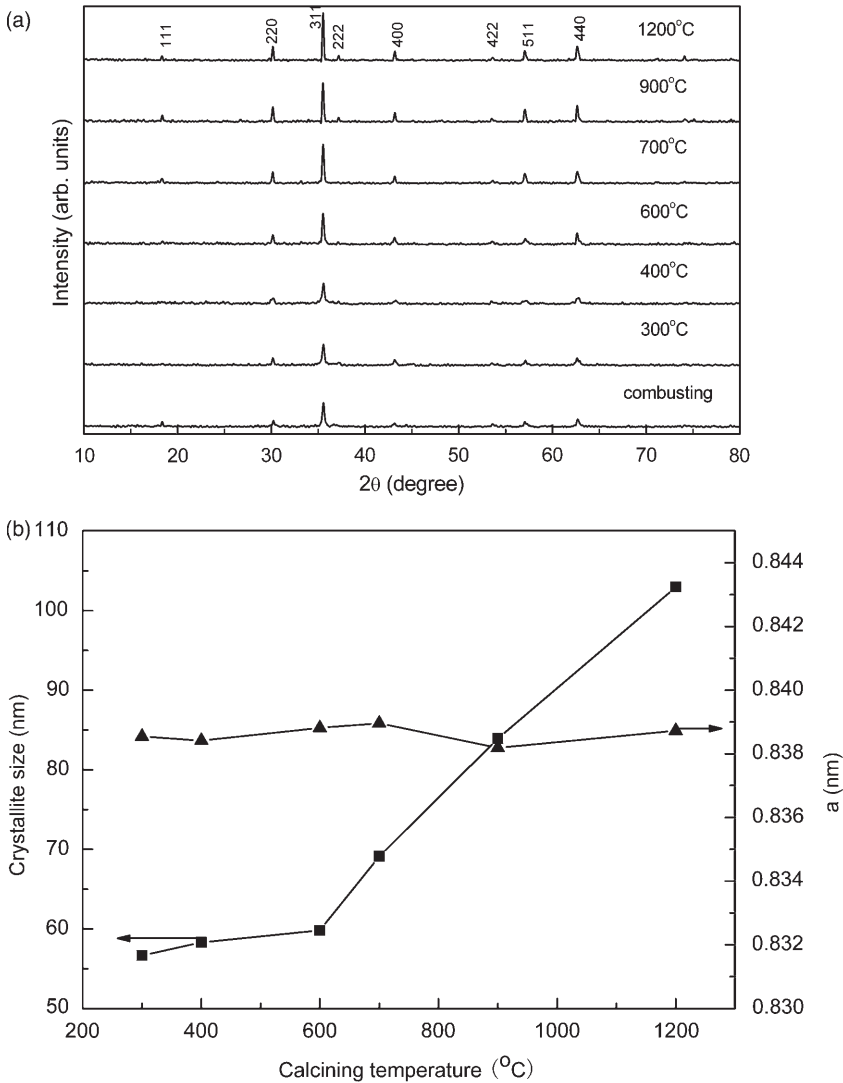


Figure 3. (a) The XRD patterns of the as-burnt powder and the sample annealed at 300, 400, 600, 700, 900 and 1200°C, respectively. (b) Particle size and lattice constant vs. annealing temperature.

It is clear that all the five Raman modes are observed. The Raman modes around 615 and 690 cm^{-1} are related to the T-site mode that reflects the local lattice effect in the tetrahedral sublattice, while other three peaks correspond to the O-site mode that reflects the local lattice effect in the octahedral sublattice.

Figure 5(a) shows the TEM images for the morphology of CoFe_2O_4 nanoparticles annealed at 400°C . It shows that there is obvious boundary in most regions. Particles of rough, irregular but generally spheroidal shapes are observed. The average particle size observed by TEM is 20–30 nm, which is much smaller than that obtained by

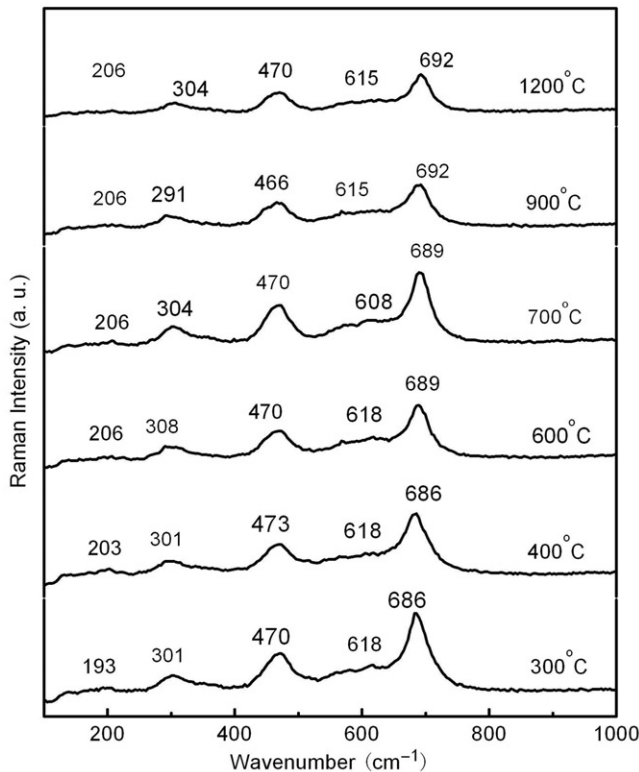


Figure 4. The Raman spectra of the samples annealed at temperature from 300 to 1200°C.

XRD observations. It is known that aggregation is common in this system due to the strong interaction between CoFe_2O_4 magnetic nanoparticles. Obviously, this aggregation combining with the annealing process results in the increasing of the average particle size of CoFe_2O_4 nanoparticles. Figure 5(b) shows the selected diffraction patterns of the same sample and the results calculated from the electron diffraction formula is given in Table 1, which is well consistent with the data of XRD.

The results of VSM measurement at room temperature are shown in Figure 6. It is obviously that the magnetic properties of CoFe_2O_4 powders show high dependence upon the annealing temperature. The M_s increases with the increase of the annealing temperature while the remanance ratio and the coercivity H_c reach its maximum value at 400°C. It indicates that the transition of M_s is highly depends upon the growth of CoFe_2O_4 nanocrystallites. Because both the crystallite size and the M_s have the same changing trend with the increasing of the annealing temperature. Also, it indicates that the size of CoFe_2O_4 nanoparticles is not only the factor in deciding H_c and the remanance ratio. It was reported that H_c is closely related to the microstructure, grain size, residual stain and many other complex factors [24,25]. As the particle size is around the single domain size, the H_c will reach a maximum value because of the coherent rotation of spins [22]. This indicates that the crystalline size of the CoFe_2O_4 powder annealed at 400°C in this work may come close to the size of single domain. The drop of H_c at 600°C and

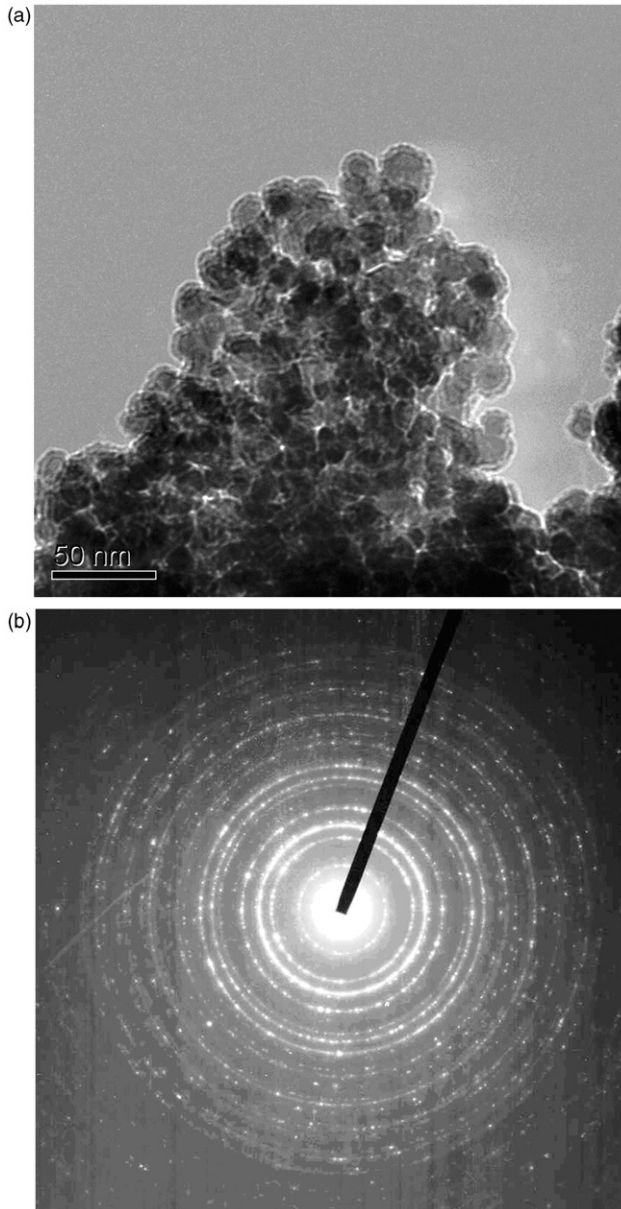


Figure 5. (a) The TEM images of the CoFe_2O_4 nanoparticles annealed at 400°C . (b) The selected diffraction patterns of the same sample.

Table 1. Values calculated from the SAD pattern of the CoFe_2O_4 nanoparticles annealed at 400°C .

hkl	111	220	311	400	422	511	400
$d_{hkl}(\text{nm})$	0.49	0.30	0.25	0.21	0.172	0.161	0.148

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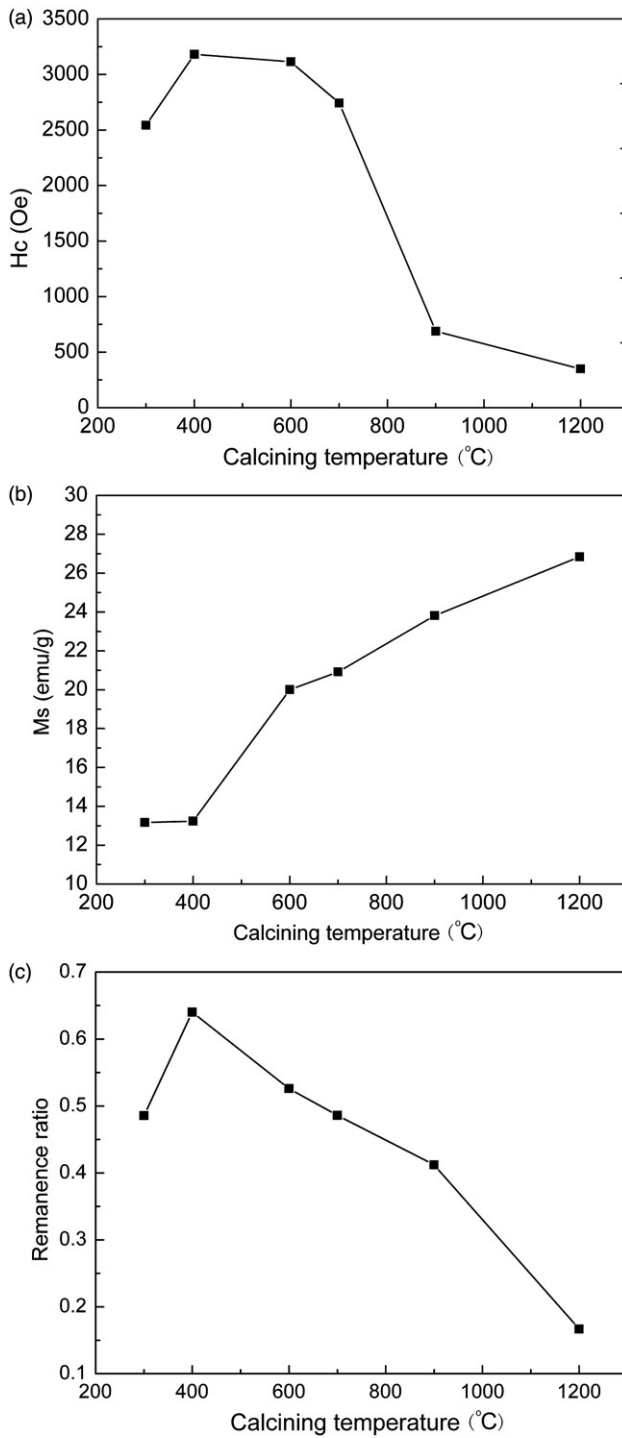


Figure 6. Dependence of (a) H_c , (b) M_s and (c) remanence ratio on the annealing temperature.

the drastic drop when the CoFe_2O_4 powder annealed at temperatures above 700°C might originate from the transition of magnetic single domains to multi-domain within a particle.

4. Conclusion

In conclusion, single-phase CoFe_2O_4 nanoparticles with different grain size have been successfully synthesised by a rapid auto-combustion method.

The results of XRD show that the crystallite size of CoFe_2O_4 increases from 57 to 105 nm with a slight change in lattice constant as the annealing temperature increases from 300 to 1200°C . Magnetic measurements show that M_s increases monotonously by increasing the annealing temperature from 300 to 1200°C , while the H_c and M_s reached a maximum when annealing temperature is at 400°C due to the change of the grain size.

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