Structural & Magnetic Properties of Cobalt Oxide Nanoparticles at Different Annealing Temperatures

Prianka Sharma and Anshu Sharma
Maharaja Agrasen University, Solan, INDIA

* Corresponding author. email: royprianka04@gmail.com
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Abstract: The effect of annealing temperature on the particle size and on the magnetic properties of cobalt oxide Co_3O_4 nanoparticle has been investigated. Single phase Co_3O_4 nanoparticles were synthesized by co-precipitation route and their structure was confirmed through X-ray diffraction analysis. The average crystallite sizes of the nanoparticles as determined from the X-ray diffraction were found to lie in the range of 22 to 29 nm. At room temperature, these particles show ferromagnetic response at 450^0C and with increasing annealing temperature, the particle size increases and the tendency of cobalt Co_3O_4 nanoparticles shifts towards slightly superparamagnetic behaviour. The coercivity decreases with increasing particle size, as the annealing temperature increases.

Key words: Cobalt Oxide nanoparticle, crystallite size, saturation magnetization, coercivity, ferromagnetism

1. Introduction

Magnetic nanoparticles, exhibit unique phenomena such as super-paramagnetism, high coercivity, high saturation field, and exchanged anisotropy due to a thin layer of antiferromagnetic oxide formed around the ferromagnetic core of the nanoparticles because of their subsequent exposure to air [1]. These phenomena are attributed to size and surface effects that dominate the behaviour of magnetic particles in nanosized range [2]. Typical examples are Co nanoparticles.

Co is a well-known ferromagnetic material which is commonly used as an alloying element in permanent magnets [3]. In recent years, transition metal cobalt (Co) and cobalt oxide (Co_3O_4) are known as promising materials due to their extensive applications in lithium-ion batteries, gas-sensing, data storage, catalysis and electro-chromic devices [4,5] . In nanosized, Co particles display a wide range of interesting size-dependent structural, electrical, magnetic, and catalytic properties [6]. Cobalt is considered to be the first catalyst made from non-precious metal with properties closely matching with those of platinum [7]. Cobalt also serves as a model system for the macroscopic magnetic response because the low to moderate crystal anisotropy allows the effects of size, shape, internal crystal structure and surface anisotropy to be observed in a single system [8,9]. In particular, because of their large surface area, Co nanoparticles showed high chemical reactivity, which makes them suitable for catalysis [10]. In particular, tricobalt tetraoxide (Co_3O_4), a p-type semiconductor with a spinel structure, has been investigated as a promising material in gas-sensing and solar energy absorption and as an effective catalyst in environmental purification and chemical engineering [11-14]. Furthermore, below a critical size of 20 nm, they behave as singe-domain particles displaying

quantum size effects, super-paramagnetism, large magnetic anisotropies, and a maximum coercivity [15].

Much attention has been paid to the characteristics of cobalt nanoparticles; however, there has been little research on the growth mechanism of cobalt nanoparticles. The shape and size of the nanoparticles influence the physical characterization of these novel materials. Therefore, the control of shape and size will increase the possibility of commercial widespread of these materials. So, it is very important to study the effect of kinetic parameters, for example, temperature and time to explain the mechanism of the morphology of the particles from the fundamental viewpoint.

In this paper, we have attempted to synthesize cobalt oxide nanoparticles at different annealing temperatures. The samples were prepared with an optimum pH 9 maintained throughout the experiment, to control the size and morphology of cobalt oxide nanoparticles. The size of the cobalt oxide nanoparticles were tuned by maintaining the stirring speed and the reaction temperature at 50°C. Standard characterization techniques XRD and SEM, were performed for study of crystal structure and surface morphology. VSM was then performed on the synthesized cobalt oxide nanoparticles to study the magnetic behaviour.

2. Experimental Method

150 mmol of (Co $(NO_3)_2 \cdot 6H_2O$) was dissolved into deionized water containing dispersant polyethylene glycol. Excessive amount of NH_4OH was added with electromagnetic stirring at 50°C to form $Co(OH)_2$ gel. pH value was maintained at 9 by dropping KOH. H_2O_2 was dropped into the above suspension. The suspension was centrifuged at 20,000 rpm for 10 min. The centrifuged suspension was placed inside an oven to be heated at 100°C then cooled to room temperature in air naturally. The black products were washed with de-ionized water and ethanol for five times and then dried in a vacuum oven at 80°C for a day. The as-prepared powder was sintered at various temperatures ranging from 450°C-650°C with a fixed annealing time of 2 h in an ambient air to obtain Co_3O_4 with different crystallite sizes.

3. Results & Discussions

Fig. 3.1 (a), (b), (c) shows X-ray diffraction patterns of Co_3O_4 at different annealing temperatures of 450°C, 550°C, and 650°C. The pre-annealed samples give a broad hump indicating that the samples are amorphous in nature [16]. The diffractogram presents the XRD pattern of nanoparticles after exposing the nanoparticles to air; no peak was related to the cobalt element in the XRD pattern. The discernible peaks can be indexed to (220), (311), (222), (400), (422), (511), (440) and (442) planes [17]. All the reflection peaks can be indexed to a cubic phase of Co_3O_4 spinel with lattice parameter a = 8.0850 Å, which is consistent with the reported value (JCPDS: 78-1969). No other peaks for impurities were detected. The spectrum consists of well-defined diffraction peaks indicating that very thin crystalline single phase is formed with cubic crystal structure. The peak broadening at each reflection is also indicative of the formation of fine size cobalt oxide powder. However, for higher annealing temperature at 650°C, it has some broad diffraction lines which remind of some inefficient crystallinity. The degree of orientation of the Co_3O_4 was strongly dependent on the annealing temperature. It increases as the annealing temperature increases. The distribution of the size becomes broader, for a higher temperature of annealing. This can happen if all the nanocrystals grow in size, at the cost of amorphous material, as annealing is performed at higher temperatures. However, the growth of smaller nanocrystals will be at a higher rate than larger crystals; because of the lower melting temperature of smaller nanocrystals [16]. The XRD patterns in figure given above show that increasing thermal treatment temperature results in the intensifying and sharpening of the diffraction peaks. This indicates that the Co_3O_4 grains grow and the nanocrystal quality is improved. To estimate the average crystallite size of nanoparticles from the measured width of their diffraction curves (XRD pattern), we used the Debye-Scherrer formula

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

In this equation, k=0.9 , λ represent the wavelength of the X-ray radiation, β is the full width at half maximum of the diffraction peak (in radians) and $\boldsymbol{\theta}_B$ the Bragg diffraction angle at full width half maximum (FWHM) of the diffraction peak. The sizes were calculated from the broadening of the three main peaks (200), (311), and (440). The crystallite sizes of Co_3O_4 are calculated and presented in Table 3.1 using the full width at oxygen defects at the grain boundaries. As a result, these defects are favourable to the merging process to form larger Co_3O_4 grains while increasing the annealing temperature.

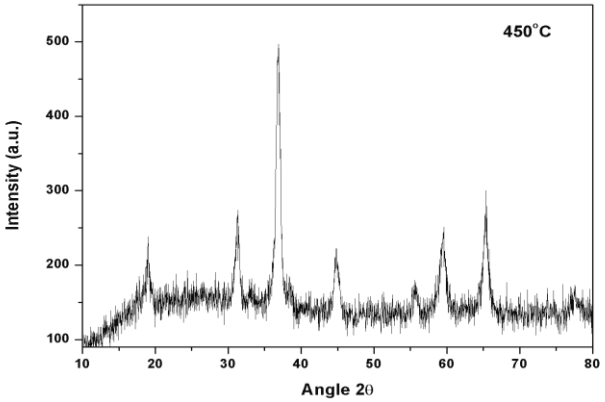

Fig. 3.1 (a) XRD pattern of Co_3O_4 at 450°C

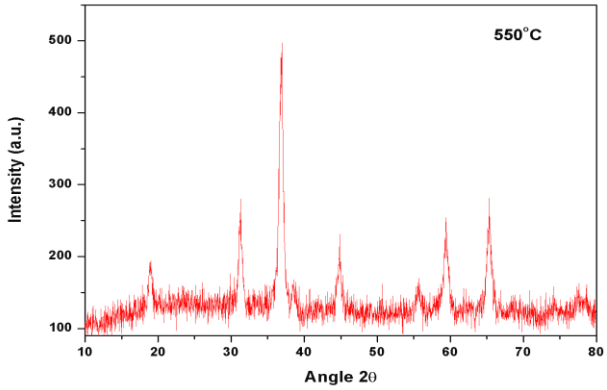

Fig. 3.1 (b) XRD pattern of Co_3O_4 at 550°C

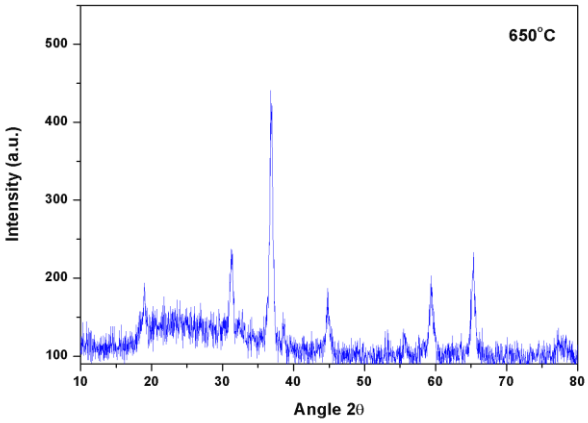

Fig. 3.1 (c) XRD pattern of Co_3O_4 at 650°C

Table 3.1. Cryatallite Size & Lattice Constant at different annealing temperatures.

Annealing Temperature (°C)	Crystallite Size (nm)	Lattice Constant (A)
450	22.10	8.08
550	28.28	8.08
650	29.48	8.08

From Table 3.1, it is seen that as the annealing temperature increases from 450°C to 650°C, the crystallite size also goes on increasing. As the annealing temperature increases, the intensity value of Co_3O_4 exhibits a tendency to decrease, which can be attributed to the coalescences of grains at higher annealing temperature. As a result, it implies that the crystallinity of the Co_3O_4 is improved at higher annealing temperatures. This

may be due to high annealing temperature providing energy to crystallite, gaining enough energy to orient in proper equilibrium sites, resulting in the improvement of crystallinity and degree of orientation of the Co_3O_4 [18]. The distribution of the size becomes broader, for a higher temperature of annealing. This can happen if all the nanocrystals grow in size, at the cost of amorphous material, as annealing is performed at higher temperatures. However, the growth of smaller nanocrystals will be at a higher rate than larger crystals; because of the lower melting temperature of smaller nanocrystals. For the nanoparticles, annealed at higher temperatures mixed phases of cobalt oxide starts appearing, and the growth kinetics of different phases may be different. At low annealing temperature around (200°C), the precursor changes into amorphous cobalt oxide, and hence the amorphous particles have large distribution of size. Any further annealing step gives asymmetric size growth of the nanocrystals and we get large size distribution [16].

Scanning electron microscopy (SEM) images of Co_3O_4 annealed at temperatures 450°C, 550°C and 650°C are shown in Fig.3.2 (a), (b), (c). Comparing them, we see that nanocubic Co_3O_4 with the average particle size of 25 nm is formed at 450°C & 550°C, and when annealing temperature increases to 650°C, some irregular Co_3O_4 including the grains that are recombined in the products are formed. This fact can be explained as the condensation reaction of $Co(OH)_2$ precursors which happens at higher annealing temperature and agglomeration of the nanoparticles occurs. From the SEM image, overgrowth of clusters is clearly seen. When we look at the images of SEM Fig. 3.2 (a), (b), (c), we can see some spherical agglomeration with some pores.

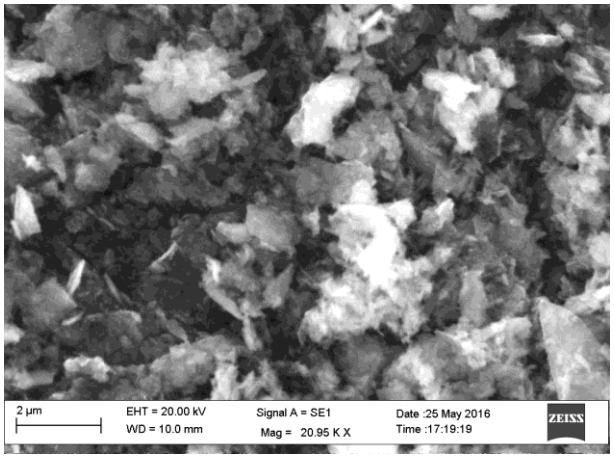

Fig. 3.2 (a) SEM image of Co_3O_4 at 450°C

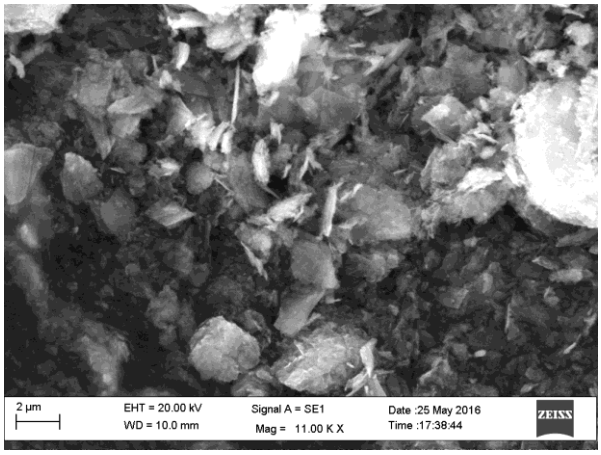

Fig. 3.2 (b) SEM image of Co_3O_4 at 550°C

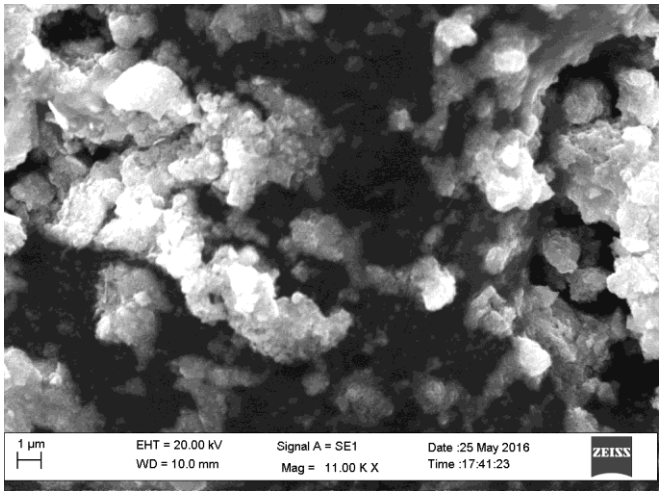

Fig. 3.2 (c) SEM image of Co_3O_4 at 650°C

The paramagnetic or superparamagnetic behavior is documented by the hysteresis loop measured for Co

nanoparticles at 300 K [17,19]. There is almost immeasurable coercivity at room temperature for Co nanoparticles, which is a very typical behaviour for a soft magnet. The hysteresis loops measured at room temperature shows a ferromagnetic behaviour of the Co_3O_4 nanoparticles [17].

In this work, we have studied the magnetic behaviour of Co_3O_4 nanoparticles, whose size variation has been obtained by the variation of the annealing temperature. The magnetic properties of Co_3O_4 nanoparticles annealed at 450°C, 550°C and 650°C were measured at room temperature (300K). The hysteresis loops of cobalt Co_3O_4 nanoparticles in Fig. 3.3 (a), (b) and (c) measured at room temperature show ferromagnetic behaviour with the coercivity (*Hc*) and remanent magnetization (*M*r) values given in the Table 3.2.

Table 3.2. Variation of Saturation Magnetization *(M_s)*, Coercivity *(H_c)* and Remanent Magnetization *(M_r)* at Different Annealing Temperatures.

Annealing Temperature (°C)	Saturation Magnetization (M_S) emu/g	Coercivity (H_c) Oe	Remanent Magnetization (M_r) emu/g
450	42.1	828.23	23.8
550	41.5	349.84	9.65
650	38.1	269.59	6.71

It is observed that saturation magnetization *(M_s)*, coercivity *(H_c)* and remanent magnetization *(M_r)* decreases as the annealing temperature increases. This could be attributed to surface oxidation of the products. This trend of decrease of the coercivity with increasing size of single domain nanoparticles (above a critical size) has been reported by various authors [20-22]. Chen et al.[21] explain this behaviour in nanoparticles in terms of an energy barrier (ΔE) for the rotation of the moments that depends on the surface area of the particle, $\Delta E = Ks\,S$. Here *Ks* is the surface anisotropy constant and *S* the surface area of the particle. This has been shown to lead to a coercivity that decreases with the size of the particles as $Hc \sim 1/d$. Thus, we understand that the observed increase in the coercivity of the particles with decreasing size reflects the increasing role of the surface in determining the anisotropy and hence the coercivity. The increase in coercivity at lower temperature could be due to the increase in the anisotropy energy.

From Fig. 3 it is observed that cobalt oxide Co_3O_4 nanoparticles show a good ferromagnetic behaviour at 450°C. This suggests that along with the increase in the size of the particles, the fraction of the ferromagnetic phase is decreasing. As the annealing temperature increases, particle size also increases and the tendency of cobalt Co_3O_4 nanoparticles shifts towards slightly superparamagnetic behaviour. At higher annealing temperature the Co_3O_4 nanoparticle may show complete superparamagnetic behaviour. The oxygen vacancies play a crucial role in producing ferromagnetism. The vacuum annealing results in the increase of the oxygen vacancy which conducts the recurrence of ferromagnetism. It is known that in a bulk system, the effect of oxygen vacancies is not important as the density of oxygen vacancies is very low. However, when the grain dimensions are reduced to nanometric scale, the translational symmetry breaking and the low coordination at the surface leads to the occurrence of oxygen vacancies, whose density strongly increases as the particle size decreases. Those oxygen vacancies, mainly located on the particle surface, are thought to play a key role for the ferromagnetism observed in nanosized cobalt oxides. Unpaired electrons can be trapped in those oxygen vacancies and their spins can polarize together via exchange interactions and lead to ferromagnetic order [22]. As the particle size increases, the ferromagnetic signal is expected to reduce since the vacancy population decreases. This is thought to be the origin of the ferromagnetism observed in nanosized Cobalt Oxides.

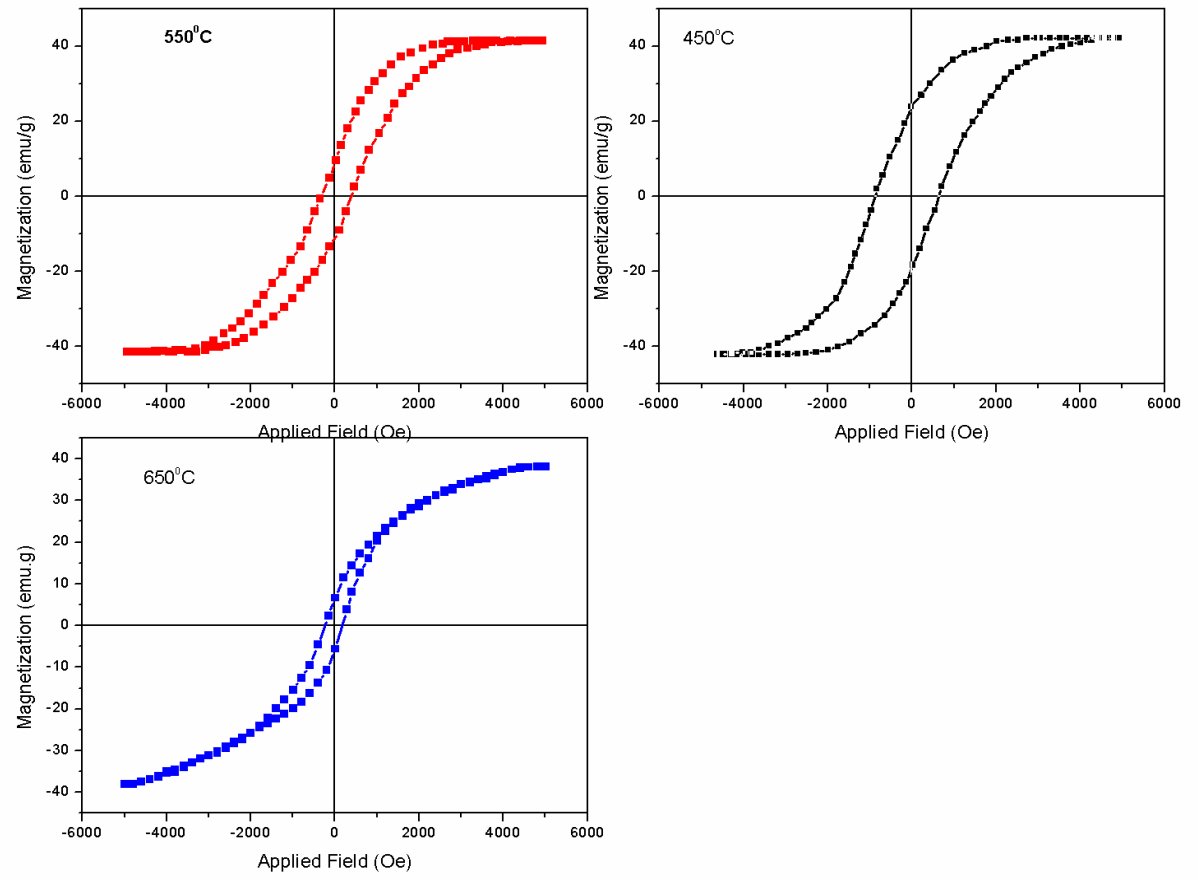

Fig. 3. M-H Curve for Co_3O_4 at 550°C, 450°C & 650°C

4. Conclusions

We conclude that the crystallite size increases as the annealing temperature is increases from 450°C to 650°C. As the annealing temperature increases, the intensity value of Co_3O_4 exhibits a tendency to decrease, which can be attributed to the coalescences of grains at higher annealing temperature. As a result, it implies that the crystallinity of the Co_3O_4 is improved at higher annealing temperatures. This may be due to high annealing temperature providing energy to crystallite gaining enough energy to orient in proper equilibrium sites, resulting in the improvement of crystallinity and degree of orientation of the Co_3O_4. From the SEM images, overgrowth of clusters is clearly seen. Nanograins may have increased their size by further deposition and come covered without any pinholes and cracks. Such surface morphology may offer increased surface area.

The magnetic properties of nanomaterials have been believed to be highly dependent on the sample shape, crystallinity, magnetization direction, and so on. Cobalt oxide nanoparticles have common features of superparamagnetic behaviour at room temperature. We find the coercivity to be decreasing with increasing size of the particles, as the annealing temperature increases. The decreasing trend of the coercivity with increasing size is attributed to the increased role of the surface anisotropy for smaller size particles. Large surface anisotropy values are quite common in nanoparticles systems. Cobalt Co_3O_4 nanoparticles show a good ferromagnetic behaviour at 450°C. This suggests that along with the increase in the size of the particles, the fraction of the ferromagnetic phase is decreasing. As the annealing temperature increases, particle size also increases and the tendency of cobalt Co_3O_4 nanoparticles shifts towards slightly superparamagnetism. At higher annealing temperature the Co_3O_4 nanoparticle may show complete superparamagnetic behaviour.

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