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EFFECT OF ANNEALING ATMOSPHERES ON COBALT FERRITE NANO-PARTICLES AND THEIR APPLICATIONS

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Cobalt ferrite nano-particles have been synthesized by co-precipitation and annealed in air and in an inert atmosphere. Change in the physical properties has been analyzed by various analytical techniques like XRD, TEM, VSM, etc. A significant change in the physical properties like structural, particle shape, size, magnetization and microwave absorption has been observed. The effect of annealing on other properties like Curie temperature, electrical conductivity is also investigated. Particles unannealed and annealed in air and in an inert atmosphere are studied for electromagnetic wave interference.

Introduction. Magnetic particles large or small in size have various applications in many devices[1, 2]. In particular, magnetic nano-particles have special magnetic and electrical properties that are important for applications like ferrofluid, microwave absorption, memory devices, etc. The size reduction of the magnetic particles leads to several unusual properties like disorder of surface spin or spin canting [3–7], surface anisotropy and superparamagnetic behaviour [8,9].

The development of novel materials is a fundamental focal point of material research, which is mandated by advancements in all areas of industry and technology. The superparamagnetic particles find good applications in ferrofluid preparation [10]. The present study aims at finding the change in physical properties of the sample annealed in air and in argon atmosphere. The crystalline phase transformation, shape and size distribution, magnetic measurements are the main aspects in the microwave absorption studies.

1. Experimental. The nano-crystalline $CoFe_2O_4$particles are synthesized by using 1 molar solution of high purity salts of $Co(NO_3)_26H_2O$, $Fe(NO_3)_39H_2O$ in water. The solutions are mixed in 1 : 2 ratios and homogenized at a constant temperature (70°C). The particles are precipated using 25% ammonia solution under a controlled pH of 10.5 with continuous stirring of the solution and dried to produce nano-particles of $CoFe_2O_4$ [11]. The so obtained particles (sample 'a') were annealed in air (sample 'b') and in argon atmosphere (sample 'c') at 1173 K for 1 hour at the maintaining heating rate 3°C/min in a UK made carbolite furnace. To understand the change in physical properties, these particles were analyzed using various analytical techniques. The crystalline phase and its transformation were analyzed by the Bruker (Germany) made D-8 advance powder X-ray diffractometer (XRD) at 40 KV and 40 mA, CuK_α radiation, maintaining the step size rate 0.02°C/sec. The shape and size distribution of the particles plays a very crucial role in producing a stable ferrofluid and other devices. The material was thus analyzed by a transmission electron microscope (TEM), model JEM-200 CX. The surface morphology of the samples was recorded by the Leo made scanning electron microscope. The magnetization of the sample was measured by a DMS–880

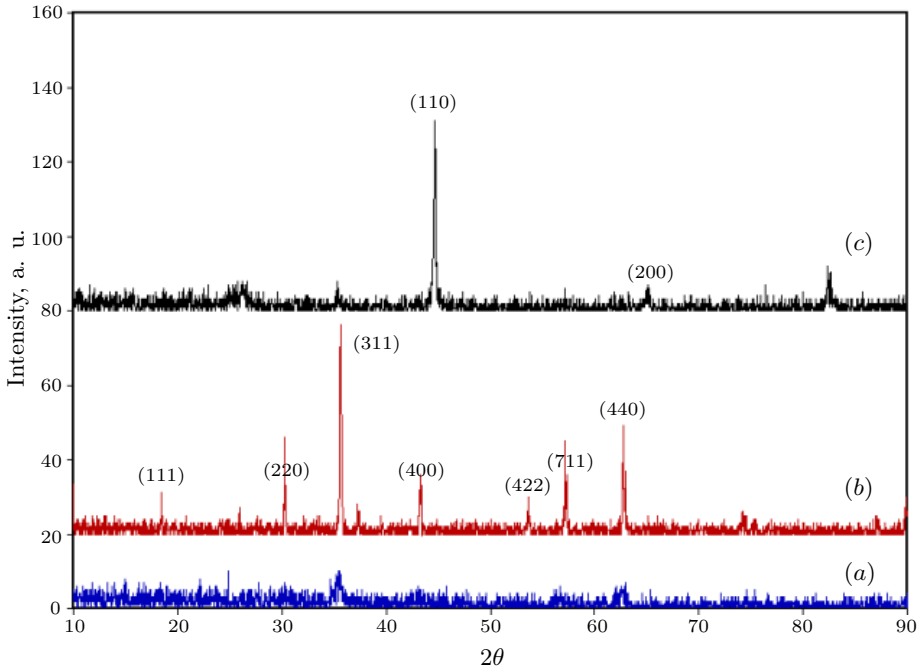

Fig. 1. X-ray diffraction pattern of $CoFe_2O_4$ samples: (*a*) synthesized at 373 K, (*b*) annealed at 1173 K in air, (*c*) annealed at 1173 K in argon.

Vibrating Sample Magnetometer (VSM) technique. Conductivity measurements were analyzed by the Keithley Nano-voltmeter model No. 2182A and the current source 6221. Further, the particles were tested for a microwave absorbing material.

2. Results and discussions. The results of our investigation on the cobalt ferrite nano-particles synthesized and further grown at a different annealing atmosphere for one hour show unique properties in the nano-region. The X-ray diffraction pattern of the synthesized particle treated in air and in argon atmosphere at 1173K are shown in Fig. 1, respectively. A broad X-ray diffraction pattern of sample (a) confirms the nano-crystalline phase formation of $CoFe_2O_4$ at 373 K (ICDD data file No. 22-1086), which shows weakly crystalline or due to ultra fine nature of particle as shown in Fig. 1*a*. By annealing the same sample at 1173 K in air, the crystalline phase of the sample remains invariant with sharp X-ray diffraction peaks and intensity, which confirm the stability of the particles in the air atmosphere even at high temperatures (Fig. 1*b*). The increase in sharpness and intensity of the diffraction pattern indicates the grain growth and an improvement in crystallite size. However, annealing the particles in argon atmosphere for one hour at 1173 K shows a complete crystalline phase transformation from cubic cobalt ferrite to cubic form of cobalt-iron (ICDD data card number 49-1567) shown in Fig. 1*c*. It is anticipated that the core-to-surface ratio of a particle is very large that creates negative pressure [12], where argon works as a reducing agent and forms a CoFe nano-alloy. In order to calculate the crystallite size of the samples, a slow scan (step size 0.005°C/min) of selected diffraction peaks (311), (400) and (711) is recorded for all samples (*a*, *b*, *c*). The crystallite size was calculated using the following relation for all samples

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

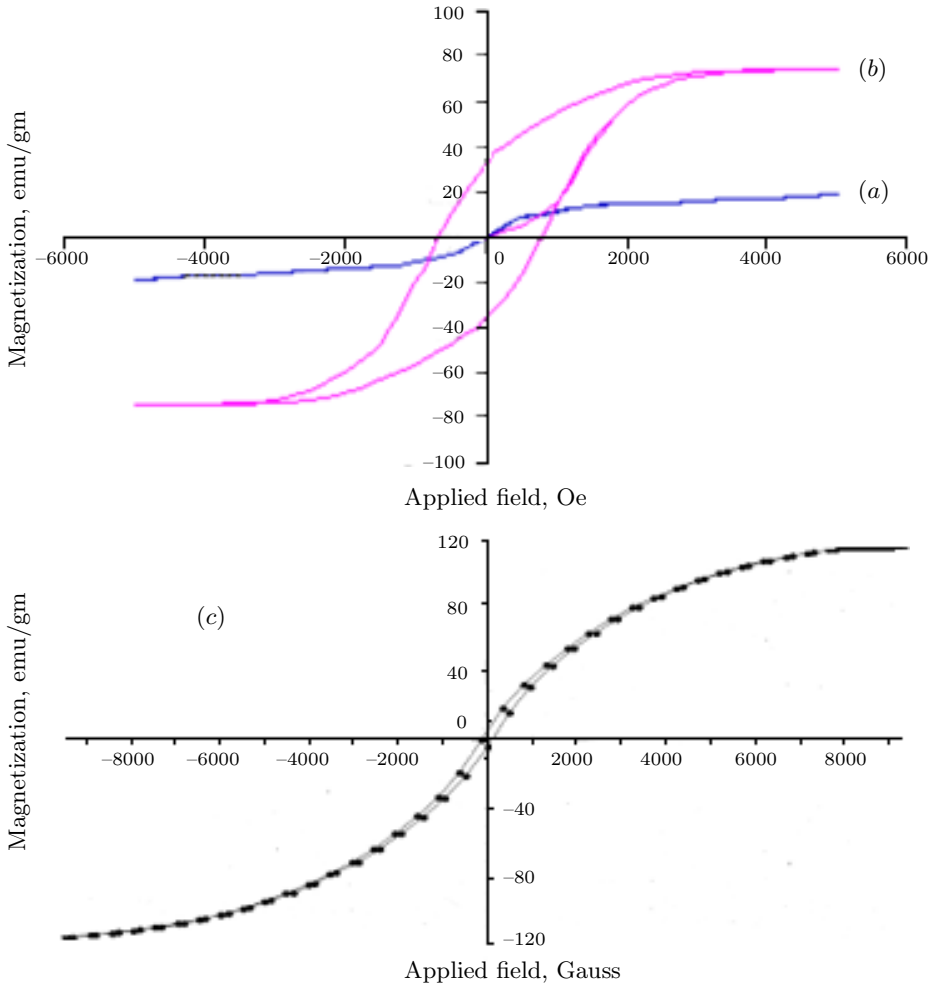

Fig. 2. $M(H)$ curves for the samples: (a) synthesized at 373 K, (b) annealed in air at 1173 K , (c) annealed at 1173 K in argon.

Comparative changes in crystallite size are calculated using the Scherer formula, which is shown in Table 1.

For magnetic materials, the magnetic moment per unit volume is a measure of strength. The magnetization curves of samples (a), (b) and (c) are shown in Fig. 2. Magnetization for the so grown material, i.e., sample (a), shows zero coreceivity and zero retentivity, which indicate the superparamagnetic nature of these

Table 1. Annealing effects on the crystallite size and particle size in air and in argon atmospheres on synthesized nano-particles of $CoFe_2O_4$.

Sr. No.	Sample	Crystallite size (nm)	Particle size (nm)
1	(a)	8	5 – 10
2	(b)	25	~ 100
3	(c)	36	~ 100

Table 2. Measured magnetization properties viz. retentivity, coreceivity and saturation magnetization for the synthesized $CoFe_2O_4$ particles as well as for the particles annealed at 1173 K in air and in argon.

Sr. No.	Sample	Retentivity (emu/gm)	Corecivity (Oe)	Saturation Magnetization (emu/gm)
1	(a)	0	0	18
2	(b)	32	1000	74
3	(c)	5	20	110

particles. The curve for sample (b) shows a relatively high saturation magnetization, corecevity and retentivity than sample (a). The $M(H)$ curve of Fig. 2c shows a further increase in saturation magnetization with a decrease in coreceivity and retentivity compared to the particles annealed at the same temperature in air. The increase in saturation magnetization in the case of nano-particles treated in air at 1173 K can be attributed to the increase in surface-to-volume ratio, direct exchange and spin canting at annealing [14]–[17]. The comparative measurements of saturation magnetization, corecivity and retentivity for samples (a), (b) and (c) are presented in Table 2.

The shape and size distribution of the particles is very important from the application point of view. The TEM measurement technique is used to determine the shape and size distribution of the particles and corresponding electron diffraction for the crystalline phase. TEM micrographs for all samples are shown in Fig. 3. The micrograph of sample (a) shows that almost all particles are spherical in shape and have a uniform size distribution in the range of 5 – 10 nm. The interplanar spacing calculated from the diameter of the diffraction rings, which perfectly match with the crystalline phase of cobalt ferrite, seem to be less crystalline. At annealing, we assumed that the particles in the nano-range were joining their neighbours by melting their surfaces at the temperatures well below the melting points of their bulk. This is due to the decrease in melting point when the surface-to-volume ratio of the particles becomes very high. The annealed particles have become nearly 100 nm in sizes.

3. Microwave application. In microwave shielding, both the conductivity and the magnetic permeability play a crucial role in determining the skin depth for the material. The skin depth is the amount of thickness of the material, which reduces the intensity of microwaves to $1/e$ times when passed through it. The skin depth (δ) is defined as

$$\delta = \frac{1}{\sqrt{\pi f \mu \sigma}}, \tag{2}$$

where, f is the frequency of microwaves, magnetic permeability $\mu = B/H$ is the relative increase or decrease in the resultant magnetic field inside a material compared with the magnetizing field, in which the given material is located, σ is the electrical conductivity of the material.

The magnetically permeability and better conductivity (σ) of the cobalt-iron metal alloy is comparatively higher ($\sim 10^3 \Omega^{-1}\mathrm{cm}^{-1}$) than the unannealed and air annealed particles of $CoFe_2O_4$, which is of the order of $10^{-6}\Omega^{-1}\mathrm{cm}^{-1}$. The results of microwave absorption of samples (a), (b) and (c) recorded at 100 GHz, 5 mW power are shown in Table 2. As per our expectations, samples (a), (b) and (c)

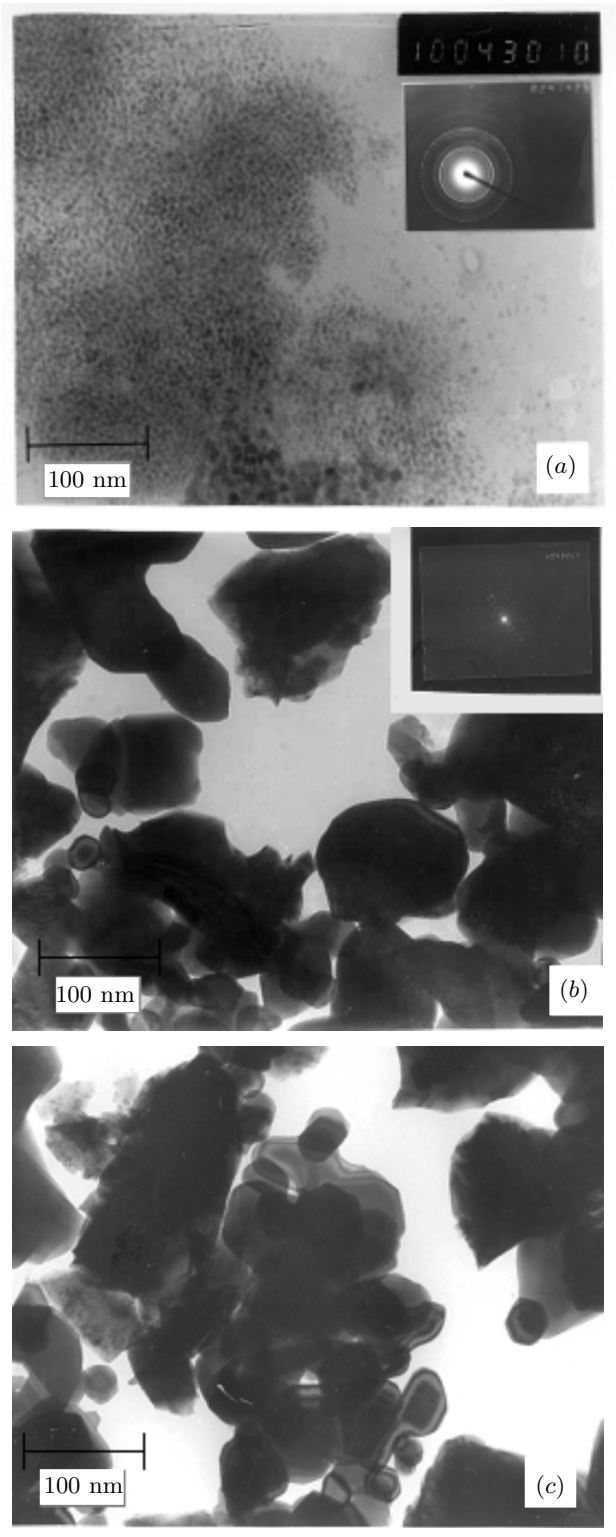

Fig. 3. Transmission Electron Micrographs (TEM) images of the $CoFe_2O_4$ samples: (*a*) synthesized at 373 K, (*b*) annealed at 1173 K in air, (*c*) annealed at 1173 K in argon.

Table 3. Experimental results of the microwave absorption by samples (*a*), (*b*). (*c*) Input signal used for microwave absorption 5 mW, frequency 100 GHz.

Sr. No.	Sample	Film thickness (mm)	Input microwave signal (mV)	Output microwave signal (mV)
1	(a)	1	1.029	0.916
2	(b)	0.5	1.029	0.743
3	(c)	0.5	1.029	0.549

show the relative increase in microwave absorption. The experimental results of the microwave absorption by the three samples are given in Table 3, where a microwave signal of 1.029 mV and frequency 100 GHz was used as an input source. Another way, all the three samples were kept in a microwave oven [18] for a period of about 10 sec. It was interesting that sample (*c*) showed a very high microwave absorption and become red hot. On the other hand, the nano-particles for samples (*a*) and (*b*) show a poor microwave absorption property and are slightly heated when kept even for more than 1 min duration in the same experimental conditions. This high absorption of microwaves by the argon treated nano-particles has paved the way for their application in microwave shielding.

4. Conclusion. The synthesized nano-particles further were used for the formation of a cobalt-iron metal alloy. These cobalt-iron particles having both conducting and magnetic properties may have suitable applications for the microwave shielding, transformer core, inductor core and so on applications. The metal alloy particles are successfully examined for the microwave absorption properties. The need for microwave absorbers is increasing day by day for many devices such as computers, cell phones and other electronics to move to higher frequencies and speeds. Therefore, it is need of the time to develop such nano-composite microwave-absorbing shielding materials.

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