The magnetic investigations of indium substituted cobalt ferrite nanoparticles

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Abstract:
The nanocrystalline In^{3+} substituted cobalt ferrite having molecular formula $CoIn_xFe_{2-x}O_4$ (x= 0.0,0.1,0.2,0.3,0.4,0.5) have been synthesised by sol-gel auto combustion technique. The magnetic properties were studied with the help of pulse field hysteresis loop tracer technique. The saturation magnetisation decreases with increase in In^{3+} substitution x. The temperature dependence of field cooled (FC) and zero field cooled (ZFC) magnetisation of indium substituted cobalt ferrite nanoparticles.
Keywords: Sol-gel, nanocrystalline, FC and ZFC

Introduction:

In the recent years, interest in nano size materials has increased due to their unusual physical and chemical properties which often differ from the bulk. The difference in the properties of nano size materials is attributed to the increase in surface area along with decreased particle size and various size effect [1-2]. The nano-size materials have become the focus of interest for several researchers not only due to their superior properties but they have many technological applications in recording media, drug delivery, catalyst, sensors, biomedical engineering and other fields [3-4]. Much attention has been recently devoted to the nano particles of spinel ferrite systems. Nanostructured iron oxide containing transition metal oxide materials are known to exhibit interesting physical and chemical properties, significantly different from bulk materials, because of their smaller size and large specific surface area. Ferrites are defined as magnetic materials composed of iron oxide as their main constituent and metal oxides. Ferrites possess both electrical and magnetic properties and have many applications in electronic computer, medical, automobile and other areas.

In the family of ferrites, cobalt ferrite with spinel structure have attracted scientists and technologists because, cobalt ferrite is a hard magnetic material with high coercivity, moderate magnetization, high Curie temperature and excellent chemical stability [5-6]. The high electrical resistivity and negligible eddy current losses makes cobalt ferrite useful in high frequency magnetic applications, magnetic recording applications (audio-video tapes) and high density digital discs etc [7]. The cobalt ferrite has cubic inverse spinel structure with Co^{2+} ions occupying half of the octahedral [B] sites whereas Fe^{3+} ions occupy all tetrahedral (A) sites and half of the octahedral [B] sites [8]. In addition to these remarkable features, the cobalt ferrite exhibits large magneto crystalline anisotropy along with (100) crystallographic direction and large magnetostriction in bulk form.

Nano size cobalt ferrite has been prepared by using physical and wet-chemical methods. Wet-chemical methods are particularly interesting and advantageous for their low cost, ease of preparation, low temperature synthesis, smaller particle size, good chemical stability and homogeneity. The wet-chemical methods include hydro-thermal [9], sol-gel [10], chemical co-precipitation [11], micro-emulsion [12], sono-chemical [13]. The sol gel auto combustion method is a well known and commonly used technique which produces high purity, homogenous powders with nano meter dimension. In the literature, a lot of work has been reported about synthesis and magnetic properties of cobalt ferrite synthesized by various methods [14-17].

A review of literature shows that very limited work has been done on infrared and cation distribution studies of nanocrystalline cobalt ferrite. The important electrical and magnetic properties of ferrites are related to the distribution of cations among the available octahedral [B] and tetrahedral sites (A) in spinel structure, therefore control of cation distribution provides a mean to tailor their properties for desired applications. In view of this, the study of cation distribution is of particular interest in understanding the structural, magnetic and electrical properties of cobalt ferrite nanoparticles. The cation distribution depends on method of preparation, valence of electrons, electronic configuration etc. parameters [18]. The changes in the particle size can also influence the magnetic properties arising due to change in the cation distribution [19].

In this study, we report the synthesis of cobalt ferrite nanoparticles using sol-gel auto combustion technique and their magnetic properties.

EXPERIMENTAL TECHNIQUE:

Cobalt ferrite ($CoFe_2O_4$) with nano size particles was synthesized by a sol-gel auto combustion technique to achieve homogeneous mixing of the chemical constituents on the atomic scale and better sinterability. The precursors used in the synthesis were cobalt nitrate [$Co(NO_3)_2.6H_2O$] and ferric nitrate [$Fe(NO_3)_3.9H_2O$], Glycine [$C_2H_5NO_2$] was added as a fuel. All the reagents used for the synthesis of cobalt ferrite nanoparticles were of an analytical grade and used as received without further purification. The stoichiometric amounts of cobalt nitrate $Co(NO_3)_2.6H_2O$ (6.2021 g) and ferric nitrate ($Fe(NO_3)_3.9H_2O$) (17.2191 g) were dissolved in deionized water under continuous magnetic stirring. Then glycine [$C_2H_5NO_2$] (12.14 g) was mixed in the metal nitrate solution to chelate Co^{2+} and Fe^{3+} ions in the solution. The molar ratio of glycine to total moles of nitrates was maintained at 1:3. A small amount of ammonia was added drop-wise into the solution to adjust pH value to about 7 and stabilize the nitrate-glycine solution. The neutralized solution was evaporated to dryness by heating at 90 ^{0}C on a hot plate with continuous stirring until it becomes viscous and finally formed a very viscous gel. The temperature is further raised up to 110 ^{0}C so that the ignition of the gel starts. The dried gel burnt completely in a self propagating combustion manner to form a loose powder. Finally, the as burnt powder was annealed at temperature 550 ^{0}C for 4 h with a heating rate of 5 ^{0}C per minute to obtain the spinel phase. The sintered powder was pressed into pellets of thickness 3 mm and diameter 10 mm using a uni-axial hydraulic press. The pressure applied on the pellet was 6 tons/cm^2.

RESULT AND DISCUSSION

Magnetic properties were measured at room temperature using pulse field hysteresis loop technique. The saturation magnetization (M_s), coercivity (H_c) and remenance magnetization (M_r) were obtained using M-H plots (Fig. 5.12) The M-H loops at 300 K exhibit superparamagnetic behaviour of the samples. From the hysteresis curves in the ferrimagnetic state the value of H_c, M_r and M_s were deduced and are given in Table.

It is observed that saturation magnetization decreases with increase in indium content x. The observed variation of magnetization can be explained on the basis of exchange interaction [20]. The saturation magnetization can be calculated as $M_s = M_B- M_A$, where M_B is the magnetic moment of ions on [B] site and M_A is the net magnetic moment of ions on (A) site. Taking only spin values of Fe^{3+} Co^{2+} and In^{3+} as 5 μ_B, 3 μ_B and 0 μ_B respectively and considering the cation distribution given in Table 5.5, the net saturation magnetization M_s values were calculated for $0.0 \leq x \leq 0.5$. The decrease in magnetization on addition of indium can be attributed to the fact that the B sub-lattice is diluted due to indium substitution which results in decrease in A-B interaction. The coercivity decreases with indium substitution x. The high values of coercivity indicate nano crystalline nature of the samples.

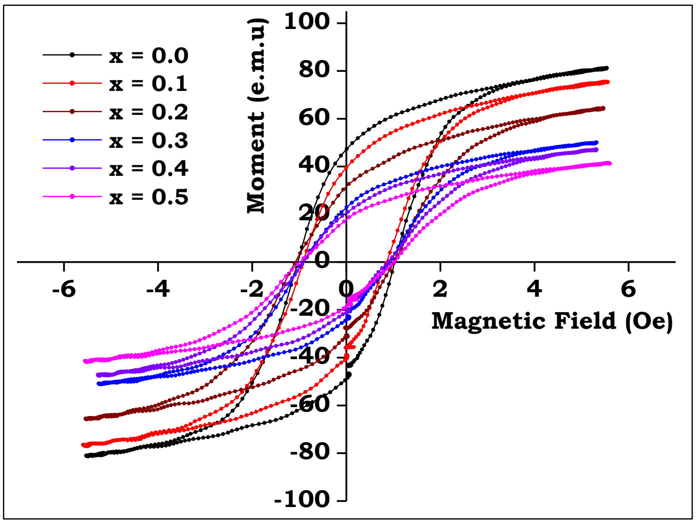

Figure 1: M-H plots recorded at room temperature fo $CoIn_xFe_{2-x}O_4$

x	M_s (emu/gm)	M_r(emu/gm)	Hc (Oe)	(Mr/Ms)	n_B (μ_B)
0.0	81.28	77.93	1028.99	0.96	3.414
0.1	75.50	52.60	886.29	0.70	3.251
0.2	64.48	38.34	1052.10	0.59	2.845
0.3	50.10	29.50	926.03	0.59	2.263
0.4	47.18	22.06	897.65	0.47	2.181
0.5	41.46	19.62	1000.42	0.47	1.961

Table 1:Saturation magnetization (Ms), Remanence magnetization (Mr), Coercivity (Hc) and Remanence ratio (Mr/Ms) and magneton number (n_B) for $CoIn_xFe_{2-x}O_4$ nanoparticles.

Under zero – field - cooled (ZFC) and field – cooled (FC) conditions; the magnetization measurements were performed for three typical samples. Figure 2 shows the ZFC-FC magnetization curves for the typical samples of $CoIn_xFe_{2-x}O_4$ system (for x = 0.0, x = 0.2, x = 0.5), all measured in the temperature range of 4.2 K - 325 K under an external static magnetic field of 50 Oe. These curve do not overlap at 325 K, this behavior is a characteristic of super-paramagnetism.

The blocking temperature of cobalt ferrite nanoparticles seems to be above room temperature. The relatively larger anisotropy contributions in cobalt ferrite nanoparticles.

The FC magnetization shows an increase with then tends to saturate with decrease in temperature. The ZFC magnetization shows the decrease continuously down to 10 K.

Conclusions:

A series of substituted indium ferrites with composition $CoIn_xFe_{2-x}O_4$ with x = 0.0, 0.1, 0.2, 0.3, 0.4 and 0.5 were prepared by sol gel auto combustion method. The effect of substitution of indium on structural, electrical, dielectric and magnetic properties of cobalt ferrite has been studied. The saturation magnetization coercivity and magneton number decreases with indium substitution x. Behavior of saturation magnetization is explained on the basis of Neel's model.

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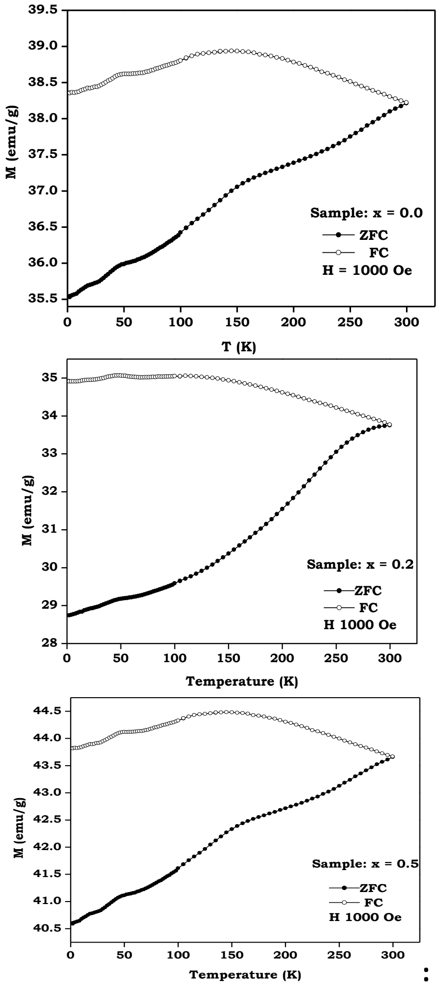

Figure 2: Temperature dependence of ZFC and FC magnetization of $CoIn_xFe_{2-x}O_4$ system for the typical samples, x =0.0, x =0.2 and x =0.5

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