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A study of effects caused by dopant copper atoms and temperature on cobalt ferrite nanoparticles

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ABSTRACT

We had prepared nano particles of Cobalt Ferrite $CoFe_2O_4$ by citrate precursor method. It is a low cost route, which ensures easy synthesis of ferrite nanoparticles samples. To find effect of doping copper in place of cobalt, we introduced 1% and 5% copper in this in calculated amount. We annealed the samples at two temperatures 450^0C and 650^0C. The structural and magnetic properties of all these samples were studied with the help of X-Ray diffractometer and vibrating sample magnetometer.

We found that particle size increased generally with temperature, but introduction of copper in more amounts seems to oppose the tendency of segregation. In the context of magnetic properties, the saturation magnetization was observed to be slightly increasing with temperature. The coercivity was also dependent of temperature, but the amount of dopant did not exhibit any effect on it.

***Keywords:* Annealing, citrate precursor, cobalt ferrite, coercivity, lattice parameter**

I.INTRODUCTION

We are already aware that particle size affects the structural and magnetic properties of cobalt ferrite nanoparticles. Specially single domain particles have properties remarkable different from bigger particles.[1]

The main cause of the special properties is magnetic relaxation process, which is due to thermal effect and existence of energy barriers separating the local minima for different equilibrium states of system. So, the magnetic behavior of a small particles depends on its relaxation time $\tau = \tau_0 \exp[\frac{KV}{K_B T}]$, where τ_0 is about 10^{-10} s and weakly depending on temperature, K_B is Boltzmann constant, T is temperature, K and V are anisotropy and average volume[2]. At very small particle size the anisotropy factor is not sufficient to stop the magnetization vector from switching to a lower energy state. Another interesting feature of nanoparticles is the due to surface spin disorder which is induced by broken exchange bonds at the surface. As a result, the system should be considered as a core shell structure with ferromagnetically aligned core spins and a spin glass like surface layer, whose thickness can vary[1].

In this work we studied few properties of cobalt ferrite nanoparticles, when we doped them with copper. In addition, we tried to do this work at two temperatures also.

II.MATERIALS AND METHODS

To synthesize cobalt ferrite, we took Cobalt nitrate Co $(NO_3)_2$ and Ferric Nitrate Fe $(NO_3)_3$ separately in stoichiometric proportion and dissolved both in minimal amount of distilled water. To dope copper, we removed 1 % and 5% of cobalt nitrate and added that much of copper nitrate so that number of moles of cobalt atoms removed is roughly compensated by copper atoms in the samples. This solution was mixed with citric acid solution and was heated for two hours with constant stirring at about 68^0C. The resulting brown jelly like substance was placed in oven for 24 hours at temperature 80^0C and became fluffy like bricks. This was sintered at two temperatures 450^0C and 650^0C. XRD and VSM measurements for these samples were carried out.

III.RESULTS AND DISCUSSIONS

The X-Ray diffraction analysis was done and crystallite size was calculated by Scherrer's formula[13,14]. At the same time, the measurements of saturation magnetization, coercivity etc. was done by vibrating sample magnetometer and overall, Table 1 was obtained.

Sample **450^0C**	Crystallite size (nm)	Saturation Magnetization Emu/g	Coercivity (G)	Retentivity (G)	Lattice parameter A^0
$CoFe_2O_4$	43.4	36.7	1460.0	19.5	2.52
$Cu_{0.01}Co_{0.99}Fe_2O4$	61.3	42.4	1768.1	24.0	2.52
$Cu_{0.05}Co_{0.95}Fe_2O4$	73.1	37.2	171.9	20.18	2.52
650^0C					
$CoFe_2O_4$	46.5	41.4	654.1	16.8	2.54
$Cu_{0.01}Co_{0.99}Fe_2O4$	73.8	66.1	171.6	26.35	2.53
$Cu_{0.05}Co_{0.95}Fe_2O4$	46.1	54.8	134.7	22.5	2.51

Table 1, Data obtained

We can see the particles size has increased with temperature in all the samples, except the sample, where doping of copper was 5%[1] . The change in particle size is almost linear with doping at 450^0C. This trend is in agreement with LD Tung et. al. It has also been found earlier that the annealing temperature affects the particle size significantly[4]. The fig 1 is a comparative view of XRD plots, showing peaks approximately at same locations in all samples. We can see that replacement of cobalt atoms, with copper atoms is not significantly changing the structure. None of the samples were found to have superparamagnetism because the selected temperature range was high and particles size was large (40 to 90 nm). Tin ferrite is seen exhibiting large change in particle size with rise of temperature shown in Figure 1. The variation of particle size is shown in Figure 2.

Coming on at magnetic properties, we analyzed the data obtained by vibrating sample magnetometer.

When the external magnetic field is applied over the sample, it tries to orient the magnetic dipoles either by domain rotation or by domain wall movement depending normally on the size of particle. At a particular field, maximum number of dipoles orient, the field is called saturation magnetization. The direction of net dipole moment of **A** sites and **B** sites are in opposite direction and their resultant decides the net field.

Saturation magnetization of cobalt ferrite samples at 650^{0}C was almost more than that at lower temperature but no relationship seems to be there with doping percentage. We have shown the graph representing this in Figure 3. This study can be extended further with the help of Mössbauer spectra in which shift in peaks may assure about existence of core shell model[3,4].

The coercivity is very important factor in defining the magnetic characteristics of a material. It is the field strength necessary to reverse the spin orientation direction[9]. The wohlfarth model assumes that there is a uniform magnetization throughout the particle and it remains so throughout the rotation process[10]. Generally the energies required to reverse the spin orientation within single domain are larger than those needed in bigger ones so coercivity is larger in small particles. In other word, when particle size decreases to single domain, the domain rotation is preferred, consuming more strength of external field making coercivity high. At the blocking temperature, when thermal energy is sufficient to break the anisotropy barrier, the coercivity gets zero. Below this temperature, the coercivity is the field which together with thermal energy can overcome the anisotropy. Therefore coercivity increases with size, below blocking temperature[10]. (Figure 4.)

In our samples, we easily conclude that there is no significant increase in coercivity with temperature and say particle size. It can be attributed to core shell structure of them already discussed above[10]. In all the samples, the coercivity is more at lower temperature which verified the established theories about dependence of coercivity with temperature[11].

Retentivity of cobalt ferrite was seen to lesser with temperature (19.5 to 16.8 G). As the doping was done this trend discontinues. The graph is also shown in Figure 5.

This anomaly can be attributed if we assume varying thickness of shell having canted spins surrounding the core. The increasing fraction of atoms having canted spin can also lead to this anomaly.

Another property is the lattice parameter, which depends on the choice of dopant atoms rather than temperature. As shown in Fig 2, At 450^{0}C, the lattice parameter of pure Cobalt ferrite is 2.52 Å. The Cobalt ferrite is an inverse spinel, in which cobalt atom and half of the iron atoms are on **B** sites, while other half of the iron atoms are on **A** sites. Copper has a tendency to go on **B** sites [12]. The Cu atoms, having affinity for **B** sites seem to replace Fe atoms only but change is not very large. Our data strengthens earlier views and it can be checked later. The change in lattice parameter with temperature is not significant. The figure 6 is representing the variation of lattice parameter.

There is always a possibity with the compromised purity of the samples. So find that we matched our data with ICDD (International centre for Diffraction Data), which indicated that the phases are sufficiently pure, but small amount of impurities were present at 450^0C, which were seen settled at high temperature. It may be due to their decomposition.

The $CoFe_2O_4$ sample had trace amounts of FeO, and Fe_2O_3, shown by lines at 33.162, 35.630, 49.465 degrees. At higher temperature these are negligible. $Cu_{0.1}Co_{0.99}Fe_2O_4$ sample was having oxides of iron in very little amount but at high temperature the oxides are absent. Overall we found that oxides of iron are more likely to be found as impurity at low temperature. At high temperature, the phases are more pure.

IV.CONCLUSION

We conclude that structural and magnetic properties can be tailored with annealing temperature and doping concentration. At the same time, we note that higher temperature is more suited for synthesis of cobalt ferrite nanoparticles. We hope that our study will help in selection of proper method of synthesizing cobalt ferrite with pre required properties in future.

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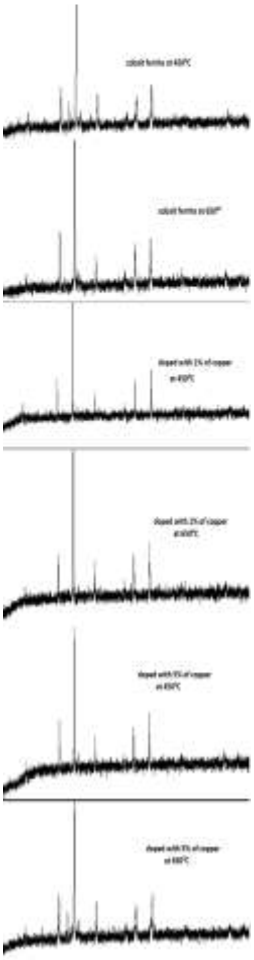

Figure 1, XRD plots together

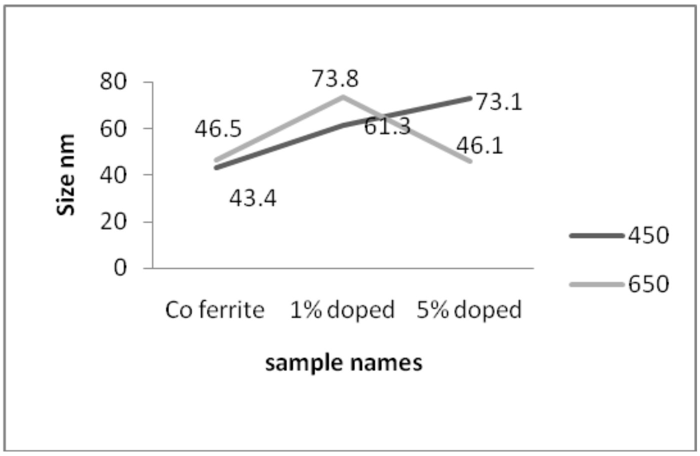

Figure 2, particle size plot

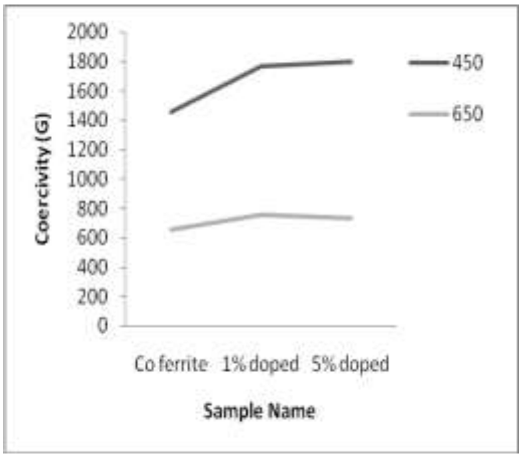

Figure 4, plot for coercivity

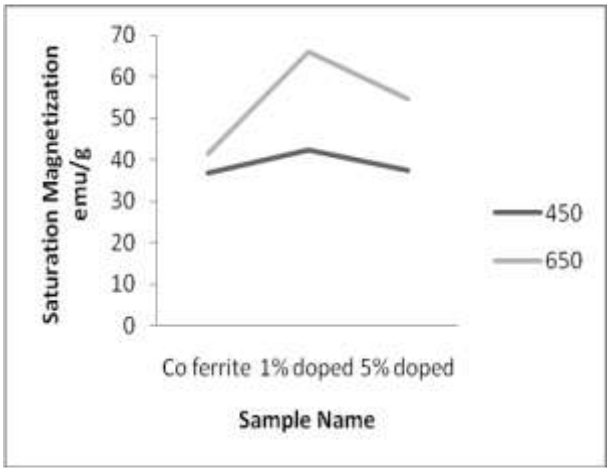

Figure 3, plots of saturation magnetization

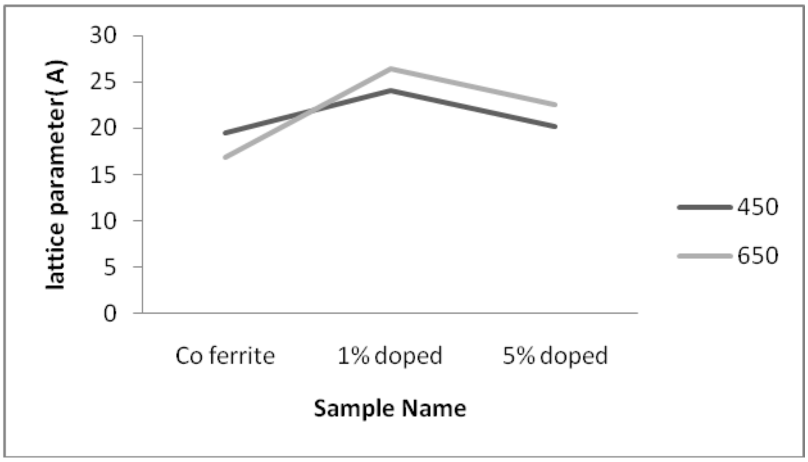

Figure 5 variations in retentivity

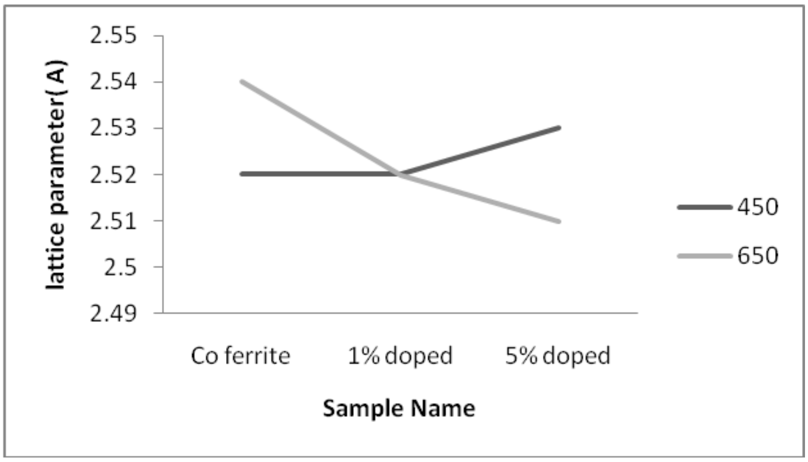

Figure 6, variation of lattice parameter