Synthesis And Properties of Ho^{+3} Doped Co-Cr-Fe Ferrite Nanoparticles Prepared by Sol-Gel Chemical Route

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ABSTRACT

Holmium doped Co-Cr-Fe spinel ferrite nanoparticles were synthesized by using sol-gel auto combustion method. X-ray diffraction patterns shows addition of Ho^{3+} ions increases the values of X-ray density and average crystallite size for all the samples. The particle size obtained from the analysis of TEM images is in good agreement with the results obtained from XRD and SEM analysis. It is also observed that the Ho^{3+} substitution in Co-Fe-Cr ferrites greatly affects on the magnetic behaviour of the samples and the saturation magnetization increases.

Keywords- Sol gel synthesis, XRD, cystallite size, hysteresis curve

I. INTRODUCTION

Recently ferrite nanoparticles have been the subject of much interest because of their unusual optical, electronic and magnetic properties, which makes them different from their bulk analogue[1]. Because of very high magnetocrystalline anisotropy cobalt ferrites become technologically important materials. Since the discovery of ferrites, they have been used in various appliances/equipments as they have very wide range of applications from microwave to radiofrequencies. Antenna cores in radio receivers, fly back transformer in TV picture tube, broad band transformer, mechanical filter, ultrasonic generator, moderators, phase shifters, isolators, etc are the components which cannot be manufactured without use of ferrites. Spinel ferrites with nano-structure have technological importance and applications in various fields due to their unique properties. High electrical resistivity, low eddy currents and dielectric losses of the ferrite materials are strongly affected by various parameters like chemical composition, type of dopant, concentration of dopant, method of preparation and position of cations over tetrahedral – A and octahedral – B sites. Cobalt ferrite nanoparticles with spinel structure show some interesting properties over the other materials such as very high saturation magnetization, high coercivity, large magnetocrystalline anisotropy, excellent chemical stability and good mechanical hardness. Cobalt ferrite shows inverse spinel structure and the percentage of inversion depends on the synthesis method and sintering conditions[2]. It has been predicted that properties such as thermal and electrical conductivity, and electromagnetic, electrical and optical behaviour could be enhanced in materials by substituting them with rare earth element cations or combinations cations, such as La^{3+}, Gd^{3+}, Nd^{3+}, Ce^{3+}, Ho^{3+} etc.

In the present investigation, nanocrystalline ferrite powders of Ho^{+3} doped cobalt ferrites with general chemical formula CoHoxFe1-0.5xCr1-0.5xO4 were synthesized by using sol-gel auto-combustion technique[3].

II. SAMPLE SYNTHESIS

In the present study Ho^{3+} doped cobalt ferrite nanoparticles with general formula CoHo$_x$Fe$_{1-0.5x}$Cr$_{1-0.5x}$O$_4$ (x= 0.0, 0.05, 0.1, 0.15) were synthesized by using sol-gel auto-combustion method. Metal nitrates of constituent elements having chemical formula Co(NO$_3$)$_2$.6H$_2$O, Ho(NO$_3$)$_3$.9H$_2$O, Fe(NO$_3$)$_3$.9H$_2$O and Cr(NO$_3$)$_3$.9H$_2$O were used as starting materials and mixed in sufficient amount of double distilled water with their weight proportion in the composition. The whole mixture was placed on hot plate with magnetic stirrer. The mixture is stirred continuously with constant heating at 80^{0}C for 2-3 hours. Citric acid was used as chelating agent in the ratio with metal nitrates as 1:3 and the pH of the mixture was maintained at 7 by adding liquid ammonia continuously. After continuous heating and stirring the density of the mixture increases and it converted into sol. After some time, the puffy sol was converted into dried gel and suddenly auto ignited which in turns converted the mixture into burnt ash. All the samples were subjected for further study such as structural, morphological and magnetic properties.

III. CHARACTERISATION TECHNIQUES

To confirm the crystal structure of all the samples of the series CoHoxFe1-0.5xCr1-0.5xO4, room temperature X-ray diffraction technique was employed. XRD patterns of all the samples were recorded by using Cu-Ka radiations (l = 1.5406 x10^{-10} m) in the 2θ range of 20^0 to 80^0. The scanning rate was maintained at 2 degree per min. the structural parameters such as lattice parameter (a), X-ray density (dX), porosity (P) and

average crystallite size were estimated by using X-ray diffraction data. Band positions and force constants at tetrahedral – A and octahedral –B sites were obtained by using Infrared spectra. Room temperature Infrared spectra of all the samples were recorded in the frequency range of 300 cm^{-1} to 800 cm^{-1}. Morphological analysis of the samples was done by using scanning electron micrographs (SEM) and transmission electron micrographs (TEM). By using SEM and TEM images, grain size of the samples was also estimated. Magnetic measurements of all the samples were taken by using Vibrating sample magnetometer (VSM) at room temperature.

IV. RESULT AND DISCUSSION

Powder X-ray diffraction pattern for prepared samples shows sharp and intensive peaks indexed with the planes (220), (311), (222), (400), (422), (333), (440) and (433) which are corresponds to the standard crystal structure of the $CoFe_2O_4$ (JCPDS card No. 22-1086). The additional peaks confirm the co-existence of a-Fe_2O_3 and $HoFe_2O_3$ ortho phase which may be due to the higher reactivity of Ho^{3+} and Fe^{3+} ions at grain boundaries [4]. The effect of Ho^{3+} ion substitution on the phase formation of cobalt ferrite has been reported in the literature [5, 6].
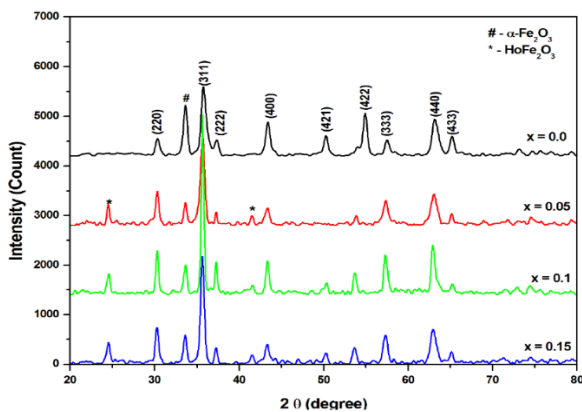

Fig. 1 XRD pattern of $CoHo_xFe_{1-0.5x}Cr_{1-0.5x}O_4$ sintered at 800^0C for 4hrs.

Lattice constant 'a' of all the samples of series $CoHo_xFe_{1-0.5x}Cr_{1-0.5x}O_4$ was calculated by using values of interplanner spacing's 'd' and miller indices in the equation.

$$d = \frac{a}{\sqrt{h^2+k^2+l^2}} \qquad (1)$$

where, 'd' is inter-atomic spacing's form adjacent planes and h, k, l are the miller indices.

Lattice constant was calculated for the most intensive peak (311) and also the average values obtained from all the reflection peaks were taken. Both values of lattice constant (average and form the plane

311) are found in good agreement with each other X-ray density and bulk density were used to calculate the percentage porosity of the samples by using the relation discussed in the literature [24]. Fig. 2 illustrates the variation of percentage porosity with the addition of Ho3+ ions in Co-Cr-Fe-O ferrites. By using the crystalline diameter of the samples obtained from XRD data and bulk density in the following relation, specific surface area of the samples was calculated [7].

$$S = \frac{6000}{Dd_B}$$

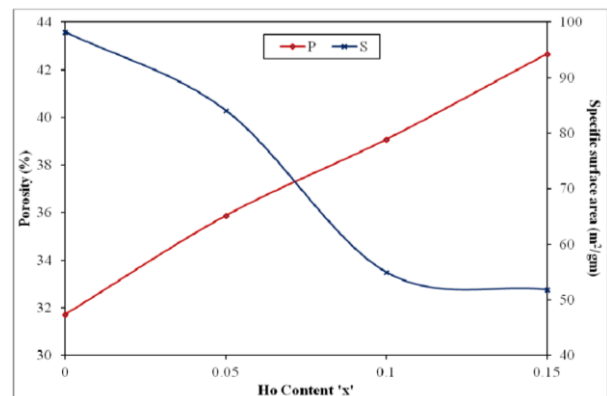It is observed that the porosity of the samples varies from 31.72 to 42.65 for the samples sintered for 4 hours.

Fig. 2 Variation of % porosity 'P' and specific surface area 'S' of $CoHo_xFe_{1-0.5x}Cr_{1-0.5x}O_4$ sintered at 800^0C for 4 hrs.

Scanning electron micrographs of the end samples of the series CoHoxFe1-0.5xCr1-0.5xO4 (x= 0.0 and x=0.15) sintered for 4h are shown in Fig. 3 (a, b). Each image shows the porous structure of the samples with well-defined grains. The average grain size for all the samples were estimated by using these SEM. The average grain size is obtained in the nanometer range for all the samples and shows increasing trend with Ho^{3+} addition and the results are in good agreement with the crystallite size obtained from the analysis of XRD data. For the samples, average grain size is obtained in the range 45 nm to 62 nm. It is also observed that the samples are amorphous in nature and shows porous structure with some agglomerates particles. [8-9].
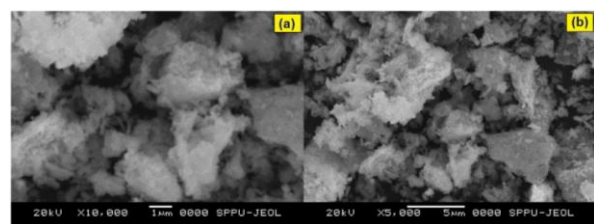

Fig. 3 SEM images of CoHoxFe1-0.5xCr1-0.5xO4 sintered at 800^0C for 4 hrs.

TEM images of the typical samples (x = 0.0 and x = 0.15 are shown in Fig. 4 Shows TEM images and the SEAD patterns of the sample (x=0.0) &(x=0.15) sintered at 800^{0}C for 4h. The observation of TEM images confirms the spherical shape of the particles with some agglomeration. The particle size obtained from the analysis of TEM images is in good agreement with the results obtained from XRD and SEM analysis. The selected area electron diffraction patterns show bright spots with sharp rings which confirm the well-defined crystalline nature of the samples.
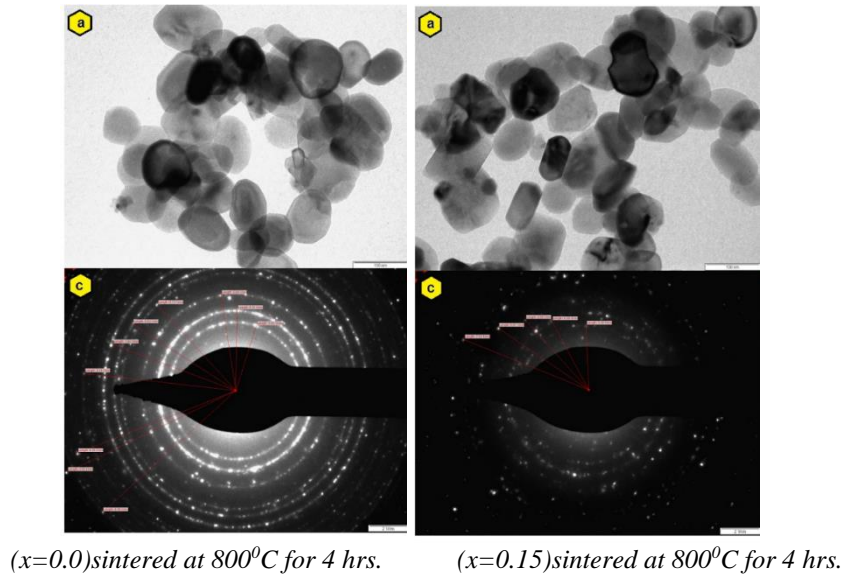

(x=0.0)sintered at 800^{0}C for 4 hrs.   *(x=0.15)sintered at 800^{0}C for 4 hrs.*

Fig. 4 TEM images & SAED pattern of CoHoxFe1-0.5xCr1-0.5xO4

Fig. 5a shows the magnetic hysteresis curves for CoHoxFe1-0.5xCr1-0.5xO4 sintered at 800^{0}C for 4h. The maximum field of 15kOe is applied for the sample. The hysteresis loops exhibits a wide cycle and gives high saturation magnetization which is the indication of formation of hard ferrites. The introduction of Ho^{3+} ions in Co-Fe-Cr ferrites increases the loop height and decreases the loop width. The values of saturation magnetization (MS), coercivity (HC) and remnant magnetization (Mr) obtained from the analysis of hysteresis loops. Variation of saturation magnetization as a function of Ho^{3+} addition is shown in Fig. 5b for the samples heated for 4h. It is observed that the Ho^{3+} substitution in Co-Fe-Cr ferrites greatly affects on the magnetic behaviour of the samples and the saturation magnetization increases. The increase in saturation magnetization with the addition of Ho^{3+} ions can be explained as,

i) In the present series Ho^{3+} ions replaces the Fe^{3+} and Cr^{3+} ions simultaneously.

ii) Ho^{3+} ions have higher magnetic moment (10.6 μB) than the Cr^{3+} (3μB) and Fe^{3+} (5μB)

iii) Due to addition of rare earth ion with higher magnetic moment enhances the overall saturation magnetization of the series.

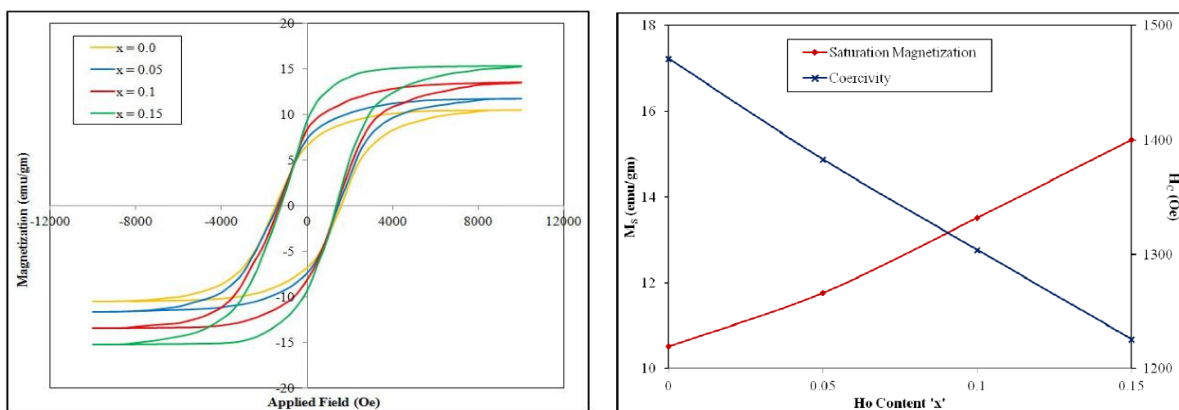**Fig. 5   a Hysteresis curves of CoHoxFe1-0.5xCr1-0.5xO4 & b Variation of saturation magnetization and coercivity of CoHoxFe1-0.5xCr1-0.5xO4**

V. CONCLUSION

Ho^{3+} doped cobalt ferrite nanoparticles with general formula CoHoxFe1-0.5xCr1-0.5xO4 (x= 0.0, 0.05, 0.1, 0.15) by using sol-gel auto-combustion method. Powder X-ray diffraction pattern for prepared samples shows sharp and intensive peaks indexed with the planes (220), (311), (222), (400), (422), (333), (440) and (433). Addition of Ho3+ ions increases the values of X-ray density for all the samples which may be related to the increasing values of molecular weight. The average crystallite size increases with the addition of Ho^{3+} ions in the Co-Cr-Fe-O ferrites. This increase in crystalline size is may be attributed to the replacement of Cr^{3+} and Fe^{3+} ions with smaller ionic radii by Ho^{3+} ions having higher ionic radii. The particle size obtained from the analysis of TEM images is in good agreement with the results obtained from XRD and SEM analysis. It is observed that the Ho^{3+} substitution in Co-Fe-Cr ferrites greatly affects on the magnetic behaviour of the samples and the saturation magnetization increases.

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