Report of Minor Research Scheme:
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Name of the Scheme:- MRP (Science)

Title of the Project:-Structural And Magnetic Properties of Indium Substituted Nano-crystalline Ferrite by Sol-gel Autocombustion Method.

I. INTRODUCTION

Ferrites are magnetic ceramics of great importance in many technological applications on account of their various electrical, dielectric and magnetic properties. The properties of ferrites are dependent on synthesis methods, synthesis parameters, type and nature of substituent and distribution of cations over the available sites . These materials find applications in the field of antenna rods, transformer cores, permanent magnet, data storage etc. . Owing to their numerous applications ferrites are being studied from last six to seven decades with a view to understand and improve their properties for suitable applications. Many efforts have been taken by researchers to study the structural, electrical and magnetic properties of ferrites . In early decades, they have been synthesized by commonly used ceramic technique. However, in the last decade, ferrites have been intensively synthesized by various chemical methods with a view to obtain nanoparticles of ferrites which can find applications in the drug delivery, ferro-fluids, catalyst, sensors etc .

In the family of ferrites, spinel ferrites with chemical formula MFe2O4 (where M represents divalent ions of the transition metal elements such as Ni, Cu, Co, Zn, Mg, Fe, Cd and Mn.) are commercially important magnetic materials because of their excellent magnetic and electrical properties. Spinel ferrites possess cubic spinel structure which belongs to space group.The unit cell of the spinel structure consists of 8 molecules. In this cubic cell, 64 tetrahedral and 32 octahedral sites are present; out of them only 8 tetrahedral sites and 16 octahedral sites in the unit cell are occupied by metal ions. These sites are also called (A) and [B] sites respectively . On the basis of distribution of metal ions at (A) and [B] site, spinel ferrites are of three types; namely normal, inverse and random spinel ferrite. The high electrical resistivity, low eddy current and dielectric loss, high saturation magnetization, high permeability, good chemical stability, ease of preparation, low cost of production etc, are the remarkable features of spinel ferrites. Among the different spinel ferrites, cobalt ferrite is a unique spinel ferrite having large magneto-crystalline anisotropy, high magnetic properties, high electrical resistivity, mechanically hard etc. interesting properties . Cobalt and substituted cobalt ferrite have been studied by many researchers for their structural, electrical, dielectric and magnetic properties . In the literature, studies on indium substituted cobalt ferrite have not been reported to our knowledge. The important structural, electrical, magnetic, dielectric, optical and other properties of spinel ferrites are strongly depend on substituent and its occupancy at (A) and [B] sites. In the literature, the properties of spinel ferrites are investigated by substituting Zn2+, Cd2+ in place of divalent metal ions and Al3+, Cr3+ in place of trivalent Fe3+ ions. However, In3+, Ga3+, Ca2+, Cd2+ etc, substituent's were rarely used for investigating the properties of spinel ferrite. The crystallite size also influences the properties of spinel ferrites. It is now, a well known fact that when size of the particles is reduced from micrometer to nanometer level, the materials shows very interesting and better properties. Therefore, research on nano-size materials has been considerably increased during the last decades. The properties of nano-size ferrite are completely different than that of bulk ferrite. The nano-size ferrites can be prepared by wet-chemical methods like sol-gel , chemical co-precipitation, hydrothermal , micro-emulsion refluxing method reverse micelles . In this work, indium substituted cobalt ferrite nanoparticles with generic formula CoInxFe2-xO4 (with x = 0.0, 0.3, 0.5) were synthesized using sol-gel auto combustion method. The prepared samples were characterized by X-ray diffraction, scanning electron microscopy, magnetization

II. EXPERIMENTAL TECHNIQUE

Indium substituted cobalt ferrite powder was prepared through nitrate-citrate sol-gel auto combustion method. Analytical grade cobalt nitrate [Co(NO3)2 6H2O], Ferric nitrate [Fe(NO3)3 9H2O], Indium nitrate [In(NO3)3 6H2O], Citric acid [C6H8O7 H2O] were used to prepare CoInxFe2-xO4 (with x = 0.0, 0.3, 0.5). Solutions of metal nitrates and citric acid were prepared using deionized water. Metal nitrate and citric acid solutions were mixed in 1:3 proportions. The pH of the solution was adjusted to 7, using ammonia solution and then the solution was heated at 80 ^{0}C to transform into gel. The temperature of the gel was increased slowly so that dried gel burnt in a self propagating combustion manner until all gel were completely burnt off to form a floppy loose ash. The auto ignition of gel was carried out in borosil glass beaker kept on a hot plate. The ash was ground for 30 minutes and then calcined at 400 ^{0}C for 4h. The powder was then pelletized using hydraulic press by applying a pressure of 6 tons. The specimens were annealed at 600 ^{0}C for 4 h in air atmosphere. The sintered specimens were used for further characterization. The sintered samples were characterized by X-ray diffraction method. The X-ray diffraction patterns were recorded at room temperature using Cu-Kα radiation on X-Ray diffractometer (BRUKER AXS D8 Advance). The X-ray diffraction patterns were recorded in 2θ range of 200 to 800. The bulk density was measured by Archimedes principle. Microstructure of the sintered samples was analyzed by scanning electron microscopy (SEM) technique performed on JEOL JSM 6480 LV system. The magnetic properties were recorded at room temperature using pulse field hysteresis loop technique. Using magnetization versus applied magnetic field (M-H plots), the saturation magnetization, coercivity, remnant magnetization of each sample was determined.

III. RESULTS AND DISCUSSIONS

A. Structural characterization

X-ray diffraction patterns of all the samples of indium substituted cobalt ferrite CoInxFe2-xO4 nanoparticles, (for x = 0.0, 0.3 and 0.5) are shown in Fig. 1. The entire samples under investigation shows the characteristics peaks of ferrite material with most intense peak (311). All the samples show good crystallization with well defined peaks. The peaks could be successfully indexed as (220), (311), (222), (400), (422), (511) and (440) which are characteristics of single phase cubic spinel structure indicating the solubility of cations into their respective lattice sites.

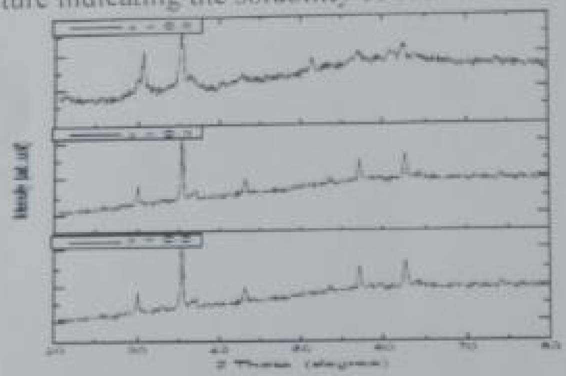

Fig.1 X-ray diffraction pattern for CoIn$_x$Fe$_{2-x}$O$_4$ nanoparticles for x= 0.0,0.3,0.5.

The XRD patterns exclude the presence of any undesirable secondary phase. The slight broadening of the XRD peaks indicates that CoInxFe2-xO4 ferrites have nano-crystalline nature. The results obtained by X-ray diffraction (XRD) data are in good agreement with the JCPDS card no. (00-022-1086).

Table. I Lattice constant (a), and unit cell volume (a³), particle size (t) for CoIn$_x$Fe$_{2-x}$O$_4$ nanoparticles

x	a (Å)	Δa (Å)	a³ (Å)³	t (nm)
0.0	8.380	—	588	24.29
0.3	8.401	0.009	592	20.81
0.5	8.412	0.003	595	12.57

The lattice constant (a) varies between 8.380 to 8.412 Å with In3+ substitution. The change in lattice constant may be due to the difference in ionic radii of In3+ and Fe3+ The ionic radii of In3+ (0.80 Å) is greater than that of Fe3+ (0.67 Å) ion and hence lattice constant of the system CoInxFe2-xO4 increases. Since larger ions (In3+) replaces smaller (Fe3+) ions, increase in lattice constant is expected. Hence the observed behaviour of lattice constant as a function of indium substitution can be understood. It is observed that, lattice constant increases linearly with In3+ substitution. The observed behaviour of lattice constant is similar to other substituted spinel ferrites [1, 2]. The particle size (t) for each composition of CoInxFe2-xO4 ferrite nanoparticles was calculated from the most intense peak (311) of XRD pattern using Debye Scherrer's formula [3]. The calculated value of particle size (t) was found to be in between 12 nm to 24 nm range and the values are given in table I. This indicates that the substitution of In3+ in place of Fe3+ ions results in decrease of the particle size. The bulk density (apparent density) of all the samples was measured using Archimedes principle. The X-ray density (theoretical density) was calculated using standard relation [3]. The variation in the X-ray density and bulk density with In3+ ions concentration is shown in Table II.

Table: II The molecular weight (M), X-ray density (dx), experimental density (dexp) and (%P) for $CoIn_xFe_{2-x}O_4$ nanoparticles

x	M (gm)	d_x (gm/cm^3)	d_{exp} (gm/cm^3)	% P
0.0	234.62	5.30	3.35	37
0.3	252.31	5.65	3.88	31
0.5	264.10	5.89	3.91	34

It is clear from table II that the X-ray density increases with the increase of In3+ ions concentration which is attributed to the fact that the density of the In atoms (7.31 gm/cm3) is less than that of Fe atoms (7.874 gm/cm3). The bulk density increases with In3+ ions concentration. This may be due to the fact that In3+ ions (114.82 a.m.u.) have greater atomic weight than that of Fe3+ (55.35 a.m.u.) atoms. It is further observed from the table II that X-ray density is higher than the bulk density. The change in the

X-ray density and bulk density may be due the existence of pores in the samples, which depends upon the method of preparation, sintering temperature and sintering conditions [4]. The porosity of each sample was calculated from the values of X-ray density and bulk density. The values of porosity are listed in table II. It can be observed from table II . that porosity value varies between 31 to 37 %. Higher values of porosity are attributed to synthesis conditions.

B. Scanning Electron Microscopy

The morphology and the average grain size of the samples were determined by scanning electron microscopy (SEM) technique. Fig.2 shows the SEM micrographs of CoInxFe2-xO4 (0.0 x 0.5) ferrite nano particles. Microstructure analysis confirms the average size and type of the grain growth of the samples, which influences the properties of the material.

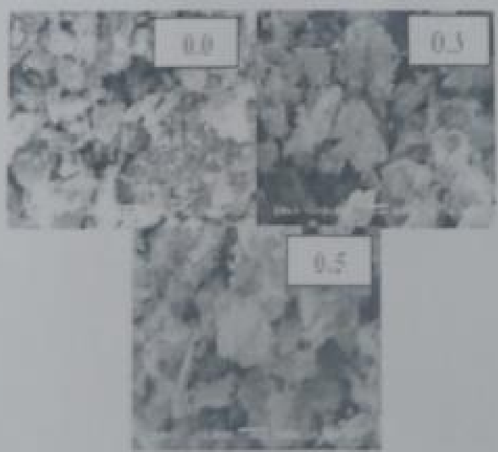

Fig.2: Scanning electron micrographs of $CoIn_xFe_{2-x}O_4$ nano-particles

It can be observed from the micrograph that, all the samples are composed of nano crystallites. The micrograph also shows uniform grain growth with spherical shape. The average grain size determined by the SEM was found to be in the range for the studied sample.

C. Magnetic Measurements

Magnetic properties were measured at room temperature using pulse field hysteresis loop tracer technique. The saturation magnetization (Ms), coercivity (Hc) and remenance magnetization (Mr) were obtained using M-H plots (Fig. 3) The M-H loops at 300 K exhibit superparamagnetic behaviour of the samples. From the hysteresis curves in the ferrimagnetic state, the value of Hc, Mr and Ms were deduced and are given in table III.

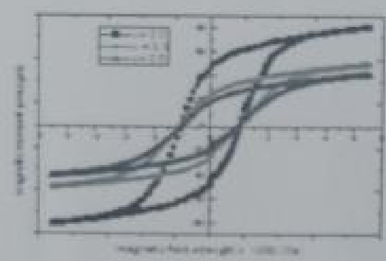

Fig 3 M-H plots recorded for of $CoIn_xFe_{2-x}O_4$ nano-particles

Table III

Saturation magnetization (Ms), Remanent magnetization (Mr), Coercivity (Hc), remanent rtio (Mr/Ms), magneton number (n_B) of $CoIn_xFe_{2-x}O_4$ nano-particles

x	M_s (emu/g)	M_r (emu/g)	Hc (Oe)	(Mr/Ms)	n_B (μ_B)
0.0	81.28	77.93	1028.99	0.96	3.414
0.3	50.10	29.50	926.03	0.59	2.263
0.5	41.46	19.62	1000.42	0.47	1.961

IV. CONCLUSIONS

A series of substituted indium ferrites with composition CoInxFe2-xO4 with x = 0.0, 0.3 and 0.5 were prepared by sol gel auto combustion method. The effect of substitution of indium on structural and magnetic properties of cobalt ferrite has been studied. X-ray diffraction analysis confirms the single phase cubic spinel structure for all the samples. The particle size estimated from Debye-Scherrer's formula varies in the range of 12 to 24 nm. The lattice constant increases with increase in indium substitution x. Average Grain size determined from SEM images shows nano meter dimension. 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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