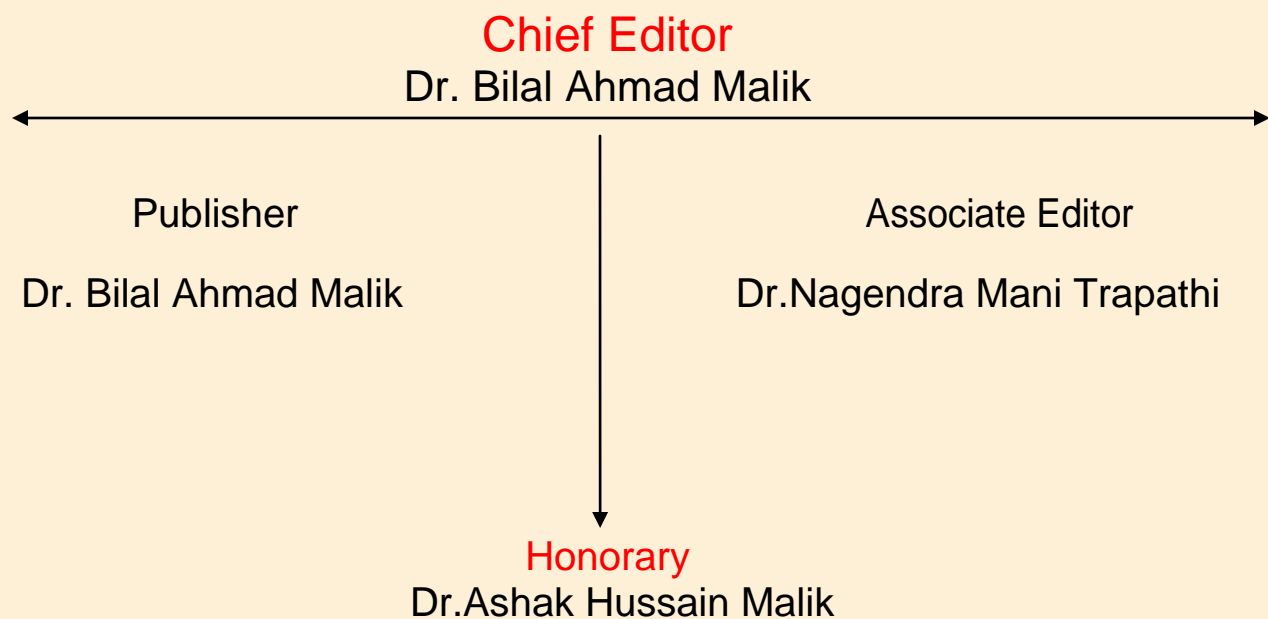


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EFFECT OF SAMARIUM SUBSTITUTION ON THE STRUCTURAL AND MAGNETIC PROPERTIES OF COBALT FERRITE

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Abstract

Samarium substituted cobalt ferrite materials with chemical formula $CoFe_2 xSm_xO_4$ ($x = 0.00$ and 0.02) have been synthesized by standard ceramic technique using AR grade CoO , Sm_2O_3 and Fe_2O_3 . The X- ray diffraction (XRD) measurements confirmed the formation of a single phase cubic spinel structure. The unit cell volume, particle size, Hopping length and lattice constant decreases, while the X- ray density, bulk density, porosity increases with samarium substituted cobalt ferrite. Infrared spectra of the samples were recorded at room temperature in the range $350cm^{-1}$ - $800cm^{-1}$ on the tetrahedral and octahedral sites respectively. Magnetic properties measurements were carried out at room temperature using pulse field hysteresis loop technique, the saturation magnetization (M_s) and magneton number decrease (nB), while the coercivity (H_c) is found to increases with samarium substituted cobalt ferrite.

KEY WORDS *Effect, Magnetic, properties. Ferrite, cobalt, samarium,*

INTRODUCTION

Spinel ferrites with general formula MFe_2O_4 (M is a divalent metal ion) are very important materials because of their high electrical resistivity, moderate saturation magnetization and low eddy current and dielectric losses, which makes them useful in many applications. The important electrical and magnetic properties of ferrite depend on chemical compositions, method of preparation and cation distribution in the two sub-lattices i.e. tetrahedral (A) and octahedral [B] site. The study of cation distribution in spinel ferrites is essential to understand structural and magnetic properties of spinel ferrites [1, 2].

In the family of spinel ferrites cobalt ferrite ($CoFe_2O_4$) is a unique ferrite having inverse spinel structure. Cobalt ferrite is a hard magnetic material possessing high magneto crystalline anisotropy, high Curie temperature, high corecivity and moderate saturation magnetization along with the chemical stability and mechanical hardness [3, 4]. Several researchers have studied pure and substituted cobalt ferrite with a view to understand their basic properties [5-7].

Spinel with rare earth ions has attracted great attention in the material science field because of their interesting properties such as infrared emission, catalytic, photoelectric and magnetic properties [8, 9]. Many investigations have been carried out to make further improvements on the structural and magnetic properties of substituted ferrites. It is known that the rare earth (RE) ions have unpaired 4f electrons which have the role of originating magnetic anisotropy because of their orbital shape. Substitution of rare earth ions into spinel

ferrites, the occurrence of 4f-3d coupling which determine the magneto crystalline anisotropy in ferrites can also improve the electrical and magnetic properties of spinel ferrites.

Recent research shows by introducing rare earth ions into the spinel lattice, can lead to small

changes in the structural, magnetization and Curie temperature of the spinel ferrite [10-12]. In the present work, we report our result on the structural and magnetic properties of samarium substituted cobalt ferrite.

EXPERIMENTAL DETAILS

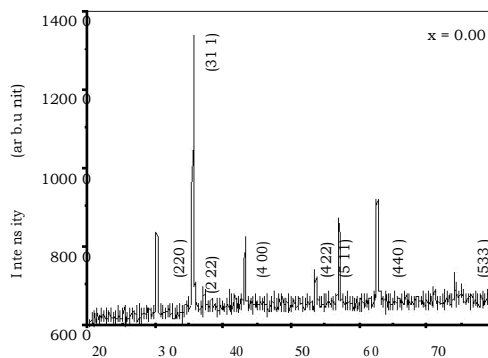
Samples with chemical formula $\text{CoFe}_{2-x}\text{Sm}_x\text{O}_4$ ($x = 0.00$ and 0.02) were prepared by standard ceramic technique [13, 14] using analytical reagent grade oxides. Compounds were accurately weighted in molecular weight percentage with single pan microbalance. The mixed powders were wet ground and pre-sintered at 9500 C for 24 hours. The sintered powder is again re-ground and pelletized. Polyvinyl alcohol was used as a binder in making circular pellets of 10mm diameter and 2–3mm thickness. The pellets were finally sintered in muffle furnace for 11800 C for 24 hours and then slowly cooled to the room temperature.

X-Ray diffraction patterns were taken at room temperature to confirm the crystal structure of the prepared samples. The XRD patterns were recorded in the 2θ range from 200 to 800 using Cu-k radiation ($\lambda = 1.5406\text{ \AA}$) with scanning rate 20 per/m. Magnetic measurements were carried out using pulse field hysteresis loop tracer at room temperature. Curie temperature of the sample was determined through a. c. susceptibility and Loria technique.

RESULTS AND DISCUSSION

• Structural analysis

Fig 1 shows X-ray powder diffraction patterns (XRD) for series having molecular formula $\text{CoFe}_{2-x}\text{Sm}_x\text{O}_4$ with $x=0.00$ and $x=0.02$ were prepared by standard ceramic technique. The Bragg reflections (hkl) belonging to the plane (220), (311), (222), (400), (422), (511), (440) and (533) confirms the formation of single phase cubic spinel structures. No characteristic peaks of impurities are detected in the pattern. It indicated that the Sm^{3+} ions ($x=0.02$) can be completely solved into the Cobalt ferrite. Similar reports of XRD pattern are available in the literature [15-18].



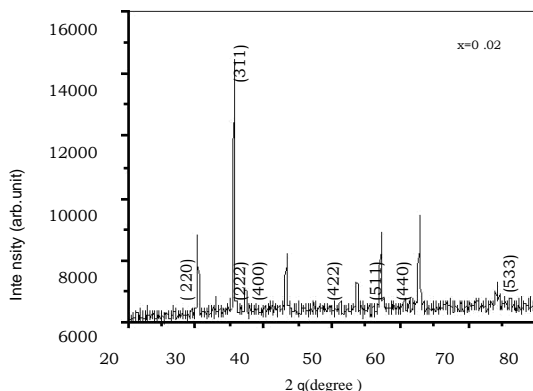


Fig 1: XRD patterns of $\text{CoFe}_{2-x}\text{Sm}_x\text{O}_4$.

Using XRD data the lattice constant (a) was calculated using standard relation [19] for cubic spinel structure. The values of lattice constant are given in Table 1 that the lattice constant of samarium substituted cobalt ferrite is less than pure cobalt ferrite [20]. A minor decreases in lattice parameter, a of CoFe_2O_4 with samarium substitution, which may be due to the compressive pressure exerted on the ferrite lattice by SmFeO_3 [21]. The X-ray density (d_x) was calculated using the equation

$$d_x = \frac{ZM}{N a^3} \quad \dots(1)$$

Where 'Z' is number of molecules per unit cell. (For spinel system $Z= 8$), 'M' is the molar mass of

the ferrite, 'N_a' is the Avogadro's number and 'a' is the unit cell volume computed from the values of lattice constant. X-ray density (d_x) increases almost linearly with the substitution of Sm^{3+} because the Fe^{3+} ions on the octahedral sites are being replaced by the larger mass Sm^{3+} ions. The bulk density of the samples was measured by using Archimedes principle [22] and the porosity of the samples was calculated by using the following relation

$$P = 1 - \frac{d_b}{d_x} \times 100\% \quad \dots(2)$$

where d_b is the bulk density and d_x is X-ray density. The particle size 't' of sample was determined by most intense peak (311) by using the relation

$$t = \frac{0.9 \lambda}{b \cos \theta} \quad \dots(3)$$

Where \hat{a} the full width at half maximum (FWHM) and \hat{e} is wavelength of the target material. The particle size values are given in Table 1. It is observed from table 1 that the particle size of samarium substitution is smaller than CoFe_2O_4 .

Table 1

Lattice constant (a), X- ray density (dx), bulk density (dB), Porosity (P) and Particle size (t) of $\text{CoFe}_{2-x}\text{Sm}_x\text{O}_4$ system.

$\text{CoSm}_x\text{Fe}_{2-x}\text{O}_4$	'a' (Å)	'a' ³ (Å) ³	dx (gm/cm ³)	dB (gm/cm ³)	P (%)	t (Å)
x = 0.00	8.376	587.64	5.305	3.864	27.16	396.71
x = 0.02	8.362	584.70	5.373	3.866	28.05	395.47

The values of the tetrahedral and octahedral bondlength (dAX and dBX), the tetrahedral edge (dAXE), and the shared and unshared octahedral edge (dBEX and dBXE) can be calculated according Eqs (4) (8). Using the value of the lattice parameter 'a' (Å) and the oxygen position parameter 'u' (u=0.381 Å).

Table 2

Hopping length (L_A, L_B), Tetrahedral bond (d_{AX}), Octahedral bond (d_{BX}), tetra edge (d_{AXE}) and octaedge (d_{BXE}) (Shared and non-shared) of $\text{CoFe}_{2-x}\text{Sm}_x\text{O}_4$ system.

$\text{CoSm}_x\text{Fe}_{2-x}\text{O}_4$	L _A (Å)	L _B (Å)	a _{AX} (Å)	a _{BX} (Å)	a _{AXE} (Å)	d _{AXE} (Å)	
						(Shared)	(Unshared)
x = 0.00	3.629	2.961	1.901	2.045	3.103	2.819	2.963
x = 0.02	3.621	2.956	1.897	2.042	3.098	2.815	2.958

The value of the bondlength of the tetrahedral and octahedral sites are shown in Table 2, It is seen that the all values are depend on the lattice parameter so, the lattice parameter decrease, then the edge and the bondlength of the tetrahedral and octahedral sites are decreases.

$$d_{AX} = \frac{a\sqrt{3}}{4} \sqrt{1-2u} \quad \dots(4)$$

$$d_{BX} = \frac{a\sqrt{3}}{4} \sqrt{1-2u} \quad \dots(5)$$

$$d_{AXE} = \frac{a\sqrt{3}}{4} \sqrt{1-2u} \quad \dots(6)$$

$$d_{BAX} = \frac{a\sqrt{3}}{4} \sqrt{1-2u} \quad \dots(7)$$

$$d_{BXE} = \frac{a\sqrt{3}}{4} \sqrt{1-2u} \quad \dots(8)$$

The distance between magnetic ions (hopping length) in the tetrahedral sites is given by Eqs (9) (10).

$$L_A = \frac{a\sqrt{3}}{4} \quad \dots(9)$$

$$L_B = \frac{a\sqrt{2}}{4} \quad \dots(10)$$

where 'a' is the lattice constant, the value Hopping length (LA, LB) are shown in Table 2, Hopping length (LA, LB) values are depend on the lattice parameter so, the lattice parameter decrease so the Hopping length (LA, LB) also decreases.

• Infrared Spectroscopy

The infrared spectra for series having molecular formula $CoFe_{2-x}Sm_xO_4$ with $x=0.00$ and $x=0.02$ are given in Table 3, that the IR spectra are found to exhibit two major absorption bans near $400cm^{-1}$ and $600 cm^{-1}$. According to Waldron [23] the vibration of unit cell of the spinel can be constructed in the tetrahedral

(A) sites and Octahedral (B) site. So, the absorption band (n_1) is caused by scratching vibrations of the tetrahedral metal-oxygen bond and absorption band (n_2) is caused by metal-oxygen vibrations in octahedral sites. The band position of n_1 and n_2 for the sample are given in Table 3. From this it is seen that the change in band position is exempted because of the different in the $Fe^{3+}-O^{2-}$ distance for the tetrahedral and octahedral complexes due to substitution of samarium [1].

Table 3

Vibrational band frequency (ν_1, ν_2), Curie temperature (T_c) measured from Loria and A.C. Susceptibility (T_c) of $\text{CoFe}_{2-x}\text{Sm}_x\text{O}_4$ system.

$\text{CoSm}_x\text{Fe}_{2-x}\text{O}_4$	ν_1 (cm^{-1})	ν_2 (cm^{-1})	T_c (K)	
			A. C. Susceptibility	Loria Technique
$x=0.00$	603.18	419.61	785	788
$x=0.02$	591.25	406.81	783	785

• **Magnetization**

Fig 2 shows the variation of saturation magnetization (M_s) and coercivity (H_c) with samarium substituted cobalt ferrite. The decrease in magnetization with samarium substituted cobalt ferrite is due to the dilution of magnetization of B-sublattice by samarium ions.

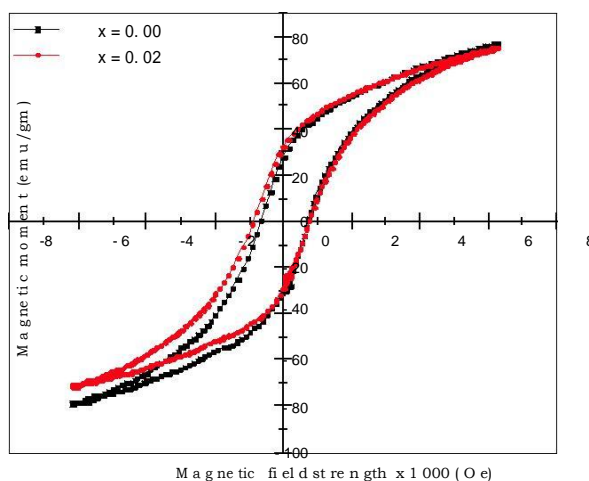


Fig 2: Hysteresis loop of $\text{CoFe}_{2-x}\text{Sm}_x\text{O}_4$

The substitution samarium ions preferably occupy B-site, when a small fraction ($x=0.02$) of Sm^{3+} ions are replaced of Fe^{3+} ions at B-sites, due to large magnetic moment of Fe^{3+} (5.9B) as compared to that of Sm^{3+} (1.5B), as the number of Fe^{3+} at B-site decreases, the magnetization of B-sublattice decreases, resulting in the observed decrease in saturation magnetization for the samarium substituted cobalt ferrite [24, 25]. Using the values of saturation magnetization (M_s), magneton number (n_B) was also calculated obtained from hysteresis loop.

$$n_B = \frac{\text{Mol.weight } M_s}{5585} \quad \dots(11)$$

The values of saturation magnetization (M_s), coercivity (H_c), magneton number (n_B) and other magnetic parameter are listed in Table 4. It is observed from M-H loop that saturation magnetization (M_s) and magneton number (n_B) decreases while Remanance magnetization (M_r), coercivity (H_c) and Remanance ratio (M_r/M_s) increases with samarium substituted cobalt ferrite. Neel's magneton number was calculated by using the relation

Table 4

Saturation magnetization (M_s), Remanance magnetization (M_r), coercivity (H_c), Remanance ratio (M_r/M_s) and Magneton number (n_B) of $CoFe_{2-x}Sm_xO_4$ system.

$CoSm_xFe_{2-x}O_4$	Tc (K)	M_s (emu/gm)	M_r (emu/gm)	H_c (Oe)	M_r/M_s	$n_B(\mu_B)$	
						Obs.	Cal.
$x = 0.00$	785	77.38	26.44	479.76	0.34	3.25	3.00
$x = 0.02$	783	74.63	32.03	717.23	0.45	3.16	2.90

$n_B = |M_B - M_A|$ and values are presented in Table 4. It evident from Table 4 that, the observed and calculated magneton number follows the decreasing trend with samarium substituted cobalt ferrite. The Curie temperature measured by A.C. susceptibility and Loria technique and the values are given in Table 3. From this it is seen that Curie temperature also decreases [26] with samarium substituted cobalt ferrite.

CONCLUSIONS

The $CoFe_{2-x}Sm_xO_4$ ($x = 0.00$ and 0.02) spinel ferrite system was successfully prepared by standard ceramic technique. The X-ray powder diffraction analysis of the samples revealed that the prepared sample posseses single phase cubic spinel structure. The lattice constant, particle size decreases but X-ray density, bulk density and porosity increases with samarium substituted cobalt ferrite. Hopping length, tetrahedral bond, Octahedral bond, tetra edge and octa edge are decreases with samarium substituted cobalt ferrite. The IR spectra are found to exhibit two major absorption bans near 400cm^{-1} and 600cm^{-1} . The saturation magnetization, magneton number decreases but coercivity increases with samarium substituted cobalt ferrite.

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