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Investigation of temperature effect on structural and magnetic properties of La-doped cobalt ferrites

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In the present work, La^{+3}- substituted Co-ferrites of chemical composition $CoLa_{0.06}Fe_{1.94}O_4$ (x = 0.06) was prepared applying the co-precipitation method and prepared samples was annealed at different temperatures such as 700-1200 °C for 6 h with step interval of 100 °C. The uniqueness of this work is that only x= 0.06 sample to study the effect of cubic spinel microstructure at different annealed temperatures was selected. The prepared samples were characterized by X-ray diffraction (XRD) technique, Scanning electron microscopy (SEM), Energy-dispersive X-ray spectroscopy (EDX), Fourier transform infrared spectroscopy (FTIR) and VSM. The XRD and FTIR techniques confirm the spinel ferrite structure. The average crystallite size was found 26.5 nm to 106 nm by using Scherer's formula. When the temperature was increased, average crystallite size also increased. SEM images showed that the size of grain increased with increase of annealing temperature and confirmed the particle size as analysed by XRD. EDX spectra clarified the presence of elements in the samples by showing their respective characteristics peaks of Co, O, La, and as per prepared composition. From M-H loop, the obtained values of Ms = 59.74 emu/g and coercivity ≥ 700 Oe showed that prepared magnetic samples may be applied as magnetic recording media.

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Keywords: Co-precipitation Method, Spinel ferrites, Characterization, M-H loop

1. Introduction

Spinel ferrites have the general formula AB_2O_4 where A shows the divalent cations and B shows the trivalent cations. Which have showed wide technological applications such as permanent magnets [1], memory chips, high-density magnetic media, and transformer cores. Mostly metal ferrites have shown the structure of inverse spinel cubic crystal in which half-sites of tetrhedral (A-sites) engaged the ions of Fe^{+3}. On the other sublattice, octahedral (B-sites) engaged the leftover Fe^{3+} along with the ions of transition metal [2]. Ferrite material have high electrical resistivity, low dielectric losses, low eddy current. These types of materials have moderate permittivity and high permeability. Due to the basic techniques, ferrites are sensitive and have some parameters such as additives, impurities, dopants, method of preparation, sintering conditions, and amount of constituent metal oxides. The studies of ferrimagnetic materials are so extensive due to their high resistivity and low magnetic coercivity and have small eddy current losses in high-frequency operation [3]. The described properties of ferrite materials strongly depend upon the arrangement of cation distribution in the A-site and B-sites. Therefore, rare earth oxides are good electrical insulators with high electrical resistivity [4]. Due to the conduction process, the occupation of rare-earth ions on 'B' sites impedes the motion of Fe^{2+} and causing an increase in resistivity [5,6]. Doped rare earth in ferrites was measured to be an effective means and improved the performance of ferrites. The main purpose of our study was to investigate the structural and magnetic properties of $CoLa_xFe_{2-x}O_4$ where (x = 0.06) ferrites and was annealed at 700-1200 °C.

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2. Materials and methods

2.1. Samples preparation and equipment

In this work to synthesize and characterizations of La^{+3}-doped Co-ferrites by using the co-precipitation method at varying sintering temperature. The desired composition of $CoLa_xFe_{2-x}O_4$ (x =0.06) was obtained using a stoichiometric amount of Co $(NO_3)_2$. $6H_2O$, La $(NO_3)_3$. $6H_2O$, Fe $(NO_3)_3$. $9H_2O$, and NaOH. They were dissolved in deionized water. As a precipitant agent, NaOH solution was used to maintain the pH at 11 and for 1 hour the solution was stirred on a magnetic stirrer. The obtained precipitate was digested in a preheated water bath at 80^oC for 30 min. To remove the byproducts the resulted precipitate was washed with deionized water. The sample was dried at 90°C in a microwave oven. With the help of mortar, the dried sample was grinded, and the prepared sample was divided into six parts for annealed at different temperatures. For microstructural studies, the XRD patterns were obtained at room temperature using powder samples in a Model PANalytical with Nickel filtered Cu-Kα radiation λ = 1.54056 Å. The study of the morphology of the prepared sample by SEM was performed using the Model JEOL-JSM 5910. The elemental composition was determined by the energy dispersive peak of the sample using the EDX Model JFC-1500 JEOL . The FTIR was measured in the frequency range of 400 -4000 cm^{-1} using Jasco-310 spectrometer. The magnetic measurements were carried out at room temperature using vibrating sample magnetometer VSM, Lake Shore 735. The XRD data were used to calculate the structural parameters such as lattice constant, average crystallite size, the volume of a unit cell, and X-ray density by these formulas as listed below [7-9].

$$A = \frac{\lambda}{2Sin\theta}\sqrt{h^2 + k^2 + l^2} \tag{1}$$

$$V_{cell} = a^3 \tag{2}$$

$$D = \frac{k\lambda}{\beta_{hkl}Cos\theta} \tag{3}$$

$$d_{x-ray} = \frac{ZM}{N_A V} \tag{4}$$

where A is a lattice parameter,V_{cell} is the volume of a unit cell, D is average crystallite size and d_{x-ray} is the X-ray density of the material, λ represents the wavelength of X-ray, θ is the Bragg's diffraction angle; 'k' is the factor of shape, 'Z' represents the atoms per unit cell of the spinel structure, 'M' is the molecular weight of the specimen and N_A is the Avogadro's number Which as have constant value $6.02x10^{23}$ g/mol.

3. Result and discussion

The XRD pattern of La^{+3}- substituted Co-ferrites with fixed content x = 0.06 annealed at different temperatures such as 700 °C to1200 °C are shown in Fig. 1. X-ray diffraction patterns confirm the spinel cubic structure with the space group $Fd\bar{3}m$. The diffraction peaks of XRD such as (220), (311), (400), (511), and (440) represent the hkl plans respectively. Some extra peaks appears between (220) and (311) planes which may be due to the La^{3+} ions substitution in ferrite structure which attribute high reactivity of Fe^{3+} ions with La^{3+}ions at the grain boundaries and appears as $LaFeO_3$ phase [10,11]. In addition, the calculated values of inter-planer distances from X-ray diffraction spectra was found in the range of 1.48-2.95 Å. The other calculations were also done such as lattice constant which was found in the range 8.3481-8.3940 Å while the volume of the unit cell was found in the range of 581.7-591.4 $Å^3$. The minimum average calculated crystallite size was found 26.5 nm. The X-ray density of the samples was found in the range 5.38 g/cm^3 to 5.47 g/cm^3 and these all calculations have been enlisted below in Table 1.

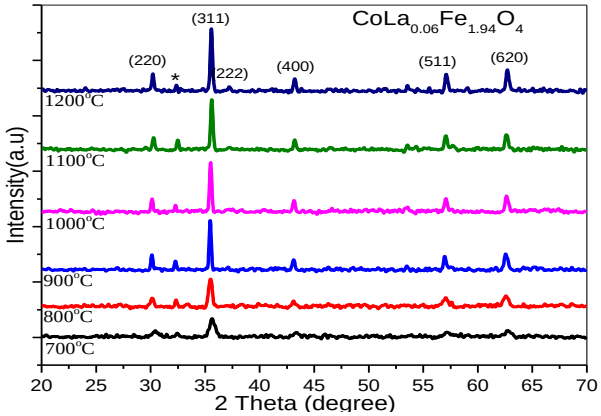

Fig. 1. X-ray diffractions patterns of $CoLa_{0.06}Fe_{1.94}O_4$ ferrites at different Sintering temperature (700-1200 ^oC).

In Table 1 the lattice parameter was found to increases in the range from 8.3481- 8.3940Å. The samples of ferrite can be explained that the lattice parameters are the basis of the radii of metal ions. The radius of La^{3+} = 1.061Å ion is larger than the Fe^{3+} = 0.67 Å ion. The replacement of Fe^{3+} ions in octahedral B-sites by La^{3+} ions would cause the expansion of the unit cell, resulting in larger lattice constants observed due to the formation of Fe^{+2} ions. However, due to the large ions, the sites of the tetrahedral are expanded and four oxygen ions shifted towards the body diagonal of the cube. From Fig. 3 it can be observed that the trend of increasing the lattice parameter and unit cell volume versus heat treatment. The crystallite diameter of $CoLa_{0.06}Fe_{1.94}O_4$ was estimated using Debye-Scherer's Equation (3). In Fig. 2(a) the average crystallite sizes of $CoLa_{0.06}Fe_{1.94}O_4$ ferrites from annealed with different temperatures such as 700-1200 °C was shown. The average crystallite size of ferrites samples increases with the increase of the annealed temperature and obtained maximum crystallite size at the temperature of 1000 °C (106 nm) except at the above temperature 1100° C the crystallite size of the synthesized sample observed that decreases with increasing heat treatment. So that, Fe^{+3} ions have a smaller size such as 0.067 nm and Fe^{+2} ions have a larger size such as 0.078 nm under the effect's high temperatures. The ions of Fe^{+3} move towards the A-sites from B sites, Fe^{+2} ions have a larger diameter.

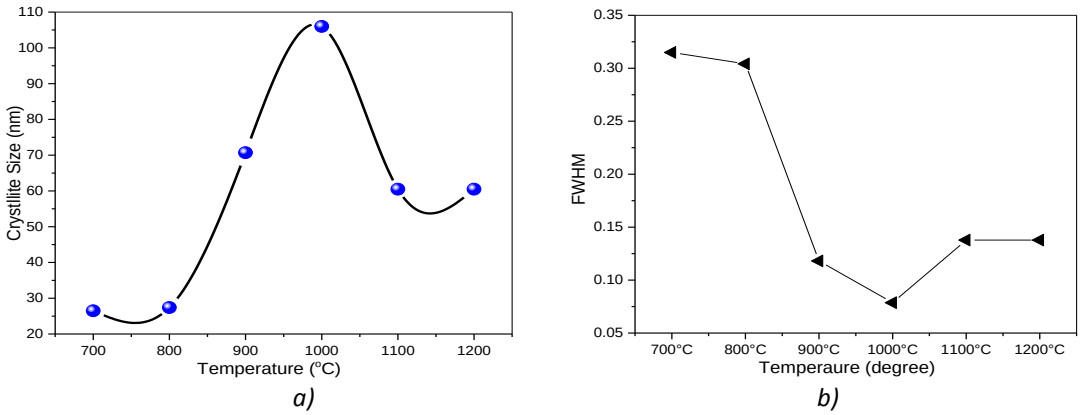

Fig. 2. (a)Average Crystalline Size (b)FWHM versus different temperatures.

To increase the average crystallite size the ions of Fe^{+3} on the octahedral sites play an important role. Similar behavior can be observed from the Fig. 2(b) there FWHM of the intense peaks at the plan (311) plot versus different temperature. From Fig. 2(a) Shows that the average

crystallite size of all samples has an inverse relation to the FWHM as per Debye-Scherer's formula.

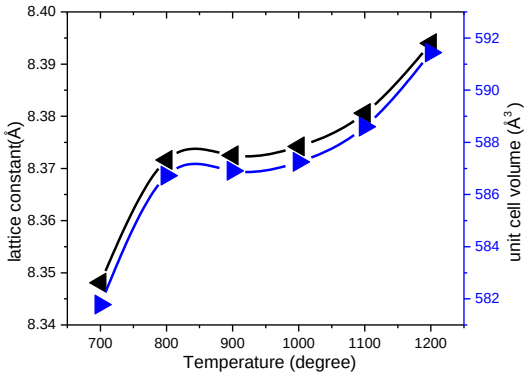

Fig. 3. Lattice constant and unit cell volume versus at different temperatures.

Using Eq. 4 for calculated the X-ray density. The resulted values have been shown in Table.1 which showed the increasing trend with the increasing temperatures.

Table. 1. Structural parameters of prepared $CoLa_{0.06}Fe_{1.94}O_4$ ferrites from XRD.

Temperature	2 Theta (311)	Intensity	FWHM	Lattice Constant (Å)	Average Crystallite Size (nm)	Volume of unit cell (Å^3)	X-ray density g/cm^3
700°C	35.6743	168	0.3149	8.3481	26.5	581.78	5.47
800°C	35.5706	243	0.3042	8.3716	27.4	586.72	5.42
900°C	35.5666	573	0.1181	8.3725	70.7	586.91	5.42
1000°C	35.5594	399	0.0787	8.3742	106	587.25	5.40
1100°C	35.5313	428	0.1378	8.3806	60.5	588.60	5.39
1200°C	35.4724	446	0.1378	8.3940	60.5	591.44	5.38

The IR spectra of $CoLa_{0.06}Fe_{1.94}O_4$ ferrites without thermal treatement was recorded in the range of 400 - 4000 cm^{-1}. The common features such as absorption peaks below 1000 cm^{-1} which represent metal-oxygen M-O vibration mode [27]. The absorption peak at 3284 cm^{-1} shows the stretching vibration. The absorption peaks of O-H, C-O, and C=H at 1000 cm^{-1} -1300 cm^{-1} and 2000 cm^{-1} -3000 cm^{-1}are the characteristics of spectrum. In IR spectra, the observed peaks centered at high frequency 525 cm^{-1} corresponds to M-O stretching at tetrahedral sites. The low frequency peaks at 440 cm^{-1} corresponds to the characteristics of the octahedral sites.

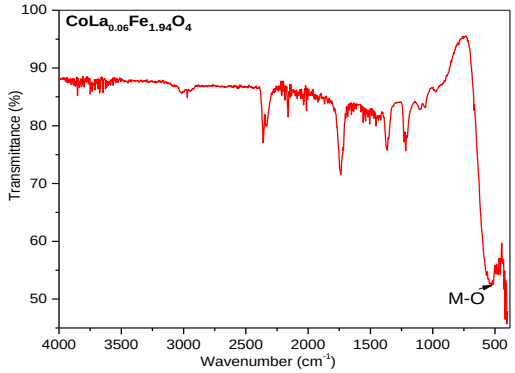

Fig. 4. IR spectra $CoLa_{0.06}Fe_{1.94}O_4$ ferrites.

The SEM images of $CoLa_{0.06}Fe_{1.94}O_4$ ferrites samples were presented in Fig. 5 (a-b) and (c-d) which were annealed at 700 °C and 800 °C for 6 hours. These images had been taken from two different scanned areas of each sample. The grain size distribution was found uniform and was calculated using the line intercept method which was found in the scale of a micrometer. The micrographs of the such samples showed few voids which may be due to the long heat treatment [12]. The increasing grain size has been visualized due to increase of temperature through SEM micrographs but has no linear variation. The SEM microscopic views have confirmed the XRD results. It is noteworthy that all the SEM micrographs were scanned without the coating of the gold. In this case, chemical reactions were produced due to the appearance of agglomeration may be attributed. When these agglomerations hold together many scientists reported that the magnetic forces or even relatively weak van der Waals bonds are responsible.

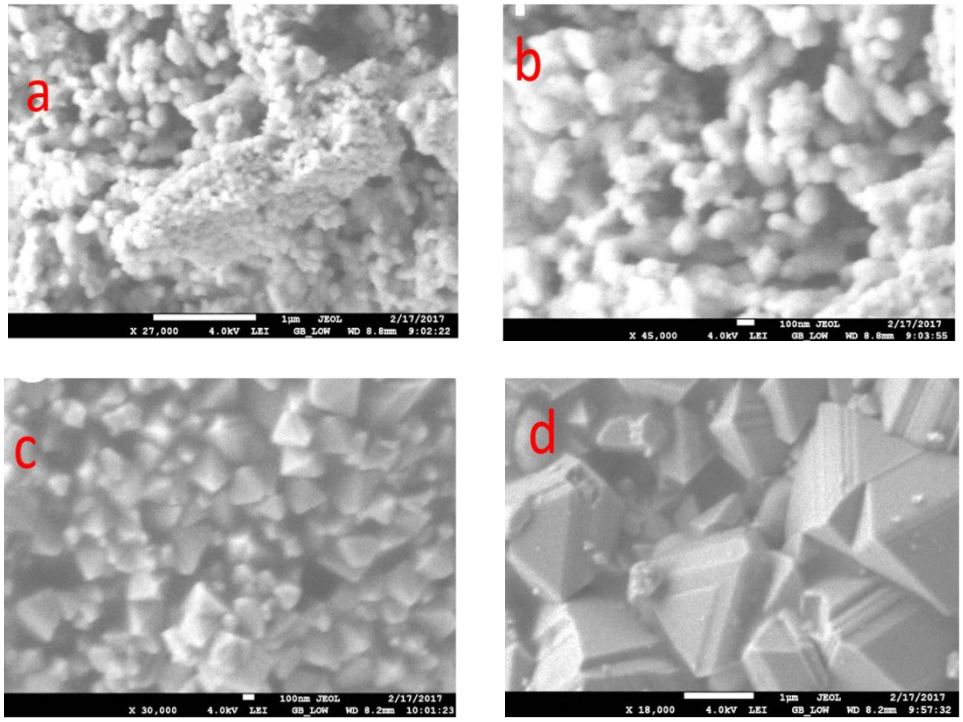

Fig. 5. (a-d) SEM micrographs of $CoLa_{0.06}Fe_{1.94}O_4$ ferrite at different temperatures (a-b) 700 °C, (c-d) 800 °C,for 6 h.

Due to the different grain size the rough surface was showed, and many dimensions made. It was also observed that the increasing the temperature the grain size increased.

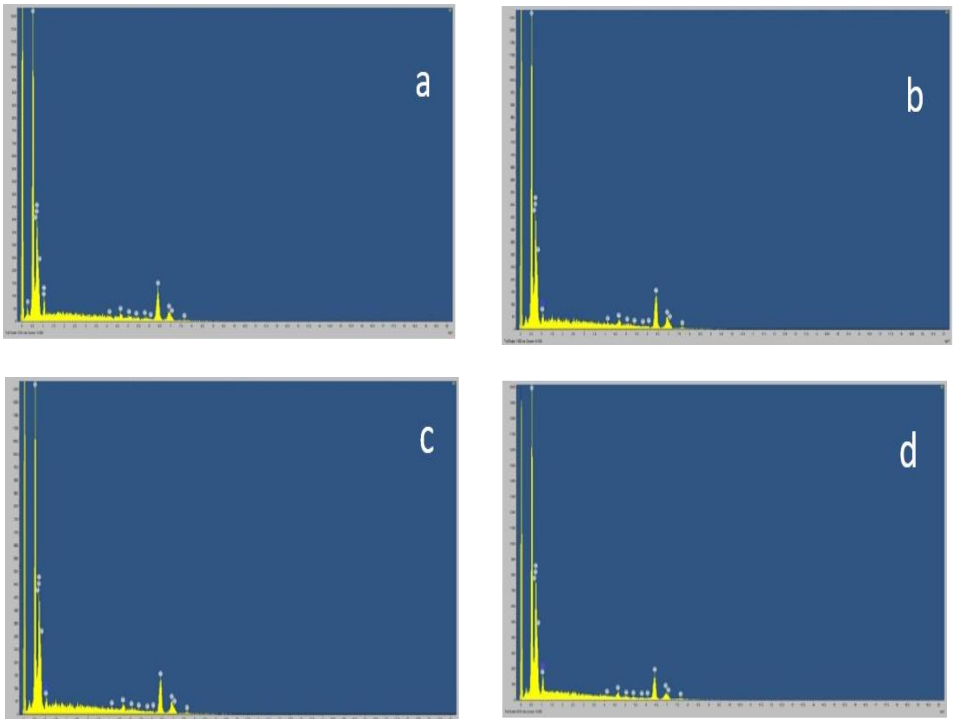

Fig. 6. EDX Spectrum for $CoLa_{0.06}Fe_{1.94}O_4$ ferrites sintered at 700- 1200°C.

Fig. 6 (a-d) showed the EDX spectra of the ferrites sample which were treated from700 °C to 1200 °C for 6 h. The observed atomic percentages of Co, La Fe, and O elements in the prepared nanoparticle samples have been tabulated in the Table 2, which suggested that the ratio of all the elements are in close to the reported values. The EDX analysis confirmed that prepared samples have required constituents and have no impurity have been observed.

Table 2. the Elemental Composition of prepared $CoLa_{0.06}Fe_{1.94}O_4$ Ferrite at different temperatures.

Elements	Temperatures			
	700 °C	800 °C	900 °C	1000 °C
O Atomic (%)	58.75	57.92	61.33	56.72
Fe Atomic (%)	26.81	25.98	26.76	26.95
Co Atomic (%)	12.63	14.34	10.11	14.44
La Atomic (%)	1.81	1.76	1.80	1.89

Fig. 7 shows that the M-H loop which of the sample which have been treated at 900 °C for the duration of 6 hour. The saturation magnetization (Ms) of the synthesized sample was recorded 59.7 emu/g while remanance (Mr) 28.6 emu/g and coercivity (Hc) 706 From the loop squareness ratio (Mr/Ms) = 0.5 was measured of the sample [13]. The increasing trend in crytsllite size was seen as thermal temperature was increased. The increasing trend have also been seen in case of saturation magnetization [14]. One of the reason of increaseng saturation magnetization (Ms) is to partial substitution of rare earth La^{+3} that change the Fe^{3+} to Fe^{2+} at the B- sites and also lead to increase the Fe-O-Fe super-exchange interactions. The ratio Mr/Ms = above 0.5 designates single domain and below 0.5 is related to the multi domain structures. Other considerable magnetic parameter is coercivity which is Hc > 700 Oe in the present situation so such material would be

suitable for application of longitudinal magnetic recording media [15]. The obtained range of coercivity also showed that magneto crystalline anisotropy of the present samples which have been annealed at higher temperature (such as 900 °C) confirmed the occupancy of Co^{2+} ions at the B-sites which as a result created surface effect.

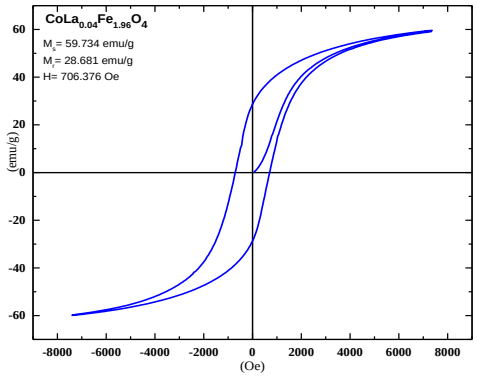

Fig. 7. M-H loops of $CoLa_{0.06}Fe_{1.94}O_4$ ferrites sintered at 900°C.

4. Conclusions

In this study La^{+3}-substituted $CoLa_{0.06}Fe_{1.94}O_4$ spinel ferrites has been successfully synthesized by using the method of co-precipitation and the prepared samples was annealed at different temperatures such as 700 °C to 1200 °C for 6 h. The microstructural characteristics have been done with X-ray Diffraction Technique (XRD). With the help of XRD spectra different parameters of the synthesized materials have been calculated that confirmed the spinel structure.

The lattice parameters were found in the range 8.3481 Å - 8.3940 Å. The average crystallite size was calculated using Scherrer formula which have been found in the range of 26.5-106 nm and was verified using SEM along with morphology of the synthesized material. The morphological results have clarified the and growth of grain which was close in agreement with results of XRD. It has also been observed that the growth of grain size increased with the increase of the temperature. The EDX spectra of the La^{+3}-substituted Co-ferrite ensured the purity of the samples.

The characteristics peaks in the spectra of EDX confirmed the presence of Fe, La, Co, and O in a definite stoichiometric ratio. From M-H loop, the values Ms 59.734 emu/g and coercivity ≥ 700 Oe were obtained. Such kind of investigatory results make path that these materials may be potential candidates as longitudinal magnetic recording media.

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