

Structural, dielectric and magnetic properties of cobalt based spinel ferrites

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ABSTRACT

CoYb_xFe_{2-x}O₄ (x = 0.00, 0.025, 0.05, 0.075, 0.10) spinel ferrites were synthesized by co-precipitation technique. Structural, dielectric and magnetic properties were measured. X-ray diffraction analysis showed that all the prepared spinel ferrites possessed cubic spinel structure. Dielectric constant, AC conductivity and dielectric loss decreased with the addition of rare earth ions. The impedance analysis explained the role of grains and grain boundaries with in prepared samples. Cole-Cole plots helped to measure the values of grains and grain boundary's resistance. The magnetic properties proved the soft nature of these ferrites. Saturation magnetization and remanence decreased while coercivity was enhanced with the addition of ytterbium concentration. All these parameters suggested that these prepared samples might be suitable for high frequency applications.

1. Introduction

Spinel ferrites are the well-known magnetic materials having various profitable electrical and magnetic properties. These properties permit nanoparticles to use in several industries. These are commonly used in microwave devices, drug delivery applications, electrical generators, magnetic diagnosis, spintronics etc. These are also used as catalyst in numerous chemical reactions like alkylation [1]. The magnetic and electrical behavior of nanoparticles depends upon nature of substituted element, size of the particle and ionic radii of substituent [2]. Many researchers are trying to obtain required properties in nanomaterials for specific applications. A lot of work has been done on metal ions substituted ferrite nanoparticles [3]. The well-known category of spinel ferrites, CoFe₂O₄ have gained more interest of researchers due to their many valuable properties like high chemical stability, remarkable mechanical hardness, moderate saturation magnetization and high coercivity. The properties of CoFe₂O₄ can be modified by addition of different divalent and trivalent metal ions according to requirement [4]. Substitution of rare earth ions in cobalt ferrites have become an interesting subject of researchers now a days. This is due to their vast applications in many fields [5]. The reported data revealed that substitution of rare earth ion cause significant changes in electrical and magnetic properties and also produce structural distortion in lattice [6,7]. This is due to the fact that rare earth ion have strong spin-orbit coupling of angular momentum and 4f unpaired electrons. The magnetic and electrical behavior is affected by Fe–Fe interactions. The rare earth ion (R) substituted spinel ferrites systems have R–Fe interactions which cause desired changes in electrical and

magnetic properties of ferrite nanoparticles. Rare earth ions have also the competency of changing electromagnetic behavior of ferrites [8–11]. In recent years, a lot of work has been done on synthesizing numerous rare earth substituted spinel ferrites to assess electrical, magnetic and optical properties. The rare earth elements belongs to lanthanide series act as good electrically insulators substances having high resistivity. Doping of these elements causes the modification of electrical, magnetic and optical properties. The ytterbium contains high value of coercivity as compared to praseodymium and holmium contents while its magnetic moment is larger as compared to gadolinium contents [12]. The values of resistivity are much higher and dielectric loss is very low as compared to holmium and praseodymium contents [12]. The reported data shows that the ytterbium substituted spinel ferrites have very low dielectric loss, high values of resistivity and coercivity.

2. Experimental

Co-precipitation method was adopted to synthesize the cobalt-based spinel ferrites. The flow chart (Fig. 1) described its step procedure clearly. The reagents Co(NO₃)₂, Fe(NO₃)₃, Yb(NO₃)₃ and NH₃ and de-ionized water were used to make the precursor. All the reagents were prepared in de-ionized water and mixed them with different amount to make solution. Solution of NH₃ dropped slowly into the former solution. On pouring the solution of NH₃ the brown precipitates formed. The temperature was observed 50–60 °C in a water bath during the reaction. The prepared solution was stirred continuously. The suspension was stirred for another 2 h after the last drop of NH₃ had been

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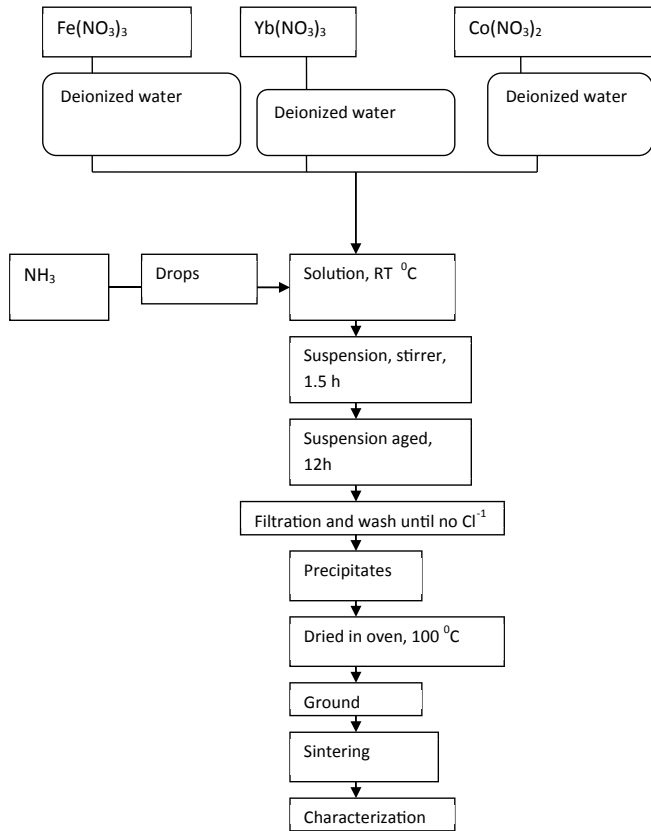


Fig. 1. Flow chart of co-precipitation method.

poured in the solution. The pH should be between 8 and 9. The suspensions were filtered by a filter paper. These precipitates also have chlorides. The precipitates are washed with de ionized water to remove chloride. The removal of chloride were then tested by adding a small drops of AgNO_3 . If no precipitates take place by addition of AgNO_3 drops, ensuring the removal of chloride. The precipitates were dried at $100\text{ }^\circ\text{C}$ for 2–3 h.

An X-ray diffractometer (D8 Advance-Bruker) with $\text{Cu-K}\alpha$ radiating source was used to observe the X-ray diffraction at room temperature. The range of XRD angle (2θ) was taken from angle $10\text{--}75^\circ$. Wayne Ker WK6500B impedance analyzer which is precision equipment was used in the range of 1 MHz–3 GHz to study the dielectric behavior of the compact pellets. The temperature was kept 300 K while studying the behavior of all prepared samples. A vibrating sample magnetometer (VSM) the Lake Shore model 7300 was used to measure the magnetic properties.

3. Results and discussions

3.1. X-ray diffraction

The XRD patterns of $\text{CoYb}_x\text{Fe}_{2-x}\text{O}_4$ spinel ferrites (nano-structured) are shown in Fig. 2. It has been observed from Fig. 2, that all the samples possessed cubic spinel structure. All these peaks were matched with the standard JCPDS card No. 22-1086. As the concentration of Yb increased ($x \geq 0.075$), few traces of secondary phase YbFeO_3 has also been observed at an angle of 32.2° . And the values of miller indices have been displayed on corresponding peaks. No extra peak of secondary phase has been observed. To calculate the average crystallite size of spinel ferrites, the well-known Scherer's formula was used. For this purpose three most intense peaks of each sample have been observed.

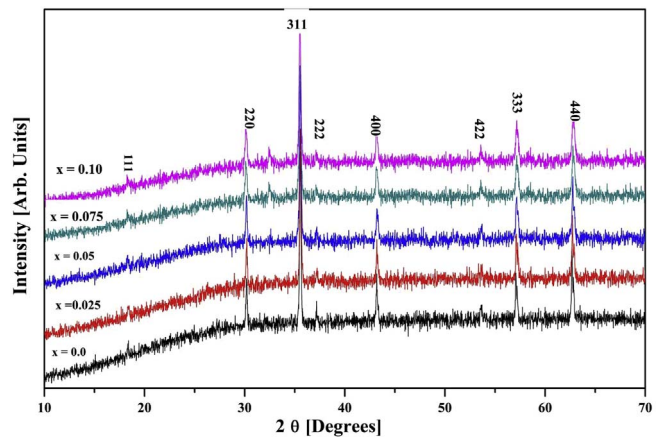


Fig. 2. X-ray diffraction of all Cobalt-based spinel ferrites.

$$D = \frac{K\lambda}{\beta \cos \theta} \tag{1}$$

here θ is called the diffraction angle while λ is the x-ray wavelength, and β is the full Width at half maximum and K is a constant approximately equal to unity and related to crystallite shape.

The values of average crystallite size are presented in Table 1. It showed the decreasing behavior with the substitution of ytterbium concentration. This decrease in crystallite size proved that substitution of ytterbium concentration is refining the cobalt-based spinel ferrites. Similar behavior was also observed by Muhammad [14].

The lattice constant ‘a’ was measured with the help of equation [13].

$$a = d_{hkl} \sqrt{h^2 + k^2 + l^2} \tag{2}$$

The values of lattice constant ‘a’ are presented in Table 1. The addition of ytterbium concentration in cobalt-based spinel ferrites increased the lattice constant. This increase in ‘a’ can be explained in such a way that ionic radius of ytterbium (100.8 pm) [14] is much larger than the ionic radius of iron ions (65 pm) [14]. This large ionic radius of ytterbium ions expands the lattice, which resulted the increase in lattice constant. This increase in lattice constant with the substitution of rare earth was already observed by different authors [15,16]. X-ray density of each sample was measured by using the values of lattice constant ‘a’, molecular weight of each composition ‘M’, Avogadro's number ‘N’ and the volume of the cubic unit cell ‘a³’ [13].

$$D_x = \frac{8M}{Na^3} \tag{3}$$

While bulk density was measures by using the relation

Table 1
Different Physical parameters for all Yb-substituted Cobalt-based Spinel Ferrites.

Composition	x = 0.00	x = 0.025	x = 0.05	x = 0.075	x = 0.10
Lattice Constant (Å)	8.364	8.391	8.432	8.456	8.473
Volume (Å ³)	585.116	590.800	599.504	604.637	608.291
Crystallite Size	62.80	54.45	50.26	46.67	41.98
X-ray Density (gm/cm ³)	5.08	5.12	5.15	5.17	5.2
Bulk Density (gm/cm ³)	4.4	4.46	4.49	4.52	4.55
P (%)	13.39	12.90	12.82	12.58	12.50
r _A (Å)	0.4609	0.4667	0.4756	0.4808	0.4845
r _B (Å)	0.7411	0.7478	0.7588	0.7644	0.7683
A-O (Å)	1.8109	1.8168	1.8256	1.8308	1.8345
B-O (Å)	2.0911	2.0978	2.1084	2.1144	2.1183
Jump Length (L _A) (Å)	3.6217	3.6334	3.6512	3.6616	3.6689
Jump Length (L _B) (Å)	2.9571	2.9667	2.9812	2.9896	2.9957

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