Substitutional effect on structural and magnetic properties of A$_x$Co$_{1-x}$Fe$_2$O$_4$ (A = Zn, Mg and x = 0.0, 0.5) ferrites

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ABSTRACT

The influence of the Zn and Mg content on the structural and magnetic properties of cubic cobalt ferrites (CoFe$_2$O$_4$) synthesized by chemical co-precipitation method was investigated using X-ray powder diffraction (XRD), Raman spectroscopy and vibrating sample magnetometer (VSM). Rietveld – refined X-ray powder diffraction patterns at room temperature confirmed the formation of single-phase cubic (FCC) structure with *Fd3m* space group for all prepared samples. Slight variation in the lattice parameter of Mg doped CoFe$_2$O$_4$ has been observed. Raman analysis reveals the doublet like nature of A$_{1g}$ mode for all synthesized samples. Small shift in Raman modes and increment in the linewidth has been observed with the doping ions. The magnetic measurement explored that the saturation value (M_s) is maximum for CoFe$_2$O$_4$ as compared to Zn and Mg doped cobalt ferrites samples.

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1. Introduction

Spinel ferrites are magnetic materials with a general formula (M$_x$Fe$_{1-x}$)[M$_{1-x}$Fe$_{1+x}$]O$_4$, where x is the cation distribution factor, the round and square brackets denote the tetrahedral (A) and octahedral (B) interstitial sites. M represents the divalent metal cation (Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, *etc.*) and Fe is the trivalent (Fe^{3+}) metal cation occupying the FCC lattice formed by O^{2-} anions. For normal spinel ferrites x = 1, with all the divalent (M^{2+}) cations on the tetrahedral (A) sites and the trivalent (Fe^{3+}) cations on the octahedral (B) sites, and is represented by the formula (M^{2+})[Fe^{3+}Fe^{3+}]O$_4$. However, x = 0 represents the "inverse" spinel ferrites, with the formula (Fe^{3+})[M^{2+}Fe^{3+}]O$_4$, in which the divalent cations occupy the B-site and the trivalent cations are equally divided among the A-site and remaining B-site. The magnetic properties of a spinel are sensitive to the types of cation and their distribution amongst the two interstitial sites of spinel lattice [1]. The cation distribution between A and B site depends on the ionic radii, the type of bonding and the preparation method. Changing the temperature, pressure, magnetocrystalline anisotropy, and composition of metal ions can change the distribution. The ferrites with spinel structure have attracted considerable interest due to their remarkable optical, electronic, mechanical, thermal, and magnetic properties. These properties are exploited in technological applications like ferrofluid, biomedicine, targeted drug delivery, magnetic resonance imaging, and recording media [2–5].

ZnFe$_2$O$_4$ is a normal spinel, where Zn^{2+} preferably occupies the tetrahedral sites due to their affinity for *sp^3* bonding with oxygen anions leaving all the ferric ions on the octahedral sites. The normal spinel structured ZnFe$_2$O$_4$ is antiferromagnetic in nature due to low Néel temperature and is paramagnetic at room temperature due to weak super exchange interaction attributed to 90° angle in Fe^{3+}–O–Fe^{3+} [6]. Thus, ZnFe$_2$O$_4$ exhibits lower magnetic moment (∼5 emu/g) at room temperature. However, on vacuum thermal annealed at 1000 °C and cooled to room temperature it becomes magnetically ordered with a large magnetic moment (∼62 emu/g). This change is attributed to the change in the cation distribution from the normal to mixed spinel type, where Fe^{3+} and Zn^{2+} occupies both sites under vacuum thermal annealing [7].

CoFe$_2$O$_4$ is typically an inverse spinel ferrite in which Fe^{3+} ions are occupied equally, with their spin in the opposite direction, in the tetrahedral (A) and octahedral (B) sites. The magnetic property is mainly dependent on the Co^{2+} (3d^7) ions that have an orbital moment of 3.7 μ_B per formula unit [1]. It has a coercivity of ∼0.75–0.98 kOe along with 80 emu/g magnetization at room temperature and is a good candidate for the magnetic recording application [8]. Magnetic coercivity of any material depends on several factors like magnetocrystalline anisotropy, shape anisotropy, strains, defects, size of the particles, doping, nature of the surface, and interface [9–13]. A number of efforts have been made to increase the coercivity in cobalt ferrite using different strategies. However, the maximum coercivity reported so far in the powders of CoFe$_2$O$_4$ is 5.3 kOe for the samples prepared

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by chemical route. Such a large coercivity is attributed to small particle size and large residual strain [14]. The maximum room temperature coercivity reported in $CoFe_2O_4$ particles synthesized by mechanical milling process is 5.1 kOe. This large coercivity is attributed to the high strain and defects produced in $CoFe_2O_4$ powders by milling [10].

On the other hand, $MgFe_2O_4$ is a soft magnetic *n*-type semiconducting material, and is very important member of ferrite family. The cation distribution in $MgFe_2O_4$, upon which many physical and chemical properties depend, is a complex function of processing parameters and mostly depends on the preparation method of the material. The earlier reported cation distribution reveals that Mg^{2+} ions exist in both sites but have a strong preference for the octahedral site [15]. The magnetic moment of Mg^{2+} is zero, so the magnetic couplings in $MgFe_2O_4$ purely originate from the magnetic moment of Fe cations and may be relatively weaker. Thus, the magnetic anisotropy in $MgFe_2O_4$ could be lower than that of other spinel ferrites. From the past few years, several researchers have incorporated various substitutions and studied the structural, vibrational and magnetic and properties of mixed ferrites. Padalia and coworkers have earlier estimated the valance state of Co as Co^{2+} and Fe as Fe^{3+} in Zn doped Cobalt ferrites using X-ray fine structure method. Additionally the bond length estimated from fine structure method was close to those obtained from crystallographic data [16]. Furthermore, Amulevicius et al. explore the dependence of average hyperfine field and temperature dependent magnetic anisotropy of mixed ferrites using multilevel relaxation model [17].

Apart from magnetization, Raman spectroscopy is also a powerful probe to reveal the structural and vibrational properties of spinel ferrites. $CoFe_2O_4$ as reported earlier belongs to cubic inverse spinel structure with $Fd3m$ space group similar to that of Fe_3O_4. Although the X-ray powder diffraction pattern of $CoFe_2O_4$ and Fe_3O_4 are quite similar, their Raman spectra are quite different. The full unit cell of cubic symmetry contains 56 atoms but the smallest Bravais cell contains only 14 atoms. Therefore, 42 vibrational modes are possible. Group theory predicts the following optical phonon distribution: $5T_{1u} + A_{1g} + E_g + 3T_{2g}$; the $5T_{1u}$ modes are IR active [18], whereas other five ($A_{1g} + E_g + 3T_{2g}$) are Raman active modes composed to the motion of O ions and both the A – site and B – site ions [19,20].

The present work aims at the investigation of structural and magnetic properties of $A_xCo_{1-x}Fe_2O_4$ (A = Zn, Mg and x = 0.0, 0.5) samples. The chemical co-precipitation method has been used to synthesize Zn and Mg doped cobalt ferrites. Detailed analyses of the structural and magnetic properties of as prepared ferrites are discussed.

2. Experimental details

2.1. 1 Materials and methods

For the synthesis of $A_xCo_{1-x}Fe_2O_4$ (A = Zn, Mg and x = 0.0, 0.5) samples through chemical co-precipitation technique all the reagents were commercial products with analytical grade without further purification. The chemical reagents for this experiment $Fe(NO_3)_3 \cdot 9H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, $Mg(NO_3)_2 \cdot 6H_2O$, and sodium hydroxide were used. The deionized water was used during the experiments. The aqueous solution of Co, Zn, Fe and Mg salts were freshly prepared by taking $Fe(NO_3)_3 \cdot 9H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, and $Mg(NO_3)_2 \cdot 6H_2O$ in appropriate molar ratio. This mixture was heated until the temperature reached 70 °C. On vigorous stirring, the *p*H of the above solution was raised to 12 rapidly, by the addition of 6 M NaOH. The particles settled at the bottom were collected and the top water layer with excess salts was discarded. The particles have been washed repeatedly with distilled water to remove salt impurities. Later, the washed particles were treated with acetone dried at room temperature and further calcined at 700 °C for 5 h.

2.2. Characterizations

The crystal structure and type of phases were identified by means of X-ray powder diffraction (XRD) at room temperature, using Bruker D8 Advance X-ray diffractometer with $CuK_{\alpha1}$ (1.5406 Å) radiation. The data was collected with a scanning speed of 2°/min. with a step size of 0.02° over the angular range 2θ (10° < 2θ < 90°) generating X-ray by 40 kV and 40 mA power settings. The Raman measurements on as synthesized samples were carried out on LABRAM-HR spectrometer with a 488 nm excitation source equipped with a Peltier cooled charge coupled device detector. Fourier Transform Infrared (FT-IR) spectra were recorded in the frequency range of 2000–400 cm^{-1} employing KBr disc technique using Bruker Germany make spectrometer model vertex-70. DC magnetization measurements on all the samples were performed using a vibrating sample magnetometer (VSM, Lakeshore 7300 model, USA) as a function of magnetic field from 0 to ±10,000 Oe.

3. Results and discussion

3.1. Structural analysis

The of X-ray diffraction pattern of $A_xCo_{1-x}Fe_2O_4$ (A = Zn, Mg and x = 0.0, 0.5) samples are shown in Fig. 1. From the X-ray diffraction pattern, it has been observed that all the reflection peaks of pure as well as doped compound matches well with Joint Committee for Powder Diffraction Set (JCPDS) Card No. 22-1086 for $CoFe_2O_4$ ferrite. Furthermore, there is no change in peak positions for all the three samples, which indicate that all the samples crystallize in single-phase cubic structure with $Fd3m$ space group.

The Rietveld refinement of X-ray powder diffraction pattern for $A_xCo_{1-x}Fe_2O_4$ (A = Zn, Mg and x = 0.0, 0.5) samples at room temperature were performed using FullPROOF program and shown in Fig. 2. The performed pattern for the structural modal with space group $Fd3m$ (227) reproduce adequately all the observed reflections and gave practically identical reliability factor. There is a good agreement between observed and calculated pattern using the Rietveld analysis, which is confirmed by observing the difference pattern. The refined parameters of as synthesized samples
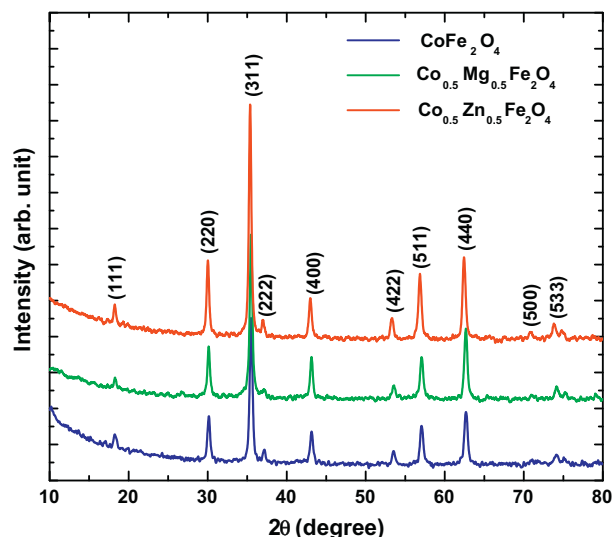

Fig. 1. X-ray diffraction pattern for $A_xCo_{1-x}Fe_2O_4$ (A = Zn, Mg and x = 0.0, 0.5) ferrite samples.