Synthesis, Structural Properties and Characterization of Co–Mg Nanoferrites

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ABSTRACT

Nanoferrite particles of $Mg_xCo_{1-x}Fe_2O_4$ (x = 0.0, 0.25, 0.50, 0.75, and 1.00) were synthesized using the citrate gel auto-combustion method and characterized by X-ray diffraction (XRD) and Fourier-transform infrared (FTIR) spectroscopy. XRD analysis confirmed the formation of a single-phase cubic spinel structure. The average crystallite size increased with increasing Mg concentration up to x = 0.75 and showed a sharp decrease at x = 1.0. The variation in lattice constant followed Vegard's law. The characteristic FTIR absorption bands confirmed the formation of the spinel nanoferrite structure. In addition, the optical absorption properties of the synthesized ferrites were investigated using UV–Visible spectroscopy.

Keywords: *Spinel structure; XRD; FTIR; UV–Visible spectroscopy.*

INTRODUCTION

The study of nanoferrites has gained significant attention due to their wide range of applications and unique properties in various fields. Nanoferrites have diverse applications in chemistry, physics, biology, medicine, and engineering. Investigating the structure and properties of nanoferrites is an important area of materials science, as their properties and applications are strongly influenced by their microstructure. Researchers have focused extensively on the synthesis of nanoferrites because of their superior optical, electrical, and magnetic properties compared with their bulk counterparts [1].

Magnetic nanoferrites have numerous technological applications and are widely used in the fabrication of magnetic devices, high-frequency transformers, storage devices, microwave components, and radar systems [2]. They are also utilized in gas sensors, heterogeneous and photocatalysis, magnetic drug delivery, data storage [3–5], magnetic resonance imaging (MRI) contrast agents [6], and thermally activated cancer treatment [7]. Spinel ferrites are also employed as magnetic adsorbents in wastewater treatment. The properties of these materials are strongly influenced by particle size distribution, morphology, shape, and density, which, in turn, depend on the method of preparation.

The physical and chemical properties of spinel ferrites are governed by the distribution of cations between the tetrahedral (A) and octahedral (B) sites of the spinel structure. Properties such as saturation magnetization and Curie temperature depend strongly on the cation distribution and the nature of the substituting cations. Spinel ferrites can generally exist as either normal or inverse spinels. In a normal spinel, the divalent metal cations occupy the tetrahedral A-sites while the Fe^{3+} ions occupy the octahedral B-sites, represented as $[M^{2+}]A[Fe^{3+}Fe^{3+}]B$. In an inverse spinel, the Fe^{3+} ions occupy the tetrahedral A-sites, while the divalent cations and remaining Fe^{3+} ions occupy the octahedral B-sites, represented as $[Fe^{3+}]A[M^{2+}Fe^{3+}]B$. These arrangements are determined by the distribution of cations between the tetrahedral and octahedral sites in the oxygen sublattice. Doping or cation substitution in ferrites can significantly modify their physical properties, and different divalent cations of appropriate ionic size can be incorporated into the interstitial sites of the spinel ferrite structure [8].

A review of the literature reveals that magnesium ferrite ($MgFe_2O_4$) is a partially inverse spinel and can be considered a collinear ferrimagnetic material. Its degree of inversion is highly sensitive to the method of sample preparation [9]. The structural and magnetic characteristics of $MgFe_2O_4$ substituted with nonmagnetic cations such as Ca, Cd, Co, and Al have been investigated using X-ray diffraction (XRD) and magnetic measurements [10]. Cobalt ferrite ($CoFe_2O_4$) is generally considered a normal spinel. The anomalous antiferromagnetic behavior observed in Co-ferrite may be attributed to the presence of a small fraction of Fe^{3+} ions at the A-sites and the formation of magnetic clusters involving neighboring Fe^{3+} ions at the B-sites. This behavior is also associated with the A–B super exchange interaction, which is stronger than the B–B interaction [11,12].

The magnetic properties of nanocrystalline Mg–Co ferrites prepared using the conventional ceramic technique have been investigated by B. R. Karche et al. [13]. In the present work, the structural, vibrational, and optical properties of the spinel ferrite system $Mg_xCo_{1-x}Fe_2O_4$ (x = 0.0, 0.25, 0.50, 0.75, and 1.00) synthesized by the citrate gel auto-combustion method are investigated. The synthesized samples were characterized using X-ray diffraction (XRD) and Fourier-transform infrared (FTIR) spectroscopy, while their optical properties were studied using UV–Visible spectroscopy.

MATERIALS AND EXPERIMENTAL METHOD

Nanoferrite particles with the chemical composition $Mg_xCo_{(1-x)}Fe_2O_4$ (x = 0.0, 0.25, 0.50, 0.75, and 1.00) were synthesized using the citrate-gel auto-combustion method. Magnesium nitrate, cobalt nitrate, ferric nitrate, citric acid, and ammonia, each with 99% purity, were used as the starting materials. The synthesis was carried out at room temperature using an appropriate stoichiometric ratio of the constituent metal nitrates and citric acid.

The calculated amounts of the metal nitrates and citric acid were separately dissolved in double-distilled water and stirred thoroughly to obtain homogeneous solutions. The resulting solutions were then mixed together and heated to approximately 80 °C under continuous stirring. The pH of the solution was adjusted to 7 by adding ammonia solution drop wise. The resulting homogeneous mixture was subsequently heated to approximately 200 °C using a magnetic stirrer. At this temperature, an auto-combustion reaction occurred, producing a voluminous ferrite powder. The obtained powder was ground thoroughly using an agate mortar and pestle and then calcined at 500 °C for 4 h. After calcinations, the samples were allowed to cool to room temperature [14].

The structural characterization of the synthesized samples was carried out using a Philips X-ray diffract meter with Cu Kα radiation (λ = 1.5355 Å). The formation of the spinel ferrite structure was further confirmed by Fourier-transform infrared (FTIR) spectroscopy. The optical properties of the synthesized nanoferrites were investigated using UV–Visible diffuse reflectance spectroscopy (UV–DRS). Barium sulfate ($BaSO_4$) was used as the reference material for the diffuse reflectance measurements, and the optical response was recorded as a function of wavelength in the UV–Visible region.

RESULTS AND DISCUSSION

XRD analysis of Mg-Co ferrite nano particles:

Figure 3.1depicts the XRD pattern of low temperature synthesized $Mg_xCo_{1-x}Fe_2O_4$ (where X=0.0 to 1.0with 0.2 variation) spinel nano ferrites. From the XRD pattern revealed that the samples consist of cubic spinel with single phase structure, there is no presence of other impurity peaks in composition of samples. Samples cubic spinel structure and belongs to Fd_3m space group[15]. The presented peak positions of XRD were also confirmed by existence of the JCPDS data. The average crystalline size of the synthesized nano ferrites were calculated from Debye Scherrer's equation [16].$l = \frac{0.94\lambda}{\beta Cos\theta}$Where λ=wavelength, β=FWHM, and θ=Brags angle.

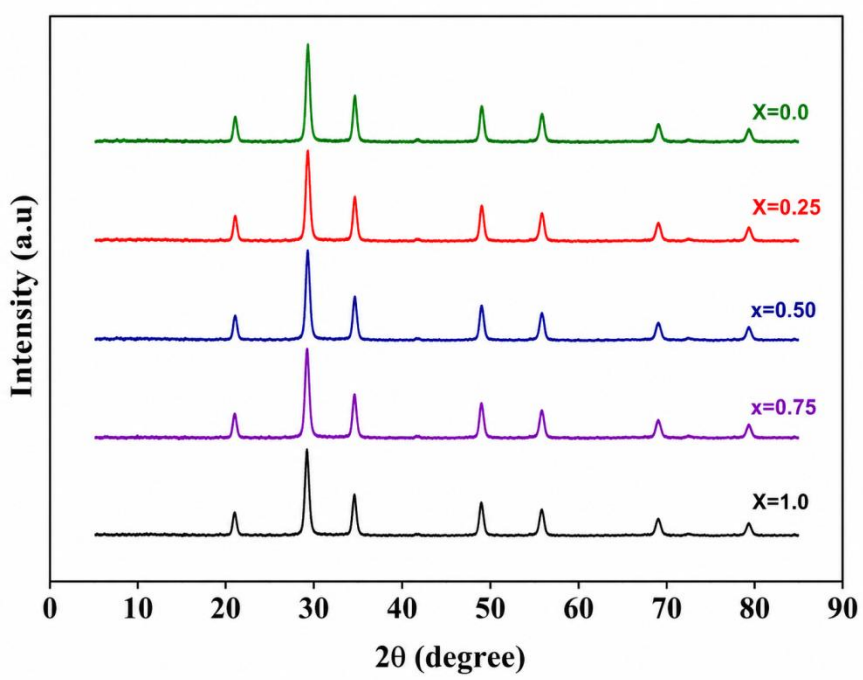

Figure 3.1 XRD patterns of Mg-Co nano ferrites

The average crystalline size of pure sample ($CoFe_2O_4$) is 36 nm. The average crystalline size increased with increasing the doping concentration on pure sample from 38 to 45 nm, it could be due to smaller ionic radios of Mg^{2+} was substituted on larger ionic radios of Co^{2+} ions. Lattice constant of fabricated nano ferrites were calculated by the following equation. $a = d\sqrt{h^2 + k^2 + l^2}$, Where hkl indicates miller indices and, d indicates lattice constant. Mg-Co nanoferrites lattice constant range from 8.9612 to 8.4659 [17]. Lattice constant was increased up to 0.8 molar ration later it was decreased (8.3679 A^O), lattice constant varies it indicates obeys Vegard's law.

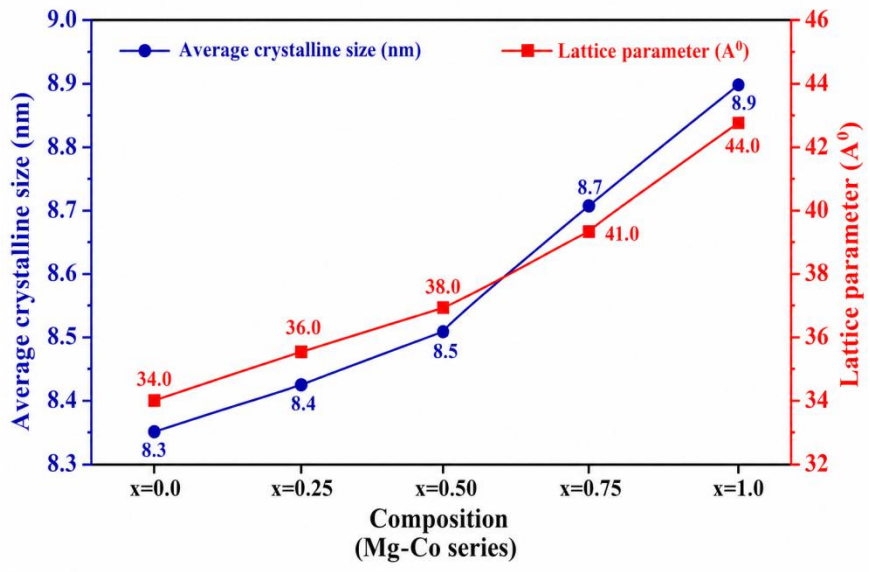

Figure 3.2 Composition Vs average crystalline size and lattice parameter

The unit cell's volume was calculated using the formula $v=a^3$, where a lattice constant The unit cell's volume changed as the dopant concentration did [18]. The material's lattice parameter determines the unit cell volume. The x-ray density of the manufactured ferrite samples was computed using the formula $d_x = {}^{8M}/_{Na^3}$, where M is the sample's molecular weight, N is its Avogadro number, and an is its lattice parameter. The x-ray density of pure Cd ferrite was determined to be 5.26 gm/cm3. The nano ferrites' X-ray density rose from 5.26 to 4.33 gm/cm3. The sample's molecular weight, lattice constant, dopant concentration, sintering temperature, and other factors all affected the x-ray density.

Mg-Co nano ferrites' FTIR spectra

FTIR spectra are a useful tool for understanding structural characteristics. The FTIR of the produced Mg-Co nano ferrites was displayed in Figure 3.3. Transmittance was plotted against wave number on the FTIR plots. Two primary absorption bands were seen in this spectrum, with a greater frequency at 600 cm^{-1} and a lower frequency at 400 cm^{-1}. These two absorption peaks indicate that the material is spinel ferrite [19]. Waldron and Hafner studied the vibrational spectra of synthetic nanoferrites and identified the tetrahedral (A) site as the source of the high frequency band (v1) at approximately 600 cm^{-1} and the octahedral (B) site as the source of the low frequency band (ω2) at approximately 400 cm^{-1}. The variation in band locations may result from variations in the distance between Fe^{3+} and O^{2-}ions.

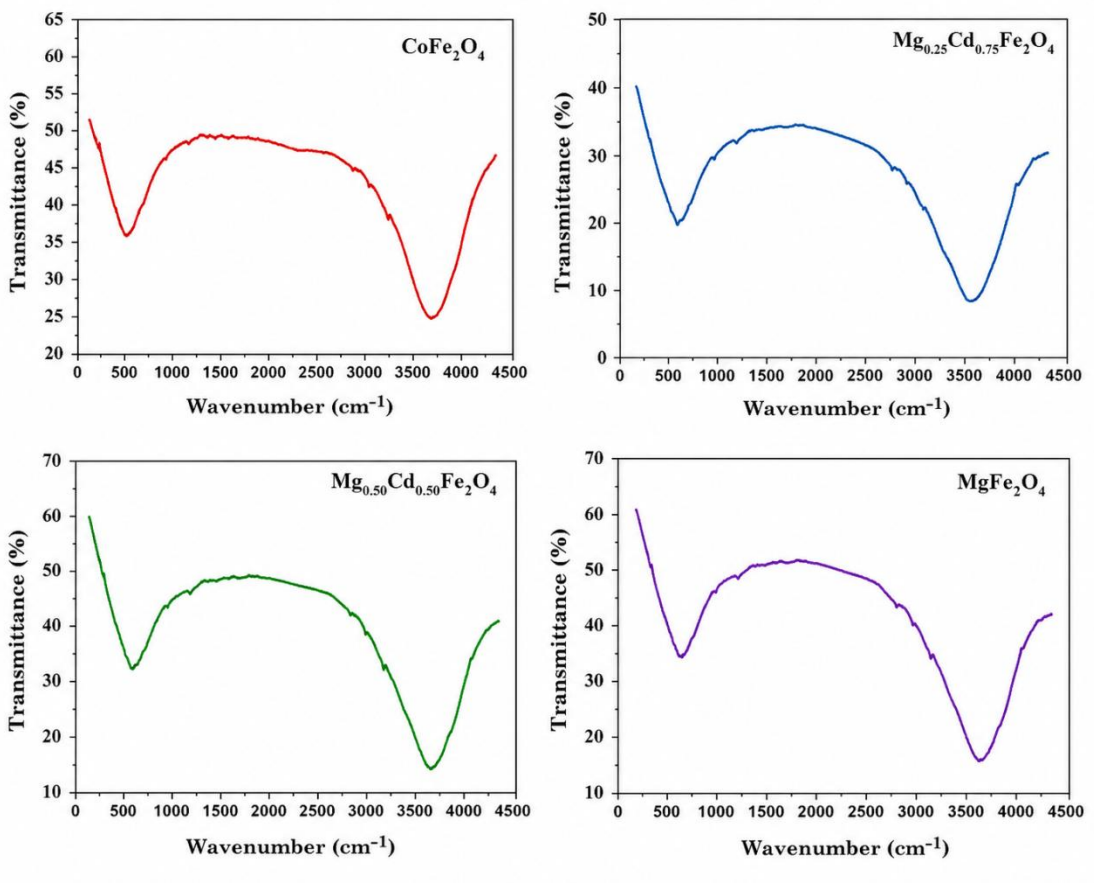

Figure 3.3 FTIR spectra of Mg-Co nano ferrites

Optical Studies of Mg-Co nano ferrites

UV-Vis spectroscopy is a potent method for determining the optical characteristics of nano ferrite samples. The UV-Vis spectra of synthetic Mg-Co micro ferrites are shown in Figure 3.4. One important technique for determining the optical band gap of spinel nanoferrrites particles is UV-Vis spectroscopy. UV-Vis spectra were captured using a UV-Vis Spectro photometer with an integrating sphere in the wavelength range of 200–800 nm [21]. Band gap energy is crucial for semiconductor materials in the field of optoelectronic applications. The band gap energy of the sample was determined from this UV-Vis spectrum using the formula E=1240◦(λ), where λ is the cutoff wavelength [22]. The band gap energy for pure $CoFe_2O_2$ was 3.36 eV, according to the equation above.

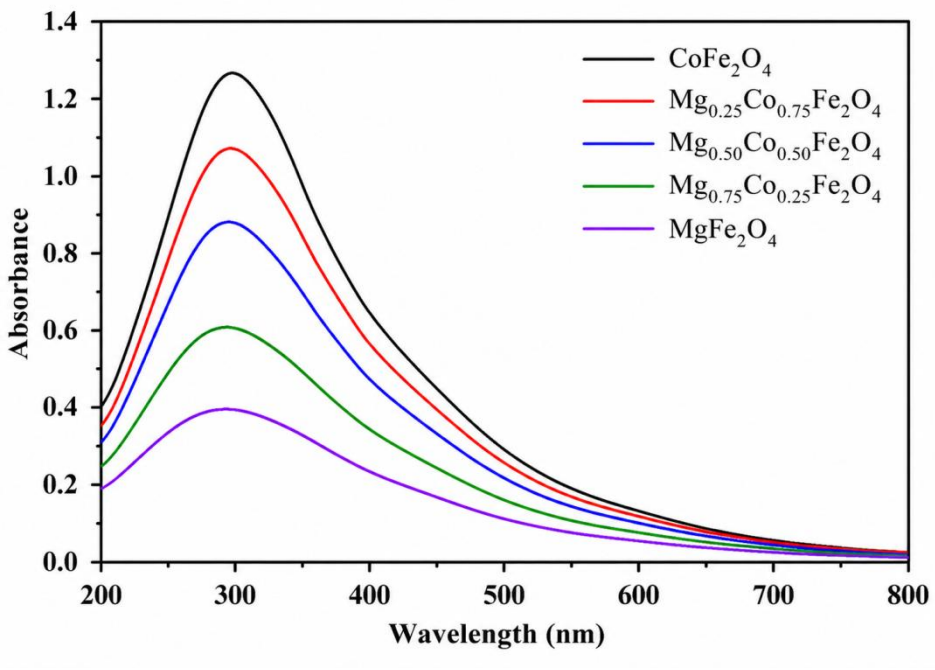

Figure 3.4. UV-Vis spectra of Mg-Co nano ferrites.

Table.2 Cut of wavelength and band gap energy of $Mg_xCo_{1-x}Fe_2O_4$ x=0.0 to 1.0

Composition name	Cut off wavelength (nm)	Band gap energy (ev)
$CoFe_2O_4$	389	3.46
$Mg_{0.25}Co_{0.75}Fe_2O_4$	375	3.58
$Mg_{0.5}Co_{0.5}Fe_2O_4$	380	3.44
$Mg_{0.75}Co_{0.25}Fe_2O_4$	367	3.38
$MgFe_2O_4$	388	3.46

CONCLUSIONS

Using the citrate gel auto combustion process, a series of spinel nano ferrites with the chemical formula $Co_{1-x}Mg_xFe_2O_4$ (where X = 0.0, 0.25, 0.50, 0.75, and 1.0) were created. X-ray diffraction examination verified the phase conformation; the produced samples have a cubic spinel structure and no additional impurity peaks.The samples' lattice parameters were found using x-ray diffraction research, and their change indicates that they follow Vigard's law. Average crystalline size, lattice parameter, unit cell volume, and x-ray density were determined from X-ray diffraction analysis samples; these parameters may depend on the material synthesis technique, sintering temperature, sintering conditions, ionic radii of the elements, etc. Two IR peaks that represent the stretching frequency of M-O bonds were found in the samples' FTIR spectra. Two IR peaks in the samples' FTIR spectra were found to be the stretching frequency of M-O bonds at tetrahedral and

octahedral sites, which may be related to the ferrites' spinel structure. The band gap energy was found to be close to 3.36 to 3.56 eV based on UV-Vis spectra. The produced samples showed signs of fluorescence, which may be useful for optoelectronic applications.

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REFERENCES

1. D. H. Chen, Y. Y. Chen, *J. Colloid Interface Sci.*, 236, 41 (2001).
2. C. Liu, B. S. Zou, A. J. Rondinone, Z. J. Zhang, *J. Am. Chem. Soc.*, 122, 6263 (2000).
3. A. C. Druc et al., "How cobalt ions substitution changes the structure and dielectric properties of magnesium ferrite?", *Ceramics International*, 40 (2014), 13573–13578.
4. K. Kirchberg et al., "Stabilization of monodisperse, phase-pure $MgFe_2O_4$ nanoparticles in aqueous and nonaqueous media and their photocatalytic behaviour," *J. Phys. Chem. C*, 121 (2017), 27126–27138.
5. K. Kombaiah et al., "Catalytic studies of $NiFe_2O_4$ nanoparticles prepared by conventional and microwave combustion method," *Materials Chemistry and Physics*, 221 (2019), 11–28.
6. C. Barcena et al., "Zinc ferrite nanoparticles as MRI contrast agents," *Chemical Communications* (2008), 2224–2226.
7. K. Kombaiah et al., "Self heating efficiency of $CoFe_2O_4$ nanoparticles: A comparative investigation on the conventional and microwave combustion method," *J. Alloys Compd.*, 735 (2018), 1536.
8. S. Krupicka, P. Novak, E. P. Wohlfarth (eds.), *Ferromagnetic Materials*, North-Holland, Amsterdam, Vol. 3 (1982).
9. H. Knock and H. Dannheim, *Physica Status Solidi (A)*, 3, k135 (1976).
10. R. V. Upadhyay and R. G. Kulkarni, *Materials Research Bulletin*, 19, 653 (1984).
11. M. Yokoyama, T. Sato, E. Ohta, T. Sato, *Journal of Applied Physics*, 80, 1015 (1996).
12. T. Kamiyama, K. Haneda, T. Sato, S. Ikeda, H. Asano, *Solid State Communications*, 81, 563 (1992).
13. B. R. Karche, B. V. Khasbardar, A. S. Vaingankar, *Journal of Magnetism and Magnetic Materials*, 168 (1997), 292–298.
14. G. Aravind et al., "Study of structural and magnetic properties of Li-Ni nano ferrites synthesized by citrate-gel auto combustion method," *Ceramics International*, 42 (2016), 2941–2950.

15. L. C. Shidaganal et al., "Al-Doped Co-Co Nanoferrites by Solution-Combustion Synthesis: Preparation and Structural Characterization," *Int. J. Self-Propagating High-Temperature Synth.*, 29 (2020), 176–180.
16. L. Yang, G. Xi, J. Liu, "MnZn ferrite synthesized by sol-gel auto-combustion and microwave digestion routes using spent alkaline batteries," *Ceramics International*, 41 (2015), 3555–3560.
17. O. Kaman et al., "Preparation of Mn-Zn ferrite nanoparticles and their silica-coated clusters: Magnetic properties and transverse relaxivity," *Journal of Magnetism and Magnetic Materials*, 427 (2017), 251–257.
18. S. B. Somvanshi et al., "Influential diamagnetic magnesium (Mg^{2+}) ion substitution in nano-spinel zinc ferrite ($ZnFe_2O_4$)," *Ceramics International*, 46 (2020), 8640–8650.
19. D. Varshney, K. Verma, A. Kumar, "Structural and vibrational properties of $Zn_xMn_{1-x}Fe_2O_4$," *Materials Chemistry and Physics*, 131 (2011), 413–419.
20. K. Hussain et al., "Study of structural, optical, electrical and magnetic properties of Cu^{2+} doped $Zn_{0.4}Co_{0.6-x}Ce_{0.1}Fe_{1.9}O_4$ spinel ferrites," *Physica B: Condensed Matter*, 584 (2020), 412078.
21. L. C. Shidaganal et al., "Al-Doped Co-Cd Nanoferrites by Solution-Combustion Synthesis: Preparation and Structural Characterization," *Int. J. Self-Propagating High-Temperature Synth.*, 29 (2020), 176–180.
22. L. Yang, G. Xi, J. Liu, "MnZn ferrite synthesized by sol-gel auto-combustion and microwave digestion routes using spent alkaline batteries," *Ceramics International*, 41 (2015), 3555–3560.
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