Structural, vibrational, electrical, and magnetic properties of mixed spinel ferrites Mg$_{1-x}$Zn$_x$Fe$_2$O$_4$ nanoparticles prepared by co-precipitation

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ABSTRACT

Mg$_{1-x}$Zn$_x$Fe$_2$O$_4$ (where $x = 0.0, 0.2, 0.4, 0.5, 0.6$ and 0.8) nanoparticles were synthesized using co-precipitation. A detailed investigation of the structural, magnetic, electrical, and optical properties was carried out for the synthesized samples using X-ray diffraction (XRD), current-voltage (I-V) measurements, vibrating sample magnetometer (VSM) and Raman spectroscopy, respectively. Rietveld refinement fitting revealed that the structure of these samples is cubic spinel with space group $Fd3m$, and the lattice parameter decreases linearly with increasing Mg-content due to the smaller ionic radius of the Mg$^{2+}$ ion. Five Raman modes were predicted for the spinel structure, and the A$_1g$ Raman mode split into three branches, where each one belong to each ions like Zn$^{2+}$, Mg$^{2+}$, and Fe$^{3+}$ in the tetrahedral positions. The magnetization showed an increasing fashion with the increasing Mg concentration due to the cation rearrangement at the tetrahedral and octahedral sites. The isothermal magnetization curves collected at room temperature showed a paramagnetic (PM) to ferrimagnetic (FiM) transition as the Mg content was increased in Mg$_{1-x}$Zn$_x$Fe$_2$O$_4$. Both magnetic and structural properties of ZnMg-ferrite nanoparticles strongly depend upon the Mg$^{2+}$ cation doping percentage. Current-voltage (I-V) measurements show that electrical resistivity increases with increasing Mg content.

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I. INTRODUCTION

Spinel ferrites containing iron oxides are important magnetic compounds and have been studied intensively due to their unique properties such as high Curie temperature,$^{1}$ high coercivity,$^{2}$ large Kerr effect,$^{3}$ Faraday rotations,$^{4}$ and insulator-metal transition.$^{5}$ Ferrites with these properties can be beneficial in many applications, such as in transformer cores, drug delivery, gas sensors and ferrofluids.$^{6}$ Complex spinels are usually represented as ABZ$_2$ (where B = Fe, Al, Cr) in the tetrahedral [A] and octahedral [B] sites in a ratio of [A]:[B] moles of 1:2, while the anions are usually (Z = O, Se, S etc.), with two distinct coordinate polyhedra for the metal atoms (cations).$^{7}$ The anions are mainly atoms of oxygen (oxospinels) in spinels. The material is known as ferrite if Fe$^{3+}$ ions reside at the B sites. Lattice occupancy of the divalent metal ions is based on the spinel structure type such as inverse, normal and mixed spinel structures. The properties of ferrite nanoparticles can be influenced by the occupancy of these metal ions on these lattice sites. Elemental composition, cation type, cation concentration, preparation methods, and external perturbations such as temperature and pressures are used as a tool to determine the electrical, magnetic or structural properties of these two lattice sites. The Mg ferrite (MgFe$_2$O$_4$) has an inverse spinel structure in which Mg$^{2+}$ ions reside on the octahedral sites,$^{8}$ whereas the Zn ferrite (ZnFe$_2$O$_4$) has a normal spinel structure where the Zn$^{2+}$ cations are placed at the tetrahedral sites.$^{9}$

Recently, these intermediate compounds have gained enormous attention due to their potential applications.$^{10,11}$ Previous...
knowledge of vibrational properties of this material is limited\cite{14} while the electrical resistivity in other spinel ferrites e.g. Zn$_{1-x}$CoFe$_2$O$_4$ revealed a decreasing trend as the Zn concentration is increased.\cite{15}

In this work, the effect of Mg-doping on the structural, vibrational, electrical, and magnetic properties of mixed cubic ferrites nanoparticles Mg$_{1-x}$Zn$_x$Fe$_2$O$_4$ (x = 0.0, 0.2, 0.4, 0.6 and 0.8) was investigated by X-ray diffraction (XRD), Raman spectroscopy, current-voltage (I-V) measurements, and vibrating sample magnetometer (VSM), respectively.

II. EXPERIMENTAL

Magnesium-doped zinc ferrite nanoparticles Mg$_{1-x}$Zn$_x$Fe$_2$O$_4$ (x = 0.0, 0.2, 0.4, 0.6 and 0.8) were synthesized using co-precipitation.\cite{12} The technique of chemical co-precipitation is relatively easy to scale and often used to synthesize ferrite nanoparticles. The chemical reagents used in this experimental study were zinc nitrate (Zn(NO$_3$)$_2$.6H$_2$O), magnesium nitrate Mg(NO$_3$)$_2$.6H$_2$O, and ferric nitrate (Fe(NO$_3$)$_3$.9H$_2$O). Under constant magnetic stirring, an aqueous solution was prepared for all three nitrates in their stoichiometry. The NaOH reagent was then quickly stirred into the above solution, until it was co-precipitated. The solution was maintained at a temperature of 70 °C for 45 mins to transform the hydroxides into ferrites. The pH value was maintained in the range of 12–13. Following the removal of chloride and sodium ions, the precipitates were washed several times with distilled water. In order to remove water content, the washed precipitates were dried in an oven at 100 °C for 12 hours. The dried powder was finally annealed in air for 5 h at 900 °C to obtain annealed nanoparticles. The structure was characterized by an X-ray diffractometer (XRD) using Cu-Kα rays with a wavelength of λ = 0.1541 nm. A laser wavelength of 532 nm and gratings of 2400 grooves/cm was used to collect the Raman spectra by a Renishaw InVia Spectrometer system. The samples were further investigated for resistivity at room temperature by using a four-probe method with a Keithley Source-meter 2410. Magnetic measurements were completed using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design, MPMS-XL-7).

III. RESULTS AND DISCUSSION

A. X-ray diffraction (XRD) analysis

The XRD analysis was performed with Cu - Kα (1.5406 Å) radiation at ambient temperature for study of phase structure, lattice parameters and crystallite size. Fig. 1(a) shows the XRD patterns of the annealed Zn$_{1-x}$Mg$_x$Fe$_2$O$_4$ (x = 0.0, 0.2, 0.4, 0.5, 0.6, 0.8) nanoparticles. All the reflections observed could be attributed to a cubic spinel lattice, with no evidence of other impurities (e.g. Fe$_2$O$_3$ or ZnO etc.), showing its single-phase structure. Peaks of the single-phase cubic spinel structure (JCPDS card no. 22-1012) could be indexed as (111), (2 2 0), (311), (2 2 2), (4 0 0), (4 2 2), (5 1 1), and (4 4 0). All Zn$_{1-x}$Mg$_x$Fe$_2$O$_4$ compositions have no additional peak, indicating that all samples crystallize into a single cubic structure.\cite{16}

Further study of the structural information and pure phase formation of the nanoparticles was attained by the Rietveld analysis of the X-ray diffraction data. Nowadays the Rietveld technique has enabled precise structural refinement to be routinely made from powder diffraction data. The structural refinement was carried out using GSAS software suite and its graphical interface EXPGUI.\cite{17} Fig. 1(b) shows the Rietveld refinement fitting results of the XRD patterns of Zn$_{1-x}$Mg$_x$Fe$_2$O$_4$, and detailed parameters obtained from the Rietveld refinement for all Mg concentration (x) = 0, 0.2, 0.4, 0.5, 0.6, 0.8, are shown in Table I. Intensive and Sharp XRD diffraction peaks represent the well-crystallized structure. All samples were thoroughly examined using the Quantitative Rietveld refinement method for traces of other impurity phases (such as Fe$_2$O$_3$, MgO and ZnO etc.) and no impurity phases were detected, which implies the formation of a single phase Zn$_{1-x}$Mg$_x$Fe$_2$O$_4$ nanoparticle, confirming our initial observation. The refinement of the structural parameters was continued until convergence was achieved with a good fit parameter (χ²) around 1.0, which is an excellent fitting result (Table I).

The major peaks at 2θ = 18.5, 30.3, 35.5, 37.2, 43.3, 53.7, 57.3, and 63 belong to the (111), (2 2 0), (311), (2 2 2), (4 0 0), (4 2 2),

### Table I. Variation of structural parameters with increasing Mg content.

| Sample       | Space Group | Lattice Parameter (Å) | Crystallite size D (nm) |
|--------------|-------------|-----------------------|-------------------------|
| ZnFe$_2$O$_4$ | Fd3m        | 8.446                 | 86.30                   |
| Zn$_{0.8}$Mg$_{0.2}$Fe$_2$O$_4$ | Fd3m        | 8.44                  | 66.78                   |
| Zn$_{0.6}$Mg$_{0.4}$Fe$_2$O$_4$ | Fd3m        | 8.435                 | 57.53                   |
| Zn$_{0.4}$Mg$_{0.6}$Fe$_2$O$_4$ | Fd3m        | 8.432                 | 51.59                   |
| Zn$_{0.2}$Mg$_{0.8}$Fe$_2$O$_4$ | Fd3m        | 8.430                 | 45.92                   |
| Zn$_{0.0}$Mg$_{1.0}$Fe$_2$O$_4$ | Fd3m        | 8.426                 | 38.17                   |

Fig. 1. (a) XRD patterns of Zn$_{1-x}$Mg$_x$Fe$_2$O$_4$ (x = 0.0, 0.2, 0.4, 0.5, 0.6, 0.8) nanoparticles (b) Rietveld refinement fitting results of the X-ray powder diffraction patterns of Zn$_{0.2}$Mg$_{0.8}$Fe$_2$O$_4$.\cite{18}
(511) and (440) crystal planes, respectively, which ensures the formation of single-phase \( \text{Zn}_{1-x}\text{Mg}_x\text{Fe}_2\text{O}_4 \) nanoparticles with cubic spinel-type structure and space group \( Fd\overline{3}m \) (227). The peak at (222) is mainly observed only for \( \text{ZnFe}_2\text{O}_4 \) nanoparticles, which increase with decreasing Mg concentration.

In the XRD profile, the average crystallite sizes of the samples are calculated by the Debye – Sherrer formula based on the diffraction peak of the (311) plane:

\[
X = \frac{0.89Y}{\beta \cos \theta}
\]

where \( X \) is crystallite size, \( Y \) is the X-ray wavelength (0.1542 nm), \( \beta \) is the full width at half maximum (FWHM), and \( \theta \) is the Bragg angle of the (311) plane. The crystallite size of the samples is summarized in Table 1. The crystallite size decreased from 86.30 to 38.17 nm with an increase in the Mg content. \(^1\) It has a minimum crystallite size of 38.17 nm for 0.8 Mg concentration, due to the smaller ionic radius of the Mg\(^{2+}\) ions. Similar results were established by Rahman et al.\(^2\), Fig. 2(a) represents the variation in average crystallite size with change in Mg concentration.

The lattice parameter (a) obtained by using XRD data lies in the range of 8.42–8.44 Å for different Mg concentrations, as shown in Fig. 2(b) and Table 1. It decreases with the increasing Mg concentration, thus, obeying Vegard’s law.\(^3\) Vegard’s law is based on the changes due to the ionic radii of replacing and replaced ions and predicts the linear change in the lattice parameter for the spinel system with the substitution of different ions. The ionic radius of the Mg\(^{2+}\) ion (0.65 Å) is smaller than that of the Zn\(^{2+}\) ion (0.83 Å), and thus, causes an effective decrease in the lattice constant. Similar results were presented earlier by Rahman et al.\(^4\) and Salah et al.\(^5\). Therefore, a linear decrease in the lattice spacing indicates that the Mg ions replace the Zn ions in the Zn ferrite matrix. \(^6\) This elucidates the decrease of the lattice constant with Mg doping, and also confirms that Mg is occupied in the spinel lattice of ferrite nanoparticles.

B. Raman spectroscopy

Raman spectra for \( \text{Zn}_{1-x}\text{Mg}_x\text{Fe}_2\text{O}_4 \)(x=0.0, 0.2, 0.4, 0.6, 0.8) samples were recorded in the range of 100–900 cm\(^{-1}\). \( \text{MFe}_2\text{O}_4 \) (ferrites) has a cubic structure (fcc) belonging to the space group \( Fd\overline{3}m \). According to the factor group analysis, some strong and weak modes were clearly observed in the Raman spectroscopy at room temperature, \( \text{A}1\text{g}, \text{E}g, \text{F}2\text{g}, \text{F}3\text{g} \), as shown in Fig. 3. Raman modes with mode frequencies of 332 cm\(^{-1}\), 484 cm\(^{-1}\), 664 cm\(^{-1}\), 688 cm\(^{-1}\) and 707 cm\(^{-1}\), are denoted as M1, M2, M3, M4, and M5, respectively.\(^7\) It is well known from the literature that the Raman modes from 650–710 cm\(^{-1}\) are related to \( \text{A}1\text{g} \) symmetry and associated with the tetrahedral sublattices.\(^8\) Previous studies also confirmed that inverse spinel ferrite such as \( \text{MgFe}_2\text{O}_4 \), \( \text{NiFe}_2\text{O}_4 \), and \( \text{Fe}_2\text{O}_4 \) only have the A-site contribute to the Raman spectrum,\(^9\) while in the case of normal spinel ferrites, \( \text{MFe}_2\text{O}_4 \) (for instance \( \text{M} = \text{Zn} \) or Mn), \( \text{M}^{2+} \) ions occupy the A-sites while \( \text{Fe}^{3+} \) ions fill in the B-sites.\(^10\) The spectrum of \( \text{Zn}_{1-x}\text{Mg}_x\text{Fe}_2\text{O}_4 \)(x=0.0, 0.2, 0.6, 0.8) recorded at ambient temperature is deconvoluted into three independent Lorentzian peaks, as illustrated in Fig. 4(a–d), by considering the mass differences among the three ions (\( \text{M}^{2+} \), \( \text{Zn}^{2+} \), and \( \text{Fe}^{3+} \)).

Raman modes at 647 and 707 cm\(^{-1}\) are related to the heaviest \( \text{Zn}^{2+} \) and lightest ions \( \text{Mg}^{2+} \) respectively, while the 688 cm\(^{-1}\) mode might be correlated to the \( \text{Fe}^{3+} \) ion in the tetrahedral sublattice.

In Fig. 3 and Fig. 4, the shape of peaks demonstrates that as the Mg concentration is increased, M5 (707 cm\(^{-1}\)) becomes clearer and M4 (647 cm\(^{-1}\)) is gradually suppressed. Since \( \text{Fe}^{3+} \) possesses an intermediate mass, we have associated the mode at 688 cm\(^{-1}\) to the \( \text{Fe}^{3+} \) ion in the tetrahedral sublattice (as shown in Fig. 4).

The Raman mode at 217 cm\(^{-1}\) is not observed in the as-synthesized samples at \( x = 0.0 \). However, for \( x = 0.2 \), it started to appear and became visible at \( x = (0.6, 0.8) \). At the same time, the...
intensity of the Raman mode around 650 cm$^{-1}$ (black) started to increase with a decrease in the Mg content for $x=0.2$. Fig. 4 clearly shows that the intensity of the Raman mode at around 670 cm$^{-1}$ is found to be increasing while the intensity of the highest wavelength Raman mode (originally at about 710 cm$^{-1}$) decreases with the increasing Mg-content.

The modes around 667 cm$^{-1}$ (light-red) and 710 cm$^{-1}$ (black) can be directly ascribed to the Fe–O and Mg–O vibrations, respectively.

C. Current-voltage (I-V) measurements

The current-voltage measurements of Zn$_{1-x}$Mg$_x$Fe$_2$O$_4$ ($x=0.0, 0.2, 0.4, 0.5, 0.6, 0.8$) nanoparticles were carried out using a 1240 source (Kiethly) at room temperature. The resistivity of all samples was evaluated using the following formula:

$$\rho = \frac{RA}{L} \tag{2}$$

where $A'$ represents the area of the pallet which is equal to $\pi R^2$ ($R$ is the resistance) while $L'$ shows the thickness of the pallet.$^{27}$ The resistivity value of ZnFe2O4 nanoparticles calculated with the help of I-V data was $5.1 \times 10^5 \Omega cm$. The ohmic and semiconducting nature of the nanoparticles is confirmed by the I-V plots and resistivity values as shown in Fig. 5.

The resistivity decreased with increased Mg concentration as shown in Table II. The replacement of the Mg$^{2+}$ ions at the octahedral B-sites leads to the decrease in the Fe$^{3+}$ concentration at the B-sites, resulting in suppression of the Fe$^{3+}$-Fe$^{3+}$ hopping. This decreased hopping may be responsible for the subsequent increase in resistivity that we observed. These electrical resistivity measurements show that both ZnFe$_2$O$_4$ and MgFe$_2$O$_4$ have high resistance.

D. Magnetic measurements

A vibrating sample magnetometer (VSM) was used to determine the magnetic properties of the prepared samples at room temperature for the applied field in range of -8000 to +8000 Oe. Fig. 6(a) shows the Hysteresis plots illustrating the variation of magnetization (Ms, emu/g) as a function of the applied magnetic field (H, Oe) for the prepared nanocrystalline Zn$_{1-x}$Mg$_x$Fe$_2$O$_4$ ($x=0.0, 0.2, 0.4, 0.5, 0.6, 0.8$) powders measured at room temperature. ZnFe$_2$O$_4$ is a soft magnetic material, and when Zn$^{2+}$ in ZnFe$_2$O$_4$ is substituted by Mg$^{2+}$ ions, its magnetic properties change, i.e., the remanent magnetization (Mr), saturation magnetization (Ms)) and coercivity (Hc), as shown in Fig. 6(a). In particular, the Ms of the Zn$_{1-x}$Mg$_x$Fe$_2$O$_4$ nanoparticles gradually increased with the increase of Mg$^{2+}$ as shown in Fig. 6(b).

For further magnetic study, we selected Zn$_{0.2}$Mg$_{0.8}$Fe$_2$O$_4$ as it has the highest magnetization among the samples studied here. The temperature dependences of magnetization of the Zn$_{0.2}$Mg$_{0.8}$Fe$_2$O$_4$ samples obtained in zero-field cooling (ZFC) and field cooling (FC) modes under six different applied magnetic fields are shown in Fig. 7. In the ZFC measurements, the Zn$_{0.2}$Mg$_{0.8}$Fe$_2$O$_4$ sample

| Sample | Resistivity  |
|--------|-------------|
| ZnFe$_2$O$_4$ | $5.1 \times 10^5 \Omega cm$ |
| Zn$_{0.8}$Mg$_{0.2}$Fe$_2$O$_4$ | $5.22 \times 10^5 \Omega cm$ |
| Zn$_{0.5}$Mg$_{0.5}$Fe$_2$O$_4$ | $5.26 \times 10^5 \Omega cm$ |
| Zn$_{0.3}$Mg$_{0.7}$Fe$_2$O$_4$ | $5.29 \times 10^5 \Omega cm$ |
| Zn$_{0.1}$Mg$_{0.9}$Fe$_2$O$_4$ | $5.32 \times 10^5 \Omega cm$ |
| Zn$_{0.2}$Mg$_{0.8}$Fe$_2$O$_4$ | $5.36 \times 10^5 \Omega cm$ |
was cooled without any applied magnetic field. Once the sample reached the lowest temperature, different magnetic fields were then applied. The magnetization values were recorded while the sample was heated gradually.

FIG. 6. (a) Magnetic hysteresis loop of Zn$_{1-x}$Mg$_x$Fe$_2$O$_4$ with different Mg concentration (b) Variation of the magnetization at 8 kOe with different Mg content.

FC measurements were also performed during warming, after the previous cooling of the sample in a magnetic field. There is a large difference between the ZFC and FC magnetization by applying different fields, as shown in Fig. 7. In ZFC, with increasing temperature, the magnetization increases and each ZFC curve has a wide cusp and reaches a maximum value at the blocking temperature TB. The bifurcation temperature of the FC and ZFC curves is observed at a temperature higher than TB which is also called as thermomagnetic irreversibility temperature ($T_{irr}$). $T_{irr}$ and TB occur at the same temperature in an ideal monodispersed system and are also sensitive to the magnetic field applied. The observed difference in the $T_{irr}$ and TB suggests the existence of a spin-spin or cluster-spin type of interaction. Furthermore, the ZFC and FC magnetization curves merge at high temperatures and gradually increase as temperature decreases, most likely attributed to local clustering of the spins or ferromagnetic domain growth.

Below a certain field depended temperature $T_f$, the ZFC and FC magnetizations start to differ, this is a phenomenon that can be interpreted in terms of freezing of the domain walls motion or a spin-glass transition, as shown previously.

Obviously, the relation between $T_f$ and the applied magnetic field is linear. However, the latter relation can be explained by Kersten within the model of domain wall pinning, in which $E \propto mH$, where $m$ is the magnetic moment and $E$ represents the electric field. However, in the most simple approximation $E_p \propto \sigma_w$ where $E_p$ is the domain wall pinning energy and $\sigma_w$ is proportional to the wall energy density. In general, the pinning of the domain-walls can be interpreted by a model in which the walls are bowed between adjacent pinning sites and can move to the next site when the applied field increases above a certain critical value. Therefore, the bifurcation between the temperature dependence of FC and ZFC can be attributed to the freezing of the domain-wall motion below the field dependent temperature $T_f(H)$, and an increase in the strength of domain wall-pinning as the temperature decreases further. On the other hand, above the $T_f$, the energy due to thermal activation of the domain-walls exceeds the pinning energy, and the walls can move between the pinning sites.

FIG. 7. Temperature dependence of ZFC and FC magnetization for different magnetic fields.
A summary of the field dependence of magnetization at various temperatures ranging from 2K to 300K is shown in Fig. 8. The saturation of magnetization decreases with the increasing temperature. The cationic distribution on the tetrahedral and octahedral lattice sites is the key factor in determining the magnetization of mixed spinel ferrites.

A misbalance of the trivalent iron ion results in the net magnetization due to the strengthening of the A–B superexchange interaction. Therefore, the magnetization of Zn$_{0.2}$Mg$_{0.8}$Fe$_2$O$_4$ depends on the distribution of the trivalent iron ion among tetrahedral (A-Sites) and octahedral (B-Sites) since both the Mg$^{2+}$ and Zn$^{2+}$ ions are non-magnetic.

IV. CONCLUSION

Nanocrystalline pure and Mg-doped ZnFe$_2$O$_4$ (Zn$_{1-x}$Mg$_x$Fe$_2$O$_4$ (x=0.0, 0.2, 0.4, 0.5, 0.6, 0.8) samples were successfully synthesized by co-precipitation method. The formation of the cubic spinel phase was confirmed by XRD refinement and the structural, optical, electrical, and magnetic properties. A single phase for the compositions was confirmed through the X-ray analysis. The lattice parameter was reduced from 8.44 Å to 8.42 Å by increasing the Mg content. Raman spectra confirmed the single-phase normal spinel Zn$_{1.8}$Mg$_{0.2}$Fe$_2$O$_4$ nanoparticles, and detailed vibrational modes alterations were studied with an increased Mg concentration. The electrical resistivity increased with increasing Mg concentration. In this study, magnetization at the maximum field M$_{\text{S}_{\text{SROE}}}$ monotonically increased with the Mg content. When the Mg$^{2+}$ ions were doped, the ferromagnetic behavior increased (up to x = 0.8), which changed the shape of the M–H loops. In our detailed magnetic study of Zn$_{0.2}$Mg$_{0.8}$Fe$_2$O$_4$, the temperature that corresponds to the bifurcation of the FC and ZFC curves ($T_{\text{B}}$) was observed at a temperature higher than TB, and it changed with the change of magnetic field.

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