Structural, optical, room-temperature and low-temperature magnetic properties of Mg–Zn nano ferrite ceramics

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ABSTRACT

Mg–Zn nanocrystalline ferrites (Mg$_{1-x}$Zn$_x$Fe$_2$O$_4$, where $x = 0.0$ to $1.0$) were synthesized by the citrate gel auto-combustion route. XRD revealed the formation of nano-sized particles with cubic spinel structure. Lattice constant and specific surface area increased with Zn substitution. SEM micrographs revealed inhomogeneous grains with agglomerates; EDS spectra confirmed the stoichiometry. HRTEM images showed agglomerated nanoparticles with average particle sizes of 21 nm and 16 nm for $x = 0.6$ and 1.0, respectively, and lattice fringe images and SAED patterns showed nanocrystalline characteristics corroborating the XRD results. FTIR and Raman spectra recorded at room temperature confirmed the spinel structure of ferrites. VSM technique at room temperature used to measure magnetic properties. $M_s$ and $H_C$ were found to decrease with increases in the Zn concentration in Mg–Zn ferrites due to a weakening of the A–B interaction and decrease in the particle size and surface effect. Low-temperature magnetic studies were carried out in the ZFC and FC modes using SQUIDS by applying 100 Oe between temperatures of 5 and 400 K, and magnetic isotherms were recorded at temperatures of 51 and 310 K. The study revealed the superparamagnetic nature of the synthesized samples showing that the blocking temperature ($T_B$) depends on interparticle interactions.

1. Introduction

Nanocrystalline ferrites, which exhibit remarkable properties, are commonly used in production of electromagnetic components for various applications [1–3]. Soft ferrites have a variety of applications due to their exotic structural, magnetic and electrical properties, making them the subject of tremendous interest among researchers and scientists. Ferrites are primarily used in various inductance components, such as magnetic filter cores, transformers, deflection antennae, video magnetic heads and magnetic heads for multiple path communications. These materials have potential applications, moreover in such technologies as magnetic liquid absorbing materials, high-density recording media, radio receivers and electromagnetic wave absorbers [4–6]. Nanocrystalline ferrite particles have a larger number of atoms at their surface than in their interior and hence they consequently possess a large surface-to-volume ratio. Their surface is considered to consist of broken exchange bonds that cause a spin disorder that produces a spin-glass-like structure. This lowers the coordination of the surface atoms and produces
a surface layer with high anisotropy, modifying their magnetic properties [7]. The disorderedly distribution of cations is different in the interior from that at the surface, causing a superexchange interaction through oxygen ions, which affects the magnetic properties [8,9]. Interest in spinal nanocrystalline ferrites [MFe$_2$O$_4$, M = Co, Ni, Mg, Zn, Mn, etc.] has significantly increased in the past few decades due to their extraordinary magnetic, electrical and optical properties. There is tremendous interest in low-temperature sintered transition metal oxides vis-à-vis Mg–Zn ferrites today for use in producing microwave devices and multilayer chip inductors due to their superior properties at high frequencies [10–12]. Nanocrystalline MgFe$_2$O$_4$ is a partially inverse spinel with large numbers of Mg$^{2+}$ ions on the octahedral site, whereas ZnFe$_2$O$_4$ is spinel. The substitution of Zn into magnesium ferrite affects the distribution of the atoms, leading to different physical properties.

The magnetic properties of these soft ferrites can be explained by studying their magnetization at low temperatures with two schemes, field-cooled (FC) and zero field-cooled (ZFC) process. In the ZFC process, the material under investigation is cooled in the absence of a field down to a very low temperature and a nominal field is applied, after which the magnetization is recorded at increasing temperatures. In the FC process, the magnetization of sample is measured in the presence of a field by cooling it to a low temperature. The effect of Zn substitution in MgF can be understood by the difference between the ZFC and FC magnetizations. At low temperatures, the MgZn ferrite exhibits a disordered spin system that can be considered as spin-glass like system. The irreversibility of FC and ZFC curves is a contributing feature to the super paramagnetism that depends mainly on magneto crystalline anisotropy [13–15]. Different protocols are being followed by different research groups for the synthesis of nano-ferrites, one of which is the citrate gel auto-combustion route of synthesis, which is simple and does not require high temperatures.

In the present study, the Mg–Zn nanocrystalline ferrite (Mg$_{1-x}$Zn$_x$Fe$_2$O$_4$, where $x$ varies from 0.0 to 1.0) were synthesized by the citrate gel auto-combustion method with the aim of studying the structural, optical and magnetic properties at room temperature and low temperatures.

2. Experimental section

2.1. Synthesis of the material

Nanoparticles of Mg–Zn nano-ferrite (Mg$_{1-x}$Zn$_x$Fe$_2$O$_4$, where $x$ varies from 0.0 to 1.0) were synthesized by the citrate gel auto-combustion method using citric acid as a fuel and chelating agent. Analytical grade chemicals comprising citric acid, ammonia and the metal nitrates Fe(NO$_3$)$_2$·9H$_2$O, Mg(NO$_3$)$_2$·6H$_2$O and Zn (NO$_3$)$_2$·6H$_2$O were used as precursors. The requisite amounts of metal nitrate as per the stoichiometric proportions were mixed in distilled water in a 1:3 nitrate-to-fuel ratio. An aqueous ammonia solution was added to the aqueous metal nitrate solution at a set speed under full stirring conditions at a reaction temperature of 80°C to adjust the pH to 7. The homogeneous solution was reduced to one-fourth the initial volume. The solution was then evaporated at a temperature of 200°C and converted into a viscous gel. After a few minutes, the gel was ignited and burned with glowing flints, and combustion was completed within a minute. The prepared sample powder was calcinated at 500°C for about 4 h and the final product was obtained. The obtained powder was ground in a binder (2% PVA) and compressed into disk-shaped pellets. The synthesis process of the samples is shown in Figure 1. The reaction involved in the synthesis of crystalline Mg–Zn ferrite (Mg$_{1-x}$Zn$_x$Fe$_2$O$_4$) is shown as follows:

**Chemical reaction:**

\[
(1 - x) \text{Mg(NO}_3\text{)}_2 \cdot 6\text{H}_2\text{O} + x \text{Zn(NO}_3\text{)}_2 \cdot 6\text{H}_2\text{O} + 2\text{Fe(NO}_3\text{)}_2 \cdot 9\text{H}_2\text{O} + 3\text{C}_6\text{H}_8\text{O}_7\text{H}_2\text{O} + 7/2 \text{O}_2 \rightarrow \text{Mg}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4 + 39 \text{H}_2\text{O} + 4 \text{N}_2 + +18\text{CO}_2
\]

2.2. Characterization techniques

Structural characterizations of the samples were carried out by X-ray diffraction (XRD) with a Shimadzu XRD700 X-ray diffractometer using Cu Kα radiation (λ = 1.54060 Å) within 2θ ranges from 10 to 80°. The surface morphology and elemental analysis of the samples were studied by scanning electron microscope (SEM) and EDAX (energy dispersive X-ray spectroscopy) using Zeiss device. To ascertain the nanocrystalline nature and to study the morphology of the synthesized samples, two sample specimens (x = 0.6 and 1.0) were analyzed by high-resolution transmission electron microscopy (HRTEM) using a JOEL JEM-2010 microscope with an operating voltage of 200 kV. Room-temperature FTIR spectra over a wave number range of 400–3500 cm$^{-1}$ were recorded using a Shimadzu FTIR 8400 spectrometer. Raman spectra were recorded at room temperature over a frequency range of 100–800 cm$^{-1}$. Room-temperature magnetizations of the samples were measured using the VSM technique with a Lakeshore VSM 7410 model with a maximum applied field of 20 kOe. Low-temperature measurements of magnetizations...
of FC and ZFC were carried out by SQUID across a temperature range of 5–400 K with an applied magnetic field of 100 Oe, and magnetic isotherms were recorded at 51 and 310 K.

3. Results and discussion

3.1. XRD analysis

As shown in Figure 2, the XRD patterns of the Mg–Zn nano-ferrite samples confirmed that the single phase cubic spinel crystal structure belong to the Fd3m space group with no impurity peaks. Diffraction pattern peaks were indexed as (111), (220), (311), (400), (511) and (422), and the broad peaks indicated that the synthesized particles of the Mg–Zn nano-ferrite system were in the nano-meter region. The average crystalline size, X-ray density, lattice parameters and unit cell volume were calculated using XRD patterns. The average crystalline size (D) of the Mg–Zn nano-ferrite system samples was calculated using Scherrer’s formula [15], \[ D = \frac{0.9 \lambda}{\beta \cos \theta} \] where \( \lambda \) is the wave length of the X-ray radiation used and \( \beta \) is the corrected half width [16]. It was observed that the crystalline size decreased with increase in the Zn concentration, which ranged from 25 to 35 nm. The lattice parameter \( a \) was found using the equation \[ a = \lambda \sqrt{(h^2 + k^2 + l^2)} / 2 \sin \theta, \] where \( \theta \) is the Bragg’s angle and \( (h, k, l) \) are the Miller indices of family of planes. It was observed that the lattice

![Figure 1. Synthesis process of Mg–Zn nanocrystalline ferrite, Mg\textsubscript{1-x}Zn\textsubscript{x}Fe\textsubscript{2}O\textsubscript{4}.](image1)

![Figure 2. (a) X-ray powder diffraction pattern of Mg\textsubscript{1-x}Zn\textsubscript{x}Fe\textsubscript{2}O\textsubscript{4} and (b) shift in the (311) peak due to Zn substitution.](image2)
parameter increased with increases in the Zn$^{2+}$ content, which could be due to the larger ionic radius of Zn$^{2+}$(0.74 Å) ions when compared to Mg$^{2+}$(0.72 Å) ions. Whenever a dopant of higher atomic radii was substituted for the host atoms, the XRD peak shifted to a lower 2θ value and the lattice parameter increased [17], the variation in the lattice parameter with Zn$^{2+}$ substitution fulfilled the conditions of Vegard’s law: as shown in Figure 2, the XRD peak (311) shifted to a lower 2θ value. The X-ray density of all the prepared Mg–Zn nano-ferrite samples was determined using the relation, $D_X = \frac{n \times M}{N_A \times a^3}$, where $n$ is the number of formula units in unit a cell, $M$ is the sample’s molecular weight, $a$ is the lattice parameter and $N_A$ is the Avogadro’s number [18]. The deviations in the crystallite size and lattice constant with varying concentrations of Zn in the samples are depicted in Figure 3. It is evident that, as the Zn concentration increased, lattice expansion took place with decreases in crystallite size. Substituting large Zn atoms are substituted in the Mg ferrite caused a change from a mixed spinel state to a normal spinel ferrite structure. Due to their stable valance state and size, the Zn$^{2+}$ ions in the structure preferred to occupy the tetrahedral sites [19].

The specific surface area $S$ of synthesized nanoparticles was determined using equation $S = \frac{6000}{D \times D_x}$, where $D_x$ is X-ray density and $D$ is crystallite size [7]. It was found that the specific surface area increased with Zn substitution in MgF. This increase in the specific surface area was mainly due to decreasing crystallite size, even though there is an increase in x-ray density. The variation of specific surface area and X-ray density with Zn concentration is shown in Figure 4.

### 3.2. Scanning electron microscopy (SEM) and EDAX analysis

SEM micrographs (Figure 5) reveal the microstructure of the Mg–Zn nano-ferrites. The micrographs show the presence of some agglomeration of particles. A close inspection reveals the presences of cubic face particles with uniform distribution. It is observed that the particles size is well below 100 nm, validating the grain size determined using Scherrer’s formula [20]. The EDAX spectrum (Figure 6) of the Mg–Zn nano-ferrites shows a quantitative and qualitative analysis of the chemical composition. The EDAX spectrum shows the existence of Zn, Mg, Fe and oxygen according to the stoichiometry of the samples without any other impurity metals. The experimentally observed weight % and atomic % of all the samples constituent atoms validate the stoichiometry of the samples: they are nearly equal to their theoretical values.

![Figure 3. Variations in the crystallite size and lattice parameters with Zn substitution.](image)

![Figure 4. Variations in X-ray density and specific surface area with Zn composition.](image)
3.3. HRTEM analysis

The morphology, crystallinity and microstructure of the synthesized nanocrystalline samples were studied by HRTEM. An HRTEM micrograph and size distribution histogram along with a lattice fringe image and the SAED pattern of Mg–Zn ferrites (Mg\(_{1-x}\)Zn\(_x\)Fe\(_2\)O\(_4\), where \(x = 0.6\) and 1.00) are depicted in Figure 7. The images indicate that the samples are agglomerated nanoparticles with a mainly non-uniform particle size distribution. The

![HRTEM micrograph of nanocrystalline Mg\(_{1-x}\)Zn\(_x\)Fe\(_2\)O\(_4\), where \(x = 0.00\), 0.6, 0.8 and 1.00.](image)

Figure 5. SEM micrographs of nanocrystalline Mg\(_{1-x}\)Zn\(_x\)Fe\(_2\)O\(_4\) (\(x = 0.00, 0.6, 0.8\) and 1.00).
average particle size as estimated by the average volume from the micrographs was 21 nm for \( x = 0.6 \) and 15.5 nm for \( x = 1.0 \), which is in agreement with the XRD results. The lattice fringes were clearly visible in both the samples. SAED showed the presence of sharp circular diffraction spots corresponding to the planes (220), (311), (400) (420), as represented in the XRD pattern. Growth of the samples along the diffraction planes, as evident from the lattice fringes and concentric circular diffraction spots of the SAED pattern, confirms the polycrystalline nature of the synthesized Mg–Zn ferrite.

### 3.4. FTIR analysis

The room-temperature FTIR spectra of an Mg–Zn ferrite (\( \text{Mg}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4 \), where \( x = 0.00–1.00 \)) recorded in the mid-IR region is shown in Figure 8. This technique is a useful means for confirming the spinel structure of ferrites. The spectral data elucidate the positions of cations in the crystal structure by their vibration
modes. In Mg–Zn ferrites, the metal cations are situated at two different sub-lattices, namely the A-site (tetrahedral) and B-site (octahedral) positions. The band \( \nu_1 \) at around 600 cm\(^{-1}\) is attributed to the stretching vibration mode of the tetrahedral complexes (A-site) and the \( \nu_2 \) band at around 400 cm\(^{-1}\) to that of the octahedral complexes (B-site) [7]. The obtained FTIR spectral data for the investigated Mg–Zn ferrite samples are represented in Table 1. The frequency bands \( \nu_1 \) ranges from 597 to 576 cm\(^{-1}\) and the lower band \( \nu_2 \) ranges from 399 to 406 cm\(^{-1}\) due to vibrations of Fe\(^{3+}\)-O\(^2-\) (metal-oxygen ions) in the stretching mode at the A-site and B-site positions. The shift of the bands \( \nu_1 \) and \( \nu_2 \) indicates distortion of the crystal [21].

The force constants (\( F_C \)), which depend on the vibrational frequencies at A and B-sites, are \( F_{CT} \) and \( F_{CO} \) respectively, as calculated by equation [22]

\[
F_C = 4\pi^2 C^2 \nu^2 m,
\]

where \( \nu \) is the vibrational frequency, \( C \) is the speed of light in a vacuum, and \( m \) is the reduced mass of the metal and oxygen system, Fe\(^{3+}\) and O\(^2-\) ions which is equivalent to \( 2.061 \times 10^{-23} \) g. As shown in Table 2, the force constant at the tetrahedral site is greater than that at the octahedral sites, and Zn\(^{2+}\) substitution in MgFe\(_2\)O\(_4\) has led to a decrease in the force constant at the tetrahedral site, indicating that Zn\(^{2+}\) ions occupy the tetrahedral positions [19,22].

### 3.5. Raman studies

Raman studies of the synthesized Mg–Zn nano-ferrite samples were carried out by recording the Raman spectra (Figure 9) at room temperature at frequencies from 100 to 800 cm\(^{-1}\). Raman spectroscopy is an important and powerful technique for analysis of the structural and vibrational characteristics of materials. In order to determine the natural tendency of the frequency, line width and lattice effect in all six synthesized samples, a least-squares fit with a Lorentzian line shape was used to fit the Raman
spectra. The thick, smooth lines shown in Figure 8 in red and green colors are fits to the Lorentzian functions. The spectra of Mg–Zn nano-ferrites consist of broadband of nearly at 224, 325, 475, 553, 703 cm\(^{-1}\) of which the 703 cm\(^{-1}\) is broadest band \[23\]. It is well known that Raman modes present in the 650–710 cm\(^{-1}\) region have \(A_{1g}\) symmetry which is related to the tetrahedral (A-site) sublattice in the system. In this study, it was found that there were five active Raman modes, which were represented by \(T = A_{1g} + E_{g1} + 3T_{2g}\). Assignment of these active Raman modes took into account the facts that MgFe\(_2\)O\(_4\) is an oxide with a partially inverse spinel structure that belongs to the space group \(Oh\) (Fd\(_{3m}\)) having eight formula per unit cell \[24,25\].

### 3.6. Room-temperature magnetic properties

The magnetic properties of the samples of nanocrystalline Mg–Zn ferrites (Mg\(_{1-x}\)Zn\(_x\)Fe\(_2\)O\(_4\), where \(x = 0.0–1.0\)) were determined using the vibrating sample magnetometer (VSM) technique at room temperature with an applied field up to 20 KOe. The magnetization curve (Figure 10) shows a hysteresis nature, and the magnetic properties coercivity (\(H_C\)), saturation magnetization (\(M_S\)), remanence magnetization (\(M_r\)) and squareness ratio (\(M_r/M_S\)) were found from the hysteresis loop. The Ms of the synthesized Mg–Zn samples was found to be between 17.9 and 2.2 emu/g it was observed that Ms decreased with the substitution of Zn in MgF. The decrease in saturation magnetization, Ms was attributed to substitution with non-magnetic zinc content \[26\]. In fact, the magnetic properties of ferrites are very much dependent on the distribution of cations in the tetrahedral and octahedral positions. \(H_C\) and \(M_r\) do not follow linearity behavior, because the large radii of zinc favors a normal spinel structure over the mixed spinel structure of nanocrystalline magnesium ferrites which causes a loss of magnetic energy that results in random remanent and coercivity values \[19\]. The low \(H_C\) and \(M_r\) indicate the soft super paramagnetic nature of synthesized Mg–Zn samples. The experimentally observed magnetic moment (per formula unit), \(\eta_B (\text{exp})\) (in \(\mu_B\)), was calculated using the formula \(\eta_B (\text{exp}) = \frac{MW \times M_a}{5585}\),
where $M_S$ is saturation magnetization (determined experimentally by the MH curve) and $MW$ is the molecular weight [27]. It was observed that Zn$^{2+}$ substitution in MgF has led to a decreased crystallite size and lattice expansion causing distortions of the lattice. The specific surface area increased and the surface was strained, which induced a broken exchange bonds at the surface. The net magnetization in ferrites depends on the interaction between magnetic ions, the atoms present at the A-site and B-site, and it was observed that the A–B interactions in ferrites are stronger than the A–A and B–B interactions [28]. The surface effect in the Mg–Zn ferrite led to a decrease in the A–B exchange interaction, resulting in lower magnetization with increases in the Zn concentration.

The squareness ratio $R^2 = M_I/M_S$ is a measurement of the ease with which the direction of magnetization can change by rotating itself to the easiest direction immediately after a magnetic field is removed. The measured magnetic properties of synthesized Mg$_{1-x}$Zn$_x$Fe$_2$O$_4$ with $x = 0.0$ to $1.0$, are tabulated in Table 2. In the present study it was observed that $R^2 < 0.5$ for all the samples suggesting that the samples were in a super paramagnetic state and that interactions occurred among grains [26,27]. The magneto crystalline anisotropy $K_1$ was determined using relationship $H_C = \frac{2K_1}{\mu_0M_S}$, where $H_C$ is coercivity, $M_S$ is saturation magnetization and $\mu_0$ is permeability of the free space [29]. It was found that $K_1$ ranged from 1.76 to 0.11 J/m$^3$, showing that substitution of Zn$^{2+}$ in MgF led to a decrease in the anisotropy constant due to the surface effect.

### 3.7. Low-temperature magnetic behavior

In order to gain insight into the magnetic behavior of Mg–Zn ferrite systems, temperature-dependent magnetization at low temperatures was studied with field-cooled (FC) and zero-field-
Figure 7. (Continued).

TEM micrograph

Lattice fringes

Particle size distribution histogram

SAED pattern nanocrystalline Mg\(_{1-x}\)Zn\(_x\)Fe\(_2\)O\(_4\) (a) \(x = 1.0\)

Figure 8. FTIR spectra of nanocrystalline Mg\(_{1-x}\)Zn\(_x\)Fe\(_2\)O\(_4\) (x = 0.00 - 1.00).
cooled (ZFC) procedures using SQUIDS. Figure 11 shows FC/ZFC magnetization curves measured in a static nominal magnetic field of 100 Oe for samples of Mg$_{1-x}$Zn$_x$Fe$_2$O$_4$ ($x = 0.00, 0.2, 0.6$ and $1.00$) over a temperature range 5–400 K along with their magnetic isotherm (M–H) curves at temperatures of 51 K and 310 K. The ZFC plot is considerably different from that of FC reflecting, irreversible behavior observed in the FC/ZFC curves due to a process of blocking and unblocking magnetic nanoparticles resulting from variation in thermal energy, which is a characteristic feature of superparamagnetism. In the ZFC process, the direction of each particle is frozen in a

Table 1. Vibrational frequencies ($\nu_1$, $\nu_2$), force constants (F$_{CT}$ and F$_{CO}$), $M_s$, Coercivity, remnant magnetization (M$_r$), squareness ration ($R^2$), anisotropy constant ($K_1$) and magnetic moment per formula unit $\eta_B$.

| Composition | $\nu_1$ (cm$^{-1}$) | $\nu_2$ (cm$^{-1}$) | F$_{CT}$ (10$^5$ dyne/cm) | F$_{CO}$ (10$^5$ dyne/cm) | $M_s$ (emu/g) | $H_c$ (Oe) | M$_r$ (emu/g) | $R^2 = M_r/M_s$ | $\eta_B$ (exp) (\mu_B) | $K_1$ (J/m$^3$) |
|-------------|---------------------|---------------------|---------------------------|-----------------------------|---------------|-------------|---------------|------------------|----------------|------------------|
| x = 0.0     | 597                 | 395                 | 2.61                      | 1.16                        | 17.9          | 157         | 1.07          | 0.06             | 0.64            | 1.76             |
| x = 0.2     | 588                 | 399                 | 2.53                      | 1.14                        | 10.4          | 127         | 0.332         | 0.03             | 0.38            | 0.82             |
| x = 0.4     | 543                 | 401                 | 2.16                      | 1.7                         | 7.84          | 193         | 1.85          | 0.23             | 0.30            | 0.95             |
| x = 0.6     | 582                 | 405                 | 2.48                      | 1.2                         | 6.27          | 182         | 1.48          | 0.24             | 0.25            | 0.71             |
| x = 0.8     | 569                 | 406                 | 2.37                      | 1.2                         | 5.77          | 96          | 0.29          | 0.05             | 0.24            | 0.35             |
| x = 1.0     | 576                 | 406                 | 2.43                      | 1.2                         | 2.2           | 83          | 0.22          | 0.1              | 0.09            | 0.11             |

Figure 9. Raman spectra of nanocrystalline Mg$_{1-x}$Zn$_x$Fe$_2$O$_4$ ($x = 0.00, 0.6, 0.8$ and $1.00$).
random direction as the samples are cooled in the absence of filed down to 5 K, and the applied nominal magnetic field of 100 Oe is not sufficiently strong to reorient the particles in field direction, showing a zero magnetization as a result [15,30]. As the temperature is increased, the magnetization builds up in the samples. It was observed that the sample Mg0.4Zn0.6Fe2O4 has showed a cusp at 270 K, and that further increases in temperature led to decreases in magnetization. This temperature at which the ZFC curve reaches the maximum is called blocking temperature, \( T_B \). No such maximum was observed in the ZFC curves of other samples at around this temperature.

When the samples were cooled in the presence of a magnetic field, moreover, irreversibility was observed in the ZFC/FC curves, which bifurcated from each other at a temperature of 330K for the Mg0.4Zn0.6Fe2O4 sample, when it reached the thermomagnetic irreversibility (TMI) temperature, \( T_{irr} \). There was a significant difference between \( T_{irr} \) and \( T_B \) for sample Mg0.4Zn0.6Fe2O4. Other samples of Mg–Zn ferrites have shown \( T_B \) and \( T_{irr} \) at above room temperature. \( T_B \) is the temperature below which the particles lack sufficient energy and the free movement of particles is blocked by anisotropy energy, while at above this temperature the thermal energy unblocks and eases the movement of moments [31]. For uniform crystallite samples, \( T_B \) coincided with \( T_{irr} \), and the difference in \( T_B \) and \( T_{irr} \) in the present case suggests that the particles in the samples are of irregular sizes, as shown in the SEM micrographs. The blocking temperature, \( T_B \), is a characteristic feature of superparamagnetism. It is similar to paramagnetism but with the difference that in superparamagnetism, the entire particle tends to align with the field direction instead of individual atoms as in case of paramagnetism [32,33]. The energy required to change the direction of magnetism is called magnetic crystalline anisotropy energy, \( K \), where \( K \) is anisotropy constant and \( V \) is the particle volume. The smaller the particles, the lower the crystalline anisotropy energy barrier, \( K \). The time scale for the successive jumps in the experimental procedure is \( \tau = \tau_0 e^{\frac{-B}{kT}} \), where \( k \) is Boltzman’s constant, \( k \) is thermal energy, \( \tau = 100 \) s and \( \tau_0 = 10^{-7} \) s for experimental DC magnetic measurements, and the blocking temperature \( T_B \) is related to KV, as \( T_B = \frac{KV}{\ln 2} \) [34,35]. The large values of \( T_B \) for samples \( x = 0.00, 0.2 \) and 1.00 are due to large variations in their particle sizes, inter-particle interactions and anisotropy. It was observed from the ZFC/FC curves that there was a large difference of 25 emu/g between the FC and ZFC magnetizations (\( M_{FC} \) and \( M_{ZFC} \)) for sample Mg0.4Zn0.6Fe2O4 when compared to other samples. It is well known that the \( T_B \) depends on the inter-particle spacing in the ferrites. A decrease in the spacing between the particles (inter-particle spacing) affects the interactions among particles, leading to an increase in the blocking temperature [35–37]. The properties of nano-ferrites such as \( T_B \), etc., are sensitive to interactions among particles, the size of nanoparticles and also on the magnetic interactions between particle.

Nanoparticles of Mg–Zn nano-ferrites (\( \text{Mg}_{1-x} \text{Zn}_x \text{Fe}_2 \text{O}_4 \)), where \( x = 0.0, 0.2 \) and 1.0) have shown that larger \( T_B \) values at above room temperature compared to 270 K for \( x = 0.6 \) may be due to the complexity of the layered structure of magnetic nanoparticles. Since the surface is strained and broken exchange bonds are induced at the surface, the MgF layer in the interior does not offset the size-related influence of the Zn-substituted MgF surface layer. These changes in \( T_B \) are due to variations in the Ms value as shown by the MH isotherms (Figure 11) which are contributed by anisotropy due to dipolar interactions or spin-orbit coupling between surface layer atoms [38,39]. The \( T_B \) of nanoparticles are greatly influenced by the spin–orbit interactions of constituent metal cations and their distribution on the tetrahedral and octahedral positions of nano-ferrites which is influenced by synthesis method [40,41].

The isotherms for variations in magnetization with applied fields at 51 and 310 K are depicted in Figure 11, and the magnetization curve reveals the soft nature of the ferrites. The magnetization of the samples at low temperatures is not fully achieved, even at an applied magnetic field of 9 kOe. This behavior is typical of nanocrystalline ferrites. The highest value
of magnetization, 85 emu/g at 51 K, was shown by the Mg$_{0.4}$Zn$_{0.6}$Fe$_2$O$_4$ sample suggesting the presence of a strong A-B interaction dominating the A–A and B–B interactions between particles.

4. Conclusions

Mg–Zn ferrite nanoparticles, Mg$_{1-x}$Zn$_x$Fe$_2$O$_4$ ($x = 0.00–1.00$) were synthesized by the citrate gel combustion method using citric acid as a fuel. An increase in the degree of Zn substitution led to lattice distortion and an increase in the specific surface area of nanoparticles. EDAX was used to confirm the stoichiometry, and SEM micrographs showed irregularly sized particles. HRTEM images confirmed the nanocrystalline nature of the samples with particle sizes of 21 nm and 15.5 nm for samples $x = 0.6$ and 1.0. The lattice fringes and concentric diffraction spots of the SAED patterns revealed their polycrystalline nature, moreover, and FTIR and Raman studies confirmed the spinel structure of the ferrites. Room-temperature magnetization decreased with increases in the Zn composition, and low-temperature magnetic studies revealed the super paramagnetic nature of the samples. The blocking temperature for content $x = 0.6$ was 270 K, while that for all other samples was above room temperature. The blocking temperature $T_B$ depended on the particle size and magnetic interactions between particles.

Figure 11. Zero-field cooled (ZFC)/field-cooled (FC) magnetization curves and magnetization isotherms at temperatures of 51 and 310 K for nanocrystalline Mg$_{1-x}$Zn$_x$Fe$_2$O$_4$ ($x = 0.00, 0.2, 0.6$ and 1.00).
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Disclosure statement

No potential conflict of interest was reported by the authors.

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References

[1] Solyman S. Transport properties of La-doped Mn-Zn ferrite. Ceramic Int. 2006;32:755–760.
[2] Sharifi I, Shokrollahi H, Amiri S. Ferrite-based magnetic nanofluids used in Hyperthermia applications. J Magn Magn Mater. 2012;324:903–915.
[3] Shokrollahi H. Magnetic properties and densification of manganese-Zinc soft ferrites (Mn1-xZnxFe2O4) doped with low melting point oxides. J Magn Magn Mater. 2008;320:463–474.
[4] Wang JM, Wang YB, Jiang CB, et al. Magnetostriatin and Magnetization of the Ni$_{29}$Mn$_{27.5}$Ga$_{2.5}$ Single Crystal. Chin Phys Lett. 2006;23:1293–1298.

[5] Upadhyay C, Verma HC. Cation distribution in nanosized Ni-zn ferrites. J Appl Phys. 2004;95:5746.

[6] Nazrul Islam M, Akther Hossain AKM. Enhancement of Neel temperature and electrical resistivity of Mn-Ni-Zn ferrite by Gd$^{3+}$ substitution. J Mater Res Tech 2018. doi:10.1016/j.jmrt.2017.11.006

[7] Ahmad SI, Ansari SA, Kumar DR. Structural, morphological, magnetic properties and cation distribution of Ce and Sm co-substituted nano crystalline cobalt ferrite. Mater Chem Phys. 2018;208:248–257.

[8] Choi EJ, Ahn Y, Kim S, et al. Superparamagnetic relaxation in CoFe$_2$O$_4$ nanoparticles. J Magn Magn Mater. 2003;262(2):L198–L202.

[9] Chundnovsky EM, Gunther L. Quantum tunneling of magnetization in small ferromagnetic particles. Phys Rev Lett. 1998;80:661–668.

[10] Fodor PS, Tsoi GM, Wigner LE. Modeling of hysteresis and magnetization curves for hexagonally ordered electrodeposited nanowires. J Appl Phys. 2003;93:7438–7445.

[11] Wang YC, Ding J, Yin JH, et al. Effects of heat treatment and magnetoannealing on nanocrystalline Co-ferrite powders. J Appl Phys. 2005;98:124306.

[12] Ahmed MA, Okasha N, El-Deik SI. Preparation and characterization of nanometric Mn ferrite via different methods. Nanotechnology. 2008;19(6):065603.

[13] Joy PA, Anil Kumar PS, Date SK. The relationship between field-cooled and zero-field-cooled susceptibilities of some ordered magnetic systems. J Phys Condens Matter. 1998;10:11049–11054.

[14] Nishigori S, Hirooka Y, Ito T. Spin-glass behavior in TbPdIn and DyPdIn. J Magn Magn Mater. 2005;292:422–427.

[15] Bakr Mohamed M, Yehia M. Cation distribution and magnetic properties of nanocrystalline gallium substituted ferrite. J Alloys Compd. 2010;509(1):213–223.

[16] Carta D, Casula MF, Falqui AD, et al. Structural and magnetic properties of Sr-doped CoFe$_2$O$_4$ ferrites. J Phys Chem C. 2007;111(33):12274–12278.

[17] Sertkol M, Koylu Y, Baykal A, et al. Synthesis and magnetic characterization of Zn$_{1-x}$Ni$_x$Fe$_2$O$_4$ nanoparticles via a polyethylene glycol-assisted hydrothermal route. J Magn Magn Mater. 2006;308:187–192.

[18] Rahman S, Nadeem K, Anees –Ur-Rahman M, et al. Structural and Magnetic Properties of Zn$_{1-x}$Fe$_2$O$_4$ nanoparticles prepared using the co-precipitation method. Cem Int. 2016;39:5235–5239.

[19] Asif Iqbal M, Islam M-U, Ashiq MN, et al. Effect of Gd-substitution on physical and magnetic properties of Li$_2$Mg$_{0.4}$Gd$_{0.6}$Fe$_2$O$_4$ ferrite. J Alloy Compd. 2013;579:181–186.

[20] Kumar R, Kar M. Correlation between lattice strain and magnetic behavior in non-magnetic Ca substituted nano-crystalline cobalt ferrite. Ceramic Int. 2016;42(6):6640–6647.

[21] Keny SJ, Manjanwa J, Venkateshwaran G, et al. Dissolution behavior of synthetic Mg/Zn-ferrite corrosion products in EDTA and NTA based formulations. Corros Sci. 2006;48:2780–2798.

[22] Gupta R, Sood AK, Metcalfe P, et al. Raman study of stoichiometric and Zn-doped Fe$_2$O$_4$. Phys Rev B. 2002;65(10):104430.

[23] Da Silva SW, Nakagomi F, Silva MS, et al. Effect of the Zn content in the structural and magnetic properties of Zn$_{1-x}$Mg$_x$Fe$_2$O$_4$ mixed ferrites monitored by Raman and Mössbauer spectroscopies. J Appl Phys. 2010;107:09B503.

[24] Wang Z, Schiferl D, Zhao Y, et al. High pressure Raman spectroscopy of spinel-type ferrite ZnFe$_2$O$_4$. J PhysChem Solid. 2003;64(12):2517–2520.

[25] Li Y, Li Q, Wen M, et al. Magnetic properties and local structure studies of Zn doped ferrites. J Elect. Spectro. 2007;60(1):1–6.

[26] Ahmed SI, Ravi Kumar D, Syed IA, et al. Structural, spectroscopic and magnetic study of nanocrystalline cerium-substituted magnesium ferrites. Arabian J Sci Eng. 2017;42:389–398.

[27] Lin Q, Lin J, He Y, et al. The structural and magnetic properties of gadolinium doped CoFe$_2$O$_4$ nanoferrites. J Nanomater. 2015;2015:1–6. Article ID 294239. doi:10.1155/2015/294239

[28] Mustafa G, Islam MU, Zhang W, et al. Investigation of structural and magnetic properties of Ce$^{3+}$-substituted nanosized Co-Cr ferrite for a variety of applications. J Alloy Compound. 2015;618:428–436.

[29] Yao C, Zeng Q, Goya GF, et al. ZnFe$_2$O$_4$ nanocrystals: synthesis and magnetic properties. J Phys Chem C. 2007;111(33):12274–12278.

[30] Ahmed SI, Ansari SA, Kumar DR. Structural, magnetic, and Mössbauer spectroscopic and magnetic study of nanocrystalline cerium-substituted magnesium ferrites. Arabian J Sci Eng. 2015;40:248–252.

[31] Bakr Mohamed M, Yehia M. Cation distribution and magnetic properties of nanocrystalline gallium substituted cobalt ferrite. J Alloys Compd. 2014;615:181–187.

[32] Mustafa G, Islam MU, Zhang W, et al. Investigation of structural and magnetic properties of Ce$^{3+}$-substituted nanosized Co-Cr ferrite for a variety of applications. J Alloy Compound. 2015;618:428–436.

[33] Carta D, Casula MF, Falqui AD, et al. Structural and magnetic investigation of the inversion degree in ferrite nanocrystals MFe$_2$O$_4$ (M= Mn, Co, Ni). J Phys Chem C. 2009;113:8606–8615.

[34] Sertkol M, Köseoglu Y, Baykal A, et al. Synthesis and magnetic characterization of Zn$_{1-x}$Ni$_x$Fe$_2$O$_4$ nanoparticles via a polyethylene glycol-assisted hydrothermal route. J Magn Magn Mater. 2009;321 (3):157–162.

[35] Obaidat IM, Issa B, Albiss BA, et al. Investigating negative magnetization and blocking temperature in aggregates of ferrite nanoparticles. IOP Conf Series Mater Sci Eng. 2015;92:021011.

[36] Rumpf K, Granitzer P, Morales PM, et al. Variable block-coating temperature of a porous silicon/Fe$_3$O$_4$ film on Si diodes. J Appl Phys. 2002;91:1034–1041.
[38] Arteaga-Cardona F, Santillán-Urquiza E, Pal U, et al. Unusual variation of blocking temperature in bi-magnetic nanoparticles. J Magn Magn Mater. 2017;441:417–423.

[39] Praveena K, Sadhana K. Ferromagnetic properties of Zn substituted spinel ferrites for high frequency applications. Int J Sci Res Pub. 2015;5(4):1–21.

[40] Ajroudi L, Mliki N, Bessaïs L, et al. Magnetic, electric and thermal properties of cobalt ferrite nanoparticles. Mater Res Bull. 2014;59:49–78.

[41] Vaishnava PP, Senaratne U, Buc E, et al. Magnetic properties of cobalt-ferrite nanoparticles embedded in polystyrene resin. J Appl Phys. 2006;99:08G702.