Impact of Ho\textsuperscript{3+} Substitution on Structural, Morphological, Optical, Electrical, Thermoelectrical and Magnetic Properties of MgCuHo\textsubscript{x}Fe\textsubscript{2-x}O\textsubscript{4} (0 < x < 0.030) System

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A series of rare earth (Ho\textsuperscript{3+}) doped magnesium-copper nanoferrites with the general chemical compositions of Mg\textsubscript{0.5}Cu\textsubscript{0.5}Ho\textsubscript{x}Fe\textsubscript{2-x}O\textsubscript{4} (where x = 0.000, 0.005, 0.010, 0.015, 0.020, 0.025 and 0.030) was fabricated by citrate sol-gel auto-combustion technique. The fabricated materials were investigated through powder XRD, FESEM, EDX, HRTEM, FTIR, UV-Vis, DC resistivity, TEP and VSM for magnetic properties. The crystallite size of the samples was determined to be in the range of 33-40 nm with increased Ho\textsuperscript{3+} content and the powder-XRD investigations validated the spinel cubic structure of the samples with the space group F\textit{d}3\textit{m}. The analysis demonstrated that the lattice constant was reduced from 8.403 to 8.356 Å and according to the FE-SEM micrographs, the morphology of the samples were found to be spherical. The HR-TEM micrographs show that average particle size decreases from 64 to 48 nm. The FTIR examination revealed that their ν\textsubscript{1} and ν\textsubscript{2} absorption bands were located between 412-401 cm\textsuperscript{-1} and 562-547 cm\textsuperscript{-1}, respectively and the optical band gap was found to be 2.77-3.28 eV. In Mg-Cu nanoferrites with Ho doping, there was no obvious increase in the elasticity moduli. It was observed that the thermal energy required to transform the p-type Mg-Cu nanoferrites from semiconducting to n-type semiconducting behaviour increases with increasing Ho doping and composition. The M-H loop saturation magnetization (M\textsubscript{s}), coercivity (H\textsubscript{c}) and retentivity (M\textsubscript{r}) values were all enhanced when the Ho\textsuperscript{3+} concentration increased and varied anisotropically with Ho doping. The findings of this study suggested that Mg-Cu ferrites doped with Ho\textsuperscript{3+} might be beneficial for magnetic resonance imaging in biomedicine.

Keywords: Ho doping, Mg-Cu nanoferrite, Electrical and Magnetic properties.

INTRODUCTION

Currently, a wide range of magnetic materials with enhanced ferromagnetic materials are produced using various nanocrystalline combinations. Owing to their unique structural, optical and magnetic characteristics, ferrites with spinel structures are significant in their own right [1-3]. There are several approaches to fine-tune these characteristics, such as doping an approved component, depending on the desired application and characterization method. The exceptional electrical and magnetic characteristics of cobalt ferrites make them a material of importance. Spinel ferrites’ tetrahedral (A) and octahedral (B) sites’ cations and their distribution are essential for these features. Ferrites exhibit ferrimagnetic properties due to a phenomenon known as super-exchange, where an interaction occurs between the oxygen ions and the magnetic moments of materials. These insulating ferrites have high electric resistance, low dielectric loss, low eddy current losses and high permeability. Ferrites exhibit diverse magnetic properties based on their composition and preparation methods [4-6].

The spinel nanoferrites are produced via a sol-gel process or precursor auto combustion, coprecipitation, hydrothermal, microwave combustion and co-precipitation [7-10]. The citrate precursor method offers several benefits, including uniform atomic level mixing of the cations, a constrained size distribution, exact stoichiometry control, cost-effectiveness and low-temperature phase formation [11-13]. Cation distribution has a significant role in controlling the magnetization of spinel nano-

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ferrite, which is proportional to the magnetization differential (M_B-M_A) between the B and A sub-lattices. Single-ion anisotropy of Co^{3+}, Fe^{3+} and Fe^{2+} depends on the occupancy site [14-18]. The cation distribution affects magnetic anisotropy, correlated coercivity and surface canting. Several publications have characterized Mg-Cu nanoferrites as magnetic materials with good transitions in their magnetization. This flexibility results from copper ferrite, depending on the inversion parameter, being either an antiferromagnetic or ferromagnetic material, while copper ferrite is ferrimagnetic [19-22].

Applications for the thermal heating of an integrated nanoferrite used in cancer treatment depend on several variables, including safe compositions, small molecular weights, small particle sizes, appropriate saturation magnetization and low coercivity. To enhance the magnetic and elastic properties of spinel ferrites, several authors have looked into the substitution of magnetic Fe^{3+} cation with nanomagnetic ones such as Sm^{3+} and Cr^{3+} at various substitution levels [23-27]. In this study, it has been observed that both the structural and magnetic characteristics exhibit non-monotonic behaviour when the substitution level increases. Those findings were discussed in the proposed sample and compared to the experimental findings from power XRD, FESEM, HRTEM, FTIR, UV-vis and VSM techniques. In present work, holonium doped magnesium and copper nanoferrites were prepared via the citrate sol-gel auto-combustion method. The impact of Ho^{3+} ions on the structural, optical, morphological and magnetic properties of magnesium and copper nanoferrites Mg_{0.5}Cu_{0.5}Ho_{x}Fe_{2-x}O_{4} (with x = 0.00-0.030) was also studied.

### EXPERIMENTAL

**Synthesis procedure:** The citrate sol-gel auto-combustion technique has been used to synthesize Ho-doped Mg-Cu ferrites, which were prepared from magnesium nitrate hexahydrate (Mg(NO_3)_2·6H_2O), copper nitrate hexahydrate (Cu(NO_3)_2·6H_2O), ferric nitrate hexahydrate (Fe(NO_3)_3·9H_2O) and holonium nitrate hexahydrate (Ho(NO_3)_3·6H_2O). To produce a homogeneous solution, the raw compounds were separately dissolved in 80 mL of deionized water at a precise stoichiometric ratio. The solution, the raw compounds were separately dissolved in 80 mL of deionized water at a precise stoichiometric ratio. The subsequent stage involved dissolving the precursors into a beaker and stirred for 45 min using a magnetic stirrer. The homogeneous solution was mixed with citric acid while using the magnetic stirrer at 70 °C. Added ammonia solution to the above mixture dropwise to maintain pH 7. The mixture was subsequently heated on a magnetic stirrer hot plate with continuous stirring until it reached a dry state, resulting in the formation of a gel. The resulting materials were calcined in a furnace at 70 °C for 5 h to obtain the spinel phase.

**Characterization:** The powder XRD analysis of the samples were conducted on the Rigaku Miniflex-600, Japan with radiation (λ = 1.5406 Å). The FESEM (Oxford Instrument Inca X-act) analysis was employed to determine grain size and morphology. The HRTEM technique (HRTEM, JEM-F200 Multi-purpose electron microscope) was used to examine the cross-sections and particle size of the nanoferrites. The FTIR spectroscopy uses confirmed the absorption bands (ν_1, ν_2). A UV-vis spectrometer (Perkin) was used to investigate the optical band gap. The Lake Shore Cryotronics 8600 Series instrument, based on the Vector Space Model (VSM), was utilized to investigate the temperature-dependent magnetic properties and M-H hysteresis loops of Ho doped magnesium and copper nanoferrites. The two-probe method was employed for this purpose, along with measurements of the DC electrical system. To investigate the connection between thermoelectric power, temperature and composition, the differential technique was adopted.

### RESULTS AND DISCUSSION

**Powder XRD studies:** Fig. 1 demonstrates the powder X-ray diffraction of Ho substituted Mg-Cu nanospinel ferrite within 10-80° 2θ at room temperatures. The XRD technique was employed to determine the crystal structure and identified the crystalline phase. The miller peaks with the following indices viz. (111), (220), (311), (222), (400), (422), (511), (440) and (533) were identified which are closely matched with the Mg-Cu ferrite peaks and belong to JCPD card no. #00-001-1109. It was evident from the P-XRD pattern that Ho^{3+} ions were appropriately doped into the prepared nanoferrite samples since no additional peaks in the Ho-doped magnesium-copper nanoferrite samples were obtained. The average crystallite size of the prepared samples was calculated using the Debye-Scherrer’s formula from the center peak (311) plane [28,29].

\[
D_{p-XRD} (\text{nm}) = \frac{k\lambda}{\beta\cos{\theta}}
\]

(1)

\[
D_{p-XRD} (\text{nm}) = \frac{K\lambda}{\beta\cos{\theta}}
\]

where \(D_{p-XRD}\) stands for crystallite size, constant \(0.9\) is the correction factor for sphere-shaped particles, \(\lambda = 1.5406 \text{ Å}\) is the wavelength of the Cu-target and indicates full-width half maximum (FWHM) and \(\theta\) is the Bragg’s angle of the peak with the highest intensity. Table-1 summarizes the computed crystallite size values \((D_{p-XRD})\). By increasing dopant Ho^{3+} content \((x = 0.00-0.030)\), the average crystallite size of the generated samples was decreased from 32.03 nm to 20.20 nm. The miller indices \((hkl)\) and interplanar spacing \((d)\) data were used to derive the lattice parameter \((a)\) as:

\[
a (\text{Å}) = d\sqrt{h^2+k^2+l^2}
\]

(2)

![](https://via.placeholder.com/150)

Fig. 1. X-ray diffraction patterns of \(\text{Mg}_{0.5}\text{Cu}_{0.5}\text{Ho}_{x}\text{Fe}_{2-x}\text{O}_{4}\) nano ferrite
The determined results of lattice constant (a) are recorded in Table-1 and Fig. 2 demonstrated the compositional variation of lattice constant (a) for the Ho concentration. The computed lattice constant values were found to be in the range 0.837 and 0.8393 nm. The variation of lattice constant (a) may be due to the replacement of Ho³⁺ (0.95 Å), more substantial ionic radii ions than Fe³⁺ (0.645 Å) ions at the octahedral site, resulting in a modest modification in the lattice constant [30].

Applying the constant lattice results and the unit cell volume (eqn. 3) of the Ho-doped Mg-Cu samples was computed [31]:

\[ V = a^3 \]  

Table-1 presents a summary of the X-ray density values obtained and illustrates the variations in the composition of these values. Due to the different ionic radii of Ho³⁺ (0.91 Å) and the ions of Fe (0.645 Å), the densities increased. The considerable increase in the value of \( d_x \) from 4.948 g cm⁻³ to 5.230 g cm⁻³ is due to the relative high atomic weight of Ho (150.36 amu) compared to iron (55.845 amu) [33]. Additionally, it can be observed that bulk density values are significantly lower than X-ray density values.

\[ d_b = \frac{m}{\pi r^2 t} \]  

where \( r \) = radius of circular pallet, \( t \) = width and \( m \) = mass (g).

The bulk density of the synthesized Mg-Cu-Ho ferrite samples doped with rare earth elements was found to be increased. The average bulk density was between 2.732 g/cm³ and 3.542 g/cm³ with additional dopant content [34]. The porosity (P%) was also calculated using eqn. 5 [35,36]:

\[ P \% = \left( 1 - \frac{d_b}{d_x} \right) \times 100 \]

where \( d_x \) is the X-ray density and \( d_b \) is the bulk density of Ho³⁺ doped samples, the measured porosity was increased from 48.78 to 56.06%. The reduced porosity of the prepared samples may be due to compressive stress caused by the negative micro-strain of lattice (Table-1). Moreover, the following relationships were used to calculate the hopping length (Lₐ and Lₖ) and the values are shown in Table-1 [37]:

\[ L_a = \frac{a \sqrt{3}}{4} \]  

\[ L_k = \frac{a \sqrt{2}}{4} \]
Morphological studies: The morphology and size of the samples have been examined using the field emission scanning electron microscope (FESEM). The FESEM and the EDS images of the synthesized $\text{Mg}_{0.5}\text{Cu}_{0.5}\text{Ho}_{x}\text{Fe}_{2-x}\text{O}_4$ ($x = 0.00-0.030$) nanoferrites are shown in Figs. 3a-f and 4a-f, respectively. The grain size of the prepared nanoferrites varies between 50 and 63 nm and is in good alignment with the P-XRD crystallite size. Prepared Cu-Mg-Ho nanoferrites with sharp edges and spherical morphologies can be observed in the FESEM images [29]. The energy dispersive (EDS) spectra (Fig. 4a-f) revealed that in all the prepared nanoferrites ($x = 0.00$ to $0.030$), only Cu, Mg, Ho, Fe and O are the main components. The quantitative analysis demonstrates that the chosen precursors were distributed uniformly following the desired composition.

The particle size distribution, agglomeration and lattice planes of the prepared nanoferrites were also analyzed in detail using high-resolution transmission electron microscopy (HR-TEM). Fig. 5a-c shows the HR-TEM images of representative Mg-Cu-Ho ferrite with $x = 0.00$, 0.015 and 0.025, which is confirmed to be the cubic spinel structural of the desired composition. The Gauss fitting of the histogram revealed that the mean particle size of the prepared nanoferrites ranged from 41 to 53 nm is well arranged through the measured FESEM spectra. Fig. 6 shows the spectra of the selected area electron diffraction (SAED) of the nanoferrites $x = 0.00$, 0.015 and 0.025. By comparing the interplanar spacing calculated from the P-XRD analysis to that observed from the selected area electron diffraction (SAED) images, it is evident that the diffraction rings observed correspond to the (440) plane. The presence of fringes at 0.245, 0.264, and 0.269 nm show that the spine nanoferrite formed a spinel cubic structure in the synthetic samples, as observed by (311) lattice planes.

FTIR studies: Fig. 7 shows the FTIR spectra of the prepared $\text{Mg}_{0.5}\text{Cu}_{0.5}\text{Ho}_{x}\text{Fe}_{2-x}\text{O}_4$ ($x = 0.00-0.030$) nanoferrites recorded in the range from 4000-250 cm$^{-1}$. The stretching vibration of oxygen bonds produces these higher and lower peaks (Table-2), which show the development of spinel structure at the tetrahedral site in the range of 578-574 cm$^{-1}$ may be due to the tetrahedral cluster stretching mode and the octahedral site in the range of 422-414 cm$^{-1}$ [38,39]. The lower frequency band may be attributed to octahedral cluster stretching. The absence of frequency bands linked to other groups suggests that the nanoferrite samples were produced, as evidenced by the spectra, which exhibit its distinctive characteristics. However, the prep-

![Fig. 3. FE-SEM images of Mg$_{0.5}$Cu$_{0.5}$Ho$_x$Fe$_2$O$_4$ ($x = 0.00$ to $0.030$) nanoferrite](image-url)

| TABLE-2 | ABSORPTION BAND AT A-SITE AND B-SITE FOR Mg$_{0.5}$Cu$_{0.5}$Ho$_x$Fe$_2$O$_4$ ($x = 0.00$ to $0.030$) NANOFERRITES |
|---|---|---|
| Samples ($x$) | High frequency ($\partial_1$) | Low frequency ($\partial_2$) |
| 0.000 | 574.90 | 414.80 |
| 0.010 | 581.04 | 412.12 |
| 0.015 | 582.88 | 414.10 |
| 0.020 | 584.32 | 416.02 |
| 0.025 | 576.81 | 419.32 |
| 0.030 | 578.14 | 422.30 |
pared Ho-doped cubic spinel nanoferite confirmed the successful development of the cubic phase. The observed band at 3420 cm\(^{-1}\) is associated with O-H vibration in the prepared spinel ferrite materials. In contrast, the absorption band in the 1546 cm\(^{-1}\) is closely connected to ambient CO\(_2\) gas. Additionally, the absorption band at 2340 cm\(^{-1}\) is associated with the C-H group [40,41].

**Absorption spectral studies:** The optical properties of Ho-doped Mg-Cu (\(x = 0.00-0.030\)) nanoferites recorded at the ambient temperature over the wavelength range of 200-650 nm were examined using a UV-visible spectrometer (Fig. 8). The Tauc’s relation was used to calculate the optical band gap, which is influenced by the wavelength-dependent absorption:

\[
(\alpha \nu)^n = A (\hbar \nu - E_g)
\]  

(a) (b) (c) (d) (e) (f) (g) (h) (i) (j) (k) (l) (m) (n) (o) (p) (q) (r) (s) (t) (u) (v) (w) (x) (y) (z)

Fig. 4. EDS images of Mg\(_{0.5}\)Cu\(_{0.5}\)Ho\(_x\)Fe\(_{2-x}\)O\(_4\) (\(x = 0.00\) to 0.030) nanoferite

Fig. 5. HR-TEM images of Mg\(_{0.5}\)Cu\(_{0.5}\)Ho\(_x\)Fe\(_{2-x}\)O\(_4\) (\(x = 0.00\) to 0.030) nanoferite
Fig. 6. SEAD images of Mg0.5Cu0.5Ho

\[ x \] Fe2-xO4 \[ x \] = (a) 0.00, (b) 0.010 and (c) 0.030] nanoferrite

\[ \text{Transmittance (%)} \]

\[ \begin{array}{cccc}
800 & 750 & 700 & 650 \\
500 & 450 & 400 & 350 \\
\end{array} \]

\[ \text{Wavenumber (cm}^{-1}\text{)} \]

\[ \begin{array}{cccc}
574.90 & 584.52 & 581.01 & 576.81 \\
582.88 & 582.14 & 514.10 & 522.30 \\
\end{array} \]

\[ \nu_1 \]

where \( \alpha \) is the absorption coefficient, \( h \) is the plank constant \((6.626 \times 10^{-34} \text{ J s})\), \( \nu \) is the photon energy (in eV), \( A \) is the proportionality constant, which depends on the probability of the transition and ‘\( n \)’ is a constant linked to the permitted direct or indirect transition probability [42]. According to reported work, spinel nanoferrites exhibit optical absorption spectra which are referred by direct electronic transitions. The optical band gap energy of the prepared materials is shown in Fig. 9. When external impurities are incorporated, semiconducting spinel ferrite usually changes the band gap. In this work, Ho3+ ions replace the B-site Fe3+ cations when the Ho3+ content is doped, which may lead to the formation of an impurity band inside the gap. Thus, the energy band gap (\( E_g \)) showed an increasing pattern and was determined to be 1.12-2.24 eV, as shown in Table-3. The reduction of Fe3+ to Fe2+ ions may be the reason for the energy band gap fluctuation [43].

\[ \begin{array}{|c|c|}
\hline
\text{Samples (x)} & \text{Band gap (eV)} \\
\hline
0.000 & 1.12 \\
0.010 & 1.83 \\
0.015 & 2.00 \\
0.020 & 2.24 \\
0.025 & 2.22 \\
0.030 & 2.24 \\
\hline
\end{array} \]

TABLE-3

BAND GAP ENERGY VALUES (\( E_g \)) FOR Mg0.5Cu0.5HoFe2-xO4 (x = 0.00 to 0.030) NANOFERRITES
Fig. 8. UV absorbance spectra of Mg$_{0.5}$Cu$_{0.5}$Ho$_x$Fe$_{2-x}$O$_4$ (x = 0.00 to 0.030) nanoferrite

Fig. 9. Tauc plots to compute indirect energy band gap Mg$_{0.5}$Cu$_{0.5}$Ho$_x$Fe$_{2-x}$O$_4$ (x = 0.00 to 0.030) nanoferrite

**I-V Measurement:** Eqn. 12 is used to evaluate the properties of a certain material that impede the flow of electrical resistance [38,39]:

$$\rho = \frac{RA}{L}$$  \hspace{1cm} (12)

The shift in DC resistivity in the Ho$^{3+}$ doped magnesium-copper nanoferrites (x = 0.00-0.030) is shown in Fig. 10. It is observed that DC resistivity rises from $5.837 \times 10^6$ to $4.105 \times 10^7$ as Ho$^{3+}$ concentration rises, which is consistent with the Verway’s hopping mechanism. The electric conduction in ferrous ions is primarily due to the movement of electrons
that are randomly distributed across the lattice sites, which are structurally comparable, and they move between ions of the same element that have different valence positions. Since the B-B sites are closer together than B-A sites, the possibility of electron jumping among B-B sites is much lower. Additionally, the microstructural elements like grain size, pores and grain boundaries have an impact on DC resistivity. The relationship between resistivity and the size of grains revealed suggests that resistivity is inversely related to the grain size. Therefore, it is anticipated that the resistivity of Cu-Mg ferrite will increase as Ho content rises.

Based on the Arrhenius relation, the curve relating log and 1000/T for samples with x = 0.00 to 0.030 is shown in Fig. 10. Temperature-dependent dc resistivity of Mg0.5Cu0.5Ho xFe2-xO4 (x = 0.00 to 0.030) nanoferrites with x = 0.00, 0.01, 0.015, 0.02, 0.025 and 0.030. At normal temperature, all ferrites except with x = 0.025 composition show a positive Seebeck coefficient, that fluctuates with temperature for the majority of nanoferrites, a straight line with a slope equivalent to activation energy can be observed throughout a broad temperature range. It is due to the fact that the Curie temperatures close to the Curie temperatures of the samples. From the linear plots (Fig. 11) of resistivity, the activation energy of each sample within the temperature range of 0.3649-0.2493 eV can be calculated and the results are shown in Table-4.

**Thermoelectric power (TEP) analysis:** Fig. 12 depicts the fluctuation of Seebeck coefficient with temperature for the Mg0.5Cu0.5Ho xFe2-xO4 nanoferrites (x = 0.00, 0.01, 0.015, 0.02, 0.025 and 0.030) at 673 K. At normal temperature, all ferrites except with x = 0.025 composition show a positive Seebeck coefficient.

---

**TABLE-4**

<table>
<thead>
<tr>
<th>Content (x)</th>
<th>Activation energies E_F (eV)</th>
<th>E_C (eV)</th>
<th>∆E (eV)</th>
<th>T_C (K)</th>
<th>Resistivity at T_C K</th>
<th>Resistivity at 673 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>0.4216</td>
<td>0.0567</td>
<td>0.3649</td>
<td>458</td>
<td>5.837 × 10^6</td>
<td>2.225 × 10^6</td>
</tr>
<tr>
<td>0.010</td>
<td>0.3860</td>
<td>0.0699</td>
<td>0.3161</td>
<td>475</td>
<td>5.452 × 10^6</td>
<td>3.137 × 10^6</td>
</tr>
<tr>
<td>0.015</td>
<td>0.3664</td>
<td>0.0716</td>
<td>0.2948</td>
<td>481</td>
<td>3.166 × 10^6</td>
<td>6.877 × 10^6</td>
</tr>
<tr>
<td>0.020</td>
<td>0.3568</td>
<td>0.0891</td>
<td>0.2677</td>
<td>486</td>
<td>3.575 × 10^5</td>
<td>6.989 × 10^5</td>
</tr>
<tr>
<td>0.025</td>
<td>0.3329</td>
<td>0.0778</td>
<td>0.2551</td>
<td>491</td>
<td>3.920 × 10^5</td>
<td>7.890 × 10^5</td>
</tr>
<tr>
<td>0.030</td>
<td>0.3178</td>
<td>0.0685</td>
<td>0.2493</td>
<td>498</td>
<td>4.105 × 10^5</td>
<td>8.567 × 10^5</td>
</tr>
</tbody>
</table>
indicating that they are all p-type semiconducting materials. The Seebeck coefficient of pure Mg-Cu nanoferrite shows positive values between 55 ºC-110 ºC, 185 ºC-310 ºC and 340 ºC-410 ºC, indicating the p-type behaviour, while it turns negative between 90 ºC-165 ºC and 290 ºC-350 ºC, indicating n-type behaviour (Fig. 12a). The Seebeck value for all Ho-doped Mg-Cu nanoferrites becomes positive between 40 ºC and 230 ºC, suggesting p-type semiconducting behaviour, while it becomes negative between 250 ºC-400 ºC, indicating n-type behaviour (Fig. 12b-f). The p-type semiconducting behaviour of the nanoferrites under study can be explained by the availability of the additional vacancies caused by the presence of Mg2+...
ions on the octahedral site instead of Fe$^{3+}$ ions in the prepared Mg$_{0.5}$Cu$_{0.5}$HoFe$_2$O$_4$ nanoferrites. Due to the lower charge of Cu$^{2+}$ ions compared to Fe$^{3+}$, the excess vacancies which arise from this would be oxygen vacancies rather than the cation vacancies. With increasing Mg$^{2+}$ occupancy, these oxygen vacancies grow, resulting in a positive Seebeck coefficient (Table-5). The Seebeck coefficient may have decreased due to a decrease in the oxygen vacancies. The hopping of electrons from Fe$^{3+}$ to Fe$^{2+}$ ions is thought to be the cause of the n-type semiconducting behaviour.

**Magnetic analysis:** Fig. 13 shows that the M-H loops of the Ho-doped Mg-Cu ferrites ($x = 0.00-0.030$) were calculated by the VSM method at room temperature (300 K). The hysteresis loops showing ferromagnetic behaviour indicate the saturation in magnetization at the high value of 20 Oe of the applied field. The magnetic parameters determined from M-H hysteresis loops of the ferrites include saturation magnetization (M$_s$), coercivity (H$_c$), retentivity (M$_r$), magnetic moment (µ), squareness ratio (SQR), anisotropy constant (K) initial permeability ($\mu_i$). The obtained values are recorded in Table-6. The S-shape with no opening cycles is shown by the Ho-doped Mg-Cu all prepared sample M-H loops (i.e. low vales retentivity and small vales coercivity). At 300 K (room temperature), this behaviour corresponds to the superparamagnetic behaviour of the prepared nanoferrites smaller than 45 nm. Nanoparticle spinel ferrites exhibited primarily superparamagnetic behaviour. The P-XRD observations above demonstrated a crystallite size of less than 42 nm. The saturation magnetization decreases and the resulting saturation (M$_s$) ranges between 6.85-4.65 emu/g. The decreasing M$_s$ values depended on several factors like crystalline size, surface spin effects, cation distribution and the M$_s$ values, which contribute the favourable super-paramagnetic behaviour [44,45]. The nanoferrite samples with $x = 0.00$ have the highest coercivity (H$_c$) value of 340.12 Oe and also exhibits the lowest M$_s$ value of 30.55 emu/g. Thus, the reported values of Ho$^{3+}$ doped Mg-Cu nanoferrites indicate that the samples have a soft nature. Furthermore, the lowered H$_c$ value indicates a reduction in the magneto-crystalline anisotropy. As the Holonium concentration in the samples increased, it was also observed that the remanence magnetization reduces from 16.25 to 10.88 emu/g. The Ho doped nanoferrites had the lowest remanent magnetization value suggesting that the sample exhibits increased superparamagnetic-like behaviour due to the low doping content of Ho$^{3+}$ ions. The lower proportion of remanent or squareness (SQR) ratio indicates the isotropic nature of the materials. The more significant proportion indicates that magnetization directions have been reoriented to the closest axis. The squareness ratio of the prepared samples in the current study ranges between 0.53 and 0.57, indicating no significant change [46].

Furthermore, the initial permeability (K) and anisotropy constant ($\mu_i$) of Ho$^{3+}$-doped Mg-Cu nanoferrites were also determined using eqns. 12 and 13 and the results are listed in Table-6.

\[
K = \frac{M_s \times H}{0.96} \tag{9}
\]

\[
\mu_i = \frac{M_s^2 \times D}{K} \tag{10}
\]

**Conclusion**

The citric sol-gel auto-combustion process has successfully produced Ho$^{3+}$ substituted Mg$_{0.5}$Cu$_{0.5}$HoFe$_2$O$_4$ ferrite systems ($x = 0.000, 0.005, 0.010, 0.015, 0.020, 0.025$ and $0.030$). The Mg-Cu ferrite matrix is replaced with holonium...
ions, which results in the development of a single cubic spinel ferrite structure and an increase in lattice constant. The FESEM, HRTEM, EDX and SEAD were employed to reveal the cubic morphology and chemical compositions. The crystallite size ranged from 17.10-32.03 nm and the lattice constant was 8.408-8.356. The most intense peak in the XRD spectra was reported at 2θ = 35° which indicate the formation of an FCC spinel structure. FTIR studies exhibited two substantial peaks in 400-562-400 cm⁻¹ region showing the metal-oxygen stretching and the formation of synthesized ferrite materials. The band gap energies were varied from 3.010 to 3.297 eV as assigned from the UV-vis spectral analysis. At ambient temperature, the saturation magnetization, coercively and remanent magnetization from M-H loops were lowered when Ho³⁺ was doped in Mg-Cu ferrites. The M-H loop analyses showed the super-paramagnetic behaviour of the prepared nanoferrites. The M-H curve demonstrates that MS initially decreases to 16.25 from 10.88 emu/g with a decrease in doping concentration. This phenomenon is brought on by an A-B type super-exchange contact in the synthesized nanoferrites. The fluctuations in the coercivity (Hc) and magnetic anisotropy (K1) indicate the thermal stability of all the samples regarding the publication of this article.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

1. N. Sanpo, C.C. Berndt, C. Wen and J. Wang, Acta Biomater., 9, 5830 (2013); https://doi.org/10.1016/j.actbio.2012.10.037
38. V. Rathod, A. Anupama, R.V. Kumar, V.M. Jali and B. Sahoo, Vib. Spectrosc., 92, 267 (2017); https://doi.org/10.1016/j.vibspec.2017.08.008
40. B.P. Jacob, S. Thankachan, S. Xavier and E.M. Mohammed, Phys. Scr., 84, 045702 (2011); https://doi.org/10.1088/0031-8949/84/04/045702