Structural and Magnetic Properties of \( \text{Mn}_{0.50-x}\text{Zn}_{0.50}\text{Cu}_x\text{Fe}_2\text{O}_4 \)

Farhad Alam\(^1\)*, Mohammad H. R. Khan\(^2\), Hari N. Das\(^3\), Akther A. K. M. Hossain\(^4\)

\(^1\)Department of Physical Sciences, School of Engineering and Computer Science, Independent University-Bangladesh, Dhaka, Bangladesh; \(^2\)Department of Arts and Sciences, Ahsanullah University of Science and Technology, Dhaka, Bangladesh; \(^3\)Materials Science Division, Atomic Energy Centre, BAEC, Dhaka, Bangladesh; \(^4\)Department of Physics, Bangladesh University of Engineering and Technology, Dhaka, Bangladesh.

Email: \*farhadiub@gmail.com; \*farhad_840@yahoo.com

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ABSTRACT

\( \text{Mn}_{0.50-x}\text{Zn}_{0.50}\text{Cu}_x\text{Fe}_2\text{O}_4 \) (where \( x = 0.0 - 0.3 \)) ferrites have been synthesized by auto combustion method. X-ray diffraction patterns reveal that all compositions are of single phase cubic spinel structure. The lattice parameter decreases with the increase in \( \text{Cu}^{2+} \) content obeying the Vegard’s law. The bulk density, average grain size, initial permeability, Néel temperature and saturation magnetic induction of \( \text{Mn}_{0.50-x}\text{Zn}_{0.50}\text{Cu}_x\text{Fe}_2\text{O}_4 \) increased with increasing \( \text{Cu}^{2+} \) content. It is observed that both density and initial permeability increase with increasing sintering temperature. The maximum initial permeability is found to be 1061 which is almost four times greater than that of the parent composition. The resonance frequency of all the samples shifts towards the lower frequency as the permeability increases with \( \text{Cu}^{2+} \) content. It is observed from B-H loops of \( \text{Mn}_{0.50-x}\text{Zn}_{0.50}\text{Cu}_x\text{Fe}_2\text{O}_4 \) that coercivity decreases and retentivity increases with \( \text{Cu}^{2+} \) content. Possible explanations for the observed magnetic properties with various \( \text{Cu}^{2+} \) contents are discussed.

Keywords: Combustion Method; Mn-Cu-Zn Ferrites; Initial Permeability; B-H Loop

1. Introduction

Polycrystalline spinel ferrites are technologically very important materials having potential applications and interesting physical properties. Mn-Zn and substituted Mn-Zn ferrites are pertinent magnetic materials due to their high permeability, high magnetization, relatively high Néel temperature, low losses, low cost and environmental stability. These ferrites have been widely used in electrical and magnetic devices for high frequency applications [1-4]. The physical and magnetic properties can be controlled by the preparation condition, chemical composition, sintering temperature and the amount of substitutions. Several investigations on the properties of Ni-Mn-Zn [5], Ni-Cu-Zn [6], Mg-Cu-Zn [7], Co-Mn-Zn [8] ferrites have been reported. It was found that the poor densification and slow grain growth rate can be remarkably improved and consequently initial permeability can be enhanced by the substitution of Cu [9]. No report has been found in the literature regarding the magnetic properties of Cu substituted Mn-Zn ferrites for Mn prepared by combustion method. In the present work, the influence of \( \text{Cu}^{2+} \) in place of \( \text{Mn}^{2+} \) on the properties of Mn-Zn ferrites has been investigated by studying the structure and some magnetic properties.

2. Experimental

The chemical compositions of \( \text{Mn}_{0.50-x}\text{Zn}_{0.50}\text{Cu}_x\text{Fe}_2\text{O}_4 \) (with \( x = 0.0 - 0.3 \) at a step of 0.1) were prepared by combustion method. The stoichiometric amounts of commercially available analytical grade powders of MnCl\(_2\)-4H\(_2\)O, Cu(NO\(_3\))\(_2\)-3H\(_2\)O, Zn(NO\(_3\))\(_2\)-6H\(_2\)O and Fe (NO\(_3\))\(_3\)-9H\(_2\)O were dissolved in ethanol to obtain a mixed homogenous solution. Ammonia solution was slowly added to adjust the pH at level 7. The solution was placed at constant temperature bath (70°C) followed by an ignition and formed a fluffy loose powders of the desired composition. The resultant powders were calcined at 700°C for five hours in air. The grounded fine powders were then pressed into disc- and toroid-shaped samples. The samples prepared from each composition were sin-
tered at 1200°C, 1250°C and 1300°C for five hours in air. During sintering, temperature ramps were 10°C/min for heating and 5°C/min for cooling. The structural characterization was carried out with an X-ray diffractometer using CuKα radiation (λ = 1.54178Å). The lattice parameter was determined using the expression 

\[ F(\theta) = 1/2 \left[ \cos^2 \theta / \sin \theta + \cos^2 \theta / \theta \right], \]

where \( \theta \) is the Bragg’s angle. The exact values of lattice constant, \( a_0 \), were estimated from the extrapolation of the best fitted line to \( F(\theta) = 0 \) or \( \theta = 90° \). The bulk density, \( \rho_b \), was determined using the expression \( \rho_b = (W x \rho) / W - W' \), where \( W \) and \( W' \) are the weight of the sample in air and water, respectively and \( \rho \) is the density of water at room temperature. The theoretical density, \( \rho_{th} \), was calculated using the relation: \( \rho_{th} = \left( Z M / N_a a^3 \right) \), where \( N_a \) is Avogadro’s number, \( M \) is the molecular weight of the corresponding composition and \( Z \) is the number of molecules per unit cell, which is 8 for the spinel cubic structure. The porosity, \( P \) was calculated from the relation \( P(\%) = \left( (\rho_{th} - \rho_b) / \rho_{th} \right) \times 100 \). The micrographs of Mn0.50-xZn0.50Cu_xFe2O4 were taken by a Scanning Electron Microscope (SEM). From these micrographs, the average grain size (D) was estimated by the linear intercept method. The frequency and temperature dependent complex initial permeability were measured using Wayne Kerr Impedance Analyzer (Model No.6500B) in the frequency range 100 Hz - 120 MHz. The real part (\( \mu' \)) and the imaginary part (\( \mu'' \)) of the complex initial permeability were calculated using the following relations: \( \mu' = L_0 / L \), and \( \mu'' = \mu / \tan \delta \), where \( L_0 \) is the self inductance of the sample core and \( L = (\mu_0 N h / 2 \pi) \ln (r_o / r_i) \), is derived geometrically. \( L \), is the inductance of the winding coil without the sample core, \( N \) is the number of turns of the coil (N = 4), \( h \) is the thickness, \( r_o \) is the outer radius and \( r_i \) is the inner radius of the toroid-shaped sample. The relative quality factor (RQF) was calculated from the relation: \( \text{RQF} = \mu / \tan \delta \), where \( \tan \delta \) is the loss factor. B-H loops were measured at room temperature using an Automatic Magnetic Hysteresis Graph Tracer (Model no. AMH-300, Laboratorio Electrofisico).

### 3. Results and Discussion

#### 3.1. Structural Analysis of Mn0.50-xZn0.50Cu_xFe2O4

Figure 1 shows the X-ray diffraction (XRD) patterns for various Mn0.50-xZn0.50Cu_xFe2O4 (with \( x = 0.0 - 0.3 \) at a step of 0.1) sintered at 1250°C. The positions of the peaks for the various compositions indicate a single phase cubic spinel crystal structure. It is seen that \( a_0 \) decreases linearly with increasing \( Cu^{2+} \) content and obeys Vegard’s law [11]. The variation of \( a_0 \) as a function of \( Cu^{2+} \) content is shown in Figure 2. The values of \( a_0 \) are shown in Table 1. The decreasing \( a_0 \) with \( Cu^{2+} \) content may be explained in terms of ionic radii. As the ionic radius of Mn2+ (0.80 Å) is larger than that of Cu2+ (0.72 Å), \( a_0 \) decreases.

![Figure 1. XRD patterns of Mn0.50-xZn0.50Cu_xFe2O4 sintered at 1250°C.](image)

![Figure 2. Variation of lattice parameter and r-variant of Mn0.50-xZn0.50Cu_xFe2O4 with \( Cu^{2+} \) content.](image)
Table 1. Lattice parameter, density, porosity, average grain size, initial permeability, resonance frequency, residual and saturation inductions, coercive field and Néel temperature of various Mn$_{0.50-x}$Zn$_{0.50}$Cu$_x$Fe$_2$O$_4$ sintered at different sintering temperatures.

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<th>$d_0$ (Å)</th>
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<th>$\rho_e$ (g/cm$^3$)</th>
<th>P (%)</th>
<th>D (μm)</th>
<th>$\mu$</th>
<th>$f_r$ (Hz)</th>
<th>$B_s$ (T)</th>
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3.2. Microstructure of Mn$_{0.50-x}$Zn$_{0.50}$Cu$_x$Fe$_2$O$_4$

The scanning electron micrographs as shown in Figure 4 reveal that the grain size is influenced by the Cu$^{2+}$ substitution, where the grain size increases with increase in Cu$^{2+}$ content in Mn$_{0.50-x}$Zn$_{0.50}$Cu$_x$Fe$_2$O$_4$ sintered at 1200°C. The D of Mn$_{0.50-x}$Zn$_{0.50}$Cu$_x$Fe$_2$O$_4$ varies from 2 μm to 4 μm at constant $T_s$. The values of D are presented in Table 1. Figure 5 shows the micrographs of Mn$_{0.40}$Zn$_{0.50}$Cu$_{0.10}$Fe$_2$O$_4$ at different $T_s$. It is seen that the D increases with increasing $T_s$. The grain size increases with increase in Cu$^{2+}$ due to the melting point of copper (1084°C) is less than that of manganese (1246°C). During sintering Cu$^{2+}$ influences...
the microstructure by the formation of liquid phase. It facilitates the grain growth and grain growth reflects the competition between the driving force for grain boundary movement and the retarding force exerted by pores [19, 20]. D increases with Tc because of homogeneous grain growth.

3.3. Magnetic Properties of Mn0.50-xZn0.50Cu_xFe_2O_4

3.3.1. Frequency Dependent Complex Initial Permeability

Figure 6 shows the complex initial permeability spectra for all Mn0.50-xZn0.50Cu_xFe_2O_4 (where x = 0.0 to 0.3 at a step of 0.1) sintered at 1200°C, 1250°C and 1300°C, respectively as a function of frequency.

The complex permeability is given by \( \mu = \mu' - i\mu'' \). Here \( \mu' \) describes the stored energy expressing the component of magnetic induction B in phase and \( \mu'' \) describes the dissipation of energy expressing the component 90° out of phase with the alternating magnetic field H. It is found that \( \mu' \) increases with increasing Cu²⁺ content for various Mn0.50-xZn0.50Cu_xFe_2O_4 at constant Tc. It is also observed that \( \mu' \) increases with increasing Tc. Highest \( \mu' \) was obtained 1061 for Mn0.20Zn0.50Cu0.30Fe2O4 at frequency 103 Hz sintered at 1300°C. \( \mu' \) remains almost constant in the frequency range up to a certain frequency, which is called the resonance frequency, \( f_r \). There is a decrease in \( \mu' \) and increase in \( \mu'' \) above \( f_r \) observed for various Mn0.50-xZn0.50Cu_xFe_2O_4. The \( f_r \) is the range of frequency of the compositions up to which these can be used efficiently. The values of \( \mu' \) and \( f_r \) for all samples sintered at various Tc are presented in Table 1.

It is observed from Figure 7 that the \( \mu' \) increases and \( f_r \) shifted towards the lower frequency with Cu²⁺ in Mn0.50-xZn0.50Cu_xFe_2O_4 at different Tc. The increasing \( \mu' \) and shifting \( f_r \) to lower frequency at constant Tc
follows the Snoek’s relation [21]. The $\mu_i$ of ferrites depends on many factors like reversible domain wall displacement, the amount and the type of dopant ions, D and intragranular porosity, etc [22-24]. It is well known that $\mu_i$ of polycrystalline ferrite is related to two magnetizing mechanisms: domain wall motion and spin rotation [25-27]. Globus et al. [22] studied several Ni-Zn ferrites and found a linear relationship between $\mu_i$ and D. Kakaktar et al. [28] studied the effect of D on $\mu_i$ and found that $\mu_i \propto D$. The $\mu_i$ can be expressed by Globus-Duplex relation $\mu_i \propto (M_s^2 D/\sqrt{|K_f|})$, where $M_s$ is the saturation magnetization; $K_f$ is the anisotropy constant [22]. In our present study of microstructure, it is seen that the D increases significantly with Cu$^{2+}$ content. Therefore, the increase of $\mu_i$ with increasing Cu$^{2+}$ content is justified. The increasing $\mu_i$ with $T_s$ is due to in both $\rho_B$ and D.

**Figure 8** shows the variation of $\mu_i$ with Cu$^{2+}$ content at different frequencies for various Mn$_{0.50-x}$Zn$_{0.50}$Cu$_x$Fe$_2$O$_4$ sintered at 1200°C, 1250°C and 1300°C. It is found that $\mu_i$ decreases at higher frequencies. This is due to the fact that at higher frequencies impurities between grains and intragranular pores act as pinning points and increasingly hinder the motion of spin and domain walls thereby decreasing their contribution to permeability and also increasing the loss [22].

For practical application the quality factor is often used as a measure of performance. The RQF increases with an increase of frequency, showing a peak and then decreases with further increase in frequency as shown in **Figure 9**. The variation of RQF with frequency showed a similar trend for all the samples. It is observed that the sample sintered at 1250°C has the highest RQF (5420) for Mn$_{0.40}$Zn$_{0.50}$Cu$_{0.10}$Fe$_2$O$_4$. The highest RQF for Mn$_{0.50}$Zn$_{0.50}$Cu$_{0.30}$Fe$_2$O$_4$ is 5420 sintered at 1250°C. This is probably due to the growth of less imperfection and defects compared to those of other samples [9].

**Figure 7** shows the variation of initial permeability and resonance frequency of Mn$_{0.50-x}$Zn$_{0.50}$Cu$_x$Fe$_2$O$_4$ at different $T_s$.

**Figure 8.** The initial permeability of Mn$_{0.50-x}$Zn$_{0.50}$Cu$_x$Fe$_2$O$_4$ with Cu$^{2+}$ content at different frequencies sintered at (a) 1200°C, (b) 1250°C and (c) 1300°C.

**Figure 9.** The RQF of Mn$_{0.50-x}$Zn$_{0.50}$Cu$_x$Fe$_2$O$_4$ with Cu$^{2+}$ content sintered at 1200°C, 1250°C and 1300°C.

### 3.3.2. Temperature Dependent Permeability

The $\mu_i$ as a function of temperature for various Mn$_{0.50-x}$Zn$_{0.50}$Cu$_x$Fe$_2$O$_4$ sintered at 1200°C is shown in **Figure 10(a)**.

It is observed that there is a sudden drop in $\mu_i$ at Néel temperature, $T_N$, where the magnetic state of the ferrite changes from ferrimagnetic to paramagnetic state. This is because at $T_N$, the thermal agitation is so high that it reduces the alignment of the magnetic moment along a given axis to zero [29]. **Figure 10(b)** shows the variation of $T_N$ with Cu$^{2+}$ content. It is observed that $T_N$ increases...
Structural and magnetic properties of Mn_{0.50-x}Zn_{0.50}Cu_{x}Fe_{2}O_{4}  

With increase in Cu^{2+} substitution for Mn^{2+} in Mn_{0.50-x}Zn_{0.50}Cu_{x}Fe_{2}O_{4} due to strengthening of A-B interaction between the two sublattices. This could be attributed to the decrease in distance (hooping length) between the magnetic ions of A- and B-sites and is confirmed by the decrease in the lattice parameter with increase in Cu^{2+} content as shown in Figure 2. The shorter distance between magnetic cations leads to the increase in A-B interaction and consequently T_N increases.

3.3.3. B-H Loops of Mn_{0.50-x}Zn_{0.50}Cu_{x}Fe_{2}O_{4}  

Figure 11(a) shows the B-H loops of Mn_{0.50-x}Zn_{0.50}Cu_{x}Fe_{2}O_{4} sintered at 1200°C at constant frequency 1000 Hz and Figure 11(b) is the B-H loops for low field.

The magnetic induction, B of all samples increases linearly with increase in applied magnetic field up to 120 A/m (depending on compositions). Beyond 120 A/m, B increases slowly and then reaches to the saturation induction, B_s. Increasing B with applied low field H indicates that all compositions are in ferromagnetic state at room temperature. From the loops B_s has been calculated. It is observed that B_s increases with increasing Cu^{2+} content which is shown in Figure 12(a).

The variation in saturation magnetization with Cu^{2+} content could be explained by cation distribution and exchange interaction. It is well known that Zn^{2+} ion has strong A-site occupancy, Mn^{2+} ions prefer to go both sites (80% A- and 20% B-sites) [16]. Also Cu^{2+} and Fe^{3+} ions can occupy both A- and B-sites. Substitution of Cu^{2+} in place of Mn^{2+} results into migration of some of Fe^{3+} from A- to B-site. The change in B_s (residual induction) and B_s with Cu^{2+} content are shown in Figure 12(b). The coercive field (H_c) for each sample has been measured from the B-H loops of Mn_{0.50-x}Zn_{0.50}Cu_{x}Fe_{2}O_{4} which is shown in Figure 12(b). It is observed that H_c decreases.
with increase in Cu\(^{2+}\) content, whereas \(\mu'\) increases. Mazen and Abu-Elsaad reported that \(H_c\) is directed to gradually decreasing with \(D\) [29]. Our experimental result is in agreement with the reported value. Therefore, samples having larger grains are expected to have lower \(H_c\).

4. Conclusion

Substitution of Cu\(^{2+}\) causes appreciable change in the structural and magnetic properties of the Mn-Cu-Zn ferrites. The XRD patterns confirm single phase cubic spinel structure of Mn\(_{0.50-x}\)Zn\(_{0.50}\)Cu\(_x\)Fe\(_2\)O\(_4\). The \(a_0\) decreases with the increase in Cu\(^{2+}\) content while \(\rho_S\), \(D\), \(\mu_i\), and \(T_N\) increase with the increase in Cu\(^{2+}\). The \(H_c\) decreases with the increase in Cu\(^{2+}\) content. \(\mu\) is greatly enhanced from 258 to 1061 (\(\sim 400\%\)). The highest RQF (5420) has been found for the sample Mn\(_{0.50}\)Zn\(_{0.50}\)Cu\(_{0.50}\)Fe\(_2\)O\(_4\) sintered at 1250°C. These ferrites are important and suitable for technological applications because of their high permeability.

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