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Effect of annealing temperature and copper mole ratio on the morphology, structure and magnetic properties of Mg_{0.5-x}Cu_{x}Zn_{0.5}Fe_{2}O_{4} nanoparticles prepared by the modified Pechini method

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Abstract

In this study, magnesium copper zinc ferrite (MCZ) nanoparticles were synthesized by the modified Pechini method. In this approach, the magnesium nitrate, copper nitrate, zinc nitrate, iron nitrate, citric acid and diethylene glycol (instead of ethylene glycol in conventional Pechini method) were used as a source of Mg^{2+}, Cu^{2+}, Zn^{2+}, complex and stabilizer and solvent agent, respectively. The effect of annealing temperature and copper mole ratio on the morphology, structural and magnetic properties of Mg_{0.5-x}Cu_{x}Zn_{0.5}Fe_{2}O_{4} (x=0-0.5) nanoparticles were investigated. Various characterization methods, including X-ray diffraction (XRD), field emission scanning electron microscope (FeSEM), energy-dispersive spectroscopy (EDS), X-ray mapping, Fourier transforms infrared spectroscopy (FTIR), adsorption-desorption isotherm and vibrating sample magnetometer (VSM) were used to study the phase, microstructure, particle size, elemental distribution, functional group determination, porosity and magnetic properties of nanoparticles, respectively. The results showed that cubic spinel phase with various
morphologies such as semi-spherical, sheet-like shapes was obtained by the modified Pechini method. Furthermore, the nanoparticles with the x value of 0.2, annealed at 700 °C have the highest saturation magnetization ($M_s = 56.5$ emu/g) among the other synthesized MCZ ferrite nanoparticles.

**Keywords:** Magnetic properties, Ferrimagnetisms, Spinel, Sol-gel.

1. **Introduction**

Today, ferrites as a subset of magnetic ceramic materials have considerable importance from radio frequency to microwave range applications. These materials have permanent magnetic moments and categorized into three groups of soft ferrite, hard ferrite, and garnets. Soft magnetic materials mainly used as magnetic cores in transformers, motors, inductors, generators and noise suppression layers. In general, Ni-Cu-Zn ferrite is famous soft magnetic materials used in multilayer chip inductors (MCLI) [1-4]. Since nickel compounds produce carcinogenic effects and environmental toxicity, despite their high permeability, high Curie temperature and high resistivity at higher frequencies, researches about replacing this material with new material were going on. On the other hand, MgCuZn ferrites are a good candidate for MLCIs due to the high magnetic permeability in a wide frequency range, cost effective, high electrical resistance, relatively low sintering temperature, and good environment stability [5, 6].

The microstructure control of ferrite powder including particle shape and size, porosity, grain boundaries, defect and etc. has an effective influence on the magnetic and physical properties of them [7, 8]. One way to control particle size is adding sintering aid such as (PbO$_2$, CaO$_2$, V$_2$O$_3$, Bi$_2$O$_3$ and etc.) during fabrication of ferrite ceramic [6-9]. However, these additives are
weakening the magnetic properties of the final product. One approach to solving this problem is the preparation of nanosized ferrite with high surface energy at low temperatures without the use of an additive [10, 11].

The MCZ ferrite nanoparticles have been synthesized get by a different chemical method including combustion, sol-gel, Pechini route (citric acid, ethylene glycol pair as a gel agent), microemulsion, co-precipitation, thermal decomposition and hydrothermal method [10-20]. Among these methods, the Pechini method has some benefits such as excellent control of stoichiometry, particle size, ability to prepare multicomponent nanostructured ceramic powders, good homogeneity through mixing at the molecular level in solution and low calcination temperatures are required for the decomposition of the gel to the metal oxide materials as compared to conventional solid-state reaction. Meanwhile, one of the problems of this method is high agglomeration degree of nanoparticles [21-24]. In the modified Pechini method (this research), MCZ ferrite nanoparticles were prepared by a pair of citric acid (CA) and diethylene glycol (DEG) i.e., EG was replaced by DEG in this approach. The modified Pechini method shares the advantages of the Pechini method with respect to chemical homogeneity and compositional control. In contrast to the conventional Pechini method, the modified Pechini method can produce nano-sized particles with a less particle size and low agglomeration degree. However, for the conventional Pechini method, hard aggregation between the nanoparticles could occur during the post-calcining process. Furthermore, the effect of annealing temperature and copper mole ratio on the morphology, structural and magnetic properties of Mg$_{0.5-x}$Cu$_x$Zn$_{0.5}$Fe$_2$O$_4$ ($x=0$-0.5) nanoparticles has been discussed.
2. Experimental

2.1. Preparation of MCZ ferrite nanoparticles

All material were purchased from Merck Co. and used without further purification. MCZ ferrite nanopowder was synthesized by the modified Pechini method including three steps described below:

(I) Sol formation:

According to Mg$_{0.5-x}$Cu$_x$Zn$_{0.5}$Fe$_2$O$_4$ (x=0-0.5) formula, the stoichiometric amount of Fe(NO$_3$)$_3$.9H$_2$O, Mg(NO$_3$)$_3$.2H$_2$O, Cu(NO$_3$)$_2$.6H$_2$O, Zn(NO$_3$)$_2$.6H$_2$O were dissolved in distilled water. Then, appropriate amounts of CA and DEG were added to the previous solution. The mole ratio of CA:DEG:M$^{n+}$ (M=Fe, Mg, Cu, Zn) was 4: 4: 1. This mole ratio was usually used in Pechini method for synthesizing of metal oxide nanoparticles [21- 24]. Then, the solution was stirred by a magnetic stirrer at 80 °C for one hour.

(II) The gel formation:

In this step, the solution was heated for 1h at 120 °C to obtain resin –like solution. The combustion of resin –like solution was performed by holding viscous gel at 250 °C for one hour.

(III) Annealing step :

The combusted gel was annealed at 600-900 °C for 2h in an air atmosphere to obtain MCZ ferrite nanoparticles. It should be mentioned that annealing step at different temperatures was
performed on \( \text{Mg}_{0.5-x}\text{Cu}_x\text{Zn}_{0.5}\text{Fe}_2\text{O}_4 \) precursor for \( x=0.2 \). The optimized temperature was selected for other samples (\( x=0-0.5 \)).

To compare the effect of the replacing DEG by EG molecules, an additional reaction was conducted with the same parameters by using conventional Pechini method (citric acid (CA): ethylene glycol (EG):\( \text{M}^{\text{st}} \) was 4: 4: 1, annealed at optimized temperatures: 700 °C). Schem.1 summarizes the experimental procedure for synthesizing MCZ ferrite samples.

### 2.2. Characterization methods

In order to identify phases of resulting nanoparticles XRD analysis (X'PertPro model, Panalytical manufacturing Co., Netherlands) with the Cu Kα of 1.54 Å was used. In this test, the voltage, current, step size and time per step was 40 kV, 30 mA, 0.05 degrees and 2 seconds, respectively. Xpert Highscore software (1.0d version) was used to phase determination. The crystallinity percent of samples was calculated with Maud software. (version 2.7). The mean crystallite size was calculated using Debye Scherrer’s equation by taking into account the instrumental line broadening factor [14, 15]:

\[
D_c = 0.9 \lambda / \beta \cos \theta
\]  

(1)

where \( \lambda \) is the wavelength of the X-rays (1.54 Å), \( \beta \) is the peak broadening (in radians) after correcting the instrumental broadening factor and \( \theta \) is the Bragg’s angle.

The lattice constant (\( a \)) of the sample was determined using Nelson–Riley (NR) extrapolation method. The values of the lattice parameter obtained from each reflected plane were plotted against the Nelson–Riley function \( F(\theta) \).
The extrapolation of the straight line to $F(\theta) = 0$ or $\theta = 90^\circ$ gives the accurate lattice constant.

The X-ray density ($\rho_x$) of as-prepared MCZ nanoparticles is calculated from the equation number (3) [25]

$$\rho_x = \frac{ZM}{N\alpha^3}$$  \hspace{1cm} (3)

where $Z$ is the number of molecules per unit cell (is 8 for the cubic spinel structure), $M$ is the molecular weight of the samples; $N$ is the Avogadro’s number and ‘$\alpha$’ is the lattice constant.

To evaluate the morphology of nanoparticles field emission electron microscopy (FESEM, TE-SCAN Co., MIRA3 model, Made in Brno – Kohoutovice, Czech Republic, with 5 nm accurately, the magnification of 20-100000 and the LaB$_6$ heated filament) analysis was used. To capture secondary electrons images, a vacuum condition with a maximum voltage of 30 kV was used. The mean particle size in FESEM images was calculated using the image analyzer software (Digimizer software, version 4.6.1).

To determine the elemental composition of nanoparticles energy dispersive spectroscopy (EDS, TE-SCAN Co., MIRA3 model) with an accelerating voltage of 20 KV and a take-off angle of 35° was performed.

In order to identify the type of functional groups, Fourier transforms infrared spectroscopy (FTIR) was done in KBr cells. The test was performed on FTIR system (JASCO Co., 6300 model made in Japan).
The magnetic properties of the sample were evaluated by vibrating sample magnetometer system (VSM, KavirMagnet model, manufactured by Daghigh Kavir Magnet Co, Kashan, Iran) with a maximum applied field 15 kOe and step size of 100 Oe at room temperature.

Adsorption-desorption isotherm was performed on Brunauer–Emmett–Teller system (BET, Belsorp-mini II model, Tuggerah NSW Australia) system. The sample was degassed and degreased at 200 °C for 2h.

3. Results and discussions

3.1. Effect of annealing temperature

The effect of annealing temperature on the crystallinity of MCZ nanoparticles (Mg$_{0.5}$$_x$Cu$_x$Zn$_{0.3}$Fe$_2$O$_4$ sample for x=0.2) is displayed in Fig. 1. To investigate the effect of temperature on the crystallization of products, the XRD of MCZ ferrite nanoparticles at four different temperatures (600, 700, 800 and 900 °C) was compared. In XRD database, there isn't any JCPDS number for three doping MgCuZn in Fe$_2$O$_3$ structure. However, the diffraction patterns in Fig.1 are in good agreement with the JCPDS card no. 0013-077-001 (CuZn ferrite with spinel phase). More accurate look at the location of the standard card diffraction and reflections of MCZ samples, it can be seen that a small amount of displacement of the peak as compared to reference standard pattern existed. This is due to the doping magnesium in CuZn ferrite network. The spinel phase in other reports (with sol-gel method [16-18]) obtained at annealing temperature above 750 °C. Thus, this approach was successful in obtaining MCZ nanoparticles at low annealing temperature (600 °C).
Also, further observation in Fig. 1 revealed that the intensity of the peaks ((222) and (511) planes) is decreased with increasing the temperature. The (222) and (511) plane are mostly sensitive to cations in octahedral site [26, 27]. Hence, the decrease in intensity of these peaks may be due to the reduction of Fe$^{3+}$ to Fe$^{2+}$ in octahedral site for Mg reduction nature upon increasing the temperature [26, 28]. A similar result was also observed by Petcharoen and coworker [28] for the tetrahedral site during synthesizing magnetite nanoparticles.

The sample crystallinity percent was (calculated with Maud software, version 2.7) improved from 84% to 98% with increasing annealing temperature from 600 °C to 900 °C. It was due to this fact that diffusion of atoms was accelerated with increasing annealing temperature. This resulted in increasing XRD peak intensity and improving the crystallinity percent of the product [29, 30].

Furthermore, the cell parameters obtained from X-ray diffraction pattern of the cubic phase MCZ ferrite annealed at 600 °C is equivalent to 8.405 Å. The absence of MgO, CuO and ZnO phases in diffraction pattern suggests the successful formation of solid solution and MCZ ferrite phase through the modified Pechini method. However, due to the XRD detection limit that is usually below 5%, it can be said that the impurity phases mentioned above if any, does not exceed 5%.

Fig. 1

Fig. 2 shows scanning electron microscope images of the MCZ sample (x = 0.2) annealed at different temperatures between 600 °C and 900 °C, respectively. According to Fig. 2a, a mixture of semi-spherical morphology with an average particle size of 50 nm and multi-dimensional sheet shapes with a thickness of about 25 nm and a length of about 250 nm were obtained at 600 °C. At
annealing temperatures of 700 °C (Fig. 2b), sheet shapes with a thickness of about 40-50 nm and a length of about 250 nm have been observed. When sample annealed at 800 °C, the thickness of sheet shape was increased to 60-70 nm (Fig. 2c). By increasing temperature up to 900 °C (Fig. 2d) most particles were sintered and grown up to one micron. According to Fig. 2d, some sheet-like particles (marked with arrows in Fig. 2d) is observed in the sintered sample.

For comparison, one sample prepared by conventional Pechini method (EG: CA: metal ions =4::4:1) and annealed at 700 °C for 2h. As can be seen from Fig. 2e, the agglomerated irregular particles exist in this sample. Therefore, this result shows the benefit of modified Pechini method as compared to classical Pechini method.

Fig. 2

To check the existence of functional groups in precursors (gel) and nanoparticles, the FTIR spectra of the samples were taken. Several FTIR bands in the gel (Fig 3a), were observed. The absorbance bands due to the stretching vibration of –OH (3407 cm\(^{-1}\)), aliphatic –CH\(_2\) (2924 and 2853 cm\(^{-1}\)), the bending vibration of –CH (1425 cm\(^{-1}\)), asymmetric and symmetric vibrations of carboxylate functional group of polyester (1624 and 1450 cm\(^{-1}\)) is observed in Fig. 3a [21-24]. Fig. 3b shows the FTIR of a gel after annealing temperature at 700 °C. The peak of carbon skeleton and carboxylate anions has been partially removed. The small amounts of the polyester agent (1136 cm\(^{-1}\) correspond to C-O group, 1624 cm\(^{-1}\) and 1425 cm\(^{-1}\) related to the bond of carbonyl –C = O group and stretching vibration of –CH\(_2\) in a polyester chain at 2853 and 2924 cm\(^{-1}\)), prevent the nanoparticles from clumping and agglomeration [23, 24]. The carbonyl group can also be related to the formation of carbonate compounds such as magnesium, copper or iron carbonate, but, due to the acidic medium of reaction (pH 1-2), the formation possibility of carbonates compound is very low. The XRD
patterns (Fig. 1) previously confirmed the absence of metal carbonate formation and is in good agreement with FTIR results. It is worth noting that the peaks in the area of 548 cm\(^{-1}\) and 423 cm\(^{-1}\) are due to the vibration frequencies of tetrahedral and octahedral positions of M-O-M bond (M=Fe, Mg, Cu and Zn) in the spinel structure, respectively [29, 30]. Moreover, in the annealed samples, a peak located at 2336 cm\(^{-1}\) can be seen. Some researchers consider this peak as the CO\(_2\) absorption in the sample [22-24].

Fig. 3

In the Pechini method, the metal salts dissolved in water and then by adding citric acid (CA), the metal ions linked to the functional groups of the CA molecules. Therefore, citric acid prevents the precipitation of ions during hydrolysis step. Usually, the reaction between citric acid and ethylene glycol (EG) occurred at temperatures of about 120 \(^\circ\)C-150 \(^\circ\)C to form a polyester and water molecules. In the presence of metal salts (such as Fe(NO\(_3\))\(_3\) and Mg(NO\(_3\))\(_2\) salts), metal ions (M=Fe\(^{3+}\), Mg\(^{2+}\), Zn\(^{2+}\) and Cu\(^{2+}\)) attached to the -COOH group of polyester and chelated polyester-M ions will be produced. Over time, the regular three-dimensional network (gel) is formed. Then, at 250 \(^\circ\)C to 300 \(^\circ\)C, the burning of gel has occurred. Then, after calcination of the polymer network, MCZ ferrite nanoparticles are formed [20]. The formation mechanism of conventional Pechini and modified method is shown in Fig. 4. According to Fig. 4b, by replacing EG with DEG molecules, more distance between chains of polyester formed and resulted in less agglomerated particles (as can be seen in FESEM images, Fig. 2).

There are generally three methods for nanoparticles stabilization [22-24]. The first method is a steric hindrance that huge groups such as surfactants or supramolecules prevent the nanoparticles from sticking together. The second method is electrostatic repulsion. In this method, molecules with
negative or positive (such as quaternary ammonium) charge are used to induce an electrical repulsion to prevent nanoparticles to be agglomerated. The third method uses a combination of the two above mentioned methods. In this case, a small amount of residual polyester (confirmed by FTIR analysis, Fig. 3b) stabilizes MCZ ferrite nanoparticles. Thus, the stabilization method in this study is the steric hindrance.

Fig. 4

VSM test results of MCZ samples annealed at different temperatures for $x = 0.2$ is shown in Fig. 5. The saturation magnetization and coercively ($H_c$) of different annealed temperatures are shown in Table 1.

According to Table 1 with increasing annealing temperature from 600 °C to 900 °C, Ms value has been increased from 54.1 emu/g to 59.4 emu/g. As the saturation magnetization is only affected by the composition and phase purity, it is reasonable that with increasing annealing temperature, enhancement of the saturation magnetization of the samples will be observed [20, 31]. The enhancement of saturation magnetization during the increment of annealing temperature is consistent with crystallinity improvement that was previously mentioned in the XRD section.

On the other hand, the coercivity ($H_c$) value decreases with increasing annealing temperature. This may be due to a reduction in crystalline defects and grain boundary in the MCZ ferrite nanoparticles [20, 31]. Moreover, the decrease in coercivity can be ascribed to particle size coarsening upon increasing annealing temperature. This may cause a decrement of domain walls contribution in the demagnetization process [20, 31]. Furthermore, as compared with Ref. 20 and 25 which synthesized MCZ with conventional and polymeric sol-gel method, the higher Ms and lower $H_c$ were obtained by the modified Pechini method at similar annealing temperatures.
According to the FESEM, XRD and VSM results, the annealing temperature at 700 °C was selected as an optimum annealing temperature due to the homogenous sheet-like morphology, narrower particle size distribution, good crystallinity and relatively high value of saturation magnetization.

![Fig. 5](image)

Table 1.

3.2. XRD analysis of MCZ ferrite nanoparticles with changing x mole ratio

The effect of copper mole ratio on the phase formation of as-synthesized samples was analyzed by XRD technique. Fig. 6 shows the XRD patterns of Mg_{0.5-x}Cu_{x}Zn_{0.5}Fe_{2}O_{4} samples for x = 0-0.5 annealed at 700 °C for 2h. According to Fig. 6, the characteristic peaks of MCZ ferrite phase (spinel phase) was clearly observed at 2θ of 30.1, 35.4, 42.6, 56.4, and 62.4 degrees. Since the substitutions of Cu^{2+} ions in the structure of MCZ ferrite particles changed the lattice spacing “d”, so, diffraction angles shifted as compared to the reference JCPDS card number (0013-77, spinel phase).

The lattice parameters and X-ray density of MCZ ferrites are given in Table 2. From this table it can be seen that, the lattice parameter is bring into decreasing with an increase of ‘X’ value. The increasing trend of lattice parameters in table 2 can be attributed to copper ion substitution in the lattice which has larger ionic radius (Cu^{2+} = 0.72˚A ) than Mg^{2+} (0.65˚A) and Fe^{2+} (0.64˚A) ions [32, 33]. Furthermore, the increasing of X-ray density of MCZ samples attributed to a higher molar mass of copper ions as compared to Mg^{2+} ions (equation 3).

![Fig. 6](image)

Table 2
3.3. FESEM, EDS and EDX mapping analysis of MCZ ferrite nanoparticles with changing x mole ratio

The effect of x mole changes on the morphology of ferrite nanoparticles was shown in Fig. 7. Figure 7a displayed scanning electron microscope image of Mg_{0.5}Zn_{0.5}Fe_{2}O_{4} sample. According to this figure, in the absence of copper, semi-spherical ferrite nanoparticles with an average particle size of 40-50 nm were obtained. Fig. 7b-f show that upon doping copper in MCZ lattice, the morphology of particles was changed from semi-spherical (x=0.1, Fig.7b) to the mixture of edge facet (angular) shape (x=0.2, Fig.7c) and irregular agglomerated nanoparticles (x=0.3-0.5, Fig.7d-f). With doping 0.2 mole of copper in ferrite lattice, MCZ nanoparticles (Figure 7c) have growth tendency to polyhedral and sheet-like shape. This could be due to a different mechanism of nucleation and growth of ferrite nanoparticles in the presence of copper ions in the MCZ.

According to Periodic Bond Chain (PBC) theory (Fig. 8) developed by Hartman and Perdok [34], for cubic structure all crystal facets divided based on the number of broken periodic bond chains on a given facet: flat surface (F-face, \{100\} faces), stepped surface (S-face, \{110\} faces) and kinked surface (K-face, \{111\} facets). Based on this hypothesis, for \{110\} a surface, each surface site is a step or ledge site, and thus any introduced atom would be integrated wherever it adsorbs. For \{111\} facets, each surface site are a kink site and would irreversibly integrate any introduced atom adsorbed onto the surface. For both S- and K-face surfaces, the above growth is recognized to as a random addition mechanism and no adsorbed atoms would get away to the solution. However, facets with fast growth rate have a propensity to disappear, i.e. surfaces with high surface energy (S- and K-faces) will disappear. In a thermo-dynamical equilibrium crystal, only those surfaces with the
lowest total surface energy (F-face) will survive. Generally, no preferred growth was observed in equilibrium condition and spherical or semi-spherical morphology due to having low surface energy was formed (see Fig. 7a, x=0). But, in the presence of CA and DEG molecules as a chelating agent and increasing x value to x=0.3-0.5, it seems S- and -K faces have less growth rate than F-face (i.e. F-faces vanished) and as a consequence in most samples semi-spherical and angular spheres were observed (Fig. 7b, 7d, 7e, 7f). However, in the case of observing sheet-like morphology, CA and DEG molecules chelated to F-faces and caused this face survive and hence the sheet-like shape was formed (Fig. 7c).

Fig. 8

EDS analysis of Mg$_{0.5-x}$Cu$_x$Zn$_{0.5}$Fe$_2$O$_4$ samples (x = 0.0-0.5) is presented in Fig. 9. EDS result revealed good consistent between designed stoichiometry formula and the experimental existence of Fe, Cu, Mg and Zn elements in the compounds. However, the values of each element have some differences as compared to its theoretical formula (Mg$_{0.5-x}$Cu$_x$Zn$_{0.5}$Fe$_2$O$_4$) due to errors such as fluorescence, absorption and etc., in this test [35].

In order to investigate the distribution of elements, X-ray map analysis from one of the samples was taken. The X-ray map analysis of Mg$_{0.3}$Cu$_{0.2}$Zn$_{0.5}$Fe$_2$O$_4$ (Figure 10) didn’t show any accumulations of elements in the sample. Therefore, homogeneous distribution of the iron, magnesium, zinc, copper and oxygen were obtained by the modified Pechini method.

Fig. 9

Fig. 10
3.4. VSM analysis of MCZ ferrite nanoparticles with changing x mole ratio

The hysteresis loops of \( \text{Mg}_{0.5-x}\text{Cu}_x\text{Zn}_{0.5}\text{Fe}_2\text{O}_4 \) nanoparticles with various x values are shown in Fig. 11. All samples show ferrimagnetic behavior. The \( M_s \) and \( H_c \) values of MCZ ferrite nanoparticles are also presented in Table 3. Changes in \( M_s \) values can be explained based on the Neel theory and cation distribution in A and B sites [36, 37]. Based on the Neel theory, three-sublattice interaction of A-A, B-B, and A-B existed in ferrite materials. The superexchange A-B interaction is predominated rather than the interactions within the A-A and B-B sublattice. The net magnetic moment vector is the sum of the magnetic moments A and B sublattice (equation 4) [38-40]:

\[
n_B^N = [MB - MA]
\]

In this equation, \( n_B^N \), \( M_B \) and \( M_A \) are the net magnetic moment, the magnetic moment of B and A sublattice, respectively. According to equation (4) and Table 3, it can be seen that the replacement of \( \text{Cu}^{2+} \) with magnetic the moment of 4.1 \( \mu \text{B} \) by nonmagnetic ions \( \text{Mg}^{2+} \) increases ferrite the magnetic moment of the MCZ nanoparticles from \( x = 0 \) to \( x = 0.2 \). The reason of reducing \( M_s \) value (Table 3) for higher doping content, can be related to changes of cation distribution in tetrahedral and octahedral sublattices. Indeed, at the higher level of copper ions in the lattice, some \( \text{Fe}^{2+} \) ions migrated from B site to A site. Accordingly, the net magnetic moment vanishes for \( x > 0.2 \).

According to Fig. 11 and Table 3, the \( \text{Mg}_{0.3}\text{Cu}_{0.2}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4 \) sample has the highest \( M_s \) value (58.6 emu/g). Saturation magnetization results are in good agreement with the results of other researchers who have synthesized MCZ with other chemical methods [6, 10, 25].

It should be noted that “\( M_c \)” values observed for MCZ ferrite nanoparticles are less than the bulk of this material. This is because the nanosized as-synthesized particle had the disorder that causes the
spins dead layer at the surface and by breaking the exchange interaction can reduce the magnetization saturation of nanosized samples [36].

Fig. 12

Table 3

As shown in Table 3, Cu-doped MCZ nanoparticles have less coercively than undoped sample (Mg$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$). It might be attributed to larger size character of doped MCZ sample (Fig. 7). In the case of larger particle size, domain wall displacement could occur easier than smaller particles. Therefore, $H_c$ will have a reducing trend. Coercivity values of Cu-doped sample are close to each other and didn’t show substantially changes. However, an increase in coercivity value from 13 Oe to 18.4 Oe was observed for Cu doping from $x=0.1$ to 0.2. This mainly attributed to the sheet-like morphology of Mg$_{0.3}$Cu$_{0.2}$Zn$_{0.5}$Fe$_2$O$_4$ sample which increases shape anisotropy contribution and higher induced coercivity [6, 10 and 20].

To investigate the effect of $x$ mole ratio on wave number shift in all specimens, the FTIR of MCZ ferrite nanoparticles (Fig. 12) was taken. As previously mentioned the presences of small quantities of polyester (confirmed by FTIR analysis) on nanoparticles stabilizes them and prevent the nanoparticles from agglomeration. It is worth noting that peaks in the range of 569-553 cm$^{-1}$ and 425-414 cm$^{-1}$ related to the vibrational frequencies of M-O-M in the octahedral and tetrahedral site, respectively [20, 26]. Commonly, the wave number is inversely proportional to atomic number, so by replacing the Fe$^{2+}$ ions (mass number= 56 g/mol) with lighter ions (Cu$^{2+}$, mass number= 63 g/mol) the peak position was shifted from 569 cm$^{-1}$ to 553 cm$^{-1}$ wave number. This result further
confirmed the entrance of Cu ions in the ferrite sublattices that affect on magnetic and structural properties as previously discussed.

Fig. 12

4. Conclusion

In this study ferrite nanoparticles, with the general formula Mg$_{0.5\times}$Cu$_x$Zn$_{0.5}$Fe$_2$O$_4$ (MCZ, x=0-0.5) were successfully synthesized by the modified Pechini method. The effect of annealing temperatures on the magnetic and structural properties of MCZ ferrite nanoparticles was investigated. XRD results showed that phase of all sample was cubic spinel. VSM analysis proved soft magnetic behavior of all samples. Various morphologies including spherical, sheet-like and irregular shapes depend on annealing temperature and copper doping value was clarified in FESEM micrographs of samples. The maximum value of saturation magnetization was obtained for Mg$_{0.3}$Cu$_{0.2}$Zn$_{0.5}$Fe$_2$O$_4$ sample with sheet-like shapes. Variation of saturation magnetization and coercivity were discussed based on phase purity, particle size and shape anisotropy in copper doped Mg$_{0.5\times}$Cu$_x$Zn$_{0.5}$Fe$_2$O$_4$ nano-ferrites.
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Figs. Captions:

Schem. 1: Schematic diagram representing preparation of Mn-Cu-Zn ferrite nanoparticles.

Fig. 1: XRD patterns of MCZ (x = 0.2) annealed at different temperatures between 600 and 900 °C.

Fig.2: Scanning electron microscope images of the MCZ samples (x = 0.2) annealed at different temperatures (a) 600 °C b) 700 °C c) 800 °C d) 900 °C e) MCZ nanoparticles prepared with conventional Pechini method.

Fig. 3: FT-IR analysis of (a) precursor or burned gel (b) ferrite nanoparticles after annealing step.

Fig. 4: Schematic of polyester formation between citric acid and ethylene glycol and chelated to metals ions in conventional Pechini method (b) the Polyester formed between citric acid and diethylene glycol in modified Pechini method.

Fig. 5: Hysteresis curves of samples annealed at different temperatures between 600 and 900 °C.

Fig. 6: X-ray diffraction pattern of Mg_{0.5-x}Cu_{x}Zn_{0.5}Fe_{2}O_{4} samples for x = 0-0.5 annealed at 700 °C.

Fig. 7: FESEM of Mg_{0.5-x}Cu_{x}Zn_{0.5}Fe_{2}O_{4} specimens with various x quantities (a) x=0 (b) x = 0.1 (c)x=0.2 (d) x = 0.3 (e) x = 0.4 and (e) x = 0.5.

Fig. 8: Schematic of Periodic Bond Chain (PBC) theory for cubic structure.

Fig. 9: EDS analysis of Mg_{0.5-x}Cu_{x}Zn_{0.5}Fe_{2}O_{4} samples for x = 0-0.5

Fig. 10: EDX mapping analysis of Mg_{0.5-x}Cu_{x}Zn_{0.5}Fe_{2}O_{4} samples for x = 0.2

Fig. 11: VSM analysis of Mg_{0.5-x}Cu_{x}Zn_{0.5}Fe_{2}O_{4} samples for various x mole ratios (a) x=0 (b) x = 0.1, (c) x=0.2 (d) x=0.3 (e) x=0.4 (f) x=0.5

Fig. 12: FTIR spectra of the nanoparticles Mg_{0.5-x}Cu_{x}Zn_{0.5}Fe_{2}O_{4} for x = 0-0.5

Table 1. Effect of annealing temperature on the saturation magnetization (Ms) and coercivity (Hc) values.

Table 2: Lattice parameter and X-ray density with changing cu ion mole ratio in MCZ structure.

Table 3: Summary of “Ms” and “Hc” values for Mg_{0.5-x}Cu_{x}Zn_{0.5}Fe_{2}O_{4} nanoparticles at different x values.
Schem. 1: Schematic diagram representing preparation of Mn-Cu-Zn ferrite nanoparticles
Table 1. Effect of calcination temperature on the saturation magnetization (Ms) and coercivity ($H_c$) values

<table>
<thead>
<tr>
<th>$H_c$ (Oe)</th>
<th>Ms (emu/g)</th>
<th>Crystallite size</th>
<th>$T$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25.0</td>
<td>54.1</td>
<td>15</td>
<td>600</td>
</tr>
<tr>
<td>18.1</td>
<td>56.5</td>
<td>24</td>
<td>700</td>
</tr>
<tr>
<td>10.0</td>
<td>57.5</td>
<td>36</td>
<td>800</td>
</tr>
<tr>
<td>10.1</td>
<td>59.4</td>
<td>49</td>
<td>900</td>
</tr>
</tbody>
</table>

Table 2: Lattice parameter and X-ray density with changing Cu ion mole ratio in MCZ structure.

<table>
<thead>
<tr>
<th>X value</th>
<th>Lattice parameter (Å)</th>
<th>X-ray density (g/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>8.3810</td>
<td>5.108</td>
</tr>
<tr>
<td>0.1</td>
<td>8.3905</td>
<td>5.112</td>
</tr>
<tr>
<td>0.2</td>
<td>8.4055</td>
<td>5.119</td>
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<tr>
<td>0.3</td>
<td>8.4069</td>
<td>5.127</td>
</tr>
<tr>
<td>0.4</td>
<td>8.4078</td>
<td>5.136</td>
</tr>
<tr>
<td>0.5</td>
<td>8.4090</td>
<td>5.145</td>
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</table>
Table 3: Summary of “$M_s$” and “$H_c$” values for $\text{Mg}_{0.5-x}\text{Cu}_x\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanoparticles at different $x$ values.

<table>
<thead>
<tr>
<th>X value</th>
<th>$M_s$ (emu/g)</th>
<th>$H_c$ (Oe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>25.7</td>
<td>24.0</td>
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<tr>
<td>0.1</td>
<td>38.4</td>
<td>13.0</td>
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<tr>
<td>0.2</td>
<td>56.5</td>
<td>18.4</td>
</tr>
<tr>
<td>0.3</td>
<td>50.0</td>
<td>17.5</td>
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<tr>
<td>0.4</td>
<td>49.3</td>
<td>17.3</td>
</tr>
<tr>
<td>0.5</td>
<td>46.9</td>
<td>19.1</td>
</tr>
</tbody>
</table>
Fig. 1: XRD patterns of MCZ (x = 0.2) calcined at different temperatures between 600 °C and 900 °C.
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(b) x = 0.1, (c) x=0.2 (d) x=0.3 (e) x=0.4 (f) x=0.5
Fig. 12. FTIR spectra of the nanoparticles $\text{Mg}_{0.5-x}\text{Cu}_x\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ for $x = 0-0.5$. 

$X=0.2$  $X=0.3$  $X=0.4$  $X=0.5$  

$553 \text{ cm}^{-1}$  $569 \text{ cm}^{-1}$  

$\text{Wavenumber (cm}^{-1})$ 

$\%T$
✓ Magnesium copper zinc ferrite synthesized by the modified Pechini method.
✓
✓ Nano-sized particles with a low agglomeration degree were obtained.
✓
✓ The Periodic Bond Chain was suggested for formation of different morphologies.