

Synthesis and Magnetic Properties of Zn, Co and Ni Substituted Manganese Ferrite Powders by Sol-gel Method

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The Zn, Co and Ni substituted manganese ferrite powders, $Mn_{1-x}(Zn, Co, Ni)_xFe_2O_4$, were fabricated by the sol-gel method, and their crystallographic and magnetic properties were studied. The Zn substituted manganese ferrite, $Zn_{0.2}Mn_{0.8}Fe_2O_4$, had a single spinel structure above 400 °C, and the size of the particles of the ferrite powder increased when the annealing temperature was increased. Above 500 °C, all the $Mn_{1-x}(Zn, Co, Ni)_xFe_2O_4$ ferrite had a single spinel structure and the lattice constants decreased with an increasing substitution of Zn, Co, and Ni in $Mn_{1-x}(Zn, Co, Ni)_xFe_2O_4$. The Mössbauer spectra of $Mn_{1-x}Zn_xFe_2O_4$ ($0.0 \leq x \leq 0.4$) could be fitted as the superposition of two Zeeman sextets due to the tetrahedral and octahedral sites of the Fe^{3+} ions. For $x = 0.6$ and 0.8 they showed two Zeeman sextets and a single quadrupole doublet, which indicated they were ferrimagnetic and paramagnetic. And for $x = 1.0$ spectrum showed a doublet due to a paramagnetic phase. For the Co and Ni substituted manganese ferrite powders, all the Mössbauer spectra could be fitted as the superposition of two Zeeman sextets due to the tetrahedral and octahedral sites of the Fe^{3+} ions. The variation of the Mössbauer parameters are also discussed with substituted Zn, Co and Ni ions. The increment of the saturation magnetization up to $x = 0.6$ in $Mn_{1-x}Co_xFe_2O_4$ could be qualitatively explained using the site distribution and the spin magnetic moment of substituted ions. The saturation magnetization and coercivity of the $Mn_{1-x}(Zn, Co, Ni)_xFe_2O_4$ ($x = 0.4$) ferrite powders were also compared with pure $MnFe_2O_4$.

Keywords : manganese ferrite, sol-gel method, mössbauer spectroscopy, coercivity, saturation magnetization

1. Introduction

Manganese ferrite, $MnFe_2O_4$, is a practical ferrite material. It has been widely used in microwave and magnetic recording applications. The crystal structure of $MnFe_2O_4$ is spinel (space group $Fd3m$) in which the lattice of O^{2-} ions forms tetrahedral and octahedral local symmetry that are referred to as A and B sites, respectively [1, 2]. In a normal spinel structure, divalent ions (Mn^{2+} in $MnFe_2O_4$) only occupy A sites, and trivalent ions (Fe^{3+} in $MnFe_2O_4$) only occupy B sites. In an inverse spinel structure, divalent ions occupy half of the B sites, and trivalent ions occupy the rest of the B sites and all the A sites. In $MnFe_2O_4$ prepared at high temperatures ($> 900^\circ C$), 20% of the Mn^{2+} ions migrate from A to B sites. This means that $MnFe_2O_4$ may be characterized as a mixture of normal and inverse spinel ferrite [3]. The Mn-Zn ferrites are ceramic materials widely used in the fabrication of transformers,

frequency filters, magnetic recording heads, etc., due to their excellent properties such as high saturation magnetization, high initial permeability, high resistivity and low losses. The sol-gel method is known as a technique for the low temperature synthesis of glass, ceramics, and other materials, using a dip coating process or spin coating for thin film [4-7]. One of the advantages of using the sol-gel method is a lower annealing temperature that enables smaller grained powders to be grown. The sol-gel method can provide multi-component oxide with a homogeneous composition, and it has been employed to prepare many high purity oxide powders, including some products with spinel-type structures [8, 9].

Synthesizing of substituted manganese ferrite is very hard by the sol-gel method, and there have been a few detailed studies on Zn, Co and Ni substituted manganese ferrites. Recently, the structure, magnetization, and susceptibility were studied in manganese ferrites synthesized by the wet-chemical method. In this study, using the sol-gel method, we synthesized Zn^{+2} , Co^{+2} and Ni^{+2} substituted manganese ferrite powders $Mn_{1-x}Zn_xFe_2O_4$, $Mn_{1-x}Co_xFe_2O_4$

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and $\text{Mn}_{1-x}\text{Ni}_x\text{Fe}_2\text{O}_4$ annealed at various temperatures ranging from 200°C to 700°C, and studied their crystallographic and magnetic properties by X-ray diffractometry (XRD), scanning electron microscopy (SEM), Mössbauer spectroscopy, and vibrating sample magnetometry (VSM).

2. Experiment

The samples of the $\text{Mn}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$, $\text{Mn}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$ and $\text{Mn}_{1-x}\text{Ni}_x\text{Fe}_2\text{O}_4$ ferrite system were prepared by the sol-gel method. Measured amounts of $\text{Mn}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{CH}_3\text{CO}_2)_2 \cdot 4\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were first dissolved in 2-Methoxyethanol for 30-50 min with an ultrasonic cleaner. The solution was refluxed at 80°C for 12 h in order to gel, and dried at 90°C in a dry oven for 24 h. The samples of the dried powders were ground and annealed at various temperatures to determine the growth of particles. All the heat-treatment process was done in a N_2 atmosphere to prevent oxidation of the Mn^{2+} . A large amount of N_2 gas was flowed early in the annealing process to remove oxygen inside a quartz tube and emitting gas from the dry powder. It is known that pure MnFe_2O_4 obtained by the sol-gel method can be formed at 250°C, and thoroughly crystallized at temperatures above 300°C, which is much lower than the required temperature used in the traditional ceramic method. To verify their purity, all samples were analyzed by an X-ray diffractometer with $\text{CuK}\alpha$ (1.54 Å) radiation. The surface microstructure was observed using SEM at room temperature. The Mössbauer spectra of the powders were recorded with a ^{57}Co source in a constant acceleration mode to identify the magnetic phase of cobalt ferrite powders. The saturation magnetization and coercivity were determined by a VSM.

3. Results and Discussion

X-ray diffraction patterns of $\text{Mn}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$ powders annealed at various temperatures are shown in Fig. 1. The X-ray diffraction measurement shows that all peaks of the $\text{Mn}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$ ferrite powders are consistent with those of a typical spinel structure of a manganese ferrite powder annealed above 400°C. The increase in the annealing temperature leads to a sharpening of the major peak, which is to a growth of a larger grain size of the spinel powders and improved crystallization. Although the formation of the spinel structure starts at 250°C, the considerable broadening of all diffraction peaks suggests that the sizes of ferrite particles are expected to be relatively small. This suggests that the low annealing temperature of powders obtained through the sol-gel method has increased

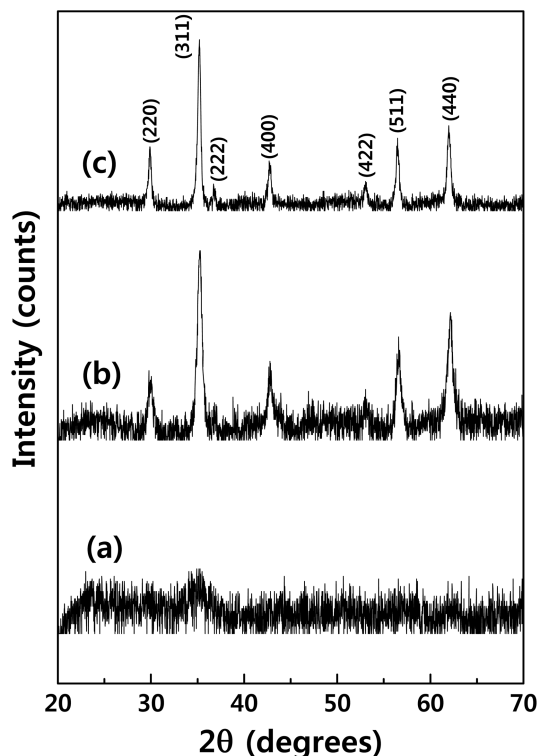


Fig. 1. X-ray diffraction patterns of $\text{Mn}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$ powder annealed at (a) 250°C, (b) 400°C and (c) 500°C.

size of the particles comparable to that of powders obtained using the ceramic and wet chemical method.

The size of the particles was determined from the diffraction peak broadening with the use of the Scherrer equation [10], $t = 0.9\lambda / (B \cos \theta_B)$, where λ represent the X-ray wavelength, B is the half width of the (311) peak, and θ_B is the angle of the (311) peak. The particle size of $\text{Mn}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$ increased with increasing annealing temperature to 20.73 nm (250°C), 45.68 nm (400°C), and 76.28 nm (500°C). Fig. 2 shows SEM images of the $\text{Mn}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$ powder. These photomicrographs were taken under the same magnification (2000 magnification) and at the same scale for sample. As the annealing temperature increase, some bigger grains are found to be embedded among the finer grains, and these grains increase in number as they increase in size.

Fig. 3 shows the X-ray diffraction patterns of the $\text{Mn}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($0.0 \leq x \leq 1.0$) powders annealed at 500°C. All peaks show the spinel ferrite. As the Zn, Co and Ni concentration increased, the lattice constants of the $\text{Mn}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$, $\text{Mn}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$ and $\text{Mn}_{1-x}\text{Ni}_x\text{Fe}_2\text{O}_4$ powders decreased linearly as shown in Fig. 4. The decrease of the lattice constant with an increasing Zn, Co and Ni concentration was related to the different radiuses of Mn^{2+} ions (0.91 Å), Zn^{2+} ions (0.74 Å), Co^{2+} ions (0.72 Å) and Ni^{2+}

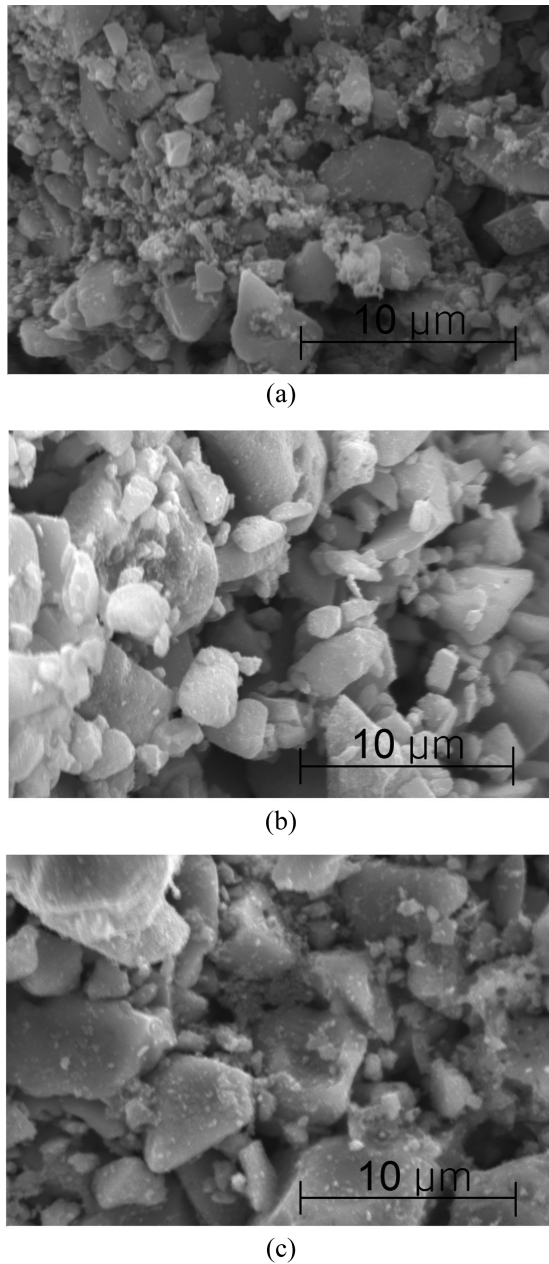


Fig. 2. SEM images of $\text{Mn}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$ powder annealed at (a) 250 °C, (b) 400 °C and (c) 500 °C.

ions (0.69 Å).

The Mössbauer absorption spectra measured at room temperature of the $\text{Mn}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ferrite powders annealed at 500 °C are shown in Fig. 5. The Mössbauer spectra of $\text{Mn}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($0.0 \leq x \leq 0.4$) could be fitted as the superposition of two Zeeman sextets due to the tetrahedral and octahedral sites of the Fe^{3+} ions. The Mössbauer spectra for $x = 0.6$ and 0.8 consisted of two Zeeman sextets and a single quadrupole doublet, which indicated the powders had a ferrimagnetic and paramagnetic nature, simultaneously.

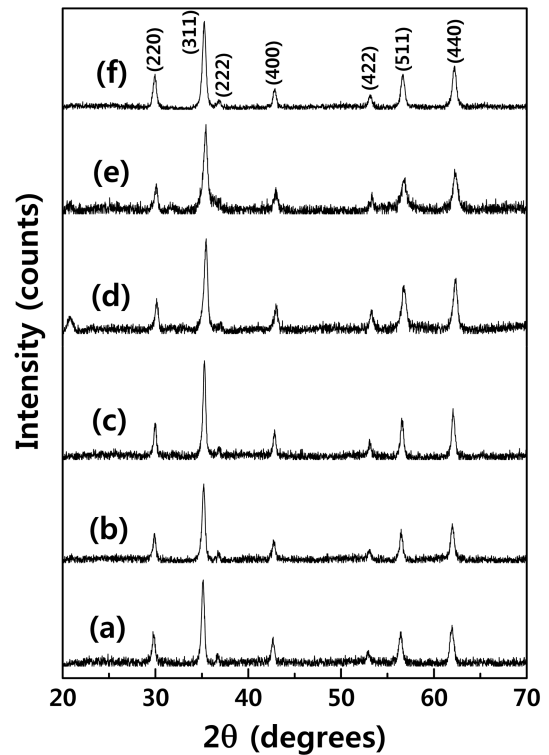


Fig. 3. X-ray diffraction patterns of $\text{Mn}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ powders annealed at 500 °C: (a) $x = 0.0$, (b) $x = 0.2$, (c) $x = 0.4$, (d) $x = 0.6$, (e) $x = 0.8$ and (f) $x = 1.0$.

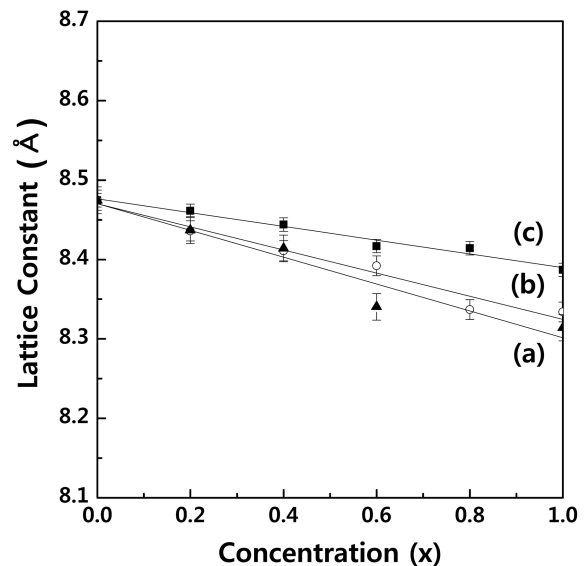


Fig. 4. The lattice constants of the $\text{Mn}_{1-x}(\text{Zn}, \text{Co}, \text{Ni})_x\text{Fe}_2\text{O}_4$ powders annealed at 500 °C: (a) Ni, (b) Co and (c) Zn.

As the Zn was introduced, the paramagnetic doublet appeared and became enhanced with increasing Zn concentration. This is partly due to the decreasing $\text{Mn}^{2+}\text{-O-Fe}^{3+}$ superexchange interaction as Zn substitutes for Mn. For x

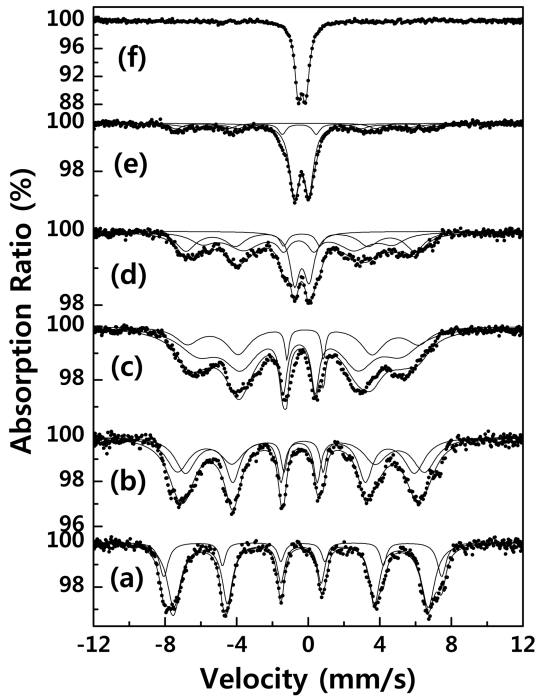


Fig. 5. Mössbauer spectra of $Mn_{1-x}Zn_xFe_2O_4$ powders at room temperature: (a) $x = 0.0$, (b) $x = 0.2$, (c) $x = 0.4$, (d) $x = 0.6$, (e) $x = 0.8$ and (f) $x = 1.0$.

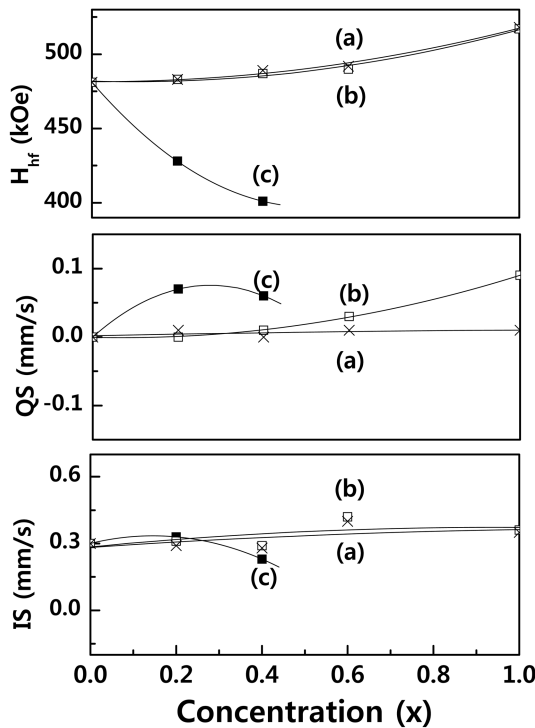
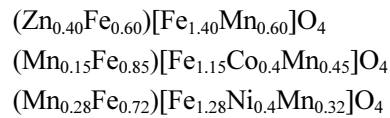


Fig. 6. Variation of the Mössbauer parameters: magnetic hyperfine field (H_{hf}), quadrupole splitting (QS), and isomer shift (IS) of the $Mn_{1-x}(Zn, Co, Ni)_xFe_2O_4$ powders: (a) Ni, (b) Co and (c) Zn.

$= 1$, we got only a paramagnetic spectrum. The Mössbauer spectra of the $Mn_{1-x}(Co, Ni)_xFe_2O_4$ ferrite samples annealed at $500^\circ C$ were also fitted with two Zeeman sextets subspectra that were assigned the tetrahedral A site and octahedral B sites of a typical spinel crystal structure [11].

Fig. 6 shows the variation of Mössbauer parameters of $Mn_{1-x}(Zn, Co, Ni)_xFe_2O_4$. H_{hf} is the magnetic hyperfine field, QS is the quadrupole splitting, and IS represent the isomer shift relative to metallic iron A-site in the Zeeman sextets. The H_{hf} is of Ni, and the Co ion-substituted Mn ferrite showed some increased values, but that of the Zn substituted Mn ferrite showed a decreased value. This can be related to the fact that Ni and Co ions are magnetic ions but Zn is a nonmagnetic ion. The increased QS values of the Zn and Co ions substituted Mn ferrite means that the electric field gradient is increased with substitution. However the IS value showed small changes with increasing substitution.

The cation distribution depends on many factors such as temperature, pressure, and composition [12, 13], as well as on the compound preparation method [14, 15]. Using an occupation preference of ions for A and B sites in a spinel structure and Zn, Co, and Ni ions located on the A and B sites, we can determine the cation distribution from the Mössbauer spectra of $Mn_{1-x}(Zn, Co, Ni)_xFe_2O_4$ ($x = 0.4$) annealed at $500^\circ C$ as



The magnetic properties of the $Mn_{1-x}(Zn, Co, Ni)_xFe_2O_4$

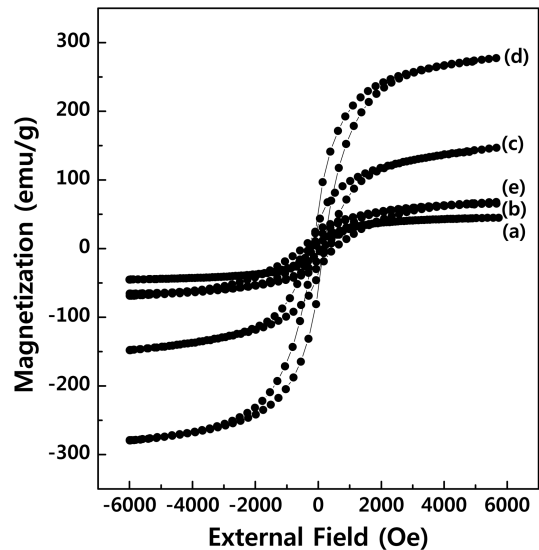


Fig. 7. Hysteresis curves of $Mn_{1-x}Co_xFe_2O_4$ ferrites: (a) $x = 0.0$, (b) $x = 0.2$, (c) $x = 0.4$, (d) $x = 0.6$ and (e) $x = 0.8$.

ferrite powders were determined at room temperature using a vibrating sample magnetometer. These hysteresis curves revealed a typical soft ferrite pattern. In Fig. 7, the magnetic properties measured at room temperature as a function of Co concentration show the hysteresis curves in the maximal field of 6 kOe. The saturation magnetization increased drastically with increasing the cobalt concentration up to $x = 0.6$ and then decreased. The coercivity increased up to $x = 0.8$ and then decreased. The increment of the saturation magnetization up to $x = 0.6$ in $Mn_{1-x}Co_xFe_2O_4$ could be qualitatively explained using the site distribution and the spin magnetic moment of the substituted ions. From the Mössbauer absorption area the octahedral Fe ions increased up to $x = 0.6$ and then decreased, and the Mn and Co ions decreased up to $x = 0.6$ and then increased. The substitution smaller magnetic moment ions ($Mn^{2+} = 5 \mu_B$, $Co^{2+} = 3 \mu_B$) by larger magnetic moment ions ($Fe^{3+} = 5 \mu_B$) could produce high values in saturation magnetization. Similar result was obtained by K. J. Kim in Mn-Co thin film [16]. In the $Mn_{1-x}Co_xFe_2O_4$ ferrite powder the maximum saturation magnetization and coercivity were 278.5 emu/g ($x = 0.6$) and 513.1 Oe ($x = 0.8$). These results are very high values in saturation magnetization and coercivity compared with pure manganese ferrite powders (53.85 emu/g and 124.64 Oe). Table 1 shows the saturation magnetization and coercivity of pure $MnFe_2O_4$ and of $Mn_{1-x}(Zn, Co, Ni)_xFe_2O_4$ ($x = 0.4$) ferrite powders annealed at 500 °C. The Zn, Co, and Ni substituted manganese ferrite powders were larger in saturation magnetization ($Mn_{0.6}Zn_{0.4}Fe_2O_4$; 62.64 emu/g, $Mn_{0.6}Co_{0.4}Fe_2O_4$; 147.30 emu/g, $Mn_{0.6}Ni_{0.4}Fe_2O_4$; 84.00 emu/g) than pure $MnFe_2O_4$ (53.85 emu/g). However, the coercivities of the $Mn_{0.6}Zn_{0.4}Fe_2O_4$ (59.49 Oe) and $Mn_{0.6}Ni_{0.4}Fe_2O_4$ (116.00 Oe) ferrite powders had smaller values than pure $MnFe_2O_4$ (124.64 Oe). However, the Co substituted manganese ferrite powders, $Mn_{0.6}Co_{0.4}Fe_2O_4$ (224.78 Oe), were larger in coercivity than pure $MnFe_2O_4$.

4. Conclusion

The Zn, Co, and Ni substituted manganese ferrite powders, $Mn_{1-x}(Zn, Co, Ni)_xFe_2O_4$, were fabricated by the sol-gel

Table 1. Saturation magnetization (M_s) and coercivity (H_c) of $Mn_{1-x}(Zn, Co, Ni)_xFe_2O_4$ ferrite powders annealed at 500 °C.

Samples	M_s (emu/g)	H_c (Oe)
$MnFe_2O_4$	53.85	124.64
$Mn_{0.6}Zn_{0.4}Fe_2O_4$	62.64	59.49
$Mn_{0.6}Co_{0.4}Fe_2O_4$	147.30	224.78
$Mn_{0.6}Ni_{0.4}Fe_2O_4$	84.00	116.00

method, and their crystallographic and magnetic properties were studied. Above 500 °C, all the ferrite powders had a single spinel structure and the lattice constants decreased with increasing substitution of Zn, Co, and Ni in $Mn_{1-x}(Zn, Co, Ni)_xFe_2O_4$.

For $Mn_{1-x}Zn_xFe_2O_4$ ($0.0 \leq x \leq 0.4$) ferrite powders, the Mössbauer spectra could be fitted as the superposition of two Zeeman sextets due to the tetrahedral and octahedral sites of the Fe^{3+} ions. However, Mössbauer spectra for $x = 0.6$ and 0.8 consisted of two Zeeman sextets and one single quadrupole doublet due to ferrimagnetic and paramagnetic. The spectrum $x = 1.0$ showed a doublet due to a paramagnetic phase. For the Co and Ni substituted manganese ferrite powders, all the Mössbauer spectra could be fitted as the superposition of two Zeeman sextets due to the tetrahedral and octahedral sites of the Fe^{3+} ions.

The hysteresis curves of the $Mn_{1-x}(Zn, Co, Ni)_xFe_2O_4$ ferrite powders revealed a typical soft ferrite pattern. The saturation magnetization increased with an increasing cobalt concentration up to $x = 0.6$ and then decreased in the $Mn_{1-x}Co_xFe_2O_4$. This increment could be explained using the site distribution and the spin magnetic moment of substituted ions. In the $Mn_{1-x}Co_xFe_2O_4$ ferrite powder the maximum saturation magnetization and coercivity were 278.5 emu/g ($x = 0.6$) and 513.1 Oe ($x = 0.8$). These results are very high values in saturation magnetization and coercivity compared with pure manganese ferrite powders (53.85 emu/g and 124.64 Oe). The saturation magnetization and coercivity of the $Mn_{1-x}Co_xFe_2O_4$ ($x = 0.4$) ferrite powders were also compared with pure $MnFe_2O_4$.

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