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Microstructure and Magnetic Property of Nanostructured NiZn Ferrite Powder

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ABSTRACT

Nanostructured spinel NiZn ferrites were prepared by the sol-gel method from metal nitrate raw materials. Analyses by X-ray diffraction and scanning electron microscopy showed the average particle size of NiZn ferrite was under 50 nm. The single phase of NiZn ferrites was obtained by firing at 250°C, resulting in nanoparticles exhibiting normal ferrimagnetic behavior. The nanostructured $Ni_{1-x}Zn_xFe_2O_4$(x = 0.0 ~ 1.0) were found to have the cubic spinel structure of which the lattice constants a_0 increases linearly from 8.339 to 8.427 Å with increasing Zn content x, following Vegard's law, approximately. The saturation magnetization M_s was 48 emu/g for x = 0.4 and decreased to 8.0 emu/g for higher Zn contents suggesting the typical ferrimagnetism in mixed spinel ferrites. Pure NiZn ferrite phase substituted by Cu was observed before using the additive but hematite phase was partially appeared at $Ni_{0.2}Zn_{0.2}Cu_{0.6}Fe_2O_4$. On the other hand, the hematite phase in this NiZnCu ferrite was disappeared after using the additive of acethyl aceton with small amount. The saturation magnetization M_S of $Ni_{0.2}Zn_{0.8-y}Cu_yFe_2O_4$(y = 0.2~0.6) as measured was about 51 emu/g at 77 K and 19 emu/g at room temperature, respectively.

Key words : Sol-gel process, Nano-ferrites, NiZn ferrites, Ferrimagnetic behavior

1. Introduction

Conventional ceramic method and coprecipitation are popular processing route of ceramics, but there are many difficulties to obtain the single phase in processing for mixed ferrites system.[1-6] The capability of producing nanosized ferrite powders is important in tailoring the geometry and properties of magnets produced by powder metallurgical processes. Recently, it is reported that the nanostructured ferrite is also expected to have many new applications with the unique properties.[7,8]

While conventional methods require high temperature to obtain ferrite powders, sol-gel processing can provide the new ways to prepare nanoparticles at relatively low temperature. The magnetic characteristics of the material are strongly affected when the particle size becomes very small, due to the influence of thermal energy over the magnetic moment ordering, originating the paramagnetic relaxation phenomenon. Microstructures and magnetic properties were investigated in this study with nanosized ferrimagnetic NiZn ferrites powders prepared by the sol-gel process at a low temperature below 300°C.

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2. Experimental Procedures

NiZn ferrite, $Ni_{1-x}Zn_xFe_2O_4$(x=0~1.0) and NiZnCu ferrite, $Ni_{0.2}Zn_{0.8-y}Cu_yFe_2O_4$(y = 0.2~0.6) were prepared by the sol-gel process using metal nitrates as precursors. Ni(II) nitrate, Zn(II) nitrate, Cu(II) nitrate and iron(III) nitrate were dissolved in ethylene glycol corresponding to the equivalent amount of each metal ion. The solution was stirred with addition of distilled water and reacted for 2 h at room temperature before holding at 80 for 3 h. The gel product from those solution was heated at 250°C for 12 h to obtain the single phase of spinel ferrites.

As prepared spinel ferrites were characterized with X-ray diffractometer to define the crystal phase and Vibrating Sample Magnetometer(VSM) for analysis of magnetic properties with applied field of 10 kOe. The morphology of ferrite nanoparticles was imaged by Field Emission-Scanning Electron Microscope(FE-SEM) with an accelerating voltage of 7 kV.

3. Results and Discussions

3.1. NiZn ferrite

X-ray diffraction patterns of $Ni_{1-x}Zn_xFe_2O_4$ powders in the composition range $0 \leq x \leq 1.0$ as received were presented in Fig. 1 which confirms the formation of good crystallization with single phase of spinel structure except for $ZnFe_2O_4$ (x = 1.0). As shown in Fig. 1, it was found that the major phase in the composition range $0 \leq x \leq 1.0$ was the spinel phase and hematite (α-Fe_2O_3) phase was observed in

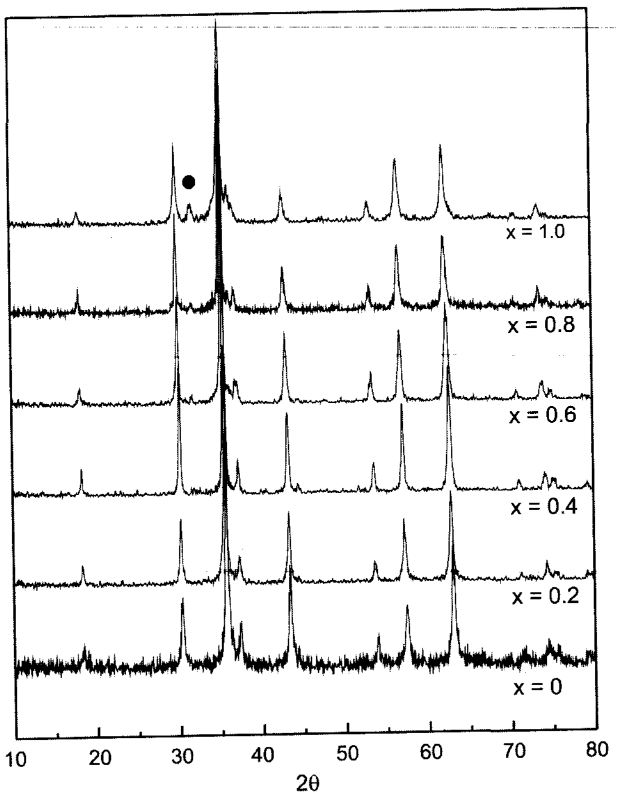

Fig. 1. X-ray diffraction patterns of $Ni_{1-x}Zn_xFe_2O_4$ in this study (as marked : α-Fe_2O_3 phase).

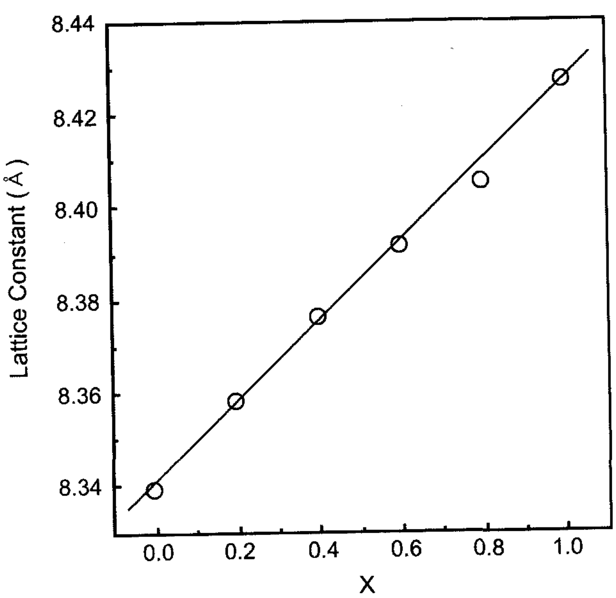

Fig. 2. Lattice constants of $Ni_{1-x}Zn_xFe_2O_4$ with Zn content x.

$ZnFe_2O_4$(x=1.0). Average particle size, as estimated by using Scherrer's equation in the range of 30~70 nm with Zn content.

The lattice constants a_0 of $Ni_{1-x}Zn_xFe_2O_4$(x=0~1.0) were calculated by using the Nelson-Riley function[9] Eq. (1) and the result was presented in Fig. 2.

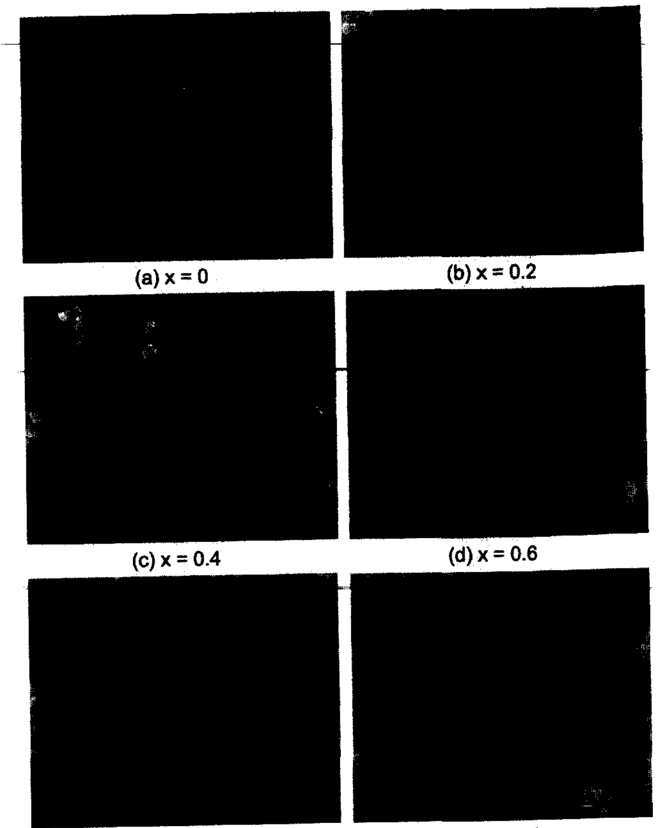

Fig. 3. FE-SEM images of $Ni_{1x}Zn_xFe_2O_4$ nanoparticles synthesized by the sol-gel process.

$$a_o = \frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta}\right) \qquad (1)$$

From the result of Fig. 2, it is shown that the variation of lattice constant for NiZn ferrite synthesized by the sol-gel process was well fitted with the Vegard's law in spinel ferrites. In general, the linear increasing of cell parameters in Fig. 2 suggests the full substitution of Zn in the spinel ferrite framework based on occupation of Zn ions due to the preference for the tetrahedral sites.[10-12] The Vegard's law confirms the formation of spinel ferrite at a low temperature in this study and allows the relationship between the composition and lattice constant as shown in Fig. 2.

Fig. 3 shows that the images of NiZn ferrite powders were observed by FE-SEM as agglomerated, but the nanosized spherical particles were under 100 nm which is expected to be applied as EMI polymer composite absorber.

Magnetic measurements of NiZn ferrrite nanoparticles carried out by VSM were shown in Fig. 4. It is shown that the result for magnetic measurements in Fig. 4 follows the typical ferrimagnetic behavior exhibited in mixed inverse spinel ferrites from ionic distribution.[12] According to the magnetic properties shown in Fig. 4, the saturation magnetization M_s was about 48 emu/g with the compostion of x = 0.4 and decreased to 12.0 emu/g with high Zn content measured at room temperature which means the typical ferri-

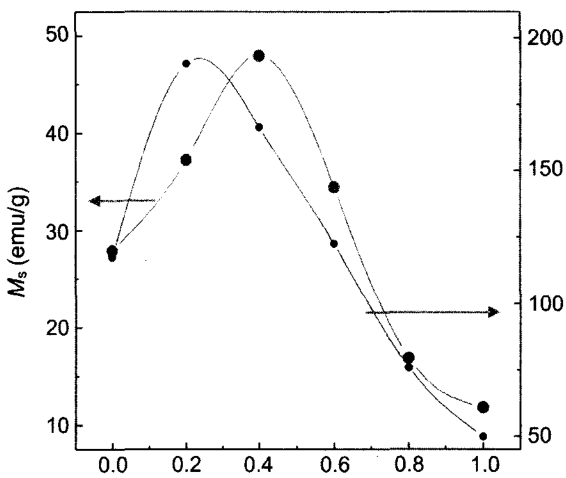

Fig. 4. Magnetic saturation (M_s) and coercivity (H_c) of $Ni_{1-x}Zn_xFe_2O_4$ powders as a function of Zn content x measured at room temperature.

Table 1. Particle Size of $Ni_{1-x}Zn_xFe_2O_4$ Powder with Zn Content x

x	0	0.2	0.4	0.6	0.8	1.0
Particle Size[a] (nm)	66.82	49.07	36.26	36.27	42.0	41.68

[a] calculated by Scherrer's equation

Table 2. The Relationship Between Particle Size and Saturation Magnetization of $NiFe_2O_4$

Particle Size (nm)	Saturation Magnetization (M_S, emu/g)
≥ 1,000	55.87[1)]
≤ 100	27.93[2)]

[1)] calculated, $\frac{M_S(emu/cm^3)}{d_x(g/cm^3)}$

d_x : X-ray density of $NiFe_2O_4$(5.3730 g/cm^3)

[*referred from E. W. Gorter, Philips Res. Rept., 9, 295(1954)*]

[2)] experimental data in this study

magnetism in mixed ferrites.

The decrease in saturation magnetization with decreasing particle size has been reported by Morrish.[13)] Furthermore, the magnetization of inverse spinel ferrites was influenced by occupation of nonmagnetic ion in spinel structure.[12)] Table 1 also indicated the particle size of NiZn ferrite powder with Zn content calculated by Scherrer's equation. The results of Fig. 4 and Table 1 suggest that NiZn ferrite synthesized at such a low temperature(250°C) formed well crystallized spinel phase in this study. As shown in Table 2, the decreasing of saturation magnetization for $NiFe_2O_4$ in this experimental result can be clearly explained from decreasing the particle size of $NiFe_2O_4$ prepared by the sol-gel process for comparison. The variation of saturation magnetization with particle size was presented in Table 2 with size over 1,000 nm which was normally prepared by conventional ceramic processing. In this experimental procedure, the particle size of NiZn ferrites was obtained below 100 nm with nanostructure and the saturation magnetization was presented which is much less than that of the calculated value in Table 2. Therefore, it is also found that the decreasing of particle size can be followed by the reduction of saturation magnetization in this study.

3.2. NiZnCu ferrite

NiZn ferrite has an attractive properties of high Curie point, high resistivity and low dielectric loss which are sensitive to the composition, microstructure and heating temperatures. By introducing a small amount of substituted ion, it is shown that an important variation of microstructure and magnetic properties.

XRD patterns of $Ni_{0.2}Zn_{0.8-y}Cu_yFe_2O_4$ powders for compositions in the range $0.2 \leq y \leq 0.6$ synthesized by the sol-gel process was obtained the single phase of well crystallized spinel structure except the composition of y = 0.6 shown in Fig. 5. The reaction between Fe^{3+} and ethylene glycol is dominantly formed in the sol-gel system using nitrates.[14)] The increas-

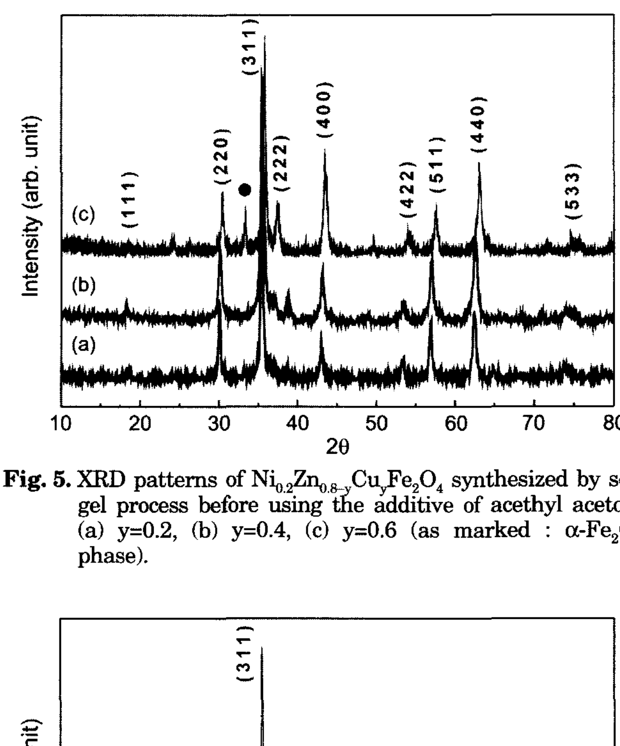

Fig. 5. XRD patterns of $Ni_{0.2}Zn_{0.8-y}Cu_yFe_2O_4$ synthesized by sol-gel process before using the additive of acethyl aceton; (a) y=0.2, (b) y=0.4, (c) y=0.6 (as marked : α-Fe_2O_3 phase).

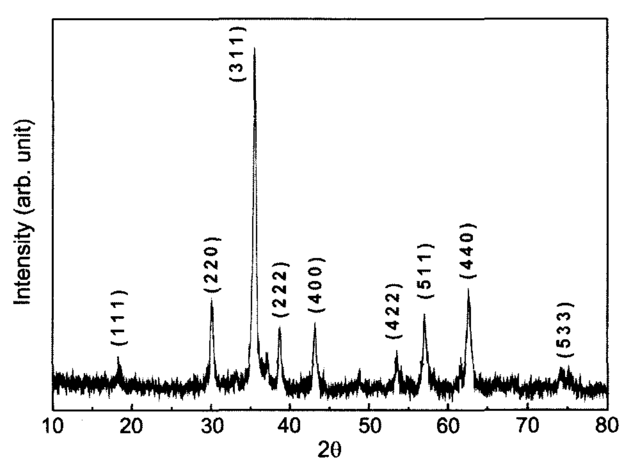

Fig. 6. XRD pattern of $Ni_{0.2}Zn_{0.2}Cu_{0.6}Fe_2O_4$ synthesized by the sol-gel process after using the additive of acethyl aceton.

Table 3. Properties of NiZnCu Ferrites with Additive in Reaction

	Lattice constant (Å)	Particle size (nm)	Saturation magnetization, M_S (emu/g)	Coercivity, H_C (Oe)
Before using AcAc[a)]	8.3948	10~20	25.3	88.6
After using AcAc	8.3492	≤ 10	19.22	48.1

[a)]Acethyl Aceton

Fig. 7. Field emission-SEM image of $Ni_{0.2}Zn_{0.6}Cu_{0.2}Fe_2O_4$ powder with addition of acethyl aceton.

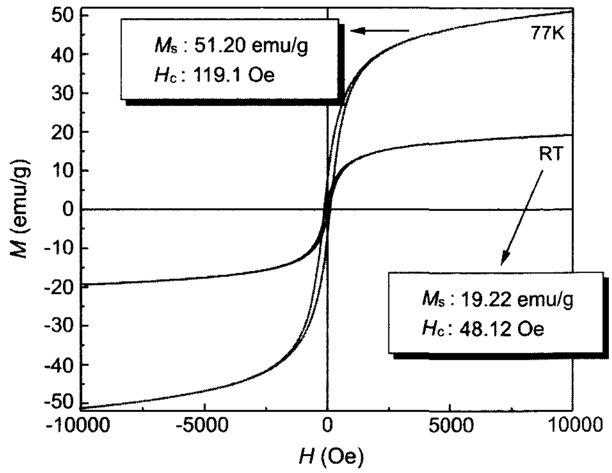

Fig. 8. Magnetic properties of $Ni_{0.2}Zn_{0.6}Cu_{0.2}Fe_2O_4$ with addition of acethyl aceton measured by vibrating sample magnetometer at room temperature and 77 K.

ing of Cu content in NiZn ferrite acts a role to make the main reaction between ferric ion(Fe^{3+}) and ethylene glycol retarded and produce extremely small amount of hematite as unreacted.

It was attempted to use an additive in order to make homogeneous particle and remove the residual hematite phase in NiZnCu ferrites. Fig. 6 shows the XRD pattern of NiZnCu ferrite synthesized by the sol-gel process with addition of acethyl aceton. It is clearly presented that hematite peak as marked in Fig. 5 was disappeared and formed the single phase of spinel NiZn ferrite. It also seems to be related with the reaction mechanism and variation of properties with starting materials including the additive as shown in Table 3.

The microstructure of NiZnCu ferrite powders was observed by FE-SEM presented in Fig. 7 which was shown as agglomerated, but it can be found that the particle size of the each spherical-shaped was around 10~20 nm. The magnetic properties of NiZnCu ferrite powders as received were measured using vibrating sample magnetometer at room temperature and 77 K, as shown in Fig. 8. The saturation magnetization M_S as measured was about 51 emu/g at 77 K and 19 emu/g at room temperature, respectively. This difference in magnetic measurement as shown in Fig. 8 can be dependent on the thermal vibration in spin moment of nanostructured NiZnCu ferrite particles at higher temperature. The magnetic characteristics of the material are strongly affected when the particle size becomes extremely small, due to the influence of thermal energy over the magnetic moment ordering which is originating the paramagnetic relaxation phenomenon of typical ferrimagnetic behavior with dependence of temperature.[11,12)]

4. Conclusion

Nanostructured NiZn ferrites powders were prepared by the sol-gel process from metal nitrates at 250°C in this study. The result of magnetic measurements(M_S, H_C) provided to indicate the formation of spinel structure of NiZn ferrites. The effect of additive on formation of NiZn ferrite was also investigated to obtain homogeneous nanosized powder and single spinel phase. As shown by VSM data measured at room temperature, NiZn ferrites nanoparticles exhibited ferrimagnetic spinel structure. These studies showed that the nanosized NiZn ferrites with good ferrimagnetism could be prepared at a low temperature 250°C. The critical difference in magnetic hysteresis measured at 77 K and room temperature showed the ferrimagnetic behavior of nanostructured NiZnCu ferrite powder with temperature dependency.

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