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Complex Permittivity and Permeability of Magnesium-Copper Spinel Ferrite under Heat-treatment Conditions

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We studied the complex permittivity and permeability properties of magnesium-copper spinel ferrite under various heat-treatment conditions. We simulated two types of materials: dielectric and magneto-dielectric. Dielectric materials show the miniaturization of the antenna; however, decreases of bandwidth and efficiency are observed. Magneto-dielectric materials show the capability of improvement of bandwidth and efficiency with a miniaturization of the antenna. The target properties were established from simulated results of permittivity and permeability <10, and permittivity/permeability ≈ 1. Magnesium spinel ferrite was shown to increase the permittivity (from 7 to 11.7) and the permeability (from 5.5 to 8.2) with an increase of sintering temperature (from 1,150°C to 1,350°C). However, the high sintering temperature (1,350°C) affected the increase of permittivity more than it did the permeability, and this condition deteriorated the ratio, loss, and resonance frequency. These problems were overcome with the substitution of copper (of formula $Mg_{0.9}Cu_{0.1}Fe_2O_4$), the addition of a sintering agent (alginate 1 wt%), and the condition of a lower sintering temperature (1,250°C). The new conditions showed equal value (≈ 9.5) of the permittivity and permeability.

Keywords: spinel ferrite, permittivity, permeability, heat treatment

1. INTRODUCTION

Recently, the miniaturization of antennas is a major issue in the RF industry. Ideas of miniaturization revolve around the physical dimensions of an antenna for the latest compact and smart phones. The antenna size is decided by the wavelength and the electrical properties of the base frame material of the antenna, such as permittivity and permeability.[1-2] Therefore, various technologies have been investigated for the improvement of these properties for miniaturization of antennas. However, these investigations were limited by an increase of the permittivity of the base frame material. High permittivity proved useful in the miniaturization of antennas, but induced a decrease of antenna bandwidth. This problem can be overcome through the inclusion of permeability. Miniaturization of an antenna follows the rule $\lambda=\lambda_0/\sqrt{\varepsilon_r\mu_r}$. Thus, the use of both permittivity and permeability is more effective than the use of one of these properties alone. Excessively high permittivity and permeability are not good for the antenna's efficiency. High permittivity and permeability are induced to maximize the miniaturization of the antennas; therefore, the radiator and base frame of an antenna can be minimized, but the antenna efficiency is decreased because the radiator of the antenna is too small. Thus, the permittivity and permeability should be under 10. The main focus for this problem is in the material design.

Ferrites show promise for technical applications, such as transformer cores, magnetic memories, noise filters, isolators, circulators, and so forth.[1-4] They are particularly in the spotlight for microwave communications because they have both dielectric and magnetic properties (they are called "magneto-dielectric" materials).[3] The properties of this compound are useful for miniaturizing antennas with wide bandwidths. The dielectric and magnetic properties of ferrite can be changed by the substitution of various elements (such as Mg^{2+}, Cu^{2+}, Co^{2+}, Zn^{2+}, Mn^{2+}, Ni^{2+} and so forth) and under certain heat-treatment conditions. Magnesium spinel ferrite has a low loss within a simple structure; however, improvement of its magnetic properties is difficult. This difficulty is overcome by the substitution of elements and by varying heat-treatment conditions.[5-7] The substitution of copper can change grain growth and high heat-treatment condition, thereby increasing permittivity and permeability. These methods do have some weak points, such as loss and resonance frequency. Thus, we need to study the change of permittivity and permeability with substituted formulas and various heat-treatment conditions.

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In this paper, magneto-dielectric materials with various heat-treatment conditions and the substitution of copper are studied.

2. EXPERIMENT

2.1. Simulation of Antenna

We simulated antennas with dielectric material that have permittivity of 25, 50, 100, and 400 and magneto-dielectric material that has permittivity of 10 and permeability of 5 and 10 at high frequency. Antenna was designed as a simple patch type and was simulated using a high frequency structuring simulation (HFSS, Ver. 11.0, Ansoft Co., Ltd.). The conditions of simulated materials are shown in Table 1.

Table 1. Conditions of simulated materials

	Permittivity	Permeability	Permittivity× Permeability	Permittivity/ Permeability
A	25	1	25	25
B	50	1	50	50
C	100	1	100	100
D	400	1	400	400
E	10	5	50	2
F	10	10	100	1

1) Antenna patch size = 150×150 mm^2

2) Substrate size = 300×300×20 mm^3

2.2. Preparation of Mg-based Spinel Ferrite Particles

Experimental raw materials were magnesium oxide (MgO, 98%, Junsei Chemical Co., Inc.), iron (III) oxide (Fe_2O_3, 99%, Kanto Chemical Co., Ltd.), and copper oxide (CuO, 97.5%, Yakuri Pure Chemicals Co., Ltd) for the preparation of spinel ferrite. Samples were studied to determine formula of start materials and heat-treatment conditions. Samples were then mixed by solid state reaction for 24~96 hours with steel balls in a jar. The mixed particles were first treated at 1,000°C for 2 hours in the air and oxygen. Then they were remixed with 0~5 wt% alginate (ammonium alginate, Waco Pure Chemical Industries, Ltd) and pressed into disk (outside diameter 18 mm, thickness > 2 mm) and toroidal (outside diameter 18 mm, inside diameter 11 mm, thickness > 2 mm) types. Finally, samples were sintered at various temperatures (from 950°C to 1,350°C) for 2 hours at a heating rate of 5°C/min.

2.3. Characterization of Properties

The phase compositions of the samples were analyzed by X-ray diffractometry (X'pert PW1827, Philips) using Cu Ka radiation. The complex permeability and permittivity of the samples were measured using an RF Impedance/Materials Analyzer (E4991A, Agilent) with test fixtures (16453A and 16454A).

3. RESULTS AND DISCUSSION

3.1. Results of Simulation

We simulated the effect of various electric and magnetic properties of certain materials. There were two types of material: dielectric and magneto-dielectric. The simulated results are summarized in Table 2.

Simulated dielectric materials (samples A, B, C, and D) show the miniaturization of the antenna; however, decreases of bandwidth and efficiency with an increase of permittivity are observed. Magneto-dielectric materials (samples E and F) show not only a miniaturization of the antenna, but also improvements in bandwidth and efficiency. In particular, permittivity = permeability (sample F) was better than permittivity > permeability (sample E) in bandwidth and efficiency. Permittivity that was too high (sample D) deteriorated the efficiency of the antenna. Thus, permittivity and permeability of the material must be under 10 for the antenna, and almost an equal value for impedance matching in free space (permittivity/permeability=1).[3] These results are interpreted in the following equations.

At the substrate of the antenna, the wavelength is estimated by Equation 1.

$$\lambda = \frac{\lambda_0}{\sqrt{\varepsilon_r}} \tag{1}$$

λ is the effective wavelength determined by the permittivity of material, and λ_0 is the wavelength in a vacuum. The effective wavelength can be derived from Equation 1. This equation is modified by the addition of permeability, as follows.

$$\lambda = \frac{\lambda_0}{\sqrt{\varepsilon_r \mu_r}} \tag{2}$$

Thus, these materials show the same effect on the miniaturization of the antenna if the square of permittivity and multiplication of permittivity and permeability show equal values.

Table 2. Bandwidth of simulated materials

	A	B	C	D	E	F
Resonant frequency (f_0, MHz)	182	129	92	47	158	110
Patch size in wave length (λ_0)	9/100	6/100	5/100	2/100	8/100	6/100
Bandwidth (%, VSWR = 3)	3.30	3.10	3.26	3.19	15.82	17.27
Efficiency (%)	51.92	42.29	36.64	35.89	81.06	88.72

For example, permittivity = permeability = 10 and permittivity = 100 are equivalent for the miniaturization of antenna.

The bandwidth of antenna can be approximated by Equation 3.

$$Bandwidth \approx \frac{96\sqrt{\frac{\mu_r}{\varepsilon_r}},\frac{t}{\lambda_0}}{\sqrt{2\left|4+17\sqrt{\mu_r\varepsilon_r}\right|}} \qquad (3)$$

In Equation 3, the bandwidth of the magneto-dielectric material is wider than that of the dielectric material.[8] Thus, a magneto-dielectric material is more useful than a dielectric material for miniaturization and a broad bandwidth of antenna.

3.2. Crystal Structures

Figures 1 and 2 are the XRD patterns of the represented Mg spinel ferrite ($MgFe_2O_4$) with two steps at different heat-treatment conditions. The fast-heated sample is not found in the second phase, but the slow heated samples were observed at the peak of the iron oxide phase. These results show that the fast heating rate is more affected by the crystallization of the main phase. In other words, supposing that the major phase grows up faster than the minor phase via fast heat treatment, a minor phase, such as that of iron oxide, is reduced by the second heat treatment. This temperature must be higher than the first heat treatment temperature. Mg-Cu spinel ferrite ($Mg_{0.9}Cu_{0.1}Fe_2O_4$) was similar to XRD patterns with Mg spinel ferrite, as shown in Figure 3. These results relate the lattice constant of Cu and Mg, the details of which were reported by D. N. Bhosale. *et al.*[9]

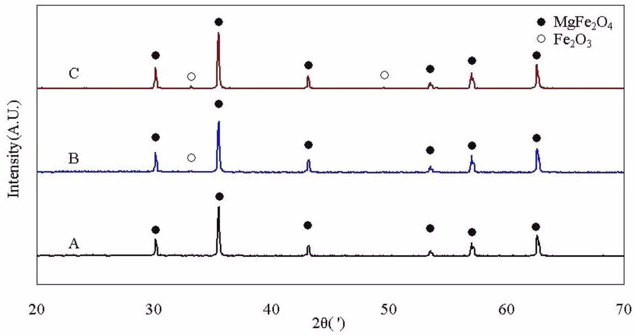

Fig. 1. XRD patterns of the $MgFe_2O_4$ with different first heat-treatment conditions, A : 5°C /min, in air, B : 1°C/min, in oxygen, C : 1°C/min, in air.

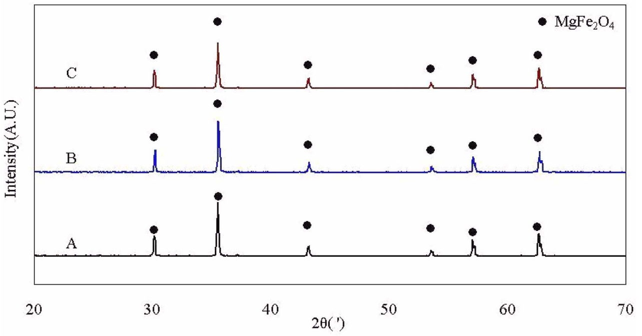

Fig. 2. XRD patterns of the $MgFe_2O_4$ with different heat-treatment conditions, after second heat-treatment at 1,150 °C, A : 5°C/min, in air, B : 1°C/min, in oxygen, C : 1°C/min, in air.

3.3. Mg-Spinel Ferrite

Figure 4 shows the complex permittivity and permeability of the $MgFe_2O_4$ at different mixing times. The real (6.9~7.3) and imaginary (close to 0) part of permittivity and the real (4 ~4.5) part of permeability show similar values. The 24-hour mixed sample (iron oxide peak observed) shows the highest

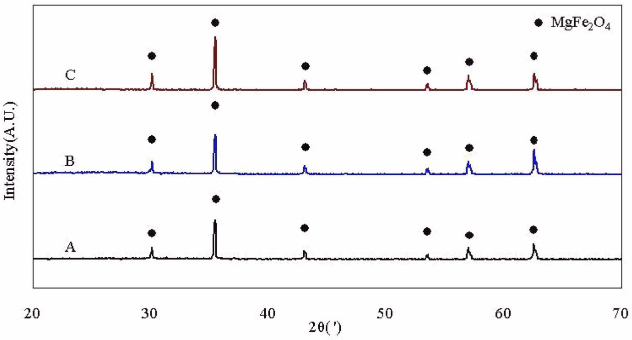

Fig. 3. XRD patterns of the $Mg_{0.9}Cu_{0.1}Fe_2O_4$ with different heat-treatment conditions. A : 1,000°C, B : 1,250°C, C : 1,350°C.

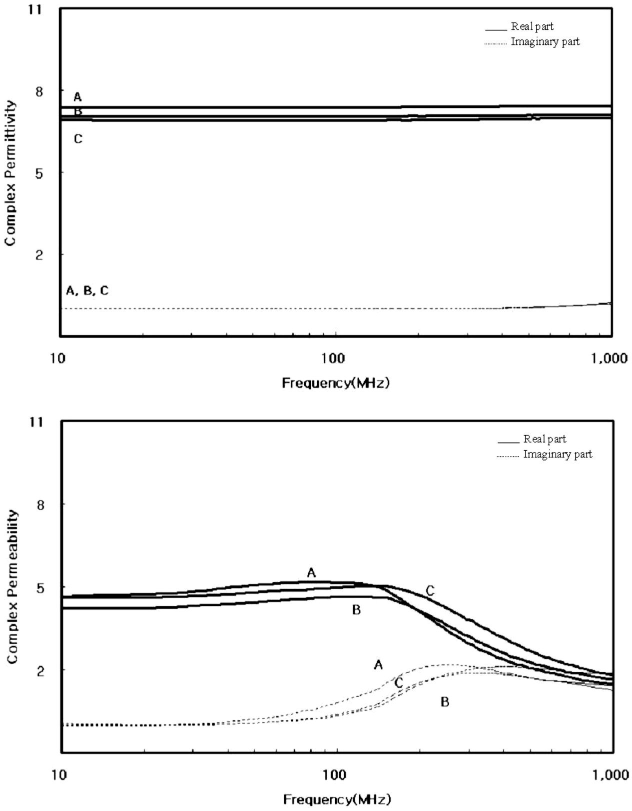

Fig. 4. Complex permittivity and permeability of the $MgFe_2O_4$ with different mixing time, A : 24 hours, B : 48 hours, C : 96 hours.

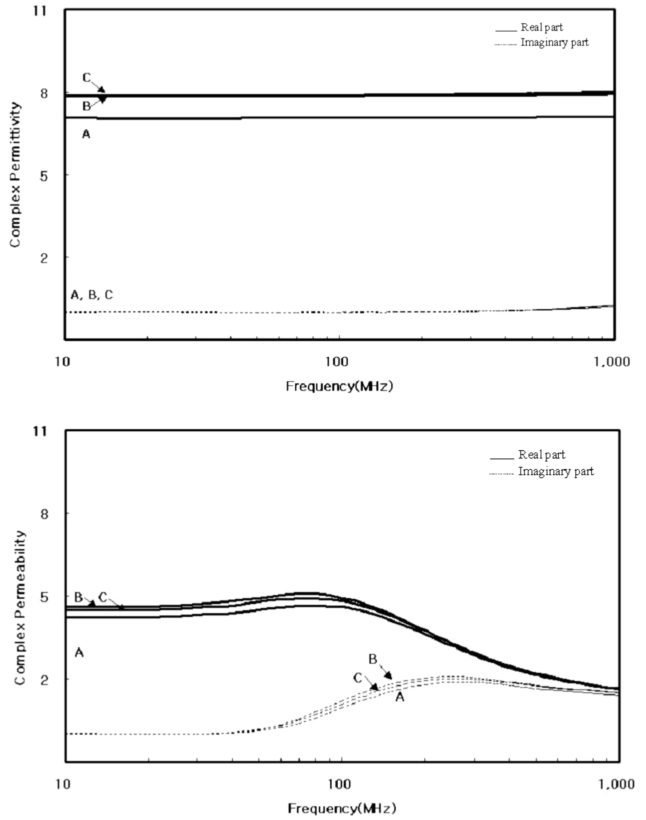

Fig. 5. Complex permittivity and permeability of the $MgFe_2O_4$ with different first heat-treatment conditions, A : 5°C/min, in air, B : 1°C/min, in oxygen, C : 1°C/min, in air.

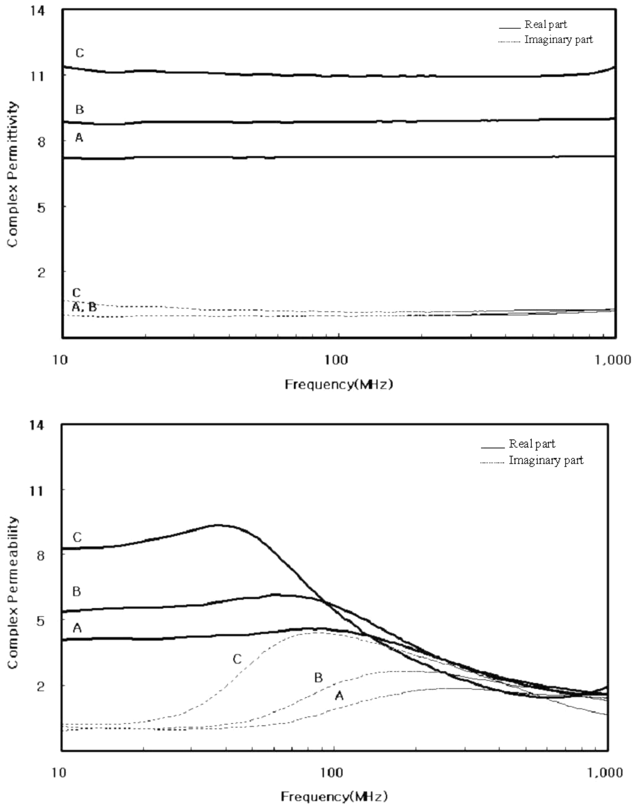

Fig. 6. Complex permittivity and permeability of the $MgFe_2O_4$ with different second heat-treatment temperature, A : 1,150°C, B : 1,250°C, C : 1,350°C.

imaginary part of permeability. The imaginary part of permeability of the 48-hour mixed sample is lower than those of the other samples. The ratio of permittivity and permeability was 1.56~1.75. The real and imaginary parts of permittivity of the 96-hour mixed sample are lower than those of the other samples and the real and imaginary part of permeability show value between the 24- and 48-hour mixed samples.

Figure 5 shows the complex permittivity and permeability of the $MgFe_2O_4$ with different first heat-treatment conditions. The real parts of permittivity and permeability of conditions B and C show a similar value (≈8 and 5.5) and ratio (≈1.45), but the imaginary part increased from 60 MHz; therefore, the loss of permeability was degraded, and the resonant frequency shifted to the low band. These results suggest that the slow heating rate affected the grain growth. Also, oxygen served to increase permittivity more than it increased permeability.

Figure 6 shows the complex permittivity and permeability of the second heat-treated $MgFe_2O_4$ (first heated at 1,000° C) at various temperatures. All samples were observed in the rapid rise of the complex permittivity and permeability with an increase of the treatment temperature. Condition C (Figure 6) shows the highest value (the real part of permittivity ≈11.7 and permeability≈8.2) and the best ratio (≈1.43) in this conditions (A≈1.78, B≈1.65); however, the imaginary part was increased from 20 MHz, and the resonant frequency was moved to the low band. The permittivity, permeability, and loss of magneto-dielectric material were related to various factors at the high frequency. These are microstructures of materials such as low volume fractions of pores, impurities, dislocations, grain size, and thickness of the grain boundary; chemical composition such as small magneto-crystalline anisotropy, magneto-striction, and saturation magnetization; and electrical resistivity.[10] Thus, the control of permittivity, permeability, and loss can be accomplished through changes in these factors. For example, high values of permittivity and permeability are achieved with an increase of heat-treatment temperature, but this method results in a deterioration of resonant frequency and loss. A small excess of Fe can minimize the hysteresis loss, but leads to a decrease in permeability. Therefore, we must control these factors through various preparation conditions. For the purposes of this paper, we designed the appropriate material (permittivity = permeability under 10) through a substitution of copper, low heat-treatment conditions, and aid for sintering.

3.4. Mg-Cu Spinel ferrite

Figure 7 shows the complex permittivity and permeability

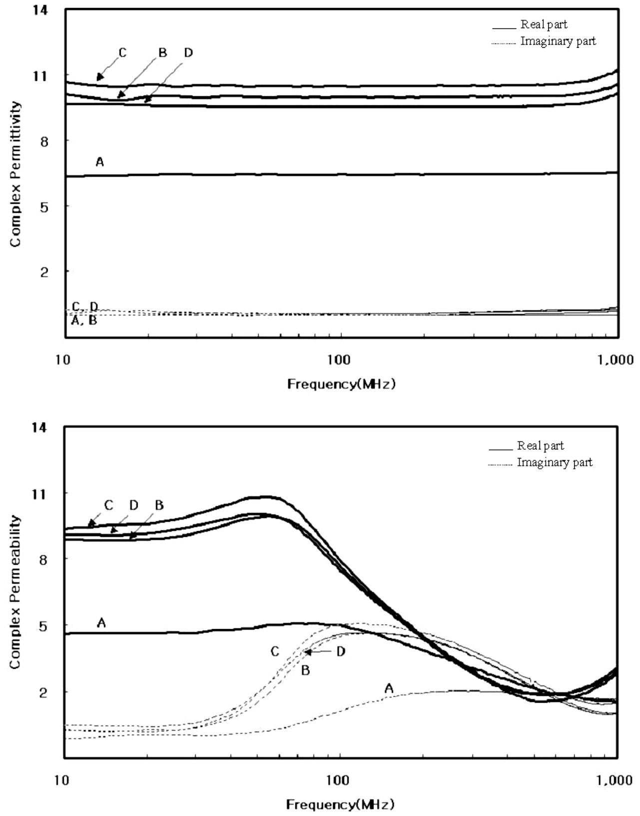

Fig. 7. Complex of permittivity and permeability of the $Mg_{0.9}Cu_{0.1}Fe_2O_4$ with different second heat-treatment (first heat-treatment at 1,000°C) conditions, A : 1,000°C, B: 1,250°C, C : 1,350°C, D: 1,250°C (with alginate 1 wt%).

of the second heat-treated $Mg_{0.9}Cu_{0.1}Fe_2O_4$ (first heated at 1,000°C) at various temperatures. The substitution of copper increased the value of the complex permittivity and permeability. Conditions B (the real part of permittivity≈10, permeability≈9) and C (the real part of permittivity≈10.6, permeability≈9.5) show a ratio (≈1.11 and 1.12) better than ratios of the previous samples. Condition B is more useful than Condition C because permittivity and permeability must be under the value of 10, as seen in Table 2. Condition B shows that the imaginary part of permeability increases from 30 MHz; therefore, a higher-frequency operation is available with the Mg-spinel ferrite, as shown in Figure 6(c). Condition D (with sintering aid) shows the best value of ratio (≈1.00), permittivity (≈9.5, at 30 MHz), and permeability (≈ 9.5, at 30 MHz) in this experiment. Copper was reported to have a low melting point (1,235°C) for liquid-phase sintering, which affected the rearrangement of grains on their formation in the liquid phase. This is due to the inclusion of copper, which affected grain growth at low temperatures. The sintering aid affected grain growth as well.[11] The alginate served to decrease permittivity and increase permeability. We found an improvement of electrical properties from the use of alginate.

4. CONCLUSIONS

This paper studied magneto-dielectric materials for the simulation of antennas and considered the importance of the preparation of materials. In simulated results, magneto-dielectric material was shown as useful not only in the miniaturization of antennas, but also in creating conditions of increased bandwidth. The target properties were established from the simulated results; in this paper, these were permittivity and permeability <10, and permittivity/permeability≈1. Magnesium spinel ferrite showed an increase in permittivity and permeability with an increase in the sintering temperature. However, the increase of the sintering temperature caused a rise of permittivity more than it did a rise of permeability; however, increase of sintering temperature also caused a deterioration of ratio of permittivity/permeability, loss, and resonance frequency. These problems were overcome through substitution of copper ($Mg_{0.9}Cu_{0.1}Fe_2O_4$), the addition of a sintering agent (alginate 1 wt%), and a lower sintering temperature (1,250°C). New conditions were shown to have an equal value (≈9.5) of permittivity and permeability.

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