THE EFFECT OF Cu SUBSTITUTION ON THE PROPERTIES OF NiZn FERRITE

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Abstract **– The effect of Cu substitution on the properties of NiZn ferrites sintered at low temperature with composition is investigated. The densification of NiCuZn ferrite is dependent upon Cu content in the composition of $(Ni_{0.5-x}Cu_xZn_{0.5}O)(Fe_2O_3)_{0.98}$. Electrical resistivity is maximum at x=0.2. Dispersion characteristics of complex permeability of $(Ni_{0.5-x}Cu_xZn_{0.5}O)(Fe_2O_3)_{0.98}$ is observed above x=0.3 and relaxation frequency increases with higher temperature. The magnetic loss of NiCuZn ferrite is occurred above the Cu content x=0.3 at a low frequency.**

I. INTRODUCTION

Polycrystalline ferrites have been used widely in many electronics devices because of its excellent characteristics in applications. Recently, the surface mounting devices have been rapidly developed for electronics applications, such as a multilayer chip bead or inductor. To achieve a reliable performance of multilayer ferrites, it is important to study the composition of low temperature-sintered ferrite co-firing with Ag electrode.

There has been a growing interest in NiCuZn ferrites for the application in producing multilayer -type chips mainly because these ferrites can be sintered at a relatively low temperature with a wide a range of composition. In particular, the addition of Cu in the composition has been known to play a crucial role in dropping the firing temperature.

The purpose of this study is to investigate the effects of Cu substitution on the properties of NiZn ferrite sintered at low temperature with composition.

II. EXPERIMENT

NiCuZn ferrites, $(Ni_{0.5-x}Cu_xZn_{0.5}O)(Fe_2O_3)_{0.98}$, were prepared by a solid-state reaction method with NiO, CuO, ZnO and α-Fe_2O_3 as starting materials. These constituent chemicals were mixed according to the stoichiometric ratios for the corresponding compositions and the mixed powders were calcined at 750℃ to obtain the spinel phase. For the measurement of properties, samples with toroid- and pellet-shape were prepared by firing relevant green bodies at 900-1300℃. The dc resistivity of the specimen was calculated from the measured resistance using a high resistance meter and a digital multimeter, while the ac resistivity was calculated from the measured resistance using an impedance analyzer. The complex permeability and dielectric constant were calculated from the measured capacitance using an impedance analyzer.

III. RESULTS AND DISCUSSION

Fig. 1 shows the variation of bulk density of NiCuZn ferrite with sintering temperature and Cu content(x). It is found that sintering density of the ferrite fired at 1000℃ is largely increased by Cu substitution to the NiZn ferrite. Above 1000℃, the sintering density was decreased slightly due to exaggerated grain growth and intergranular micropore. The observed phenomena caused by the addition of Cu is evident in the densification of NiCuZn ferrite, since the iron deficiency in this study is constant. This is caused by the great atomic mobility of Cu at a relatively low sintering temperature.

Fig. 2 shows the variation of dc resistivity of the ferrites sintered at 950℃, 1000℃, and 1050℃ versus the Cu contents(x). The dc resistivity was increased up to a near maximum value at x=0.2

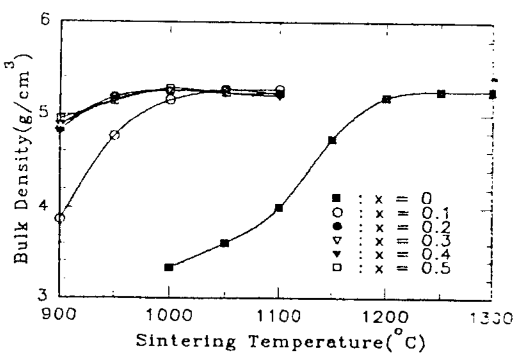

Fig. 1. Bulk density of $(Ni_{0.5-x}Cu_xZn_{0.5}O)(Fe_2O_3)_{0.98}$ as a function of sintering temperature.

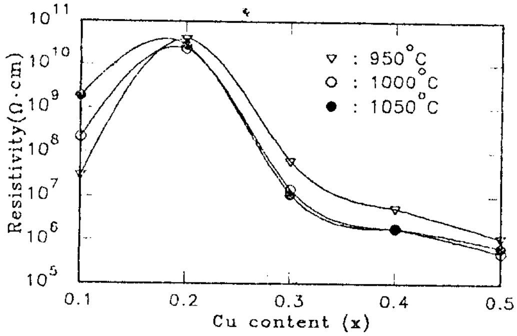

Fig. 2. DC resistivity of $(Ni_{0.5-x}Cu_xZn_{0.5}O)(Fe_2O_3)_{0.98}$ at various sintering temperatures as a function of x.

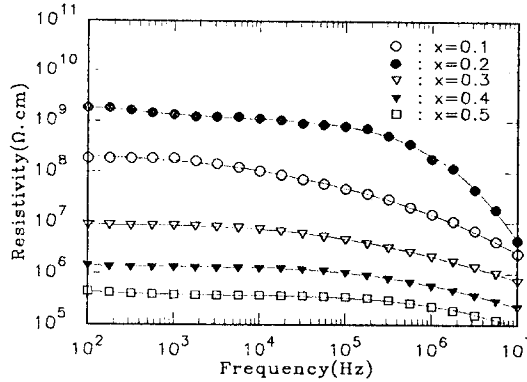

Fig. 4. AC resistivity of $(Ni_{0.5-x}Cu_xZn_{0.5}O)(Fe_2O_3)_{0.98}$ sintered at 1000℃ as a function of frequency.

and dropped above x=0.2. In general, the dominant electrical conductivity mechanism in the iron deficient NiZn ferrite is *p*-type up to a firing temperature of 1300℃. The effect of the Ni to Zn composition ratio on the electrical conductivity cannot be negligible at a low sintering temperature, so that Cu substituted for Ni plays a significant role in the conductivity of NiCuZn ferrites. Previous work[1] has shown that high resistivity of NiCu ferrite can be obtained from the Ni^{2+}-Ni^{3+} electron transition but Cu^{2+}-Cu^{+} transition makes dc resistivity lowered as the variation of Cu content in NiCu ferrite.

Fig. 3 shows the activation energy above and below the Curie temperature, which is related to the change of dc resistivity. From the results shown in Fig. 2 and Fig. 3, it can be seen that activation energy up to x=0.2 increases with the reduction of carrier number due to the protection of $Ni^{2+} \rightarrow Ni^{3+}$ oxidation by Cu substitution but decreases with increasing Cu content due to its dominant role in conductivity.

The ferrite resistivity increases at low frequency because motion of electrons occurs readily through grains under an electric field but is interrupted if they reach the interfaces. The ferrite permittivity also increases with the large polarization formed on the grain boundary interface at a low frequency[2,3].

Fig. 4 shows the dependence of the ac resistivity and Fig. 5 shows the dependence of the dielectric constant of the ferrites sintered at 1000℃ on frequency. From these results, it is determined that the dielectric constant at a low frequency with low ac resistivity is much higher than with high ac resistivity. However, the dielectric constant of $(Ni_{0.5-x}Cu_xZn_{0.5}O)(Fe_2O_3)_{0.98}$ decreases as increasing frequency and become constant for all Cu contents. Therefore, it is found that the dielectric constant of $(Cu_{0.5}Zn_{0.5}O)(Fe_2O_3)_{0.98}$(x=0.5) is much higher than that of $(Ni_{0.3}Cu_{0.2}Zn_{0.5}O)(Fe_2O_3)_{0.98}$(x=0.2) due to its low ac resistivity because of large polarization having small amount of charge carrier.

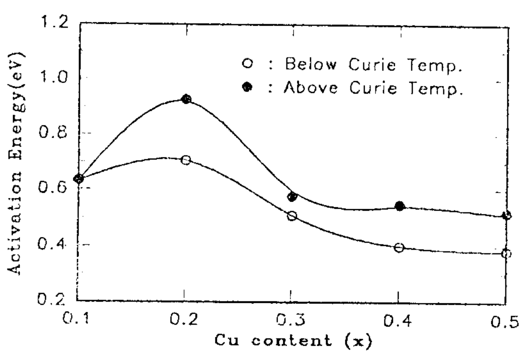

Fig. 3. Activation energy of $(Ni_{0.5-x}Cu_xZn_{0.5}O)(Fe_2O_3)_{0.98}$ sintered at 1000℃ as a function of x.

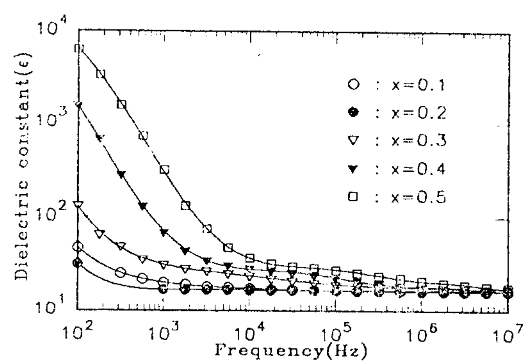

Fig. 5. Dielectric constant(ε) of $(Ni_{0.5-x}Cu_xZn_{0.5}O)(Fe_2O_3)_{0.98}$ sintered at 1000℃ as a function of frequency.

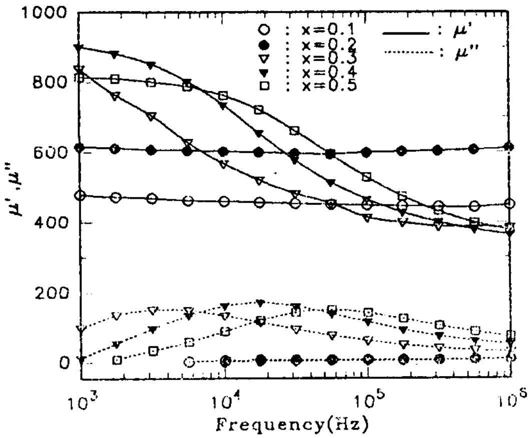

Fig. 6. Complex permeability of $(Ni_{0.5-x}Cu_xZn_{0.5}O)(Fe_2O_3)_{0.98}$ sintered at 1000℃ with variation of frequency.

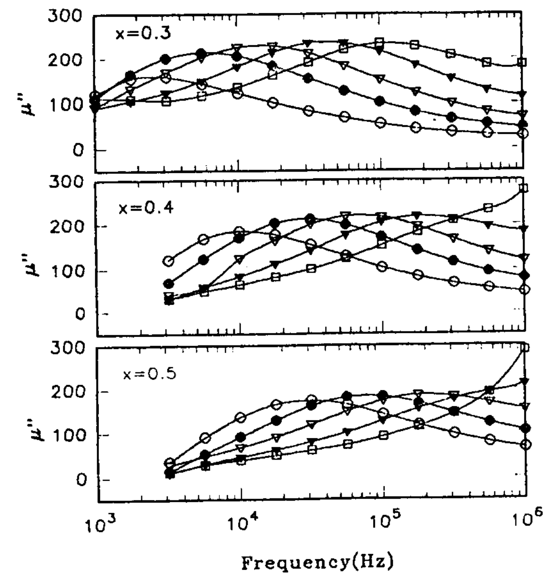

Fig. 7. Imaginary part(μ'') of the permeability of $(Ni_{0.5-x}Cu_xZn_{0.5}O)(Fe_2O_3)_{0.98}$ sintered at 1000℃ with variation of frequency. [measured at 20 ℃(○), 40 ℃(●), 60 ℃(▽), 80 ℃(▼), 100 ℃(□)]

Fig. 6 gives the dispersion characteristics for the ferrites of the variation complex permeability with frequency. The relaxation seems to occur in the frequency range of 1-1000 kHz above x=0.3. This tendency seems to be connected with the relaxation process. Losses of this kind occur in all Cu-containing ferrites with spinel structure and can be described in terms of an activation energy E_m[4,5] by

$$\omega = \omega_{\infty} \cdot \exp(-E_m/kT) \qquad (1)$$

where k is Boltzmann's constant, T is absolute temperature and ω_{∞} is the relaxation frequency with infinite temperature. To explain this phenomena it is supposed that the magnetic energy levels of the magnetic ions depend on the orientation of the magnetization. For each orientation there will be an equilibrium Boltzmann distribution. In a moving domain wall, the magnetization changes its direction, and the energy levels, so that the equilibrium distribution changes. A thermally activated redistribution will occur in a finite relaxation time, causing the magnetization to lag behind the applied field. Therefore, it is determined that a high activation energy for domain wall motion needs to occur for this relaxation phenomena above room temperature.

Fig. 7 shows the variation of the imaginary part of permeability of the ferrites sintered at 1000℃ as a function of the frequency and temperature above x=0.3. It is observed that the range of relaxation

TABLE I

THE ACTIVATION ENERGY(E_m) OF MAGNETIC RELAXATION AND THE ACTIVATION ENERGY(E_ρ) OF THE DC RESISTIVITY OF $(Ni_{0.5-x}Cu_xZn_{0.5}O)(Fe_2O_3)_{0.98}$ SINTERED AT 1000℃ FOR 4 HOURS

Composition $(Ni_{0.5-x}Cu_xZn_{0.5}O)(Fe_2O_3)_{0.98}$	Resistivity at Room Temp. [Ω·cm]	E_m [eV]	E_ρ [eV]
x=0.1	2.17×10^8	-	0.632
x=0.2	2.24×10^{10}	-	0.705
x=0.3	1.42×10^7	0.452	0.507
x=0.4	1.80×10^6	0.438	0.399
x=0.5	5.10×10^5	0.399	0.382

frequency moves to a higher frequency range with increasing temperature. But the relaxation phenomena do not appear in the ferrite of x=0.4 above 100℃, and for x=0.5 above 80℃. These tendencies, therefore, are well fitted to equation (1) and the relation between dc resistivity and activation energy with various x value in $(Ni_{0.5-x}Cu_xZn_{0.5}O)(Fe_2O_3)_{0.98}$ is given in Table I.

Fig. 8 shows the variation of magnetic loss tangent of NiCuZn ferrites sintered at 1000℃ as a function of frequency. The magnetic loss peak appears above x=0.3 in this study, which is related to the relaxation phenomena at a low frequency range.

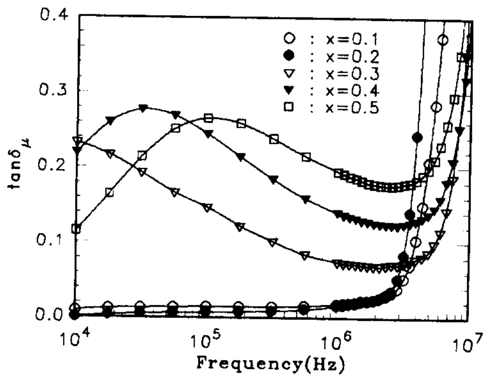

Fig. 8. The magnetic loss tangent of $(Ni_{0.5-x}Cu_xZn_{0.5}O)(Fe_2O_3)_{0.98}$ sintered at 1000℃ with frequency.

Ⅳ.CONCLUSION

The most significant result of this study is to provide the characteristics of Cu substitution for Ni in the NiZn ferrite. It is found that NiCuZn ferrite can be prepared by the Cu substitution at a lower firing temperature than NiZn ferrite, while not increasing the sintering density above the proper Cu content. Furthermore, the spectrums of electrical and magnetic properties indicate that techniques for controlling the Cu substitution for Ni in NiZn ferrite will be an important factor in improving its properties and applications at the RF region.

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