Electric and Magnetic Properties of Ta-Doped Polycrystalline Mn-Zn Ferrite

Y. Yamamoto, A. Makino and T. Nikaidou

Central Research Laboratory, Alps Electric Co., Ltd., 1-3-5 Higashitakami, Nagaoka 940, Japan

Abstract. The effect of Ta₂O₅ additive on the electric and magnetic properties of MnZn ferrites with fine grain size was studied. A adding small amounts of Ta₂O₅ to the MnZn ferrite increased electric resistivity, while an excessive addition of Ta₂O₅ caused decrease in resistivity without significant grain growth. In a small amount of Ta₂O₅ the change in the electric resistivity can be explained by Ta⁵⁺ substitution for Fe³⁺ entailing disappearance of the oxygen defects. The excessive addition of Ta₂O₅ created the oxygen defects and the electrons which are promoted by the metallic ion defects and the thermal dissociation of oxygen.

1. Introduction

It is well known [1] that MnZn ferrites with small amounts of the additives such as SiO₂ and CaO have good magnetic properties at high frequency because of their high electric resistivity. These effects of CaO and SiO₂ are generally described [1] that a glassy high resistivity layer envelopes the grains. The excessive addition of additives makes the grain size large and the resistivity decreases [2]. However, TEM and AES analyses have shown that the presence of a high-resistivity glassy layer has not been proved and the high resistivity is caused by segregation of Ca [3]. Furthermore, EELS and STEM-EDX analyses have shown [4] that the Ca²⁺ segregation to boundaries and a decrease in Fe²⁺ content and thus high resistivity of boundaries caused by the inhibition of the $\text{Fe}^{2+} \rightleftharpoons \text{Fe}^{3+} + e^-$ equilibrium. We have already reported [5] that the addition of a small amount of Ta₂O₅ to the MnZn ferrite improves the core losses at the frequency range of 0.5 to 2 MHz. In this study, we used the sintered MnZn ferrite with a composition of 53.2 mol% Fe₂O₃, 37.1 mol% MnO and 9.7 mol% ZnO, which were made from hydrothermal-precipitated ferrite powders with spinel structure. The purpose of this study is to understand the additional effect of Ta₂O₅ on the resistivity and the core loss for the MnZn ferrite.

2. Experimental Procedure

The MnZn ferrite powder for the sintered bodies was prepared by the hydrothermal method. Figure 1 shows a TEM image of the hydrothermal ferrite powder and Table 1 shows composition of the powder. The powder was annealed at 973 K in Nitrogen for 10.8 ks. Ta₂O₅ was added to the ferrite powder in 0, 0.03, 0.05, 0.10 mol% and the powder was mixed by ball-milling method, mixed with proper quantity of an organic binder, pelletized and sintered at different temperatures, in the interval 1273 K-1473 K for 14.4 ks in a reduced atmosphere. The microstructure was observed with a scanning electron microscope. The resistivity (ρ) was measured by the four-point probe method. The coercive force (H_c) was measured under a field of 800 A/m with a dc B-H loop tracer, and the core loss was measured with Ryowa dc loop tracer MMS-0375-2.1B. The samples were ring-shaped, with outer and inner diameters of 10 and 6 mm respectively, and a thickness of 1.5 mm. All measurements were carried out at room temperature.

Fig.1 TEM image of the powder prepared by hydrothermal method.

Table 1 Composition and particle size of the powder prepared by hydrothermal method.

Particle size	(μm)	0.125
Fe ₂ O ₃	(mol%)	53.17
MnO	(mol%)	37.08
ZnO	(mol%)	9.75
FeO	(wt%)	0.96
SiO ₂	(wt%)	0.007
CaO	(wt%)	0.012
Na ₂ O	(wt%)	0.009

3. Results and Discussion

Figure 2 shows the effect of Ta₂O₅ addition on the grain size and the ρ of the samples sintered between 1273K to 1473K. The sintered samples had the porosity less than 2.2% because the powders are relatively easy to sinter. The grain size is strongly dependent on the sintering temperature and in the lower sintering temperature below 1373K the Ta₂O₅ content dependence of grain size was negligible and the grain sizes were almost constant. At higher sintering temperatures, 1423K and 1473K, a exaggerate grain growth was observed in the amount of Ta₂O₅ less than 0.05mol% and no exaggerate grain growth was observed at 0.10mol%. The ρ increases with increasing of the amount of Ta₂O₅ and decrease in 0.10mol% after indicating the maximum value with 0.05mol%. The ρ of 0.10mol% indicated lower value than 0mol% of Ta₂O₅ at each sintering temperature. The increase of ρ in the amount of Ta₂O₅ not more than 0.05mol% can explain the inhibition of the hopping mechanism [4], $\text{Fe}^{2+} \rightleftharpoons \text{Fe}^{3+} + e^-$, owing to the Ta⁵⁺ segregation to boundaries. However, the ρ decreases without grain growth in the amount of Ta₂O₅ more than 0.05mol%.

Figure 3 shows the Ta₂O₅ quantity dependence of H_c and the core loss. H_c decreases as the sintering temperature becomes higher. At the low sintering temperature between 1273K-1323K, H_c decreases as a amount of Ta₂O₅ becomes much and shows minimum value and then increases as an amount of Ta₂O₅. The increase of H_c is assumed that the domain wall moving is damped with precipitating Ta₂O₅ on boundaries. The change of core losses show the minimum value upon the amount of Ta₂O₅ and indicates the similar dependence of ρ .

Therefore, we may propose the following mechanism to explain the effects of Ta₂O₅ on ρ and magnetic properties. (A) On doping Ta⁵⁺ onto ferrite, the oxygen vacancies disappear to compensate for the excess plus charge originated from replacing Ta⁵⁺ for Fe³⁺.

(B) Ta is consumed for the production of vacancies $\text{V}_{\text{Fe}}^{3+}$ to maintain the electroneutrality. Vacancies $\text{V}_{\text{Fe}}^{3+}$ invite the thermal dissociation of Oxygen and the thermal formation of Oxygen vacancies can occur more easily.

It is important to note that eq.(1) does not create electrons and eqs.(2,3) create electrons. In the range of small amount of Ta₂O₅, the ρ increases because the $\text{Fe}^{2+} \rightleftharpoons \text{Fe}^{3+} + e^-$ equilibrium governing the conduction mechanism at grain boundaries was inhibited with Ta⁵⁺ substitution for Fe³⁺. On the other hand, in the range of excess amount of Ta₂O₅ the creation of the cation vacancies become predominant and the ρ decreases with increase of electrons as a result of dissociation of oxygen in the vicinity of cation vacancies. Therefore, the dependence of the ρ on Ta₂O₅ content should be closely related to the density of the oxygen vacancy and cation vacancy. The reason for core loss to have a minimum value is qualitatively explained by the disappearance and the creation of defects.

Fig. 3 Change in the core loss and the coercive force as a function of Ta₂O₅ contents for the ferrites sintered at various temperatures.

Fig. 2 Change in the electric resistivity and the grain size as a function of Ta₂O₅ contents for the ferrites sintered at various temperatures.

References

- [1] T. Akashi: Trans. Japan Inst. Metals 2, (1961) 171.
- [2] T. Hiraga, K. Okutani and T. Ojima: "Electronic material series Ferrite", Maruzen (1986).
- [3] P. E. C. Franken and W. T. Stacy: Journal of The American Ceramic Society 63 (1980) 315.
- [4] M. H. Berger, J. Y. Laval, F. Kools and J. Roelffama: Proceedings of 5th International Conference on Ferrite, (1989) 619.
- [5] Y. Yamamoto, M. Yokoyama and A. Makino: Digests of the 17th Annual Conference on Magnetism in Japan 12pE-9(1993).