Synthesis and Magnetic Properties of Ferroxplana Type Ferrite

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The purposes of this study are to investigate the sintering conditions of single Z-type with high electrical resistivity for enhancing the resonance frequency. A mixture of BaCO₃, CoO and Fe₂O₃ powders (final product : Ba₃Co₂Fe₂₄O₄₁) was calcined at 1273K, sintered at 1473-1623K and then furnace-cooled. The sintering atmospheres used vacuum, Ar, O₂, air and mixtures of O₂ and Ar. The following properties of sintered samples were examined about bulk density, saturation magnetization, magnetic permeability, dc electrical resistivity and also phase composition. The single phase Z-type ferrite was found in the sample sintered under oxygen at 0.1MPa. The sample sintered at 1573K for 24h under oxygen at 0.1MPa showed a higher resonance frequency over 1.8GHz for having high electrical resistivity and 50% higher value of the real part of permeability than the previously reported results.

*keywords: synthesis, magnetic properties, sintering atmosphere, dc electrical resistivity,
Z-type ferrite, frequency dispersion, single phase*

I . Introduction

Recently downsizing of electronic parts has been required for small-sized and high frequency electronic devices. Now Ni-ferrite (NiO · Fe₂O₃) is used for magnetic materials in the order of 10MHz frequency range⁽¹⁾⁻⁽⁴⁾. However magnetic loss drastically increases in the range over 100MHz, which is well known as Snoek's limit, which means that it is impossible to use this ferrite as magnetic core materials in GHz range.

In place of this material, ferroxplana type ferrite has been studied and developed. Among ferroxplana type ferrites, Z-type ferrite whose chemical formula is 2MeO · 3BaO · 12Fe₂O₃ (Me means divalent metal ion), has a hexagonal structure like M-type ferrite. The Z-type ferrite with Me=Co has a high calculated resonance frequency of 3.4GHz, in virtue of its basal plane anisotropy and large anisotropy field⁽¹⁾. However in previously reported results, Z-type ferrite exhibited a resonance frequency 1.4GHz lower than the calculated value⁽¹⁾⁻⁽³⁾. Those reasons were explained by stress and shape anisotropy⁽³⁾.

We consider that there are two methods of enhancing

the resonance frequency. Firstly, by the substitution of Sr for Ba, which recently enabled Kimura et al⁽⁵⁾ to increase the resonance frequency from 1.4GHz to 2.5GHz. Secondly, by changing the processing conditions in order to try to obtain single phase Z-type ferrite, which has a high electrical resistivity. We decided to investigate the second method.

It is well known that the magnetic properties of ferroxplana type ferrite are effected by other phases. The presence of phases such as the W-type, lead to a deterioration in properties. These phases appear when sintering under oxygen atmospheres with various pressures⁽⁶⁾⁻⁽⁸⁾. It is anticipated that single Z-type ferrite can be obtained by controlling the oxygen content during sintering, however, the necessary conditions are not clear yet.

Electron hopping between Fe²⁺ and Fe³⁺ gives rise to electrical conduction in Z-type ferrite⁽⁴⁾. It is considered that the electrical resistivity is enhanced by heat treatment under an oxygen-rich atmosphere because of decreasing amount of Fe²⁺ in Z-type ferrite. Therefore, we consider that the resonance frequency can be enhanced by varying the oxygen content during sintering. But the relationship between resonance frequency and sintering atmosphere in ferrite has not been extensively reported.

Therefore the purpose of this work is to investigate the sintering conditions of single phase Z-type ferrite with

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Fig. 1 X-ray intensities of the observed phases in $\text{Ba}_3\text{Co}_2\text{Fe}_{24}\text{O}_{41}$ after sintering at 1473K (a), at 1523K (b), at 1573K (c), at 1623K (d) for 3h in various atmospheres. The indices of the representative reflections of Z, Y, W, Co spinel, M and Fe_3O_4 phases were chosen: (1016), (119), (1010), (311), (107) and (220), respectively.

high electrical resistivity for enhancing the resonance frequency, by sintering under various oxygen atmosphere.

II. Experimental

Samples were prepared using a conventional ceramic technique, and the sample composition is represented by the chemical formula $2\text{CoO} \cdot 3\text{BaO} \cdot 12\text{Fe}_2\text{O}_3^{(9)}$. We used α - Fe_2O_3 (purity:99.9%), CoO (99.9%) and BaCO_3 (99%) as raw materials, and mixtures of these materials were calcined at 1273K for 1h. Then the pellets were formed and sintered at 1473-1623K in vacuum, air, O₂ and mixtures of Ar and O₂ (at the ratios of 1:1 and 19:1), for 3-24h. The flow rate of the gas atmosphere was $500 \times 10^{-4} \text{m}^3 \cdot \text{min}^{-1}$. Heating rate to sintering temperature is for $400 \text{K} \cdot \text{h}^{-1}$ and furnace-cooling to 473K was used after sintering.

Bulk density was measured by Archimedes' method.

Saturation magnetization was estimated from the value of magnetization at a magnetic field of $1.2 \text{MA} \cdot \text{m}^{-1}$ using a VSM. Frequency dispersion of the real part of permeability μ' and μ'' of all samples were measured at the frequencies from 5Hz to 13MHz, by preparing cylindrical samples. However, for some samples measuring frequencies were extended up to 1.8GHz using a toroidal coil. Dc electrical resistivity was measured by four point contact method. The observed phases were identified by X-ray diffraction and magnetic balance studies. All the measurement were performed at room temperature except magnetic balance.

III. Results and Discussion

Figure 1 shows the dependence of the X-ray intensities of the observed phases in the samples, on various sintering atmospheres. The following indices of the representative reflections of Z, Y, W, Co-spinel, M

Fig. 2 Dependence of magnetization on temperature of samples sintered at 1573K for 3h in 1:1 (Ar:O₂) mixture (a) and O₂ (b).

Fig. 3 Dependence of bulk density, magnetization and the real part of permeability on various sintering atmospheres.

and Fe₃O₄ phases were chosen: (10 $\bar{1}$ 6), (119), (10 $\bar{1}$ 0), (311), (107) and (220), respectively. Several phases coexist in the samples sintered under a low oxygen pressure. It is considered that the Z-type phase

transforms or decomposes into stable phases such as Y, M and Co-spinel, at low oxygen content whilst furnace-cooling. Therefore, Z-type phase coexists with those phases. On the other hand, when the sintering temperature is higher, the Z-type phase coexists with W and Fe₃O₄ phases. The single phase Z-type ferrite was obtained in samples sintered for 3h at 1573K in 1:1 (Ar:O₂) mixture and O₂, according to X-ray diffraction measurements. Figure 2 shows the temperature dependence of magnetization of samples sintered in the 1:1 (Ar:O₂) mixture (a) and O₂ (b). In the 1:1 (Ar:O₂) mixture, there is a kink around 683K, but the curve does not flatten until 728K. It is thought that this high temperature effect can be attributed to the presence of another phase, such as M or W, which coexists with the Z-type phase. In pure O₂, the Magnetization-temperature curve flattens at about 692K, which is consistent with the Currie temperature value of the Z-type ferrite (683K), previously reported⁽³⁾.

Figure 3 shows the dependence of bulk density, saturation magnetization and the real part of permeability μ' measured at 10MHz on various sintering atmospheres. There is a small in density decrease with increasing oxygen pressure, which indicates that the sintering process is greatly effected by the presence of oxygen ion vacancies. The density of the sample sintered at 1573K for 3h under oxygen at 0.1MPa, which is confirmed from X-ray diffraction analysis and magnetic balance as single phase Z-type ferrite, is $4.64 \times 10^3 \text{ Kg} \cdot \text{m}^{-3}$. This value is small in

Fig. 4 Dependence of dc electrical resistivity on various sintering atmospheres.

Fig. 5 Frequency dispersion of samples sintered at 1573K for 3h in 1:1 (Ar:O₂) mixture (a) and for 24h under oxygen at 0.1MPa (b).

comparison with the X-ray density of $5.33 \times 10^3 \text{ Kg} \cdot \text{m}^{-3}$. The saturation magnetization for the 1573K sintered sample was found to be $64.88 \mu \text{ Wb} \cdot \text{m} \cdot \text{Kg}^{-1}$, which is comparable to previously reported results⁽³⁾. When sintering temperature and oxygen pressure are low, samples contains Y and magnetic hard phases such as M, W and Co spinel phases, and have a smaller real part of permeability, when compared with single phase Z-type ferrite. In sample sintered at 1573K for 3h in the 1:1 (Ar:O₂) mixture, the highest real part of permeability of 8.01 is obtained. In sample sintered at 1573K for 3h under oxygen at 0.1MPa, regardless of the single phase Z-type ferrite, has smaller real part of permeability of 6.31 than previously reported results⁽³⁾ because of demagnetization effects during measurement caused by the cylindrical shape of the sample.

Figure 4 shows the dependence of dc electrical resistivity on sintering atmosphere. For every sintering temperature, the resistivity of the samples increases with increasing oxygen content, from Ar to the 1:1 (Ar:O₂) mixture. The resistivity reaches a maximum with the 1:1 (Ar:O₂) mixture, and then decreases with pure O₂. It is considered that this variation in resistivity is caused by an increase of metal vacancies. Resistivities of the single phase Z-type ferrite, which was confirmed from X-ray diffraction analysis (Fig. 1) sintered at 1573K for 3h in the 1:1 (Ar:O₂) mixture and under oxygen at 0.01MPa are $8.6 \times 10^4 \Omega \cdot \text{m}$ and $2.8 \times 10^4 \Omega \cdot \text{m}$, respectively. The sample sintered at 1573K for 3h under oxygen at

0.1MPa has low resistivity regardless of the single Z-type ferrite confirmed from X-ray diffraction analysis and magnetic balance. And when sintering time is long, sample sintered at 1573K for 24h under oxygen at 0.1MPa has the highest resistivity of $1.1 \times 10^7 \Omega \cdot \text{m}$.

It has been known from Figure 3 that sample sintered at 1573K for 3h in the 1:1 (Ar:O₂) mixture had the highest real part of permeability regardless of representing mixture phases. Figure 5 shows the frequency dispersion of the samples sintered at 1573K for 3h in the 1:1 (Ar:O₂) mixture (a) and sintered at 1573K for 24h under oxygen of 0.1MPa (b). The real part of permeability of the sample sintered at 1573K for 3h in the 1:1 (Ar:O₂) mixture tends to decrease gradually in the 300MHz range. This sample exhibits lower resonance frequency of 800MHz than previous reported results, because of low resistivity. The sample sintered under oxygen at 0.1MPa exhibits a constant value of the real part of permeability near to 1GHz, for having the highest resistivity. The real part of permeability of $\mu' = 18$ at 1GHz is 50% higher than the previously reported results⁽³⁾. The imaginary part of permeability does not exhibit the maximum value up to 1.8GHz. This fact means that the resonance frequency had been enhanced over 1.8GHz, for having the highest resistivity. These results are higher than those previously reported⁽¹⁾⁻⁽³⁾, but lower than those of Sr substituted Z-type ferrite⁽⁴⁾.

IV. Conclusions

Electrical and magnetic properties were measured in the ferroxplana Z-type Ba₃Co₂Fe₂₄O₄₁ ferrite sintered in various atmospheres. Samples sintered at 1573K for more than 3h in O₂ showed the single phase Z-type ferrite. The results was the follow: bulk density was $4.64 \times 10^3 \text{ Kg} \cdot \text{m}^{-3}$; magnetization was $64.88 \mu \text{ Wb} \cdot \text{m} \cdot \text{Kg}^{-1}$; Currie temperature was 692K; and the dc electrical resistivity was $2.8 \Omega \cdot \text{m}$. These values are comparable to previously reported results. The sample sintered at 1573K for 24h under oxygen at 0.1MPa showed $1.1 \times 10^7 \Omega \cdot \text{m}$ of the highest electrical resistivity and a higher value of the real part of permeability at 1GHz than the previously reported results. This sample exhibits the resonance frequency over 1.8GHz.

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