二流体ノズルを用いた噴霧熱分解法による Y 型フェライトの作製

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Preparation of Y-type ferrite particles by the Spray-Pyrolysis method using a two-fluid nozzle

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諸言

噴霧熱分解法は均一なナノサイズ粒子の作製、連続的に作製することが期待できる方法である。しかし、この方法のみを用いた M 型を除く六方晶フェライトの作製の報告は非常に少ない [1)]。本研究ではこの方法のみを用い、六方晶 Y 型フェライト $Ba_2Co_2Fe_{12}O_{22}$ の作製を行った。従来は噴霧する液滴の粒形を最も小さくできる超音波スプレーノズル [1)]を利用し、噴霧化を行っていた。超音波スプレーノズルに内蔵されている圧電セラミックスの耐久温度は約 120ºC である。しかし、電気炉内を 1300ºC にすると、電気炉上部とノズルの結合部分の温度が 65～280ºC まで上昇する。このような高温域では超音波スプレーノズルの噴霧化は停止し、使用を続けることはできない。そこで本研究では、より単純な機構で高温下でも連続的に噴霧化をする事ができる二流体ノズルを利用した。

実験方法

$Ba(NO_3)_2$、$Co(NO_3)_2・6H_2O$、$Fe(NO_3)_3・9H_2O$ を六方晶 Y 型フェライト $Ba_2Co_2Fe_{12}O_{22}$ の組成になるように秤量し、純水に溶かした。この溶液を撹拌しながら 70ºC まで加熱し、クエン酸を金属イオンと等モル加えた。室温まで下げた後、アンモニア水溶液で pH7.0 に調整し、12 時間撹拌した。これを原料溶液とした。二流体ノズルに原料溶液を流量 1.0 mL/s で供給し、電気炉中の石英管内に噴霧した。この時の空気量を 10～15 L/min にし、電気炉内を 1150～1300ºC にすることで熱分解を行った。得た試料を X 線回折装置(XRD)、振動試料型磁力計(VSM)により測定した。

実験結果

図 1 は熱分解温度 1150～1300ºC で作製した試料の X 線回折図である。熱分解温度 1250ºC で六方晶 Y 型フェライト $Ba_2Co_2Fe_{12}O_{22}$ が最も生成している。図 2 と六方晶 Y 型フェライト $Ba_2Co_2Fe_{12}O_{22}$ のキュリー点が 340ºC であることからこの試料の主相が Co_2Y フェライトであることが確認できた。以上から、二流体ノズルを利用した噴霧熱分解法による六方晶フェライトの作製に成功した。

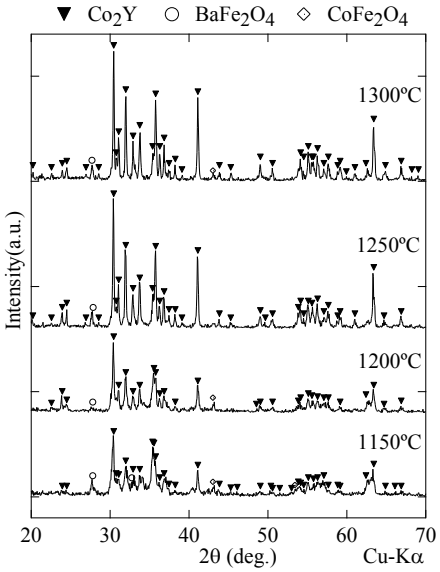

図 1：焼成温度 1150～1300ºC で熱分解した試料の X 線回折図

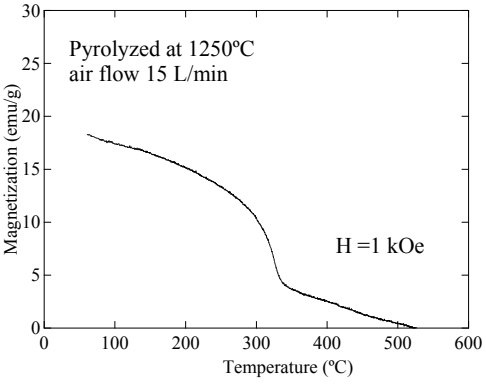

図 2 : 1250ºC で焼成した試料の磁化の温度依存性

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Characterization of Nanocrystalline Fine $MgFe_2O_4$ Soft Ferrite Powder Synthesized by Ultrasonic Spray Pyrolysis Method

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Ultrasonic spray pyrolysis (USP) has been successfully used to synthesize fine ceramic particles with several advantage such as convenient, controllable and continuous process [(1)]. In the present work, nano-magnetic unsintered magnesium ferrite as dried powder has been synthesized using ultrasonic spray pyrolysis technique without any additives and post-annealing processes. Magnesium ferrite is a very useful soft magnetic ceramic material and it expected to be suitable for local hyperthermia when compared with other ferrites [(2)]. Spherical nano-sized magnesium ferrite powders were obtained using ultrasonically atomized aqueous solutions of iron (III) nitrate and magnesium nitrate mixture followed by thermal decomposition of dried mist in nitrogen atmosphere. Different pyrolysis temperature applied to the reactor furnace was found to have a significant impact on the crystallinity and morphology of the magnesium ferrite powders. Structural characterization was carried out using x-ray powder diffraction (XRD) method to evaluate crystallographic analysis and crystallite size. Figure 1 shows that all the samples are single phase cubic ferrites particles with the space group Fd-3m and lattice constant vary from 0.829 nm to 0.838 nm with increasing pyrolysis temperature from 600 °C to 800 °C. Crystallite size of the nanoparticles increased from 5.24 ± 51 to 15.97 ± 45 nm when pyrolysis temperature increased from 600 °C to 800 °C. Formation of ferrites was examined using Fourier transform infrared spectroscopy (FT-IR). The nanocrystallite nature and morphology of the as dried powder was evidenced by transmission electron microscopy (TEM) (Fig. 2). The effects of the pyrolysis temperature on the particle size distribution were investigated using laser particle size analyzer. Results showed that particle sizes were decreased from 253 nm to 67 nm by increasing pyrolysis temperature from 600 °C to 800 °C and also narrower size distribution was obtained using higher pyrolysis temperature. The agglomerates observed by field-emission scanning electron microscopy (FE-SEM) proved that $MgFe_2O_4$ nanocrystallites shows high dispersibility. Also, particles prepared at 800 °C had less aggregated structure than those prepared from 600 °C to 700 °C. The composition examined using energy-dispersive spectroscopy (EDS) was stoichiometric. Magnetic properties of synthesized $MgFe_2O_4$ powder were examined using VSM.

Reference:

1) Kang et al. *Mat. Sci. Eng. B*, **127** (2006) 99.
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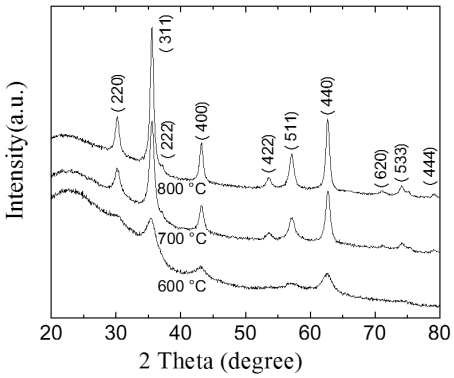

Fig. 1. XRD patterns of Mg-ferrite nanoparticles synthesized at various pyrolysis temperature.

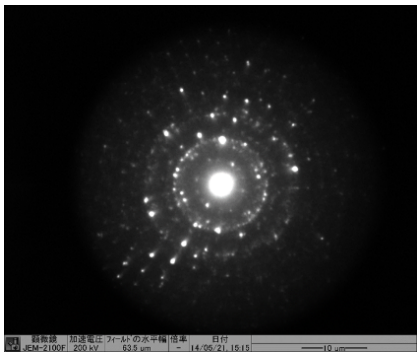

Fig. 2. SAED pattern of Mg-ferrite nanoparticles synthesized at 600 °C.

Controlled microwave-assisted synthesis of nano-crystalline zinc ferrite

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Controlled synthesis of nanocrystalline spinel ferrites are of immense importance owing to their interesting magnetic characteristics at nanoscale that leads not only to study the process of magnetization in them at that scale but also to use them for the development of various functional devices. Among largely-favoured low-temperature solution-based processing methods, as demonstrated in our earlier work[1], microwave-irradiation-assisted synthesis technique (MAST) offers rapid way to obtain pure crystallites with very narrow size distribution. However, the use of surfactant and the need of post-synthesis anneal was unavoidable in order to control distribution and growth of particle size. In this work we will demonstrate surfactant-free and anneal-free synthesis of zinc ferrite nanocrystallites with tunable physical and chemical properties by same MAST but with slightly altered synthesis conditions. Furthermore we will also show the effect of processing conditions on their properties.

For the synthesis of zinc ferrite by MAST, metalorganic complexes such as $Zn(acac)_2$ and $Fe(acac)_3$ were chosen (in stoichiometric ratio) as precursors and taken in a solvent mixture containing ethanol, 1-decanol, and a small quantity of de-ionized water (5:8:1) and stirred mildly until a clear solution resulted. The clear solution was then transferred to a Pyrex glass vessel, designed for 'Discover SP' system (Microwave reactor, CEM Corp., US), and placed inside the microwave cavity for the exposure of microwave irradiation (2.45 GHz, 300 W) for just 10 minutes so as to complete the reaction that resulted in pure nanocrystalline zinc ferrite powder (sample name: N10x) as precipitate at the bottom of the vessel. 1-decanol, being a high boiling point solvent, pushed the overall boiling point of the solution mixture near to 200 °C, while serving the purpose of surfactant due to its high viscosity. Therefore, the inclusion of 1-decanol was found to be crucial to control shape and size of the nanocrystallites. The purity and crystallinity of the samples were confirmed through powder X-ray diffraction (PXRD; Fig. 1) and X-ray photoelectron spectroscopy (XPS). Scanning electron microscopy (SEM) image of the crystallites revealed mono-dispersed particles of ~ 5-7 nm diameters in agglomerated state. Magnetization of these nanocrystallites, measured at low (3 K) temperature by using SQUID magnetometer, revealed (Fig. 3) hysteresis with saturation magnetization (M_S) and coercivity of 30 emu/g and 400 Oe respectively. Zinc ferrite – a normal spinel, which ideally is antiferromagnetic (below T_N=10 K) in bulk, displayed superparamagnetism even at room temperature (Fig. 1c). This observation is a clear evidence of process-induced distribution of cations in the lattice that in turn enables ferrimagnetically coupled superexchange interactions among the Fe^{3+} ions present both in tetrahedral and octahedral sites. It is also to be noted that the inversion was infused in the crystal structure only at ~190 °C and is believed to be influenced heavily by the presence of microwave irradiation. Prolonged exposure (1 hour; sample name: N10 x-1H) of microwave irradiation, however, resulted in a little reduction in M_S (23 emu/g), while uniform growth of nanocrystallites up to 20 nm was observed (Fig. 1 and 2). Therefore, an anneal-free alternative to crystal growth was evidenced.

Reference

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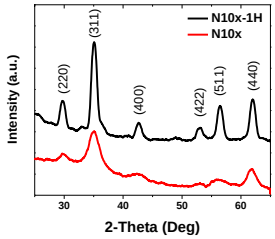

Fig. 1: XRD patterns of N10x and N10x-1H

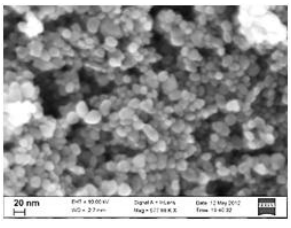

Fig. 2: SEM image of N10x-1H

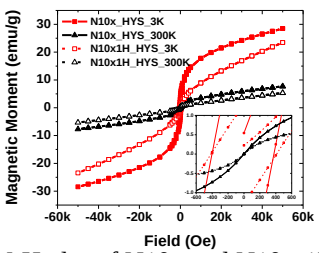

Fig. 3: M-H plot of N10x and N10x-1H measured at 3 K and 300 K

短絡・開放同軸線路を用いた透磁率・誘電率の相互補正測定

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Inter correction measurement of permeability and permittivity by short and open circuited coaxial line

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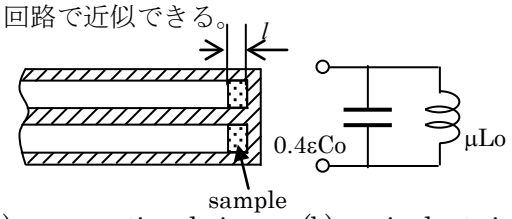
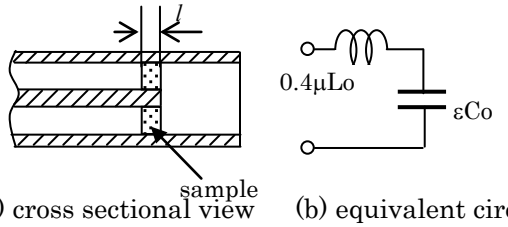
はじめに　短絡・開放同軸線路を用いて透磁率・誘電率を測定する方法はよく知られている 1)。この方法では、お互いの効果を考慮する必要があるが、一般に解析手法は面倒である。今回、解析方法として、集中定数回路近似を用いることにより、両者の効果を簡単に補正できる方法を考案したので報告する。

測定理論　Fig.1 に短絡同軸線路を、Fig.2 に開放同軸線路を示す。円筒形試料が内外導体に緊密に接触した状態で挿入されている。それぞれの線路は、試料表面を基準面とすると等価回路として並列 LC 回路と直列 LC 回路で近似できる。



(a) cross sectional view　(b) equivalent circuit

Fig.1 Short circuited coaxial line



(a) cross sectional view　(b) equivalent circuit

Fig.2 Open circuited coaxial line

図中、Lo=Ll, Co=Cl であり、L=166.7[nH/m], C=66.7[pF/m]は 50Ω同軸線路の単位長当たりのインダクタンスと静電容量である。また l は試料の厚みである。試料の透磁率と誘電率をμとεで示した。等価回路の 0.4 の係数は、位相変化がπ/2 以下であれば、集中定数近似が 5%以下で成立するためのものである。このような配置で、試料がある場合とない場合の S_{11} パラメータを測定する。Fig.1 の場合はεが既知であればμを求めることができ、Fig.2 の場合はμが既知であればεを求めることができる。そこで、最初、ε=1 としてμを求め、これをμ_1 とする。同じように、μ=1 としてεを求め、これをε_1 とする。次に、ε=ε_1 としてμを求め、これをμ_2 とする。同じように、μ=μ_1 としてεを求め、これをε_2 とする。この操作を続ければ、補正の精度は向上する。しかし、実際には 1 回の操作で十分であり、2 回目以降はほとんど変化しない。また、最終的に得られたμ, εを用いて、$\beta=(2\pi f/c)\sqrt{\varepsilon\mu}\ l$ を計算して、各周波数 f で β<π/2 であることを確認する。ただし、c は真空中の光速である。

実験結果　同軸線路としては APC-7 を用いた。円筒形試料の寸法は 7mmϕ x 3mmϕであり、金型で打ち抜いて作成した。試料の端部は凹凸を示すが、外導体と内導体との試料の接触状況は、軽く金型で押しても外れないほどの緊密さである。被測定試料は NEC トーキン製 K4E 材で、厚みは 0.3mm である。Fig.3 に測定結果を示す。複数回測定で、透磁率の測定値はほとんど変化しなかったが、誘電率測定はε'の最大値で 20%～30%のばらつきがあった。図は最大のものを示している。

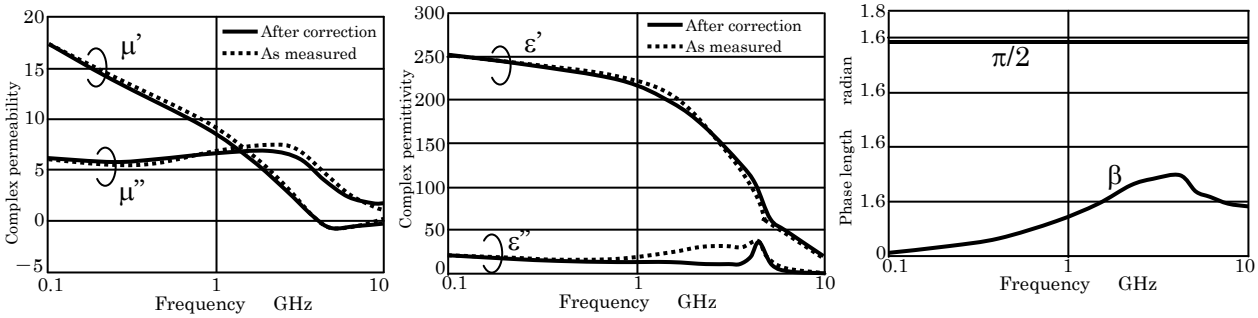


Fig.3 Measurement results of permeability (a) and permittivity (b) and judgment (c)

透磁率と誘電率の両者はお互いに影響を受けるが、実数部より虚数部の方が補正後変化は大きかった。特に誘電率の虚数部は透磁率の影響を受ける。位相変化βは 3.7GHz で最大をとるが、π/2 より十分に小さく、今回の測定が集中定数近似範囲内であることを示している。

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High frequency soft-magnetic properties and thermal stability of CoPd-$SrTiO_3$ nano-composite films

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Soft magnetic films with high permeability and ferromagnetic resonance frequency have been studied intensively for the application in micro-electronic device components. Recent work has been done on soft-magnetic Co-based nano-composite films to keep their permeability as high as possible to GHz frequency.[1)] However, the resonance frequency (*fr*) of the films is still low which may limit the application in higher-frequency magnetic devices. According to the modified Landau-Lifshitz equation, it is required of large values of magnetic anisotropy field (H_k) and saturation magnetization (M_s) to obtain high *fr*. Soft-magnetic films studied to date have large M_s, but show rarely high H_k. Recently, a few films demonstrate high H_k. whereas, they show low thermal stability, which is a big disadvantage for the high temperature processing in practical applications (such as Surface mounted technology at 250℃ for Printed circuit board). In this report, $SrTiO_3$ (STO) is employed as nonmagnetic ceramic phase due to its thermal stability and high resistivity (ρ). Pd is induced to form CoPd alloy nanoparticles to enlarge anisotropy (H_k). To prevent oxidation of Co metal, a kind of tandem sputtering method is used. The composition, structure, magnetic properties and thermal stability of the CoPd-STO films have been investigated.

The CoPd-STO nano-composite films were deposited onto Si and quartz substrates by sputtering methods, using a STO target and a composite target composed of a Co disk, Pd chips. The chemical composition of the films was analyzed by X-ray photoelectron spectroscopy (XPS). Film structures were investigated by XRD. The microstructure of films was characterized by TEM. The magnetization was measured with VSM. The permeability (μ) was determined by a shielded loop coil method.

The CoPd-STO films consist of amorphous STO matrix and CoPd nano-particles. The CoPd phase shows fcc structure. The CoPd-STO films have a typical in-plane uniaxial soft magnetic properties, with the easy axis (parallel) and hard axis (perpendicular to easy magnetic direction) (Fig. 1). The magnetization hysteresis loops of the films show magnetization (B_s) of about 10 kG, H_k of around 950 Oe, and ρ of 300 μΩ･cm. It is noteworthy that the magnetic properties of the sample after annealing treatment at 250 ℃ shows no obvious change compared with that of the as-deposited film. Form XRD analysis (Fig. 2), it is clearly proved that the CoPd particles have no change after annealing treatment for both size and crystalline structure. The measured μ' is approximately 10, which keeps constant up to 3 GHz. The calculated μ' by L.L.G. formula is consistent with the measured results and shows the resonance frequency at about 9 GHz.

Reference

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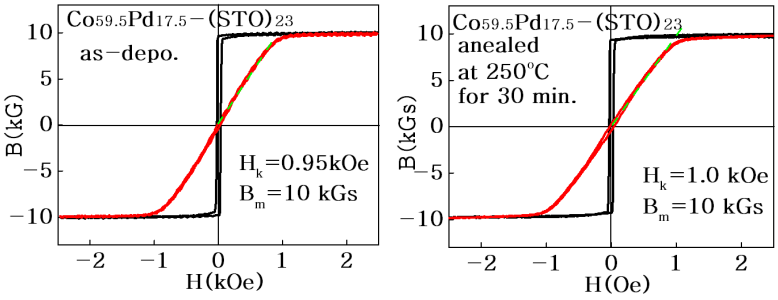

Fig.1 Hysteresis loops of CoPd-(STO) nano-composite film: a) as deposited, b) annealed at 250 ℃ for 30 min.

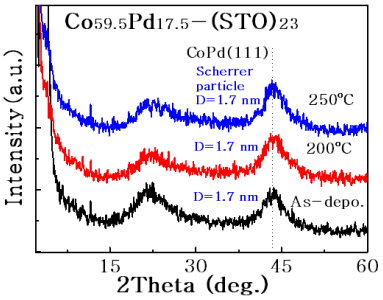

Fig.2 XRD spectra of the as-deposited and annealed CoPd-STO samples.