

The magnetic properties of porous Ni-Zn ferrites prepared from wood templates

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The crystallographic and magnetic properties of porous $\text{Ni}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.1, 0.5$ and 0.9) from wood templates were investigated in this study. The nitrates aqueous precursor solution was infiltrated into the wood specimen at 60°C to retain the original shape and the microstructure of wood. The sintered bodies contained elongated pores enclosed by a thin layer of wall with the thickness about $1\text{-}2 \mu\text{m}$. The grain size of polycrystalline ferrite was observed to be in the range of $1\text{-}1.5 \mu\text{m}$. Each grain was horizontally connected to form polycrystalline walls of single-layered grains. The VSM measurement showed that there is an obvious difference of magnetic properties in the parallel and perpendicular direction due to the anisotropic structure of wood template. The coercivity perpendicular to the pores orientation was larger compared to the coercivity parallel to the pores orientation. It is also discovered that the optimum saturation magnetization was achieved at $x = 0.5$.

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1. Introduction

Porous ceramics are well-recognized to be resistance to a wide range of chemicals, high melting temperature and superior mechanical strength (citation needed). Due to their unique properties and availability, a significant number of researches have been studied the method to exploit their unique properties.¹⁾ We had developed several types of ceramics with enhanced specific properties from wood templates with a bio-casting method.^{2)–4)} Most of the products are developed to by retain the original pore structures of woods by ceramitization, where the pore structures are used as the frame for the ceramics.

NiZn ferrites which are characterized in the class of spinel have high electrical resistivity, have wide variation of operating frequencies, stable at high range of temperature, low loss and high permeability.^{4)–6)} In this work we focus on the development of porous ferrite ceramic from wood templates to investigate the effect of the shape anisotropy on the magnetic properties of $\text{Ni}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$, which might be suitable to be applied in electromagnetic interference EMI at high frequency range. M. Abe et al. has successfully produced Ni-Zn ferrite films by spin-spray plating. The films have high permeability and high resonance frequency (exceeds Snoek's limit for bulk ferrite specimens). In 2004, D. Guo et al. reported that Ni-Zn ferrite film fabricated by magnetron sputtering has the capability to withstand high frequency settings. Such phenomenon is believed to be influenced by coercive anisotropy due to the elongated pore structures of ferrite wood, which acts as multilayer films.

2. Experimental procedures

Nickel nitrate (Wako), zinc nitrate (Wako) and iron (III) nitrate (Wako) were weighed according to the required stoichiometric proportion $\text{Ni}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.1, 0.5$ and 0.9) and mixed at 65°C for 10–15 min under stirring. Cedar (the wood specimens) was boiled with 25% ammonia for 1 h to remove the wood

extractive compounds. The specimens were washed with distilled water before they were re-boiled with de-ionized water for 1–2 h. Then, aqueous nitrates precursor solution was infiltrated onto the wood template at 60°C . Finally, the samples were sintered at 1200°C for 8 h in air.⁴⁾ The crystal structures of the ferrite wood specimens were investigated with X-ray diffraction (XRD) (RINT 1100, Rigaku Co.) with Cu K α radiation. The microstructures were observed by Scanning electron Microscope SEM (JSM-6100, JEOL Ltd.). Magnetic hysteresis was measured at parallel and perpendicular directions (at room temperature) using the vibrating sample magnetometer (VSM, TOEI) to investigate the effect of shape anisotropy on the magnetic properties.

3. Results and discussion

3.1 Preparation of ferrite woods

Figure 1 shows the X-ray diffraction patterns of the infiltrated specimens sintered at 1200°C for 8 h. The characteristic peaks are the sign of spinel NiZn ferrite. The peaks shifted to higher diffraction angles with the increase of x . In Ni-Zn ferrite, Zn $^{2+}$ and Ni $^{2+}$ ions occupied A sites (tetrahedral) and B sites (octahedral) in the spinel structure, respectively. The introduction of Ni $^{2+}$ ions into the B sites forced the transfer of the same quantity of Fe $^{3+}$ ions from the B site to the A site. This can be expressed by $[\text{Zn}^{2+}]_{1-x}, \text{Fe}^{3+}]_{\text{A site}} [\text{Ni}^{2+}_x, \text{Fe}^{3+}_{2-x}]_{\text{B site}} \text{O}_4$. The ionic radius of Zn $^{2+}$ (0.082 nm) is much larger than that of Fe $^{3+}$ (0.064 nm) in

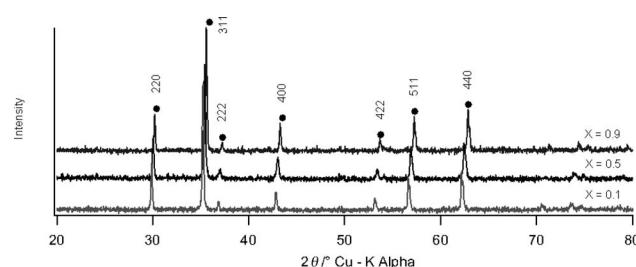


Fig. 1. XRD patterns of $\text{Ni}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ specimens sintered at 1200°C 8 h.

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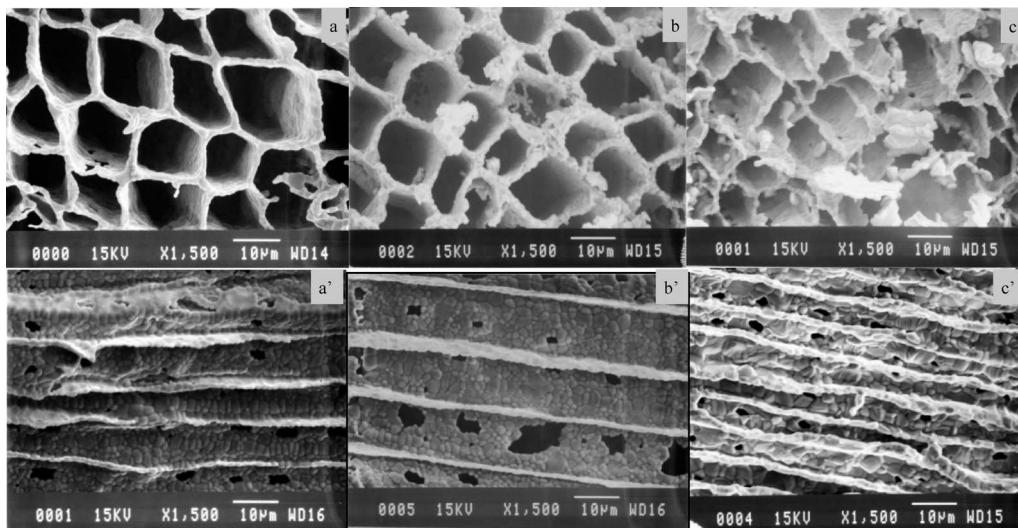


Fig. 3. SEM images of $\text{Ni}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ sintered at 1200°C for 8 h, $x = 0.1$ (a) and (a'), $x = 0.5$ (b) and (b'), $x = 0.9$ (c) and (c'). (front view = a, b and c) and (side view = a', b' and c').

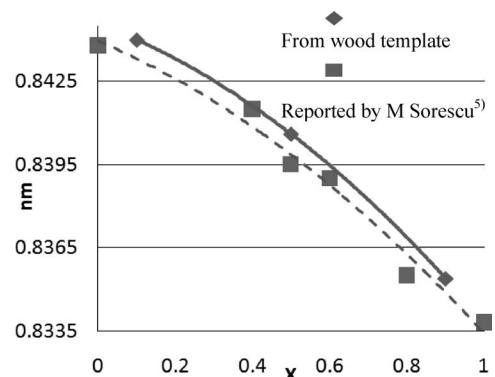


Fig. 2. Lattice constant as function of x for $\text{Ni}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$.

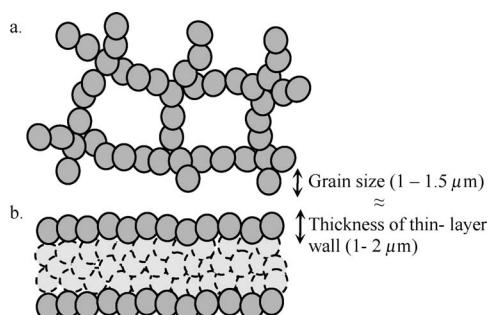


Fig. 4. Schematic of grains distribution of NiZn ferrite wood (a) front view, (b) site view.

the tetrahedral site. The ionic radius of Ni^{2+} (0.078 nm) is slightly larger than Fe^{3+} (nm) in octahedral site. Therefore, with increasing x , the lattice parameters decrease in total. **Figure 2** illustrates the plot of lattice constant versus x for $\text{Ni}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ where plot from this study is not much different compared to the values reported by M. Sorescu.⁵⁾ This suggests that each composition in a solution of mixed nitrates corresponds to the composition in a product.

Figure 3 shows the microstructures of sintered ferrite woods. The images confirmed that the pore structures of cedar wood are

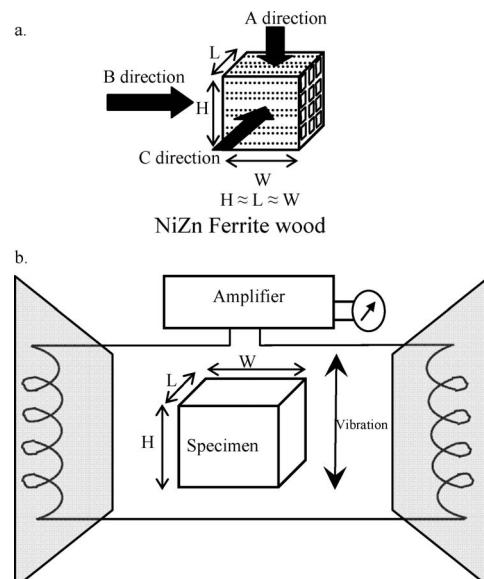


Fig. 5. Schematic diagram of (a) and (b) specimens setting for VSM measurements.

retained. However, the cell wall in the original cedar wood transformed to polycrystalline thin layers to form a micro honeycomb ceramic. The elongated pores were enclosed by the thin layer wall. The thickness of the thin layer wall was within the range of 1–2 μm. The grain size of polycrystalline ferrite was approximated to be in the range of 1–1.5 μm. Each grain was only horizontally connected together to form polycrystalline walls of single layered grains as shown in **Fig. 4**.

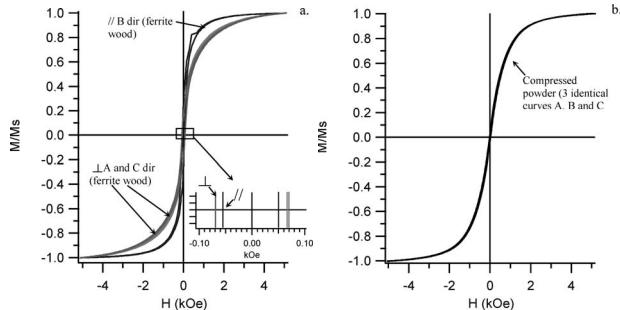
3.2 Magnetic properties of ferrite woods

As illustrated in **Fig. 5(a)** the specimen was cut into cubic shape ($\text{height} \approx \text{width} \approx \text{length}$). A and C are perpendicular to the thin layer wall and B is parallel. Magnetic hystereses of the cubic-shaped specimens were measured in the A, B and C directions by VSM as shown in **Fig. 5(b)**.

All samples exhibited the similar magnetic properties as shown in **Table 1**. Therefore, magnetization curves in the three

Table 1. Magnetic Data of $\text{Ni}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ from Wood Templates

X	Ms		Hc (Oe)		
	(emu/g)	(emu/cc)	A dir	B dir	C dir
0.1	15.5	9.86	39.1	33.7	40.5
0.5	56	38.12	68.7	55.8	68.8
0.9	49	44.35	89	71	88

Fig. 6. The hysteresis loops for $x = 0.5$ in A, B and C directions (a) ferrite wood and (b) compressed ferrite powder.Table 2. Magnetic Data of $\text{Ni}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ Compressed Powder

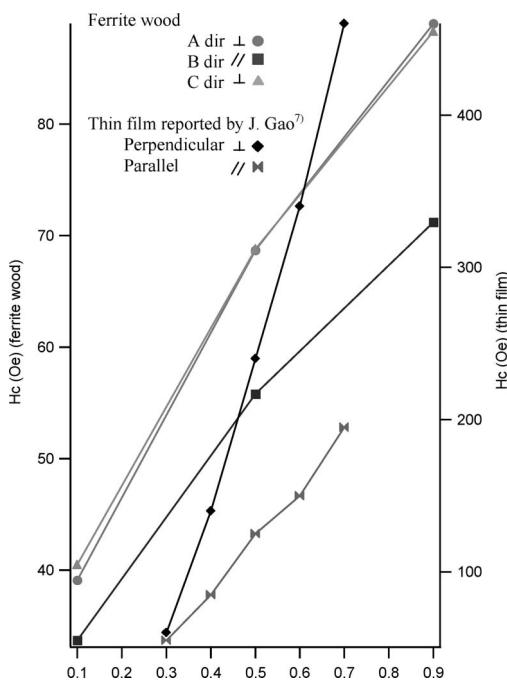
X	Ms (emu/g)	Hc (Oe)		
		A dir	B dir	C dir
0.5	59	42.8	42.8	42.8

directions for the sample with $x = 0.5$ was shown in **Fig. 6(a)**. Table 1 lists the magnetic properties for the samples with different compositions. As a results, we observed significant difference in the B direction (parallel) compared with the A and C direction (perpendicular). The curve rapidly approached to Ms in the case of measurement in B direction compared with A and C directions.

In magnetic thin films, the value of the magnetic susceptibility becomes consecutively higher in the direction parallel to the film, because the domains have a lower barrier for reorientation.⁸⁾ Therefore, the distinct difference of the M-H curve in direction B ascribed to the domain motion originated from the structural anisotropy derived from the wood template. The wood pore structure consists of many wall cells by nature. These thin-layered walls could be considered as multilayer of thin films.

To understand the different between bulk shape and wood-shape, the obtained ferrite wood was crushed and compressed into bulk shape of $3.5 \times 3 \times 2 \text{ mm}^3$ and the magnetic hysteresis was measured in three directions using VSM. The hysteresis readings of the compressed, crushed-ferrite wood as shown in Fig. 6(b) is similar in all directions. This demonstrated that the wood shaped ferrite caused an anisotropic magnetization parallel and perpendicular to the growth direction of the wood. The values of Ms for the compressed powder (59 emu/g) were almost same as that for the ferrite wood (56 emu/g, 38 emu/cc **Table 2**). Although they were much lower than that of a thin films (400 emu/cc),⁷⁾ they were comparable to those of some powder (30–67 emu/g)^{8,9)} and the composite film (110 emu/g).⁸⁾ Highly porous ferrite woods have low value of Ms per volume.

Figure 7 shows the coercive field, Hc as the function of the composition x . The coercive field, Hc increased monotonously with the increase of x , where the coercivities in the A and C directions (perpendicular) were larger than that in the B direction (parallel to pores orientation). Therefore it is obvious that the dif-

Fig. 7. Coercivity H_c as a function composition in A, B and C directions for ferrite wood and parallel and perpendicular for thin film.

ference of H_c in the parallel and perpendicular directions was an effect due to the anisotropic structure of wood template. The effect also can be observed in the thin film case,⁷⁾ although the coercivities H_c of thin film were much higher.

4. Conclusions

The magnetic properties of layered porous NiZn ferrite from wood template were studied as a function of composition ratio. The wood template gives the unique structural anisotropy to show the different magnetic properties in the different directions. This magnetic anisotropy was ascribed to the structural anisotropy derived from the wood template. The sintered body exhibited elongated pores enclosed by the thin layer wall. The anisotropic structure of the ferrite wood acts as multilayer films and the magnetic susceptibility was observed to be the same as the magnetic thin films.

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