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Improvement of initial permeability for Z-type ferrite by Ti and Zn substitution

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Abstract

We have found that the initial permeability μ' of Co_2Z ferrite is improved by the substitution of Ti^{4+} and Zn^{2+} ions for Fe^{3+} ions. The substituted sample of $Ba_3Co_2Ti_xZn_xFe_{24-2x}O_{41}$ with $x = 0.85$ has a maximum μ' of 24, which is twice as large as that of the non-substituted sample with $x = 0$. The particle size and shape are changed by the substitution. This is influential in the densification and the preferential orientation of a toroidal-shape sample, which results in the improvement of μ'.

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1. Introduction

In the magnetic iron oxides — ferrite — an O^{2-} ion has a radius of 0.13 nm and the radii of 3d transition metal cations (Fe^{3+} and M^{2+} ions; M = Zn, Mn, Fe, Co, Ni, Cu) are 0.06–0.08 nm. Therefore, Fe^{3+} and M^{2+} ions fill in the gap between the O^{2-} ions which form a crystal frame work. The frame work of the O^{2-} ions has a close-packed structure, so that it basically becomes hexagonal or cubic. The [1 1 1] direction of the cubic lattice corresponds to the *c*-axis direction of the hexagonal lattice [1]. The typical ferrite with a chemical formula of MFe_2O_4 has the cubic spinel crystal structure, where a metal cation is located at an octahedral site with six oxygen ligands or at a tetrahedral site with four oxygen ligands. The radii of Ba^{2+}, Sr^{2+} and Pb^{2+} ions are 0.14, 0.13 and 0.13 nm, respectively, which can compare with that of an O^{2-} ion. Thus, Ba^{2+}, Sr^{2+} and Pb^{2+} ions cannot fill in the gap between the O^{2-} ions in contrast with Fe^{3+} and M^{2+} ions. Consequently, these ions make the layer which borders on the (1 1 1) plane of a spinel structure layer. These layers are stacked up and form a hexagonal crystal. As shown in Table 1, the structures of M-type, W-type, Y-type and Z-type ferrites depend on the combination of layers, where R and T layers contain Ba^{2+}, Sr^{2+} or Pb^{2+} ions [2]. The S layer has the spinel ferrite structure. Fig. 1(a) shows these basic layers. It should be emphasized that the R layer has the cuboid site with five oxygen ligands, which produce a uniaxial ligand field for the metal cation.

The crystal magnetic anisotropy energy E_A of these oxides is firstly expressed as $E_A = K_{u1}\sin^2\theta + K_{u2}\sin^4\theta$, where K_{u1} and K_{u2} are uniaxial magnetic anisotropy constants and θ is the angle from the *c*-axis, reflecting the uniaxial crystal structure. By differentiating this energy with respect to the angle, the minimum stable energy and its angle θ_0 can be determined depending on K_{u1} and K_{u2}. When $K_{u1} > 0$ and $K_{u1} + K_{u2} > 0$, the stable angle θ_0 is zero and the anisotropy becomes uniaxial. When $K_{u1} < 0$ and $K_{u1} + 2K_{u2} > 0$, the easy axis becomes canted from *c*-axis for θ_0, where $\sin\theta_0 = (-K_{u1}/2K_{u2})^{1/2}$. In the other cases, planar anisotropy with $\theta_0 = \pi/2$ takes place. The anisotropy of hexagonal ferrite is shown in Table 2. Y-type ferrite tends to have planar anisotropy, which may be due to the lack of R layer, as mentioned above. Also, it can be seen that Co^{2+} ions tend to change the anisotropy to be

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planar [2,3]. If the anisotropy is planar, another anisotropy in the plane should be considered. Nevertheless, the latter is rather small because of the high symmetry of a hexagonal structure in the *c*-plane. Therefore, the magnetic moment can rotate in the plane rather freely and consequently initial permeability becomes relatively high. Also, considering the precession motion of the magnetic moment, the difference between the strong out-of-plane and the weak in-plane anisotropy makes a higher resonance field, by which it is possible to overcome the difficulty of Snoek's limit [2]. So, for soft magnetism, stronger out-of-plane anisotropy to make $\theta_0 = \pi/2$ stable and weaker in-plane anisotropy for smooth motion of a magnetic moment in the plane are desired. This hexagonal ferrite with planar anisotropy is called a "ferroxplana" [4].

Table 1
Chemical formula and unit cell structure of hexagonal ferrite

Type	Chemical formula[a]	Unit cell structure[b]	Number of molecules in a unit cell
M	$BaO \cdot 6Fe_2O_3$	SRS*R*	2
W	$BaO \cdot 2MO \cdot 8Fe_2O_3$	SSRS*S*R*	2
Y	$2BaO \cdot 2MO \cdot 6Fe_2O_3$	STST	3
Z	$3BaO \cdot 2MO \cdot 12Fe_2O_3$	TSRS*T*S*R*S	2

[a]M is basically a 3d transition metal element.
[b]The R, T and S layers are shown in Fig. 1(a). An asterisk denotes that the layer is turned for 180° around *c*-axis.

The Z-type Co_2Z ferrite ($Ba_3Co_2Fe_{24}O_{41}$) is one of the ferroxplana type hexagonal ferrites found in 1950 [4,5]. The crystal structure is hexagonal with a space group of P63/mmc. The lattice constants of *a* and *c* are 0.588 and 5.231 nm, respectively [6]. So, the unit cell is long as shown in Fig. 1(b). This Co_2Z ferrite has a relatively high μ' of about 15 up to a high frequency region (300–1000 MHz) because of in-plane magnetic anisotropy as mentioned above [2,7].

There is an increasing demand to miniaturize electronic devices, and to develop surface mounting technology. Also, the operating frequency of the devices is in the GHz region.

Table 2
Magnetic anisotropy of hexagonal ferrite

Description	Chemical formula	Anisotropy
BaM	$BaFe_{12}O_{19}$	Uniaxial
Fe_2W	$BaFe_{18}O_{27}$	Uniaxial
FeZnW	$BaZnFe_{17}O_{27}$	Uniaxial
$Fe_{0.5}Zn_{1.5}W$	$BaZn_{1.5}Fe_{16.5}O_{27}$	Uniaxial
$Fe_{0.5}Co_{0.75}Zn_{0.75}W$	$BaCo_{0.75}Zn_{0.75}Fe_{16.5}O_{27}$	Weakly planar
FeCoW	$BaCoFe_{17}O_{27}$	Weakly uniaxial
Co_2W	$BaCo_2Fe_{16}O_{27}$	Weakly planar
Ni_2W	$BaNi_2Fe_{16}O_{27}$	Uniaxial
Mg_2Y	$Ba_2Mg_2Fe_{12}O_{22}$	Weakly planar
Ni_2Y	$Ba_2Ni_2Fe_{12}O_{22}$	Planar
Zn_2Y	$Ba_2Zn_2Fe_{12}O_{22}$	Planar
Co_2Y	$Ba_2Co_2Fe_{12}O_{22}$	Planar
Co_2Z	$Ba_3Co_2Fe_{24}O_{41}$	Planar

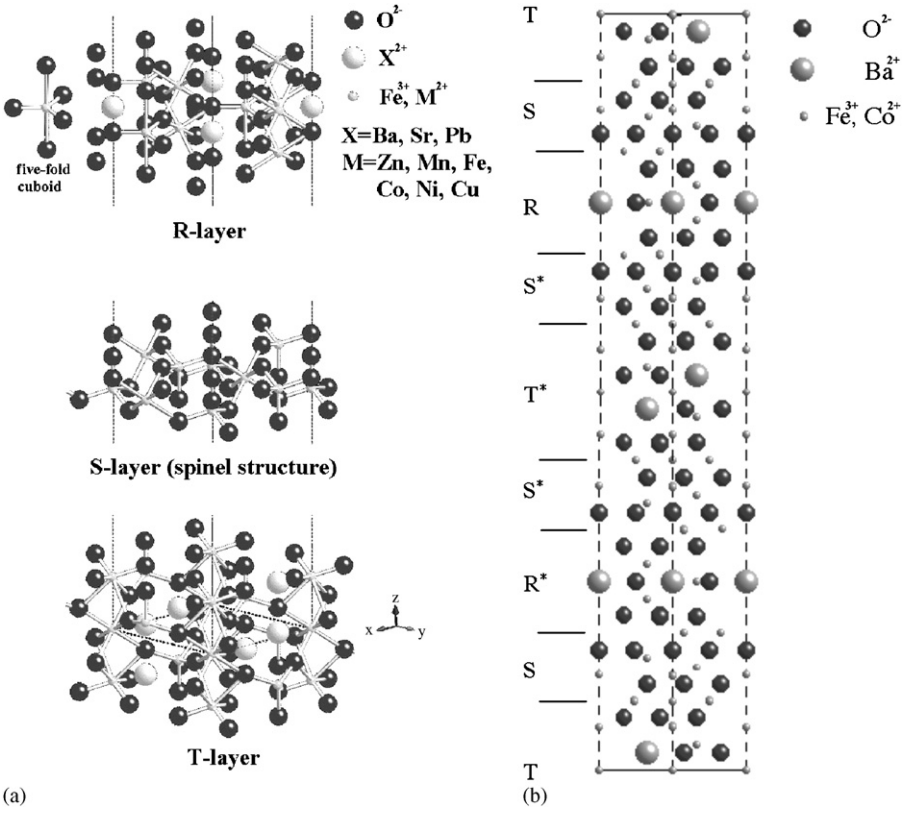

Fig. 1. (a) Basic layers for a hexagonal ferrite and (b) crystal structure of Co_2Z ferrite ($Ba_3Co_2Fe_{24}O_{41}$).