New MnZn Ferrites with High Saturation Flux Density

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Abstract

New and emerging ferrite applications where significant power is involved (i.e. in automotive), impose stronger demands on the performance of magnetic cores, such as that the components should exhibit higher saturation flux densities at high temperatures, than those currently exhibited by existing components, with the lowest possible effects on other important magnetic properties (i.e. initial magnetic permeability, power losses). In this article the development of a MnZn ferrite polycrystalline material is reported with a saturation flux density of 642 mT at 10 kHz, 1200 A/m, 25°C and 550 mT at 100°C. The initial permeability is 1020 (10 kHz, 0.1 mT, 25°C) and the power losses 800 mW cm⁻³ (100 kHz, 200 mT, 100°C). The previous results place this material among the best in its class. The improvements have been realized through optimizations in the design of the antiferrimagnetic unit cell lattice as well as through optimizations on the processing and the microstructural evolution of the polycrystalline structure.

Key Words: High saturation flux density, Iron excess MnZn ferrites

I. INTRODUCTION

MnZn ferrites can be found in almost all nowadays electric or electronic equipment of industrial sectors [1]. New applications possess stronger demands on the performance of the magnetic cores. These applications require that the magnetic components exhibit a higher saturation flux density (B_s) than those currently existing, with the lowest possible counter effects on other important magnetic properties. Commercially available materials exhibit power losses (P_v) below 400 mW cm⁻³ (at 100 kHz, 200 mT, 100°C) and $B_s \sim 450$ mT (at 10 kHz, 1200 A/m, 100°C). The new arising applications (i.e. inverter units) require 20% higher B_s at 100°C with P_v levels preferably below 1000 mW cm⁻³. The reported P_v of MnZn ferrite materials with $B_s \geq 550$ mT exceed 1000 mW cm⁻³. At 100 kHz, 200 mT the hysteresis loss contribution dominates the total losses. In general a μ_i of at least 1000 is required for high B_s applications. Although this requirement is fulfilled for most materials with $B_s < 500$ mT (at 100°C), it is not satisfied by existing MnZn ferrites with higher B_s .

II. EXPERIMENTAL PART

MnZn ferrite materials of the cubic spinel structure and with the general formula $\text{Mn}_{1-x}\text{Zn}_x\text{Fe}_{2+2\delta}\text{O}_4$ have been synthesized according to the mixed oxide method, as reported elsewhere [2]. The toroidal compacted specimens were sintered at 1325°C at various oxygen partial pressures in nitrogen. The cooling of the samples took place under controlled oxygen partial pressures, so that no additional oxidation or reduction occurs during cooling [3].

III. RESULTS AND DISCUSSION

The effect of Fe_2O_3 excess of the basic composition is investigated as shown in Table I. It is expected that an excess (δ) of Fe_2O_3 in the system $(1+\delta)\text{Fe}_2\text{O}_3+x\text{ZnO}+(1-x)\text{MnO}$ will lead to the creation of cation vacancies in the A-sublattice in order to compensate for the Fe^{3+} excess. If the iron excess will be reduced then Fe^{2+} will also be present. A-sublattice defect concentrations will diminish the concentration of the divalent manganese cations. Since Fe^{2+} has a spin magnetic moment of $4\mu_B$ and Mn^{2+} of $5\mu_B$ the total magnetization of the A-sublattice is expected to be reduced. The total saturation magnetization (M_s), i.e. the difference between the two magnetizations of the two sublattices, is expected to increase. The X-ray pattern shows that specimens 1-3 consist only of the spinel phase. By increasing Fe_2O_3 content further, secondary phase appears. These include Fe_3O_4 (Nr.4) and additionally even Fe_2O_3 (Nr.6). The B_s of synthesis Nr.1 is measured to be 465 mT, while that of synthesis Nr.3 (65 mol%) is measured to be 478 mT. Syntheses 4-6 give lower B_s values. This is

attributed to the presence of the previously mentioned secondary phases.

In addition, iron contents higher than 65 mol% result to even lower sintered densities (SD). Fe_2O_3 excess ferrites basically have lower densities since cation vacancies are introduced into the unit cell. These result to lower anion vacancy concentrations, which means lower oxygen diffusion rates and therefore also lower densification rates. Lower SD reduces the magnetic flux per unit volume, reduces the μ_i and increases the P_v . Higher iron contents also lead to higher $[\text{Fe}^{2+}]/[\text{Fe}^{3+}]$ ratios, which leads to lower specific resistivities (ρ). The conductivity occurs by electron hopping between Fe^{2+} and Fe^{3+} ions located on crystallographically equivalent lattice sites. Increase of Fe_2O_3 , increases the concentration of Fe^{2+} - Fe^{3+} pairs and the conductivity, which leads to increased eddy current losses and therefore to increased total P_v [4].

Table I Chemical composition of $\text{Mn}_{1-x}\text{Zn}_x\text{Fe}_{2+2\delta}\text{O}_4$ ferrite synthesis and influence of iron excess (δ) on magnetic properties.

Synthesis Nr.	δ	x	SD (g cm^{-3})	B_s (mT) at 10 kHz, 1200 A/m, 100°C	μ_i at 10 kHz, 0.1 mT, 25°C	P_v (mW cm^{-3}) at 100 kHz, 200 mT, 100°C
1	0.156	0.131	4.94	465	1850	380
2	0.5	0.131	4.80	470	510	1250
3	0.857	0.131	4.75	478	332	1460
4	1.333	0.131	4.67	450	170	>>2000
5	2	0.131	4.62	440	82	>>2000
6	3	0.131	4.49	430	46	>>2000

Having established the optimum Fe_2O_3 at around 65 mol% (i.e. $\delta=0.857$), further material development efforts follow:

(i) the Mn/Zn mol ratio is decreased from ~ 6.63 to ~ 1.1 . The replacement of almost half of the Mn^{2+} with non magnetic Zn^{2+} will cause an additional disproportionation between the total magnetic moments of the A- and B-sublattices and a further increase in B_s . The B_s that gives the synthesis with Mn/Zn mol ratio at ~ 6.63 is measured to be 570 mT at 25°C and 475 mT at 100°C, while when the Mn/Zn mol ratio is ~ 1.1 the B_s is measured to be 600 mT at 25°C and 510 mT at 100°C. Zn ions preferentially occupy the A sites of the spinel lattice. The magnetization $M=|M_B-M_A|$ will increase since the magnetization of the A-sublattice is reduced due to the presence of Zn. This occurs up to Mn/Zn mol ratio ~ 1 , because at higher Zn contents the A-B distance increases, thereby the A-B exchange interaction reduces and finally the magnetic coupling is reduced so that the total M also reduces.

(ii) addition of NiO in the composition, actually Ni^{2+} cations in the unit cell, at amounts of 0-5 mol%. NiFe_2O_4 is known for its high ρ in relation to MnZn ferrites and is expected to play an important role in the P_v due to depression of the eddy current loss contribution. It has also higher T_C in relation to MnZn ferrites. NiO raises the T_C and leads to increase of the B_s . The ρ of sintered samples is measured within a range between DC and 1 MHz. It is found that NiO addition increases the ρ during the whole frequency range. The samples without NiO have typical DC resistivity of 1.41 Ωm , while for the samples in which NiO is added is 1.72 Ωm . Zn and Ni ions occupy tetrahedral and octahedral positions respectively. Fe and Mn ions occupy both A-sites and B-sites. The probability of finding Mn and Fe ions at A- and B-sites respectively, is bigger. Fe and Mn ions exist in 2+ as well in 3+ states. When Ni^{2+} ions are introduced, some of the Fe ions migrate from B-site to A-site, decreasing thereby the Fe^{3+} ion concentration at octahedral (B-sites). The probability of Fe^{2+} - Fe^{3+} electron hopping is reduced resulting in increase in resistivity. Higher ρ can also be attributed to the smaller grain size. As it is evident in Fig. 1, in the case of the samples which contain no NiO the mean grain diameter is $4.2\pm 0.3 \mu\text{m}$, while is $3.5\pm 0.3 \mu\text{m}$ in that cases of the samples in which NiO is added. Small grains give a large number of grain boundaries, acting as scattering centers for the flow of electrons and results to the increase of ρ . A high B_s at 100°C is not only a question of high moment lattice but also a question of temperature stable magnetization. B_s can be further increased by increasing the T_C , as happens with NiO addition. The shortage in distances between the moments of A- and B-sublattices leads the A-B interactions to increase and consequently T_C is increased. The B_s at 10 kHz, 1200 A/m and at 100°C is 510 mT in the case of the samples that have no NiO, while it increases to 540 mT when NiO is added, as shown in Table II.

(iii) Co_3O_4 is added into the Ni rich sample (Table II) in order to increase further the μ_i and decrease the P_v . If K_I is the magnetocrystalline anisotropy constant of the cubic crystal system, it represents the resistance of the energy barriers that the magnetic dipoles must overcome in order to be aligned in agreement with the direction of the applied field. K_I

depends on the interactions between the ions at various lattice sites. When K_I is small, the orientation of the magnetic dipoles to favorable directions of the external magnetic field is easier and then the μ_i becomes higher and the P_v lower. K_I decreases with temperature until a certain temperature T_o where it is zero. It takes negative values at higher temperatures, which means that the anisotropy field changes directions. Co^{2+} ion is known to contribute positively to the anisotropy in cubic spinel system. Its anisotropy constant dominates the temperature dependence of μ_i under the same iron content and increases with the increase of Co^{2+} which also results in the decrease of T_o . The increase of cobalt content increases also the saturation magnetization as shown in Table III. As Cobalt is a bulk dopant that dissolves into the spinel lattice, Co^{2+} enter the lattice at interstitial sites. The magnetic ions are dissolved in the spinel lattice and thus the M_s is increased.

Table II Influence of NiO on microstructure and magnetic properties.

	no NiO	0-5 mol% NiO
Number of grains (Fig. 1)	66	103
Mean grain diameter (μm)	4.2 ± 0.3	3.5 ± 0.3
DC resistivity (Ωm)	1.41	1.72
P_v (mW cm^{-3}) at 100 kHz, 200 mT, 25°C	1800	1630
P_v (mW cm^{-3}) at 100 kHz, 200 mT, 100°C	1350	1100
B_s (mT) at 10 kHz, 1200 A/m, 25°C	600	630
B_s (mT) at 10 kHz, 1200 A/m, 100°C	510	540

Fig. 1 SEM images of the polycrystalline microstructure of samples without (A) and with (B) NiO

Table III Influence of Co_3O_4 addition on magnetic properties.

	no Co_3O_4	0-2 mol% Co_3O_4 , typical values
μ_i at 10 kHz, 0.1 mT, 25°C	760	1020
P_v (mW cm^{-3}) at 100 kHz, 200 mT, 25°C	1630	1500
P_v (mW cm^{-3}) at 100 kHz, 200 mT, 100°C	1100	800
P_v (mW cm^{-3}) at 10 kHz, 400 mT, 25°C	495	350
P_v (mW cm^{-3}) at 10 kHz, 400 mT, 100°C	310	275
B_s (mT) at 10 kHz, 1200 A/m, 25°C	630	642
B_s (mT) at 10 kHz, 1200 A/m, 100°C	540	550

IV. CONCLUSIONS

A synthesis with ~65 mol% Fe_2O_3 and Mn/Zn mol ratio ~1.1 that combines the absence of non magnetic secondary phases and the replacement of the Mn^{2+} with non magnetic Zn^{2+} , results to high B_s . NiO addition results to higher ρ and higher T_C , consequently B_s increases more. Co^{2+} which dissolves into the spinel lattice and contributes positively to the anisotropy is added. This leads to a further improvement on B_s , increase of μ_i and decrease of P_v . The development of a new MnZn ferrite with B_s of 550 mT (at 10 kHz, 1200 A/m, 100°C), μ_i of 1020 (10 kHz, 0.1 mT, 25°C) and P_v of 800 mW cm^{-3} (100 kHz, 200 mT, 100°C), has been realized through optimizations in the design of the antiferrimagnetic unit cell lattice as well as through optimizations on the microstructural evolution of the polycrystalline structure.

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