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Measuring and modeling broadband magnetic losses versus temperature and aging effects in CoO-doped Mn-Zn ferrites

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Abstract — We analyze the physical mechanisms associated with addition of CoO to sintered Mn-Zn ferrites and the ensuing stabilization versus temperature of their magnetic properties. We determine, in particular, the value and behavior of the magnetic anisotropy as a function of doping and temperature and we model in physical terms the evolution of the energy loss in the investigated frequency (DC – 1 GHz) and temperature (-20 °C – +130 °C) ranges. We show that magnetic aging by long exposure of the CoO-doped ferrites at 200 °C is minimized by additional TiO₂ doping. This is observed to restrain the increase of the extra-anisotropy induced by directional ordering of the Co²⁺ cations.

Keywords—Mn-Zn ferrites, magnetic anisotropy, magnetic losses.

I. INTRODUCTION

Modern power electronic applications, such as those in mobile communications, automotive, electric charging, and other sectors, often require the development of soft magnetic materials operating over a wide range of temperatures with the lowest possible power losses. To this end, it is common practice in the conventional ceramic/industrial manufacturing of sintered Mn-Zn ferrites to introduce selected additives, with the objective of achieving the best compromise between intrinsic and structural dependent magnetic properties [1], [2]. Solute cations can modify, in particular, sign and value of the magnetic anisotropy in a temperature dependent fashion, leading to the phenomenon of anisotropy compensation [3]. For example, Co²⁺ ions, obtained by dissolution of CoO added to the prefired powders, combine their anisotropy with the native anisotropy, associated with the Fe³⁺ cations, of the host lattice. With appropriate concentrations of CoO, the temperature dependence of the resulting anisotropy constant $\langle K_{\text{eff}} \rangle$, that is, of magnetic permeability and losses, can be effectively loosened, with obvious benefits in many applications [4], [5]. However, CoO-doped ferrites are prone to magnetic aging, when

exposed for a long time to sufficiently high temperatures, because the Co²⁺ cations tend to diffuse in anisotropic fashion. This becomes an obvious drawback, because recent material requirements, like those imposed by automotive applications, call for a stable magnetic performance of the Mn-Zn ferrite cores against thermal exposure. On the other hand, it is known that Ti⁴⁺ ions can hinder the diffusion of Co²⁺ [6]. Consequently, addition of TiO₂ has been investigated as a tool for compensating the aging effect promoted by Co²⁺ [7]. But a coherent physical approach to the manifold magnetic phenomenology ensuing from manipulation of such additives lacks at present time in the literature.

In this work, we investigate by experiment and theory the magnetic properties of CoO-added Mn-Zn ferrites, their dependence on temperature and magnetizing frequency, the effect of aging, and its control by addition of TiO₂. The strict relationship existing between magnetic permeability and energy loss is highlighted and the way these quantities are influenced by doping upon an extremely wide range of frequencies is quantified. The underlying physical approach relies, on the one hand, on the principle of loss decomposition and, on the other hand, on the role of ferromagnetic resonance.

II. EXPERIMENTAL METHOD

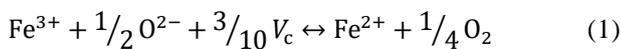
The preparation of the investigated ferrite specimens included the solidstate processing of selected high-purity raw materials following the proportion of 0.487 mol % Fe₂O₃, 0.421 mol % MnO and 0.092 mol % ZnO, which were weighed, mixed and prefired at 850°C in air. Certain additives, such as CaO and Nb₂O₅ were pre-selected [8, 9], while CoO addition varied between 0 and 6000 ppm. The 3000 ppm CoO-doped ferrite, which shows the best stability of the magnetic properties versus temperature, was then enriched by TiO₂ = 1000 and 5000 ppm. The doped batches

were milled for 9 hours and were subsequently granulated using 0.2 wt % Polyvinyl Alcohol. The specimens, uniaxially compacted with a press density of $2.90 \pm 0.02 \text{ g/cm}^3$, were sintered at 1325°C according to the Morineau-Paulus equilibrium [10], in order to reach a constant oxidation degree of the material during heating and cooling. The prepared powders were morphologically and structurally evaluated by means of laser scattering, N_2 adsorption-desorption and X-Ray Diffraction respectively, while the sintered specimens were examined in terms of sinter density and polycrystalline microstructure by means of Archimedes' method and scanning electron microscopy, respectively. The aging test of the specimens containing TiO_2 was performed by thermal exposure of the cores at 200°C for 100 hours in air. Ring samples of outside diameter $D_o = 14 \text{ mm}$, inside diameter $D_i = 9 \text{ mm}$, and thickness of $4.55 - 5.02 \text{ mm}$ were prepared. Selected specimens of each doping level had their thickness reduced to about 1 mm, in order to make negligible the eddy current losses at all frequencies.

The DC magnetization curve, measured on the ring samples up to $H = 6 \text{ kA/m}$ and extrapolated in the $(J, 1/H)$ plane to the limit $1/H \rightarrow 0$ provided saturation polarization values J_s at room temperature ranging between 0.540 T (without CoO and TiO_2 additions) and 0.504 T (with $\text{CoO} = 3000 \text{ ppm}$ and $\text{TiO}_2 = 5000 \text{ ppm}$). The AC characterization was performed applying the fluxmetric method up to a few MHz and a transmission line method, based on the use of a Vector Network Analyzer (VNA), between a few hundred kHz and 1 GHz. Details on the employed fluxmetric setup and the VNA procedure are provided in [7, 11]. Measurements of the real ρ' and imaginary ρ'' parts of the electrical resistivity, carried out by the four-point method up to 20 MHz, reveal the typical RC response of the Mn-Zn sintered ferrites. ρ' attains a constant value (corresponding to the average resistivity of the grains) and ρ'' becomes negligible, because of the capacitive short provided by the nanometer thick grain boundaries, above about 1 MHz [12].

III. EXPERIMENTAL RESULTS AND DISCUSSION

The preliminary evaluation of the ferrite material showed that all prepared Co-doped and Co-Ti-doped Mn-Zn ferrite powders are morphologically and structurally comparable. All sintered specimens are of pure cubic (spinel) structure. The comparison of the polycrystalline microstructure of the sintered Co-doped samples shown in Figs. 1a-c revealed that the addition of Co does not affect grain growth, as the average grain size ($\langle s \rangle \sim 11.8 \mu\text{m}$) remains basically unchanged. However, the introduction of TiO_2 is known to limit to some extent the grain growth [13], as confirmed by the images presented in Fig. 1d ($\langle s \rangle \sim 10.1 \mu\text{m}$). This can be explained, according to (1), in terms of equilibrium between the material and the atmosphere during the sintering process



Because of the presence of Ti^{4+} and the associated creation of cation vacancies V_c , the diffusion mechanism for impurity ions is enhanced and so is their segregation at the grain boundaries. The reaction (1) is retarded (shifted to the left) and the concentration of Fe^{2+} is limited by the formation

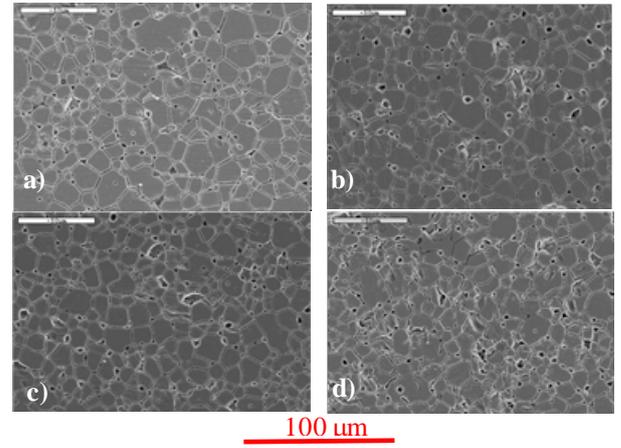


Fig. 1. SEM micrographs of Mn-Zn ferrites with different degrees of doping: a) Undoped; b) Doped with addition of 3000 ppm CoO; c) 5000 ppm CoO; d) 3000 ppm CoO + 5000 ppm TiO_2 .

of tightly bound $\text{Ti}^{4+}\text{-Fe}^{2+}$ pairs.

The basic outcome of optimal CoO addition is the reduced dependence of magnetic loss and initial permeability on temperature. Such property bears an obvious advantage in applications (e.g. in power electronics), where working temperatures around 100°C are the rule. It chiefly arises from the smoothing of the dependence of the magnetocrystalline anisotropy $\langle K_{\text{eff}} \rangle$ versus temperature, which we have quantitatively estimated across the whole spectrum of adopted CoO additions [12]. Such estimate, going beyond the usual qualitative assumptions of the literature, follows from the identification of the rotational permeability μ_{rot} , as distinguished from the domain wall (DW) permeability μ_{dw} . A procedure has in fact been devised, by which, starting from the idea that the imaginary permeability μ'' (i.e. the loss) at low (quasi-static) frequencies is exclusively due to the DW motion, we can eventually obtain the permeability components $\mu'_{\text{dw}}, \mu''_{\text{dw}}, \mu'_{\text{rot}}, \mu''_{\text{rot}}$ as a function of frequency [14]. To remark that the concept of complex permeability holds and $\mu = \mu' - j\mu''$ can be taken as a magnetic constitutive equation of typical Mn-Zn ferrites up to peak polarization value $J_p \sim 100 - 200 \text{ mT}$. We thus arrive, by knowledge of the DC relative rotational permeability $\mu_{\text{rot,DC}}$, at the following estimate for the effective anisotropy constant

$$\langle K_{\text{eff}} \rangle \cong J_s^2 / 3\mu_0 \mu_{\text{rot,DC}} \quad , \quad [\text{J/m}^3] \quad (2)$$

where μ_0 is the magnetic constant and, according to the experiments, $\mu_{\text{rot,DC}} \gg 1$. With the concept of effective anisotropy we account for the contributions arising, besides the one-ion term provided by the crystalline symmetry, from the internal (grain-to-grain) magnetostatic fields and possible directional ordering effects. The latter contribution is what is expected to occur in the aged CoO-doped ferrites, as the result of the anisotropic diffusion of the Co^{2+} cations towards the B-sites. Whatever the magnetization process (DW motion, rotations, their resonant phenomena), $\langle K_{\text{eff}} \rangle$ is involved, the lower $\langle K_{\text{eff}} \rangle$ the softer the magnetization process and the lower the resonance frequency. The overall view of the evolution of $\langle K_{\text{eff}} \rangle$ with temperature shown in Fig. 2 for different degrees of doping, before and after aging, makes clear how, by suitable CoO addition, $\langle K_{\text{eff}} \rangle$ is

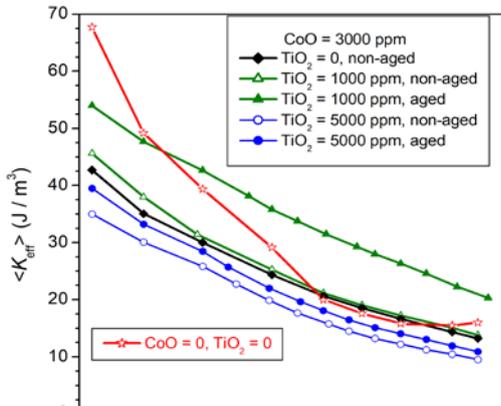


Fig. 2. Effective average anisotropy constant $\langle K_{\text{eff}} \rangle$ versus temperature, as calculated, according to (2), from the rotational DC permeability $\mu_{\text{rot,DC}}$. The smoothing out of the $\langle K_{\text{eff}} \rangle$ vs. T dependence by 3000 ppm CoO doping is apparent. With the addition of 5000 ppm TiO_2 , the increase of $\langle K_{\text{eff}} \rangle$ upon aging (100 hours at 200 °C) is dramatically reduced.

decreased in value and smoothed in its dependence on temperature. However, a prolonged treatment at 200 °C, emulating likely working conditions of the magnetic cores, is conducive to an increase of $\langle K_{\text{eff}} \rangle$ by directional ordering in the CoO-doped ferrites. Here the role of the Ti^{4+} ions, resulting from the dissolution of additional 5000 ppm TiO_2 , in curbing this process is apparent.

This evolution of $\langle K_{\text{eff}} \rangle$ with doping and temperature has an obvious counterpart in the behavior of the magnetic loss $W(f, J_p)$ versus frequency f and J_p . It is a matter best assessed by adopting the concept of loss separation, both for what concerns the standard decomposition of W into the hysteresis W_h , excess W_{exc} , and classical W_{cl} components [15] and the separation between rotational and DW related losses [16].

On the one hand, the DW energy, directly affecting W_h and W_{exc} , is proportional to $K_{\text{eff}}^{1/2}$. On the other hand, the energy dissipated via damped spin rotation inside the

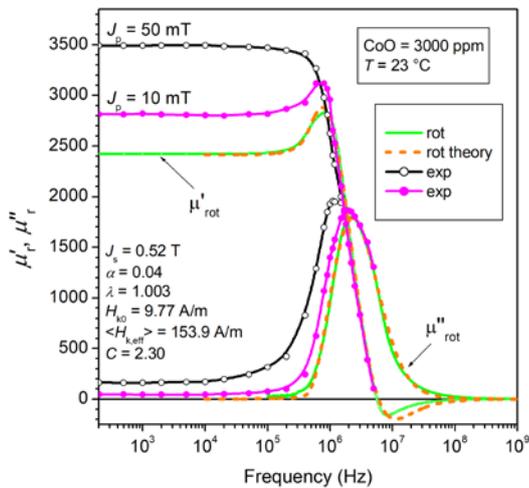


Fig. 3. An example of behavior of the relative rotational permeabilities $\mu'_{\text{rot}}(f)$ and $\mu''_{\text{rot}}(f)$ versus frequency (solid lines), as extracted from the complex permeability $\mu(f)$ in a CoO-doped Mn-Zn ferrite. The DW permeabilities $\mu'_{\text{dw}}(f)$ and $\mu''_{\text{dw}}(f)$ are obtained by subtracting the rotational quantities from the measured ones. The dashed lines are calculated starting from the Landau-Lifshitz equation for the damped spin precession, as discussed in [12, 14].

domains peaks at the resonance frequency $f_0 \propto K_{\text{eff}}$. It is then possible to qualitatively and quantitatively understand the behavior of magnetic loss and permeability versus frequency under the different conditions and parameters to be faced in applications by separating the DW and rotational contributions by separating the magnetization process and by correspondingly assessing the behaviors of the loss components. To this end, a specific methodology has been devised, where the measured permeability is decomposed in the rotational $\mu_{\text{rot}} = \mu'_{\text{rot}} - j\mu''_{\text{rot}}$ and DW $\mu_{\text{dw}} = \mu'_{\text{dw}} - j\mu''_{\text{dw}}$ contributions [12, 14]. An example of such decomposition in the 3000 ppm CoO ferrite is shown in Fig. 3. The experimental μ'_{rot} and μ''_{rot} are theoretically predicted (dashed lines) as solutions of the Landau-Lifshitz equation with distributed anisotropy fields $H_{k,\text{eff}} = 2\langle K_{\text{eff}} \rangle / J_s$ [17]. It is then immediate to translate the calculated μ'_{rot} and μ''_{rot} into the corresponding $W_{\text{rot}}(f) \equiv W_{\text{cl}}(f)$ and obtain the loss decomposition shown in Fig. 3 (thin sample, dashed lines). To note in this figure that CoO doping brings about a remarkable decrease of the hysteresis loss, which increases to some extent again after aging. This effect is quantified by the expression

$$W_h(J_p) = 8a(J_p)\sqrt{A} \frac{\sqrt{\langle K_{\text{eff}} \rangle}}{J_s \langle s \rangle} \cdot \frac{\mu_{\text{dw,dc}}}{\mu_{\text{dw,dc}} + \mu_{\text{rot,dc}}} J_p, \quad [\text{J/m}^3] \quad (3)$$

where $a(J_p)$ is a parameter lumping the effect of the material microstructure and A is the exchange stiffness constant [12]. Fig. 4 shows that the eddy current losses are confined to very high frequencies, beyond a few MHz, and become negligible in sufficiently thin samples ($d \leq 1.5 - 1.0 \text{ mm}$). The corresponding term $W_{\text{eddy}}(f)$ is calculated by a simple

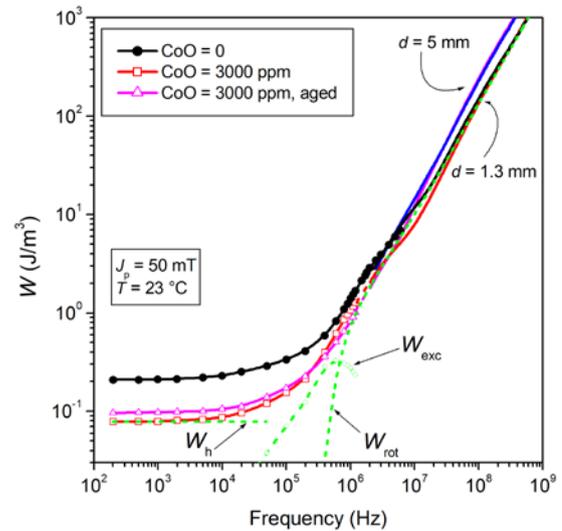
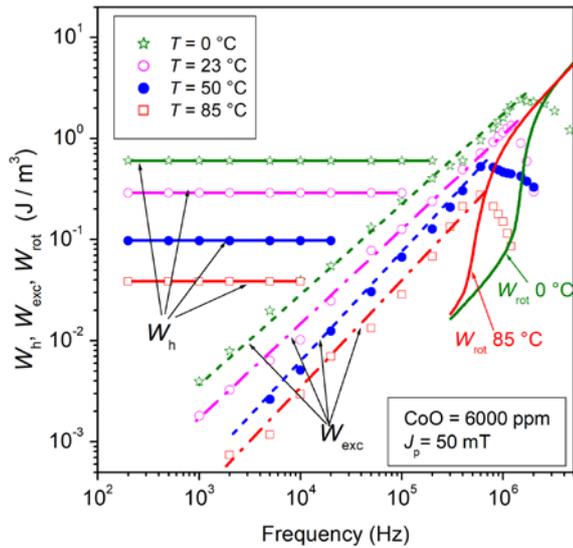


Fig. 4. Magnetic energy loss $W(f)$ before and after 3000 ppm CoO addition. The doped material is eventually subjected to 100-hour aging at 200 °C. The dashed lines show an example of decomposition of the measured loss according to $W(f) = W_h + W_{\text{exc}}(f) + W_{\text{rot}}(f)$, where $W_{\text{rot}}(f)$ is calculated starting from the solution of the Landau-Lifshitz equation with distributed anisotropy field. The hysteresis component behaves according to (3). The bifurcation of $W(f)$ beyond a few MHz is related to the dissipation by eddy currents in the thicker sample.



analytical expression [18] and can be singled out. W_h , $W_{exc}(f)$, and $W_{rot}(f)$ are then extracted, as shown in the example of Fig. 5, where temperatures T ranging between 0 °C and 85 °C are considered. W_h and $W_{exc}(f)$, both originating from the dissipative dynamics of the DWs, follow a same monotonic decreasing trend with increasing T , consistent with the corresponding behavior of $\langle K_{eff} \rangle$ (see Fig. 1). Their combined contribution to $W(f)$ is eventually overcome at high

Fig. 5. Decomposition of the energy loss $W(f)$ measured at $J_p = 50$ mT in a high-CoO (6000 ppm) Mn-Zn ferrite sample. W_h and $W_{exc}(f)$ monotonically decrease with increasing the temperature T , following the decrease of $\langle K_{eff} \rangle$. The contribution by W_{rot} can be appreciated on approaching the MHz range.

frequencies by $W_{rot}(f)$, whose dependence on T (i.e. on $\langle K_{eff} \rangle$) is somewhat opposite to the one followed by W_h and $W_{exc}(f)$. This is understood in terms of distribution of resonance frequencies $f_0 \propto K_{eff}$, which move downward, together with their dissipative effects, on increasing T .

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