Published in IEEE TRANSACTIONS ON MAGNETICS CTOBER 2011

Pressure Dependence of the Frequency Permeability Spectra of Soft Ferrite Composite Materials: A Method of Measuring the Natural Ferromagnetic Resonance Frequency

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Experimental studies on the complex susceptibility of soft magnetic composite materials (magnetostrictive Ni-Zn and Ni-Zn-Co spinels) in their region of ferrimagnetic resonance (FMR) show that the FMR is an increasing function of the applied pressure. It is shown that powders could advantageously replace their sintered materials counterpart to measure without any ambiguity the natural ferrimagnetic resonance (NFMR) frequencies of bulk materials. It is also shown that such soft ferrite composites can be realized in order to shift FMR to higher values, and to obtain low magnetic losses up to 900 MHz. High frequencies applications can be envisaged.

***Index Terms*—Ferrimagnetic materials, ferrites, microwave materials, natural ferrimagnetic resonance measurements.**

I. Introduction

THIS study deals with investigations on the ferrimagnetic resonance (FMR) of various types of spinel ferrites powders. In particular, it is shown how powders might advantageously replace sintered materials to measure their natural ferrimagnetic resonance (NFMR) frequency. The studied materials are different in their chemical nature (Ni-Zn and Ni-Zn-Co-In spinels) as well as in their preparation mode (powders obtained either by grinding sintered ferrites or by co-precipitation method). Regarding ground powders, it is well known that residual stresses are able to partially screen the intrinsic magnetic properties by introducing additional anisotropy terms. This is true in particular for stress sensitive materials for which the FMR frequency deviates far from NFMR value. The experimental value of the effective anisotropy field $\mathrm{H_K}$ is then hardly accessible. Therefore, through a study of the stamping effects observed on the high frequency susceptibility in the FMR region, this work shows how powders provide an efficient way to overcome the problem of the uncontrolled internal stresses. This study also shows that the shifting to higher frequencies of the dispersive region (and of the associated magnetic losses) allow to considerate stressed ferrites as potential candidates for frequencies applications up to 900 MHz.

II. Experiments

Nano-sized particles (diameter = 30 nm) of spinel ferrite $\mathrm{Ni_{0.7}Zn_{0.3}Fe_2O_4}$, $\mathrm{Ni_{0.4}Zn_{0.6}Fe_2O_4}$, and $\mathrm{Ni_{0.5}Zn_{0.3}Co_{0.2}In_{0.02}Fe_{1.98}O_4}$ were prepared by co-precipitation method. More details on synthesis process and on structural characterization can be found in [1]. Soft magnetic composite materials were prepared by mixing epoxy resin with ferrite particles (with a magnetic load C at about 0.5). This value must be carefully chosen. Actually, it is an experimental fact that inner demagnetizing effects turn to outer effects when the fraction in magnetic matter goes through a particular value [2], [3]. For heterogeneous and randomly structured materials, cooperative phenomena in the composite arise at a percolation threshold Cp that lies between filler fractions from 20 to 40-vol.% [2], [4]. Therefore, in order to avoid such inner demagnetizing effects on the FMR value, C value was chosen above the percolation threshold. It has been demonstrated that, above $\mathrm{C_P}$ the resonance frequency no longer depends on the magnetic load [5], [13]. The mixture was moulded under uniaxial stress, with various applied pressure values. It must be obvious that for further experiments, the sample thickness will be reduced by the applied pressure; consequently the magnetic load will increase. However this will not affect the measured resonance frequency, precisely because the magnetic load remains well above the percolation threshold. Because C is well above the percolation threshold, the magnetic particles are expected to form a percolating cluster. Therefore a pressure applied on the sample would lead the magnetic particles to be strongly fitted into each other. The anisotropy induced by the pressure is therefore not expected to relax, and this is will be well confirmed by the experiments.

A Hewlett Packard HP 8753ES network analyzer and APC7 coaxial-line setup was used for the measurements of the complex permeability ($\mu = \mu' - \mathrm{j}\mu''$) in the frequency range [10 MHz–6 GHz]. The measured FMR frequencies $\mathrm{F_R}$ are obtained from permeability spectra measurements (maximum of the imaginary part), for various applied pressures. The accuracy on the measured values of $\mathrm{f_R}$ is always better than 50 MHz. The reproducibility of the presented experiments have been checked, on these spinels ferrites, as well as on other soft ferrites (not shown in this paper).

Manuscript received February 21, 2011; revised May 17, 2011; accepted May 20, 2011. Date of current version September 23, 2011. Corresponding author: J.-L. Mattei (e-mail: mattei@univ-brest.fr; jean-luc.mattei@univ-brest.fr).

Digital Object Identifier 10.1109/TMAG.2011.2157899

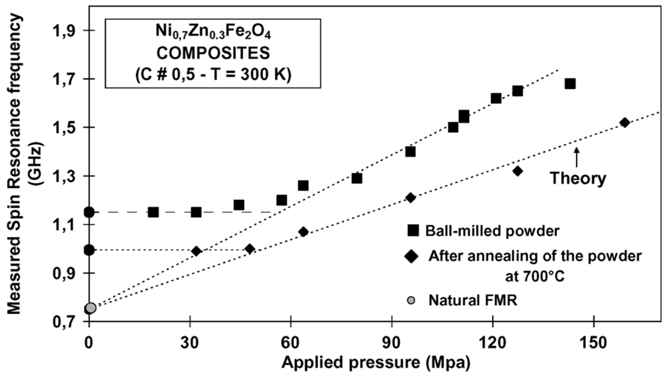

Fig. 1. Effect of the moulding pressure on the FMR of $Ni_{0.7}Zn_{0.3}Fe_2O_4$ composite materials and for different treatment applied on materials.

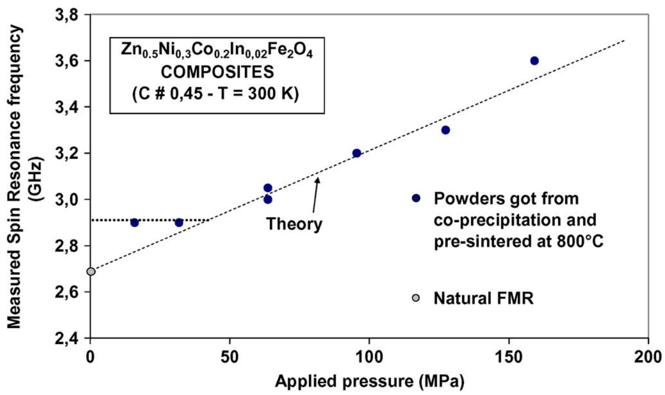

Fig. 2. Effect of the moulding pressure on the FMR of $Ni_{0.5}Zn_{0.3}Co_{0.2}In_{0.02}Fe_{1.98}O_4$ composite materials.

III. Discussion

Let first focus on Fig. 1, that shown results concerning ball-milled powders, together with those of annealed particles (700°C/1 hour). The FMR frequency increases linearly with the compression strength only beyond a pressure threshold (50MPa). Below this threshold value, FMR remains insensitive to variations of the applied pressure. This is well confirmed by annealing.

These results show how the pressure applied during the moulding phase may have a persistent action on the value of the FMR. As expected annealing reduces the amount of internal stresses and simultaneously reduces the FMR values. Whatever the treatment applied to the particles during the manufacturing process, the straight lines converges towards the measured NFMR frequency of the bulk material (750 MHz for $Ni_{0.7}Zn_{0.3}Fe_2O_4$ [6]).

Fig. 2 is another example still concerning spinel materials, but with addition of cobalt and substitution of Indium ($Ni_{0.5}Zn_{0.3}Co_{0.2}In_{0.02}Fe_{1.98}O_4$). It is known that such changes in the chemical composition lead to an increase of the effective anisotropy field [7], [8] and of the magnetization [9], and then to the simultaneous decrease of the FMR. The data shown Fig. 2 are consistent with that. Here again two regions appear in which the behaviors are very different: below 50 MPa the FMR does not depend on the compression strength, whereas beyond it increases linearly.

Interpretation of these experiments is detailed in that what follows. Assuming isotropic magnetostriction the sum of the magnetocrystalline anisotropy energy with the magnetoelastic energy writes: $E = (K + 3/2\lambda_S\sigma_i)\sin^2\varphi$. K is the magnetocrystalline anisotropy constant, λ_S is the magnetostriction constant, and σ_i the local stress on the grains (correlated to the moulding pressure P). Assuming that the angle φ between the magnetization and the easy axe is low, an effective anisotropy field can be defined by [10]: $E = -\mu_0 M_S . H_{eff} . \cos\varphi$. Straightforward calculations on [111] axe (the studied materials present four easy axes) leads to

$$H_{eff} = \frac{4}{3}\frac{(K + 3/2\lambda_S\sigma_i)}{\mu_0 M_S}. \tag{1}$$

The ferrimagnetic resonance frequency F_R is given by $F_R = \gamma H_{eff}$ where γ is the gyromagnetic ratio ($\gamma = 35.185$ $MHz/kA \cdot m^{-1}$), that is

$$F_R = F_0 + \frac{2\gamma}{\mu_0}\left(\frac{\lambda_S}{M_S}\right)\sigma_i. \tag{2}$$

Here F_0 is the NFMR frequency of the bulk which is linked to the magnetocrystalline anisotropy field H_K through the gyromagnetic ratio: $F_0 = \gamma H_K$.

Relation (2) applies for a material in which the particles would be submitted to internal stresses σ_i all applied along the magnetization direction (say along one of the easy axes). Although it might be difficult to theoretically correlate the internal stress σ_i to the moulding pressure P, our experiments allow to think that, inside the domain of strength investigated, σ_i is proportional to P ($\sigma_i = \alpha . P$) so that an empirical law fairly similar to (2) can be expressed as

$$F_R = F_0 + \alpha\frac{2\gamma}{\mu_0}\left(\frac{\lambda_S}{M_S}\right)P \tag{3}$$

where α is an unknown factor to be determined experimentally. The physical meaning of the factor α is sketched in Fig. 3: because of the existing voids in the ferrite compact, the local strengths are most probably higher than the applied strength itself. Its values might depend on mechanical properties of the particles. All our experiments on $Ni_xZn_{1-x}Fe_2O_4$ ferrites (where x belongs to [0.3, 0.7]) led to an experimental value $\alpha \cong 2$. Relation (3) establishes a linear variation of the FMR with the applied pressure P from which one would get the ratio λ_S/M_S and the NFMR frequency F_0 of the bulk. The same behavior was observed for $Ni_{0.4}Zn_{0.6}Fe_2O_4$ composites (magnetic load $C = 0.5$). The obtained data are summarized Table I. The magnetostriction constants were obtained after magnetization measurements by SQUID experiments. They are in agreement with published data [7]. The obtained values for H_{eff} are also consistent with published data on the magnetocrystalline anisotropy constant K [11].

The region below 50 MPa, where the FMR is constant, but higher than usual values for bulk materials, may correspond to permanent internal stresses that exist before moulding.

Another benefit of this study is that it may open to soft ferrites the field of microwave applications up to 1 GHz. Actually spinel ferrite materials usually exhibit high magnetic losses limiting their potential to be used as high frequency devices below 400 MHz.

Fig. 4 shows the effect of the moulding pressure on the permeability. Thanks to adequate manufacturing process and to the magnetostrictive effect demonstrated on Figs. 1 and 2, soft ferrite composites can be realized in order to shift FMR to

TABLE I
λ_S, F_0 AND H_K GOT FROM PERMEABILITY MEASUREMENTS ON COMPOSITE MATERIALS

Sample type	M_S (kA/m)	λ_S x10^6	F_0 (GHz)	H_K (kA/m)
$Ni_{0.4}Zn_{0.6}Fe_2O_4$	345	-6.5	0.27	7.5
$Ni_{0.7}Zn_{0.3}Fe_2O_4$	410	-17.5	0.75	21.3
$Ni_{0.5}Zn_{0.3}Co_{0.2}In_{0.02}Fe_{1.98}O_4$	420	-21	2.68	76.2

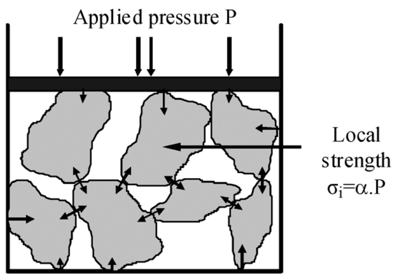

Fig. 3. Relation between applied and local strengths.

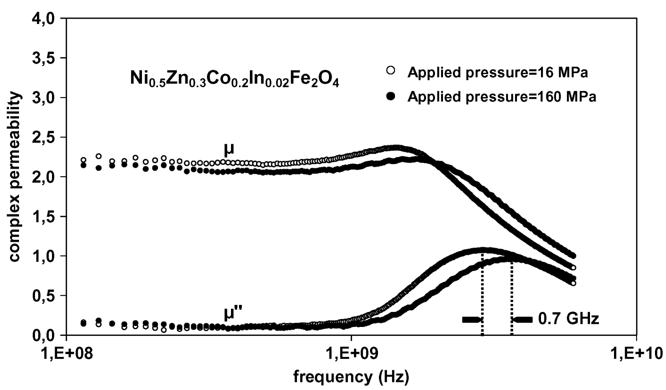

Fig. 4. Effect of the moulding pressure on the permeability spectrum of $Ni_{0.5}Zn_{0.3}Co_{0.2}In_{0.02}Fe_{1.98}O_4$ composite materials. In the presented data, the shift of FMR is 700 MHz.

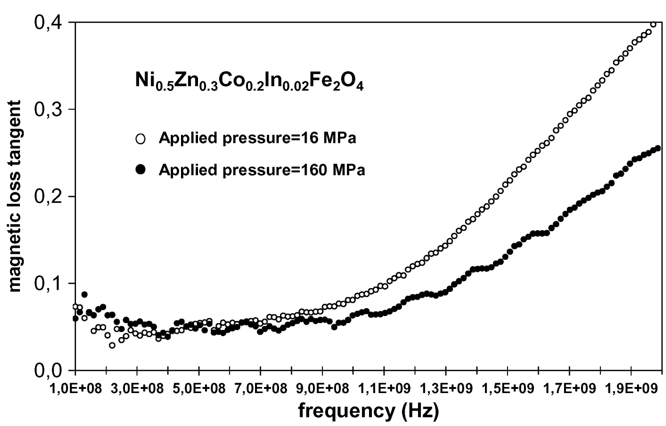

Fig. 5. Effect of the moulding pressure on the magnetic losses.

higher values, and to obtain low magnetic losses up to 900 MHz (Fig. 5). Such high frequency properties make them envisaged candidates for digital video broadcast handled (DVB-H) applications (Frequency ranging (462–870 MHz).

Fig. 4 underlined a remarkable behavior of the static permeability μ_S. Actually μ_S seems to be nearly insensitive when the applied pressure P varies from16 Mpa and 160 Mpa., whereas the resonance frequency shows a linear variation in the same time. This behavior has been recorded on other ferrites we studied as well. This behavior seems to be in discrepancy with the well-known Snoëk's law [12]. Snoëk's relation expresses that a change in μ_S due to variations in the material structure is followed by a opposite change in f_R. This may be written as: $(\mu_S - 1) \propto 1/f_R$. Nevertheless the present experimental data can be understood as resulting from a balance between two phenemenons, as explained in what that follows. On one hand, as explained in the second part of this paper, the magnetic load is *increased* by the applied pressure (the sample thickness being reduced by the applied pressure). But in the other hand, and accordingly to Snoëk's law, the increase of fR leads to a *decrease* of μ_S. These two competing behaviors result in a remarkable constant value of μ_S.

IV. CONCLUSION

Soft magnetic composite materials have FMR frequencies which tend towards the NFMR of bulks (sintered materials). Powders seem to be, thus, a very interesting aspect of matter to develop useful methods for investigating anisotropy fields by high frequency measurements. Concerning the difficult question of stresses induced by the moulding phase, it has been shown how a simple technique of extrapolation can lead to the expected NFMR frequency. Because of their low magnetic losses up to 900 MHz these composites can be envisaged as devices for high frequencies applications.

REFERENCES

[1] D. Souriou, J. L. Mattei, A. Chevalier, and P. Quéffélec, "Influential parameters on magnetic properties of Nickel Zinc ferrites for antenna miniaturisation," *J. Appl. Phys.*, vol. 107, no. 9, p. 09A518, May 2010.
[2] J.-L. Mattei and M. Le Floc'h, "Percolative behaviour and demagnetizing effects in disordered heterostructures," *J. Magn. Magn. Mater.*, vol. 257, pp. 335–345, 2003.
[3] M. Anhalt and B. Weidenfeller, "Permeability of soft magnetic FeCoV-PP composites for varying filler fractions," *IEEE Trans. Magn.*, vol. 46, pp. 440–442, 2010.
[4] M. Anhalt, B. Weidenfeller, and J.-L. Mattei, "Inner demagnetizing factor in polymer bonded soft magnetic composites," *J. Magn. Magn. Mater.*, vol. 320, pp. e844–e848, 2008.
[5] J.-L. Mattei and M. Le Floc'h, "Effects of the magnetic dilution on the ferromagnetic resonance of disordered heterostructures," *J. Magn. Magn. Mater.*, vol. 264, pp. 86–94, 2003.
[6] J. Gieraltowski, *J. Physique IV France*, vol. 38, pp. C1–57, 1977.
[7] E. du Tremolet de Lacheisserie, *Magnetostriction*. Boca Raton, FL: CRC Press , 1993.
[8] J. G. M. De Lau, *Philips Research Reports Supplements*, vol. 6, 1975.
[9] B. P. Rao and K. H. Rao, "Distribution of In^{3+} ions in indium-substituted Ni-Zn-Ti ferrites," *J. Magn. Magn. Mater.*, vol. 292, pp. 4–48, 2005.
[10] S. Chikazumi, *Physics of Magnetism*. New York: Wiley, 1964.
[11] A. Globus and P. Duplex, "Effective anisotropy in polycrystalline materials. Separation of components," *J. Appl. Phys*, vol. 39, no. 2, pp. 727–729, 1968.
[12] O. Acher and S. Dubourg, "Generalization of Snoék's law to ferromagnetic films and composites," *Phys. Rev. B*, vol. 77, p. 104440, 2008.
[13] A. Chevalier and M. Le Floc'h, "Dynamic permeability in soft magnetic composite materials," *J. Appl. Phys.*, vol. 90, no. 7, pp. 3462–3466, 2001.