Measurement of Dielectric and Magnetic Constants of Ferrofluid-Doped Sol-Gels by a Resonant Cavity Method

ABSTRACT

Materials with specific electromagnetic properties are increasingly used for the realization of passive components. Therefore, electromagnetic characterization is a priority to know these materials properties. This study focuses on the electromagnetic characterization of 10 nm maghemite ferrofluid doped sol-gel using a resonant cavity method. We deposited the sol-gel by dipping/removal on an alumina substrate in order to make measurements on the cavity to determine the complex permittivity and permeability. Two studies were carried out; the first consisted in varying the doped sol-gel thickness of layers of the same concentration in the realization of samples; and the second consisted in varying the volume concentration of ferrofluid according to the matrix dimensions. The first study showed that the dielectric constants do not vary with the thickness of the magnetic sol-gel layers. In the second study, measurements also showed that the gyromagnetic resonance is the same for all samples regardless of the ferrofluid volume concentration.

Keywords: Characterization, Permittivity, Permeability, Doped sol-gel, Cavity

1. INTRODUCTION

Given the evolution of systems and technologies in telecommunications field, the use of new microwave materials as multilayer materials becomes more important. The understanding of the propagation characteristics of the electromagnetic wave in these media requires a good knowledge of the electromagnetic properties (dielectric and magnetic), and therefore to be able to characterize them in microwave [1].

There are different methods for electromagnetic characterization of materials in the microwave domain [2] [3]. The choice of a cell characterization depends on the desired accuracy of various electrical parameters of the material (Table 1). There are two classes of characterization methods, namely broadband and narrowband methods. We can see from this table that the free space method is limited to loss tangents greater than 10^{-2} due to the high losses induced by its principle. On the other hand, the transmission line method allows the characterization of materials of different shapes such as platelets, granular, etc. Especially in the coaxial configuration, this method allows a good accuracy on the permittivity. The resonant cavity technique gives better accuracy but at a single frequency.

All these methods have their own advantages and inconveniences. It is therefore important to combine them to obtain very efficient hybrid methods that exploit their common advantages.

Table 1. Comparison of the main characterization methods

Measuring cell	Measured parameters	Physical quantities	Frequency range	Relative errors	Tangent loss
Free space	Sii and/or Sij	ε_r and/or μ_r	Wide or narrow band	--	> 10^{-2}
Resonant cavity	Sii or Sij	ε_r or μ_r	Single frequency (resonance)	<2% on ε_r	> 10^{-3}
Transmission line	Sii and Sij	ε_r and/or μ_r	Wide band	<5% on ε_r	> 10^{-3}

For example, the combination of the resonant cavity method and the coaxial probe method constitutes an accurate hybrid method (loss tangents <10^{-2}) over a wide frequency range. Since the concern is often for good measurement accuracy over a wide frequency range, the hybridization of methods is important in the field of characterization. In practice, it is a compromise between the accuracy required on the different dielectric parameters of the material (ε_r or $\tan\delta$), the width of the frequency band, the ease of sample preparation and also the ability to operate at high temperature.

The principle of the resonant cavity method is to place the material in a resonant cavity and go back to the value of ε_r from the variation of the resonant frequency and the quality factor of the cavity, as shown on the example in figure 1.

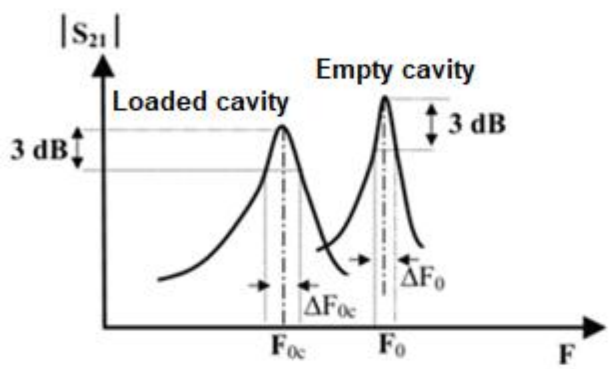

Fig. 1. Transmission response of a resonant cavity

Thus, our choice is the resonant cavity method for its accuracy and sensitivity [4], but also, this method allows to determine the electrical and magnetic properties of composites [5]. Several massive magnetic materials have been synthesized in the form of ferrofluids, i.e., nanoparticles (NP) dispersed in a solvent [6].

The materials to be characterized in this work are magnetic sol-gel composites [7] obtained by mixing silica precursors, which constitute the matrix, with maghemite nanoparticles of about 10 nm (ferrofluid) [8], which represent the dopant of the solution [9] [10] [11]. This solution is deposited on a substrate by the dip coating method [12].
The complex permittivity ε^* is an essential constitutive parameter for the macroscopic description of the dielectric medium. It is given by:

$$\varepsilon^* = \varepsilon' - j\varepsilon'' \qquad (1)$$

ε' and ε'' respectively represent the real (non-dissipative component) and imaginary (dissipative component) parts of the permittivity.

The complex permeability μ^* is also a main constitutive parameter for the macroscopic description of the magnetic medium. It is given by the expression:

$$\mu^* = \mu' - j\mu'' \quad (2)$$

μ' and μ'' are respectively the real and imaginary parts of the permeability.

These parameters will allow us to measure the electromagnetic properties of the magnetic sol-gel.

2. PRINCIPLE OF CAVITY MEASUREMENT

The principle of material characterization, based on the measurement of the perturbation of the resonant frequency of a cavity has been studied and developed for several decades [13]. It is based on the resonant frequency (Δf) measurement and the variation of the quality factor (ΔQ) of the cavity, when inserting a sample in an area where the electric field is maximum (to extract the permittivity) or where the magnetic field is maximum (to determine the permeability).

The extraction of these electromagnetic parameters is done from the reflection or transmission parameters (S_{11} or S_{21}) measurement. The electromagnetic analysis of the cavity then allows an approximation for a small perturbation of the complex effective dielectric constant by [5]:

$$\varepsilon' = 1 + \frac{\Delta f}{2 f_0} \frac{V_c}{V_e} \qquad (3)$$

$$\varepsilon'' = \frac{1}{4}\left(\frac{1}{Q_1} - \frac{1}{Q_0}\right)\frac{V_c}{V_e} \qquad (4)$$

Δf is the resonant frequency offset given by the expression $\Delta f = f_0 - f_1$; with f_0 and f_1 representing the no-loaded and loaded resonance frequencies; Q_0 and Q_1 respectively representing the quality of no-loaded and loaded coefficients of the cavity.

The cavity used in this study is rectangular (Figure 2).

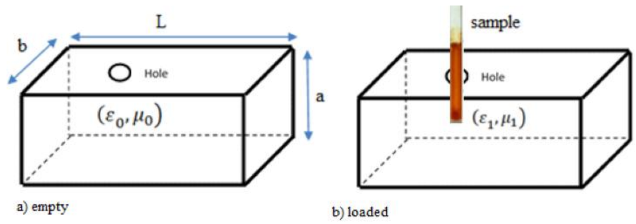

Fig. 2. Rectangular cavity: a) empty cavity, b) loaded cavity

V_c is the cavity volume given by the expression $V_c = a \times b \times L$ with respectively *a, b* and *L* denote the width, thickness and length of the cavity;

V_e is the volume of the sample given by the expression with $V_e = a_1 \times b_1 \times (d_1 + d_2)$ with a_1 and b_1 representing the width, the length of the sample, and d_1 and d_2 are respectively the thickness of alumina substrate and ferrofluid doped sol-gel (Figure 3).

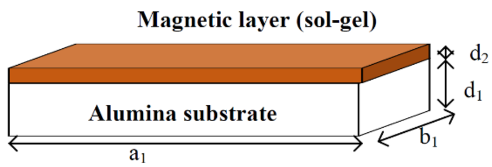

Fig. 3. Sample dimensions

The dimensions of the cavity and the substrate are known. The thicknesses of the doped sol-gel thin films are measured by profilometer.

Therefore, the electromagnetic analysis of the cavity allows an approximation for weak perturbation by the following complex permeability equations [10].

$$\mu' = 1 + \frac{\Delta f}{2 f_0} \frac{V_c}{V_e} \quad (5)$$

$$\mu'' = \frac{1}{4}\left(\frac{1}{Q_1} - \frac{1}{Q_0}\right)\frac{V_c}{V_e} \quad (6)$$

In this work, we present two studies to determine the electromagnetic properties (complex permittivity and permeability) of doped sol-gel. The first one consists in measuring the complex permittivity and permeability of two sol-gel layers of the same volume concentration but different thicknesses. For the second one, we always measure the complex electromagnetic parameters of sol-gel layers having different volume concentrations.

3. THICKNESS VARIATION OF MAGNETIC SOL-GEL LAYERS ON THE SUBSTRATE

This step consists in soaking substrates in a solution of the same volume concentration (sol-gel) with different withdrawal speeds. So, we obtain layers with different thicknesses of doped sol-gels.

We have prepared two sol-gel samples of different thicknesses but with the same volume concentration of ferrofluid/silica matrix (8.8%). We will present the measurements of dielectric and magnetic properties in the following paragraphs.

3.1. Dielectric measurement and sol-gel thickness study

The aim is to measure the complex relative permittivity of different ferrofluid-doped sol-gel layers, deposited on alumina substrates.

By measuring the reflection response of the cavity (figure 3), we will estimate the change of the resonance parameters (f, Q) caused by the presence of the sample (layer/substrate) in the cavity. Then we apply the perturbation method to extract the effective dielectric constants (equations (3) and (4)). After extracting the effective quantities, the following equations allow us to calculate the dielectric constants of the doped sol-gel.

$$\varepsilon'_{Sol-gel} = \frac{\varepsilon' \times (d_1 + d_2) - d_1 \times \varepsilon'_{substrat}}{d_2} \quad (7)$$

$$\varepsilon''_{sol-gel} = \frac{\varepsilon'' \times (d_1 + d_2) - d_1 \times \varepsilon''_{substrat}}{d_2} \quad (8)$$

$$\tan(\delta) = \frac{\varepsilon''_{sol-gel}}{\varepsilon'_{sol-gel}} \quad (9)$$

The cavity measurements give a no-load resonant frequency of 8.73 GHz at -38 dB and a loaded resonant frequency of 8.66 GHz at -18 dB (Figure 4). Using the perturbation method equations (equations (7), (8) and (9)) on these results, the dielectric values of the doped sol-gel are given in Table 2.

Table 2. Permittivity of doped sol-gels of two samples of same concentration and different thicknesses

Samples	ε'	ε''	$tan\delta$
24 µm (8.8%)	4.4327	0.0680	$1.5.10^{-2}$
32 µm (8.8%)	4.3770	0.09380	$2.1.10^{-2}$

We note that the extracted permittivity values are almost identical in both cases. We can note that the signal interacts with the same types of nanoparticles in the sol-gel. This allows to confirm that the dielectric constant is the same for this 8.8% doped sol-gel whatever its thickness. This small variation is due to measurement errors and the positioning of the sample in the cavity hole, which is introduced in the hole manually.

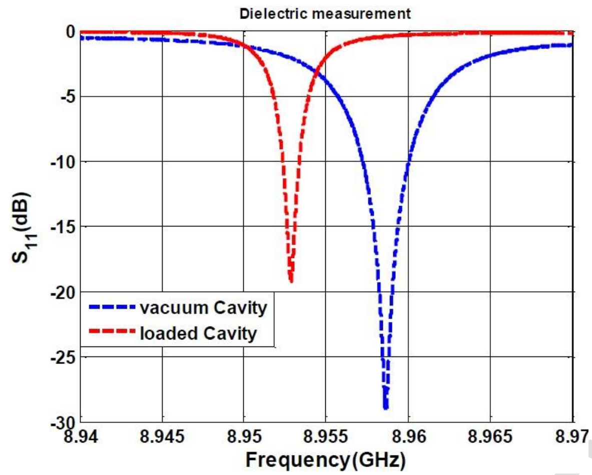

Fig. 4. Frequency-dependent reflection parameter

3.2. Magnetic measurement and Sol-gel thickness study

This involves measuring the relative permeability of the different samples that have been previously measured. When the sample is magnetized, its magnetic permeability is a tensor quantity at microwave frequencies. The evolution of the permeability as a function of frequency depends strongly on the state of the material magnetization. These measurements are always carried out in an applied parallel field to the plane of the sample. For this measurement, the cavity is used, with the sample placed at the point where the microwave magnetic field is maximal. This complex quantity can be determined from the proposed approach linking the effective permeability of a bi-layer material with the resonance frequency variation, the quality factor and equations (5) and (6) (figure 5).

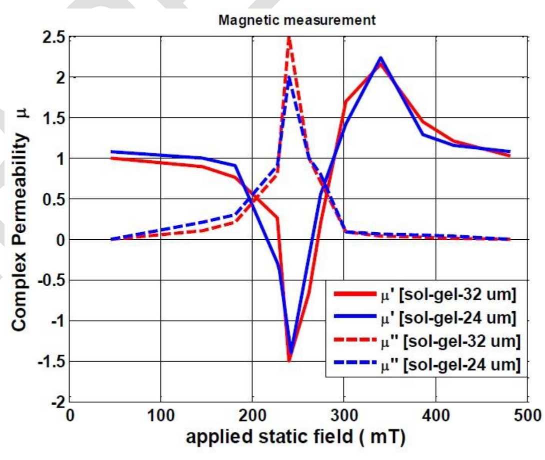

Fig. 5. Variation of complex permeability as a function of a doped sol-gel applied field with same concentration and two thicknesses

The variation of the permeability is observed as a function of the external excitation field (figure 5). We note that the real parts of the permeability μ' of two samples (24 um and 32 um sol-gel) vary between -1.4 and 2.3 with the external excitation field H_0. We find that the gyromagnetic resonance is always at a magnetic bias field around H_0=240mT. This study confirms that whatever the thickness of the doped sol-gel layer, the gyromagnetic resonance zone does not change, because the magnetic nanoparticles in the doped solutions are of the same nature. The electromagnetic signal interacts with sol-gel layers of the same particle type in the realization.

4. VARIATION OF THE VOLUME CONCENTRATION OF DOPED SOL-GEL

For the second study, we made three samples by varying the volume concentration of the magnetic ferrofluid with respect to the silica matrix to obtain three doped sol-gels. Then, we performed dipping/withdrawal of three substrates in the different doped solutions.

4.1. Dielectric measurement and sol-gel concentration study

We measured three samples of different volume concentrations for the mixture of magnetic ferrofluid and silica matrix in the preparation. When a sample is introduced into the cavity, the resonance frequency shifts (figure 7). This variation allows us to extract the effective permittivity values of the samples using the perturbation method. The complex relative permittivity of three samples are presented in Table 3.

Table 3. Permittivity of doped sol-gels of three samples of different volume concentrations

Samples	ε'	ε''	$tan\delta$
(13%) 9.2 µm	4,2467	0.03447	0.0812
(18%) 3.7 µm	4,3683	0.03444	0.0788
(23%) 2 µm	4,1692	0.0730	0.0175

The extracted permittivity values are almost identical in the three cases. This small variation is due to measurement errors and especially the sample positioning in the cavity. In these structures, the wave-matter interaction occurs with the same types of nanoparticles in the mixture. So, we can deduce that the dielectric constant is the same for a material whatever the volume concentration of sol-gel in the mixture. We have made a summary of the complex permittivity values of all the samples made with different thicknesses of doped sol-gel in figure 6.

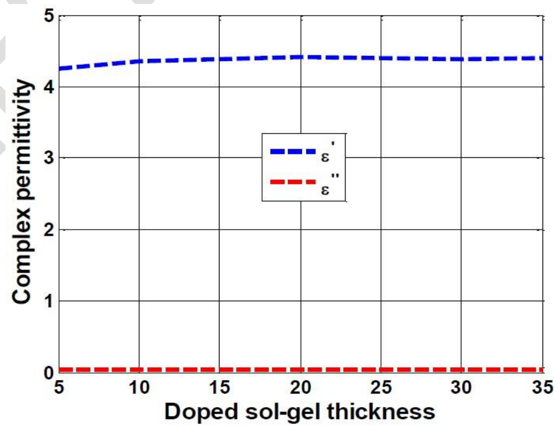

Fig. 6. Recap on the complex permittivity of sol-gel layers of different concentrations and thicknesses

We observe that the permittivity of the three samples is constant regardless of the thickness of the sol-gel layer. This is normal, since the same types of nanoparticles in the sol-gel mixture interact with the electrical signal. We can conclude that the increase of sol-gel layer thickness does not affect their dielectric constants. Similarly, the volume concentration of sol-gel does not change the dielectric quantities.

4.2. Magnetic measurement and sol-gel concentration study

We also measured the three samples with different volume concentrations of sol-gels in the mixture of ferrofluid and silica matrix. The results of complex permeability μ' and μ'' measurements on these samples are respectively shown in Figures 7 and 8.

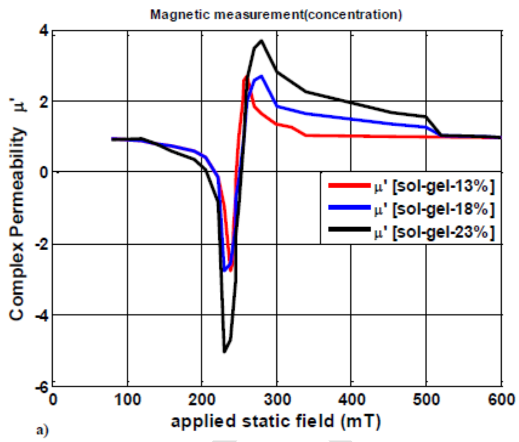

Fig. 7. Variation of permeability μ' as a function of applied field for a doped sol-gel

It can be seen that the permeability varies with the applied magnetic field. On these three samples doped at 13%, 18%, and 23%, the permeability varies in the same way but there is an evolution of the peak with the increase of the concentration (figure 7). This is due to the fact that the quantity of magnetic nanoparticles in the sol-gel mixture is not identical for the three cases but the gyromagnetic resonance zone is the same. This zone is around 240 mT (figures 7 and 8). We also note that the higher the concentration is, the stronger is the signal absorption (figure 8).

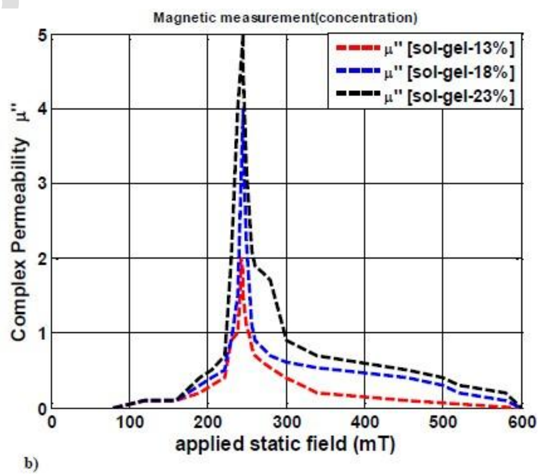

Figure 8. Variation of permeability μ'' as a function of applied field for doped sol-gel

We still observe the same gyromagnetic resonance in the three cases (at 240 mT) but there is a peak broadening of the permeability variation for the last case (23%). This broadening is due to the quantity of particles in the sol-gel being greater than in the two previous cases. We can conclude from this study that the gyromagnetic resonance is the same whatever the volume concentration. In conclusion, for the same nature of matrix and ferrofluid (silica and maghemite in our case), the nanoparticles that interact with the electromagnetic wave are the same.

5. CONCLUSION

In this paper, we have presented an experimental study on the determination of the permittivity and permeability of a magnetic sol-gel layer deposited on an alumina substrate. A simple proportionality relationship was used to determine these parameters of magnetic sol-gel layers of different concentrations and thicknesses.

The first series of experimental measurements on the samples showed that the complex permittivity and permeability of the magnetic sol-gel mixture of different thicknesses are identical. The second series were made on three samples with different volume concentrations of magnetic sol-gel composites. The dielectric measurements showed that the values of the complex permittivity on these samples are close to each other whatever their volume concentrations. As for the magnetic measurements, the gyromagnetic resonance zone is the same but there is an evolution of the peak with the increase of the concentration. This is explained by the strong absorption of the electromagnetic wave when the volume of magnetic ferrofluid is large in the sol-gel matrix.

The disadvantage of the cavity measurement is its narrow bandwidth, so it is necessary to multiply the cavities of different dimensions for a more extensive characterization. However, this approach is very simple to determine the electromagnetic properties of thin films.

REFERENCES

1. J. C. Maxwell. A Treatise on Electricity and Magnetism. Doveq N.Y, 1954.
2. Kern D.J., Werner D.H. and Lisovich. Metaferrites: using electromagnetic bandgap structures to synthesize metamaterial ferrites. IEEE Trans. On Anten. Propag. 2005; 53:1382-1389.
3. K. Buell and K. Sarabandi. A method for characterizing complex permittivity and permeability of meta-materials. Proceeding of IEEE, Antennas and Propagation Society International, Symposium. 2002; 2:408-411.
4. Michael D. Janezic, James Baker-Jarvis, B. Riddle, C. L. Holloway N. G. Paulter and J. E. Blendell. Dielectric and Conductor-Loss Characterization & Measurements on Electronic Packaging Materials. NIST Technical note 1520. Boulder, Colorado, USA, July 2001.
5. R. A. Waldron. Perturbation theory of resonant cavities. Proceedings of the IEE. 1960; 170(C):272-274.

6. S. Neveu, A. Bee, M. Robineau, and D. Talbot. Size-Selective Chemical Synthesis of Tartrate Stabilized Cobalt Ferrite Ionic Magnetic Fluid. J. Colloid Interface Sci. 2002; 255:293.

7. Robina Ashraf, Saira Riaz, Mahwish Bashir, Usman Khan, and Shahzad Naseem. Structural and Magnetic Properties of Mn/Fe CoDoped ZnO Thin Films Prepared by Sol-Gel Technique. IEEE Transactions on Magnetics. 2014; 50(8).

8. Chang Young Kim, Se Chan Jang, Sung-Chul Yi and J. Cer. Proc. Res, Vol. 5, No. 264, 2004.

9. Mornet, J. Portier, and E. Duguet. A method for synthesis and functionalization of ultrasmall superparamagnetic covalent carriers based on maghemite and dextran. Journal of Magnetism and Magnetic Materials. 2005; 293(1):127-134.

10. F. Chen, R. Shi, Y. Xue, L. Chen, Q. H. Wan, J. Magn. Magn. Mater, Vol. 322, No. 2439, 2010.

11. V. A. Kalmyk, S. B. Rayevskiy and V. P. Ygryumov. An experimental verication of existence of complex waves in a two-layer circular, shielded waveguide. Radio Engineering and Electronic Physics. 1978; 23:16 -19.

12. F. Choueikani, F. Royer, D. Jamon, A., Siblini, J. J.Rousseau, N., Sophie, and J., Charara. Magneto-optical waveguides made of cobalt ferrite nanoparticles embedded in silica/zirconia organic-inorganic matrix. Appl. Phys. Lett. 2009 ; 94.

13. H. M. Altschuler, M. Sucher and J. Fox. Dielectric Constant. Handbook of Microwave Measurements, Brooklyn, Polytechnic Press, New York. 1963; 2:518-548.