Magneto-dielectric characterization of TiO₂-CoFe₂O₄ derived ceramic composites

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Abstract

Dielectric permittivity (ε′), magnetic permeability (µ′) and dielectric and magnetic loss (tan δε and tan δµ, respectively) of magneto-dielectric cobalt ferrite-titania (CFO-TO) ceramic composites are determined from 200 to 300 MHz. The four different combinations of phases - that can be produced in the sintered composite, according to the starting CFO/TO molar ratio - allow to tune the macroscopic permittivity and permeability. For the first time impedance, miniaturization and magneto-dielectric loss of the four classes of composites are calculated and discussed. The displayed miniaturization factors between 4.4 and 8.2 in the very-high frequency (VHF) range corroborate their potential application as magneto-dielectric substrate materials for antennas. Remarkably, the ceramic composites characterized by 2 vol. % and 3 vol. % of CFO and TO, respectively, dispersed in Fe₂CoTi₃O₁₀ (FCTO) matrix display a magneto-dielectric loss lower than 0.07 and a miniaturization factor of 4.8.

Keywords: composites, ferrites, titanates, dielectric properties, magnetic properties

I. Introduction

The possibility of easily tuning or enhancing certain properties of multifunctional materials paves the way for new applications [1]. Composite materials answer to this technological demand [2–4], and increasing efforts are being focused on ferrites and their composites with dielectric, ferroelectric, and optoelectronic materials. Among such materials, magneto dielectrics (MDs) show properties that can easily be tuned, as required in the case of substrates for miniaturized antennas [5]. In particular, MDs allow to tune their permeability and permittivity values as demanded by the working frequency range, while keeping low loss [6–8].

By combining a relative magnetic permeability (µr) greater than unity with a reasonably low value of relative dielectric permittivity (εr) it is possible to achieve a favourable miniaturization factor [n = (µr · εr)¹/²] without affecting the radiating properties. However, reducing the magnetic and dielectric loss at the same time is still a challenge [9–11]. It is well-known that ferrites are the best candidates for antenna substrates and a number of compositions have been investigated, including spinel ferrites and hexagonal ferrites, in some cases combined with other ceramics. Zheng et al. [12] were able to reduce loss by combining NiZn ferrite with Ba hexaferrite, or Co-Zn hexaferrite [13], bringing the εr/µr ratio down to about one over a wide frequency range (1–10¹² MHz). Two-step sintering allowed to obtain very low magnetic and dielectric loss tangent [14], while improved magneto-dielectric effect was found by Banerjee et al. [15] in composites of NiZn ferrite nanoparticles with BaTiO₃, synthesized by a chemical method.

Magnetic/dielectric properties of ceramic composites can be tuned by tailoring composition, interconnectivity and interfaces. Overall properties of the composite may follow the rule of mixtures as well as more complex combinations of the properties of the side phases,
or may be dominated by one or more phases of the composite [16]. Moreover, even a limited interaction between the two components of a binary ceramic composite may cause novel properties to appear, which were absent in both components [17–19].

In search for new candidates for magneto-dielectric materials, we studied the system cobalt ferrite (CoFe$_2$O$_4$, CFO) and titanium oxide (TiO$_2$, TO), owing to high coercivity, and moderate magnetic moment of the CFO, and low eddy current and dielectric loss of TO [20–25]. However, ceramic composites based on the binary system TiO$_2$/CoFe$_2$O$_4$ are sintered at temperatures lower than about 600 °C, in order to avoid the anatase-to-rutile transformation [26] which generally reduces the photocatalytic properties. To the best of our knowledge, there is scanty literature about the properties of the Fe$_2$CoTi$_4$O$_{10}$ (FCTO) compound resulting from the reaction between CFO and TO at temperature higher than 800 °C [7,27,28].

In this work, we focus on the dielectric and magnetic characterization of in situ synthesized ceramic composites derived from displacement reactions between TiO$_2$ and CoFe$_2$O$_4$. By using in situ, we intend to contrast these materials with the more conventional composites, in which the side phases are the same as the final ones, the materials being obtained starting from TiO$_2$ and CoFe$_2$O$_4$ powder mixtures. By exploiting the displacement reactions (i.e. by changing the starting TO/CFO molar ratio) four different phases mixtures can be produced [27]: i) TO + FCTO, for TO/CFO starting molar ratio higher than 3; ii) FCTO + TO + CFO, for TO/CFO starting molar ratio equal to 3; iii) FCTO + CFO, for 1–2 < TO/CFO < 3 (in fact the lower bound has never been investigated [29]); and iv) CFO + CoTiO$_3$ + Fe$_2$O$_3$, for 0 < TO/CFO < 0.8–1 (the upper bound has never been investigated [29]). In situ synthesized ceramic composites provide good trade-off between dielectric/magnetic constants and dielectric/magnetic loss and allow to optimize their intrinsic impedance and magneto-dielectric efficiency for their possible application as antenna substrates in the very-high frequency (VHF) range.

II. Materials and methods

Cobalt ferrite-titania ceramic composites are produced by conventional sintering at 1200 °C starting from mixtures of said phases (cobalt ferrite, CFO and titania, TO), according to the compositional scheme (100 − x)TO−xCFO, with x = 20, 49.5, 57 and 80 wt.%. In Table 1 the correlation between samples’ IDs, starting CFO content, and final composition of the samples is reported. Further details on powder’s synthesis, densification and microstructural features of the produced samples are reported in a previously published work [27]. The microstructure of the sintered samples is investigated on polished cross section by SEM (Quanta, FEI).

For dielectric measurements over the 200–300 MHz frequency range, the samples are prepared by applying Ag electrodes onto the polished surfaces of properly machined cylinders and placed at the end of short-circuited coaxial line between the inner conductor and the terminating contact. Measurements are performed using an Agilent 8714ET network analyser. The complex reflection coefficient of the electromagnetic wave is measured and the dielectric permittivity is calculated using the parallel-plate capacitor formula:

$$\varepsilon^* = \frac{(C^* - C_0) \cdot d}{\varepsilon_0 \cdot A}$$  

where $C$ is the complex capacitance of the sample, $d$ is its thickness, $A$ is the area of the sample and $\varepsilon_0 = 8.85 \cdot 10^{-12}$ F/m is the permittivity of free space. Capacitance $C_0$ is estimated by measuring an air gap of length $d$. Magnetic measurements of the ceramic composites over the 200–300 MHz frequency range are performed by applying the inductance measurement method. A 3 mm diameter hole is machined in the centre of disk-shaped ceramics having external diameter 9 mm and thickness 3.1 mm for CFT20, and 4.8 mm for the others. The ring-shaped samples are mounted into a measurement test fixture forming an ideal (no magnetic flux leakage) one-turn inductor which is placed in an homemade sample holder (analogous to the Agilent 16454A magnetic test fixture [29]), which is connected to the Agilent E8363B network analyser. The complex relative permeability is calculated from the measured complex impedance values using the formula:

$$\mu^* = \frac{2\pi \cdot \left( Z_m^* - Z_r^* \right)}{j \cdot \omega \cdot \mu_0 \cdot h \ln \frac{R}{r}} + 1$$  

Here $Z_m$ and $Z_r$ denote the impedance of the measurement cell with and without the sample, respectively, $R$ and $r$ are the outer and inner radiuses of the ring-shaped sample, $h$ is its thickness, and $\mu_0$ is the magnetic permeability of free space.

III. Results and discussion

In Fig. 1 the microstructure of the produced samples is shown. The different phases are evidenced by

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Starting composition [wt. %]</th>
<th>Final composition [vol. %]</th>
<th>Porosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>CFT20</td>
<td>20.0</td>
<td>0 60 39 0 0 1</td>
<td></td>
</tr>
<tr>
<td>FCTO</td>
<td>49.5</td>
<td>2 3 90 0 0 5</td>
<td></td>
</tr>
<tr>
<td>CFT57</td>
<td>57.0</td>
<td>12 0 83 0 0 5</td>
<td></td>
</tr>
<tr>
<td>CFT80</td>
<td>80.0</td>
<td>19 0 0 37 36 8</td>
<td></td>
</tr>
</tbody>
</table>
different grey scale according to their density (i.e. the phases with higher density show pale grey that darkens with decreasing density). Hence, in case of the CFT20, Fig. 1a, the black areas are pores (as for all the other samples), the darker grains are TiO$_2$ (rutile, density, $\rho = 4.25$ g/cm$^3$), and the brighter grains are Fe$_2$CoTi$_3$O$_{10}$ ($\rho = 4.31$ g/cm$^3$). For the FCTO sample, Fig. 1b, the darker grains are TiO$_2$, those displaying medium grey are Fe$_2$CoTi$_3$O$_{10}$, and the brighter ones are CoFe$_2$O$_4$ ($\rho = 5.30$ g/cm$^3$). In case of the CFT57, Fig. 1c, the darker grains are Fe$_2$CoTi$_3$O$_{10}$, and the brighter ones are CoFe$_2$O$_4$. For the CFT80 it is more difficult to distinguish the phases, even if, in principle, the darker grains are CoTiO$_3$ ($\rho = 4.98$ g/cm$^3$), those displaying medium grey are Fe$_2$O$_3$ (hematite, $\rho = 5.27$ g/cm$^3$), and the brighter ones are CoFe$_2$O$_4$.

In Fig. 2a the spectra for the real permeability $\mu'$ are shown. In the investigated frequency range, all the $\mu'$ curves display the typical trend of a plateau below a certain frequency and the distinct peaking behaviour that is modelled by Snoek’s law [30].

As expected, higher $\mu'$ values are shown by the samples with the highest amount of CFO, i.e. CFT80 and CFT57 display permeability value of 1.22 and 1.16, respectively. These compounds show the highest $\mu''$ values too (Fig. 2b). Even though the FCTO has 2 vol.% of CFO, its $\mu'$ spectra is comparable with the dielectric CFT20. This could be attributed to the microstructure and shape of the CFO grains [31–34]. In fact, the small amount of CFO in the FCTO sample, compared to the CFT80 and CFT57 samples, allows the development of smaller CFO grains [27], which, on the one hand reduce the contribution of the domain-wall motion [22,33,34], and on the other hand enhance spin rotation owing to the higher weight of surface’s effects. It is worth noting that spin rotation is an intrinsic property of the bulk material, but in material’s surface it is influenced by extrinsic properties such as grain size and shape [35]. Anyway, spin rotation contribution is not negligible, since the ferromagnetic resonance is expected at higher frequencies (about 2–4 GHz [36]).

The frequency dependence of permittivity $\varepsilon'$ and dielectric loss tangent (tan $\delta$) are shown in Fig. 3. It can be seen that for the heterostructures containing TO and/or FCTO components the dielectric permittivity is almost constant over the whole analysed frequency range, and its average value decreases with decreasing the titania content. The permittivity of FCTO is normally lower than that of TiO$_2$, so the presence of FCTO in the composites will produce a dilution effect. For the CFT80 sample, which has 19 vol.% CFO and 36 vol.% Fe$_2$O$_3$, respectively, the dielectric permittivity is higher at low frequencies and decreases with increasing frequency, as expected from the Maxwell-Wagner theory applied to ferrite-containing composites [37,38], and according to the Kramers-Kroning relations since the 12%
The dielectric loss tangent (tan δε) of the CFT20 and FCTO samples is negligibly small and remains stable in the whole frequency range. Titania significantly flattens both ε′ and tan δε curves. The tan δε values of samples can be correlated with the amount of porosity (Table 1) because tan δε values grow with increasing porosity.

The increase of a few orders of magnitude of tan δε in the CFT80 sample, beside porosity contribution, can be due to its complex microstructure which promotes the accumulation of free charge carriers at the interfaces between the magnetic and dielectric phases causing the so-called space charge polarization which can be accounted by the above mentioned Maxwell-Wagner theory. Contrary to other ferrites, where the dielectric constant is closely related to the concentration of Fe²⁺ ions [39–42], for cobalt ferrites this contribution is missing since the iron cations are stabilized in the Fe³⁺ state due to the presence of Co²⁺.

Owing to the easily adjustable permeability and per-
mittivity, the developed CFT composites can be used as a magneto-dielectric antenna substrate. The spectra of normalized impedance $(\mu'/\varepsilon')^{1/2}$ and miniaturization factor $(\mu'/\varepsilon')^{1/2}$ are shown in Fig. 4a and 4b, respectively. It can be observed that the impedance $(\mu'/\varepsilon')^{1/2}$ value for the CFT57 sample is the highest among the investigated compositions and is always higher than 0.25. On the other hand, the characteristic impedance is four times lower than the impedance of the free space. A miniaturization factor of about 8 is achieved with the samples CFT80 and CFT20. Despite the smaller miniaturization factor (about 4.5), the CFT57 sample, is also desirable for using it as a magneto-dielectric antenna substrate material [43].

Magneto-dielectric loss $P_{MD}$ (Fig. 4c) is calculated as:

$$ P_{MD} = (\tan \delta_\mu + \tan \delta_\varepsilon) \cdot (\varepsilon'/\mu')^{1/2} $$

where the $(\varepsilon'/\mu')^{1/2}$ term is related to the stored energy. Consequently, the performances of an antenna printed on those magneto-dielectric substrates, and particularly its radiation efficiency and bandwidth will be better in materials with lower $P_{MD}$ values [44]. In particular, FCTO composites display the lowest $P_{MD}$, lower than 0.07. Among the other, FCTO/CFO system seems to be the most promising and suitable for very-high-frequency applications.

IV. Conclusions

In this paper, the magneto-dielectric properties of novel titania-cobalt ferrite in situ synthesized ceramic composites are characterized. Due to the high reactivity of the two starting phases the final composition of the composite material changes significantly and the different microstructures result in significantly different functional properties. Therefore, the titania-cobalt ferrite system provides an accurate composition-dependent control of the microstructure and, thus, the possibility to easily tailor the magneto-dielectric properties. The best compromise among magnetic permeability, dielectric permittivity and loss is achieved in the samples with the starting TO/CFO ratio 43/57 and 50.5/49.5. These samples, based on FCTO/CFO and FCTO/CFO/TO phases mixture, respectively, show a combination of properties (FCTO/CFO: $1.15 < \mu' < 1.16$, $16.9 < \varepsilon' < 18.4$, $0.66 < P_{MD} < 0.75$; and FCTO/CFO/TO: $1 < \mu' < 1.02$, $22.6 < \varepsilon' < 23.6$, and $0.03 < P_{MD} < 0.07$) that can be exploited for the design of miniaturized antennas for very-high-frequency applications.

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References


