

Measurement of dielectric properties at low temperatures: application to the study of magnetoresistive manganite/insulating oxide bulk composites

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Abstract. In this paper, we report low temperature dielectric measurements of bulk composite electroceramic samples containing a colossal magnetoresistive (CMR) manganite phase ($\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ [abbreviated LCMO]) and an insulating phase (Mn_3O_4). Details of the experimental system are given and possible experimental artefacts due to moisture are outlined. For a LCMO volume fraction of $\sim 16\%$, the permittivity of the LCMO/ Mn_3O_4 composite at $T = 50$ K is found to be much higher than that of pure Mn_3O_4 and magnetic field dependent. This effect is related to an extrinsic space charge polarization mechanism between the insulating phase (Mn_3O_4) and the conducting magnetoresistive phase (LCMO).

1. Introduction

In the past few years there has been a significant interest in functional materials which exhibit a coupling between ferroelectric and magnetic properties [1]. These materials had already been characterised in the 1960s [2], but the interest was renewed recently, due to the discovery of new compounds with remarkable properties [3-6] as well as the perspective of engineering applications in which the electric polarization can be tuned magnetically. The general term “magnetodielectric” can be used to describe materials whose permittivity is sensitive to an external magnetic field (“magnetocapacitance”), whereas “multiferroic” refers specifically to compounds where ferroelectric and ferromagnetic orders can coexist simultaneously [1]; the latter include e.g. several transition metal perovskites [7] or some rare-earth manganites [3-9]. In addition to such “intrinsic” magnetoelectric materials, it has also been shown that magnetocapacitance properties can be observed due to an “extrinsic” effect caused by the combination of magnetoresistance and Maxwell-Wagner effect at the electrode/ceramic interface or at grain boundaries, e.g. in composites [8]. Such interfacial magnetocapacitive effects are usually associated to a strong frequency dependence of the parameters of the parallel $R \parallel C$ equivalent circuit of the material [7,8]. Although such properties are not directly related to a “true” magnetoelectric coupling, they are nevertheless of definite technological interest.

In the present study, we report the dielectric properties of bulk composite samples containing a (conducting) Colossal Magneto Resistive (CMR) manganite phase [10-12] and an (insulating) oxide secondary phase. We focus on the $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3/\text{Mn}_3\text{O}_4$ composite system, where $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ (LCMO) is the manganite phase and Mn_3O_4 the insulating phase. In our previous works, we have shown that such composite materials can be prepared with almost constant manganite compositions throughout the series of samples with different proportions of the two phases [13]. We have shown that the electrical properties of this system exhibit a clear percolation threshold for a volume fraction of the conducting phase (f_{LCMO}) of ~ 0.19 , i.e. for $f_{LCMO} > 0.19$, the composite material is conducting (resistivity $\rho < 10^3 \Omega\cdot\text{cm}$) whereas for $f_{LCMO} < 0.19$, the resistivity exceeds $10^6 \Omega\cdot\text{cm}$. The fundamental reason for studying such composites is that, in the conducting regime ($f_{LCMO} > 0.19$), the presence of the insulating Mn_3O_4 phase forces the electric current to meander through the LCMO grains, thereby increasing significantly the colossal magnetoresistance effect at low magnetic fields [14,15]. Due to the fact that the insulating phase (Mn_3O_4) is ferrimagnetic for $T < 42 \text{ K}$, these materials are characterised by unusual magnetoresistive properties at low temperature [16]. In addition to affecting the electrical properties, grain boundaries in these materials were also shown to affect the thermal conductivity of the composite [17]. In this paper, we concentrate on the insulating regime ($f_{LCMO} < 0.19$) and consider the low temperature dielectric properties of such composites and investigate possible magnetic field dependence of the permittivity. We first describe the experimental system used for characterising the dielectric properties at low temperature and then compare the behaviour of a LCMO/ Mn_3O_4 composite sample to that of pure Mn_3O_4 .

2. Experiment

The composite $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3/\text{Mn}_3\text{O}_4$ materials were synthesized from precursor powders obtained by the spray drying technique [18]. This consists in spraying an aqueous solution of metallic cations into droplets, which are dried by a hot air flow. The detailed synthesis process has been described previously (see [13] and references therein). The samples were characterised by several techniques. Powder X-ray diffraction patterns were collected with a Siemens D5000 diffractometer (Cu K_α radiation). The morphology of the samples was studied by scanning electron microscopy using a Philips XL30 FEG-ESEM. The cationic composition was checked by an Energy Dispersive X-ray Analysis (EDAX system), coupled to the electron microscope. The density was measured using the Archimedes method in order to calculate the volume fraction of each phase, i.e. the LCMO phase, the Mn_3O_4 phase and the total (open + closed) porosity.

The dielectric properties were measured as a function of temperature and magnetic field in a home-made experimental set-up based on a Quantum Design PPMS (Physical Property Measurement System) [19-22]. Our experimental arrangement is shown schematically in Figure 1. Either silver or gold electrodes are first deposited on both sides of the ceramic sample in order to realize a parallel plate capacitor. A circular guard ring is also deposited around the low voltage (V-) electrode and connected to earth. The sample holder is based on the sample puck of the PPMS (figure 1): the low voltage electrode is thermally anchored to the puck itself through silver paste and a small brass disk, but isolated electrically using a thin cigarette paper and 7031 GE varnish. A brass cap around the system, acting as electric shield, is connected to earth. In view of minimizing thermal conduction through the wires within the experimental chamber, no additional coaxial cable is used; connexions between the sample and the measuring instruments are achieved with the existing wires along the external face of the sample chamber of the PPMS. The sample chamber itself is connected to earth and parasitic capacitance between the three wires (shown in red, blue and green colours in figure 1) is minimized by choosing the wires that are positioned at approx. 120° from each other. The dielectric properties are measured using a Perkin Elmer 7260 Lock-In amplifier acting both as a voltage source and high sensitivity ammeter. For each measuring frequency (in the range 5 Hz – 250 kHz), phase correction is achieved by measuring a Solartron calibrated reference capacitor (11.92 pF).

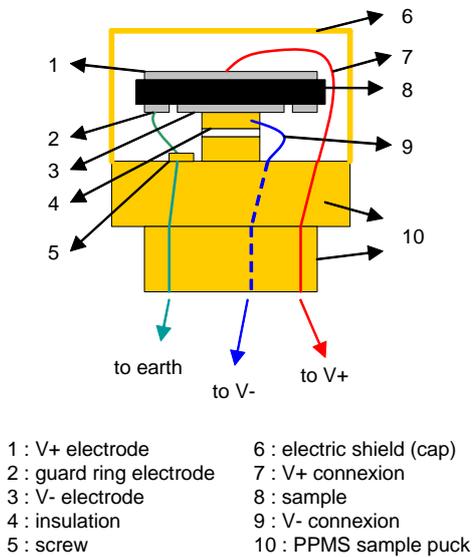


Figure 1. Schematic illustration of the experimental system for dielectric measurements

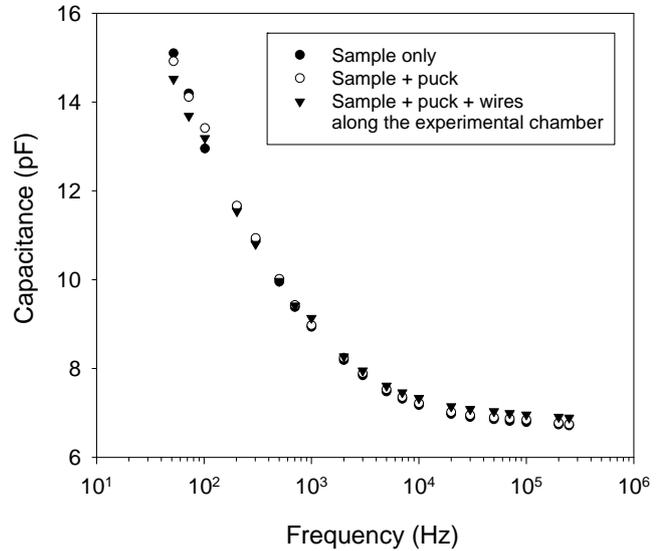


Figure 2. Room-temperature frequency dependence of the capacitance of a composite sample (LCMO/ Mn_3O_4) having a LCMO volume fraction equal to ~ 0.16 for 3 different experimental arrangements.

3. Results and discussion

3.1. Experimental system

Figure 2 shows the room-temperature frequency dependence of a composite sample (LCMO/ Mn_3O_4) for which the dimensionless LCMO volume fraction is equal to 0.16. The volume fraction of the pores in this sample is evaluated to 0.24; the volume fraction of Mn_3O_4 is 0.60. Three different experimental arrangements are used. The first is the system described in the paragraph above, where the sample is placed on the PPMS puck, inserted in the sample chamber. In order to evaluate possible sources of parasitic capacitances, the sample was also measured (i) placed on the PPMS puck, but inserted in an electric shield or (ii) removed from the puck holder (“sample only” in figure 2) and placed in an electric shield. As can be seen in figure 2, the capacitance measured by the three methods leads to results that are close to each other; the agreement is found to be better than 4% at 10 Hz and better than 1% at 10 kHz. The parasitic capacitance between the connecting wires along the sample chamber was evaluated to 0.3 pF, almost frequency independent. The result shown in figure 2 shows that the simple experimental system described in figure 1 is perfectly appropriate for measuring the dielectric properties of the composite ceramic samples.

In the experimental chamber, the temperature of the sample can be varied using the temperature control system of the PPMS. The temperature dependence of parameters R and C of the parallel equivalent circuit of the material are shown in figure 3. If no particular precaution is taken (blue triangle symbols) the $R(T)$ and $C(T)$ curves are found to exhibit a clear anomaly at $T \sim 238$ K : a significant jump is observed in the $C(T)$ plot whereas the resistance displays a sharp (negative) peak. The particular temperature at which the anomaly appears is not reproducible and is found to vary within a ~ 40 K window from one experimental run to another. These features are related to the presence of moisture in the pores of the ceramic sample and / or in the experimental chamber.

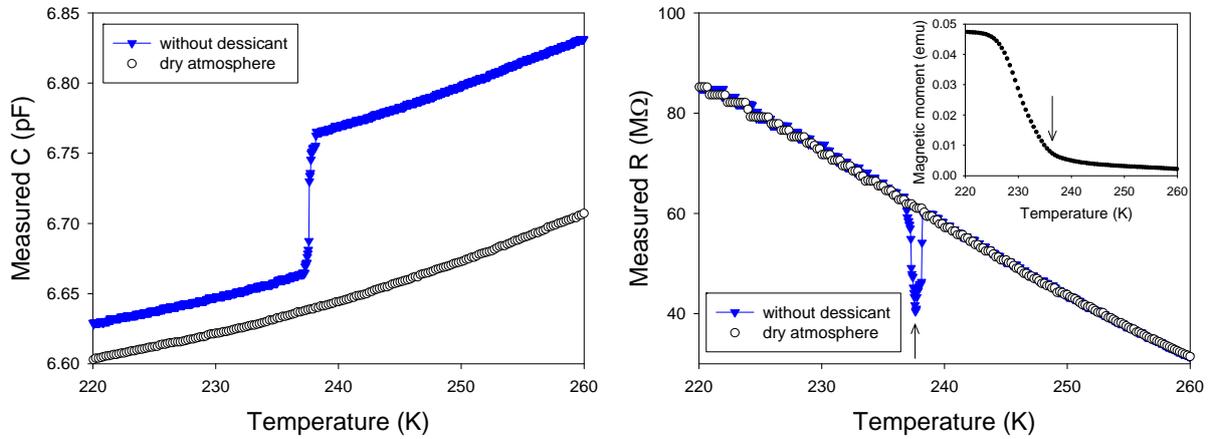


Figure 3. Measured temperature dependence of the capacitance C and parallel resistance R of a composite sample (LCMO/ Mn_3O_4) with a LCMO volume fraction equal to ~ 0.16 . The data shows that a significant experimental artefact can be observed due to moisture in the pores of the sample and / or in the experimental chamber. The inset of in the left graph shows the temperature dependence of the DC magnetic moment of the same material measured under a 0.1 T applied magnetic induction.

After 72 h of conditioning the samples in dry atmosphere and turbomolecular pumping the sample chamber for 24 h, both the jump in $C(T)$ and the peak in $R(T)$ disappear (white symbols in figure 3). These peaks are related to the change of dielectric properties of water at solid-vapor or solid-liquid phase transitions [23], arising at temperatures that are strongly pressure dependent. The data shown in figure 3 give thus experimental evidence that spurious experimental artefacts can be observed in measuring the dielectric properties of bulk porous ceramics that have not been kept in dry atmosphere. It can be noted that the jump and peaks observed in figure 3 might be particularly misleading since they occur at a temperature (indicated by an arrow) close to the ferromagnetic – paramagnetic transition temperature of the LCMO phase in our composite samples (cf. inset in figure 3).

3.2. Dielectric properties of composite samples

At $T = 300$ K, the capacitance of a bulk composite sample (LCMO/ Mn_3O_4) with $f_{\text{LCMO}} = 0.16$ is a decreasing function of frequency, as shown in figure 2. At 1 kHz, the absolute value of in-phase permittivity of the bulk composite is found to be approximately 2.7 times that of bulk Mn_3O_4 . The presence of interfaces with different densities of charge carriers, e.g. at dielectric – electrode interfaces or at grain boundaries can be responsible for the behaviour shown in figure 2. In the particular case of the composite sample, the manganite phase produces an extrinsic interfacial or space-charge polarization mechanism, resulting in a noticeable increase in the real part of the permittivity with respect to that of Mn_3O_4 [24-26].

Figure 4 shows the magnetic field dependence of the in-phase permittivity of the composite sample at $T = 50$ K, for a magnetic field ramped from 0 to 4 teslas and then cycled between two symmetric values. The data for the composite material (red curve) are compared to the behaviour of Mn_3O_4 (black curve). As can be seen, the LCMO/ Mn_3O_4 sample displays a perceptible magnetocapacitance (relative variation ~ 0.4 % in the magnetic field range investigated) and the $C(H)$ plot displays a hysteretic behaviour. Conversely, the permittivity of the Mn_3O_4 sample at 50 K is almost magnetic field independent. More precisely the in-phase permittivity decreases slightly with the applied field but the relative variation of permittivity is smaller than 0.02 % in the magnetic field range investigated.

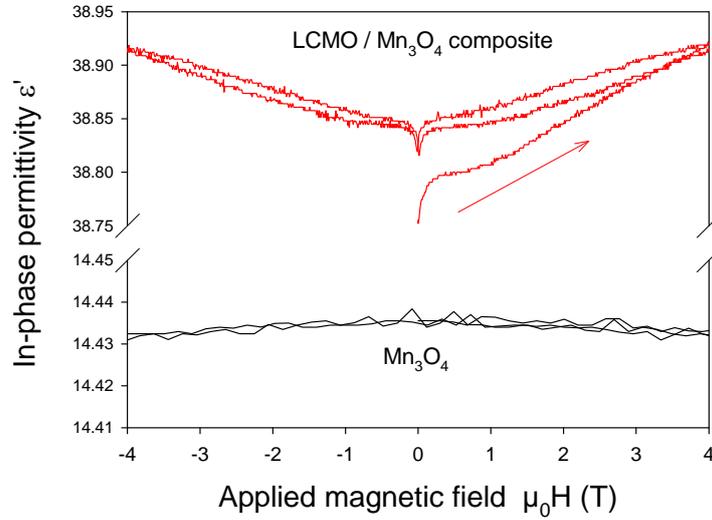


Figure 4. Comparison of the magnetic field dependence of the in-phase permittivity measured at $T = 50$ K for pure Mn_3O_4 and for a composite ($\text{LCMO} / \text{Mn}_3\text{O}_4$) ceramic.

The behaviour of Mn_3O_4 depicted in figure 4 is in agreement with recent literature data putting into evidence a magnetodielectric coupling associated with specific magnetic structures and understood with a spin-phonon coupling model [27,28]. These intrinsic magnetodielectric effects are linked to complex magnetic phase transitions arising at $T = 34, 40$ and 42 K but the permittivity decreases very slightly with magnetic field in the paramagnetic phase ($T > 42$ K). By contrast, the permittivity of our $\text{LCMO} / \text{Mn}_3\text{O}_4$ composite is found to increase with magnetic field. Combined with the pronounced frequency dependence (figure 2), this magnetodielectric effect is linked to the heterogeneous nature of the composite and can be understood through a combination of the magnetoresistive phase (LCMO) and the Maxwell-Wagner effect at interfaces [8]. As can be seen in figure 4, the magnetodielectric effect is more pronounced around zero. The intrinsic low-field magnetoresistance of the conducting LCMO phase [15] below its transition temperature (~ 230 K, cf. inset in figure 3) is likely to be responsible for this effect. Similarly, the hysteretic behaviour shown in figure 4 is reminiscent of the hysteretic resistance vs. magnetic field properties of the composite in the vicinity of the percolation threshold ($f_{\text{LCMO}} \sim 0.19$).

4. Conclusions

We have measured the dielectric properties of a bulk manganite/insulator polycrystalline composite ($\text{LCMO} / \text{Mn}_3\text{O}_4$) at relatively low manganite content (16%), so that the whole material is insulating. We have described the experimental set-up for measurements at low temperature and emphasized artefacts that can be observed if the bulk ceramic is not kept in dry atmosphere. The permittivity of the composite is found to be frequency dependent and much higher than that of pure Mn_3O_4 . A clear magnetic field dependence of the permittivity is observed at $T = 50$ K. At this temperature, intrinsic magnetodielectric effects of Mn_3O_4 are very small. The behaviour observed in the composite is therefore ascribed to Maxwell-Wagner effects arising at the interfaces between the insulating and the conducting magnetoresistive phase.

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