

Increase of the dielectric constant near a magnetic phase transition in $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$

P.M. Botta*, J. Mira, A. Fondado, J. Rivas

Departamento de Física Aplicada, Facultad de Física, Universidad de Santiago de Compostela, E-15782, Santiago de Compostela, Spain

Received 13 September 2006; accepted 21 October 2006

Available online 9 November 2006

Abstract

The dielectric response of polycrystalline $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ as a function of frequency and temperature was studied. The semiconducting nature of this oxide gave rise to very high dielectric constant values, which were mainly attributed to interfacial polarization (grain boundaries and contacts sample-electrode). However, an increase of the permittivity at temperatures close to a magnetic phase transition suggests the contribution of intrinsic effects to the observed high dielectric constants.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Dielectrics; Magnetic materials; Semiconductors; Manganites

1. Introduction

Materials with high dielectric constant are currently an important challenge for new applications in electronics [1]. Although ferroelectric materials have been the standard solution by decades, they exhibit some limitations because of the strong dependence of the dielectric permittivity with temperature. Recently, some results concerning huge dielectric constant in systems with charge condensation have been reported [2]. Although these colossal values ($>10^4$) seem to be strongly influenced by non-intrinsic properties of the solid [3], the phenomenon could be very interesting, since could yield high dielectric constants by non-conventional ferroelectric mechanisms.

The system $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ has a rich magnetic phase diagram [4] where paramagnetic (PM), ferromagnetic (FM), antiferromagnetic (AF), and charge ordered (CO) states are determined by temperature and doping level, x . The phase boundary point $x=0.5$ is a focus of great interest. This compound undergoes a transition from PM to FM state ($T \cong 225$ K), and then transforms to a COAF phase at temperatures between

160 and 180 K, depending on the synthesis conditions [5]. Moreover, the competition between FM and CO states gives rise to an electronic phase separation into nano-scale regions of FM and CO below 150 K [5,6].

In this context, the main objective of this work is to provide experimental evidence that support the apparent link between the electronic state and the dielectric response in $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$.

2. Experimental

Polycrystalline $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ was prepared by conventional solid-state reaction method. Stoichiometric amounts of pure and dried La_2O_3 , CaO , and Mn_2O_3 were well-ground in an agate ball-mortar. This powder was pressed and thermally treated in air at 1473 and 1573 K with intermediate grindings. The sample calcined at 1573 K was ground, cold-pressed into pellets and sintered for 24 h at 1623 K.

The phase evolution of the obtained material was followed by X-ray powder diffraction (XRD). The oxygen content was determined using iodometric titrations. Magnetization between 5 and 300 K was measured in a commercial SQUID magnetometer. A ZFC–FC loop was performed for each sample. Both measurements were made by heating from 5 to 300 K. In the case of ZFC the sample was cooled to 5 K without applying a magnetic field, while for FC curves a magnetic field of 100 Oe was applied during the cooling.

* Corresponding author. Dept. Física Aplicada, Facultad de Física — Campus Sur, 15782 Santiago de Compostela, Spain. Tel.: +34 981563100x14014; fax: +34 981520676.

E-mail address: pbotta@usc.es (P.M. Botta).

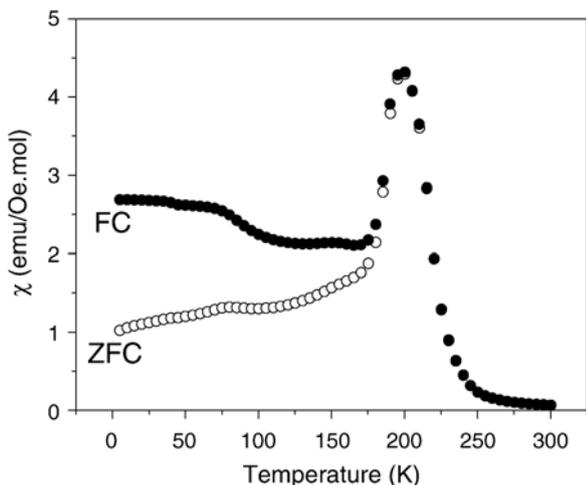


Fig. 1. Magnetic susceptibility as a function of temperature after zero-field cooling (ZFC) and field cooling (FC) at 100 Oe.

The complex dielectric permittivity was measured at temperatures from 100 to 300 K in frequencies ranging from 20 to 1×10^6 Hz. The ceramic pellets (5 mm diameter \times 1 mm thickness) were sputtered with gold on their surfaces to ensure good electrical contacts with the electrodes.

3. Results and discussion

XRD analysis showed the completion of the solid-state reaction and the absence of secondary phases. Iodometric titrations resulted in an oxygen content of 3.01, very close to the stoichiometric value.

Fig. 1 shows the magnetic susceptibility (χ) as a function of temperature for the prepared material. A COAF–FM transition at about 185 K and a FM–PM transition at 220 K are observed. The large hysteresis exhibited between ZFC and FC curves can be explained taking into account the nature of these magnetic transitions, in which the transformation from PM to FM state involves a progressive appearance of FM domains. Upon cooling, the application of a magnetic field (FC curves) enlarges the size of these domains, provoking higher magnetic susceptibilities than those displayed for ZFC curves at temperatures below T_C .

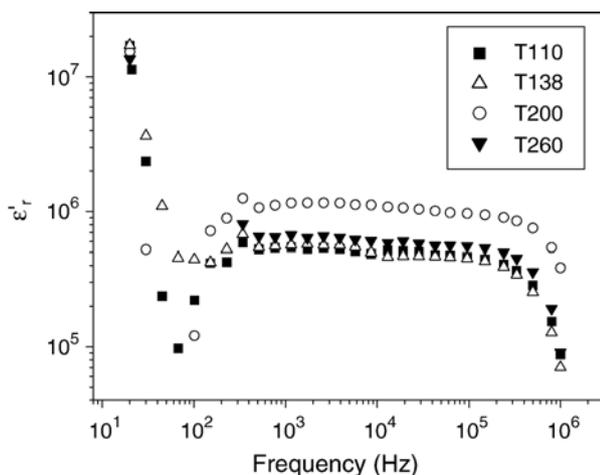


Fig. 2. Real part of the complex relative dielectric permittivity vs. frequency at selected temperatures.

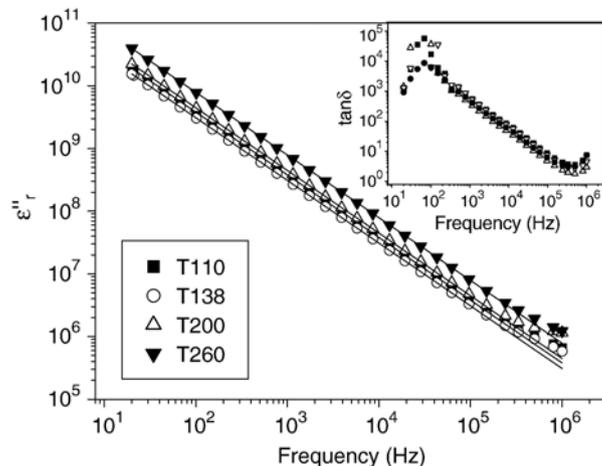


Fig. 3. Imaginary part of the complex relative dielectric permittivity vs. frequency at selected temperatures. Straight lines indicate the contribution to ϵ''_r of dc conduction. The inset shows the loss tangent vs. frequency at the same temperatures.

Fig. 2 shows the real part of the relative permittivity (dielectric constant, ϵ'_r) as a function of frequency at several temperatures. A plateau of ϵ'_r between 5×10^5 and 1×10^6 can be observed at frequencies from 300 to 3×10^5 Hz. These abnormally high dielectric constant values are the result of a combination of intrinsic and extrinsic effects.

Besides charge condensation, the intrinsic effects could be related to semiconducting character of $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$, which presents relatively high dc conductivity. In fact, very high dielectric losses were measured (Fig. 3). The straight lines represent the contribution to ϵ''_r of dc conduction. This was calculated using the following expression:

$$\epsilon_{r,dc}'' = \sigma_{dc} / \omega \cdot \epsilon_0,$$

where σ_{dc} is the dc conductivity, ω is the angular frequency ($\omega = 2 \cdot \pi \cdot \nu$) and ϵ_0 is the dielectric permittivity of free space ($8.85 \times 10^{-12} \text{ F m}^{-1}$). σ_{dc} values were estimated from conductivity data measured at the lowest frequency for each temperature. As it can be seen, dc conduction is the main contribution to the dielectric losses. The inset shows the variation of loss tangent ($\tan \delta = \epsilon''_r / \epsilon'_r$) with

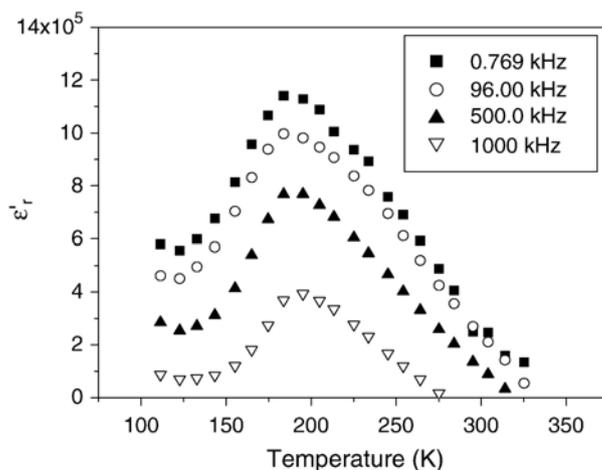


Fig. 4. Dielectric constant of $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ as a function of temperature at several frequencies.

frequency. Extremely high values were measured, especially at the lowest frequencies. This implies a serious limitation to the application of the material as a condenser. However, taking into account the main origin of the losses, they can be reduced by using $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ as a part of a composite material together with an electrical insulator, like Al_2O_3 or SiO_2 .

The extrinsic contribution to the high dielectric constant is associated to the interfacial polarization produced in grain boundaries and contacts sample-electrode [3,7]. For semiconducting materials, the last ones arise mainly due to the formation of Schottky barriers in the region near the metallic electrodes. When the electron work function in a metal is higher than a semiconductor, the electrons flow from the semiconductor to the electrode, making equal both Fermi levels. The electron consumption in the semiconductor gives rise to a net positive charge localized in the region close to interphase sample-electrode, the so-called depletion layer. This thin layer of small conductivity behaves as a high capacitance condenser parallel with a resistor, connected in series with the sample. In Fig. 2 the relaxation of both interfacial and contact phenomena can be distinguished. The first one begins at frequencies lower than 100 Hz whereas the second takes place from 10^5 Hz on.

In order to evaluate the relative significance of both extrinsic and intrinsic contributions to polarization, the realization of dielectric measurements at higher frequencies would be necessary. Unfortunately, due to limitations of our instrument, this could not be carried out. However, we have estimated the intrinsic value of ϵ'_r performing dielectric measurements on samples, in which Teflon films (this polymer has a very high electric resistivity and $\epsilon'_r=2$) were interposed between the material and the electrodes. In this way, the Schottky barriers (and consequently the most part of extrinsic effects) are minimized. Dielectric constants of about 45 were found at high frequencies. This value agrees with that obtained by means of a linear extrapolation of ϵ'_r curves (Fig. 2) up to high enough frequencies to consider the complete relaxation of the extrinsic factors (1×10^9 Hz). Taking into account that the studied manganite is considered a non-ferroelectric oxide, a dielectric constant of 45 represents a relatively high value. Therefore an intrinsic effect seems to be playing an important role in the dielectric response of $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$.

The dependence of ϵ'_r with temperature is shown in Fig. 4. A clear maximum (of increasing intensity for lower frequencies) is observed. This peak is centered on 185 K, fitting in with the observed COAF–FM transition temperature (Fig. 1).

A similar behavior has been reported for $\text{Pr}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ at 225 K (the CO transition temperature for this compound) [8,9]. Several explanations for linking the observed dielectric response to the charge-order state have been suggested. One of them considers that the CO in these systems could be in an intermediate state between the classical CO (charge localized on Mn ions, or site-centered CO) and an oxygen-centered ordering (charge localized on the bonding interaction Mn–O–Mn, or bond-ordering). The CO pattern of such intermediate state lacks inversion symmetry and exhibits a net ferroelectric moment. By means of theoretical calculations, an electronic phase diagram was obtained for manganites, the ferroelectric state being predicted in a composition range of $0.4 < x < 0.5$ [10]. The idea of non-centrosymmetric CO states as origin of an incipient ferroelectricity is also supported by the behavior recently observed in $\text{La}_{1.5}\text{Sr}_{0.5}\text{NiO}_4$ [11].

Electronic phase separation has been invoked as another possibility to explain the observed dielectric behavior of these manganites. The

coexistence of FM (metallic) and COAF (insulating) regions in the solid could increase the capacitive response of the system, as reported in several studies dealing with metallic particles embedded in insulating matrixes [12]. This behavior is controlled by the volume fraction of the metal in the composite. When this fraction reaches the percolation threshold, a divergence in ϵ'_r is observed. For $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ the fraction of the FM region strongly depends on temperature, as was reported in Ref. [6], where the maximum fraction of ferromagnetic phase was found about the Néel temperature.

4. Conclusions

A very high dielectric constant in a wide temperature and frequency range was measured for $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$. This value is mainly due to the Schottky barriers formed at the interface sample-electrode and the semiconducting characteristics of the material, which cause very high losses by dc conduction. The intrinsic contribution to the dielectric constant of this manganite was estimated about 45. The dependence of this parameter with temperature revealed a maximum near a COAF–FM transition, supporting the existence of intrinsic dielectric phenomena. The origin of this anomaly could be associated to the presence of a CO pattern with a net ferroelectric moment or the proximity to the percolation threshold in the phase separated system.

Acknowledgements

This work was financed by MAT2004-05130-C02-01 from MEC (Spain). PMB thanks MEC for the support under the program Juan de la Cierva.

References

- [1] R.J. Cava, *J. Mater. Chem.* 11 (2001) 54.
- [2] C.C. Homes, T. Vogt, S.M. Shapiro, S. Wakimoto, A.P. Ramirez, *Science* 293 (2001) 673.
- [3] P. Lunkenheimer, V. Bobnar, A.V. Pronin, A.I. Ritus, A.A. Volkov, A. Loidl, *Phys. Rev.*, B 66 (2002) 052105.
- [4] S.-W. Cheong, C.H. Chen, in: C.N.R. Rao, B. Raveau (Eds.), *Colossal Magnetoresistance, Charge Ordering and Related Properties of Manganese Oxides*, World Scientific, Singapore, 1998, p. 241.
- [5] P. Levy, F. Parisi, G. Polla, D. Vega, G. Leyva, H. Lanza, R.S. Freitas, L. Ghivelder, *Phys. Rev. B* 62 (2000) 6437.
- [6] F. Rivadulla, M. Freita-Alvite, M.A. López-Quintela, L.E. Hueso, D.R. Miguéns, P. Sande, J. Rivas, *J. Appl. Phys.* 91 (2002) 785.
- [7] D.C. Sinclair, T.B. Adams, F.D. Morrison, A.R. West, *Appl. Phys. Lett.* 80 (2002) 2153.
- [8] F. Rivadulla, M.A. López-Quintela, L.E. Hueso, C. Jardón, A. Fondado, J. Rivas, M.T. Causa, R.D. Sánchez, *Solid State Commun.* 110 (1999) 179.
- [9] S. Mercone, A. Wahl, A. Pautrat, M. Pollet, C. Simon, *Phys. Rev.*, B 69 (2004) 174433.
- [10] D.V. Efremov, J. van den Brink, D.I. Khomskii, *Nat. Mater.* 3 (2004) 853.
- [11] J. Rivas, B. Rivas-Murias, A. Fondado, J. Mira, M.A. Señaris-Rodríguez, *Appl. Phys. Lett.* 85 (2004) 6224.
- [12] C. Pecharrmán, J.S. Moya, *Adv. Mater.* 12 (2000) 294.