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Physics Letters A 323 (2004) 473–476

PHYSICS LETTERS A

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Influence of charge-ordering on the dielectric response of $La_{1-x}Sr_xMnO_3$

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Received 23 December 2003; accepted 11 February 2004

Communicated by J. Flouquet

Abstract

The low- and audio-frequency dispersions of the complex relative dielectric permittivity of $La_{1-x}Sr_xMnO_3$ ($x = 0.15$ and 0.33) have been investigated. It is found that $La_{0.85}Sr_{0.15}MnO_3$ shows an extra contribution to the dielectric response that is not present in $La_{2/3}Sr_{1/3}MnO_3$. This extra contribution makes the dielectric constant to be quite stable in a relatively high value to at least 1 MHz and up to around 270 K. The difference between the dielectric responses of both materials is attributed to the charge-ordered state and the polaronic regime that are present in $La_{0.85}Sr_{0.15}MnO_3$ below its Curie temperature.

PACS: 75.47.Lx; 77.22.Ch; 77.22.Gm; 71.45.Gm

Keywords: Manganites; Dielectric properties; Charge ordering

1. Introduction

The technological applications of materials with high dielectric permittivity make interesting any improvement of this property. Since the discovery of ferroelectricity in single crystal materials in the 20s the field has developed rapidly [1] due to pressures of economic origin in parallel with the obvious scientific interest. In fact, ferroelectrics are the standard systems used in industry to obtain devices based on strong dielectric responses.

It is worth then investigating alternatives to the current resources. Our report on the finding of a high dielectric permittivity in the manganese-based perovskite $Pr_{2/3}Ca_{1/3}MnO_3$ [2,3] started a promising line in which an important boost has been given by Homes et al. [4], who found a dielectric constant of $\sim 80\,000$ in $CaCu_3Ti_4O_{12}$, and more recently with the report of similar values at room temperature and above in $La_{1.5}Sr_{0.5}NiO_4$ [5].

These results have created strong debate about the nature of the effect. Several groups have claimed that it is due to extrinsic reasons [6,7]. In our first reports on the topic [2,3] we suggested that the charge ordered state of $Pr_{2/3}Ca_{1/3}MnO_3$ might be playing the decisive role. In order to test the intrinsic or extrinsic character of the anomalous dielec-

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doi:10.1016/j.physleta.2004.02.030

tric properties of these manganites and, more specifically, to determine the role of the charge ordered state, we have studied the dielectric response of the $La_{1-x}Sr_xMnO_3$ system with $x = 0.15$ and $x = 0.33$. $La_{0.85}Sr_{0.15}MnO_3$ presents charge order below $T_{CO} = 192$ K [8], whereas $La_{2/3}Sr_{1/3}MnO_3$ is a prototype of double-exchange ferromagnet with a conventional second-order ferromagnetic–paramagnetic phase transition at $T_C = 360$ K [9], and its electrical and magnetic behaviour does not present anomalies due to lattice effects as in manganites exhibiting colossal magnetoresistance [10,11].

2. Experimental details

$La_{1-x}Sr_xMnO_3$ ($x = 0.15$ and 0.33) polycrystalline samples were synthesized by solid state reactions from stoichiometric mixtures of La_2O_3, SrO, Mn_2O_3 and MnO_2. La_2O_3 was previously heated at 1000 °C for 8 h in order to eliminate CO_2. The starting materials were ground in an agata mortar and then fired in air at 1100 °C for 70 h and 1300 °C for 70 h with intermediate grindings. The X-ray diffraction powder analysis showed single phase.

The complex dielectric permittivity was measured with a parallel-plate capacitor coupled to a precision LCR meter Agilent 4284 A, capable to measure in frequencies ranging from 20 to 10^6 Hz. The capacitor was mounted in an aluminium box refrigerated by liquid nitrogen, that incorporates a mechanism to control the temperature. The samples were prepared to fit in the capacitor, and gold was sputtered on their surfaces to ensure good electrical contact with the electrodes of the capacitor. The measurements were carried out in pellets of about 1 cm of diameter and 1 mm thick, prepared by pressing the powders at $6.4\ \mathrm{ton/cm^2}$.

3. Results

In their reaction to sinusoidal electric fields, the frequency response of dielectrics can be expressed by their complex relative dielectric permittivity [12]:

$$\varepsilon_r(\omega) = \varepsilon_r'(\omega) - i\varepsilon_r''(\omega), \tag{1}$$

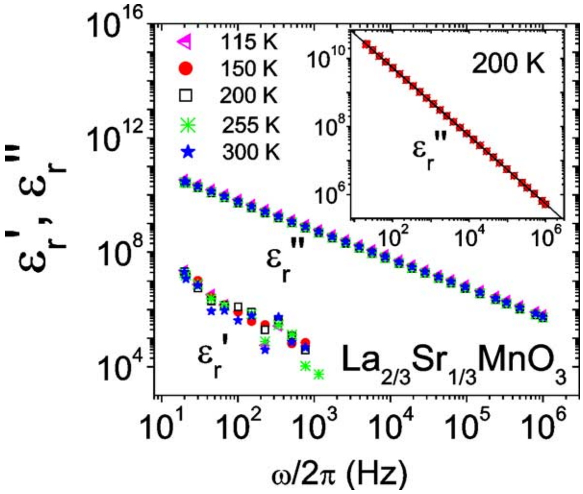

Fig. 1. Real part (dielectric constant, ε_r') and imaginary part (ε_r'') of the complex relative dielectric permittivity of $La_{2/3}Sr_{1/3}MnO_3$ versus frequency at selected temperatures. The dissipative effects are due to the contribution of "free" charge carriers only, as concluded from the fit of ε_r'' measured at $T = 200$ K shown in the inset. Points are experimental data, the line corresponds to the fit. The labels of the inset axes are the same as those of the main figure.

where we will use complex quantities (with $i = \sqrt{-1}$) $\varepsilon_r = \varepsilon/\varepsilon_0$ ($\varepsilon_0 = 8.85 \times 10^{-12}$ F/m) is the permittivity of free space and ω is the angular frequency.

In Fig. 1 we show the real component of the relative permittivity (dielectric constant), ε_r', and the imaginary component, ε_r'', of $La_{2/3}Sr_{1/3}MnO_3$ in the frequency range from 20 Hz to 1 MHz at several temperatures. This system is an electrical conductor, which causes a drop of the dielectric constant to negligible values above 1 kHz.

In order to obtain information about the origin of this dielectric response, that at first sight resembles a diffusion process [12], we have analyzed the imaginary component. This parameter describes the dissipation of electric energy, and, if it is assumed that the material obeys Ohm's law, the dc electric conductivity, σ_{dc}, and ε_r'' are related through the defining equation of the Maxwell's displacement current, giving [12,13]

$$\varepsilon''_{r,\mathrm{die}}(\omega) = \varepsilon_r''(\omega) - \frac{\sigma_{dc}}{\varepsilon_0\omega} \tag{2}$$

($\varepsilon''_{r,\mathrm{die}}$ = contribution associated to true dipolar processes).

Using (2) we can separate the true conductivity created by migrating charge carriers from any other polar

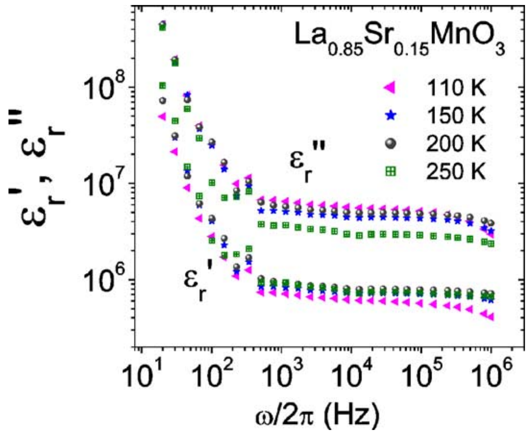

Fig. 2. Real part (dielectric constant, ε_r') and imaginary part (ε_r'') of the complex relative dielectric permittivity of $La_{0.85}Sr_{0.15}MnO_3$ versus frequency at selected temperatures. The plateaus both in ε_r' and ε_r'' are revealing the presence of another mechanism that gives rise to the dielectric constant in this system, out of the contribution of free charge carriers.

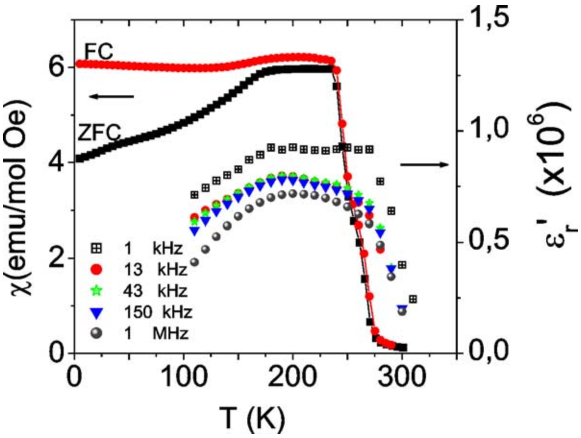

Fig. 3. Dielectric constant at selected frequencies vs. temperature, and zero field cooled (ZFC) and field cooled (FC) magnetization (measured at a magnetic field $H = 120$ Oe) of $La_{0.85}Sr_{0.15}MnO_3$. It is clear the correlation between the anomalous dielectric constants found in the system with its magnetic response.

dissipative action. The fits (an example is presented in the inset of Fig. 1) show that there are no other contributions different from the conductivity term, and therefore the energy dissipation is due only to migration of charge carriers. The "giant" polarizabilities observed at low frequencies in this perovskite can be explained if we take into account the accumulation of charge carriers at the sample-electrode interface. Additionally, the observed dielectric spectroscopy can be explained assuming that the charge carriers dominate with a relatively free possibility to move between the electrodes of the capacitor, as suggested by Jonscher in similar cases [14].

The dielectric response of $La_{0.85}Ca_{0.15}MnO_3$ is qualitatively different, as is obvious from Fig. 2. Although for low frequencies the behaviour is the same as in $La_{2/3}Sr_{1/3}MnO_3$, a very high stable value of dielectric constant is observed for frequencies higher than about 500 Hz. This is a clear indication of the subsistence, within a single volume of the material, of two differently dispersive mechanisms, of which the more strongly dispersive becomes important at higher frequencies. One of such mechanisms is responsible for the plateau-like behaviour of ε_r'. The analysis of ε_r' versus temperature allows to observe that it sets in between 250–300 K (Fig. 3), like the magnetic ordered phase of the system. It is worth mentioning that the maxima of the dielectric response versus temperature are around 180 K, i.e., near the charge-ordering transition point, marked also by the kink in the magnetic data at that temperature.

4. Discussion

The dielectric behaviour of $La_{1-x}Sr_xMnO_3$ with $x = 0.15$ and $x = 1/3$ is very different, as it can be seen in Fig. 1. The difference is not only quantitative, but also qualitative. For $x = 0.15$ ε_r' decreases monotonically, whereas for $x = 1/3$ there is a plateau, with a quite stable and high value of the dielectric constant up to the maximum frequency studied, 1 MHz. What is the reason for that? As stated in the introduction, the main difference between both systems is the charge ordered state present in the $x = 0.15$ sample. This seems to be another confirmation of the link between both phenomena, in line with the results obtained in Refs. [2,3,5], although now there is a difference: in the case of $Pr_{2/3}Ca_{1/3}MnO_3$ the onset of the high dielectric response at high frequencies coincides with that of the charge ordering, but in the case of $La_{0.85}Sr_{0.15}MnO_3$ the high dielectric constant is present above the starting temperature of the charge ordering, T_{CO}. Only at the Curie point, T_C, it starts to decrease. What happens between T_{CO} and T_C? Zhou et al. [15] have demonstrated that, contrary to the assessment of de Gennes [16], the electrons are not itinerant below T_C; moreover, they found a polaronic (vibronic) regime in the range $T_{CO} < T < T_C$. After our result it is clear, therefore, that the charge ordered state is a sufficient rather than a necessary condition for the observed ε'_r. Also, a polaronic regime such as that present in $La_{0.85}Sr_{0.15}MnO_3$ at $T_{CO} < T < T_C$, together with sample-electrode interfacial effects, produces a high ε'_r, as in the case $T < T_{CO}$. The essential point seems to be the existence of a strong electron coupling to orbital fluctuations that distinguish these electrons from the itinerant electrons in the $x = 1/3$ case. In this line, Ciuchi and de Pasquale [17] have observed theoretically, applying the dynamical mean field model to the problem of charge ordering, that in the normal state as well as in the charge ordered state the existence of polarons is associated to the qualitative properties of the lattice polarization distribution function, that could give rise to an enhancement of the dielectric constant [18].

In summary, we have found an anomalous high dielectric response of $La_{0.85}Sr_{0.15}MnO_3$ below its Curie temperature. Such behaviour is not observed in $La_{2/3}Sr_{1/3}MnO_3$. As the main difference between both systems from the electrical point of view is the charge-ordered state followed by a polaronic regime that are present in the former, we attribute to this difference the anomalous high dielectric response measured.

Acknowledgements

We thank the financial support of the DGI of the Ministry of Science and Technology of Spain under project FEDER MAT2001-3749. M.P. Gutiérrez also acknowledges the CONACyT of Mexico, for her postdoctoral fellowship.

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