Dielectric response of the charge-ordered two-dimensional nickelate La$_{1.5}$Sr$_{0.5}$NiO$_4$

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We report the dielectric response of La$_{1.5}$Sr$_{0.5}$NiO$_4$, a system that experiences charge ordering above room temperature ($T_{CO}=480$ K) and a rearrangement of its charge-order pattern in the temperature region 160–200 K. A careful analysis of the role of the electrical contacts used, sample thickness, and grain size on the experimental data allows us to determine that this material exhibits a high intrinsic dielectric constant. In addition, the temperature dependence of the dielectric constant, that shows a maximum in the region of the rearrangement of the charge-order pattern, points to a link between the two phenomena. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1834998]

Ferroelectrics are the standard solution to obtain devices that make use of notable dielectric properties. In them, the ferroelectric state arises because the centers of positive charges in the crystalline lattice do not coincide with those of negative charges; i.e., the ultimate origin of the ferroelectric state is structural. Among the alternative strategies to find materials with high dielectric constant are those that involve condensation of electronic charges. The interest on these alternatives has grown since the report by Homes *et al.*[1] of a high-dielectric constant of about 8×10^4 in CaCu$_3$Ti$_4$O$_{12}$ at temperatures as high as 250 K and frequencies up to 1 MHz. The origin of this finding has been discussed by Lunkenheimer *et al.*,[2,3] who attribute it to extrinsic effects. Basically, they argue that the temperature independent dielectric constant in a broad temperature range found by Homes *et al.* cannot stem from permanent dipoles or off-center ions. He *et al.*[4] and Cohen *et al.*[5] also attribute to extrinsic effects the dielectric response of CaCu$_3$Ti$_4$O$_{12}$, after a first-principles study of its structural and lattice dielectric response. In the same line, Sinclair *et al.*[6] stress the apparent character of this colossal dielectric constant and explain it by Maxwell–Wagner-type contributions of depletion layers at the interface between sample and contacts and at grain boundaries.

Despite this controversy, it seems admissible to think about a correlation between the dielectric properties and the electronic state. In this context, we have focused on systems with charge condensation, starting with charge-ordered manganese perovskites. Our report on the finding of a high capacitive behavior in Pr$_{2/3}$Ca$_{1/3}$MnO$_3$ that appears just below its charge ordering temperature, $T_{CO}=250$ K (Refs. 7 and 8), is evident demonstration of the link between the electronic state and the increase of the dielectric response.

In this letter we are focusing on a system with charge ordering temperature above room temperature, the mixed oxide La$_{1.5}$Sr$_{0.5}$NiO$_4$, with $T_{CO}=480$ K (Ref. 9), with the aim of getting a high dielectric constant at ambient conditions. In order to test the role of intrinsic and extrinsic factors, and on the basis of Refs. 2–6, the sample contacts were changed, the sample thickness was modified, and two kinds of samples were synthesized by two routes giving different grain sizes. On one hand, a La$_{1.5}$Sr$_{0.5}$NiO$_4$ ceramic sample was prepared by a conventional solid-state reaction, starting from stoichiometric amounts of dry La$_2$O$_3$, SrCO$_3$, and NiO, that were thoroughly mixed and grinded together, pressed into pellets and fired at 1373, 1473, and 1573 K with intermediate grindings. The sample was then cooled to room temperature at the rate of 1 K/min. On the other hand, the same compound was synthesized by the Pechini method using La$_2$O$_3$, SrCO$_3$ and Ni(NO$_3$)$_2 \cdot$6H$_2$O as starting materials. The procedure was as follows: La$_2$O$_3$ was first converted into the corresponding nitrate by dissolution in 30% nitric acid. This product was then added to a 1 M citric acid aqueous solution, in which stoichiometric amounts of SrCO$_3$ and Ni(NO$_3$)$_2 \cdot$6H$_2$O were also dissolved. After diluting the so-obtained solution, we carefully added ethyleneglycol in a proportion of 10% v/v. The resulting solution was heated at 473 K until we obtained a brown resin, whose organic matter was subsequently decomposed at 673 K. The obtained ashes were given accumulative heating treatments at 873, 973, 1073, and 1173 K followed by intermediate grindings, and the pelletized sample was finally annealed at 1273 K.

Both samples were characterized by x-ray powder diffraction, that showed that they are single phase, with a structure related to the perovskite: La$_{1.5}$Sr$_{0.5}$NiO$_4$ displays a quasi-two-dimensional structure (K$_2$NiF$_4$) in which perovskite blocks, that are one-octahedra thick, are separated from one another by the presence of rock-salt type (La–Sr/O) layers along the c axis. Also, the obtained polycrystalline materials have an averaged particle diameter of 0.7 μm in the case of the Pechini sample and several micrometers in the case of the ceramic sample, as seen by scanning electron microscopy. 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 aluminum box refrigerated with liquid nitrogen, and incorporating a mechanism to control the temperature. The samples were prepared to fit in the capacitor, and alternatively gold or silver were sputtered on their surfaces to ensure good electrical contact with the electrodes of the capacitor. The system was tested using a commercial SrTiO$_3$ sample, and gave values similar to those reported in the literature.[10]
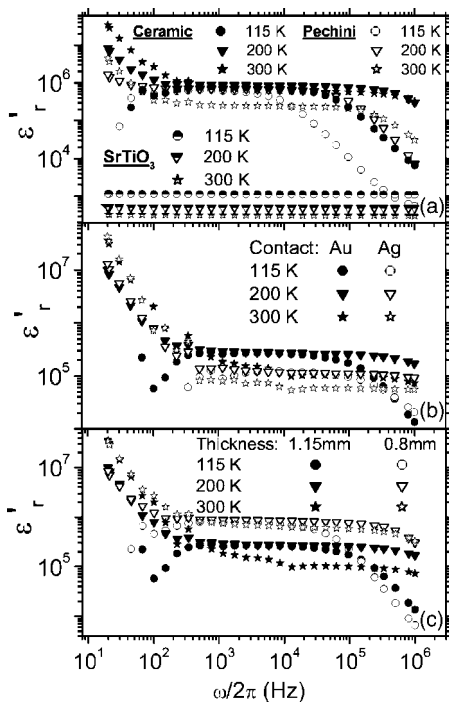
FIG. 1. Real part of the complex relative dielectric permittivity, ε_r', of La$_{1.5}$Sr$_{0.5}$NiO$_4$ vs frequency at selected temperatures: (a) comparison between samples with different grain size. Data taken in a commercial SrTiO$_3$ sample are included as reference. Results obtained in the ceramic sample, using two different types of contacts (b) and two different sample thicknesses (c).

The complex relative dielectric permittivity of La$_{1.5}$Sr$_{0.5}$NiO$_4$;

$$\varepsilon_r(\omega) = \varepsilon_r'(\omega) - i\varepsilon_r''(\omega), \qquad (1)$$

($\varepsilon_r = \varepsilon/\varepsilon_0$; where $\varepsilon_0 = 8.85 \times 10^{-12}$ F/m is the permittivity of free space and ω is the angular frequency) was measured as a function of frequency and temperature. In Fig. 1(a) we show the real part of the relative permittivity (dielectric constant, ε_r') of the ceramic sample with sputtered gold contacts, in the frequency range from 20 Hz to 1 MHz at several temperatures. It is higher than 10^6 at very low frequencies, keeps well above 10^5 at room temperature up to 100 kHz, and decreases to 3×10^4 at 1 MHz.

The same measurement was done in the sample of smaller grain size, and the values changed [Fig. 1(a)], indicating a dependence on the grain size. Additionally, it was observed that sample contacts play also a certain role as can be seen in Fig. 1(b). Finally, the thickness of the sample was changed and it was observed that it altered the dielectric response [Fig. 1(c)]. It is therefore clear that extrinsic factors are contributing to the measurement of the dielectric constant of La$_{1.5}$Sr$_{0.5}$NiO$_4$.

The frequency dependence of the imaginary part, ε_r'' was also measured [Fig. 2(a)]. In order to study frequency dependent or purely ac relaxation effects, it is better to substract the dc contribution from the observed ε_r'' value, taking into account that[11]

$$\varepsilon_{r,\text{die}}''(\omega) = \varepsilon_r''(\omega) - \frac{\sigma_{dc}}{\varepsilon_0 \omega}, \qquad (2)$$

($\varepsilon_{r,\text{die}}''$ = loss factor due to a true dielectric response, σ_{dc} = dc electric conductivity). In this context, we have substracted
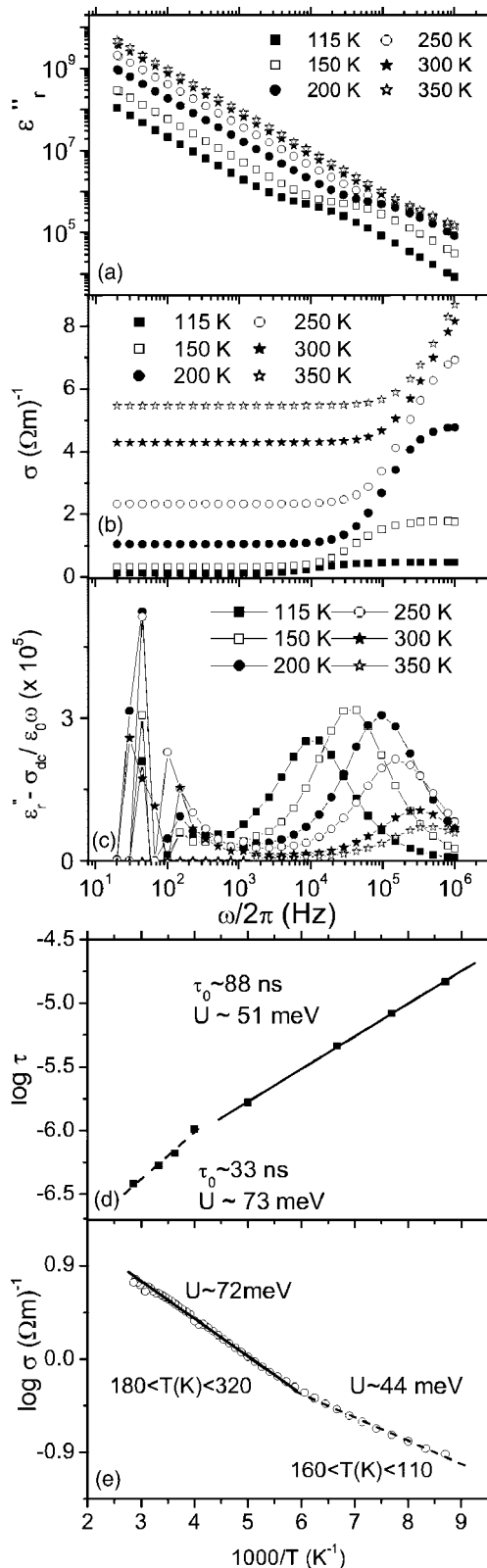

FIG. 2. Results for the La$_{1.5}$Sr$_{0.5}$NiO$_4$ sample synthesized by the Pechini method: (a) imaginary part of the complex relative dielectric permittivity, ε_r'', vs frequency at selected temperatures, measured with gold contacts; (b) conductivity vs frequency at diverse temperatures. Extrapolation of the curves to zero frequency gives σ_{dc}; (c) frequency dependence of the imaginary part of the complex relative dielectric permittivity after substraction of the contribution from free charge carriers. The maxima define the characteristic frequencies; (d) logarithm of the characteristic times vs the inverse of temperature. From linear fits we obtain two activation energies, with a boundary around 200 K; (e) logarithm of σ_{dc} vs the inverse of temperature.
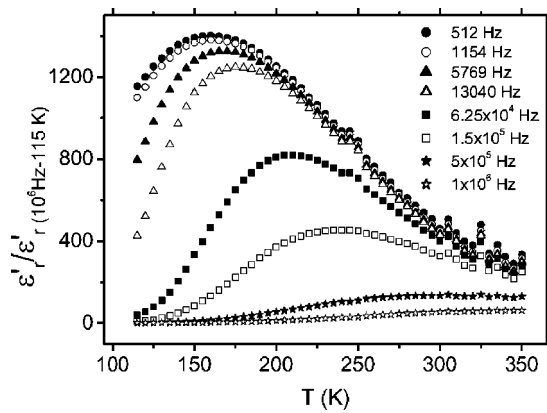
FIG. 3. ε_r' vs temperature at selected frequencies in the Pechini sample. The maxima separate two different behaviors in the dielectric response of $La_{1.5}Sr_{0.5}NiO_4$.

from the data of Fig. 2(a) the contribution from migrating charge carriers, $\sigma_{dc}/(\varepsilon_0\omega)$, where the dc conductivity, σ_{dc} has been obtained from the extrapolation at low frequencies of the conductivity, $\sigma(\omega)$, shown in Fig. 2(b). The obtained results, corresponding to the Pechini sample, are presented in Fig. 2(c), and enable us to observe the evolution with frequency and temperature of the dielectric relaxation, and to obtain the characteristic frequency of the relaxation with increasing temperature. There is a noticeable increase in the characteristic relaxation times, $\tau = 1/\omega$, with decreasing temperatures. A logarithmic fit of the characteristic times versus the inverse of temperature shows two different regimes with Arrhenius behavior, $\tau = \tau_0 \exp[U/(K_BT)]$, where U is the activation energy and k_B the Boltzmann constant [Fig. 2(d)]: one at high temperatures (>200 K) with activation energy $U \sim 73$ meV and another at lower temperatures with $U \sim 51$ meV.

On the other hand, if we examine the temperature dependence of σ_{dc} we observe a thermal activated behavior, with activation energy ~ 72 meV, in the high temperature regime [Fig. 2(e)]. This behavior changes in the region 160–200 K, to another with activation energy of ~ 44 meV. This situation correlates well with that of characteristic times [Fig. 2(d)], establishing a link between its dielectric relaxation and its conductivity. What is the reason for this change at 160–200 K? We think that it could be found in a recent work by Kajimoto *et al.*,[9] who have studied in detail the charge ordering of $La_{1.5}Sr_{0.5}NiO_4$ by neutron diffraction: they found, at 180 K, a spontaneous rearrangement of such charge ordering, from a checkerboard pattern to a stripe-type charge order. This rearrangement does not only affect the activation energies commented before, but also the high dielectric constant itself, that falls below this temperature (Fig. 3).

From the results of Fig. 1 we observe the influence of extrinsic factors, such as sample contacts, thickness, and grain size. The dielectric spectra reveal a quasi-Debye relaxation which can be explained satisfactorily with the help of a two- or trilayer Maxwell–Wagner capacitor.[12] In this line, the dispersion of ε_r' can be modeled taking into account the interfacial polarization due to the existence of depletion layers near the Au/Ag contacts, and considering the polycrystalline solid as consisting of conducting grains separated by grain boundaries (layers) of lower conductivity.[6] In this phenomenological model, if we assume that the true dielectric con-

stant is almost the same in all the sample (in the contacts zone and grain boundaries the conductivity of the material changes, but the dielectric constant should not be altered too much), then it can be demonstrated[12] that the ε_r' measured at low frequencies is strongly enhanced by extrinsic contributions that multiply the intrinsic (true) dielectric constant of the compound. The intrinsic ε_r' would directly correspond to ε_r' at its optical value ($\omega \to \infty$), ε_∞'. Although this optical value is out of the limits of our experimental device, by extrapolation at higher frequencies we have estimated a value around $\varepsilon_\infty' \approx 40$ at room temperature for this nickelate.

The role of the intrinsic part can be clearly seen from the variation of ε_r' with temperature, that goes through a maximum in the interval 160–200 K (Fig. 3). Given that the conductivity increases monotonically with temperature [Fig. 2(b)], the extrinsic contribution also changes monotonically with temperature,[12] and therefore the temperature dependence of ε_r' must be shaped by the intrinsic term. The maximum of the measured ε_r' found around 160–200 K (indicating that the intrinsic term should peak in a similar temperature range), falls in a temperature region where, as noted before, $La_{1.5}Sr_{0.5}NiO_4$ undergoes a spontaneous rearrangement of its charge ordering pattern.[9] Therefore, there seems to be a link between the electronic state of the material and its dielectric function.

In summary, we believe that this work is of general interest due to: (i) it reports rather high values of the dielectric constant in $La_{1.5}Sr_{0.5}NiO_4$; (ii) this dielectric response shows a correlation with the charge-order pattern of the material, indicating a link of both phenomena; (iii) from the applied point of view, it proposes new work to be done in other charge-ordered compounds, more suitable to minimize the dielectric losses, while keeping ε_r' as high as possible.

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