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Colossal dielectric constants in $\text{La}_{15/8}\text{Sr}_{1/8}\text{NiO}_4$

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Abstract. We report the results of dielectric spectroscopy on $\text{La}_{15/8}\text{Sr}_{1/8}\text{NiO}_4$, performed in a broad temperature and frequency range. This material exhibits extremely high ("colossal") dielectric constants ϵ' . Room-temperature values $\epsilon' > 10^4$ are found, remaining colossal up to the GHz-regime, which is of high relevance for possible applications. The charge transport in $\text{La}_{15/8}\text{Sr}_{1/8}\text{NiO}_4$ is found to be dominated by hopping conductivity. The material is prone to charge order, which can be assumed to play an important role in the generation of its unusual dielectric properties.

1. Introduction

Materials with high dielectric constants for future electronics have aroused tremendous interest. Among them, $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) stands out due to its "colossal" dielectric constant (CDC) up to 10^5 , which is constant in a relatively broad temperature region [1,2]. Aside of the extensively investigated CCTO, there are further materials, mainly transition metal oxides, which show CDCs [3,4,5]. In contrast to ferroelectrics, in CCTO and other materials the CDCs are nearly constant over a broad temperature range, an important prerequisite for technical applications. They reveal, however, a strong frequency dependence, which shows the signature of relaxational contributions. It is more or less commonly accepted nowadays, that this feature is due to a non-intrinsic effect, termed Maxwell-Wagner (MW) relaxation [3,6,7]. Within this scenario, heterogeneity, caused by the fact that the sample is composed of relatively high-conducting areas and insulating parts, is the origin for the relaxation and the CDCs. Especially, thin insulating layers can arise from surface effects (e.g., Schottky diodes at the electrodes) or internal barriers (e.g., grain boundaries). The exact mechanism responsible for the generation of the CDCs in CCTO is still a matter of debate. A significant problem of CCTO in terms of application, like capacitive elements in wireless electronics, is the fact that at room temperature the MW relaxation leads to an ϵ' value of only 100 for frequencies beyond 10 MHz [7,8]. Thus, CCTO does not meet the requirements, e.g., for telecommunications, where the dielectric properties in the GHz regime are important.

As was shown by us [9], $\text{La}_{15/8}\text{Sr}_{1/8}\text{NiO}_4$ (LSNO) seems to be a better suited material. In the present work, we will provide temperature-dependent dielectric spectra on single-crystalline LSNO covering the barely investigated, but important frequency range up to 1 GHz. Extending a previous work [9], here we also focus on the temperature-dependent conductivity, the dielectric loss and the relaxation times, which provides new insight into the electrical properties of LSNO including the prevailing charge-transport process. Early investigations of the system $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ revealed the presence of

charge stripe order in this material for a broad range of Sr-substitution levels [10]. The occurrence of charge order can be assumed to be of high relevance for the relaxational contributions in LSNO.

The LSNO crystals were prepared by the travelling solvent floating-zone growth technique. Details of preparation and measurement techniques are described in [9] and references therein.

2. Results and discussion

Figure 1 shows the temperature dependence of ϵ' and the conductivity σ' of LSNO for various frequencies. The data in the left frames ((a) and (b)) were measured using silver-paint contacts and those in the right frames ((c) and (d)) using sputtered gold contacts, applied after removing the silver paint. In both cases, pronounced steps in $\epsilon'(T)$ are observed from relatively low values at low temperatures ($\epsilon' \approx 300 - 600$) to colossal values up to 17000 in the case of silver paint and even higher values (4×10^5) if sputtered gold is applied. They shift to higher temperatures with increasing frequency. The conductivity (figures 1(b) and (d)) shows well-pronounced peaks, located at the points of inflection of $\epsilon'(T)$. These are typical signatures of a relaxation process, most probably of MW type. The overall behaviour qualitatively resembles that of single-crystalline CCTO (see, e.g., [2,11]). However, for LSNO the steplike increase in $\epsilon'(T)$ occurs at significantly lower temperatures than for CCTO. Thus the region of constant ϵ' is much broader in LSNO.

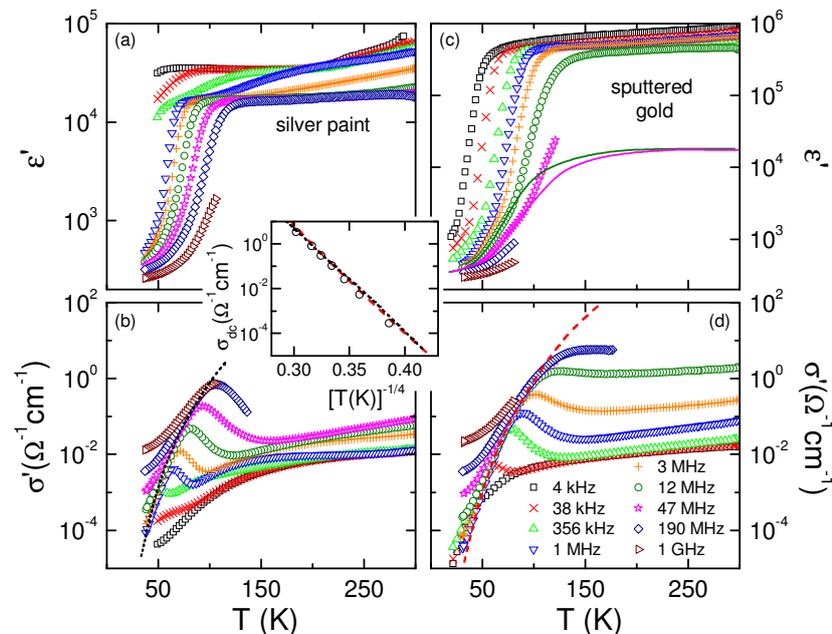


Figure 1. Temperature dependence of ϵ' ((a) and (c)) [9] and σ' ((b) and (d)) of LSNO for various frequencies. The left and right frames show the results obtained with silver paint and sputtered gold contacts, respectively. The lines in (c) represent an educated guess for a second relaxation. The dashed lines in (b) and (d) provide an estimate of the intrinsic dc-conductivity. The inset shows these curves (dashed lines) in VRH representation and results for σ_{dc} from fits of the frequency dependence (cf. figure 2 and [9]).

Using silver paint contacts, in LSNO a second relaxation step becomes clearly evident (figure 1a), leading to even higher values of $\epsilon'(T)$. Taking a closer look at the measurement with sputtered gold contacts (figure 1c), also there two relaxations can be suspected: The observed change of slope in the region of 50 - 75 K could indicate a first relaxation (indicated by the lines in figure 1(c)) superimposed

by a stronger second one. Just as for CCTO [7,8,11], the observed strong variation of ϵ' when the contact material is changed (figure 1) cannot be explained with an intrinsic mechanism. This implies that also in LSNO surface effects play an important role. However, the first relaxation may not be affected by the type of contact material.

The dashed lines in figures 1(b) and (d) provide estimates of the intrinsic dc-conductivity σ_{dc} [11]. The deviations from these lines at low temperatures and high frequencies are a signature of a frequency-dependent increase of σ' due to hopping conductivity. In the inset of figure 1 these $\sigma_{dc}(T)$ curves are shown in a representation leading to a linear behaviour for three-dimensional variable range hopping (VRH) [12]. For both contact types, almost identical dc conductivities are obtained as expected for an intrinsic bulk quantity. In addition, results from fits of the frequency dependence (cf. [9] and figure 2) are included (circles), well matching $\sigma_{dc}(T)$ extracted from the temperature-dependent data. The nearly linear behaviour of $\sigma_{dc}(T)$ in the inset of figure 1 points towards VRH behaviour, $\sigma_{dc} \propto \exp[-(T_0/T)^{1/4}]$. For VRH a frequency dependence $\sigma = \sigma_{dc} + \sigma_0 \omega^s$ ($s < 1$) is expected [12]. This is consistent with the mentioned intrinsic frequency dependence of σ' observed at low temperatures and high frequencies in figures 1(b) and (d). Via the Kramers-Kronig relation, $\sigma'(\nu)$ also influences $\epsilon'(\nu)$. Figure 2(a) shows $\epsilon'(\nu)$ of LSNO for various temperatures. For example, at 45 K and $10^6 \text{ Hz} < \nu < 10^9 \text{ Hz}$ a shallow power-law increase of ϵ' with decreasing frequency up to values of about 600 is observed. This can be ascribed to the mentioned VRH contribution [9].

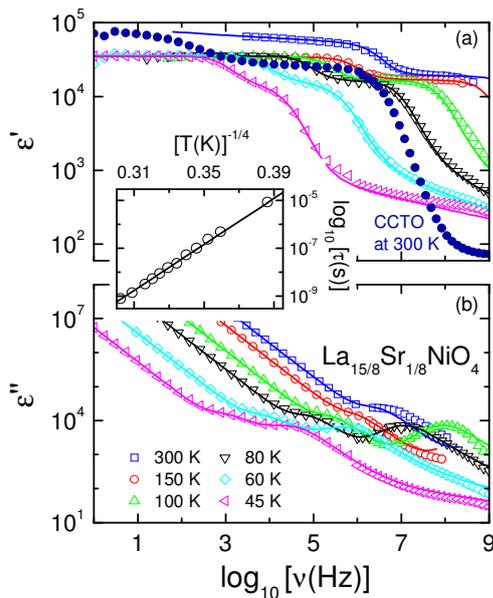


Figure 2. Frequency-dependent dielectric constant (a) and loss (b) of LSNO for various temperatures measured with silver paint contacts. The lines are fits with an equivalent circuit as used in [9]. (a) also contains a spectrum of CCTO obtained at room temperature [11]. The inset shows the VRH representation of the characteristic times of the main relaxation as determined from the fits. The line is a linear fit.

Figure 2 shows the frequency dependence of ϵ' and the loss ϵ'' . The steps in $\epsilon'(\nu)$ and peaks in $\epsilon''(\nu)$, both shifting with temperature, are ascribed to MW relaxations [9]. As revealed by figure 2(a), in contrast to CCTO (closed circles [11]), at room temperature $\epsilon'(\nu)$ of LSNO remains colossal up to the highest investigated frequency (430 MHz). Above this frequency, the resolution limit of the measurement device was exceeded. To obtain information on the frequency location of the main relaxation at room temperature, its relaxation time $\tau(T)$ has to be analyzed. Within an equivalent-circuit description [9], τ can be approximated by $\tau \approx R_b C_i$ with the bulk resistance R_b and the capacitance of the insulating layer C_i . The lines in figure 2 are fits with an equivalent-circuit model as discussed in [9]. The relaxation times calculated from the fit parameters R_b and C_i are shown in the inset of figure 2. They are nearly identical to the values determined from the positions ν_p of the loss peaks in figure 2(b) via $\tau = 1/(2\pi\nu_p \tau)$ (not shown), corroborating the validity of the chosen approach. The VRH representation of the inset of figure 2 was chosen because the temperature dependence of τ can be assumed to be dominated by that of R_b , which itself is proportional to $1/\sigma_{dc}$. Indeed $\tau(T)$ could

be linearized by this representation. An extrapolation leads to a value of $\tau = 1.0 \times 10^{-12}$ s at 300 K. This corresponds to a relaxation step in $\epsilon''(\nu)$ at about 160 GHz. Using instead an Arrhenius law to extrapolate $\tau(T)$, a value of 12 GHz is obtained. In any case, at room temperature the colossal ϵ' in LSNO persists well up to the GHz regime.

In summary, we have provided a detailed analysis of the dielectric properties of LSNO, in which the presence of charge-order seems likely. In contrast to CCTO, at room temperature ϵ' is found to remain colossal up to the technically important GHz regime. Two relaxations are found in this material, both most likely of MW type. The second relaxation leading to higher values of ϵ' clearly is sensitive to the variation of the contact material and thus can be ascribed to electrode effects. Concerning the origin of the first relaxation, currently only speculations are possible: For the CDCs in $\text{La}_{5/3}\text{Sr}_{1/3}\text{NiO}_4$ [5] and $\text{La}_{3/2}\text{Sr}_{1/2}\text{NiO}_4$ [13], "charge-glassiness" or polaron hopping were invoked, respectively. Alternatively, charge-order-induced heterogeneity is an interesting candidate to explain the detected MW-like behaviour. This corresponds to an internal barrier effect that is driven by an intrinsic mechanism, quite in contrast to CCTO where extrinsic mechanisms as, e.g., grain boundaries are considered. Thus the CDCs in LSNO should also be present on a much finer length scale, e.g., in thin films. The synthesis of high quality thin films with industrial throughput, as demonstrated, e.g., for CCTO [14], is a challenge to make LSNO suitable for applications. Another interesting feature of LSNO is the relatively high intrinsic (i.e., not MW related) ϵ' . The present results provide evidence for charge transport via VRH in LSNO. Via the Kramers-Kronig relation it leads to an increase of the intrinsic ϵ' up to 600 at 1 MHz. This high intrinsic dielectric constant as well as the CDC up to GHz at room temperature demonstrates the high potential of this charge-ordered nickelate both from a technical and scientific point of view.

Acknowledgments

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