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Strain-induced enhancement of the thermoelectric power in thin films of hole-doped La$_2$NiO$_{4+\delta}$

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We propose a novel route for optimizing the thermoelectric power of a polaronic conductor, independent of its electronic conductivity. This mechanism is exemplified here in thin-films of La$_2$NiO$_{4+\delta}$. Tensile stress induced by epitaxial growth on SrTiO$_3$ doubles the thermoelectric power of $\approx$15 nm thick films relative to $\approx$90 nm films, while the electronic conductivity remains practically unchanged. Epitaxial strain influences the statistical contribution to the high temperature thermopower, but introduces a smaller correction to the electronic conductivity. This mechanism provides a new way for optimizing the high temperature thermoelectric performance of polaronic conductors. © *2013 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License.* [http://dx.doi.org/10.1063/1.4818356]

I. INTRODUCTION

Lanthanum nickelate, La$_2$NiO$_4$, crystallizes in the 2D-K$_2$NiF$_4$ structure, in common with several cuprate high-temperature superconductors. The formally negative NiO$_2$ (3d^8) planes constitute the electronically active units, which can be hole-doped into the narrow $d(x^2\text{-}y^2)$ band by replacement of La^{3+} in the rock-salt layer with an A^{2+} ion.[1] However, in spite of the similarities with the cuprates, hole-doped La$_{2-x}$Sr$_x$NiO$_4$ never becomes a superconductor; instead it develops charge-ordered stripes of small polarons at large doping,[2] pointing to a stronger Coulomb repulsion in the Ni-O band compared to Cu–O.[3] In addition, La$_2$NiO$_4$ incorporates interstitial oxygen spontaneously to release the compressive stress of the Ni^{2+}–O bond. While strong correlations and the effective reduction of the bond-stress hamper the formation of multihole polarons as in the cuprates,[3,4] spectroscopic studies suggest that carriers in La$_2$NiO$_{4+\delta}$ are slightly above the small polaron limit.[5]

Recent *ab initio* calculations have found potential for La$_2$NiO$_{4+\delta}$ as a thermoelectric material.[6] Pardo *et al*.[6] suggested that the thermoelectric power factor (S^2/ρ) is optimized for La$_2$NiO$_{4.05}$, and suggested that this performance might be further enhanced by increasing the lattice parameter, via epitaxial strain in a film.[7] The range of oxygen content and lattice parameters suggested by these authors should be attainable, at least in their lower limit, via epitaxial growth on SrTiO$_3$ (STO). In spite of extensive literature about the effect of epitaxial stress on the physical properties of thin-films (structural, electronic, magnetic, etc.), its effect on the thermoelectric power has not been systematically investigated.[8]

Here we report the effect of tensile stress on the thermoelectric power and electrical resistivity of La$_2$NiO$_{4+\delta}$ thin films. Our results demonstrate that the thermoelectric power in the films can be manipulated by epitaxial stress, independently of the electrical resistivity. This effect can be understood by considering the role of tensile stress on the polaron size and its contribution to the entropy per added carrier.
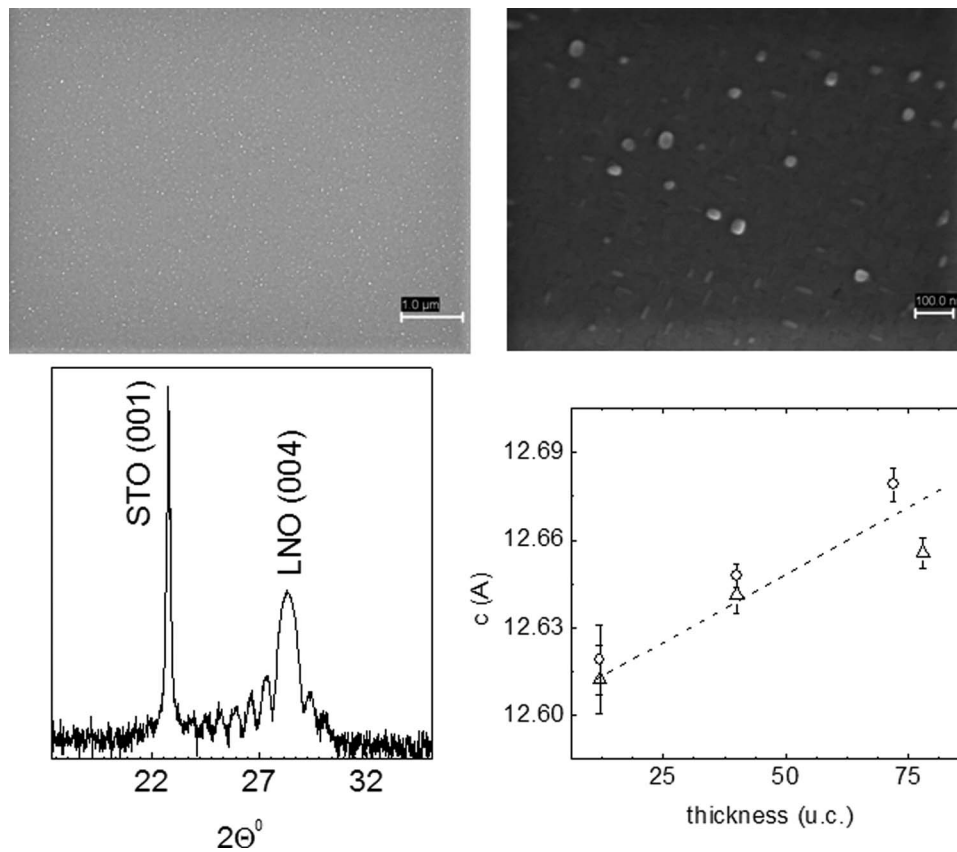
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FIG. 1. (Top) SEM picture of a 40 nm thick film grown at 200 mTorr O_2 at different magnifications. The size of the scale bars are 1 μm (left) and 100 nm (right). (Left, bottom) Detail of the x-ray pattern around the (004) peak of La_2NiO_4 for a film of 14 nm (from x-ray reflectivity). From the position of the Laue fringes, a thickness of 13.3 nm is estimated for this film. (Right, bottom) Dependence of the c axis (out of plane) parameter on the film thickness, for samples grown at 10 mTorr (triangles) and 200 mTorr (circles).

II. RESULTS AND DISCUSSION

In order to discuss a possible relationship between epitaxial strain and transport properties, two series of films of different thicknesses were grown either at 10 mTorr or 200 mTorr of oxygen (see the supplementary material[17]). A summary of the morphological and structural quality of the films is shown in Figures 1 and 2. Tetragonal *I4/mmm* La_2NiO_4 (bulk: a = b = 3.876 Å, c = 12.673 Å)[9] is grown epitaxially under tensile stress on (001)-oriented cubic $SrTiO_3$ (STO, a = 3.905 Å). The out-of-plane lattice parameter expands as a function of thickness (Figure 1), confirming the relaxation of the stress induced by epitaxial growth in the *ab*-plane (Figure 2).

The epitaxial growth of the La_2NiO_4 film has been confirmed by high resolution TEM. Figure 2(a) shows that the different layers of La_2NiO_4 are free of defects or stacking faults. Fourier transforms (Figures 2(b) and 2(c)) confirm crystalline growth in the *I4/mmm* structure along the [010] zone axis. The epitaxial analysis confirms that the ⟨001⟩ La_2NiO_4 crystalline direction is perpendicular to the initial surface of the STO substrate. Surprisingly, we have observed that this epitaxial relationship is only kept at low oxygen pressures; samples grown at 600 mTorr show a reorientation from a-domain (a axis perpendicular to the film surface) close to the substrate, to c-domain (c axis perpendicular to the film surface) (see the supplementary material[17]). A change in the growth direction (c-domain to a-domain) was previously reported[10] in thick films (several hundreds of nanometers), but we show here that it can happen also in thin films, as a function of oxygen pressure.
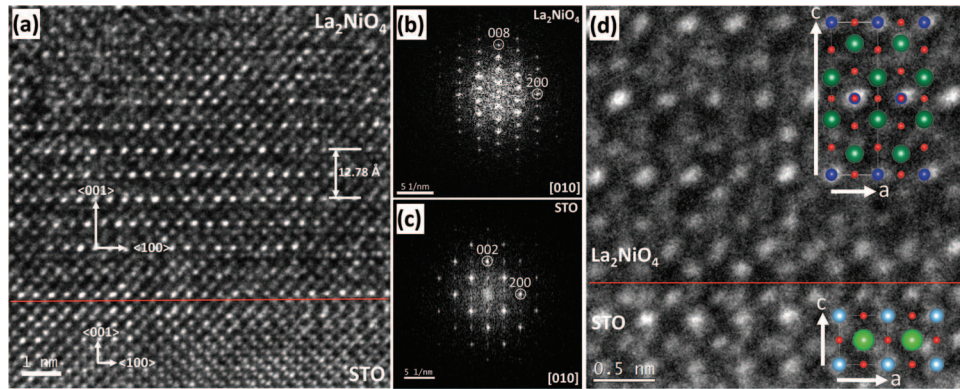
FIG. 2. (a) High resolution TEM image of a La_2NiO_4 film grown epitaxially over the STO. (b) and (c) Fourier transforms of the La_2NiO_4 film and STO substrate respectively, confirming the epitaxial growth (see text). (d) Close up view of the interface region, showing the c axis perpendicular to the STO surface.
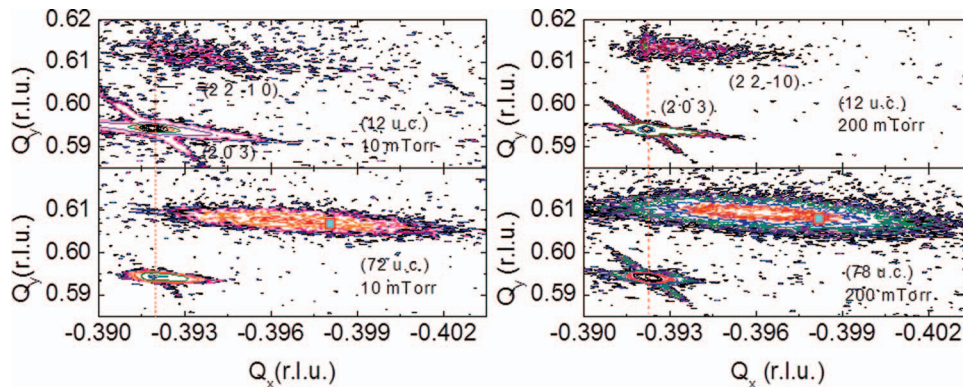

FIG. 3. High resolution RSM around the (2 2–10) reflection of $La_2NiO_{4+\delta}$ films grown at 10 mTorr (left) and 200 mTorr (right) oxygen pressure. Thinner films (top) are very much stretched by the substrate, while the thicker ones (bottom) are almost fully relaxed. The square in the bottom panels marks the lattice parameter for bulk $I4/mmm$ La_2NiO_4.

In order to study the effect of lattice strain and relaxation we have performed high-resolution x-ray reciprocal space maps (RSM) around the asymmetric (2 2 −10) reflection of $La_2NiO_{4+\delta}$, for different film thicknesses. The data in Figure 3 show that the in-plane lattice parameters are almost fully relaxed for the thicker films ($\approx$70–80 unit cells), while the thinner films are very stretched due to lattice mismatching with STO. In addition, there is a larger distribution of the in-plane and out of plane lattice parameter in the thicker samples synthesized at 200 mTorr (a = 3.88(2) Å), with respect to the analogous at 10 mTorr (a = 3.88(1) Å), which is most probably reflecting an inhomogeneous distribution of interstitial oxygen.

In order to corroborate whether interstitial oxygen produces an effective electronic doping, we have measured the electrical resistivity of the samples synthesized at different O_2 pressures. The results are shown in Figure 4. As expected, the resistivity shows temperature-activated behavior, with smaller values for the samples grown at the higher oxygen pressure due to hole-doping. However, we observe that tensile stress quantified by the RSM data of Figure 3 has a negligible effect in the electrical conductivity of the samples. Therefore, samples with different thickness grown at the same oxygen pressure show essentially the same resistivity.

The activation energy for the charge transport was estimated $\approx$83(3) meV, from the fitting to a conventional activated behavior ($\rho = \rho_0 \exp(\Delta E/k_B T)$; inset to Figure 4). This value is independent of the film thickness and oxygen content. The small value of the activation energy is in agreement with previous reports for bulk $La_2NiO_{4+\delta}$[11] and suggests that the conduction mechanism is dominated by in-gap states produced by interstitial (oxygen) dopants. Increasing the oxygen content increases
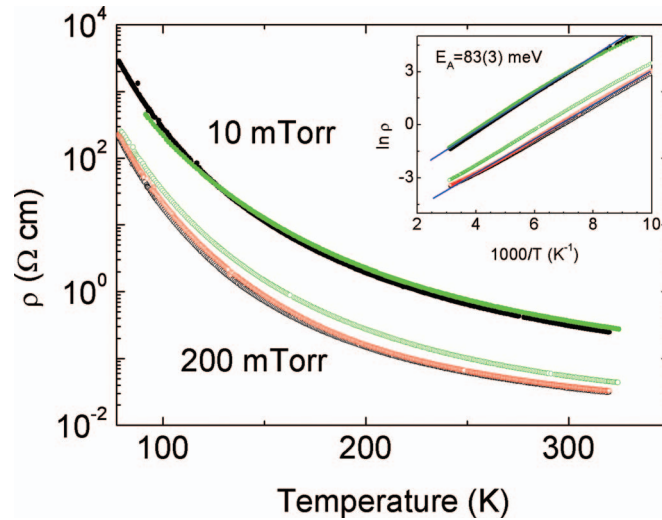
FIG. 4. Temperature dependence of the electrical resistivity for the series of samples grown at 10 mTorr and 200 mTorr of O_2. The resistivity decreases as the oxygen content increases, but is independent of tensile stress. (Inset) Fit of log resistivity to inverse temperature to calculate the activation energy. $E_A \approx 83(3)$ meV is constant, within the error, for all the samples measured.

the number of in-gap states and hence the number of charge carriers, consistent with the reduction in the electrical resistivity in spite of $\Delta E \approx$ constant.

Previous studies[4,5] in doped $La_{2-x}Sr_xNiO_4$ have shown that this material is a polaronic conductor, in which strong Coulomb correlations and release of compressive stress at the Ni^{2+}–O bonds determine the evolution of polaron size with doping. In a narrow band polaronic conductor, the temperature-independent limit for the thermoelectric power will be the dominant contribution at low-to-moderate temperatures. In this limit, the thermoelectric power is completely determined by the statistical distribution of polarons among the available lattice sites (the entropy per charge carrier).[12] Strong correlations, which will determine the size of the polarons, and therefore the ratio of carriers to sites for a fixed level of doping, will determine the high temperature value of the thermopower.

Consequently, controlling the tensile/compressive stress induced by epitaxial growth on a substrate could open a path to control, independently, the electrical conductivity and the thermoelectric power in polaronic materials.

The temperature dependence of the thermopower is shown in Figure 5. Measurements below 200 K became noisy due to the rapid increase of the electrical resistance, which limits our measurement capabilities. In any case, we have a wide range of more than 150 K to study the evolution of the thermopower of all samples. The samples show positive thermopower, suggesting that the main carriers are holes, as expected in this system. The thermopower decreases with increased oxygen content, which is consistent with hole doping. At both oxygen concentrations, the thermopower is largest in the thinnest (most highly stressed films) and then decreases in the thicker films as their lattice parameters relax toward the bulk value. Therefore, considering that $S(T)$ for the thicker (almost relaxed) films must be very close to the intrinsic value, we estimate the films grown at 10 mTorr to be close to $\delta \approx 0.07$ and 200 mTorr, $\delta \approx 0.15$, by comparison with bulk $La_2NiO_{4+\delta}$.[13] A more accurate determination through Hall effect measurement was impossible due to the very low carrier mobility. Moreover in polaronic conductors, Hall resistance is not directly related to the actual carrier concentration.[14]

The results demonstrate that the thermoelectric power of $La_2NiO_{4+\delta}$ films is sensitive to both oxygen content and lattice strain. The decrease of $S(T)$ with oxygen is expected due to the increase in the number of charge carriers, but the observed dependence on tensile stress is surprising given the negligible effect on the resistivity. This effect of stress is actually very large, the thermopower of the thinner samples increasing by more than 100% with respect to the thicker ones.
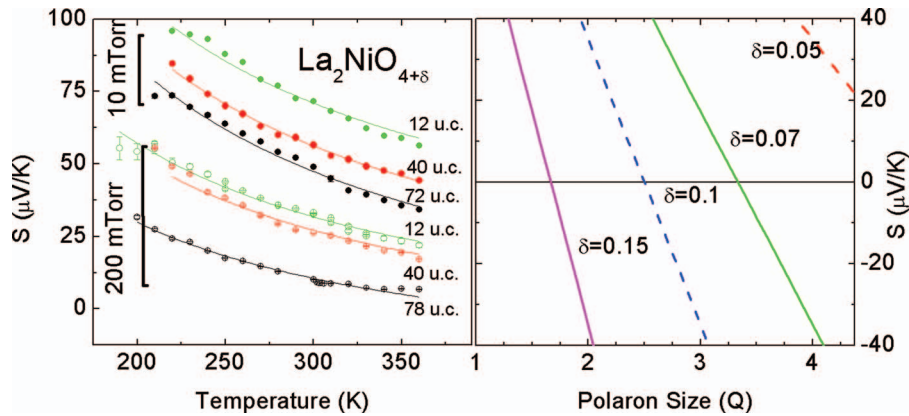
FIG. 5. (Left) Temperature dependence of the thermoelectric power for the samples grown at 10 mTorr (closed symbols) and 200 mTorr (open symbols) of O_2. Lines are fittings to Eq. (1). (Right) Polaron-size dependence of the high-temperature limit of the thermoelectric power (Eq. (2)) for different dopings. Solid lines correspond to the most probable level of oxygen in our samples.

The dependence of the thermopower for different film thicknesses is qualitatively consistent with the predictions by Pardo *et al.*[7] However, the temperature dependence of the thermopower calculated by these authors shows a positive slope, typical of metallic conductors. Therefore, their proposed mechanism will probably lead to the same strain dependence in the electronic conductivity. Hence, the activated behavior observed experimentally in the resistivity and $S(T)$ suggests an alternative explanation for the strain dependence of the thermopower.

Indeed, the curves of $S(T)$ for different samples are fairly parallel to each other, a behavior that is qualitatively consistent with a constant activation energy plus a sample dependent, temperature independent term. The thermopower of a thermally activated polaronic system is expected to be described by

$$S = -\frac{k_B}{|e|}\left(\frac{\Delta E}{T}\right) + S_\infty, \tag{1}$$

$$S_\infty = \frac{k_B}{e}\ln\left(\frac{1 - Qx}{Qx}\right), \tag{2}$$

where ΔE, x, and Q are the activation energy, concentration, and size of the polarons, respectively.[12] Note that a parameter like Q does not appear explicitly in the original formulation discussed in Ref. 12. However, given that the most important contribution to the thermopower at this temperature comes from the degeneracy of the system, the ratio of particles to sites must be explicitly considered in this equation (see the supplementary material[17]).

We have fitted the experimental data to Eq. (1), and the best results show that the activation energy is constant for each series of samples ($\approx$15 meV for 10 mTorr; and $\approx$25 meV for 200 mTorr), while $|S_\infty|$ decreases from sample to sample as thickness does (tensile stress increases). The difference between these activation energies derived from the thermopower and those from electrical resistivity (83 meV) is a signature of small polaron conduction.[15]

The dependence of S_∞ on Q, calculated from Eq. (2) is shown in the right panel of Figure 5 for different levels of doping in $La_2NiO_{4+\delta}$. In the negative part of S_∞ (corresponding to light doping, i.e., $Qx < 0.5$) and for a fixed doping level, a slight increase in the polaron size Q increases $|S_\infty|$. Therefore, if we accept the most probable oxygen content in our samples to be δ = 0.07 (for the 100 mTorr series) and δ = 0.15 (200 mTorr), a polaron size in the range $\approx$1.8 (200 mTorr) to $\approx$3.3 (10 mTorr) lattice sites explains the experimental thermopower of $La_2NiO_{4+\delta}$. These values are consistent with spectroscopic observations of carriers above the small polaron limit in this material.[5] Therefore, although the actual polaron sizes obtained from these fitting are approximate, the continuous decrease of $|S_\infty|$ with the decrease in film thickness in both series of

samples shows a clear trend of a decreasing polaron size as tensile stress increases. Note also that a very small change in the polaron size produces a large change in the Seebeck coefficient.

In bulk $La_{2-x}Sr_xNiO_{4+\delta}$ the ratio c/a increases with δ.[16] In thin-films, this effect is dominated by tensile stress: as shown in Figures 1 and 3, c/a decreases in the thinner films. This will shrink the $d(x^2-y^2)$ band, increasing the Coulomb repulsion and localizing the polarons in the *ab*-plane. Although polaron localization should also have a contribution to the resistivity, this effect is expected to be negligible in this temperature range in a narrow band polaronic conductor.

On the other hand, we have confirmed the reduction of the thermopower in samples grown under compressive stress on $LaAlO_3$ (LAO) with respect to identical samples grown on STO (see the supplementary material[17]).

Finally, in order to verify whether this is a general phenomenon in polaronic conductors, we studied the effect of strain in thin films of $La_{1/2}Ca_{1/2}MnO_3$ (details in the supplementary material[17]). Bulk $La_{1/2}Ca_{1/2}MnO_3$ shows a thermopower already flat at room temperature, so the effect of tensile stress according to Eq. (2) can be better verified. Films 35 nm thick indeed show a constant S(T) above $\approx$225 K, similar to the bulk, while strained films of $\approx$5 nm, show a substantial reduction of $|S$(T)$|$, consistent with a reduction of the polaron size. The resistivity remains unchanged in this thickness range (see the supplementary material[17]).

III. CONCLUSIONS

We have shown that the statistical contribution to the thermopower, which is dominant at moderate temperatures in polaronic conductors, can be influenced by lattice stress in epitaxial films of $La_2NiO_{4+\delta}$. This term does not contribute directly to the electronic conductivity, and hence could be used as a channel to tune independently these two magnitudes. We have shown this effect to be common to other polaronic materials, and hence could be a useful strategy for optimizing their thermoelectric performance.

ACKNOWLEDGMENTS

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[17] See supplementary material at http://dx.doi.org/10.1063/1.4818356 for details of the fabrication, resistivity as well as the resistivity and thermoelectric power of $La_{1/2}Ca_{1/2}MnO_3$ thin films.