Correlation of O (1s) and Fe (2p) near edge x-ray absorption fine structure spectra and electrical conductivity of $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{0.75}\text{Ni}_{0.25}\text{O}_{3-\delta}$

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A-site substitution of La^{3+} by Sr^{2+} in polaron conducting ABO_3 -type perovskite $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{0.75}\text{Ni}_{0.25}\text{O}_{3-\delta}$ causes oxidation of Fe^{3+} toward Fe^{4+} and formation of conducting electron holes, as evidenced by Fe (2p) and O (1s) near edge x-ray absorption fine structure spectra. Hole doping is reflected by linear variation of the prepeak ratio $e_g(\uparrow)/[t_{2g}(\downarrow) + e_g(\downarrow)]$ of oxygen spectra, along with increased conductivity. The significant increase in conductivity due to NiO doping in $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$ is caused by increased overlap between Fe (3d) and O (2p) and charge transfer from the O (2p) to the Ni (3d) states, as concluded from near edge x-ray absorption fine structure spectra and ligand field multiplet calculations. © 2009 American Institute of Physics.

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Battery and solid oxide fuel cell (SOFC) cathodes are typically based on transition metal (TM) oxides, often with noninteger average metal oxidation states. Adding large rare earth cations to the TM oxides facilitates phases with metal insulator transitions, charge ordering, superconductivity, or colossal magnetoresistance. These TM have a high oxidation state and their ground state is dominated by O (2p) band holes, and not by the metal 3d electrons.¹

This work is about $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{0.75}\text{Ni}_{0.25}\text{O}_{3-\delta}$ (LSFN), an ABO_3 perovskite. The iron in the parent compound LaFeO_3 is in the high spin (HS), trivalent insulating oxidation state ($3d^5$), making it a charge transfer insulator.²

Substitution of the A-site La^{3+} by Sr^{2+} causes oxidation of Fe toward Fe^{4+} with $3d^5\bar{L}$ state, $\bar{L}$ denoting an electron ligand hole.³ The temperature (T) dependence of the electric conductivity $\sigma(T)$ in this class of materials follows often an exponential and is known as polaron activated conductivity.⁴

The maximum conductivity of LaSrFe -oxide (LSF) is around 500 °C, a temperature range relevant for intermediate temperature SOFC. $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_3$ has the highest conductivity in the LSF series, but substituting B-site with nickel increases $\sigma(T)$ significantly to around 700 S/cm.⁵ Similar holds for Sr_3FeMO_7 ($M=\text{Fe}, \text{Co}, \text{Ni}$), where $\sigma(T)$ increases from Fe to Ni,⁶ while the p - d transfer integral decreases.

X-ray spectroscopy has contributed to the understanding of hole doping by A-site substitution in LSF.⁷ In analogy to A-site substitution in LaFeO_3 ,⁸ substitution of Sr creates new features in the oxygen near edge x-ray absorption fine structure (NEXAFS) spectra, along with increasing $\sigma(T)$.

We extend the previous studies toward LSFN and rationalize the quantitative correlation of conductivity and electronic structure, as obtained by x-ray spectroscopy and supported with ligand field multiplet calculation (LFMC), in terms of d -type and p -type holes formed by Sr doping.

Polycrystalline LSFN with $x=0.0, 0.25, 0.50, 0.75$, and 1.0 were prepared by solid state reaction of La_2O_3 (>99.99%), SrCO_3 (99.9%), Fe_2O_3 (>99.0%), and NiO (99.8%) in stoichiometric proportions, calcined at 1200 °C for 4 h and sintered at 1400 °C for 12 h (5 K/min). The oxygen deficiency δ was obtained by thermogravimetry. X-ray powder diffractograms (XRD) were collected with a Philips X'Pert diffractometer (40 kV, 40 mA, $\text{Cu } K\alpha$ radiation) at 300 K in steps of 0.02° for $20^\circ \leq 2\theta \leq 80^\circ$. The 4-point dc conductivity of sintered slabs (size $\sim 5 \times 3 \times 25 \text{ mm}^3$) was measured for $300 \text{ K} < T < 1300 \text{ K}$ in air during cooling (2 K/min). NEXAFS spectra at 300 K were recorded with total electron yield at Beamline 9.3.2, Advanced Light Source, in Berkeley (photon energy range 200–1200 eV, energy resolution up to 1/10 000). The vacuum chamber base pressure was below 5×10^{-10} Torr. Powder samples were dispersed on conducting carbon tape and then mounted on a copper sample holder. Iron L -edge and oxygen spectra were recorded in steps of 0.1 eV from 690 to 750 eV and 520 to 560 eV, respectively.

Rietveld refinement of the XRD showed orthorhombic phase for $x=0$, and for $x=1$ cubic phases with two different cell parameters, as justified by the distinct splitting of reflections. The other samples are rhombohedral with minor amount of a tetragonal phase.

In general, LSF conductivity $\sigma(T)$ increases to a maximum upon annealing and then decreases. The effect of T on σ for LSF has been explained in terms of small-polaron hopping and follows an exponential $\sigma T \sim \exp(E_p/kT)$ with activation energy E_p and Boltzmann constant k .⁹ Analysis

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FIG. 1. (Color online) Conductivity of $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{0.75}\text{Ni}_{0.25}\text{O}_{3-\delta}$. E_p is calculated for low temperature region (305–465 K).

of the Arrhenius plots for $300\text{ K} < T < 1273\text{ K}$ (Fig. 1) shows that LSFN with $x=0$ ($x=0.5$) has the lowest (highest) conductivity and highest (lowest) E_p . The trend that LSF with $x=0.5$ have highest conductivity is thus maintained in LSFN. Upon further substitution, $\sigma(T)$ increases and E_p decreases. The fact that LSFN has generally a higher conductivity than LSF has motivated us to study this system. LSF samples with $x=0.50$ have highest conductivity (352 S/cm at 823 K). The maximum conductivity of $\text{La}_{0.5}\text{Sr}_{0.5}\text{Fe}_{0.8}\text{Ni}_{0.2}\text{O}_3$ ($\text{La}_{0.5}\text{Sr}_{0.5}\text{Fe}_{0.4}\text{Ni}_{0.6}\text{O}_3$) is around 700 S/cm (350 S/cm).⁵ Our sample $\text{La}_{0.5}\text{Sr}_{0.5}\text{Fe}_{0.75}\text{Ni}_{0.25}\text{O}_{3-\delta}$ has 678 S/cm. This maximum apparently decreases at doping levels from 20% to 60%. Our sample with $x=1.0$ was very brittle and could not be subjected to conductivity measurements.

The area normalized Fe $L_{2,3}$ edge spectra of LSFN in Fig. 2 show the spin-orbit split L_3 and L_2 edges of the Fe 2p core hole.⁸ Each edge is additionally split by multiplet effects and crystal field splitting. The spectrum for $x=0$ has the overall sharpest features, i.e. a set of reasonably well separated $2p_{3/2} t_{2g}$ and e_g resonances. Comparison with literature⁸ suggests and simulation by LFMC confirms—that for $x=0$ Fe is in $\text{Fe}^{3+} 3d^5$ high spin state—in similarity to LaFeO_3 . LFMC was made assuming octahedral symmetry with Slater

FIG. 2. (Color online) Experimental and simulated spectra of Fe $L_{2,3}$ edge.

TABLE I. Oxygen nonstoichiometry δ and valency for Fe, τ and spectral ratio S in LSFN. The τ calculation is based on valency of $3+$ for Ni.

x	δ	Ox Fe for $\delta=0$	Ox Fe for $\delta=\text{exp}$	Ox Fe from simulation	τ for $\delta=0$	τ for $\delta=\text{exp}$	S
0	0.000	3.00	3.00	3.00	0.00	0.00	1/4
1/4	0.035	3.33	3.24	3.25	0.33	0.24	1/3
1/2	0.053	3.67	3.53	3.50	0.67	0.53	1/2
3/4	0.069	4.00	3.82	3.95	1.00	0.82	3/4

integrals scaled down to 50% of their atomic values in order to mimic covalency effects. With increased Sr doping, the spectra lose their discrete features. The differences in the electronic structure of LaFeO_3 and $\text{LaFe}_{0.75}\text{Ni}_{0.25}\text{O}_3$ are reduced Slater integrals and crystal field splitting. Our sample has stronger Slater integral reduction, indicating that the Fe 3d orbital becomes broader, decreasing $d-d$ and $p-d$ interactions. Fe is substituted by Ni, the $M-O$ (M indicates metal) distance is reduced causing an increase in the O 2p bandwidth. Thus, the $p-d$ bandgap decreases and consequently σ increases.¹⁰ Therefore, $\text{LaFe}_{0.75}\text{Ni}_{0.25}\text{O}_3$ is a semiconductor whereas LaFeO_3 is an insulator at RT, despite their similar electronic configuration.

Comparison between experiment and simulation (Fig. 2) shows that LSFN with $x=0.25$ and $x=0.5$ have the percentage of Fe^{4+} as expected from stoichiometry. However, LSFN with $x=0.75$ shows larger amount of Fe^{4+} (95%) than suggested by stoichiometry. Fe is in all samples in HS with crystal field $10Dq=1.85\text{ eV}$ and with Slater integral reduced to 50%. We thus conclude that increasing Sr content changes the valency of Fe and Ni, but no other electronic structure parameters. The valency of Fe, which is calculated assuming that Ni is Ni^{3+} and corrected by the experimental δ , are quite close to that obtained by LFMC, except for high Sr doping level ($x=0.75$), Table I.

The spectra in Fig. 3 represent the unoccupied O 2p orbitals and reflect the empty Fe/Ni 3d bands at the pre-edge (524–527 eV). The triplet at around 525 eV is attributed to $e_g(\uparrow)$, $t_{2g}(\downarrow)$, and $e_g(\downarrow)$ bands.¹¹ The intensity of the $e_g(\uparrow)$ peak is due to doped holes, increases upon Sr doping,⁸ and shifts slightly to the Fermi level (E_F) depending on the hole/Sr doping concentration. Interestingly, this shift is larg-

FIG. 3. (Color online) Normalized oxygen K edge x-ray absorption spectra of $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{0.75}\text{Ni}_{0.25}\text{O}_{3-\delta}$.

FIG. 4. (Color online) Comparison of d -type hole with conductivity (left), and with S ratio.

est for $x=0.50$, which has maximum σ . The hole concentration τ relates to the stoichiometry as follows.¹² $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{1-\tau}\text{Fe}^{4+}_\tau\text{O}_{3-\delta}$. We illustrate the evolution of τ as a function of the A -site substitution, and begin with $x=0$ and the simplified assumption that $\delta=0$, Ni is Ni^{3+} and La and Sr retain their formal valences as La^{3+} and Sr^{2+} . The formal charge of the iron is thus Fe^{3+} and $\tau=[\text{Fe}^{4+}]=0$. The values corrected for the experimental δ are listed in Table I. We have recently shown¹¹ that the ratio S of spin up to spin down peaks of the upper Hubbard band in O NEXAFS spectra (pre-edge peaks) correlates with the conductivity in A - and B -site substituted LSF. We exercise this for the O spectra of our samples and find that the ratio S is not for all samples close to simple rational numbers (Table I). We thus conclude that the p -projected electrons do not only go to Fe $3d$ but also to Ni $3d$ states. The evolution of S which is linear in the substitution parameter x , and the relative Fe hole density τ are shown in Fig. 4. When La^{3+} is substituted by Sr^{2+} , one hole is created. The hole concentration τ $[\text{Fe}^{4+}/(\text{Fe}^{3+} + \text{Fe}^{4+})]$, of LSFN increases with increasing Sr content, Fig. 4. σ and τ increase upon Sr doping up to 50%. In the high doping region, σ decreases while τ increases. The mobility of free electrons increases with increasing Sr content in the low doping region: Coulomb repulsion by La^{3+} around oxygen in the superexchange unit ($\text{Fe}^{4+}-\text{O}^{2-}-\text{Fe}^{3+}$) is stronger than the barrier by Sr^{2+} . In the high Sr doping region, the oxygen vacancy concentration increases along the migration pathway.¹³ Therefore, an electron needs higher energy to hop across ($\text{Fe}^{3+}-\text{O}^{2-}-\text{Fe}^{4+}$), which results in decreased mobility and consequently in a decrease of σ . This conclusion is supported by the increasing activation energy, $E_p=72$ meV for $x=0.75$ whereas $E_p=39$ meV for $x=0.50$. The interaction of $\text{Fe}^{3+}-\text{O}-\text{Fe}^{3+}$ is antiferromagnetic whereas that of $\text{Fe}^{3+}-\text{O}-\text{Fe}^{4+}$ is ferromagnetic.¹⁴ Once Fe^{3+} is oxidized to Fe^{4+} , the number of unpaired electrons decreases and the antiferromagnetic structure is lifted in favor of ferromagnetic interaction.

We compare the p -type and d -type hole concentration depending on the Sr content (Fig. 4). P -type holes are created on the O site by transition of electrons from O ($2p$) to Fe $3d$ or Ni $3d$, which scale with the ratio S . Since there are two different B -site species, Fe and Ni, assessing the p -type hole concentration will not allow to conclude on whether electrons go to Fe $3d$ or Ni $3d$ orbitals. The Fe spectra basically show us Fe d -type hole concentration. Unfortunately, we cannot do so for the Ni because the Ni and

La edges coincide. We begin with $\text{LaFe}_{0.75}\text{Ni}_{0.25}\text{O}_3$, which has Fe in $3d^5$ configuration and not in $3d^5\text{L}$, suggesting there is no charge transfer from O to Fe. We anticipate hence no contribution from Fe to the O $e_g(\uparrow)$ peak for the hole, i.e. $S=0$. However, the S -ratio in fact is $S=0.25$. We conclude that this charge transfer must have occurred from O $2p$ to Ni $3d$. It is known that $\text{Fe}(\epsilon_d - \epsilon_p) > \text{Ni}(\epsilon_d - \epsilon_p)$, where ϵ_d and ϵ_p are the energy of $3d$ and $2p$ states of Fe/Ni and oxygen, respectively.¹⁵ As is shown in Fig. 4 (right), increasing the Sr content increases the Fe oxidation state and the S -ratio. When the p -electrons go to Fe $3d$ orbitals, Fe should become reduced. Therefore, we can also conclude for the Sr doped samples that the charge transfer occurs predominantly between oxygen $2p$ and Ni $3d$. In LSFN we showed that increasing the Sr content increases the number of d -type $[\text{Fe}^{4+}/(\text{Fe}^{4+} + \text{Fe}^{3+})]$ and p -type holes $\{[e_g(\uparrow)/t_{2g}(\downarrow) + e_g(\downarrow)]\}$.¹¹ We conclude that charge transfer occurred mostly from O to Ni, and not to Fe. The conductivity which has contributions from d - and p -holes increases up to 50% of Sr doping. At low Sr doping level, we find that the Fe^{4+} concentration determined by LPMC is similar to the Sr concentration. At high Sr doping, the conductivity decreases while the d - and the p -type hole concentration increase, and this because of the vacancies created along the migration pathway. Increasing the Sr content increases the Fe^{4+} concentration, but does not affect crystal field ($10Dq=1.85$ eV) and the Fe spin state.

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