Iron-resonant valence band photoemission and oxygen near edge x-ray absorption fine structure study on La$_{1-x}$Sr$_x$Fe$_{0.75}$Ni$_{0.25}$O$_{3-\delta}$

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Iron resonant valence band photoemission spectra (VB PES) of Sr substituted LaFe$_{0.75}$Ni$_{0.25}$O$_{3-\delta}$ have been recorded across the Fe 2p-3d absorption threshold to obtain Fe specific spectral information on the 3d projected partial density of states. Comparison with La$_{1-x}$Sr$_x$FeO$_3$ resonant VB PES literature data suggests that substitution of Fe by Ni forms electron holes which have mainly O 2p character. Substitution of La by Sr increases the hole concentration to an extent that the e$_g$ structure vanishes. The variation in the e$_g$ and t$_{2g}$ structures is paralleled by the changes in the electrical conductivity. © 2010 American Institute of Physics. [doi:10.1063/1.3484960]

The electronic structure of defect regulated materials is important for understanding their functional relationship such as transport properties. The electrical conductivity of oxides with perovskite structure depends on their valence band (VB) characteristic.1 La$_{1-x}$Sr$_x$FeO$_3$ (LSFO) is a parent compound that can be used in solid oxide fuel cell cathodes,2 and the conductivity particularly at high temperature is an important quantity for its functionality as a cathode. Sr substitution of LaFeO$_3$, which is an insulator, forms electron holes which are associated with nominally tetravalent Fe having the electronic structure of 3d$^2$L, L denoting the electron hole from the oxygen. Substitution by 50% (Fe$^{3+}$/Fe$^{4+}$=1/1) warrants that the electron hopping across the Fe$^{3+}$–O–Fe$^{4+}$ superexchange unit occurs with maximum probability. It has been shown that Fe substitution of La$_{1-x}$Sr$_x$FeO$_3$ on the B-site by Ni (Ref. 3) or Co improves the conductivity, with a conductivity maximum at temperatures around 650–750 K, making them attractive for intermediate temperature proton conducting ceramic fuels.3 The structural and transport properties of La$_{1-x}$Sr$_x$Fe$_{1-y}$Ni$_y$O$_3$, have been studied for different stoichiometries (x, y). It has also been explained how the electronic structure evolves from charge transfer type insulator LaFeO$_3$ (2 eV band gap) to the “oxygen-hole metal” SrFeO$_3$ (Ref. 8) using in situ photoemission spectroscopy (PES) on thin films. Out of the rare-earth nickel oxides, LaNiO$_3$ is the only metallic member.9 Chainani et al.10 showed a systematic x-ray photoemission study on bulk LSFO. However, the influences of Ni and Sr substitution on electronic structure, especially for occupied states of Fe, are still not clear.

We employ Fe resonant VB PES to investigate the influence of the Ni-substitution and Sr-substitution with respect to the Fe, which is the main player for the electrical conductivity via the Fe$^{3+}$–O–Fe$^{4+}$ superexchange unit.

The A-site substitution of LaFeO$_3$ by Sr (La$_{1-x}$Sr$_x$FeO$_3$) and its impact on the electronic conductivity is well understood. In the oxygen near edge x-ray absorption fine structure (NEXAFS) spectra this substitution manifests in a so-called hole doping state with e$_g$ symmetry as the leading peak in the O 1s pre-edge, preceding the two t$_{2g}$ and e$_g$ orbital symmetry peaks from the hybridized O 2p–Fe 3d states. Interestingly, B-site substitution with Ni, too, shows such extra peak. The question naturally arises as to which role Fe and Ni play for the corresponding spectra.

High purity precursors (La$_2$O$_3$>99.99%, SrCO$_3$, 99.9% Fe$_2$O$_3$>99.0%, and NiO 99.8%, purities given in weight %) were mixed in stoichiometric proportions, ball milled for 24 h, calcined for 4 h at 1473 K and for 12 h at 1673 K so as to obtain La$_{1-x}$Sr$_x$Fe$_{0.75}$Ni$_{0.25}$O$_{3-\delta}$ (LSFN) with x=0, 0.50, 0.75.11 X-ray powder diffractionograms confirmed that the samples had rhombohedral symmetry (space group: R$\bar{3}$c, space group number: 167), with a barely noticeable contamination of a tetragonal phase.12 The four-point dc conductivity shows the same trend like in Ref. 11. For VB PES measurements the fine powders were uni-axially pressed into disks (~$\phi$ 13 mm) at 40 KN and then sintered at 1673 K for 12 h. Photoemission spectra were recorded at end station at beamline 9.3.2 of the Advanced Light Source, Lawrence Berkeley National Laboratory. The energy resolution of the beamline is E/ΔE=3000.14 The spectra were recorded in the maximum transmission mode. During measurements the base pressure of the main chamber was maintained at 10$^{-9}$ Torr. The resonant VB PES spectra for Fe metal were measured using photon energies between 704 and 716 eV, leading up to the 2p/3s resonance energies. NEXAFS spectra were measured at beamline 8.0.1 in total electron yield mode at 300 K.

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Upon substitution of Sr by 50% and by 75%, this we, therefore, conclude that substitution of Fe shows the normalized Fe L\(_{\text{2}}\) edge. Visual inspection of the two spectra suggests that the transitions that arise from states with electronic configurations corresponding to the one known for La\(_{1-x}\)Sr\(_{x}\)FeO\(_{3-\delta}\) samples studied here are polycrystalline sintered bodies with a finite porosity. Such samples have a larger surface-to-volume ratio than single crystals. It is known that La\(_{1-x}\)Sr\(_{x}\)FeO\(_{3-\delta}\) has a larger surface-to-volume ratio than single crystals. It is known that La\(_{1-x}\)Sr\(_{x}\)FeO\(_{3-\delta}\) surfaces are slightly understoichiometric and oxygen deficient, thus providing the iron atoms near the surface a less than sixfold octahedral coordination. This may be a reason why the VB structures near EF, particularly the t\(_{2g}\) and e\(_{g}\) structures are less pronounced in our sintered polycrystalline samples than those in single crystals.

A comparison of the VB PES spectra for La\(_{1-x}\)Sr\(_{x}\)FeO\(_{3-\delta}\) and La\(_{1-x}\)Sr\(_{x}\)FeO\(_{3-\delta}\) shows that the e\(_{g}\) peak (A) is virtually absent in La\(_{1-x}\)Sr\(_{x}\)FeO\(_{3-\delta}\). Upon substitution of Sr by 50% and by 75%, this e\(_{g}\) (A) structure is not noticeable anymore. The next observation is that the energy position of the t\(_{2g}\) (B) structure seems to move towards higher binding energy, i.e., from 3.5 eV for x=0 to just below 4.0 eV for x=0.5, and also for x =0.75. This is in contrast to observations made on La\(_{1-x}\)Sr\(_{x}\)FeO\(_{3-\delta}\). It appears also that the relative intensity of the t\(_{2g}\) peak decreases as x is increasing. Thus, the general picture is that spectral intensity moves away from the Fermi energy E\(_{\text{F}}\) with increasing substitution parameter x, as it is particularly evidenced for the peaks due to transitions from states with the e\(_{g}\) and t\(_{2g}\) orbital symmetry. For La\(_{1-x}\)Sr\(_{x}\)FeO\(_{3-\delta}\), the intensity decrease in the e\(_{g}\) (A) structure upon Sr substitution was rationalized by transfer of doped electron holes towards the Fe e\(_{g}\) band. Since states with an e\(_{g}\) orbital symmetry correspond to Fe in octahedral coordination with the oxygen ions, the diminishing of the e\(_{g}\) state can be interpreted as a deviation of crystal field effect in octahedral coordination: the crystal field effect increases from 1.80 eV to 1.85 eV by substituting Fe with Ni. We, therefore, conclude that substitution of Fe by Ni, too, leads to formation of electron holes, which move to the Fe e\(_{g}\) bands, and therefore, Ni substitution has the similar effect on the depletion of the e\(_{g}\) structure like Sr-substitution. In addition, as evidenced in our spectra, the established trend that substitution of La by Sr increases the doped hole concentration in La\(_{1-x}\)Sr\(_{x}\)FeO\(_{3-\delta}\) is also recovered in our LSFN samples: The hole states formed upon Sr substitution was rationalized by transfer of doped electron holes towards the Fe e\(_{g}\) band.
how the Ni interacts in relation to the Fe with oxygen is not yet clear. Quite interestingly, we notice that the $e_g$ intensity for $x=0.75$ in the VB PES is a little yet noticeable larger than that for $x=0.50$. The same holds for the larger extent for the $t_{2g}$ intensity, corroborating how the electrical conductivity depends systematically on the VB PES intensity.

We have performed resonant VB PES, and NEXAFS at the O K edge and Fe $L_2,3$ edges on $La_{1-x}Sr_{x}FeO_{3-d}$ ($x=0.0, 0.5, \text{and} 0.75$). The spectral weight of occupied $e_g$ and $t_{2g}$ states of Fe is reduced upon electron hole doping up to 50% and then starts to increase which is parallel to changes in electrical conductivity. The spectral weight of the prepeak in the oxygen NEXAFS spectra due to the p-type electron holes created on Ni 3$d$ increases with increasing $x$. With respect to $La_{1-x}Sr_{x}FeO_3$, it is observed that the spectral weight transfers from below $E_F$ to above it across the gap. However, in $La_{1-x}Sr_{x}FeO_{3-d}$ it is difficult to conclude this since the Ni 3$d$ states are located closer to $E_F$ than those of the Fe 3$d$ and we do not consider any metal-metal (Fe-Ni and/or Ni-Fe) electron hole transfer.

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substitution in $La_{1-x}Sr_{x}FeO_{3-d}$ and LSFN deplete the $e_g$ states. This suggestion finds further confirmation when looking at the oxygen NEXAFS spectra of $La_{1-x}Sr_{x}Fe_{0.75}Ni_{0.25}O_3$ for $x=0$ and 0.5, as shown in Fig. 3. $La_{1-x}Sr_{x}FeO_{3-d}$ has an $e_g$ spin up orbital symmetry state from doped holes, and a $t_{2g}$ and $e_g$ spin down doublet from hybridized O 2$p$–Fe 3$d$ states as the O 1$s$ NEXAFS pre-edge structure. The intensities of the $e_g$ states in $La_{1-x}Sr_{x}FeO_{3-d}$ scale roughly with the Sr content. 15

Due to the exponential dependence between the relative spectral intensity ratio $e_g\uparrow/(t_{2g}\uparrow+e_g\downarrow)$ and the conductivity was found, 16 it is possible to investigate the transport property of this type material through their pre-edge structures. $La_{1-x}Sr_{x}Fe_{0.75}Ni_{0.25}O_3$ with $x=0$ has a small such leading $e_g\uparrow$ peak, which supports the aforementioned suggestion that Ni substitution has the same effect like hole doping. It has recently been shown that increasing Ni concentration in $LaFe_{1-x}NiO_3$ increases the intensity of prepeak and also shifts it towards $E_F$. 17 The intensity of the corresponding $e_g$ spin up peak in $La_{1-x}Sr_{x}Fe_{0.75}Ni_{0.25}O_3$ for $x=0.50$ is much higher than the intensity of that for $x=0$, i.e., by a factor of six. In addition we do notice a small shift in the $e_g$ spin up peak energy position toward $E_F$ upon hole doping. We have recently shown that, since the Ni 3$d$ states are closer to $E_F$ than the Fe 3$d$ states, the doped holes go predominantly to Ni. 11 The changes in the electronic structure of the $La_{1-x}Sr_{x}Fe_{0.75}Ni_{0.25}O_3$ upon Sr substitution are qualitatively reflected by the electrical conductivity, as shown in ref. 11. The well known conductivity maximum of $La_{1-x}Sr_{x}FeO_{3-d}$ at $x=0.50$ is also observed for $La_{1-x}Sr_{x}Fe_{0.75}Ni_{0.25}O_{3-d}$ for the same $x$; this is also corroborated by the $e_g\uparrow$ peak intensity in the oxygen NEXAFS spectra for $x=0$ and 0.50, see Fig. 3.

The influence of the Ni-when to 25% substituting the Fe in $La_{1-x}Sr_{x}FeO_{3-d}$ on the conductivity and on the electronic structure appears clear now. However, the mechanism of

FIG. 3. (Color) Normalized O K edge x-ray absorption spectra of $La_{1-x}Sr_{x}Fe_{0.75}Ni_{0.25}O_3$ for $x=0$, and $x=0.50$ with suggested peak decomposition into Voigt functions. Arrow in top panel spectrum shows the difference between $e_g\uparrow$ peak intensity and normalization level (dashed horizontal line). Spectrum in bottom panel has additional peak at $\sim 528 \text{ eV}$.

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