Electronic Structure of Nd$_{1-x}$Sr$_x$FeO$_3$ Probed by Soft-X-Ray Spectroscopy

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The electronic structure of Nd$_{1-x}$Sr$_x$FeO$_3$ ($x=0$, 0.1 and 0.4) has been studied by soft-X-ray spectroscopy. The Nd$_{1-x}$Sr$_x$FeO$_3$ has the mixed valence states of Fe$^{3+}$ and Fe$^{2+}$. The intensity of hole-induced state at the bottom of the conduction band increases with increasing Sr concentration. This result indicates that the lattice constant of $a$-axis increases and those of $b$- and $c$-axes decrease with Sr concentration.

1 Introduction
Sr-doped NdFeO$_3$ (Nd$_{1-x}$Sr$_x$FeO$_3$) with perovskite structure is expected as a $p$-type thermoelectric material due to its high chemical stability in air. The electrical conductivity for the oxygen gas partial pressure exhibits hole-ion mixed conduction, which needs for electrode of solid state oxide fuel cell (SOFC), at high temperature region [1]. The mixed conduction is useful for the performance of SOFC. However, details of structural and electrical properties have not been clarified far.

In this study, the authors have prepared the Nd$_{1-x}$Sr$_x$FeO$_3$ bulk ceramics and probed their electronic structures by X-ray absorption spectroscopy (XAS) and high-resolution photoemission spectroscopy (PES). The Nd$_{1-x}$Sr$_x$FeO$_3$ has hole and oxygen vacancies in the crystal lattice by Sr substitution. In this paper, the authors discuss about the valence state of Fe, oxygen vacancies and electronic structures of the valence band for Nd$_{1-x}$Sr$_x$FeO$_3$ ($x=0$, 0.1, 0.2, and 0.4) in comparison with electrical conductivity.

2 Experiment
Nd$_{1-x}$Sr$_x$FeO$_3$ ($x=0$, 0.1, 0.2, and 0.4) bulk ceramics were prepared by the solid-state reaction method. Nd$_2$O$_3$, SrCO$_3$, and Fe$_2$O$_3$ powders were mixed using a wet ball mill. The mixture was pressed into a disk shape at 14 kN and sintered for 24 h at 1300°C. The crystallization of the prepared target was confirmed using X-ray diffraction (XRD) using CuKα.

The electronic structure was confirmed by photoemission spectroscopy (PES) and X-ray absorption spectroscopy (XAS), which was installed at the undulator beamline BL-2A in Photon Factory, KEK. The XAS spectra were measured by total-electron-yield mode. The kinetic energy of photoelectron for PES was measured using Gammadata-Scienta SES-2002. The energy resolutions of PES and XAS were 100 meV and 60 meV, respectively, at $h

3 Results and Discussion
Table 1 shows peak positions of (110), (112) and (202) for Sr concentration estimated from XRD patterns. The (110) and (112) peaks shifts to higher diffraction angle side and (202) peak shifts to lower diffraction angle side with increasing Sr concentration. This result indicates that the lattice constant of $a$-axis increases and those of $b$- and $c$-axes decrease with Sr concentration.

![Temperature dependence of electrical resistivity of Nd$_{1-x}$Sr$_x$FeO$_3$](image)

Figure 1 shows the temperature dependence of electrical resistivity of Nd$_{1-x}$Sr$_x$FeO$_3$. The NdFeO$_3$ exhibits insulator-like behavior. The resistivities of $x=0.1$ and 0.2 decrease with decreasing temperature between 400 and 1000°C. However, those increase below 400°C. On the other hand, the resistivity of $x=0.4$ decreases with decreasing temperature, which corresponds to the metallic behavior. The resistivity of Nd$_{1-x}$Sr$_x$FeO$_3$ is lower than that of La$_{1-x}$Sr$_x$FeO$_3$.

Figure 2 shows the Fe 2p XAS spectra of Nd$_{1-x}$Sr$_x$FeO$_3$. Each spectrum consists of two parts derived from the spin-orbit split of $L_3$ ($2p_{3/2}$) and $L_2$ ($2p_{1/2}$) states. They are...
Fig. 2 O 1s XAS spectra of Nd$_{1-x}$Sr$_x$FeO$_3$ ($x$=0, 0.1, 0.2, and 0.4).

Fig. 3 Fe 2p XAS spectra of Nd$_{1-x}$Sr$_x$FeO$_3$ ($x$=0, 0.1, 0.2, and 0.4).

Further split into the $t_{2g}$ and $e_g$ states due to the octahedral ligand field. The crystal-field splitting ($10Dq$) corresponding to the energy separation between $t_{2g}$ and $e_g$ states is 1.5 eV. The spectral shape and peak position are similar to those of La$_{1-x}$Sr$_x$FeO$_3$, which was calculated assuming a high-spin [t$_{2g}$]$_3$[e$_g$]$_2$ ground state [2]. The intensity of $t_{2g}$-subband increases with Sr concentration, indicating that the doped Sr ions are doped as hole.

Figure 3 shows the O 1s-XAS spectra of Nd$_{1-x}$Sr$_x$FeO$_3$. The O 1s XAS of Fe oxide corresponds to the transition from O 1s core level to unoccupied O 2p state hybridized with Fe 3d state. The conduction band is mainly composed of Fe 3d state. Hole or oxygen vacancies induced state ($h$) is observed at the bottom of the conduction band. The intensity of the structure increases with Sr concentration.

Figure 4 shows the resonant-PES spectra of Nd$_{0.9}$Sr$_{0.1}$FeO$_3$ measured at various excitation energies of Fig. 3.

O 2p state and Fe 3d ($t_{2g}$) state. The on.2 spectrum corresponding to $e_g$-resonance exhibits strong resonance effect at peak $\alpha$ at near the Fermi level ($E_F$). This result indicates that the $e_g$-subband of Fe 3d state is closely related to the electrical conductivity of Nd$_{0.9}$Sr$_{0.1}$FeO$_3$.

**4 Summary**

We have studied the electrical resistivities and electronic structures of Nd$_{1-x}$Sr$_x$FeO$_3$. The lattice constant of $a$-axis increases and those of $b$- and $c$-axes decrease with Sr concentration. The Fe has the mixed valence states of Fe$^{2+}$ and Fe$^{3+}$. The hole-induced state with Sr doping is observed at the bottom of the conduction band. The valence band is mainly composed of $t_{2g}$- and $e_g$-subbands of Fe 3d states hybridized with O 2p states. The electrical conductivity of Nd$_{0.9}$Sr$_{0.1}$FeO$_3$ is achieved by the $e_g$-subband at $E_F$.

**References**


**Research Achievements**


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