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XAS Study on Oxygenated LaSrNiO_4 and $\text{La}_2\text{NiO}_{4+\delta}$

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Abstract. XANES studies at Ni K-edge have been performed for $\text{LaSrNiO}_{3.99}$ and $\text{La}_2\text{NiO}_{4+\delta}$ treated under various atmosphere conditions as well as chemical and electrochemical oxidation methods. XRD patterns of polycrystalline have shown a well crystallized single phase, and valence states of Ni were carefully determined by iodometric titration, resulting in $\delta = 0.01 \sim 0.17$. The oxidation from Ni(II) to Ni(III) is indicated by an absorption edge shift to higher energy side, which is in good agreement with the amount of excess oxygen determined by iodometric titration. XANES study suggests that the doped holes in nickelates are more localized on nickel sites than those in cuprate.

1. INTRODUCTION

Since the discovery of superconductivity through the partial substitution of Ba for La in the La_2CuO_4 system [1], La_2CuO_4 and its related compounds have been regarded as model compounds for understanding superconductivity due to their structural simplicity. Recently we reported the X-ray absorption spectroscopy (XAS) study on the partial formation of Cu(III) in the superconducting $\text{La}_2\text{CuO}_{4.08}$, indicating that the dop-induced holes are present on the copper sites.[2] However the isostructural La_2NiO_4 -related compounds show a metallic behavior only at a very high doping level and do not exhibit a superconducting transition, unlike La_2CuO_4 -ones. In this respect, we have studied Ni K-edge XAS for $\text{La}_2\text{NiO}_{4+\delta}$ compounds including $\text{LaSrNiO}_{3.99}$ in order to evaluate the electronic structure of nickel upon oxygen doping.

2. EXPERIMENTAL

Using as-sintered $\text{La}_2\text{NiO}_{4+\delta}$ prepared in air at 1050 °C, $\text{La}_2\text{NiO}_{4+\delta}$ having different oxygen contents were prepared under reaction conditions shown in Table 1. Especially, a stoichiometric La_2NiO_4 was prepared by a direct reaction of La_2O_3 and NiO in a sealed quartz tube at 1100 °C for 30 hrs. All samples were found to be single phase by X-ray powder diffraction. The oxygen contents were determined by a conventional iodometric titration. The XANES spectra at the nickel K-edge were recorded on beam line 7C of the Photon Factory in the transmission mode at room temperature. Polarization-dependent spectra for a single crystal La_2NiO_4 were recorded using the fluorescence-yield mode. For XANES spectra, a linear background was subtracted from the experimental spectra by extrapolating the least-square fitting of the pre-edge experimental points, and the edge jump was set to unity.

3. RESULTS AND DISCUSSION

From the Ni K-edge XANES spectra of Fig. 1, it is shown that the overall spectral feature shifts to higher energies upon the

Table 1. Samples and reaction conditions.

sample	reaction condition
$\text{La}_2\text{NiO}_{4.01}$ (A)	1100 °C, quartz sealed
$\text{La}_2\text{NiO}_{4.13}$ (B)	900 °C, N_2 flowing
$\text{La}_2\text{NiO}_{4.16}$ (C)	500 °C, O_2 flowing
$\text{La}_2\text{NiO}_{4.17}$ (D)	chemical oxidation with KMnO_4 ^a
$\text{La}_2\text{NiO}_{4.17}$ (E)	electrochemical oxidation ^a
$\text{LaSrNiO}_{3.99}$ (F)	1050 °C, via sol-gel synthetic route

^a Detailed preparation methods are reported in ref. [3,4].

Figure 1: Ni K-edge XANES spectra for samples A (—), B (---), C (....), D (— · —), E (— — —), and F (— · —).

Figure 2: The second derivatives of Ni K-edge XANES spectra shown in Fig. 1.

Figure 3: The second derivatives of polarized Ni K-edge spectra for a single crystal La_2NiO_4 . The value of ϕ indicates the angle between incident beam and ab plane of single crystal.

increasing oxygen content. It has been also found that the nominal oxidation states of nickel for the present compounds are in a linear relation with the edge energies defined by the first inflection point of absorption edge. The difference of edge energy between $\text{LaSrNi(III)O}_{3.99}$ and $\text{La}_2\text{Ni(II)O}_{4.01}$ is about 2.3 eV. The second derivatives in Fig. 2 show that the preedge peak at ~ 8330 eV, which is assigned to $1s \rightarrow 3d$ quadrupole transition, shifts to higher energies and also increases in area, indicating the increasing density of Ni 3d states. In addition, the main absorption peak at about 8345 eV actually consists of two peaks except for the case of $\text{LaSrNiO}_{3.99}$. For the detailed assignment of the main peak, the polarized Ni K-edge spectra were measured for a single crystal, La_2NiO_4 as shown in Fig. 3, where spectra at $\phi = 5^\circ$ and 85° approximately correspond to those for X-ray polarization vector ϵ parallel to the c axis ($\epsilon \parallel c$) and to the ab plane ($\epsilon \perp c$), respectively. Based on both dipole selection rule and symmetry consideration, $1s \rightarrow 4p_\pi$ transition is allowed for $\epsilon \parallel c$ and $1s \rightarrow 4p_\sigma$ one is allowed for $\epsilon \perp c$. Thus, the two peaks in Fig. 2 can be assigned to transition to final states of out-of-plane Ni $4p_\pi$ and in-plane Ni $4p_\sigma$, respectively. The reason why the main peak in $\text{LaSrNiO}_{3.99}$ consists of one peak can be explained by energy separation between in-plane and out-of-plane states. That is, as the oxidation state of nickel increases, in-plane and out-of-plane Ni-O distances become closer so that $4p_\pi - 4p_\sigma$ energy splitting is finally vanishing. This fact is well consistent with the previous results of polarized spectra for single crystals of $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$. [5] From this view point, it is of interest to compare the XANES spectral features between chemically and electrochemically oxidized nickelates. Even though both nickelates were determined to have almost the same content of excess oxygen by iodometric titration as shown in Table 1, the degree of $4p_\pi - 4p_\sigma$ energy splitting in Fig. 2 suggests that chemically oxidized nickelate has higher valent nickel than electrochemically oxidized one. The possible existence of manganese oxides due to KMnO_4 used as an oxidant makes the exact iodometric titration for chemically oxidized nickelate difficult.

4. Conclusion

This work presents the continuous evolution of Ni K-edge XANES spectra upon the oxidation states of nickel. Consequently it is clear that the doped hole in the present nickelates has a substantial Ni(III) character. Comparing to La_2CuO_4 -related materials, isostructural nickelates have shown more distinct changes in spectral features upon hole doping, which suggests that the doped holes in nickelates are more localized on nickel sites than those in cuprates.

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