

Synchrotron X-ray Diffraction Study for High- $T_c$  candidate  $\text{Nd}_{3.5}\text{Sm}_{0.5}\text{Ni}_3\text{O}_8$ Masatomo Uehara\*, Kai Kobayashi, Hiroki Yamamoto, Akitoshi Nakata,  
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## 1 Introduction

$\text{Ln}_4\text{Ni}_3\text{O}_8$  (Ln=La, Nd, Sm) contains 2-dimensional  $\text{NiO}_2$  planes and its crystal structure is basically the same with high- $T_c$  cuprate as shown in fig.1. Moreover, the formal valence of Ni is +1.33 consisting of  $\text{Ni}^+ 3d^9$  and  $\text{Ni}^{2+} 3d^8$  states, being the same with high- $T_c$  cuprate. Therefore,  $\text{Ln}_4\text{Ni}_3\text{O}_8$  is a promising candidate for new high- $T_c$  material. Despite these similarities with cuprate,  $\text{Ln}_4\text{Ni}_3\text{O}_8$  had showed neither metallic characteristic nor superconductivity. [1-3]

Recently, we found that the intercalation and subsequent deintercalation treatment with sulfur induces the metallic nature from 300 down to  $\sim 20$  K in  $\text{Nd}_{3.5}\text{Sm}_{0.5}\text{Ni}_3\text{O}_8$ . [4] This is the first observation of the metallic state in this system. As the origin of this behavior, it can be guessed that the additional oxygens at apical site of Ni is removed by S-treatment, because a similar phenomenon has been observed in  $T$ -type high- $T_c$  cuprate having similar structure with present system.

In this study, synchrotron X-ray diffraction experiment was performed to investigate what happens structurally by S-intercalation and deintercalation.

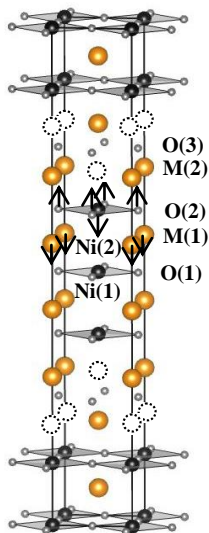


Fig. 1. The crystal structure of  $\text{Nd}_{3.5}\text{Sm}_{0.5}\text{Ni}_3\text{O}_8$ . The arrows show the displacement-directions of M(1), Ni(2) and O(2) atoms by S-treatment. The circles with broken lines are possible additional apical oxygens.

## 2 Experiment

The detail of sample preparation was reported in our previous paper. [5] The intercalation and deintercalation by sulfur is called as ‘‘S-treatment’’ hereafter.

Also, we call the sample without S-treatment to be the ‘‘as-synthesized sample’’ and the sample after S-treatment

to be the ‘‘S-deintercalated samples’’ hereafter. The as-synthesized and S-deintercalated samples show the semiconducting and the metallic behavior (300 -  $\sim 20$  K), respectively.

High-resolution synchrotron X-ray powder diffraction data were collected at BL-4B2 beam line with an incident beam wavelength of 1.19735 Å at room temperature.

## 3 Results and Discussion

Figure 2(a) and (b) show the synchrotron X-ray data for as-synthesized and S-deintercalated samples, respectively. S-deintercalated sample contains very tiny amount of impurity phase shown by asterisk marks. The electrical resistivity data for the samples used in synchrotron X-ray experiments are displayed in the inset of the figures. These data were analysed by Rietveld method by using RIETAN program, [6] assuming  $I4mmm$  (No. 139) space group. M(1) and M(2) are imaginary atoms of  $(\text{Nd}_{3.5}\text{Sm}_{0.5})$ . Blue solid and dotted lines are observed and calculated data respectively. The difference between observed and calculated data is displayed below X-ray profile. The vertical tick marks correspond to the Bragg positions. For S-deintercalated sample, two-theta ranges shown below where tiny amount of impurity phases are detected were not used. 16.7-17.03°, 20.0-20.76°, 22.47-23.18°, 23.92-24.29°, 28.5-29.5°.

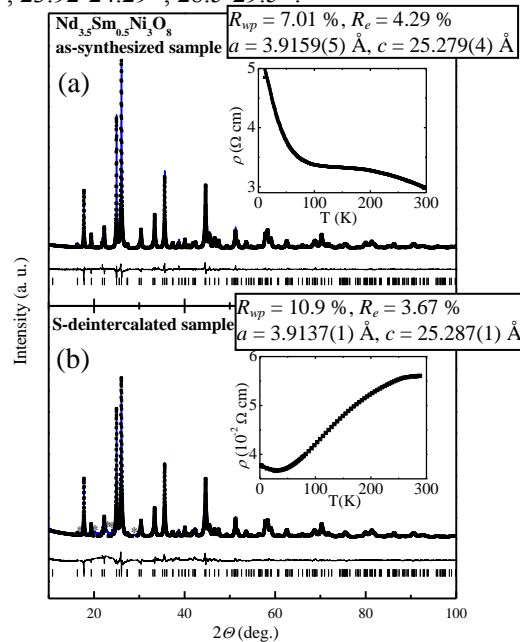


Fig. 2(a)(b). Synchrotron XRD patterns of as-synthesized (a) and S-deintercalated (b) samples of  $\text{Nd}_{3.5}\text{Sm}_{0.5}\text{Ni}_3\text{O}_8$ . Inset shows the temperature dependence of electrical resistivity of the samples used in synchrotron XRD experiments.

For isotropic atomic displacement parameters of oxygen, those determined by neutron diffraction experiment in ref. [7] were used. For S-deintercalated sample, Rietveld analysis was performed with the same isotropic atomic displacement parameters with the values determined in the analysis for as-synthesized sample. The occupation factors for all ions were fixed to be 1.0 according to the previous neutron diffraction result. [7] For as-synthesized sample, the analysed crystal data is almost consistent to published data by neutron diffraction experiments. [7] In order to see what was changed structurally by S-treatment, figure 3 shows the displacement-length (Å) along *c*-axis of Ni(2), O(2), M(1) and M(2) positions for S-deintercalated sample, relative to those of as-synthesized sample. O(2) atoms are being away from NiO<sub>2</sub> plane and close to block layer by S-treatment. In contrast, Ni(2) atoms move with opposite way of O(2) atoms. This can be understood qualitatively by removal of O<sup>2-</sup> ion at apical site (broken circles in Fig. 1) of Ni(2) by intuitive electrostatic consideration. The position of M(2) atoms is almost unchanged, while M(1) atoms moves with the same direction of Ni(2) atoms. This might be understood by the Coulomb repulsion from Ni(2)<sup>1.33+</sup> ions overcoming the Coulomb attraction from O(2)<sup>2-</sup>. This situation is schematically shown in the picture of crystal structure by using arrows (Fig. 1).

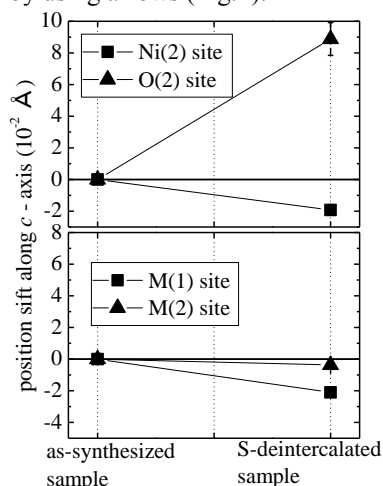


Fig. 3. The position shift along *c*-axis of Ni(2), O(2), M(1) and M(2) sites for as-synthesized and S-deintercalated samples of Nd<sub>3.5</sub>Sm<sub>0.5</sub>Ni<sub>3</sub>O<sub>8</sub>, comparing to those of as-synthesized sample.

#### 4 conclusion

We have performed synchrotron X-ray diffraction experiment for “semiconductive” as-synthesized and “metallic” S-deintercalated Nd<sub>3.5</sub>Sm<sub>0.5</sub>Ni<sub>3</sub>O<sub>8</sub> samples in order to elucidate the origin of metallization by S-treatment from a structural point of view. Synchrotron X-ray diffraction study suggests that the appearance of metallic behavior for Nd<sub>3.5</sub>Sm<sub>0.5</sub>Ni<sub>3</sub>O<sub>8</sub> by S-treatment is associated with the removal of additional apical oxygen, similar to the situation of *T'*-type high-*T<sub>c</sub>* cuprate.

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