MLF Experimental Report	提出日 Date of Report May 4, 2013
課題番号 Project No. 2012B0247 実験課題名 Title of experiment Detailed crystal structural study on highly hole doped $R_{2-x}Sr_xNiO_4$ with $x > 1/2$ 実験責任者名 Name of principal investigator Ryoichi Kajimoto 所属 Affiliation J-PARC Center, Japan Atomic Energy Agency	装置責任者 Name of responsible person Takashi Kamiyama 装置名 Name of Instrument/（BL No.） SuperHRPD/(BL08) 実施日 Date of Experiment 9:00 on Feb. 7 – 9:00 on Feb. 13, 2013

試料、実験方法、利用の結果得られた主なデータ、考察、結論等を、記述して下さい。（適宜、図表添付のこと）
Please report your samples, experimental method and results, discussion and conclusions. Please add figures and tables for better explanation.

1. 試料 Name of sample(s) and chemical formula, or compositions including physical form.

Powder samples of $Pr_{2-x}Sr_xNiO_4$ with x = 0.5, 0.7, and 0.9

2. 実験方法及び結果（実験がうまくいかなかった場合、その理由を記述してください。）
Experimental method and results. If you failed to conduct experiment as planned, please describe reasons.

Layered perovskite nickel oxide, $R_{2-x}Sr_xNiO_4$ (R = La, Pr, Nd, etc.) shows charge and spin orderings upon hole doping. The holes enter the x^2-y^2 orbitals of Ni ions when the hole concentration per nickel site x is less than 1/2, which results in a so-called stripe ordering of charges and spins in the NiO_2 planes. On the other hand, when $x > 1/2$, the holes also enter the $3z^2-r^2$ orbitals, and the x^2-y^2 character in e_g orbitals of the Ni^{3+} ions becomes dominant [1]. In order to clarify structural changes caused by the change of orbital character as well as the charge and spin ordering in $R_{2-x}Sr_xNiO_4$ with $x > 1/2$, we performed high-resolution powder neutron diffraction measurements on $Pr_{2-x}Sr_xNiO_4$ with x = 0.7, 0.8, and 0.9. We utilized a 4–5 g powder sample for each composition, and measured the powder diffraction patterns with changing the temperature from 10 K to 310 K in 20 K step. Unfortunately, observed data were contaminated by the diffraction profile from an unused time-frame due to a failure of synchronization of the frame-overlap choppers. Therefore, we could not obtain high-quality data of x = 0.5 and x = 0.7 for a precise analysis. Though the contamination of the x = 0.9 data is less severe, the data contains small spurious peaks caused by this contamination. We are now trying to get rid of the contamination from the data by manipulating the raw event data.

2. 実験方法及び結果（つづき） Experimental method and results (continued)

Figure 1 shows the powder diffraction pattern of x = 0.9 measured at 10 K and the result of its Rietveld analysis. The Rietveld analysis was performed using the software package Z-Rietveld (ver. 0.9.36). We removed the spurious peaks described above in the analysis as much as possible, fixed the site occupancies to their nominal values, and assumed the isotropic temperature factor for each atom. Though the observed peak positions are describable in the space group *I4/mmm*, the goodness of the fit (*R*-factor) is not satisfactory, partly because the profile shapes of several peaks are not reproduced by the refinement. A previous neutron powder diffraction work on $LaSrNiO_4$ (x = 1) reported that multiple phases and anisotropic strain broadening were required to reach a satisfactory refinement due to a distribution of La/Sr ratios throughout the sample [2]. We should also try to incorporate these effects to improve the refinement.

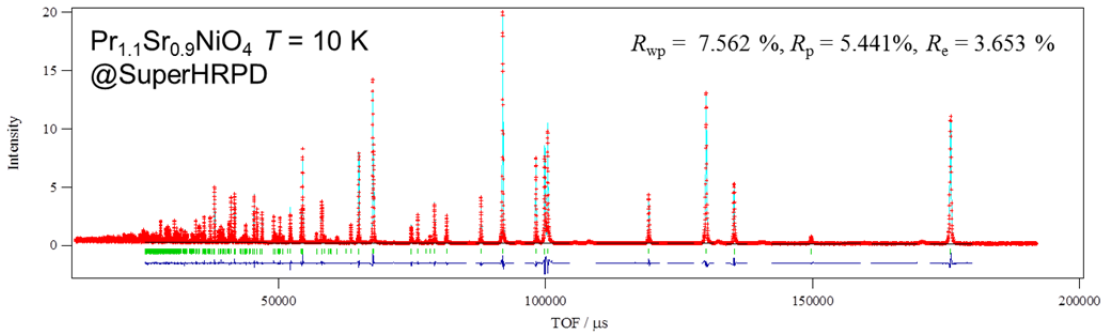

Fig. 1. Powder diffraction pattern of $Pr_{1.1}Sr_{0.9}NiO_4$ at 10 K as a function of time-of-flight. Red marks show the observed data. Light blue line, green vertical bars, and dark blue line show the calculated diffraction pattern, peak positions, and difference between the observed and calculated patterns obtained by the Rietveld analysis.

Figure 2 shows temperature dependence of the ratio of the axial [Ni-O(1)] to equatorial [Ni-O(2)] Ni-O bond length, which were obtained by the Rietveld refinement of each temperature data. The ratio decreases as temperature decreases, but it shows a kink around 100 K. This temperature corresponds to the one where the sign of the Hall coefficient changes [1]. Since the ratio of the Ni-O bond lengths reflects the character of e_g orbitals of Ni ions, the change of the temperature dependence may indicate the change of the orbital character concomitant with the change of the character of carriers. Though it is an interesting interpretation, we need further analysis and comparison of the data of the other compositions to conclude.

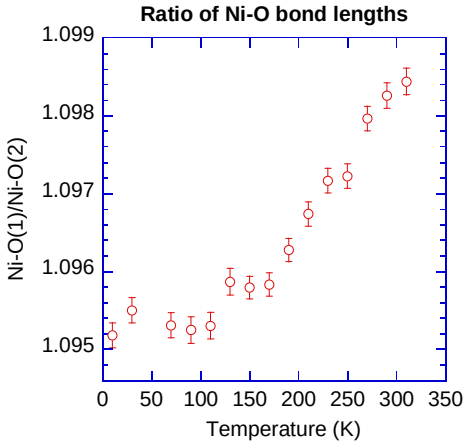

Fig. 2. Temperature dependence of the ratio of the axial to equatorial Ni-O bond lengths in $Pr_{1.1}Sr_{0.9}NiO_4$.

References

[1] M. Uchida *et al.*, Phys. Rev. B **86**, 165126 (2012).

[2] J. E. Millburn *et al.*, J. Solid State Chem **145**, 401 (1999).