MLF Experimental Report	提出日 Date of Report February 1, 2013
課題番号 Project No. 2012B0217 実験課題名 Structural Origin of Large Oxygen Permeability in the K_2NiF_4-Type Mixed and Ionic Conductors 実験責任者名 Name of principal investigator Masatomo Yashima 所属 Affiliation Department of Chemistry and Materials Science, Graduate School of Science and Engineering, Tokyo Institute of Technology	装置責任者 Name of responsible person Toru Ishigaki 装置名 Name of Instrument/（BL No.） BL-20 実施日 Date of Experiment December 25-27, 2012 January 14, 18, 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.

AA′BO$_4$- and *ABO*$_3$-based materials (*A*: large cations such as rare earth La, Ce, Pr, Nd, Y and Ba, Sr, Ca; *B*: smaller cations as In, Si, Sn, Ge, Ga, Mn, Fe, Co).

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.

Experimental methods

Neutron powder diffraction data of *AA′BO*$_4$- and *ABO*$_3$-based materials were measured at room temperature and at high temperatures by a high-resolution neutron powder diffractometer iMateria installed at the beam line BL20 of J-Parc facility, Japan. The sintered or the powder samples were introduced into 6 mmϕ vanadium sample holders and were used for the diffraction measurements. The diffraction data were analyzed by the Rietveld method with the computer program Z-Rietveld.

Experimental results

The crystal structure of $BaNdInO_4$ has previously unknown structural type and we have recently solved its crystal structure from the powder X-ray diffraction data. The Rietveld analysis of $BaNdInO_4$ was initially carried out using the structural model obtained by the powder X-ray diffraction analysis. However, the analysis did not give a good quality fitting as shown in the Figure 1a (R_{wp} = 0.1350 and R_B = 0.1767).

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

Because some diffraction peaks could not be explained by the initial structural model, the unit cell parameters were re-examined and it was found that the correct structure has a doubled unit cell of the initial model. Using a new structural model, a good quality fitting was finally achieved with R_{wp} = 0.0417 and R_B = 0.0441 (Figure 1b). Neutron diffraction profiles include useful information on oxygen, because the scattering ability of the oxygen nucleus (amplitude of coherent scattering length) is relatively large and independent of diffraction angle. In the present case, both the initial and final structural models of $BaNdInO_4$ have almost same atomic positions for the metal atoms and small difference could be recognized in the oxygen atomic positions. Because of the low scattering power for oxygen in the X-ray diffraction data, it was very difficult to determine the correct crystal structure only from the powder X-ray diffraction data. Thus, the present study has clearly showed that the neutron powder diffraction experiments provide the critical information for a correct crystal structure of the metal oxide materials. Finally, the validity of the analyzed crystal structure of $BaNdInO_4$ was confirmed from bond valence sums (BVS). The BVSs of the cations were calculated to be 3.00 for In, 1.75 for Ba and 2.95 for Nd. The formal charges of In, Ba and Nd are +3, +2 and +3, and well agree with the calculated BVSs.

In the crystal structure of $BaNdInO_4$, the Ba and In construct the two-dimensional slabs (BaInO slabs) which are interleaved with the two-dimensional NdO layers (Figure 2). Such layered structure could have an advantage for the oxide-ion conduction and we are currently carrying out the electrical-conductivity measurements with the aim for the application as a mixed oxide-ion conductor.

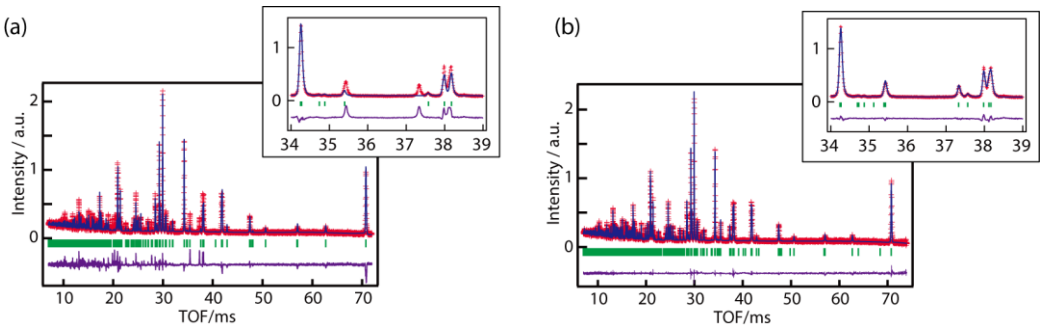

Figure 1. Rietveld plot of $BaNdInO_4$ with (a) the initial wrong structural model and (b) the final correct structural model.

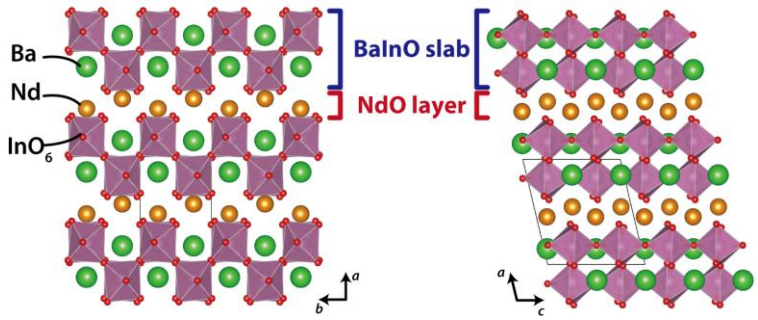

Figure 2. Refined crystal structure of $BaNdInO_4$.