

## Discovery of a New Crystal Structure Family of Oxide-Ion Conductors NdBaInO<sub>4</sub>

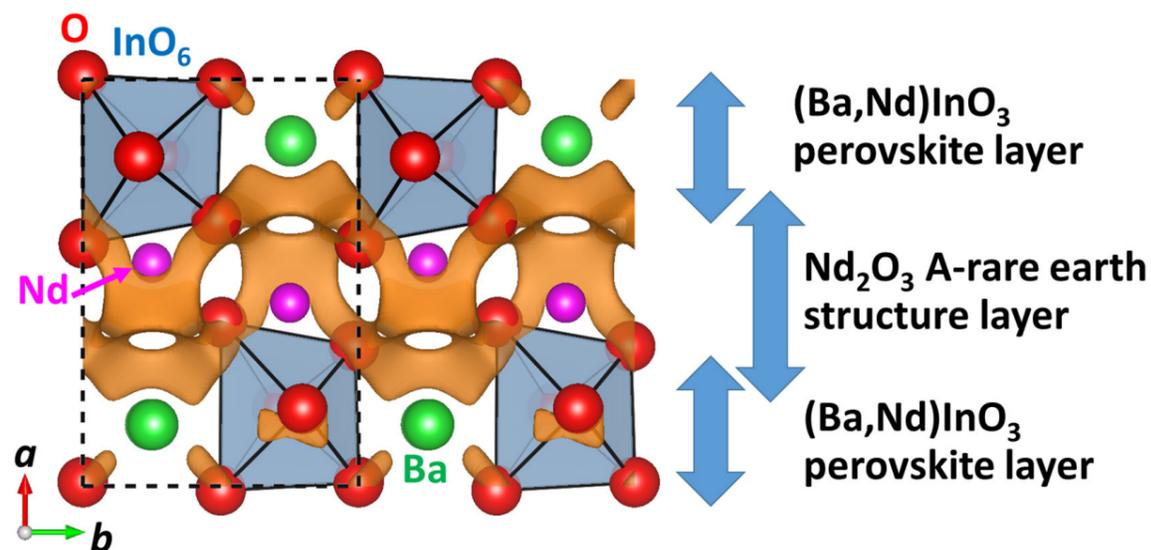
We have discovered a new structure family of oxide-ion (O<sup>2-</sup>) conducting material, NdBaInO<sub>4</sub> [1]. It was found that Sr doping improves the oxide-ion conductivity [2]. We have successfully determined the crystal structure and visualized the oxide-ion diffusion pathway of the material (Fig. 1). This discovery may lead to the development of new ionic conductors for better solid oxide fuel cells and oxygen concentrators, and of electronic materials.

Oxide-ion conducting materials such as pure oxide-ion conductors and mixed oxide-ion electronic conductors have a wide variety of applications in fuel cells, oxygen separation membranes and gas sensors. Since the oxide-ion conductivity is strongly dependent on the crystal structure, the discovery of a new oxide-ion conductor belonging to a new structure family may pave the way for further innovative developments in the application of oxide-ion conductors.

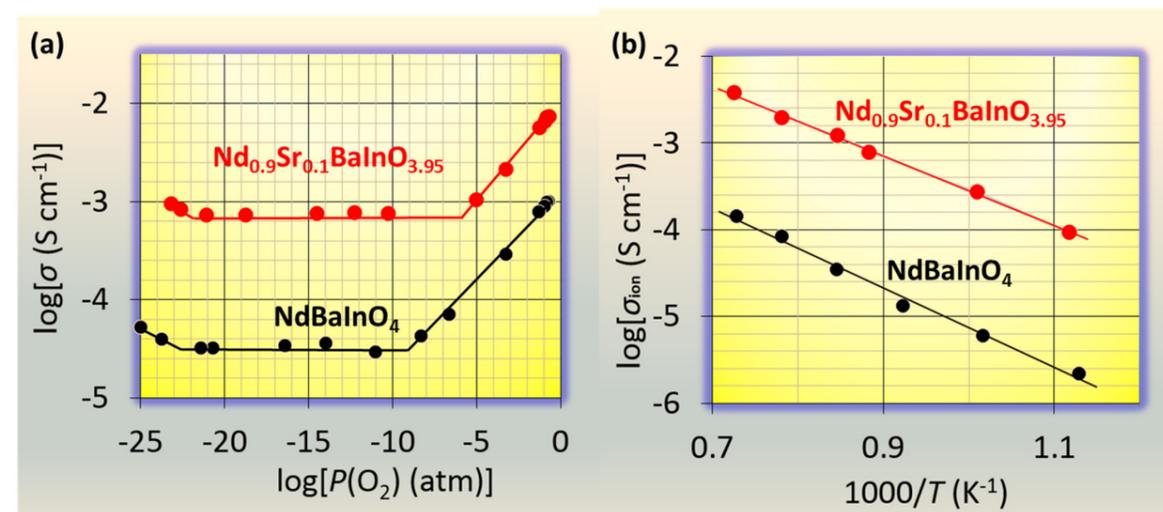
To design a new perovskite-related layered structure, we have studied various chemical compositions of AA'BO<sub>4</sub> where A and A' are larger cations and B is a smaller cation. After examining a number of chemical compositions, we discovered a new structure family of oxide-ion conducting material, NdBaInO<sub>4</sub> [1]. Nd, Ba and In were chosen as cations because (i) the different sizes of Nd and Ba can lead to Ba/Nd cation ordering and (ii) the BaInO<sub>2.5</sub> perovskite unit can form in view of the sizes of Ba and In cations. NdBaInO<sub>4</sub> and Nd<sub>0.9</sub>Sr<sub>0.1</sub>BaInO<sub>3.95</sub> were prepared by solid-state reactions at 1400°C using BaCO<sub>3</sub>, SrCO<sub>3</sub>, In<sub>2</sub>O<sub>3</sub> and Nd<sub>2</sub>O<sub>3</sub> powders. NdBaInO<sub>4</sub> and Nd<sub>0.9</sub>Sr<sub>0.1</sub>BaInO<sub>3.95</sub> exhibit oxide-ion conduction as shown in Fig. 2. The present NdBaInO<sub>4</sub> and

Nd<sub>0.9</sub>Sr<sub>0.1</sub>BaInO<sub>3.95</sub> samples were a single monoclinic phase with a new crystal structure as described below. Thus a new structure family of oxide-ion conducting material, NdBaInO<sub>4</sub>, was discovered in this study. Furthermore, it was found that the oxide-ion conductivity of Nd<sub>0.9</sub>Sr<sub>0.1</sub>BaInO<sub>3.95</sub> ( $7.7 \times 10^{-4}$  S cm<sup>-1</sup>) is about 20 times higher than that of NdBaInO<sub>4</sub> ( $3.6 \times 10^{-5}$  S cm<sup>-1</sup>) at 858°C (Fig. 2) [2].

The crystal structure of NdBaInO<sub>4</sub> was investigated by neutron and synchrotron X-ray powder diffractometry and *ab initio* electronic calculations. The synchrotron X-ray powder diffraction data were measured at BL-4B2 of the Photon Factory and at BL02B2 of SPring-8. The multi-detector system at BL-4B2 yields high angular resolution synchrotron data with extremely low background. We carried out *ab initio* crystal structure analysis using the X-ray powder diffraction data. Neutron diffraction enables precise determination of the positional parameters of oxygen atoms. Neutron powder diffraction data were taken using the diffractometers iMATERIA (J-PARC), Echidna (ANSTO) and HRPD (KAERI). The space group was found to be monoclinic *P*2<sub>1</sub>/*c*. The validity of the crystal structure of NdBaInO<sub>4</sub>



**Figure 1:** Refined crystal structure and orange isosurface of the difference bond valence sum (DBVS) for an oxide ion (O<sup>2-</sup>) of NdBaInO<sub>4</sub>. The structure consists of (i) Nd<sub>2</sub>O<sub>3</sub> A-rare earth structure layers and (ii) (Ba,Nd)InO<sub>3</sub> perovskite layers. The DBVS map strongly suggests that the oxide-ion conduction occurs in the Nd<sub>2</sub>O<sub>3</sub> layer.



**Figure 2:** (a) Oxygen partial pressure dependence of total electrical conductivity at 858°C of NdBaInO<sub>4</sub> (Black) and Nd<sub>0.9</sub>Sr<sub>0.1</sub>BaInO<sub>3.95</sub> (Red). (b) Arrhenius plots of oxide-ion conductivity of NdBaInO<sub>4</sub> (Black) and Nd<sub>0.9</sub>Sr<sub>0.1</sub>BaInO<sub>3.95</sub> (Red).

(Fig. 1) was confirmed (i) by Rietveld refinements of the synchrotron X-ray and neutron powder diffraction data, (ii) by bond valence sums (BVS) of Nd, Ba and In atoms, and (iii) by structural optimization based on density functional theory calculations. The refined crystal structure of NdBaInO<sub>4</sub> consists of the Nd<sub>2</sub>O<sub>3</sub> A-rare earth structure and (Ba,Nd)InO<sub>3</sub> perovskite layers (Fig. 1) [1], which indicates a new Ba/Nd (A/A') cation ordered perovskite-related layered structure. An outstanding and unique feature of this new structure is that the edge of the InO<sub>6</sub> octahedron faces the Nd<sub>2</sub>O<sub>3</sub> (A<sub>2</sub>O<sub>3</sub>) unit. Structure analysis of Nd<sub>0.9</sub>Sr<sub>0.1</sub>BaInO<sub>3.95</sub> and NdBaInO<sub>4</sub> revealed Sr cations at the Nd site and oxygen vacancies in Nd<sub>0.9</sub>Sr<sub>0.1</sub>BaInO<sub>3.95</sub>. This result indicates that the increase of the oxide-ion conductivity is mainly due to the increase of the carrier (oxygen vacancy) concentration. The oxide-ion diffusion path of NdBaInO<sub>4</sub> was

studied by the bond valence method, which strongly suggests that the oxide ions diffuse two-dimensionally in the Nd<sub>2</sub>O<sub>3</sub> (A<sub>2</sub>O<sub>3</sub>) unit (Fig. 1).

### REFERENCES

- [1] K. Fujii, Y. Esaki, K. Omoto, M. Yashima, A. Hoshikawa, T. Ishigaki and H. R. Hester, *Chem. Mater.*, **26**, 2488 (2014).
- [2] K. Fujii, M. Shiraiwa, Y. Esaki, M. Yashima, S. J. Kim and S. Lee, *J. Mater. Chem. A*, **3**, 11985 (2015).

### BEAMLINE

BL-4B2

M. Yashima<sup>1</sup>, K. Fujii<sup>1</sup>, M. Shiraiwa<sup>1</sup>, Y. Esaki<sup>1</sup>, K. Omoto<sup>1</sup>, A. Hoshikawa<sup>2</sup>, T. Ishigaki<sup>2</sup>, H. R. Hester<sup>3</sup>, S. J. Kim<sup>4</sup> and S. Lee<sup>4</sup> (<sup>1</sup>Tokyo Inst. of Tech., <sup>2</sup>Ibaraki Univ., <sup>3</sup>ANSTO, <sup>4</sup>KAERI)