Discovery and development of BaNdInO₄ —A brief review—

Kotaro FUJII¹,† and Masatomo YASHIMA¹,‡

¹Department of Chemistry, School of Science, Tokyo Institute of Technology, 2-12-1-W4-17 O-okayama, Meguro-ku, Tokyo 152-8551, Japan

This article provides the first critical review on the discovery and development of BaNdInO₄. Exploring a new structure family of ionic conductors is an important task to develop ceramic ionic conductors. Since some A₂B₂O₆ compositions exhibit high oxide-ion conductivities, we investigated ABCO₄ compositions to explore new oxide-ion conductors with A/B/C cation-ordered structures. Here A, B, and C are cations [ionic radii: (A) ≥ r(B) ≥ r(C)]. In 2014, we discovered a new material BaNdInO₄ which belongs to a new structure family of perovskite-related structures. This BaNdInO₄-type structure (monoclinic, P2₁/c) consists of alternative stacking of the A rare earth oxide unit and perovskite unit with a b c tilt system. We also discovered new materials BaRInO₄ (R = Sm, Y, Ho, Er, Yb) having the BaNdInO₄-type structure, and report their lattice parameters and anisotropic chemical expansion. Electrical conductivity of BaNdInO₄ was higher than those of BaRInO₄ (R = Sm, Y, Er). Oxide-ion conduction was dominant for BaNdInO₄ in the P(0) region from 3.8 x 10⁻²² to 5.5 x 10⁻⁹ atm at 858°C. Oxide-ion conductivities of Ba₁Nd₀.₉InO₃.₉₅, BaSr₀.₁Nd₀.₉InO₃.₉₅ and BaCa₀.₂Nd₀.₈InO₃.₉ were higher than that of BaNdInO₄. Structure analyses of Ba₁₁Nd₉InO₃₉₅ and BaSr₁₁Nd₉InO₃₉₅ indicated that the excess Ba and doped Sr cations were partially substituted for Nd cation and that there existed oxygen vacancies, leading to the increase of the carrier concentration and higher oxide-ion conductivity. Following the discovery of BaNdInO₄, BaRScO₄ (R = Nd, Eu, Y, Yb) and SrYbInO₄ were reported as new ABCO₄ materials. BaYSrO₄ and BaYbScO₄ have the BaNdInO₄-type structure. BaNdScO₄ and BaEuScO₄ crystallize into the space group Cmcm, which has a higher symmetry than P2₁/c for BaNdInO₄. SrYbInO₄ is the first example of pure oxide-ion conductors with CaFe₂O₄-type structure. Further investigations of ABCO₄ compositions and BaNdInO₄ related materials will lead to development of materials science and solid state ionics.

©2018 The Ceramic Society of Japan. All rights reserved.

Key-words : Oxide-ion conductor, Perovskite-related material, Crystal structure, Layered perovskite

1. Introduction

Ceramic oxide-ion conductors have attracted considerable attention because of their potential applications such as solid oxide fuel cells (SOFCs), catalysts, gas sensors, and oxygen separation membranes.¹⁻⁵ Oxide-ion conductivity of the oxide-ion conductor is strongly dependent on its crystal structure.²⁻¹⁻³ Several structure families, such as fluorite,⁻⁵⁻⁷ pyrochlore,⁻⁵⁻¹⁰ perovskite,⁻¹¹⁻¹⁵ K₂NiF₄,⁻¹⁶⁻²¹ mellilite,⁻²²⁻²³ and apatite-type⁻²⁴⁻²⁹ structures are known to exhibit high oxide-ion conductivities. Most of researches have studied only materials with known crystal structures. The discovery of a new structure family of oxide-ion conductors is obviously necessary for further development of ceramic science and solid state ionics. We have tackled this issue and successfully found several new structure families of oxide-ion conductors.²⁰⁻²⁴ In 2014, our group discovered a new structure family of oxide-ion conductors BaNdInO₄ by exploring ABCO₄ materials.²⁰ Here A, B, and C are cations where their ionic radii have the following relationship: r(A) ≥ r(B) ≥ r(C). In this review paper, we briefly overview the discovery and development of BaNdInO₄, its solid solutions and several new ABCO₄ materials.

2. Discovery of a new structure family of oxide-ion conductors BaNdInO₄. Structure and electrical conduction of BaRInO₄ (R = Nd, Sm, Y, Ho, Er and Yb)

Since some A₂B₂O₆-based materials such as K₂NiF₄-type (Pr,La)₂(Ni,Cu,Ga)O₄₁₈₋₂₀,²⁰⁻³⁵,³⁷ exhibit high oxide-ion conductivities, our group has explored new structure families of oxide-ion conductors with ABCO₄ compositions. In the structure field map of M₂MO₄ compounds, K₂NiF₄-type oxides exist in the area where the sizes of M cations are relatively large [violet squares in Fig. 1, r(M) > 1 Å]. Here, M is a₅B₀.₅ and M’ is C of ABCO₄ for
K₂NiF₄-type oxides. ABCO₄ compounds such as SrErAlO₄ have the K₂NiF₄-type structure where A and B cations occupy the same crystallographic site and are fully disordered in the average structure, because A and B cations have similar ionic sizes: 1 ≤ r(A)/r(B) < 1.25 (violet circles in Fig. 2). On the other hand, there were no reported structures in the area of r(A)/r(B) > 1.25 in Fig. 2. A/B/C cation ordering in layered perovskites ABCO₆−δ such as BaPrCo₂O₆−δ is known to enhance the oxide-ion conductivity where δ is the content of oxygen vacancies. Thus, we explored new A/B/C cation-ordered ABCO₄ materials with higher ratios of r(A)/r(B) > 1.25. In the exploration, we selected BaNdInO₄ (A = Ba, B = R: rare earths and C = In), which satisfies r(A)/r(B) > 1.25 (Fig. 2). In Fig. 1, BaNdInO₄ materials are expressed by either red closed circles (M = Ba₉₀In₈₀, M’ = In) or red crosses (M = Ba₉₀In₈₀, M’ = Ba). Since there were no reports on BaNdInO₄ materials, we prepared BaNdInO₄ samples and investigated their crystal structures and electrical properties, in order to explore a new structure family of oxide-ion conductors.

BaNdInO₄ was synthesized by the solid-state reactions at 1400°C. Because the existing phase of BaNdInO₄ was not able to be identified by X-ray powder diffraction, the ab initio structure determination was carried out using the synchrotron X-ray powder diffraction and time-of-flight neutron powder diffraction data of BaNdInO₄ in 2014. In 2017, the crystal structure of BaNdInO₄ was also analyzed using the single-crystal X-ray diffraction data. The crystal structure of BaNdInO₄ consists of A rare earth oxide (Nd,Ba)₂O₃ and perovskite (Ba₃/₂Nd₁/₂)InO₃ units giving a new perovskite-related structure with monoclinic P2₁/c symmetry (Fig. 3). The crystal structure of

![Fig. 1. Structure field map of M₂M’O₄ compounds (224 compositions).](image1)

![Fig. 2. Structure field map of ABCO₄ compounds with K₂NiF₄-, BaNdInO₄-, and BaNdScO₄-type structures. The tolerance factor for A₁/₂B₁/₂O₃ perovskite unit in a K₂NiF₄-type ABCO₄ is defined as t = [(r(A) + r(B))/2 + r(O)]/(√2(r(C) + r(O))). The t for the A₂/₃B₁/₃O₄ perovskite unit is defined as t = [(3r(A) + r(B))/4 + r(O)]/(√2(r(C) + r(O)))] for BaNdInO₄ and BaNdScO₄-type ABCO₄. r(A), r(B), r(C) and r(O) denote the ionic radii of A, B, C and O cations and oxide ion, respectively. For the K₂NiF₄-type structure, the coordination numbers of A, B, C, and O are eleven, seven, six, and six, respectively.](image2)

![Fig. 3. (a) Crystal structure of BaNdInO₄ viewed along the c axis (left) and b axis (right). The solid lines represent the unit cells. (b) Schematic figures to show the apical oxygen facing the rock-salt unit in a K₂NiF₄-type oxide (left) and the edge facing the (Nd,Ba)₂O₃ unit (right) in BaNdInO₄. Copyright 2014, American Chemical Society.](image3)
BaNdInO$_4$ is called as BaNdInO$_4$-type structure. The lattice parameters and volume of BaNdInO$_4$ were determined using the X-ray powder diffraction data as $a = 9.0939(3)$ Å, $b = 6.04831(12)$ Å, $c = 8.2595(2)$ Å, $\beta = 103.4280(19)\degree$, and $V = 441.87(4)$ Å$^3$. There are seven independent sites, Ba, Nd, In, O1, O2, O3 and O4, which are all in the 4e general positions of $P2_1/c$ (Fig. 3). Ba, Nd, and In are fully ordered at Ba, Nd, and In sites, respectively, which were confirmed in the refinement of occupancy factors. Thus, an $ABCO$ material with a new $A/B/C$ cation-ordered perovskite-related layered structure, BaNdInO$_4$ was successfully discovered. The structure of the A rare earth oxide (Nd$_2$Ba$_2$O$_5$) unit is similar to that of Nd$_2$O$_3$ with the A-rare earth oxide structure (La$_2$O$_3$-type structure). In most of perovskite-related structures, such as Ruddlesden–Popper–$\textit{P}_{2-\text{}}/\text{c}$ structures, $\textit{P}_{2-\text{}}/\text{c}$ unit in K$_2$NiF$_4$-type structure (Left figure of Fig. 3(b)). La$_3$RuO$_4$ has a layered structure consisting of La-O and LaRuO$_3$ perovskite units and has a similar and different edge-facing feature.$^{51-53}$ The structure of La$_3$RuO$_4$ contains additional oxygen atoms in the La-O unit, compared with that of BaNdInO$_4$. BaYInO$_4$, BaSmInO$_4$, BaHoInO$_4$, BaErInO$_4$ and BaYbInO$_4$ were also synthesized by the solid-state reactions at 1400°C.$^{54,55}$ All the reflections in CuK$\alpha$ X-ray powder diffraction patterns of BaYInO$_4$, BaSmInO$_4$, BaHoInO$_4$, BaErInO$_4$, and BaYbInO$_4$ were indexed to a primitive monoclinic cell, indicating the single monoclinic phase with the BaNdInO$_4$-type structure. The lattice parameters $a$ and $b$, and volume $V$ of BaNdInO$_4$ increased with an increase of the ionic radius of rare earth cation $r(R)$, while the lattice parameter $c$ and $\beta$ angle decreased with $r(R)$ (Fig. 5). We calculated the chemical expansions for the lattice parameters $a$, $b$, $c$, and $\beta$, and cube root of the lattice volume $V^{1/3}$, which are defined as $\Delta a/L_a \equiv [L(BaNdInO_4) - L(BaYbInO_4)]/L(BaYbInO_4)$ where the $L(BaNdInO_4)$ is the lattice parameter $a$, $b$, $c$, $\beta$ or $V^{1/3}$ of BaNdInO$_4$ (Fig. 5). With increasing the ionic radius of $R$, the chemical expansions $\Delta a/a_0$ and $\Delta b/b_0$ increased, whereas $\Delta c/c_0$ decreased. Average chemical expansion coefficients between $R =$ Yb and Nd were estimated to be $\alpha_a^{\text{chem}} = 0.197 \, \AA^{-1}$, $\alpha_b^{\text{chem}} = 0.195 \, \AA^{-1}$, $\alpha_c^{\text{chem}} = -0.09 \, \AA^{-1}$, and $\Delta \beta/\beta_0 = -0.109 \, \AA^{-1}$, which indicates the anisotropy in the chemical expansion: $\alpha_a^{\text{chem}} > \alpha_b^{\text{chem}} > \alpha_c^{\text{chem}}$. Similar anisotropy was observed in the thermal expansion of lattice parameters of BaNdInO$_4$ and its solid solutions: $\alpha_a > \alpha_b$, and $\alpha_a > \alpha_c^{30,45,56}$.

The electrical conductivities of BaNdInO$_4$ (R = Nd, Er, Y, Sm) were measured in air by a dc 4-probe method (Fig. 6). The total electrical conductivity of BaNdInO$_4$ was the highest among BaNdInO$_4$ (R = Nd, Er, Y, Sm)$^{54,55}$, thus, we mainly focused on BaNdInO$_4$ in further researches. The total electrical conductivity of BaNdInO$_4$ was measured by controlling oxygen partial pressure $P(O_2)$. In the high $P(O_2)$ region [e.g. $P(O_2)$ = 5.9 x $10^{-4}$ to 2.1 x $10^{-1}$ atm at 858°C], BaNdInO$_4$ exhibited mixed oxide-ion and electron–hole conduction. On the other hand, the total electrical conductivity of BaNdInO$_4$ was constant in the intermediate $P(O_2)$ region [e.g. $P(O_2)$ = 3.8 x $10^{-2}$ to 5.5 x $10^{-9}$ atm at 885°C], indicating that oxide-ion conduction is dominant. Therefore, the oxide-ion conductivities were measured in the intermediate $P(O_2)$ region, in which the total electrical conductivities were independent of $P(O_2)$. BaNdInO$_4$ showed oxide-ion conductivity of 3.6 x $10^{-5}$ $\text{S cm}^{-1}$ at 885°C (black line in Fig. 7), and the activation energy for oxide-ion conduction of BaNdInO$_4$ was 0.91(4) eV.$^{56}$

The crystal structure of BaNdInO$_4$ at 1000°C was analyzed by BaNdInO$_4$-type structure.$^{30}$ The lattice parameters $a$, $b$ and $c$ were higher, while the $\beta$ angle was lower at 1000°C, compared with those at 20°C. The average thermal expansion coefficients of BaNdInO$_4$ between 20 and 1000°C were $\alpha_a = 1.42(2) \times 10^{-5}$ K$^{-1}$, $\alpha_b = 1.176(14) \times 10^{-5}$ K$^{-1}$, $\alpha_c = 0.77(3) \times 10^{-5}$ K$^{-1}$, $\alpha_\beta = -3.81(4) \times 10^{-5}$ K$^{-1}$, and $\alpha_\gamma = 1.176(15) \times 10^{-5}$ K$^{-1}$. Here, the average thermal expansion coefficients between $T_{\text{min}}$ and $T_{\text{max}}$ ($^\circ$C) are defined as $\alpha_L = [L(T_{\text{max}}) - L(T_{\text{min}})]/[L(T_{\text{max}}) \times (T_{\text{max}} - T_{\text{min}})]$ and $\alpha_R = [\sqrt{V(T_{\text{max}})} - \sqrt{V(T_{\text{min}})}]/[\sqrt{V(T_{\text{max}})} \times (T_{\text{max}} - T_{\text{min}})]$, where $L(T_{\text{min}})$ and $V(T_{\text{min}})$ are the lattice parameter $a$, $b$, $c$ or $\beta$ and lattice volume $V$, respectively, at the temperature $T_{\text{min}}$. These results indicate the anisotropic thermal expansion: $\alpha_a > \alpha_b > \alpha_c$. The average linear thermal expansion

---

**Fig. 4.** Tilting of the InO$_6$ octahedra in BaNdInO$_4$. Projection of the crystal structure of BaNdInO$_4$ along the (a) [−0.33564 0.5 −0.0868], (b) [0.33564 0.5 0.0868], and (c) [0 0 1] axes. The tilt system is $a$–$b$–$c$. The numbers denote the tilt angles. The tilt angles along the [−0.33564 0.5 −0.0868], [0.33564 0.5 0.0868] and [0 0 1] axes were estimated to be 5.5, 5.5 and 4.2°, respectively, averaging two angles shown in the figures.
The average thermal expansion coefficients of 3 and 8 mol% YSZ between 20 and 1000°C were reported as $1.08 \times 10^{-5}$ and $4.5 \times 10^{-5}$, respectively.

Fig. 6. Arrhenius plots of total electrical conductivities $\sigma_{\text{total}}$ of BaNdInO$_4$, BaErInO$_4$, BaYInO$_4$, and BaSmInO$_4$ in air.

Fig. 7. Arrhenius plots of oxide-ion conductivities $\sigma_{\text{ion}}$ of BaNdInO$_4$, BaNd$_{0.9}$Sr$_{0.1}$InO$_{3.95}$, Ba$_{1.1}$Nd$_{0.9}$InO$_{3.95}$, BaNd$_{0.8}$Ca$_{0.2}$InO$_{3.9}$, and BaNdIn$_{0.8}$Ti$_{0.2}$O$_{4.1}$. The $\sigma_{\text{ion}}$ were measured in reduced atmosphere for BaNdInO$_4$, BaNd$_{0.9}$Sr$_{0.1}$InO$_{3.95}$, Ba$_{1.1}$Nd$_{0.9}$InO$_{3.95}$, and BaNd$_{0.8}$Ca$_{0.2}$InO$_{3.9}$. The $\sigma_{\text{ion}}$ of BaNdIn$_{0.8}$Ti$_{0.2}$O$_{4.1}$ was calculated multiplying the oxide-ion transport number by total electrical conductivity measured in air. See the details in the literature.
3. Improvement of oxide-ion conductivity of BaNdInO₄ by cation doping

3.1 BaNd₀.₉Sr₀.₁InO₃.₉₅ and Ba₁₁Nd₀.₉InO₃.₉₅

Aliovalent cation doping can increase the oxide-ion conductivity. As shown in Fig. 7, the oxide-ion conductivities of Ba₁₁Nd₀.₉InO₃.₉₅ and BaNd₀.₉Sr₀.₁InO₃.₉₅ were higher than that of the basic material BaNdInO₄. The activation energies for oxide-ion conduction were 0.8₆₃ (eV) for Ba₁₁Nd₀.₉InO₃.₉₅ and 0.₇₉₅ (10) eV for BaNd₀.₉Sr₀.₁InO₃.₉₅, which were lower than that of BaNdInO₄ [0.₉₁(₄) eV]. Using the activation energies for oxide-ion conduction, the apparent carrier concentrations were found to have larger contributions to the increase of oxide-ion conductivities compared to the mobility of oxide ion.⁴₅,⁵₆ The existence of oxygen vacancies in the crystal structures of Ba₁₁Nd₀.₉InO₃.₉₅ and BaNd₀.₉Sr₀.₁InO₃.₉₅ were experimentally confirmed by the crystal structure analyses of the single-crystal X-ray and neutron powder diffraction data.⁴₅,⁵₆ There were no vacancy cavities in BaNd₀.₉Sr₀.₁InO₃.₉₅ and Ba₁₁Nd₀.₉InO₃.₉₅.⁴₅,⁵₆ The doped Sr and excess Ba cations existed at the Nd site in BaNd₀.₉Sr₀.₁InO₃.₉₅ and Ba₁₁Nd₀.₉InO₃.₉₅, respectively.⁴₅,⁵₆ Rietveld analyses of neutron-diffraction data indicated that BaNd₀.₉Sr₀.₁InO₃.₉₅ and Ba₁₁Nd₀.₉InO₃.₉₅ have the P₂₁/c BaNdO₄-type structure from room temperature to 8₀₀°C.⁴₅,⁵₆ In both compositions, the lattice parameters a, b and c at higher temperatures were higher, while the β angle at higher temperatures was lower compared with those at room temperature as well as BaNdInO₄. The average thermal expansion coefficients (TECs) of BaNd₀.₉Sr₀.₁InO₃.₉₅ between 2₄ and 8₀₀°C were αₐ = 1.₂₃₄ (10) × 1₀⁻⁵ K⁻¹, α₆ = 1.₃₇₃ (10) × 1₀⁻⁵ K⁻¹, α₇ = 0.₇₂₄ (10) × 1₀⁻⁵ K⁻¹, α₈ = 3.₇₃₇ (10) × 1₀⁻⁵ K⁻¹, and α₉ = 1.₀₆₂ (10) × 1₀⁻⁵ K⁻¹.⁵₆ The average TECs of Ba₁₁Nd₀.₉InO₃.₉₅ between 2₇ and 8₀₀°C were αₐ = 1.₄₇₂ (10) × 1₀⁻⁵ K⁻¹, α₆ = 0.₉₆₃ (10) × 1₀⁻⁵ K⁻¹, α₇ = 0.₅₀₃ (10) × 1₀⁻⁵ K⁻¹, α₈ = 3.₅₃₇ (10) × 1₀⁻⁵ K⁻¹, and α₉ = 1.₁₁₂ (10) × 1₀⁻⁵ K⁻¹.⁴₅ Thus, BaNd₀.₉Sr₀.₁InO₃.₉₅ and Ba₁₁Nd₀.₉InO₃.₉₅ exhibit anisotropic thermal expansions: αₐ > α₆ > α₇ > α₈, as well as BaNdInO₄.

3.2 BaNd₀.₈Ca₀.₂InO₃.₉

Yang et al.⁵₈ reported that BaNd₀.₈Ca₀.₂InO₃.₉ exhibited higher oxide-ion conductivities (Fig. 7) and lower activation energy for oxide-ion conduction 0.₇₀₂ (2) eV than BaNd₀.₉Sr₀.₁InO₃.₉₅. The higher oxide-ion conductivity of BaNd₀.₈Ca₀.₂InO₃.₉ than BaNd₀.₉Sr₀.₁InO₃.₉₅ and Ba₁₁Nd₀.₉InO₃.₉₅ is attributable to the higher carrier (oxygen vacancy) concentration and lower activation energy. The higher solubility limit of M = Ca in BaNd₁₋ₓMₓInO₄₋₂ (xₐ ≥ 0.₂)⁵₈ compared to those xₐ = 0.₁₁ for M = Ba⁴₅ and 0.₁ < xₐ < 0.₂ for M = Sr⁵₆ might enable the formation of solid solution of x = 0.₂ with higher carrier concentration for M = Ca. The inequality of the solubility limits xₐ > xₐ > xₐ can be ascribed to that in the size mismatch, |r(Ca) − r(Nd)| < |r(Sr) − r(Nd)| < |r(Ba) − r(Nd)| = 0.₀₁₄ < 0.₁₆₄ < 0.₃₃₄ Å. The inequality of the activation energy for oxide-ion conduction, Eᵣ = [0.₇₀(₂) eV] for BaNd₁₋ₓSrₓInO₃.₉₅ < Eᵣ = [0.₇₉₅(₁₀) eV] for BaNd₁₋ₓSrₓInO₃.₉₅ and Eᵣ = [0.₈₆₃(₃) eV] for Ba₁₁Nd₀.₉InO₃.₉₅ is also attributable to that of the size mismatch.

3.3 BaNd₁₋ₓTiₓO₄₋₅

Ishihara et al.⁵₉ reported the P(₂) dependencies of the electrical conductivities of BaNd₁₋ₓMₓO₃₋₄ (M = Mg, Ce, Ga, Cr, Nb, Zr, Ta, Ti, Si, and Sn). Here δ is the content of oxygen vacancies or excess oxygens, but they did not determine the δ values.⁵₉ Among these compositions, BaNd₁₋ₓSrₓO₄₋₅ showed the highest oxide-ion conductivity. They examined the electrical properties of BaNd₁₋ₓSrₓO₄₋₅ (x = 0.₁, 0.₂, 0.₂₅, 0.₃). Oxide-ion conduction in BaNd₁₋ₓSrₓO₄₋₅ was confirmed by the measurements of oxide-ion transport number. BaNd₁₋ₓSrₓO₄₋₅ showed the highest oxide-ion conductivity among the BaNdInO₄-based materials (Fig. 7). Ishihara et al. described the possibility of the interstitial oxygen ions in the rock-salt block of BaNd₁₋ₓSrₓO₄₋₅, however, further investigations are necessary due to the following reasons. (i) There is no direct evidence for the interstitial oxygen through neutron-diffraction and single-crystal X-ray diffraction analyses. (ii) In BaNdInO₄-type structure there is no rock-salt block, but A rare earth oxide unit [Fig. 3(a)]. (iii) There could be an influence of impurity phases such as Ba₂In₂O₅ and Ba₂In₂₋₂Ti₂O₄₋₅, which were confirmed in the BaNd₁₋ₓSrₓO₄₋₅ sample synthesized by our group. Ba₂In₂O₅ and Ba₂In₂₋₂Ti₂O₄₋₅ exhibit high oxide-ion conductivities.⁶₀ Thus, to solve these issues in the future, it is required to analyze the precise crystal structure and to measure the oxide-ion conductivity of impurity-free BaNd₁₋ₓTiₓO₄₋₅ samples.

4. Oxide-ion migration paths in BaNdInO₄ and its solid solutions

Oxide-ion migration paths in BaNdInO₄ and its solid solutions were investigated using the bond-valence method of our group,⁴₅,⁵₆ and using the static lattice simulations and molecular dynamics by Yang et al.⁵₈ Oxygen vacancy migrations were assumed in all cases. All the results suggested two-dimensional oxide-ion migrations in the A rare earth oxide (Nd,Ba)₂O₅ unit on the bc plane in BaNdInO₄ and its solid solutions. Figure 8 shows the bond-valence-based energy (BVE) landscape of a test oxide ion for the refined crystal structure of Ba₁₁Nd₀.₉InO₃.₉₅ at 2₄°C.⁴₅ BVE isosurfaces around O₁ and O₂ sites are more mobile than O₁ and O₂.⁵₈ The molecular dynamics simulations also supported that the oxide ions at the O₃ and O₄ sites are more mobile than O₁ and O₂.⁵₈ The activation energies for the oxide-ion conduction in Ba₁₁Nd₀.₉InO₃.₉₅ and BaNd₁₋ₓSrₓO₄₋₅ were lower than...
that of BaNdInO₄. Thus, the increase of mobility by cation substitution also contributes to the increase of oxide-ion conductivity of BaNdInO₄, although the increase of the carrier (oxygen vacancy) concentration has larger contributions. Lower energy barriers for oxide-ion migration in Ba₁.₁Nd₀.₉InO₃.₉₅ and BaNdₙ₀.₉Sr₀.₁InO₃.₉₅ were confirmed in the BVE landscapes, which are attributable to the larger bottleneck sizes in Ba₁.₁Nd₀.₉InO₃.₉₅ and BaNd₀.₉Sr₀.₁InO₃.₉₅ compared to BaNdInO₄.⁴⁵,⁵⁶)

5. New ABCO₄ materials having similar chemical formulae with BaNdInO₄

BaRS rêScO₄ (R = Nd, Eu, Y, Yb) and SrYbInO₄ having similar chemical formulae with BaNdInO₄ were reported after the discovery of BaNdInO₄. In 2016, Cochran et al. discovered new materials BaReScO₄ (R = Nd, Eu, Y, Yb).⁶⁴) BaYScO₄ and BaYbScO₄ have the monoclinic P₂₁/c BaNdInO₄-type structure. BaNdScO₄ and BaEuScO₄ crystallize into the space group Cmcm, which is a supergroup of P₂₁/c and has a higher symmetry than P₂₁/c for BaNdInO₄. Here, we call the crystal structure of Cmcm BaNdScO₄ and BaEuScO₄ as BaNdScO₄-type structure. The P₂₁/c BaNdInO₄-type structure is a distorted structure of the Cmcm BaNdScO₄-type structure. There is no tilting of ScO₆ octahedron in Cmcm BaNdScO₄-type structure. BaRScO₄ (R = Nd and Eu), while a P₂₁/c BaNdInO₄-type oxide has out-of-phase tilting of octahedron (Fig. 4). The tolerance factor t for the A₃B₁₁/₄CO₄ perovskite unit is defined as t = [(3r(A) + r(B))/4 + r(O)]/√2[2(r(C) + r(O))] for BaNdInO₄— and BaNdScO₄-type ABCO₄. Here, the ionic radii for the coordination numbers of eleven for A = Ba, seven for B = R, and six for C (= In or Sc) and O are used. The tolerance factors of BaNdScO₄ and BaEuScO₄ are higher and closer to unity than those of BaNdInO₄, BaYInO₄ and BaYbInO₄ (P₂₁/c) (Fig. 2). Thus, BaNdScO₄ and BaEuScO₄ have higher symmetry Cmcm compared with P₂₁/c BaNdInO₄, BaYInO₄ and BaYbInO₄.

We have discovered a new material SrYbInO₄.³²) SrYbInO₄ is the first example of pure oxide-ion conductor with CaFe₂O₄-type structure (Fig. 1).³²) The crystal structure of SrYbInO₄ consists of Sr and two types of double octahedra, B₂O₁₀ and C₂O₁₀. Here, B and C are Yb₀.₅₇₄(²)In₀.₄₂₆(²) and In₀.₅₇₄(²)Yb₀.₄₂₆(²), respectively, indicating partial Yb/In occupational disorder. Both B₂O₁₀ and C₂O₁₀ double octahedra form infinite columns along the b axis. The BVE landscape of a test oxide ion indicates one-dimensional diffusion of oxide ions along the edges of double-octahedra in the b direction.

In this brief review, we have described the discovery and development of BaNdInO₄ and several ABCO₄ materials (Figs. 1 and 2). Further investigations of ABCO₄ compositions and BaNdInO₄ related materials will lead to the development of the ceramic materials and ionic conductors.

Acknowledgments We would like to express special thanks to Mr. M. Shiraiwa, Mr. Y. Esaki, Ms. C. Saito, Dr. K. Omoto, the co-authors of the cited works and the staff of the neutron and synchrotron X-ray diffractometers and facilities. Part of this work was supported by a Grant-in-Aid for Scientific Research (KAKENHI, Nos. JP24850009, JP24226016, JP24246107, JP25630365, JP15H02291, JP26870190, JP16H00884, JP16H06293, JP16H06440, JP16H06438, JP16K21724, JP17H06222) from the Ministry of Education, Culture, Sports, Science and Technology of Japan, and Murata Science Foundation. The neutron diffraction measurements were performed with the approval (JPARC: proposal Nos. 2012B0217, 2013A0136, 2013B0100, 2013B0178, 2013B0198, 2014A0011, 2014B0233, 2014A0011, 2015A0146, 2015A0190, 2015A0249, 2016A0175, 2017A0053, 2017A0111, 2017L1300; ANSTO: Proposal Nos. P2696, DB2638, M12673, P3209, P3648, P4008, P4501, P4682, P4943, PP5198; HANARO: Proposal Nos. NB-HRPD/2013-00026, 27, 2014-0071, and 72). The synchrotron experiments were performed as projects approved by the Photon Factory of KEK (Proposal Nos. 2011G185, 2013G216, 2013G053, 2014G508, 2015G047, 2016G644, 2017G168).
and by the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal Nos. 2012B1696, 2013B1718, 2014A1510, 2014B1660, 2014B1922, 2015B1596, 2015A1674, 2015B1901, 2016A1616). Travel costs were partially supported by Institute for Solid State Physics, The University of Tokyo (proposal Nos. 12725, 13679, 14643, 15617, 16604, and 16595), Japan Atomic Energy Agency, Tokai, Japan.

Reference
1) J. C. Boivin and G. Mairesse, Chem. Mater., 10, 2870–2888 (1998).
2) M. Yashima, J. Ceram. Soc. Jpn., 117, 1055–1059 (2009).
3) C. Sun, R. Hui and J. Roller, J. Solid State Electr., 14, 1125–1144 (2010).
4) J. A. Kilner and M. Burriel, Catal. Today, 253, 3–19 (2015).
5) M. Yashima, Solid State Ionics, 179, 797–803 (2008).
6) H. L. Tuller, Solid State Ionics, 94, 63–74 (1997).
7) S. A. Kramer and H. L. Tuller, Solid State Ionics, 82, 15–23 (1995).
8) W. Uno, K. Fujii, E. Niwa, S. Torii, P. Miao, T. Kamiyama and M. Yashima, J. Ceram. Soc. Jpn., 126, 341–345 (2018).
9) T. Ishihara, H. Matsuda and Y. Takita, J. Am. Chem. Soc., 116, 3801–3803 (1994).
10) T. Ishihara, J. Tabuchi, S. Ishikawa, J. Yan, M. Enoki and H. Matsumoto, Solid State Ionics, 177, 1949–1953 (2006).
11) A. S. Bhalha, R. Guo and R. Roy, Mater. Res. Innov., 4, 3–26 (2000).
12) R. E. Schaak and T. E. Mallouk, Chem. Mater., 14, 1455–1471 (2002).
13) S. Stolen, E. Bakken and C. E. Mohn, Phys. Chem. Chem. Phys., 8, 429–447 (2006).
14) V. V. Kharton, A. P. Viskup, E. N. Naumovich and F. M. B. Marques, J. Mater. Chem., 9, 2623–2629 (1999).
15) S. Miyoshi, T. Furuno, O. Sangoanruang, H. Matsumoto and T. Ishihara, J. Electrochem. Soc., 154, B57–B62 (2007).
16) T. Ishihara, K. Nakashima, S. Okada, M. Enoki and H. Matsumoto, Solid State Ionics, 179, 1367–1371 (2008).
17) M. Yashima, M. Enoki, T. Wakita, R. Ali, Y. Matsushita, F. Izumi and T. Ishihara, J. Am. Chem. Soc., 130, 2762–2763 (2008).
18) M. Yashima, N. Sirikanda and T. Ishihara, J. Am. Chem. Soc., 132, 2385–2392 (2010).
19) M. Yashima, H. Yamada, S. Niu, P. J. Zajdel, C. Dickinson, J. B. Claridge, L. Jantsky and M. J. Rosseinsky, Nat. Mater., 7, 498–504 (2008).
20) C. Tealdi, P. Mustarelli and M. S. Islam, Adv. Funct. Mater., 20, 3874–3880 (2010).
21) S. Nakayama and M. Sakamoto, J. Eur. Ceram. Soc., 18, 1413–1418 (1998).
52) S. G. Ebbinghaus, *Acta Crystallogr. C*, 61, i96–i98 (2005).
53) S. Riegg, A. Reller and S. G. Ebbinghaus, *J. Solid State Chem.*, 188, 17–25 (2012).
54) M. Yashima, K. Fujii, K. Omoto, Y. Esaki and C. Saito, Perovskite related compound, US9656878B2 (2017).
55) M. Yashima, K. Fujii, K. Omoto, Y. Esaki and C. Saito, Perovskite related compound, JP2015-63438, (2018).
56) K. Fujii, M. Shiraiwa, Y. Esaki, M. Yashima, S. J. Kim and S. Lee, *J. Mater. Chem. A*, 3, 11985–11990 (2015).
57) I. Yasuda and M. Hishinuma, *Electrochemistry*, 68, 526–531 (2000).
58) X. Yang, S. Liu, F. Lu, J. Xu and X. Kuang, *J. Phys. Chem. C*, 120, 6416–6426 (2016).
59) T. Ishihara, Y. Yan, T. Sakai and S. Ida, *Solid State Ionics*, 288, 262–265 (2016).
60) V. Jayaraman, A. Magrez, M. Caldes, O. Joubert, M. Ganne, Y. Pifferaud and L. Brohan, *Solid State Ionics*, 170, 17–24 (2004).
61) S. Adams, *Solid State Ionics*, 136–137, 1351–1361 (2000).
62) M. Sale and M. Avdeev, *J. Appl. Crystallogr.*, 45, 1054–1056 (2012).
63) M. Avdeev, M. Sale, S. Adams and R. P. Rao, *Solid State Ionics*, 225, 43–46 (2012).
64) A. K. Cochrane, M. Telfer, C. A. L. Dixon, W. Zhang, P. S. Halasyamani, E. Bousquet and P. Lightfoot, *Chem. Commun.*, 52, 10980–10983 (2016).

Kotaro Fujii is an assistant professor of Department of Chemistry, School of Science, Tokyo Institute of Technology. He earned Bachelor (2004), Master (2006), and Doctor (2009) degrees from Tokyo Institute of Technology. After working for School of Chemistry, Cardiff University (2009–2010) and Tokyo Institute of Technology (2010–2012), he moved to the present position. He earned Seiichi Tejima Doctoral Dissertation Award (Tokyo Institute of Technology) in 2010, and CrSJ Young Scientist Award (Crystallographic Society of Japan) in 2014. He is specialized in chemical crystallography of organic and inorganic materials.