Change of octahedral tilting by topochemical anion insertion

D. Kato[A]

[A]Kyoto Univ.

A common strategy for inducing ferroelectric distortion is to utilize a second-order Jahn－Teller (SOJT) distortion to break the inversion symmetry. However, d^0 (e.g. Ti^{4+} in $BaTiO_3$) and ns^2 (e.g. Bi^{3+} in $BiFeO_3$) is necessary and restrict available element. Recently, it has been demonstrated that ferroelectricity can be induced in layered perovskite-type structures by a new mechanism originating from octahedral rotation [1, 2]. In particular, it has been demonstrated that $n = 2$ Ruddlesden-Popper (RP) oxides with the composition of $A_3B_2O_7$ (Fig 1, left) show a linear relationship between the tolerance factor and ferroelectric transition temperature, indicating its high designability. In the $n = 2$ RP-type structure, the tolerance factor has been controlled by substituting the A- and B-site cations. [2] On the other hand, although there have been some recent attempts at anion (O^{2-}) substitution [3, 4], a systematic understanding of the relationship between anion substitution and octahedral rotation is limited. In this context, we have attempted to F^-/H^- exchange with O^{2-} to control octahedral tilting.

Topochemical F^-/H^- exchange in $n = 2$ (RP) oxides was carried out in Kyoto university. CaH_2 and PVFF were used for hydridation and fluorination, respectively. Laboratory XRD demonstrated the large expansion of c axis, indicating insertion of F^-/H^- into the inter-layer interstitial site (Fig 2, right). Because it is difficult to determine the position of light element using XRD, ND is necessary for these compounds to discuss its octahedral rotations.

Neutron diffraction measurement is performed in JRR-3 at HERES. Compared with ideal RP structure with $a_p \times b_p \times c$ lattice parameters ($a_p \sim b_p \sim 4$ Å, $c \sim 20$ Å), the patterns of both oxyhydride and oxyfluoride can be indexed using $\sqrt{2}a_p \times \sqrt{2}b_p \times c$ superlattice, which was difficult to be observed using synchrotron X-ray diffraction, indicating the presence of octahedral tilting as with oxide starting materials. In addition, we found changes of reflection condition, indicating the change of octahedral tilting after anion insertion. The detailed structural refinement is on-going.

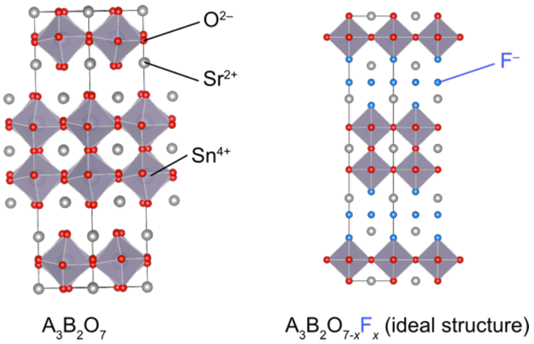

Fig. 1. The crystal structure of ferroelectric $n = 2$ RP oxides (left) and ideal structure obtained by anion exchange in our study (right).

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[3] Zhang, R., *et al., Chem. Mater.* **2016**, 28 (22), 8399-8406.

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