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## 論 文 要 約

Organic-inorganic hybrid perovskites have been explored by utilizing the diversity of organic ions. Organic cations incorporated into inorganic crystals act as spacers that separate the inorganic framework, enabling the formation of perovskite derivatives with diverse crystal structures. The monovalent organic anion, thiocyanate ion, can serve as a useful tool to control the structure by directly bonded to the inorganic framework. This thesis focused on unveiling the role of thiocyanate ion in inorganic crystals and utilizing it as a tool for defect generation in a perovskite lattice. Inspired by the anisotropic bonding nature of the thiocyanate ion towards lead ions, this study proposed a strategy for controlling the crystal structure of perovskites by employing it as a bond-terminating agent to cleave the inorganic framework. This thesis reported the synthesis, structures, properties, and functionalities of the layered perovskite containing thiocyanate anion and defect-ordered perovskites stabilized by thiocyanate ion.

In Chapter 2, I report the temperature-induced structural phase transition of  $(MA)_2PbI_{2-x}Br_x(SCN)_2$  ( $0 \leq x \leq 1.2$ ). The first-order structural transition in  $(MA)_2PbI_2(SCN)_2$  can be attributed to dynamic disorder of molecular ions, similar to the melting transition in the layered perovskites with alkylammonium chains. The transition temperature becomes lower and broadened with Br substitution. These changes can be explained by the strength of hydrogen bonds between  $MA^+$  and  $SCN^-$ . The decomposition temperature also decreases with Br substitution due to weakening of interlayer bonding. Thus, tuning the interlayer bonding leads to tuning the stability of layered hybrid perovskites. The photophysical properties of  $(MA)_2PbI_2(SCN)_2$  were also reported that the fast decay component of transient photocurrent significantly decreases with the transition due to random distortion of the perovskite layer derived from disordering of molecular ions. This study reveals the temperature behavior of the crystal structure and physical properties of organic-inorganic hybrid compounds containing  $SCN^-$ .

In Chapter 3, I report thiocyanate-stabilized new perovskite derivative  $FA_6Pb_4I_{13.5}(SCN)_{0.5}$  ( $\alpha'$ -phase) with ordered columnar defects in  $\alpha$ -FAPbI<sub>3</sub> perovskite.  $\alpha$ -FAPbI<sub>3</sub> ( $FA^+ = CH(NH_2)_2^+$ ) with a cubic perovskite structure is promising for solar cell applications. However,  $\alpha$ -FAPbI<sub>3</sub> is metastable at room temperature and transforms to the  $\delta$ -phase at a certain period at room temperature. The newly identified  $FA_6Pb_4I_{13.5}(SCN)_{0.5}$  possesses a superstructure based on the perovskite structure represented as  $\sqrt{5}a_p \times \sqrt{5}a_p \times a_p$  tetragonal unit cell ( $a_p$ : cell parameter of primitive perovskite cell). The optical band gap is  $\sim 2.0$  eV, and it is stable at room temperature in a dry atmosphere. Furthermore, the presence of the  $\alpha'$ -phase in a mixed sample with the  $\delta$ -phase drastically reduces the  $\delta$ -to- $\alpha$  transition temperature upon heating, suggesting the reduction of the nucleation energy of the  $\alpha$ -phase or thermodynamic stabilization of the  $\alpha$ -phase through epitaxy. The defect-ordered pattern in the  $\alpha'$ -phase forms a coincidence-site lattice at the twinned boundary of the single crystals, thus hinting at an epitaxy- or strain-based mechanism of  $\alpha$ -phase formation and/or stabilization. This study presents a new strategy to generate defect-ordering in halide perovskites and provided insight into stabilizing  $\alpha$ -FAPbI<sub>3</sub> by pseudo-halide anion and grain-boundary engineering.

In Chapter 4, a new defect-ordered perovskite  $FA_4Pb_2I_{7.5}(SCN)_{0.5}$  with columnar defect ordering is reported. The defects are arranged along the  $(110)_p$  planes to the perovskite lattice, forming a layered perovskite structure with  $3\sqrt{2}a_p \times \sqrt{2}a_p \times a_p$  superstructure based on FAPbI<sub>3</sub> perovskite. Here, the thiocyanate ion substituted at the iodine site

acts as a Pb-I bond termination and creates columnar defect orderings. Together with  $\text{FA}_6\text{Pb}_4\text{I}_{13.5}(\text{SCN})_{0.5}$ , they are members of the  $\text{FA}_{n+1}\text{Pb}_n\text{I}_{3n-1.5}(\text{SCN})_{0.5}$  structural family with columnar defects, the first homologous series of defect-ordered hybrid perovskites. As the ratio of SCN to Pb increases, the amount of defect increases and the band gap becomes larger. I also show an application of the defect-ordered perovskite for the photovoltaic cell as a buffer layer stabilizing  $\alpha$ -FAPbI<sub>3</sub>. This study introduces a new strategy for defect engineering in organic-inorganic hybrid perovskite compounds by an analogy to the defect-ordered perovskite oxides.

In Chapter 5, a new one-dimensional defect-ordered perovskite homologue was synthesized. Columnar defect-ordering with a defect concentration of 1/2 is alternately arranged within the perovskite lattice, forming a 2-fold superstructure. This compound can be organized as a member of the defect-ordered homologous series. The absorption and emission wavelengths change depending on the value of  $n$ . This study paves the way for extended dimensional reduction of defect-ordering within a perovskite lattice from three-dimensional to one-dimensional frameworks, enabling the tuning their properties.

In conclusion, this thesis demonstrated a new strategy for controlling the crystal structure of organic-inorganic hybrid perovskites using molecular anions and revealed how these anions play a role in the inorganic lattice. My approach, focusing on the anisotropic bonding nature of the thiocyanate ion, enabled the discovery of a new perovskite homologous series based on defect-ordering.