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論文題目	Synthesis, Anion Ordering, and Properties of Mixed-anion Hydrides （複合アニオン水素化物の合成、アニオン秩序、および性質）		
Hydrides, compounds where hydrogen exists as a negatively charged anion (H^-), have attracted significant attention as key materials for next-generation energy devices, catalysis, and other advanced functional materials. The hydride ion (H^-) itself has unique properties, such as high polarizability, strong reducing ability, large ionic size, and the absence of p orbitals, distinguishing it from other anionic species. However, its thermal lability and propensity to form covalent bonds often hinder compositional tuning and structural control, thereby limiting broader exploitation of its chemical and physical potential. To address these challenges, the incorporation of additional anionic species has led to the development of mixed-anion hydrides, such as oxyhydrides (containing both H^- and O^{2-}). These materials offer expanded platforms for manipulating chemical and physical properties beyond those of single-anion hydrides, even giving rise to unprecedented functionalities, such as ionic conductors, heterogenous catalysts and supports, superconductors, magnetic materials, hydrogen storage materials, photoluminescent materials, and photochromic materials. This makes mixed-anion hydrides a highly promising but largely unexplored frontier in solid-state chemistry and anion chemistry. In contrast to cation order, which has been extensively investigated and is known to critically influence chemical and physical properties, anion order remains less understood. Fully ordered anions on long-range (and short-range) scales are often observed in mixed-anion compounds with significant anionic differences like charge, ionic radii, electronegativity, and polarizability, particularly in layered compounds with alternating stacks of different anion layers. Between the limits of fully ordered and fully disordered anions lies correlated anion disorder, where local-scale ordering exists within globally disordered frameworks. Although various ordered and disordered anion structures have been observed, reports on controlling anion arrangements within a given composition—such as anion order–disorder transitions—are much rarer. Moreover, the influence of such anion arrangements on material properties remains poorly understood, highlighting a significant knowledge gap in solid-state chemistry and anion engineering. In <i>Chapter 1</i>, the author explored the induction of anion ordering in anion-disordered hydride-fluorides by applying external pressure. Hydride-fluorides, composed of H^- and F^- with the same charge and similar ionic sizes, typically exhibit anion disorder. The high-pressure structures of alkaline earth metal hydride-fluorides ($A\text{HF}$s) ($A = \text{Ca}, \text{Sr}, \text{and Ba}$) were investigated up to 8 GPa. While $A\text{HF}$s adopt a fluorite-type structure ($Fm\bar{3}m$) at ambient pressure without anion ordering, pressurization leads to the formation of a PbCl_2-type (cotunnite-type) structure ($Pnma$) with partially H^-/F^- anion ordering. In contrast to PbCl_2-type LaHO and LaOF whose anions are fully ordered, the partially H^-/F^- ordered in PbCl_2-type SrHF and BaHF have a preferential occupation of H^- at square-pyramidal sites (vs. tetrahedral sites). First-principles calculations partially support this preferential anion occupation and suggest occupation switching at higher pressure. These results provide a strategy for controlling anion ordering and local structure in mixed-anion hydrides by creating different internal factors (i.e., coordination numbers) induced by external factors (i.e., pressure).			

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In <i>Chapter 2</i>, the author successfully realized a pressure-induced H^-/O^{2-} order–disorder transition in $\text{Sr}_2\text{CuO}_2\text{Cl}_2$-type layered perovskite $\text{Sr}_2\text{LiHOCl}_2$. Oxyhydrides, composed of O^{2-} and H^- with a small charge difference and similar ionic sizes, can exhibit diverse anion order/disorder behaviors. By controlling these behaviors, interesting anion order–disorder transitions can be achieved. While cation order–disorder transitions have been extensively investigated because of their decisive impact on chemical and physical properties, anion order–disorder transitions remain rare and largely unexplored. When synthesized at ambient and low pressures (≤ 2 GPa), $\text{Sr}_2\text{LiHOCl}_2$ is isostructural to orthorhombic $\text{Eu}_2\text{LiHOCl}_2$ (<i>Cmcm</i>) with a H^-/O^{2-} order at the equatorial sites. However, applying a higher pressure (5 GPa) during synthesis causes the equatorial anions to be disordered, leading to a tetragonal symmetry (<i>I4/mmm</i>) with a loss of the superstructure. The structural analysis revealed that, in the ambient pressure phase, HLi_2Sr_4 and OLi_2Sr_4 octahedra have distinct sizes to stabilize otherwise underbonded oxide ions, which is less important at the higher pressure. Given the abundant layer-type anion order in perovskite-based oxyhydrides (La_2LiHO_3), the incorporation of additional anions (chloride) broadens the frontiers of anion ordering patterns and control. This research leverages different internal factors (compressibility) induced by external factors (pressure), offering potential benefits such as enhanced ionic conduction in solids. In <i>Chapter 3</i>, the author explores the synthesis and physical properties of new lanthanide nitride-hydrides, $\text{Ln}_2\text{H}_{3-x}\text{N}$ ($\text{Ln} = \text{La}, \text{Nd}, \text{and Gd}, P\text{--}3m1$). Nitrides-hydrides, composed of N^{3-} and H^- with a large charge difference yet similar ionic sizes, are generally expected to exhibit only anion ordering. However, the claim of near-ambient superconductivity in nitrogen-doped lutetium hydride ($\text{LuH}_{3-\delta}\text{N}_\delta$, <i>Fm</i>–$3m$) with disordered anions, although later retracted by Nature, has sparked significant interest in the potential of nitride-hydrides for novel properties. Different from previous studies with unclear compositions and (disordered) structures via high-pressure gas-solid reactions, an anion-layered-ordered structure with substantial hydrogen vacancies ($x \sim 0.7$) in $\text{La}_2\text{H}_{2.3}\text{N}$ was obtained via a high-pressure solid-state reaction. $\text{La}_2\text{H}_{2.3}\text{N}$ exhibits metallic behavior at ambient pressure due to electron donation by hydrogen vacancies, but unexpectedly, a semiconducting behavior was found at 70 GPa without an apparent structural change, suggesting a potential subtle changes in H concentrations near a quantum critical point. Our findings highlight the novel electronic properties and structural versatility achievable in mixed-anion hydrides, underscoring the importance of further investigations into their potential applications in advanced materials, such as lowering the required pressure for (super)hydride superconductors. In <i>Chapter 4</i>, the first hydroxide-borohydride to the author’s knowledge, $\text{Li}_2(\text{OH})(\text{BH}_4)$, featuring $\text{O}\text{--}\text{H}\cdots\text{H}\text{--}\text{B}$ dihydrogen bonds, was synthesized. The coexistence of proton (H^+) and hydride (H^-) ions in solid-state materials is highly challenging, due to their strong tendency to form hydrogen gas. This obstacle can be overcome by introducing covalent bonding to form complex ions. As expected, hydroxide-borohydrides, despite having the same charge, exhibit anion ordering due to the significant size difference between OH^- and BH_4^-. Thus, this study on hydroxide-borohydride introduces a new system of H^+/H^--coexisting materials for hydrogen storage and lithium-ion electrolytes, offering advantages over the previously studied amine–borane derivatives.			