SYNTHESIS OF NOVEL METAL HALIDES AND THEIR STRUCTURE-PROPERTY RELATIONS(Digest_要約)

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学位論文の要約

題目　SYNTHESIS OF NOVEL METAL HALIDES AND THEIR STRUCTURE-PROPERTY RELATIONS
（新規金属ハライドの合成とその構造物性相関）

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Metal halides are an interesting class of crystalline materials because they show diverse chemical and physical properties. Due to the multifunctional properties, they are also attracting much attention for energy applications such as solar cells and all-solid Li-ion batteries. In this thesis, Ag-Bi-I solid solution system which can be used for absorbers in solar cells and antiperovskite Li-OH-X (X = Cl and Br) compounds used for solid electrolytes in all-solid Li-ion batteries were studied. The detailed crystal structures and the properties were presented and their relations were discussed.

1. Structure-property relations in Ag-Bi-I compounds: potential Pb-free absorbers in solar cells

$Ag_{2-3x}Bi_xI_2$ ($0.33 \le x \le 0.60$) compounds were prepared and their phase-pure compositions, crystal structures, and optical and electrical properties were investigated. Ag-rich compositions stabilize a rhombohedral phase and phase-pure samples are obtained with $x = 0.45 – 0.48$. The rhombohedral phase crystalizes in a $CdCl_2$-type crystal structure with the space group $R\bar{3}m$. The Ag and Bi ions fully occupy the octahedral sites and additional Ag ions occupy the interstitial sites between the octahedral layers. Bi-rich compositions, on the other hand, stabilize a cubic phase and phase-pure samples are obtained with $x = 0.52 – 0.57$. The cubic phase crystalizes in a defect-spinel-type crystal structure with the space group $Fd\bar{3}m$. The Ag and Bi ions partially occupy the octahedral sites, producing cation vacancies at the sites. Both rhombohedral and cubic crystal structures have similar cubic close-packed I-ion arrangements, and thus the small variation in the Ag/Bi composition causes the structure difference. Both the rhombohedral and the spinel-type cubic phases show suitable band-gap energies for potential absorbers in solar cells. The rhombohedral compounds exhibit shallower valence band energies, larger indirect band gap energies, and higher electrical conductivity with lower activation energy than the cubic compounds. The difference in the physical properties are resulted from the structural defects, the additional Ag ions in the rhombohedral phase and the cation deficiencies in the cubic phase.

2. Crystal structures and ionic conductivity in Li_2OHX (X = Cl, Br) antiperovskites

Antiperovskite structure Li_2OHX (X = Cl, Br) compounds were prepared, and their crystal structures and ionic conducting properties were examined. Li_2OHCl shows an orthorhombic structure at room temperature and changes to a cubic one between 27 and 37 °C. Li_2OHBr, in contrast, shows a cubic structure and no structural phase transition is observed. The crystal structures of both cubic Li_2OHCl and Li_2OHBr are an antiperovskite type with the space group $Pm\bar{3}m$ and include Li-ion vacancies. The orthorhombic Li_2OHCl crystalizes with the space group $Pmc2_1$ and the ordered Li-ion vacancies make this structure anisotropic and two-dimensional. The distinct structural property between the Cl- and Br-compounds can be explained by the difference in size mismatch of the crystal structure. The significant size mismatch in Li_2OHCl induces the Li-ion vacancy ordering and the structural phase transition. While the cubic phase shows high Li-ion conductivity, the orthorhombic one exhibits significantly reduced conductivity because of its distorted two-dimensional structure.

3. Ruddlesden-Popper phases of lithium-hydroxide-halide antiperovskites: two dimensional Li-ion conductors

Novel Ruddlesden-Popper (RP) lithium-hydroxide-halide antiperovskite phases $LiX(Li_{3-p}OH_pX)_n$ with X = Br and Cl, n = 1, 2, and 3, and p = 0, 0.5, and 1, were explored. The n = 2 RP phase $LiBr(Li_2OHBr)_2$ is stabilized with a tetragonal structure with the space group $I4/mmm$. The crystal structure consists of double antiperovskite Li_2OHBr layers intercalated with rock-salt type LiBr layers. Li-ion vacancies are introduced selectively to the antiperovskite layers but not in the rock-salt type LiBr layers. Cl-containing compounds, in contrast, cannot be crystallized with the RP phases due to the structural mismatch between the antiperovskite layers and the rock-salt type LiCl layers. The RP $LiBr(Li_2OHBr)_2$ exhibits ionic conductivity of 1.27×10^{-7} S/cm at 30 °C with the activation energy of 0.57 eV. The rigid rock-salt type LiBr layers contribute less in Li-ion hopping and thus the Li-ion conduction occurs through the Li-ion vacancies within the antiperovskite layers, resulting in the two-dimensional ion conduction.