学 位 論 文 内 容 の 要 旨

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学 位 論 文 題 名

Structure and Electronic Properties of Layered Organic-Inorganic Hybrid Metal-Halide Perovskites Based on Tin, Lead and Copper

（スズ、鉛、銅を用いた有機 - 無機ハイブリッド金属ハロゲン化物層状ペロブスカイトの構造と物性）

In this study, the structure and electronic properties of metal-halide hybrid organic-inorganic perovskites (Fig.1) were investigated. In Chapter 1, the structure and properties of metal-halide perovskites were briefly discussed giving special focus to the highly conducting tin-iodide system. For the tin-iodide system, it had been determined that the origin of high conductivity was due to spontaneous hole doping in the material (Fig. 2). This study on tin-iodide perovskite system was previously conducted in the same laboratory and was used as basis for comparison with the present results. Were it not for its chemical instability (high redox activity of iodide), tin iodide based perovskites would be the perfect soluble semiconductor especially since it also showed high carrier mobility and electronic tunability. It was therefore imperative to study other metal-halide based perovskites with potentially better chemical stability.

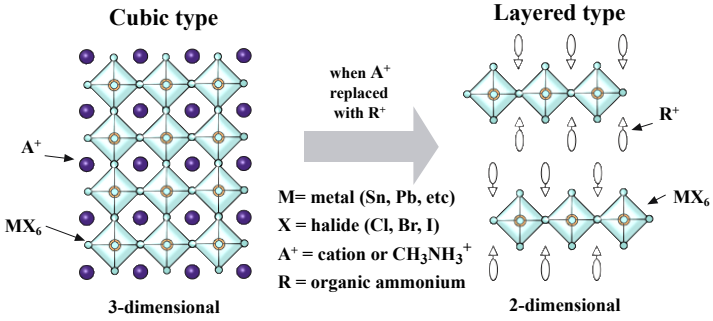

Figure 1. Organic-inorganic metal-halide perovskites with Cubic type (left) and layered type (right) shown.

The bromide counterpart seemed like a good candidate since the redox activity of bromide are lower than iodides. Thus in Chapter 2, layered tin and lead bromide based perovskites were investigated. Although, structurally similar to layered tin iodide based perovskites, these compounds showed considerably lower conductivities. Hole doping with M^{IV} was therefore attempted to enhance the conductivity. The results of the hole doping showed two orders of magnitude increase in conductivity for the doped compounds. Moreover, the activation energy of these compounds was found to be significantly lower than the optical band gap, this led to the conclusion that similarly for tin iodide system, tin bromide and lead bromide compounds also behaved as extrinsic semiconductors. It was therefore hypothesized that doping of M^{IV} leads to increase $(MBr_4)^{(2-x)-}$ species which lead to an enhancement of conductivity through the formation of acceptor levels above the valence band (Fig. 3). Although the conductivity of tin bromide and lead bromide perovskites were far from that of tin iodide perovskite, these materials can be considered alternatives to tin iodide since these are undoubtedly more chemically stable.

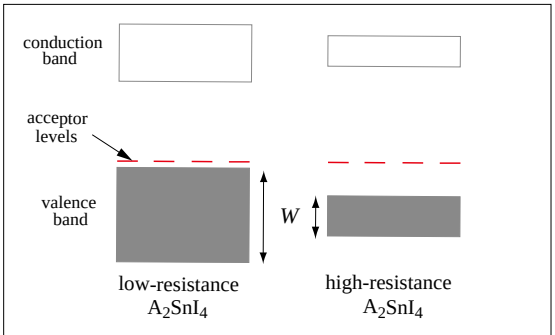

Figure 2. Schematic representation of formation of acceptor levels for tin-iodide perovskite

In Chapter 3, the study was extended to include transition metal based layered copper-halide perovskites. These copper-halide perovskites were easily processed in solution. Furthermore, the optical band gap of about 1.12 eV seemed similar to the highly conducting tin iodide based perovskites. In addition, before this study there were no reports on the study of the electronic properties of these materials. The structure of copper-halide based perovskites showed the similar organic-inorganic layering but these compounds showed *z* elongation type of Jahn-Teller distortion within the metal-halide octahedra. This led to the elongation of two of the copper-halide bonds, which were then arranged orthogonally relative to the adjacent CuX_6 octahedra (Fig.4). Within the copper-halide layer, this distortion of the bonds can be viewed as practically each individual $[CuX_4]^{2-}$ units are independent of each other. The highly resistive property was corroborated by the observed band structure of these compounds, with very narrow band widths since there was virtually no inter $[CuX_4]^{2-}$ interaction. The charge transport probably occurs via electron hopping between $[CuX_4]^{2-}$ units. Attempts at carrier doping with Cu^{I} were done since the reduction process of Cu^{II} to Cu^{I} could lead to an increase in electron carriers in these compounds. The results showed a small increase in conductivity for the doped compounds, however virtually no change in activation energy was observed and thus probably artificial doping could increase the concentration however the hopping process remained unaffected. Furthermore, the magnetic properties of these copper-halide based perovskites were also investigated. Thermal variation of molar magnetic susceptibility and temperature clearly shows ferromagnetic behavior. This is similar to previously reported copper-halide perovskites. This magnetic behavior was determined to be due to the orthogonal arrangement of the semicoordinate copper-halide bonds within the inorganic layer, which leads to a ferromagnetic superexchange interaction.

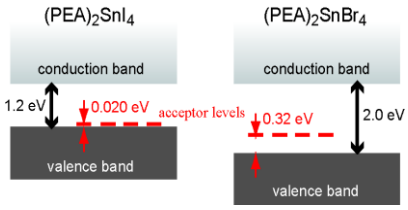

Figure 3. Schematic representation of the formation of acceptor levels for $(PEA)_2SnI_4$ and $(PEA)_2SnBr_4$ perovskite systems (where PEA=Phenylammonium)

In Chapter 4, due to the recent interest in metal-halide perovskites especially in the field of high efficiency solar cells, this study was also extended to the investigation on the photovoltaic properties of metal-halide perovskites. Although, the photovoltaic mechanism is not yet well understood, the basic structure was based on the perovskite layers acting as the absorbing (active layer), which would generate electrons and holes carriers upon the absorption of photons. Two types of perovskite system for solar cell application were conceptualized, type 1 was based on the cubic $CH_3NH_3SnI_2Br$ mixed halide tin based perovskite and type 2 was based on double layers of perovskites using $CH_3NH_3PbI_3$ and $CH_3NH_3SnI_3$. The initial results showed photovoltaic effect for both types of configuration of the perovskite solar cells. Although, both types of configuration showed relatively low device efficiency, it was nonetheless important since it showed photovoltaic properties for both types of perovskite compounds.

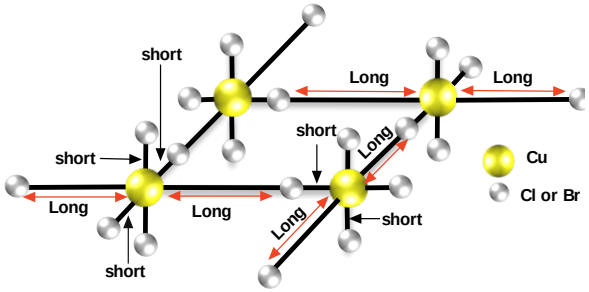

Figure 4. Antiferrodistortive arrangement of copper-halide bonds within the extended 2D octahedral layer of copper-halide based perovskites.

In Chapter 5, a summary and concluding remarks of this study is given.