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Structure and charge transport properties of tin-iodide perovskites

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Introduction

Tin and iodide can be employed to construct a series of perovskites; the composition is denoted by $A_2(Me-NH_3)_{n-1}Sn_nI_{3n+1}A_2Sn^{II}I_4$, where A=organic ammonium cation, and the number of the layer (n) can be adjusted. The compounds with $n = 1$ are primarily semiconductors with wide energy gaps ($E_g > 1$ eV), but the electrical conductivity was found to be tunable by doping treatment (Sn(II) is partly replaced with Sn(IV)). Therefore, relatively high conductivity of as-grown A_2SnI_4 was interpreted by spontaneous hole-doping [1]. It should be noted that even $Me-NH_3SnI_3$ ($n=\infty$) is also a semiconductor as shown by recent theoretical calculations, though the pressed powder sample showed metallic conductivity [2]. Therefore, the high conductivity of cubic perovskite $Me-NH_3SnI_3$ is also considered to be due to spontaneous hole doping. In the present study, doping effects on the transport properties in the double layer Sn-I perovskite, $(PhEtNH_3)_2(Me-NH_3)Sn_2I_7$ (n=2) and cubic perovskite $Me-NH_3SnI_3$ ($n=\infty$) have been investigated.

Experiment

The double layer perovskite of $(PhEtNH_3)_2(Me-NH_3)Sn_2I_7$ was prepared by adding anhydrous ethanol to stoichiometric amounts of purified SnI_2, $PhEtNH_3I$, and $Me-NH_3I$ under nitrogen atmosphere, followed by slow cooling of the solution (from 65 ˚C to 5 ˚C at a rate of 2 ˚C h^{-1}). Black aggregated platelet crystals with size as large as $1.5 \times 1.5 \times 1$ mm^3 were obtained. The same method was employed to prepare $Me-NH_3SnI_3$ (black and block crystals with size $1.2 \times 1.2 \times 1$ mm^3) by just using stoichiometric SnI_2 and $Me-NH_3I$.

Results and analysis

According to the single crystal X-ray diffraction at 153 K, $(PhEtNH_3)_2(Me-NH_3)Sn_2I_7$ has the space group of P-1 with cell parameters: $a = 8.683$, $b = 8.659$, $c = 22.409$ Å, $\alpha = 93.74$, $\beta = 97.42$, $\gamma = 90.24˚$. Although the diffraction data of the crystal were not good enough, its double-layer feature was confirmed as shown in Fig. 1. The $PhEtNH_3^+$ ions are located

between the tin-iodide perovskite double layers while Me-NH$_3^+$ ions are embedded into the intra-layer. The band calculation based from the inorganic framework indicates its semiconducting electronic structure with an approximate E_g of 1.0 eV. The primary electrical conductivity experiment (four-probe method) indicates that (PhEtNH$_3$)$_2$(Me-NH$_3$)Sn$_2$I$_7$ has the resistivity of 30-75 $\Omega\cdot$ cm at 300K, comparable with that of the single layer perovskite (PhEtNH$_3$)$_2$SnI$_4$ [1].

In the following work, we will further carry out the electrical conductivity measurements of the single crystals of these two perovskites and their artificial Sn(IV)-doping, and investigate the relationship between the conductivity and the doping level.
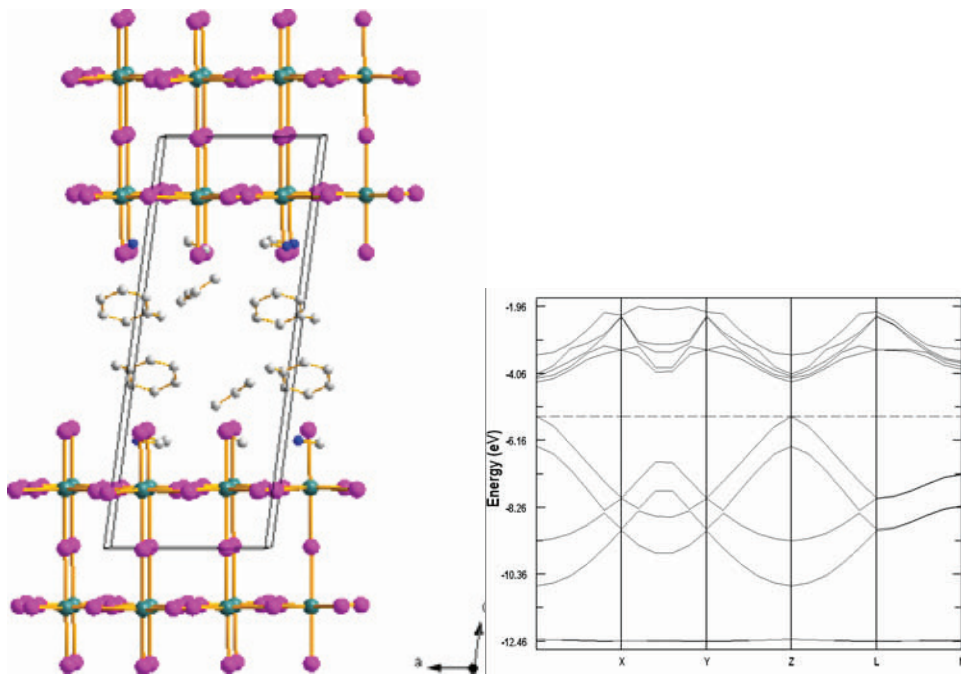

Fig.1 double layer configuration (left) of the (PhEtNH$_3$)$_2$(Me-NH$_3$)Sn$_2$I$_7$ (the PhEtNH$_3^+$ cations are not well resolved) and its band structure (right).

References

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