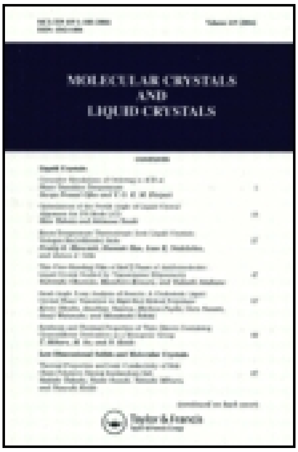

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Structures and Electrical Properties of the Layered Tin-Iodide Perovskite Compounds with Various Organic Cations

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Abstract A series of the layered tin-iodide perovskite compounds with a general formula $(RNH_3)_2SnI_4$ have been prepared. The RNH_3 species adopted are normal-alkyl ammonium, cyclic-alkylammonium, and phenylethylammonium, and as the $(RNH_3)_2$ unit alkyldiammonium is adopted. The obtained single crystals have been subjected to X-ray diffraction experiments. The structures of the SnI_4^{2-} layers, their bond lengths and angles, are widely varied depending on the cationic organic species between the perovskite layers.

Keywords layered perovskite; organic-inorganic compound; tin-iodide; crystal structure

INTRODUCTION

In contrast to most of the metal-halide perovskites, which are generally electrically insulating, tin-halide perovskites form an interesting class of conducting materials. The typical compound is $ASnI_3$ ($A = CH_3NH_3^+$), which is reported to be highly conducting[1]. Partial replacement of A in this cubic perovskite by monoalkyl ammonium (RNH_3) produces a series of the layered perovskites, $(RNH_3)_2A_{n-1}Sn_nI_{3n+1}$. In the family

$(C_4H_9NH_3)_2A_{n-1}Sn_nI_{3n+1}$, for example, conducting "n"-layer-thick perovskite-based anion slabs alternate with much wider band gap butylammonium cation bilayers, leading to multiple quantum well structures with controllable well width. The conductivity of these compounds has been reported to depend on the "n"-layer thickness; from the powder mesurements the conductivity is changed from semiconducting to metal-like as increasing the layer thickness ("n")[2]. On the other hand, $(C_6H_5C_2H_4NH_3)_2SnI_4$ was reported to show much different (metal-like) temperature dependence of the conductivity, although "n" equals to 1[3].

We paid attention to the structure of these compounds, since there seems to be a relation between the structure of the perovskite sheet and the conductivity. In this study, we synthesized the "n=1" compounds [$(RNH_3)_2SnI_4$] using various ammonium cations, then carried out their X-ray structure analyses. The RNH_3 or $(RNH_3)_2$ species are $CH_3(CH_2)_xNH_3$, cyclopentylammonium, phenylethylammonium, and alkyldiammonium (H_3N-$(CH_2)_x$-NH_3), which are abbreviated to Cx, CyPe, PhEt, and CxDi, respectively. The formulae of the last compounds are $[H_3N(CH_2)_xNH_3]SnI_4$, which are similier to the lead-iodide analogue $[H_3N(CH_2)_6NH_3]PbI_4$[4].

EXPERIMENTAL

To synthesize $(RNH_3)_2SnI_4$ or $[H_3N(CH_2)_xNH_3]SnI_4$, tin(II) iodide was first dissolved in concentrated (57% by weight) aqueous HI, then at 80°C, the solution was added to the aqueous HI solution containing monoalkylamine (Cx, CyPe or PhEt) or alkyldiamine (CxDi). Crystals of these compounds were grown from the slowly cooled solutions. Both SnI_2 and amines were mixed stoichiometrically for the desired compounds. All procedures were carried out under a nitrogen atomosphere. Suitable single crystals for X-ray diffraction experiments were selected and coated by epoxy adhesive to protect from air. Data were collected on a Rigaku RAXIS-RAPID Imaging Plate X-ray diffractometer with graphite-monochromated Mo-Kα radiation.

RESULTS AND DISCUSSION

The crystal structures of the three compounds are shown in FIGUREs 1-3. The orthorhombic unit lattice of $(CyPe)_2SnI_4$ consists of the SnI_4^{2-} perovskite sheets of corner-shared SnI_6 octahedra, which are separated by bilayers of cyclopentylammonium cations. The ammonium group is positionally disorderd and hydrogen/ionic bonding to iodines in the perovskite sheets (FIGURE 1). The relatively weak van der Waals force between the cyclopentyl groups separating the layers provides for a

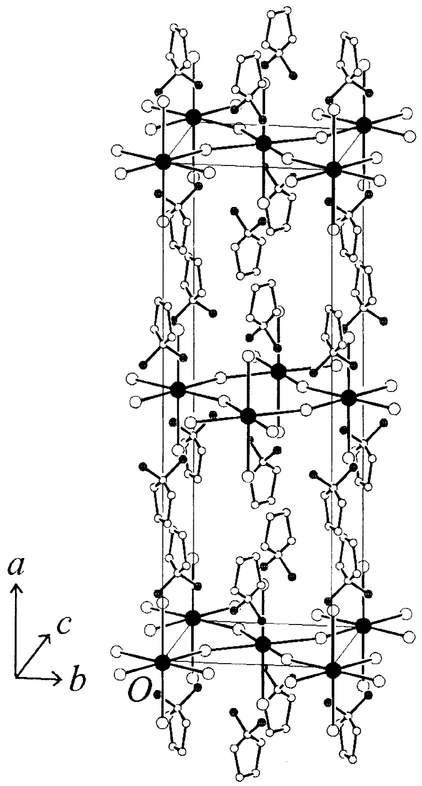

FIGURE 1 Crystal structure of $(CyPe)_2SnI_4$.

highly two-dimensional structure. The framework consisting of tin and equatorial iodine atoms is nearly planar. The bond length of Sn-$I_{equatorial}$ is 3.21 Å, and that of Sn-I_{axial} is 3.17 Å. The bond angle of Sn-$I_{equatrial}$-Sn is 155.5°.

In the monoclinic unit lattice of (C5Di)SnI_4, the Sn-$I_{equatorial}$ plane is considerably distorted; the angle between the SnI_4 least-squares planes is 24.4°. The distance between the two perovskite layers is about 10.2 Å, which is shorter than that in $(CyPe)_2SnI_4$ (~13.3 Å). The bond lengths of Sn-$I_{equatorial}$ are 3.13-3.19 Å, and those of Sn-I_{axial} are 3.07 and 3.23 Å. The bond angles of Sn-$I_{equatrial}$-Sn are 155.1-176.4°. The corrugation of the perovskite layer is also observed for the C4Di, C6Di, and C8Di compounds.

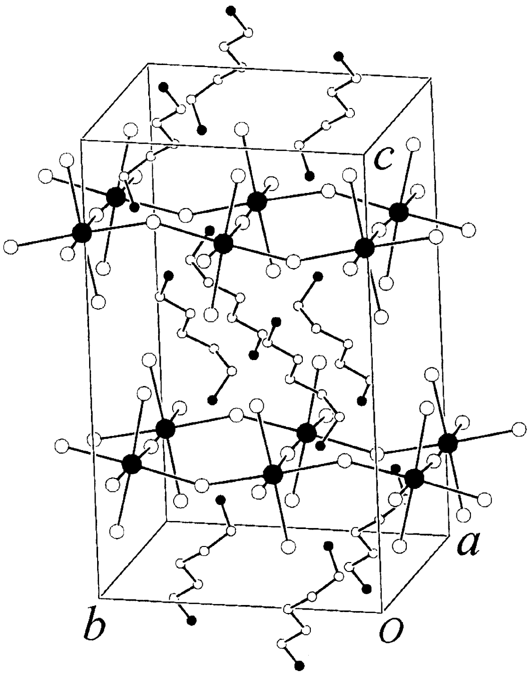

FIGURE 2 Crystal structure of (C5Di)SnI_4.

For (C9Di)SnI_4, it was difficult to determine the structure at room temperature because of heavy disorder of the ammonium cation, and the structure was determined using the data collected at -40°C (there is no structural transition in the temperature range between -40 and 23°C). In the monoclinic structure of this crystal, the $Sn\text{-}I_{equatorial}$ framework is planar compared with C5Di-SnI_4. The angle between the SnI_4 least-squares planes is 2.8°. The distance between the two perovskite layers is about 13.4 Å. The bond length of $Sn\text{-}I_{equatorial}$ is 3.14 Å, and those of $Sn\text{-}I_{axial}$ are 3.12 and 3.26 Å. The bond angle of $Sn\text{-}I_{equatrial}\text{-}Sn$ is 155.9°. Distortion of the perovskite layer is more pronounced in CxDi-

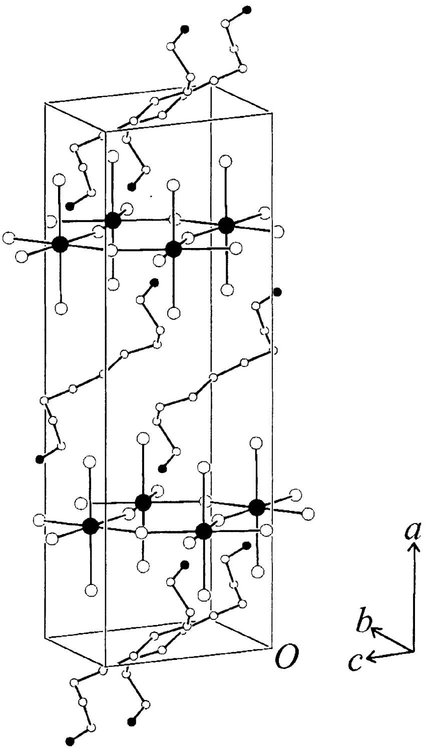

FIGURE 3 Crystal structure of (C9Di)SnI_4. The data were collected at -40°C.

SnI_4 with x=4, 5, 6 and 8, in which the angles between the SnI_4 least-squares planes are 24-28°. The structures of the perovskite layers in $(C6)_2SnI_4$ and $(PhEt)_2SnI_4$[5] are similar to that in $(C9Di)SnI_4$, while those in $(C4)_2SnI_4$[6], $(C5)_2SnI_4$ are similar to that in $(C5Di)SnI_4$.

In conclusion, we have found that the structures of the perovskite layers are notably different with the species of ammonium cations. The $Sn\text{-}I_{equatorial}$ bond lengths change in a range from 3.12 Å to 3.21 Å, and the $Sn\text{-}I_{equatrial}\text{-}Sn$ bond angles from 149.2° to 176.4°. The compounds with short alkyldiammonium cations form "corrugated layers". Moreover, in $(CxDi)SnI_4$, the structure of the perovskite layers may have some correlation with the conformation of alkyldiammonium cations. When x is an odd number (5, or 9), the bond lengths of $Sn\text{-}I_{equatorial}$ are 3.14-3.15 Å, and the bond angles of $Sn\text{-}I_{equatrial}\text{-}Sn$ are 155.9-176.4°. On the other hand, when x is an even number (4, 6, or 8), the bond lengths of $Sn\text{-}I_{equatorial}$ are longer (3.16-3.17 Å), and the bond angles of $Sn\text{-}I_{equatrial}\text{-}Sn$ are smaller (150.4-151.6°) than those of "odd"s. Therefore there may be odd-even-effect to the structure.

These factors may effect the overlap integrals, and may influence the electrical properties in turn. The details of their electrical properties will be published elsewhere.

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