Perovskite Phases

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Synthesis, Single-Crystal Structure and Characterization of $(CH_3NH_3)_2Pb(SCN)_2I_2$

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layered compounds · organic–inorganic hybrid composites · perovskite phases

$CH_3NH_3PbI_3$ ($MAPbI_3$) is an effective material for dye solar cells. Jiang et al. have shown that the partial substitution of I^- by SCN^- results in a new dye with enhanced stability against hydrolysis.[1] They proposed $MAPb(SCN)_2I$ as the active material and reported a structure closely related to the cubic perovskite, as it is known for $MAPbI_3$. However, for a more detailed characterization we considered to investigate single crystals and phase-pure samples. As a first step, the conditions for the deposition of the dye on the photocell as they were described by Jiang et al. were simulated for the growth of single crystals. $Pb(SCN)_2$ was prepared according to Brauer[2] as a single-phase product. Pure MAI was obtained with the method of Poglisch et al.[3] 0.20 g $Pb(SCN)_2$ and 0.15 g MAI were dissolved in 0.6 mL DMF and heated under stirring to 60 °C. Upon cooling and evaporation of DMF black single crystals precipitated from the solution.

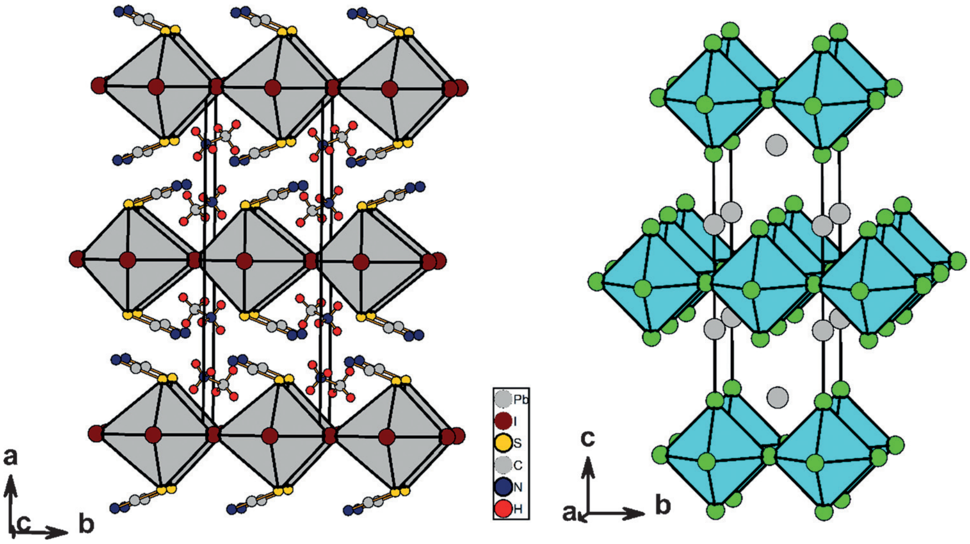

Figure 1. Crystal structures of $(CH_3NH_3)_2Pb(SCN)_2I_2$ (left) and K_2NiF_4 (right).

The single-crystal investigation[4] revealed an orthorhombic unit cell ($a = 18.580(2)$, $b = 6.2668(6)$, $c = 6.4658(6)$ Å). Structure solution and refinement in space group $Pnm2_1$ were performed without difficulties. The compound turned out to be $MA_2Pb(SCN)_2I_2$ with a structure closely related to the K_2NiF_4-type (Figure 1) as indicated by the pseudotetragonal metric. Accordingly, Pb is octahedrally coordinated by four I^- and two S-bonded SCN^- ligands in *trans* position. The $Pb(SCN)_2I_4$ octahedra (Figure S1 in the Supporting Information) are linked to layers through corner-sharing I^- ligands. The MA^+ cations are located between the layers of $Pb(SCN)_2I_2$ octahedra. The polarity of the direction [001] results from the orientation of the MA^+ cations and a slight bent of the SCN^- ligands.

The easy formation of $MA_2Pb(SCN)_2I_2$ and its high stability is supported by the following observation: Grinding of a 1:2 molar mixture of $Pb(SCN)_2$/MAI in an agate mortar yielded a dark red powder. The experimental XRD pattern is in excellent agreement with the pattern calculated from the single-crystal data (Figure S2, Supporting Information). Furthermore, the pattern of $MA_2Pb(SCN)_2I_2$ is in good agreement with the pattern presented by Jiang et al., which was obtained directly from the device. The UV/Vis spectrum (Figure S3, Supporting Information) matches the spectrum published by Jiang et al. and shows a sharp absorption onset at 790 nm in good agreement with the color of the crystal. The fluorescence spectrum (Figure S4, Supporting Information) shows a strong emission at 702 nm and a shoulder at 760 nm. The IR spectrum (Figure S5, Supporting Information) con-

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tains the characteristic features of the CH_3NH_3 cation and the SCN ligand.

The realization of a K_2NiF_4-type structure by $MA_2Pb(SCN)_2I_2$ is not surprising. According to the connectivity of the anions four I^- ligands are in a planar arrangement, while the ligands in *trans* position are terminal.

Jiang et al. communicated EDX (energy-dispersive X-ray analysis) results of active layers of $MAPbI_3$ and „$MAPb(SCN)_2I$“. Besides other elements contained in the underlying material they detected Pb and I, which are only contained in the dyes. The Pb:I ratios were 1:3 and 1:2, respectively. This confirms $MAPbI_3$ and $MA_2Pb(SCN)_2I_2$ as active materials.

Jiang et al. have shown that the electrochemical performance of the SCN^--containing perovskite variant is comparable to $MAPbI_3$ when processed under similar conditions. With $(CH_3NH_3)Pb(SCN)_2I_2$ as the active dye the conclusion is that perovskite variants of the K_2NiF_4-type are also powerful dyes. This extends the range of potential dyes for solar cell applications to a class of perovskite-related structures of the general composition $(AMX_3)_n(AX)_m$. These systems are known as Ruddleson–Popper phases and play a pivotal role in superconducting cuprates ($La_{1-x}Sr_xCuO_4$, YBa_2CuO_3, …). Very recently Kanatzidis et al. reported that 2D perovskites exist in the system $(n\text{-}C_4H_9NH_3)_2(CH_3NH_3)_{n-1}Pb_nI_{3n+1}$ and are suitable as dyes for solar cells.[5]

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[4] Data collection with Bruker APEX II with CCD and microsource, data handling with SAINT, numerical absorption correction with SADABS, structure solution and refinement by direct methods using the SHELXTL program package with anisotropic displacement parameters for all atoms, crystal as twin of inversion. Summary of the crystal data: Dark red platelet ($0.2\times0.1\times0.02\ mm^3$), $Pnm2_1$, $Z=2$, $a=18.580(2)$, $b=6.2668(7)$, $c=6.4658(6)$ Å, ρ(X-ray) $=2.829\ g\,cm^{-3}$, $2\Theta_{max}=50°$, $Mo_{K\alpha1}$, 298 K, 4866 reflections, 2129 unique reflections (2004 observed), $R_{int}=0.022$, $R_{sigma}=0.036$, $\mu=15.55\ mm^{-1}$, min./max. transmission $=0.385/0.746$, full-matrix least-square refinement on F^2, 68 parameters, BASF 0.656(7), $R_1=0.026$, $wR_2=0.060$, $R_1=0.028$, for all reflections, max./min. residual electron density $=+1.36/-1.19\ e\,Å^{-3}$. Atom coordinates, displacement parameters and selected distances can be found in the Supporting information. CCDC 1409175 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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