(CH$_3$NH$_3$)$_2$Pb(SCN)$_2$I$_2$: A More Stable Structural Motif for Hybrid Halide Photovoltaics?

Alex M. Ganose, †‡ Christopher N. Savory, † and David O. Scanlon*†‡

†University College London, Kathleen Lonsdale Materials Chemistry, Department of Chemistry, 20 Gordon Street, London WC1H 0AJ, United Kingdom
‡Diamond Light Source, Ltd., Diamond House, Harwell Science and Innovation Campus, Didcot, Oxfordshire OX11 0DE, United Kingdom

Supporting Information

ABSTRACT: Hybrid halide perovskites have recently emerged as a highly efficient class of light absorbers; however, there are increasing concerns over their long-term stability. Recently, incorporation of SCN$^-$ has been suggested as a novel route to improving stability without negatively impacting performance. Intriguingly, despite crystallizing in a 2D layered structure, (CH$_3$NH$_3$)$_2$Pb(SCN)$_2$I$_2$ (MAPSI) possesses an ideal band gap of 1.53 eV, close to that of the 3D connected champion hybrid perovskite absorber, CH$_3$NH$_3$PbI$_3$ (MAPI). Here, we identify, using hybrid density functional theory, the origin of the smaller than expected band gap of MAPSI through a detailed comparison with the electronic structure of MAPI. Furthermore, assessment of the MAPSI structure reveals that it is thermodynamically stable with respect to phase separation, a likely source of the increased stability reported in experiment.

The past three years have witnessed an explosion of interest into hybrid halide perovskite solar cells.1–3 Power conversion efficiencies (PCEs) have skyrocketed to 20.1%,4 quickly surpassing other third-generation devices such as dye-sensitized solar cells,5 organic photovoltaics,6 and the champion inorganic earth-abundant absorber, Cu$_2$ZnSn(S,Se)$_4$ (CZTSSe).7,8 Currently, the highest performing hybrid perovskite is CH$_3$NH$_3$PbI$_3$ (MAPI), which can be easily solution processed for widespread application with a direct band gap of 1.55 eV, close to that of the 3D connected champion hybrid perovskite absorber, CH$_3$NH$_3$PbI$_3$ (MAPI). Here, we identify, using hybrid density functional theory, the origin of the smaller than expected band gap of MAPSI through a detailed comparison with the electronic structure of MAPI. Furthermore, assessment of the MAPSI structure reveals that it is thermodynamically stable with respect to phase separation, a likely source of the increased stability reported in experiment.

Unfortunately, despite these excellent properties, chemical stability is still a major concern facing hybrid perovskites as they move toward industrial deployment.22–24 Indeed, while suitable encapsulation should reduce decomposition by hydrolisis,22–24 the fundamental long-term stability of the MAPI structure is still a topic of dispute.25 Much effort has been devoted to increasing the stability of MAPI based devices, however, these stable cells generally perform with reduced PCEs of 10–13%.26–28 Preserving high efficiencies while demonstrating increased chemical and thermodynamic stability is therefore a significant challenge facing the hybrid halide perovskite community.29

In the past six months, the substitution of iodine with the pseudohalide ion, SCN$^-$, has been proposed as a novel method for increasing the stability of MAPI based devices.30–33 Chen et al. reported that the incorporation of SCN$^-$ (which has a similar ionic radius to I$^-$) for CH$_3$NH$_3$PbI$_3$ (SCN)$_x$ resulted in larger crystal sizes and fewer trap states than pure MAPI.30 The authors reported a PCE of 11% for planar CH$_3$NH$_3$PbI$_3$ (SCN)$_x$/PC61BM bilayer heterojunction solar cells, finding that 5% SCN$^-$ incorporation was the optimum in the range of 1–10%, and that the CH$_3$NH$_3$PbI$_3$ (SCN)$_x$ films displayed greater stability, higher reproducibility, and lower amounts of hysteresis than similarly prepared MAPI films.34,35 The reason for this extra stability was not elucidated.

Halder et al. subsequently observed that incorporation of SCN$^-$ as a dopant opened up the fundamental band gap versus MAPI by 8 meV, and had a remarkable effect on the photoluminescence response, concluding that SCN$^-$ incorporation is a valuable addition to the hybrid halide family.31

Jiang et al. recently reported that CH$_3$NH$_3$Pb(SCN)$_2$I films crystallized in the perovskite structure, with a band gap of 1.53 eV.32 These CH$_3$NH$_3$Pb(SCN)$_2$I films were found to be much more stable after 4 h in air with 95% humidity compared to MAPI films.36 The reason for this stability, however, is not explained. Overall, the CH$_3$NH$_3$Pb(SCN)$_2$I films displayed an efficiency of 8.3%, with a larger open circuit voltage (0.87 eV versus 0.80 eV), but a smaller fill factor (52 versus 63) than MAPI films.32

Very recently, Daub and Hillebrecht have reported that the reaction of MAI and Pb(SCN)$_2$ results in the formation of (CH$_3$NH$_3$)$_2$Pb(SCN)$_2$I$_2$ (herein denoted MAPSI).33 MAPSI crystallizes in a layered orthorhombic pattern with space group Pnma, in which the Pb is octahedrally coordinated to four axial I$^-$ and two apical (or trans) S-bonded SCN$^-$ ions. The MA
molecules are situated between the layers, resulting in a structure that is similar to the K$_2$NiF$_4$-type structure, as indicated in Figure 1. Daub and Hillebrecht demonstrated that the X-ray diffraction (XRD) pattern for MAPSI is actually an excellent fit for the XRd patterns of the CH$_3$NH$_3$PbI$_3$ films produced by Jiang et al. 33

Intriguingly for a 2D layered inorganic hybrid halide, MAPSI possesses an optical band gap of 1.56 eV, very close to that of quasi-cubic MAPI. 12, 37 Typically, upon moving from a 3D to a 2D connectivity of the Pb-halide octahedra, the band gap opens up, 38, 39 severely affecting solar cell absorber ability. Therefore, an open question remains: why can MAPSI possess a smaller band gap than other 2D hybrid halides?

In this Letter we investigate the fundamental electronic structure of MAPSI using hybrid density functional theory (DFT). We demonstrate: (i) that MAPSI does indeed possess a band gap suitable for PV applications, and explain why this is so via a detailed comparison with the electronic structure of MAPI, and (ii) show that MAPSI should be more stable against decomposition than MAPI. Lastly we speculate on the ability of MAPSI and (ii) show that MAPSI should be more stable against decomposition than MAPI. Lastly we speculate on the ability of MAPSI against those in MAPI reveals an average shift in energy difference stems from the N

| Table 1. Calculated Lattice Parameters of (CH$_3$NH$_3$)$_2$Pb(SCN)$_2$I$_2$  

| Functional | a (Å) | b (Å) | c (Å) | Volume (Å$^3$) |
|------------|-------|-------|-------|----------------|
| PBEsol     | 18.268| 6.230 | 6.475 | 736.917        |
| PBEsol+D3  | 17.657| 6.134 | 6.388 | 691.872        |
| PBE+D3     | 18.323| 6.274 | 6.525 | 746.379        |
| experiment | 18.580| 6.267 | 6.466 | 752.907        |

In all cases, the a parameter is underestimated compared to the experimental structure, indicating that thermal effects may play a role in determining the distance between the layers.

**Electronic Structure.** To test the effect of a-parameter variation on the electronic structure, we calculated the band structures at the experimental (room temperature, RT) and at the Heyd–Scuseria–Ernzerhof hybrid DFT functional 45 with the addition of spin orbit coupling (SOC) to accurately treat known relativistic effects experienced by lead-iodide-based hybrid halides. The shortening of the a parameter shortens the calculated band gap of MAPSI from 1.79 to 1.57 eV (Figure S1 of the Supporting Information), remarkably close to the experimental optical band gap. 33 The partial (ion decomposed) density of states of MAPSI is presented in Figure 2a. It is immediately clear that the valence band maximum (VBM) is dominated by I $p$ states, similar to the electronic structure of MAPI (Figure 2c). The main difference stems from the N $p$ and S $p$ states, which are present ~1 eV below the valence band maximum.

In semiconductors, $d$–$p$ repulsion has been shown to play a role in determining the absolute ionization potential and, as such, the position of the VBM. 31 Comparison of the Pb $d$ states in MAPSI against those in MAPI reveals an average shift in energy of only 0.15 eV, indicating a slight increase in Pb $5d$–$1s$ $p$ repulsion but unlikely to be sufficient to account for the smaller than expected band gap. Instead, the SCN states must act to push up the VBM of MAPSI, maintaining a small band gap despite the layered nature of the system. This is corroborated by analysis of the S–C–N bond lengths, which reveals an increase in the covalent character of the pseudohalide, as evidenced by the shortening of the S–C and lengthening of the C–N bonds in MAPSI ($\tilde{S}$–C = 1.601 eV, C–N = 1.169 eV) when compared to the ionic AgSCN (S–C = 1.783 eV, C–N = 1.144 eV). 52 The SCN therefore plays an active role in bonding, in contrast to other polyanion substituted MAPI structures, 53 which is supported by the charge density isosurfaces presented in Figure 3. Here, it can be seen that the VBM is dominated by Pb 6p/1 5p with a small contribution from the S 3p and N 2p of the SCN, with the CBM dominated by Pb 6p states.

The HSE06+SOC-calculated band gap for the RT MAPSI structure is presented in Figure 2b. The fundamental band gap is 1.57 eV, with the CBM and VBM situated just off the U point (0.0, 0.5, 0.5). There is noticeably no dispersion in the X–S direction, which is to be expected as this spans across the layers in the [100] direction. The calculations indicate that mild relativistic Dresselhaus splitting is present in the lower conduction band, and to a lesser extent in the upper valence band, due to the lack of the inversion symmetry in the MAPSI
structure. We note that similar Dresselhaus splitting has previously been predicted for BF$_4$-substituted MAPI.\textsuperscript{53}

The average effective masses of the VBM and CBM were found to be 0.20 $m_0$ and 0.14 $m_0$, respectively, indicating that both electrons and holes will be mobile in the MAPSI system, although the conductivity should be somewhat anisotropic due to its layered nature. We also tested the effect of SOC on the electronic structure of this system, with the results displayed in Figure S2 of the Supporting Information. Similar to MAPI,\textsuperscript{54,55} the relativistic renormalization of the conduction band is large ($\sim 0.68$ eV), indicating that proper treatment of relativistic effects is of vital importance. It should be noted that many body effects will also likely play a role in this Pb–I based system,\textsuperscript{56,57} although the size of the MAPSI unit cell (50 atoms) means they are currently beyond the scope of this study.

Stability. The chemical stability of MAPI has been the subject of much debate in the past half decade.\textsuperscript{20,21} It has been suggested that moisture or oxygen in the environment causes the poor stability of MAPI fi lms,\textsuperscript{24,36} but recent theoretical analysis suggests that the material is intrinsically thermodynamically unstable with respect to phase separation into PbI$_2$ and CH$_3$NH$_3$I.\textsuperscript{58} To test the stability of MAPSI with regard to decomposition, we have tested two decomposition pathways, with their energetics compared to the decomposition of MAPI:

\begin{equation}
\text{CH}_3\text{NH}_3\text{PbI}_3 \rightarrow \text{CH}_3\text{NH}_3\text{I} + \text{PbI}_2, \\
\Delta_R H = -0.09 \text{ eV}
\end{equation}

\begin{equation}
(\text{CH}_3\text{NH}_3)_2\text{Pb(SCN)}_2\text{I}_2 \rightarrow 2\text{CH}_3\text{NH}_3\text{I} + \text{Pb(SCN)}_2, \\
\Delta_R H = 0.38 \text{ eV}
\end{equation}

Figure 2. (a,c) Ion decomposed partial and total density of states and (b,d) band structure along the high symmetry directions for (CH$_3$NH$_3$)$_2$Pb(SCN)$_2$I$_2$ and CH$_3$NH$_3$PbI$_3$, respectively. In all cases, the HSE06+SOC method was used, and the VBM is set to 0 eV. The valence band and conduction band of panels b and d are denoted by blue and orange, respectively.

Figure 3. Charge density isosurfaces of (a) the VBM and (b) the CBM. Regions of low and high electron density are shown in blue and red, respectively. Pb, I, C, H, N, and S atoms are denoted by dark gray, purple, brown, pink, light gray/blue, and yellow spheres, respectively. The Journal of Physical Chemistry Letters

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We find that the decomposition routes into either CH$_3$NH$_3$I and Pb(SCN)$_2$ (the starting materials in the synthesis of MAPSI) or CH$_3$NH$_3$(SCN) and PbI$_2$ are both positive, indicating that MAPSI does not spontaneously decompose, unlike MAPI, in which it is favorable to decompose to CH$_3$NH$_3$I and PbI$_2$. This is the likely origin of the increased stability reported for materials with SCN incorporation.

We have demonstrated using DFT that MAPSI has an appropriate electronic structure for PV application, displaying a band gap of ~1.57 eV, low effective masses for both holes and electrons, and improved chemical stability against phase separation when compared to MAPI. Experimentally, the addition of MAPSI to MAPI films seems to promote stability, and to be able to maintain reasonable e$\rightarrow$ff, and improved chemical stability against phase separation. These results open up some fundamental questions. As ABX$_3$ perovskite structured MAPI can be electronically tuned by adding of MAPSI to MAPI

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