Electronic Supplementary Information

Enhanced Yield-Mobility Products in Hybrid Halide Ruddlesden–Popper Compounds with Aromatic Ammonium Spacers

Naveen R. Venkatesan,^{ab} Ali Mahdi,^{bc} Brian Barraza,^c Guang Wu,^c Michael L. Chabinyc,^{*ab} and Ram Seshadri^{*abc}

^a Materials Department, University of California, Santa Barbara, CA 93106, United States

- Materials Research Laboratory, University of California, Santa Barbara, CA 93106, United States
- ^c Department of Chemistry and Biochemistry, University of California, Santa Barbara, CA 93106, United States

*Corresponding Authors: <u>mchabinyc@engineering.ucsb.edu</u> seshadri@mrl.ucsb.edu

S1. Single-crystal X-ray diffraction patterns

Single-crystal X-ray diffraction data was collected using a Bruker KAPPA APEX II diffractometer equipped with an APEX II CCD detector utilizing a TRIUMPH monochromator and a Mo-K α X-ray source ($\lambda = 0.71703$ Å). Diffraction images are shown below in Figures S1 and S2.



Figure S1. Sample X-ray diffraction image of (BPEA)₂PbI₄ obtained from grown single-crystals.



Figure S2. Sample X-ray diffraction image of (BPEA)₂(CH₃NH₃)Pb₂I₇ obtained from grown single-crystals.

S2. Observed bond angles and distances in $(BPEA)_2PbI_4$ and $(BPEA)_2(CH_3NH_3)Pb_2I_7$

Structural details of $(BPEA)_2PbI_4$ and $(BPEA)_2(CH_3NH_3)Pb_2I_7$ are tabulated below. Bond distances for the four equatorial and two axial iodides, along with all I-Pb-I and Pb-I-Pb (if applicable) bond angles are presented. For comparison, the bond lengths and angles from $(BA)_2PbI_4$ and $(BA)_2(MA)Pb_2I_7$ are listed in Table S2.¹

	(BPEA) ₂ PbI ₄	(BPEA) ₂ (CH ₃ NH ₃)Pb ₂ I ₇
	Bond Distances	
Pb-I _{axial (1)} (Å)	3.2073(14)	3.131(3)
Pb-I _{axial (2)} (Å)	3.2073(14)	3.2617(12)
Pb-I _{axial (3)} (Å)	N/A	3.2617(12)
Pb-I _{axial (4)} (Å)	N/A	3.131(3)
Pb-I _{equatorial (1)} (Å)	3.108(5)	3.141(4)
Pb-l _{equatorial (2)} (Å)	3.174(5)	3.179(3)
Pb-l _{equatorial (3)} (Å)	3.222(5)	3.191(4)
Pb-I _{equatorial (4)} (Å)	3.154(5)	3.157(4)
	Bond Angles	
I-Pb-I _{axial (1)} (°)	176.4(3)	176.38(9)
I-Pb-I _{axial (2)} (°)	N/A	176.38(9)
I-Pb-I _{equatorial (1)} (°)	179.25(14)	176.31(8)
I-Pb-I _{equatorial (2)} (°)	178.18(16)	176.28(9)
Pb-I-Pb _{axial} (°)	N/A	179.2(3)
Pb-I-Pb _{equatorial} (°)	152.49(15)	154.52(11)

Table S1. Structural details of (BPEA)₂PbI₄ and (BPEA)₂(CH₃NH₃)Pb₂I₇

	(BA) ₂ PbI ₄	(BA) ₂ (CH ₃ NH ₃)Pb ₂ I ₇	
	Bond Distances		
Pb-I _{axial (1)} (Å)	3.201(16)	3.08(3)	
Pb-I _{axial (2)} (Å)	3.213(13)	3.28(3)	
Pb-I _{axial (3)} (Å)	N/A	3.25(3)	
Pb-I _{axial (4)} (Å)	N/A	3.08(3)	
Pb-I _{equatorial (1)} (Å)	3.164(7)	3.171(4)	
Pb-I _{equatorial (2)} (Å)	3.212(8)	3.169(5)	
Pb-I _{equatorial (3)} (Å)	3.191(6)	3.169(5)	
Pb-l _{equatorial (4)} (Å)	3.160(7)	3.171(4)	
	Bond Angles		
I-Pb-I _{axial (1)} (°)	178.6(3)	177.3(3)	
I-Pb-I _{axial (2)} (°)	N/A	177.3(3)	
I-Pb-I _{equatorial (1)} (°)	179.2(5)	175.5(9)	
I-Pb-I _{equatorial (2)} (°)	179.1(5)	175.5(9)	
Pb-I-Pb _{axial} (°)	N/A	165.64(16)	
Pb-I-Pb _{equatorial} (°)	155.1(3)	164.2(10)	

Table S2. Structural details of $(BA)_2PbI_4$ and $(BA)_2(CH_3NH_3)Pb_2I_7$ taken from reference 1.

S3. Qualitative comparison of $(BPEA)_2(CH_3NH_3)Pb_2I_7$ with isotropic and textured XRD simulations

The single-crystal structures of (BPEA)₂PbI₄ and (BPEA)₂(CH₃NH₃)Pb₂I₇ were used to simulate powder diffraction patterns and compared with actual measurements. Figure S3 shows the comparison of (BPEA)₂(CH₃NH₃)Pb₂I₇ to a completely isotropic, untextured simulation of powder diffraction, showing poor agreement (isotropic (BPEA)₂PbI₄ is presented as the simulation in Figure 2 of the main manuscript). When texturing along the layer stacking direction ([010]) is added, the agreement between simulation and experiment is clear.



Figure S3. Powder X-ray diffraction of synthesized powder of (BPEA)₂(CH₃NH₃)Pb₂I₇ compared to simulated diffraction patterns of an isotropic sample and a [010]-textured sample, illustrating structural agreement with the latter.

S4. PXRD of aged powders compared to Pbl₂

The aged (5 weeks in ambient) powders of $(BPEA)_2PbI_4$ and $(BPEA)_2(CH_3NH_3)Pb_2I_7$ were compared to the expected diffraction pattern of PbI_2 to show that there was no material degradation after exposure to ambient conditions.



Figure S4. Powder X-ray diffraction patterns of (BPEA)₂PbI₄ and (BPEA)₂(CH₃NH₃)Pb₂I₇ powders aged for five weeks in ambient conditions, along with simulated diffraction pattern of PbI₂. Comparison with the simulated pattern illustrates no degradation of Ruddlesden–Popper phases into lead iodide.

References

 C. C. Stoumpos, D. H. Cao, D. J. Clark, J. Young, J. M. Rondinelli, J. I. Jang, J. T. Hupp and M. G. Kanatzidis, *Chem. Mater.*, 2016, **28**, 2852–2867.