Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

SUPPORTING INFORMATION

Substitutional doping of hybrid organic-inorganic perovskite crystals for thermoelectrics

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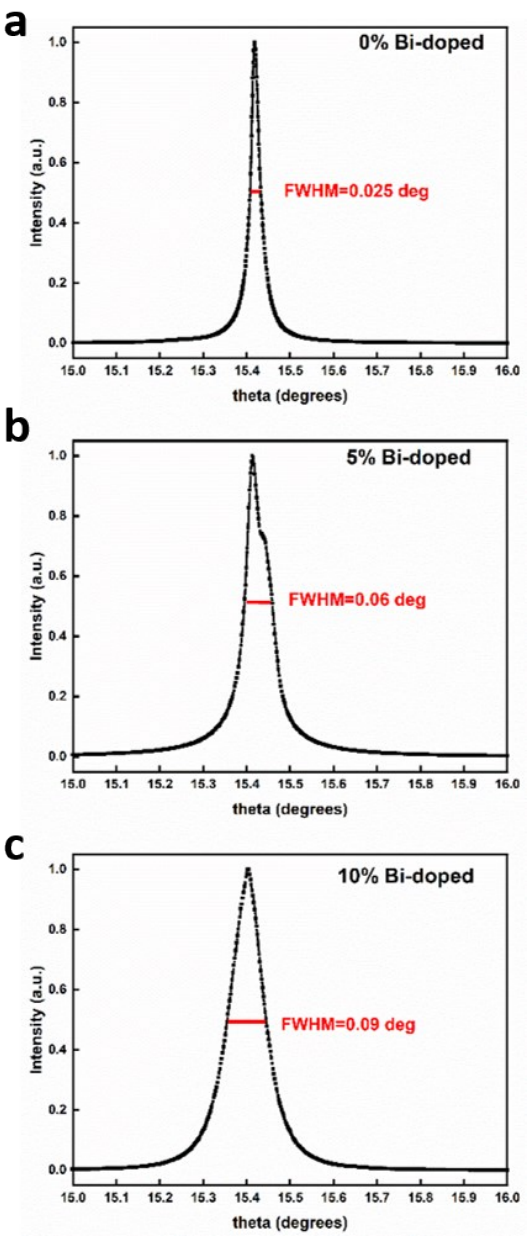


Figure S1: High-resolution XRD rocking curves around the (002) peak at θ =15.4° for 0%, 5% and 10% Bi-doped $MAPbBr_3$ single.

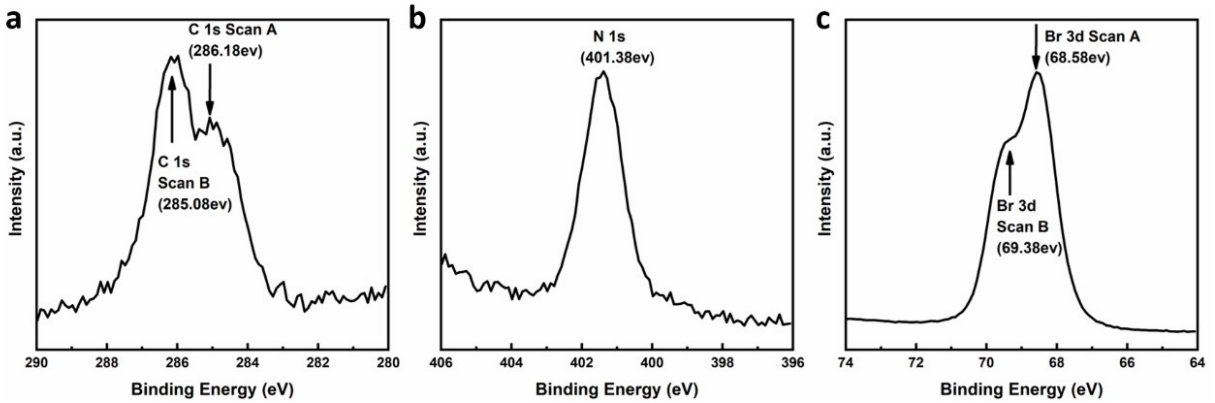


Figure S2: XPS spectra of (a) C 1s**,** (b) N 1s and (c) Br 3d in 15% Bi-doped freshly cleaved $MAPbBr_3$ single crystals.

Table S1: Density of pristine and Bi-doped $MAPbBr_3$ single crystals. The average density and standard deviation are calculated from measurements of 4 samples.

Materials / Density	0% doped	1% doped	5% doped	10% doped	15% doped
Density(g/cm^{-3})	3.665	3.654	3.652	3.657	3.647
Std. Dev.	0.01	0.008	0.013	0.013	0.007

The density (ρ) was determined using Archimedes' principle: $\rho = \frac{mass\ of\ crystal}{displaced\ volume\ of\ fluid}$. We cut and polished the pristine and Bi-doped crystals to a regular cubic size and then measured their volume (v) and mass (m), respectively. For each Bi concentration, we measured four crystals and obtained an average density and its stand deviation.

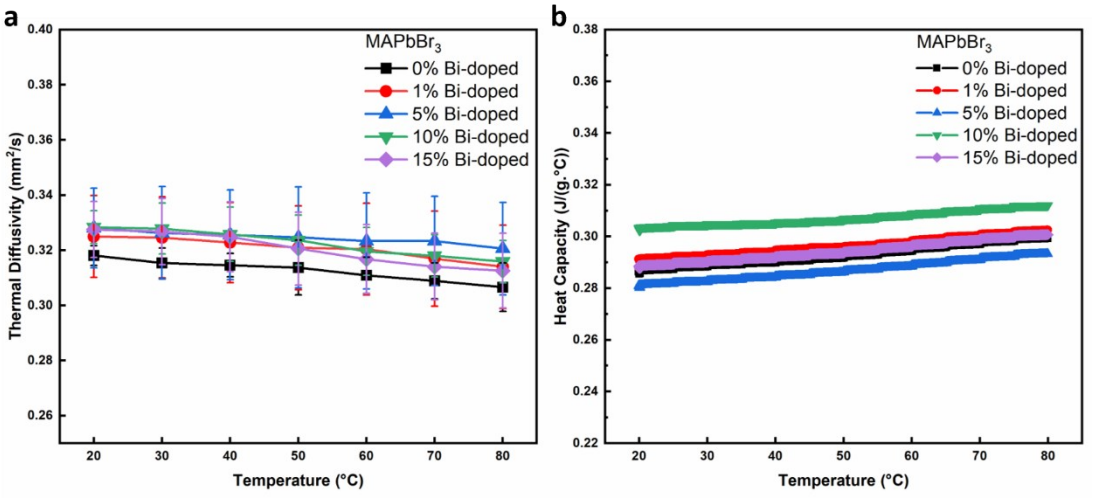


Figure S3: Thermal properties of pristine and Bi-doped $MAPbBr_3$ single crystals. (a) Temperature-dependent thermal diffusivity, *D*. (b) Temperature dependence of heat capacity C_p.

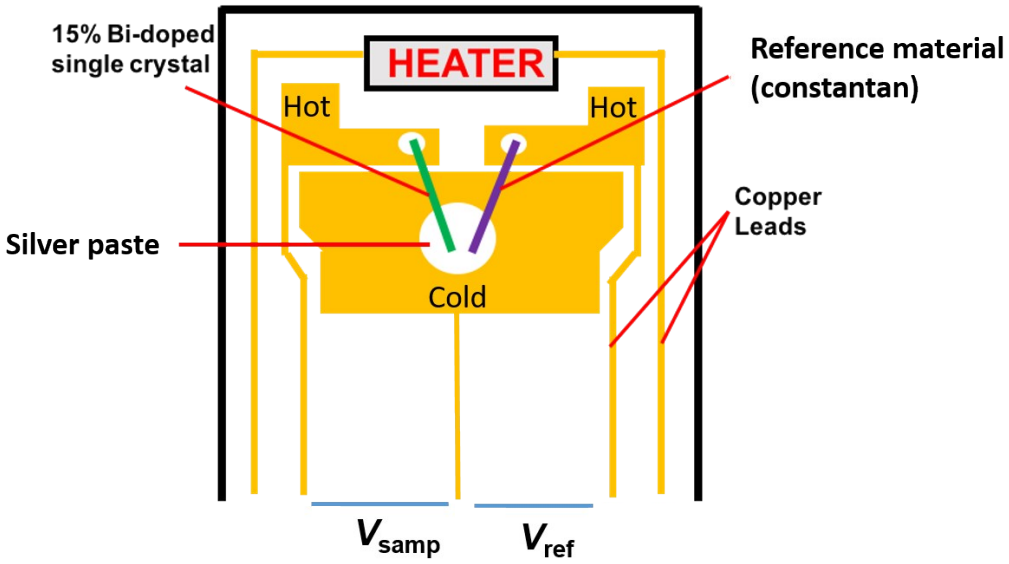


Figure S4: The arrangement of the Bi-doped crystal under investigation and reference material wire relative to the hot- and cold-reservoirs used in the MMR Seebeck Measurement System.

Figure S4 is a schematic of the sample holder of the Seebeck coefficient measurement system. The 15% Bi-doped crystals were cleaved to suitable dimensions and mounted on the holder, along with the constantan reference wire (constantan wire of diameter 300 μm), to the hot- and cold-reservoirs. Silver paste was used to guarantee electrical and thermal contact with the reservoirs. The holder was then mounted on a variable-temperature stage within a vacuum chamber, which provided the stable absolute temperature for the measurement. During the measurement, the on-holder heater provided the approximately one degree temperature difference between hot- and cold-reservoirs.

For a single Seebeck coefficient measurement, the system records V_{samp} and V_{ref} for two values of electrical power supplied to the on-holder heater, P_1 and P_2. The Seebeck coefficient of the sample is given by,

$$S_{samp} = S_{ref}\frac{[V_{samp}(P_1) - V_{samp}(P_2)]}{[V_{ref}(P_1) - V_{ref}(P_2)]}$$

The system is calibrated against a standard temperature variation of S_{ref}. The data points in **Figure 4** of the main text are the average of ten measurements, the error bars are the standard deviation.

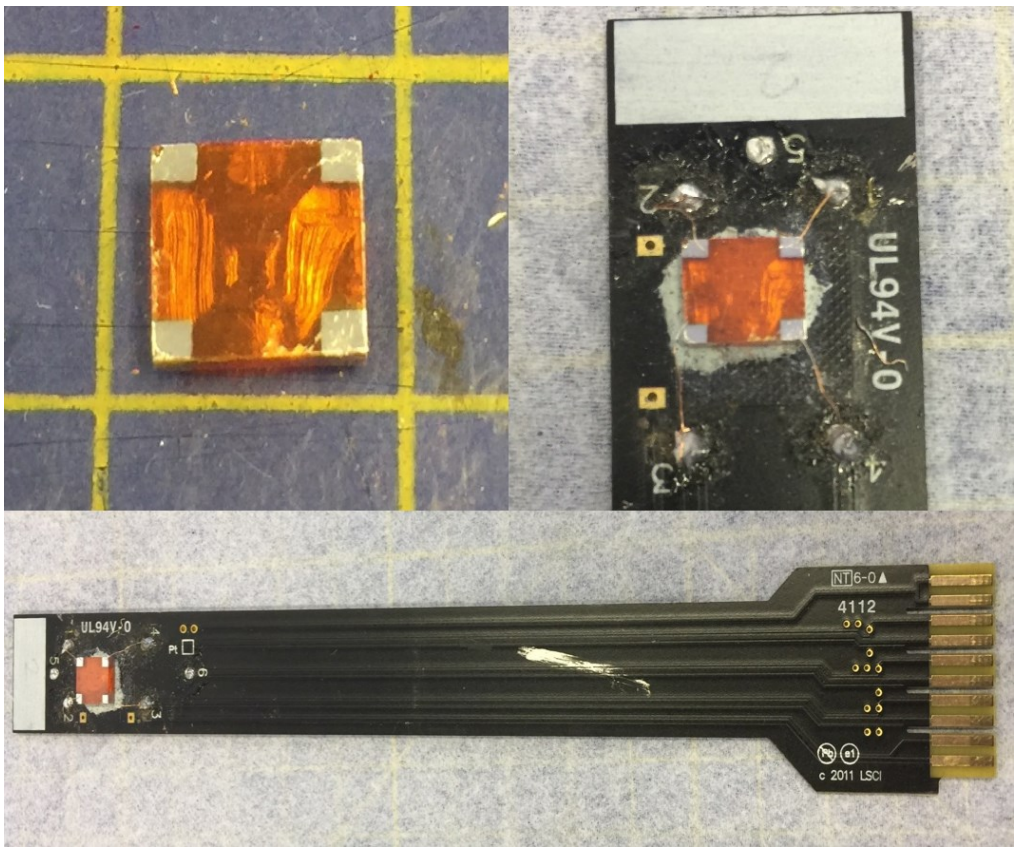


Figure S5: The configuration of Hall Effect sample and stage.

Model 8404 AC/DC Hall Effect Measurement System
(Lake Shore Cryotronics, Inc)

Measured on 11/09/2019

SPECIMEN

Materials: $MAPbBr_3$
Thickness: 1.86 mm

MEASURING CONDITIONS

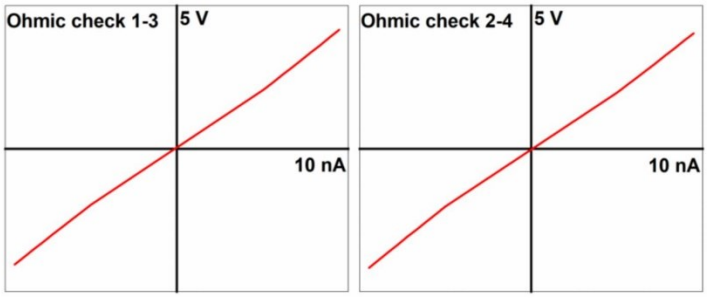
Excitation current: 7 nA
Field: 1.19 T

RESULTS SUMMARY

μ_H [$cm^2/V{\cdot}s$]: $8.15E^{-1}$
n [$1/cm^3$]: $1.19E^{11}$
n_{sheet} [$1/cm^2$]: $2.22E^{10}$
R_H [cm^3/C]: $5.23E^{7}$

R_{Hsheet} [cm^2/C]: $2.81E^{8}$
P [$\Omega{\cdot}cm$]: $6.42E^{7}$
ρ_{sheet} [$\Omega/\square$]: $3.45E^{8}$
V_H [V]: $2.3517E^{-4}$

CONTACT CHECK



RESISTIVITY

Intermediate results	Geometry A		Geometry B	
	R2134	R3241	R4312	R1423
Resistance [Ω]	9.30E+07	6.28E+07	8.90E+07	6.32E+07
Standard deviation of resistance [Ω]	3.74E+04	7.90E+03	2.57E+04	8.36E+03
Voltage [V]	6.52E-01	4.41E-01	6.24E-01	4.43E-01
Standard deviation of voltage [V]	2.62E-04	5.46E-05	1.80E-04	5.84E-05
Current [A]	7.01E-09	7.01E-09	7.01E-09	7.01E-09
Standard deviation of current [A]	1.18E-13	1.47E-13	1.14E-13	8.35E-14

HALL MEASUREMENTS

Average measurements	Geometry C			Geometry D		
	I+(P1)	I-(N1)	I+(P2)	I+(P1)	I-(N1)	I+(P2)
Voltage [V]	2.26E-04	2.52E-04	1.80E-04	1.41E-04	3.49E-04	1.41E-04
Standard deviation of voltage [V]	4.64E-05	1.32E-05	1.16E-05	1.28E-05	1.54E-06	4.12E-06
Phase [deg.]	-2.00E-01	-1.78E+02	-8.00E+00	-9.90E+00	-1.75E+02	-1.15E+01
Current [A]	7.01E-09	-7.01E-09	7.01E-09	7.01E-09	-7.01E-09	7.01E-09
Misalignment voltage [DC V]	N/A	N/A	N/A	N/A	N/A	N/A
Current lead voltage [DC V]	N/A	N/A	N/A	N/A	N/A	N/A

Figure S6: AC Hall Effect results of non-doped $MAPbBr_3$ single crystals.

Model 8404 AC/DC Hall Effect Measurement System (Lake Shore Cryotronics, Inc)

Measured on 23/08/2019

SPECIMEN

Materials: $MAPbBr_3$
Thickness: 2.02 mm

MEASURING CONDITIONS

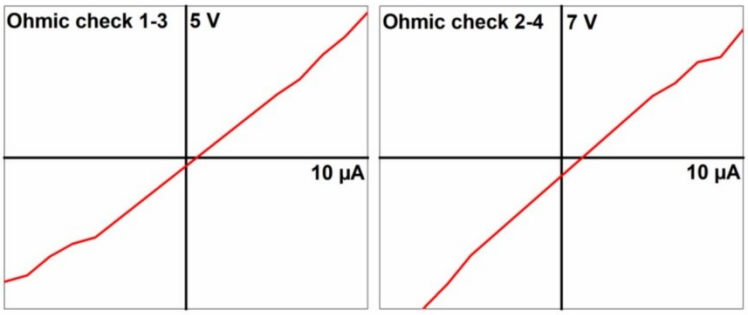
Excitation current: 10 uA
Field: 1.19 T

RESULTS SUMMARY

μ_H [$cm^2/V{\cdot}s$]: 2.09
n [$1/cm^3$]: $4.48E^{14}$
n_{sheet} [$1/cm^2$]: $1.08E^{14}$
R_H [cm^3/C]: $1.39E^{4}$

R_{Hsheet} [cm^2/C]: $5.77E^{4}$
P [$\Omega{\cdot}cm$]: $6.66E^{3}$
ρ_{sheet} [$\Omega/\square$]: $2.76E^{4}$
V_H [V]: $6.8932E^{-5}$

CONTACT CHECK



RESISTIVITY

Intermediate results	Geometry A		Geometry B	
	R2134	R3241	R4312	R1423
Resistance [Ω]	8.02E+03	4.81E+03	7.56E+03	4.55E+03
Standard deviation of resistance [Ω]	1.21E+01	8.64E+01	1.53E+02	1.69E+02
Voltage [V]	8.02E-02	4.81E-02	7.56E-02	4.55E-02
Standard deviation of voltage [V]	1.21E-04	8.64E-04	1.53E-03	1.69E-03
Current [A]	1.00E-05	1.00E-05	1.00E-05	1.00E-05
Standard deviation of current [A]	1.70E-11	3.96E-11	7.02E-11	3.33E-11

HALL MEASUREMENTS

Average measurements	Geometry C			Geometry D		
	I+(P1)	I-(N1)	I+(P2)	I+(P1)	I-(N1)	I+(P2)
Voltage [V]	4.78E-05	3.65E-05	2.04E-04	6.08E-04	1.09E-04	8.75E-05
Standard deviation of voltage [V]	2.57E-04	1.65E-04	3.06E-04	6.47E-04	2.79E-04	1.42E-04
Phase [deg.]	-1.57E+02	3.83E+01	-1.19E+02	1.49E+02	1.66E+02	-1.14E+02
Current [A]	1.00E-05	-1.00E-05	1.00E-05	1.00E-05	-1.00E-05	1.00E-05
Misalignment voltage [DC V]	N/A	N/A	N/A	N/A	N/A	N/A
Current lead voltage [DC V]	N/A	N/A	N/A	N/A	N/A	N/A

Figure S7: AC Hall Effect results of 15% Bi-doped $MAPbBr_3$ single crystals.

Table S2: AC Hall Effect results of pristine and Bi-doped $MAPbBr_3$ single crystals.

Bi/Pb atomic ratio % in solution	Hall Mobility ($cm^2/V{\cdot}s$)	Carrier Concentration (cm^{-3})	Charge Type (N/P)
0	0.58	1.19×10^{11}	P
1	1.86	4.49×10^{13}	N
5	5.41	5.41×10^{13}	N
10	7.51	8.60×10^{13}	N
15	2.09	4.48×10^{14}	N