Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Mixed Ge/Pb Perovskite Light Absorbers with an Ascendant Efficiency Explored from Theoretical View

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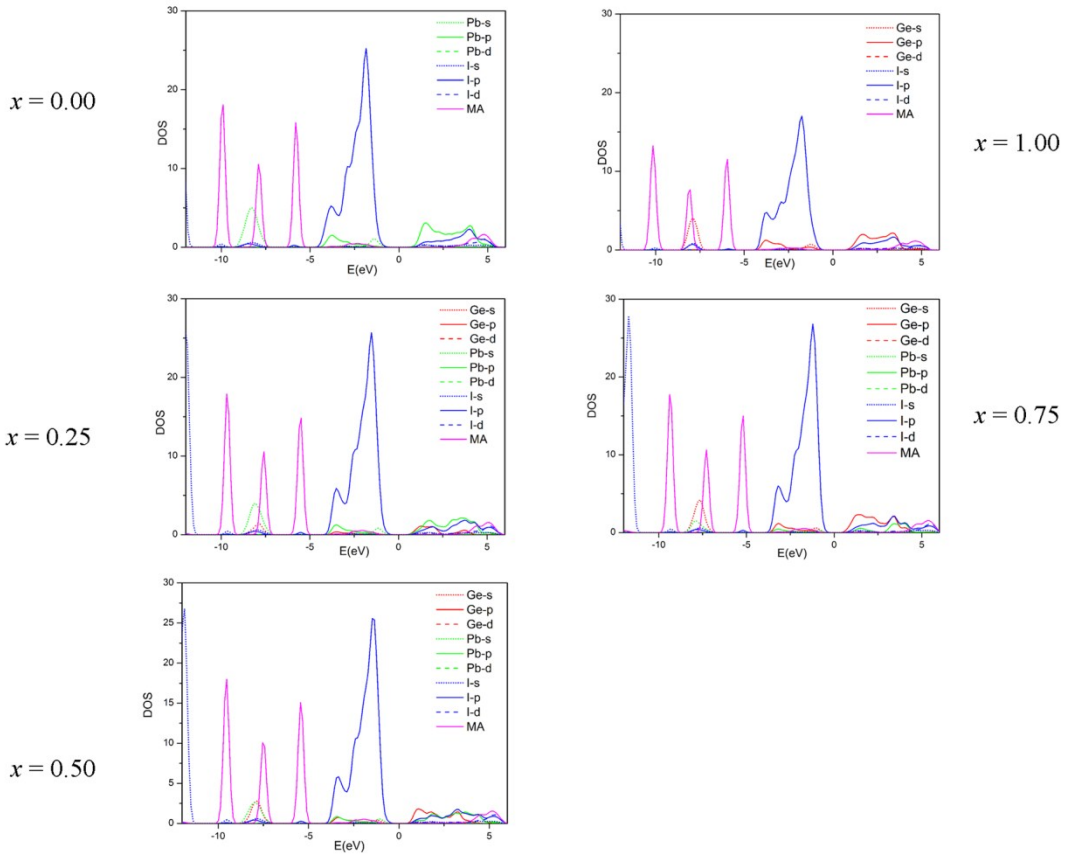

Figure S1. PDOS structures of the mixed $MAGe_xPb_{(1-x)}I_3$ perovskites. The short dot, solid and dash lines are the s-orbital, p-orbital and d-orbital states of the corresponding atoms (Pb/Ge/I), respectively. The green, red, blue and magenta colors are the orbital contributions of Pb, Ge, I atoms and MA^+ cation. It is clear to see that for x = 0, the CBM is controlled by the p-orbital states of Pb, and the VBM is mainly from the contribution of the hybrid states of Pb s-orbital and I p-orbitals. With the increase of Ge, for the three mixed systems x = 0.25, 0.50, 0.75, both CBM and VBM of the mixed systems are composed of similar the states, CBM is mainly from the hybrid p-orbitals Pb and Ge atoms, VBM is from hybrid s-orbitals Pb and Ge atoms and p-orbitals of I atoms. When x increases to 1.00, the CBM is controlled by the p-orbital states of Ge, and the VBM is made up of s-orbital of Ge atom and p-orbitals of I atom.

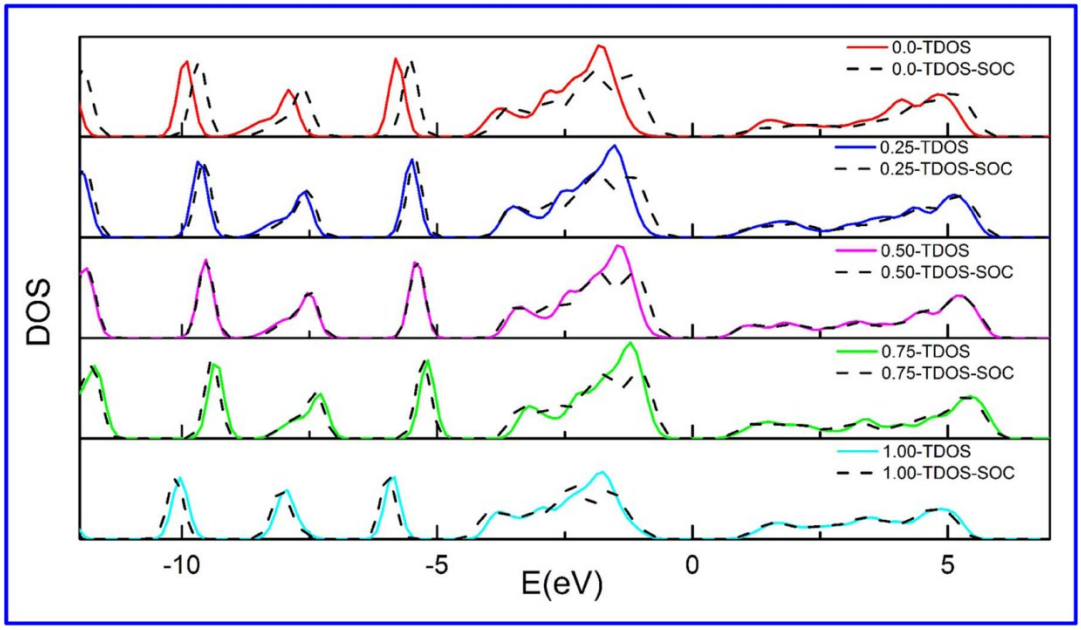

Figure S2. TDOS structures of the mixed $MAGe_xPb_{(1-x)}I_3$ perovskites shown with and without SOC methods. The solid line is the TDOS with PBE method, the dashed line is with PBE-SOC method. All the dashed lines in the valence band split into two peaks and with weaker peak intensities while the solid lines are with a single peak, which indicates that the SOC also gives rise to a weak energy splitting on the valence bands. Besides, it is clear to see that with the increase of x, the dashed lines make an increasing degree of shift to the left, and overlap with the solid line when x = 1.00, which indicates that the SOC also has an effect to reduce the band gap of the mixed perovskites by lifting the valence bands, and the effects reduce with the decreasing content of Pb atom.

Table S1. Calculated lattice parameters and corresponding experimental data of mixed $MAGe_xPb_{(1-x)}I_3$ perovskites.

Structure	*a* /Å	*b* /Å	*c* /Å	*α* /°	*β* /°	*γ* /°	V/ Å^3
x = 0.00	8.89	8.92	13.20	90.06	89.96	90.01	1048.25
x = 0.00/Exp.	8.93	8.93	12.67	90	90	90	1011.50
x = 0.25	8.88	8.86	13.11	89.92	90.98	89.96	1031.91
x = 0.50	8.81	8.95	12.87	88.96	89.97	89.99	1016.02
x = 0.75	8.76	8.83	12.84	88.86	89.14	89.89	994.81
x = 1.00	8.84	8.68	11.53	88.25	91.62	121.42	756.06
x = 1.00/Exp.	8.55	8.55	11.16	90	90	120	707.2

Table S2. Calculated range of bond lengths and bond angles for mixed $MAGe_xPb_{(1-x)}I_3$ systems.

sort	$x = 0.00$	$x = 0.25$	$x = 0.50$	$x = 0.75$	$x = 1.00$
H_N-X/Å	2.61-3.62	2.62-3.66	2.60-3.21	2.61-3.45	2.67-3.55
H_C-X/Å	3.11-3.37	3.27-3.50	3.31-3.48	3.26-3.42	3.24-3.62
M-I1(equatorial) /Å	3.20-3.28	2.78-3.50	2.72-3.72	2.72-3.68	2.73-3.67
M-I2(apical) /Å	3.22-3.40	2.86-3.67	2.90-3.54	2.82-3.66	2.79-3.42
M-I-M(equatorial)/deg	151-154	151-163	151-169	152-171	152-169
M-I-M(apical)/deg	171-172	169-173	165-172	166-170	162-165

Table S3 Effective masses m* (electron and hole effective mass m_e and m_h) and the corresponding reduced masses μ for the researched systems in Γ-F, F-Q, Q-Z, Z-Γ directions for the three mixed $MAGe_xPb_{(1-x)}I_3$ series with HSE-SOC method.

	$MAGe_{0.25}Pb_{0.75}I_3$			$MAGe_{0.50}Pb_{0.50}I_3$			$MAGe_{0.75}Pb_{0.25}I_3$		
	m_e	m_h	μ	m_e	m_h	μ	m_e	m_h	μ
Γ-F	0.128	0.137	0.066	0.122	0.127	0.062	0.113	0.119	0.058
F-Q	0.133	0.142	0.069	0.124	0.131	0.064	0.117	0.124	0.060
Q-Z	0.128	0.151	0.069	0.119	0.139	0.064	0.111	0.132	0.060
Z-Γ	0.125	0.146	0.067	0.115	0.134	0.062	0.108	0.113	0.055