Supporting Information

Improved Phase Stability of CsPbI₃ Perovskite via Organic Cation

Doping

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Table S1. Calculated lattice parameters, cell volumes and band gaps of $CsPbI_3$ with and without spinorbit coupling (SOC) for cubic α and orthorhombic δ unit cells. The experimental values are also presented for comparison.

		a (Å)	b (Å)	c (Å)	Volume (Å ³)	Band gap (eV)
α	PBE	6.364			257.8	1.50
	PBE+SOC	6.664			296.0	0.65
	Exp. ¹	6.289			248.7	1.70
δ	PBE	10.630	4.874	18.077	936.5	2.50
	PBE+SOC	11.751	5.131	19.112	1152.3	2.00
	Exp. ^{2,3}	10.434	4.791	17.761	887.9	2.82

Table S2. Calculated energy differences between α and δ phases ($\Delta E = E_{\alpha} - E_{\delta}$) for pure CsPbI₃ and M_xCs_{1-x}PbI₃ (M= DMA⁺, EA⁺ or GA⁺; x=0.125) with first-principles molecular dynamics simulations at 100, 200 and 300 K. (Unit: eV/formula unit)^a

	pure	DMA^+	EA^+	GA^+
100 K	0.24	0.08	0.14	0.11
200 K	0.23	0.07	0.13	0.17
300 K	0.19	-0.14	0.14	0.12

^aAll molecular dynamics simulations in NPT ensemble are performed using VASP code.⁴ Because the simulations are time consuming, the total simulation time is set to 1.5 ps with a time step of 2 fs for each system, which can reflect the change trend of phase stability of CsPbI₃ perovskite upon doping. The values are the averaged energies corresponding to the last 0.5 ps. Clearly, the energy differences between α and δ phases for the organic cation doped systems are lower than that of the pure CsPbI₃, regardless of the simulation temperature, indicating the improved stability for CsPbI₃ perovskite. In particular, DMA⁺ is more efficient in reducing the energy differences of α and δ phases than EA⁺ and GA⁺, and even invert the energy order of the two phases at 300 K. These results are in agreement with the change trend of the predicted α -to- δ phase transition temperature upon organic cation doping, where all dopants can lower the transition temperature of CsPbI₃ and DMA⁺ is found to be particularly effective.



Figure S1. Diagram of bonding (σ) and antibonding (σ^*) orbitals in APbI₃ (A is monovalent cation). Reprinted from Ref. 5 with permission of Materials Research Society, Copyright 2015. The interaction between Pb(6*p*) and I(5*p*) leads to the creation of middle part of valence band, which is mainly contributed by I(5*p*), and the bottom part of conduction band, which is composed of Pb(6*p*). This indicates that the charge transfers from Pb(6*p*) to I(5*p*), which is the feature of ionic bonding. The overlap of Pb(6*s*) and I(5*p*) creates a pair of bonding/antibonding orbital. The bonding orbital is at the deep part of valence band, while the antibonding one constitutes the valence band maximum, which is commonly contributed by Pb(6*s*) and I(5*p*). Thus, Pb(6*s*) has covalent coupling with I(5*p*). Overall, CsPbI₃ perovskite is a mixed ionic and covalent compound.

Supporting References:

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