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Supporting Information for:

Bi³⁺ doping in 1D ((CH₃)₃SO)Pbl₃: a model for defect interactions in halide perovskites

Candida Pipitone, Silvia Carlotto, Maurizio Casarin, Alessandro Longo, Antonino Martorana, Francesco Giannici

Computational details: chemical potentials

To avoid precipitation of the elements, for every element X, it holds that $\Delta \mu_X < 0$. In addition, to avoid segregation of simpler iodides from solid solutions, further constraints must hold at the same time:

$$\begin{split} \Delta \mu_{TMSO} + & \Delta \mu_{Pb} + 3 \ \Delta \mu_{I} = \ \Delta H_{(TMSO)PbI3} \\ \Delta \mu_{Pb} + 2 \ \Delta \mu_{I} < \Delta H_{PbI2} \\ \Delta \mu_{TMSO} + & \Delta \mu_{I} < \Delta H_{TMSOI} \\ \Delta \mu_{Bi} + 3 \ \Delta \mu_{I} < \Delta H_{BiI3} \\ 3 \ \Delta \mu_{TMSO} + 2 \ \Delta \mu_{Bi} + 9 \ \Delta \mu_{I} < \Delta H_{(TMSO)3Bi2I9} \end{split}$$

Where ΔH is the formation enthalpy of each compound. From an inspection of the total energy of (TMSO)Pbl₃ supercell and simpler compounds, it is found that (TMSO)Pbl₃ is indeed stable (by about 0.14 eV) against decomposition into Pbl₂ and (TMSO)I. It may be argued that there is likely more vibrational and configurational entropy in (TMSO)Pbl₃, where the organic cations are less densely packed than in (TMSO)I. Therefore the free energy stabilization of (TMSO)Pbl₃ compared to simple iodides precursors is likely higher.





Figure S1 Stability phase diagram of (TMSO)PbI₃ (Bi-doped) against decomposition as PbI₂ (upper right) and (TMSO)I (bottom left) at different Bi chemical potential, shown below the plot. BiI₃ precipitation occurs above the horizontal line. The yellow area defines the stability region of (TMSO)PbI₃. The precipitation of the (TMSO)₃Bi₂I₉ secondary phase is out of range for these diagrams and does not influence the stability region for (TMSO)PbI₃. Black dots show the chemical potential conditions 1 (a), 2 (b) and 3 (c).

	Table S1	Formation	energies	of neutral	clusters	of defects.
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Supercell	Defects	□□□□□, 1 (eV)	(eV)	3 (eV)
(TMSO) ₇ Pb ₈ l ₂₃	$V_I^{\bullet} + V_{TMSO}$	0.88	1.78	0.89
(TMSO) ₈ Pb ₅ Bi ₂ I ₂₄	$2Bi_{Pb}^{\bullet} + V_{Pb}^{"}$	-0.24	6.36	-0.29
(TMSO) ₇ Pb ₇ Bil ₂₄	$Bi_{Pb}^{\bullet} + V_{TMSO}$	0.34	3.64	0.33
(TMSO) ₈ Pb ₇ Bil ₂₅	$Bi_{Pb}^{\bullet} + I_i$	1.31	3.71	1.29

Computational details: corrections to the formation energy

The formation energy of charged defects was corrected for electrostatic defect-defect interactions using the CoFFEE package. Three different correction terms $(^{E^{lat}, \Delta V_{0/p}, \Delta V_{q-0/m}})$ are introduced. The first two terms account for the finite size of the model supercell and the alignment between the electrostatic potential of the neutral defective and undefective supercells, respectively. $^{\Delta V_{q-0/m}}$ accounts for the alignment of the electrostatic potential difference between the charged and neutral defective supercells, as modeled by DFT and the Poisson equation. To calculate the latter two terms, the dielectric

constant of $(TMSO)PbI_3$ is taken to be equal to that of $((CH_3)_3S)PbI_3$ due to its chemical and structural similarity. (A. Kaltzoglou, *Inorg. Chem.* 2017, 56, 6302-6309).

Computational details: defect configurations

Longer distance effects due to the interaction between defects residing in two adjacent chains are neglected in the present analysis. The transition matrix describing the probability of each sequence is independent of the content of neighboring chains. Configurations described by the same transition matrix but differing in the mutual position of two neighboring chains (e.g., G and H in the table above) only differ as what concerns the longer-distance interactions between cations at 9-10 Å and above, while maintaining all the other first-neighbor and second-neighbor distances. Such structural differences account for energy differences around 0.01-0.07 eV in total. Considering that the multiplicity of each cation-cation distance between adjacent chains is high (around 10-20), the energy contribution of a single M-M interaction at 10 Å is estimated to be on the order of 10⁻³ eV. This considered, neglecting farther cation-cation distances beyond 8 Å: a) allows to simplify significantly subsequent algebraic expressions; b) has little effect on the energy; c) is consistent with the transition matrix formulation of the cation sequences.

Table S2. Defect configurations used in the atomistic simulations of $(TMSO)_8Pb_5Bi_2I_{24}$. The first neighbor cation-cation distances are enumerated for each configuration. Calculated energy from DFT is reported relative to configuration A (i.e., the configuration with the lowest energy).

Configuration	Chains (unit cell)		Pb-Pb bonds	Bi-Bi bonds	Pb-Bi bonds	V-Bi bonds	V-Pb bonds	Calculated E _{tot} (eV)
	(1)	V-Bi-Pb-Bi	٨	0	0			
A —	(2)	Pb-Pb-Pb-Pb	- 4	0	2	2	0	0.000
D	(1)	V-Bi-Bi-Pb	٨	4	4	4	4	0.583
D —	(2)	Pb-Pb-Pb-Pb	- 4	I	I	I	I	
0	(1)	V-Bi-Pb-Pb	2	0	3	1	1	0.577
U =	(2)	Pb-Pb-Pb-Bi	- 3					
D —	(1)	V-Bi-Pb-Pb	2	0	3	1	1	0.560
	(2)	Pb-Pb-Bi-Pb	- 3					
	(1)	V-Bi-Pb-Pb	- 3	0	3	1	1	0.484
E —	(2)	Pb-Bi-Pb-Pb						
F —	(1)	V-Bi-Pb-Pb	- 3	0	3	1	1	0.516
	(2)	Bi-Pb-Pb-Pb						
0	(1)	V-Pb-Bi-Pb	- 2	0	4	0	2	1.109
G —	(2)	Pb-Pb-Pb-Bi						
	(1)	V-Pb-Bi-Pb	- 2	0	4	0	2	1.042
н —	(2)	Pb-Pb-Bi-Pb						
I —	(1)	V-Pb-Bi-Pb	- 2	0	4	0	2	0.966
	(2)	Pb-Bi-Pb-Pb						
L —	(1)	V-Pb-Bi-Pb	- 2	0	4	0	2	1.031
	(2)	Bi-Pb-Pb-Pb						
Μ —	(1)	V-Pb-Pb-Pb	2	1	2	0	2	1.475
	(2)	Bi-Bi-Pb-Pb	– ວ					

N —	(1)	V-Pb-Pb-Pb	2	0	4	0	2	1.393
	(2)	Bi-Pb-Bi-Pb	Z					
0 —	(1)	V-Pb-Pb-Pb	2	1	2	0	2	1.543
	(2)	Bi-Pb-Pb-Bi	3					
P –	(1)	V-Pb-Pb-Pb	3	1	2	0	2	1.471
	(2)	Pb-Bi-Bi-Pb						
Q -	(1)	V-Pb-Pb-Pb	2	0	4	0	2	1.391
	(2)	Pb-Bi-Pb-Bi	Z					
R -	(1)	V-Pb-Pb-Pb	2	1	2	0	2	1.537
	(2)	Pb-Pb-Bi-Bi	5					

Table S3. Defect configurations used in the atomistic simulations of $(TMSO)_8Pb_2Bi_4I_{24}$. The first neighbor cation-cation distances are enumerated for each configuration. Calculated energy from DFT is reported relative to configuration A (i.e., the configuration with the lowest energy) of $(TMSO)_8Pb_5Bi_2I_{24}$ and corrected for the different composition using the chemical potentials of Pb and Bi.

Configuration	Chains (unit cell)		Pb-Pb bonds	Bi-Bi bonds	Pb-Bi bonds	V-Bi bonds	V-Pb bonds	Calculated E _{tot} (eV)
	(1)	V-Bi-Pb-Bi	0	0	4	4	0	-0.276
AB —	(2)	Pb-Bi-V-Bi	- 0					
AC —	(1)	V-Pb-Pb-Bi	1	2	1	3	1	0.441
	(2)	Bi-Bi-Bi-V	- 1					
AE —	(1)	V-Pb-Bi-Bi	0	2	2	2	2	0.907
	(2)	Bi-Bi-V-Pb	- 0					
AF —	(1)	V-Pb-Bi-Pb	0	2	2	2	2	0.926
	(2)	Bi-Bi-V-Bi	- 0					



