Supplementary information

Lead-free double perovskites: how divalent cations tune the electronic structure for photovoltaic applications

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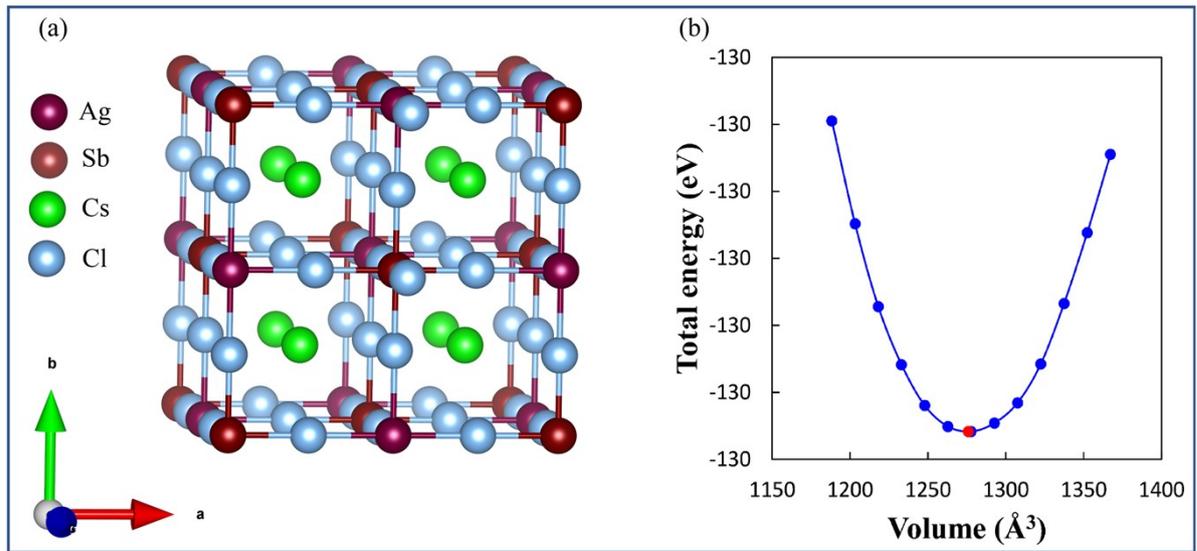chanyeup@kicet.re.kr (Chan-Yeup Chung)

Figure S1: (a) Conventional cell and (b) Total energy–Volume curve of pristine $Cs_2AgSbCl_6$ double perovskite. The red ball represents the equilibrium volume by the third-order Birch-Murnaghan equation of states.
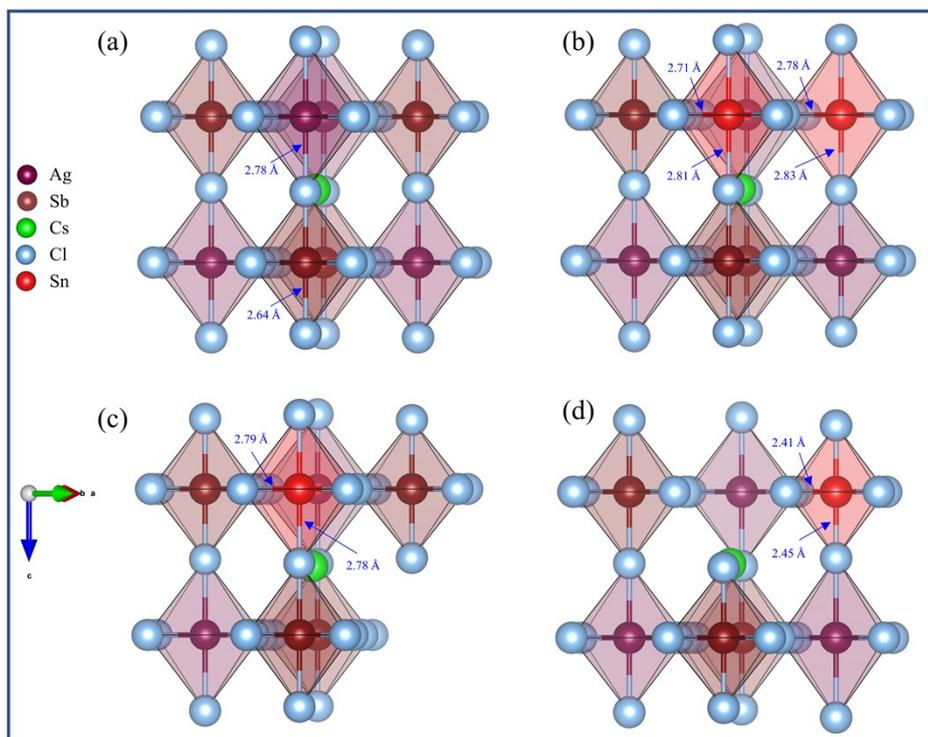

Figure S2: Octahedral symmetry in (a) the pristine, and (b) Sn^{2+}–Sn^{2+}, (c) Sn^{2+}–V_{Ag}, and (d) Sn^{4+}–V_{Ag} doped perovskites.
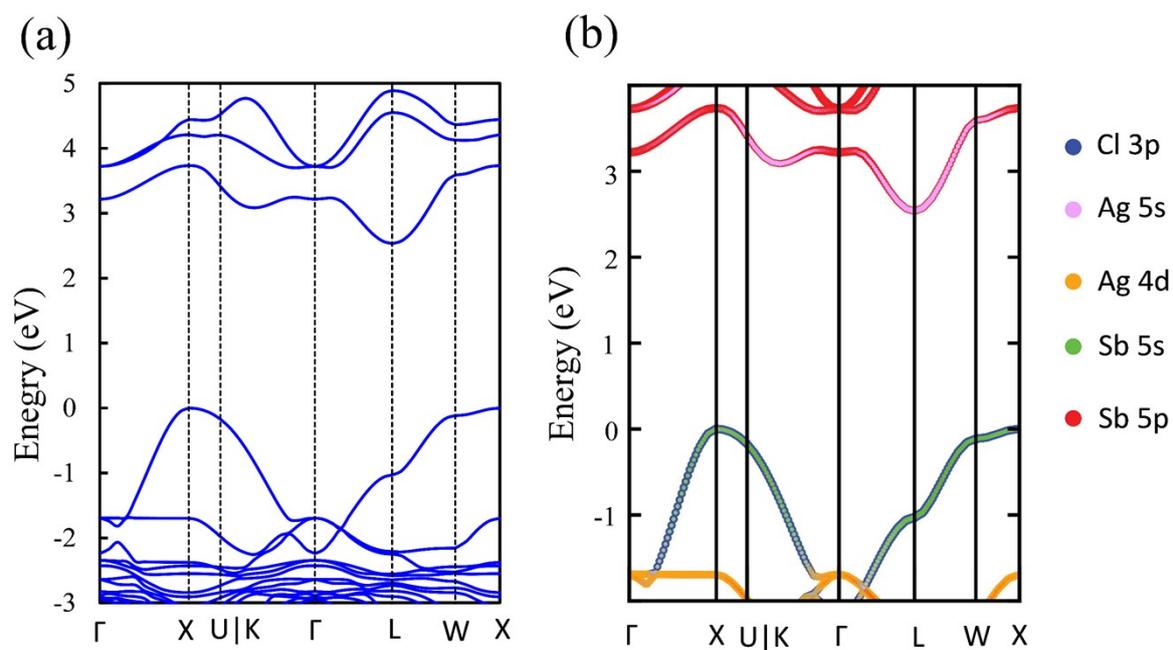
Figure S3: (a) Band structure and (b) partial band structure of pristine $Cs_2AgSbCl_6$ primitive cell.

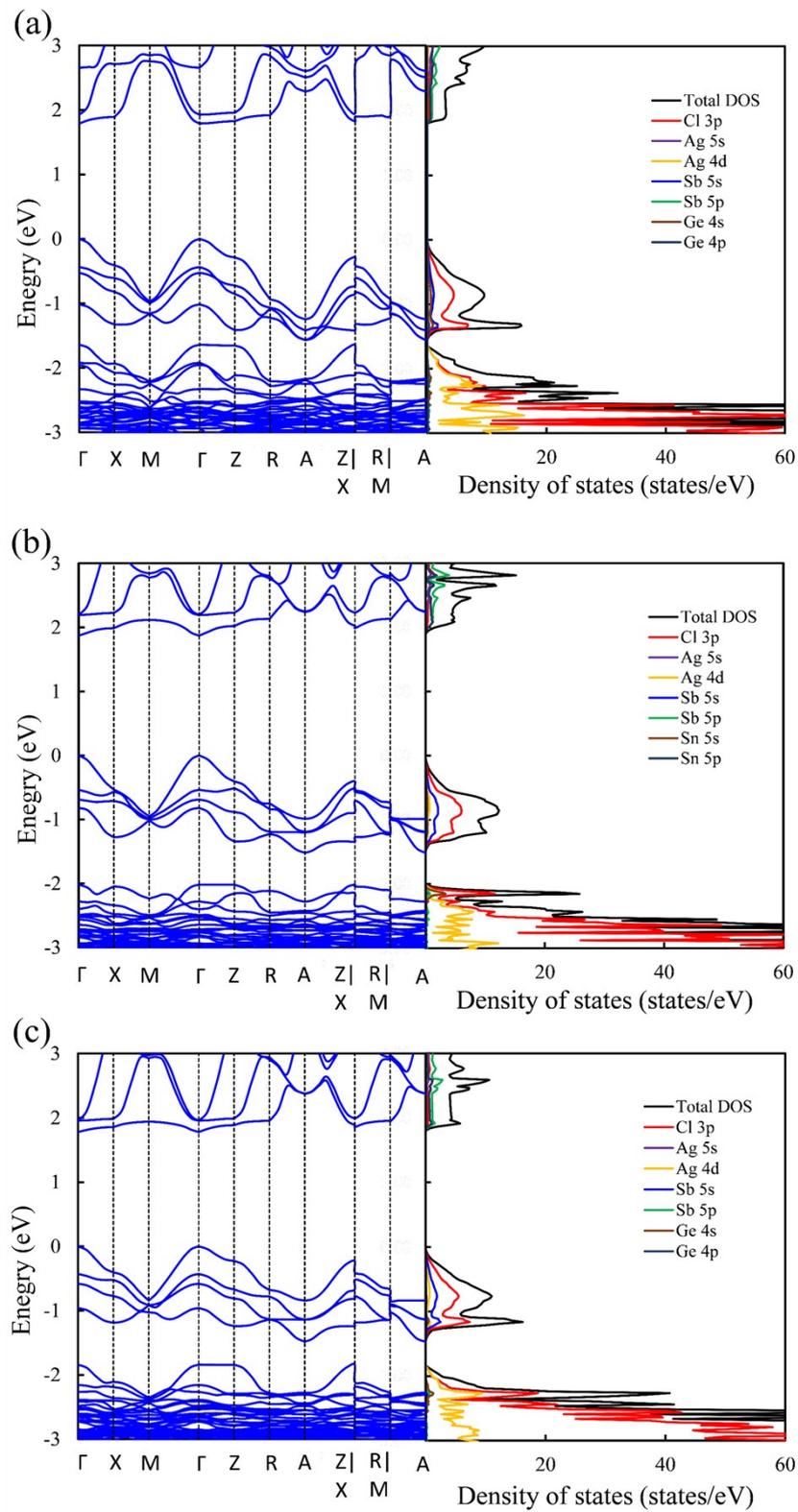**Figure S4:** Band structure (left) and density of states (right) of (a) Ge^{2+}–Ge^{2+}, (b) Sn^{2+}–V_{Ag}, and (c) Ge^{2+}–V_{Ag} doped perovskites.
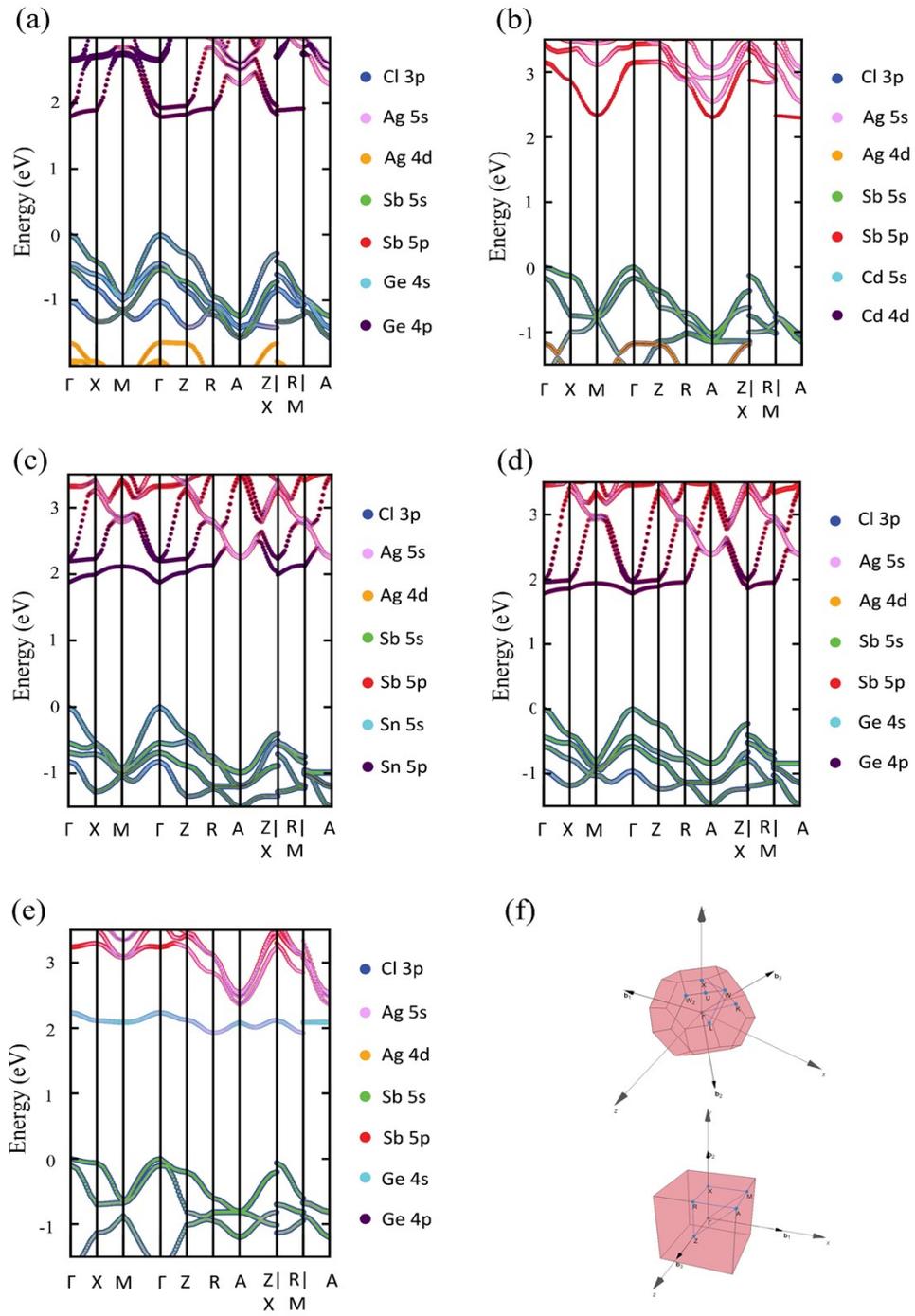
Figure S5: Partial band structure of (a) Ge^{2+}–Ge^{2+}, (b) Cd^{2+}–Cd^{2+}, (c) Sn^{2+}–V$_{Ag}$, (d) Ge^{2+}–V$_{Ag}$, and (e) Ge^{4+}–V$_{Ag}$ doped perovskites. (f) The suggested Brillouin zone path of the pristine primitive cell (up) and doped perovskites (down).
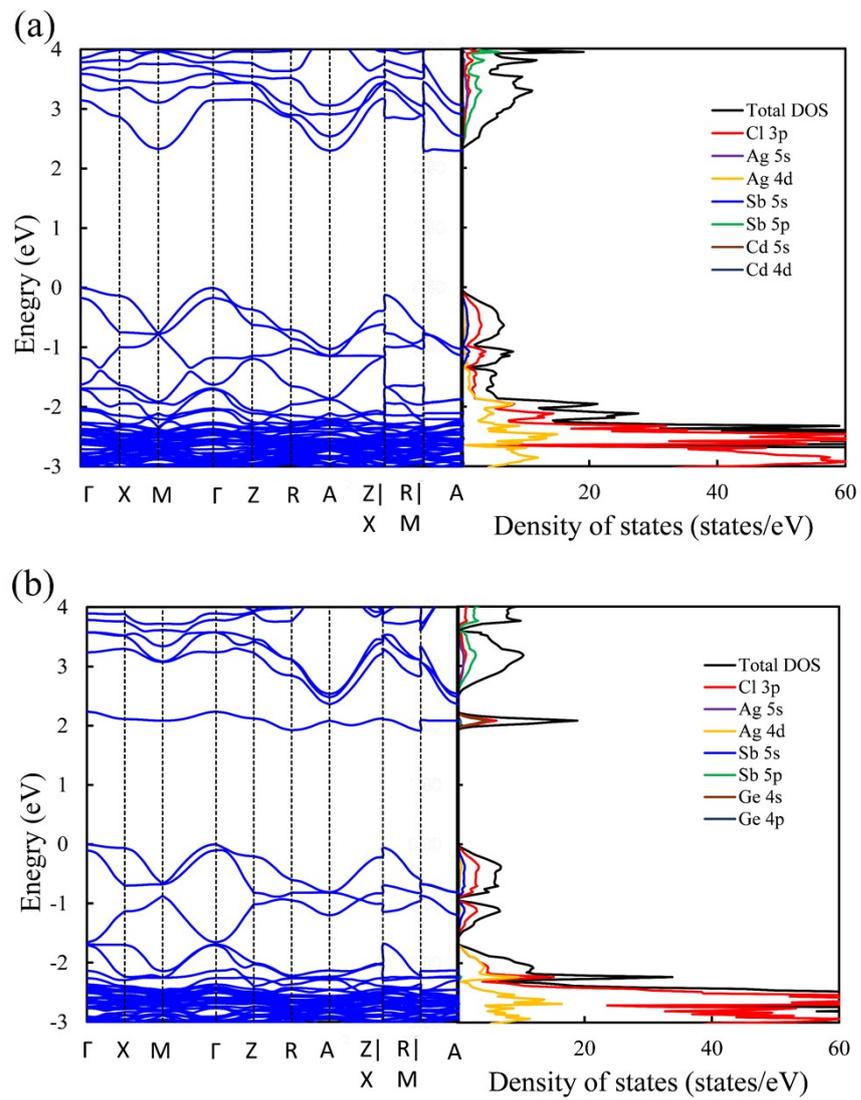
Figure S6: Band structure (left) and density of states (right) of (a) Cd^{2+}–Cd^{2+} and (b) Ge^{4+}–V_{Ag} doped perovskites.

Table S1: Average Bader charge (e) per atom in the pristine and all of the doped perovskites. Negative charges indicate gain of electrons and positive charges indicate loss of electrons.

Perovskite	Bader charge (e)				
	Cs	Ag	Sb	Cl	M
Pristine	0.888	0.610	1.767	−0.692	
Sn^{2+}–Sn^{2+}	0.906	0.673	1.752	−0.718	1.358
Ge^{2+}–Ge^{2+}	0.897	0.636	1.718	−0.691	1.174
Zn^{2+}–Zn^{2+}	0.901	0.608	1.836	−0.701	1.146
Cd^{2+}–Cd^{2+}	0.901	0.635	1.805	−0.699	1.127
Sn^{2+}–V_{Ag}	0.905	0.650	1.759	−0.704	1.305
Ge^{2+}–V_{Ag}	0.905	0.640	1.719	−0.692	1.221
Sn^{4+}–V_{Ag}	0.899	0.597	1.733	−0.670	1.909
Ge^{4+}–V_{Ag}	0.899	0.567	1.760	−0.659	1.658

Table S2: The calculated effective mass ($|m^*|$) of electrons and holes (in a unit of bare electron mass m_e) along the Γ–M path for the proposed Sn^{2+} and Ge^{2+}-based perovskites.

Perovskite	$|m^*|$	
	electron	hole
Sn^{2+}–Sn^{2+}	0.257	0.365
Ge^{2+}–Ge^{2+}	0.252	0.361
Sn^{2+}–V_{Ag}	0.719	0.326
Ge^{2+}–V_{Ag}	1.184	0.403