

Supporting Information

B-site Co-doping-Induced Symmetry Breaking for Enhanced Optoelectronic Properties in Vacancy-Ordered Double Perovskites

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S1. Structural Stability and Electronic Calculation Details

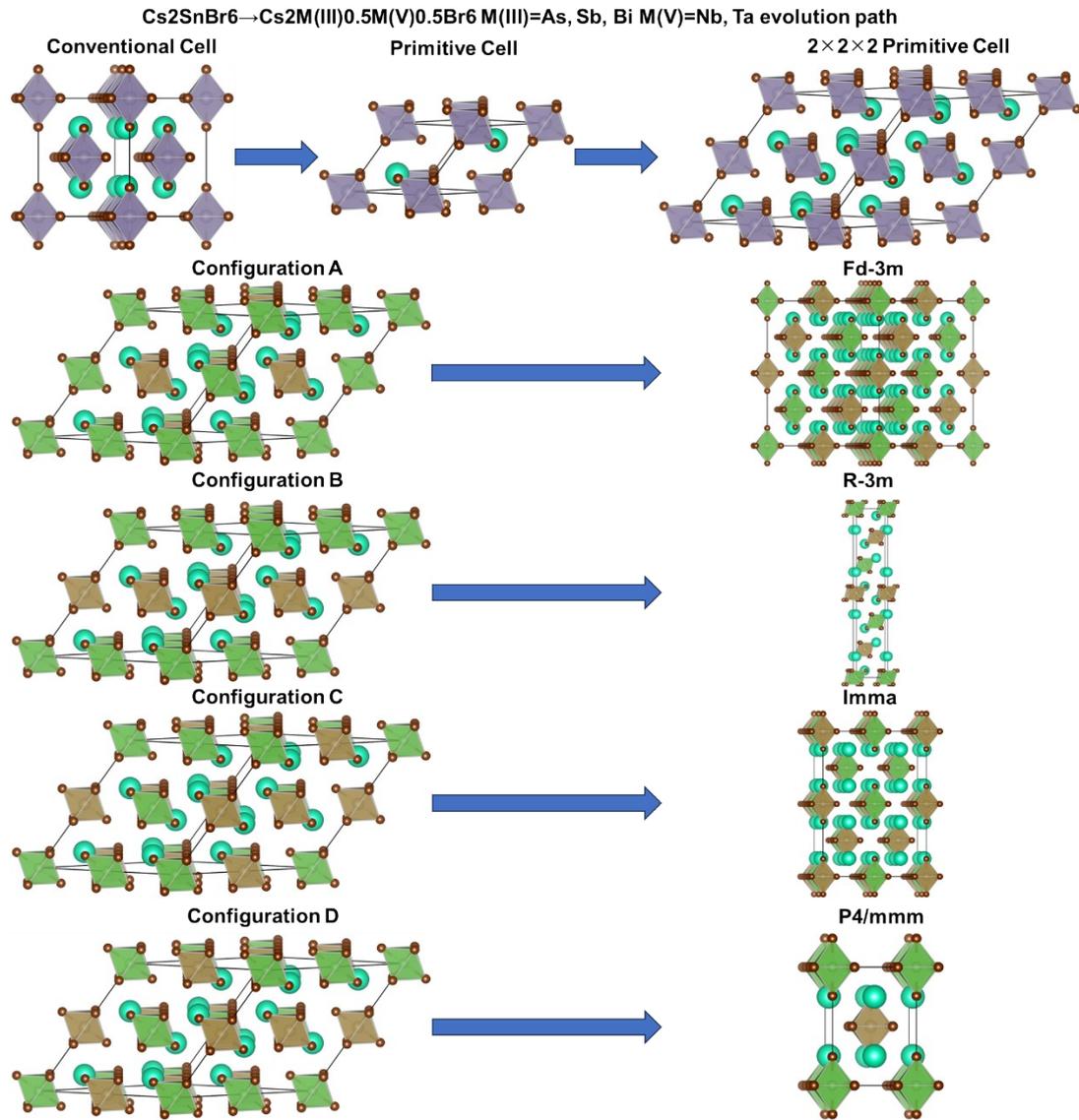
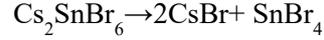


Figure S1 Shows the possible configurational transformation paths during the structural relaxation process.

Table S1 Total Energy Comparison of Crystal Phases. Total energies (in eV per formula unit, f.u.) for the six co-doped systems in various candidate crystal phases (Fd-3m, R-3m, Imma, and P4/mmm).

Compound	Fd-3m (eV/f.u.)	R-3m (eV/f.u.)	Imma (eV/f.u.)	P4/mmm (eV/f.u.)
Cs ₂ (As _{0.5} Nb _{0.5})Br ₆	-64.303	-64.311	-64.384	-64.461
Cs ₂ (As _{0.5} Ta _{0.5})Br ₆	-66.221	-66.228	-66.310	-66.395
Cs ₂ (Bi _{0.5} Nb _{0.5})Br ₆	-64.613	-64.622	-64.694	-64.776
Cs ₂ (Bi _{0.5} Ta _{0.5})Br ₆	-66.549	-66.557	-66.638	-66.718
Cs ₂ (Sb _{0.5} Nb _{0.5})Br ₆	-64.464	-64.471	-64.529	-64.595
Cs ₂ (Sb _{0.5} Ta _{0.5})Br ₆	-66.360	-66.367	-66.441	-66.519

Table S2 Thermodynamic Stability Calculations. Total energies of the co-doped compounds and their potential decomposition products, along with the calculated decomposition enthalpy (ΔH) for the specified decomposition pathways.



Compounds	SG	E _{total} (eV/f.u.)
Cs ₂ SnBr ₆	Fm-3m	-28.614
Cs ₄ AsNbBr ₁₂	P4/mmm	-64.457
Cs ₄ SbNbBr ₁₂	P4/mmm	-64.590
Cs ₄ BiNbBr ₁₂	P4/mmm	-64.776
Cs ₄ AsTaBr ₁₂	P4/mmm	-66.391
Cs ₄ SbTaBr ₁₂	P4/mmm	-66.515
Cs ₄ BiTaBr ₁₂	P4/mmm	-66.714
CsBr	Pm-3m	-6.354
SnBr ₄	P2 ₁ /c	-14.760
AsBr ₃	P2 ₁ 2 ₁ 2 ₁	-12.255
SbBr ₃	Pnma	-12.370
BiBr ₃	P2 ₁ /c	-12.765
NbBr ₅	Pnma	-25.344
TaBr ₅	Pnma	-27.210

Table S3 Average radius of B-site atoms (r_B) in various materials, tolerance factor(t), and octahedral factor (μ).

Compounds	r_B (Å)	t	μ
Cs_2SnBr_6	0.69	1.0246	0.352
$\text{Cs}_2(\text{As}_{0.5}\text{Nb}_{0.5})\text{Br}_6$	0.61	1.0565	0.3112
$\text{Cs}_2(\text{As}_{0.5}\text{Ta}_{0.5})\text{Br}_6$	0.61	1.0565	0.3112
$\text{Cs}_2(\text{Bi}_{0.5}\text{Nb}_{0.5})\text{Br}_6$	0.835	0.9715	0.426
$\text{Cs}_2(\text{Bi}_{0.5}\text{Ta}_{0.5})\text{Br}_6$	0.835	0.9715	0.426
$\text{Cs}_2(\text{Sb}_{0.5}\text{Nb}_{0.5})\text{Br}_6$	0.7	1.0208	0.3571
$\text{Cs}_2(\text{Sb}_{0.5}\text{Ta}_{0.5})\text{Br}_6$	0.7	1.0208	0.3571

Table S4 Elastic Tensors and Mechanical Stability. Calculated elastic constants (C_{ij}) and derived mechanical properties for all materials.

Compound	SG	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	C_{66}	B	E	G	v	B/G
Cs_2SnBr_6	Fm-3m	15.869	7.470	—	—	7.673	—	10.270	15.117	6.024	0.255	1.705
Cs_2SnBr_6	P4/mmm	19.692	4.897	8.100	15.579	7.376	4.839	10.791	15.102	5.961	0.267	1.810
$\text{Cs}_2(\text{As}_{0.5}\text{Nb}_{0.5})\text{Br}_6$	P4/mmm	20.492	6.004	7.189	14.412	7.048	4.670	10.585	14.990	5.930	0.264	1.785
$\text{Cs}_2(\text{As}_{0.5}\text{Ta}_{0.5})\text{Br}_6$	P4/mmm	19.926	5.319	6.282	12.889	6.468	4.646	9.676	14.284	5.696	0.254	1.699
$\text{Cs}_2(\text{Bi}_{0.5}\text{Nb}_{0.5})\text{Br}_6$	P4/mmm	17.330	5.339	6.295	12.725	5.975	4.398	9.185	12.977	5.131	0.265	1.790
$\text{Cs}_2(\text{Bi}_{0.5}\text{Ta}_{0.5})\text{Br}_6$	P4/mmm	18.815	6.779	6.152	11.322	5.414	4.813	9.370	12.785	5.023	0.273	1.865
$\text{Cs}_2(\text{Sb}_{0.5}\text{Nb}_{0.5})\text{Br}_6$	P4/mmm	20.613	6.778	8.331	15.481	6.859	4.205	11.453	14.513	5.630	0.289	2.034
$\text{Cs}_2(\text{Sb}_{0.5}\text{Ta}_{0.5})\text{Br}_6$	P4/mmm	17.364	4.830	6.564	12.908	6.065	4.951	9.246	13.299	5.276	0.260	1.752

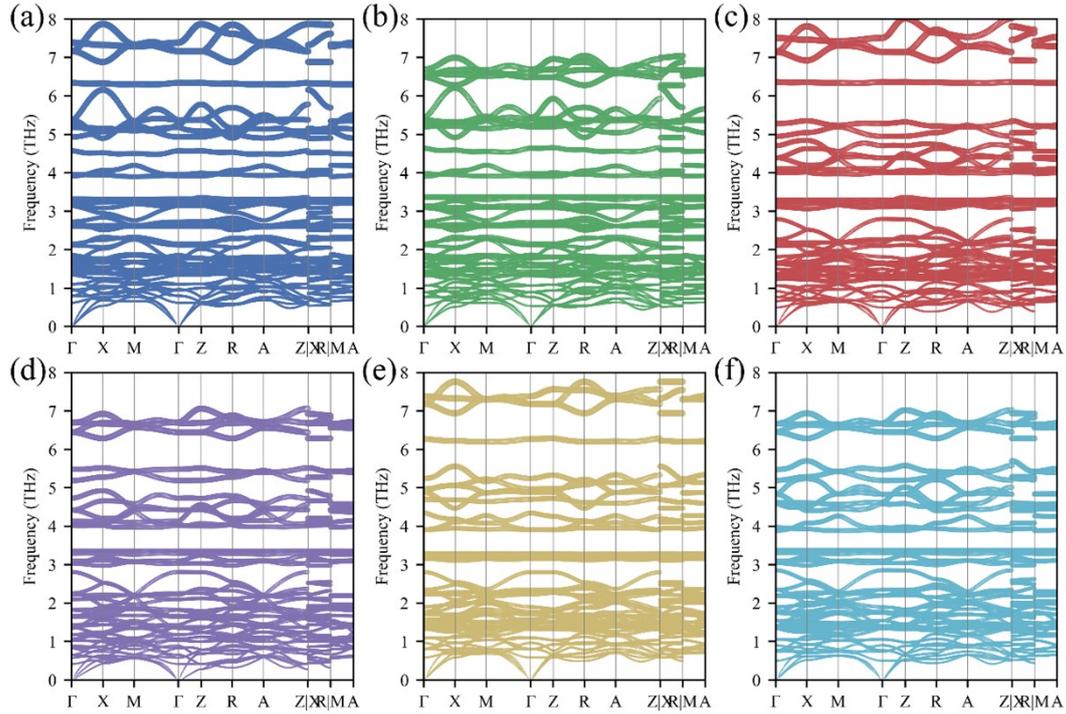


Figure S2. Phonon Dispersion Spectra. Calculated phonon dispersion spectra for the six co-doped systems in the P4/mmm phase: (a) $\text{Cs}_2(\text{As}_{0.5}\text{Nb}_{0.5})\text{Br}_6$, (b) $\text{Cs}_2(\text{As}_{0.5}\text{Ta}_{0.5})\text{Br}_6$, (c) $\text{Cs}_2(\text{Bi}_{0.5}\text{Nb}_{0.5})\text{Br}_6$, (d) $\text{Cs}_2(\text{Bi}_{0.5}\text{Ta}_{0.5})\text{Br}_6$, (e) $\text{Cs}_2(\text{Sb}_{0.5}\text{Nb}_{0.5})\text{Br}_6$, and (f) $\text{Cs}_2(\text{Sb}_{0.5}\text{Ta}_{0.5})\text{Br}_6$.

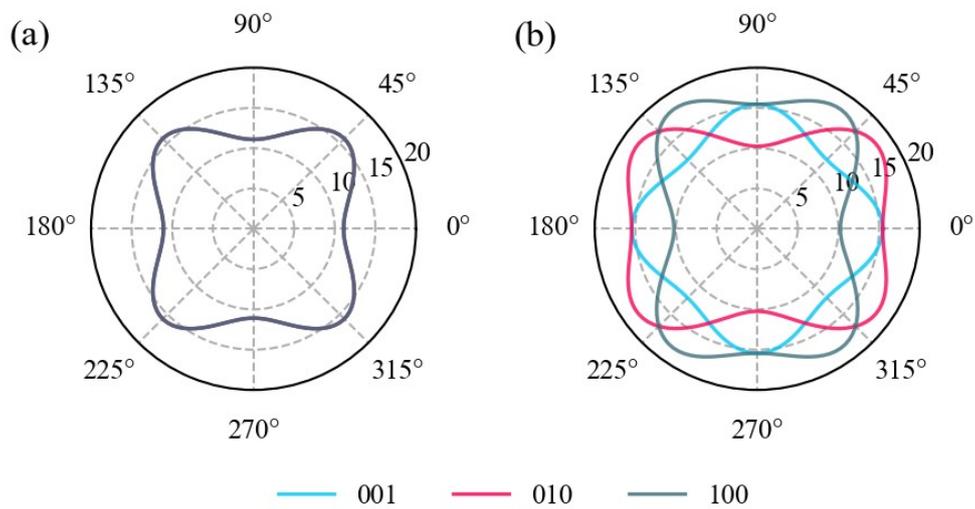


Figure S3. Anisotropy of Young's Modulus. Polar plots of the Young's modulus for (a) pristine Fm-3m and (b) P4/mmm Cs_2SnBr_6 .

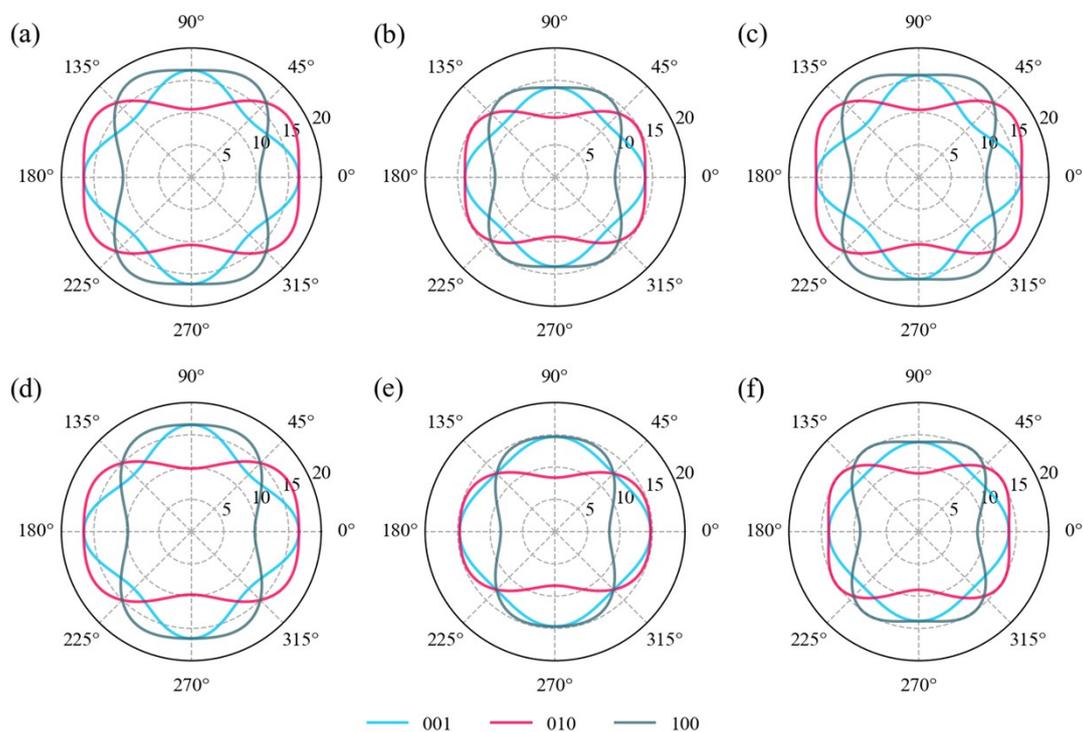


Figure S4. Anisotropy of Young's Modulus for Co-doped Systems. Polar plots of the Young's modulus for the six co-doped systems: (a) $\text{Cs}_2(\text{As}_{0.5}\text{Nb}_{0.5})\text{Br}_6$, (b) $\text{Cs}_2(\text{Sb}_{0.5}\text{Nb}_{0.5})\text{Br}_6$, (c) $\text{Cs}_2(\text{Bi}_{0.5}\text{Nb}_{0.5})\text{Br}_6$, (d) $\text{Cs}_2(\text{As}_{0.5}\text{Ta}_{0.5})\text{Br}_6$, (e) $\text{Cs}_2(\text{Sb}_{0.5}\text{Ta}_{0.5})\text{Br}_6$, and (f) $\text{Cs}_2(\text{Bi}_{0.5}\text{Ta}_{0.5})\text{Br}_6$.

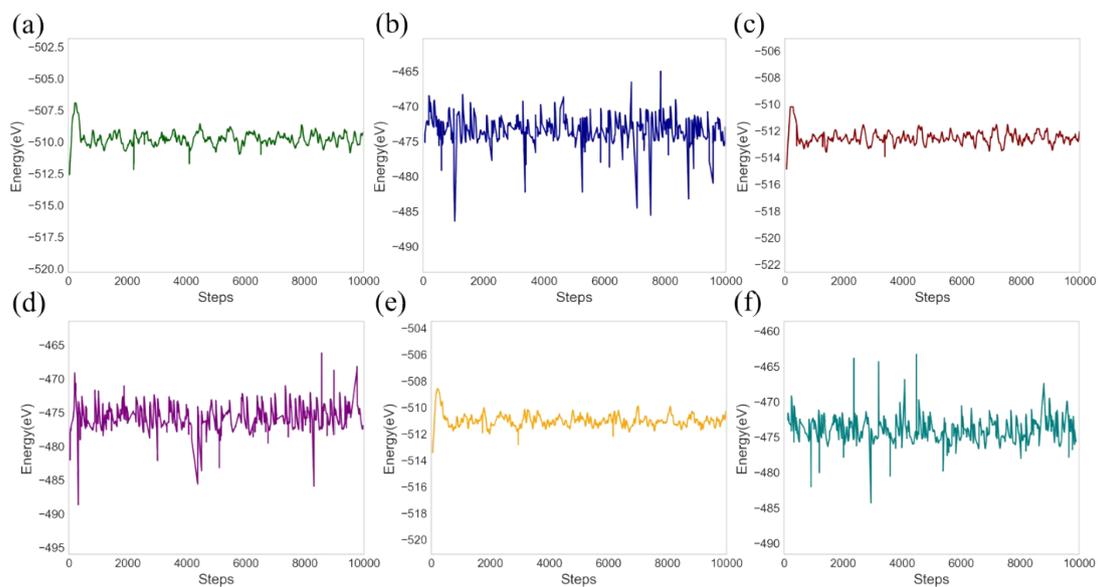


Figure S5 Ab Initio Molecular Dynamics (AIMD) Trajectories at 300 K. The total energy as a function of simulation steps for the six co-doped (a) $\text{Cs}_2(\text{As}_{0.5}\text{Nb}_{0.5})\text{Br}_6$, (b) $\text{Cs}_2(\text{Sb}_{0.5}\text{Nb}_{0.5})\text{Br}_6$, (c) $\text{Cs}_2(\text{Bi}_{0.5}\text{Nb}_{0.5})\text{Br}_6$, (d) $\text{Cs}_2(\text{As}_{0.5}\text{Ta}_{0.5})\text{Br}_6$, (e) $\text{Cs}_2(\text{Sb}_{0.5}\text{Ta}_{0.5})\text{Br}_6$, and (f) $\text{Cs}_2(\text{Bi}_{0.5}\text{Ta}_{0.5})\text{Br}_6$.

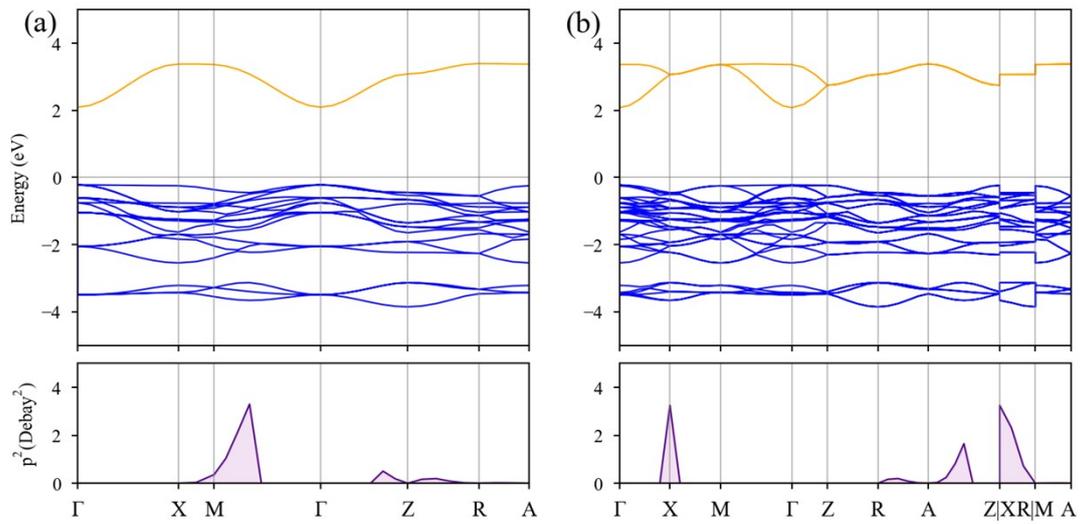


Figure S6 Cs₂SnBr₆(a) Fm-3m HSE BAND and TDM (b) P4/mmm HSE BAND and TDM

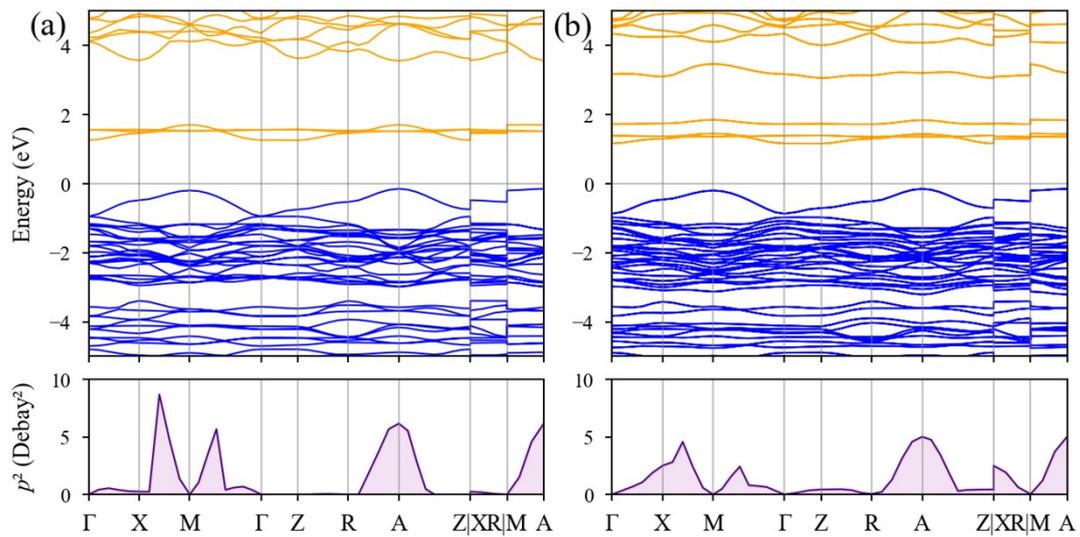


Figure S7. Effect of Spin-Orbit Coupling (SOC) on Electronic Structure. Comparison of the band structures for the Cs₂(Bi_{0.5}Ta_{0.5})Br₆ system calculated with (a) HSE and (b) HSE+SOC functionals.

S2. Optical Properties and SLME

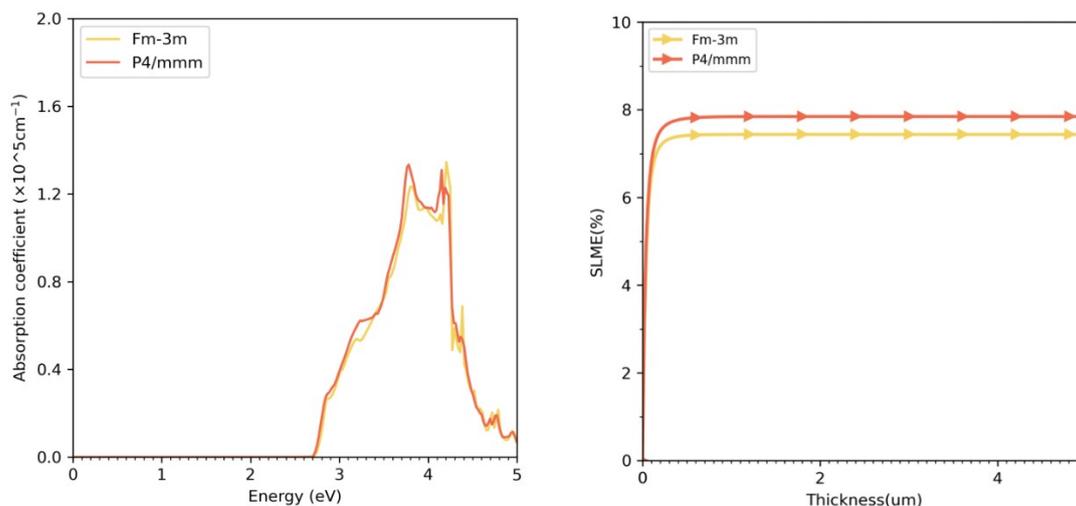


Figure S8 Optical Properties of Pristine Cs_2SnBr_6 . Comparison of the (left) optical absorption coefficient and (right) Spectroscopic Limited Maximum Efficiency (SLME) for pristine Cs_2SnBr_6 in the Fm-3m and P4/mmm phases.

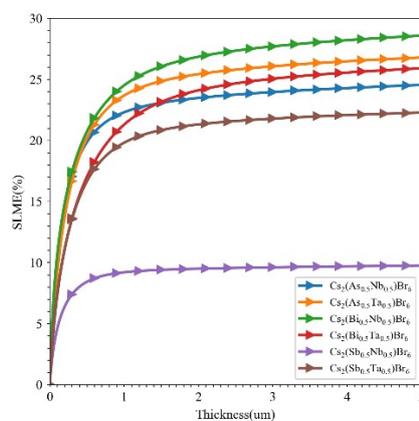


Figure S9 Spectroscopic Limited Maximum Efficiency (SLME) as a function of film thickness for the six co-doped systems: $\text{Cs}_2(\text{As}_{0.5}\text{Nb}_{0.5})\text{Br}_6$ (blue), $\text{Cs}_2(\text{As}_{0.5}\text{Ta}_{0.5})\text{Br}_6$ (orange), $\text{Cs}_2(\text{Bi}_{0.5}\text{Nb}_{0.5})\text{Br}_6$ (green), $\text{Cs}_2(\text{Bi}_{0.5}\text{Ta}_{0.5})\text{Br}_6$ (red), $\text{Cs}_2(\text{Sb}_{0.5}\text{Nb}_{0.5})\text{Br}_6$ (purple), and $\text{Cs}_2(\text{Sb}_{0.5}\text{Ta}_{0.5})\text{Br}_6$ (brown).

S3. Carrier Transport Properties

These are the inputs for AMSET in Cs₂SnBr₆

Hole doping = [1.0e14, 1.0e15, 1.0e16, 1.0e17, 1.0e18, 1.0e19]

Electron doping = [-1.0e14, -1.0e15, -1.0e16, -1.0e17, -1.0e18, -1.0e19]

Temperatures = 300

Interpolation factor = 60

$$\text{Elastic constant (GPa)} = \begin{bmatrix} 15.869 & 7.470 & 7.470 & 0 & 0 & 0 \\ 7.470 & 15.869 & 7.470 & 0 & 0 & 0 \\ 7.470 & 7.470 & 15.869 & 0 & 0 & 0 \\ 0 & 0 & 0 & 7.673 & 0 & 0 \\ 0 & 0 & 0 & 0 & 7.673 & 0 \\ 0 & 0 & 0 & 0 & 0 & 7.673 \end{bmatrix}$$

$$\text{Static dielectric} = \begin{bmatrix} 6.967888 & 0 & 0 \\ 0 & 6.967888 & 0 \\ 0 & 0 & 6.967888 \end{bmatrix}$$

$$\text{High-frequency dielectric} = \begin{bmatrix} 3.585533 & 0 & 0 \\ 0 & 3.585533 & 0 \\ 0 & 0 & 3.585533 \end{bmatrix}$$

Pop frequency = 0.24

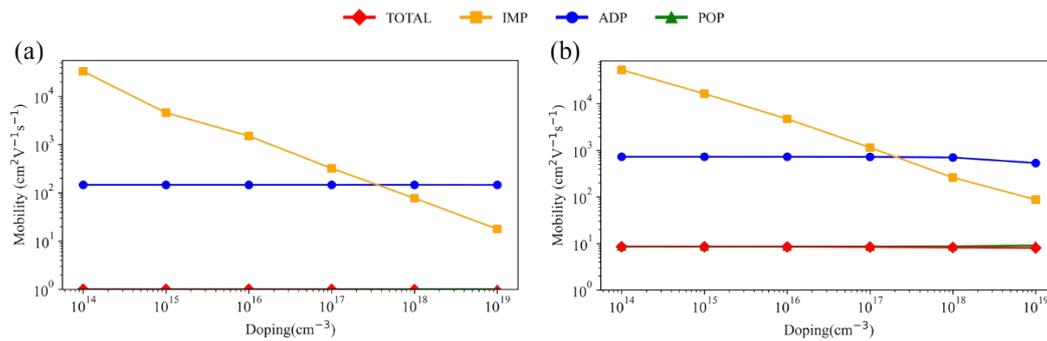


Figure S10. Transport Properties of Pristine Fm-3m Cs₂SnBr₆. Mobility as a function of carrier

concentration at 300 K for pristine Fm-3m Cs₂SnBr₆: (a) n-type mobility with scattering mechanism decomposition, (b) p-type mobility with scattering mechanism decomposition.

These are the inputs for AMSET in Cs₂(As_{0.5}Nb_{0.5})Br₆

Hole doping = [1.0e14, 1.0e15, 1.0e16, 1.0e17, 1.0e18, 1.0e19]

Electron doping = [-1.0e14, -1.0e15, -1.0e16, -1.0e17, -1.0e18, -1.0e19]

Temperatures = 300

Interpolation factor = 60

$$\text{Elastic constant (GPa)} = \begin{bmatrix} 20.492 & 6.004 & 7.189 & 0 & 0 & 0 \\ 6.004 & 20.492 & 7.189 & 0 & 0 & 0 \\ 7.189 & 7.189 & 14.412 & 0 & 0 & 0 \\ 0 & 0 & 0 & 7.048 & 0 & 0 \\ 0 & 0 & 0 & 0 & 7.048 & 0 \\ 0 & 0 & 0 & 0 & 0 & 4.670 \end{bmatrix}$$

$$\text{Static dielectric} = \begin{bmatrix} 10.942473 & 0 & 0 \\ 0 & 10.942473 & 0 \\ 0 & 0 & 11.210766 \end{bmatrix}$$

$$\text{High-frequency dielectric} = \begin{bmatrix} 4.942725 & 0 & 0 \\ 0 & 4.942725 & 0 \\ 0 & 0 & 5.588822 \end{bmatrix}$$

Pop frequency = 0.27

These are the inputs for AMSET in Cs₂(As_{0.5}Ta_{0.5})Br₆

Hole doping = [1.0e14, 1.0e15, 1.0e16, 1.0e17, 1.0e18, 1.0e19]

Electron doping = [-1.0e14, -1.0e15, -1.0e16, -1.0e17, -1.0e18, -1.0e19]

Temperatures = 300

Interpolation factor = 60

$$\text{Elastic constant (GPa)} = \begin{bmatrix} 19.926 & 5.319 & 6.282 & 0 & 0 & 0 \\ 5.319 & 19.926 & 6.282 & 0 & 0 & 0 \\ 6.282 & 6.282 & 12.889 & 0 & 0 & 0 \\ 0 & 0 & 0 & 6.468 & 0 & 0 \\ 0 & 0 & 0 & 0 & 6.468 & 0 \\ 0 & 0 & 0 & 0 & 0 & 4.646 \end{bmatrix}$$

$$\text{Static dielectric} = \begin{bmatrix} 8.524522 & 0 & 0 \\ 0 & 8.524522 & 0 \\ 0 & 0 & 8.643849 \end{bmatrix}$$

$$\text{High-frequency dielectric} = \begin{bmatrix} 4.235180 & 0 & 0 \\ 0 & 4.235180 & 0 \\ 0 & 0 & 4.460564 \end{bmatrix}$$

Pop frequency = 0.25

These are the inputs for AMSET in Cs₂(Bi_{0.5}Nb_{0.5})Br₆

Hole doping = [1.0e14, 1.0e15, 1.0e16, 1.0e17, 1.0e18, 1.0e19]

Electron doping = [-1.0e14, -1.0e15, -1.0e16, -1.0e17, -1.0e18, -1.0e19]

Temperatures = 300

Interpolation factor = 60

$$\text{Elastic constant (GPa)} = \begin{bmatrix} 17.330 & 5.339 & 6.295 & 0 & 0 & 0 \\ 5.339 & 17.330 & 6.295 & 0 & 0 & 0 \\ 6.295 & 6.295 & 12.725 & 0 & 0 & 0 \\ 0 & 0 & 0 & 5.975 & 0 & 0 \\ 0 & 0 & 0 & 0 & 5.975 & 0 \\ 0 & 0 & 0 & 0 & 0 & 4.398 \end{bmatrix}$$

$$\text{Static dielectric} = \begin{bmatrix} 9.887553 & 0 & 0 \\ 0 & 9.887553 & 0 \\ 0 & 0 & 9.421203 \end{bmatrix}$$

$$\text{High-frequency dielectric} = \begin{bmatrix} 4.398486 & 0 & 0 \\ 0 & 4.398486 & 0 \\ 0 & 0 & 4.749813 \end{bmatrix}$$

Pop frequency = 3.25

These are the inputs for AMSET in Cs₂(Bi_{0.5}Ta_{0.5})Br₆

Hole doping = [1.0e14, 1.0e15, 1.0e16, 1.0e17, 1.0e18, 1.0e19]

Electron doping = [-1.0e14, -1.0e15, -1.0e16, -1.0e17, -1.0e18, -1.0e19]

Temperatures = 300

Interpolation factor = 60

$$\text{Elastic constant (GPa)} = \begin{bmatrix} 18.815 & 6.779 & 6.152 & 0 & 0 & 0 \\ 6.779 & 18.815 & 6.152 & 0 & 0 & 0 \\ 6.152 & 6.152 & 11.322 & 0 & 0 & 0 \\ 0 & 0 & 0 & 5.414 & 0 & 0 \\ 0 & 0 & 0 & 0 & 5.414 & 0 \\ 0 & 0 & 0 & 0 & 0 & 4.813 \end{bmatrix}$$

$$\text{Static dielectric} = \begin{bmatrix} 10.331313 & 0 & 0 \\ 0 & 10.331313 & 0 \\ 0 & 0 & 8.756491 \end{bmatrix}$$

$$\text{High-frequency dielectric} = \begin{bmatrix} 4.007451 & 0 & 0 \\ 0 & 4.007451 & 0 \\ 0 & 0 & 4.159804 \end{bmatrix}$$

Pop frequency = 3.18

These are the inputs for AMSET in Cs₂(Sb_{0.5}Nb_{0.5})Br₆

Hole doping = [1.0e14, 1.0e15, 1.0e16, 1.0e17, 1.0e18, 1.0e19]

Electron doping = [-1.0e14, -1.0e15, -1.0e16, -1.0e17, -1.0e18, -1.0e19]

Temperatures = 300

Interpolation factor = 60

$$\text{Elastic constant (GPa)} = \begin{bmatrix} 20.613 & 6.778 & 8.331 & 0 & 0 & 0 \\ 6.778 & 20.613 & 8.331 & 0 & 0 & 0 \\ 8.331 & 8.331 & 15.481 & 0 & 0 & 0 \\ 0 & 0 & 0 & 6.859 & 0 & 0 \\ 0 & 0 & 0 & 0 & 6.859 & 0 \\ 0 & 0 & 0 & 0 & 0 & 4.205 \end{bmatrix}$$

$$\text{Static dielectric} = \begin{bmatrix} 11.745154 & 0 & 0 \\ 0 & 11.745154 & 0 \\ 0 & 0 & 13.48814 \end{bmatrix}$$

$$\text{High-frequency dielectric} = \begin{bmatrix} 6.089959 & 0 & 0 \\ 0 & 6.089959 & 0 \\ 0 & 0 & 7.412938 \end{bmatrix}$$

Pop frequency = 3.75

These are the inputs for AMSET in Cs₂(Sb_{0.5}Ta_{0.5})Br₆

Hole doping = [1.0e14, 1.0e15, 1.0e16, 1.0e17, 1.0e18, 1.0e19]

Electron doping = [-1.0e14, -1.0e15, -1.0e16, -1.0e17, -1.0e18, -1.0e19]

Temperatures = 300

Interpolation factor = 60

$$\text{Elastic constant (GPa)} = \begin{bmatrix} 17.364 & 4.830 & 6.564 & 0 & 0 & 0 \\ 4.830 & 17.364 & 6.564 & 0 & 0 & 0 \\ 6.564 & 6.564 & 12.908 & 0 & 0 & 0 \\ 0 & 0 & 0 & 6.065 & 0 & 0 \\ 0 & 0 & 0 & 0 & 6.065 & 0 \\ 0 & 0 & 0 & 0 & 0 & 4.951 \end{bmatrix}$$

$$\text{Static dielectric} = \begin{bmatrix} 11.04053 & 0 & 0 \\ 0 & 11.04053 & 0 \\ 0 & 0 & 9.57087 \end{bmatrix}$$

$$\text{High-frequency dielectric} = \begin{bmatrix} 4.413127 & 0 & 0 \\ 0 & 4.413127 & 0 \\ 0 & 0 & 4.779305 \end{bmatrix}$$

Pop frequency = 3.40

Table S5 Analysis of Dielectric Constants for Pristine and Co-doped Systems. The table summarizes the electronic contribution (ϵ^{ele}), ionic contribution (ϵ^{ion}), and static dielectric constant (ϵ^{st}) tensors along the three principal directions (xx, yy, zz).

Compound	SG	ion_{xx}	ion_{yy}	ion_{zz}	ele_{xx}	ele_{yy}	ele_{zz}	st_{xx}	st_{yy}	st_{zz}
Cs ₂ SnBr ₆	Fm-3m	3.382	3.382	3.382	3.586	3.586	3.586	6.968	6.968	6.968
Cs ₂ SnBr ₆	P4/mmm	4.416	4.416	4.013	3.591	3.591	3.590	7.007	7.007	7.603
Cs ₂ (As _{0.5} Nb _{0.5})Br ₆	P4/mmm	6.000	6.000	5.622	4.943	4.943	5.589	10.942	10.942	11.211
Cs ₂ (As _{0.5} Ta _{0.5})Br ₆	P4/mmm	4.289	4.289	4.183	4.235	4.235	4.461	8.525	8.525	8.644
Cs ₂ (Bi _{0.5} Nb _{0.5})Br ₆	P4/mmm	5.489	5.489	4.671	4.398	4.398	4.750	9.888	9.888	9.421
Cs ₂ (Bi _{0.5} Ta _{0.5})Br ₆	P4/mmm	6.324	6.324	4.597	4.007	4.007	4.160	10.331	10.331	8.756
Cs ₂ (Sb _{0.5} Nb _{0.5})Br ₆	P4/mmm	5.655	5.655	6.075	6.090	6.090	7.413	11.745	11.745	13.488
Cs ₂ (Sb _{0.5} Ta _{0.5})Br ₆	P4/mmm	6.627	6.627	4.792	4.413	4.413	4.779	11.041	11.041	9.571