Supplementary Information

First-Principles DFT+U Investigation of Eco-Friendly K_2AgPBr_6 Double Perovskite: Mechanical Ductility and Optoelectronic Resilience for Near-Infrared Harvesting and Tandem Photovoltaics

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Section S1: Detailed Structural and Atomic Parameters

The K_2AgPBr_6 compound stabilizes in the cubic elpasolite structure with the $Fm\bar{3}m$ space group (No. 225). The detailed atomic coordinates and Wyckoff positions after geometric optimization are summarized in **Table S1**.

Table S1: *Atomic coordinates and Wyckoff positions for K_2AgPBr_6 lattice.*

Atom	Wyckoff Site	x	y	z	Occupation
K	8c	0.25	0.75	0.75	1.0
Ag	4b	0.5	0.5	0.5	1.0
P	4a	0	0	0	1.0
Br	24e	0.5	0.248	0.5	1.0

Detailed Electronic Configuration and Pseudopotential Information

The specific valence electronic configurations and pseudopotential definitions used for each element are listed in **Table S2**. The very low charge spilling parameter (0.19%) confirms the high quality of the basis set and the accuracy of the electronic wavefunctions.

Table S2: *Electronic configurations and Pseudopotential details.*

Element	Valence Configuration	Ionic Charge	Potential Type
K	$3s^2 3p^6 4s^1$	9.00	Koelling-Harmon
Ag	$4s^2 4p^6 4d^{10} 5s^1$	19.00	Koelling-Harmon
P	$3s^2 3p^3$	5.00	Koelling-Harmon
Br	$4s^2 4p^5$	7.00	Koelling-Harmon

Section S2: Computational Convergence Tests

To ensure the highest degree of numerical accuracy and reproducibility, all calculations were performed using the **Ultra-fine** quality settings within the CASTEP code. The specific convergence tolerances and electronic parameters used for the geometry optimization and property calculations are detailed in **Table S3** and **Table S4**.

Table S3: *Convergence tolerances for Geometry Optimization (Ultra-fine quality).*

Parameter	Convergence Criterion	Unit
Total Energy	5.0×10^{-6}	eV/atom
Maximum Ionic Force	0.01	eV/Å
Maximum Stress	0.02	GPa
Maximum Displacement	5.0×10^{-4}	Å
Optimization Algorithm	BFGS	-

Table S4: *Electronic and SCF Parameters for GGA-PBE and DFT+U calculations.*

Parameter	Setting/Value
Energy Cut-off (Customized)	500 eV
SCF Tolerance	2.0×10^{-6} eV/atom
Max. SCF Cycles	100
K-point Mesh (Monkhorst-Pack)	4×4×4
K-point Mesh (For accurate optical response and Charge Density mapping)	8×8×8
Pseudopotentials	OTFG Ultrasoft
Relativistic Treatment	Koelling-Harmon
Electronic Minimizer	Density Mixing
Hubbard U (for Ag-4d orbitals)	2.00 eV

Section S3: Comparison of Theoretical Frameworks

The accuracy of the electronic properties of K_2AgPBr_6 was evaluated using both standard GGA-PBE and the DFT+U framework. As shown in **Table S5**, standard GGA-PBE tends to underestimate the bandgap, a common limitation in DFT studies of transition metal-based semiconductors. The application of the Hubbard U parameter (2.0 eV for Ag-4d) significantly improves the agreement with the expected bandgap range by correcting the self-interaction errors.

Table S5: *Comparison of calculated bandgap (E_g) and lattice constant (a) using different functionals.*

Method	**Lattice Constant a (Å)**	**Bandgap E_g (eV)**	**Gap Nature**
GGA-PBE	12.150	0.422	Indirect (L→X)
DFT+U (U=2.0 eV)	**12.150**	**0.529**	**Indirect (L→X)**

To provide quantitative evidence of our parameterization process, we have summarized the influence of the Hubbard U parameter on the bandgap and electronic character in **Table S6**. While increasing the U value leads to a wider bandgap, a value of **2.0 eV** was identified as the physical limit. Beyond this value (i.e., U > 2.0 eV), we observed a significant suppression of the Ag 4*d* and Br 4*p* orbital hybridization at the valence band maximum (VBM). We prioritized maintaining the correct electronic band topology and orbital character over simply 'fitting' the bandgap to a larger value, identifying U = 2.0 eV as the most scientifically consistent parameter for this system.

Table S6: *Benchmarking of Hubbard U parameter for Ag 4d states in K_2AgPBr_6.*

Hubbard U value (eV)	**Bandgap (E_g, eV)**	**ΔE_g from GGA (eV)**	**Remarks on Electronic Structure and Physicality**
0.0 (Standard GGA)	**0.422**	0.000	Significant self-interaction error; overly delocalized Ag 4*d* states.

1.0	0.475	0.053	Partial correction of SIE; bandgap remains below literature standards.
2.0 (Selected)	**0.529**	**0.107**	Optimal *p*−*d* hybridization at VBM; consistent with d^{10} benchmarks.
3.0	0.584	0.162	Onset of over-localization; Ag 4*d* contribution to VBM begins to diminish.
4.0	0.641	0.219	Unphysical isolation of *d*-states; distorted band curvature at high-symmetry points.
5.0	0.698	0.276	Severe over-localization; suppression of essential *p*−*d* anti-bonding character.

Section S4: Impact of Spin-Orbit Coupling (SOC) on Band Structure

To address the concerns regarding relativistic effects in the K_2AgPBr_6 system, we performed additional electronic band structure calculations including Spin-Orbit Coupling (SOC). **Figure S1** illustrates the comparison. The inclusion of SOC leads to minor splitting of the Ag-4d and Br-4p states in the valence band regions; however, the fundamental indirect bandgap (L→X) and the overall electronic topology remain remarkably stable. The calculated bandgap with SOC is approximately **0.556 eV**, which is very close to the DFT+U value (0.529 eV). This justifies that the DFT+U framework without SOC is sufficiently accurate for describing the optoelectronic properties of this specific halide system.

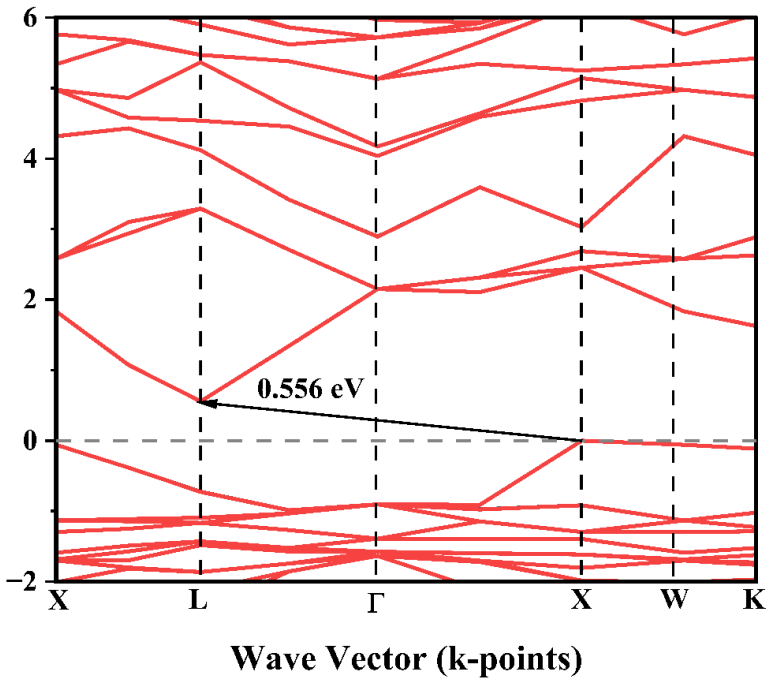
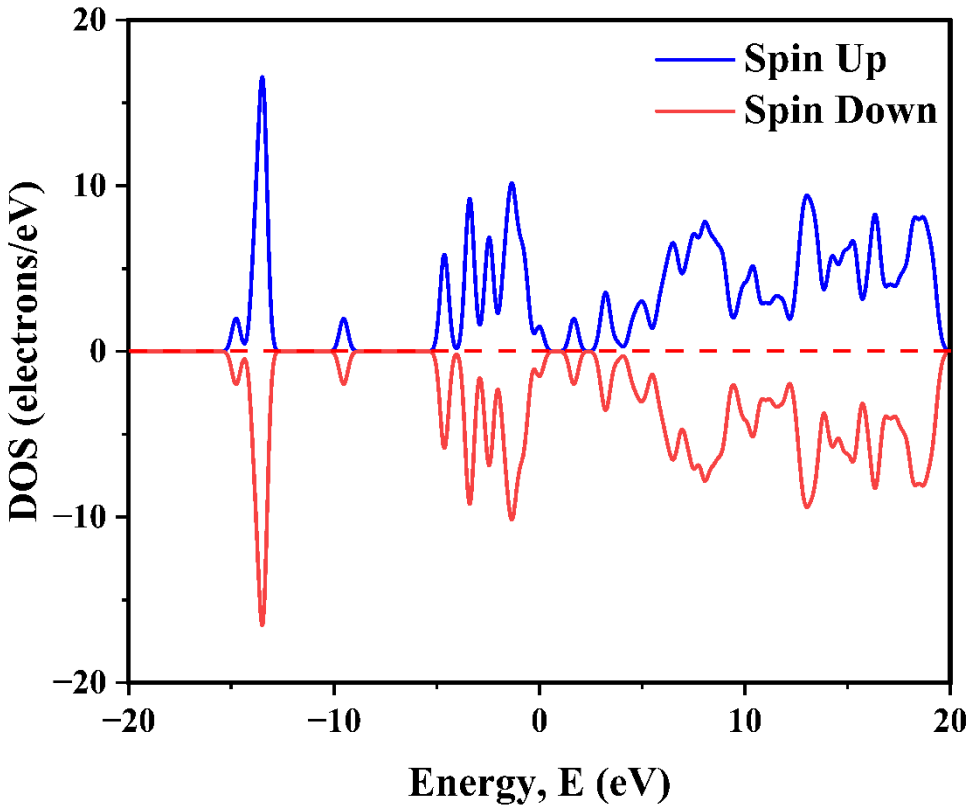


Figure S1: *Calculated electronic band structure of K_2AgPBr_6 including Spin-Orbit Coupling (SOC) effects.*



Section S5: Numerical Data for Mulliken Population and Bond Overlap

To quantitatively support the bonding analysis discussed in the main text, the detailed Mulliken orbital populations and bond overlap values are provided in **Table S7** and **S8**.

Table S7: *Detailed Atomic Populations (Mulliken).*

Species	s-orbital	p-orbital	d-orbital	Total (e)	Charge (e)
P	2.035	2.604	0.000	4.638	+0.362
K	2.109	6.279	0.226	8.614	+0.386
Ag	2.588	6.718	9.903	19.209	-0.209
Br	1.821	5.334	0.000	7.154	-0.154

Table S8: *Calculated Bond Overlap Populations and Bond Lengths.*

Bond Type	Overlap Population	Length (Å)
Ag – Br	0.11	2.82455
P – Br	-0.02	2.59826

Section S6: Thermophysical and Acoustic Properties

The elastic constant calculations also provide insights into the thermophysical and acoustic nature of K_2AgPBr_6. The averaged sound velocity (v_m) and the elastic Debye temperature (θ_D) were derived from the calculated elastic moduli.

Table S9: *Calculated Acoustic and Thermal Properties.*

Property	Value	Unit
Bulk Modulus (B)	19.06375	GPa
Shear Modulus (G)	9.13946	GPa

Young's Modulus (E)	23.64049	GPa
Poisson Ratio (v)	0.29332	-
Vickers Hardness (H_V)	1.91024	GPa
Universal Anisotropy (A^U)	0.50766	-
Averaged Sound Velocity (v_m)	1759.18	m/s
Debye Temperature (θ_D)	164.91	K