Electronic Supplementary Material (ESI) for Materials Advances.

Supporting Information

Black Single Crystals of Lead-free Perovskite $Cs_2Ag(Bi:Ru)Br_6$ with Intermediate Band

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Experimental Methods

Materials: CsBr (≥99.9%) was obtained from Xi'an Polymer Light Technology Corp(PLT). $BiBr_3$ (≥ 98%) was purchased from Aldrich. Ruthenium(III) bromide hydrate (Ru 25% min) was purchased from Alfa. AgBr (99.9%) and 48% HBr were purchased from Aladdin. All these commercially available materials were used as received without any further purification.

Preparation of $Cs_2AgBiBr_6$ Crystals (Ru-0): Solid CsBr (424 mg, 2.0 mmol), $BiBr_3$ (448 mg, 1.0 mmol) and AgBr (188 mg, 1.0 mmol) were dissolved in 10~12 mL of 48% HBr and then transferred into a 25 mL or 50 mL Teflon-lined autoclave. The autoclave was sealed and placed in the Muffle furnace where it was heated to 120 °C for 24 h. After being slowly cooled to room temperature at a rate of 1 °C h^{-1}, red single crystals were obtained. Finally, the crystals were dried.

Preparation of $Cs_2AgBiBr_6$ Crystals with Ru-doping (Ru-x): x% (molar ratio) $BiBr_3$ is replaced by equimolar $RuBr_3$ in the precursor solutions. The synthesis approach is the same as that used for pristine $Cs_2AgBiBr_6$.

Device Fabrication: Au electrode was deposited by thermal evaporation at a rate of 0.3 nm s^{-1} using a shadow mask to pattern the electrode. The electrode spacing is 0.2 mm.

Characterization: UV–visible absorption spectrum was measured by using a UV–vis–NIR spectrophotometer (UV3600 Plus). ICP-OES analysis of the samples was performed by Prodigy 7 (Leeman). PL, excited at 400 nm, was measured with NanoLog infrared fluorescence spectrometer (Nanolog L3-2Ihr). The XRD patterns were measured using X-ray diffraction system (PANalytical Inc.) with monochromatic Cu Kα irradiation (λ = 1.5418 Å). VB-XPS was measured using the X-ray Photoelectron Spectrometer (AXIS Supra, Kratos Analytical Ltd.) The power of the 980 nm laser is 85 mW. The volt-ampere characteristic curve of the device is measured by the probe station (TTPX, LakeShore).

DFT calculation: Our first-principles calculations are performed using the projector augmented wave (PAW) method[1, 2] as implemented in the Vienna ab initio simulation

package (VASP) code[3]. The generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE)[4] is used for exchange correlation functional. The cutoff energy is set to 500 eV for the plane-wave expansion. The 7×7×7, 11×11×11, and 13×13×13 *Γ*-centered Monkhorst-Pack *k*-point meshes are employed for structure optimization, self-consistent calculation, and DOS calculations, respectively. In the calculations of the halide perovskite $Cs_2Ag(Bi:Ru)Br_6$, the convergence tolerance of energy (residual atomic forces) is less than 10^{-6} eV (10^{-2} eV/Å).

Table S1. ICP-OES measurement of crystals powder (molar ratio:Ru/(Ru+Bi))

Sample	Molar ratio of Ru/(Ru+Bi) in precursor	Cs (μg/ml)	Bi (μg/ml)	Ru (μg/ml)	Molar ratio of Ru/(Ru+Bi) in single crystals
Ru-0.7	7:1000	31.7495	23.8543	0.0003	< 0.01%
Ru-1	1:100	33.0088	24.6628	0.0357	0.30 %
Ru-3	3:100	35.6166	26.4831	0.1390	1.07 %
Ru-5	1:20	33.5736	24.3427	0.2217	1.85 %

Table S2. The crystal system and the lattice constants of $Cs_2Ag(Bi:Ru)Br_6$. Here, Exp. and Cal. indicate the results by experiment and calculation, respectively.

Sample	Crystal System	Lattice Constant (Å)	
		Exp.	Cal.
Ru-0	Cubic	11.280	11.292
Ru-1	Cubic	11.280	-
Ru-3	Cubic	11.278	-
Ru-5	Cubic	11.268	-

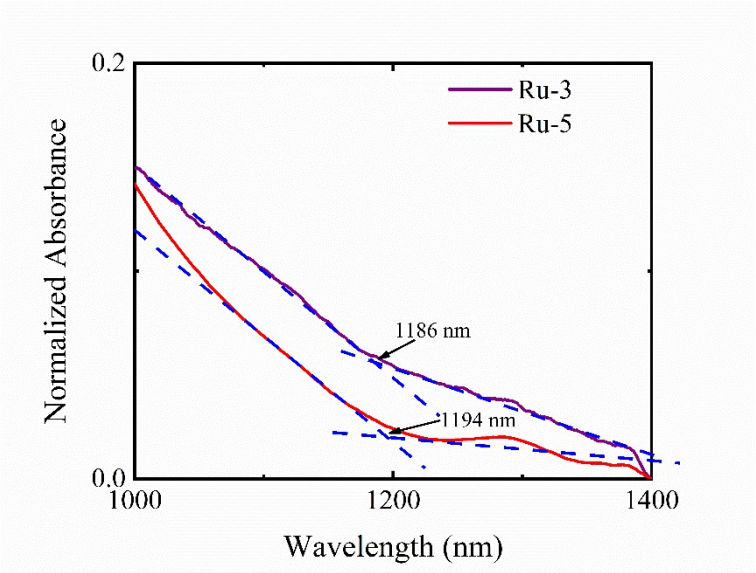

Figure S1. Locally amplified absorption spectra of Ru-3 and Ru-5

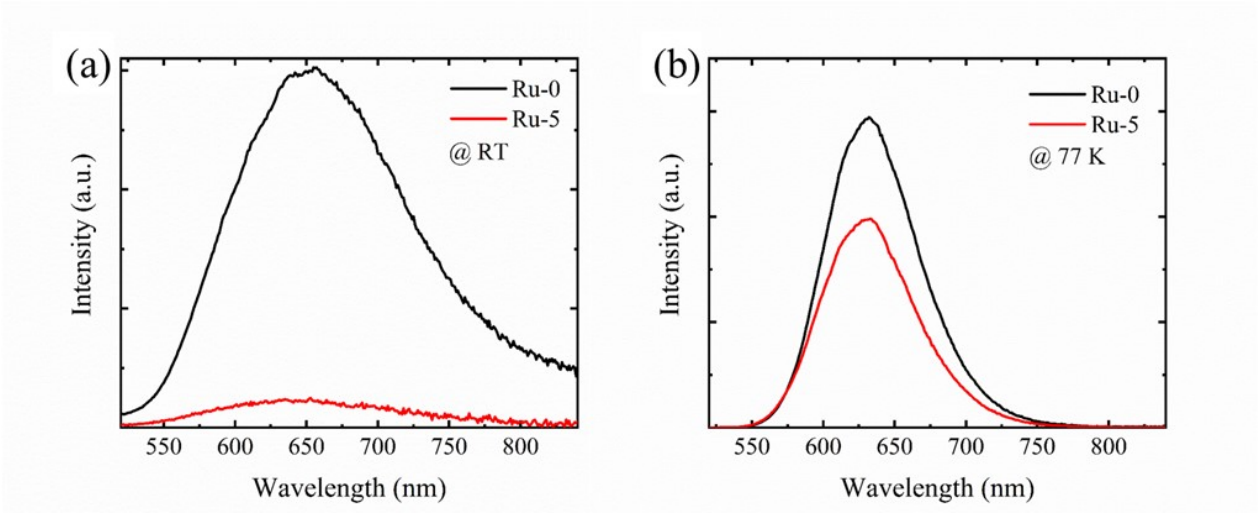

Figure S2. The PL (a) in the visible region at room temperature (RT), (b) at 77 K and of Ru-0 and Ru-5 powders.

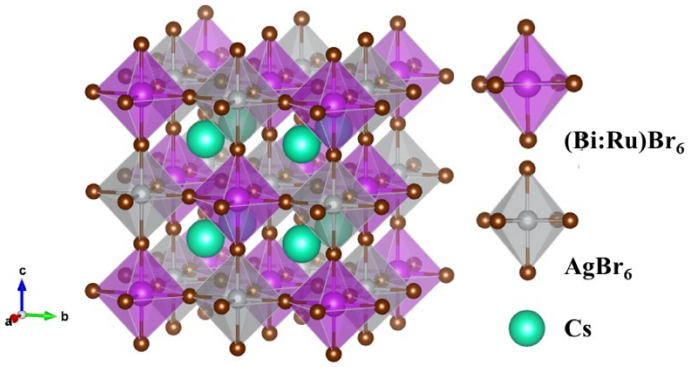

Figure S3. The simulated crystal structure of $Cs_2Ag(Bi:Ru)Br_6$.

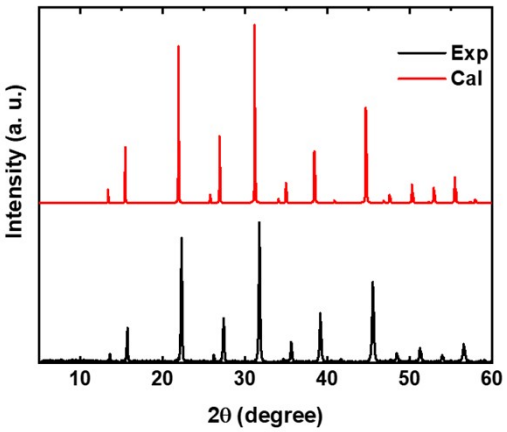

Figure S4. The comparison of experimental (Exp) and calculated (Cal) XRD spectrum of $Cs_2AgBiBr_6$.

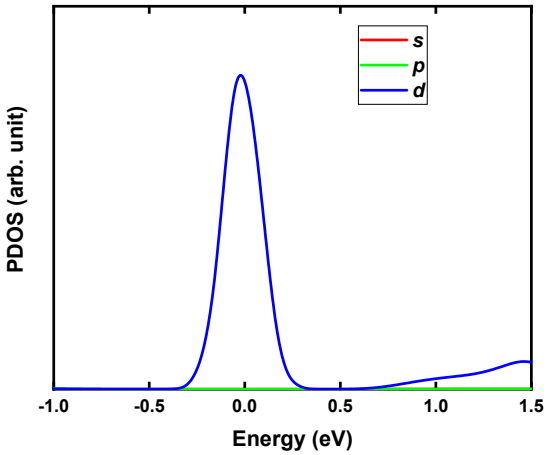

Figure S5. The partial density of states of Ru-*s*/*p*/*d* of Ru-25.

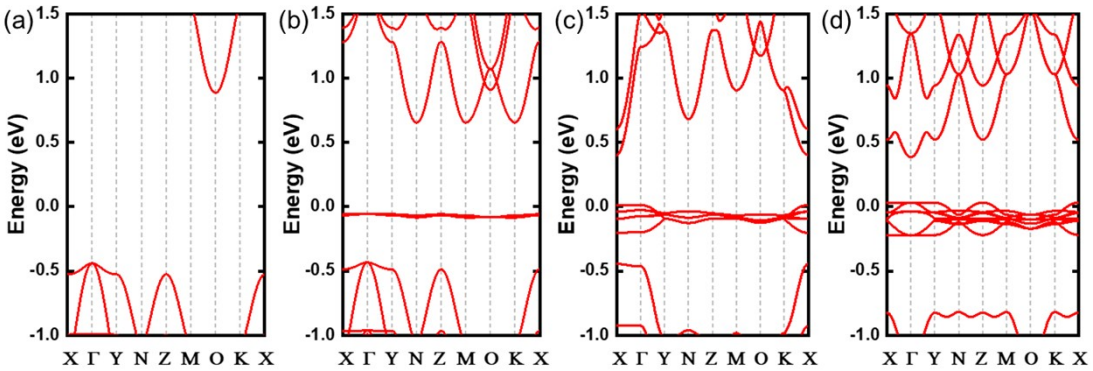

Figure S6. The calculated band structures of (a) $Cs_2Ag(Bi_1Ru_0)Br_6$, (b) $Cs_2Ag(Bi_{0.75}Ru_{0.25})Br_6$, (c) $Cs_2Ag(Bi_{0.5}Ru_{0.5})Br_6$ and (d) $Cs_2Ag(Bi_{0.25}Ru_{0.75})Br_6$. Here, the Fermi level is set at 0 eV.

References:

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[2] P. E. Blöchl, *Physical Review B* **1994**, 50, 17953.
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[4] J. P. Perdew, K. Burke,M. Ernzerhof, *Physical Review Letters* **1996**, 77, 3865.