Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Annex 1: Absorption model used to fit the PDS spectra

The α·d spectra (**Figure 4**a) has been fitted using the following equations of the Urbach-Tauc combined model,

$$for\ E < E_1 \rightarrow \alpha_{1,Urbach} = \alpha_0 \cdot exp\left(\frac{E}{E_U}\right)$$

$$for\ E > E_1 \rightarrow \alpha_{2,Tauc} = \beta \cdot \frac{\sqrt{E - E_g}}{E}$$

where E is the energy ($h\nu$), E_g is the bandgap, E_U is the Urbach energy, α_0 and β are constants of the model, and E_1 is a transition energy near the optical bandgap where the following boundary conditions must be fulfilled,

$$\alpha_{1,Urbach}(E_1) = \alpha_{2,Tauc}(E_1)$$

$$\frac{d\alpha_{1,Urbach}}{dE}(E_1) = \frac{d\alpha_{2,Tauc}}{dE}(E_1)$$

Once the value of E_1 is determined, the system of equations is solved, which determines the value of the direct bandgap (E_g).

Annex 2: Additional figures and tables

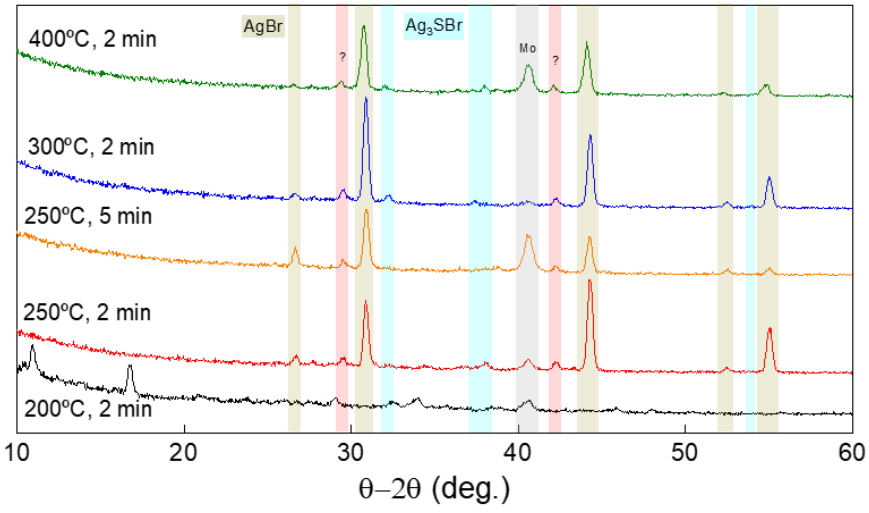

Figure S1: GIXRD patterns of samples prepared with AgBr and TU (1:2) dissolved in DMF. Samples were prepared following this procedure: dissolution of AgBr and TU precursors in DMF to obtain a 0.5 M solution; deposition of solution by drop-casting on Mo-coated glass substrate; drying at 50ºC using hot-plate; annealing at temperatures between 200ºC-400ºC using a hot-plate under N_2 atmosphere

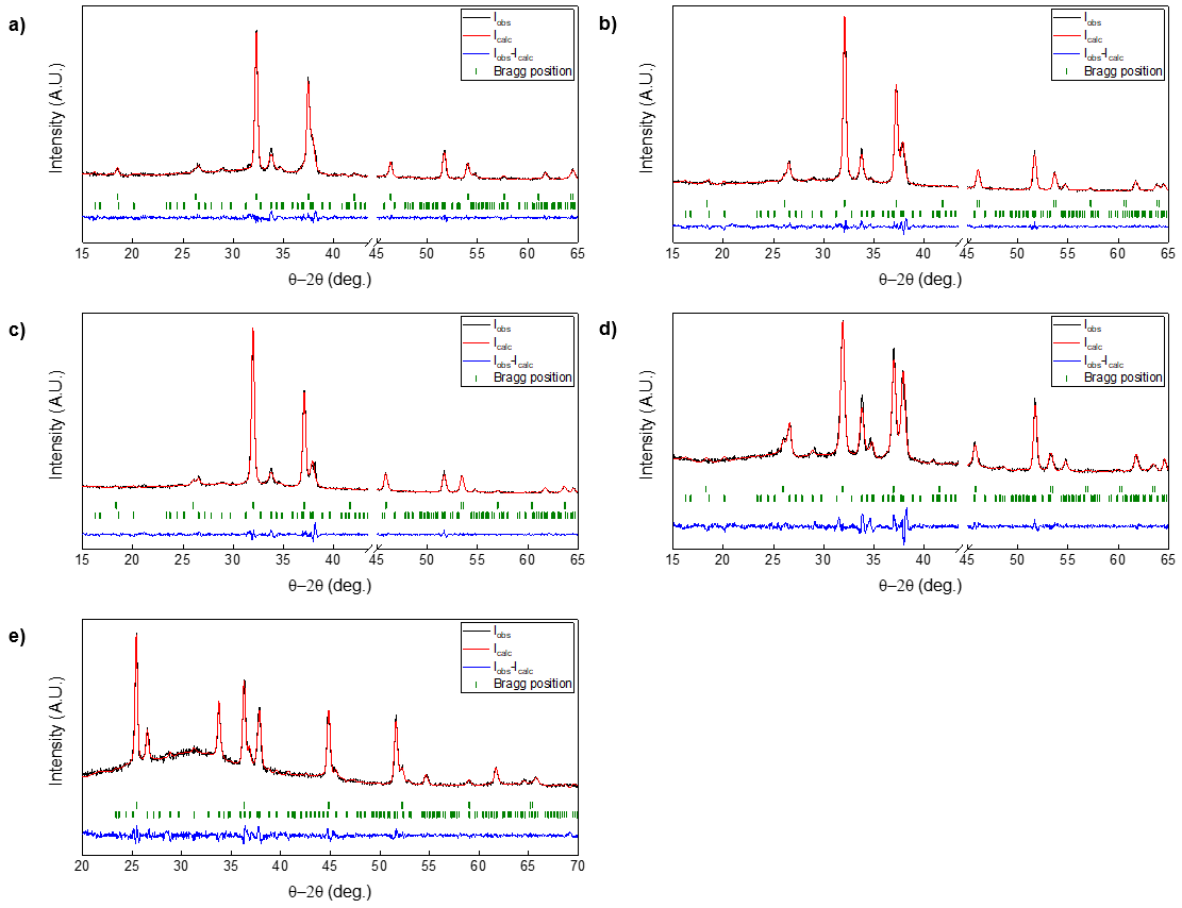

Figure S2: Experimental (red points) and Le Bail (black) refined patterns, along with the difference profile (blue curve) and Bragg reflections (green sticks) of $Ag_3S(Br_xI_{1-x})$ anti-perovskite samples

Table S1: Cell volume and parameters of $Ag_3S(Br_xI_{1-x})$ samples. Calculated from Le Bail refinement using the FullProf suite software

x	Vol. (Å^3)	Cell p. (Å)	χ
1	110.61	4.800	1.43
0.7	112.70	4.830	1.80
0.5	113.97	4.849	1.73
0.3	114.74	4.859	2.03
0	121.42	4.952	1.37

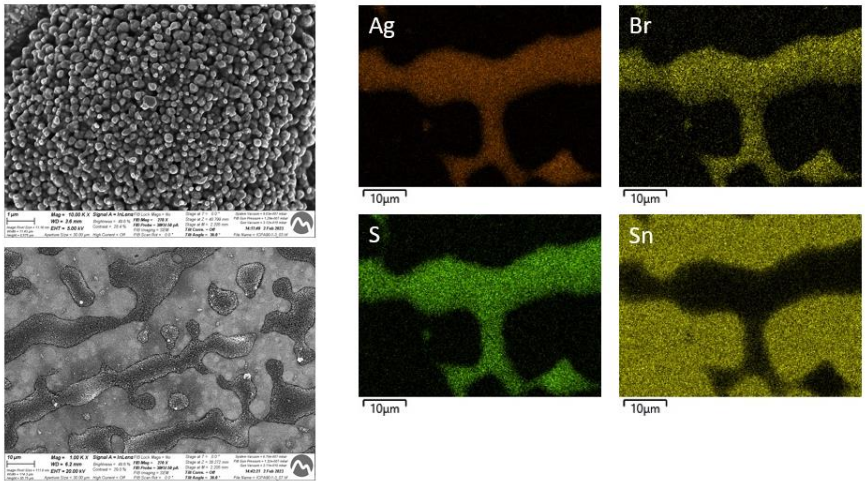

Figure S3: SEM and EDX micrographs of an FTO/Ag_3SBr sample

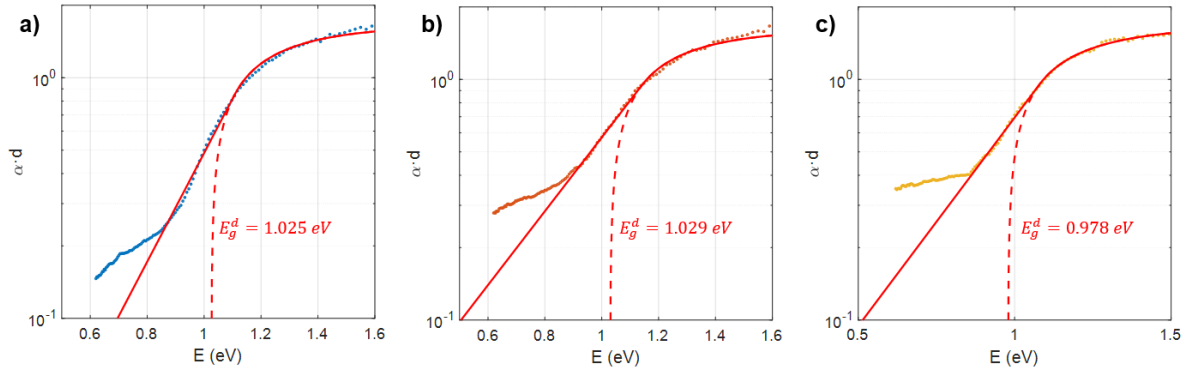

Figure S4: Absorption (α·d) spectra of $Ag_3S(Br_xI_{1-x})$, measured with PDS. **a)** x=0.7 **b)** x=0.5 **c)** x=0.3

Table S2: Urbach energies of $Ag_3S(Br_xI_{1-x})$ samples. Calculated from PDS measurements

x	Urbach energy (meV)
1	287
0.7	251
0.5	283
0.3	192
0	285

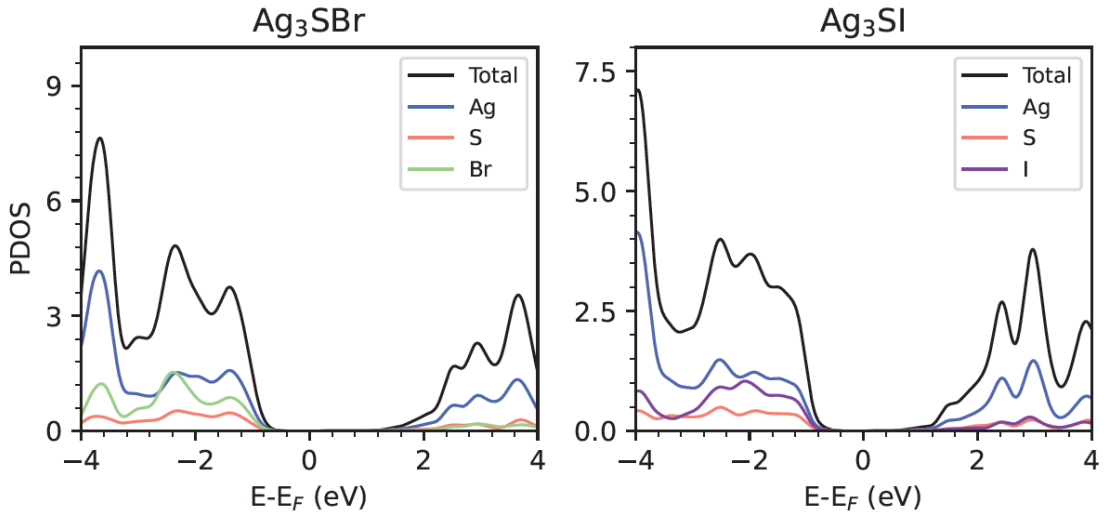

Figure S5: Total and projected density of electronic states calculated for Ag_3SBr and Ag_3SI with first-principles DFT methods. The largest contribution to the top of the valence band and bottom of the conduction band stem from the electronic Ag orbitals.

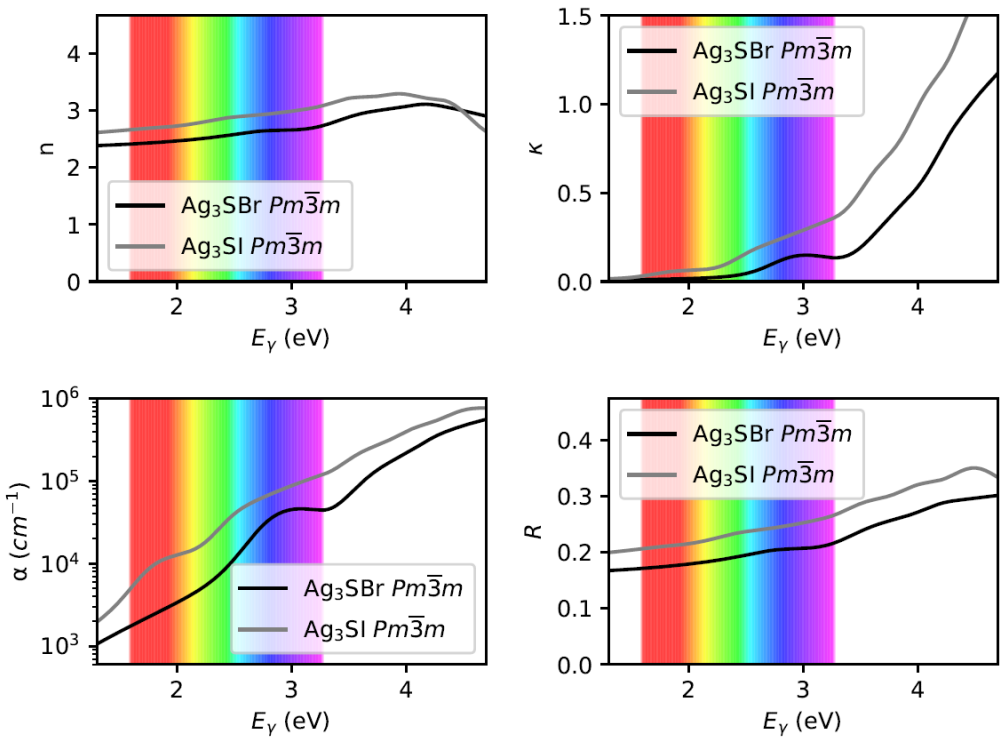

Figure S6: Refractive index (n), extinction coefficient (κ), absorption coefficient (α), and reflectivity (R) estimated as a function of the incident photon energy