Supplementary Information

Hydrothermal Growth and Characterization of Large Rb_2SnBr_6 Double Perovskite Crystals: A Promising Semiconductor Material for Photocatalysis and Optoelectronics

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Note about notation: *Going forward, we will use (Rb:Sn:X) ratio notation to indicate the nominal stoichiometry used where relevant: Rb_2SnBr_6 (2:1:6) or Rb_2SnBr_6 (4:3:10).*

Table S1. Experimental results of several adopted techniques for fabricating the Rb_2SnBr_6 halide double perovskite.

Synthesis technique	**Hydrothermal**		**Evaporation**	
Solvent	H_2O	H_2O	H_2O	DMF
Temperature (°C)	220	150	120	120
Crystal size	Centimeter	Millimeter	Micron	Micron
Crystal Color	Light Yellow	Light Yellow	Dark Brown	Dark Yellow
Product Stability	Air and moisture stable	Air and moisture stable	Air and moisture stable	Air and moisture stable
Phase formed	$Rb_2Sn\mathit{X}_6$, *Fm*-3*m*			

Table S2. The unit cell dimension of the pristine, 50% Cl-doped and 10% I-doped Rb_2SnBr_6

Sample	**Rb2SnBr6 (2:1:6)**	**$Rb_2SnBr_3Cl_3$(2:1:6)**	**$Rb_2SnBr_{5.5}I_{0.5}$(2:1:6)**
Space group	*Fm*-3*m*	*Fm*-3*m*	*Fm*-3*m*
a (Å)	10.678	10.57478	10.77
Rwp (%)	4.38	3.7	4.67
Volume (Å^3)	1217.71	1182.53	1251.48
α = β = γ =	90	90	90

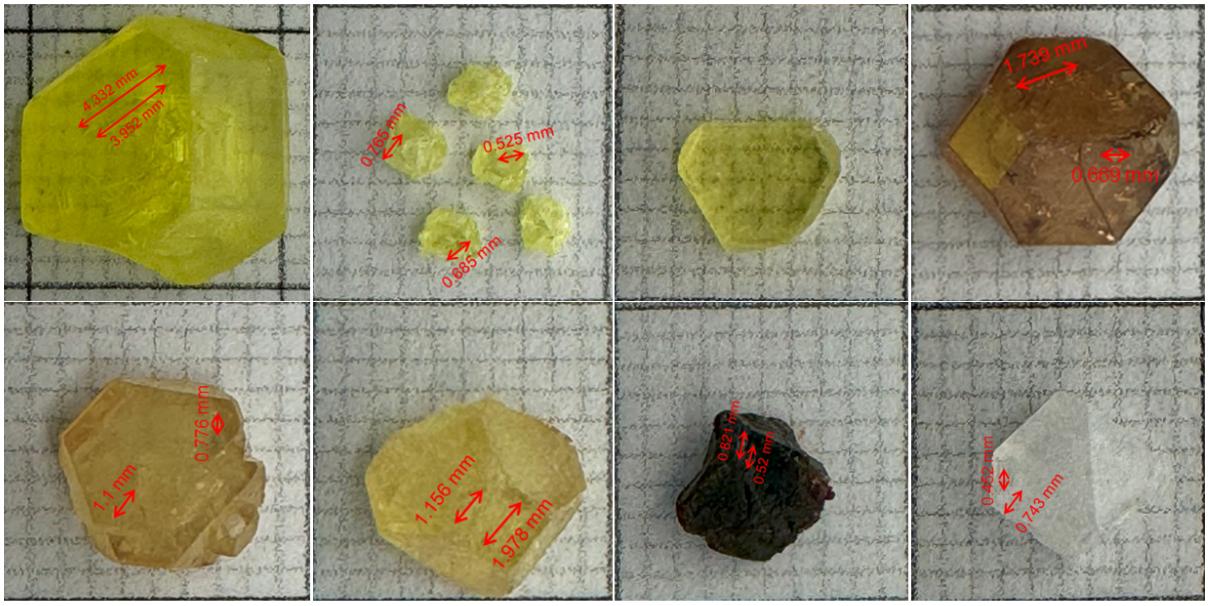

Figure S1: The measured crystal domain size of the single crystal in **(a)** Rb_2SnBr_6 (4:3:10), **(b)** Rb_2SnBr_6 (2:1:6), **(c)** $Rb_2SnBr_{5.4}Cl_{0.6}$ (2:1:6), **(d)** $Rb_2SnBr_{4.5}Cl_{1.5}$ (2:1:6), **(e)** $Rb_2SnBr_3Cl_3$ (2:1:6), **(f)** $Rb_2SnBr_{1.5}Cl_{4.5}$ (2:1:6), **(g)** $Rb_2SnBr_{5.5}I_{0.5}$ (2:1:6), and **(h)** Rb_2SnCl_6 (2:1:6). The grid is 1x1 mm^2.

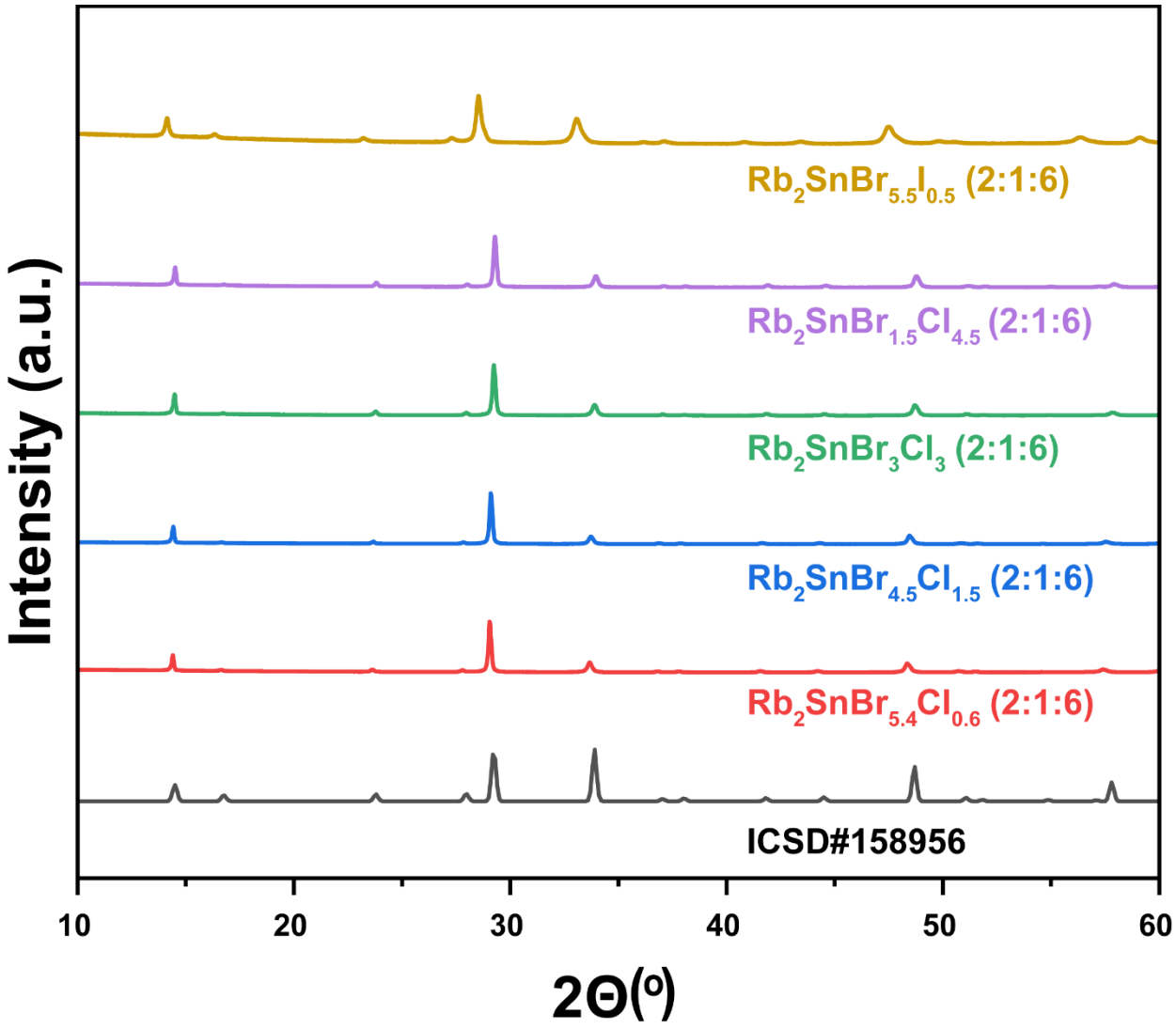

Figure S2. Powder XRD data for Cl- and I-doped Rb_2SnBr_6 (2:1:6).

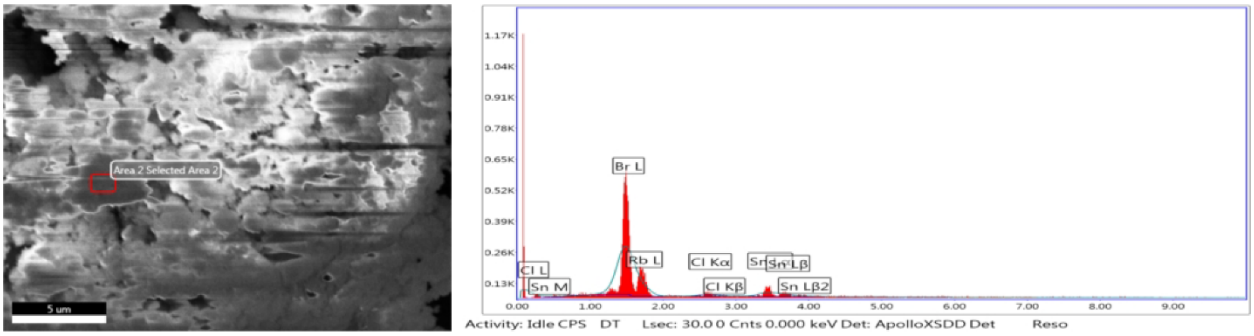

Table. EDS single point analysys of the Cl-doped $Rb_2SnBr_{4.5}Cl_{1.5}$ (2:1:6)

Element	At.%
Rb	17.03
Sn	12.38
Br	62.06
Cl	8.53
Total	100
Experimental composition	$Rb_{1.99(\pm 0.5\%)}Sn_{1.04(\pm 4\%)}Br_{7.76(\pm 72\%)}Cl_{2.4(\pm 60\%)}$

Figure S3. Energy-dispersive X-ray spectroscopy (EDS) single spot analysis of the $Rb_2SnBr_{4.5}Cl_{1.5}$ (2:1:6) powder sample.

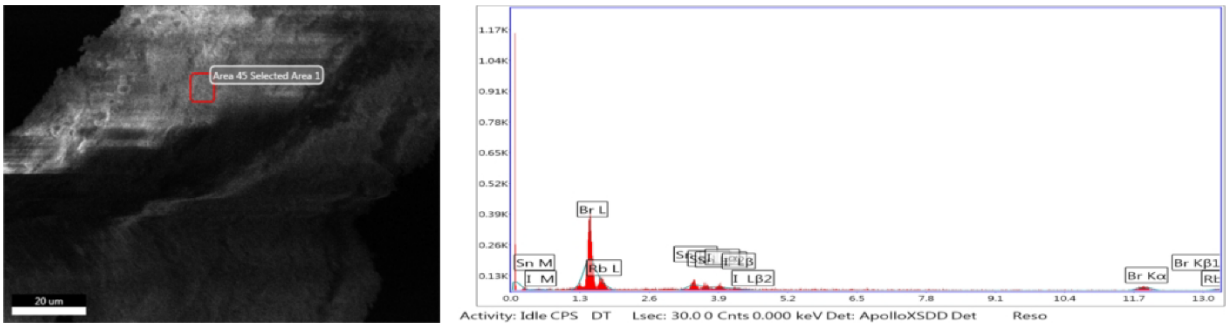

Table. EDS point analysys of the I-doped $Rb_2SnBr_{5.4}I_{0.6}$ (2:1:6)

Element	At.%
Rb	16.15
Sn	16.09
Br	58.36
I	9.4
Total	100
Experimental composition	$Rb_{1.88(\pm 6\%)}Sn_{1.35(\pm 35\%)}Br_{7.3(\pm 35.18\%)}I_{0.7(\pm 16\%)}$

Figure S4. Energy-dispersive X-ray spectroscopy (EDS) analysis of the powder sample of the $Rb_2SnBr_{5.4}I_{0.6}$ (2:1:6) .

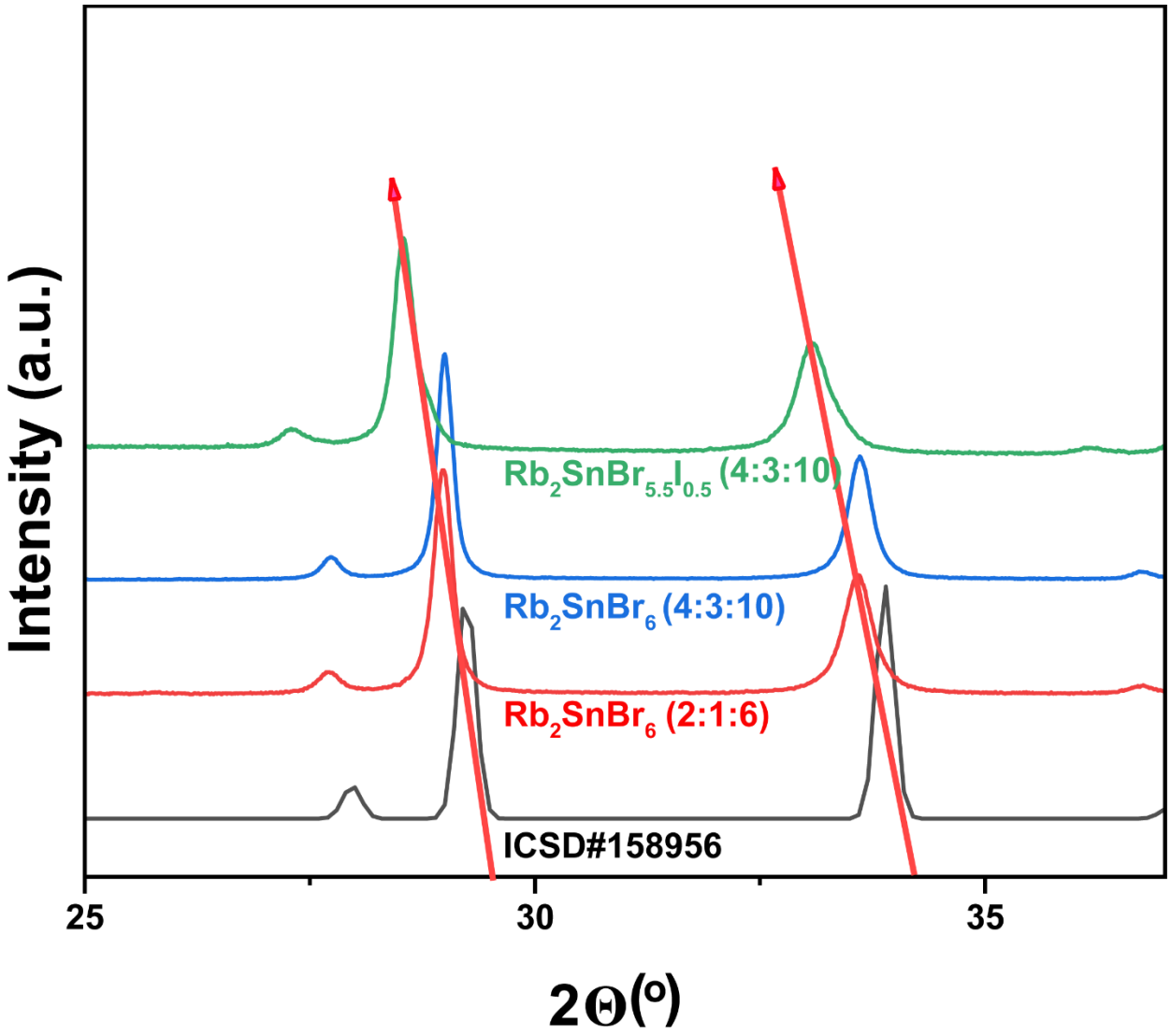

Figure S5. Lower angle peak shifting of the pristine and doped Rb_2SnBr_6.

Figure S6. Extracted powder samples from the low-temperature process for the fabrication of Rb_2SnBr_6; **(a)** Rb_2SnBr_6 (2:1:6) from hydrothermal process (T = 150°C, H_2O); **(b)** Rb_2SnBr_6 (4:3:10) from hydrothermal process (T = 150°C, H_2O); **(c)** Rb_2SnBr_6 (2:1:6) from evaporation process (T = 120°C, H_2O); and **(d)** Rb_2SnBr_6 (2:1:6) from evaporation process (T = 120°C, DMF).

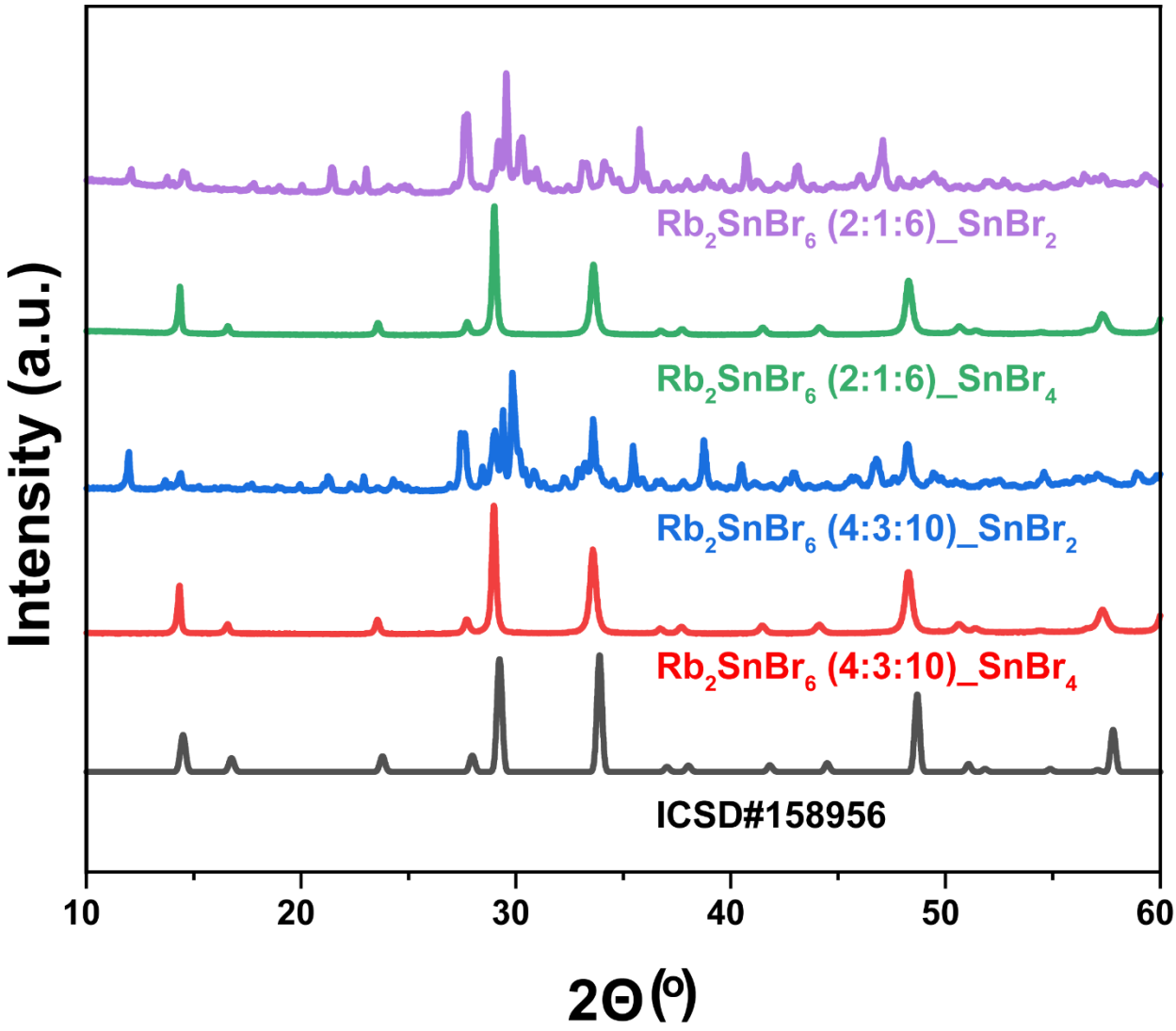

Figure S7. PXRD analysis of the low-temperature synthesis compositions of Rb_2SnBr_6 (2:1:6) and Rb_2SnBr_6 (4:3:10) from the $SnBr_2$ and $SnBr_4$ salts as Sn sources. The unidentified peaks in the XRD plots of Rb_2SnBr_6 (4:3:10) are from the corresponding raw materials peaks of $SnBr_2$ and $SnBr_4$.

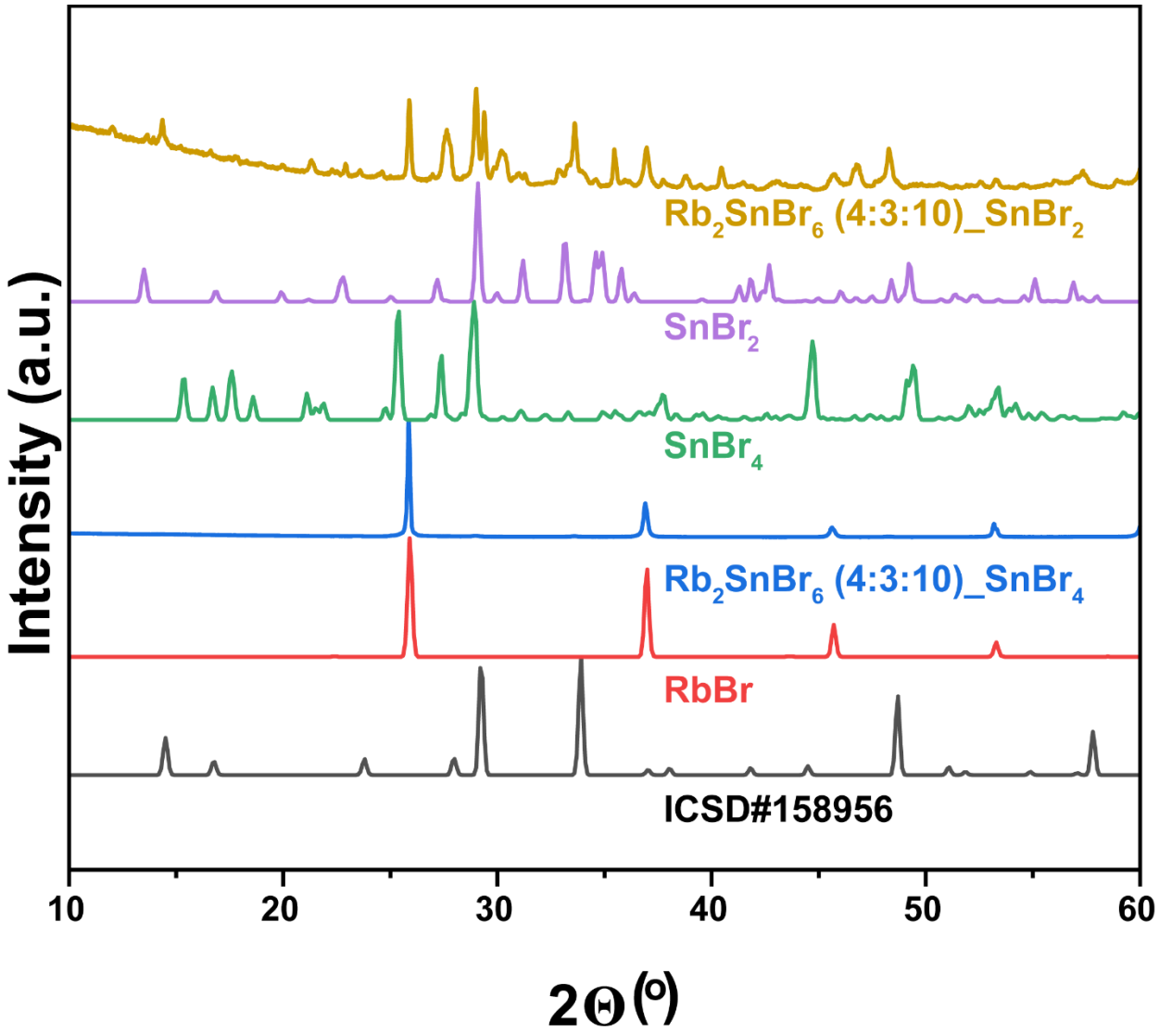

Figure S8. Powder XRD data for the Hydrothermal process (120 ℃) to synthesize Rb_2SnBr_6 (4:3:10) single crystal. The unidentified peaks in the XRD plots of Rb_2SnBr_6 (4:3:10) are from the corresponding raw materials peaks of $SnBr_2$ and $SnBr_4$.

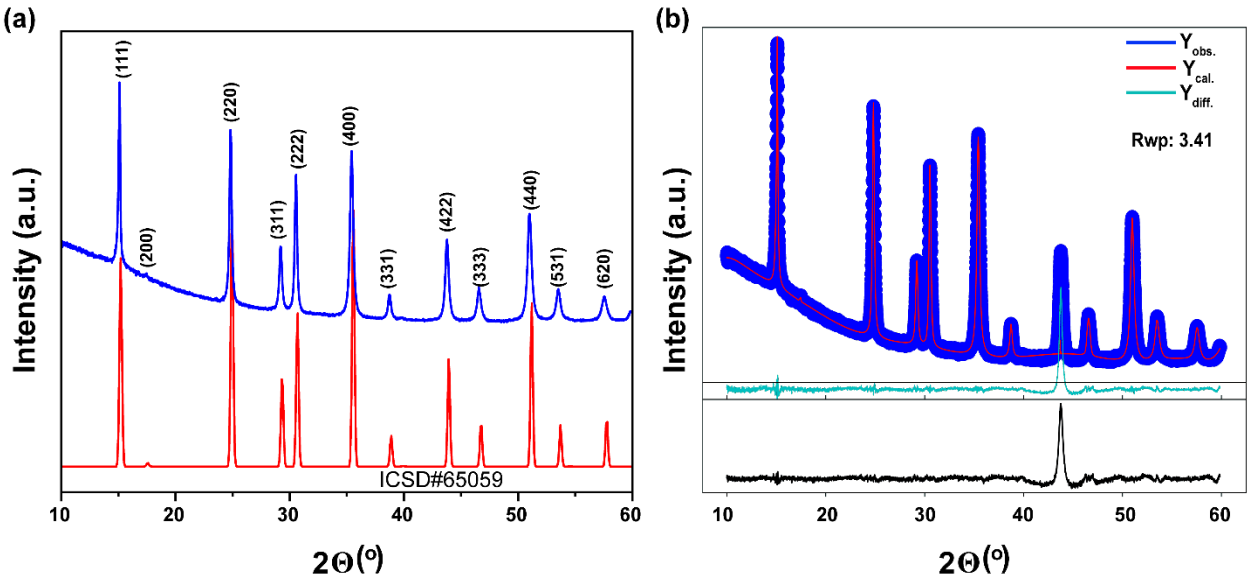

Figure S9. It has analyzed Powder crystal XRD of Rb_2SnCl_6 and its Rietveld refinement crystal structure synthesized by hydrothermal process (*Fm*-3*m*, a = 10.14 Å, V^3 = 1042.68 $Å^3$, R_{wp} = 3.41).

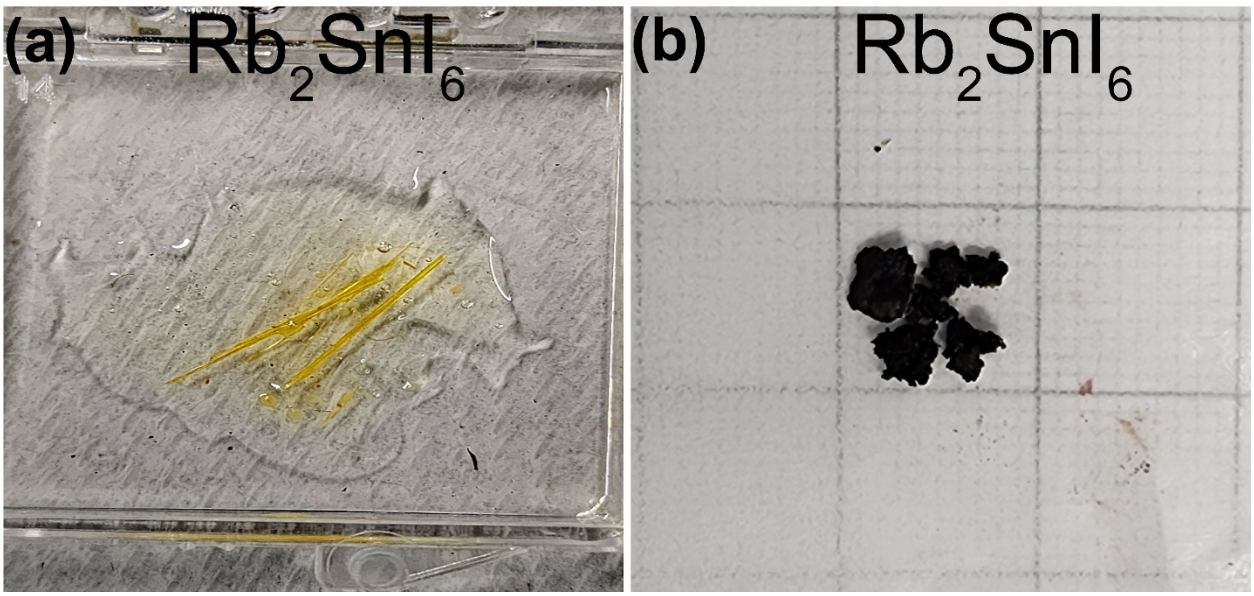

Figure S10. Hydrothermal synthesized crystals of (a) as-synthesized Rb_2SnI_6 and (b) oxidized product of Rb_2SnI_6.

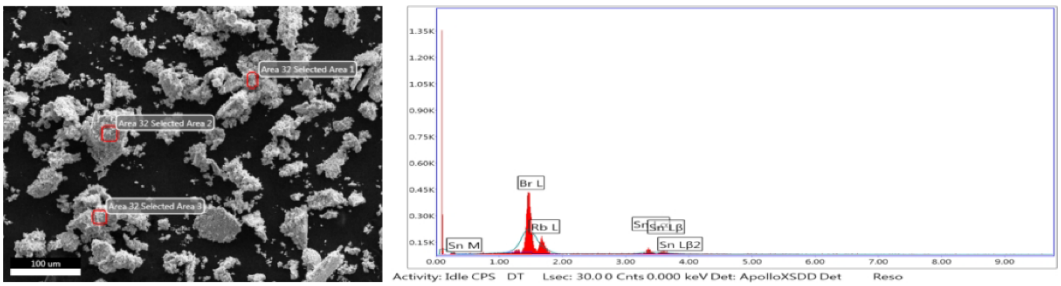

Table. Three point EDS analysis of the Rb_2SnBr_6 (2:1:6) crystal powder.

Selected point	Elements	At.%
Point 1	Rb	21.09
	Sn	15.97
	Br	62.93
	Total	100
	Experimental composition	$Rb_{2.46(\pm21\%)}Sn_{1.35(\pm35\%)}Br_{7.87(\pm31\%)}$
Point 2	Rb	13.31
	Sn	13.12
	Br	73.57
	Total	100
	Experimental composition	$Rb_{1.56(\pm22\%)}Sn_{1.1(\pm10\%)}Br_{9.2(\pm53\%)}$
Point 3	Rb	16.39
	Sn	19.25
	Br	64.36
	Total	100
	Experimental composition	$Rb_{1.92(\pm4\%)}Sn_{1.6(\pm60\%)}Br_{8.05(+34\%)}$

Figure S11. Three-point energy-dispersive X-ray spectroscopy (EDS) analysis of the powder sample of the Rb_2SnBr_6 (R2).

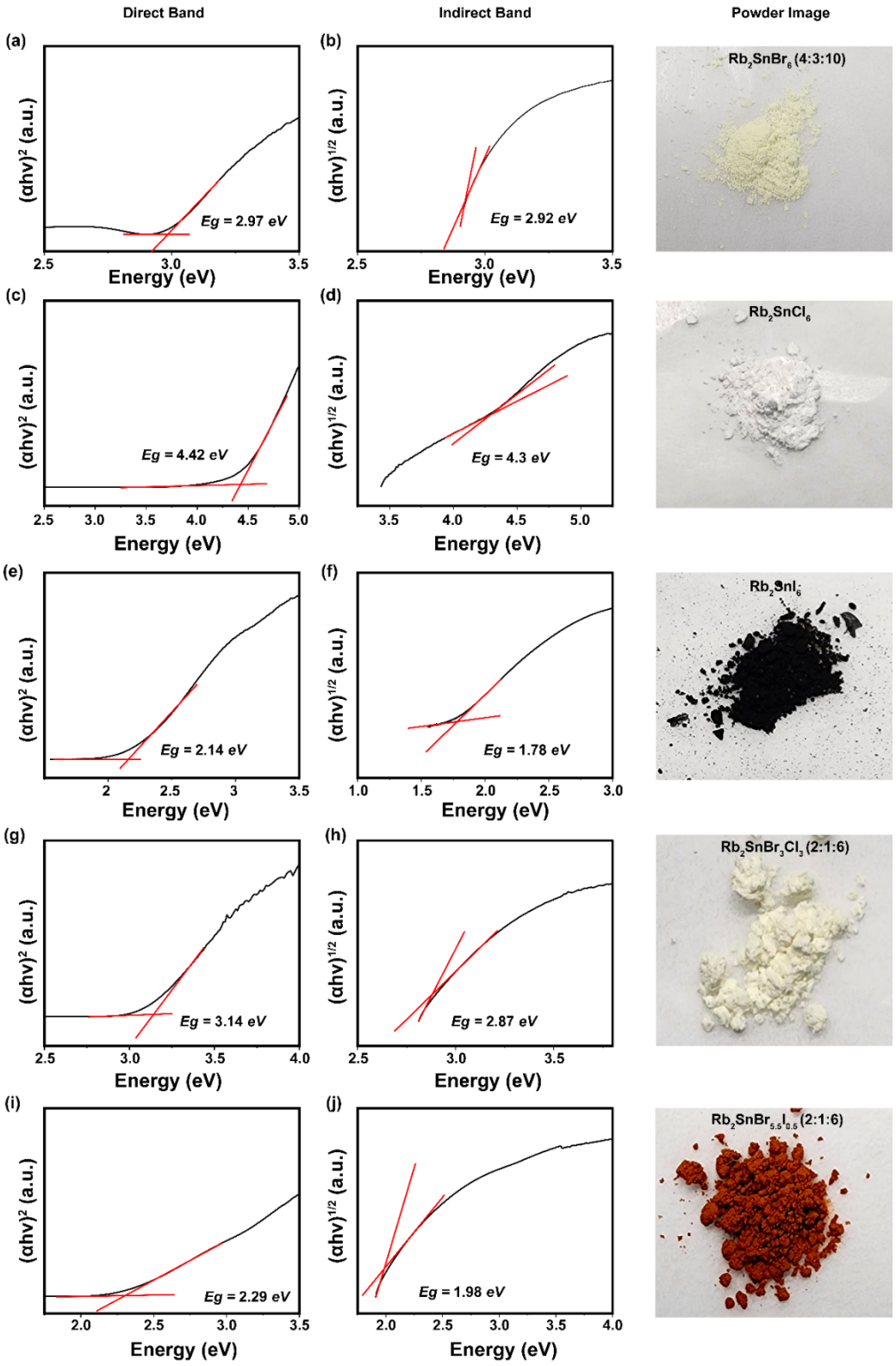

Figure S12. Calculated direct and indirect optical bandgap of the pristine and doped Rb_2SnBr_6 (2:1:6) from powder samples using the UV-absorption data: (**a,b**) (Rb_2SnBr_6 (2:1:6), (**c,d**) Rb_2SnCl_6, (**e,f**) Rb_2SnI_6, (**g,h**) $Rb_2SnBr_3Cl_3$ and (**g,h**) $Rb_2SnBr_{5.5}Cl_{0.5}$.

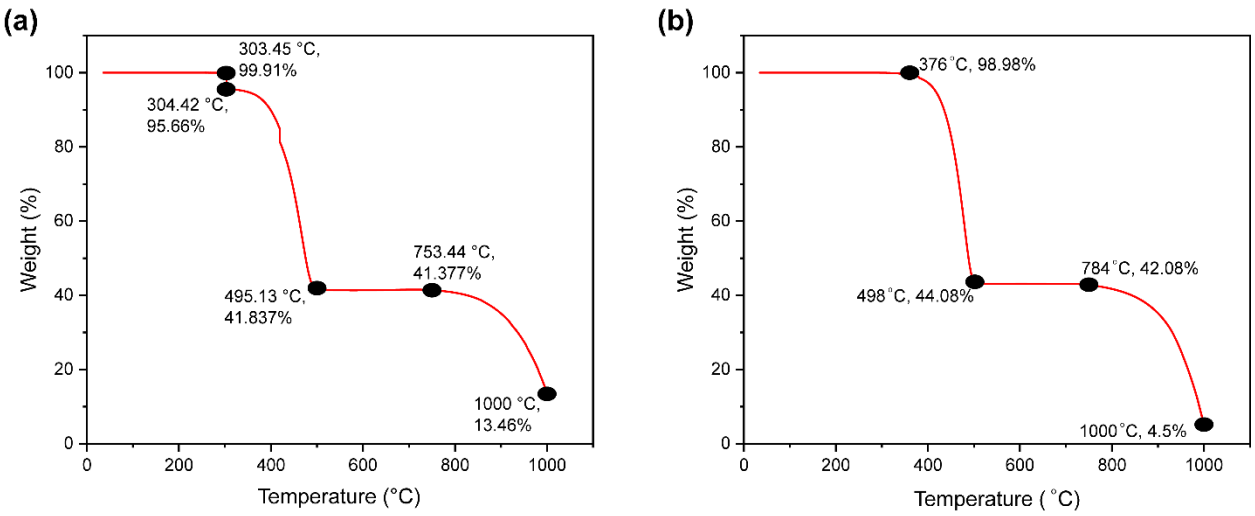

Figure S13. Thermogravimetric analysis (TGA) of the Rb_2SnBr_6 halide double perovskite single crystals; (a) Rb_2SnBr_6 (2:1:6) (b) Rb_2SnBr_6 (4:3:10).