Antimony-Doping Enhanced Photoluminescence Quantum Yield in Zero-Dimensional Lead-Free Metal Halide Rb$_2$CsBiCl$_6$ Crystals

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Table S1. Crystallographic and structure refinement data of $Rb_2CsBiCl_6$ at RT.

Empirical formula	$Rb_2CsBiCl_6$
Formula weight	725.53
Crystal system	orthorhombic
Space group	*Pbcm*
Cell dimensions/Å	$a = 8.1044(4)$, $b = 12.9295(6)$, $c = 25.8508(10)$
Cell parameters /°	$\alpha = \beta = \gamma = 90.00$
Z	8
Cell Volume/Å^3	2708.8(2)
Calculated density (g/cm^3)	3.55789
Color	colorless
F(000)	2512
μ/mm^{-1}	23.936
Data collection range/deg	$2.51 < \theta < 30.85$
Index ranges	$-10 \leq h \leq 10$, $-14 \leq k \leq 18$, $-36 \leq l \leq 30$
Data/restraints/parameters	3551/0/96
GOF(F^2)	1.039
Final R indices [Fo^2>2σ(Fc^2).]^a	$R_1 = 0.0361$, wR$_2 = 0.0862$
Final R indices (all data)^a	$R_1 = 0.0495$, wR$_2 = 0.0904$

$$^aR_1 = \sum \left\| F_0 \right| - \left| F_c \right\| / \sum \left| F_0 \right| \ and \ wR_2 = \left[\sum w(F_0^2 - F_c^2) / \sum wF_0^4 \right]^{\frac{1}{2}} \ for \ F_0^2 > 2\sigma(F_c^2)$$

Table S2. Atomic coordinates of $Rb_2CsBiCl_6$ measured at RT.

Atom	Wyckoff	S.O.F.	x/a	y/b	z/c
Rb1	8e	1	0.19039(9)	-0.09342(5)	0.65514(3)
Rb2	8e	1	0.31539(10)	0.25515(6)	0.66207(3)
Cs1	8e	1	0.76108(8)	0.08664(4)	0.54998(2)
Bi1	4c	2	0.28213(4)	1/4	1/2
Bi2	4d	m	0.75582(5)	0.08114(3)	3/4
Cl1	4d	m	0.8998(4)	-0.10851(19)	3/4
Cl2	4d	m	0.6144(4)	0.27275(19)	3/4
Cl3	8e	1	0.5272(3)	0.17456(16)	0.43926(7)
Cl4	8e	1	0.2724(3)	0.08152(14)	0.55966(8)
Cl5	8e	1	0.9598(3)	0.13932(18)	0.67229(8)
Cl6	8e	1	0.5503(3)	0.02172(17)	0.67445(8)
Cl7	8e	1	0.0497(3)	0.16218(15)	0.43954(8)

Table S3. Selected bond lengths (Å) of $Rb_2CsBiCl_6$ measured at RT.

Rb1-Cl1 (x1)	3.406(2)	Rb1-Cl2 (x1)	3.393(2)
Rb1-Cl3 (x1)	3.506(2)	Rb1-Cl4 (x1)	3.413(2)
Rb1-Cl5 (x1)	3.570(3)	Rb1-Cl5 (x1)	3.690(3)
Rb1-Cl6 (x1)	3.313(2)	Rb1-Cl7 (x1)	3.251(2)
Rb2-Cl1 (x1)	3.364(2)	Rb2-Cl2 (x1)	3.330(2)
Rb2-Cl3 (x1)	3.261(2)	Rb2-Cl4 (x1)	3.488(2)
Rb2-Cl5 (x1)	3.259(2)	Rb2-Cl6 (x1)	3.583(3)
Rb2-Cl6 (x1)	3.628(2)	Rb2-Cl7 (x1)	3.561(2)
Cs1-Cl3 (x1)	3.616(2)	Cs1-Cl3 (x1)	3.634(2)
Cs1-Cl3 (x1)	4.116(2)	Cs1-Cl4 (x1)	3.582(2)
Cs1-Cl4 (x1)	3.969(3)	Cs1-Cl5 (x1)	3.613(2)
Cs1-Cl6 (x1)	3.738(3)	Cs1-Cl7 (x1)	3.574(2)
Cs1-Cl7 (x1)	3.818(2)	Cs1-Cl7 (x1)	4.011(2)
Bi1-Cl3 (x2)	2.7133(19)	Bi1-Cl4 (x2)	2.6703(18)
Bi1-Cl7 (x2)	2.6981(19)	Bi2-Cl1 (x1)	2.715(3)
Bi2-Cl2 (x1)	2.730(3)	Bi2-Cl5 (x2)	2.708(2)
Bi2-Cl7 (x2)	2.679(2)		

Table S4. Selected bond angles (°) of $Rb_2CsBiCl_6$ measured at RT.

Cl4-Bi1-Cl4 (x1)	176.62(11)	Cl6-Bi2-Cl6 (x1)	93.60(11)
Cl4-Bi1-Cl7 (x4)	89.32(7)	Cl6-Bi2-Cl5 (x2)	85.31(8)
Cl7-Bi1-Cl7(x1)	91.45(10)	Cl6-Bi2-Cl5 (x2)	178.90(7)
Cl4-Bi1-Cl3 (x2)	93.59(7)	Cl5-Bi2-Cl5 (x1)	95.77(10)
Cl4-Bi1-Cl3 (x2)	88.89(7)	Cl6-Bi2-Cl1 (x2)	90.46(7)
Cl7-Bi1-Cl3 (x2)	175.98(7)	Cl5-Bi2-Cl1 (x2)	89.35(7)
Cl7-Bi1-Cl3 (x2)	91.40(7)	Cl6-Bi2-Cl2 (x2)	89.96(7)
Cl3-Bi1-Cl3 (x1)	85.89(9)	Cl5-Bi2-Cl2 (x2)	90.24(7)
		Cl1-Bi2-Cl2 (x1)	179.39(9)

Table S5. Molar ratios of $M_{Sb^{3+}}/M_{(Sb^{3+}+Bi^{3+})}$ in solutions and in $Rb_2CsBiCl_6:Sb^{3+}$ single crystals, respectively.

$M_{Sb^{3+}}/M_{(Sb^{3+}+Bi^{3+})}$ (%) in saturated solutions	5	10	15	20	25	30
$M_{Sb^{3+}}/M_{(Sb^{3+}+Bi^{3+})}$ (%) in single crystals	0.3	1.0	1.6	1.9	2.2	3.5

Table S6. Crystallographic and structure refinement data of $Rb_2CsBiCl_6$ at 100 K.

Empirical formula	$Rb_2CsBiCl_6$
Formula weight	725.53
Crystal system	orthorhombic
Space group	*Pbcm*
Cell dimensions/Å	$a = 8.0294(3)$, $b = 12.7822(5)$, $c = 25.7036(8)$
Cell parameters /°	$\alpha = \beta = \gamma = 90.00$
Z	8
Cell Volume/Å^3	2638.05(16)
Calculated density (g/cm^3)	3.654
Color	colorless
F(000)	2512
μ/mm^{-1}	24.578
Data collection range/deg	$2.556 < \theta < 26.320$
Index ranges	$-10 \leq h \leq 8$, $-14 \leq k \leq 15$, $-29 \leq l \leq 32$
Data/restraints/parameters	2752/0/97
GOF(F^2)	1.037
Final *R* indices [Fo$^2 > 2\sigma$(Fc^2).]^a	$R_1 = 0.0351$, wR$_2 = 0.0885$
Final *R* indices (all data)^a	$R_1 = 0.0401$, wR$_2 = 0.0908$

$$^a R_1 = \sum \left\| F_0 \right| - \left| F_c \right\| / \sum \left| F_0 \right| \ and \ wR_2 = \left[\sum w(F_0^2 - F_c^2) / \sum wF_0^4 \right]^{\frac{1}{2}} \ for \ F_0^2 > 2\sigma(F_c^2)$$

Table S7. Cell parameters of $Rb_2CsBiCl_6$ measured at 293(2) K and 100 K, respectively.

Measured temperature	Space group	a/Å	b/Å	c/Å	V/Å^3
293(2) K	*Pbcm*	8.1044(4)	12.9295(6)	25.8508(10)	2708.8(2)
100 K	*Pbcm*	8.0294(3)	12.7822(5)	25.7036(8)	2638.05(16)
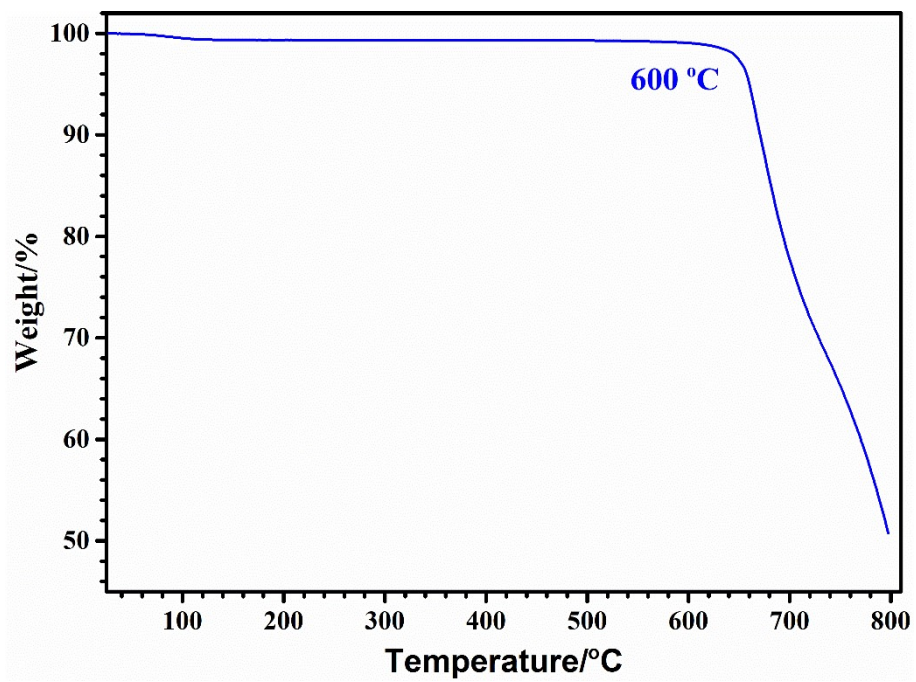
Figure S1. Thermal analysis curve of $Rb_2CsBiCl_6$.
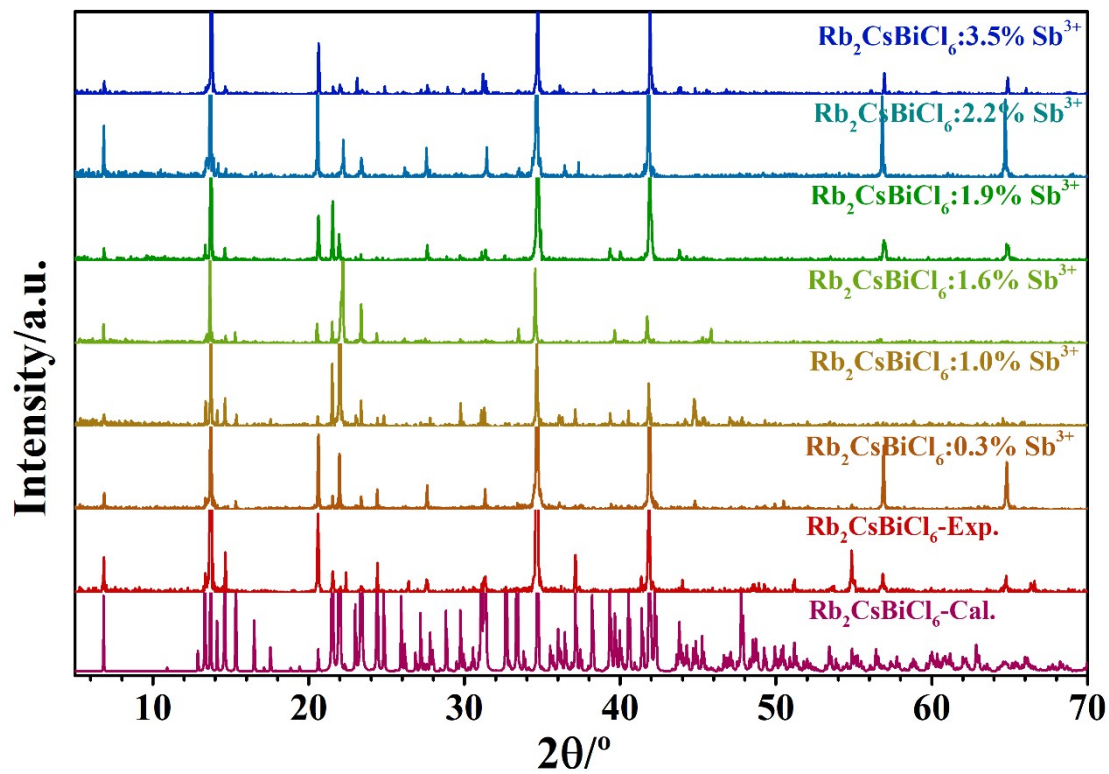
Figure S2. Calculated and experimental powder XRD patterns of undoped and Sb^{3+}-doped $Rb_2CsBiCl_6$ (with $M_{Sb^{3+}}/M_{(Bi^{3+}+Sb^{3+})}$ less than 30% in solutions).
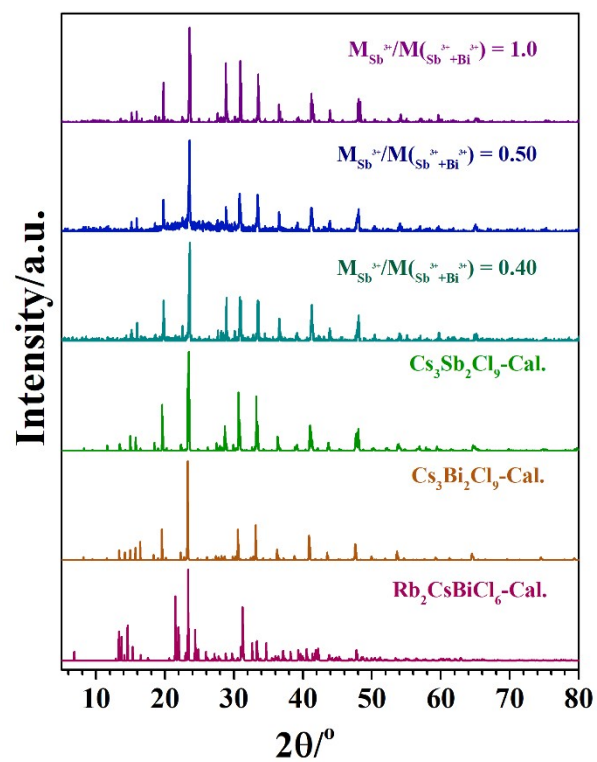
Figure S3. Calculated and experimental powder XRD patterns of undoped and Sb^{3+}-doped $Rb_2CsBiCl_6$ (with $M_{Sb^{3+}}/M_{(Bi^{3+}+Sb^{3+})}$ greater than 30% in solutions).

Figure S4. Photograph of crystals grown in a solution with $M_{Sb^{3+}}/M_{(Bi^{3+}+Sb^{3+})}$ of 40%.
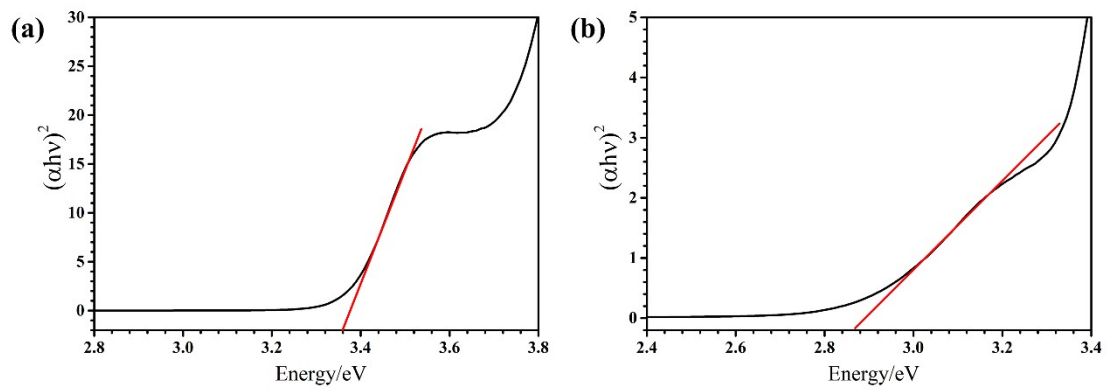
Figure S5. (a) Tauc plots of $Rb_2CsBiCl_6$, and (b) $Rb_2CsBiCl_6:Sb^{3+}$ samples.
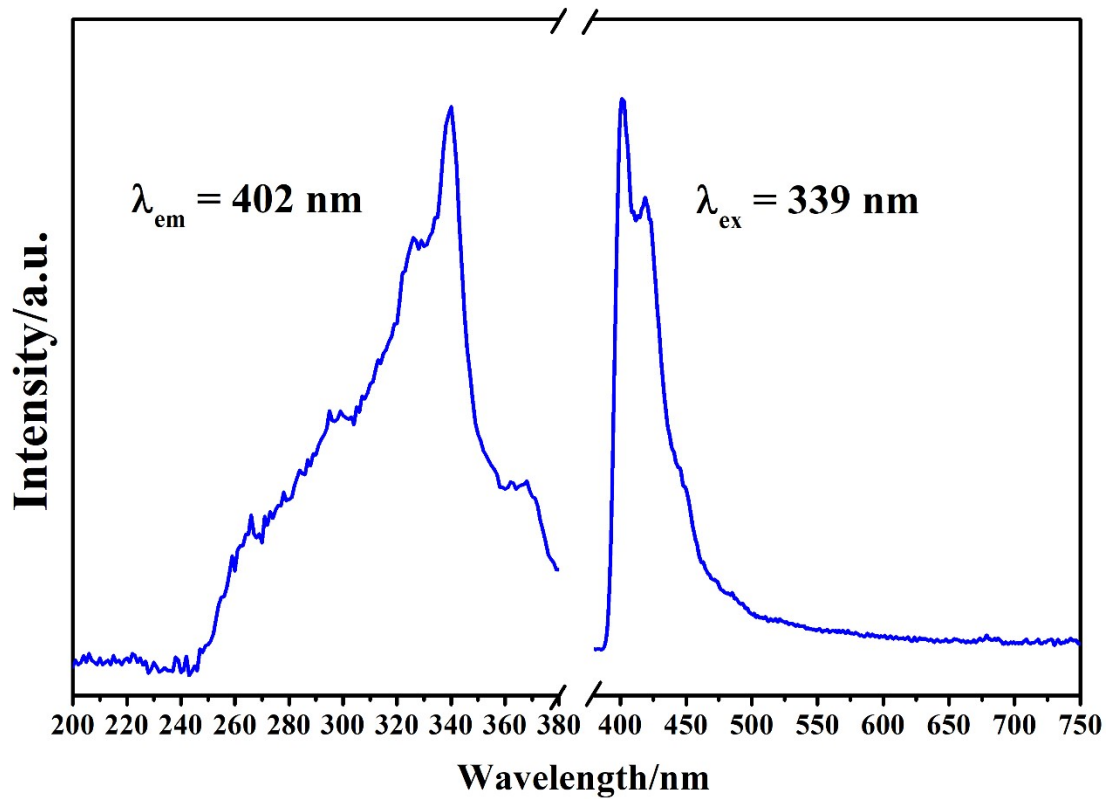
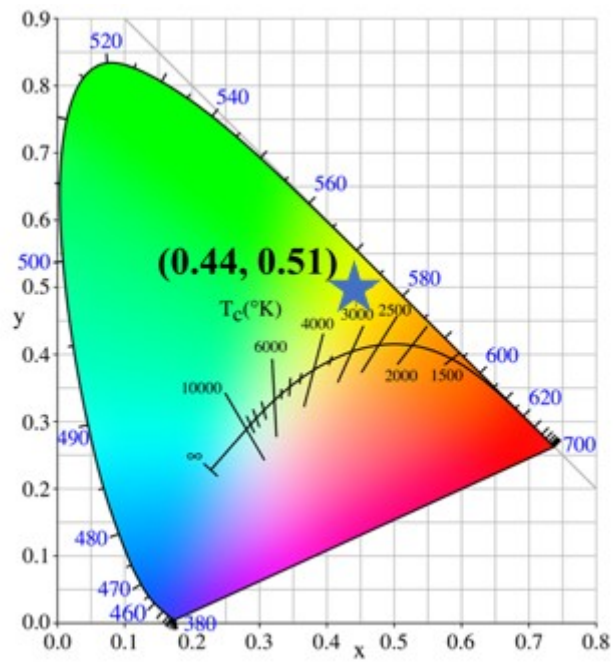**Figure S6**. Excitation and emission spectra of the $Rb_2CsBiCl_6$.

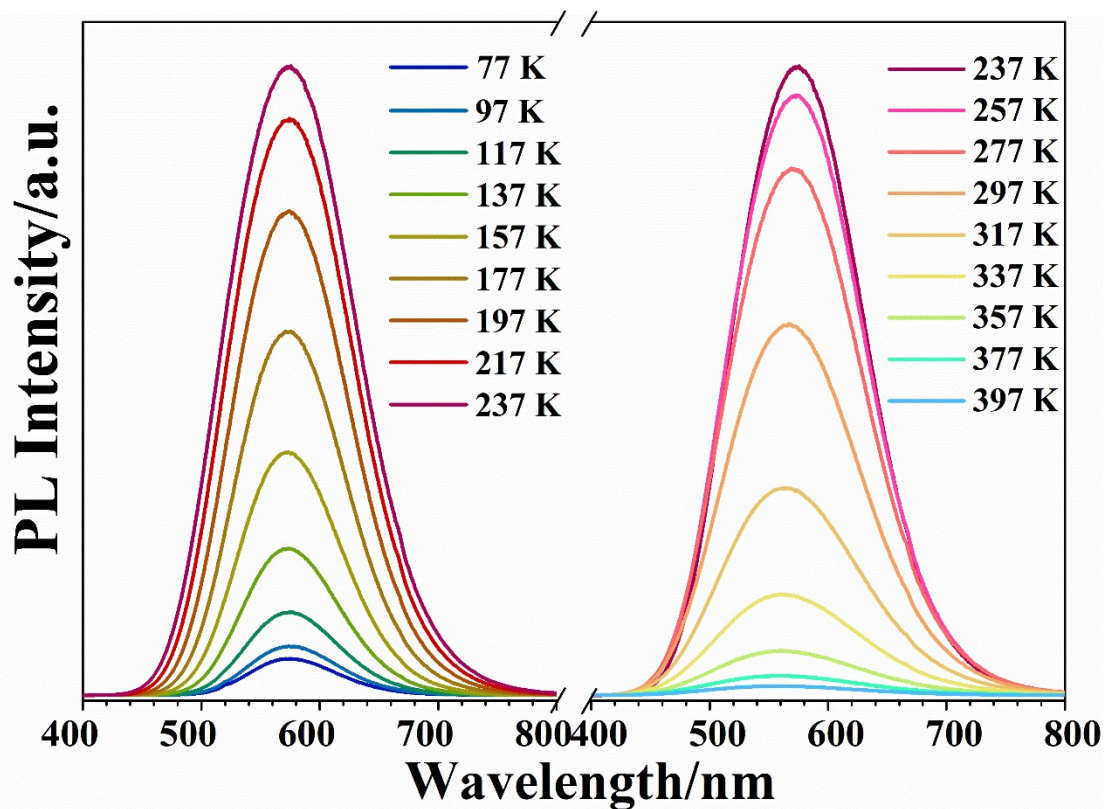**Figure S7**. Calculated CIE chromaticity coordinates of Sb^{3+}-doping $Rb_2CsBiCl_6$.

Figure S8. Normalized temperature-dependent emission spectra.

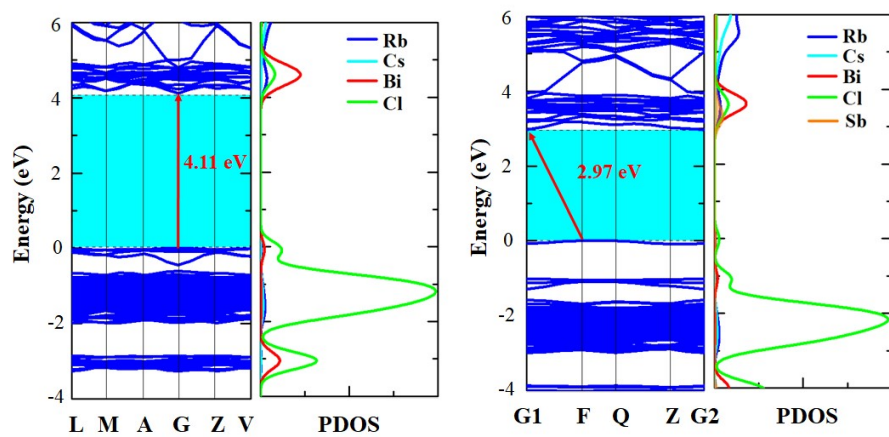Figure S9. Calculated band gap and PDOS for undoped and Sb^{3+}-doped $Rb_2CsBiCl_6$.