Supplementary Information

Syntheses, crystal structure, and photoelectric properties of two selenoantimonate A-Zn–Sb–Se (A = Rb and Cs)

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1. Computational Details

Spin-polarized first-principles-based calculations were performed with Cambridge Sequential Total Energy Package (CASTEP)[1-2] with Perdew–Burke–Ernzerhof (PBE) functional[3] within GGA.[4] The crystal structures of compounds $Rb_4Zn_2Sb_2Se_7$ (**1**) and $Cs_4Zn_2Sb_2Se_7$ (**2**) were firstly fully optimized without any constrains. All the calculations were performed with On-the-fly-generated (OFTG) ultrasoft pseudopotentials and the energy cutoff was set as 435.40 eV based on convergence tests.[5-6] Monkhorst k-point grids with separation smaller than 0.03 Å were used for the Brillouin-zone integrations.[7]

2. Figures and Tables

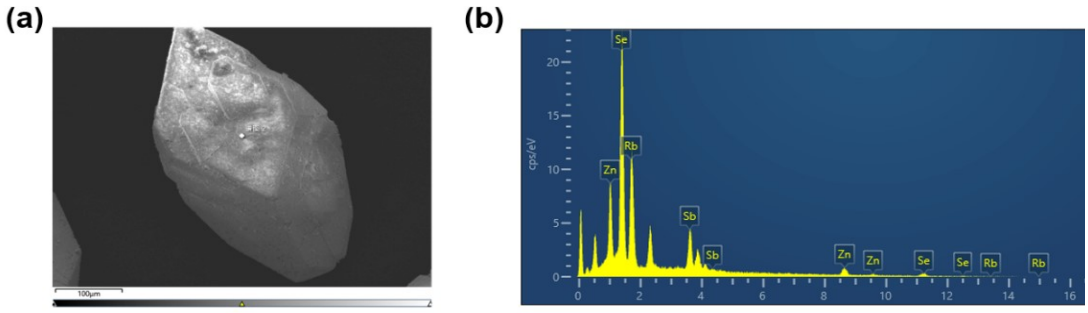

Figure S1. SEM image (a) and EDS analysis (b) of **1**.

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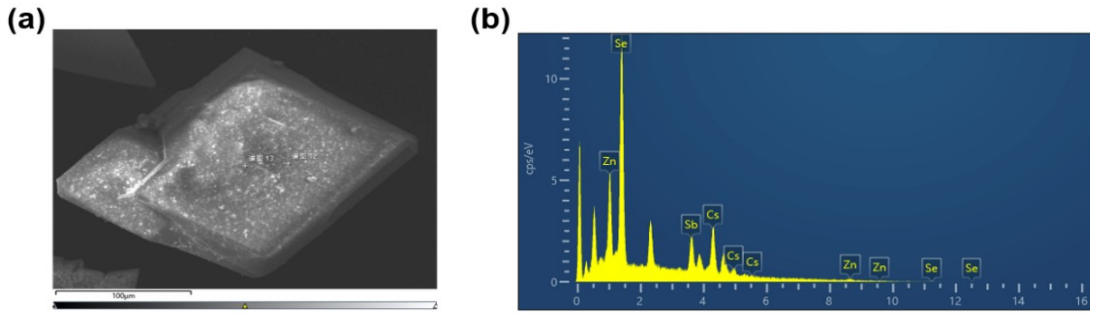

Figure S2. SEM image (a) and EDS analysis (b) of **2**

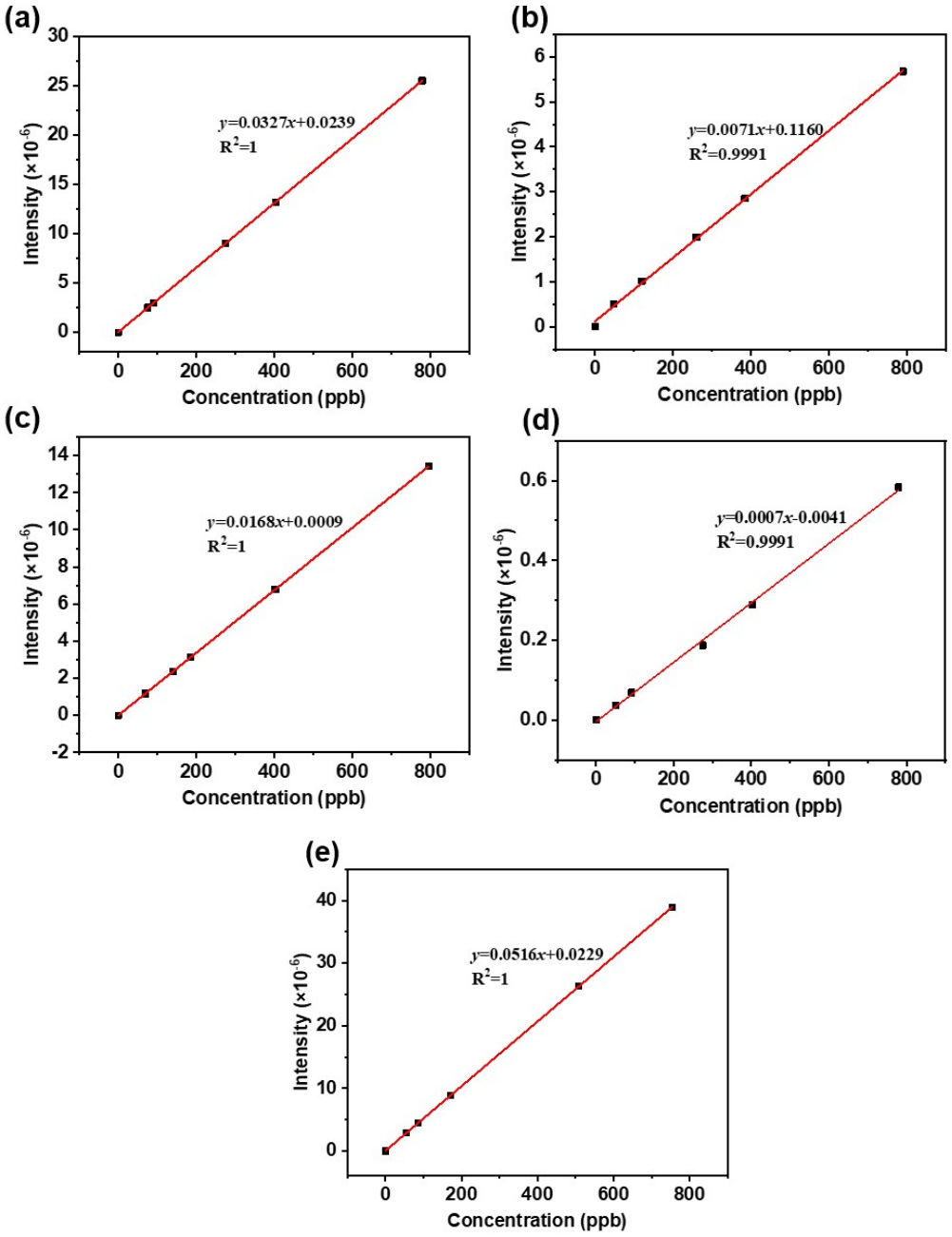

Figure. S3. Calibration curves (a) Rb; (b) Zn; (c) Sb; (d) Se; (e) Cs.

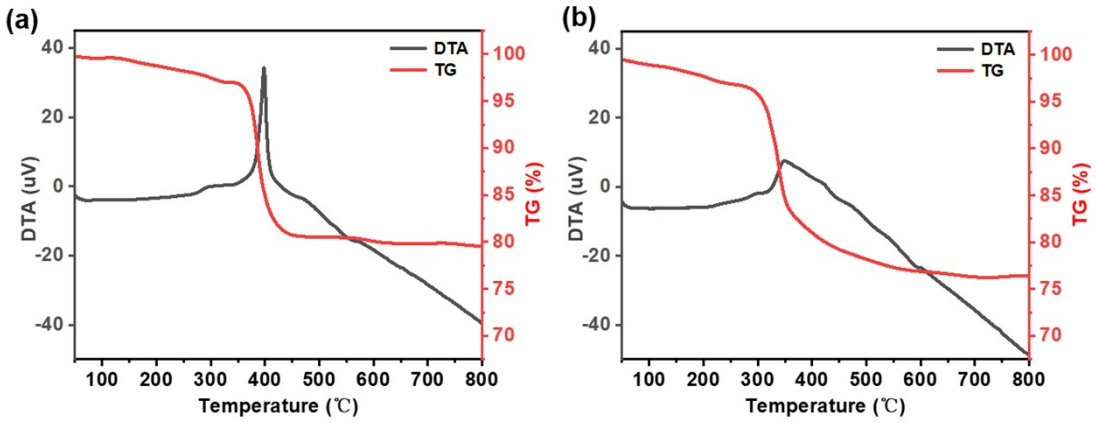

Figure S4. TG-DSC curves figure of the compounds **1** and **2**

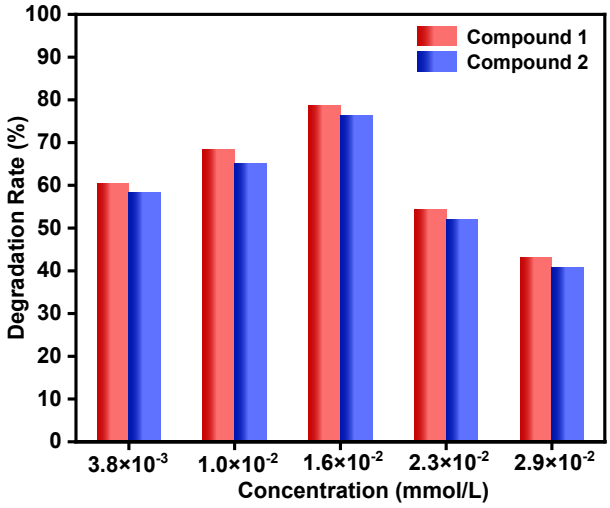

Figure S5. Degradation rate of compounds **1** and **2** to different concentrations of MB.

Table S1. Selected bond lengths (Å) and angles (°) for **1**.

Sb1-Se1	2.5005(17)	Se4-Sb2-Se6[1]	99.59(6)
Sb1-Se2	2.5239(19)	Se5-Sb2-Se6[1]	102.95(6)
Sb1-Se3[2]	2.5733(18)	Se5-Sb2-Se4	96.87(6)
Sb2-Se4	2.5141(17)	Se2-Zn1-Se3	124.14(8)
Sb2-Se5	2.5301(16)	Se2-Zn1-Se4	105.12(8)
Sb2-Se6[1]	2.5593(17)	Se2-Zn1-Se7[8]	104.99(7)
Zn1-Se2	2.409(2)	Se3-Zn1-Se7[8]	105.33(7)
Zn1-Se3	2.406(2)	Se4-Zn1-Se7[8]	112.32(7)
Zn1-Se4	2.475(2)	Se4-Zn1-Se3	105.04(8)
Zn2-Se5	2.474(2)	Se5-Zn2-Se6	108.25(7)

Zn2-Se6	2.486(2)	Se5-Zn2-Se7	116.85(7)
Zn2-Se7	2.4650(19)	Se5-Zn2-Se7^{4}	109.29(8)
Se2-Sb1-Se1	100.30(6)	Se6-Zn2-Se7	108.79(7)
Se2-Sb1-Se3^{2}	95.79(6)	Se6-Zn2-Se7^{4}	113.71(7)
Se3^{2}-Sb1-Se1	100.53(6)		

Symmetry transformations used to generate equivalent atoms: ^{1}-*x*, -*y*, 1-*z*; ^{2}1-*x*, 2-*y*, 1-*z*; ^{4}-*x*, -*y*, 1-*z*; ^{8}+*x*, 1+*y*, +*z*

Table S2. Selected bond lengths (Å) and angles (°) for **2**.

Zn-Se1	2.470(3)	Se6-Sb2-Se7	100.72(9)
Zn1-Se2	2.488(3)	Se6-Sb2-Se5^{2}	96.79(9)
Zn1-Se3	2.492(3)	Zn2^{3}-Se1-Zn1	125.51(10)
Zn2-Se5	2.402(3)	Zn2^{3}-Se1-Zn1^{4}	120.10(9)
Zn2-Se4	2.479(3)	Se2-Zn1-Se1	109.67(10)
Zn2-Se6	2.407(3)	Se2-Zn1-Se1^{4}	114.44(10)
Sb1-Se2^{1}	2.544(2)	Se3-Zn1-Se1	118.23(10)
Sb1-Se3	2.536(2)	Se3-Zn1-Se1^{4}	110.25(10)
Sb1-Se4	2.512(2)	Se3-Zn1-Se2	106.41(10)
Sb2-Se5^{2}	2.556(3)	Se5-Zn2-Se1^{5}	107.90(10)
Sb2-Se6	2.526(3)	Se4-Zn2-Se1^{5}	112.35(10)
Sb2-Se7	2.495(2)	Se4-Zn2-Se5	104.05(11)
Se3-Sb1-Se2^{1}	102.73(8)	Se6-Zn2-Se1^{5}	105.53(11)
Se4-Sb1-Se2^{1}	99.91(8)	Se6-Zn2-Se5	121.39(11)
Se4-Sb1-Se3	98.01(8)	Se6-Zn2-Se4	105.73(11)
Se5^{2}-Sb2-Se7	100.51(8)		

Symmetry transformations used to generate equivalent atoms: ^{1}-*x*, -*y*, 1-*z*; ^{2}1-*x*, 2-*y*, 1-*z*; ^{3}+*x*, 1+*y*, +*z*; ^{4}-*x*, 2-*y*, 1-*z*; ^{5}+*x*, -1+*y*, +*z*

Table S3. List of photocurrent densities of antimony chalcogenides

Compounds	Photocurrent density (μA/cm^2)	Ref.
$[pipH_2]_{0.5}[Ag_2SbS_3]$	0.430	[8]
$[pipH_2]_{0.5}[Ag_2SbSe_3]$	0.495	
KCu_2SbS_3	~2.60	[9]
$BaCuSbS_3$	~0.06	[10]
$BaCuSbSe_3$	~0.03	
$SrOCuSbS_2$	~1500	[11]
$Rb_2Ba_3Cu_2Sb_2S_{10}$	~0.05	[12]

$Rb_2CuSb_7S_{12}$	~0.01	[13]
$(C_4H_{14}N_2)_{0.5}Cu_2SbSe_3$	1.42	[14]
$Sr_6Cd_2Sb_6S_{10}O_7$	2.5	[15]
$[Mn(en)_3]CdSb_2Se_5$	2.59	[16]
$[Ga_{10}S_{19}SHSb]\cdot 3[Mn(TEPA)]\cdot xH_2O$	7.16	[17]
$[Ga_{10}S_{19}SHSb]\cdot 3[Ni(TEPA)]\cdot xH_2O$	2.63	
$[Ga_{10}S_{19}SHSb]\cdot 3[Fe(TEPA)]\cdot xH_2O$	0.75	
$Mn(tren)GaSbS_4$	~7.41	[18]
$Fe(tren)GaSbS_4$	~3.23	
$[V^{III}(dap)_2SbS_3]$	5.8	[19]
$[V^{III}(dap)_2SbSe_3]$	67.5	
$[H_2dien][V^{III}_2(en)_2(dien)_2(\mu_2\text{-}O)][SbSe_4]_2$	5.5	
$[V^{III}(dien)_2SbSe_4]$	19.3	
$Mn(en)_3Sb_2S_4$	1.12	[20]
$Co(en)_3Sb_2Se_4$	0.68	
$[Zn(tren)_2H]SbSe_4$	~6.3	[21]
$[Ni(1, 2\text{-dap})_3]_2Zn(1, 2\text{-dap})Sb_2Se_8$	~7.4	
$Rb_2ZnSb_4S_8$	~11.3	
$Cs_2ZnSb_2S_5$	~2.9	[22]
$[Zn(tren)]_2Sb_2Se_5$	1.86	[23]
$[Zn(tepa)H]_2Sb_2S_6$	0.88	
$Rb_4Zn_2Sb_2Se_7$	27.22	This work
$Cs_4Zn_2Sb_2Se_7$	25.50	

Table S4. Summary of MB degradation rates of antimony chalcogenides containing Zn

Compounds	Efficiency (%)	Ref.
$[Zn(trien)]Sb_4S_7$	Not found	[24]
$[Zn(dap)_3]_2(Sb_2Se_5)\cdot H_2O$	Not found	[25]
$[Zn(C_4H_{13}N_3)_2]_n[CdSb_2Se_5]_n$	Not found	[26]
$[Zn(tren)Sb_4S_7]$	Not found	[27]
$[Zn(tren)_2H]SbSe_4$ $[Ni(1,2\text{-dap})_3]_2Zn(1,2\text{-dap})Sb_2Se_8$ $Rb_2ZnSb_4S_8$	Not found	[21]
Cu_2ZnSbS_4	Not found	[28]
$Cs_2ZnSb_2S_5$	69 %	[22]
$[Zn(tren)]_2Sb_2Se_5$	88.2 %	[23]
$[Zn(tepa)H]_2Sb_2S_6$	82.4 %	
$Rb_4Zn_2Sb_2Se_7$	78.8%	This work
$Cs_4Zn_2Sb_2Se_7$	76.4%	

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