Electronic Supplementary Information (ESI)

Syntheses, crystal structure, and photoelectric properties of two Zn-based chalcogenidoantimonates Zn-Sb-Q (Q=S, Se) †

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1. Experimental Section

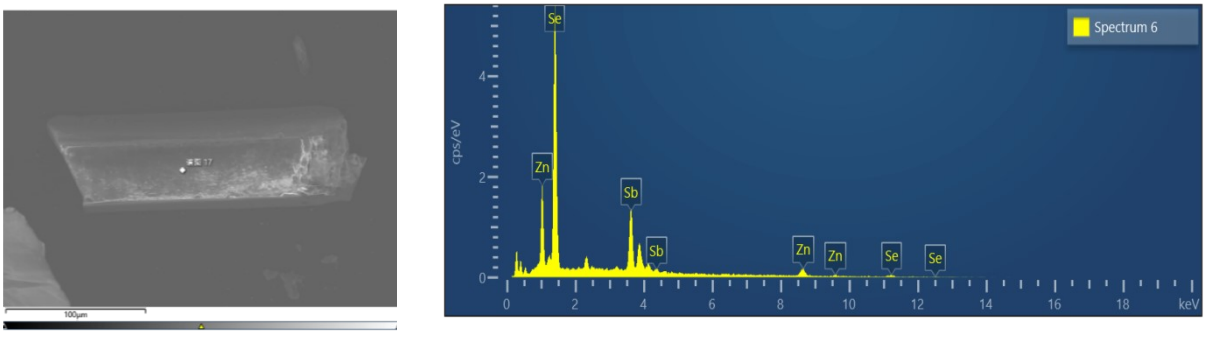
1.1 Single-Crystal Structure Characterizations

Structural analyses were carried out on a Rigaku Raxis-Rapid X-ray diffractometer (Rigaku, Japan), and diffracted structural data were collected using an APEX-II CCD single-crystal diffraction from Bruker, Germany, with a graphite monochromator and Mo-Kα radiation (λ = 0.071073 nm). All calculated diffracted structural data were corrected for L_p factor and empirical absorption factor, structural data were solved by direct calculation method, all non-hydrogen atom coordinate data were determined directly by difference Fourier synthesis method, and all non-hydrogen atom coordinate parameters and anisotropic thermal parameters were corrected by full-matrix least squares method. The structural calculation data were done directly with the *Olex2* program.[1] The CCDC numbers for compounds **1** and **2** are 2280314 and 2280315, respectively.

2. Computational Details

Spin-polarized first-principles-based calculations were performed with Cambridge Sequential Total Energy Package (CASTEP)[2-3] with Perdew–Burke–Ernzerhof (PBE) functional[4] within GGA.[5] The crystal structures of compounds $[Zn(tren)]_2Sb_2Se_5$ (**1**) and and $[Zn(tepa)H]_2Sb_2S_6$ (**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.[6-7] Monkhorst k-point grids with separation smaller than 0.03 Å were used for the Brillouin-zone integrations.[8]

3. Figures and Tables



(a) (b)

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

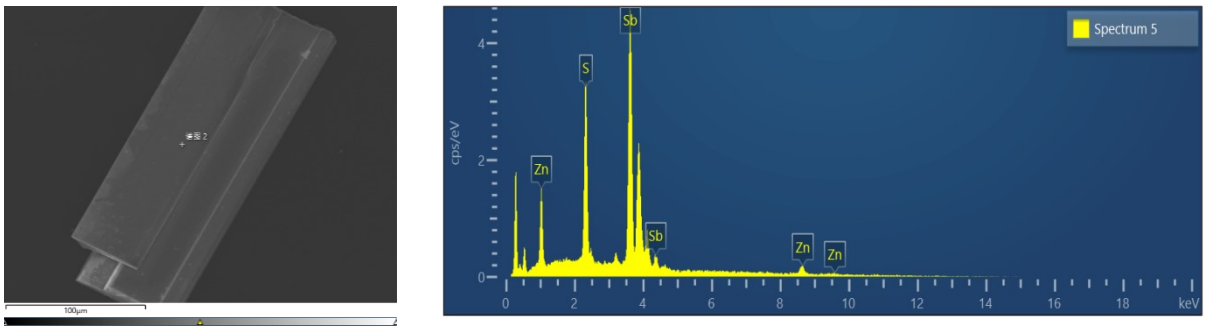


Figure S2. SEM image (a) and EDS analysis (b) of **2**.

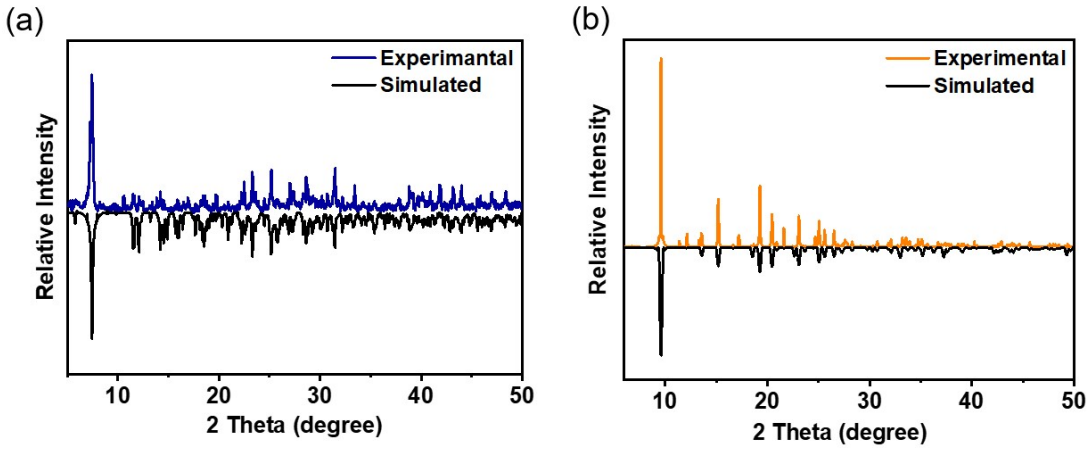


Figure S3. Powder XRD pattern of **1** (a) and **2** (b).

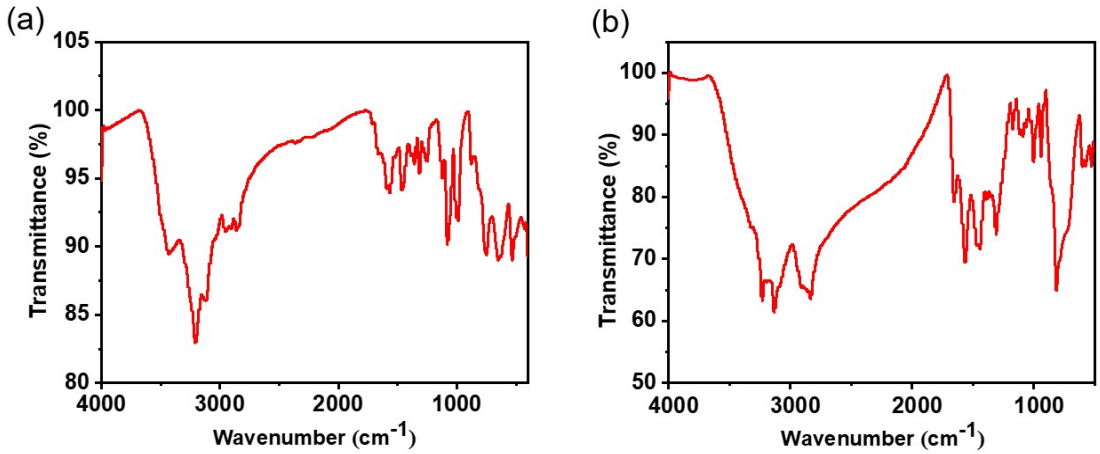


Figure S4. Infrared spectra of **1** (a) and **2** (b).

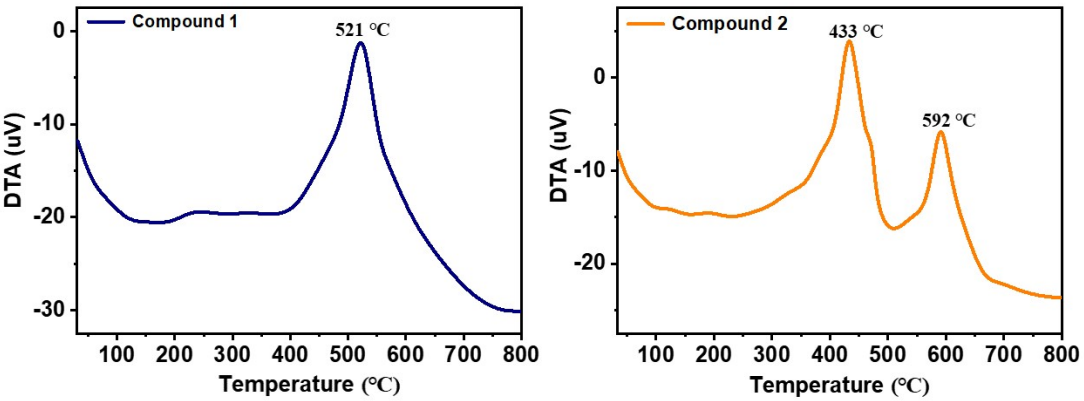


Figure S5. DTA curves for **1** (a) and **2** (b).

Table S1. Summary table of coordination numbers and degradation rates of MB for antimony chalcogenides containing zinc.

Formula	Coordination number of Zn and Sb atoms	Efficiency (%)	Ref.
$[Zn(trien)]Sb_4S_7$	Zn (5); Sb (3 and 4)	Not found	[9]
$[Zn(dap)_3]_2(Sb_2Se_5)\cdot H_2O$	Zn (6); Sb (3)	Not found	[10]
$[Zn(C_4H_{13}N_3)_2]_n[CdSb_2Se_5]_n$	Zn (6); Sb (3)	Not found	[11]
$[Zn(tren)Sb_4S_7]$	Zn (5); Sb (4)	Not found	[12]
$[Zn(tren)_2H]SbSe_4$	Zn (5); Sb (4)	Not found	[13]
$[Ni(1,2\text{-dap})_3]_2Zn(1,2\text{-dap})Sb_2Se_8$	Zn (4); Sb (4)	Not found	[13]
$Rb_2ZnSb_4S_8$	Zn (4); Sb (3)	Not found	[13]
Cu_2ZnSbS_4	Zn (4); Sb (4)	Not found	[14]
$Cs_2ZnSb_2S_5$	Zn (4); Sb (3 and 4)	69 %	[15]
$[Zn(tren)]_2Sb_2Se_5$	Zn (5); Sb (3)	88.2 %	This work
$[Zn(tepa)H]_2Sb_2S_6$	Zn (6); Sb (4)	82.4 %	This work

Table S2. Selected bond lengths [Å] and angles [º] for **1**.

Zn1-N1	2.068(4)	N2-Zn1-N3	75.73(15)
Zn1-N2	2.438(4)	N3-Zn1-N4	116.81(18)
Zn1-N3	2.114(4)	N4-Zn1-N1	109.21(18)
Zn1-N4	2.053(4)	N5-Zn2-N6	118.6(2)
Zn1-Se1	2.4842(8)	N6-Zn2-N7	77.89(17)
Zn2-N5	2.094(5)	N7-Zn2-N8	78.03(15)
Zn2-N6	2.110(5)	Se1-Sb1-Se2	100.59(2)
Zn2-N7	2.358(4)	Se3-Sb2-Se4	97.67(2)
Zn2-N8	2.069(4)	N2-Zn1-Se1	172.33(11)

Zn2-Se4	2.4637(8)	N4-Zn1-Se1	109.43(12)
Sb1-Se1	2.5646(6)	N3-Zn1-Se1	97.47(12)
Sb1-Se2	2.4978(7)	N5-Zn2-Se4	95.62(15)
Sb2-Se3	2.4734(7)	N7-Zn2-Se4	171.66(11)
Sb2-Se4	2.5210(7)	N8-Zn2-Se4	108.53(11)
N1-Zn1-N2	77.23(15)		

Table S3. Selected bond lengths [Å] and angles [º] for **2.**

Zn1-N1	2.147(6)	N4-Zn1-N5	87.8(2)
Zn1-N2	2.193(5)	N4-Zn1-N2	141.7(2)
Zn1-N3	2.237(5)	S1-Sb1-S3	119.10(6)
Zn1-N4	2.164(5)	S1-Sb1-S2[1]	108.69(6)
Zn1-N5	2.234(5)	S1-Sb1-S2	111.45(6)
Sb1-S1	2.3144(15)	S2[1]-Sb1-S2	94.00(5)
Sb1-S2	2.4587(15)	S3-Sb1-S2[1]	110.11(6)
Sb1-S3	2.3549(17)	S3-Sb1-S2	110.59(6)
Zn1-S3	2.5821(18)	N1-Zn1-S3	165.9(2)
N1-Zn1-N2	95.6(2)	N2-Zn1-S3	90.91(15)
N1-Zn1-N3	165.9(2)	N3-Zn1-S3	81.63(14)
N2-Zn1-N3	76.7(2)	N4-Zn1-S3	111.83(15)
N3-Zn1-N4	76.7(2)	N5-Zn1-S3	113.6(2)

Symmetry transformations used to generate equivalent atoms: [1]-*X*, -*Y*, 1-*Z*

4. References

[1] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, OLEX2: A complete structure solution, refinement and analysis program. *J. Appl. Cryst*. 2009, **42**, 339-341.

[2] M. C. Payne, M. P. Teter, D. C. Allan, T. A. Arias and J. D. Joannopoulos, Iterative minimization techniques for ab initio total-energy calculations: molecular dynamics and conjugate gradients. *Rev. Mod. Phys.* 1992**, 64**, 1045-1097.

[3] S. J. Clark, M. D. Segall, C. J. Pickard, P. J. Hasnip, M. J. Probert, K. Refson and M. C. Payne, First principles methods using CASTEP. *Z Krist-Cryst Mater.* 2005**, 220**, 339-341.

[4] J. P. Perdew, K. Burke and M. Ernzerhof, Generalized gradient approximation made simple. *Phys. Rev. Lett.* 1996**, 77**, 3865-3868.

[5] J. P. Perdew and Y. Wang, Accurate and simple analytic representation of the electron-gas correlation energy. *Phys. Rev. B*, 1992**, 45**, 13244-13249.

[6] K. Lejaeghere, V. V. Speybroeck, G. O. Van and S. Cottenier, Error Estimates for Solid-State Density-Functional Theory Predictions: An Overview by Means of the Ground-State Elemental Crystals. *Crit. Rev. Solid State Mat. Sci.* 2014, **39**, 1-24.

[7] D. Vanderbilt, Soft Self-Consistent Pseudopotentials in a Generalized Eigenvalue Formalism. *Phys. Rev. B* **1990,** *41*, 7892-7895.

[8] H. J. Monkhorst, J. D. Pack. Special Points for Brillouin-zone Integrations. *Phys. Rev. B* **1976,** *13*, 5188-5192.

[9] H. Lühmann, Z. Rejai, K. Möller, P. Leisner, M. E. Ordolff, C. Näther and W. Bensch, On the Flexibility of Thioantimonate Networks: Solvothermal Syntheses and Crystal Structures of Six New Thioantimonates(III) with the $[Sb_4S_7]^{2-}$ Anion, *Z. Anorg. Allg. Chem*., 2008, **634**, 1687-1695.

[10] G. Q. Bian, J. Zhou, C. Y. Li, N. Cheng, X. M. Lin, Y. Zhang and J. Dai, Solvothermal synthesis and crystal structure of $[M(dap)_3]_2(Sb_2Se_5) \cdot xH_2O$ (M=Ni, x=2; M=Zn, x=0), *Chemical research and application*., 2008, **20**, 53-57.

[11] H. Jiang, X. Wang, T. L. Sheng, S. M. Hu, R. B. Fu, Y. H. Wen, C. J. Shen, N, Yuan and X. T. Wu, Solvothermal synthesis and characterization of a novel selenidoantimonate: $[M^1(C_4H_{13}N_3)_2]_n[M^2Sb_2Se_5]_n$ (M^1 = Mn、Co, M^2 = Zn、Cd), *Sci China Chem*., 2011, **41**, 726-731.

[12] B. Seidlhofer, E. Antonova, J. Wang, D. Schinkel and Wolfgang Bensch, On the Complexity of Crystallization of Thioantimonates: In-situ Energy Dispersive X-ray Diffraction (EDXRD) Studies of the Solvothermal Formation of the Isostructural Thioantimonates $[TM(tren)Sb_4S_7]$ (TM = Fe, Zn), *Z. Anorg. Allg. Chem*. 2012, **15**, 2555-2564.

[13] M. G. Shele, X. Y. Tian and M. H. Baiyin, Solvothermal synthesis and properties of three antimony chalcogenides containing transition metal zinc, *J Solid State Chem*., 2021, **302**, 122401.

[14] E. M. Heppke, S. Klenner, O. Janka, R. Pöttgen, T. Bredow and M. Lerch, Cu_2ZnSbS_4: A Thioantimonate (V) with Remarkably Strong Covalent Sb-S Bonding, *Inorg. Chem*., 2021, **60**,

2730-2739.

[15] N. Li, G. L. Teri, M. G. Shele, Sagala, Namila, M. H. Baiyin, The Solvothermal Synthesis and Properties of Thioantimonates Rb(1,4-DABH)Sb_4S_7 and $Cs_2ZnSb_2S_5$: 1D Anion Chains and 2D Anion Layer, *J Clust Sci*., 2023, **34**, 1853-1860.