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Electronic Supplementary Information (ESI)

$CsCu_3SbS_4$: rational design of a two-dimensional layered material with giant birefringence derived from Cu_3SbS_4

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Figure S1. (a) Coordination environment of a $Cs_2@S_{16}$ polyhedron, (b) single 2D Cs–S layer, and (c) the 3D unique Cs–S network is made of these 2D Cs–S layers via S−S

1. Experimental Section

Physical Measurements. The optical diffuse reflectance spectra were measured on a Hitachi UH4150 UV–vis-NIR spectrometer equipped with an integrating sphere at room temperature. The picked polycrystalline samples were ground into fine powders before measurement. The absorption (α/S) data were calculated from reflectance with the Kubelka–Munk function: $\alpha/S = (1-R)^2/2R$, in which α is the absorption coefficient, R is the reflectance at a specified wavelength, and S is the scattering coefficient.[1] The

elemental analyses of Cs, Cu, Sb, and S have been examined with via an EDX-equipped JEOL/JSM-6360A SEM. Powder X-ray diffraction data were collected on a Bruker D8 Advance diffractometer with a graphite-monochro-matized Cu K_α radiation. The operating 2θ angle ranges from 10° to 70°. Simulation of XRD patterns were carried out by the single-crystal data and diffraction-crystal module of the Mercury (Hg) program version 1.4.2 available free of charge through the website http://www.iucr.org.

Synthesis of $CsCu_3SbS_4$. The starting reagents $CsOH·H_2O$ (99.7%), Cu powder (99.7%), S powder (99.5%) and hydrazine monohydrate (85%) purchased from Sinopharm Chemical Reagent Co., Ltd. were used as obtained. The binary starting material Sb_2S_3 (99.9%) was purchased from Aladdin Co., Ltd. All the chemicals used for synthesis are of analytical grade and directly used without further purification.

After numerous explorations on the experimental conditions including starting reactant, loading ratio, annealing temperature, the optimal synthesis condition was established as follows: 1.0 mmol of $CsOH·H_2O$, 3.0 mmol of Cu, 0.5 mmol of Sb_2S_3, 2.5 mmol of S, and 0.5 mL of hydrazine monohydrate (98%) and 2.0 mL PEG-400 were mixed together and sealed in a 25 mL Teflon-lined stainless autoclave and heated at 160 °C for 7 days. The resultant reaction mixtures were washed with deionized water and ethanol, respectively, and the yield is about 55% (based on Cu).

Energy-dispersive X-ray analysis of $CsCu_3SbS_4$ was shown in Figure S2. The EDX results confirmed the presence of Cs, Cu, Sb and S in an approximate molar ratio of $Cs_{1.0}Cu_{3.1(2)}Sb_{1.0(8)}S_{4.1(2)}$, which is in good agreement with the refined

compositions obtained from the single-crystal XRD data. Compound $CsCu_3SbS_4$ was characterized by powder XRD and the experimental XRD patterns of the title compound was agreed well with the simulated patterns (Figure S3).

Single-Crystal Structure Characterizations. Suitable single crystals of the title compounds were mounted on the glass fibers. Diffraction data were collected by an Oxford Xcalibur (Atlas Gemini ultra) diffractometer with a graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) at room temperature. The absorption corrections were based on the multi-scan method. The structures were solved by the direct methods and refined by the full-matrix least-squares fitting on F^2 using the *SHELXL-2014* software package.[2] The assignments of Cs, Cu, Sb, and S were determined on the basis of the interatomic distances, coordination environments and relative displacement parameters. The structure was verified using the *ADDSYM* algorithm from the program *PLATON*.[3] The final atomic positions were standardized with the *STRUCTURE TIDY* program.[4] Crystal data and refinement details are summarized in Tables S2-3, the selected bond lengths are listed in Table S4. CCDC number: 2109895.

Computational Details. Crystallographic data determined by single crystal X-ray diffraction were used for theoretical calculations of their electronic band structures. The density functional theory (DFT) calculations have been performed using the Vienna ab initio simulation package (VASP)[5-7] with the Perdew-Burke-Ernzerhof (PBE)[8] exchange correlation functional. The projected augmented wave (PAW)[9] potentials have been used to treat the ion-electron interactions . A Γ-centered 5×5×7

Monkhorst-Pack grid for the Brillouin zone sampling and a cutoff energy of 700 eV for the plane wave expansion were found to get convergent lattice parameters and self-consistent energies.

3. Figures and Tables

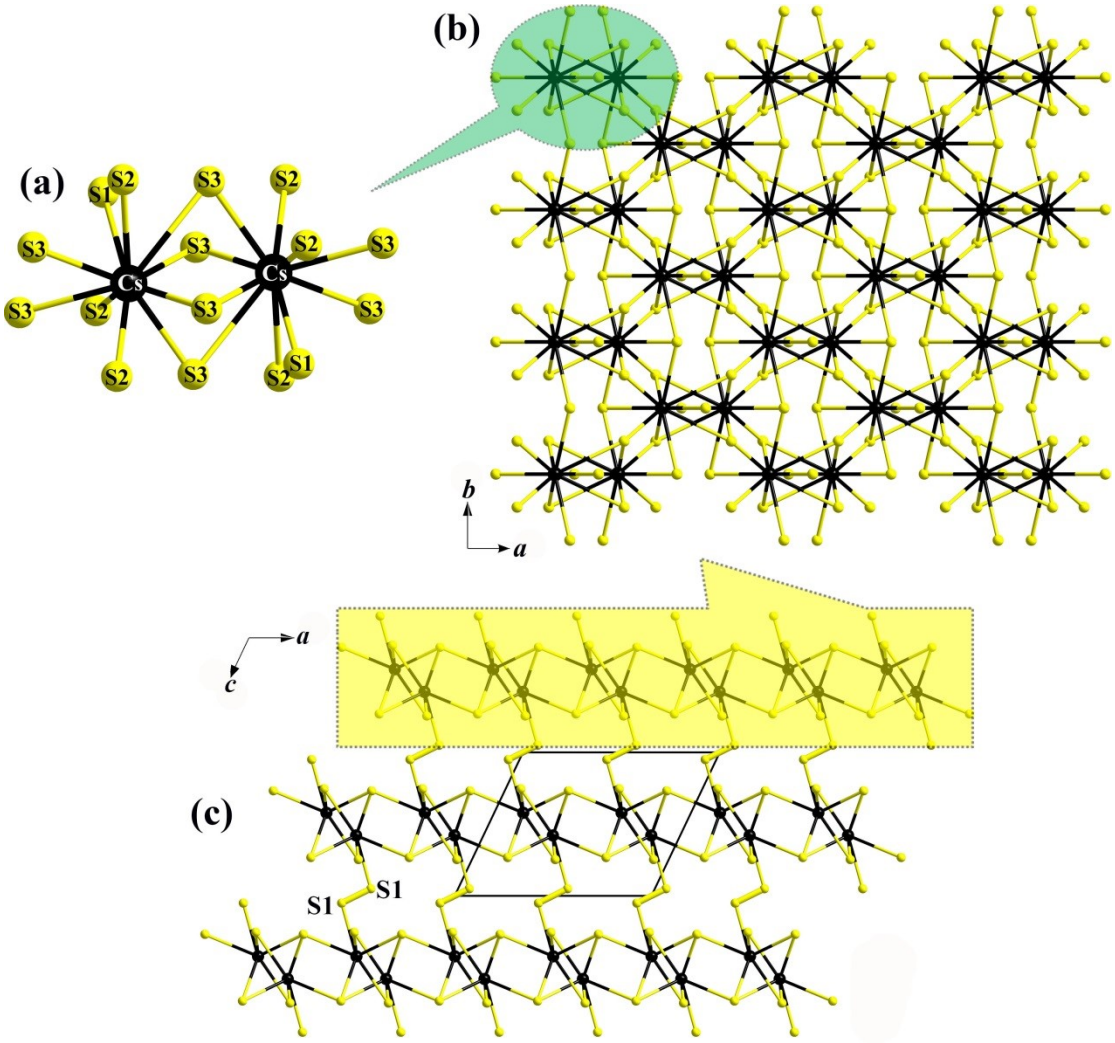

Figure S1. (a) Coordination environment of a $Cs_2@S_{16}$ polyhedron, (b) single 2D Cs–S layer, and (c) the 3D unique Cs–S network is made of these 2D Cs–S layers via S−S bonds.

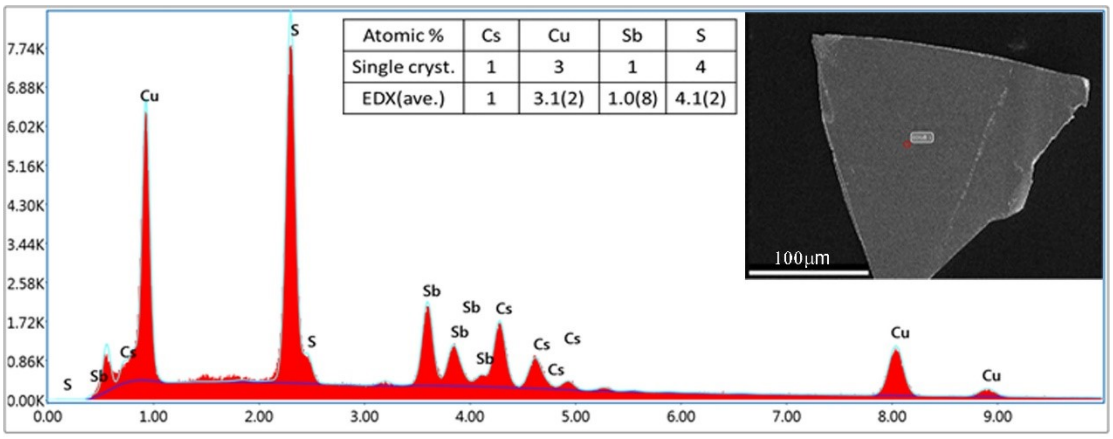

Figure S2. Energy-dispersive X-ray spectroscopy analysis of $CsCu_3SbS_4$ (insert: SEM image).

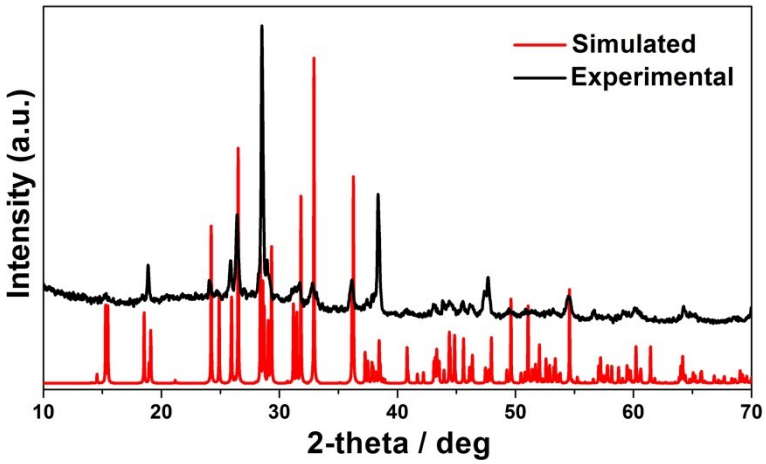

Figure S3. The experimental (black) and simulated (red) powder XRD of $CsCu_3SbS_4$.

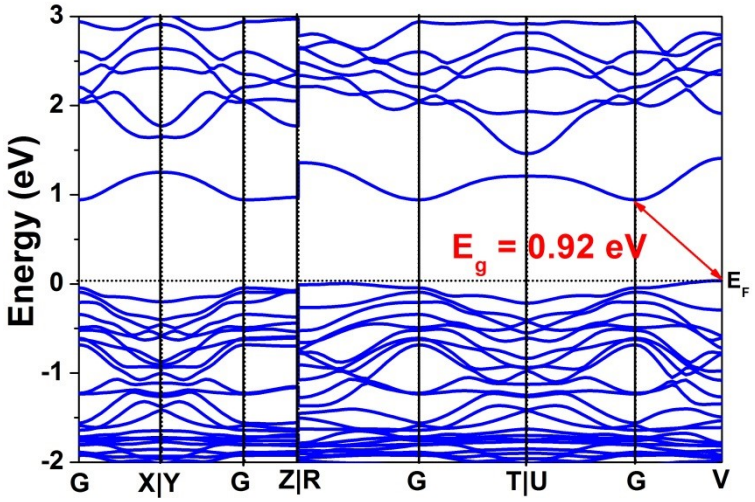

Figure S4. Electronic band structure of $CsCu_3SbS_4$.

Table S1. Structural features of quaternary X/Cu/Sb/Q (A = cations; Q = chalcogen) system.

Compounds	Crystal system	Space group	Cu/Sb ratio	Dimension of anionic substructure	Ref.
$CsCu_3SbS_4$	**monoclinic**	***C*2/*m* (12)**	**3.0**	**2D**	**This work**
$[M(NH_3)_6][Cu_8Sb_3S_{13}]$ (M = Mn, Fe, Ni)	cubic	$F\bar{4}3c$（no. 219）	2.67	3D	10
ACu_2SbS_3 (A = K, Rb, Cs)	triclinic	$P\bar{1}$（no. 2）	2.0	2D	11
KCu_2SbSe_3	monoclinic	$P2_1/c$ (14)	2.0	2D	12
$(C_2N_2H_8)_{0.5}[Cu_2SbS_3]$	monoclinic	$P2_1/c$ (14)	2.0	2D	13
$(C_4N_3H_{15})_{0.5}[Cu_2SbS_3]$	monoclinic	$P2_1/c$ (14)	2.0	2D	14
$(C_6N_2H_{18})_{0.5}[Cu_2SbS_3]$	monoclinic	$P2_1/c$ (14)	2.0	2D	14
$(C_8N_4H_{22})_{0.5}[Cu_2SbS_3]$	monoclinic	$P2_1/c$ (14)	2.0	2D	14
$[Ni(pda)_2][Cu_4Sb_2S_6]$	monoclinic	$P2_1/c$ (14)	2.0	2D	15
$(C_6N_4H_{20})_{0.5}[Cu_3Sb_2S_5]$	triclinic	$P\bar{1}$（no. 2）	1.5	2D	14

$(C_4N_3H_{14})[Cu_3Sb_2S_5]$	monoclinic	*C*2/*c* (15)	1.5	2D	14
A_2CuSbS_3 (A = Na, K)	monoclinic	$P2_1/c$ (14)	1.0	2D	16
$Rb_2Cu_2Sb_2S_5$	monoclinic	$P2_1/c$ (14)	1.0	2D	17
$Cs_2Cu_2Sb_2Q_5$ (Q = S, Se)	triclinic	$P\bar{1}$（no. 2）	1.0	2D	18
$BaCuSbQ_3$ (Q = S, Se)	orthorhombic	*Pbam* (55)	1.0	3D	19
$PbCuSbS_3$	orthorhombic	$Pmn2_1$ (31)	1.0	3D	20
$ACuSb_2S_4$ (A = Rb, Cs)	monoclinic	*C*2/*c* (15)	0.5	3D	21
$[Ni(dien)_2][CuSb_3S_6]$	monoclinic	$P2_1/c$ (14)	0.33	2D	15
$[C_4H_{12}N_2]_{0.5}[CuSb_6S_{10}]$	monoclinic	$P2_1/c$ (14)	0.17	3D	22
$Rb_2CuSb_7S_{12}$	triclinic	$P\bar{1}$（no. 2）	0.14	3D	23

Table S2. Crystal data and structure refinements for $CsCu_3SbS_4$.

Empirical formula	$CsCu_3SbS_4$
Formula weight	573.52
Color	Dark red
Crystal system	Monoclinic
Space group	*C*2/*m* (no. 12)
a (Å)	12.840(2)
b (Å)	7.1481(8)
c (Å)	10.3659(18)
α (deg)	90
β (deg)	115.49(2)
γ (deg)	90
V (Å^3)	858.8(3)
Z	4
D_{cal} (g/cm^3)	4.436
μ(mm^{-1})	15.495
F(000)	1028
R_1, wR_2 ($I > 2\sigma(I)$)	0.0591,0.1662
R_1, wR_2 (all data)	0.0669,0.1709
GOOF on F^2	1.065

$R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. $wR_2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

Table S3. Atomic coordinates and equivalent isotropic displacement parameters of $CsCu_3SbS_4$.

Atom	*Wyckoff*	*x*	*y*	*z*	$U_{(eq)}$*	*Occu.*
Cs	4*i*	0.35284(15)	0	0.57909(17)	0.0354(5)	1.0
Cu1	4*i*	0.7398(3)	0	0.1274(3)	0.0280(8)	1.0
Cu2	8*j*	0.43916(18)	0.2797(3)	0.1528(2)	0.0304(6)	1.0
Sb	4*i*	0.19946(12)	0	0.12864(15)	0.0171(5)	1.0
S1	4*i*	0.4436(4)	0	0.0501(6)	0.0188(11)	1.0
S2	4*i*	0.0770(5)	0	0.2526(6)	0.0217(12)	1.0
S3	8*j*	0.3240(3)	0.2502(5)	0.2677(4)	0.0184(8)	1.0

*$U_{(eq)}$ is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table S4. Selected bond lengths (Å) for $CsCu_3SbS_4$.

Cu1–S3 ×2	2.262(4)	∠S3–Cu1–S3	104.2(2)
Cu1–S1	2.281(6)	∠S3–Cu1–S1	124.09(12)
Cu2–S2	2.260(4)	∠S3–Cu1–S1	124.09(12)
Cu2–S3	2.272(4)	∠S2–Cu1–S3	112.50(19)
Cu2–S1	2.277(3)	∠S2–Cu1–S1	130.82(19)
Sb–S3 ×2	2.419(4)	∠S3–Cu1–S1	108.44(17)
Sb–S2	2.421(6)	∠S3–Sb–S3	95.37(19)
S1–S1	2.116(2)	∠S3–Sb–S2	95.61(13)
Cs–S3 ×2	3.568(4)	∠S3–Sb–S2	95.61(13)
Cs–S1	3.600(6)		
Cs–S2	3.698(6)		
Cs–S3 ×2	3.738(4)		
Cs–S2 ×2	3.908(3)		
Cs–S3	4.155(4)		

Table S5. The direction and magnitude (in Debye) of the polyhedral dipole moments for ABUs in $CsCu_3SbS_4$.

ABUs	*x*(*a*)	*y*(*b*)	*z*(*c*)	Magnitude
$[Cu1S_3]$	-0.962	0	-1.549	1.823
$[Cu2S_3]$	4.724	2.265	-3.447	6.271
$[SbS_3]$	16.176	0	-24.362	29.243

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