Electronic Supplementary Information (ESI)

Stereochemically-active-lone-pair-driven giant enhancement of birefringence from three-dimensional $CsZn_4Ga_5Se_{12}$ to two-dimensional $CsZnAsSe_3$

Chao Zhang,‡[a] Mao-Yin Ran,‡[b,c,d] Xin Chen,[a] Sheng-Hua Zhou,[b,c,d] Hua Lin,*[,b,c] and Yi Liu*[,a]

[a]*Institute for Composites Science Innovation (InCSI), School of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, China*

[b]*Fujian Science & Technology Innovation Laboratory for Optoelectronic Information of China, Fuzhou 350108, China*

[c]*State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, China*

[d]*University of Chinese Academy of Sciences, Beijing 100049, China*

‡*C. Zhang and M. Y. Ran contributed equally to this work.*

*E-mail: liuyimse@zju.edu.cn and linhua@fjirsm.ac.cn.

Electronic Supplementary Information Index

1. Experimental Section

1.1 Birefringence Measurements

The birefringence (Δn) was characterized by using the polarizing microscope (ZEISS Axio Scope, A1) equipped with Berek compensator. The wavelength of the light source was 546 nm. The formula for calculating the Δn is $R = | N_e – N_o | \times T = \Delta n \times T$. Here, R represents the optical path difference and T denotes the thickness of the crystal.

1.2 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.[1] The assignments of Cs, Zn, As, and Se 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*.[2] Crystal data and refinement details are summarized in Tables 1 and 2, the selected bond lengths are listed in Table S1. CCDC number: 2215339.

2 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)[3-5] with the Perdew-Burke-Ernzerhof (PBE)[6] exchange correlation functional. The projected augmented wave (PAW)[7] potentials have been used to treat the ion-electron interactions. A Γ-centered 7×7×9 Monkhorst-Pack grid for the Brillouin zone sampling and a cutoff energy of 800 eV for the plane wave expansion were found to get convergent lattice parameters and self-consistent energies.

3. Figures and Tables

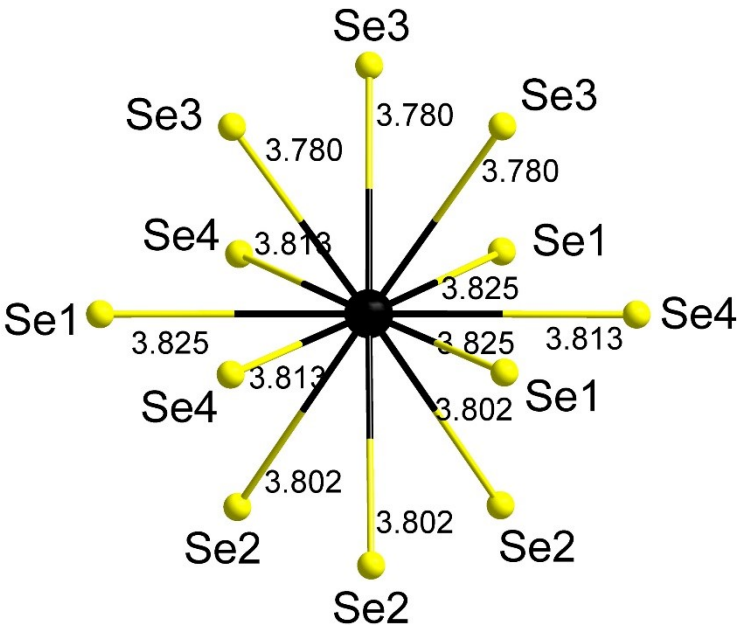


Figure S1. Coordination environment and bond lengths (Å) of a $Cs@Se_{12}$ polyhedron in $CsZn_4Ga_5Se_{12}$.

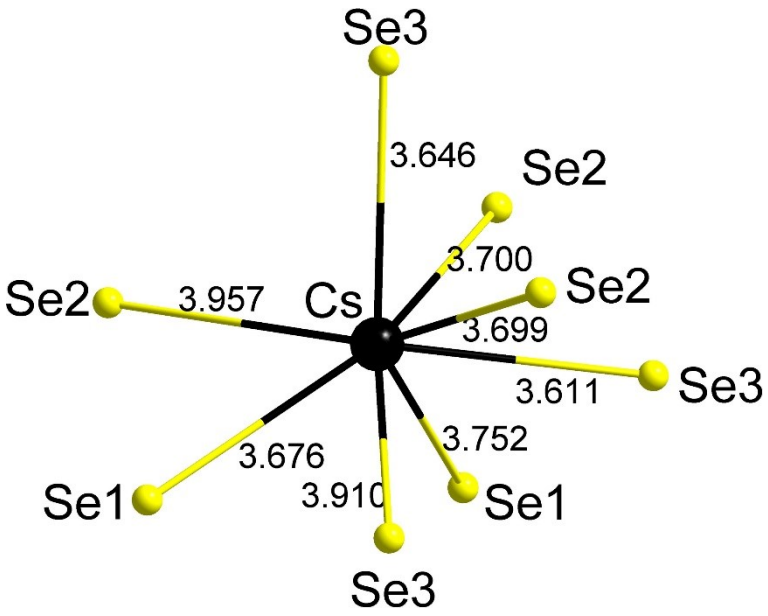
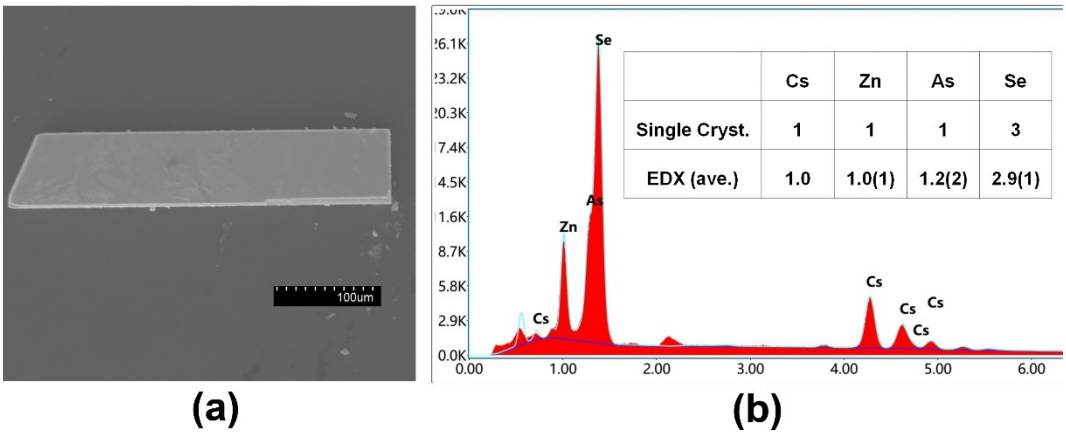


Figure S2. Coordination environment and bond lengths (Å) of a $Cs@Se_8$ polyhedron in $CsZnAsSe_3$.



	Cs	Zn	As	Se
Single Cryst.	1	1	1	3
EDX (ave.)	1.0	1.0(1)	1.2(2)	2.9(1)

Figure S3. (a) SEM image and (b) EDX analysis of $CsZnAsSe_3$.

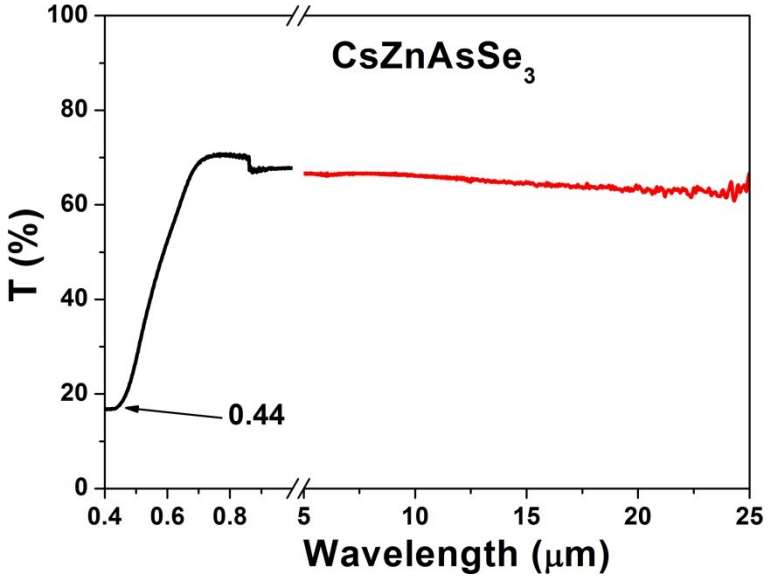


Figure S4. Optical transmittance spectra of $CsZnAsSe_3$.

Table S1. Selected bond lengths (Å) for $CsZnAsSe_3$.

Zn–Se3	2.4439(14)	∠S3–Zn–S2	117.32(5)
Zn–Se2	2.4440(13)	∠S3–Zn–S1	118.52(5)
Zn–Se1	2.4680(13)	∠S2–Zn–S1	102.15(5)
Zn–Se1	2.5316(13)	∠S3–Zn–S1	97.98(5)
As–Se3	2.3605(11)	∠S2–Zn–S1	108.48(5)
As–Se2	2.3710(12)	∠S1–Zn–S1	112.42(5)
As–Se1	2.4196(11)	∠S3–As–S2	102.38(4)
Cs–Se3	3.6111(9)	∠S3–As–S1	102.47(4)
Cs–Se3	3.6459(9)	∠S2–As–S1	97.89(4)
Cs–Se1	3.6758(9)		
Cs–Se2	3.6994(9)		
Cs–Se2	3.7000(9)		
Cs–Se1	3.7517(9)		
Cs–Se3	3.9104(10)		
Cs–Se2	3.9570(2)		

4. References

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