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Stereochemically active lone-pair-driven giant enhancement of birefringence from three-dimensional CsZn₄Ga₅Se₁₂ to two-dimensional CsZnAsSe₃†

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Birefringent crystals are highly desirable for their important applications in optoelectronic fields. However, the rational design of novel birefringent materials with large birefringence (Δn) has always faced great challenges. In this work, a novel quaternary thioarsenate, CsZnAsSe₃, has been rationally designed and successfully obtained based on a stereochemically active lone pair (SCALP) induction strategy *via* the facile surfactant–thermal method. In the structure of CsZnAsSe₃, isolated [AsSe₃] triangular pyramids and one-dimensional infinite [Zn–Se]_∞ chains are alternately connected with each other to generate a two-dimensional [ZnAsSe₂][−] layer and the charge-balanced Cs⁺ cations are occupied between them. The introduction of SCALP cations not only induces structural dimension transformation but also significantly improves optical anisotropy. Remarkably, CsZnAsSe₃ exhibits a significantly increased Δn (*ca.* 0.223), which is about 28 times that of the previously reported three-dimensional parent CsZn₄Ga₅Se₁₂ (*ca.* 0.008). Moreover, detailed theoretical investigation has aided in the deep understanding of the electronic structure and the source of large Δn . This research offers a useful structural design strategy for discovering new chalcogenides with enhanced Δn in the future.

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Introduction

Birefringent crystals have attracted continuously intensive studies owing to their capability of modulating the polarization of light and they are critically important for many optoelectronic fields such as optical communication, polarization information processing and laser polarization technology.¹ To date, commercially leading birefringent crystals have been mainly used in oxides, such as α -BaB₂O₄ (0.2–2.5 μm),² CaCO₃ (0.35–2.3 μm),³ YVO₄ (0.4–5 μm),⁴ and LiNbO₃ (0.42–5.2 μm),⁵ and widely used in the spectral interval from UV to near-IR.

Unfortunately, the disadvantageous absorption of the M–O bonds limits their further application in mid- and far-IR regions. Therefore, there is a very urgent need to discover novel mid- and far-IR birefringent crystals with large birefringence (Δn).

In terms of the structure–active relationship, Δn is largely dependent on the anisotropic polarization of the crystal structures.⁶ Over the last ten years, various structural design strategies have been widely applied to discover excellent birefringent crystals. Among them, stereochemically active lone pair (SCALP) induction is one of the most useful strategies.⁷ For example, by reacting HIO₃ with potassium sulfate, K₂SO₄·HIO₃ has been successfully obtained by Ok and co-workers and it displays a 70 times increase in Δn when compared to K₂SO₄ at 589.3 nm.⁸ Another classic example, Sn₂PO₄X (X = Cl, Br, and I), was discovered by Pan's group by introducing Sn(II)–O–X groups into phosphates, which displayed enhanced Δn of larger than 0.2 at 1064 nm.⁹ Recently, Zou's group found that Sb(III)-based sulfates and phosphates, such as CsSbSO₄F₂ and K₂SbP₂O₇F, respectively, show dramatically improved Δn .¹⁰ Benefiting from the wide transmission range and rich structural chemistry, metal chalcogenides are considered one of the best candidates for developing new MIR and FIR birefringent crystals.¹¹ Although some chalcogenide birefringent crystals

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have been discovered recently, obtaining novel chalcogenides with large Δn by the SCALP induction strategy based on the known structure is rarely reported.

The well-known quaternary polar I-II₄-III₅-Q₁₂ (I = K, Rb, and Cs; II = Mn, Zn, and Cd; III = Ga and In; Q = S, Se, and Te), is a large family of IR nonlinear optical (NLO) candidates featuring three-dimensional (3D) networks and exhibits remarkable second-harmonic-generation effects.¹² Unfortunately, most of them cannot realize effective phase-matching in the IR region owing to their too small Δn . To obtain improved Δn , a series of new chalcogenides, such as KHg₄Ga₅Se₁₂,¹³ AM^{II}₃Ga₅S₁₁ (A = K, Rb, and Cs; M^{II} = Mn and Cd),¹⁴ and AM^{III}₂Sn₂Se₆ (A = Rb and Cs; M^{III} = Ga and In),¹⁵ has been designed and successfully prepared by different structural strategies with the I-II₄-III₅-Q₁₂ type compounds as the template in the past ten years. However, the improvement of the Δn of the aforementioned compounds is not very significant, which can be attributed to the fact that all materials retain the 3D diamond-like frameworks with poor anisotropy in the parent structure. It is widely known that the anisotropic polarization of the crystal structure is the key factor for Δn . Therefore, finding ways to obtain a low-dimensional structure with significant anisotropy is the most effective strategy to achieve large Δn values of materials.¹⁶

Driven by the above-mentioned SCALP induction strategy, a novel quaternary thioarsenate with a two-dimensional (2D) layered structure, namely, CsZnAsSe₃, has been successfully obtained by a facile surfactant-thermal method, which exhibits significantly improved Δn (*ca.* 0.223) when compared to the parent CsZn₄Ga₅Se₁₂ (*ca.* 0.008). Moreover, we show the detailed investigations of crystal synthesis, structural evolution, optical characterization, and theoretical calculations to aid the understanding of the electronic structure and the source of large Δn .

Experimental section

Synthesis and characterization

The starting reagents CsOH·H₂O (2 N), Zn powder (3 N), 1,2-propanediamine and PEG-400 were purchased from Sinopharm Chemical Reagent Co., Ltd. Se (4 N) and As₂Se₃ (3 N) were purchased from Aladdin Co., Ltd. The aforementioned chemicals were directly used for the reaction without further purification. Compound CsZnAsSe₃ was used in the reaction as follows: 1 mmol of CsOH·H₂O, 0.4 mmol of Zn, 0.5 mmol of As₂Se₃, 2.5 mmol of Se, 2.0 mL of PEG-400 and 1 mL of 1,2-propanediamine. All reactants were sealed in a 25 mL Teflon-lined stainless autoclave, which was held at 453 K for one week, and then naturally cooled to room temperature. The reaction mixture was washed with distilled water and ethanol, respectively. A large number of yellow block-shaped CsZnAsSe₃ crystals (close to 40% yield based on Zn) were discovered and a pure phase could be easily obtained by manually selecting crystals from the mixture. Single-crystal XRD data of CsZnAsSe₃ were collected using an Oxford Xcalibur (Atlas

Gemini ultra) diffractometer with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) at 273 K. Elemental analysis was performed using an EDX-equipped JEOL/JSM-6360A SEM. Powder XRD data were obtained on a Bruker D8 Advance diffractometer with graphite-monochromated Cu-K α radiation. Thermogravimetry (TG) analysis was performed under a flowing N₂ atmosphere at 313–1273 K using a NETZSCH STA 449C simultaneous analyzer. The optical band gap was collected on a Hitachi UH4150 UV-vis-NIR spectrometer equipped with an integrating sphere from 200 nm to 2500 nm. The birefringence of the single-crystal CsZnAsSe₃ was observed using a ZEISS Axio A1 polarizing microscope. Theoretical results were also carried out based on the DFT method (see the ESI† for the detailed discussion).

Results and discussion

CsZn₄Ga₅Se₁₂ belongs to the acentric R3 (no. 146) trigonal space group and possesses the following crystallographically unique positions in its asymmetric unit: 1 Cs, 3 M (M = Zn/Ga) and 4 Se atoms. Each M is bonded with 4 Se atoms to give rise to an [MSe₄] tetrahedron which has 4 normal M–Se bonds with 2.379(3)–2.482(2) Å bond lengths. The Cs atom coordinates with 12 Se atoms to generate a cuboctahedron, showing the Cs–Se bond lengths of 3.769(2)–3.843(3) Å (Fig. S1†). Three [M(2)Se₄] tetrahedra are arranged in a six-membered ring and alternately interconnected with other [M(1)Se₄] and [M(3)Se₄] tetrahedra, creating an [M₉Se₂₄] functional primitive (Fig. 1a). These functional primitives are interconnected *via* Se-sharing to form 2D [Zn₄Ga₅Se₁₂][–] layers (Fig. 1b) that are further interlinked *via* M–Se–M bonds to construct a 3D diamond-like framework, in which charge-balanced Cs⁺ cations are filled between the 2D layers (Fig. 1c). Regrettably, such a dense 3D framework structure with poor anisotropy results in an extremely low Δn of CsZn₄Ga₅Se₁₂.

CsZnAsSe₃ crystallizes in the monoclinic system with the centrosymmetric space group of P2₁/c (no. 14) (Table 1). Each asymmetric unit contains 1 independent Cs site (Wyckoff position: 4e), 1 Zn site (4e), 1 As site (4e), and 3 Se sites (4e) (Table 2). The coordination modes of Zn and As atoms are given in Fig. 1d. The selected bond distances and angles are shown in Table S1.† The bond lengths of Zn–Se in [ZnSe₄] are in the range of 2.444–2.532 Å, while the As–Se bond lengths in [AsSe₃] are between 2.360 and 2.420 Å (Fig. 1d). Two [ZnSe₄] tetrahedra are interconnected with each other through Se-sharing to build [Zn₂Se₇]^{10–} dimers that are further interlinked *via* Zn–Se–Zn bonds to construct a wave one-dimensional (1D) infinite [Zn–Se]_∞ chain extending along the *b* axis. These 1D [Zn–Se]_∞ chains further form a 2D [ZnAsSe₃] layer with discrete [AsSe₃] triangular pyramids (Fig. 1e), with Cs⁺ acting as a charge-balanced cation located between these layers (Fig. 1f). Compared with the Cs atom that centers the Se₁₂ cuboctahedron in the CsZn₄Ga₅Se₁₂, the Cs atoms are coordinated by 8 Se atoms to generate a highly twisted CsSe₈ bicapped trigonal prism in CsZnAsSe₃ (Fig. S2 in the ESI†). Similar examples are

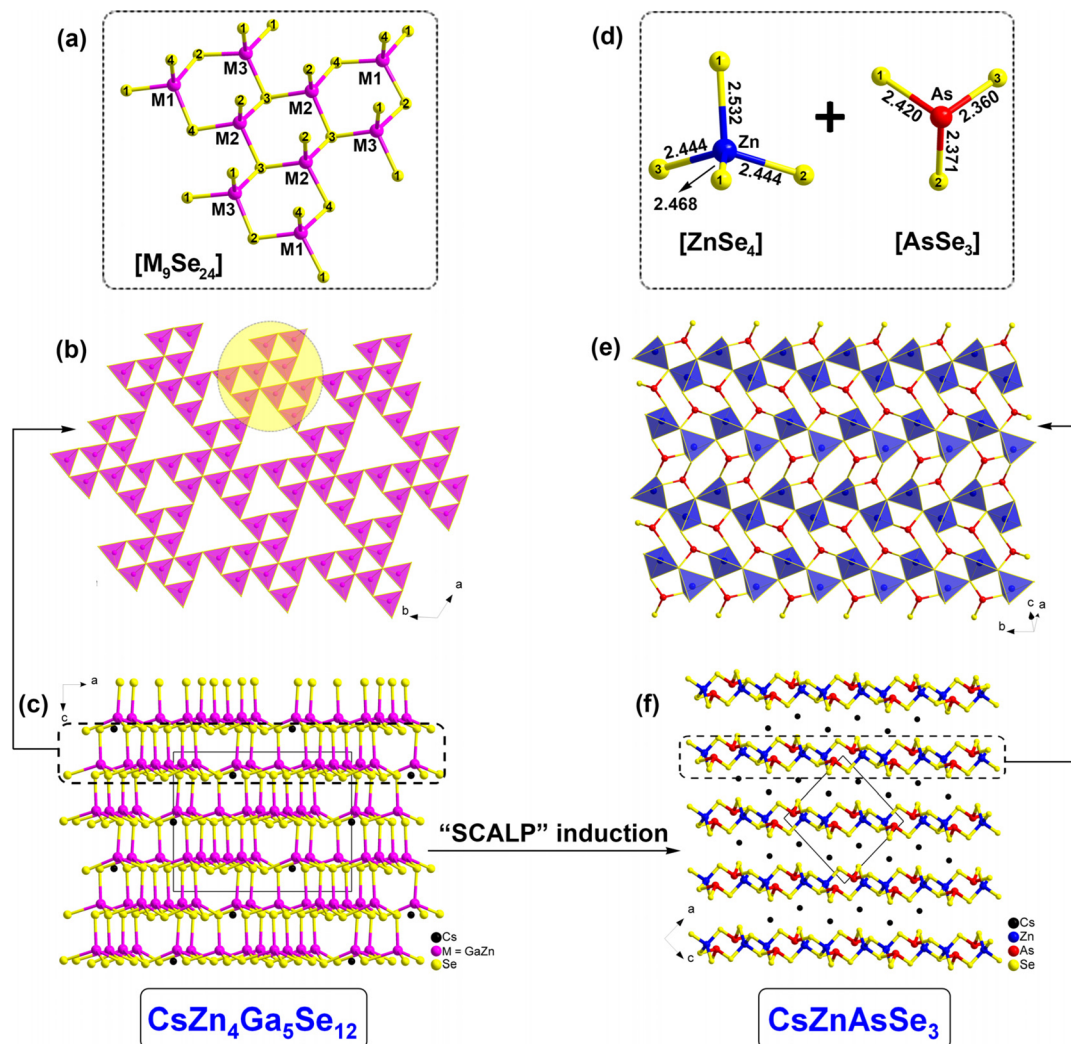


Fig. 1 Structural evolution from 3D $\text{CsZn}_4\text{Ga}_5\text{Se}_{12}$ to 2D CsZnAsSe_3 : (a and d) coordination environment of $[\text{M}_5\text{Se}_{24}]$ ($\text{M} = \text{Zn}/\text{Ga}$), $[\text{ZnSe}_4]$ and $[\text{AsSe}_3]$ FBBs with the atom numbers and bond distance marked; (b and e) projection of 2D $[\text{Zn}_4\text{Ga}_5\text{Se}_{12}]^-$ and 2D $[\text{ZnAsSe}_3]^-$ layers along the ab - and ac -planes, respectively; (c and f) the ball-and-stick models of 3D $\text{CsZn}_4\text{Ga}_5\text{Se}_{12}$ and 2D CsZnAsSe_3 with the unit cell outlined.

also found in some other Cs-based chalcogenides.¹⁷ It is interesting to note that the selenide of CsZnAsSe_3 is the first quaternary phase discovered within the A–Zn–As–Q (A = alkali metals; Q = chalcogen) systems.

Structural evolution from 3D $\text{CsZn}_4\text{Ga}_5\text{Se}_{12}$ to 2D CsZnAsSe_3 based on the SCALP induction strategy is illustrated in Fig. 1. CsZnAsSe_3 might be considered the two-step substitution compound from $\text{CsZn}_4\text{Ga}_5\text{Se}_{12}$. First, the tetrahedral $[\text{GaSe}_4]$ basic building units are replaced by $[\text{AsSe}_3]$ triangular pyramids. Second, the charge shortage caused by the reduction of the coordination number is supplemented by charge-balanced Cs^+ cations. Similar structural evolution processes can be found in some other chalcogenide systems.¹⁸ From the point of chemical design, the As atom was chosen to change the crystal structure owing to the following considerations: (i) As and Ga belong to the same period and the ionic radius is close to $r(\text{As}^{3+}) = 0.58 \text{ \AA}$ vs. $r(\text{Ga}^{3+}) = 0.62 \text{ \AA}$.

Theoretically, free substitution can be realized between them according to the Goldschmidt rule.¹⁹ (ii) The introduction of SCALP groups is conducive to symmetry breaking and thereby obtaining a low-dimensional structure. (iii) The highly polarizable As–Se bond is beneficial for the improvement of Δn .²⁰

Single crystals of CsZnAsSe_3 were prepared by the facile surfactant–thermal method²¹ and yellow block-shaped crystals were chosen for characterization. The elemental distribution of Cs : Zn : As : Se was determined to be 1 : 1.0(1) : 1.2(2) : 2.9(1) by EDX mapping (Fig. S3, ESI[†]), which is close to the result of single-crystal XRD analysis. In addition, the phase of CsZnAsSe_3 was verified by powder XRD measurements, as shown in Fig. 2a. The results indicate that the experimental patterns match well with the simulated ones derived from the CIF data. The result of the UV-Vis-NIR diffuse reflectance spectrum shows that the experimental energy gap (E_g) is about 2.25 eV for CsZnAsSe_3 (Fig. 2b), which is wider than those of other

Table 1 Crystallographic information and refinement results for CsZnAsSe₃

Empirical formula	CsZnAsSe ₃
CCDC number	2215339
Formula weight	510.08
Temperature (K)	293(2)
Crystal system	Monoclinic
Space group	<i>P2₁/c</i> (no. 14)
<i>a</i> (Å)	10.2443(4)
<i>b</i> (Å)	6.6430(3)
<i>c</i> (Å)	10.6276(5)
α (°)	90
β (°)	93.871(4)
γ (°)	90
<i>V</i> (Å ³)	721.59(5)
<i>Z</i>	4
<i>D_c</i> (g cm ⁻³)	4.695
μ (mm ⁻¹)	44.141
GOOF on <i>F</i> ²	1.102
<i>R</i> ₁ , <i>wR</i> ₂ (<i>I</i> > 2 σ (<i>I</i>)) ^a	0.0457, 0.1219
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0467, 0.1226
Largest diff. peak and hole (e Å ⁻³)	3.312, -2.944

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

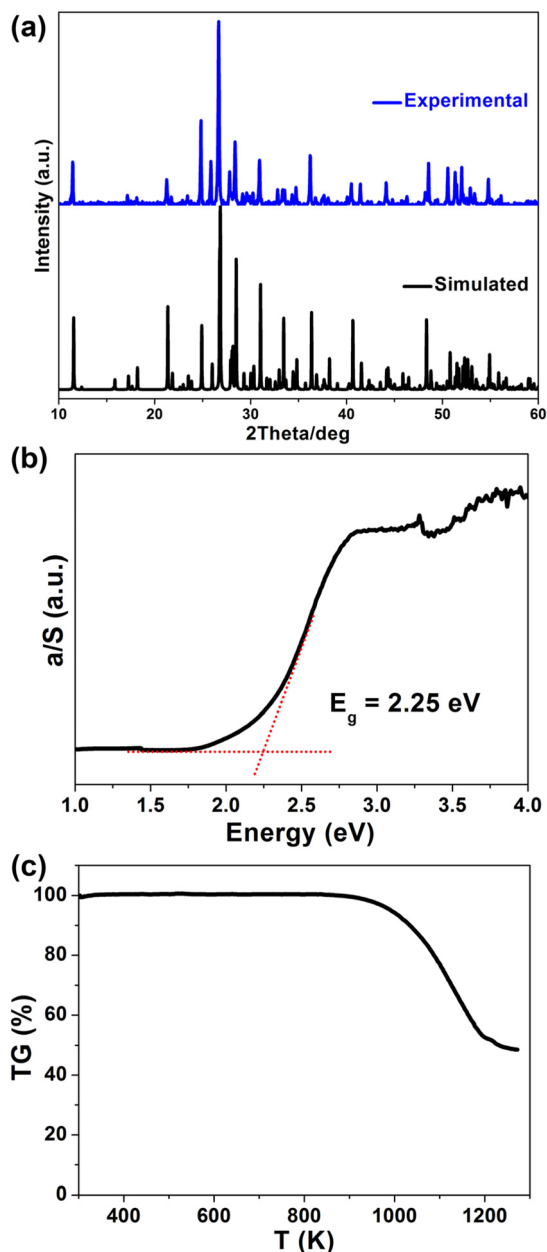
Table 2 The atomic coordinates and equivalent isotropic displacement parameters for CsZnAsSe₃

Atom	Wyckff.	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i> /Å ²
Cs	4e	0.07666(4)	0.80032(7)	0.67533(4)	0.0064(2)
Zn	4e	0.33503(2)	0.19131(2)	0.34814(2)	0.0024(3)
As	4e	0.38109(8)	0.66019(2)	0.46021(8)	0.0024(2)
Se1	4e	0.21283(8)	0.87236(2)	0.35947(7)	0.0027(2)
Se2	4e	0.24498(7)	0.38994(2)	0.51540(7)	0.0038(2)
Se3	4e	0.42689(8)	0.82296(2)	0.65564(8)	0.0042(2)

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

reported quaternary alkali metal-based thioarsenates, including K₇As₃(P₂Se₆)₄ (*E_g* = 2.0 eV),²² Cs₃CuAs₄Se₈ (*E_g* = 1.83 eV),²³ K₂Sm₂As₂Se₉ (*E_g* = 1.70 eV),²⁴ K₃BiAs₆Se₁₂ (*E_g* = 1.65 eV),²⁵ and RbAg₂As₃Se₆ (*E_g* = 1.44 eV).²⁶ Besides, CsZnAsSe₃ exhibits desirable thermal stability (up to 900 K) under N₂ conditions according to the TG curve, as shown in Fig. 2c. Additionally, the optical transmittance spectra of CsZnAsSe₃ are depicted in Fig. S4,† indicating that no bond absorption occurs in a broad spectral range from 0.44 to 25 μm, which covers two important atmospheric transparent windows (3–5 and 8–14 μm). Such a result suggests that CsZnAsSe₃ may be suitable for applications in the mid- and far-IR regions.

Furthermore, the Δn of CsZn₄Ga₅Se₁₂ and CsZnAsSe₃ was observed using a ZEISS Axio A1 cross-polarizing microscope. The observed interference colours of CsZn₄Ga₅Se₁₂ and CsZnAsSe₃ at 546 nm under cross-polarized light are shown in Fig. 3. In terms of the Michel–Levy chart, their retardations (*R* values) and crystal thicknesses (*T* values) were measured as 117 nm and 13.8 μm for CsZn₄Ga₅Se₁₂ and 1381 nm and 6.2 μm for CsZnAsSe₃, respectively. Therefore, their Δn values in the visible range were calculated as 0.008 for CsZn₄Ga₅Se₁₂

**Fig. 2** Experimental characterization of CsZnAsSe₃: (a) powder XRD patterns, (b) the reflectance spectrum transformed using the Kubelka–Munk function and (c) TG curve.

and 0.223 for CsZnAsSe₃ based on the formula of $\Delta n = R/T$.²⁷ It is worth recalling that the experimental Δn shows about a 28 times increase for 2D CsZnAsSe₃ compared to that of 3D CsZn₄Ga₅Se₁₂. Notably, the Δn of CsZnAsSe₃ is close to or higher than those of most commercial birefringent materials, such as YVO₄ (0.23 at 630 nm),⁴ α -BaB₂O₄ (0.12 at 544 nm),² and LiNbO₃ (0.08 at 632 nm),⁵ and also larger than those of many recently reported chalcogenides, such as LiBaSbS₃ (0.05 at 532 nm),²⁸ α -CsBa₂SnSe₄Cl (0.06 at 532 nm),²⁹ K₂Na₂Sn₃S₈ (0.07 at 546 nm),³⁰ Cs₂ZnSn₃S₈ (0.12 at 546 nm),³¹ β -CsBa₂SnSe₄Cl (0.14 at 532 nm)²⁹ and Rb₃NaSn₃S₈ (0.20 at

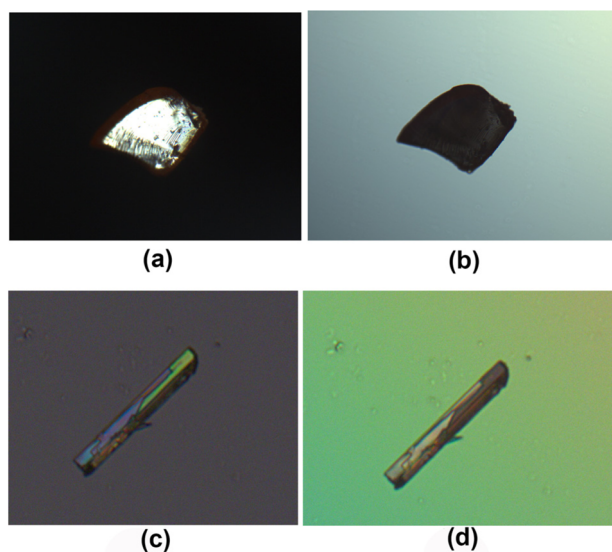


Fig. 3 (a and b) $\text{CsZn}_4\text{Ga}_5\text{Se}_{12}$ and (c and d) CsZnAsSe_3 crystals for Δn determination and the interference colors observed before and after complete extinction.

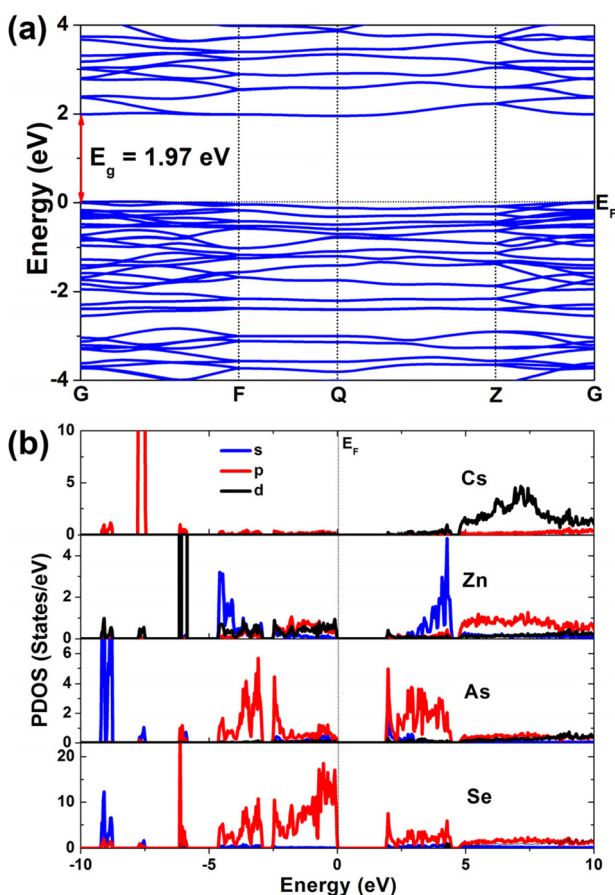


Fig. 4 Theoretical calculations of CsZnAsSe_3 : (a) calculated band structure and (b) PDOS.

546 nm),³⁰ suggesting that it has potential as an IR birefringent candidate. This result suggests that the SCALP induction strategy is very effective for improving optical anisotropy and enhancing Δn in chalcogenide systems.

Furthermore, the detailed energy band structure and partial density of states (PDOS) have aided in a better understanding of the electronic structure and the source of large Δn . It is evident from Fig. 4a that the valence band maximum (VBM) and the conduction band minimum (CBM) occupy the same G points, suggesting that CsZnAsSe_3 is a direct band-gap semiconductor. The calculated E_g of 1.97 eV is slightly less than the corresponding experimental value of 2.25 eV, which can be attributed to the well-known discontinuity of exchange correction energy in the GGA.³² The PDOS analysis of CsZnAsSe_3 was performed as shown in Fig. 4b. As can be seen, the top of the VBs mainly consists of Se-4p states, while the bottom of CBs mainly consists of Cs-6d, Zn-4s/3p/3d, and As-4s/4p orbital states. The high density and overlap of the Zn-4s/3p/3d, As-4s/4p, and Se-4p orbitals near the Fermi level (E_F is fixed to 0 eV, *i.e.*, $E_{\text{VBM}} = 0$) reveal that $[\text{AsSe}_3]$ triangular pyramids and $[\text{ZnSe}_4]$ tetrahedra mainly determine the optical E_g of the structure.

On the basis of the electronic structure, we also calculated the Δn values of $\text{CsZn}_4\text{Ga}_5\text{Se}_{12}$ and CsZnAsSe_3 , respectively. The calculated result is shown in Fig. 5a. It can be

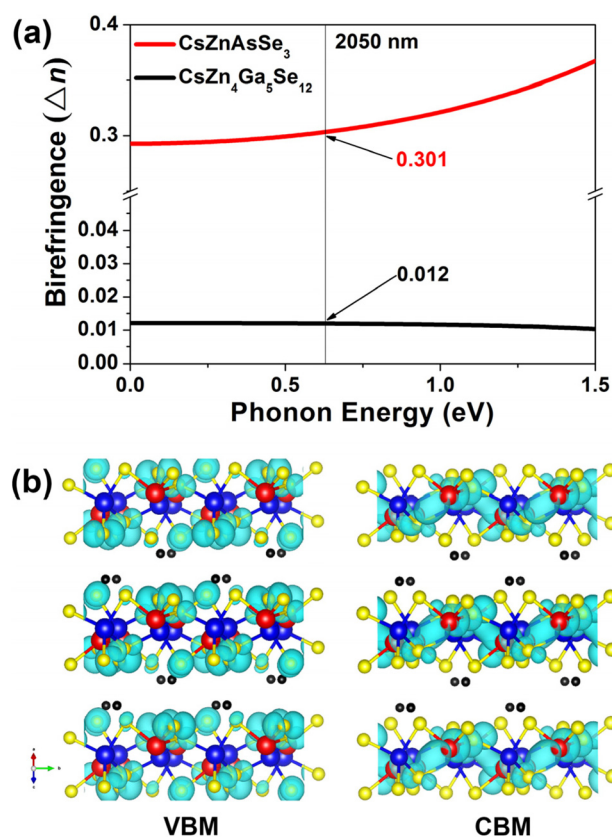


Fig. 5 (a) Calculated birefringence of CsZnAsSe_3 . (b) Projection of the partial charge density maps in the VBM and CBM parts.

seen that their Δn values at 2050 nm are 0.012 and 0.301 for $\text{CsZn}_4\text{Ga}_5\text{Se}_{12}$ and CsZnAsSe_3 , respectively. The increase of Δn from $\text{CsZn}_4\text{Ga}_5\text{Se}_{12}$ to CsZnAsSe_3 is very consistent with the structural analysis and experimental results. Moreover, partial charge density maps in the VBM and CBM parts to visualize the distribution of the bonding and SCALP electrons are given in Fig. 5b. It confirms the strong lone electron density clouds around the As^{3+} cations and the optical anisotropy is closely related to the $[\text{AsSe}_3]$ unit arrangement modes.

Conclusions

In summary, a novel birefringent crystal containing a 2D unique layered structure, CsZnAsSe_3 , has been successfully designed by the SCALP induction strategy and synthesized by the surfactant-thermal reaction. In particular, the birefringence of CsZnAsSe_3 is about 28 times higher than that of previously reported $\text{CsZn}_4\text{Ga}_5\text{Se}_{12}$ with a dense 3D framework structure, which can be attributed to the successful introduction of SCALP $[\text{AsSe}_3]$ triangular pyramids. Our study not only offers a deep understanding of the role of the SCALP effect in the birefringence property of CsZnAsSe_3 but also suggests that the CsZnAsSe_3 crystal may be used for polarization-dependent optical applications.

Author contributions

C. Zhang designed and carried out the experiments and finished the manuscript. M. Y. Ran performed the characterization of optical properties. X. Chen prepared the samples. S. H. Zhou carried out the theoretical calculations. H. Lin and Y. Liu analyzed the results and edited the manuscript. All the authors have approved the final version of the manuscript. C. Zhang and M. Y. Ran contributed equally to this work.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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