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Interesting dimensional transition through changing cations as the trigger in multinary thioarsenates displaying variable photocurrent response and optical anisotropy†

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Due to the intriguing component variability and structure–property flexibility, lone-pair cation-based chalcogenides have garnered substantial interest in recent years. Herein, two new multinary thioarsenates, $Cs_2ZnAs_4S_8$ and $[(NH_4)Cs]CdAs_4S_8$, were successfully discovered via a surfactant–thermal reaction. Both of them possess identical stoichiometry 2-1-4-8, but they exhibit surprisingly different structural features. $Cs_2ZnAs_4S_8$ demonstrates a three-dimensional (3D) $[ZnAs_4S_8]^{2-}$ framework made from the cornersharing $[ZnS_4]$ tetrahedra and one-dimensional (1D) $[As_4S_8]^{4-}$ chains, whereas $[(NH_4)Cs]CdAs_4S_8$ exhibits a two-dimensional (2D) $[CdAs_4S_8]^{2-}$ layer constructed from the corner-sharing $[CdS_4]$ tetrahedra and tetranuclear $[As_4S_8]$ clusters. Photoelectric measurements display that $Cs_2ZnAs_4S_8$ has higher photogenerated electron–hole pair separation efficiency than $[(NH_4)Cs]CdAs_4S_8$ under visible light irradiation. Moreover, both of them show large optical anisotropy $(\Delta n > 0.17$ at 1064 and 2050 nm), while the low dimensional structure is more conducive to enhancing the optical anisotropy based on the theoretical calculations. These findings will provide inspiration for the exploration of multifunctional chalcogenides.

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Introduction

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Over the past few decades, inorganic chalcogenides containing $[M^{III}Q_n]$ ($M^{III}=As$, Sb, Bi) polyhedra have attracted increasing attention because of their intriguing structural and compositional diversity. These M^{III} cations with stereochemically active lone-pair electrons are favorable to form different asymmetric coordination modes, which will further influence the electronic structures and physical properties of the resultant chalcogenides. For example, $M_2As_2Q_5$ (M=Ba, Pb; Q=S, Se) exhibit excellent overall infrared nonlinear optical (IR-NLO) performance thanks to their zero-dimensional (0D) discrete arsenate anions. Pentanary thioantimonate $Rb_2Ba_3Cu_2Sb_2S_{10}$

adopts a one-dimensional (1D) chain structure and displays a wide-bandgap and an intriguing photocurrent response.9 The narrow gap semiconductor RbBi_{11/3}Te₆, which consists of a two-dimensional (2D) infinite Bi₂Te₃-like layer, exhibits a sharp superconducting transition at ~3.2 K.4 The three-dimensional (3D) frameworks A₃Mn₂Sb₃S₈ (A = K and Rb) not only display IR-NLO performances but also possess temperaturedependent paramagnetism and photocurrent responses.¹³ On the other hand, transition-metal-based chalcogenides with d10 electronic configurations (e.g., Zn²⁺, Cd²⁺, Hg²⁺) have also been extensively investigated as these cations tend to show flexible coordination geometries, and hence engender an efficient route to design functional materials.¹⁶ For instance, $Na_6Zn_3M_2Q_9$ (M = Ga, In; Q = S, Se), 2D layered chalcogenides made of unprecedented T3-supertetrahedra, exhibit desirable photoluminescence performances. T KCd3Ga5S11 adopts a diamond-like framework structure and achieves a strong second-harmonic-generation intensity $(1.7 \times \text{AgGaS}_2)$. Ternary IR-NLO BaHgSe2 shows large susceptibility and physicochemical stability activated by the trigonal planar [HgSe₃]⁴⁻ motif.¹⁹

A tremendous amount of multinary lone-pair cation-based chalcogenides have been discovered so far, however, the systematic investigation of the A/TM/As/Q system (A = alkali metals; TM = group 12 metals; Q = chalcogen) is rarely reported. To the best of our knowledge, only 3 compounds in this system are known, namely NaCdAsS₃, ²⁰ Rb₄CdAs₂S₉, ²¹ and

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CsHgAsS₃.²² The first two are obtained by the solid-state method, while the last one is prepared by solvothermal synthesis. Recently, a surfactant-thermal reaction has been proved to be a facile method for exploring novel chalcogenides.²³⁻³¹ In this study, our continuous explorations based on the surfactant-thermal method have led to the discovery of two new thioarsenates, Cs₂ZnAs₄S₈ and [(NH₄)Cs]CdAs₄S₈. Although these two compounds have identical stoichiometry 2-1-4-8, they are not isostructural and undergo an interesting dimensional transition from a 3D framework to a 2D layered structure. Herein, the crystal structure, physical properties, and corresponding theoretical studies are systematically investigated.

Results and discussion

Single-crystal X-ray diffraction (SXRD) test results show that Cs₂ZnAs₄S₈ and [(NH₄)Cs]CdAs₄S₈ belong to different space

Table 1 Crystallographic data and refinement details of Cs₂ZnAs₄S₈ and [(NH₄)Cs]CdAs₄S₈

Formula FW	Cs ₂ ZnAs ₄ S ₈ 887.35	[(NH ₄)Cs]CdAs ₄ S ₈ 819.51
Crystal system	Tetragonal	Tetragonal
Temperature (K)	Yellow	Orange
Crystal color	$I4_1/a$ (no. 88)	P4/n (no. 85)
Space group	11.0828(5)	10.3879(2)
a (Å)	11.0828(5)	10.3879(2)
b (Å)	13.2303(8)	7.7691(2)
c (Å)	90	90
$\alpha (\circ)$	90	90
β (\circ)	90	90
γ (°)_	1625.06(18)	838.35(4)
$V(A^3)$	4	2
Z	3.627	3.246
$D_{\rm c}$ (g cm ⁻³)	15.004	12.243
$\mu (\mathrm{mm}^{-1})$	1.039	1.071
$\stackrel{'}{\text{GOOF}}$ on F^2	0.0265, 0.0603	0.0152, 0.0300
R_1 , w R_2 $(I > 2\sigma(I))^a$	0.0369, 0.0645	0.0189, 0.0316
R_1 , w R_2 (all data)	1.826/-1.271	0.818/-0.552
Largest diff. peak/hole (e Å ⁻³)	887.35	819.51

^a $R_1 = \sum ||F_0| - |F_c||/\sum |F_0|$, $wR_2 = \left[\sum w(F_0^2 - F_c^2)^2/\sum w(F_0^2)^2\right]^{1/2}$.

groups, i.e., tetragonal I4₁/a (no. 88) for Cs₂ZnAs₄S₈ with cell parameters of a = b = 11.0828(5), c = 13.2303(8) Å, and Z = 4and tetragonal P4/n (no. 85) for [(NH₄)Cs]CdAs₄S₈ with cell parameters of a = b = 10.3879(2), c = 7.7691(2) Å, and Z = 2. The detailed crystallographic information is listed in Table 1. There are 1 unique Cs atom (Wyckoff site: 8e), 1 unique As atom (Wyckoff site: 16f), 1 unique Zn atom (Wyckoff site: 4a), and 2 unique S atoms (Wyckoff sites: 16f and 16f) in its asymmetric unit (Table 2). As illustrated in Fig. 1a, the three-dimensional (3D) crystal structure of Cs2ZnAs4S8 is constructed from charge-balanced Cs⁺ cations, regular [ZnS₄] tetrahedra, (Fig. 1b) and one-dimensional (1D) anionic chains $[As_4S_8]^{4-}$ made of the corner-sharing $[As_4S_9]$ groups (Fig. 1c). The important bond distances of Cs2ZnAs4S8 are listed in Table S1.† The As atom adopts a common coordination with 3 S atoms in the bond distance range of 2.2143(5)-2.3267(5) Å to build a [AsS₃]³⁻ triangular pyramid. The Zn-S bond distance in the [ZnS₄] tetrahedron is 2.3309(5) Å. The S-As-S angles in $Cs_2ZnAs_4S_8$ range from 98.07(2)° to 103.28(2)°, while the S–Zn– S angles vary from 105.79(2)° to 117.12(2)°. These bond distances and angles in Cs2ZnAs4S8 are normal and can also be comparable to the reported Cs-based chalcogenides. 32-34

There are 7 unique crystallographic atoms in the asymmetric unit of the structure of [(NH₄)Cs]CdAs₄S₈, including 1 Cs (Wyckoff site: 2c), 1 Cd (Wyckoff site: 2a), 1 As (Wyckoff site: 8g), 2 S (Wyckoff sites: 8g and 8g), 1 N (Wyckoff site: 2b) and 1 H (Wyckoff site: 8g) (Tables 1 and 2). As given in Fig. 1d, the crystal structure of [(NH₄)Cs]CdAs₄S₈ is composed of regular [CdS₄] tetrahedra with $d_{\text{(Cd-S)}} = 2.5481(5) \text{ Å}$ and tetranuclear [As₄S₈] clusters with $d_{\text{(As-S)}} = 2.2676(5)-2.3008(5) \text{ Å}$, which interconnect with each other by sharing vertexes to form a two-dimensional (2D) [CdAs₄S₈]²⁻ layer filling the dispersed $(NH_4)^+$ and Cs^+ cations.

The interesting structural evolution between Cs₂ZnAs₄S₈ and [(NH₄)Cs]CdAs₄S₈ is illustrated in Fig. 1. Both of them possess an identical stoichiometry of 2-1-4-8 and belong to the same tetragonal system, but they are not isostructural and have some significantly different structural features: (i) pyramidal [AsS₃] units in Cs₂ZnAs₄S₈ forms a 1D infinite [As₄S₈]⁴⁻

Table 2 Atomic coordinates and equivalent isotropic displacement parameters of Cs₂ZnAs₄S₈ and [(NH₄)Cs]CdAs₄S₈

Atom	Wyckoff	x	y	z	$U_{(\mathrm{eq})}^{a}$	Occu.
Cs ₂ ZnAs ₄ S ₈						
Cs	8 <i>e</i>	0	0.25	0.45521(2)	0.02597(6)	1.0
As	16f	0.16243(2)	0.01798(2)	0.00487(2)	0.01245(5)	1.0
Zn	4a	0	0.25	0.125	0.01320(8)	1.0
S2	16f	0.17589(5)	0.21445(4)	0.03310(3)	0.01605(9)	1.0
S1	16f	0.31599(5)	0.51563(5)	0.10909(3)	0.01892(10)	1.0
[(NH ₄)Cs]Cd					,	
Ĉs	2c	0.25	0.25	0.68028(3)	0.02210(7)	1.0
Cd	2a	0.25	0.75	0	0.01361(7)	1.0
As	8 <i>g</i>	0.04860(2)	0.15875(2)	0.14479(2)	0.01204(6)	1.0
S2	8 <i>g</i>	0.16315(4)	0.02562(4)	0.31813(6)	0.01556(10)	1.0
S1	8 <i>g</i>	0.07233(4)	0.64420(4)	0.17643(6)	0.01402(9)	1.0
N	$2\overset{\circ}{b}$	0.25	0.75	0.5	$0.0082(5)^{'}$	1.0
H	8 <i>g</i>	0.2013(19)	0.724(2)	0.446(3)	0.014(6)	1.0

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

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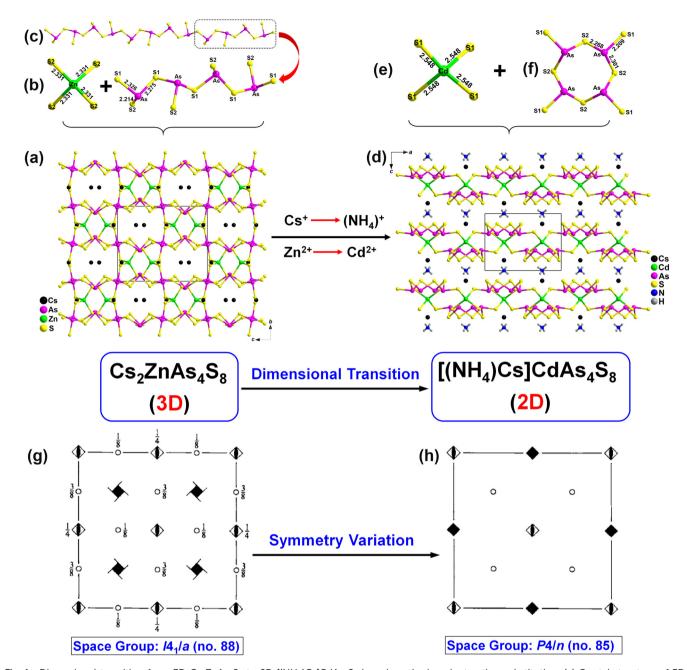


Fig. 1 Dimensional transition from 3D $Cs_2ZnAs_4S_8$ to 2D $[(NH_4)Cs]CdAs_4S_8$ based on the isovalent cation substitution. (a) Crystal structure of 3D $Cs_2ZnAs_4S_8$ viewed down the a-direction; (b) 1D $[As_4S_8]$ chain with the coordination environment of the $[As_4S_9]$ unit marked; (c) the coordination environment of the tetrahedral [ZnS₄] unit; (d) crystal structure of 2D [(NH₄)Cs]CdAs₄S₈ viewed down the a-direction; (e, f) the coordination environment of the tetrahedral [ZnS₄] unit and tetra-nuclear [As₄S₈] cluster; (g, h) spatial symmetry operation from $I4_1/a$ (no. 88) to P4/n (no. 85).

chain by vertex-sharing S1 atoms, while in [(NH₄)Cs]CdAs₄S₈, the tetra-nuclear [As₄S₈] cluster is constructed from the same [AsS₃] units; (ii) the coordination number (CN) of the crystallographically independent Cs atom in Cs2ZnAs4S8 is 10 and the Cs-S bond distances are in the range of 3.617 (5)-4.116 (6) Å, which are different from those of [(NH₄)Cs]CdAs₄S₈ [CN = 8, $d_{(Cs-S)} = 3.696(5)-3.76(5)$ Å] (Fig. S1†). Such differences between them can be attributed to the different sizes of cations, i.e., the 3D $[ZnAs_4S_8]^{2-}$ framework in $Cs_2ZnAs_4S_8$ can be viewed as [ZnS₄] tetrahedra connected by 1D infinite [As₄S₈]⁴

chains by sharing S atoms and relatively large Cs⁺ cations occupied the space of the framework. However, when one of the "large" radius Cs⁺ cations was replaced by smaller radius (NH₄)⁺ cations, the linkages between the [As₄S₈]⁴⁻ chains in Cs₂ZnAs₄S₈ are broken, and the 3D $[ZnAs_4S_8]^{2-}$ framework in $Cs_2ZnAs_4S_8$ transforms into the 0D [As₄S₈] clusters in [(NH₄)Cs]CdAs₄S₈. In addition, the above-mentioned structural evolution is ultimately reflected by their space groups, from $I4_1/a$ (for $Cs_2ZnAs_4S_8$) to P4/n(for [(NH₄)Cs]CdAs₄S₈). The detailed symmetric operation change based on isovalent cation substitution is shown in Fig. 1g and h.

Polycrystalline samples of Cs₂ZnAs₄S₈ and [(NH₄)Cs] CdAs₄S₈ were prepared by a facile surfactant-thermal method at 413 K for 7 days with CsOH·H₂O, Zn (or Cd), As₂S₃, S, oleic acid, hydrazine monohydrate (98%) and PEG-400 as staring materials, in a yield of approximately 80-90% based on Zn (or Cd) (further experimental details see the ESI†). As displayed in Fig. S2 and S3,† semi-quantitative energy-dispersive X-ray (EDX) elemental analysis provides the average atomic ratios of 2.0/1.1(2)/3.9(8)/8.2(1) and 1.0/1.1(4)/4.0(5)/7.9(7) for $Cs_2ZnAs_4S_8$ and [(NH₄)Cs]CdAs₄S₈, respectively. In addition, the purity of the polycrystalline samples was confirmed by powder X-ray diffraction (XRD) analysis (Fig. S4 and S5†). Moreover, both of them exhibit desirable thermal stability (up to 700 K) under N₂ conditions, as shown in Fig. S6 and S7.† Based on the different calculated formulas for direct semiconductors $((\alpha hv)^2)$ vs. energy) or indirect semiconductors $((\alpha h v)^{1/2} \text{ vs. energy})^{35}$ the experimental energy gaps (E_{φ}) of Cs₂ZnAs₄S₈ and $[(NH_4)Cs]$ CdAs₄S₈ are about 2.24 and 2.36 eV, respectively (Fig. 2). These values are compared to those of other reported quaternary thioarsenates, such as RbCu₄AsS₄ ($E_g = 2.15 \text{ eV}$), ³⁶ Cs₃CuAs₄S₈

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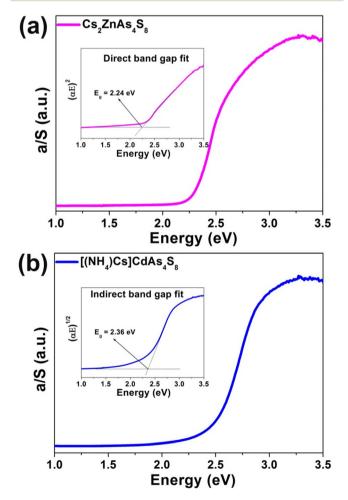


Fig. 2 UV-vis-NIR diffuse reflectance spectra of (a) Cs₂ZnAs₄S₈ and (b) [(NH₄)Cs]CdAs₄S₈ (inset: direct or indirect band gap fit based on the DFT results)

 $(E_g = 2.26 \text{ eV})$, 30 Rb₈Cu₆As₈S₁₉ $(E_g = 2.29 \text{ eV})$, 37 and CsCu₂AsS₃ $(E_g = 2.30 \text{ eV}).^{27}$

In addition, inspired by recent reports that most of the lone-pair-based chalcogenides display intriguing photocatalytic properties, 38-43 the photoelectrochemical experiment was performed through a standard three-electrode system using simulated solar light illumination to study the photoelectric properties of Cs2ZnAs4S8 and [(NH4)Cs]CdAs4S8. As illustrated in Fig. 3, the photocurrent-time curves exhibit a rapid and consistent photocurrent response in a multiple 20 s switching period. Clearly, Cs2ZnAs4S8 shows a remarkable transient photocurrent response, which is about 4 times that of [(NH₄)Cs]CdAs₄S₈, that is, Cs₂ZnAs₄S₈ possesses higher photogenerated electron-hole pair separation efficiency than [(NH₄)Cs]CdAs₄S₈ under visible light irradiation. Meanwhile, these repeatable anodic photocurrent responses suggest that Cs₂ZnAs₄S₈ and [(NH₄)Cs]CdAs₄S₈ belong to n-type semiconductors. It is worth mentioning that these values of photocurrent densities (ca. 3.0 and 0.75 µA cm⁻² for Cs₂ZnAs₄S₈ and [(NH₄)Cs]CdAs₄S₈, respectively) are much higher than those of most recently reported chalcogenides, such as $Rb_2Ba_3Cu_2Sb_2S_{10}$ (ca. 6 nA cm⁻²), BaCuSbSe₃ (ca. 30 nA cm⁻²),³⁸ and BaCuSbS₃ (ca. 55 nA cm⁻²).³⁸

To well understand the origin of difference of electronic structures and structure-activity relationships, theoretical calculations of Cs2ZnAs4S8 and [(NH4)Cs]CdAs4S8 have been systematically carried out based on DFT methods. As shown in Fig. 4a and b, the valence band maximum (VBM) and the conduction band minimum (CBM) located at the same high-symmetry points (i.e., Z|R) indicate that Cs2ZnAs4S8 is a directband-gap (E_g = 1.92 eV) semiconductor, while [(NH₄)Cs] $CdAs_4S_8$ is an indirect-band-gap ($E_g = 2.13 \text{ eV}$) semiconductor since the VBM and the CBM are located at different high-symmetry points (i.e., Z|R and V, respectively). These calculated values are slightly smaller than the experimental observations

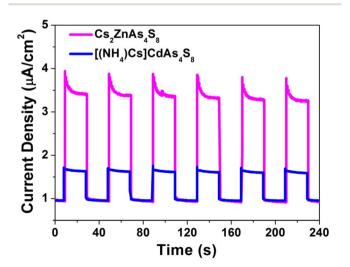


Fig. 3 Photocurrent response curves of Cs₂ZnAs₄S₈ and [(NH₄)Cs] CdAs₄S₈.

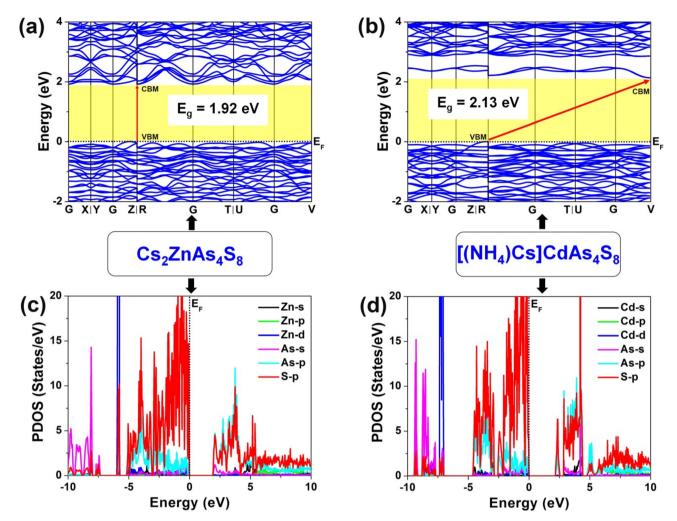


Fig. 4 Theoretical calculated results of $Cs_2ZnAs_4S_8$ and $[(NH_4)Cs]CdAs_4S_8$: (a, b) electronic band structures; (c, d) PDOSs ((states with fewer contributions are omitted for a better view). The Fermi level E_F is set at 0.0 eV.

(2.24 eV for Cs₂ZnAs₄S₈ and 2.36 eV for [(NH₄)Cs]CdAs₄S₈, as given in Fig. 2), which is a well-known phenomenon for the local approximations to DFT.44 It is widely known that the photocatalytic activity mainly depends on the separation and diffusion rate of the photogenerated charge carriers, which can be judged by calculating the relative effective masses of electrons and holes based upon the electronic structures of the VBM and CBM in the title compounds.³⁸ Through comparison, we can clearly see that the electronic bands of Cs2ZnAs4S8 are steeper than those of [(NH₄)Cs]CdAs₄S₈. Namely, Cs₂ZnAs₄S₈ is more conducive to improving the efficiency of photocatalysis, which is basically consistent with the experimental observation (Fig. 3). In addition, the projected density of states (PDOSs) with major contributions of title compounds is illustrated in Fig. 4c and d. Cs₂ZnAs₄S₈ and [(NH₄)Cs]CdAs₄S₈ exhibit similar results: the band from -5 eV to the Fermi level (EF), S-3p as well as As-4p and Zn-3d (or Cd-4d) states makes the main contribution, while the bottom of the CB is mainly composed of electronic hybridization of S-3p, As-4p and As-4s

states. Consequently, the optical Eg values of Cs2ZnAs4S8 and [(NH₄)Cs]CdAs₄S₈ mainly come from the charge transfer of Zn (or Cd)-S and As-S units, in which charge-balancing cations $(e.g., Cs^+, (NH_4)^+)$ show negligible contributions for the DOS. On the basis of their electron structures, we also calculated the birefringence (Δn) of $Cs_2ZnAs_4S_8$ and $[(NH_4)Cs]CdAs_4S_8$, respectively. As displayed in Fig. 5, their Δn values in both the important wavelengths can be calculated as 0.17@1064 nm and 0.18@2050 nm for Cs2ZnAs4S8 and 0.29@1064 nm and 0.31@2050 nm for [(NH₄)Cs]CdAs₄S₈, which are comparable with some recently reported chalcogenides, indicating that they have potential as UV-vis or IR birefringent crystals. As known, the Δn value will mainly depend on the anisotropy of the anionic substructure, whereas the contribution of chargebalancing cations can be neglected. 45-50 In other words, compared with the 3D anionic $[CdAs_4S_8]^{2-}$ framework in $[(NH_4)Cs]$ $CdAs_4S_8$, the anisotropy of the 2D anionic $[ZnAs_4S_8]^{2-}$ layer in Cs₂ZnAs₄S₈ is more obvious, which is more beneficial for producing larger Δn values.

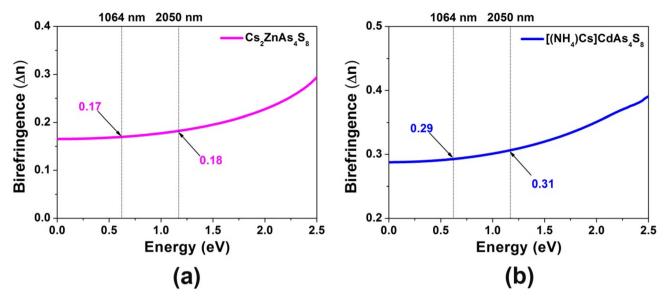


Fig. 5 Curves of the calculated birefringence (Δn) as a function of energy (eV) for (a) Cs₂ZnAs₄S₈ and (b) [(NH₄)Cs]CdAs₄S₈.

Conclusions

In conclusion, two new members of the multinary X-TM-As-S family, Cs₂ZnAs₄S₈ and [(NH₄)Cs]CdAs₄S₈, have been prepared by a simple surfactant-thermal method. Although they have similar chemical stoichiometry 2-1-4-8, they undergo an intriguing dimensional transition from a 3D framework to a 2D layered structure. The optical absorption spectra and photoelectric results confirm that both the thioarsenates are widebandgap semiconductors and Cs2ZnAs4S8 exhibits a better photocurrent response than [(NH₄)Cs]CdAs₄S₈ under the same test conditions. Meanwhile they also show large birefringence. In particular for [(NH₄)Cs]CdAs₄S₈, the calculated birefringence values are 0.29@1064 nm and 0.31@2050 nm, respectively, suggesting its potential for application as a dual-waveband birefringent crystal. The analysis results of the structure-activity relationship show that the low dimensional structure of this family will be favorable for the generation of large optical anisotropy, that is, to obtain high birefringence. These results provide new insights into the exploration of novel functional chalcogenides and further research on the other physical properties of the title compounds is ongoing.

Author contributions

C. Zhang prepared the samples, and designed and carried out the experiments. S. H. Zhou carried out the theoretical calculations. Y. Xiao measured the optical properties. H. Lin and Y. Liu conceived the experiments, analyzed the results and wrote and edited the manuscript. All the authors have approved the final version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

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