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A new infrared nonlinear optical material BaZnGeS₄ with a wide band gap and large nonlinear optical response†

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Developing high-performance infrared (IR) nonlinear optical (NLO) materials is essential for modern laser technology, but challenging due to the competition of the NLO coefficient and band gap in the structure. Based on the “electronic structure engineering bucket effect” and systematic experimental investigations on the A^{II}B^{II}C^{IV}D₄^{VI} family, three new alkaline earth metal sulfides Mg_{0.6}Cd_{1.4}GeS₄, CaCdGeS₄, and BaZnGeS₄ have been developed. The compounds show a structural change from the *Pnma* (CaCdGeS₄) to the *Fdd2* (BaZnGeS₄) space group. Among them, BaZnGeS₄ exhibits a phase-matching NLO response of ~0.8× AGS, a wide band gap of 3.36 eV, and a high laser-induced damage threshold of ~5.4× AGS, achieving a good balance between the NLO response and band gap, which makes it an excellent IR NLO material. Theoretical calculations show that the NLO effects of BaZnGeS₄ originated from the [ZnS₄] and [GeS₄] NLO-active motifs. The results indicate that BaZnGeS₄ is a promising anti-laser damage IR NLO material and enriches the chemical diversity of the A^{II}B^{II}C^{IV}D₄^{VI} family.

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Introduction

Nonlinear optical (NLO) crystals, as the critical optical devices of all-solid-state lasers, play a critical role in the development of coherent light sources through frequency-conversion technology, which shows wide applications in the fields of laser photolithography, medical diagnostics, environmental monitoring, remote sensing, communication, and so on.^{1–3} Over the past decades, borate-based NLO crystals, such as β-BaB₂O₄, LiB₃O₅, and KBe₂BO₃F₂, have achieved great success in ultraviolet (UV) and deep-UV regions.^{4–9} In IR regions, the commercially available IR NLO crystals AgGaS₂ (AGS), AgGaSe₂ (AGSe), and ZnGeP₂ (ZGP) show strong NLO responses,^{10–12} but low laser-induced damage thresholds (LIDTs) (AGS/Se) or narrow band gap induced two-photon absorption around 1 μm (ZGP), which limits their further applications in modern laser technology.^{13–17} Hence, the development of new IR NLO materials with wide band gaps and strong NLO responses is still a hot topic in this field.

For an excellent IR NLO material, the following requirements related to optical properties are highly expected: (i) a high NLO effect ≥0.5× AGS, preferably ≥1.0× AGS to improve the frequency conversion efficiency; (ii) a large band gap ($E_g > 3.0$ eV) to prevent two-photon absorption around 1 μm and achieve high LIDT; (iii) a wide IR transparency range covering the two important IR atmospheric windows (3–5 μm and 8–12 μm); and (iv) moderate birefringence to meet the phase-matching (PM) condition.^{18–20} To obtain a strong NLO response and wide IR transparent region, chalcogenides have been regarded as a promising system,^{21–26} and to produce a wide band gap, introducing alkali and/or alkaline earth metal (AEM) without d–d and f–f electron transitions has been recognized as a feasible strategy.^{27–32} Recently, the quaternary A^{II}B^{II}C^{IV}D₄^{VI} family compounds with abundant and adjustable structure sites have received considerable attention in the design of high-performance IR NLO materials.³³ However, most of the developed compounds in the A^{II}B^{II}C^{IV}D₄^{VI} family show narrow band gaps (≤3.0 eV).³⁴ Based on the “electronic structure engineering bucket effect” promoted by Chen *et al.*,³⁵ BaZnGeS₄ could be predicted as a promising wide band gap IR NLO material considering the wide band gaps of the involved binary phases (BaS: 3.88 eV; ZnS: 3.87 eV; GeS₂: 3.54 eV) in the structure. Moreover, the A-site atom in this family is limited to Sr and Ba, and the number (~26, Table S1†) of A^{II}B^{II}C^{IV}D₄^{VI} family compounds is far less than the one (more than 38) of A₂^IB^{II}C^{IV}D₄^{VI} family compounds.^{34,36}

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In this work, systematic experimental investigations were carried out on quaternary AEM-Zn/Cd-Ge-S systems, and three new AEM-containing sulfides $\text{Mg}_{0.6}\text{Cd}_{1.4}\text{GeS}_4$, CaCdGeS_4 , and BaZnGeS_4 were synthesized through high-temperature solid-state reactions. The compounds show an interesting structural change from the centrosymmetric (CS) *Pnma* ($\text{Mg}_{0.6}\text{Cd}_{1.4}\text{GeS}_4$ and CaCdGeS_4) to the non-centrosymmetric (NCS) *Fdd2* (BaZnGeS_4) space group. It is worth noting that BaZnGeS_4 is composed of $[\text{BaS}_8]$, $[\text{ZnS}_4]$, and $[\text{GeS}_4]$ units and belongs to the $A^{\text{II}}B^{\text{IV}}C^{\text{IV}}D_4^{\text{VI}}$ family, while CaCdGeS_4 and $\text{Mg}_{0.6}\text{Cd}_{1.4}\text{GeS}_4$ are isostructural compounds consisting of $[\text{Ca}/\text{CdS}_6]$ / $[\text{Mg}/\text{CdS}_6]$ and $[\text{GeS}_4]$ units that are derived from the $A_2^{\text{II}}C^{\text{IV}}D_4^{\text{VI}}$ family. Among them, BaZnGeS_4 exhibits excellent optical properties including a large NLO response ($\sim 0.8 \times \text{AgGaS}_2$), a high LIDT ($5.4 \times \text{AgGaS}_2$), a wide experimental band gap ($E_g = 3.36 \text{ eV}$), and a large birefringence ($\Delta n_{\text{cal}} = 0.135@1064 \text{ nm}$), and could be a promising IR NLO material for high power IR lasers.

Experimental section

Materials

The high-purity starting materials BaS (99.99%), SrS (99.99%), CaS (99.99%), MgS (99.99%), Zn (99.99%), Cd (99.99%), Ge (99.99%), and S (99.99%), which are utilized for the experimental preparations, were purchased from the Aladdin website. To prevent the possible oxidation and deliquescence of sulfides, they were stored in dry argon-filled glove boxes.

Chemical syntheses

The single crystals for structural determinations of $\text{Mg}_{0.6}\text{Cd}_{1.4}\text{GeS}_4$, CaCdGeS_4 , and BaZnGeS_4 were prepared through high-temperature solid-state reactions. The starting mixtures of BaS/CaS/MgS, Zn/Cd, Ge, and S with stoichiometric ratios of 1 : 1 : 1 : 3 were weighed and loaded into quartz tubes with an inner diameter of 10 mm. After initial mixing, the samples were vacuumed to 10^{-3} Pa and then flame sealed. The sealed quartz tubes were placed in a muffle furnace with programmed temperature, slowly heated to 800 °C (BaZnGeS_4) or 900 °C ($\text{Mg}_{0.6}\text{Cd}_{1.4}\text{GeS}_4$, CaCdGeS_4) at a speed of 6 °C h^{-1} , held for 60 h to complete the reactions, and then slowly cooled to room temperature at 8 °C h^{-1} . Finally, tablet-like BaZnGeS_4 / CaCdGeS_4 / $\text{Mg}_{0.6}\text{Cd}_{1.4}\text{GeS}_4$ single crystals were harvested. The pure-phase powder samples of BaZnGeS_4 and $\text{Mg}_{0.6}\text{Cd}_{1.4}\text{GeS}_4$ were synthesized through similar procedures with the chemical stoichiometric ratios of BaS : Zn : Ge : S = 1 : 1 : 1 : 3 and MgS : Cd : Ge : S = 0.6 : 1.4 : 1 : 3.4, respectively, and the holding time at the reaction temperatures (800 °C for BaZnGeS_4 and 900 °C for $\text{Mg}_{0.6}\text{Cd}_{1.4}\text{GeS}_4$) was set to 100 h.

Single crystal X-ray diffraction (XRD) measurements

The single-crystal XRD data of the three compounds were collected on a Bruker SMART APEX III CCD single-crystal X-ray diffractometer with Mo K_α radiation ($\lambda = 0.71073 \text{ \AA}$) at room temperature. The collected data of these crystals were integrated using the SAINT program and the multi-scan type

absorption correction of the structures was performed using the SADABS program, and then refined using the structure resolution program package SHELXL by full-matrix least-squares fitting on F^2 .^{37,38} In BaZnGeS_4 , there is no atomic co-occupation. While in $\text{Mg}_{0.6}\text{Cd}_{1.4}\text{GeS}_4$ and CaCdGeS_4 , the Mg/Ca is co-occupied with Cd atoms at two crystallographically unique sites, owing to the similar cationic radii and coordination configurations of Mg/Ca and Cd. For a clearer ratio, based on free occupancy refinement initially, the occupancies of Mg/Cd were fixed to 0.1/0.9 for Mg(1)/Cd(1), 0.5/0.5 for Mg(2)/Cd(2) in $\text{Mg}_{0.6}\text{Cd}_{1.4}\text{GeS}_4$, and 0.8/0.2 for Ca(1)/Cd(1), 0.2/0.8 for Ca(2)/Cd(2) in CaCdGeS_4 , respectively. The PLATON program was used to check the lacking symmetry elements and no higher symmetries were found.³⁹

Powder XRD (PXRD) characterization

The PXRD measurements were performed on a Bruker D2 PHASER diffractometer with Cu K_α radiation ($\lambda = 1.5418 \text{ \AA}$) at room temperature. The PXRD data were collected with the 2θ ranging from 10 to 70° and a scan step rate of 0.02°. The theoretical XRD patterns of BaZnGeS_4 and $\text{Mg}_{0.6}\text{Cd}_{1.4}\text{GeS}_4$ were obtained using Mercury software based on their CIF files.

Energy-dispersive spectroscopy (EDS)

The EDS and mapping of $\text{Mg}_{0.6}\text{Cd}_{1.4}\text{GeS}_4$, CaCdGeS_4 , and BaZnGeS_4 single crystals were performed on a field emission scanning electron microscope (FE-SEM, JEOL JSM-7610F Plus, Japan) equipped with an energy-dispersive spectrometer (Oxford, X-Max 50). It was operated at 5 kV.

UV-vis-near-IR (NIR) diffuse-reflectance spectroscopy

The ultraviolet-visible-near infrared (UV-vis-NIR) diffuse-reflectance spectra of BaZnGeS_4 and $\text{Mg}_{0.6}\text{Cd}_{1.4}\text{GeS}_4$ polycrystalline powder samples were recorded on a ShimadzuSolidSpec-3700 DUV UV-Vis-IR spectrometer. The measurement range was from 200 to 2600 nm, and BaSO_4 was used as the diffuse reflection standard. The diffuse reflection data were converted into absorption data using the Kubelka-Munk function $F(R) = \alpha/S = (1 - R)^2/2R$, where $F(R)$ means the ratio of the absorption coefficient to the scattering coefficient; α , R , and S represent the absorption coefficient, reflectance, and scattering coefficient, respectively.

Raman spectroscopy

Raman spectra of the three compounds in the 4000–100 cm^{-1} region (2.5–100 μm) were recorded on a LABRAM HR Evolution spectrometer equipped with a CCD detector using 532 and 633 nm radiation from a diode laser. High-quality crystals of samples were selected and placed on a glass slide for measurement. The maximum power of the laser was set to 60 mW, and the data collection was completed within 15 s.

Second-harmonic generation (SHG) measurements

The powder SHG responses of BaZnGeS_4 were measured using the Kurtz-Perry method (It is widely applied for the evaluation of SHG response of a new NLO material.^{40–42}) on a 2.09 μm Q-switched laser, and the SHG signals were detected on a

photomultiplier tube and recorded using an oscilloscope. Before the experiments, the polycrystalline powder samples were ground and sieved in the range of ≤ 45 , 45–63, 63–90, 90–125, 125–180, and 180–212 μm , respectively. Commercial AGS samples with the same particle size distribution were used as the references.

Laser-induced damage threshold (LIDT) measurements

The LIDT of BaZnGeS_4 micro-crystal samples was evaluated using the single-pulse LIDT method under a pulsed Nd: YAG laser (1.06 μm , 9 ns, 1 Hz).^{43,44} The AGS sample with a similar size (≤ 45 μm) distribution was utilized as the reference. The laser output energy was gradually increased until the sample was damaged (color changed) on the surface. The damaging energies were found to be ~ 240 μJ for BaZnGeS_4 and ~ 45 μJ for AaGaS_2 . The LIDT of BaZnGeS_4 samples can be derived as follows:

$$\begin{aligned} \text{LIDT}_{\text{BaZnGeS}_4} &= L_{\text{AGS}} \frac{E(\text{BaZnGeS}_4)}{\frac{\pi r^2 \tau_p}{E(\text{AGS})}} \\ &= L_{\text{AGS}} \frac{E(\text{BaZnGeS}_4)}{E(\text{AGS})} \approx 5.4 \times \text{AGS} \end{aligned} \quad (1)$$

where E is the laser energy of a single pulse, r is the spot radius, and τ_p is the pulse width.

Computational descriptions

The electronic band structure, the density of states, and the optical properties of BaZnGeS_4 were investigated using density functional theory (DFT) calculations in the CASTEP package.⁴⁵ To describe the exchange–correlation energy, the Perdew–Burke–Ernzerhof (PBE)⁴⁶ exchange–correlation of generalized gradient approximation (GGA)⁴⁷ was used for the calculations. The HSE06 band gap of BaZnGeS_4 was investigated in PWmat code based on the Heyd–Scuseria–Ernzerhof (HSE06) hybrid functional with a plane wave cut off of 50 Ryd.⁴⁸ Meanwhile, the interaction between the ionic core and valence electrons was described using the norm-conserving pseudopotential (NCP).⁴⁹ The following valence-electron configurations were considered in the computation: Ba $5s^2 5p^6 6s^2$, Zn $3d^{10} 4s^2$, Ge $4s^2 4p^2$, and S $3s^2 3p^4$ for BaZnGeS_4 . Moreover, the kinetic energy cut-off was set to be 720.0 eV, and the Monkhorst–Pack k -point meshes of $7 \times 7 \times 7$ with a density of 0.015 \AA^{-1} in the Brillouin zone (BZ) were utilized.⁵⁴ The real part of the dielectric function $\epsilon(\omega)$, refractive index n and other linear optical properties were calculated according to the Kramers–Kronig transformation. Meanwhile, the SHG-density method was used to analyze the contributions of the orbitals or bands to the second-order susceptibility.

Results and discussion

Crystal structures

$\text{Mg}_{0.6}\text{Cd}_{1.4}\text{GeS}_4$, CaCdGeS_4 , and BaZnGeS_4 transparent crystals for single-crystal XRD were picked under an optical micro-

scope. The results of single-crystal XRD show that the three compounds crystallize in the orthorhombic system but in different space groups (Table S2†). Specifically, BaZnGeS_4 belongs to the $A^{\text{II}}B^{\text{II}}C^{\text{IV}}D_4^{\text{VI}}$ family and crystallizes in the $Fdd2$ (No. 43) space group with cell parameters $a = 21.0291(6) \text{ \AA}$, $b = 21.7992(6) \text{ \AA}$, $c = 12.3028(3) \text{ \AA}$, $Z = 32$. In its asymmetric unit, there are three crystallographically unique Ba (Ba (1), Ba (2), Wyckoff site $8a$; Ba (3), Wyckoff site $16b$), two Zn (Wyckoff site $16b$), two Ge (Wyckoff site $16b$), and eight S (Wyckoff site $16b$) atoms. The Zn and Ge atoms are bonded to four S atoms to form tetrahedral $[\text{ZnS}_4]$ units with the bond lengths $d_{\text{Zn-S}} = 2.288\text{--}2.403 \text{ \AA}$, and $[\text{GeS}_4]$ units with $d_{\text{Ge-S}} = 2.187\text{--}2.225 \text{ \AA}$, respectively (Fig. 1a and b). The formed $[\text{ZnS}_4]$ and $[\text{GeS}_4]$ tetrahedral units are edge-sharing in a $[\text{ZnGeS}_6]$ dimer (Fig. 1c) and further connected *via* corner-sharing to build the $[\text{Zn}_3\text{Ge}_3\text{S}_{16}]_{\infty}$ layer in the ac and ab planes (Fig. 1e and f). Ba atoms are bound with eight S atoms to form $[\text{BaS}_8]$ polyhedra with $d_{\text{Ba-S}} = 3.188\text{--}3.256 \text{ \AA}$, and the $[\text{BaS}_8]$ polyhedra are further connected to form a channel-like three-dimensional (3D) $[\text{BaS}_8]_{\infty}$ framework (Fig. 1d and g). The $[\text{ZnS}_4]$ and $[\text{GeS}_4]$ tetrahedra fill the channels to result in the final crystal structure of BaZnGeS_4 (Fig. 1h).

Different from BaZnGeS_4 , $\text{Mg}_{0.6}\text{Cd}_{1.4}\text{GeS}_4$ and CaCdGeS_4 are isostructural compounds and crystallize in the $Pnma$ space group (Table S2†). Since they show similar structure features (Fig. S1 and S2†), CaCdGeS_4 is used as an example to illustrate their crystal structures here. In the asymmetric unit of CaCdGeS_4 , there are two crystallographically independent M (Ca/Cd) (M (1), Wyckoff site $4c$; M (2), Wyckoff site $4b$), one Ge (Wyckoff site $4c$), and three S (S (1), S (3), Wyckoff site $4c$; S (2), Wyckoff site $8d$) atoms. The Ge atoms are coordinated with four S atoms to form $[\text{GeS}_4]$ tetrahedral units with $d_{\text{Ge-S}} = 2.177\text{--}2.234 \text{ \AA}$ (Fig. S1a†). The $[\text{GeS}_4]$ tetrahedral units are isolated from each other to construct the $[\text{GeS}_4]_{\infty}$ pseudo-chain

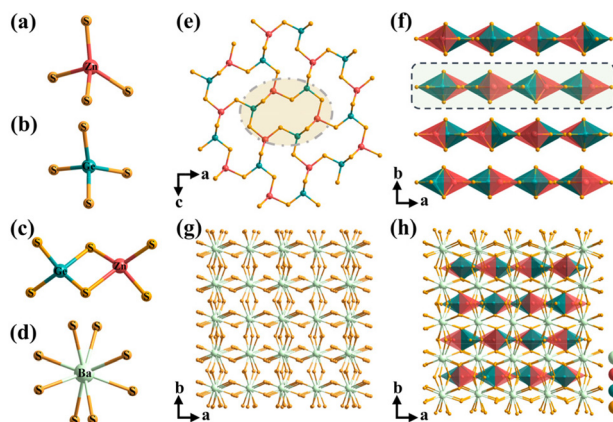


Fig. 1 Crystal structure of BaZnGeS_4 . (a, b and d) The coordination environments of Zn, Ge, and Ba atoms; (c) the formed $[\text{ZnGeS}_6]$ dimer; (e and f) the formed 2D $[\text{Zn}_3\text{Ge}_3\text{S}_{16}]_{\infty}$ layers with 12-membered rings viewed in the ac and ab planes; (g) the formed channel-like $[\text{BaS}_8]_{\infty}$ framework; (h) the 3D crystal structure of BaZnGeS_4 viewed along the c direction.

and $[\text{GeS}_4]_\infty$ pseudo-layer structures in the *ac* and *ab* planes (Fig. S1d–f†), and the $[\text{GeS}_4]$ units in each two adjacent $[\text{GeS}_4]_\infty$ pseudo-chains (Fig. S1d and f†)/pseudo-layers (Fig. S1e†) show reverse arrangements. It is worth noting that the Ca/Cd occupancy at the M(1) site was refined to 0.5/0.5, while to 0.1/0.9 at the M(2) site. Different from the 8-coordinated Ba and 4-coordinated Zn in BaZnGeS_4 , the Ca/Cd atoms are 6-coordinated with S atoms to form the $[\text{Ca/CdS}_6]$ octahedral units, as shown in Fig. S1b and c.† The resulting $[\text{Ca/Cd}(1)\text{S}_6]$ and $[\text{Ca/Cd}(2)\text{S}_6]$ units are further linked by corner-sharing to build a 3D $[\text{MS}_6]$ structural framework with channels, and the $[\text{GeS}_4]$ units fill the channels to form the final crystal structure of CaCdGeS_4 (Fig. S1g and h†).

Although CaCdGeS_4 and BaZnGeS_4 have a similar formula, their crystal structures are totally different, and CaCdGeS_4 and $\text{Mg}_{0.6}\text{Cd}_{1.4}\text{GeS}_4$ belong to the $\text{A}_2^{\text{II}}\text{C}^{\text{IV}}\text{D}_4^{\text{VI}}$ family, rather than the $\text{A}^{\text{II}}\text{B}^{\text{II}}\text{C}^{\text{IV}}\text{D}_4^{\text{VI}}$ family. To elucidate the structural difference in the two families, a detailed structure comparison was implemented, as shown in Fig. 2a–d. In CaCdGeS_4 and BaZnGeS_4 , the atomic coordination environments of Zn (coordination number: 4) and Cd (coordination number: 6) atoms and their connections with $[\text{GeS}_4]$ tetrahedra are different. Moreover, there are 6 crystallographically unique atom sites in the asymmetric unit of CaCdGeS_4 and 15 crystallographically unique atom sites in BaZnGeS_4 , resulting in the degradation of structural symmetry from CaCdGeS_4 to BaZnGeS_4 (Fig. 2e and f).⁵⁰

The computed bond valence sums (BVSs) (Ba: 2.31–2.32, Zn: 1.89–1.90, Ge: 4.02–4.05, and S: 2.01–2.14 in BaZnGeS_4 ;

Mg/Cd: 2.11–2.18, Ge: 4.02, and S: 1.92–2.11 in $\text{Mg}_{0.6}\text{Cd}_{1.4}\text{GeS}_4$; Ca/Cd: 2.20, Ge: 4.03, and S: 2.06–2.30 in CaCdGeS_4) verify the reasonability of the crystal structures. The crystal data and structure refinement information, including atomic coordinates and equivalent isotropic displacement parameters, bond length, and angle information, are provided in the ESI (Tables S2–14†). To further confirm the compositions and chemical bonding in the three compounds, energy-dispersive X-ray spectroscopy (EDS) and Raman spectroscopy were performed. The EDS spectra and mapping confirm the presence and homogeneous distributions of Ba, Zn, Ge, and S elements in BaZnGeS_4 , and Ca/Mg, Cd, Ge, and S elements in $\text{CaCdGeS}_4/\text{Mg}_{0.6}\text{Cd}_{1.4}\text{GeS}_4$ (Fig. S3†). Meanwhile, the vibration peaks at 315.03 and 377.47 cm^{-1} in BaZnGeS_4 , 375.69 cm^{-1} in $\text{Mg}_{0.6}\text{Cd}_{1.4}\text{GeS}_4$, and 370.75 cm^{-1} in CaCdGeS_4 can be attributed to the vibrations of Ge–S bonds; the peak at 244.93 cm^{-1} in BaZnGeS_4 (293.52 cm^{-1} in $\text{Mg}_{0.6}\text{Cd}_{1.4}\text{GeS}_4$ and 280.91 cm^{-1} in CaCdGeS_4) can be assigned to the vibrations of Zn–S (Cd–S) bonds (Fig. S4†).^{27,51–55}

Optical properties

To evaluate the optical properties, BaZnGeS_4 and $\text{Mg}_{0.6}\text{Cd}_{1.4}\text{GeS}_4$ polycrystalline powder samples were synthesized through conventional solid-state reactions at 800 and 900 °C, respectively. The experimental PXRD patterns of BaZnGeS_4 and $\text{Mg}_{0.6}\text{Cd}_{1.4}\text{GeS}_4$ matched well with the theoretical results derived from their Cif files (Fig. S5†), indicating high purity of the obtained polycrystalline samples. To detect the optical band gap, the UV-vis-NIR diffuse reflectance spectra of BaZnGeS_4 and $\text{Mg}_{0.6}\text{Cd}_{1.4}\text{GeS}_4$ were measured on the polycrystalline powder samples. Based on the Kubelka–Munk function,^{26,56,57} the experimental band gaps of BaZnGeS_4 and $\text{Mg}_{0.6}\text{Cd}_{1.4}\text{GeS}_4$ are determined to be ~3.36 (Fig. 3a) and 2.94 eV (Fig. S6†). The band gap (3.36 eV) of BaZnGeS_4 is far larger than the ones in commercial IR NLO materials such as AGS (2.73 eV), AGSe (1.83 eV), and ZGP (2.34 eV), and larger than the ones in most of the $\text{A}^{\text{II}}\text{B}^{\text{II}}\text{C}^{\text{IV}}\text{D}_4^{\text{VI}}$ family compounds such as BaZnSnS_4 (3.25 eV),⁵⁸ SrZnSnS_4 (2.83 eV),⁵⁹ $\beta\text{-BaHgSnS}_4$ (2.77 eV),⁶⁰ and SrHgSnS_4 (2.72 eV).⁶⁰ It is comparable with the ones in the recently developed IR NLO compounds, such as $[\text{Ba}_4(\text{S}_2)][\text{ZnGa}_4\text{S}_{10}]$ (3.39 eV),⁵⁵ AGa_5S_8 (A = K, Rb, Cs) (3.23, 3.10, 3.37 eV),⁶¹ and $\text{Na}_2\text{Ba}[\text{Na}_2\text{Sn}_2\text{S}_7]$ (3.42 eV).⁶² Generally, a wide band gap inherently contributes to a high LIDT,^{63–65} and it was evaluated by the single-pulse LIDT method with AGS as the reference. The LIDT of BaZnGeS_4 was found to be ~5.4 times that of AGS under the same test conditions (Fig. S7†).

Since BaZnGeS_4 crystallizes in the NCS orthorhombic *Fdd2* space group, its SHG properties were evaluated using the Kurtz–Perry method under 2.09 μm irradiation, and AGS samples were utilized as the references. As shown in Fig. 3b, the measured SHG response (180–212 μm) of BaZnGeS_4 is about ~0.8 \times AGS. Meanwhile, the SHG intensities are increased with the particle sizes, implying that BaZnGeS_4 is a phase-matching compound with 2.09 μm pumping which is important for practical applications.⁵⁷ As shown in Fig. 3c, the



Fig. 2 Structural difference in CaCdGeS_4 and BaZnGeS_4 . (a) The formed 6-coordinated $[\text{Ca/CdS}_6]$ octahedra in CaCdGeS_4 ; (b) the formed 4-coordinated $[\text{ZnS}_4]$ tetrahedra in BaZnGeS_4 ; (c) and (d) the crystal structures of CaCdGeS_4 and BaZnGeS_4 viewed along the *c* direction; (e and f) detailed spatial symmetry operations in CaCdGeS_4 (*Pnma*) and BaZnGeS_4 (*Fdd2*).



Fig. 3 (a) Experimental band gap of BaZnGeS₄; (b) the SHG intensities versus particle sizes with AGS as the references under 2.09 μm irradiation; (c) the comparison of optical properties between BaZnGeS₄ and benchmark AGS; (d) the typical alkali- and/or AEM-containing sulfide IR NLO candidates with PM behavior, AGS is used as the reference.

experimental results indicate that BaZnGeS₄ achieves a good balance between a wide band gap ($E_g \geq 3.0$ eV) and large SHG response ($\geq 0.5 \times$ AGS) for an anti-laser damage IR NLO material,^{22,66–68} which are comparable with those of typical alkali- and/or AEM-containing sulfide IR NLO materials developed recently, such as LiGaS₂,⁶⁹ α -Li₂ZnGeS₄,⁷⁰ Li₄MgGe₂S₇,⁵² SrZnGeS₄,³⁴ and SrCdSiS₄⁷¹ (Fig. 3d).

Theoretical calculations

To clarify the origin of the optical properties, the electronic structure of BaZnGeS₄ was calculated using the first-principles calculations based on DFT.^{72–75} The calculated band structure (Fig. 4a) shows that BaZnGeS₄ has a direct band gap of 2.71 eV, which is smaller than the experimental value due to the discontinuity of exchange–correlation energy of the GGA.^{76,77} Hence, the HSE06 band gap is investigated,^{78,79} and the calculated HSE06 band gap of BaZnGeS₄ is about 3.52 eV, which matches with the experimental result (3.36 eV), illustrating the reliability of the HSE06 hybrid functional. Moreover, the top of the valence band (VB) of BaZnGeS₄ is mainly occupied by the S 3p, Ge 4s, and Zn 4s orbitals, while the bottom of the conduction band (CB) is primarily composed of S 3p, Ge 4p, and Zn 4s orbitals (Fig. 4b), indicating that the optical band gap of BaZnGeS₄ is mainly determined by the [GeS₄] and [ZnS₄] tetrahedral units.

To evaluate the birefringence of the title compound, the refractive indices along the optical axes (n_x , n_y , n_z) were computed. As shown in Fig. S8a,† the dielectric constants of BaZnGeS₄ show the trends of $n_z > n_y > n_x$ and $n_z - n_y < n_y - n_x$. It means that BaZnGeS₄ is a negative biaxial crystal. The calculated birefringence of BaZnGeS₄ is 0.135@1064 nm (Fig. S8b†), which matches the PM behavior, as shown in Fig. 3b. The large birefringence could be related to the formed

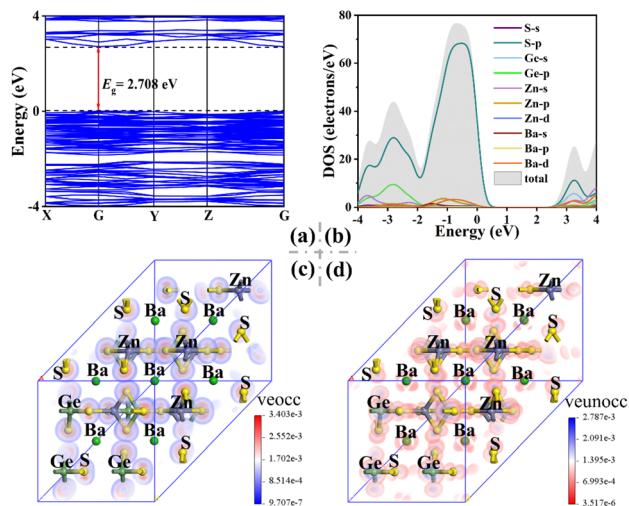


Fig. 4 (a) Band structure; (b) the density of states (DOS) and partial DOS; (c and d) the SHG-density maps of the occupied (c) and unoccupied (d) orbitals in the virtual-electron process of BaZnGeS₄.

[Zn₃Ge₃S₁₆]_∞ layers with large optical anisotropy in the structure. To uncover the origin of the NLO effect in BaZnGeS₄, the SHG density maps of occupied (Fig. 4c) and unoccupied (Fig. 4d) states in the virtual-electron (VE) process were calculated. The results confirm that [ZnS₄] and [GeS₄] units make significant contributions to the SHG responses.

Conclusions

In conclusion, three new AEM-containing sulfides, Mg_{0.6}Cd_{1.4}GeS₄, CaCdGeS₄, and BaZnGeS₄ with a structural change from the CS *Pnma* (Mg_{0.6}Cd_{1.4}GeS₄ and CaCdGeS₄) to the NCS *Fdd2* (BaZnGeS₄) space group, have been successfully synthesized through conventional solid-state reactions. Among them, BaZnGeS₄ belongs to the A^{II}B^{IV}C^{IV}D₄^{VI} family, and Mg_{0.6}Cd_{1.4}GeS₄ and CaCdGeS₄ are isostructural compounds belonging to the A₂^{II}C^{IV}D₄^{VI} family. Based on the “electronic structure engineering bucket effect”, BaZnGeS₄ exhibits a wide band gap of 3.36 eV, larger than most of the values for the A^{II}B^{IV}C^{IV}D₄^{VI} family compounds. Meanwhile, it has a large SHG response ($\sim 0.8 \times$ AGS), a large birefringence ($\Delta n_{\text{cal}} = 0.135@1064$ nm), and a high LIDT (5.4 \times AGS). It could be a promising anti-laser damage IR NLO candidate. The theoretical calculations indicate that the optical band gap and SHG response in BaZnGeS₄ mainly stem from the NLO-active [ZnS₄] and [GeS₄] tetrahedral units. The results verify the feasibility of designing wide band gap chalcogenides using the “electronic structure engineering bucket effect”.

Conflicts of interest

The authors declare that they have no conflict of interest.

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