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Heteroanion-introduction-driven birefringence enhancement in oxychalcogenide $Ba_3M^{II}Ge_3O_2S_8$ (M^{II} = Mn, Cd)†

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Birefringent crystals play a crucial role in regulating the polarization of light and are widely used in optoelectronic fields. However, the effective design of novel infrared (IR) birefringent crystals with large birefringence (Δn) still face significant challenges. In this study, we present the rational design and successful synthesis of two novel quinary oxychalcogenides with the formula $Ba_3M^{II}Ge_3O_2S_8$ (M^{II} = Mn, Cd), employing a heteroanion-introduction strategy *via* high-temperature solid-state reactions. $Ba_3M^{II}Ge_3O_2S_8$ (M^{II} = Mn, Cd) crystallized in the monoclinic space group $P2_1/n$ (no. 14) and the structures comprised one-dimensional (1D) $[M^{II}Ge_3S_8O_2]^{6-}$ chains arranged in an antiparallel manner and separated by Ba^{2+} cations. The coexistence of multiple heteroanionic ligands ($[M^{II}OS_5]$ octahedra, $[GeOS_3]$, and $[GeO_2S_2]$ tetrahedra) in one material was surprisingly discovered for the first time in the realm of oxychalcogenides. It was revealed that the heteroanion-introduction strategy not only leads to a reduction in the structural dimensionality but also enhances the optical anisotropy significantly. Notably, $Ba_3M^{II}Ge_3O_2S_8$ (M^{II} = Mn, Cd) demonstrated large Δn values of 0.11 and 0.14, which represent a remarkable improvement compared to the three-dimensional (3D) parent $AE_3M^{II}M_2^{IV}Q_8$ system (Δn = 0). Furthermore, theoretical calculations suggest that the significant Δn of $Ba_3M^{II}Ge_3O_2S_8$ (M^{II} = Mn, Cd) resulted primarily from the combination of polarizabilities from the various heteroanionic groups. Overall, these results highlight the potential of the heteroanion-introduction strategy for designing novel IR birefringent materials for optoelectronic applications.

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1. Introduction

Birefringent crystals play a crucial role in high-performance optics, especially in polarization apparatus, phase-matching elements, and laser processing.[1] Currently, the majority of the commercially available birefringent crystals are inorganic oxides, such as YVO_4,[2] $CaCO_3$,[3] and α-BaB_2O_4.[4] However, these materials have their limitations. For instance, they suffer from detrimental metal–oxygen (M–O) bond absorptions, which restrict their usage in the infrared (IR) region. Conversely, the current commercially available birefringent crystals are suitable for the ultraviolet and visible region, and few birefringent crystals has been explored for the IR region. In addition, the excellent birefringence (Δn) of crystals enables the downsizing of crystal optical devices.[5] Consequently, there is an increasing demand for high-performance IR birefringent crystals in both the scientific research and technological development fields.

The analysis of the structure–property relationships of birefringent crystals revealed a positive correlation between the Δn and anisotropy.[6] In other words, a larger anisotropy corresponds to a greater Δn. Effective structural design strategies can be employed to modulate the Δn, such as introducing π-conjugated units,[7] stereochemically active lone pairs (SCALPs),[8] and functional building units (FBUs) with large polarizability anisotropy.[9] Recently, the heteroanion-introduction strategy has been proved to be an effective and direct approach for boosting the Δn, such as $Rb_2VO(O_2)_2F$ (Δn = 0.189 @ 546 nm),[10] Sn_2BO_3I (Δn = 0.393 @ 546 nm), Sn_2PO_4I (Δn = 0.664 @ 546 nm),[11] $RbTeMo_2O_8F$ (Δn = 0.263 @ 546 nm),[12] and $K_2Sb(P_2O_7)F$ (Δn = 0.157 @ 546 nm).[13]

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Oxychalcogenides with rich structures, varying from isolated zero-dimensional (0D) to dense three-dimensional (3D) frameworks, are an exciting class of heteroanionic system that have attracted significant attention in recent years owing to their high Δn, which can obtained by partial anion substitution from the parent structure.[14] Some examples include $Ba_3Ge_2O_4Te_3$ (0.14 @ 2090 nm, maternal structure: $Ba_2ZnGe_2O_7$),[15] $SrGeOSe_2$ (0.16 @ 2050 nm, maternal structure: $SrGeO_3$),[16] $Sr_2CdGe_2OS_6$ (0.193 @ 2050 nm, maternal structure: $Sr_2CdGe_2O_7$),[17] $Nd_3[Ga_3O_3S_3][Ge_2O_7]$ (0.091 @ 2050 nm, maternal structure: $Cs_3[Sb_3O_6][Ge_2O_7]$),[18] and $Sr_2ZnSn_2OS_6$ (0.12 @ 2050 nm, maternal structure: $Sr_2ZnSi_2O_7$).[19] The parent structures mentioned above are all oxides. However, no examples have been reported using chalcogenides as parent structures to generate new oxychalcogenides by introducing oxygen atoms.

The quaternary $AE_3M^{II}M^{IV}_2Q_8$ (AE = Sr, Ba; M^{II} = divalent transition metals; M^{IV} = Ge, Sn; Q = chalcogen) family is a complex system that distinguishes itself as an intriguing nonlinear optical (NLO) system owing to its structural flexibility at every crystallographic site.[20] However, its crystallization in the cubic space group results in the Δn values of 0, rendering it incapable of achieving phase-matching in NLO applications. Inspired by the previous strategy of introducing heteroanions, we successfully obtained two new oxychalcogenides, *i.e.* $Ba_3M^{II}Ge_3O_2S_8$ (M^{II} = Mn, Cd). In this study, the syntheses, structures, optical properties, and birefringent characteristics of the title compounds are described. Furthermore, theoretical calculations were conducted to achieve a better understanding of the structure–activity relationships.

2. Results and discussion

In the structure of $AE_3M^{II}M^{IV}_2Q_8$, the $[M^{IV}Q_4]$ tetrahedron links 3 $[M^{II}Q_4]$ tetrahedra while $[M^{II}Q_4]$ links 4 $[M^{IV}Q_4]$ tetrahedra to build up a 3D framework. Inside this framework, charge-balanced AE^{2+} cations are located in the cavity (Fig. 1a and c). Unfortunately, the dense 3D structure, which crystallizes in the cubic system (space group $I\bar{4}3d$ (no. 220)), has an inappropriate anisotropy, resulting in a Δn value of 0 for $AE_3M^{II}M^{IV}_2Q_8$, and thereby rendering phase-matching impossible. It is widely recognized that the anisotropic polarization of a structure significantly impacts its Δn. Hence, the search for low-dimensional structures exhibiting significant anisotropy is considered one of the most effective means to obtain materials with a large Δn.[21]

The oxychalcogenides $Ba_3M^{II}Ge_3O_2S_8$ (M^{II} = Mn, Cd) represent a novel type of quinary compound discovered in AE/M^{II}/M^{IV}/Q/O systems. These compounds crystallize in the centrosymmetric monoclinic space group $P2_1/n$ (no. 14); their detailed crystallographic information is shown in Table 1. The asymmetric unit consists of three independent Ba sites, one independent M^{II} site, three independent Ge sites, two independent O sites, and eight independent S sites. All the independent atom sites are located in the Wyckoff position 4*e*. The

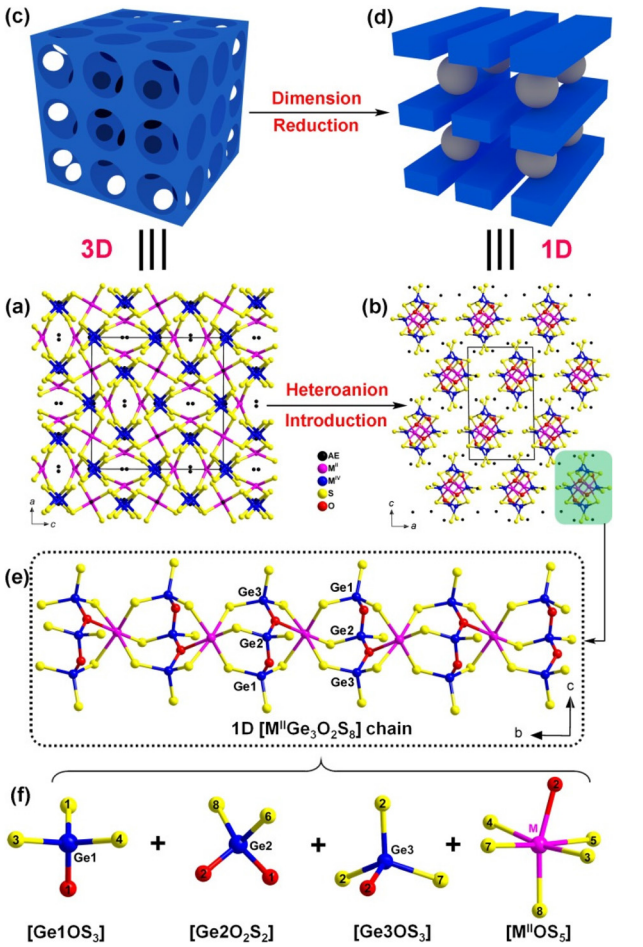

Fig. 1 Structural evolution from 3D $AE_3M^{II}M^{IV}_2Q_8$ to 1D $Ba_3M^{II}Ge_3O_2S_8$: (a and b) ball-and-stick models viewed from the *ac*-plane; (c and d) schematic diagram of equivalent models; (e) projection of the 1D $[MGe_3O_2S_8]^{6-}$ chain along the *bc*-plane; (f) coordination environment of $[GeOS_3]$, $[GeO_2S_2]$, and $[M^{II}OS_5]$ (M^{II} = Mn, Cd) FBUs with the atom numbers marked.

basic structure of $Ba_3M^{II}Ge_3O_2S_8$ can be seen as composed of 1D $[M^{II}Ge_3O_2S_8]^{6-}$ infinite chains, while AE^{2+} cations fill the space to balance the charge (refer to Fig. 1b and d). The coordination environments of Ge and M^{II} atoms are shown in Fig. 1f, and the key bond distances and angles are given in Table S1.† Ge1 and Ge3 atoms are linked to 1 O atom and 3 S atoms, forming heteroanionic $[GeOS_3]$ FBUs with Ge–S bond lengths in the regular range of 2.174–2.205 Å and Ge–O bond distances of 1.806–1.838 Å. The Ge2 atom, on the other hand, is linked to 2 O atoms and 2 S atoms, forming heteroanionic $[GeO_2S_2]$ FBUs with Ge–S bond lengths in the range of 2.137–2.178 Å and Ge–O bond lengths in the range of 1.779–1.787 Å. The M^{II} atom is coordinated with 1 O and 5 S atoms to form a highly distorted $[M^{II}OS_5]$ octahedron, with M^{II}–S and M^{II}–O bond lengths falling within the normal ranges.[22] Two $[GeOS_3]$ FBUs and one $[GeO_2S_2]$ FBU form a $[Ge_3O_2S_8]$ cluster through bridging O atoms. These clusters are then interconnected with octahedral $[M^{II}OS_5]$ FBUs, resulting

Table 1 Crystal data and structural refinement details for $Ba_3M^{II}Ge_3O_2S_8$ (M^{II} = Mn, Cd)

Empirical formula	$Ba_3CdGe_3O_2S_8$	$Ba_3MnGe_3O_2S_8$
CCDC	2234469	2234468
Formula weight	1030.67	973.21
Temperature (K)	293(2)	293(2)
Crystal system	Monoclinic	Monoclinic
Crystal color	Light yellow	Light yellow
Size (mm^3)	0.08 × 0.10 × 0.10	0.07 × 0.10 × 0.11
Space group	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)
a (Å)	8.8294(10)	8.8298(7)
b (Å)	11.9334(13)	11.8254(11)
c (Å)	15.2993(17)	15.2442(11)
β (°)	90.839(2)	90.548(7)
V ($Å^3$)	1611.8(3)	1591.7(2)
Z	4	4
D_c (g cm^{-3})	4.247	4.061
μ (mm^{-1})	15.037	14.684
GOOF on F^2	1.139	1.119
R_1, wR_2 ($I > 2\sigma(I)$)[a]	0.0265, 0.0720	0.0456, 0.1248
R_1, wR_2 (all data)	0.0290, 0.0725	0.0483, 0.1233
Largest diff. peak and hole (e $Å^{-3}$)	1.512, −1.727	2.520, −1.257

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

in the formation of 1D $[M^{II}Ge_3O_2S_8]^{6-}$ infinite chains through face-sharing (Fig. 1e). The Ba atoms also have different coordination behaviors. For instance, Ba1 and Ba3 atoms are surrounded by 8 S atoms, forming a $[BaS_8]$ bicapped trigonal prism. On the other hand, the Ba2 atom is surrounded by 1 O atom and 7 S atoms, resulting in a more twisted $[BaOS_7]$ bicapped trigonal prism (Fig. S1 and S2†).

The detailed structural evolution from 3D $AE_3M^{II}M_2^{IV}Q_8$ to 1D $Ba_3M^{II}Ge_3O_2S_8$ is depicted in Fig. 1. The introduction of O atoms, which have a different electronegativity (χ_O = 3.44 *vs.* χ_S = 2.58), can be viewed as acting like structural scissors to break the dense high-dimensional framework structure, resulting in the formation of a loosely connected low-dimensional chain structure. Consequently, a significantly anisotropic structure was obtained. This could be further confirmed by the experimental results and theoretical research on birefringence discussed in the following section.

Furthermore, through comparing and analyzing the reported oxychalcogenides, we discovered that $Ba_3M^{II}Ge_3O_2S_8$ (M^{II} = Mn, Cd) demonstrated structural novelty in three distinct aspects. First, the heteroanionic $[GeO_xQ_{4-x}]$ FBUs can only exist in a singular form in oxychalcogenides,[23–28] such as $[GeOTe_3]$, $[GeO_2S_2]$, and $[GeO_3Se]$, identified in $AE_3Ge_2O_4Te_3$,[15,23] $AEGeOS_2$,[25] and $Sr_3Ge_2O_4Se_3$,[27] respectively. However, the title compounds simultaneously contained two $[GeO_xS_{4-x}]$ FBUs, namely, $[GeOS_3]$ and $[GeO_2S_2]$. Second, it has been reported that there are relatively few oxychalcogenides with transition-metal-based $[TMO_xQ_y]$ FBUs,[29] but some examples include $[ZnO_2S_2]$ in BaZnOS,[30] $[ZnOS_3]$ in $SrZn_2S_2O$,[31] $[CoO_2S_2]$ in BaCoOS,[32] and $[CoOS_3]$ in CaCoOS.[33] Notably, in contrast to the previously reported four-coordinated $[TMO_xQ_y]$, two new heteroanionic FBUs, $[MnOS_5]$ and $[CdOS_5]$, were successfully observed in $Ba_3M^{II}Ge_3O_2S_8$ (M^{II} = Mn, Cd) for the first time, which enhances the diversity of oxychalcogenides. Third, compounds with two or more heteroanionic FBUs are currently very rare, with the few examples limited to $Ba_6V_4O_5S_{11}$ ($[VOS_3]$ + $[VO_2S_2]$)[34] and $(Ba_{19}Cl_4)(Ga_6Si_{12}O_{42}S_8)$ ($[GaOS_3]$ + $[GaO_2S_2]$).[35] The coexistence of multiple heteroanionic FBUs (octahedral $[M^{II}OS_5]$, tetrahedral $[GeOS_3]$ and $[GeO_2S_2]$) in the title compounds was surprisingly discovered for the first time in the realm of oxychalcogenides.

The compounds $Ba_3M^{II}Ge_3O_2S_8$ (M^{II} = Mn, Cd) were synthesized using a traditional high-temperature solid-state method. Single crystals with a millimeter-size were carefully selected for characterization and measurement (Fig. 2). The elemental analysis of $Ba_3M^{II}Ge_3O_2S_8$ (M^{II} = Mn, Cd) confirmed the symmetrical distribution through EDX mapping, and the Ba : M^{II} : Ge : O : S ratio was found to be highly consistent with the results obtained from single-crystal XRD (Fig. S3 and S4†). The purity phase of $Ba_3M^{II}Ge_3O_2S_8$ (M^{II} = Mn, Cd) was examined by powder XRD measurements (see Fig. 2a and b). The experimental results matched well with the simulated patterns derived from the single-crystal XRD measurements. The UV–Vis–NIR diffuse reflectance spectrum revealed optical energy gap (E_g) values of 3.82 and 3.39 eV for $Ba_3CdGe_3O_2S_8$ and $Ba_3MnGe_3O_2S_8$ (Fig. 2c and d), respectively, using the Kubelka–Munk function.[36] These values are higher compared to other reported TM-based oxychalcogenides, such as $Sr_6Cd_2Sb_6O_7S_{10}$ (1.89 eV),[37] $Sm_3NbS_3O_4$ (2.68 eV),[38] and $[Sr_3VO_4][InSe_3]$ (2.62 eV).[39] Additionally, $Ba_3M^{II}Ge_3S_8O_2$ (M^{II} = Mn, Cd) exhibited high thermal stability up to 1100 K under a N_2 atmosphere based on the thermal analysis (Fig. S5†). There were no melting or phase transition behaviors observed in the corresponding DSC curves, which was consistent with the powder XRD results (Fig. S6†). Furthermore, $Ba_3CdGe_3O_2S_8$ (M^{II} = Mn, Cd) demonstrated a broad IR transmission cut-off

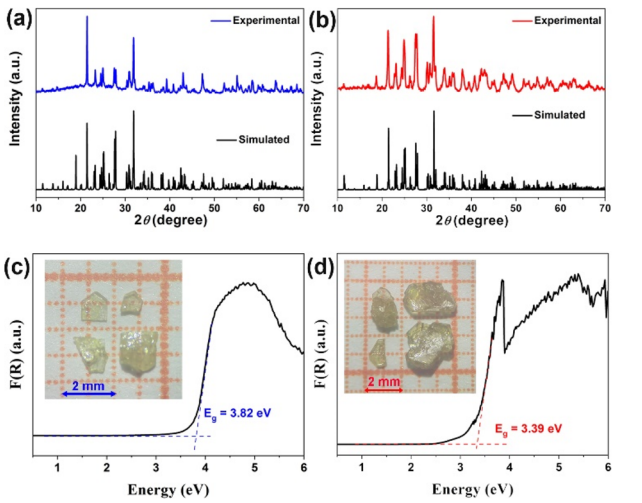

Fig. 2 Characterization of $Ba_3M^{II}Ge_3O_2S_8$ (M^{II} = Mn, Cd): experimental and simulated powder XRD patterns for the as-synthesized (a) $Ba_3CdGe_3S_8O_2$ and (b) $Ba_3MnGe_3S_8O_2$; optical E_g for (c) $Ba_3CdGe_3S_8O_2$ and (d) $Ba_3MnGe_3S_8O_2$ (inset: optical images of the target single crystals).

region from 2.5 to 13.3 μm (Fig. S7†), indicating their potential as IR birefringent candidates.

Inspired by oxychalcogenides that exhibit an appropriate Δn value,[40] the Δn of $Ba_3CdGe_3O_2S_8$ (M^{II} = Mn, Cd) was also measured using a ZEISS Axio A1 cross-polarizing microscope. The retardations (R values) and crystal thicknesses (T values) were tested as 1.073 μm and 9.8 μm for $Ba_3MnGe_3O_2S_8$, and 0.85 μm and 5.9 μm for $Ba_3CdGe_3O_2S_8$ respectively. Notably, the measured Δn values for $Ba_3MnGe_3O_2S_8$ and $Ba_3CdGe_3O_2S_8$ were found to be 0.11 and 0.14, respectively, using the formula $\Delta n = R/T$ (Fig. 3).[41] These values are larger than those of commercial materials like MgF_2 (0.012 @ 632 nm)[42] and $LiNbO_3$ (0.08 @ 632 nm),[43] as well as many recently reported chalcogenides, such as $[Ba_4(S_2)][ZnGa_4S_{10}]$ (0.053 @ 1064 nm),[44] $LiBaSbS_3$ (0.045 at 532 nm),[45] and $K_2Na_2Sn_3S_8$ (0.070 at 546 nm).[46] This indicates that the target compounds have potential as birefringent materials. Moreover, it is noteworthy that compared to the 3D $AE_3M^{II}M_2^{IV}Q_8$ with a Δn value of 0, the 1D $Ba_3M^{II}Ge_3O_2S_8$ (M^{II} = Mn, Cd) oxychalcogenides displayed appropriate Δn values. These findings indicate that the heteroanion-introduction strategy is effective in increasing optical anisotropy and boosting Δn in the oxychalcogenide family.

For a more comprehensive understanding of the electronic structures and optical performances of $Ba_3M^{II}Ge_3O_2S_8$ (M^{II} = Mn, Cd), detailed theoretical calculations were conducted using the DFT method. As depicted in Fig. S8† and Fig. 4a, $Ba_3MnGe_3O_2S_8$ and $Ba_3CdGe_3O_2S_8$ exhibited direct band gaps, with calculated E_g values of 1.53 and 2.47 eV, respectively. These values were notably different from the tested values obtained from the UV–vis–NIR spectra (3.39 and 3.82 eV). This discrepancy may be attributed to the limited accuracy of the conventional DFT functional in describing band gaps.[47] A detailed Brillouin zone plot with high symmetry points is provided in Fig. S9.† Since the $Ba_3MnGe_3O_2S_8$ and $Ba_3CdGe_3O_2S_8$ compounds demonstrated similarities in the partial density of states (PDOS) curves (Fig. 4b and S8†), $Ba_3CdGe_3O_2S_8$ was chosen as the representative compound for further elucidation. In the PDOS graphs, the valence band maximum (VBM) was defined by the S-3p and O-2p nonbonding states, while the conduction band minimum (CBM) was dominated by the unoccupied Cd-4s, Ge-3s, and Ba-4p orbitals. Thus, the E_g of $Ba_3CdGe_3O_2S_8$ was primarily determined by the heteroanionic $[GeOS_3]$, $[GeOS_3]$ and $[CdOS_5]$ FBUs, namely, 1D $[CdGe_3O_2S_8]^{6-}$ chains.

Besides, based on DFT calculations, the Δn of $Ba_3M^{II}Ge_3O_2S_8$ (M^{II} = Mn, Cd) was also calculated (Fig. 5a and S10†). The results reveal that the calculated Δn of $Ba_3CdGe_3O_2S_8$ was 0.15 @ 2050 nm. Additionally, when combined with the analysis by the partial charge density graphs in the VBM and CBM ranges (Fig. 5b), it was evident that the het-

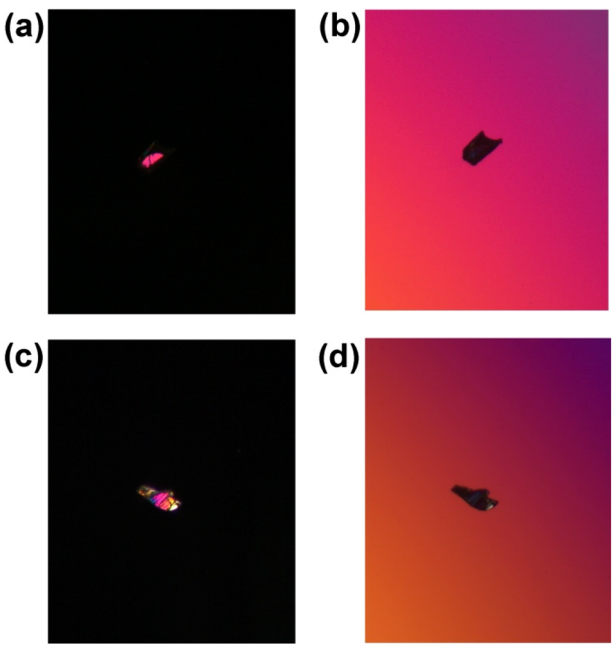

Fig. 3 (a and b) $Ba_3MnGe_3O_2S_8$ and (c and d) $Ba_3CdGe_3O_2S_8$ crystals for birefringence determination and the interference colors observed before and after complete extinction.

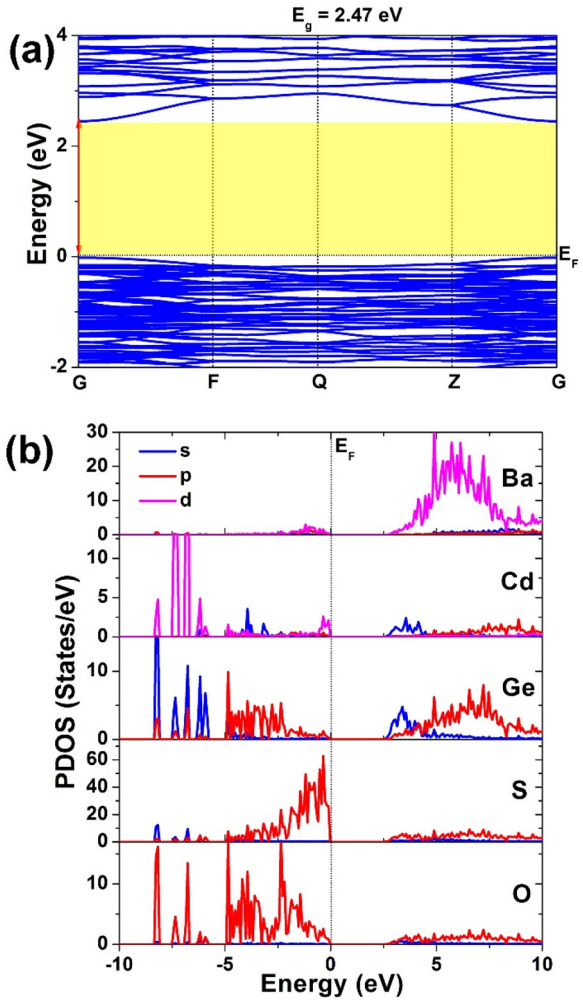

Fig. 4 Theoretical calculated results of $Ba_3CdGe_3O_2S_8$: (a) electronic band structure; (b) PDOS curve.

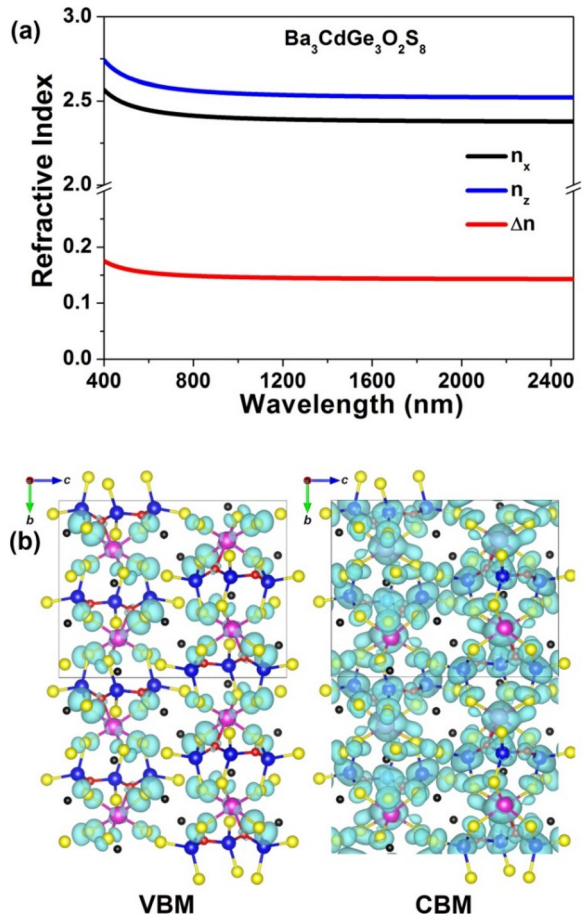

Fig. 5 (a) Calculated refractive index dispersion curves and birefringence of $Ba_3CdGe_3O_2S_8$; (b) distribution of the partial charge density maps in the VBM and CBM parts. Black atoms: Ba; pink atoms: Cd; blue atoms: Ge; yellow atoms: S; red atoms: O.

eroanionic FBUs play a significant role in achieving a large Δn. This implies that the introduction of heteroanions into the structure is favorable to the structural anisotropy.

3. Conclusions

With the aim of obtaining new IR birefringent materials in the AE–TM–M^{IV}–O–Q system, two novel oxychalcogenides $Ba_3M^{II}Ge_3O_2S_8$ (M^{II} = Mn or Cd) were successfully synthesized by employing a heteroanion-introduction strategy of replacing part of the Q atoms from the parent $AE_3M^{II}M^{IV}_2Q_8$. This is the first case that contains multiple heteroanionic ligands in oxychalcogenides, and the 1D anionic $[M^{II}Ge_3O_2S_8]^{6-}$ chain is exclusively constructed by three heteroanionic units, that is, octahedral $[M^{II}OS_5]$, and tetrahedral $[GeOS_3]$ and $[GeO_2S_2]$. Both compounds exhibited a large E_g (3.39 and 3.82 eV), a broad IR transparency region (2.5–13.3 μm), and good thermal stability (approximately 1100 K). Specifically, $Ba_3M^{II}Ge_3O_2S_8$ (M^{II} = Mn or Cd) demonstrated a large Δn (0.11 and 0.14 @ 549 nm), implying its potential application as an IR birefringent candidate. Analysis of their structure–property relationships displayed that the 1D chains in a reversed arrangement is favorable for generating a large Δn. Overall, this study represents significant progress in the field of IR birefringent materials and presents a new paradigm for developing crystal structures with enhanced Δn that are suitable for optoelectronic applications.

Author contributions

Sheng-Hua Zhou: investigation, methodology, validation, writing – original draft. Mao-Yin Ran: investigation, formal analysis, writing – original draft. Wen-Bo Wei: formal analysis, validation. A-Yang Wang: formal analysis, validation. Xin-Tao Wu: conceptualization, writing – review & editing. Hua Lin: supervision, conceptualization, writing – review & editing. Qi-Long Zhu: supervision, writing – review & editing.

Conflicts of interest

There are no conflicts to declare.

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