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From oxides to oxysulfides: the mixed-anion GeS₃O unit induces huge improvement in the nonlinear optical effect and optical anisotropy for potential nonlinear optical materials†

 Xinyu Tian,[‡] Xiaodong Zhang,[‡] Yan Xiao,[‡] Xiaowen Wu,[‡] * Bingbing Zhang,[‡]  Daqing Yang[‡]  and Kui Wu[‡] *

Oxysulfides combining intrinsic performance advantages between sulfides (strong NLO response) and oxides (wide optical bandgap) are proposed as potential infrared (IR) NLO materials. Theoretical calculation shows that the mixed-anion GeS₃O tetrahedron has a stronger polarizability anisotropy and hyperpolarizability than that of the typical GeO₄ unit. Based on this, two Sr₂MGe₂S₆O (M = Zn, Cd) oxysulfides with the GeS₃O unit show dozens of times improvement in critical birefringence and the NLO effect compared with those of isostructural Sr₂ZnGe₂O₇. Moreover, structure–property study further verifies that the mixed-anion GeS₃O ligand is a useful NLO-active unit and can offer great influence over the NLO origin. This research result also gives us a feasible design strategy and research system to explore new IR NLO candidates.

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Nonlinear optical (NLO) crystals have shown extensive applications in extending the conventional laser wavelengths to unusual short deep-ultraviolet (DUV) or mid- and far infrared (MFIR) regions through frequency-conversion technology.^{1–4} As for the IR region, inherent performance drawbacks (low laser damage threshold (LDT) and harmful two-photon absorption (TPA)) in commercial NLO crystals have seriously limited their applications.⁵ As we know, the optical bandgap is proportional to the LDT but shows an inverse relationship with the NLO response; thus, it is extremely challenging to design new promising IR NLO crystals with balanced performances, such as wide bandgap (≥ 3.0 eV) and large second harmonic generation (SHG) effect ($\geq 0.5 \times \text{AgGaS}_2$).⁶ Recently, researchers have proposed several feasible design strategies to regulate the crystal structures and performances. Incorporation of mixed-anion functional groups into crystal structure was regarded as one good way to solve the above problem.⁷ Based on this, several of chalcogenides have been synthesized and shown the excellent performances compared with halogen-free analogues.⁸ Nowadays, oxysulfides have been also attracted increasing attentions because this system can be viewed as the modification of

sulfides and oxides, and oxysulfides exhibit the performance advantages in both of them (good NLO response and wide bandgap).⁹ Besides, chalcogenides often appear the structural changes by anion-substitution of S²⁻ with halogen (X⁻) owing to different valence states, but the atom substitution with same valence (such as O²⁻ to S²⁻) can maintain the similar structural features, thus, oxysulfide system provides one good way to investigate the influence of mixed-anion ligand on property while compared with their isostructural oxides. With this in mind, two oxysulfides Sr₂MGe₂S₆O (M = Zn, Cd) were successfully synthesized and their properties were systematically compared with Sr₂MGe₂O₇ in this work. Among them, crystal structure of Sr₂ZnGe₂S₆O was reported in 1985 but its performances have not been studied so far.¹⁰ Besides, optical performances of Sr₂CdGe₂S₆O were reported in the Lin's master's thesis in 2019.¹¹ However, in view of the similar structures between Sr₂MGe₂S₆O oxysulfides and Sr₂ZnGe₂O₇ oxides, this is good case to compare the performance change rule and study the inherent ligand-property relationship, such as from typical GeO₄ to mixed-anion GeS₃O unit. Herein, we have done the detailed performance comparison between title oxysulfides and isostructural oxides based on experimental and theoretical methods. Critical performances in Sr₂MGe₂S₆O (such as optical anisotropy and SHG response) show the obvious enhancement compared with those of Sr₂ZnGe₂O₇, which indicates that oxysulfides have good potential to be used as IR NLO candidates.

Sr₂MGe₂S₆O (M = Zn, Cd) crystallize in the tetragonal *P421m* space group (Table S1†). Among them, we have chosen Sr₂CdGe₂S₆O as the representative to discuss their structural

College of Chemistry and Environmental Science, Hebei University, Baoding, China.

E-mail: wuxiaowen1114@163.com; wukui@hbu.edu.cn

† Electronic supplementary information (ESI) available: Experimental details; PXRD, bandgap, BS, PDOS of Sr₂ZnGe₂O₇; birefringence. CCDC 2159655 and 2159656 for Sr₂CdGe₂S₆O and for Sr₂ZnGe₂S₆O, respectively. For ESI and crystallographic data in CIF or other electronic format see <https://doi.org/10.1039/d2ra02605h>

‡ Xinyu Tian, Xiaodong Zhang and Yan Xiao contributed equally.



features (Fig. 1). In its asymmetric unit, there is composed of one Sr, one Cd, one Ge, one O and two S atoms (Table S2[†]). Ge atom exhibits the four-coordination mode with one O and three S atoms to form mixed-anion GeS₃O tetrahedron with $d(\text{Ge-S}) = 2.147\text{--}2.206 \text{ \AA}$ and $d(\text{Ge-O}) = 1.834 \text{ \AA}$ (Fig. 1d). Two GeS₃O units link together by sharing one O atom to compose the isolated Ge₂S₆O dimer. Typical CdS₄ units link with Ge₂S₆O dimers to form the two-dimensional (2D) [CdGe₂S₁₀O] layers (Fig. 1e). Sr atoms connect with one O and seven S atoms to form the SrS₇O dodecahedron with $d(\text{Sr-S}) = 3.014\text{--}3.278 \text{ \AA}$ and $d(\text{Sr-O}) = 2.829 \text{ \AA}$ (Fig. 1c). SrS₇O units are located at the interlayers and further link with these 2D layers to form a 3D network (Fig. 1b). From another point of view, Sr atoms are located within the tunnels seen from the *c*-axis (Fig. 1a). Sr₂MGe₂S₆O are isostructural and their whole structures are composed of 2D [MGe₂S₁₀O] layers and Sr atoms are located within the interlayers. Note that MS₄ (M = Zn, Cd) are regular tetrahedral units and one MS₄ unit is connected with four (Ge₂S₆O) dimers to form the windmill shapes. We have added the structural diagrams of Sr₂MGe₂S₆O from the same direction (along the *c*-axis) (Fig. S1[†]). Compared with the distortion degree of GeS₃O unit, they have the tiny differences, such as $\Delta d = 5.42 \times 10^{-3}$ in Sr₂CdGe₂S₆O and $\Delta d = 5.05 \times 10^{-3}$ in Sr₂ZnGe₂S₆O. Besides, ZnS₄ and CdS₄ can be viewed as the regular tetrahedral units with the same $d(\text{Zn-S}) = 2.327 \text{ \AA}$ and $d(\text{Cd-S}) = 2.494 \text{ \AA}$. We have surveyed the compounds with O-Ge-S tetrahedron based on the Inorganic Crystal Structure Database and the result shows that MGeOS₂ (M = Sr, Ba)^{9g} have another special GeO₂S₂ unit and these GeO₂S₂ units further link together to compose the (GeO₂S₂)_{*n*} chains, which is different with that (isolated Ge₂S₆O dimer) in Sr₂MGe₂S₆O. Note that GeO₂S₂ unit shows close relationship with SHG effect but the specific contribution of GeS₃O unit on the SHG origin has not been studied. In view of the disparity

between Ge-S and Ge-O bond length, GeS₃O exhibits the higher distortion degree than that of GeO₄, which is conducive to the generation of large SHG response.

Microcrystals of Sr₂MGe₂S₆O were successfully synthesized in vacuum-sealed silica tubes and their experimental powder XRD patterns are in consistence with corresponding calculated ones (Fig. 2a and b). Their polycrystalline samples show the good chemical stability and can be stably stored in air more than half a year. We have also investigated their thermal behaviour and measured the differential thermal curves in the customized tiny silica tubes. Sr₂MGe₂S₆O have the explicit endothermic and exothermic peaks in the heating and cooling process, for example, Sr₂ZnGe₂S₆O has the single melting temperature (1030 °C) and crystallization point (832 °C), whereas the melting and crystallization points of Sr₂CdGe₂S₆O are 941 and 776 °C, respectively (Fig. 2c and d). We have also studied the XRD patterns before and after recrystallization process and they still have the similar XRD patterns, which verifies that Sr₂MGe₂S₆O are congruent-melting compounds (Fig. 2a and b). Thus, Sr₂MGe₂S₆O oxysulfides could be grown as large-size single-crystals by the conventional Bridgman-Stockbarger (BS) method. Their diffuse-reflection spectra were measured and their experimental bandgaps are 3.30 eV for Sr₂ZnGe₂S₆O (colorless) and 3.13 eV for Sr₂CdGe₂S₆O (pale-yellow) (Fig. 2e), respectively, which are smaller than that of Sr₂ZnGe₂O₇ (4.31 eV) (Fig. S2 and S3[†]). First principles calculation was used to analyze the inherent structure-property relationship.¹² Seen from their electronic structures, Sr₂MGe₂S₆O are indirect bandgap compounds and their theoretical bandgaps are calculated to be 2.77 and 2.67 eV, respectively (Fig. 3a and b), such theoretical values are often estimated due to the GGA calculation problem. Besides, they have the similar density of states (DOS) and Sr₂ZnGe₂S₆O was chosen as representative to be discussed (Fig. 3c and d). Near the top of valence band (VB: -5 to 0 eV), this region is mainly composed of S-p orbital with minor contribution from Ge-p and Zn-p orbitals. On the bottom of conduction band (CB), Zn-s, Ge-s, Ge-p and S-p orbitals produce the major contribution on this region, thus, optical absorption of Sr₂ZnGe₂S₆O can be attributed as the synergistic effect between ZnS₄ and GeS₃O units. Compared with the DOS diagram of Sr₂ZnGe₂O₇ (Fig. S5[†]), S-p orbital makes the great influence on the Fermi-level and further induces the obvious red shift of short absorption edge in Sr₂ZnGe₂S₆O.

In view of the isostructural NCS structures between Sr₂MGe₂S₆O and Sr₂ZnGe₂O₇, their powder SHG responses have been tested with a 2.09 μm Q-switch pulse laser and commercial AgGaS₂ was chosen as the reference (Fig. 2f). SHG signal intensities of Sr₂MGe₂S₆O show the continuously increasing trend with the enhanced particle sizes range from 38 to 250 μm, which shows that they satisfy the phase-matching (PM) condition. And at the maximum particle size (200–250 μm), they exhibit the good SHG responses about 0.6 for Sr₂ZnGe₂S₆O and 0.7 times that of AgGaS₂ for Sr₂CdGe₂S₆O, respectively, which are comparable to those of other reported NLO oxysulfides, such as Sr₅Ga₈O₃S₁₄ (0.8 × AgGaS₂),^{9d} SrGeOS₂ (0.4 × AgGaS₂)^{9g} and BaGeOS₂ (0.5 × AgGaS₂)^{9g} signal under the 2.09 μm about 1/20

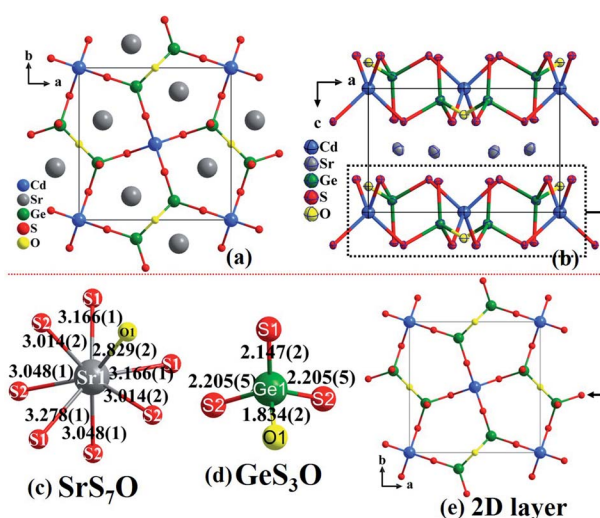


Fig. 1 (a) Crystal structure of Sr₂CdGe₂S₆O seen from *c*-axis (Sr-S/Sr-O bonds were omitted for clearly); (b) crystal structure of Sr₂CdGe₂S₆O seen from *b*-axis (Sr-S/Sr-O bonds were omitted for clearly); coordination modes of SrS₇O (c) and GeS₃O (d) units with bond-length (Å); (e) 2D layer composed of CdS₄ and GeS₃O units.

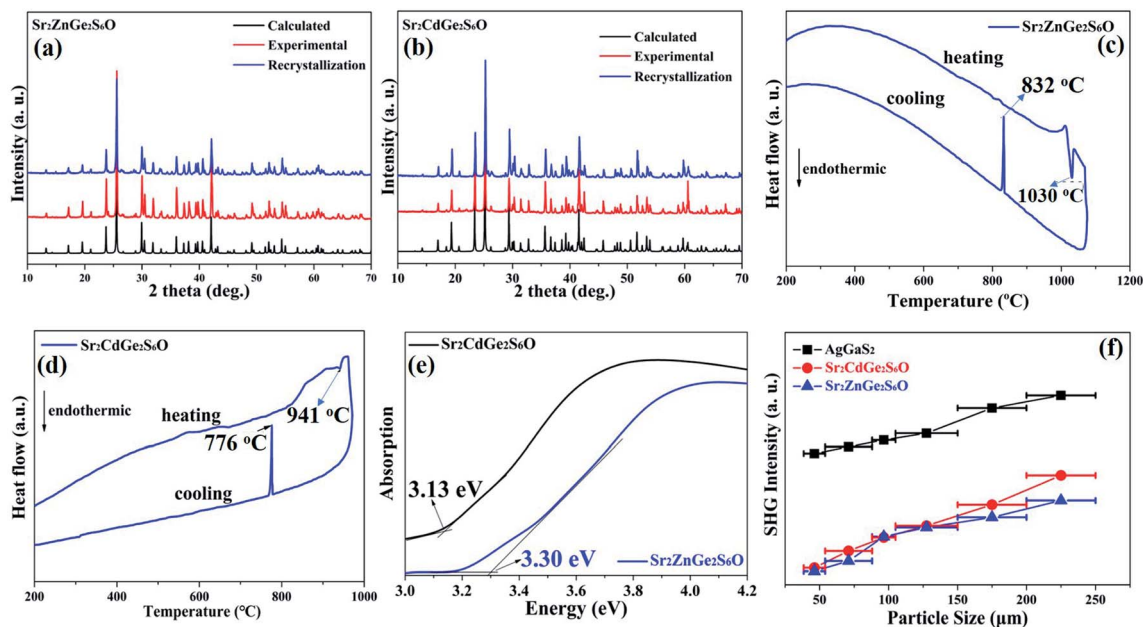


Fig. 2 Powder XRD patterns of Sr₂ZnGe₂S₆O (a) and Sr₂CdGe₂S₆O (b); DSC curves of Sr₂ZnGe₂S₆O (c) and Sr₂CdGe₂S₆O (d); (e) optical bandgaps of Sr₂MGe₂S₆O; (f) SHG response versus particle size in Sr₂MGe₂S₆O with AgGaS₂ as reference.

times than of AgGaS₂ at the maximum particle size and they cannot achieve the PM behavior (Fig. S4†). Theoretical NLO coefficients are calculated to be -3.71 for Sr₂ZnGe₂S₆O and -3.53 pm V^{-1} for Sr₂CdGe₂S₆O, respectively, which are much larger than that (-0.144 pm V^{-1}) of Sr₂ZnGe₂O₇. Therefore, SHG responses of Sr₂MGe₂S₆O undergo the great promotion about 25 times that of Sr₂ZnGe₂O₇, which agree well with the As for the previously Lin' reported Sr₂CdGe₂S₆O,¹¹ its SHG effect about $0.3 \times$ AgGaS₂ was measured at one particle size at 125–150 μm . Unfortunately, Sr₂ZnGe₂O₇ only shows the very weak SHG data. In order to verify the specific PM condition, we have also calculated their optical anisotropy (Δn) between Sr₂MGe₂S₆O

and Sr₂ZnGe₂O₇ (Fig. S6†). The result shows that Sr₂MGe₂S₆O exhibit the significant increase (0.126–0.141 @ 2 μm) about up to dozens of times that of Sr₂ZnGe₂O₇ (0.011 @ 2 μm), thus, mixed-anion units have a good chance to enhance the birefringence for critical phase-matching demand, which is also corresponding to the change rules of polarizability anisotropy from GeO₄ to GeS₃O ligand (Fig. 5a). SHG-density calculation (Fig. 4) was also used to analyse the origin of NLO effect in oxysulfides and their SHG responses can be attributed as the collaborative contribution from MS₄ and GeS₃O units, which

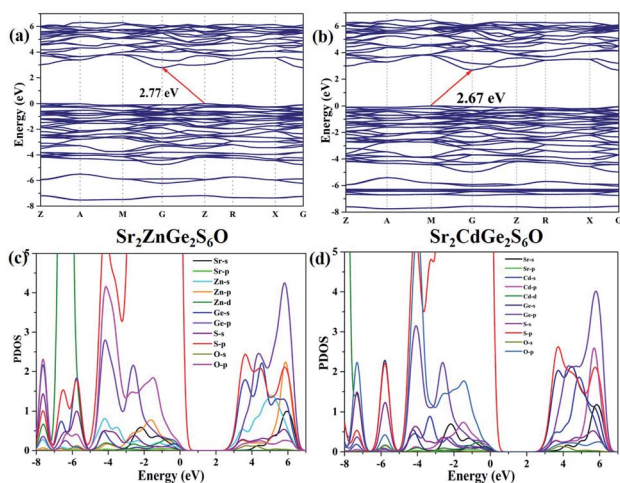


Fig. 3 (a) Band structure of Sr₂ZnGe₂S₆O; (b) band structure of Sr₂-CdGe₂S₆O; (c) PDOS diagram of Sr₂ZnGe₂S₆O; (d) PDOS diagram of Sr₂CdGe₂S₆O.

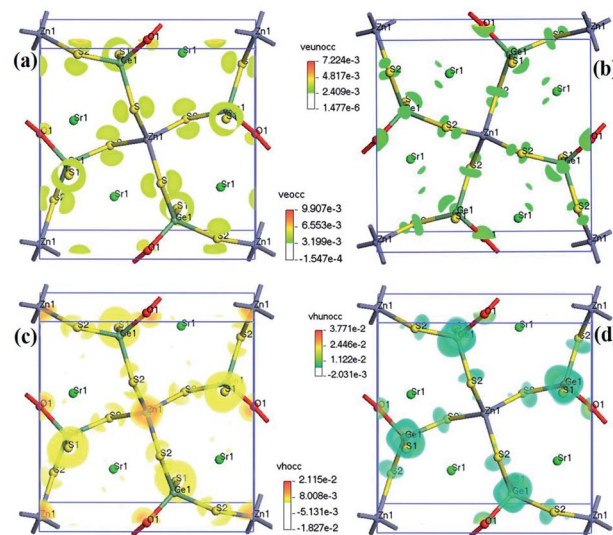


Fig. 4 SHG-density maps of Sr₂ZnGe₂S₆O. (a) Occupied and (b) unoccupied states in the virtual-electron (VE) process; (c) occupied and (d) unoccupied states in the virtual-hole (VH) process.

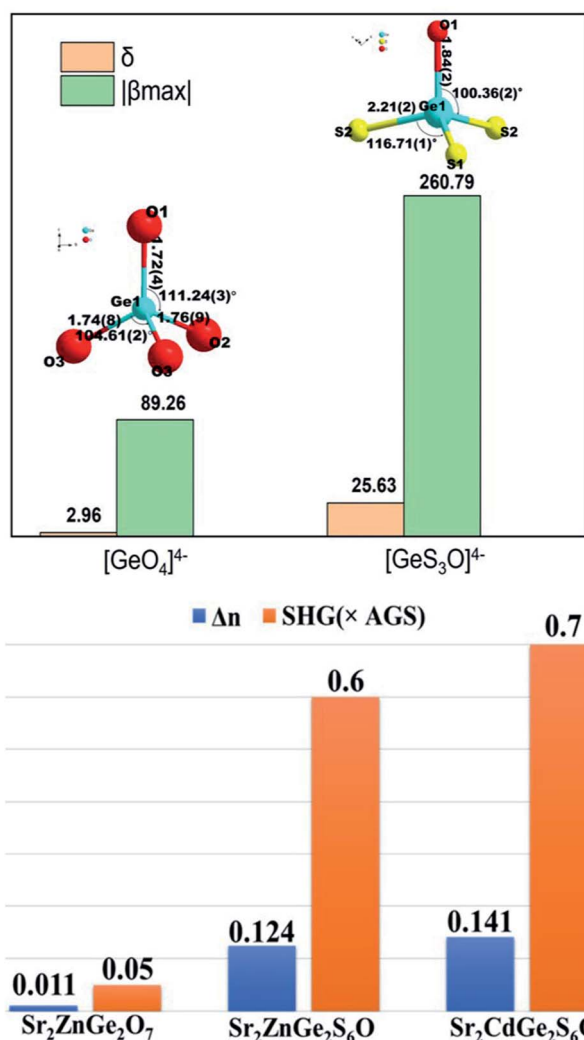


Fig. 5 Calculated hyperpolarizability (β_{\max}) and polarizability anisotropy (δ) of GeO_4 and GeS_3O units (upper); property comparison between birefringence and SHG response among $\text{Sr}_2\text{ZnGe}_2\text{O}_7$ and $\text{Sr}_2\text{MGe}_2\text{S}_6\text{O}$ (lower).

indicates that GeS_3O unit is one useful NLO-active unit and offer the positive effect on the SHG origin. Moreover, gaussian calculation shows that GeS_3O exhibits the stronger hyperpolarizability (β_{\max}) and polarizability anisotropy (δ) than those of GeO_4 , which are consistency with the variation of experimental results from $\text{Sr}_2\text{ZnGe}_2\text{O}_7$ to $\text{Sr}_2\text{MGe}_2\text{S}_6\text{O}$ (Fig. 5). Moreover, increase optical bandgaps and decreased SHG responses were appeared from $\text{Sr}_2\text{ZnGe}_2\text{S}_6\text{O}$ to $\text{Sr}_2\text{CdGe}_2\text{S}_6\text{O}$ with the Cd was replaced with Zn atoms. This study also verifies the oxy-sulfides as the optimal research system for the exploring the new IR NLO materials.

Conclusions

In summary, through the partial substitution of O with S atoms in the structure of $\text{Sr}_2\text{ZnGe}_2\text{O}_7$, $\text{Sr}_2\text{MGe}_2\text{S}_6\text{O}$ IR NLO oxy-sulfides with specific GeS_3O unit were successfully synthesized. Research result shows that $\text{Sr}_2\text{MGe}_2\text{S}_6\text{O}$ achieve the good

balanced performances between wide bandgap (3.13–3.30 eV) and good SHG response ($0.6\text{--}0.7 \times \text{AgGaS}_2$), showing the potential application as IR NLO materials. Besides, $\text{Sr}_2\text{MGe}_2\text{S}_6\text{O}$ satisfy the PM condition and their birefringence ($\Delta n = 0.126$) are much larger than that ($\Delta n = 0.011$) of $\text{Sr}_2\text{ZnGe}_2\text{O}_7$ due to the great contribution of mixed-anion units. Theoretical analysis indicates that mixed-anion GeS_3O unit offers the positive influence on the SHG origin. Furthermore, oxy-sulfides coexisting the property advantages between oxides and sulfides could be regarded as a good system choice for the future exploration of new IR NLO crystals.

Conflicts of interest

There are no conflicts to declare.

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