A$_2$SrM$^{IV}$S$_4$ (A = Li, Na; M$^{IV}$ = Ge, Sn) concurrently exhibiting wide bandgaps and good nonlinear optical responses as new potential infrared nonlinear optical materials†

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Exploration of new nonlinear optical (NLO) materials is of importance for infrared (IR) applications. However, it is an extremely tough challenge to design and synthesize excellent IR NLO materials with optimal performances (e.g., concurrently a large NLO response and wide bandgap). Herein, four new mixed alkali/alkaline earth metal sulfides, A$_2$SrM$^{IV}$S$_4$ (A = Li, Na; M$^{IV}$ = Ge, Sn), were successfully synthesized by a motif-optimization approach using the classical AgGaS$_2$ as a template. Note that all of them concurrently exhibit wide bandgaps (3.1–3.8 eV) and good NLO responses (0.5–0.8 × AgGaS$_2$) with phase-matching behavior, which satisfy the balance conditions ($E_g \approx 3.0$ eV and $d_{ij} \approx 0.5 \times$ benchmark AgGaS$_2$) of optical performances and hence are outstanding IR NLO materials. Remarkably, both of Na$_2$SnM$^{IV}$S$_4$ have the same structure without the structural transformation (Ge to Sn) in the reported related analogues and an interesting cation-dependent structural change is also found in Na$_2$MIISnS$_4$ (M$^{II}$: Sr, Na; M$^{IV}$: Ge, Sn), respectively. For ESI and XRD, BS and DOS. CCDC 1888059, 1888058, 1888057, and 1888060 for structural distortion, BVS and GII, performance comparison, LDTs, powder XRD, BS and DOS. CCDC 1888059, 1888058, 1888057, and 1888060 for Li$_2$SrGeS$_4$, Li$_2$SrSnS$_4$, Na$_2$SrGeS$_4$, and Na$_2$SrSnS$_4$, respectively. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c9sc00028c

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**Introduction**

Nonlinear optical (NLO) materials are of great importance in achieving the output of tunable lasers ranging from ultraviolet (UV)/deep-UV to the infrared (IR) region. In the deep-UV to visible regions, many kinds of oxides including borates, phosphates, carbonates, and iodates have been developed as worthy exploring systems for the discovery of NLO candidates. Unfortunately, most oxides are limited in the IR region because of their low IR absorption edges induced by the strong absorption of metal/metalloid-oxygen bands. So far, commercially available NLO materials have been rarely discovered in the IR region and all of them still exhibit some inherent performance drawbacks (low laser damage threshold (LDT) and two-photon absorption (TPA)) that seriously hinder their wide applications. Therefore, a critical prerequisite for the future exploration of IR NLO materials is to achieve a suitable balance between the large second harmonic generation (SHG) response ($d_{ij}$) and wide bandgap ($E_g$) in view of their inversely proportional relationship; thus, the two important parameters ($E_g$ and $d_{ij}$) must satisfy the following balance conditions ($E_g \approx 3.0$ eV and $d_{ij} \approx 0.5 \times$ benchmark AgGaS$_2$) for one outstanding IR NLO material. After decades of exploration and development, hundreds of IR NLO materials have been synthesized and note that chalcogenides are the main research source for the exploration of new IR NLO materials. The previously reported results show that by incorporation of the second-order Jahn–Teller (SOJT) effect transition-metals or/and lone-pair cations into crystal structures it is hard to obtain suitable balanced performances for IR NLO materials. Thus, an efficient design strategy that could enhance the $E_g$ and simultaneously maintain good $d_{ij}$ appears to be particularly important. After a detailed literature survey, to the best of our knowledge, about dozens of chalcogenides satisfy the demand of performance balance so far and most of them are sulfides. Besides, this investigation also shows that almost all their cations are alkali or/alkaline earth metals without d–d or f–f electronic
transitions and several anionic groups, e.g., typical MS\(_4\) (M = Ga, In, Ge, Sn) tetrahedra, act as critical “NLO active units” and provide the main contribution to the origin of the SHG response.\(^{11}\) Recently, considering the structural and performance features of commercial IR NLO materials, a targeted element-cosubstitution strategy has been used to design new potential IR NLO materials by the replacement of cations or/and anionic groups with classical materials as templates.\(^2\) For example, many diamond-like (DL) and chalcopyrite-like (CL) sulfides can be structurally designed from the prototype compound AgGaS\(_2\).\(^{13}\) With this in mind, the classical AgGaS\(_2\) is chosen as a template, through substituting the Ag cation with alkali (Li, Na) and alkaline earth (Sr) metals and the GaS\(_4\) anionic group with MIVS\(_4\) (MIV = Ge, Sn) NLO active units to afford the successful discovery of four new noncentrosymmetric (NCS) sulfides in this work, A\(_2\)SrMIVS\(_4\) (A = Li, Na; MIV = Ge, Sn). The experimental results show that all of them exhibit excellent performances (E\(_g\) = 3.1–3.8 eV; \(d_{ij}\) = 0.5–0.8 \(\times\) AgGaS\(_2\)) and achieve the optimal balance of wide E\(_g\) and good \(d_{ij}\), which indicates that they satisfy the performance demands as outstanding IR NLO candidates and can further remove the low LDTS and TPA of commercial materials. Moreover, the above results also confirm the feasibility of the motif-optimization strategy for exploring new IR NLO materials.

**Results and discussion**

Single crystal X-ray analysis shows that Li\(_2\)SrMIVS\(_4\) crystallize in the \(\overline{I}42m\) space group whereas Na\(_2\)SrMIVS\(_4\) crystallize in the \(R3c\) space group (Table S1\(^\dagger\)). Note that an interesting structural change is found in Na\(_2\)SrSnS\(_4\) (\(R3c\)) and Na\(_2\)BaSnS\(_4\) (\(I42d\)), but Na\(_2\)SrMIVS\(_4\) do not undergo the structural transformation with different MIV (Ge to Sn) atoms in comparison with other reported analogues, such as Ag\(_2\)BaGeS\(_4\) (\(I42m\)) vs. Ag\(_2\)BaSnS\(_4\) (\(I222\))\(^1\) and Na\(_2\)BaGeS\(_4\) (\(R3c\)) vs. Na\(_2\)BaSnS\(_4\) (\(I42d\))\(^2\) (Table S2\(^\dagger\)). Bond valences and the global instability index (GII) are also calculated and the results verify their structural reasonability (GII = 0.10–0.13) (Tables S3–S6\(^\dagger\)). Herein, we have chosen Li\(_2\)SrGeS\(_4\) and Na\(_2\)SrGeS\(_4\) as the representatives to depict their structural differences. As for Li\(_2\)SrGeS\(_4\), its three-dimensional (3D) network structure is composed of 2D corner-sharing (LiS\(_4\)) layers (Fig. 1a) and isolated GeS\(_4\) ligands, where the Sr atoms are located in the tunnels (Fig. 1b); in other words, its structure can be also depicted as a 3D framework composed by the interconnection of edge-sharing SrS\(_4\) dodecahedra with Li and Ge atoms located at the channels (Fig. 1c). More importantly, it appears that the interesting compression of the unit cell along the c-axis and Li\(_2\)SrGeS\(_4\) can be considered as the “compressed CL material”, which is also similar to the reported CL structures. According to the following equation of the structural distortion degree (\(\Delta d = 2 – (c/a)\), a and c are the cell parameters),\(^3\) the calculated results show that Li\(_2\)SrMIVS\(_4\) exhibit a large \(\Delta d\) (Ge: 0.815 vs. Sn: 0.811), thus leading to severe compression along the c axis because of the larger coordination number (8) of Sr atoms than only 4 in classical AgGaS\(_2\) (Table S7\(^\dagger\)). Moreover, based on the similar structures of known Li-based compressed CL sulfides,\(^3\) the interlayer spacing between two adjacent (LiS\(_4\)) layers (1 and 2) was also calculated and the interlayer spacing increases gradually from 2.5160 to 2.5497 Å with the increase of the cation radius of Sr\(^{2+}\) (1.40 Å) to Ba\(^{2+}\) (1.56 Å),\(^\dagger\) which indicates that a large cation radius corresponds to a wide interlayer spacing but is inversely proportional to the large \(\Delta d\) in compressed CL materials (Fig. 1d and Table S7\(^\dagger\)). This result may give us a feasible way to predict the interlayer spacing and \(\Delta d\) for new compressed CL materials.

\[\text{Na}_2\text{M}_{11}\text{SnS}_4\ (M_{11} = \text{Sr, Ba})\] undergo the interesting structural transformation (Sr, \(R3c\) vs. Ba, \(I42d\)) with the different alkaline-earth metals (Fig. 2). Based on the previous analysis,\(^2\) the whole structure of Na\(_2\)SrSnS\(_4\) can be depicted as the combination of numerous three-types of rings including the outermost 24-NaS\(_6\)-MR ring, inner fake ring (composed of six isolated SnS\(_4\) tetrahedra) and innermost 6-(SrS\(_4\))-MR circle (Fig. 2b). Interestingly, both of the similar isolated SnS\(_4\) tetrahedron and NaS\(_6\) octahedron exist in the structures of Na\(_2\)M\(_{11}\)SnS\(_4\) although they...
still have several obviously different structural features. The prominent structural difference is the connection modes of NaS₄ and Ba₅Sn/Sr₅S₆ polyhedra, for instance, the Ba₅S₆ polyhedra connect with each other by sharing edges to form a 3D network in Na₅BaS₅Sn (Fig. 2a), whereas the Sr₅S₆ ligands link together by sharing corners and edges to make up the tunnel structure in Na₅SrS₅Sn; besides, note that the NaS₄ octahedra are connected together to form 24-MRs in Na₅SrS₅Sn, which is obviously different from that (all Na atoms exist in the tunnels linking together to form a 3D framework structure) in Na₅BaS₅Sn. Moreover, Na₅SrS₅Sn show distinguished structures compared with those of Li₅SrS₅Sn (R₃c vs. I₄₂/m) because of the different coordination numbers for monovalent cations (Na: 6 vs. Li: 4).

We have also investigated the effect of distortion degrees (Δd = (d(\text{longest}) − d(\text{shortest})) and Δθ = (θ(\text{largest}) − θ(\text{smallest}))) of I₄ tetrahedra (I = Ag, Cu, Na, Li) on the structural changes of the I₄–AE–M–S₃ system (Table S2†). The result shows that the distortion degrees (Δd and Δθ) of I₄ units exhibit significant changes while the series of compounds undergo the space group transformations. After analysis of their structural features, it is clear that their structural transformations have a close relationship with the sizes and coordination numbers of cations. The above results also verify that the variable structural dimensionality and symmetry can be attributed to the cationic size effect, and similar phenomena were discovered in many relative systems, such as BaGa₃S₅ (Pmmn) vs. PbGa₃S₅ (Pc), Ba₅GeS₆ (P₂/m) vs. Mg₅GeS₆ (Pmaa). More importantly, our previous work has also reported the rising structural symmetries (Cs, P1; Rh, P₂/m; α-K, Aŭa2; and Na, P4/m) in the A₂Hg₃GeS₈ (A = alkali metal) system with the element substitutions (Cs to Na). Thus, a slight change of the cation size can lead to structural changes and future structure prediction should pay close attention to the effect of cation sizes on crystal structures.

Air-stable high quality single crystals of millimeter dimension for title compounds were successfully prepared by spontaneous crystallization in vacuum-sealed silica tubes (Fig. 4a and b). Their experimental XRD patterns are in agreement with the simulated ones derived from the crystal data, which further verify the purity of polycrystalline samples (Fig. 3). We have also compared the powder XRD patterns before and after melting for the title compounds. Comparison results show that all of them exhibit identical patterns before and after melting, which demonstrates that they are congruently melting compounds (Fig. S1†). Besides, as seen from Fig. S2† there are no obvious absorption peaks in the range from 4000 to 500 cm⁻¹, which indicates that they have a wide IR transmission region (~20 μm). In addition, critical optical parameters including Eₚ, dₚ and LDTs of the title compounds were systematically measured. All of them exhibit a wider Eₚ than the benchmark AgGaS₂ (2.73 eV), such as Li₅SrGeS₄ (3.75 eV), Li₅SrSnS₄ (3.10 eV), Na₅SrGeS₄ (3.80 eV), and Na₅SrSnS₄ (3.12 eV), which is similar to those of other reported A₅BaM₅S₁₄ compounds (Fig. 4a and b). The above results also indicate that the cosubstitution of alkali or alkaline earth metals in the same main group has little influence on the material Eₚ, which can also be confirmed in relative systems including AZ₅Ga₃S₁₂ (A = K, Rb, Cs; ~3.65 eV) and A₅Ga₃PSi₁Cl (A = K, Rb; 3.60 vs. 3.65 eV). Besides, their shortwave absorption edges are lower than 400 nm and such a low absorption edge can remove the effect of harmful TPA at 1 μm for another classical ZnGeP₂; thus, recent mature laser sources (e.g. 1.06 μm) may be utilized to achieve the frequency-conversion in the title compounds. Besides, based on density functional theory, their band structures have been calculated and the results indicate that their optical absorptions (2.20–2.84 eV) are mainly derived from the M⁵S₄ units for the title compounds (Fig. 5 and S3†). Moreover, a wide Eₚ is helpful to improve the LDT and further ensures the normal use without damage or breakdown under the high-power laser system for one of the materials. Recently, estimating the LDTs of new NLO compounds on powder samples has become a feasible method according to the previously reported research results. Herein, powder LDTs of the title compounds were investigated under...
the excitation of a 1.06 μm pulse laser with AgGaS2 as the reference (Table S8†). The experimental result shows that the title compounds have higher LDTs than AgGaS2, for example, Li2SrGeS4 and Na2SrSnS4 (10 × AgGaS2), Li2SrSnS4 (5.0 × AgGaS2), and Na2SrSnS4 (6.0 × AgGaS2), which are comparable to those of other famous IR NLO crystals, such as LiGaS2 (11 × AgGaS2), LiInS2 (2.5 × AgGaS2), HgGa2S4 (3.0 × AgGaS2), BaGa2S4 (3.0 × AgGaS2), BaGa2Se2 (3.7 × AgGaS2), and HgGa2Se4 (4.75 × AgGaS2). The experimental result shows that the title compounds have higher LDTs than AgGaS2, for example, Li2SrGeS4 and Na2SrSnS4 (10 × AgGaS2), Li2SrSnS4 (5.0 × AgGaS2), and Na2SrSnS4 (6.0 × AgGaS2), which are comparable to those of other famous IR NLO crystals, such as LiGaS2 (11 × AgGaS2), LiInS2 (2.5 × AgGaS2), HgGa2S4 (3.0 × AgGaS2), BaGa2S4 (3.0 × AgGaS2), BaGa2Se2 (3.7 × AgGaS2), and HgGa2Se4 (4.75 × AgGaS2). The experimental result shows that the title compounds have higher LDTs than AgGaS2, for example, Li2SrGeS4 and Na2SrSnS4 (10 × AgGaS2), Li2SrSnS4 (5.0 × AgGaS2), and Na2SrSnS4 (6.0 × AgGaS2), which are comparable to those of other famous IR NLO crystals, such as LiGaS2 (11 × AgGaS2), LiInS2 (2.5 × AgGaS2), HgGa2S4 (3.0 × AgGaS2), BaGa2S4 (3.0 × AgGaS2), BaGa2Se2 (3.7 × AgGaS2), and HgGa2Se4 (4.75 × AgGaS2). The experimental result shows that the title compounds have higher LDTs than AgGaS2, for example, Li2SrGeS4 and Na2SrSnS4 (10 × AgGaS2), Li2SrSnS4 (5.0 × AgGaS2), and Na2SrSnS4 (6.0 × AgGaS2), which are comparable to those of other famous IR NLO crystals, such as LiGaS2 (11 × AgGaS2), LiInS2 (2.5 × AgGaS2), HgGa2S4 (3.0 × AgGaS2), BaGa2S4 (3.0 × AgGaS2), BaGa2Se2 (3.7 × AgGaS2), and HgGa2Se4 (4.75 × AgGaS2). The experimental result shows that the title compounds have higher LDTs than AgGaS2, for example, Li2SrGeS4 and Na2SrSnS4 (10 × AgGaS2), Li2SrSnS4 (5.0 × AgGaS2), and Na2SrSnS4 (6.0 × AgGaS2), which are comparable to those of other famous IR NLO crystals, such as LiGaS2 (11 × AgGaS2), LiInS2 (2.5 × AgGaS2), HgGa2S4 (3.0 × AgGaS2), BaGa2S4 (3.0 × AgGaS2), BaGa2Se2 (3.7 × AgGaS2), and HgGa2Se4 (4.75 × AgGaS2). The experimental result shows that the title compounds have higher LDTs than AgGaS2, for example, Li2SrGeS4 and Na2SrSnS4 (10 × AgGaS2), Li2SrSnS4 (5.0 × AgGaS2), and Na2SrSnS4 (6.0 × AgGaS2), which are comparable to those of other famous IR NLO crystals, such as LiGaS2 (11 × AgGaS2), LiInS2 (2.5 × AgGaS2), HgGa2S4 (3.0 × AgGaS2), BaGa2S4 (3.0 × AgGaS2), BaGa2Se2 (3.7 × AgGaS2), and HgGa2Se4 (4.75 × AgGaS2). The experimental result shows that the title compounds have higher LDTs than AgGaS2, for example, Li2SrGeS4 and Na2SrSnS4 (10 × AgGaS2), Li2SrSnS4 (5.0 × AgGaS2), and Na2SrSnS4 (6.0 × AgGaS2), which are comparable to those of other famous IR NLO crystals, such as LiGaS2 (11 × AgGaS2), LiInS2 (2.5 × AgGaS2), HgGa2S4 (3.0 × AgGaS2), BaGa2S4 (3.0 × AgGaS2), BaGa2Se2 (3.7 × AgGaS2), and HgGa2Se4 (4.75 × AgGaS2). The experimental result shows that the title compounds have higher LDTs than AgGaS2, for example, Li2SrGeS4 and Na2SrSnS4 (10 × AgGaS2), Li2SrSnS4 (5.0 × AgGaS2), and Na2SrSnS4 (6.0 × AgGaS2), which are comparable to those of other famous IR NLO crystals, such as LiGaS2 (11 × AgGaS2), LiInS2 (2.5 × AgGaS2), HgGa2S4 (3.0 × AgGaS2), BaGa2S4 (3.0 × AgGaS2), BaGa2Se2 (3.7 × AgGaS2), and HgGa2Se4 (4.75 × AgGaS2). The experimental result shows that the title compounds have higher LDTs than AgGaS2, for example, Li2SrGeS4 and Na2SrSnS4 (10 × AgGaS2), Li2SrSnS4 (5.0 × AgGaS2), and Na2SrSnS4 (6.0 × AgGaS2), which are comparable to those of other famous IR NLO crystals, such as LiGaS2 (11 × AgGaS2), LiInS2 (2.5 × AgGaS2), HgGa2S4 (3.0 × AgGaS2), BaGa2S4 (3.0 × AgGaS2), BaGa2Se2 (3.7 × AgGaS2), and HgGa2Se4 (4.75 × AgGaS2).
structures and performances and then further design promising IR NLO candidates. Furthermore, considering the characteristics of optimized cations or anionic groups, the A-AE-M-S system was identified as the preferred system for the future exploration of new IR NLO materials.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

