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Effectively designing infrared nonlinear optical materials with magnetism, $MMn_6Ga_6S_{16}$ (M = Ca, Sr, Ba, and Pb), aided by stable open frameworks†

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Infrared nonlinear optical (NLO) materials are crucial to the development of laser technology. However, finding ways to effectively synthesize them is still a big challenge. Herein, aided by a stable open framework, four IR NLO materials, $MMn_6Ga_6S_{16}$ (M=Ca, Sr, Ba, and Pb), have been effectively synthesized in a high-temperature vacuum sealing system. They all crystallize in a non-centrosymmetric (NCS) space group, $P\bar{6}$, and their structures feature a three-dimensional open framework composed of Mn-S single and double chains and Ga-S single and double chains, in which these one-dimensional chains increase the structural flexibility and adjustability to accommodate varied cations with different ionic radii. Remarkably, $MMn_6Ga_6S_{16}$ (M=Ca, Sr, Ba, and Pb) exhibit not only comprehensive NLO performances including appropriate NLO responses and band gaps and a wide transmission range but also para-magnetism in magnetic properties, indicating that $MMn_6Ga_6S_{16}$ (M=Ca, Sr, Ba, and Pb) are potential IR multifunctional materials. This work suggests that a stable open framework can be used to construct varied structures, which brings a new platform for effectively designing multifunctional materials.

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Introduction

Infrared (IR) coherent lights, covering two important atmospheric windows (3-5 and 8-12 µm), have important applications in laser guidance and radar, atmospheric detection, and infrared remote sensing. Utilizing the frequency conversion of nonlinear optical (NLO) crystals is an effective way to generate coherent radiation over a range of different wavelengths. 1-6 Presently, a large number of nonlinear optical materials have been discovered and synthesized, including oxides and chalcogenides,7-12 but in reality, the insufficient optical transparency and low second-harmonic generation (SHG) response of oxides are not suitable for their application in the IR region. Chalcogenides have been considered the preferred candidates to explore IR materials due to their unique structures composed of typical tetrahedral NLO-active genes, i.e. the main-group metal elements (e.g., Ga, In, Si, Ge, and Sn) coordinated with chalcogen atoms to form asymmetric configurations. 13-17 These structural advantages are favorable for large SHG coefficients and a wide optical transparency

window up to the IR region, such as those of commercialized chalcopyrite-type $AgGaQ_2$ (Q = S, Se) and $ZnGeP_2$. However, own performance defects hinder their application ranges, and with this background, effectively designing and synthesizing IR NLO materials have become the important task for researchers.

In crystal engineering, taking classical structures as templates or evolving these structures is an efficient way to explore new IR NLO materials in chalcogenides. 21-24 For example, based on the type of melilite structure, a number of chalcogenides, i.e. $Sr_2ZnSn_2OS_6$, ²⁵ $Ca_2GeGa_2OS_6$ ²⁶ and $Sr_2MnGe_2OS_6$, ²⁷ have been developed. Sr₂ZnSn₂OS₆ shows excellent NLO properties including a high SHG (0.7 × AGS), a wide optical band gap ($E_g = 3.52$ eV), and suitable birefringence ($\Delta n = 0.14@2090$ nm). Besides, by assembling different host and guest functional units in salt inclusion chalcogenides (SICs), many new compounds can be designed and synthesized with diverse structures and unique properties, 28 such as the nano-tunnel type [K₃Cl][Mn₂Ga₆S₁₂] and $[Cs_6Cl][Ga_5GeQ_{12}]$ (Q = S, Se) in the $[R_aX_b][M_cQ_d]$ family (R = alkali or alkali-earth metals; X = halogen; M = main-group or transition metals; and Q = chalcogen) and $[NaSr_4Cl][Ge_3S_{10}]$ with isolated [Ge₃S₉] rings and one-dimensional [ClNaSr₃]_∞⁶⁺ chains.^{29–31} Based on the above analysis, it is not hard to notice that the selection of a suitable framework is conducive to designing new NLO materials.32

After extensive screening and in-depth analysis, we noticed that the $A(\iota)B_3C_3Q_8$ (A = Ag, Li, Na, Cu; B = Mg; C = Al, Ga; Q =

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S, Se) family exhibits excellent linear or nonlinear performances, and in the structures, 33 the A-, B-, and C-sites can be replaced by various cations with different electronic configurations, in which, the framework is still stable, suggesting that it may be a good template to design NLO materials combined with the chemical substitution method. In this series of compounds, alkali metal AMg₃Ga₃S₈ (A = Li, Na) and AE(II) $Mg_6Ga_6Q_{16}$ (AE = Ca, Sr, Ba, Q = S, Se) with two types of alkaline earth metals have been reported, and among them, the optical band gaps of LiMg₃Ga₃S₈ and NaMg₃Ga₃S₈ are up to 3.86 and 3.70 eV, respectively, but their second harmonic coefficients are relatively small. However, under the action of 'the two types of alkaline earth metals' or 'rare earth metals and alkaline earth metals', AEMg₆Ga₆S₁₆ (AE = Ca, Sr, Ba) and LaMg₆Ga₆S₁₆ not only have large second harmonic effects ($\approx 0.7-0.8 \times AGS$), but also possess wide optical band gaps ($E_g =$ 3.00-3.54 eV). 34-36 It can be seen that in the family of A(1) B₃C₃Q₈, the A-site cations have a significant effect on their performances. To date, the element substitution of A- and C-sites has led to the formation of many new compounds and the substitution effects on the structure and performances have been investigated, whereas there are no direct studies on the B-sites, as an important component of the structural framework, to determine their effect on the stability of structures and properties. Not long ago, our group had successfully synthesized NaMn₃Ga₃S₈.³⁷ In this work, we will continue to change the B-site of the $AEMg_6Ga_6S_{16}$ (AE = alkaline earth metals) family by introducing Mn2+ cations and further study the effects of chemical substitution on its structure and properties. Four new non-centrosymmetric (NCS) chalcogenides MMn₆Ga₆S₁₆ (M = Ca, Sr, Ba, Pb) have been successfully synthesized. Structurally, all these compounds crystallize in the NCS hexagonal space group P6 and contain Mn-S and Ga-S single and double chains, which provide the flexibility for the formation of open frameworks to match different A-site cations. Property measurements show that $MMn_6Ga_6S_{16}$ (M = Ca, Sr, Ba, Pb) not only exhibit NLO performances but also possess magnetic properties compared with the Ga-based family.38 Besides, a detailed structural comparison has been carried out in A(1) B₃C₃Q₈ and AE(II)Mg₆Ga₆Q₁₆ to elaborate on the designability of the structure.

Results and discussion

Crystal structures

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The structures of CaMn₆Ga₆S₁₆ (CMGS), SrMn₆Ga₆S₁₆ (SMGS), BaMn₆Ga₆S₁₆ (BMGS), and PbMn₆Ga₆S₁₆ (PMGS) were determined by single-crystal XRD. The results showed that they were isostructural and crystallized in the NCS hexagonal space group $P\bar{6}$ (Table S1, ESI†). Taking CMGS as an example, its asymmetric unit contains 3 unique Ca atoms, 6 unique Mn atoms, 3 unique Ga atoms, and 11 S atoms (Table S2†). The Mn atom is linked with six S atoms to form a MnS₆ octahedron, with Mn-S distances of 2.524(3)-2.769(4) Å. Furthermore, the MnS₆ octahedra are connected with each

other to construct one-dimensional (1D) Mn-S single and double chains (Fig. 1a). The Mn-S single chains are linked with Mn-S double chains to form 1D tunnels along the c-axis (Fig. 1b). Also, the Ga atoms are coordinated with four S atoms to form GaS₄ tetrahedra (Fig. 1c), and their combination subsequently results in the formation of Ga-S single and double chains with Ga-S distances ranging from 2.221(3)-2.322(2) Å. Then, Ga-S double chains are linked with 1D tunnels composed of MnS₆ to construct an open framework, in which the GaS₄ single chains and Ca²⁺ cations are located in the space (Fig. 1d). The values for the bond valence sum (BVS) for each atom are in the range of 1.57-1.60 for Ca, 1.78-1.84 for Sr, 2.11-2.21 for Ba, 1.59-1.68 for Pb, 2.93-2.97 for Ga, 1.90-1.98 for Mn and 1.82-2.12 for S (Table S2†). 39 These are all consistent with the expected oxidation states. By comparing the structures of CMGS, SMGS, BMGS, and PMGS, it was found that the open [Mn/Ga-S]_∞ framework can be filled by cations of different sizes (Ca: 197 pm, Sr: 215 pm, Ba: 222 pm, and Pb: 175 pm), indicating that their structural framework is stable and flexible.

Structural comparison

In the systems of $A(I)B_3C_3Q_8$ (A = alkali metal) and AE(II)Mg₆Ga₆Q₁₆ (AE = alkaline-earth metal), there are 21 compounds containing the title compounds $MMn_6Ga_6S_{16}$ (M = Ca, Sr, Ba, and Pb). They all crystallize in the same NCS space group of $P\bar{6}$. They also contain a similar structural framework. These compounds all can be seen as the derivative of A(1) B₃C₃Q₈. Owing to the similarity of these structures, their lattice constants are also related. For $A(I)B_3C_3Q_8$ to AE(II) $Mg_6Ga_6Q_{16}$, $a = b_{(A)} \approx a = b_{(AE)}$, while the length of the crystallographic c-axis of AE(II)Mg₆Ga₆Q₁₆ is almost two times that of A(1)B₃C₃Q₈ due to the substitution of the alkali metal by the alkaline-earth metal. This substitution results in the ordered vacancies forming at the A site in $MMn_6Ga_6S_{16}$ (M = Ca, Sr) or partially occupied by the Ba or Pb atoms in $M'Mn_6Ga_6S_{16}$ (M' = Ba, Pb) (Fig. S6†). As for B and C site substitution, the lattice constants hardly changed in AE(II)Mg₆Ga₆Q₁₆ (Table S3†). Structurally, all structures contain an open framework composed of a series of B- and C-based chains. These chains provide the flexibility and adjustability for scaling up and down of channels in the structures that can accommodate different A-site cations. For example, as the radius increases from Li to Na in AMg₃Ga₃S₈ (Fig. 2a and b), the radii of the tunnels composed of the Mg- and Ga-based chains also increase (Fig. 2g). However, when A = Ag, the coordination environment changes from six-fold coordinated LiS6 or NaS6 to three-coordinated AgS3, and the location of A-site cations also changes, i.e. in LiMg₃Ga₃S₈ and NaMg₃Ga₃S₈, the Li and Na atoms are nearly coplanar with Mg atoms, while the Ag atoms are coplanar with Ga atoms in AgMg₃Ga₃S₈ (Fig. 2f). Besides, at A-sites, the alkali metals were replaced by the alkali earth metals, and accordingly, the radius of the tunnels also increases (Table S6†). This analysis indicates that the sites of filled cations can self-adjust with the difference in their radii and coordination environment, further presenting the flexi-

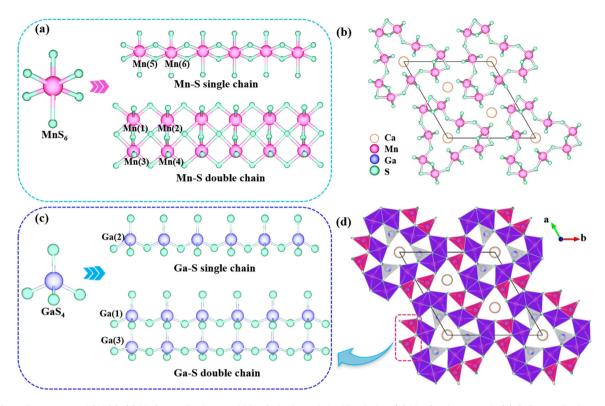
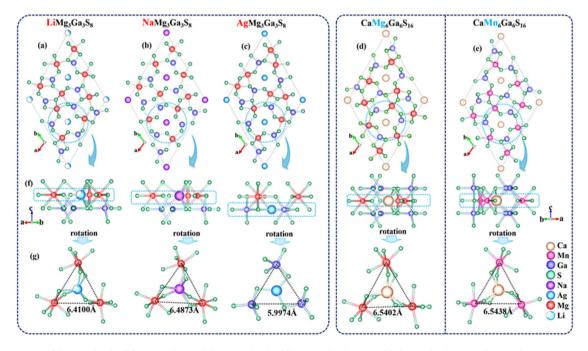


Fig. 1 Crystal structure of CMGS: (a) MnS₆ octahedron and Mn-S single and double chains; (b) Mn₉S₃₉ framework; (c) GaS₄ tetrahedron and Ga-S single and double chains; and (d) structure of CMGS viewed along the c-axis.



 $\textbf{Fig. 2} \quad \textbf{Structures of (a) LiMg}_3Ga_3S_8; \textbf{ (b) NaMg}_3Ga_3S_8; \textbf{ (c) AgMg}_3Ga_3S_8; \textbf{ (d) CaMg}_6Ga_6S_{16}; \textbf{ and (e) CaMn}_6Ga_6S_{16}; \textbf{ and (f and g) the location of different and good and good accordance on the contraction of the contractio$ cations.

bility of these constituted chains. However, to date, there is no related report about the B-site substitution in AE(II)Mg₆Ga₆Q₁₆. So, the title compounds, $MMn_6Ga_6S_{16}$ (M = Ca, Sr, Ba, Pb), represent the first example of B-site change based on the structure of AE(II)Mg₆Ga₆Q₁₆. It is worth noting that the B-site substitution results in some structural difference; for example, when

Mg²⁺ ions were successfully replaced by Mn²⁺ ions, the radii of the channels increased, suggesting that the atomic radius of the Mn ion as an important component of the channels directly affects the size of the channels' radii. Based on the above analysis, we can conclude that the varied chain structure may provide the flexibility to build the open framework to accommodate different cations, which is favorable for the design of new compounds.

Optical properties

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The polycrystalline samples were synthesized using a hightemperature solid-state reaction in a closed vacuum environment, and the purity was checked by powder X-ray diffraction (Fig. S1†). The Rietveld refinement of the powder XRD profile for CMGS is shown in Fig. 3a. The R value of $R_P = 0.08$ indicates that the fitted profile matches the experimental data well. Then, the polycrystalline samples were used for the performance characterization. The UV-vis-NIR diffuse reflectance spectra for these compounds are shown in Fig. S2.† Converting the diffuse reflectance spectra to absorption by the Kubelka-Munk equation is shown in Fig. 3b. It is clear that the experimental band gaps of the title compounds were 2.58 eV (CMGS), 2.40 eV (SMGS), 2.55 eV (BMGS), and 2.05 eV (PMGS), which are consistent with their crystal colors (their crystal colors are cyan, light green, green, and orange, respectively). In addition, the laser induced damage threshold (LIDT) was determined using the single-pulse measurement method, and the values were 40.5, 45.4, 47.7 and 41.3 MW cm⁻² for $MMn_6Ga_6S_{16}$ (M = Ca, Sr, Ba, Pb) with the particle size ranging from 180-250 µm, respectively, which were higher than that of AGS (8.5 MW cm⁻²) under the same conditions.⁴⁰ These

results indicated that $MMn_6Ga_6S_{16}$ (M = Ca, Sr, Ba, Pb) can withstand higher power laser irradiation. The IR spectra are shown in Fig. 3c. It was found that these title compounds have a wide infrared transmission range from 600 to 4000 cm⁻¹ that covers the two atmospheric windows (3–5 and 8–12 μ m) for the important applications in telecommunications, laser guidance, and explosive detection.

Besides, the birefringence of the crystals of MMn₆Ga₆S₁₆ (M = Ca, Sr, Ba, Pb) has been measured by using a cross-polarization microscope based on the formula $R = \Delta n \times d$, where R, Δn , and d represent the optical path difference, birefringence, and thickness, respectively. The original interference color is shown in Fig. 3d-f (Fig. S3†). The crystal thickness was measured by using a single crystal diffractometer, and the thicknesses were 26.6 µm (CMGS), 28.8 µm (SMGS), 19.9 µm (BMGS) and 28.3 µm (PMGS). The optical path differences were obtained to be 1200, 1300, 1300 and 1400 nm for CMGS, SMGS, BMGS and PMGS, respectively, by comparing with the Michel-Lévy chart. Then, the birefringence values were determined to be 0.045 (CMGS), 0.046 (SMGS), 0.060 (BMGS) and 0.049 (PMGS) in the visible region. The suitable birefringence is favorable to achieve a wide phase matching (PM) region. 43

These title compounds are all NCS structures, which is an essential prerequisite for an NLO response. So, the SHG intensity *versus* the particle sizes of MMn₆Ga₆S₁₆ (M = Ca, Sr, Ba, Pb) has been investigated based on the Kurtz–Perry method with a Q-switched Ho:Tm:Cr:YAG laser (2.09 μ m, 3 Hz, 50 ns). As shown in Fig. 4a, the SHG intensities increase with the particle size increasing in the range of 30–210 μ m, indicating that MMn₆Ga₆S₁₆ are phase-matchable and the SHG intensities of these compounds are 0.4–0.7 times that of AGS with

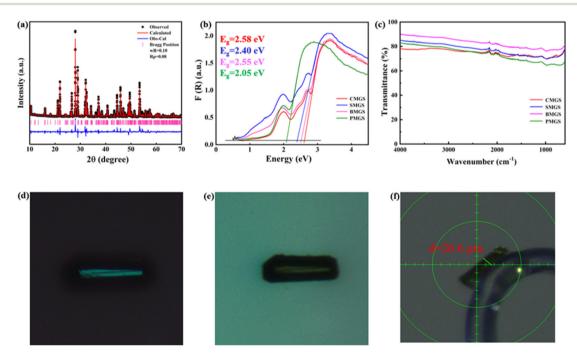


Fig. 3 (a) Rietveld refinement of the powder XRD profile for CMGS; (b) band gaps of $MMn_6Ga_6S_{16}$ (M = Ca, Sr, Ba, and Pb); (c) IR spectra of $MMn_6Ga_6S_{16}$ (M = Ca, Sr, Ba, and Pb); and (d-f) the original interference color, extinction, and thickness of the CMGS crystal, respectively.

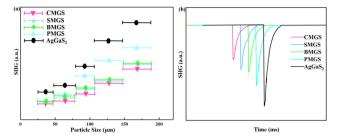


Fig. 4 (a) Phase-matching results of $MMn_6Ga_6S_{16}$ (M = Ca, Sr, Ba, and Pb) and the benchmark AGS at 2090 nm and (b) SHG intensities of $MMn_6Ga_6S_{16}$ (M = Ca, Sr, Ba, and Pb) and AGS with the particle size ranging from 150-200 μm.

the particle size ranging from 150-210 µm. For PMGS, its SHG strength is up to 0.7 times that of AGS (Fig. 4b), greatly improving the NLO response compared with A(1)B₃C₃S₈ (Table S3b†). To further investigate the NLO properties, we further analyzed the distortion (Δd) of MnS₆ or MgS₆ and GaS₄ in MMn₆Ga₆S₁₆ (M = Ca, Sr, Ba, Pb), La₆MnGe₂S₁₄, La₃MnGaS₇, LiGaS₂, LiGaS α -BaGa₄S₇⁴⁷ and AeMg₆Ga₆S₁₆ (Ae = Ca, Sr, Ba). The calculated results show that the distortion of the MnS₆ octahedron is larger than that in La₆MnGe₂S₁₄ and La₃MnGaS₇, while the GaS₄ tetrahedron exhibits similar distortion to that in α-BaGa₄S₇ and AeMg₆Ga₆S₁₆ (Ae = Ca, Sr, Ba) (Tables S5a and b†). These indicate that the distorted MnS₆ and GaS₄ and their regular arrangement are conducive to the SHG response (Fig. S4†).

Magnetic properties

The title compounds all contain the Mn²⁺ ions, which may make these compounds exhibit magnetic properties. As such, the dependence of magnetization (M-T) of polycrystalline powder was tested in the temperature range of 3-300 K (zero field cooling (ZFC) and field cooling (FC)) with an applied electric field of H = 5000 Oe. ^{48,49} The molar magnetic susceptibility (χ) and the inverse molar magnetic susceptibility (χ^{-1}) as a function of temperature $(T \text{ K}^{-1})$ are shown in Fig. S5.† The magnetic susceptibility decreases gradually with the increase in temperature, which is a typical characteristic of a paramagnetic compound conforming to the Curie-Weiss law. In addition, according to the Curie-Weiss law, by extrapolating the high-temperature paramagnetic curve of χ^{-1} -T as a straight line, we can obtain the intercept on the T-axis, which is the Curie-Weiss temperature $(T_{\rm W})$ and the slope is 1/C (C is the Curie constant). 50,51 The fitted Curie constant (C) and Weiss temperature $(T_{\rm W})$ are 4.73 emu K mol⁻¹ and -130.71 K for CMGS, respectively. Similar results were obtained for compounds SrMn₆Ga₆S₁₆, BaMn₆Ga₆S₁₆ and PbMn₆Ga₆S₁₆ (Table S3a \dagger). The negative $T_{\rm W}$ values suggest weak short-range antiferromagnetic interactions among the adjacent magnetic cations. Then, according to the $\mu_{\rm eff}$ = $(8C)^{1/2}\mu_{\rm B}$ equation, the experimental effective magnetic moment (μ_{eff}) of Mn(II) in CMGS is $6.15\mu_B$, which is consistent with the theoretical one of Mn(II) $(5.92\mu_B)$.⁵²

Furthermore, we noted that CMGS has a similar structure to that of NaMn₃Ga₃S₈ previously reported by our group; however, NaMn₃Ga₃S₈ exhibits antiferromagnetic behavior.³⁷ Structural analysis shows that the substitution of A-site cations has some effects on the local chemical environment, bonding distance, and bonding angle of Mn²⁺ ions in the structure. In the structures of $NaMn_3Ca_3S_8$ and CMGS, the A-based (A = Naor Ca) polyhedra are surrounded by Mn-S single chains composed of edge-sharing MnS₆ octahedra (Fig. 5a and b). When the Na⁺ cations are replaced by the Ca²⁺ cations, it causes a slight squeeze between the MnS₆ octahedra. As a result, the Mn(3) atoms deviate off the chains extending along the *c*-axis, which leads to a change in the distances of Mn-Mn between two chains from 6.5144 Å in NaMn₃Ca₃S₈ to 6.5642 Å in CMGS. Also, the distance between two Mn atoms in the same chain changes (Fig. 5c and d). Accordingly, the distances of Mn-Mn in the double chains composed of a MnS₆ octahedron also change. Besides, the arrangement mode of Ca²⁺ cations is different from that of Na⁺ cations, resulting in a change in the local chemical environment of Mn²⁺. As such, the increased

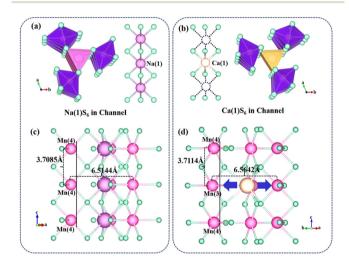


Fig. 5 Distribution of A-site cations in channels of NaMn₃Ga₃S₈ and CaMn₆Ga₆S₁₆.

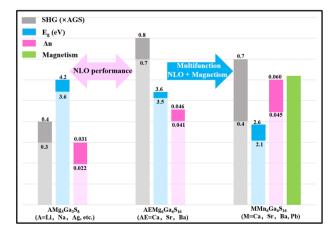


Fig. 6 Performance changes of $A(i)B_3C_3S_8$ and $(AE/M)Mg_6Ga_6S_{16}$ after element substitution.

distances of Mn–Mn in two chains and the different local chemical environments around Mn–S single chains caused by the substituted cation may be the reason for the difference in the magnetic properties. During the research process, it was found that the substitution of A- and C-sites in the $A_{\rm I}B_3C_3Q_8$ and $AE_{\rm II}Mg_6Ga_6Q_{16}$ systems can improve their linear or nonlinear optical performances. However, in this study, by replacing their B-sites with Mn atoms, $MMn_6Ga_6S_{16}$ (M = Ca, Sr, Ba, Pb) exhibit not only NLO performances but also paramagnetism (Fig. 6). This indicates that $MMn_6Ga_6S_{16}$ (M = Ca, Sr, Ba, Pb) can serve as potential multifunctional materials.

Conclusions

In summary, four NCS chalcogenides, MMn₆Ga₆S₁₆ (M = Ca, Sr, Ba, Pb), were successfully synthesized using the high-temperature sealed-tube method. They all crystallize in the space group $P\bar{6}$ of the hexagonal system, featuring open frameworks built by Mn-S and Ga-S single/double chains, and channels filled with alkaline-earth metal cations. The systematic structural analysis indicates that the low-dimensional structure, i.e. these 1D chains, brings great flexibility and adjustability to different-site substitution in A(I)B₃C₃Q₈ and AE(II)Mg₆Ga₆Q₁₆. Performance measurement shows that $MMn_6Ga_6S_{16}$ (M = Ca, Sr, Ba, Pb) not only exhibit a wide IR transmission region, suitable SHG response (0.4–0.7 \times AGS) and high LIDT (4.8–5.6 \times AGS) but also possess the temperature-dependent paramagnetism. Besides, the study of the structure-property relationship indicates that distorted MnS₆ octahedra and GaS₄ tetrahedra and their well-ordered arrangement are responsible for the NLO response of MMn₆Ga₆S₁₆ (M = Ca, Sr, Ba, Pb) and structural anisotropy. This work not only provides a wide material platform to explore new IR-NLO chalcogenides by coupling different kinds of chains in one structure but also can improve or enrich material functionality by introducing functional element-based chains.

Author contributions

Writing – original draft: Kaixuan Li, Yujie Zhang and Xianchao Zhu; writing – review and editing: Hongping Wu; resources: Zhanggui Hu; and supervision: Jiyang Wang and Yicheng Wu.

Data availability

- 1. The data supporting this article have been included as part of the ESI. \dagger
- 2. Crystallographic data for 2350610–2350613 have been deposited at the CCDC. \dagger

Conflicts of interest

There are no conflicts to declare.

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