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## A high-performance IR nonlinear optical material $\text{Sr}_3\text{MnGe}_2\text{S}_8$ achieved via partial cation substitution-induced structural transformation

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The development of Mn-based infrared nonlinear optical (IR-NLO) materials that concurrently exhibit a large second-harmonic generation response ( $\text{SHG} > 1.0 \times \text{AgGaS}_2$ ) and a wide band gap ( $E_g > 3.0 \text{ eV}$ ) remains a formidable challenge. Herein, we demonstrate a partial cation substitution strategy to address this issue, successfully transforming centrosymmetric  $\text{Sr}_2\text{GeS}_4$  into a novel non-centrosymmetric quaternary sulfide,  $\text{Sr}_3\text{MnGe}_2\text{S}_8$ . The compound features a three-dimensional framework constructed from corner-sharing  $[\text{MnS}_4]$  and  $[\text{GeS}_4]$  tetrahedra, with  $\text{Sr}^{2+}$  cations residing in the interstitial spaces.  $\text{Sr}_3\text{MnGe}_2\text{S}_8$  achieves an outstanding balance of key IR-NLO properties: it shows a strong SHG response ( $2.4 \times \text{AgGaS}_2$  at 2050 nm), a high laser-induced damage threshold ( $13.4 \times \text{AgGaS}_2$ ), and a wide  $E_g$  of 3.06 eV—ranking it among the best-performing Mn-based chalcogenides. Theoretical calculations and structural analysis reveal that the excellent NLO performance originates from the synergistic effects between the two distinct types of functional units. This work provides a valuable paradigm for designing high-performance IR-NLO materials through rational structural transformation, highlighting the power of chemical substitution in overcoming property trade-offs.

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## Introduction

Nonlinear optical (NLO) crystals serve as the cornerstone materials for laser frequency conversion and play a pivotal role in a variety of applications, including environmental monitoring, medical imaging, infrared (IR) remote sensing, and national defense and security.<sup>1</sup> Currently, commercially available NLO crystals operating in the mid- to far-IR region—such as  $\text{AgGaS}_2$ ,  $\text{AgGaSe}_2$ , and  $\text{ZnGeP}_2$ —suffer from intrinsic limitations, notably a narrow bandgap ( $E_g$ ), which leads to a low laser-induced damage threshold (LIDT) and undesirable two-photon absorption (TPA).<sup>2</sup> These drawbacks significantly restrict their application in high-power infrared laser systems. Consequently, there is an urgent need to explore and synthesize new IR-NLO crystals that exhibit superior overall per-

formance, particularly those possessing both a wide  $E_g$  and a large second-harmonic generation (SHG) response.<sup>3</sup>

Transition metal-based chalcogenides have garnered significant attention as a compelling class of materials for IR-NLO applications, distinguished by their structurally tunable frameworks, adaptable electronic band structures, strong nonlinear susceptibilities, high LIDTs, and excellent physicochemical stability.<sup>4</sup> While over 500 compounds in this family have been explored to date, research efforts remain heavily concentrated on systems containing  $d^{10}$ -configured metal centers, leaving those with alternative electron configurations—such as manganese-based compounds with a  $d^5$  configuration—relatively underexplored. Despite their limited investigation, the known Mn-based IR-NLO materials already exhibit remarkable structural diversity.<sup>5–22</sup> These range from simple chalcogenides (e.g.,  $\text{RbMn}_4\text{In}_5\text{Se}_{12}$ ,<sup>5</sup>  $\text{Pb}_{0.65}\text{Mn}_{2.85}\text{Ga}_3\text{S}_8$ ,<sup>7</sup> and  $\text{Li}_2\text{MnSnS}_4$ <sup>10</sup>) to complex heteroanionic systems including oxychalcogenides (e.g.,  $\text{Ba}_{10}\text{In}_2\text{Mn}_{11}\text{Si}_3\text{O}_{12}\text{S}_{18}$ <sup>12</sup> and  $\text{Eu}_2\text{MnGe}_2\text{OS}_6$ <sup>13</sup>) and salt-inclusion chalcogenides (e.g.,  $[\text{Ba}_4\text{Cl}_2][\text{MnGa}_4\text{Se}_{10}]$ <sup>16</sup>). However, a critical challenge persists across these systems: their relatively narrow  $E_g$  fundamentally limits practical utility by inducing TPA and constraining the LIDT. Consequently, achieving a balanced combination of wide  $E_g$  ( $>3.0 \text{ eV}$ ) and strong SHG response ( $>1.0 \times \text{AgGaS}_2$ ) represents a pivotal yet unresolved

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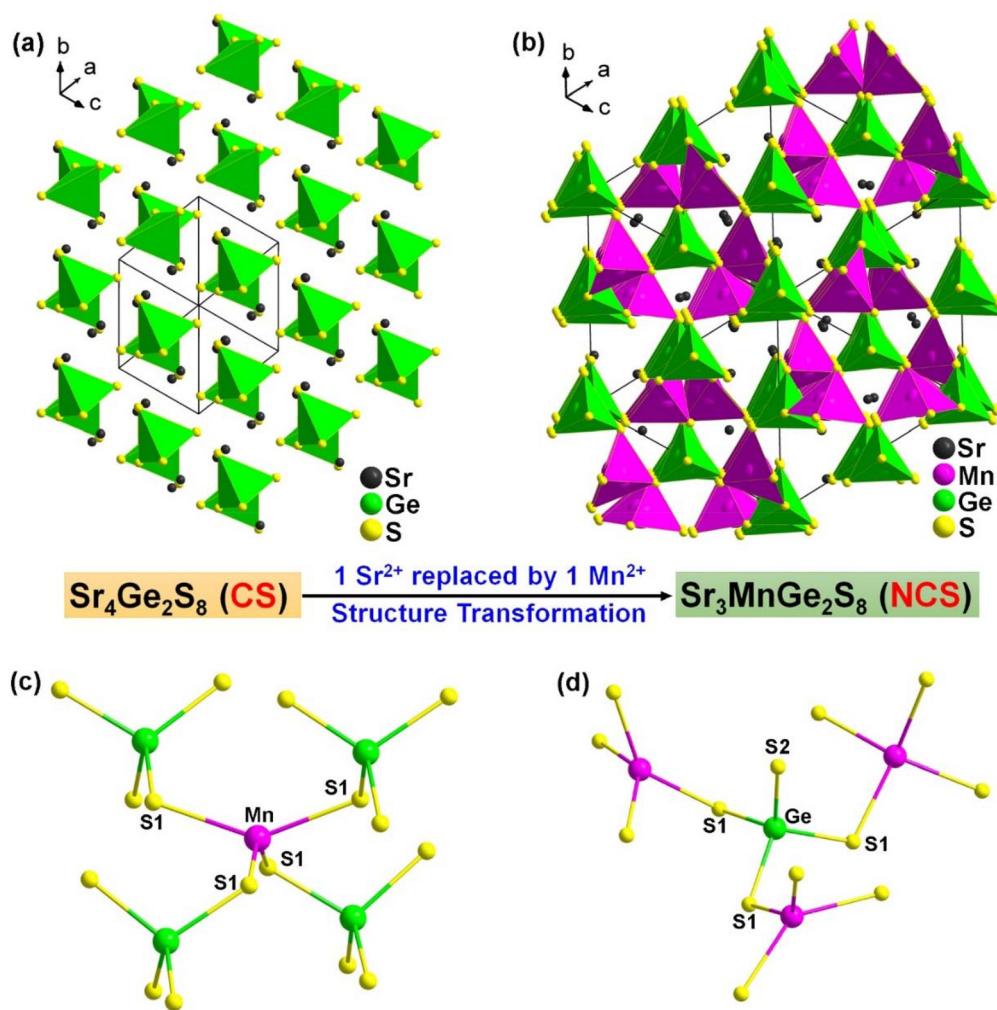


pursuit in the development of high-performance Mn-based IR-NLO materials.

Beyond the performance limitations previously discussed, a more fundamental challenge in the development of Mn-based IR-NLO materials lies in the intentional design of noncentro-symmetric (NCS) structures—a strict prerequisite for any second-order NLO material.<sup>23</sup> Over decades, multiple synthetic strategies have been developed to promote NCS formation, among which chemical substitution has gained considerable attention due to its operational simplicity and structural predictability.<sup>24</sup> This approach typically employs a known centrosymmetric (CS) parent phase as a template, where targeted replacement of cationic or anionic motifs induces symmetry breaking, thereby activating the SHG response. Notable successes of this strategy include the transformation from CS-CsGaS<sub>2</sub> to NCS-[CsBa<sub>2</sub>Cl][Ga<sub>4</sub>S<sub>8</sub>],<sup>25</sup> CS-Rb<sub>4</sub>P<sub>2</sub>S<sub>6</sub> to NCS-RbBiP<sub>2</sub>S<sub>6</sub>,<sup>26</sup> CS-SnBr<sub>2</sub> to NCS-Sn<sub>7</sub>Br<sub>10</sub>S<sub>2</sub>,<sup>27</sup> and CS-PbBr<sub>2</sub> to NCS-Pb<sub>4</sub>SeBr<sub>6</sub>.<sup>28</sup> Building on this methodology, our group recently demonstrated that chemical substitution can be stra-

tegically applied to wide- $E_g$  CS templates to simultaneously achieve a large SHG response and retain a wide  $E_g$ . Representative examples include: CS-SrGeO<sub>3</sub> to NCS-SrGeOSe<sub>2</sub> ( $E_g = 3.16$  eV, SHG =  $1.3 \times$  AgGaS<sub>2</sub>),<sup>29</sup> CS-Sr<sub>2</sub>GaS<sub>4</sub> to NCS-SrCdSiS<sub>4</sub> ( $E_g = 3.61$  eV, SHG =  $1.1 \times$  AgGaS<sub>2</sub>),<sup>30</sup> and CS-Cs<sub>3</sub>[Sb<sub>3</sub>O<sub>6</sub>][Ge<sub>2</sub>O<sub>7</sub>] to NCS-Nd<sub>3</sub>[Ga<sub>3</sub>O<sub>3</sub>S<sub>3</sub>][Ge<sub>2</sub>O<sub>7</sub>] ( $E_g = 4.35$  eV, SHG =  $0.8 \times$  AgGaS<sub>2</sub>).<sup>31</sup> These results highlight the potential of rational substitution strategies to overcome the traditional trade-off between wide  $E_g$  and large SHG response—paving a viable pathway toward high-performance Mn-based NLO systems.

Based on the aforementioned design strategy, we herein report the rational synthesis of a novel Mn-based IR-NLO candidate, Sr<sub>3</sub>MnGe<sub>2</sub>S<sub>8</sub>, through a partial cation substitution approach, starting from the wide- $E_g$  CS phase Sr<sub>2</sub>GeS<sub>4</sub> as a structural template.<sup>32</sup> The resulting Sr<sub>3</sub>MnGe<sub>2</sub>S<sub>8</sub> achieves an outstanding balance of key IR-NLO properties, exhibiting a strong SHG response ( $2.4 \times$  AgGaS<sub>2</sub> at 2050 nm), a high LIDT ( $13.4 \times$  AgGaS<sub>2</sub>), and a wide  $E_g$  of 3.06 eV. These merits place it



**Fig. 1** Structural evolution from (a) CS Sr<sub>2</sub>GeS<sub>4</sub> to (b) NCS Sr<sub>3</sub>MnGe<sub>2</sub>S<sub>8</sub> via partial cation substitution. The local coordination environments of the (c) [MnS<sub>4</sub>] and (d) [GeS<sub>4</sub>] tetrahedral units in the resulting Sr<sub>3</sub>MnGe<sub>2</sub>S<sub>8</sub> structure are also displayed.



**Table 1** Crystal data and structure refinement for  $\text{Sr}_3\text{MnGe}_2\text{S}_8$ 

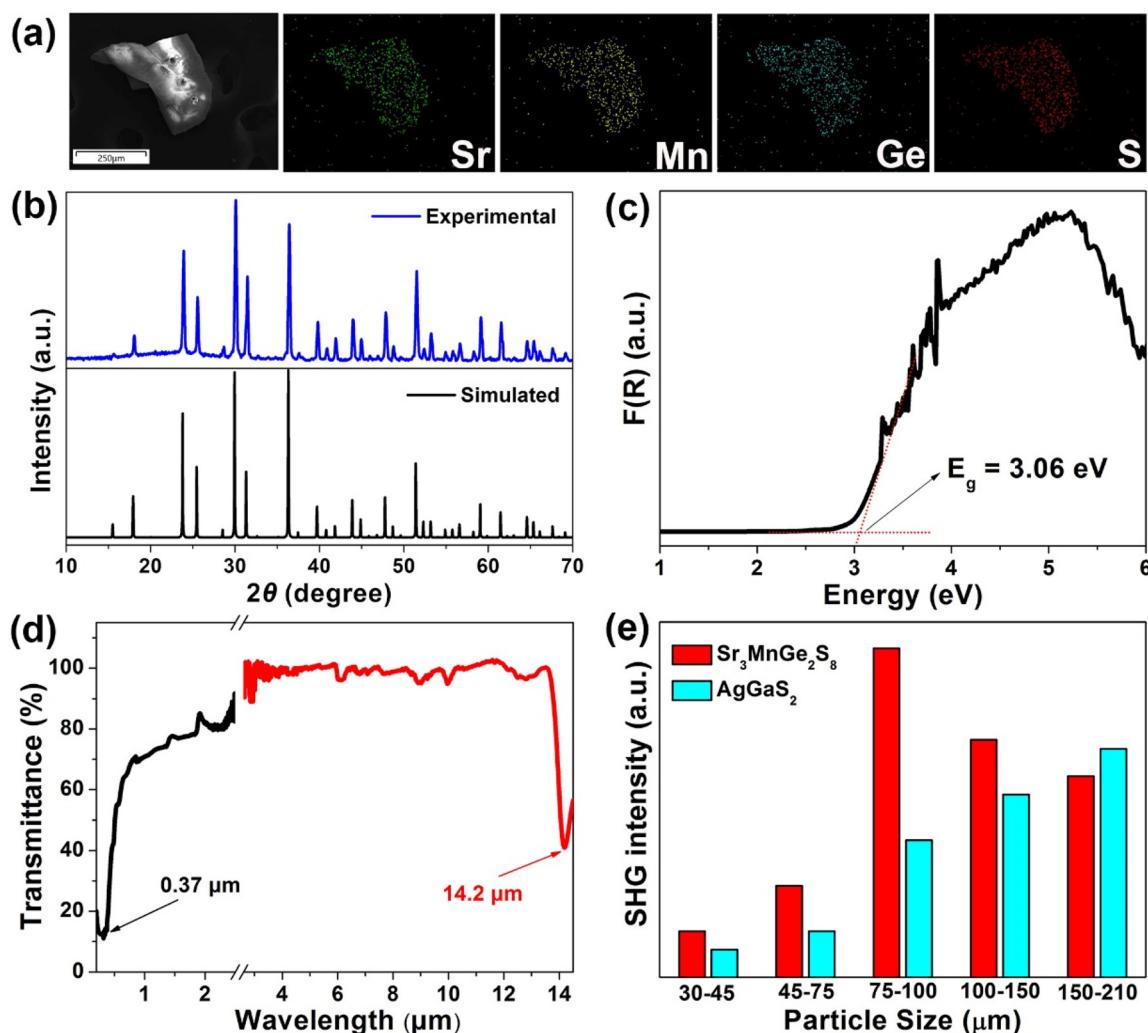
Molecular formula	$\text{Sr}_3\text{MnGe}_2\text{S}_8$
CCDC number	2488264
Formula weight	719.46
Crystal system	Cubic
Space group	$\bar{F}\bar{4}3d$
Temperature (K)	293(2)
Radiation	Mo K $\alpha$ ( $\lambda = 0.71073$ )
$F(000)$	2648.0
$a$ (Å)	13.97941(15)
$\alpha$ (°)	90
$V$ (Å $^3$ )	2731.91(9)
$Z$	8
$\rho_{\text{cal.}}$ (g cm $^{-3}$ )	3.50
$\mu$ (mm $^{-1}$ )	25.6
GOOF on $F^2$	1.08
Flack factor	0.04(3)
$R_1$ , $wR_2$ [ $I > 2\sigma(I)$ ] <sup>a</sup>	0.0413, 0.1056
$R_1$ , $wR_2$ (all data) <sup>a</sup>	0.0428, 0.1079
Largest diff. peak and hole (e Å $^{-3}$ )	0.82/-1.66

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

among the top-performing Mn-based chalcogenides reported to date. This work comprehensively describes its synthesis, crystal structure, optical properties, and the underlying structure–property relationships.

## Results and discussion

The successful implementation of a chemical substitution strategy for structural transformation and IR-NLO material design critically depends on the judicious selection of a parent structure. In this work, the CS  $\text{Sr}_2\text{GeS}_4$  was chosen as the template based on two key considerations. First, it contains conventional NLO-active motifs—specifically, isolated  $[\text{GeS}_4]$  tetrahedra—that are essential for generating a SHG response.<sup>33</sup> Second, its zero-dimensional (0D) structural architecture (Fig. 1a), characterized by well-separated structural units, contributes to a wide experimental  $E_g$  (3.46 eV), which is highly



**Fig. 2** Characterization of  $\text{Sr}_3\text{MnGe}_2\text{S}_8$ : (a) SEM image with the corresponding elemental maps, (b) experimental (blue) and simulated (black) powder XRD patterns, (c) solid-state diffuse reflectance spectrum, (d) optical transmission spectra across UV-Vis-NIR and mid-IR regions, and (e) particle size-dependent SHG responses relative to the reference  $\text{AgGaS}_2$ .

desirable for achieving a high LIDT.<sup>34</sup> By partially substituting  $\text{Sr}^{2+}$  with transition-metal  $\text{Mn}^{2+}$ , we aimed to leverage the inherent size mismatch to break inversion symmetry—inducing a CS-to-NCS transition—while largely retaining the wide  $E_g$  characteristic imparted by the parent structure. Single-crystal X-ray diffraction (XRD) analysis confirms that  $\text{Sr}_3\text{MnGe}_2\text{S}_8$  crystallizes in the cubic crystal system with the NCS space group  $I\bar{4}3d$  (no. 220). The unit cell parameters are  $a = b = c = 13.9794(2)$  Å (Table 1). The asymmetric unit comprises one independent Sr atom (Wyckoff site 24*d*), one Ge atom (16*c*), one Mn atom (12*a*), and two S atoms (sites 48*e* and 16*c*) (Table S1). As depicted in Fig. 1b, the crystal structure of  $\text{Sr}_3\text{MnGe}_2\text{S}_8$  is characterized by  $\text{Mn}^{2+}$  and  $\text{Ge}^{4+}$  ions in tetrahedral coordination with S atoms, forming  $[\text{MnS}_4]$  and  $[\text{GeS}_4]$  units. These tetrahedra interconnect through vertex-sharing, assembling into a three-dimensional (3D) anionic  $[\text{MnGe}_2\text{S}_8]^{6-}$  framework, charge-balanced by  $\text{Sr}^{2+}$  cations residing in the interstitial sites. Fig. 1c and d illustrate the local coordination geometry of the  $[\text{MnS}_4]$  and  $[\text{GeS}_4]$  tetrahedra, respectively. It is noteworthy that each  $[\text{MnS}_4]$  tetrahedron shares its four S1 atoms with four adjacent  $[\text{GeS}_4]$  units. In contrast, the  $[\text{GeS}_4]$  tetrahedron on the three-fold axis is surrounded by three distorted  $[\text{MnS}_4]$  tetrahedra *via* shared S1 atoms, whereas its S2 atom remains as the terminal atom.

A key structural consequence of the partial substitution of  $\text{Sr}^{2+}$  by  $\text{Mn}^{2+}$  is the pronounced distortion observed in both the  $[\text{GeS}_4]$  and  $[\text{MnS}_4]$  tetrahedra, attributable to the ionic size mismatch between the substituents. In  $\text{Sr}_3\text{MnGe}_2\text{S}_8$ , the degree of distortion of the  $[\text{GeS}_4]$  unit is larger than that in the parent  $\text{Sr}_2\text{GeS}_4$  structure ( $15.44^\circ$  *vs.*  $14.88^\circ$ ), as quantified by the formula  $\sum = \sum_{i=1}^4 (|\varphi_i - 109.47^\circ|)$ .<sup>35</sup> Similarly, the newly

formed  $[\text{MnS}_4]$  tetrahedron displays substantial angular distortion, with a maximum S–Mn–S bond angle of  $139.67^\circ$  and a corresponding gaint degree of distortion of  $110.94^\circ$  (Tables S2 and S3). The local dipole moment also serves as a metric for the tetrahedral distortion, yielding values of 0.84 D and 28.55 D for the  $[\text{GeS}_4]$  and  $[\text{MnS}_4]$  units, respectively.<sup>36</sup> Moreover, the charge-balancing Sr atoms exhibit notable differences in their coordination configuration and structure assembly. Specifically, Sr is six-coordinate within the CS  $\text{Sr}_2\text{GeS}_4$ , constituting a 2D layered structure. Conversely, in the NCS  $\text{Sr}_3\text{MnGe}_2\text{S}_8$ , Sr adopts an eight-coordinate geometry, resulting in a 3D network structure, as shown in Fig. S1. These geometric perturbations collectively underscore the efficacy of chemical substitution in modulating local symmetry and bonding geometry, which is critical for activating and enhancing second-order SHG responses.

The pale yellow crystalline compound  $\text{Sr}_3\text{MnGe}_2\text{S}_8$  was synthesized *via* a high-temperature solid-state reaction under vacuum, using stoichiometric mixtures of Sr, Mn, Ge, and S. The resulting product (with a yield of approximately 70%) demonstrated excellent stability, remaining unaltered after more than one year of storage in ambient air (see the SI for details). Energy dispersive X-ray spectroscopy (EDX) confirmed the homogeneous distribution of Sr, Mn, Ge, and S throughout the crystal, with an average atomic ratio of approximately 3 : 1.1 : 2 : 7.9 (Fig. 2a and Fig. S2), in good agreement with the stoichiometry derived from single-crystal XRD structure analysis. Phase purity was further verified by powder XRD, as shown in Fig. 2b. UV-vis-NIR absorption spectroscopy revealed that  $\text{Sr}_3\text{MnGe}_2\text{S}_8$  possesses a wide optical  $E_g$  of 3.06 eV, as estimated using the Kubelka–Munk function<sup>37</sup> (Fig. 2c). This

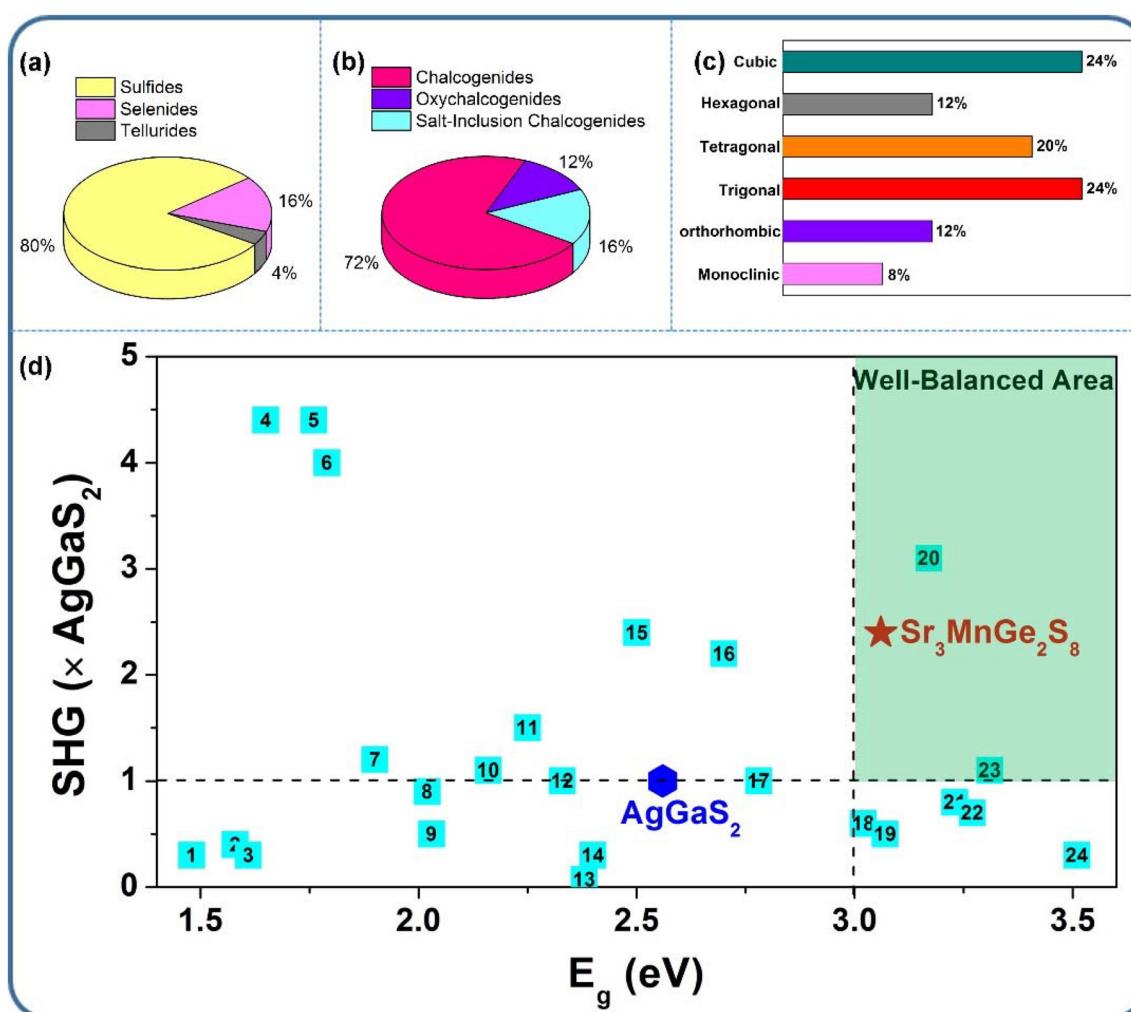
**Table 2** Properties comparison of the reported Mn-based IR-NLO chalcogenides

Number	Compounds	Unit cell	Space group	$E_g$ (eV)	SHG ( $\times \text{AgGaS}_2$ )	Ref.
1	$\text{CsMn}_4\text{In}_5\text{Te}_{12}$	$R\bar{3}$ (no. 146)	Trigonal	1.48	0.3	5
2	$\text{K}_3\text{Mn}_2\text{Sb}_3\text{S}_8$	$I\bar{4}2m$ (no. 121)	Tetragonal	1.58	0.4	6
3	$\text{Rb}_3\text{Mn}_2\text{Sb}_3\text{S}_8$	$I\bar{4}2m$ (no. 121)	Tetragonal	1.61	0.3	6
4	$\text{Pb}_{0.72}\text{Mn}_{2.84}\text{Ga}_{2.95}\text{Se}_8$	$P\bar{6}$ (no. 174)	Hexagonal	1.65	4.4	7
5	$\text{RbMn}_4\text{In}_5\text{Se}_{12}$	$R\bar{3}$ (no. 146)	Trigonal	1.76	4.4	5
6	$\text{CsMn}_4\text{In}_5\text{Se}_{12}$	$R\bar{3}$ (no. 146)	Trigonal	1.79	4.0	5
7	$\text{BaMnSn}_4$	$Fdd2$ (no. 43)	Orthorhombic	1.90	1.2	8
8	$\text{CsMnAs}_3\text{S}_6$	$I\bar{4}$ (no. 82)	Trigonal	2.02	0.9	9
9	$\text{Li}_2\text{MnSn}_4$	$Pmn2_1$ (no. 33)	Orthorhombic	2.03	0.5	10
10	$\text{RbMnAs}_3\text{S}_6$	$R\bar{3}$ (no. 146)	Trigonal	2.16	1.1	9
11	$\text{Pb}_{0.65}\text{Mn}_{2.85}\text{Ga}_3\text{S}_8$	$P\bar{6}$ (no. 174)	Hexagonal	2.25	1.5	7
12	$\text{Sr}_3\text{MnSn}_2\text{S}_8$	$I\bar{4}3d$ (no. 220)	Cubic	2.33	1.0	11
13	$\text{Ba}_{10}\text{In}_2\text{Mn}_{11}\text{Si}_3\text{O}_{12}\text{S}_{18}$	$I\bar{4}3m$ (no. 217)	Cubic	2.38	$3 \times \alpha\text{-SiO}_2$	12
14	$\text{Eu}_2\text{MnGe}_2\text{OS}_6$	$P\bar{4}2_1m$ (no. 113)	Tetragonal	2.40	0.3	13
15	$\text{Ba}_4\text{Cu}_{2.2}\text{Mn}_{0.8}(\text{SnS}_4)_4$	$I\bar{4}3d$ (no. 220)	Cubic	2.5	2.4	14
16	$\text{Ba}_6\text{Ge}_2\text{Mn}_3\text{S}_16$	$I\bar{4}3d$ (no. 220)	Cubic	2.70	2.2	15
17	$[\text{Ba}_4\text{Cl}_2][\text{MnGa}_4\text{S}_{16}]$	$I\bar{4}$ (no. 82)	Tetragonal	2.78	1.0	16
18	$[\text{K}_4\text{Cl}][\text{MnGa}_9\text{S}_{16}]$	$P\bar{1}$ (no. 1)	Triclinic	3.02	0.6	17
19	$\text{Li}_2\text{MnGeS}_4$	$Pmn2_1$ (no. 33)	Orthorhombic	3.07	0.5	18
20	$[\text{K}_3\text{Cl}][\text{Mn}_2\text{Ga}_6\text{S}_{12}]$	$P\bar{3}1c$ (no. 159)	Trigonal	3.17	3.10	19
21	$\text{CsMn}_3\text{Ga}_5\text{S}_{11}$	$P\bar{c}$ (no. 7)	Monoclinic	3.23	0.8	20
22	$\text{RbMn}_3\text{Ga}_5\text{S}_{11}$	$P\bar{c}$ (no. 7)	Monoclinic	3.27	0.7	20
23	$\text{K}_3\text{Rb}_3[\text{K}_3\text{Cl}][\text{Li}_2\text{Mn}_4\text{Ga}_{12}\text{S}_{27}]$	$P\bar{6}_3mc$ (no. 186)	Hexagonal	3.31	1.1	21
24	$\text{Sr}_2\text{MnGe}_2\text{OS}_6$	$P\bar{4}2_1m$ (no. 113)	Tetragonal	3.51	0.3	22
★	$\text{Sr}_3\text{MnGe}_2\text{S}_8$	$I\bar{4}3d$ (no. 220)	Cubic	<b>3.06</b>	<b>2.4</b>	<b>This work</b>



value represents one of the largest  $E_g$  reported to date among Mn-based IR-NLO materials, exceeding the threshold of 3.0 eV (see Table 2 for details). Notably, the optical  $E_g$  of  $\text{Sr}_3\text{MnGe}_2\text{S}_8$  is substantially broader than those of well-established IR-NLO crystals such as  $\text{AgGaS}_2$  (2.56 eV),<sup>38</sup>  $\text{AgGaSe}_2$  (1.83 eV),<sup>39</sup> and  $\text{ZnGeP}_2$  (2.0 eV).<sup>2</sup> A large  $E_g$  is beneficial for minimizing TPA and achieving a high LIDT. In light of this, we evaluated  $\text{Sr}_3\text{MnGe}_2\text{S}_8$ 's performance in high-power applications by measuring its powder LIDT. The obtained value of 37.52 MW cm<sup>-2</sup> at 1064 nm is 13.4 times that of  $\text{AgGaS}_2$  (2.8 MW cm<sup>-2</sup>).<sup>40</sup> Additionally, transmission measurements based on the single-crystal sample indicate that  $\text{Sr}_3\text{MnGe}_2\text{S}_8$  exhibits a broad transparency window spanning from 0.37  $\mu\text{m}$  (UV-Vis) to 14.2  $\mu\text{m}$  (far-IR) (Fig. 2d). This value is comparable to recently reported IR-NLO materials, such as  $\text{Cs}_3\text{In}(\text{In}_4\text{Se}_7)(\text{P}_2\text{Se}_6)$  (0.41–19.5  $\mu\text{m}$ ),  $[\text{Ba}_{22}(\text{SO}_4)_5][\text{Zn}_{14}\text{Ga}_{18}\text{S}_{58}]$  (0.35–10.2  $\mu\text{m}$ ),  $[\text{K}_4\text{BaCl}_2][\text{In}_6\text{Se}_{11}]$  (0.7–17.1  $\mu\text{m}$ ), and  $[\text{Ba}_4\text{Cl}_2][\text{CdGa}_4\text{S}_{10}]$

(0.28–18.6  $\mu\text{m}$ ).<sup>41</sup> The compound also displays remarkable thermal stability, maintaining its structural integrity up to 1100 K under a nitrogen atmosphere, as evidenced by thermogravimetric analysis (Fig. S3). The exceptional thermal stability of this compound—outperforming recent chalcogenides such as  $\text{LiPb}_3\text{GeS}_4\text{Cl}_3$  (693 K),  $\beta\text{-EuZnGe}_4$  (1073 K), and  $(\text{Na}_3\text{Rb})\text{Hg}_2\text{Ge}_2\text{S}_8$  (717 K)<sup>42</sup>—makes it highly promising for applications demanding harsh-environment operation. Owing to its NCS crystal structure, the NLO properties of  $\text{Sr}_3\text{MnGe}_2\text{S}_8$  were systematically evaluated using the powder SHG method. Polycrystalline samples of  $\text{Sr}_3\text{MnGe}_2\text{S}_8$ , along with  $\text{AgGaS}_2$  as a reference, were carefully ground and sieved into five distinct particle size ranges. SHG measurements were conducted using a 2050 nm laser. As shown in Fig. 2e, the SHG intensity of  $\text{Sr}_3\text{MnGe}_2\text{S}_8$  does not increase monotonically with the increase of particle size, indicating non-phase-matching behavior—consistent with its cubic crystal system, which lacks sufficient bire-



**Fig. 3** Statistical distribution of Mn-based IR-NLO chalcogenides categorized by (a and b) chemical composition and (c) crystallographic system. (d) Mapping the balance between SHG and  $E_g$  for Mn-based IR-NLO chalcogenides. The outlined area identifies the most promising candidates with a wide  $E_g$  ( $>3.0$  eV) and large SHG efficiency ( $>1.0 \times \text{AgGaS}_2$ ). Detailed data are provided in Table S2.



fringence for phase matching. Notably,  $\text{Sr}_3\text{MnGe}_2\text{S}_8$  exhibits a strong SHG response, reaching approximately 2.4 times that of  $\text{AgGaS}_2$  in the particle size range of 75–100  $\mu\text{m}$  (Fig. 2e).

To contextualize the performance of the newly discovered  $\text{Sr}_3\text{MnGe}_2\text{S}_8$ , we have benchmarked it against known Mn-based IR-NLO materials. As shown in Fig. 3 and summarized in Table 2, sulfides represent the majority of materials in this category, comprising 80% of reported compounds, whereas selenides and tellurides account for 16% and 4%, respectively (Fig. 3a). When classified by anionic composition, these chalcogenides can be categorized into two groups: single-anion chalcogenides, which constitute the predominant fraction (72%), and mixed-anion chalcogenides, representing a smaller proportion (28%). The latter includes oxychalcogenides (12%) and salt-inclusion chalcogenides (16%) (Fig. 3b). Statistical analysis indicates that Mn-based IR-NLO chalcogenides crystallize in all six crystal systems, with the following distribution: cubic (24%), tetragonal (20%), orthorhombic (12%), trigonal (24%), hexagonal (12%), and monoclinic (8%) (Fig. 3c). This distribution reflects a pronounced preference for high-symmetry systems (approximately 80%), whereas low-symmetry structures, such as the triclinic and monoclinic system, are relatively uncommon. Fig. 3d summarizes two critical performance indicators for these compounds—the SHG response and the  $E_g$ —with detailed data provided in Table 2. Notably,  $\text{Sr}_3\text{MnGe}_2\text{S}_8$  achieves a remarkable balance between a wide  $E_g$  ( $>3.0$  eV) and a strong SHG response ( $>1.0 \times \text{AgGaS}_2$ ), a combination that effectively overcomes the typical performance trade-off in Mn-based NLO systems.

To elucidate the optical properties and structure–performance correlations of the title compound, first-principles calculations of DFT were conducted using the VASP package. The electronic band structure along high-symmetry paths (Fig. S4)

confirms that  $\text{Sr}_3\text{MnGe}_2\text{S}_8$  is an indirect bandgap semiconductor with a theoretical  $E_g$  of 2.23 eV. The computed value is moderately lower than the experimental result, a discrepancy commonly associated with the discontinuity in the exchange–correlation energy inherent to the GGA.<sup>43</sup> The partial density of states (PDOS) in Fig. 4 reveals pronounced orbital hybridization between Mn and S, as well as between Ge and S, across both the valence bands (VBs) and conduction bands (CBs), indicative of strong covalent character. The upper VB is mainly constituted by Ge 4s, Ge 4p, Mn 3d, and S 3p orbitals, while the lower CB is primarily contributed by Ge 4s, Ge 4p, Mn 3d, and S 3p orbitals. Since electronic transitions near the band edges are critical in governing optical behavior, the Ge–S and Mn–S groups are considered key structural units responsible for the optical  $E_g$  and NLO properties of  $\text{Sr}_3\text{MnGe}_2\text{S}_8$ . Furthermore, the SHG coefficients of  $\text{Sr}_3\text{MnGe}_2\text{S}_8$  were evaluated based on the electronic structure using the length-gauge formalism.<sup>44</sup> In accordance with Kleinman's symmetry<sup>45</sup> and the  $I\bar{4}3d$  space group, only one independent SHG tensor element,  $d_{14}$ , is present, and its value is calculated as 15.72 pm V<sup>−1</sup>, showing good consistency with experimental findings.

## Conclusions

In summary, a novel NCS Mn-based quaternary sulfide,  $\text{Sr}_3\text{MnGe}_2\text{S}_8$ , has been successfully synthesized *via* an equivalent partial cation substitution strategy, using the CS compound  $\text{Sr}_2\text{GeS}_4$  as the parent template. This material demonstrates outstanding IR-NLO performance, characterized by a strong SHG response ( $2.4 \times \text{AgGaS}_2$  at 2050 nm), a wide  $E_g$  (3.06 eV), a high LIDT ( $13.4 \times \text{AgGaS}_2$ ), and a broad transparency range (0.37–14.2  $\mu\text{m}$ ). These properties are attributed to the synergistic effect arising from the distortion and favorable alignment of the constituent  $[\text{MnS}_4]$  and  $[\text{GeS}_4]$  tetrahedral units. Notably,  $\text{Sr}_3\text{MnGe}_2\text{S}_8$  stands out as one of the very few Mn-based chalcogenides that simultaneously surpass the benchmark thresholds of large SHG efficiency ( $>1.0 \times \text{AgGaS}_2$ ) and wide  $E_g$  ( $>3.0$  eV). Through detailed structural and theoretical analysis, we establish that the partial substitution of Sr by Mn not only triggers a CS-to-NCS structural transformation but also significantly enhances the NLO activity. This work provides an effective chemical design strategy for achieving balanced NLO performance and opens a viable pathway for the discovery of high-performance IR-NLO materials through targeted structural engineering.

## Author contributions

A-Lan Xu: investigation, formal analysis, writing – original draft. Mao-Yin Ran: investigation, formal analysis, writing – review & editing. Zuju Ma: methodology, validation. Xin-Tao Wu: conceptualization, writing – review & editing. Hua Lin: supervision, conceptualization, writing – review & editing. Qi-Long Zhu: supervision, writing – review & editing.

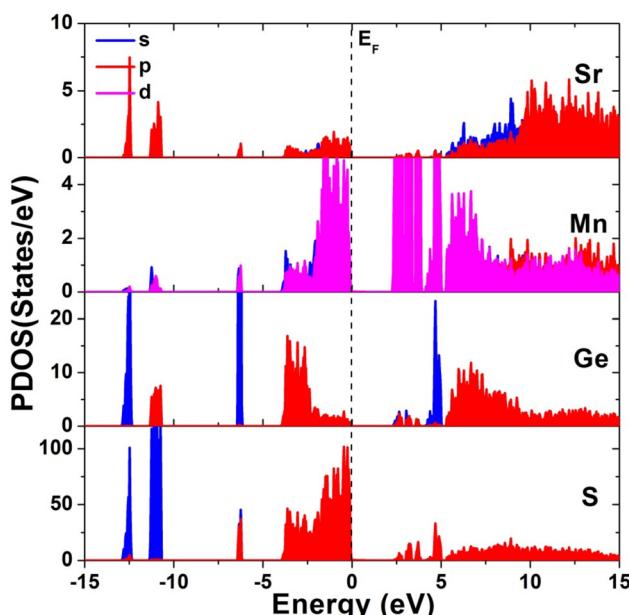


Fig. 4 The partial density of states (PDOS) of  $\text{Sr}_3\text{MnGe}_2\text{S}_8$ .



## Conflicts of interest

There are no conflicts to declare.

## Data availability

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information: additional experimental and theoretical results, together with additional tables and figures. See DOI: <https://doi.org/10.1039/d5qi02182k>.

CCDC 2488264 contains the supplementary crystallographic data for this paper.<sup>46</sup>

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