

## REVIEW

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## An overview of Mg-based IR nonlinear optical materials

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Infrared nonlinear optical (IR-NLO) materials play a vital role in generating IR laser output and have significant applications in the fields of communication, medicine, and security. At present, commercial IR-NLO crystals suffer from various performance drawbacks that constrain their range of applications. Therefore, the pursuit of designing and exploring new IR-NLO materials has emerged as an important avenue for the advancement of the IR laser industry. Benefiting from the various structural compositions, wide energy gaps, sufficient second-harmonic-generation intensities, strong laser-induced damage thresholds and favorable phase matching features, Mg-based IR-NLO materials have attracted wide attention in recent years. However, there has not been a specific review of this attractive family. In this overview, the recent advancements of Mg-based IR-NLO materials are summarized. These non-centrosymmetric compounds (including 36 chalcogenides and 4 pnictides) can be categorized into three types based on their chemical compositions: (i) ternary  $\text{MgGa}_2\text{Se}_4$ ,  $\text{MgSiP}_2$ ,  $\text{MgSiAs}_2$ , and  $\text{Mg}_3\text{Si}_6\text{As}_8$ ; (ii) quaternary  $\text{Li}_4\text{MgGe}_2\text{S}_7$ ,  $\text{Li}_2\text{Mg}_2\text{M}^{\text{III}}\text{S}_6$  ( $\text{M}^{\text{III}} = \text{Si, Ge}$ ),  $\text{AEMg}_6\text{Ga}_6\text{S}_{16}$  ( $\text{AE} = \text{Ca, Sr, Ba}$ ),  $\text{RE}_6\text{MgSi}_2\text{S}_{14}$  ( $\text{RE} = \text{Y, La-Nd, Sm, and Gd-Er}$ ),  $\text{Li}_2\text{MgM}^{\text{IV}}\text{Se}_4$  ( $\text{M}^{\text{IV}} = \text{Ge, Sn}$ ),  $\text{Na}_4\text{MgM}^{\text{III}}\text{Se}_6$  ( $\text{M}^{\text{III}} = \text{Si, Ge}$ ),  $\text{Cu}_2\text{MgM}^{\text{IV}}\text{Q}_4$  ( $\text{M}^{\text{IV}} = \text{Si, Ge; Q} = \text{S, Se}$ ),  $\text{M}^{\text{I}}\text{Mg}_3\text{M}^{\text{III}}\text{Q}_8$  ( $\text{M}^{\text{I}} = \text{Na, Cu, Ag; M}^{\text{III}} = \text{Al, Ga; Q} = \text{S, Se}$ ), and  $\text{Mg}_2\text{In}_3\text{Si}_2\text{P}_7$ ; and (iii) quinary  $\text{Ba}_6\text{Cu}_{1.9}\text{Mg}_{1.1}\text{Ge}_4\text{S}_{16}$  and  $\text{Ba}_6\text{Cu}_{1.94}\text{Mg}_{1.06}\text{Sn}_4\text{S}_{16}$ . Their solid-state synthesis, crystal structures, optical properties and structure–activity relationships are systematically discussed. Finally, some useful conclusions and outlooks on this topic have been put forward.

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## 1. Introduction

Nonlinear optical (NLO) crystals are crucial components of full-state lasers as they possess the capacity to enhance the frequency range, making them applicable in a variety of aspects such as laser spectroscopy, long distance laser communication, signal processing and so on.<sup>1–18</sup> Due to the limitations of laser wavelength, significant research has been conducted on second order NLO materials, owing to their eminent ability to generate second harmonic generation (SHG). According to the various application bands, NLO materials can be divided into three groups, including ultraviolet (UV), visible-near infrared (Vis-NIR), mid- and far-infrared (MFIR) groups. Among them, NLO materials of UV and Vis-NIR wavelengths have already been deeply researched and commercialized in the past decades, such as  $\text{KBe}_2\text{BO}_3\text{F}_2$  (KBBF),<sup>19</sup>  $\beta\text{-BaB}_2\text{O}_4$

( $\beta\text{-BBO}$ ),<sup>20</sup>  $\text{LiB}_3\text{O}_5$  (LBO),<sup>21</sup>  $\text{KH}_2\text{PO}_4$  (KDP),<sup>22</sup> and  $\text{KTiOPO}_4$  (KTP).<sup>23</sup> Although traditional commercialized IR-NLO materials, such as  $\text{AgGaS}_2$ ,<sup>24</sup>  $\text{AgGaSe}_2$ ,<sup>25</sup> and  $\text{ZnGeP}_2$ ,<sup>26</sup> have strong SHG coefficients ( $d_{\text{eff}}$ ), they still possess some inevitable drawbacks such as an imperfect laser-induced damage threshold (LIDT) of  $\text{AgGaS}_2$ , non-phase-matching property of  $\text{AgGaSe}_2$  and negative two-photon absorption of  $\text{ZnGeP}_2$ .<sup>27,28</sup> Therefore, the development of new outstanding IR-NLO materials is not only urgent but also challenging.

In order to meet the requirements of modern laser technology, high-performance IR-NLO materials need to fulfil the following conditions: (1) suitable birefringence ( $\Delta n$  at the range of 0.03–0.10) for phase-matching; (2) sufficient  $d_{\text{eff}}$  ( $>0.5 \times \text{AgGaS}_2$ ,  $13 \text{ pm V}^{-1}$  for  $\text{AgGaS}_2$ ); (3) high LIDT ( $>1 \times \text{AgGaS}_2$ ); (4) wide band gap  $E_g$  ( $>3.0 \text{ eV}$ ) and transparent range (covering the 3–5  $\mu\text{m}$  and 8–12  $\mu\text{m}$  atmospheric windows); (5) easiness to achieve growth of large size single crystals; and (6) satisfactory chemical and physical stability (mainly low hygroscopicity, resistance to the atmosphere, and possibility of cutting and grinding).<sup>29–40</sup> In addition to the performance requirements mentioned above, it is also imperative that the material be crystallized in a non-centrosymmetric space group. This is because it is a prerequisite for it to function as an IR-NLO

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candidate.<sup>41–43</sup> In recent decades, several design strategies have been developed. Among these, the most commonly used method for obtaining non-centrosymmetric structures is the introduction of various asymmetric building units (ABUs) into one structure. The common ABUs for IR-NLO materials are as follows: (i) distorted  $[MQ_4]$  tetrahedra (M = main-group elements; Q = chalcogen);<sup>44–52</sup> (ii)  $[MQ_n]$  polyhedra (M = transition-metal elements;  $n = 2, 3$ , and  $4$ );<sup>53–57</sup> (iii) distorted  $[REQ_n]$  polyhedra (RE = rare-earth-metal elements);<sup>58–61</sup> (iv) lone-pair-cation-based  $[MQ_n]$  polyhedra (M = As(III), Sb(III), Bi(III), Pb(II), and Sn(II));<sup>62–71</sup> and (v) mixed-anion  $[MO_xQ_y]$  polyhedra.<sup>72–81</sup>

Recently, the introduction of Mg-based ABUs into the non-centrosymmetric structures has attracted considerable interest due to the following reasons: (i) Mg possesses large electropositivity ( $\chi = 1.31$ ), has a high Z/R ratio of 2.8 (Z, cation charge; R, cation radius), has light atomic mass and is non-poisonous. (ii) Mg is more inclined to form stable covalent bonds with chalcogen and pnictide atoms than are Ca, Sr, and Ba, which have strong ionic properties within the same family, for example, tetrahedral  $[MgQ_4]$  and  $[MgP_n]$  ( $P_n = P, As$ ) ABUs and octahedral  $[MgQ_6]$  ABUs. (iii) Due to the absence of d–d and f–f electron transitions, Mg is beneficial for obtaining wide  $E_g$  values and expanding the IR transparent region.<sup>82–96</sup> Moreover, highly polarizable Mg-based ABUs are helpful in maintaining strong  $d_{eff}$  and suitable  $\Delta n$ . However, a specific summary of non-centrosymmetric Mg-based materials has not been provided, even though they have been discovered to display excellent IR-NLO performances.

In this review, the recent advancements of Mg-based IR-NLO materials are summarized. These non-centrosymmetric compounds (including 36 chalcogenides and 4 pnictides) can be categorized into three types based on their chemical composition: (i) ternary  $MgGa_2Se_4$ ,  $MgSiP_2$ ,  $MgSiAs_2$ , and  $Mg_3Si_6As_8$ ; (ii) quaternary  $Li_4MgGe_2S_7$ ,  $Li_2Mg_2M^{III}S_6$  ( $M^{III} = Si, Ge$ ),  $AEMg_6Ga_6S_{16}$  (AE = Ca, Sr, Ba),  $Li_2MgM^{IV}Se_4$  ( $M^{IV} = Ge, Sn$ ),  $RE_6MgSi_2S_{14}$  (RE = Y, La–Nd, Sm, and Gd–Er),  $Na_4MgM^{III}Se_6$  ( $M^{III} = Si, Ge$ ),  $Cu_2MgM^{IV}Q_4$  ( $M^{IV} = Si, Ge; Q = S, Se$ ),  $M^IMg_3M^{III}Q_8$  ( $M^I = Na, Cu, Ag; M^{III} = Al, Ga; Q = S, Se$ ), and  $Mg_2In_3Si_2P_7$ ; and (iii) quinary  $Ba_6Cu_{1.9}Mg_{1.1}Ge_4S_{16}$  and  $Ba_6Cu_{1.94}Mg_{1.06}Sn_4S_{16}$ . Their solid-state synthesis, crystal structures, optical properties and structure–activity relationships are systematically discussed. Finally, some useful conclusions and outlooks on this topic have been put forward.

## 2. The survey on Mg-based IR-NLO materials

### 2.1 Ternary Mg-based chalcogenides and pnictides

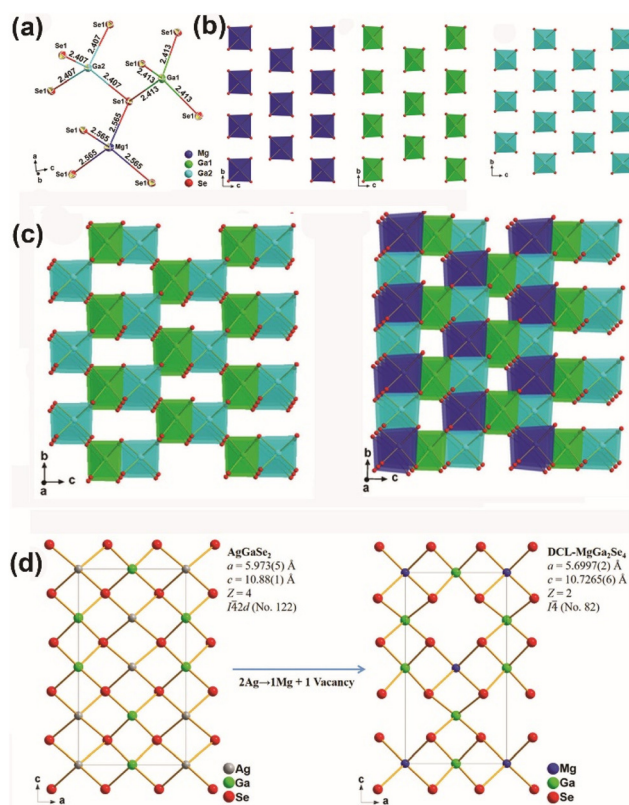
**2.1.1  $MgGa_2Se_4$ .** The first defect-chalcopyrite-like Mg-based chalcogenide  $MgGa_2Se_4$ , with a non-centrosymmetric  $I\bar{4}$  space group, was successfully designed and constructed *via* a structure prediction and experiment combined method by Li and co-workers in 2022. They used high-temperature solid-state

reactions to create it, by mixing  $MgSe$ ,  $Ga$ , and  $Se$  in a stoichiometric ratio of 1 : 2 : 3 at 1223 K.<sup>82</sup>

As shown in Fig. 1,  $Mg$  and  $Ga$  atoms both coordinate with  $Se$  atoms, forming a four-coordinated model represented by tetrahedral  $[MgSe_4]$  and  $[GaSe_4]$  ABUs. In the  $[Ga_2Se_7]$  channel,  $[MgSe_4]$  ABUs are embedded *via* corner-sharing with adjacent  $[Ga_1Se_4]$  and  $[Ga_2Se_4]$ , as depicted in Fig. 1b and c, resulting in a three-dimensional (3D) defect-chalcopyrite-like structure. Furthermore, this structure can also be achieved by utilizing chalcopyrite-like  $AgGaSe_2$ , as depicted in Fig. 1d. When one  $Mg$  atom and one vacancy replace two  $Ag$  atoms in  $AgGaSe_2$ , defect-chalcopyrite-like  $MgGa_2Se_4$  is produced.

The developed  $MgGa_2Se_4$  possesses a wide optical  $E_g$  (*ca.* 2.96 eV), a high LIDT (*ca.*  $3.0 \times AgGaSe_2$ ), a broad transparency window (covering 3–12  $\mu m$ ), and a suitable phase-matching  $d_{eff}$  (*ca.*  $0.9 \times AgGaSe_2$  @150–200  $\mu m$ ). Therefore,  $MgGa_2Se_4$  shows great potential as an IR-NLO candidate. Additionally, theoretical calculations reveal that the strong  $d_{eff}$  of  $MgGa_2Se_4$  mainly originates from the  $[GaSe_4]$  ABUs and nonbonding  $Se$  4p states, and indicate that the tetrahedral  $[MgSe_4]$  ABUs can effectively broaden the  $E_g$  of chalcopyrite-like compounds.

**2.1.2  $MgSiP_2$  and  $MgSiAs_2$ .** In 2018, He's group conducted a systematic study of the electronic structures, linear and NLO



**Fig. 1** (a) Coordination environment of asymmetric building units in  $MgGa_2Se_4$ ; (b) the arrangement of isolated  $[MgSe_4]$ ,  $[Ga_1Se_4]$ , and  $[Ga_2Se_4]$  tetrahedra in the  $bc$  plane; (c)  $[Ga_2Se_7]^{4-}$  anionic framework (left) and 3D structure of  $MgGa_2Se_4$  (right); (d) structural evolution from  $AgGaSe_2$  (left) to  $MgGa_2Se_4$  (right). Copyright 2022 Wiley.

properties, and thermodynamic stability of the  $\text{MgM}^{\text{IV}}\text{P}_n\text{As}_2$  ( $\text{M}^{\text{IV}} = \text{Si, Ge, Sn}$ ;  $\text{P}_n = \text{P, As}$ ) system through first-principles research. The aim of the study was to evaluate their potential in IR-NLO applications.<sup>83</sup> In the same year, Kovnir and his colleagues successfully synthesized  $\text{MgSiAs}_2$  by reacting raw materials in the molar ratio of  $\text{Mg}:\text{Si}:\text{As} = 1.2:1:2$  at the temperature of 1123 K.<sup>84</sup> To obtain a single crystal, they performed three cycles of annealing and grinding coupled with acid treatment ( $\text{HCl}:\text{H}_2\text{O} = 1:1$ ). Recently, Ye and co-workers successfully obtained millimeter-level crystals of  $\text{MgSiP}_2$  ( $1.3 \times 2.3 \times 0.5 \text{ mm}^3$ ) by mixing Mg, Si, P, and  $\text{BaCl}_2$  flux in a molar ratio of 1.33 : 1 : 2 : 2.67 and heating it to 1373 K.<sup>85</sup>

$\text{MgSiAs}_2$  and  $\text{MgSiP}_2$  possess a classical chalcopyrite structure (space group:  $I42d$ ), with a 3D covalent framework comprising tetrahedral  $[\text{SiP}_n\text{As}_2]$  ( $\text{P}_n = \text{P, As}$ ) ABUs. The tunnels are filled with  $\text{Mg}^{2+}$  cations, which are coordinated with four closest  $\text{P}_n$  atoms (as depicted in Fig. 2). Computational and optical investigations have revealed that  $\text{MgSiAs}_2$  and  $\text{MgSiP}_2$  display direct  $E_g$  semiconductor properties with an optical  $E_g$  of 1.83 eV and 2.33 eV, respectively.  $\text{MgSiAs}_2$  exhibits a moderate  $d_{\text{eff}}$  (ca.  $0.6 \times \text{AgGaS}_2@55\text{--}88 \mu\text{m}$ ) and comparable LIDT (ca.  $1.1 \times \text{AgGaS}_2$ ), while  $\text{MgSiP}_2$  possesses a strong  $d_{\text{eff}}$  ( $3.5 \times \text{AgGaS}_2@150\text{--}212 \mu\text{m}$ ), and a broad IR transparency window (0.53–10.3  $\mu\text{m}$ ). These studies indicate that the desired balance between  $E_g$  and  $d_{\text{eff}}$  can be achieved by rationally adjusting the ionicity–covalency–metallicity properties.

**2.1.3  $\text{Mg}_3\text{Si}_6\text{As}_8$ .** In 2018, Kovnir and co-workers reported the discovery of  $\text{Mg}_3\text{Si}_6\text{As}_8$ , which is the second ternary pnictide in the Mg–Si–As family. Single crystals of  $\text{Mg}_3\text{Si}_6\text{As}_8$  ( $3 \times 1.5 \times 1 \text{ mm}^3$ ) were prepared through stoichiometric ratios of Mg, Si, and As and a 50 molar excess of Bi flux at 1150 K.<sup>84</sup> It represents a new structure type and belongs to the non-centrosymmetric  $P4_332$  space group. The crystal structure of  $\text{Mg}_3\text{Si}_6\text{As}_8$  is composed of a complex 3D Si–As network with interspersed Mg cations. Two distinct environments can be observed for the Mg cations: *i.e.*, tetrahedral  $[\text{MgAs}_4]$  and octahedral  $[\text{MgAs}_6]$  ABUs. Moreover, the Si–As network found in  $\text{Mg}_3\text{Si}_6\text{As}_8$  is similar to that of the binary  $\text{SiAs}$ , where six As atoms surround Si–Si dumbbells in both cases. The structure of  $\text{Mg}_3\text{Si}_6\text{As}_8$  creates a 3D rhombus grid fashion of  $\text{Si}_2\text{As}_6$  octahedra, as depicted in Fig. 3a. In contrast, these octahedra in the  $\text{SiAs}$  crystal structure form two-dimensional (2D) layers, as shown in Fig. 3b.



Fig. 2 Crystal structure of II–IV–V<sub>2</sub>. Copyright 2018 IOP Publishing.

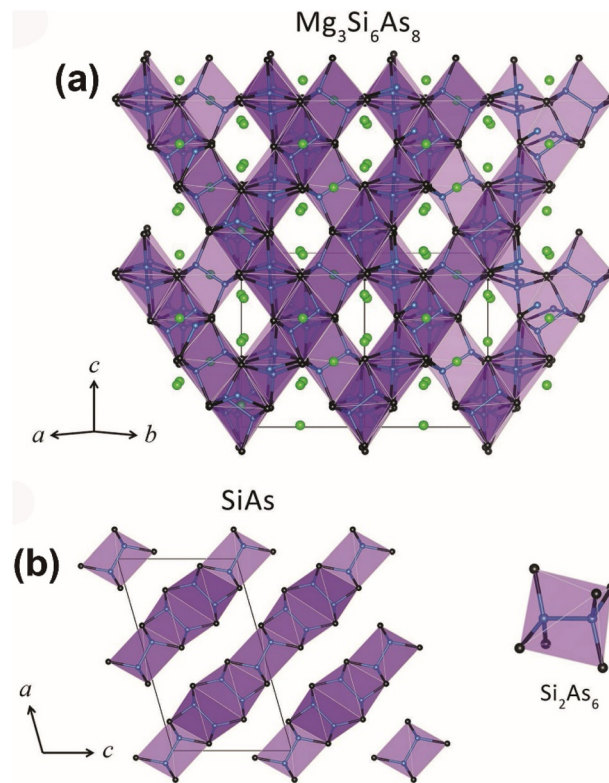


Fig. 3 (a) Crystal structure of the 3D Si–As network in  $\text{Mg}_3\text{Si}_6\text{As}_8$  and (b)  $\text{SiAs}$  with  $\text{Si}_2\text{As}_6$  marked as purple octahedra. Green atom: Mg; blue atom: Si; black atom: As. Copyright 2018 Wiley.

$\text{Mg}_3\text{Si}_6\text{As}_8$  displays more significant thermal stability than  $\text{MgSiAs}_2$  with a difference of 100 K (1240 K compared to 1140 K). Additionally, its experimental  $E_g$  is recorded as 2.02 eV. Unfortunately, it does not have SHG response due to its 432 Laue class.

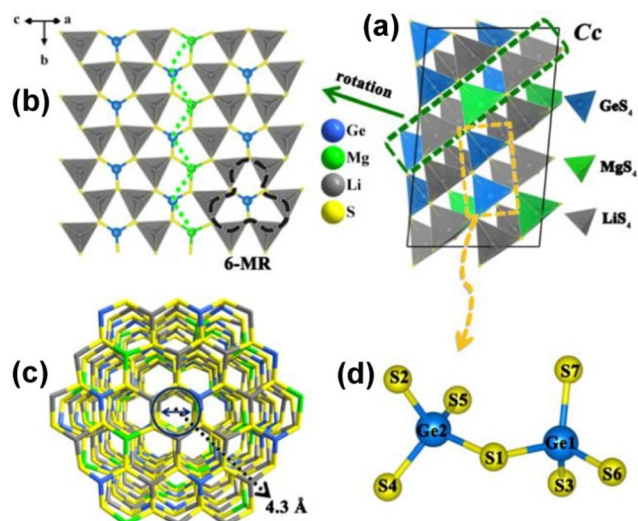
## 2.2 Quaternary Mg-based chalcogenides and pnictides

**2.2.1  $\text{Li}_4\text{MgGe}_2\text{S}_7$ .** The first alkali and alkaline-earth metal defect-chalcopyrite-like Mg-based chalcogenide  $\text{Li}_4\text{MgGe}_2\text{S}_7$ , with a monoclinic  $Cc$  space group, was successfully designed based on the chemical substitute-oriented strategy in the  $\text{M}_4^{\text{I}}\text{--M}^{\text{II}}\text{--M}_2^{\text{IV}}\text{--Q}_7$  system by Li and co-workers in 2021.<sup>86</sup> Colorless block-shaped crystals of  $\text{Li}_4\text{MgGe}_2\text{S}_7$  were prepared by a high-temperature solution reaction using the starting materials  $\text{Li}_2\text{S}$ , Mg, Ge, and S in the molar ratio of 2.5 : 1 : 2 : 5 at 1223 K.

Like other diamond-like chalcogenides,  $\text{Li}_4\text{MgGe}_2\text{S}_7$  can be seen as a derivative of wurtzite  $\beta\text{-ZnS}$ .<sup>97</sup> Each metal is coordinated by four S atoms, forming tetrahedral  $[\text{LiS}_4]$ ,  $[\text{MgS}_4]$ , and  $[\text{GeS}_4]$  ABUs. The six  $[\text{LiS}_4]$  ABUs are interconnected by sharing common sulfur atoms, creating a fascinating 6-membered ring (6-MR), with the  $[\text{GeS}_4]$  tetrahedron located in the middle of this unit. Furthermore, the one-dimensional (1D)  $[\text{GeMgS}_5]$  zigzag chains connect to the 6-MRs to construct a 2D honeycomb-like layer (Fig. 4a). The assembly of this honeycomb layer along the  $[101]$  direction is achieved *via* shared S atoms, resulting in the final 3D diamond-like framework







**Fig. 4** Crystal structure of  $\text{Li}_4\text{MgGe}_2\text{S}_7$ : (a) 3D diamond-like structure; (b) single 2D layered fragment viewed along the [102] direction; (c) honeycomb-like 3D framework with an internal diameter of about 4.3 Å; (d) coordination environment of  $[\text{Ge}_2\text{S}_7]^{6-}$  dimers. Copyright 2021 Wiley.

(Fig. 4b). When viewed along the [203] direction, a clear depiction of the honeycomb-like 3D framework with an internal diameter of about 4.3 Å is observed (Fig. 4c). Additionally, unique  $[\text{Ge}_2\text{S}_7]^{6-}$  dimers are discovered in  $\text{Li}_4\text{MgGe}_2\text{S}_7$  (Fig. 4d).

The obtained  $\text{Li}_4\text{MgGe}_2\text{S}_7$  exhibits the widest experimental  $E_g$  of 4.12 eV among reported quaternary metal chalcogenides. Additionally, it shows a suitable phase-matching  $d_{\text{eff}}$  (ca.  $0.7 \times \text{AgGaS}_2$  at 2090 nm, granularity range 15–200 μm) and a high LIDT ( $7 \times \text{AgGaS}_2$  at 1064 nm), making it an excellent IR-NLO candidate for high-power laser applications. Theoretical calculations indicate that alkali metal Li and alkaline-earth metal Mg effectively enhance  $E_g$ , while covalent  $[\text{Ge}_2\text{S}_7]^{6-}$  dimers contribute to a strong  $d_{\text{eff}}$ . This study enriches the diversity of diamond-like chalcogenides and offers a new route for the design and exploration of new IR-NLO materials with broad  $E_g$  and significant  $d_{\text{eff}}$ .

**2.2.2  $\text{Li}_2\text{Mg}_2\text{M}_2^{\text{III}}\text{S}_6$  ( $\text{M}^{\text{III}} = \text{Si, Ge}$ ).** The first Li-containing members of the  $\text{A}_{12-n}\text{M}_x^{\text{III}}(\text{T}_2\text{Q})_2$  family,  $\text{Li}_2\text{Mg}_2\text{Si}_2\text{S}_6$  and  $\text{Li}_2\text{Mg}_2\text{Ge}_2\text{S}_6$ , were reported by Aitken and co-workers in 2022.<sup>87</sup> Transparent and colorless single crystals of  $\text{Li}_2\text{Mg}_2\text{Si}_2\text{S}_6$  and  $\text{Li}_2\text{Mg}_2\text{Ge}_2\text{S}_6$  were obtained by the traditional high-temperature solid-phase technology using stoichiometric amounts of the reagents at 1173 K.

These two new compounds belong to the non-centrosymmetric polar space group  $P31m$  (No. 157) and represent a new structure type. As indicated in Fig. 5, each octahedral  $[\text{LiS}_6]$  ABU shares its edge with three other  $[\text{LiS}_6]$  ABUs to build a 2D layer in the  $ab$  plane, resulting in holes in the  $c$  direction. This layer is designated as “layer 1”. Similarly, along the  $c$  axis, there exist nearly identical layers formed by the octahedral  $[\text{MgS}_6]$  ABUs, which are subsequently referred to as “layer 2”. These two layers, layer 1 and layer 2, are then interconnected along the  $c$  axis via face sharing of their respective octahedra



**Fig. 5** Polyhedral stacking structure of  $\text{Li}_2\text{Mg}_2\text{M}_2^{\text{III}}\text{S}_6$  viewed along the  $bc$  plane. Copyright 2022 Wiley.

to generate a 3D framework. These staggered ethane-like  $[\text{Si}_2\text{S}_6]^{6-}$  groups are nestled within the holes present in layer 2 of the Mg–S layer, whereas the holes in layer 1 of the Li–S layer remain unoccupied. Each  $[\text{MgS}_6]$  corner shares six of its corners with three ethane-like  $[\text{Si}_2\text{S}_6]^{6-}$  units, and the orientation of Si–Si bonds is perpendicular to the  $[\text{MgS}_6]$  layers.

The optical  $E_g$  values of  $\text{Li}_2\text{Mg}_2\text{Si}_2\text{S}_6$  and  $\text{Li}_2\text{Mg}_2\text{Ge}_2\text{S}_6$  have been estimated through optical diffuse reflectance spectra, which are 3.24 eV and 3.18 eV, respectively. These compounds exhibit moderate  $d_{\text{eff}}$  of approximately  $0.24 \times \text{KDP}$  and  $2.9 \times \alpha\text{-SiO}_2$  for  $\text{Li}_2\text{Mg}_2\text{Si}_2\text{S}_6$ , and  $0.17 \times \text{KDP}$  and  $2.1 \times \alpha\text{-SiO}_2$  for  $\text{Li}_2\text{Mg}_2\text{Ge}_2\text{S}_6$  when exposed to a Nd:YAG laser at 1064 nm.

The theoretical calculation results indicate that the atomic orbitals of Li and Mg atoms do not significantly contribute to the state near the valence band maximum. This finding is significant due to their positive electrical properties and the potential interaction with the primary sulfur ions.

**2.2.3  $\text{AEMg}_6\text{Ga}_6\text{S}_{16}$  ( $\text{AE} = \text{Ca, Sr, Ba}$ ).** The first examples of a double alkaline-earth metal chalcogenide,  $\text{AEMg}_6\text{Ga}_6\text{S}_{16}$  ( $\text{AE} = \text{Ca, Sr, Ba}$ ), were successfully discovered by Yu's group in 2022.<sup>88</sup> Millimeter-level pale-yellow crystals of  $\text{AEMg}_6\text{Ga}_6\text{S}_{16}$  were prepared by the solid-state method in sealed silica tubes using the starting materials  $\text{MgS}$ ,  $\text{Ga}_2\text{S}_3$ , and  $\text{AES}$  in the molar ratio 1.22 : 0.6 : 0.21 at 1323 K.

As a representative,  $\text{SrMg}_6\text{Ga}_6\text{S}_{16}$  (space group:  $P\bar{6}$ ) is adopted to describe the structure. In this structure, octahedral  $[\text{MgS}_6]$  ABUs share both corners and faces to form  $[\text{Mg}_3\text{S}_{14}]$  trimers, while tetrahedral  $[\text{GaS}_4]$  ABUs interconnect through vertex-sharing to create two distinct kinds of 1D Ga–S chains along the  $c$  direction, namely,  $[\text{Ga}(1)\text{S}_3]_\infty$  single chains (Fig. 6a) and  $[\text{Ga}(2,3)_2\text{S}_4]_\infty$  double chains (Fig. 6b). Then, these  $[\text{Mg}_3\text{S}_{14}]$





**Fig. 6** (a) Coordination environment of  $[\text{Mg}_3\text{Si}_{14}]$  trimers and 1D  $[\text{Ga}(1)\text{S}_3]$  chain; (b) 1D  $[\text{Ga}(2,3)_2\text{S}_4]$  chain; (c) 3D  $[(\text{Mg}/\text{Ga})\text{S}]_\infty$  framework and (d) crystal structure of  $\text{SrMg}_6\text{Ga}_6\text{S}_{16}$  viewed along the  $ab$  plane. Copyright 2022 Wiley.

trimers connect through vertex-sharing (in the  $a$ - $b$  plane) and edge-sharing (along the  $c$ -axis) with two types of 1D Ga-S chains to form a 3D open  $[\text{Mg}_6\text{Ga}_6\text{S}_{16}]^{2-}$  framework (Fig. 6c). Finally, charge-balancing Sr atoms are introduced to fill the channels of this framework (Fig. 6d).

The obtained chalcogenides melt congruently and are stable in both air and water, which facilitates the growth of single crystals. Performance characterization demonstrates that they can achieve a well-balanced combination of large phase-matching  $d_{\text{eff}}$  (ca.  $0.7$ – $0.8 \times \text{AgGaS}_2$  at  $2090$  nm, granularity range  $180$ – $250$   $\mu\text{m}$ ), wide  $E_g$  ( $3.50$ – $3.54$  eV), high LIDTs (ca.  $11 \times \text{AgGaS}_2$  at  $1064$  nm), and broad IR transparent windows ( $0.35$ – $20$   $\mu\text{m}$ ), which suggests that  $\text{AEMg}_6\text{Ga}_6\text{S}_{16}$  are potential IR-NLO candidates. Upon further studying the structure–property relationships, it has been shown that the excellent NLO properties of the material predominantly arise from the combined contribution of the polarizable  $[\text{GaS}_4]$  and  $[\text{MgS}_6]$  ABUs in the 3D open  $[\text{Mg}_6\text{Ga}_6\text{S}_{16}]^{2-}$  framework. These findings offer a brand-new family for developing IR-NLO candidates with stable framework structures and excellent properties.

**2.2.4  $\text{RE}_6\text{MgSi}_2\text{S}_{14}$  (RE = Y, La–Nd, Sm, and Gd–Er).**  $\text{RE}_6\text{MgSi}_2\text{S}_7$  (RE = Y, La–Nd, Sm, and Gd–Er) with a NCS  $P6_3$

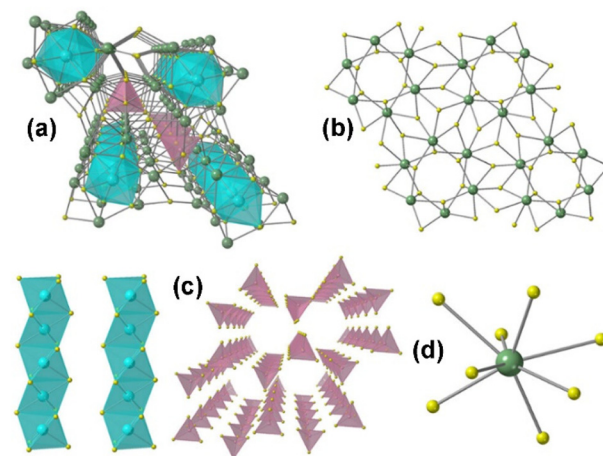
space group were systematically researched by zur Loye's group in 2023.<sup>89</sup> With the exception of  $\text{La}_6\text{MgSi}_2\text{S}_7$ ,<sup>98</sup> these compounds were all discovered for the first time. These compounds were synthesized by the flux method and crystallized by combining the boron chalcogen mixture method<sup>99</sup> and the molten flux method.

The crystal structure of  $\text{RE}_3\text{Mg}_{0.5}\text{Si}_7$  contains three types of polyhedral:  $[\text{MgS}_6]$ ,  $[\text{SiS}_4]$ , and  $[\text{RES}_8]$ . The 3D structure (Fig. 7a) is constructed from bi-capped trigonal prisms of  $[\text{RES}_8]$ , which are shared at the edges and corners to produce a ring-shaped arrangement (Fig. 7b). Isolated  $[\text{SiS}_4]$  tetrahedra (Fig. 7c) are distributed throughout the structure, positioned between the ring-shaped  $[\text{RES}_8]$  assemblies (Fig. 7d). Furthermore, face-sharing  $[\text{MgS}_6]$  octahedra are situated centrally within each ring arrangement and interact with their neighbouring assemblies.

The experimental values for  $\text{RE}_3\text{Mg}_{0.5}\text{Si}_7$  are an  $E_g$  of  $2.77$  eV and an approximate  $d_{\text{eff}}$  of  $0.16 \times \text{KDP}$  at a wavelength of  $1064$  nm. However, the SHG activity was not tested in any other samples due to difficulties in measuring it arising from crystal colouration in other compositions.

**2.2.5  $\text{Li}_2\text{MgM}^{\text{IV}}\text{Se}_4$  ( $\text{M}^{\text{IV}} = \text{Ge}, \text{Sn}$ ).** Two new diamond-like chalcogenides with the formula of  $\text{Li}_2\text{MgM}^{\text{IV}}\text{Se}_4$  ( $\text{M}^{\text{IV}} = \text{Ge}, \text{Sn}$ ) have been reported by Pan and co-workers in 2021.<sup>90</sup> Both of them adopt the NCS space group of  $Pmn2_1$  and were synthesized by direct combination of the stoichiometric elements at  $1153$  K. As depicted in Fig. 8, all of the ions within the structures occupy general sites and exhibit tetrahedral coordination models. The 3D diamond-like framework of  $\text{Li}_2\text{MgM}^{\text{IV}}\text{Se}_4$  is formed by tetrahedral  $[(\text{Li}/\text{Mg})\text{Se}_4]$   $[\text{LiSe}_4]$  and  $[\text{M}^{\text{IV}}\text{Se}_4]$  ABUs through corner-sharing Se atoms (Fig. 8a and c). For both compounds, there are similar channel-like structures with a channel diameter of approximately  $6$  Å on the  $ab$  direction, as given in Fig. 8b and d.

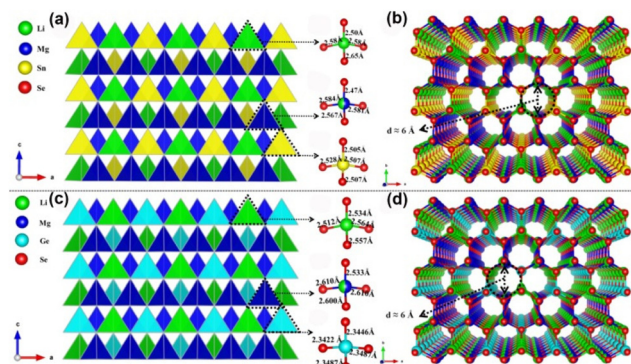
The calculated results suggest that the  $d_{33}$  of  $\text{Li}_2\text{MgSnSe}_4$  and  $\text{Li}_2\text{MgGeSe}_4$  are  $12.19$  and  $14.77$  pm  $\text{V}^{-1}$ , respectively,



**Fig. 7** (a) Crystal structure of  $\text{RE}_6\text{MgSi}_2\text{S}_{14}$  from the  $c$ -axis; coordination environment of (b) 3D RE-S network, (c) 1D chains of face-sharing  $[\text{MgS}_6]$  octahedra (left) and isolated  $[\text{GeS}_4]$  tetrahedra (right), and (d)  $[\text{RES}_8]$  polyhedron. Copyright 2023 American Chemistry Society.







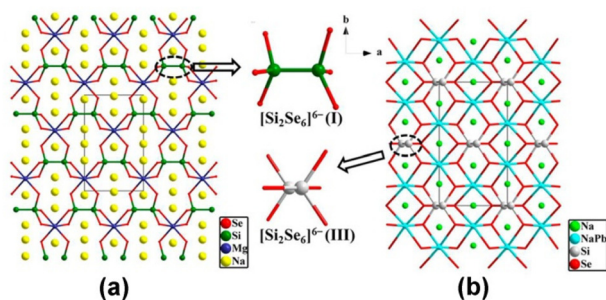
**Fig. 8** Crystal structure of  $\text{Li}_2\text{MgM}^{\text{IV}}\text{Se}_4$  ( $\text{M}^{\text{IV}} = \text{Ge}, \text{Sn}$ ): (a and c) 3D diamond-like structures viewed along the  $c$  direction; (b and d) 3D channel-like structures viewed along the  $ab$  plane.

which primarily stem from the tetrahedral  $[\text{M}^{\text{IV}}\text{Se}_4]$  ABUs and are comparable to that of the widely accepted reference material  $\text{AgGaS}_2$  ( $d_{14} = 13.7 \text{ pm V}^{-1}$ ). The calculated  $E_g$  for  $\text{Li}_2\text{MgSnSe}_4$  and  $\text{Li}_2\text{MgGeSe}_4$  was 2.42 and 2.44 eV, correspondingly. Notably, these two selenides represent the first series in the  $\text{M}_2^{\text{I}}\text{--M}^{\text{II}}\text{--M}^{\text{IV}}\text{--Q}_4$  system to feature alkali and alkaline-earth metals, thereby expanding the variety of structures found among diamond-like chalcogenides.

**2.2.6  $\text{Na}_4\text{MgM}^{\text{III}}\text{Se}_6$  ( $\text{M}^{\text{III}} = \text{Si}, \text{Ge}$ ).**  $\text{Na}_4\text{MgM}^{\text{III}}\text{Se}_6$  ( $\text{M}^{\text{III}} = \text{Si}, \text{Ge}$ ), with a  $C2$  non-centrosymmetric space group, were first reported by Pan's group in 2015.<sup>91</sup> They were discovered using traditional solid-state reactions with reaction materials Na, Mg,  $\text{M}^{\text{III}}$ , Ge in a molar ratio of 4:1:2:6 at 973 K (for  $\text{Na}_4\text{MgSi}_2\text{Se}_6$ ) and 873 K (for  $\text{Na}_4\text{MgGe}_2\text{Se}_6$ ).

Due to their similar structures,  $\text{Na}_4\text{MgSi}_2\text{Se}_6$  has been chosen as the representative. The Mg atoms are coordinated with six Se atoms to generate octahedral  $[\text{MgSe}_6]$  ABUs, which are then connected with  $[\text{Si}_2\text{Se}_6]$  ABUs to build a 2D layered structure. Finally, charge-balancing  $\text{Na}^+$  cations fill the channels and interlayer spaces to further form a 3D framework (Fig. 9a). When compared to the formerly reported  $\text{Na}_8\text{Pb}_2(\text{Si}_2\text{Se}_6)_2$  (Fig. 9b),<sup>100</sup> which also owns the same ethane-like  $[\text{Si}_2\text{Se}_6]$  dimers, a significant difference occurs in their different space groups ( $C2/m$  vs.  $C2$ ).

Significantly, they display high power LIDTs of 9 and 7 times that of  $\text{AgGaS}_2$ , moderate phase-matching  $d_{\text{eff}}$  of 0.5 and



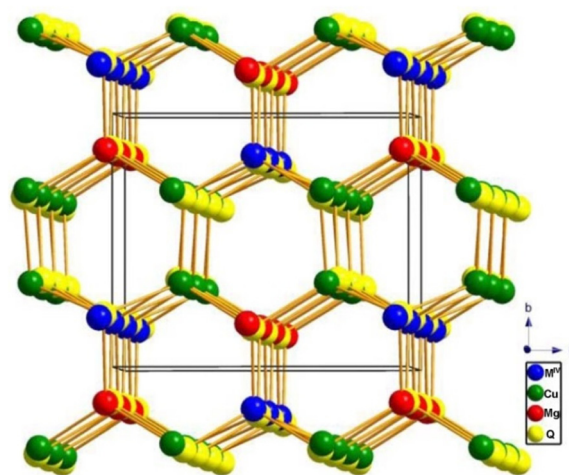
**Fig. 9** Crystal structures of (a)  $\text{Na}_4\text{MgSi}_2\text{Se}_6$  and (b)  $\text{Na}_8\text{Pb}_2(\text{Si}_2\text{Se}_6)_2$  viewed along the  $ab$  plane. Copyright 2015 American Chemistry Society.

1.3 times that of  $\text{AgGaS}_2$  within the particle size range of 150–200  $\mu\text{m}$ , and wide IR transmission windows of 0.45–20  $\mu\text{m}$ . These properties could potentially remove the key drawbacks, such as small LIDTs and harmful TPA, observed in commercially available IR-NLO crystals. Based on the calculation results, that calculated  $\Delta n$  values are close to 0.10 for  $\text{Na}_4\text{MgM}^{\text{III}}\text{Se}_6$  at the wavelength of 1064 nm and the charge transitions from Se 4p,  $\text{M}^{\text{III}}$  3p/4p and Mg 2p play the important role for  $d_{\text{eff}}$ .

**2.2.7  $\text{Cu}_2\text{MgM}^{\text{IV}}\text{Q}_4$  ( $\text{M}^{\text{IV}} = \text{Si}, \text{Ge}$ ;  $\text{Q} = \text{S}, \text{Se}$ ).** Three new diamond-like chalcogenides with the formula  $\text{Cu}_2\text{MgM}^{\text{IV}}\text{Q}_4$  ( $\text{M}^{\text{IV}} = \text{Si}, \text{Ge}$ ;  $\text{Q} = \text{S}, \text{Se}$ ) have been obtained by the traditional high-temperature solid-state method by Guo and co-workers in 2013.<sup>92</sup> All of them belong to the non-centrosymmetric space group of  $Pmn_21$  in the wurtzite-type superstructure and synthesized by direct combination of the stoichiometric elements at 1223 K. As depicted in Fig. 10, all of the ions within the structures occupy general sites and exhibit tetrahedral coordination models. Each  $\text{Q}^{2-}$  anion is tetrahedrally coordinated with one  $\text{Mg}^{2+}$  cation, one  $\text{M}^{4+}$  cation, and two  $\text{Cu}^+$  cations, resulting in a 3D honeycomb structure. The remarkable structural characteristic of  $\text{Cu}_2\text{MgM}^{\text{IV}}\text{Q}_4$  is the introduction of a tetrahedrally coordinated  $\text{Mg}^{2+}$  cation to the  $\text{M}^{\text{II}}$  sites of diamond-like chalcogenides with the formula  $\text{M}_2^{\text{I}}\text{--M}^{\text{II}}\text{--M}^{\text{IV}}\text{--Q}_4$  (where  $\text{M}^{\text{I}} = \text{group 11 metals and Li}$ ;  $\text{M}^{\text{II}} = \text{group 12 metals}$ ;  $\text{M}^{\text{IV}} = \text{group 14 metals}$ ;  $\text{Q} = \text{S}, \text{Se}$ ).

The experimental  $E_g$  were determined to be 3.20 and 2.36 eV for  $\text{Cu}_2\text{MgSiS}_4$  and  $\text{Cu}_2\text{MgGeS}_4$ , respectively. Although both of them belong to the non-centrosymmetric space group, no noticeable SHG response was observed when testing a modified /Kurtz-NLO system with 1064 and 2100 nm laser radiation.

**2.2.8  $\text{M}^{\text{I}}\text{Mg}_3\text{M}^{\text{III}}\text{Q}_8$  ( $\text{M}^{\text{I}} = \text{Na}, \text{Cu}, \text{Ag}$ ;  $\text{M}^{\text{III}} = \text{Al}, \text{Ga}$ ;  $\text{Q} = \text{S}, \text{Se}$ ).**  $\text{M}^{\text{I}}\text{Mg}_3\text{M}^{\text{III}}\text{Q}_8$  ( $\text{M}^{\text{I}} = \text{Na}, \text{Cu}, \text{Ag}$ ;  $\text{M}^{\text{III}} = \text{Al}, \text{Ga}$ ;  $\text{Q} = \text{S}, \text{Se}$ ) represents a newly discovered quaternary chalcogenide family within the  $\text{M}_2^{\text{I}}\text{Q--M}^{\text{II}}\text{Q--M}^{\text{III}}\text{Q}_3$  system. These 9 materials constitute the first series discovered in this family by Li and co-workers in 2022.<sup>93</sup> The  $\text{NaMg}_3\text{Ga}_3\text{Q}_8$ ,  $\text{NaMg}_3\text{Al}_3\text{Q}_8$  and



**Fig. 10** 3D diamond-like structure of  $\text{Cu}_2\text{MgM}^{\text{IV}}\text{Q}_4$  viewed slightly along the  $c$  direction. Copyright 2013 Elsevier.

$\text{CuMg}_3\text{Ga}_3\text{S}_8$  compounds were synthesized utilizing a flux method. The necessary initial reactant, Na/Cu, Mg, and Ga/Al, along with S/Se, were used in a molar ratio of 2 : 3 : 3 : 8. The synthesis process was carried out at a temperature of 1273 K. For the  $\text{AgMg}_3\text{Ga}_3\text{S}_8$  and  $\text{LiMg}_3\text{Ga}_3\text{S}_8$  compounds, the same method was applied; however,  $\text{Ga}_2\text{O}_3$  replaced Ga as the raw material.

Given that  $\text{M}^{\text{I}}\text{Mg}_3\text{M}_3^{\text{III}}\text{Q}_8$  adopt the same non-centrosymmetric  $P\bar{6}$  space group and exhibit similar structural features,  $\text{AgMg}_3\text{Ga}_3\text{S}_8$  has been chosen as the representative. The S atoms are coordinated with Mg, Ga and Ag atoms to form octahedral  $[\text{MgS}_6]$ , tetrahedral  $[\text{GaS}_4]$  and triangle-planar  $[\text{AgS}_3]$  ABUs (Fig. 11a). Interestingly, diverse connection modes such as vertex-, edge-, and face-sharing between these ABUs can be found in this structure. For example,  $[\text{GaS}_4]$  ABUs interconnect to form 1D  $[\text{GaS}_4]_\infty$  and  $[\text{Ga}_2\text{S}_7]_\infty$  via corner-sharing. Meanwhile,  $[\text{MgS}_6]$  ABUs connect together to construct 1D  $[\text{MgS}_6]_\infty$  and  $[\text{Mg}_2\text{S}_9]_\infty$  chains via edge- or/and face-sharing

(Fig. 11b). Moreover, the resulting 1D  $[\text{GaS}_4]_\infty$  and  $[\text{MgS}_6]_\infty$  chains arrange alternately by vertex-sharing, creating a distinctive windmill-like  $[\text{Mg}_3\text{Ga}_3\text{S}_{24}]$  unit (Fig. 11c). Finally, the  $[\text{Mg}_3\text{Ga}_3\text{S}_{24}]$  units are linked by the 1D  $[\text{Ga}_2\text{S}_7]_\infty$  and  $[\text{Mg}_2\text{S}_9]_\infty$  chains, and the Ag atoms are positioned in the interior of the  $[\text{Mg}_3\text{Ga}_3\text{S}_{24}]$  channels, forming the 3D framework of  $\text{AgMg}_3\text{Ga}_3\text{S}_8$  (Fig. 11d). Compared to the  $[\text{Ga}_6\text{S}_{18}]$  unit in  $\text{AgGaS}_2$ , the  $[\text{Mg}_3\text{Ga}_3\text{S}_{24}]$  unit is formed by replacing three *meta*-position  $[\text{GaS}_4]$  ABUs with three  $[\text{MgS}_6]$  ABUs (Fig. 11d).

The experimental results suggest that  $\text{NaMg}_3\text{Ga}_3\text{S}_8$  has potential as an IR-NLO candidate due to its sufficient  $d_{\text{eff}}$  ( $\sim 1 \times \text{AgGaS}_2 @ 180\text{--}212 \mu\text{m}$ ), wide selenide  $E_g$  (2.77 eV), suitable  $\Delta n$  (0.079@546 nm), and large LIDT ( $\sim 2.3 \times \text{AgGaS}_2$ ). Moreover, the SHG-density maps indicate that the large  $d_{\text{eff}}$  in  $\text{NaMg}_3\text{Ga}_3\text{S}_8$  is mainly provided by the NLO-active  $[\text{GaSe}_4]$  ABUs. Besides, the optical and NLO parameters of other compounds are presented in Table 1.

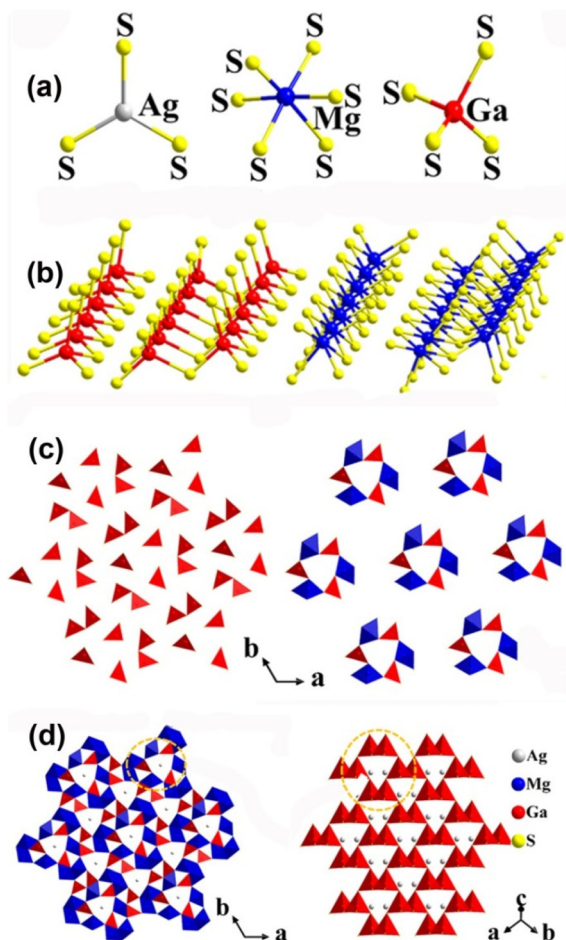
**2.2.9  $\text{Mg}_2\text{In}_3\text{Si}_2\text{P}_7$ .** By implementing a “rigidity-flexibility coupling” approach, a quaternary Mg-based phosphide  $\text{Mg}_2\text{In}_3\text{Si}_2\text{P}_7$  was successfully discovered by Ye’s group in 2021.<sup>94</sup> Millimeter-level red crystals of  $\text{Mg}_2\text{In}_3\text{Si}_2\text{P}_7$  ( $2.5 \times 1.5 \times 0.5 \text{ mm}^3$ ) were obtained by the solid-state method in sealed silica tubes using the starting materials of Mg, In, Si, P and flux  $\text{BaBr}_2$  in the molar ratio of 1.33 : 1.5 : 1 : 3.5 : 2.67 at 1073 K.

The  $\text{Mg}_2\text{In}_3\text{Si}_2\text{P}_7$  crystal structure displays a diamond-like pattern, which is created by the vertex-sharing  $[(\text{Mg}/\text{In})\text{P}_4]$ ,  $[(\text{In}/\text{Si})\text{P}_4]$  and  $[\text{SiP}_4]$  ABUs (Fig. 12a). The tetrahedral  $[\text{SiP}_4]$  ABUs are integrated into the 12-MR rings of  $[(\text{Mg}/\text{In})_6\text{P}_6]$ , thereby generating 1D  $[(\text{Mg}/\text{In})_6\text{SiP}_{16}]_\infty$  chains (Fig. 12a), and the tetrahedral  $[(\text{In}/\text{Si})\text{P}_4]$  ABUs interlink through corner-sharing and form zigzag 1D  $[(\text{In}/\text{Si})\text{P}_3]_\infty$  chains. These two kinds of 1D chains are interconnected to build 2D layers (Fig. 12b), which are arranged in an *ABAB* fashion, giving rise to a 3D polar structure (Fig. 12a). Additionally,  $\text{Mg}_2\text{In}_3\text{Si}_2\text{P}_7$  exhibits a hexagonal close-packed structure that closely resembles wurtzite (Fig. 12c), which was confirmed by the experimental results of the selected area electron diffraction patterns (Fig. 12d).

Noticeably,  $\text{Mg}_2\text{In}_3\text{Si}_2\text{P}_7$  has achieved rare coexistence of huge  $d_{\text{eff}}$  ( $2 \times \text{ZnGeP}_2$  and  $7.1 \times \text{AgGaS}_2$ , granularity range 150–212  $\mu\text{m}$ ), a sufficient  $E_g$  of 2.21 eV, a large  $\Delta n$  of 0.107, and a wide IR transparent window of 0.56–16.4  $\mu\text{m}$ . Theoretical calculations have revealed that the colossal  $d_{\text{eff}}$  and large  $\Delta n$  can be attributed to the favorable arrangement of tetrahedral  $[\text{InP}_4]$  and  $[\text{SiP}_4]$  ABUs. These findings not only open up a new route for sophisticated IR-NLO crystal design but also have the potential to inspire more discoveries in the quaternary diamond-like families.

## 2.3 Quinary Mg-based chalcogenides

**2.3.1  $\text{Ba}_6\text{Cu}_{1.9}\text{Mg}_{1.1}\text{Ge}_4\text{S}_{16}$  and  $\text{Ba}_6\text{Cu}_{1.94}\text{Mg}_{1.06}\text{Sn}_4\text{S}_{16}$ .**  $\text{Ba}_6\text{Cu}_{1.9}\text{Mg}_{1.1}\text{Ge}_4\text{S}_{16}$  and  $\text{Ba}_6\text{Cu}_{1.94}\text{Mg}_{1.06}\text{Sn}_4\text{S}_{16}$  were reported by Wang’s group in 2021 and 2022, respectively.<sup>95,96</sup> Both of them can be obtained through the traditional high-temperature solid-state method using the stoichiometric amounts of the reagents at 1073 K, with the difference being that the



**Fig. 11** (a) Coordinated environment of  $[\text{AgS}_3]$ ,  $[\text{MgS}_6]$ , and  $[\text{GaS}_4]$  atoms; (b) 1D  $[\text{GaS}_4]$ ,  $[\text{Ga}_2\text{S}_7]$ ,  $[\text{MgS}_6]$ , and  $[\text{Mg}_2\text{S}_9]$  chains; (c) 1D Ga–S chains and  $[\text{Mg}_3\text{Ga}_3\text{S}_{24}]$  groups viewed along the *ab* plane; (d) 3D structure of  $\text{AgMg}_3\text{Ga}_3\text{S}_8$  (left) and  $\text{AgGaS}_2$  (right) with the  $[\text{Ga}_6\text{S}_{18}]$  units marked (yellow dashed circle). Copyright 2022 American Chemistry Society.



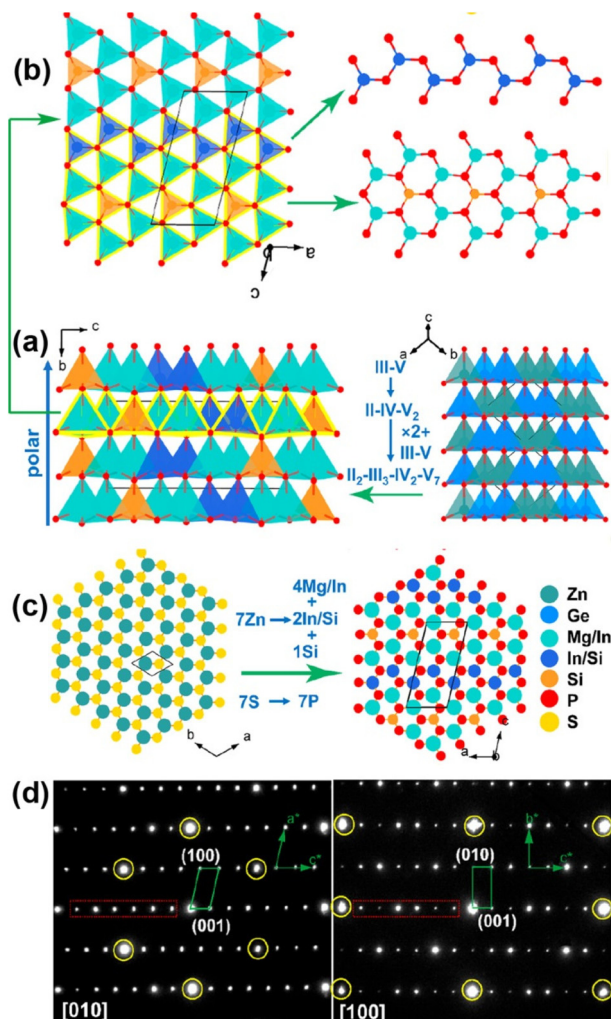
Table 1 A summary of reported Mg-based IR-NLO materials

Compound	Mg polyhedron	Unit cell	Space group	$E_g^a$ (eV)	Window of transparency ( $\mu\text{m}$ )	$d_{\text{eff}}^b$	LIDT <sup>b</sup>	$\Delta n^c$	PM/NPM <sup>d</sup>	Ref.
MgGa <sub>3</sub> Se <sub>4</sub>	MgSe <sub>4</sub>	Tetragonal	$\bar{I}4$	2.96	1.35–12.43	$0.9 \times \text{AgGaS}_2$ (@2.09 $\mu\text{m}$ )	$3.0 \times \text{AgGaS}_2$	0.048 (@0.55 $\mu\text{m}$ )	PM	82
MgSiP <sub>2</sub>	MgP <sub>4</sub>	Tetragonal	$\bar{I}42d$	2.34	0.53–10.3	$3.5 \times \text{AgGaS}_2$ (@2.05 $\mu\text{m}$ )	N/A <sup>e</sup>	N/A	PM	84
MgSiAs <sub>2</sub>	MgAs <sub>4</sub>	Tetragonal	$\bar{I}42d$	1.83	N/A	$0.6 \times \text{AgGaS}_2$ (@2.09 $\mu\text{m}$ )	$1.12 \times \text{AgGaS}_2$	N/A	PM	85
Li <sub>4</sub> MgGe <sub>2</sub> S <sub>7</sub>	MgS <sub>4</sub>	Monoclinic	$Cc$	4.12	N/A	$0.7 \times \text{AgGaS}_2$ (@2.09 $\mu\text{m}$ )	$7.0 \times \text{AgGaS}_2$	0.035 (@1.06 $\mu\text{m}$ ) (exp.)	PM	86
Li <sub>2</sub> Mg <sub>2</sub> Si <sub>2</sub> S <sub>6</sub>	MgS <sub>6</sub>	Trigonal	$P31m$	3.24	N/A	$0.3 \times \text{KDP}$ (@1.06 $\mu\text{m}$ )	$\text{AgGaS}_2$	N/A	N/A	87
Li <sub>2</sub> Mg <sub>2</sub> Ge <sub>2</sub> S <sub>6</sub>	MgS <sub>6</sub>	Trigonal	$P31m$	3.18	N/A	$0.2 \times \text{KDP}$ (@1.06 $\mu\text{m}$ )	N/A	N/A	N/A	87
CaMg <sub>6</sub> Ga <sub>8</sub> S <sub>16</sub>	MgS <sub>6</sub>	Hexagonal	$P6$	3.54	0.35–20	$0.7 \times \text{AgGaS}_2$ (@2.09 $\mu\text{m}$ )	$11.7 \times \text{AgGaS}_2$	0.046 (@1.06 $\mu\text{m}$ ) (exp.)	PM	88
SrMg <sub>6</sub> Ga <sub>6</sub> S <sub>16</sub>	MgS <sub>6</sub>	Hexagonal	$P6$	3.51	0.35–20	$0.7 \times \text{AgGaS}_2$ (@2.09 $\mu\text{m}$ )	$11.5 \times \text{AgGaS}_2$	0.042 (@1.06 $\mu\text{m}$ ) (exp.)	PM	88
BaMg <sub>6</sub> Ga <sub>6</sub> S <sub>16</sub>	MgS <sub>6</sub>	Hexagonal	$P6$	3.50	0.35–20	$0.7 \times \text{AgGaS}_2$ (@2.09 $\mu\text{m}$ )	$11.5 \times \text{AgGaS}_2$	0.041 (@1.06 $\mu\text{m}$ ) (exp.)	PM	88
Gd <sub>6</sub> MgGe <sub>2</sub> S <sub>14</sub>	MgS <sub>6</sub>	Hexagonal	$P6_3$	2.77	N/A	$0.2 \times \text{KDP}$ (@1.06 $\mu\text{m}$ )	$\text{AgGaS}_2$	N/A	N/A	89
Li <sub>2</sub> MgGeSe <sub>4</sub>	(Li/Mg)Se <sub>4</sub>	Orthorhombic	$Pmn2_1$	2.44 (cal.)	N/A	$d_{33} = 12.19 \text{ pm V}^{-1}$ (cal.)	N/A	0.012 (@1.06 $\mu\text{m}$ )	N/A	90
Li <sub>2</sub> MgSnSe <sub>4</sub>	(Li/Mg)Se <sub>4</sub>	Orthorhombic	$Pmn2_1$	2.62	N/A	$d_{33} = 14.77 \text{ pm V}^{-1}$ (cal.)	N/A	0.011 (@1.06 $\mu\text{m}$ )	N/A	90
Na <sub>4</sub> MgSi <sub>2</sub> Se <sub>6</sub>	MgSe <sub>6</sub>	Monoclinic	$C2$	2.53	0.45–20	$0.5 \times \text{AgGaS}_2$ (@2.09 $\mu\text{m}$ )	$9.0 \times \text{AgGaS}_2$	0.100 (@1 $\mu\text{m}$ )	PM	91
Na <sub>4</sub> MgGe <sub>2</sub> Se <sub>6</sub>	MgSe <sub>6</sub>	Monoclinic	$C2$	2.85	0.45–20	$1.3 \times \text{AgGaS}_2$ (@2.09 $\mu\text{m}$ )	$7.0 \times \text{AgGaS}_2$	0.092 (@1 $\mu\text{m}$ )	PM	91
AgMg <sub>3</sub> Ga <sub>3</sub> S <sub>8</sub>	MgS <sub>6</sub>	Hexagonal	$P6$	3.59	N/A	$d_{11} = 3.74 \text{ pm V}^{-1}$ (cal.)	N/A	0.091 (@1.06 $\mu\text{m}$ )	N/A	93
AgMg <sub>3</sub> Ga <sub>3</sub> Se <sub>8</sub>	MgS <sub>6</sub>	Hexagonal	$P6$	2.43 (cal.)	N/A	$d_{11} = 10.2 \text{ pm V}^{-1}$ (cal.)	N/A	0.17 (@1.06 $\mu\text{m}$ )	N/A	93
NaMg <sub>3</sub> Ga <sub>3</sub> S <sub>8</sub>	MgS <sub>6</sub>	Hexagonal	$P6$	3.70	N/A	$d_{11} = 3.24 \text{ pm V}^{-1}$ (cal.)	N/A	0.030 (@1.06 $\mu\text{m}$ )	N/A	93
NaMg <sub>3</sub> Ga <sub>3</sub> Se <sub>8</sub>	MgSe <sub>6</sub>	Hexagonal	$P6$	2.77	N/A	$1.0 \times \text{AGS}$ (@2.09 $\mu\text{m}$ )	$2.3 \times \text{AgGaS}_2$	0.079 (@0.55 $\mu\text{m}$ ) (exp.)	PM	93
NaMg <sub>3</sub> Al <sub>3</sub> S <sub>8</sub>	MgS <sub>6</sub>	Hexagonal	$P6$	4.20	N/A	$d_{11} = 2.45 \text{ pm V}^{-1}$	N/A	0.010 (@1.06 $\mu\text{m}$ )	N/A	93
NaMg <sub>3</sub> Al <sub>3</sub> Se <sub>8</sub>	MgS <sub>6</sub>	Hexagonal	$P6$	3.72 (cal.)	N/A	$d_{11} = 3.93 \text{ pm V}^{-1}$	N/A	0.038 (@1.06 $\mu\text{m}$ )	N/A	93
Mg <sub>2</sub> In <sub>3</sub> Si <sub>2</sub> P <sub>7</sub>	(In/Mg)P <sub>4</sub>	Monoclinic	$P2_1$	2.21	0.56–16.4	$7.1 \times \text{AgGaS}_2$ (@2.05 $\mu\text{m}$ )	N/A	0.107 (@2.05 $\mu\text{m}$ )	PM	94
Ba <sub>6</sub> Cu <sub>1.9</sub> Mg <sub>1.1</sub> Ge <sub>4</sub> S <sub>16</sub>	(Cu/Mg)S <sub>4</sub>	Cubic	$I43d$	2.92	N/A	$2.3 \times \text{AgGaS}_2$ (@2.09 $\mu\text{m}$ )	$6.2 \times \text{AgGaS}_2$	N/A	NPM	95
Ba <sub>6</sub> Cu <sub>1.9</sub> Mg <sub>1.1</sub> Sn <sub>4</sub> S <sub>16</sub>	(Cu/Mg)S <sub>4</sub>	Cubic	$I43d$	2.4	N/A	$2.5 \times \text{AgGaS}_2$ (@2.09 $\mu\text{m}$ )	$2.5 \times \text{AgGaS}_2$	N/A	NPM	96

<sup>a</sup> Experimental value. <sup>b</sup> Powder sample. <sup>c</sup> Theoretical value. <sup>d</sup> PM = phase-matchability, NPM = nonphase-matchability. <sup>e</sup> N/A = not available.



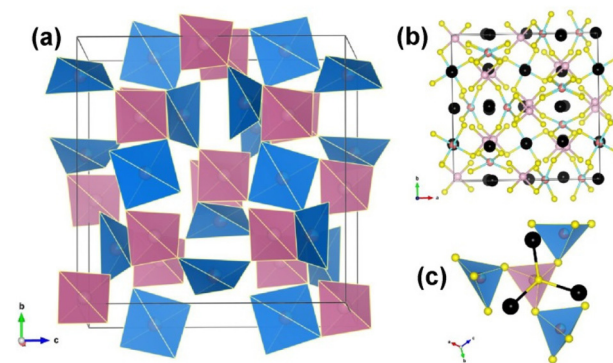




**Fig. 12** (a) Structural evolution from ZnGeP<sub>2</sub> (right) to Mg<sub>2</sub>In<sub>3</sub>Si<sub>2</sub>P<sub>7</sub> (left); (b) single 2D tetrahedral-stacking layer composed of 1D [(Mg/In)<sub>6</sub>SiP<sub>16</sub>] and [In/SiP<sub>3</sub>] chains in Mg<sub>2</sub>In<sub>3</sub>Si<sub>2</sub>P<sub>7</sub>. (c) Structural evolution from wurtzite ZnS (left) to Mg<sub>2</sub>In<sub>3</sub>Si<sub>2</sub>P<sub>7</sub> (right); (d) electron diffraction patterns of Mg<sub>2</sub>In<sub>3</sub>Si<sub>2</sub>P<sub>7</sub> along the [010] and [100] zone axes. Copyright 2021 American Chemistry Society.

former requires the use of KI salt as the flux, while the latter does not.

Ba<sub>6</sub>Cu<sub>1.9</sub>Mg<sub>1.1</sub>Ge<sub>4</sub>S<sub>16</sub> and Ba<sub>6</sub>Cu<sub>1.94</sub>Mg<sub>1.06</sub>Sn<sub>4</sub>S<sub>16</sub> are both members of the M<sup>II</sup><sub>6</sub>M<sup>I</sup><sub>4</sub>M<sup>IV</sup><sub>4</sub>Q<sub>16</sub> (M<sup>II</sup> = Sr, Ba; M<sup>I</sup> = Li, Cu, Ag; M<sup>IV</sup> = Ge, Sn; Ch = S, Se) family.<sup>101,102</sup> These two compounds feature mixed locations at the Li/Cu/Ag atomic sites, where M<sup>I</sup> metals are replaced by M<sup>II</sup> metals. Since both compounds belong to the same non-centrosymmetric *I*43d space group and exhibit similar structural features, Ba<sub>6</sub>Cu<sub>1.9</sub>Mg<sub>1.1</sub>Ge<sub>4</sub>S<sub>16</sub> has been chosen as the representative. The 3D framework is formed by tetrahedral [(Cu/Mg)S<sub>4</sub>] and [GeS<sub>4</sub>] ABUs through corner-sharing S atoms, where the charge-balanced Ba<sup>2+</sup> packing in the empty spaces. The polyhedral and ball-stick modes of Ba<sub>6</sub>Cu<sub>1.9</sub>Mg<sub>1.1</sub>Ge<sub>4</sub>S<sub>16</sub> are displayed in Fig. 13a and b, respectively. Besides, the coordination environment between the tetrahedral [(Cu/Mg)S<sub>4</sub>] and [GeS<sub>4</sub>] ABUs is highlighted in Fig. 13c.



**Fig. 13** Crystal structural of Ba<sub>6</sub>Cu<sub>1.9</sub>Mg<sub>1.1</sub>Sn<sub>4</sub>S<sub>16</sub>: (a) polyhedral packing model; (b) ball-and-stick model; (c) coordination environment of [(Cu/Mg)S<sub>4</sub>] (pink) and [SnS<sub>4</sub>] (blue) tetrahedra. Black: Ba; red: Mg; blue: Cu; pink: Sn; yellow: S. Copyright 2021 American Chemistry Society.

The experimental  $E_g$  was determined to be 2.92 and 2.24 eV for Ba<sub>6</sub>Cu<sub>1.9</sub>Mg<sub>1.1</sub>Ge<sub>4</sub>S<sub>16</sub> and Ba<sub>6</sub>Cu<sub>1.94</sub>Mg<sub>1.06</sub>Sn<sub>4</sub>S<sub>16</sub>, respectively. Through the placement of monovalent Cu<sup>+</sup> with divalent Mg<sup>2+</sup>, the optical properties can be shifted to promote a good balance between  $d_{\text{eff}}$  and LIDT. For instance, Ba<sub>6</sub>Cu<sub>1.9</sub>Mg<sub>1.1</sub>Ge<sub>4</sub>S<sub>16</sub> possesses a strong non-phase-matching  $d_{\text{eff}}$  and a high LIDT of  $2.3 \times \text{AgGaS}_2$  and  $6.2 \times \text{AgGaS}_2$  within the particle size range of 28–55  $\mu\text{m}$ , respectively. Theoretical calculations confirmed that the [(Cu/Mg)S<sub>4</sub>] and [GeS<sub>4</sub>] ABUs are the major role of the SHG responses.



**Fig. 14** Distributions of the Mg-based IR-NLO materials according to (a) material type, (b) chemical component and (c) the space groups in different crystal systems.



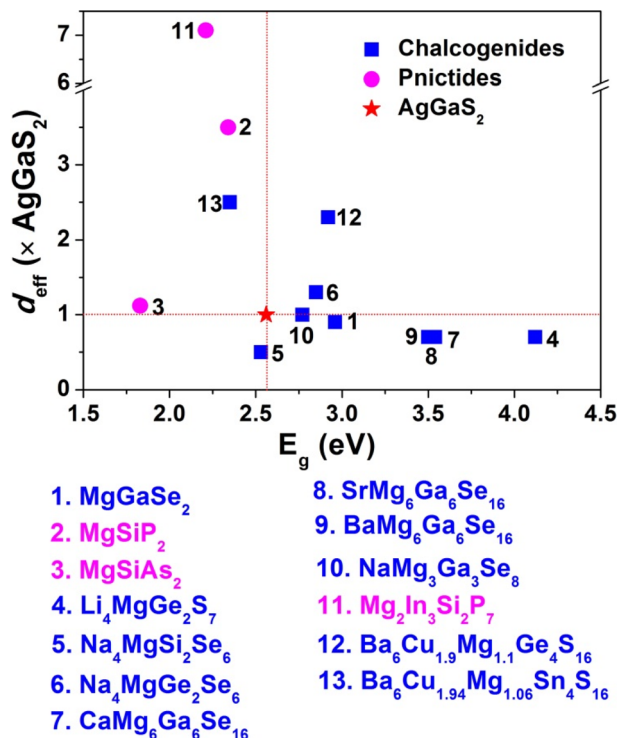


Fig. 15 Comparison of the  $d_{eff}$  ( $\times$  AGS) and  $E_g$  (eV) for selected Mg-based materials with IR NLO properties.

### 3. Conclusions and perspectives

Research interest in new IR-NLO candidates has stimulated the rapid development of new NCS Mg-based chalcogenides and pnictides. In this review, we presented a brief introduction to the solid-state synthesis, structural design, and NLO properties together with the structure–property relationship of the recently reported Mg-based IR-NLO materials. The distribution of  $E_g$  (eV) in relation to  $d_{eff}$  ( $\times$  AgGaS<sub>2</sub>) and detailed performance comparison for previously reported Mg-based IR-NLO materials are illustrated in Fig. 14, 15 and Table 1, respectively. From this, certain characteristics can be inferred:

(i) The currently reported Mg-based IR-NLO materials (including 36 chalcogenides and 4 pnictides) are mainly quaternary compounds (87.5%), with a small amount of ternary (7.5%) and pentagonal (5%) compounds (Fig. 14a and b). Moreover, they mainly belong to the highly symmetrical crystal systems, such as the hexagonal space group of  $P6_3$  (27.5%) and  $P\bar{6}$  (30%) (Fig. 14c).

(ii) The Mg-based compounds mentioned above are synthesized using traditional high-temperature solid-state methods. Some of them require the use of fluxes to assist in the reaction, including Bi, NaCl, NaI, KI, CsCl, CaCl<sub>2</sub>, BaCl<sub>2</sub>, and BaBr<sub>2</sub>. Furthermore, it is worth noting the synthesis of RE<sub>6</sub>MgSi<sub>2</sub>S<sub>14</sub>, which utilizes a boron chalcogen mixture method. It is anticipated that this method can be expanded to other chalcogenide systems, allowing for the exploration of further captivating physical properties.

(iii) As displayed in Fig. 15, most of them are stronger than commercial AgGaS<sub>2</sub> ( $E_g = 2.56$  eV and  $d_{eff} = 1 \times$  AgGaS<sub>2</sub>).

Remarkably, quaternary pnictide Mg<sub>2</sub>In<sub>3</sub>Si<sub>2</sub>P<sub>7</sub> exhibits the largest  $d_{eff}$  ( $7.1 \times$  AgGaS<sub>2</sub>) due to the most favorable combination and arrangement of ABUs, while NaMg<sub>3</sub>Al<sub>3</sub>S<sub>8</sub> possesses the widest  $E_g$  of 4.20 eV in this system.

(iv) Due to the incompatibility of optical parameters, there are currently no reports of IR-NLO Mg-based materials that can achieve a balance between large  $E_g$  ( $>3.0$  eV) and strong phase-matching  $d_{eff}$  ( $>1.0 \times$  AgGaS<sub>2</sub>).

Many distinguished researchers have made significant contributions in exploring and verifying the potential of Mg-based IR NLO materials. However, more research is required to fully uncover the potential of these materials. Some possible avenues for further progress are outlined below:

(1) The pnictide system shows promise for further exploration. However, only a few Mg-based pnictides have been reported, and their usability has been limited by their narrow  $E_g$ . To increase the  $E_g$ , an effective solution could be to introduce high electronegativity “structure scissors” ions, such as alkali metals, alkaline earth metals, and halogens.

(2) Efforts are underway to synthesize high-performance Mg-based IR-NLO compounds by combining other ABUs. Currently, distorted [MQ<sub>4</sub>] tetrahedra (M = group 13 and 14 metal elements) are the most commonly used second ABUs, but it would be worthwhile to experiment with introducing other ABUs, such as, lone-pair-cation-based [MQ<sub>n</sub>] ABUs, distorted [REQ<sub>n</sub>] ABUs, or mixed-anion [MO<sub>x</sub>Q<sub>y</sub>] ABUs.

(3) The theoretical calculation system for IR-NLO materials requires further study. Researchers can gain crucial properties through first-principles calculations, reducing the experimental blind spots and deepening the understanding of structure–activity relationships. Due to the development of anionic group theory in the research of oxide systems, there is still a significant difference between the calculation results and single crystal tests when applied to chalcogenides and pnictides. Therefore, there is an urgent need to establish a theoretical system that is suitable for IR-NLO materials.

(4) The study of large-sized crystal growth still requires further enhancement. After identifying crystals with exceptional properties, it is crucial for their scientific and technological development to investigate the possibility of growing them into large-sized crystals for commercial purposes.

### Author contributions

Jia-Xiang Zhang: investigation and writing – original draft. Mao-Yin Ran: investigation and formal analysis. Xin-Tao Wu: conceptualization and formal analysis. Hua Lin: supervision, conceptualization and writing – review and editing. Qi-Long Zhu: supervision and writing – review and editing.

### Conflicts of interest

There are no conflicts to declare.



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