Syntheses, Structures and Properties of Alkali and Alkaline Earth Metal Diamond-Like Compounds Li$_2$MgMSe$_4$ (M = Ge, Sn)

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1. Introduction

The exploration of advanced functional materials, as well as the development of structural chemistry, depends on the fabrication of new compounds with a special crystal structure, which contains distinctive physical and chemical behaviors [1–12]. A diamond-like (DL) structure compound, exhibiting abundant chemical diversities and adjustable optical properties, has been proven as a valid structural framework for the design and fabrication of new infrared (IR) optical materials, especially for the mid- or far-IR nonlinear optical (NLO) materials. Over the past few decades, a large number of non-centrosymmetric DL chalcogenide compounds, such as Li$_4$HgGe$_2$S$_7$ [13] and Li$_4$MgGe$_2$S$_7$ [14] in the I$_4$-II-IV-VI$_2$ family, and Li$_2$CdGeS$_4$ [15], Li$_2$CdGeSe$_4$ [16], Li$_2$ZnGeSe$_4$ [17] and Cu$_2$ZnSnS$_4$ [18] in the I$_2$-II-IV-VI$_3$ family, with outstanding optical properties, have been developed using an atomic substitution or co-substitution strategy.

In a DL compound, the cation is coordinated with four anions, and follows the Pauling’s electrostatic valency rule [19–23]. Hence, the optical properties including band gap and SHG response in the DL chalcogenide compounds could be effectively regulated by organizing proper tetrahedral units in the structure. On the basis of the statistical gap and SHG response in the DL chalcogenide compounds could be effectively regulated.
analyses, the DL chalcogenide compounds mainly consisted of univalent metal tetrahedral units, such as alkali metal tetrahedral LiQ\textsubscript{4} (Q = S, Se) and/or IB group metal tetrahedral M\textsuperscript{4}Q\textsubscript{4} (M\textsuperscript{4} = Cu, Ag; Q = S, Se), with IB (Zn, Cd and Hg), IIIA (Al, Ga and In), IVA (Si, Ge and Sn) and VA (P and As) group element tetrahedral units [24–27]. Most recently, Pan and Li et al. [14] demonstrated that the alkaline-earth metal AQ\textsubscript{4} (A = Be, Mg; Q = S, Se) tetrahedral units, which without \textit{d}-\textit{d} and \textit{f}-\textit{f} electronic transitions, can be used to regulate the optical properties of DL chalcogenide compounds. By introducing alkaline-earth metal tetrahedral unit Mg\textsubscript{4} into the I\textsubscript{2}-II-IV-\textit{V}\texttextsubscript{7} system, the first alkali and alkaline-earth metal DL sulfide Li\textsubscript{4}MgGe\textsubscript{3}S\textsubscript{7} with excellent IR NLO optical performances was discovered. However, owing to the experimental challenges to obtain the four-coordinated alkaline-earth metal AQ\textsubscript{4} tetrahedral units in a crystal structure, the number of reported alkaline-earth metal containing DL compounds is very limited, and the exploration of new IR NLO materials, especially with excellent optical properties in alkali and alkaline-earth metal DL chalcogenide compounds, is just in the initial stage.

Considering the above discussions, the alkali metal tetrahedral Li\textsubscript{4} and alkaline-earth metal tetrahedral MgSe\textsubscript{4} units were successfully introduced into the classical I\textsubscript{2}-II-IV-V\textsubscript{4} family in this work. Two new alkali and alkaline-earth metal DL selenides Li\textsubscript{2}MgMSe\textsubscript{4} (M = Ge, Sn) were synthesized by conventional high temperature solid state reactions in sealed quartz tubes. Li\textsubscript{2}MgMSe\textsubscript{4} (M = Ge, Sn) are isostructural compounds, crystallizing in the orthorhombic \textit{Pmmn} space group. The compounds exhibit a three dimensional channel structure, which is built by [LiSe\textsubscript{4}], [[Li/Mg]Se\textsubscript{4}] and [MSe\textsubscript{4}] (M = Ge, Sn) tetrahedral units.

The theoretical investigations show that the calculated band gap for the two compounds is 2.44 eV for Li\textsubscript{2}MgGeSe\textsubscript{4}, and 2.42 eV for Li\textsubscript{2}MgSnSe\textsubscript{4} (matched with the experimental value of 2.62 eV). The calculated SHG coefficients of the title compounds are \textit{d}_{33} = 12.19 pm/V for Li\textsubscript{2}MgSnSe\textsubscript{4} and \textit{d}_{33} = −14.77 pm/V for Li\textsubscript{2}MgGeSe\textsubscript{4}, which are close to the one in AgGa\textsubscript{2} (\textit{d}_{\text{AgGa}_{2}} = 13.7 pm/V) [28]. The SHG coefficients are mainly contributed by the MSe\textsubscript{4} (M = Ge, Sn) tetrahedral units. Meanwhile, the calculated birefringences are 0.011 for Li\textsubscript{2}MgSnSe\textsubscript{4} and 0.012 for Li\textsubscript{2}MgGeSe\textsubscript{4}.

2. Experimental Sections

2.1. Chemical Syntheses

High purity (99.99%) raw materials (Li, Mg, Sn, Ge and Se) were obtained from Aladdin Industrial Corporation (Fengxian District, Shanghai, China) and utilized without extra purification.

Li\textsubscript{2}MgMSe\textsubscript{4} (M = Ge, Sn) single crystals for structural determination were prepared using a melting method in sealed quartz tubes. The starting mixture samples (Li:Mg:Ge:Se = 2:1:1:4; Li:Mg:Sn:Se = 2:1:1:4) were packaged in graphite crucibles in a glove box. After that the samples were heated to 880 °C in 46 h, and kept at 880 °C for 50 h, then cooled to room temperature in 48 h. Breaking the tubes, the yellow Li\textsubscript{2}MgGeSe\textsubscript{4} and Li\textsubscript{2}MgSnSe\textsubscript{4} single crystals were harvested in the graphite crucibles. It is worth mentioning that the two crystals show strong moisture absorptions in air.

The syntheses of Li\textsubscript{2}MgMSe\textsubscript{4} (M = Ge, Sn) powder samples for performance characterization were tried at a higher temperature. The mixtures of Li, Mg, Ge/Sn and Se elements with an atomic stoichiometric ratio were first weighed, ground and sealed in quartz tubes. The sealed samples were slowly heated to 900 °C (in 60 h) in a muffle furnace, and kept at this temperature for 100 h, then cooled to room temperature in 100 h.

2.2. Single-Crystal X-ray Diffractions

Li\textsubscript{2}MgMSe\textsubscript{4} (M = Ge, Sn) single crystals were manually picked out and utilized for structural determinations. The X-ray diffraction data of Li\textsubscript{2}MgMSe\textsubscript{4} (M = Ge, Sn) single crystals were collected in a Bruker D8 Venture diffractometer that was equipped with monochromatic Mo-K\alpha radiation (\textit{λ} = 0.71073 Å) operating at 50 kV and 40 mA. The
structure refinements of the two compounds were carried out in the SHELX-97 crystallography software package. The XPREP program was used for the absorption correction (multiscan), the structures of Li$_2$MgMSe$_4$ (M = Sn, Ge) were checked by PLATON in case of additional symmetry elements [29–31]. It is worth noting that the initial Li/Mg occupation from refinement was 0.53715:0.462850 for Li$_2$MgSnSe$_4$, and 0.489330:0.51067 for Li$_2$MgGeSe$_4$, which is close to 1:1. To maintain the charge balance in the whole structures, the atomic ratio of Li/Mg in both title compounds was set to 1:1. The crystal data and structural refinements of Li$_2$MgMSe$_4$ (M = Ge, Sn) are listed in Table 1. Meanwhile, the corresponding atomic coordinates, bond distances and angles, isotropic displacement parameters and atomic parameters are shown in Tables S1–S7. Since Li$_2$MgGeSe$_4$ deliquesces quickly in air, the data collection for Li$_2$MgGeSe$_4$ was repeated several times using different single crystals. However, the data integrity of Li$_2$MgGeSe$_4$ is still lower than Li$_2$MgSnSe$_4$.

Table 1. Crystal data and structural refinements of Li$_2$MgSnSe$_4$ and Li$_2$MgGeSe$_4$.

| Empirical Formula | Li$_2$MgSnSe$_4$ | Li$_2$MgGeSe$_4$ |
|-------------------|------------------|------------------|
| Formula weight    | 472.72 g/mol     | 426.62 g/mol     |
| Temperature       | 296.15 K         | 153 (2) K        |
| Crystal system    | Orthorhombic     | Orthorhombic     |
| Space group       | Pmn2$_1$ (No. 31) | Pmn2$_2$ (No. 31) |
| a = 8.402 (14) Å  | a = 8.2961 (7) Å |
| b = 7.181 (12) Å  | b = 7.0069 (5) Å |
| c = 6.728 (11) Å  | c = 6.6116 (6) Å |
| Volume            | 405.9 (12) Å$^3$ | 384.33 (5) Å$^3$ |
| Z                 | 2                | 2                |
| Calculated density| 3.867 g/cm$^3$   | 3.686 g/cm$^3$   |
| Absorption coefficient | 21.047 mm$^{-1}$ | 22.891 mm$^{-1}$ |
| Goodness-of-fit on $F^2$ | 0.993          | 1.110            |
| Final R indices   | $R_1 = 0.0349; \omega R_2 = 0.0750$ | $R_1 = 0.0350; \omega R_2 = 0.0783$ |
| R indices         | $R_1 = 0.0401; \omega R_2 = 0.0784$ | $R_1 = 0.0413; \omega R_2 = 0.0831$ |
| Largest diff. peak and hole | 2.08 e·Å$^{-3}$ and −0.93 e·Å$^{-3}$ | 1.55 e·Å$^{-3}$ and −2.46 e·Å$^{-3}$ |

The Powder X-ray diffraction (PXRD) pattern of Li$_2$MgSnSe$_4$ was characterized using a Bruker D2 Phaser diffractometer (Bruker Corporation, Karlsruhe, Germany) under Cu-Kα radiation ($\lambda = 1.5418$ Å) with a metal holder. Meanwhile, the experimental XRD pattern of Li$_2$MgSnSe$_4$ (Figure S1) was recorded from 10 to 70° (2$\theta$) with a scan step width of 0.02°. The experimental and calculated PXRD patterns of Li$_2$MgSnSe$_4$ are shown in Figure S1. Owing to the experimental challenge in synthesizing and characterizing the moisture-sensitive compounds, impurities such as SnSe$_2$ and SnSe were observed in the synthesized Li$_2$MgSnSe$_4$ powder samples. However, based on the XRD patterns, the main phase can be determined to be Li$_2$MgSnSe$_4$. Meanwhile, compared with Li$_2$MgSnSe$_4$, Li$_2$MgGeSe$_4$ powder samples exhibit more serious moisture absorption. It was deliquesced too fast in air (the samples were deliquesced in 1 min at room temperature) to finish the PXRD measurement. GSAS was used to fit and refine the powder diffraction data of Li$_2$MgSnSe$_4$. The main phase Li$_2$MgSnSe$_4$ and impurity phases SnSe$_2$ and SnSe were refined. A certain peak function was fitted with experimental intensity data, and the values of peaks and structural parameters (including background function, lattice parameters, peak parameters, atomic position, preference orientation, etc.) were constantly adjusted during the fitting process until the difference between calculated intensity and experimental intensity stabilized [34]. The multi-phase Rietveld refinement yielded tiny impurities contents such as SnSe$_2$ and SnSe (total 9.7%) remaining from the staring materials, and a weight fraction of 90.3% of target Li$_2$MgSnSe$_4$ (Figure S2). The refined structural parameters are provided in Table S8. The large difference in the refinement can be attributed to the
experimental challenge to obtain long time and high quality PXRD data for the moisture-sensitive Li$_2$MgSnSe$_4$. However, the refined results are helpful in judging the purity of the product.

2.4. UV–Vis–NIR Diffuse Reflectance Spectroscopy

The diffuse reflectance spectrum of the synthesized Li$_2$MgSnSe$_4$ powder samples was characterized using a DUV spectrophotometer (Shimadzu SolidSpec-3700, Shimadzu Corporation, Shanghai, China) at room temperature in air. Based on the reflection spectrum, the corresponding absorption spectrum was obtained using the Kubelka–Munk formula [35,36]. The process was completed in 5–10 min.

2.5. Raman Spectroscopy

The Raman spectrum of Li$_2$MgSnSe$_4$ was characterized on a single crystal in a LABRAM HR Evolution spectrometer.

The Li$_2$MgSnSe$_4$ single crystal was firstly placed onto a transparent glass slide. Then, a suitable objective lens was used to select the measured area on the crystal. The maximum power of the used laser beam was about 60 mW with a spot size of ~35 µm.

2.6. Theoretical Calculations

Based on the density functional theory (DFT) and CASTEP program, the plane wave pseudopotential was applied to calculate the electronic structures of Li$_2$MgMSe$_4$ (M = Ge, Sn) [37]. Meanwhile, the exchange-correlation effects of the compounds were analyzed by using the generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) function [38,39]. Under the norm conserving pseudopotentials for wave function expansion, the kinetic energy cutoff of the models was set to 450 eV. Moreover, the Brillouin zone [40] contained $2 \times 2 \times 2$ Monkhorst-pack k-point sampling [41]. The virtual unit cells were used to process the occupancy [42,43].

3. Results and Discussion

3.1. Crystal Structure

As shown in Figure 1a,f, the two compounds are isomorphic structures. Herein, Li$_2$MgSnSe$_4$ is taken as an example of the structure description. Li$_2$MgSnSe$_4$ crystallizes in the noncentrosymmetric space group Pmn2$_1$ with $a = 8.402$ (14) Å, $b = 7.181$ (12) Å, $c = 6.728$ (11) Å and $Z = 2$. In the asymmetric unit of Li$_2$MgSnSe$_4$, there are two Li, one Mg, one Sn and three Se atoms that are crystallographically independent. In Li$_2$MgSnSe$_4$, the Li2 and Sn1 atoms are bonded to four Se atoms to build up the [LiSe$_4$] and [SnSe$_4$] tetrahedra with Li-Se bond lengths ranging from 2.50 Å–2.65 Å and Sn-Se bond lengths ranging from 2.505 Å–2.528 Å, respectively. The Li1 and Mg1 atoms are set to share the same sites with the atomic ratio of 1:1 in the initial refinements with the identical anisotropic displacement parameters, which can help to obtain better R values and reasonable temperature factors, similar to the situation of Cu/Mg atomic co-occupation in Cu$_2$MgSiS$_4$ [44], Cu$_2$MgGeS$_4$ [44] and Cu$_2$MgSiSe$_4$ [44]. Furthermore, Li/Mg atomic co-occupation is very common, which can be found in the LiMg(IO$_3$)$_3$ [45] and Li$_{0.8}$Mg$_{2.1}$B$_2$O$_5$F [46]. Similar to the Li2 and Sn1 atoms, the co-occupied Li1 and Mg1 atoms are bonded to four Se atoms to construct the [(Li/Mg)Se$_4$] tetrahedra units at the Wyckoff position 4b (Table S7). Furthermore, the formed tetrahedra groups are connected with each other by sharing Se atoms to constitute the final DL structure. For both compounds, there is a similar channel-like structure with a channel diameter of about 6 Ångstrom on the ab plane, as shown in Figure 1e,j. On the basis of the detailed investigations in the Inorganic Crystal Structure Database (ICSD), the two compounds should be the first series of alkali and alkaline earth metal DL compounds in the I$_2$-II-IV-VI$_4$ family.
The DL structure of Li$_2$MgSnSe$_4$ (a) and Li$_2$MgGeSe$_4$ (f) on the ac plane; (b–d,g–i) The structures of [LiSe$_4$], [(Li/Mg)Se$_4$], [SnSe$_4$] and [GeSe$_4$] tetrahedral units. The channel-like structures of Li$_2$MgSnSe$_4$ (e) and Li$_2$MgGeSe$_4$ (j) on ab plane.

3.2. Optical Properties

Based on the UV–Vis–NIR diffuse-reflectance spectrum, the experimental band gap of Li$_2$MgSnSe$_4$ was determined to be 2.62 eV (Figure 2a). To confirm chemical bonding, the Raman spectrum of Li$_2$MgSnSe$_4$ was characterized on a single crystal. As shown in Figure 2b, the peaks below 193 cm$^{-1}$ are related to the vibrations of Li-Se and Mg-Se bonding, matched with the previous results [47–49]. The peak at 193 cm$^{-1}$ and the overlapping peaks around 235 cm$^{-1}$ could be assigned to the asymmetric and symmetric stretching vibrations of Sn-Se bonding in SnSe$_4$ tetrahedral groups [49,50].

![Figure 2. (a) Experimental band gap of Li$_2$MgSnSe$_4$ samples; and (b) Raman spectrum of Li$_2$MgSnSe$_4$ single crystal.](image)

3.3. Theoretical Calculations

To study the linear and nonlinear optical properties of Li$_2$MgMSe$_4$ (M = Ge, Sn), DFT calculations were implemented. Considering the Li/Mg atomic co-occupation at the Wyckoff position 4b in the structures, the virtual unit cells were built for the calculations, as shown in Table S9 and Figure S3. The calculated theoretical band gaps, SHG coefficients and birefringences of the two compounds are shown in Table 2; the calculated band gap for the two compounds is 2.44 eV for Li$_2$MgGeSe$_4$, and 2.42 eV for Li$_2$MgSnSe$_4$ (matched with
the experimental value of 2.62 eV). The SHG coefficients of Li₂MgSnSe₄ in d₁₃ = 12.19 pm/√V and Li₂MgGeSe₄ in d₁₃ = −14.77 pm/√V are close to the one of AgGaS₂ in d₁₄ = 13.7 pm/√V. The calculated birefringences for the two compounds are 0.011 (Li₂MgSnSe₄) and 0.012 (Li₂MgGeSe₄), respectively.

Table 2. Calculated band gaps, SHG coefficients and birefringence of Li₂MgSnSe₄ and Li₂MgGeSe₄.

| Compound         | Eg (cal/EV) | d₁₃ (pm/√V) | d₁₄ (pm/√V) | d₁₅ (pm/√V) | Δn@1064 nm |
|------------------|-------------|-------------|-------------|-------------|------------|
| Li₂MgSnSe₄       | 2.42        | −4.68       | −5.81       | 12.19       | 0.011      |
| Li₂MgGeSe₄       | 2.4         | 5.53        | 7.14        | −14.77      | 0.012      |

To detect the origin of the optical properties, the electronic structures, SHG densities and band-resolved NLO susceptibilities of Li₂MgMSe₄ (M = Ge, Sn) were further investigated. Figure 3 shows the calculated band structures, total and partial density of states and the band-resolved NLO susceptibility \( \chi^{(2)} \) of the two compounds. The band structures (Figure 3a,b) indicate that Li₂MgGeSe₄ is an indirect band gap compound with a band gap of 2.44 eV, while Li₂MgSnSe₄ is a direct band gap compound with a band gap of 2.42 eV (matched with the experimental value of 2.62 eV). Furthermore, as shown from the total and partial density of states (PDOS) curves (Figure 3c,d), the valence bands maximum (VBM), which, around the Fermi level, is mainly occupied by Se-4p (83%) orbitals with the minor contribution of Sn-5p (8%), Li/Mg-2p (5%) and Li-2s (4%) orbitals for Li₂MgSnSe₄ and Se-4p (83%) orbitals with the minor contribution of Ge-4p (8%), Li/Mg-2p (5%) and Li-2s (4%) orbitals for Li₂MgGeSe₄, respectively (the range from -4.0 to 0 eV). The conduction bands minimum (CBM) originates from Se-4p (10%), Sn-5p (9%), Li-2s (19%) and Li/Mg-2p (21%) orbitals for Li₂MgSnSe₄, Se-4p (11%), Ge-4p (8%), Li-2s (17%) and Li/Mg-2p (21%) orbitals for Li₂MgGeSe₄, respectively (the range from 2.4 to 12 eV). The results indicate that the optical band gaps of Li₂MgMSe₄ (M = Ge, Sn) are mainly determined by the Se-4p, Li/Mg-2p and Li-2s orbitals.

Figure 3. Calculated band structures of (a) Li₂MgSnSe₄ and (b) Li₂MgGeSe₄; total and partial density of states and the band-resolved NLO susceptibility \( \chi^{(2)} \) of (c) Li₂MgSnSe₄ and (d) Li₂MgGeSe₄.

Figure 4 shows the calculated SHG densities for the two compounds. Combined with the band-resolved NLO susceptibility \( \chi^{(2)} \) in Figure 3c–d, the SHG responses of Li₂MgMSe₄...
(M = Ge, Sn) can be mainly derived from the [MSe₄] (M = Ge, Sn) tetrahedra units and with minor contributions from [LiSe₄] and [(Li/Mg)Se₄] groups.

**Figure 3.** Calculated band structures of (a) Li₂MgSnSe₄ and (b) Li₂MgGeSe₄.

**4. Conclusions**

In summary, the first series of DL selenides in the I₂-II-IV-VI₄ family, Li₂MgGeSe₄ and Li₂MgSnSe₄, have been rationally designed and synthesized. Their crystal structures were determined using single crystal X-ray diffractions, and the optical properties were studied using experimental spectra and DFT calculations. Li₂MgMSe₄ (M = Ge, Sn) crystallize in the non-centrosymmetric space group Pmn2₁ and show channel structures built by [LiSe₄], [(Li/Mg)Se₄] and [MSe₄] (M = Ge, Sn) tetrahedra units. The two compounds exhibit large theoretical SHG coefficients in 𝑑₃₃ (12.19 pm/v for Li₂MgSnSe₄, and −14.77 pm/v for Li₂MgGeSe₄), moderate band gaps (2.42 for Li₂MgSnSe₄, and 2.44 for Li₂MgGeSe₄) in selenides. The results demonstrated that introducing alkali metal and alkaline earth metal tetrahedral units into the I₂-II-IV-VI₄ family is a feasible way for the development of diamond-like IR nonlinear optical materials with good properties.

**Supplementary Materials:** The following are available online at https://www.mdpi.com/article/10.3390/ma14206166/s1, Table S1: Atomic coordinates and equivalent isotropic displacement parameters of Li₂MgSnSe₄, Table S2: Anisotropic displacement parameters (Å² × 10³) of Li₂MgSnSe₄, Table S3: Symmetry, selected bond lengths and angles of crystal data and structural refinements of Li₂MgSnSe₄, Table S4: Atomic coordinates and equivalent isotropic displacement parameters of Li₂MgGeSe₄, Table S5: Anisotropic displacement parameters (Å² × 10³) of Li₂MgGeSe₄, Table S6: Symmetry, selected bond lengths and angles of crystal data and structural refinements of Li₂MgGeSe₄, Table S7: Atomic parameters of Li₂MgSnSe₄ and Li₂MgGeSe₄, Table S8: The refined structural parameters of Li₂MgSnSe₄, Table S9: The crystallographic data of Li₂MgMSe₄ (M = Sn, Ge), Figure S1: Experimental and calculated PXRD patterns of Li₂MgSnSe₄, Figure S2: The PXRD Rietveld refinement of the obtained Li₂MgSnSe₄ samples, Figure S3: The atomic models of (a) Li₂MgSnSe₄ and (b) Li₂MgGeSe₄.

**Author Contributions:** H.G. synthesized the crystals, tested the samples, and wrote the manuscript. K.Z. and Z.Y. performed the electronic structure and optical property calculations. A.A. provided the support for the syntheses and structure determination of crystals. C.B. and J.L. provided comments on the revision of the manuscript. J.L., K.L. and S.P. designed and supervised the study. All authors have read and agreed to the published version of the manuscript.

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**Data Availability Statement:** The data presented in this study are available in Supplementary Material. The X-ray crystallographic coordinates for structures reported in this study have been deposited at the Cambridge Crystallographic Data Centre (CCDC), under deposition numbers.
References

1. Geng, L.; Meng, C.; Lu, H.; Luo, Z.; Lin, C.; Cheng, W. Bi$_2$Te$_4$(IO$_3$)$_2$: A novel polar iodate oxychloride exhibiting a second-order nonlinear optical response. *Dalton Trans.* 2015, 44, 2469–2475. [CrossRef]

2. Lu, X.; Chen, Z.; Shi, X.; Jing, Q.; Lee, M. Two Pyrophosphates with Large Birefringences and Second-Harmonic Responses as Ultraviolet Nonlinear Optical Materials. *Angew. Chem. Int. Ed.* 2020, 59, 17648–17656. [CrossRef]

3. Liang, F.; Kang, L.; Lin, Z.; Wu, Y. Mid-Infrared Nonlinear Optical Materials Based on Metal Chalcogenides: Structure–Property Relationship. *Cryst. Growth Des.* 2017, 17, 2254–2289. [CrossRef]

4. Kotb, H.; Khater, H.; Saber, O.; Ahmad, M. Sintering Temperature, Frequency, and Temperature Dependent Dielectric Properties of Na$_5$Sm$_2$Cu$_3$Ti$_4$O$_{12}$ Ceramics. *Materials 2021*, 14, 4805. [CrossRef] [PubMed]

5. Rong, L.; Xu, Z.; Sun, J.; Guo, G. New methyl formate synthesis method: Coal to methyl formate. *J. Energy Chem.* 2018, 27, 238–242. [CrossRef]

6. Wang, C.; Yang, G.; Humphrey, M.G.; Zhang, C. Recent Advances in Ultraviolet and Deep-Ultraviolet Second-Order Non-linear Optical Crystals. *Coord. Chem. Rev.* 2018, 375, 459–488. [CrossRef]

7. Mutailipu, M.; Zhang, M.; Zhang, B.B.; Wang, L.Y.; Yang, Z.H.; Zhou, X.; Pan, S.L. SrBi$_2$O$_5$F$_3$ Functionalized with [B$_5$O$_9$F$_3$]$^-$–Chromophores: Accelerating the Rational Design of Deep-Ultraviolet Nonlinear Optical Materials. *Angew. Chem. Int. Ed.* 2018, 57, 6095–6099. [CrossRef]

8. Wang, Y.; Zhang, Z.; Yang, Z.; Pan, S. Cation-Tuned Synthesis of Fluorooxoborates: Towards Optimal Deep-Ultraviolet Nonlinear Optical Materials. *Angew. Chem. Int. Ed.* 2018, 57, 2150–2154. [CrossRef]

9. Huang, Y.; Gao, L.; Yu, H.; Yang, Z.; Li, J.; Pan, S. Na$_5$Mg$_6$Q$_6$ (M = Zn, Cd; Q = S, Se): Promising New Ternary Infrared Nonlinear Optical Materials. *Chem. Eur. J.* 2021, 27, 6538–6544. [CrossRef]

10. Xu, F.; Peng, G.; Lin, C.; Zhao, D.; Li, B.-X.; Zhang, G.; Yang, S.; Ye, N. Na$_5$Sc$_2$(PO$_4$)$_2$F$_3$: Rational design and synthesis of an alkali rare-earth phosphate fluoride as an ultraviolet nonlinear optical crystal with an enlarged birefringence. *J. Mater. Chem. C* 2020, 8, 4965–4972. [CrossRef]

11. Lee, H.; Ok, K.M. Na$_5$Mg$_6$-xZn$_2$Si$_4$(0 ≤ x ≤ 1): Noncentrosymmetric Sodium Metal Silicate Solid Solutions with Ultraviolet Nonlinear Optical Properties. *Bull. Korean Chem. Soc.* 2020, 41, 139–142. [CrossRef]

12. Kee, J.; Ok, K.M. Hydrogen-Bond-Driven Synergistically Enhanced Hyperpolarizability: Chiral Coordination Polymers with Nonpolar Structure Exhibiting Unusually Strong Second-Harmonic Generation. *Angew. Chem. Int. Ed.* 2021, 60, 20656–20660. [CrossRef]

13. Wang, K.; Yang, Z.; Pan, S. The first quaternary diamond-like semiconductor with 10-membered Li$_4$S$_4$ rings exhibiting excellent nonlinear optical performances. *Chem. Commun.* 2017, 53, 3010–3013. [CrossRef]

14. Abudurusulli, A.; Huang, J.; Wang, P.; Yang, Z.; Pan, S.; Li, J. Li$_2$MgGe$_2$S$_7$: The First Alkali and Alkaline-Earth Diamond-Like Infrared Nonlinear Optical Material with Exceptional Large Band Gap. *Angew. Chem. Int. Ed.* 2021. [CrossRef]

15. Lekse, J.W.; McNerny, K.L.; Yeon, J.; Halasyamani, S.; Aitken, J. Second-Harmonic Generation and Crystal Structure of the Diamond-like Semiconductors Li$_2$CdGeS$_4$ and Li$_2$CdSnS$_4$. *Inorg. Chem.* 2009, 48, 7516–7518. [CrossRef]

16. Zhang, J.H.; Clark, D.J.; Weiland, A.; Stoyko, S.S.; Kim, Y.S.; Jang, J.I.; Aitken, J.A. Li$_2$CdGeSe$_4$ and Li$_2$CdSnSe$_4$: Biaxial Nonlinear Optical Materials with Strong Infrared Second-Order Responses and Laser-Induced Damage Thresholds Influenced by Photoluminescence. *Inorg. Chem. Front.* 2017, 4, 1472–1484. [CrossRef]

17. Zhang, J.-H.; Clark, D.J.; Brant, J.A.; Sinagra, C.W.; Kim, Y.S.; Jang, J.I.; Aitken, J.A. Infrared nonlinear optical properties of lithium-containing diamond-like semiconductors Li$_2$ZnGeSe$_4$ and Li$_2$ZnSnSe$_4$. *Dalton Trans.* 2015, 44, 11212–11222. [CrossRef]

18. Ritscher, A.; Hoelzel, M.; Lerch, M. The order-disorder transition in Cu$_2$ZnSnS$_4$-A neutron scattering investigation. *J. Solid State Chem.* 2016, 238, 68–73. [CrossRef]

19. Liang, F.; Kang, L.; Lin, Z.; Wu, Y.; Chen, C. Analysis and prediction of mid-IR nonlinear optical metal sulfides with diamond-like structures. *Coord. Chem. Rev.* 2017, 333, 57–70. [CrossRef]

20. Kang, L.; Liang, F.; Jiang, X.; Lin, Z.; Chen, C. First-Principles Design and Simulations Promote the Development of Nonlinear Optical Crystals. *Accounts Chem. Res.* 2019, 53, 209–217. [CrossRef] [PubMed]

21. Chen, M.-M.; Xue, H.-G.; Guo, S.-P. Multinary metal chalcogenides with tetrahedral structures for second-order nonlinear optical, photocatalytic, and photovoltaic applications. *Coord. Chem. Rev.* 2018, 368, 115–133. [CrossRef]

22. Pauling, L. The principles determining the structure of complex ionic crystals. *J. Am. Chem. Soc.* 1929, 51, 1010–1026. [CrossRef]

23. Wu, H.; Zhang, B.; Yu, H.; Hu, Z.; Wang, J.; Wu, Y.; Halasyamani, P.S. Designing Silicates as Deep-UV Nonlinear Optical (NLO) Materials using Edge-Sharing Tetrahedra. *Angew. Chem. Int. Ed.* 2020, 59, 8922–8926. [CrossRef]

24. Zhang, J.-H.; Clark, D.J.; Brant, J.A.; Rosmus, K.A.; Grima, P.; Lekse, J.W.; Jang, J.I.; Aitken, J.A. α-Li$_2$ZnGeSe$_4$: A Wide-Bandgap Diamond-like Semiconductor with Excellent Balance between Laser-Induced Damage Threshold and Second Harmonic Generation Response. *Chem. Mater.* 2020, 32, 8947–8955. [CrossRef]
