

# Article K<sub>2</sub>CdGe<sub>3</sub>S<sub>8</sub>: A New Infrared Nonlinear Optical Sulfide

Zi-Xuan Wu<sup>1,2</sup>, Wen-Fa Chen<sup>1,2</sup>, Bin-Wen Liu<sup>1</sup>, Xiao-Ming Jiang<sup>1,\*</sup> and Guo-Cong Guo<sup>1,\*</sup>

- State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, China
- <sup>2</sup> University of Chinese Academy of Sciences, Beijing 100190, China
- \* Correspondence: xmjiang@fjirsm.ac.cn (X.-M.J.); gcguo@fjirsm.ac.cn (G.-C.G.)

**Abstract:** A quaternary metal chalcogenide, namely  $K_2CdGe_3S_8$  (I), is obtained through a hightemperature solid-state approach. Compound I crystallizes with the non-centrosymmetric space group  $P2_12_12_1$ . It features a 2D layer structure with  $[CdGe_3S_8]$  layers consisting of tetrahedral GeS<sub>4</sub> and CdS<sub>4</sub> units, and counter K<sup>+</sup> embedded between the layers. The compound exhibits a powder second-harmonic generation (SHG) response of ~0.1 times that of KH<sub>2</sub>PO<sub>4</sub> (KDP) with phase-matchable character at the laser wavelength of 1064 nm. Remarkably, it has a wide band gap (3.20 eV), which corresponds to a favorable high laser-induced damage threshold of 6.7 times that of AgGaS<sub>2</sub>. In addition, the calculated birefringence ( $\Delta n$ ) is 0.039 at the wavelength of 1064 nm, which satisfies the  $\Delta n$  criteria for a promising infrared NLO material.

**Keywords:** nonlinear optical material; metal chalcogenide; second-harmonic generation; crystal structure; density functional theory

## 1. Introduction

Nonlinear optical (NLO) materials play a crucial role in laser technology due to the frequency conversion effect and have wide applications in science and industrial fields, such as medical treatment, radar, and remote sensing [1-11]. For practical laser uses, a promising NLO crystal must meet the following technical requirements [12–14], namely, broad transparent region, large second-harmonic generation (SHG) coefficient, wide band gap for improved laser-induced damage threshold (LIDT), moderate birefringence  $\Delta n$ (~0.03–0.10), low dn/dT as material requirements, good crystal growth habit, and good chemical stability. Typical crystals including LiB<sub>3</sub>O<sub>5</sub>, β-BaB<sub>2</sub>O<sub>4</sub>, KH<sub>2</sub>PO<sub>4</sub>, and KTiPO<sub>4</sub> are mostly used in the deep ultraviolet, ultraviolet, and visible-near infrared (IR) regions, while they are seriously limited in the mid- and far-IR regions due to their strong chemical absorptions. During the past decades, a series of excellent IR NLO crystals have been successfully synthesized and commercialized in the chalcogenide and pnictide systems, including AgGaS<sub>2</sub> (AGS) [15], AgGaSe<sub>2</sub> (AGSe) [16], and ZnGeP<sub>2</sub> [17], which demonstrate the merits of a broad IR transparency and large NLO coefficients. However, all these crystals have serious drawbacks such as a low laser-induced damage threshold (LIDT), and strong two and multiphoton absorptions, thus considerably restricting their high-power applications. Therefore, exploring new high-performance IR NLO materials is of great importance, but comes with a big challenge.

The family of non-centrosymmetric metal chalcogenides is one of the best candidates to achieve excellent IR NLO properties due to their structural diversity and functional flexibility. Chalcogenides of group 14 elements have a strong tendency to exist with tetrahedral coordination, including MQ<sub>4</sub> (M = Si, Ge, and Sn; Q = S, Se) [18] tetrahedra, the corner-sharing M<sub>2</sub>Q<sub>7</sub> [19] unit, edge-sharing M<sub>2</sub>Q<sub>6</sub> dimer [17], isolated M<sub>3</sub>Q<sub>9</sub> ring [20] and adamantane M<sub>4</sub>Q<sub>10</sub> unit [21,22]. These M<sub>m</sub>Q<sub>n</sub> units can be further assembled into 1D chains, 2D layers and 3D networks, which can be modulated by the template role of counter cations. The architectures that are constructed of acentric MQ<sub>4</sub> tetrahedra



Citation: Wu, Z.-X.; Chen, W.-F.; Liu, B.-W.; Jiang, X.-M.; Guo, G.-C. K<sub>2</sub>CdGe<sub>3</sub>S<sub>8</sub>: A New Infrared Nonlinear Optical Sulfide. *Symmetry* **2023**, *15*, 236. https://doi.org/ 10.3390/sym15010236

Academic Editor: Wiesław Leoński

Received: 10 November 2022 Revised: 29 December 2022 Accepted: 4 January 2023 Published: 15 January 2023



**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). tend to form non-centrosymmetric structures, which is a prerequisite and challenging condition for NLO materials [23–30]. Moreover, most metals in chalcogenides, especially transition  $d^{10}$  metals, are usually tetra-coordinated to form distorted tetrahedral units; this fact increases the chance of SHG generation. Moreover, to expand the optical energy gap, a good molecular design strategy would be the introduction of alkali and alkaline earth metal cations (Li<sup>+</sup>, Na<sup>+</sup>, Mg<sup>2+</sup>, and so on), which are beneficial to high LIDTs. Under the guidance of these ideas, the I-IIB-IVA-VI compounds would be promising IR NLO candidates with a non-centrosymmetric structure for the SHG effect, wide band gap, and high LIDT. For example, in the structure of Na<sub>2</sub>ZnGe<sub>2</sub>S<sub>6</sub> [31], each [GeS<sub>4</sub>] tetrahedron is corner-shared to form  $[GeS_3]_n$  chains, which further connect with discrete  $[ZnS_4]$  tetrahedra to build a 3D framework. Na<sub>2</sub>ZnGe<sub>2</sub>S<sub>6</sub> has been reported to possess optimal comprehensive performances with a wide band gap of 3.25 eV for a high LIDT ( $7 \times AgGaS_2$ ), and a remarkable phase matchable SHG intensity ( $\sim 0.9 \times \text{AgGaS}_2$ ). Similarly, AZn<sub>4</sub>Ga<sub>5</sub>Se<sub>12</sub> (A = K, Rb, or Cs) [32] in the non-centrosymmetric space group R3 feature 3D diamondlike frameworks and exhibit strong SHG responses ( $2.8-3.7 \times AgGaS_2$ ) and high LIDTs  $(19.2-23.4 \times \text{AgGaS}_2)$  as well as moderate band gaps (2.41–2.49 eV). It has been evident that these examples are good candidates for IR NLO materials; however, the I-IIB-IVA-VI system is far from fully exploited.

Herein, the simultaneous introduction of the tetrahedral  $CdS_4$  and  $GeS_4$  units affords a new quaternary IR NLO chalcogenide, namely,  $K_2CdGe_3S_8$  (I). We will report its synthesis, crystal structure, linear and nonlinear optical properties, theoretical calculation of electronic structure band, and optical properties of I.

## 2. Experiment Section

## 2.1. Synthesis

For the preparation of I, reactants of  $CdCl_2$  powder (0.10 mmol, Aladdin, 99%), Ge metal (1.03 mmol, Alfa, 99.99%), S powder (2.59 mmol, Sinopharm, 99.9%), Li metal (1.05 mmol, Sinopharm, 99%), and KCl powder (1.55 mmol, Aladdin, 99%) were weighed in an argon-filled glovebox. All reagents were loaded into a quartz tube with a carbon crucible inside and sealed under a vacuum with  $10^{-3}$  Torr; the tube was then put into a furnace with the following temperature curves. First heating to 400 °C for 5 h and holding there for 5 h, then heating to 700 °C for 5 h and keeping at that temperature for 100 h; subsequently, cooling it down to 400 °C for 96 h at a rate of 3 °C/h before turning down the furnace. Single crystals of I were finally obtained and were separated manually after washing the products with alcohol and deionized water.

#### 2.2. Single-Crystal X-ray Diffraction (XRD) Analysis

A transparent crystal of  $0.12 \times 0.12 \times 0.02 \text{ mm}^3$  was choosen for single-crystal XRD analysis. Generally, the growth of bulk crystal is difficult; some methods can be used for sulfides, such as Bridgman, chemical vapor deposition and horizontal gradient freeze. A diffraction dataset was collected by using a Rigaku FR-X Microfocus diffractometer, which was equipped with Mo-*K* $\alpha$  radiation ( $\lambda = 0.71073$  Å) and operated at 45 kV and 66 mA at 297 K. The CrysAlisPro software [33] was used to reduce the dataset. The structure of I was solved based on the direct method, and *F*<sup>2</sup> full matrix least squares method was used to perform the structural refinement. The structure of I was analyzed using the crystal software SHELXL 97 package [34]. The PLATON program [35] was adopted to check the symmetry of the final structure, and no higher symmetry was found. Details of data collection, structure refinements, and crystal parameters are given in Table 1. Detailed asymmetric atomic parameters and selected bond lengths are presented in Tables 2 and 3, respectively.

Empirical formula	K <sub>2</sub> Ge <sub>3</sub> CdS <sub>8</sub>
CCDC	2,215,394
Formula weight	664.85
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	$P2_{1}2_{1}2_{1}$
a/Å	7.3758(3)
b/Å	12.1051(5)
c/Å	16.8658(6)
Volume/Å <sup>3</sup>	1505.86(10)
Z	4
$\rho_{\rm calc}  ({\rm g/cm^3})$	2.933
$\mu/mm^{-1}$	8.945
F(000)	1240.0
Crystal size/mm <sup>3</sup>	0.12 imes 0.12 imes 0.02
Radiation	Mo $K\alpha$ ( $\lambda = 0.71073$ )
$2\theta$ range for data collection/°	4.83 to 51
Index ranges	$-8 \le h \le 6$ , $-14 \le k \le 14$ , $-16 \le l \le 20$
Reflections collected	8972
Independent reflections	2792 [ $R_{int} = 0.0236$ , $R_{sigma} = 0.0262$ ]
Data/restraints/parameters	2792/0/133
Goodness-of-fit on $F^2$	0.717
Final <i>R</i> indexes $[I > = 2\sigma(I)]$	$R_1 = 0.0327, wR_2 = 0.0835$
Final R indexes [all data]	$R_1 = 0.0367, wR_2 = 0.0872$
Largest diff. peak/hole/e Å <sup>-3</sup>	1.84/-1.32
Flack parameter	-0.01(3)
${}^{a}R = \Sigma \mid  F_{o}  -  F_{c}  \mid /\Sigma \mid F_{o} \mid , {}^{b}wR$	$R = \Sigma (w(F_o^2 - F_c^2)^2) / \Sigma (w(F_o^2)^2))^{1/2}.$

Table 1. Crystal data and structure refinements for I.

Table 2. Fractional atomic coordinates  $(\times 10^4)$  and equivalent isotropic displacement parameters  $(\AA^2\times 10^3)$  for I.

Atom	X	Y	Z	U(eq)
K1	12,537(8)	3585(4)	4448(3)	65.1(13)
K2	7684(12)	1998(7)	1683(5)	115(2)
Cd1	4694.9(14)	4981.9(10)	542.7(8)	32.0(3)
Ge1	9689.7(19)	5293.1(12)	1540.8(10)	24.1(4)
Ge2	7686(3)	5666.3(13)	4867.9(9)	29.3(4)
Ge3	7374(2)	4561.0(13)	3275.4(8)	26.2(4)
S1	7314(5)	6326(3)	1580(2)	27.7(7)
S2	7807(7)	3886(3)	4507(2)	36.2(10)
S3	7192(8)	6341(3)	3650(2)	38.1(10)
S4	9962(6)	4246(4)	2649(3)	39.4(10)
S5	4971(7)	3817(4)	2776(3)	49.8(14)
S6	9766(10)	3997(6)	582(3)	78(2)
S7	2106(6)	6311(4)	1442(3)	46.0(12)
S8	10,430(40)	6120(30)	5266(19)	37(6)
S8B	9840(60)	6460(30)	5470(16)	50(8)

 $\overline{U_{\text{eq}}}$  is defined as 1/3 of the trace of the orthogonalized  $U_{ij}$  tensor.

Table 3. Selected bond distances (Å) in I.

Bond	Distance/Å	Bond	Distance/Å	Bond	Distance/Å
Ge(1)-S(1)	2.154(4)	Ge(3)-S(4)	2.215(5)	K(1)-S(5) <sup>#5</sup>	3.355(7)
Ge(1)-S(4)	2.267(4)	Ge(3)-S(5)	2.160(5)	K(1)-S(7) <sup>#6</sup>	3.376(7)
Ge(1)-S(6)	2.254(5)	Cd(1)-S(1)	2.526(4)	K(2)-S(3) <sup>#7</sup>	3.725(10)
Ge(1)-S(7) <sup>#5</sup>	2.173(4)	Cd(1)-S(5)	2.521(5)	K(2)-S(4)	3.590(10)

Bond	Distance/Å	Bond	Distance/Å	Bond	Distance/Å
Ge(2)-S(2)	2.241(4)	Cd(1)-S(7)	2.502(4)	K(2)-S(5)	3.500(11)
Ge(2)-S(3)	2.241(4)	Cd(1)-S(8) <sup>#8</sup>	2.510(8)	K(2)-S(6)	3.415(12)
Ge(2)-S(6) <sup>#6</sup>	2.211(6)	K(1)-S(1)#4	3.239(6)	K(2)-S(7) <sup>#7</sup>	3.274(10)
Ge(2)-S(8)	2.211(6)	K(1)-S(2) <sup>#1</sup>	3.477(6)	K(2)-S(8) <sup>#8</sup>	3.681(12)
Ge(3)-S(2)	2.255(4)	K(1)-S(3)	3.509(8)	K(1)-K(1) <sup>#1</sup>	4.896(7)
Ge(3)-S(3)	2.250(4)	K(1)-S(4)	3.667(7)	K(1)-K(2) <sup>#3</sup>	4.553(10)

Table 3. Cont.

Symmetry transformation used to generate equivalent atoms: (#1) 1/2 + X, 1/2-Y, 1-Z; (#3) 2-X, 1/2 + Y, 1/2-Z; (#4) 2-X, -1/2 + Y, 1/2-Z; (#5) 1 + X, +Y, +Z; (#6) 3/2-X, 1-Y, 1/2 + Z; (#7) 1-X, -1/2 + Y, 1/2-Z; (#8) 3/2-X, 1-Y, -1/2 + Z; (#9) 1-X, 1/2 + Y, 1/2-Z; (#10) -1 + X, +Y, +Z.

#### 2.3. Powder XRD Analysis

The purity of sample I was checked by powder XRD analysis using a Rigaku Flex600 X-ray diffractometer equipped with Cu K $\alpha$  ( $\lambda$  = 1.54057 Å) radiation in the 2 $\theta$  range of 5° to 65° with the scan step size of 0.02° at 293 K. The experimental and simulated powder XRD patterns of I are shown in Figure 1; the experimental XRD pattern is consistent with the simulation one, indicating that the powder sample of compound I is a pure phase (Figure 1a).



Figure 1. Simulated and experimental powder XRD patterns (a) and EDS (b) of compound I.

## 2.4. Energy-Dispersive X-ray Spectroscopy (EDS) Analysis

Element analysis of the title compound was performed using a Hitachi S-3500 SEM spectrometer equipped with an EDS. The result demonstrates that the concentration of each element in **I**, K:Cd:Ge:S = 2.3:1:3.7:9.6, is consistent with the experimental formula of **I** determined from single-crystal XRD measurement (Figure 1b).

## 2.5. IR and UV-Vis-NIR Diffuse-Reflectance Spectroscopy

The Fourier transform IR spectrum (Figure 2b) of I with the wavelength from 4000 to  $400 \text{ cm}^{-1}$  was recorded on a Nicolet Magana 750 FT-IR spectrophotometer. The UV-Vis-NIR diffuse reflectance spectrum (Figure 2a) of I was collected on the Perkin-Elmer Lambda 950 UV-Vis-NIR spectrophotometer with the wavelength ranging from 200 to 2500 nm, and BaSO<sub>4</sub> as a reference. The Kubelka–Munk formula [36] was applied to transform the reflection spectra into the absorption spectra:  $\alpha/S = (1 - R)^2/2 R$ , where  $\alpha$  represents the absorption coefficient, *S* represents the scattering coefficient, and *R* represents the reflectance.



**Figure 2.** (a) Absorption spectrum of I transformed from UV-Vis-NIR diffuse reflectance; (b) IR spectrum of I.

#### 2.6. Powder SHG and LIDT Measurements

Powder SHG of I was characterized by the Kurtz–Perry method [37] under the polarized laser irradiation of 2 mJ and 1064 nm with transmission mode at room temperature. Manually selected crystals and benchmark KDP were screened into five particle size ranges, namely, 30–50, 50–75, 75–100, 100–150, and 150–200 µm, for phase matching measurements. The frequency-doubling signals (532 nm) were detected by an Andor's DU420A-BR-DD CCD. The powder LIDT of compound I and the reference AGS were assessed by the singlepulse powder LIDT method with the same particle size range [38]. The samples were irradiated with a 1064 nm (pulse width  $\tau_p$  is 10 ns) laser beam until damage occurred on the surface of the sample. Then, the apparent color change was observed by an optical microscope. The LIDT was computed by the equation LIDT =  $E/\pi r^2 \tau_p$ , where *E*, *r*, and  $\tau_p$ are the energy of a single pulse, the spot radius, and the pulse width, respectively.

#### 2.7. Computational Methods

Based on density functional theory (DFT) [39–42], the electronic band structure, density of states (DOS), and optical properties of compound I were calculated by the ABINIT software package. The orbital electrons of S-3s<sup>2</sup>3p<sup>4</sup>, K-3s<sup>2</sup>3p<sup>6</sup>4s<sup>1</sup>, Ge-3d<sup>10</sup>4s<sup>2</sup>4p<sup>2</sup>, and Cd-4d<sup>10</sup>5s<sup>2</sup> were set as valence electrons. Exchange and correlation effects were addressed by generalized gradient approximation (GGA). The plane-wave cutoff energy was set to 18 Hartree, and a 5 × 3 × 2 Monkhorst–Pack *k*-point grid was adopted. Four hundred empty bands were used for optical calculations. Linear optical properties were described by the complex dielectric function  $\varepsilon_{ij} = \varepsilon_{ij,re}(\omega) + \varepsilon_{ij,im}(\omega)$ , where the imaginary part  $\varepsilon_{ij,im}(\omega)$ generated other optical constants by Kramers–Kroning transformation.

The frequency dependence of SHG tensors  $\chi_{ijk}(-2\omega, \omega, \omega)$  were theoretically calculated by the "sum over states" and density functional perturbation method. SHG susceptibility is mainly from three parts: (1) the intra-band transition term  $\chi_{intra}(-2\omega, \omega, \omega)$ ; (2) the pure inter-band transition term  $\chi_{inter}(-2\omega, \omega, \omega)$ ; and (3) the modulation term  $\chi_{mod}(-2\omega, \omega, \omega)$  of intra-band contribution by the inter-band motion-related polarization energy [43].

#### 3. Results and Discussion

#### 3.1. Crystal Structure

Compound I was synthesized by the high-temperature solid-state method with a yield of 40% based on Ge, the compound was stable in the atmosphere for more than half a year. Phase I crystallizes in the orthorhombic space group of  $P2_12_12_1$  (No. 19, Table 1), and there are two independent K, one Cd, three Ge, and eight S atoms in the asymmetric unit. The Cd–S and Ge–S bond distances fell in the ranges of 2.503(4)–2.529(4) Å and 2.143(7)–2.262(4) Å, respectively, which are close to those in a series of chalcogenides, such as Na<sub>2</sub>CdGe<sub>2</sub>S<sub>6</sub> (2.510–2.534 Å) [44], BaCdGeS<sub>4</sub> (2.451–2.613 Å) [45], K<sub>2</sub>ZnGe<sub>3</sub>S<sub>8</sub> (2.148–2.285 Å) [46], KLaGeS<sub>4</sub> (2.175–2.220 Å) [47],

KBiGeS<sub>4</sub> (2.181–2.239 Å) [48] and Na<sub>5</sub>AgGe<sub>2</sub>S<sub>7</sub> (2.189–2.247 Å) [49]. Meanwhile, the  $\angle$ S–Cd– S bond angles in I range from 98.62° to 118.50°, which differ significantly from the bond angle of 109.5° in the regular tetrahedral coordination, indicating that the [CdS<sub>4</sub>] tetrahedra in I are distorted. This phenomenon is caused by the second-order Jahn–Teller distortion of Cd<sup>2+</sup> in a tetrahedral coordination environment. As illustrated in Figure 3a, compound I features a 2D layer structure. All Cd and Ge atoms are tetrahedrally coordinated to form CdS<sub>4</sub> and GeS<sub>4</sub> units, respectively. Each three GeS<sub>4</sub> and one CdS<sub>4</sub> tetrahedra share corners with each other to form a [CdGe<sub>3</sub>S<sub>11</sub>] cluster, all of which further share edges of GeS<sub>4</sub> tetrahedra along the *c* direction and sulfur corners of GeS<sub>4</sub> and CdS<sub>4</sub> tetrahedra along the *a* direction, establishing the [CdGe<sub>3</sub>S<sub>8</sub>] layers (Figure 3b). All potassium cations in I are surrounded by six sulfur atoms with K–S distances of 3.239–3.725 Å (Table 3), which benefits the structural stabilization of I.



**Figure 3.** (a) Ball and stick representation of the layered structure of I as viewed down the *a*-axis. (b) A [CdGe<sub>3</sub>S<sub>8</sub>] layer, dark green and purple tetrahedral present GeS<sub>4</sub> and CdS<sub>4</sub> units, respectively. The [CdGe<sub>3</sub>S<sub>11</sub>] cluster is identified using dotted ellipse.

#### 3.2. Optical Properties

As depicted in Figure 2a, the absorption spectrum of I transformed from UV-Vis-NIR diffuse reflectance indicates that compound I has an optical band gap of 3.20 eV, which is larger than that of commercial IR NLO crystals AgGaS<sub>2</sub> (2.73 eV) [26], and comparable to those of the newly reported Cs<sub>2</sub>ZnGe<sub>3</sub>S<sub>8</sub> (3.32 eV) [17], Cs<sub>2</sub>CdGe<sub>3</sub>S<sub>8</sub> (3.38 eV) [17], K<sub>2</sub>ZnGe<sub>3</sub>S<sub>8</sub> (3.36 eV) [42], K<sub>2</sub>MnGe<sub>3</sub>S<sub>8</sub> (2.95 eV) [50] and Rb<sub>2</sub>CdGe<sub>3</sub>S<sub>8</sub> (3.16 eV) [51]. It can be seen from the IR spectrum (Figure 3b) that compound I possesses a characteristic absorption at 6.25 µm, which can be attributed to the absorption arising from the stretching vibration in H<sub>2</sub>O. Therefore, compound I is transparent in the wide infrared range of 0.78–12 µm, where 0.78 µm corresponds to one-half of the band gap. The infrared transparent range covers the two most important atmosphere transparency windows at 3–5 and 8–12 µm.

## 3.3. SHG and LIDT Properties

To further evaluate the SHG property of **I**, the Kurtz and Perry method was used to measure the frequency doubling signal of powdery samples under the irradiation of a fundamental frequency 1064 nm laser. Crystalline KDP is selected as the reference for SHG comparison. As shown in Figure 4a, the measured SHG intensity of **I** was positively correlated with the particle size, indicating that the title compound is phase matchable. For the sample with the particle range of 75–100  $\mu$ m, the SHG intensity of **I** is about 0.1 times that of benchmark KDP at 1064 nm (Figure 4b).

In addition, the well-known one single pulse method was adopted to measure the powder LIDT of compound I and AGS at 1064 nm. As presented in Table 4, compound I exhibits a LIDT of 268.05 mJ/cm<sup>2</sup>, approximately 6.7 times that of AGS powder (42.32 mJ/cm<sup>2</sup>). The positive correlation between LIDT and optical band gap has been widely accepted. Although the wide band gap can avoid two-photon and three-photon absorptions, the thermal expansion characteristic of NLO crystal also has a great influence on the LIDT. Therefore, the temperature dependence of cell lengths of compound I were characterized to investigate the thermal-expansion coefficient (TEC) by single crystal X-ray diffraction at 100–340 K with a step of 20 K. As displayed in Figure 5 the corresponding TEC values of I along the *a*-, *b*- and *c*-axes were  $1.55 \times 10^{-5}$ ,  $4.86 \times 10^{-5}$ , and  $2.05 \times 10^{-5}$ , respectively. The thermal-expansion anisotropy (TEA,  $\delta$ ; defined as  $\delta = \max\{(\alpha_i - \alpha_j)/\alpha_i(i, j = a, b, c)\})$  of I is 2.12, which is remarkably lower than that of the AGS (2.95) [24,52], indicating that compound I has superior LIDT than that of AGS.



**Figure 4.** (**a**) Particle size dependence of SHG intensities of **I** and KDP under 1064 nm laser irradiation. (**b**) SHG signals of **I** and KDP in the size range of 75–100 μm.

LIDT		Band Gap		TEC (×10 <sup>-5</sup> )		
Compounds (r	(mJ/cm <sup>2</sup> )	(eV)	а	b	С	IEA
I	268.05	3.20	1.56	4.88	2.09	2.12
AGS	42.32	2.62	2.09	2.09	-1.07	2.95

Table 4. LIDT Comparison of I and AGS.



Figure 5. Temperature variation of the lattice parameters of I along the *a*, *b*, and *c* directions.

## 3.4. Electronic Structure and NLO Coefficient Calculations

To further investigate the intrinsic relationships between structure and the secondorder NLO properties of I, first-principles calculations of electronic structure and NLO coefficients with the single crystal structure were performed. As can be seen from the calculated band structure (Figure 6a), compound I is an indirect band gap material with a theoretical band gap of 2.51 eV, which is smaller than the experimental result (3.20 eV). This phenomenon is reasonable because of the limitations of DFT calculations. The partial density of states (PDOS) of the title compound (Figure 6b) show that the top of the valence band is mainly constituted by S–3*p* states, and S–3*p* and Ge–4*s* states contribute mostly to the conduction band bottom. Therefore, GeS<sub>4</sub> units are mainly responsible for the band gap absorptions.



**Figure 6.** Calculated electronic band structure (**a**), partial densities of states (PDOS) (**b**), SHG coefficient tensor  $d_{123}$  and effective SHG coefficient  $d_{\text{eff}}$  (**c**), and the energy-dependent birefringence (**d**) of **I**.

Due to the point group of 222, only one independent nonzero SHG tensor, namely  $d_{123}$ , is left for compound **I**, under the restriction of Kleinman symmetry. As shown in Figure 6c, the calculated  $d_{123}$  of **I** is  $-0.067 \text{ pm} \cdot \text{V}^{-1}$  at a wavelength of 1064 nm. In addition, the effective NLO coefficient at 1064 nm is  $0.057 \text{ pm} \cdot \text{V}^{-1}$  (Figure 6c), which is in agreement with the experimental results. The refractive indexes  $n_x$ ,  $n_y$  and  $n_z$  along x, y and z directions at 1064 nm are 1.729, 1.747 and 1.769, respectively, among which  $n_z$  and  $n_x$  are the largest and smallest of all the refractive indices along different directions, respectively. As shown in Figure 6d, the calculated  $\Delta n$  is 0.039 at 1064 nm, supporting the phase-matching behavior, while in the region of 2–5 µm, compound **I** is non-phase-matchable.

## 4. Conclusions

A new quaternary chalcogenide  $K_2CdGe_3S_8$  has been synthesized by utilizing the high-temperature solid-state method. The compound features a 2D layer structure, in which the [CdGe<sub>3</sub>S<sub>8</sub>] layers are comprised of tetrahedral GeS<sub>4</sub> and CdS<sub>4</sub> units. The counter K<sup>+</sup> cations are embedded between the layers. Particle size-dependent powder SHG studies reveal that compound I exhibits a phase-matchable SHG response of ~0.1 times that of KH<sub>2</sub>PO<sub>4</sub> (KDP) at 1064 nm. The compound presents a favorable laser-induced damage threshold of 6.7 times that of AgGaS<sub>2</sub>, which is consistent with its relatively wide band gap of 3.2 eV and low thermal-expansion anisotropy. DFT calculations reveal that the valence band top and conduction band bottom of I are dominated by the states of GeS<sub>4</sub> units, which are mainly responsible for the band gap absorptions. The theoretical birefringence index ( $\Delta n$ ) of I is 0.039 at 1064 µm, which satisfies the  $\Delta n$  criteria for a promising IR NLO material.

**Author Contributions:** Conceptualization, Z.-X.W. and B.-W.L.; methodology, Z.-X.W.; theoretical calculation, W.-F.C.; writing—original draft preparation, Z.-X.W.; writing—review and editing, B.-W.L. and X.-M.J.; supervision, G.-C.G. All authors have read and agreed to the published version of the manuscript.

**Funding:** This work was funded by the National Natural Science Foundation of China (21827813, 21921001, 22175172, 22075283, 92161125), the Youth Innovation Promotion Association of Chinese Academy of Sciences (2020303, 2021300).

**Data Availability Statement:** CCDC 2215394 contains the crystallographic data for this paper. These data can be obtained free of charge via https://www.ccdc.cam.ac.uk/Community/Depositastructure/CSDCommunications/ (accessed on 3 January 2023).

Conflicts of Interest: The authors declare no conflict of interest.

#### References

- 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]
- Julià-López, A.; Hernando, J.; Ruiz-Molina, D.; González-Monje, P.; Sedó, J.; Roscini, C. Temperature-Controlled Switchable Photochromism in Solid Materials. *Angew. Chem. Int. Ed.* 2016, 55, 15044–15048. [CrossRef]
- 3. Zhang, W.; Ye, H.Y.; Graf, R.; Spiess, H.W.; Yao, Y.F.; Zhu, R.Q.; Xiong, R.G. Tunable and switchable dielectric constant in an amphidynamic crystal. *J. Am. Chem. Soc.* 2013, 135, 5230–5233. [CrossRef] [PubMed]
- Jiang, X.M.; Guo, S.P.; Zeng, H.Y.; Zhang, M.J.; Guo, G.C. Large Crystal Growth and New Crystal Exploration of Mid-Infrared Second-Order Nonlinear Optical Materials; Springer: Berlin/Heidelberg, Germany, 2012; Volume 145, pp. 1–44.
- 5. Ok, K.-M. Toward the rational design of novel noncentrosymmetric materials: Factors influencing the framework structures. *Acc. Chem. Res.* **2016**, *49*, 2774–2785. [CrossRef]
- 6. Guo, S.P.; Chi, Y.; Guo, G.C. Recent achievements on middleand far-infrared second-order nonlinear optical materials. *Coord. Chem. Rev.* 2017, 335, 44–57. [CrossRef]
- Lin, H.; Wei, W.-B.; Chen, H.; Wu, X.-T.; Zhu, Q.-L. Rational design of infrared nonlinear optical chalcogenides by chemical substitution. *Coord. Chem. Rev.* 2020, 406, 213150. [CrossRef]
- 8. Jiang, X.-M.; Deng, S.; Whangbo, M.-H.; Guo, G.-C. Material research from the viewpoint of functional motifs. *Natl. Sci. Rev.* 2022, *9*, nwac017. [CrossRef]
- 9. Guo, G.-C.; Yao, Y.-G.; Wu, K.-C.; Wu, L.; Huang, J.-S. Studies on the Structure-Sensitive Functional Materials. *Prog. Chem.* 2001, 13, 151–155. (In Chinese)
- 10. Wang, Y.L.; Li, X.Y.; Han, S.D.; Pan, J.; Xue, Z.Z. A Cu<sub>2</sub>I<sub>2</sub>-Based Coordination Framework as the Selective Sensor for Ag<sup>+</sup> and the Effective Adsorbent for I<sub>2</sub>. *Cryst. Growth Des.* **2022**, *22*, 3719–3726. [CrossRef]
- Xue, Z.Z.; Meng, X.D.; Li, X.Y.; Han, S.D.; Pan, J.; Wang, G.M. Luminescent Thermochromism and White-Light Emission of a 3D [Ag<sub>4</sub>Br<sub>6</sub>] Cluster-Based Coordination Framework with Both Adamantane-like Node and Linker. *Inorg. Chem.* 2021, 60, 4375–4379. [CrossRef]
- 12. Kang, L.; Zhou, M.; Yao, J.; Lin, Z.; Wu, Y.; Chen, C. Metal Thiophosphates with Good Mid-infrared Nonlinear Optical Performances: A First-Principles Prediction and Analysis. *J. Am. Chem. Soc.* **2015**, *137*, 13049–13059. [CrossRef] [PubMed]
- Bera, T.K.; Jang, J.I.; Song, J.-H.; Malliakas, C.D.; Freeman, A.J.; Ketterson, J.B.; Kanatzidis, M.G. Soluble Semiconductors AAsSe<sub>2</sub> (A = Li, Na) with a Direct-Band-Gap and Strong Second Harmonic Generation: A Combined Experimental and Theoretical Study. J. Am. Chem. Soc. 2010, 132, 3484–3495. [CrossRef] [PubMed]
- 14. Yang, C.; Liu, X.; Teng, C.; Cheng, X.; Liang, F.; Wu, Q. Hierarchical molecular design of high-performance infrared nonlinear Ag<sub>2</sub>HgI<sub>4</sub> material by defect engineering strategy. *Mater. Today Phys.* **2021**, *19*, 100432. [CrossRef]
- 15. Akiko Harasaki, A.H.; Kiyoshi Kato, K.K. New Data on the Nonlinear Optical Constant, Phase-Matching, and Optical Damage of AgGaS<sub>2</sub>. *Jpn. J. Appl. Phys.* **1997**, *36*, 700. [CrossRef]
- Catella, G.C.; Shiozawa, L.R.; Hietanen, J.R.; Eckardt, R.C.; Route, R.K.; Feigelson, R.S.; Cooper, D.G.; Marquardt, C.L. Mid-IR absorption in AgGaSe(2) optical parametric oscillator crystals. *Appl. Opt.* 1993, 32, 3948–3951. [CrossRef] [PubMed]
- 17. Boyd, G.D.; Buehler, E.; Storz, F.G. Linear and Nonlinear Optical Properties Of ZnGeP<sub>2</sub> AND CdSe. *Appl. Phys. Lett.* **1971**, *18*, 301–304. [CrossRef]
- 18. Heine, J.; Dehnen, S. From Simple Chalcogenidotetrelate Precursors to Complex Structures and Functional Compounds. Z. Anorg. Allg. Chem. 2012, 638, 2425–2440. [CrossRef]
- Morris, C.D.; Li, H.; Jin, H.; Malliakas, C.D.; Peters, J.A.; Trikalitis, P.N.; Freeman, A.J.; Wessels, B.W.; Kanatzidis, M.G. Cs<sub>2</sub>MIIMIV<sub>3</sub>Q<sub>8</sub> (Q = S, Se, Te): An Extensive Family of Layered Semiconductors with Diverse Band Gaps. *Chem. Mater.* 2013, 25, 3344–3356. [CrossRef]
- 20. Trikalitis, P.N.; Rangan, K.K.; Kanatzidis, M.G. Platinum Chalcogenido MCM-41 Analogues. High Hexagonal Order in Mesostructured Semiconductors Based on  $Pt^{2+}$  and  $[Ge_4Q_{10}]^{4-}$  (Q = S, Se) and  $[Sn_4Se_{10}]^{4-}$  Adamantane Clusters. *J. Am. Chem. Soc.* 2002, 124, 2604–2613. [CrossRef]

- 21. Liao, J.H.; Varotsis, C.; Kanatzidis, M.G. Syntheses, structures, and properties of six novel alkali metal tin sulfides: K<sub>2</sub>Sn<sub>2</sub>S<sub>8</sub>, alpha-Rb<sub>2</sub>Sn<sub>2</sub>S<sub>8</sub>, beta-Rb<sub>2</sub>Sn<sub>2</sub>S<sub>8</sub>, K<sub>2</sub>Sn<sub>2</sub>S<sub>5</sub>, Cs<sub>2</sub>Sn<sub>2</sub>S<sub>6</sub>, and Cs<sub>2</sub>SnS<sub>14</sub>. *Inorg. Chem.* **1993**, *32*, 2453–2462. [CrossRef]
- Rangan, K.K.; Trikalitis, P.N.; Canlas, C.; Bakas, T.; Weliky, D.P.; Kanatzidis, M.G. Hexagonal Pore Organization in Mesostructured Metal Tin Sulfides Built with [Sn<sub>2</sub>S<sub>6</sub>]<sup>4-</sup> Cluster. *Nano Lett.* 2002, 2, 513–517. [CrossRef]
- Li, H.; Li, G.M.; Wu, K.; Zhang, B.B.; Yang, Z.H.; Pan, S.L. BaB<sub>2</sub>S<sub>4</sub>: An Efficient and Air-Stable Thioborate as Infrared Nonlinear Optical Material with High Laser Damage Threshold. *Chem. Mater.* 2018, *30*, 7428–7432. [CrossRef]
- Liu, B.W.; Jiang, X.M.; Zeng, H.Y.; Guo, G.C. [ABa<sub>2</sub>Cl][Ga<sub>4</sub>S<sub>8</sub>] (A = Rb, Cs): Wide-Spectrum Nonlinear Optical Materials Obtainedby Polycation-Substitution-Induced Nonlinear Optical (NLO)-Functional Motif Ordering. *J. Am. Chem. Soc.* 2020, 142, 10641–10645. [CrossRef] [PubMed]
- Feng, K.; Kang, L.; Lin, Z.; Yao, J.; Wu, Y. Noncentrosymmetric Chalcohalide NaBa<sub>4</sub>Ge<sub>3</sub>S<sub>10</sub>Cl with Large Band Gap and IR NLO Response. J. Mater. Chem. C 2014, 2, 4590–4596. [CrossRef]
- 26. Liu, B.W.; Jiang, X.M.; Li, B.X.; Zeng, H.Y.; Guo, G.C. Li[LiCs<sub>2</sub>Cl][Ga<sub>3</sub>S<sub>6</sub>]: ANanoporous Framework of GaS4 Tetrahedra with Excellent Nonlinear Optical Performance. *Angew. Chem. Int. Ed.* **2020**, *59*, 4856–4859. [CrossRef] [PubMed]
- Chu, Y.; Wu, K.; Su, X.; Han, J.; Yang, Z.H.; Pan, S.L. Intriguing Structural Transition Inducing Variable Birefringences in ABa<sub>2</sub>MS<sub>4</sub>Cl (A = Rb, Cs; M = Ge, Sn). *Inorg. Chem.* 2018, *57*, 11310–11313. [CrossRef] [PubMed]
- Liu, B.W.; Zeng, H.Y.; Jiang, X.M.; Guo, G.C. Phase Matching Achieved by Bandgap Widening in Infrared Nonlinear Optical Materials [ABa<sub>3</sub>Cl<sub>2</sub>][Ga<sub>5</sub>S<sub>10</sub>] (A= K, Rb, and Cs). CCS Chem. 2021, 3, 964–973. [CrossRef]
- Zhou, J.Z.; Chu, Y.; Li, J.J.; Pan, S.L. Ba<sub>2</sub>BS<sub>3</sub>Cl and Ba<sub>5</sub>B<sub>2</sub>S<sub>8</sub>Cl<sub>2</sub>: First Alkaline-Earth Metal Thioborate Halides with [BS<sub>3</sub>] Units. *Chem. Commun.* 2021, 57, 6440–6443. [CrossRef]
- Berseneva, A.A.; Aziziha, M.; Schorne-Pinto, J.; Besmann, T.M.; zur Loye, H.-C. All-Inorganic Open-Framework Chalcogenides, A<sub>3</sub>Ga<sub>5</sub>S<sub>9</sub>·xH<sub>2</sub>O (A = Rb and Cs), Exhibiting Ultrafast Uranyl Remediation and Illustrating a Novel Post-Synthetic Preparation of Open-Framework Oxychalcogenides. *Chem. Mater.* 2022, *34*, 8366–8378. [CrossRef]
- Li, G.; Wu, K.; Liu, Q.; Yang, Z.; Pan, S. Na<sub>2</sub>ZnGe<sub>2</sub>S<sub>6</sub>: A New Infrared Nonlinear Optical Material with Good Balance between Large Second-Harmonic Generation Response and High Laser Damage Threshold. *J. Am. Chem. Soc.* 2016, 138, 7422–7428. [CrossRef]
- Chen, M.M.; Zhou, S.; Wei, W.; Wu, X.; Lin, H.; Zhu, Q.L. AZn<sub>4</sub>Ga<sub>5</sub>Se<sub>12</sub> (a = K, Rb, or Cs): Infrared Nonlinear Optical Materials with Simultaneous Large Second Harmonic Generation Responses and High Laser-Induced Damage Thresholds. *Inorg. Chem.* 2022, 60, 10038–10046. [CrossRef] [PubMed]
- 33. Rigaku Oxford Diffraction. CrysAlisPro Software System, Version v40.67a; Rigaku Corporation: Oxford, UK, 2019.
- 34. Sheldrick, G. SHELXS-97: Program for X-ray Crystal Structure Solution; University of Gottingen: Gottingen, Germany, 1997.
- 35. Spek, A. PLATON, A Multipurpose Crystallographic Tool; Utrecht University: Utrecht, The Netherlands, 2005.
- 36. Gustav, K. Reflectance Spectroscopy; Springer: Berlin/Heidelberg, Germany, 1969; pp. 1–366.
- Kurtz, S.K.; Perry, T.T. A Powder Technique for the Evaluation of Nonlinear Optical Materials. J. Appl. Phys. 1968, 39, 3798–3813.
  [CrossRef]
- Zhang, M.-J.; Jiang, X.-M.; Zhou, L.-J.; Guo, G.-C. Two phases of Ga<sub>2</sub>S<sub>3</sub>: Promising infrared second-order nonlinear optical materials with very high laser induced damage thresholds. *J. Mater. Chem. C* 2013, 1, 4754–4760. [CrossRef]
- Gonze, X. Perturbation expansion of variational principles at arbitrary order. *Phys. Rev. A* 1995, 52, 1086–1095. [CrossRef] [PubMed]
- 40. Gonze, X. Adiabatic density-functional perturbation theory. Phys. Rev. A 1995, 52, 1096–1114. [CrossRef] [PubMed]
- 41. Baroni, S.; de Gironcoli, S.; Dal Corso, A.; Giannozzi, P. Phonons and related crystal properties from density-functional perturbation theory. *Rev. Mod. Phys.* 2001, *73*, 515–562. [CrossRef]
- 42. Ghosez, P.; Gonze, X.; Godby, R.W. Long-wavelength behavior of the exchange-correlation kernel in the Kohn-Sham theory of periodic systems. *Phys. Rev. B* 1997, *56*, 12811–12817. [CrossRef]
- 43. Sharma, S.; Ambrosch-Draxl, C. Second-Harmonic Optical Response from First Principles. Phys. Scr. 2004, 109, 128. [CrossRef]
- Yohannan, J.P.; Vidyasagar, K. Syntheses and structural characterization of non-centrosymmetric Na<sub>2</sub>M<sub>2</sub>M'S<sub>6</sub> (M, M'=Ga, In, Si, Ge, Sn, Zn, Cd) sulfides. J. Solid State Chem. 2016, 238, 147–155. [CrossRef]
- 45. Teske, L. Zur Kenntnis von BaCdGeS4 mit einem Beitrag | zur | Kristallchemie von Verbindungen des Typs BaABS<sub>4</sub>. Z. Anorg. Allg. Chem. **1980**, 468, 27–34. [CrossRef]
- Luo, X.; Liang, F.; Zhou, M.; Guo, Y.; Li, Z.; Lin, Z.; Yao, J.; Wu, Y. K<sub>2</sub>ZnGe<sub>3</sub>S<sub>8</sub>: A Congruent-Melting Infrared Nonlinear-Optical Material with a Large Band Gap. *Inorg. Chem.* 2018, *57*, 9446–9452. [CrossRef] [PubMed]
- 47. Wu, P.; Ibers, J.A. Synthesis and Structures of the Quaternary Chalcogenides of the Type KLnMQ<sub>4</sub> (Ln = La, Nd, Gd, Y; M = Si, Ge; Q = S, Se). *J. Solid State Chem.* **1993**, 107, 347–355. [CrossRef]
- Mei, D.; Lin, Z.; Bai, L.; Yao, J.; Fu, P.; Wu, Y. KBiMS<sub>4</sub> (M=Si, Ge): Synthesis, structure, and electronic structure. *J. Solid State Chem.* 2010, 183, 1640–1644. [CrossRef]
- 49. Zhang, C.; Wang, K.-N.; Ji, M.; An, Y.-L. Mild Solvothermal Syntheses of Thioargentates A-Ag-S (A = K, Rb, Cs) and A-Ag-Ge-S (A = Na, Rb): Crucial Role of Excess Sulfur. *Inorg. Chem.* **2013**, *52*, 12367–12371. [CrossRef] [PubMed]
- Li, Z.; Jiang, X.; Yi, C.; Zhou, M.; Guo, Y.; Luo, X.; Lin, Z.; Wu, Y.; Shi, Y.; Yao, J. K<sub>2</sub>MnGe<sub>3</sub>S<sub>8</sub>: A new multifunctional semiconductor featuring [MnGe<sub>3</sub>S<sub>8</sub>]<sup>2-</sup> layers and demonstrating interesting nonlinear optical response and antiferromagnetic properties. *J. Mater. Chem. C.* 2018, 6, 10042–10049. [CrossRef]

- Guo, G.; Jiang, X.; Liu, B.; Yan, Q.; Chen, W.; Chai, X. Rb<sub>2</sub>MGe<sub>3</sub>S<sub>8</sub> (M=Zn, Cd): Non-Centrosymmetry Transformation Led by Structure Change of [MGe<sub>3</sub>S<sub>8</sub>]<sup>2-</sup> Unit. *Acta Chim. Sin.* 2022, *80*, 633–639.
- Li, S.-F.; Jiang, X.-M.; Fan, Y.-H.; Liu, B.-W.; Zeng, H.-Y.; Guo, G.-C. New strategy for designing promising mid-infrared nonlinear optical materials: Narrowing the band gap for large nonlinear optical efficiencies and reducing the thermal effect for a high laser-induced damage threshold. *Chem. Sci.* 2018, *9*, 5700–5708. [CrossRef]

**Disclaimer/Publisher's Note:** The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.