

Second-Harmonic Generation and Crystal Structure of the Diamond-like Semiconductors $\text{Li}_2\text{CdGeS}_4$ and $\text{Li}_2\text{CdSnS}_4$

Jonathan W. Lekse,[†] Meghann A. Moreau,[†] Katie L. McNerny,[†] Jeongho Yeon,[‡] P. Shiv Halasyamani,[‡] and Jennifer A. Aitken^{*†}

[†]Department of Chemistry and Biochemistry, 600 Forbes Avenue, Duquesne University, Pittsburgh, Pennsylvania 15282, and [‡]Department of Chemistry, 136 Fleming Building, University of Houston, Houston, Texas 77204-5003

Received May 29, 2009

The semiconductors $\text{Li}_2\text{CdGeS}_4$ and $\text{Li}_2\text{CdSnS}_4$, which are of interest for their nonlinear optical properties, were synthesized using high-temperature solid-state and polychalcogenide flux syntheses. Both compounds were found to crystallize in $Pmn2_1$, with R_1 (for all data) = 1.93% and 1.86% for $\text{Li}_2\text{CdGeS}_4$ and $\text{Li}_2\text{CdSnS}_4$, respectively. The structures of both compounds are diamond-like with the tetrahedra pointing in the same direction along the c axis. The alignment of the tetrahedra results in the structure lacking an inversion center, a prerequisite for second-harmonic generation (SHG). A modified Kurtz nonlinear optical powder technique was used to determine the SHG responses of both compounds. $\text{Li}_2\text{CdGeS}_4$ displayed a type I phase-matchable response of approximately $70\times$ α -quartz, while $\text{Li}_2\text{CdSnS}_4$ displayed a type I non-phase-matchable response of approximately $100\times$ α -quartz. Diffuse-reflectance spectroscopy was used to determine band gaps of 3.10 and 3.26 eV for $\text{Li}_2\text{CdGeS}_4$ and $\text{Li}_2\text{CdSnS}_4$, respectively.

Beginning with the first observation of nonlinear optical (NLO) behavior in quartz crystals in 1961,¹ researchers have been finding uses for second-harmonic-generation (SHG) materials in optical communications, laser medicine, and molecular spectroscopy, among others. There are several notable materials, such as KTiOPO_4 (KTP),² LiNbO_3 ,^{3–5} and LiB_3O_5 (LBO)⁶ that have found uses in either the ultraviolet or visible region, while several chalcopyrites are

commonly used in the IR region, such as AgGaS_2 ,^{7–9} CuGaS_2 ,¹⁰ and AgGaSe_2 .¹¹ These materials possess higher SHG coefficients than the above-mentioned oxides because of the presence of highly polarizable M–S or M–Se bonds, yet they are somewhat limited in their applications because of lower laser-damage thresholds, which are correlated to their relatively small band gaps.¹⁰ Consequently, new materials with exceptional SHG properties and higher laser-damage thresholds are required for applications in the IR region.

Toward this goal, we have prepared two compounds, $\text{Li}_2\text{CdGeS}_4$ and $\text{Li}_2\text{CdSnS}_4$. These materials have polarizable M–S bonds resulting in high NLO coefficients, yet they also have wider band gaps, which may result in higher laser-damage thresholds. Like chalcopyrites, $\text{Li}_2\text{CdGeS}_4$ and $\text{Li}_2\text{CdSnS}_4$ are diamond-like semiconductors (DLSs),^{12–16} which means that the structures of these compounds are derived from that of diamond, either the cubic or hexagonal form.^{12,13} These compounds are built from tetrahedral building blocks that are oriented along one crystallographic axis, rendering the structures inherently noncentrosymmetric, the first criterion for SHG.¹⁷

Much of the previous work with DLSs has been focused on binary and ternary compounds, with less exploration in the area of quaternary materials.^{14–16} Admittedly, there are difficulties involved in the synthesis of quaternary DLSs that deter many researchers from exploiting the diversity that exists in these systems. The principle issue is the tendency of high-temperature, solid-state reactions to favor the

*To whom correspondence should be addressed. E-mail: aitkenj@duq.edu.

- (1) Franken, P. A.; Hill, A. E.; Peters, C. W.; Weinrich, G. *Phys. Rev. Lett.* **1961**, 7, 118–119.
- (2) Kato, K. *IEEE J. Quantum Electron.* **1991**, 27, 1137–1140.
- (3) Miller, R. C.; Nordland, W. A. *Phys. Rev.* **1970**, B2, 4896–4902.
- (4) Brosnan, S. J.; Byer, R. L. *IEEE J. Quantum Electron.* **1979**, 15, 415–431.
- (5) Dmitriev, V. G.; Gurzadyan, G. G.; Nikogosyan, D. N. *Handbook of Nonlinear Optical Crystals*; Springer: New York, 1999.
- (6) Chen, C.; Wu, Y. *J. Opt. Soc. Am.* **1989**, B6, 616–621.
- (7) Ruderman, W.; Maffettone, J.; Zelman, D.; Poirier, D. *Mater. Res. Soc. Symp. Proc.* **1998**, 484, 519–524.
- (8) Bhar, G. C.; Smith, R. C. *Phys. Status Solidi* **1972**, 13, 157–168.
- (9) Chemla, D. S.; Kupecek, P. J.; Robertson, D. S.; Smith, R. C. *Opt. Commun.* **1971**, 3, 29–31.

- (10) Jackson, A. G.; Ohmer, M. C.; LeClair, S. R. *Infrared Phys. Technol.* **1997**, 38, 233–244.
- (11) Catella, G. C.; Burlage, D. *MRS Bull.* **1998**, 23, 28–36.
- (12) Goryunova, N. A. *The Chemistry of Diamond-Like Semiconductors*; Anderson, J. C., Ed.; The MIT Press: Cambridge, U.K., 1965.
- (13) Parthé, E. *Crystal Chemistry of Tetrahedral Structures*; Gordon and Breach Science Publishers: New York, 1964.
- (14) Parthé, E.; Yvon, K.; Dietch, R. H. *Acta Crystallogr., Sect. B* **1969**, 25, 1164–1174.
- (15) Schleich, D. M.; Wold, A. *Mater. Res. Bull.* **1977**, 12, 111–114.
- (16) Quintero, M.; Barreto, A.; Grima, P.; Tovar, R.; Quintero, E.; Porras, G. S.; Ruiz, J.; Woolley, J. C.; Lamarche, G.; Lamarche, A. M. *Mater. Res. Bull.* **1999**, 34, 2263–2270.
- (17) Ohmer, M. C.; Pandey, R. *MRS Bull.* **1998**, 23, 16–20.

Table 1. Selected Crystallographic Data for $\text{Li}_2\text{CdGeS}_4$ and $\text{Li}_2\text{CdSnS}_4$

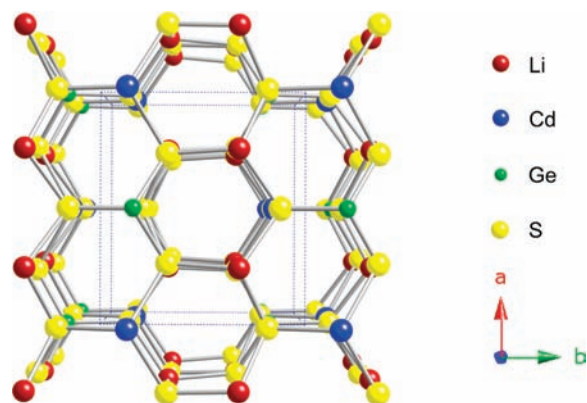
	$\text{Li}_2\text{CdGeS}_4$	$\text{Li}_2\text{CdSnS}_4$
crystal system	orthorhombic	orthorhombic
space group	$Pmn2_1$	$Pmn2_1$
unit cell parameters	$a = 7.7374(1) \text{ \AA}$ $b = 6.8498(1) \text{ \AA}$ $c = 6.3688(1) \text{ \AA}$	$a = 7.9555(3) \text{ \AA}$ $b = 6.9684(3) \text{ \AA}$ $c = 6.4886(3) \text{ \AA}$
Z	2	2
reflections collected	5848	6530
independent reflections	1228 [$R(\text{int}) = 0.0289$]	1345 [$R(\text{int}) = 0.0211$]
goodness of fit	0.949	1.149
R indices (all data)	$R1 = 0.0193$, $wR2 = 0.0273$	$R1 = 0.0186$, $wR2 = 0.0419$
largest peak/hole	$0.608/-0.716 \text{ e/\AA}^3$	$0.854/-0.847 \text{ e/\AA}^3$

formation of the most thermodynamically stable phases, which are quite frequently binary compounds. Despite this synthetic challenge, it is worth pursuing quaternary materials because of their increased compositional flexibility,^{12,13} compared to binary and ternary phases. It is this flexibility that allows for the potential to tune the physical properties of the material for applications in nonlinear optics, as well as other areas where DLSs have found utility such as light-emitting diodes¹⁸ and solar cells.¹⁹

The general formula used to represent the DLSs reported here is $\text{I}_2\text{-II-IV-VI}_4$, where the roman numeral corresponds to the number of valence electrons and the subscript denotes the number of that particular ion in the formula unit. While there are many known compounds with this formula where $\text{I} = \text{Ag}$ or Cu ,^{16,20} there are few where $\text{I} = \text{Li}$.^{21,22} The “replacement” of Ag or Cu with Li widens the band gap in these materials, increasing their potential in SHG applications because of the possibility of increased laser-damage thresholds. Additionally, the presence of Li as the univalent cation allows for the use of a lithium polysulfide flux²³ as a reaction medium to promote crystal growth.

A phase-pure, polycrystalline powder of $\text{Li}_2\text{CdGeS}_4$ was synthesized by heating stoichiometric amounts of lithium sulfide, cadmium, germanium, and sulfur at $525 \text{ }^\circ\text{C}$. However, single crystals of $\text{Li}_2\text{CdGeS}_4$ were obtained from a lithium polysulfide flux at $650 \text{ }^\circ\text{C}$. Both single-crystal and polycrystalline samples of $\text{Li}_2\text{CdSnS}_4$ were synthesized using a polychalcogenide flux at 750 and $650 \text{ }^\circ\text{C}$, respectively. Though this is the first report of $\text{Li}_2\text{CdGeS}_4$, $\text{Li}_2\text{CdSnS}_4$ has been previously reported.²¹ A synthesis using conditions identical to those reported by Devi and Vidyasagar²¹ was also attempted; however, the product was primarily CdS with a small amount of the quaternary phase present. In our work, it was determined that the flux ratio, $\text{Li}_2\text{S}:\text{S}$, is very important in determining the product of these reactions. Varying this ratio by ~ 0.02 produces pure CdS and none of the quaternary phase. Additional experimental details can be found in the Supporting Information.

$\text{Li}_2\text{CdGeS}_4$ and $\text{Li}_2\text{CdSnS}_4$ are both predicted to be diamond-like based upon a set of rules used to identify

**Figure 1.** Structure of $\text{Li}_2\text{CdGeS}_4$ viewed down the c axis.

DLSs.^{12,13} The first of four rules is that the average valence electron concentration must be 4. The second rule is that the valence electron concentration per anion must be 8. The last two are Pauling’s first and second rules.²⁴ In a DLS, the atoms should be tetrahedrally coordinated and therefore should follow Pauling’s first rule and have cation-to-anion ratios that lead to tetrahedral coordination. A DLS should also conform to Pauling’s second rule, also known as the electrostatic valence sum rule. In order to satisfy this rule, the charge of the anion should be compensated for by the valence bonds from the cations in the immediate coordination sphere.

Single-crystal X-ray diffraction was used to determine that both compounds are indeed diamond-like and possess the wurtz–stannite structure type. The term wurtz–stannite does not represent a particular compound. Instead, it was first used in 1974 to describe the distorted wurzite structure adopted by several compounds with the general formula $\text{Cu}_2\text{-II-IV-S}_4$.²⁵ $\text{Li}_2\text{CdGeS}_4$ and $\text{Li}_2\text{CdSnS}_4$ crystallize in the orthorhombic space group $Pmn2_1$ (Table 1 and Figure 1). In accordance with Pauling’s second rule, each S anion is tetrahedrally coordinated to one Cd cation, one Ge/Sn cation, and two Li cations, forming a three-dimensional, honeycomb structure. However, if the Li-S bonds are considered to be more ionic than either the Cd-S or Sn/Ge-S bonds, the structure can be thought of as two-dimensional, with Li^+ cations separating $[\text{Cd}(\text{Ge}/\text{Sn})\text{S}_4]^{2-}$ layers, which extend in the ab plane. All of the tetrahedra are fairly regular, with the greatest distortion from ideal occurring in the LiS_4 polyhedra, with values for S-Li-S angles ranging from $106.3(5)^\circ$ to $113.4(5)^\circ$. This is in contrast to the previously reported structure of $\text{Li}_2\text{CdSnS}_4$ in the centrosymmetric

(18) Bachmann, K. J.; Buehler, E.; Shay, J. L.; Wernick, J. H. *U.S. Pat. Appl. B* 382,021.

(19) Goetzberger, A.; Hebling, C.; Schock, H. *Mater. Sci. Eng.* **2003**, *40*, 1–46.

(20) Davidiyuk, G. E.; Parasyuk, O. V.; Semenyuk, S. A.; Romanyuk, Ya. E. *Inorg. Mater.* **2003**, *39*, 919–923.

(21) Devi, M. S.; Vidyasagar, K. *J. Chem. Soc., Dalton Trans.* **2002**, 2092–2096.

(22) Lekse, J. W.; Leverett, B. M.; Lake, C. H.; Aitken, J. A. *J. Solid State Chem.* **2008**, *181*, 3217–3222.

(23) Kanatzidis, M. G.; Sutorik, A. C. *Progress in Inorganic Chemistry*; Karlin, K. D., Ed.; John Wiley & Sons, Inc.: Hoboken, NJ, 1999; Vol. 43.

(24) Pauling, L. *J. Am. Chem. Soc.* **1929**, *51*, 1010–1026.

(25) Schäfer, W.; Nitsche, R. *Mater. Res. Bull.* **1974**, *9*, 645–654.

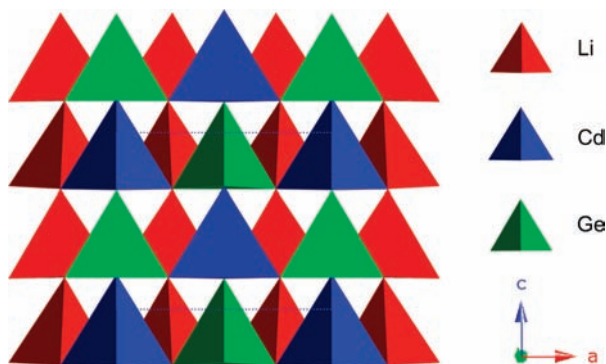


Figure 2. Polyhedral representation of the structure of $\text{Li}_2\text{CdGeS}_4$ that shows all tetrahedra oriented in the same direction along the c axis, thus demonstrating the lack of an inversion center.

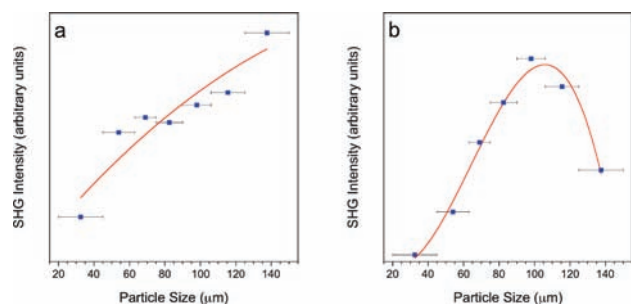


Figure 3. SHG measurements of (a) $\text{Li}_2\text{CdGeS}_4$ and (b) $\text{Li}_2\text{CdSnS}_4$. $\text{Li}_2\text{CdGeS}_4$ exhibits a type I, phase-matchable response of approximately $70\times$ α -quartz, while $\text{Li}_2\text{CdSnS}_4$ exhibits a type I, non-phase-matchable response of approximately $100\times$ α -quartz. The line in both plots is not a fit to the data but rather a guide for the eye.

space group $Pm\bar{m}n$ using a disorder model.²¹ Powder X-ray diffraction was also used to determine the phase purity of the obtained products and validate the crystal structures (see the Supporting Information).

By virtue of being diamond-like, the compounds synthesized in this work are noncentrosymmetric (Figure 2), a prerequisite for SHG. A modified Kurtz NLO system was used to measure the SHG responses of both compounds.²⁶ Samples of $\text{Li}_2\text{CdGeS}_4$ displayed a type I, phase-matchable, SHG response of approximately $70\times$ α -quartz (ungraded) (Figure 3a). $\text{Li}_2\text{CdSnS}_4$ was also found to be SHG-active, with a type I, non-phase-matchable response of $100\times$ α -quartz (ungraded) (Figure 3b). However, this does not preclude the possibility that $\text{Li}_2\text{CdSnS}_4$ could display another type of phase matchability, i.e., type II, that cannot be measured on powder samples. Larger crystals than those obtained here are required to test for other types of phase matchability. The presence of an SHG response by $\text{Li}_2\text{CdSnS}_4$ validates our structure solution in space group $Pmn2_1$.

Fourier transform IR spectroscopy was used to determine that these compounds are transparent in the IR region (see the Supporting Information). Transparency in this region is an additional criterion for practical NLO applications. In addition to IR spectroscopy, optical diffuse-reflectance UV/vis/near-IR spectroscopy was used to determine the band gaps of the compounds. $\text{Li}_2\text{CdGeS}_4$, a pale-yellow compound, was found to have a band gap of 3.10 eV, while the pale-orange $\text{Li}_2\text{CdSnS}_4$ was determined to have a band gap

(26) Kurtz, S. K.; Perry, T. T. *J. Appl. Phys.* **1968**, *39*, 3798–3813.

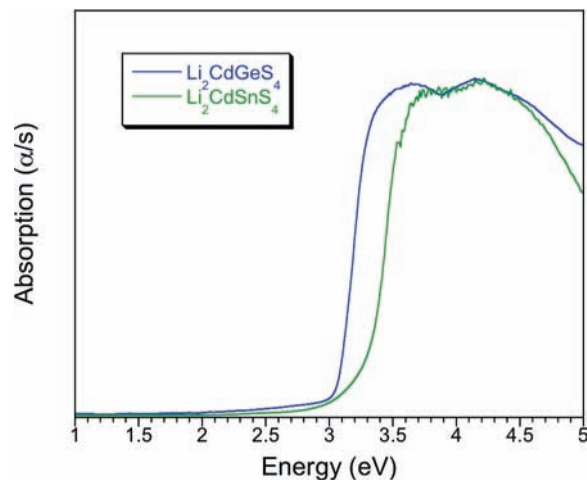


Figure 4. Optical diffuse-reflectance spectra, converted to absorption, of $\text{Li}_2\text{CdGeS}_4$ and $\text{Li}_2\text{CdSnS}_4$.

of 3.26 eV (Figure 4). The result for $\text{Li}_2\text{CdSnS}_4$ is in sharp contrast to the report from Devi and Vidyasagar that this compound does not show any absorption edge.²¹ These band gaps are significantly larger than those of the analogous Cu-containing compounds, $\text{Cu}_2\text{CdGeS}_4$ (2.05 eV)²⁷ and $\text{Cu}_2\text{CdSnS}_4$ (1.38 eV),²⁸ and the commercially available chalcopyrites used for SHG applications, AgGaS_2 (2.73 eV),¹⁷ AgGaSe_2 (1.83 eV),¹⁷ and CuGaS_2 (2.469 eV).²⁹ Larger band gaps are important because the laser-damage threshold of a material is dependent upon the compound's band gap, with larger gaps leading to increased thresholds.¹⁰ The wide gaps of $\text{Li}_2\text{CdSnS}_4$ and $\text{Li}_2\text{CdGeS}_4$ coupled with their substantial SHG response make these and related compounds promising for NLO applications.

In conclusion, two DLSs, $\text{Li}_2\text{CdGeS}_4$ and $\text{Li}_2\text{CdSnS}_4$, were synthesized and found to display relatively wide band gaps in addition to significant SHG responses. These properties warrant further investigation of quaternary Li-containing DLS compounds for NLO applications. Electronic band structure calculations are being conducted to understand the origin of the band gaps. Additionally, $\text{Li}_2\text{ZnSnS}_4$ ²² and $\text{Li}_2\text{ZnGeS}_4$ are being synthesized and characterized to expand the library of compounds at our disposal for physical property tuning.

Acknowledgment. J.A.A. thanks the National Science Foundation (NSF; Grant DMR-0645304) for a CAREER award. We also thank Duquesne University's Bayer School of Natural and Environmental Sciences and the NSF (Grants DUE-0511444 and CRIF-02-34872) for equipment and funding. J.Y. and P.S.H. thank the Robert A. Welch Foundation, the ACS PRF (47345-AC10), and the NSF (Grant DMR-0652150) for support.

Supporting Information Available: Additional synthetic details, a CIF file for both compounds, a comparison of experimental and calculated powder diffraction patterns, and IR spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

(27) Davidiyuk, G. E.; Parasyuk, O. V.; Semenyuk, S. A.; Romanyuk, Ya. E. *Inorg. Mater.* **2003**, *39*, 919–923.

(28) Ichikawa, T.; Maeda, T.; Matsushita, H.; Katsui, A. *J. Adv. Sci.* **2000**, *12*, 99–100.

(29) Horinaka, H.; Yamamoto, N.; Miyauchi, T. *J. Appl. Phys.* **1978**, *17*, 521–526.