Electronic Supplementary Information

Li_2ZnGeS_4: A Promising Diamond-like Infrared Nonlinear Optical Material with High Laser Damage Threshold and Outstanding Second-Harmonic Generation Response

Yi Huang[#], Kui Wu[#], Jianian Cheng, Yu Chu, Zhihua Yang[*], Shilie Pan[*]

CAS Key Laboratory of Functional Materials and Devices for Special Environments, Xinjiang Technical Institute of Physics & Chemistry, CAS; Xinjiang Key Laboratory of Electronic Information Materials and Devices, 40-1 South Beijing Road, Urumqi 830011, China

To whom correspondence should be addressed:

** E-mail: slpan@ms.xjb.ac.cn (Shilie Pan).*

**E-mail: zhyang@ms.xjb.ac.cn (Zhihua Yang)*

CONTENTS

1. Synthesis of Title Compound

2. Structural Refinement and Crystal Data

3. Property Characterization

4. Figure and Tables

5. References

1. Synthesis of Title Compounds

Purchased high-purity (4N) chemicals were directly used for the material synthesis. To better ensure the reliability of raw material ratio, vacuum glove box was chosen to complete the preparation process and avoid the effect of air oxidation.

***β*-Li_2ZnGeS_4**. Raw mixture (Li : ZnS : Ge : S) with stoichiometric proportion of 2 : 1 : 1 : 3 was firstly loaded into the graphite crucible and then put it into silica tube, which is different with that (Li_2S:Zn:Ge:S = 2:1:1:8) of *α*-Li_2ZnGeS_4. Using the flame gun and air extractor, silica tube was carefully vacuum-sealed with the internal vacuum degree about 10^{-3} Pa. Muffle furnace was used to complete the crystallization reaction and the setting temperature process was shown as follows: firstly heated to 300 °C in 10 h and left at this temperature for 20 h to make the partial S participate into the reaction, further heated to 900 °C that is different with the maximum temperature (750 °C) of *α*-Li_2ZnGeS_4 to ensure the mixture melt completely while kept at this temperature within 4 days, then slowly cooled down to 300 °C in 100 h, finally quickly down to the room temperature in one day. Many air-stable colorless crystals with about 95% yield were found under the optical microscope.

Carefully ground microcrystal powders were used for powder X-ray diffraction (PXRD) measurement by an automated Bruker D2 X-ray diffractometer at room temperature. Experimental results of title compounds are essentially in accordance with the calculated ones from the single-crystal data respectively (Fig. 1). Compared with the powder XRD patterns of *α*/*β*-Li_2ZnGeS_4, they exhibit the similar peak positions, but their peak intensities are obviously different, such as 19.5°. Besides, *β*-Li_2ZnGeS_4 exhibit only one peak in the 22.5° while *α*-Li_2ZnGeS_4 has the two split peaks: 22.5° and 23.5°. Moreover, the intensities of several peaks between 25° and 30° are also different.

2. Structural Refinement and Crystal Data

A Bruker SMART APEX II 4K CCD diffractometer with Mo Ka radiation (λ = 0.71073 Å) was used to complete the crystal data collection at room temperature. Multi-scan method was used for absorption correction. The crystal structure was solved by the direct method and refined using the SHELXTL program package[1]. Note

that all atom sites are completely occupied by each atom in β-Li_2ZnGeS_4. Crystal data and structure refinements of title compound are given in Table S1 and Table S2 summarizes the atomic coordinates and isotropic displacement parameters of title compound. The subsequent analysis of the element content in the crystal with an energy-dispersive X-ray (EDX) equipped Hitachi JSM-7610F PLUS (Fig S1, Table S3) shows that the molar ratio (Zn : Ge : S) of Li_2ZnGeS_4 is approximately about 1:1:4, which is consistent with that of β-Li_2ZnGeS_4.

3. Property Characterization

UV–Vis–NIR Diffuse-reflectance Spectroscopy. Shimadzu SolidSpec-3700 DUV spectrophotometer was used to measure the diffuse-reflectance spectra within the wavelength range from 200 to 2500 nm.

Infrared Spectroscopy. Ground micro-crystals mixed with KBr powder were used to complete the IR spectroscopy measurement on a Shimadzu IRAffinity-1 Fourier transform infrared spectrometer within the range from 400 to 4000 cm^{-1}.

Second-Harmonic Generation Measurements. The SHG response measurement was performed by the Kurtz and Perry method with a 2.09 μm Q-switched laser.[2] The crystals were ground and sieved into five particle size ranges of 38-55, 55-88, 88-105, 105-150, and 150- 200 μm, with microcrystalline $AgGaS_2$ of the same particle size ranges serving as references. The samples were placed on a glass microscope cover slide, secured by a 1 mm thick silicone insole with an 8 mm diameter hole, and then covered with another glass slide. Then, they were placed into light-tight boxes and explored under a pulsed infrared beam from a Q-switched Ho:Tm:Cr:YAG laser with wavelength of 2.09 μm. The SHG signals were recorded on the oscilloscope that was connected with the detector. The procedure was repeated using the standard IR NLO material of $AgGaS_2$.

LDT Measurements. We have estimated the LDT of powdered β-Li_2ZnGeS_4 with powdered $AgGaS_2$ sample as the reference by a pulse laser (1.06 μm, 10 Hz, and 10 ns) in the same condition. The detailed test procedure is as follows: the LDT of β-Li_2ZnGeS_4 was evaluated on microcrystal powders (150-200 μm) with a pulsed Nd:YAG laser (1.06 μm, 10 ns, 10 Hz). Similar size of $AgGaS_2$ is chosen as the

reference. The judgment criterion is as follows: with increasing laser energy, the color change of the powder sample is constantly observed by optical microscope to determine the damage threshold. To adjust different laser beams, an optical concave lens is added into the laser path. The size of damage spot is measured on the scale of optical microscope.

Computational Description

The theoretical electronic and band structures as well as NLO properties were obtained within the framework of density functional theory (DFT) using the CASTEP Package[3]. The generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) functional and norm-conserving pseudopotentials (NCP) were performed under the geometry optimization[4]. During the calculations, pseudo atomic was adopted with the following valence electrons: Li $2s^1$, Zn $3d^{10}$ $4s^2$, Ge $4s^2$ $4p^2$, S $3s^2$ $3p^4$. And a plane wave cutoff of 650 eV along with 4 × 4 × 3 k-point sampling was set to achieve the convergence of calculations. Additionally, a formalism developed by Aversa and Sipe was applied to calculate the NLO coefficients at a zero frequency[5]. Since the previous calculation has been shown that the two band contributions are proved to be nearly zero, the static second-order nonlinear coefficients $\chi_{\alpha\beta\gamma}^{(2)}$ can be simplified as[6]: $\chi_{\alpha\beta\gamma}^{(2)} = \chi_{\alpha\beta\gamma}^{(2)}$ (VE) + $\chi_{\alpha\beta\gamma}^{(2)}$ (VH) (1)where, (VE), (VH) on behalf of virtual-electron process and virtual-hole process, respectively.

4. Figure and Tables

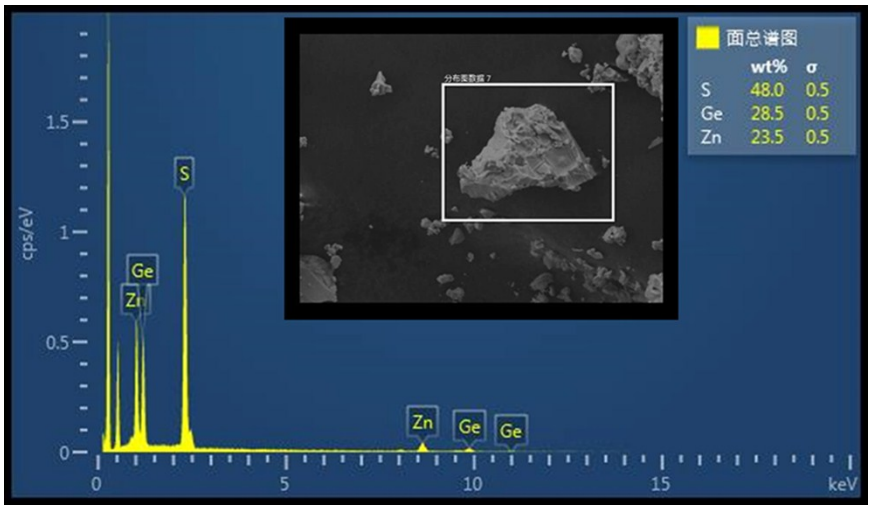

Fig. S1. EDX spectrum of β-Li_2ZnGeS_4.

Table S1. Crystal Data and Structure Refinement for Li_2ZnGeS_4

Empirical formula	**β-Li_2ZnGeS_4**
Formula weight	280.08
Crystal system	monoclinic
Space group	*Pn*
Unit cell dimensions	a = 6.213 (5) Å b = 6.525(5) Å c = 7.830 (6) Å β=90.7°
Z , V	2, 317.4(5) Å^3
Density (calculated)	2.931 g/cm^3
Absorption coefficient	9.687 mm^{-1}
F (000)	264
Completeness to theta	99.8 %
Goodness-of-fit on F^2	1.166
Final R indices [$F_o^2 > 2\sigma(F_o^2)$][a]	R_1= 0.0580, wR_2 = 0.1404
R indices (all data) [a]	R_1= 0.0795, wR_2 = 0.1617
Largest diff. peak and hole	1.960 and -1.170 e·Å^{-3}
[a]$R_1 = F_0 - F_c/F_0$ and $wR_2 = [w(F_0^2 - F_c^2)^2/wF_o^4]^{1/2}$ for $F_0^2 > 2\sigma(F_0^2)$.	

Table S2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for β-Li_2ZnGeS_4

Atom	**x**	**y**	**z**	**Ueq**	**Occupancy**
Li(1)	0.314(6)	0.672(3)	-0.005(4)	0.000(8)	1
Li(2)	0.307(6)	0.173(4)	0.287(5)	0.000(10)	1
Zn(1)	0.3098(4)	0.1776(3)	-0.2333(3)	0.0202(12)	1
Ge(1)	-0.1892(3)	0.3221(2)	0.0222(2)	0.0055(6)	1
S(1)	0.1709(6)	0.3152(7)	0.0132(6)	0.0093(9)	1
S(2)	-0.3176(7)	0.1812(7)	-0.2169(6)	0.0139(10)	1
S(3)	-0.3055(7)	0.6480(7)	0.0291(6)	0.0092(9)	1
S(4)	-0.3035(7)	0.1572(7)	0.2561(6)	0.0116(10)	1

Table S3. Average EDX data of β-Li_2ZnGeS_4

Element	Calc.(molecular mass)	Exp.
Zn	65.38(24.47)	23.5
Ge	72.63(27.18)	28.5
S	128.24(48.00)	48

Table S4. Properties Comparison of α/β-Li_2ZnGeS_4, $LiGaS_2$ and $AgGaS_2$.

Formula	E_g (eV)	d_{ij} (× AGS)	LDT (×AGS)
$AgGaS_2$	2.64	1	1
$LiGaS_2$	4.15	0.4	11
α-Li_2ZnGeS_4	3.92	100×α-SiO_2	-
β-Li_2ZnGeS_4	3.49	0.7	8

Table S5. Comparisons of the calculated SHG coefficients with a correction of the band gap by using a scissor operator for β-Li_2ZnGeS_4.

Cal. d_{ij} (pm/V)		VE (pm/V)	VH (pm/V)
d_{11}	14.16	13.65	0.49
d_{12}	-5.86	-6.45	0.61
d_{13}	-4.70	-5.34	0.64
d_{15}	-2.61	-1.95	-0.66
d_{24}	2.80	1.88	0.92
d_{33}	0.06	0.036	-0.03

Table S6. The contributions of different ions or groups to total d_{11} by real-space atom-cutting.

Cation/group	d_{11}(pm/V)	Contribution
Li	0.54	3.81%
ZnS_4	5.39	38.06%
GeS_4	9.80	69.21%

5. References

1 Sheldrick, G. M. *SHELXTL*, version 6.14, Bruker Analytical X-ray Instruments, Inc. Madison, WI, 2008.

2 Kurtz, S. K.; Perry, T. T. *J. Appl. Phys.* 1968, **39**, 3798.

3 Clark, S. J.; Segall, M. D.; Pickard, C. J.; Hasnip, P. J.; Probert, M. J.; Refson, K.; Payne, M. C. Z. Kristallogr. 2005, **220**, 567.

4 Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* 1996, **77**, 3865-3870. Kohn, W.; Sham, L. J. *Phys. Rev.* 1965, **140**, 1133.

5 Aversa, C.; Sipe, J. E. *Phys. Rev. B* 1995, **52**, 14636.

6 Lin, J.; Lee, M. H.; Liu, Z. P.; Chen, C.; Pickard, C. J. *Phys. Rev. B* 1999, **60**, 13380.