

Electronic Supplementary Information (ESI)

Li₃Ge₃Se₆: The First Ternary Lithium Germanium Selenide with Interesting ∞ [Ge₆Se₁₂]_n Chains Constructed by Ethane-like [Ge₂Se₆]⁶⁻ Clusters

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2. Experimental sections

Synthesis

All the substances used are purchased from Shanghai Aladdin biochemistry technology Co., Ltd and listed as follows: Li metal, Ge powder and Se powder. All the reactants have the purities higher than 99.99% and are stored in a glove box filled with dry Ar without oxygen and moisture. The crystal and pure phase sample of $\text{Li}_3\text{Ge}_3\text{Se}_6$ were synthesized by solid-state reaction with all elementary substances of Li, Ge and Se at a ratio of 1:1:2. The mixture of Li, Ge and Se was weighted and placed into the graphite crucible in the Ar atmosphere, and then sealed into a 10 mm (inner diameter) fused-silica tube with methane-oxygen flame under a high vacuum of 10^{-3} Pa. The tubes were moved into a computer-controlled furnace, heated to 850 °C in 50 h, dwelled there for 30 h, cooled to 650 °C at a rate of 5 °C /h, then rapidly

cooled to room temperature at a rate of 10 °C /h.

Structural refinement and crystal data

Experimental single crystals of $\text{Li}_3\text{Ge}_3\text{Se}_6$ are selected mechanically and fixed on the top of a glass fiber with epoxy for single crystal X-ray crystallography. All above operations was made under a $40\times$ microscope. All structure data were collected with a Bruker SMART APEX II 4K CCD diffractometer which was equipped with Mo Ka radiation ($\lambda = 0.71073 \text{ \AA}$) operating at 50 kV and 40 mA at 296(2) K. Then the data were refined through full-matrix least-squares on F^2 using SHELXTL program package.¹ Structure determination is based on direct method, and face-indexed absorption correction was made with XPREP Program. The final structure was checked with PLATON² and no higher symmetries were provided. Structure parameters in detail are listed in Table S1 and their atomic bond-valence and isotropic displacement parameters are listed in Table S2. Selected bond length and angles are listed in Table S3.

Powder X-ray diffraction (PXRD)

An automated Bruker D2 X-ray diffractometer equipped with a diffracted monochromator set for Cu KR ($\lambda = 1.5418 \text{ \AA}$) radiation was used to measure the XRD. The measurement was performed at 298 K in the angular range of $2\theta = 10^\circ - 70^\circ$. The scan step width was 0.02° and the fixed counting time was 1 s/step.

Infrared spectrum

The IR spectrum was recorded on a Shimadzu IRAffinity-1 Fourier transform infrared spectrometer with a resolution of 2 cm^{-1} covering the wave number range of $400 - 4000 \text{ cm}^{-1}$. The samples used to measure were the mixture of crystals of title compounds and KBr with the ratio of about 1:100. Firstly the mixture was dried and ground into fine powder, and then pressed into a transparent sheet through mechanical method. Finally the sheet was loaded in the sample chamber and then the IR spectrum was measured.

UV-Vis-NIR diffuse reflectance spectroscopy

Optical diffuse reflectance spectrum data were collected at 298 K with Shimadzu SolidSpec-3700DUV spectrophotometer. Spectral data cover a wavelength range of 190–2600 nm, which can provide the visible or UV cut-off edge. Besides, the reflectance spectra can be converted to absorbance through Kubelka-Munk function³, with which we got the experimental band gaps for title compound.

Raman spectroscopy

The Raman data were collected with a LABRAM HR Evolution spectrometer equipped with a CCD detector using 532 nm radiations from a diode laser on small single crystals, which were selected and loaded on a glass slide. A 50× objective lens was used to choose the area to be measured on the crystal. The beam has a spot size of 35 μm and its maximum power was 60 mW. All the spectrum data collection processes finished in 15 s.

Theoretical calculations

The first principle calculations for the experimental crystal structure were obtained based on *ab initio* calculations implemented in the CASTEP package through density functional theory (DFT).⁴ The generalized gradient approximation (GGA) was adopted and Perdew–Burke–Ernzerhof (PBE) functional was chosen to calculate the exchange-correlation potential, with an energy cutoff of 900.0 eV. The k integration over the Brillouinzone was performed by the tetrahedron method⁴¹ using a Monkhorst–Pack grid of $4 \times 4 \times 2$.

Table S1. Crystal data and structure refinements for Li₃Ge₃Se₆.

Empirical formula	Li ₃ Ge ₃ Se ₆	
Formula weight	712.35	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system, space group	<i>P</i> -1	
Unit cell dimensions	a = 6.7728(3) Å	α = 74.519(4)°
	b = 8.6804(5) Å	β = 76.334(4)°
	c = 10.6300(5) Å	γ = 69.185(4)°
Volume	555.98(5) Å ³	
Z, Calculated density	2, 4.255 kg/m ³	
Absorption coefficient	27.629 mm ⁻¹	
F(000)	618	
Crystal size	0.248×0.228×0.183 mm ³	
Theta range for data collection	2.56 to 27.53°.	
Limiting indices	-8 ≤ h ≤ 8, -11 ≤ h ≤ 11, -13 ≤ h ≤ 13	
Reflections collected / unique	9499 / 2550 [<i>R</i> _(int) = 0.0407]	
Completeness to theta = 27.53	99.40%	
Refinement method	Full-matrix least-squares on <i>F</i> ²	
Data / restraints / parameters	2550 / 0 / 113	
Goodness-of-fit on <i>F</i> ²	0.999	
Final <i>R</i> indices [<i>I</i> > 2sigma(<i>I</i>)]	<i>R</i> ₁ = 0.0265, <i>wR</i> ₂ = 0.0471	
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0386, <i>wR</i> ₂ = 0.0502	
Largest diff. peak and hole	0.851 and -0.747 e·Å ⁻³	

^a*R*₁ = $F_0 - F_c / F_0$ and *wR*₂ = $[w(F_0^2 - F_c^2)^2 / wF_0^4]^{1/2}$ for $F_0^2 > 2\sigma(F_0^2)$.

Table S2. Atomic bond-valence and isotropic displacement parameters for $\text{Li}_3\text{Ge}_3\text{Se}_6$.

atoms	x	y	z	δ_{iso}	BVS
Li1	1	1	0	0.034(3)	0.635
Li2	0.0301(16)	0.6879(13)	0.3226(9)	0.037(2)	0.741
Li3	0.5	1	0.5	0.037(3)	0.794
Li4	0.5123(17)	0.3509(12)	0.1913(9)	0.038(2)	0.710
Ge1	0.56771(8)	0.61650(6)	0.44715(4)	0.014(1)	3.871
Ge2	0.55315(8)	0.74147(6)	0.09507(4)	0.014(1)	3.975
Ge3	0.45759(8)	0.97254(6)	0.20559(4)	0.014(1)	3.979
Se1	0.25734(7)	0.85751(6)	0.40466(4)	0.016(1)	1.949
Se2	0.77538(8)	0.52995(6)	0.24387(4)	0.016(1)	1.889
Se3	0.79862(8)	0.78454(6)	-0.10436(4)	0.018(1)	1.900
Se4	0.74589(8)	1.01802(6)	0.24942(5)	0.019(1)	1.739
Se5	0.76359(8)	0.66601(6)	0.57205(5)	0.019(1)	1.696
Se6	0.26720(8)	0.66959(6)	0.07830(5)	0.019(1)	1.727

Table S3. Selected bond distances (Å) and angles (°) for Li₃Ge₃Se₆.

Li(1)-Se(4)#7	2.8089(5)	Se(6)-Li(2)-Se(1)	97.0(3)
Li(1)-Se(6)#2	2.8182(5)	Se(5)#6-Li(2)-Se(1)	91.4(3)
Li(1)-Se(6)#1	2.8182(5)	Se(4)#6-Li(2)-Se(1)	84.2(3)
Li(2)-Se(5)#6	2.835(10)	Se(6)-Li(2)-Se(5)#4	92.6(3)
Li(2)-Se(4)#6	2.850(10)	Se(5)#6-Li(2)-Se(5)#4	82.5(2)
Li(2)-Se(5)#4	2.915(10)	Se(4)#6-Li(2)-Se(5)#4	167.6(4)
Li(2)-Se(2)#6	2.921(10)	Se(1)-Li(2)-Se(5)#4	103.3(3)
Li(3)-Se(4)#8	2.7856(5)	Se(6)-Li(2)-Se(2)#6	85.2(3)
Li(3)-Se(5)#8	2.8215(5)	Se(5)#6-Li(2)-Se(2)#6	86.5(3)
Li(3)-Se(1)#8	2.8564(5)	Se(4)#6-Li(2)-Se(2)#6	93.0(3)
Li(4)-Se(4)#9	2.737(10)	Se(1)-Li(2)-Se(2)#6	176.6(4)
Li(4)-Se(5)#4	2.760(10)	Se(5)#4-Li(2)-Se(2)#6	79.1(3)
Li(4)-Se(6)#3	2.922(10)	Se(4)#8-Li(3)-Se(4)	180
Li(4)-Se(3)#3	3.151(11)	Se(4)#8-Li(3)-Se(5)#8	89.023(15)
Ge(1)-Se(5)	2.2912(7)	Se(4)-Li(3)-Se(5)#8	90.977(15)
Ge(1)-Ge(1)#4	2.4109(10)	Se(4)#8-Li(3)-Se(5)	90.977(15)
Ge(2)-Se(6)	2.2920(7)	Se(4)-Li(3)-Se(5)	89.023(15)
Ge(2)-Ge(3)	2.4080(7)	Se(5)#8-Li(3)-Se(5)	180.000(1)
Ge(3)-Se(3)#2	2.3845(7)	Se(4)#8-Li(3)-Se(1)#8	86.987(14)
Se(1)-Ge(3)	2.4068(7)	Se(4)-Li(3)-Se(1)#8	93.013(14)
Se(1)-Ge(1)	2.4121(7)	Se(5)#8-Li(3)-Se(1)#8	85.796(14)
Se(1)-Li(3)	2.8564(5)	Se(5)-Li(3)-Se(1)#8	94.204(14)
Se(1)-Li(2)	2.868(10)	Se(4)#8-Li(3)-Se(1)	93.013(14)
Se(2)-Ge(2)	2.3977(6)	Se(4)-Li(3)-Se(1)	86.987(14)
Se(2)-Ge(1)	2.4272(7)	Se(5)#8-Li(3)-Se(1)	94.204(14)
Se(2)-Li(2)#1	2.921(10)	Se(5)-Li(3)-Se(1)	85.796(14)
Se(2)-Li(4)	2.967(11)	Se(1)#8-Li(3)-Se(1)	180
Se(3)-Ge(3)#2	2.3845(7)	Se(4)#9-Li(4)-Se(5)#4	93.3(3)
Se(3)-Ge(2)	2.3982(7)	Se(4)#9-Li(4)-Se(6)	166.4(4)
Se(3)-Li(4)#3	3.151(11)	Se(5)#4-Li(4)-Se(6)	94.7(3)
Se(4)-Ge(3)	2.2938(7)	Se(4)#9-Li(4)-Se(6)#3	84.3(3)
Se(4)-Li(4)#5	2.737(10)	Se(5)#4-Li(4)-Se(6)#3	165.0(4)
Se(4)-Li(3)	2.7856(5)	Se(6)-Li(4)-Se(6)#3	85.2(2)
Se(4)-Li(1)	2.8089(5)	Se(4)#9-Li(4)-Se(2)	104.2(3)
Se(4)-Li(2)#1	2.850(10)	Se(5)#4-Li(4)-Se(2)	100.1(3)
Se(5)-Li(4)#4	2.760(10)	Se(6)-Li(4)-Se(2)	85.2(3)
Se(5)-Li(3)	2.8215(5)	Se(6)#3-Li(4)-Se(2)	94.8(3)
Se(5)-Li(2)#1	2.835(10)	Se(4)#9-Li(4)-Se(3)#3	84.3(3)
Se(5)-Li(2)#4	2.915(10)	Se(5)#4-Li(4)-Se(3)#3	82.9(3)
Se(6)-Li(2)	2.724(10)	Se(6)-Li(4)-Se(3)#3	85.9(3)
Se(6)-Li(4)	2.785(9)	Se(6)#3-Li(4)-Se(3)#3	82.1(3)
Se(6)-Li(1)#6	2.8182(5)	Se(2)-Li(4)-Se(3)#3	170.7(3)
Se(6)-Li(4)#3	2.922(10)	Se(1)-Ge(1)-Se(2)	111.43(2)
Se(4)#7-Li(1)-Se(4)	180	Se(5)-Ge(1)-Se(2)	113.48(3)
Se(4)#7-Li(1)-Se(6)#2	95.085(15)	Se(5)-Ge(1)-Se(1)	110.50(3)
Se(4)-Li(1)-Se(6)#2	84.915(15)	Se(6)-Ge(2)-Se(2)	112.29(3)

Se(4)#7-Li(1)-Se(6)#1	84.915(15)	Se(6)-Ge(2)-Se(3)	116.65(3)
Se(4)-Li(1)-Se(6)#1	95.085(15)	Se(2)-Ge(2)-Se(3)	103.66(2)
Se(6)#2-Li(1)-Se(6)#1	180.000(19)	Se(4)-Ge(3)-Se(3)#2	115.75(3)
Se(6)-Li(2)-Se(5)#6	171.1(4)	Se(4)-Ge(3)-Se(1)	111.39(2)
Se(6)-Li(2)-Se(4)#6	96.3(3)	Se(3)#2-Ge(3)-Se(1)	104.89(2)
Se(5)#6-Li(2)-Se(4)#6	87.5(3)		

Symmetry transformations used to generate equivalent atoms:

#1 $x+1, y, z$ #2 $-x+1, -y+2, -z$ #3 $-x+1, -y+1, -z$ #4 $-x+1, -y+1, -z+1$
#5 $x, y+1, z$ #6 $x-1, y, z$ #7 $-x+2, -y+2, -z$ #8 $-x+1, -y+2, -z+1$
#9 $x, y-1, z$

Table S4. List of ethane-like $[M_2Q_6]^{6-}$ (M= Si, Ge; Q = S, Se, Te) clusters-obtained compounds and their belonging space groups.

NO.	Formula	Space Group	NO.	Formula	Space Group
1	Na ₄ Si ₄ Se ₁₀	<i>P2₁/c</i>	17	Na ₈ Eu ₂ (Ge ₂ Se ₆) ₂	<i>C2/m</i>
2	K ₆ Sn ₂ Te ₆	<i>P2₁/c</i>	18	Na ₈ Eu ₂ (Ge ₂ Te ₆) ₂	<i>C2/m</i>
3	Na ₆ Ge ₂ Se ₆	<i>P2₁/c</i>	19	Na ₉ Sm(Si ₂ Se ₆) ₂	<i>C2/m</i>
4	Na ₆ Ge ₂ Te ₆	<i>P2₁/c</i>	20	Na ₉ Sm(Ge ₂ Se ₆) ₂	<i>C2/m</i>
5	K ₆ Si ₂ Te ₆	<i>C2/c</i>	21	Na ₉ La(Ge ₂ Se ₆) ₂	<i>C2/m</i>
6	K ₆ Ge ₂ Te ₆	<i>C2/c</i>	22	Na ₄ MgSi ₂ Se ₆	<i>C2</i>
7	Na ₉ Sb(Ge ₂ Se ₆) ₂	<i>C2/c</i>	23	Na ₄ MgGe ₂ Se ₆	<i>C2</i>
8	K ₆ Ge ₂ S ₆	<i>C2/m</i>	24	Na ₈ Ge ₄ Se ₁₀	<i>P-1</i>
9	K ₆ Ge ₂ Se ₆	<i>C2/m</i>	25	Al ₂ Si ₂ Te ₆	<i>P-3</i>
10	Na ₉ Sb(Ge ₂ S ₆) ₂	<i>C2/m</i>	26	In ₂ Si ₂ Te ₆	<i>P-3</i>
11	Na ₈ Pb ₂ [Ge ₂ S ₆] ₂	<i>C2/m</i>	27	Cr ₂ Si ₂ Te ₆	<i>R-3h</i>
12	Na ₈ Sn ₂ [Ge ₂ S ₆] ₂	<i>C2/m</i>	28	Cr ₂ Ge ₂ Te ₆	<i>R-3h</i>
13	Na ₈ Pb ₂ [Ge ₂ Se ₆] ₂	<i>C2/m</i>	29	Sc ₂ Si ₂ Te ₆	none
14	Na ₈ Pb ₂ [Si ₂ Se ₆] ₂	<i>C2/m</i>	30	Na ₆ Si ₂ S ₆	none
15	Na ₈ Pb ₂ [Ge ₂ Se ₆] ₂	<i>C2/m</i>	31	Na ₆ Si ₂ Se ₆	none
16	Na ₈ Eu ₂ (Si ₂ Se ₆) ₂	<i>C2/m</i>			

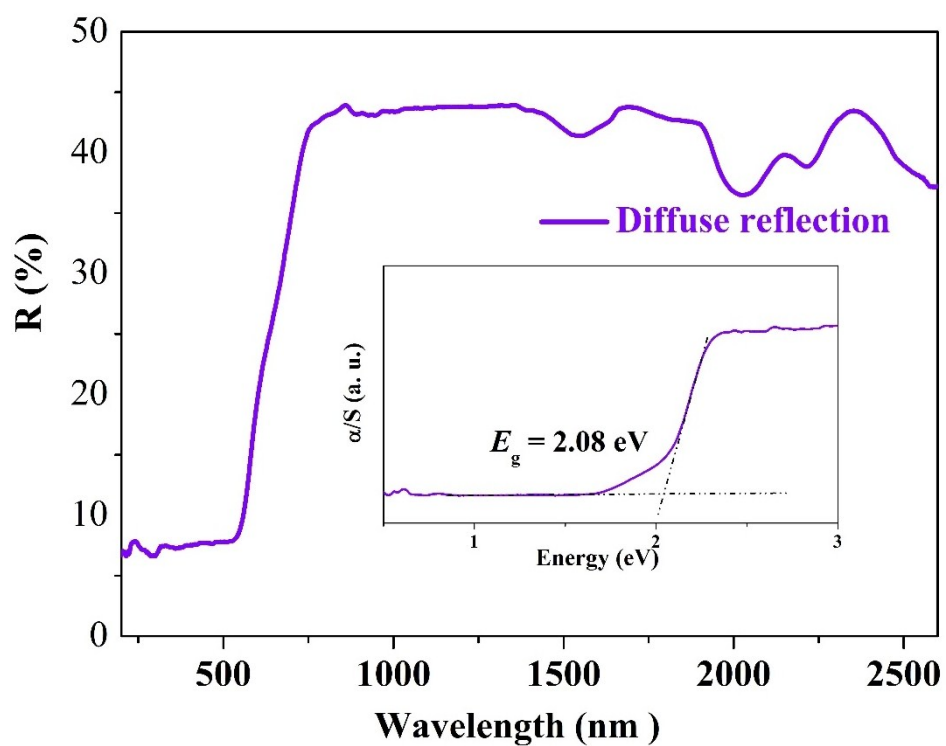


Figure S1. The converted UV-vis-NIR diffuse reflection spectrum and the inserted diagram is experimental band gap for $\text{Li}_3\text{Ge}_3\text{Se}_6$.

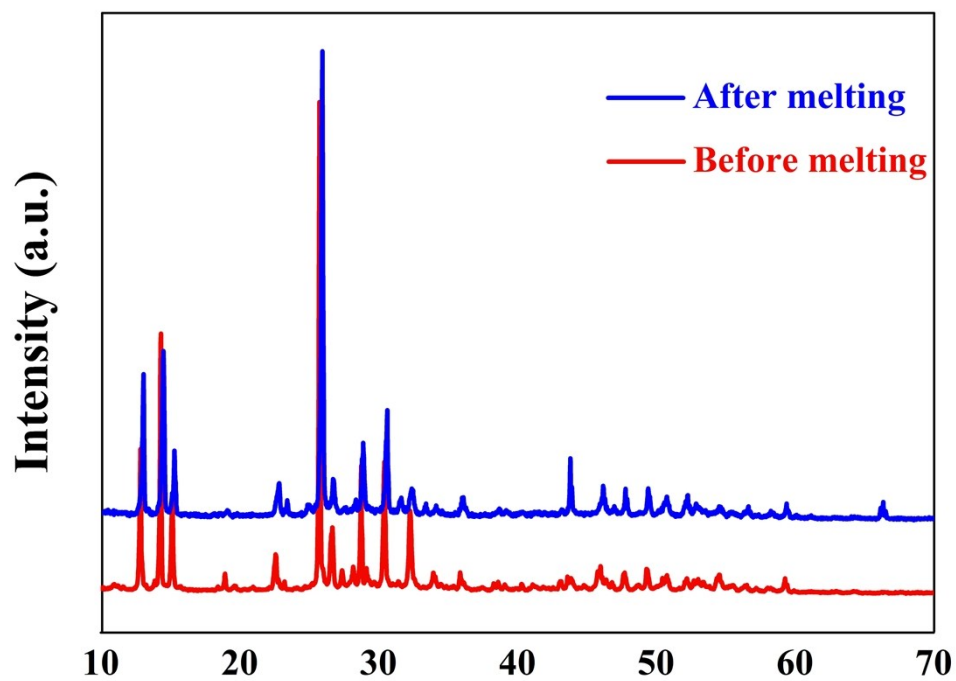


Figure 2. Comparison of PXRD spectra between samples before and after melting.

Reference

- (1) Sheldrick, G. M. *SHELXTL, Bruker Analytical X-ray Instruments, Inc.* Madison, WI, **2008**.
- (2) Spek, A. L. *J. Appl. Crystallogr.* 2003, **36**, 7-13.
- (3) Kortüm, G. *Reflectance Spectroscopy*. Springer Verlag, New York, 1969.
- (4) Clark, S. J.; Segall, M. D.; Pickard, C. J.; Hasnip, P. J.; Probert, M. J.; Refson, K.; Payne, M. C. *Z. Kristallogr.* 2005, **220**, 567-570.