

SUPPORTING INFORMATION

Lithium metal atoms fill vacancies in the germanium network of a type-I clathrate: Synthesis and structural characterization of $\text{Ba}_8\text{Li}_5\text{Ge}_{41}$

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Table S1. Selected crystallographic data for Ba₈Li₅Ge₄₁ synthesized by *B* synthesis method; *T* = 200(2) K; Mo K α , λ = 0.71073 Å; space group $Pm\bar{3}n$, *Z* = 1. CCDC no. 2257290.

Chemical formula	Ba ₈ Li _{5.1(1)} Ge _{40.9}
<i>a</i> / Å	10.8048(11)
<i>V</i> / Å ³	1261.39(13)
$\rho_{\text{calc.}}$ / g cm ⁻³	5.40
$\mu(\text{Mo-K}\alpha)$ / cm ⁻¹	300.5
<i>R</i> ₁ (<i>I</i> > 2 σ (<i>I</i>)) ^a	0.0292
<i>wR</i> ₂ (<i>I</i> > 2 σ (<i>I</i>)) ^a	0.0680
<i>R</i> ₁ (all data) ^a	0.0354
<i>wR</i> ₂ (all data) ^a	0.0698
$\Delta\rho_{\text{max,min}}$ / e ⁻ · Å ⁻³	1.12, -1.21

^a $R_1 = \sum ||F_o| - |F_c| / \sum |F_o|$; $wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$,
where $w = 1 / [\sigma^2 F_o^2 + (0.0360 \cdot P)^2 + (3.264 \cdot P)]$, and $P = (F_o^2 + 2F_c^2) / 3$

Table S2. Selected crystallographic data for Ba₈Li₅Ge₄₁ synthesized by *C* synthesis method; *T* = 200(2) K; Mo K α , λ = 0.71073 Å; space group $Pm\bar{3}n$, *Z* = 1. CCDC no. 2257291.

Chemical formula	Ba ₈ Li _{5.1(1)} Ge _{40.9}
<i>a</i> /Å	10.8098(12)
<i>V</i> /Å ³	1263.14(14)
$\rho_{\text{calc.}}$ /g cm ⁻³	5.40
$\mu(\text{Mo-K}\alpha)$ /cm ⁻¹	300.1
$R_1 (I > 2\sigma(I))^{\text{a}}$	0.0223
$wR_2 (I > 2\sigma(I))^{\text{a}}$	0.0444
R_1 (all data) ^a	0.0269
wR_2 (all data) ^a	0.0455
$\Delta\rho_{\text{max,min}}$ / e ⁻ ·Å ⁻³	0.85, -0.72

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$,
where $w = 1 / [\sigma^2 F_o^2 + (0.0155 \cdot P)^2 + (6.60 \cdot P)]$, and $P = (F_o^2 + 2F_c^2) / 3$.

Table S3. Selected crystallographic data for Ba₈Li₅Ge₄₁ synthesized by *A* synthesis method with doubly-reduced amount of Li in the nominal composition; *T* = 200(2) K; Mo K α , λ = 0.71073 Å; space group $Pm\bar{3}n$, *Z* = 1. CCDC no. 2257292.

Chemical formula	Ba ₈ Li _{5.1(1)} Ge _{40.9}
<i>a</i> / Å	10.8090(7)
<i>V</i> / Å ³	1262.86(14)
$\rho_{\text{calc.}}$ / g cm ⁻³	5.40
$\mu(\text{Mo-K}\alpha)$ / cm ⁻¹	300.7
$R_1 (I > 2\sigma(I))^{\text{a}}$	0.0321
$wR_2 (I > 2\sigma(I))^{\text{a}}$	0.0646
R_1 (all data) ^a	0.0451
wR_2 (all data) ^a	0.0694
$\Delta\rho_{\text{max,min}}$ / e ⁻ · Å ⁻³	1.84, -1.40

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$,
where $w = 1 / [\sigma^2 F_o^2 + (0.0201 \cdot P)^2 + (18.213 \cdot P)]$, and $P = (F_o^2 + 2F_c^2) / 3$;

Table S4. Refined atomic coordinates and equivalent isotropic displacement parameters (U_{eq}^a) for $Ba_8Li_5Ge_{41}$ synthesized by *B* synthesis method.

<i>Atom</i>	<i>Wyckoff Site</i>	<i>Occupancy /%</i>	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq} / \text{\AA}^2$
Ba1	2 <i>a</i>	100	0	0	0	0.0099(3)
Ba2 ^b	6 <i>d</i>	100	0	½	¼	0.0364(3)
Li/Ge1	6 <i>c</i>	84.5(7)/15.5(7)	¼	½	0	0.007(2)
Ge2	16 <i>i</i>	100	0.18312(4)	<i>x</i>	<i>x</i>	0.0112(2)
Ge3	24 <i>k</i>	100	0.11636(6)	0.31002(7)	0	0.0138(2)

^a U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

^b Ba2 can also be refined as off-centered at the 48*l* site (1/8 occupancy) with coordinates 0.011(1) 0.05127(9) 0.243(2) $U_{eq} = 0.022(3)$

Table S5. Refined atomic coordinates and equivalent isotropic displacement parameters (U_{eq}^a) for $Ba_8Li_5Ge_{41}$ synthesized by *C* synthesis method.

<i>Atom</i>	<i>Wyckoff Site</i>	<i>Occupancy /%</i>	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq} / \text{\AA}^2$
Ba1	2 <i>a</i>	100	0	0	0	0.0087(2)
Ba2 ^b	6 <i>d</i>	100	0	½	¼	0.0354(2)
Li/Ge1	6 <i>c</i>	84.6(9)/15.4(9)	¼	½	0	0.009(2)
Ge2	16 <i>i</i>	100	0.18305(3)	<i>x</i>	<i>x</i>	0.010(2)
Ge3	24 <i>k</i>	100	0.11607(5)	0.30970(5)	0	0.011(2)

^a U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

^b Ba2 can also be refined as off-centered at the 48*l* site (1/8 occupancy) with coordinates 0.016(3) 0.0506(1) 0.252(2) $U_{eq} = 0.029(1)$

Table S6. Refined atomic coordinates and equivalent isotropic displacement parameters (U_{eq}^a) for $Ba_8Li_5Ge_41$ synthesized by *A* synthesis method with doubly-reduced amount of Li in the nominal composition.

<i>Atom</i>	<i>Wyckoff Site</i>	<i>Occupancy /%</i>	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}/\text{\AA}^2$
Ba1	<i>2a</i>	100	0	0	0	0.0083(3)
Ba2 ^b	<i>6d</i>	100	0	1/2	1/4	0.0384(4)
Li/Ge1	<i>6c</i>	83(1)/17(1)	1/4	1/2	0	0.009(2)
Ge2	<i>16i</i>	100	0.18318(5)	<i>x</i>	<i>x</i>	0.0108(3)
Ge3	<i>24k</i>	100	0.11652(8)	0.31035(9)	0	0.0138(3)

^a U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

^b Ba2 can also be refined as off-centered at the *48l* site (1/8 occupancy) with coordinates 0.0143(8) 0.0512(1) 0.241(2) $U_{eq} = 0.021(3)$

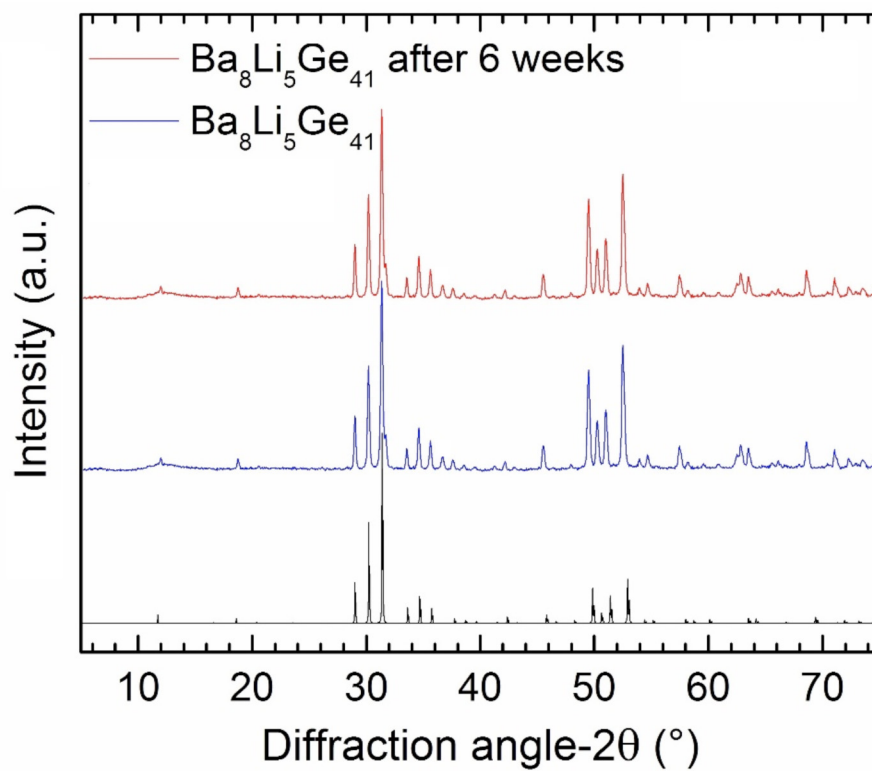


Figure S1. Powder X-ray diffraction pattern of $\text{Ba}_8\text{Li}_5\text{Ge}_{41}$ and the same after 6 weeks being exposed to the ambient atmosphere. For comparison, the simulated pattern of $\text{Ba}_8\text{Li}_5\text{Ge}_{41}$ is also provided (black trace).

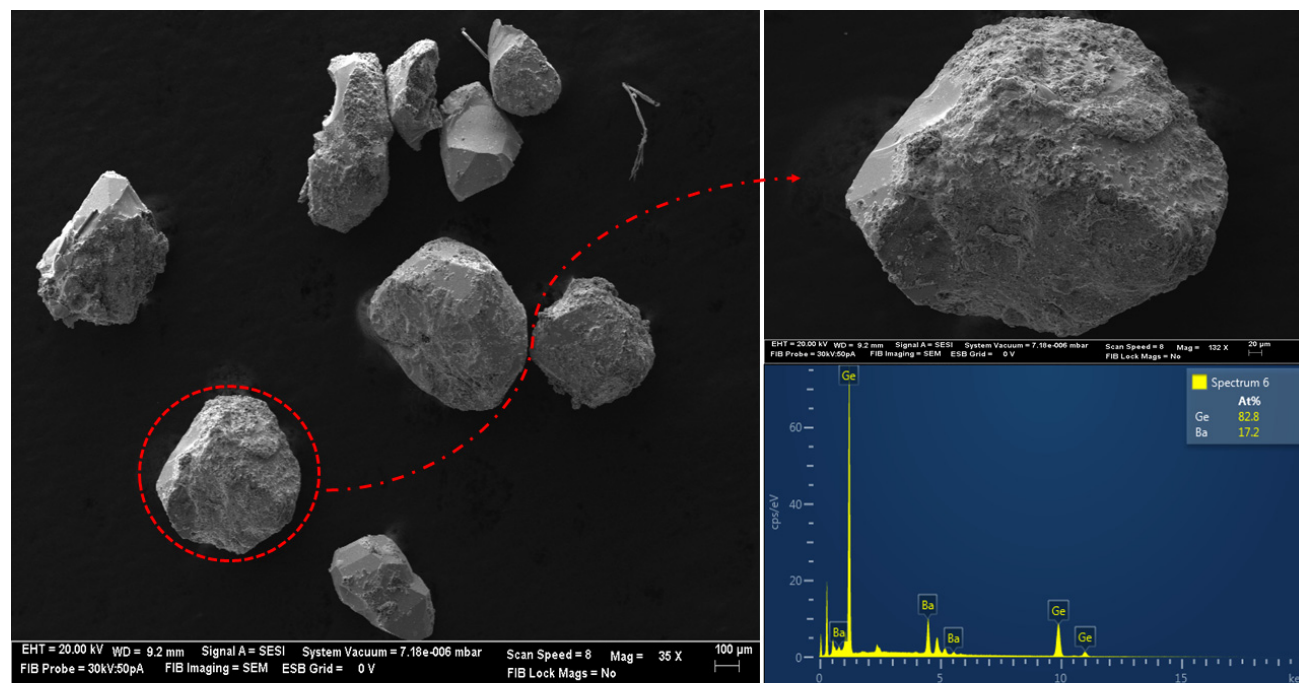


Figure S2. Scanning Electron Microscopy (SEM) image and atomic percentages measured by the X-ray energy-dispersive method for crystals of $\text{Ba}_8\text{Li}_5\text{Ge}_{41}$ (sample from method *A*).

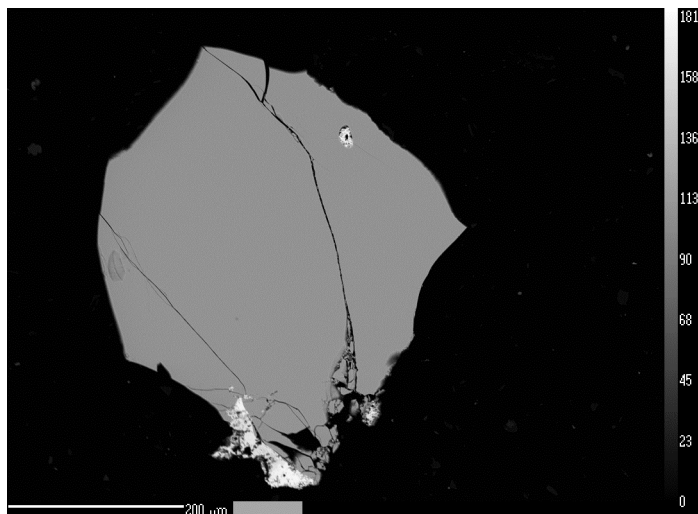


Figure S3. Scanning Electron Microscopy (SEM) image of the cross-section of a Ba₈Li₅Ge₄₁ crystal (sample from method *A*).

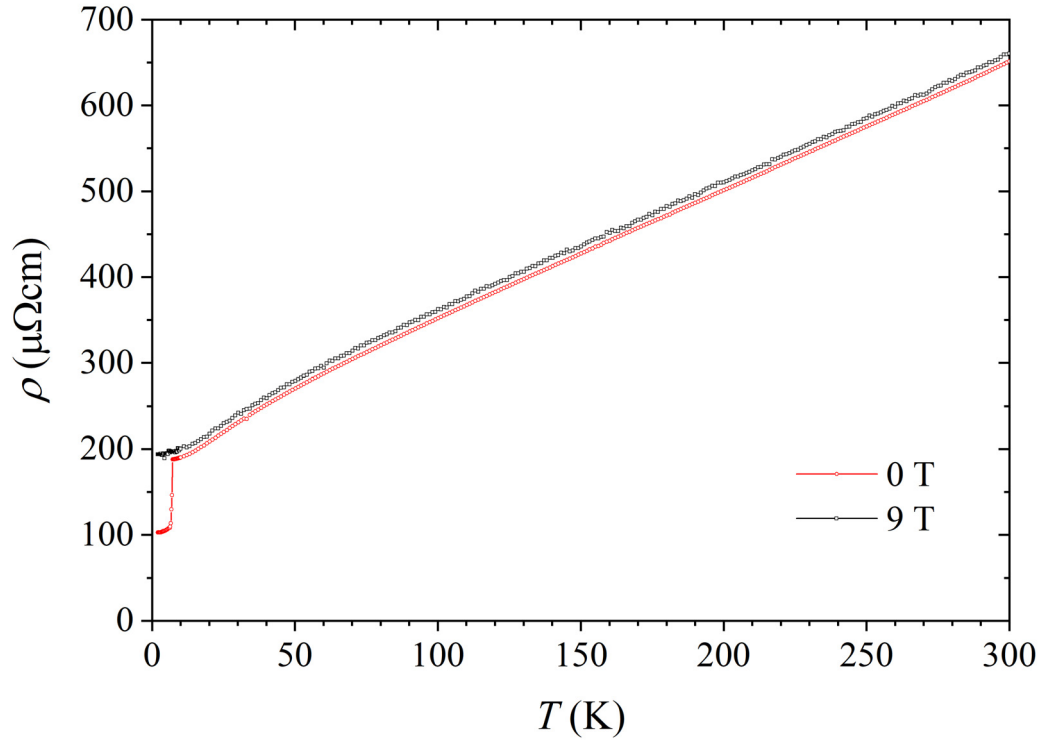


Figure S4. Electrical resistivity of a single-crystal of the $\text{Ba}_8\text{Li}_5\text{Ge}_{41}$ clathrate (A synthesis method) in the temperature range 2–300 K.

Away from the low-temperature limit, the $\rho(T)$ increases linearly with temperature, like in standard metals. The positive temperature coefficient in $\rho(T)$ demonstrates the dominant role of the electron-phonon inelastic scattering mechanism. In zero magnetic field, a sudden drop of resistivity is observed at $T = 7.2$ K, which can be attributed to superconducting (SC) transition of Pb. Pb is a starting material (flux) present in the synthesis of $\text{Ba}_8\text{Li}_5\text{Ge}_{41}$ and thus an impurity that cannot be avoided. Since the Pb to sample volume ratio is small, $\rho(T)$ does not drop to zero. In $\mu_0 H = 9$ T field $\rho(T)$ shows a saturation to a constant plateau in the $T \rightarrow 0$ limit due to scattering of electrons on quenched defects in the structure in the normal state. The SC transition

is suppressed in $\mu_0 H = 9$ T field and the difference between $\mu_0 H = 0$ T and 9 T resistivity values at $T = 300$ K is within the experimental error of a few %. According to the high resistivity values at $T = 2$ K ($\rho_{2K} \approx 190 \mu\Omega \text{ cm}$) and 300 K ($\rho_{300K} \approx 650 \mu\Omega \text{ cm}$) this material can be considered as a bad metal and a moderate electrical conductor.