SUPPORTING INFORMATION

Structural and Thermodynamic Similarities of Phases in the Li–*Tt* (*Tt* = Si, Ge) Systems: Redetermination of the Lithium-Rich Side of the Li–Ge Phase Diagram and Crystal Structures of $Li_{17}Si_{4.0-x}Ge_x$ for x = 2.3, 3.1, 3.5, and 4 as well as $Li_{4.1}Ge$

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Details on the structure refinement of $Li_{4.096(4)}Ge$

The structure of $Li_{16.38(2)}Ge_4$ is isotypic with $Li_{4.11}Si$ ($Li_{16.42(1)}Si_4$) and the disorder model highlighted in this article corresponds to the one reported for $Li_{16.42(1)}Si_4$. Atom positions Li4A on 4*c* (½, *y*, ¼), Li4B on 8*g* (*x*, *y*, ¼), and Li5 on 8*f* (0, *x*, *y*) are affected by disorder (cf. Table 2). A free refinement of occupancy factors for Li4A and Li4B delivers values of 0.669(15) und 0.390(8). Within standard deviations (3σ), those values are in agreement with refinement results using the constraint *occ*(Li4A) + *occ*(Li4B) = 1 (0.616(8) and 0.384(8)) which excludes their simultaneous occupancy since otherwise meaningless Li–Li distances are observed.

For Li5 on 8*f* (0, *x*, *y*), a split position was introduced. The split fractions converged to 0.25(4) and 0.75(4) which is identical with results obtained from a free refinement of occupancy factors for these positions (0.74(4) and 0.25(4)). The *R*-values of the final model are R_1 = 0.023 and wR_2 = 0.027 for all data and residual electron densities are +0.69 e·Å^{-3} and −0.52 e·Å^{-3}. Ignoring the atom split, the reliability factors for all data are slightly higher (R_1 = 0.024 and wR_2 = 0.030) but significant residual electron density is almost exactly located at the former Li5B position (+1.134 e·Å^{-3}).

Regarding the relevance of the atom split for Li5, it demonstrates structural flexibility which comes along with the disorder of Li4A and Li4B. In detail, if position Li4B is occupied, a simultaneous occupancy of Li5B is excluded due to unreasonably short Li–Li distances (2.02(4) Å). In case of an occupied Li4A site, either Li5A or Li5B can be occupied (2.86(3) Å (Li4A–Li5B), 3.220(7) Å (Li4A–Li5B)).

$Li_{17}Si_{4-x}Ge_x$ [x = 2.30(2), 3.08(4), 3.53(3)]: Single Crystal X-ray diffraction and crystallographic details

The preparation of crystals from $Li_{17}Si_{4-x}Ge_x$ [x = 2.30(2), 3.08(4), 3.53(3)] exactly follows the procedure described in the main article. For $Li_{17}Si_{4-x}Ge_x$ [x = 2.30(2), 3.08(4)], single crystal diffraction data were collected at 123 K on an OXFORD XCALIBUR3 diffractometer (SAPPHIRE3 CCD detector) equipped with a graphite monochromated MoK_α radition (λ = 0.71073 Å) using the Oxford CrysAlisRED software.[1] Empirical absorption correction was carried out with the SCALE3 ABSPACK scaling algorithm as implemented in CRYSALISRED. For $Li_{17}Si_{0.47(3)}Ge_{3.53(3)}$, intensity data were collected at 123 K on a BRUKER X-ray diffractometer equipped with a CCD detector (APEX II, κ-CCD), a rotating anode (NONIUS, FR591) with MoK_α radiation (λ = 0.71073 Å) and a Montel mirror using the BRUKER APEX Software Suite.[2] Integration, data reduction and absorption correction was done with SAINT and SADABS.[3, 4]

In case of $Li_{17}Si_{0.92(4)}Ge_{3.08(4)}$, penetration twinning along [1 1 1] was detected (twin fraction 0.45). Only single reflections of the main domain were used, composite reflections from both domains were omitted. For all compounds, the space group $F\bar{4}3m$ was assigned on the basis of the systematic absences and the statistical analysis of the intensity distributions. Since $F\bar{4}3m$ is non-centrosymmetric, only identical indices were merged. Fractional atomic coordinates and atomic displacement parameters for Si/Ge mixed sites were set equal. The structures were solved with direct methods (SHELXS-97) and refined with full-matrix least squares on F^2 (SHELXL-97).[5, 6] Table S1–S4 list refinement results, fractional atomic coordinates, and isotropic equivalent atomic displacement parameters for $Li_{17}Si_{4-x}Ge_x$ [x = 2.30(2), 3.08(4), 3.53(3)].

Table S1. Crystallographic data and structure refinement for $Li_{17}Si_{4-x}Ge_x$ [x = 2.30(2), 3.08(4), 3.53(3)].

empirical formula	$Li_{17}Si_{1.70(2)}Ge_{2.30(2)}$	$Li_{17}Si_{0.92(4)}Ge_{3.08(4)}$	$Li_{17}Si_{0.47(3)}Ge_{3.53(3)}$
T / K	123(2)	123(2)	123(2)
diffractometer	Oxford Xcalibur	Oxford Xcalibur	Bruker APEX II
formula weight / g·mol^{-1}	332.69	367.44	387.34
crystal size / mm^3	0.20 × 0.20 × 0.10	0.10 × 0.10 × 0.10	0.20 × 0.20 × 0.15
crystal color	metallic silver	metallic silver	metallic silver
crystal shape	block	block	block
space group	$F\bar{4}3m$	$F\bar{4}3m$	$F\bar{4}3m$
structure type	$Li_{17}Pb_4$	$Li_{17}Pb_4$	$Li_{17}Pb_4$
unit cell dimension / Å	a = 18.7125(1)	a = 18.7515(2)	a = 18.7721(5)
V / Å^3	6552.33(6)	6593.4(1)	6615.1(3)
Z	20	20	20
ρ (calc.) / (g·cm^{-3})	1.686	1.851	1.945
μ / mm^{-1}	5.354	6.995	7.928
F (000)	2968	3249	3410
θ - range / °	3.61–30.45	3.07–30.00	2.17–30.03
index range hkl	$-26 \le h \le +14$,	$-26 \le h \le +25$,	$-26 \le h \le +18$,
	$-26 \le k \le +26$,	$-26 \le k \le +26$,	$-26 \le k \le +19$,
	$-26 \le l \le +26$	$-26 \le l \le +26$	$-24 \le l \le +22$
reflections collected	31663	26446	19618
independent reflections	1035 (R_{int} = 0.032)	952 (R_{int} = 0.061)	1019 (R_{int} = 0.041)
reflections with $I > 2\sigma(I)$	991 (R_σ = 0.010)	880 (R_σ = 0.021)	1016 (R_σ = 0.015)
data/restraints/parameter	1035/0/72	952/0/72	1019/0/72
absorption correction	multi-scan	multi-scan	multi-scan
goodness-of-fit on F^2	1.260	1.000	1.202
Final R indices [$I > 2\sigma(I)$][a, b]	R_1 = 0.016	R_1 = 0.022	R_1 = 0.014
	wR_2 = 0.036	wR_2 = 0.047	wR_2 = 0.036
R indices (all data)[a, b]	R_1 = 0.017	R_1 = 0.025	R_1 = 0.014
	wR_2 = 0.036	wR_2 = 0.048	wR_2 = 0.037
extinction coefficient	4.4(3)×10^{-4}	2.4(3)×10^{-4}	0.9(1)×10^{-4}
Flack parameter	0.42(3)	0.54(5)	0.54(3)
Largest diff. peak and hole / e·Å^{-3}	0.45 and −0.28	0.32 and −0.26	0.28 and −0.37

[a] $R_1 = \sum \big| |F_o| - |F_c| \big| / \sum |F_o|$

[b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$

Table S2. Fractional atomic coordinates and isotropic equivalent atomic displacement parameters for $Li_{17}Si_{1.70(2)}Ge_{2.30(2)}$ ($F\bar{4}3m$, $Z = 20$, $T = 123$ K, estimated standard deviations in parentheses).

Atom	Wyckoff position	*x*	*y*	*z*	U_{eq} / ($Å^2 \cdot 10^{-3}$)	*s.o.f.*
Si/Ge1	16*e*	0.15972(2)	*x*	*x*	7.2(2)	0.41(1) / 0.59(1)
Si/Ge2	16*e*	0.91675(2)	*x*	*x*	6.6(2)	0.522(9) / 0.478(9)
Si/Ge3	24*f*	0.32154(3)	0	0	7.6(2)	0.39(1) / 0.61(1)
Si/Ge4	24*g*	0.57001(3)	¼	¼	7.8(1)	0.40(1) / 0.60(1)
Li1	16*e*	0.0743(3)	*x*	*x*	16(2)	1
Li2	16*e*	0.3027(2)	*x*	*x*	11(1)	1
Li3	16*e*	0.4187(3)	*x*	*x*	12(1)	1
Li4	16*e*	0.5573(2)	*x*	*x*	12(1)	1
Li5	16*e*	0.6882(2)	*x*	*x*	15(1)	1
Li6	16*e*	0.8325(2)	*x*	*x*	19(2)	1
Li7	24*f*	0.1686(4)	0	0	19(2)	1
Li8	24*g*	0.0746(3)	¼	¼	10(2)	1
Li9	48*h*	0.0909(2)	*x*	0.2625(3)	19(1)	1
Li10	48*h*	0.0907(2)	*x*	0.7609(3)	21(1)	1
Li11	48*h*	0.1550(2)	*x*	0.5211(2)	21(1)	1
Li12	48*h*	0.1632(2)	*x*	0.0026(3)	12(1)	1
Li13	4*a*	0	0	0	13(3)	1

Table S3. Fractional atomic coordinates and isotropic equivalent atomic displacement parameters for $Li_{17}Si_{0.92(4)}Ge_{3.08(4)}$ ($F\bar{4}3m$, $Z = 20$, $T = 123$ K, estimated standard deviations in parentheses).

Atom	Wyckoff position	*x*	*y*	*z*	U_{eq} / ($Å^2 \cdot 10^{-3}$)	*s.o.f.*
Si/Ge1	16*e*	0.15999(3)	*x*	*x*	9.5(2)	0.22(2) / 0.78(2)
Si/Ge2	16*e*	0.91708(3)	*x*	*x*	8.6(2)	0.30(2) / 0.70(2)
Si/Ge3	24*f*	0.32192(4)	0	0	9.6(2)	0.22(2) / 0.78(2)
Si/Ge4	24*g*	0.56959(4)	¼	¼	10.8(2)	0.21(2) / 0.79(2)
Li1	16*e*	0.0732(5)	*x*	*x*	29(4)	1
Li2	16*e*	0.3019(3)	*x*	*x*	17(2)	1
Li3	16*e*	0.4186(5)	*x*	*x*	20(3)	1
Li4	16*e*	0.5578(3)	*x*	*x*	16(2)	1
Li5	16*e*	0.6893(4)	*x*	*x*	20(3)	1
Li6	16*e*	0.8329(5)	*x*	*x*	45(5)	1
Li7	24*f*	0.1694(7)	0	0	27(5)	1
Li8	24*g*	0.0755(6)	¼	¼	12(4)	1
Li9	48*h*	0.0910(4)	*x*	0.2622(4)	22(2)	1
Li10	48*h*	0.0919(5)	*x*	0.7631(6)	41(3)	1
Li11	48*h*	0.1553(3	*x*	0.5218(4)	23(2)	1
Li12	48*h*	0.1636(3)	*x*	0.0031(5)	15(2)	1
Li13	4*a*	0	0	0	17(6)	1

Table S4. Fractional atomic coordinates and isotropic equivalent atomic displacement parameters for $Li_{17}Si_{0.47(3)}Ge_{3.53(3)}$ ($F\bar{4}3m$, $Z = 20$, $T = 123$ K, estimated standard deviations in parentheses).

Atom	Wyckoff position	*x*	*y*	*z*	U_{eq} / ($Å^2 \cdot 10^{-3}$)	*s.o.f.*
Si/Ge1	16*e*	0.15962(1)	*x*	*x*	7.5(1)	0.10(1) / 0.90(1)
Si/Ge2	16*e*	0.91657(1)	*x*	*x*	6.2(1)	0.18(1) / 0.82(1)
Si/Ge3	24*f*	0.32124(2)	0	0	7.3(1)	0.10(1) / 0.90(1)
Si/Ge4	24*g*	0.57034(2)	¼	¼	7.3(1)	0.11(1) / 0.89(1)
Li1	16*e*	0.0740(3)	*x*	*x*	20(2)	1
Li2	16*e*	0.3028(2)	*x*	*x*	14(1)	1
Li3	16*e*	0.4179(3)	*x*	*x*	14(2)	1
Li4	16*e*	0.5573(2)	*x*	*x*	14(1)	1
Li5	16*e*	0.6872(2)	*x*	*x*	15(1)	1
Li6	16*e*	0.8317(2)	*x*	*x*	18(2)	1
Li7	24*f*	0.1672(4)	0	0	19(2)	1
Li8	24*g*	0.0747(3)	¼	¼	12(2)	1
Li9	48*h*	0.0908(2)	*x*	0.2622(3)	22(1)	1
Li10	48*h*	0.0900(2)	*x*	0.7614(3)	18(1)	1
Li11	48*h*	0.1553(2)	*x*	0.5197(2)	17.1(9)	1
Li12	48*h*	0.1633(2)	*x*	0.0018(3)	14(1)	1
Li13	4*a*	0	0	0	8(3)	1

Table S5.[8] Comparison of experimental and computational relaxed fractional atomic coordinates for $Li_{21}Si_5$[7, 8] ($a_{exp.}$ = 18.710(2) Å (T = 298 K), $a_{calc.}$ = 18.55411 Å, $F\bar{4}3m$, Z = 16) and $Li_{17}Si_4$[8] ($a_{exp.}$ = 18.6563(2) Å (T = 123 K) and $a_{calc..}$ = 18.57319 Å, $F\bar{4}3m$, Z = 20). Estimated standard deviations are given in parentheses; most differing Li1 is marked in bold.

Atom	Wyck. pos.	x ($Li_{21}Si_5$)	x ($Li_{21}Si_5$ calc.)	z ($Li_{21}Si_5$)	z ($Li_{21}Si_5$ calc.)	x ($Li_{17}Si_4$)	x ($Li_{17}Si_4$ calc.)	z ($Li_{17}Si_4$)	z ($Li_{17}Si_4$ calc.)
*Tt*1	16*e*	0.1595(2)	0.1605	*x*	*x*	0.15976(1)	0.1600	*x*	*x*
*Tt*2	16*e*	0.9175(2)	0.9149	*x*	*x*	0.91660(1)	0.9167	*x*	*x*
*Tt*3	24*f*	0.3220(3)	0.3219	0	0	0.32133(1)	0.3215	0	0
*Tt*4	24*g*	0.5691(3)	0.5700	¼	¼	0.57031(1)	0.5708	¼	¼
Li1	16*e*	**0.071(2)**	**0.0553**	*x*	*x*	**0.07410(6)**	**0.0750**	*x*	*x*
Li2	16*e*	0.304(1)	0.3027	*x*	*x*	0.30284(5)	0.3031	*x*	*x*
Li3	16*e*	0.417(1)	0.4189	*x*	*x*	0.41794(7)	0.4180	*x*	*x*
Li4	16*e*	0.559(2)	0.5572	*x*	*x*	0.55713(5)	0.5572	*x*	*x*
Li5	16*e*	0.688(2)	0.6862	*x*	*x*	0.68687(5)	0.6867	*x*	*x*
Li6	16*e*	0.829(1)	0.8301	*x*	*x*	0.83168(6)	0.8311	*x*	*x*
Li7	24*f*	0.174(2)	0.1725	0	0	0.16807(8)	0.1691	0	0
Li8	24*g*	0.073(2)	0.0747	¼	¼	0.07492(9)	0.0750	¼	¼
Li9	48*h*	0.092(1)	0.0910	0.262(1)	0.2630	0.09068(4)	0.0907	0.26186(6)	0.2616
Li10	48*h*	0.088(1)	0.0905	0.761(1)	0.7616	0.09013(5)	0.0900	0.76176(6)	0.7604
Li11	48*h*	0.153(1)	0.1550	0.521(1)	0.5203	0.15503(4)	0.1551	0.51978(6)	0.5193
Li12	48*h*	0.164(1)	0.1607	0.000(1)	0.0068	0.16327(4)	0.1635	0.00286(7)	0.0029
Li13	4*a*	-	-	-	-	0	0	0	0

Table S6. Comparison of experimental fractional atomic coordinates for $Li_{17}Si_4$[8] (a = 18.6563(2) Å, T = 123 K), $Li_{17}Ge_4$ (a = 18.8521(3) Å, T = 298 K), $Li_{17-\varepsilon}Zn_\varepsilon Ge_4$[9] ($a$ = 18.842(1) Å, T = 173 K), and $Li_{16.95}Ge_4$[10] (a = 18.756(2) Å, T = 160 K; space group $F\bar{4}3m$, Z = 20). Estimated standard deviations are given in parentheses.

Atom	Wyck. pos.	x ($Li_{17}Si_4$)	x ($Li_{17}Ge_4$)	x ($Li_{17-\varepsilon}Zn_\varepsilon Ge_4$)	x ($Li_{16.95}Ge_4$)	z ($Li_{17}Si_4$)	z ($Li_{17}Ge_4$)	z ($Li_{17-\varepsilon}Zn_\varepsilon Ge_4$)	z ($Li_{16.95}Ge_4$)
*Tt*1	16*e*	0.15976(1)	0.15955(1)	0.15958(2)	0.15952(5)	*x*	*x*	*x*	*x*
*Tt*2	16*e*	0.91660(1)	0.91657(1)	0.91667(3)	0.91684(5)	*x*	*x*	*x*	*x*
*Tt*3	24*f*	0.32133(1)	0.32102(1)	0.32118(4)	0.32112(7)	0	0	0	0
*Tt*4	24*g*	0.57031(1)	0.57015(1)	0.57020(4)	0.56965(7)	¼	¼	¼	¼
Li1A	16*e*	0.07410(6)	0.0734(2)	0.0747(6)	0.0775	*x*	*x*	*x*	*x*
Li1B	16*e*	-	-	-	0.0587	-	-	-	*x*
Li2	16*e*	0.30284(5)	0.3031(2)	0.3033(3)	0.3032(6)	*x*	*x*	*x*	*x*
Li3	16*e*	0.41794(7)	0.4175(2)	0.4179(5)	0.4169(9)	*x*	*x*	*x*	*x*
Li4	16*e*	0.55713(5)	0.5575(2)	0.5584(4)	0.5579(6)	*x*	*x*	*x*	*x*
Li5	16*e*	0.68687(5)	0.6877(2)	0.6864(4)	0.6876(7)	*x*	*x*	*x*	*x*
Li6	16*e*	0.83168(6)	0.8314(2)	0.8331(4)	0.8329(7)	*x*	*x*	*x*	*x*
Li7	24*f*	0.16807(8)	0.1677(3)	0.1678(6)	0.170(1)	0	0	0	0
Li8	24*g*	0.07492(9)	0.0743(3)	0.0740(6)	0.075(1)	¼	¼	¼	¼
Li9	48*h*	0.09068(4)	0.0913(2)	0.0906(3)	0.0907(7)	0.26186(6)	0.2624(2)	0.2631(4)	0.2660(8)
Li10	48*h*	0.09013(5)	0.0896(2)	0.0904(4)	0.0914(7)	0.76176(6)	0.7612(2)	0.7613(4)	0.7597(9)
Li11	48*h*	0.15503(4)	0.1547(1)	0.1554(3)	0.1540(5)	0.51978(6)	0.5205(2)	0.5216(4)	0.5216(9)
Li12	48*h*	0.16327(4)	0.1637(1)	0.1632(3)	0.1625(5)	0.00286(7)	0.0027(2)	0.0025(5)	0.005(1)
Li13	4*a*	0	0	0	0	0	0	0	0
Zn1	4*a*	-	-	0	-	-	-	0	-

Table S7. Comparison of experimental fractional atomic coordinates for $Li_{16.95}Ge_4$[10] (a = 18.756(2) Å, T = 160 K; space group $F\bar{4}3m$, Z = 20) and computational relaxed ones for $Li_{21}Si_5$[8] ($a_{calc.}$ = 18.55411 Å, $F\bar{4}3m$, Z = 16). Estimated standard deviations are given in parentheses.

Atom	Wyck. pos.	x ($Li_{16.95}Ge_4$)	x ($Li_{21}Si_5$ calc.)	z ($Li_{16.95}Ge_4$)	z ($Li_{21}Si_5$ calc.)
*Tt*1	16*e*	0.15952(5)	0.1605	*x*	*x*
*Tt*2	16*e*	0.91684(5)	0.9149	*x*	*x*
*Tt*3	24*f*	0.32112(7)	0.3219	0	0
*Tt*4	24*g*	0.56965(7)	0.5700	¼	¼
Li1A	16*e*	0.0775	0.0553	*x*	*x*
Li1B	16*e*	0.0587	-	*x*	-
Li2	16*e*	0.3032(6)	0.3027	*x*	*x*
Li3	16*e*	0.4169(9)	0.4189	*x*	*x*
Li4	16*e*	0.5579(6)	0.5572	*x*	*x*
Li5	16*e*	0.6876(7)	0.6862	*x*	*x*
Li6	16*e*	0.8329(7)	0.8301	*x*	0
Li7	24*f*	0.1697(12)	0.1725	0	0
Li8	24*g*	0.0752(12)	0.0747	¼	¼
Li9	48*h*	0.0907(7)	0.0910	0.2660(8)	0.2630
Li10	48*h*	0.0914(7)	0.0905	0.7597(9)	0.7616
Li11	48*h*	0.1540(5)	0.1550	0.5216(9)	0.5203
Li12	48*h*	0.1625(5)	0.1607	0.005(1)	0.0068
Li13	4*a*	0	-	0	-

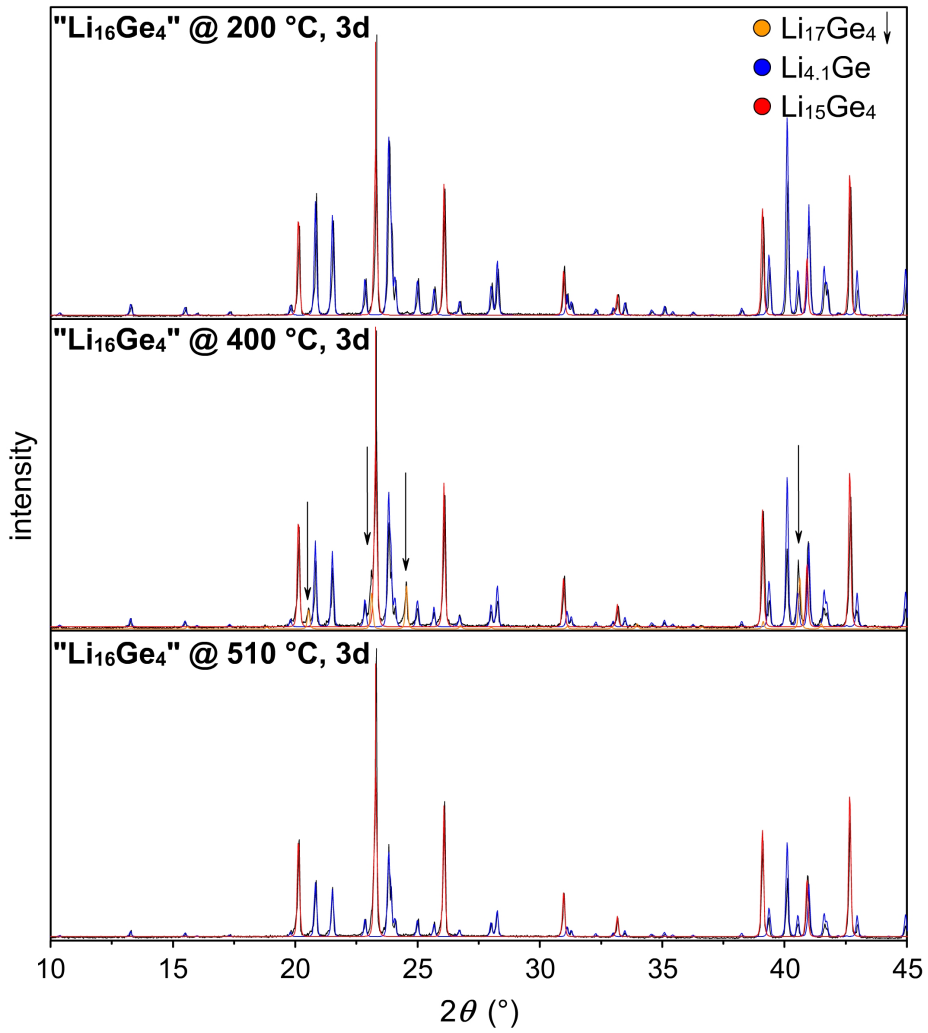

Figure S1. PXRD patterns of "$Li_{16}Ge_4$" samples annealed at 200, 400 and 510 °C in tantalum ampules for three days followed by quenching in water (experimental = black, $Li_{17}Ge_4$ (calc.) = yellow, $Li_{4.10}Ge$ (calc.) = blue, $Li_{15}Ge_4$ (calc.) = red).

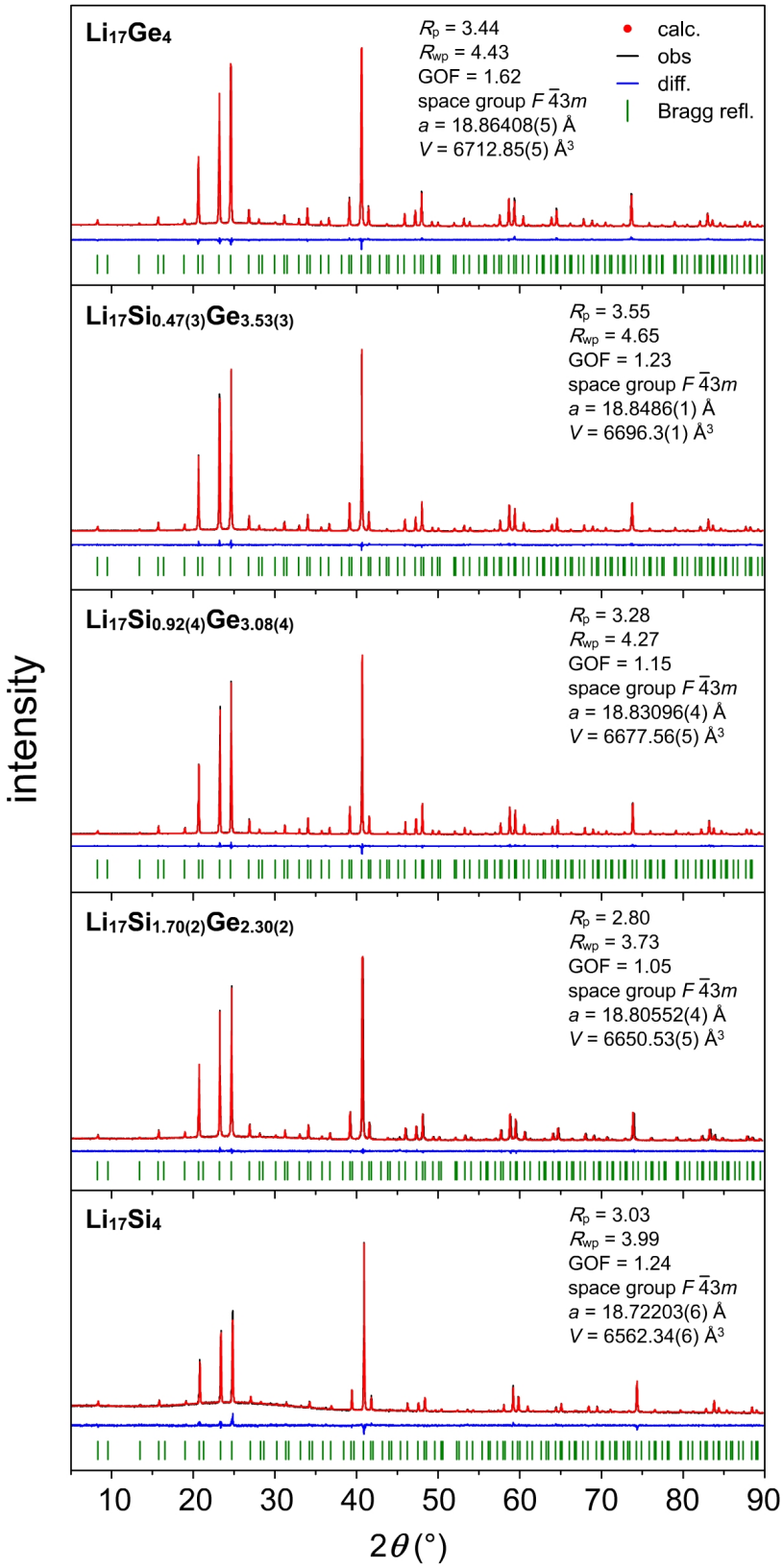

Figure S2. Rietveld[11] fits of the $Li_{17}Si_4$ model to PXRD patterns of ground single crystals of $Li_{17}Si_{4-x}Ge_x$ (x = 0, 2.30(2), 3.08(4), 3.53(3), 4).

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