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Electronic Supplementary Information

Synthesis, Structure and Conduction Mechanism of the Lithium Superionic Conductor $Li_{10+\delta}Ge_{1+\delta}P_{2-\delta}S_{12}$

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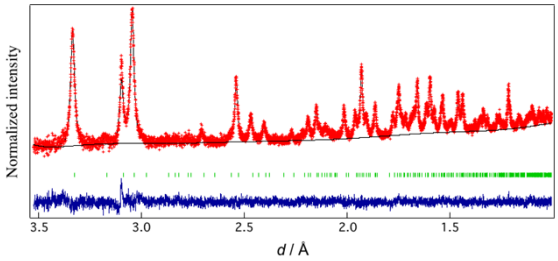

Figure S1. Neutron Rietveld refinement pattern of $Li_{10.5}Ge_{1.5}P_{1.5}S_{12}$ at 300 K. Red: observed intensities; black: calculated intensities; blue: difference plot. The green markers indicate the positions of the diffraction lines.

Table S1. (a) Rietveld refinement results for $Li_{10.5}Ge_{1.5}P_{1.5}S_{12}$ at 300 K ($Li_{10+\delta}Ge_{1+\delta}P_{2-\delta}S_{12}$, $\delta = 0.50$)

Atom	Site	*g*	*x*	*y*	*z*	*U* / Å²
Ge(1)	4*d*	0.750 (15)	0	1/2	0.6902 (2)	0.039
P(1)	4*d*	0.250 (15)	=*x*(Ge1)	=*y*(Ge1)	=z(Ge1)	=*B*(Ge1)
Ge(2)	2*b*	0.00 (3)	0	0	1/2	0.034
P(2)	2*b*	1.00 (3)	=*x*(Ge2)	=*y*(Ge2)	=*z*(Ge2)	=*B*(Ge2)
S(1)	8*g*	1	0	0.1897 (5)	0.4099 (4)	0.027
S(2)	8*g*	1	0	0.29268 (6)	0.0971 (4)	0.034
S(3)	8*g*	1	0	0.6953 (6)	0.7911 (4)	0.025
Li(1)	16*h*	0.51 (3)	0.2557 (17)	0.2624 (18)	0.1915 (12)	0.110
Li(2)	4*d*	1.00 (4)	0	1/2	0.9431 (9)	0.070
Li(3)	8*f*	0.75 (4)	=*y*(Li3)	0.2478 (9)	0	0.121
Li(4)	4*c*	0.67 (8)	0	0	0.233 (2)	0.111

Atom	U_{11} / Å²	U_{22} / Å²	U_{33} / Å²	U_{12} / Å²	U_{13} / Å²	U_{23} / Å²
Ge(1)	0.064 (3)	0.031 (2)	0.022 (2)	0	0	0
P(1)	=U_{11}(Ge1)	=U_{22}(Ge1)	=U_{33}(Ge1)	=U_{12}(Ge1)	=U_{13}(Ge1)	=U_{23}(Ge1)
Ge(2)	=U_{22}(Ge2)	0.023 (3)	0.057 (5)	0	0	0
P(2)	=U_{11}(Ge2)	=U_{22}(Ge2)	=U_{33}(Ge2)	=U_{12}(Ge2)	=U_{13}(Ge2)	=U_{23}(Ge2)
S(1)	0.052 (4)	0.008 (3)	0.021 (4)	0	0	0.012 (2)
S(2)	0.055 (5)	0.019 (4)	0.029 (5)	0	0	-0.015 (3)
S(3)	0.046 (4)	0.011 (4)	0.018 (4)	0	0	0.012 (3)
Li(1)	0.053 (9)	0.056 (10)	0.222 (19)	0.014 (6)	-0.045 (6)	-0.056 (11)
Li(2)	0.118 (9)	0.069 (7)	0.024 (5)	0	0	0
Li(3)	=U_{22}(Li3)	0.055 (6)	0.254 (16)	-0.015 (6)	=-U_{23}(Li3)	-0.067 (4)
Li(4)	0.110 (2)	0.143 (3)	0.081 (3)	0	0	0

Space group $P4_2/nmc$, $a = 8.7025(11)$ Å, $c = 12.6251(3)$ Å, $R_{wp} = 3.27\%$, $R_p = 2.77\%$.

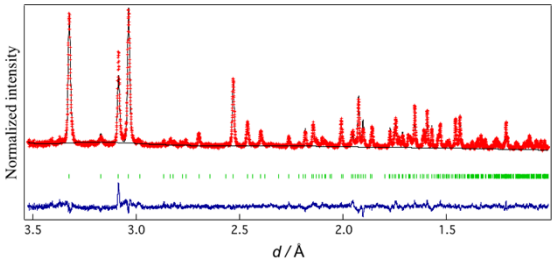

Figure S2. Neutron Rietveld refinement pattern of $Li_{10.35}Ge_{1.35}P_{1.65}S_{12}$ at 4.8 K. Red: observed intensities; black: calculated intensities; blue: difference plot. The green markers indicate the positions of the diffraction lines.

Table S2. Rietveld refinement results for $Li_{10.35}Ge_{1.35}P_{1.65}S_{12}$ at 4.8 K ($Li_{10+\delta}Ge_{1+\delta}P_{2-\delta}S_{12}$, $\delta = 0.35$)

Atom	Site	g	*x*	*y*	*z*	*U* / Å²
Ge(1)	4*d*	0.675 (8)	0	1/2	0.6891 (10)	0.033
P(1)	4*d*	0.325 (8)	=*x*(Ge1)	=*y*(Ge1)	=z(Ge1)	=*B*(Ge1)
Ge(2)	2*b*	0.00 (2)	0	0	1/2	0.043
P(2)	2*b*	1.00 (2)	=*x*(Ge2)	=*y*(Ge2)	=*z*(Ge2)	=*B*(Ge2)
S(1)	8*g*	1	0	0.1892 (2)	0.4082 (2)	0.0184 (5)
S(2)	8*g*	1	0	0.2936 (2)	0.0935 (2)	0.0081 (5)
S(3)	8*g*	1	0	0.7009 (2)	0.7910 (2)	0.0067 (5)
Li(1)	16*h*	0.462 (18)	0.2388 (7)	0.2675 (9)	0.1865 (9)	0.073
Li(2)	4*d*	1.00 (2)	0	1/2	0.9428 (4)	0.016 (2)
Li(3)	8*f*	0.79 (3)	=*y*(Li3)	0.2461 (4)	0	0.102
Li(4)	4*c*	0.738 (17)	0	0	0.2507 (4)	0.008 (3)

Atom	U_{11} / Å²	U_{22} / Å²	U_{33} / Å²	U_{12} / Å²	U_{13} / Å²	U_{23} / Å²
Ge(1)	0.052 (10)	0.0213 (9)	0.0251 (11)	0	0	0
P(1)	=U_{11}(Ge1)	=U_{22}(Ge1)	=U_{33}(Ge1)	=U_{12}(Ge1)	=U_{13}(Ge1)	=U_{23}(Ge1)
Ge(2)	=U_{22}(Ge2)	0.0323 (8)	0.0629 (8)	0	0	0
P(2)	=U_{11}(Ge2)	=U_{22}(Ge2)	=U_{33}(Ge2)	=U_{12}(Ge2)	=U_{13}(Ge2)	=U_{23}(Ge2)
Li(1)	0.052 (7)	0.050 (8)	0.117 (9)	0.019 (4)	-0.065 (5)	-0.048 (5)
Li(3)	=U_{22}(Li3)	0.065 (5)	0.177 (9)	-0.043 (4)	=-U_{23}(Li3)	0.093 (5)

Space group $P4_2/nmc$, $a = 8.67026$ (5) Å, $c = 12.6031$ (12) Å, $R_{wp} = 3.61\%$, $R_p = 2.97\%$.

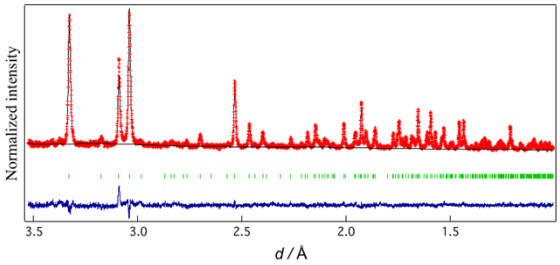

Figure S3. Neutron Rietveld refinement pattern of $Li_{10.35}Ge_{1.35}P_{1.65}S_{12}$ at 135 K. Red: observed intensities; black: calculated intensities; blue: difference plot. The green markers indicate the positions of the diffraction lines.

Table S3. Rietveld refinement results for $Li_{10.35}Ge_{1.35}P_{1.65}S_{12}$ at 135 K ($Li_{10+\delta}Ge_{1+\delta}P_{2-\delta}S_{12}$, $\delta = 0.35$)

Atom	Site	g	*x*	*y*	*z*	*U* / Å²
Ge(1)	4*d*	0.675 (8)	0	1/2	0.6888 (10)	0.036
P(1)	4*d*	0.325 (8)	=*x*(Ge1)	=*y*(Ge1)	=z(Ge1)	=*B*(Ge1)
Ge(2)	2*b*	0.00 (2)	0	0	1/2	0.048
P(2)	2*b*	1.00 (2)	=*x*(Ge2)	=*y*(Ge2)	=*z*(Ge2)	=*B*(Ge2)
S(1)	8*g*	1	0	0.1900 (2)	0.4073 (2)	0.032
S(2)	8*g*	1	0	0.2944 (4)	0.0970 (2)	0.037
S(3)	8*g*	1	0	0.7005 (9)	0.7892 (8)	0.043
Li(1)	16*h*	0.465 (14)	0.2453 (9)	0.2642 (9)	0.1875 (8)	0.102
Li(2)	4*d*	1.00 (10)	0	1/2	0.9475 (5)	0.040
Li(3)	8*f*	0.76 (2)	=*y*(Li3)	0.2454 (4)	0	0.116
Li(4)	4*c*	0.74 (2)	0	0	0.2540 (8)	0.048

Atom	U_{11} / Å²	U_{22} / Å²	U_{33} / Å²	U_{12} / Å²	U_{13} / Å²	U_{23} / Å²
Ge(1)	0.0440 (15)	0.0343 (14)	0.0282 (11)	0	0	0
P(1)	=U_{11}(Ge1)	=U_{22}(Ge1)	=U_{33}(Ge1)	=U_{12}(Ge1)	=U_{13}(Ge1)	=U_{23}(Ge1)
Ge(2)	=U_{22}(Ge2)	0.042 (2)	0.060 (3)	0	0	0
P(2)	=U_{11}(Ge2)	=U_{22}(Ge2)	=U_{33}(Ge2)	=U_{12}(Ge2)	=U_{13}(Ge2)	=U_{23}(Ge2)
S(1)	0.056 (2)	0.010 (2)	0.029 (2)	0	0	-0.003 (10)
S(2)	0.026 (2)	0.045 (3)	0.041 (3)	0	0	-0.013 (2)
S(3)	0.044 (2)	0.045 (2)	0.041 (2)	0	0	-0.005 (2)
Li(1)	0.053 (9)	0.054 (9)	0.198(14)	0.025 (5)	-0.067 (8)	-0.085 (9)
Li(2)	0.055 (5)	0.036 (5)	0.029 (5)	0	0	0
Li(3)	=U_{22}(Li3)	0.059 (6)	0.231 (11)	-0.047 (5)	=-U_{23}(Li3)	0.085 (4)
Li(4)	0.029 (9)	0.032 (9)	0.084 (9)	0	0	0

Space group $P4_2/nmc$, $a = 8.67989$ (5) Å, $c = 12.6121$ (2) Å, $R_{wp} = 3.28\%$, $R_p = 2.76\%$.

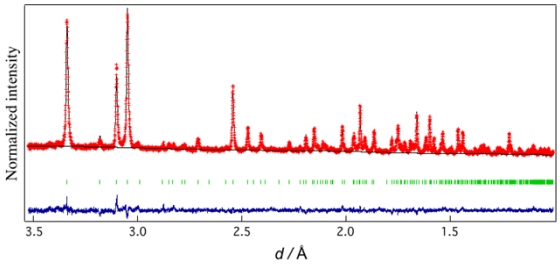

Figure S4. Neutron Rietveld refinement pattern of $Li_{10.35}Ge_{1.35}P_{1.65}S_{12}$ at 300 K. Red: observed intensities; black: calculated intensities; blue: difference plot. The green markers indicate the positions of the diffraction lines.

Table S4. Rietveld refinement results for $Li_{10.35}Ge_{1.35}P_{1.65}S_{12}$ at 300 K ($Li_{10+\delta}Ge_{1+\delta}P_{2-\delta}S_{12}$, $\delta = 0.35$)

Atom	Site	g	*X*	*y*	*z*	*U* / Å²
Ge(1)	4*d*	0.675 (12)	0	1/2	0.6885 (10)	0.046
P(1)	4*d*	0.325 (12)	=*x*(Ge1)	=*y*(Ge1)	=z(Ge1)	=*B*(Ge1)
Ge(2)	2*b*	0.00 (2)	0	0	1/2	0.046
P(2)	2*b*	1.00 (2)	=*x*(Ge2)	=*y*(Ge2)	=*z*(Ge2)	=*B*(Ge2)
S(1)	8*g*	1	0	0.1920 (2)	0.4090 (2)	0.046
S(2)	8*g*	1	0	0.2958 (2)	0.0989 (2)	0.048
S(3)	8*g*	1	0	0.7005 (3)	0.7885 (2)	0.035
Li(1)	16*h*	0.473 (11)	0.2477 (9)	0.2616 (13)	0.2018 (11)	0.108
Li(2)	4*d*	1	0	1/2	0.9524 (4)	0.060
Li(3)	8*f*	0.75 (2)	=*y*(Li3)	0.2463 (4)	0	0.118
Li(4)	4*c*	0.77 (2)	0	0	0.2585 (7)	0.077

Atom	U_{11} / Å²	U_{22} / Å²	U_{33} / Å²	U_{12} / Å²	U_{13} / Å²	U_{23} / Å²
Ge(1)	0.052 (10)	0.044 (14)	0.043 (13)	0	0	0
P(1)	=U_{11}(Ge1)	=U_{22}(Ge1)	=U_{33}(Ge1)	=U_{12}(Ge1)	=U_{13}(Ge1)	=U_{23}(Ge1)
Ge(2)	=U_{22}(Ge2)	0.038 (11)	0.062 (3)	0	0	0
P(2)	=U_{11}(Ge2)	=U_{22}(Ge2)	=U_{33}(Ge2)	=U_{12}(Ge2)	=U_{13}(Ge2)	=U_{23}(Ge2)
S(1)	0.078 (2)	0.023 (2)	0.038 (3)	0	0	0.014 (10)
S(2)	0.055 (2)	0.036 (2)	0.052 (3)	0	0	-0.010 (10)
S(3)	0.044 (2)	0.009 (2)	0.052 (2)	0	0	0.002 (2)
Li(1)	0.074 (8)	0.050 (8)	0.20 (2)	0.019	-0.097 (11)	-0.059 (11)
Li(2)	0.104 (4)	0.051(6)	0.024 (5)	0	0	0
Li(3)	=U_{22}(Li3)	0.048 (5)	0.259 (11)	-0.0335 (3)	=-U_{23}(Li3)	-0.0929 (4)
Li(4)	0.026 (9)	0.096 (11)	0.108 (10)	0	0	0

Space group $P4_2/nmc$, a = 8.713023 (5) Å, c = 12.639695 (2) Å, R_{wp} = 3.06%, R_p = 2.52%.

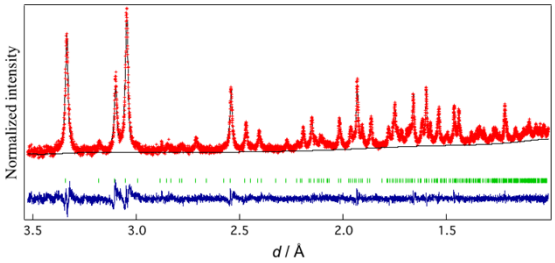

Figure S5. Neutron Rietveld refinement pattern of $Li_{10.2}Ge_{1.2}P_{1.8}S_{12}$ at 300 K. Red: observed intensities; black: calculated intensities; blue: difference plot. The green markers indicate the positions of the diffraction lines.

Table S5. Rietveld refinement results for $Li_{10.2}Ge_{1.2}P_{1.8}S_{12}$ at 300 K ($Li_{10+\delta}Ge_{1+\delta}P_{2-\delta}S_{12}$, $\delta = 0.20$)

Atom	Site	g	*x*	*y*	*z*	*U* / Å²
Ge(1)	4*d*	0.60 (2)	0	1/2	0.6904 (2)	0.026
P(1)	4*d*	0.40 (2)	=*x*(Ge1)	=*y*(Ge1)	=z(Ge1)	=*B*(Ge1)
Ge(2)	2*b*	0.00 (3)	0	0	½	0.032
P(2)	2*b*	1.00 (3)	=*x*(Ge2)	=*y*(Ge2)	=*z*(Ge2)	=*B*(Ge2)
S(1)	8*g*	1	0	0.1870 (4)	0.4092 (3)	0.024
S(2)	8*g*	1	0	0.2952 (5)	0.0976 (4)	0.029
S(3)	8*g*	1	0	0.6967 (5)	0.7920 (3)	0.027
Li(1)	16*h*	0.43 (2)	0.2572 (16)	0.2678 (16)	0.1867 (14)	0.112
Li(2)	4*d*	1.00 (4)	0	1/2	0.9473 (2)	0.079
Li(3)	8*f*	0.80 (4)	=*y*(Li3)	0.2436 (7)	0	0.176
Li(4)	4*c*	0.78 (6)	0	0	0.2443 (13)	0.089

Atom	U_{11} / Å²	U_{22} / Å²	U_{33} / Å²	U_{12} / Å²	U_{13} / Å²	U_{23} / Å²
Ge(1)	0.046 (2)	0.024 (2)	0.0090 (13)	0	0	0
P(1)	=U_{11}(Ge1)	=U_{22}(Ge1)	=U_{33}(Ge1)	=U_{12}(Ge1)	=U_{13}(Ge1)	=U_{23}(Ge1)
Ge(2)	=U_{22}(Ge2)	0.030 (3)	0.036 (4)	0	0	0
P(2)	=U_{11}(Ge2)	=U_{22}(Ge2)	=U_{33}(Ge2)	=U_{12}(Ge2)	=U_{13}(Ge2)	=U_{23}(Ge2)
S(1)	0.040 (3)	0.015 (3)	0.018 (3)	0	0	0.013 (2)
S(2)	0.036 (4)	0.025 (3)	0.026 (4)	0	0	-0.006 (2)
S(3)	0.042 (4)	0.025 (3)	0.014 (3)	0	0	0.006 (2)
Li(1)	0.051 (17)	0.054 (16)	0.23 (2)	0.030 (2)	-0.026 (2)	-0.034 (2)
Li(2)	0.099 (12)	0.079 (11)	0.058 (10)	0	0	0
Li(3)	=U_{22}(Li3)	0.081 (10)	0.366 (10)	-0.068 (8)	=-U_{23}(Li3)	-0.125 (9)
Li(4)	0.058 (18)	0.11 (2)	0.098 (16)	0	0	0

Space group $P4_2/nmc$, $a = 8.7043$ (2) Å, $c = 12.6160$ (2) Å, $R_{wp} = 3.99\%$, $R_p = 3.40\%$.

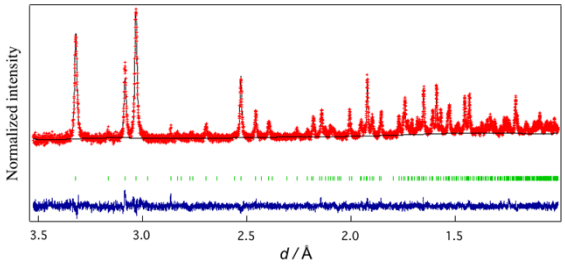

Figure S6. Neutron Rietveld refinement pattern of $Li_{10.05}Ge_{1.05}P_{1.95}S_{12}$ at 10 K. Red: observed intensities; black: calculated intensities; blue: difference plot. The green markers indicate the positions of the diffraction lines.

Table S6. Rietveld refinement results for $Li_{10.05}Ge_{1.05}P_{1.95}S_{12}$ at 10 K. ($Li_{10+\delta}Ge_{1+\delta}P_{2-\delta}S_{12}$, $\delta = 0.05$)

Atom	Site	g	*x*	*y*	*Z*	*U* / Å²
Ge(1)	4*d*	0.525 (13)	0	1/2	0.6898 (2)	0.0061 (9)
P(1)	4*d*	0.475 (13)	=*x*(Ge1)	=*y*(Ge1)	=z(Ge1)	=*B*(Ge1)
Ge(2)	2*b*	0.00 (3)	0	0	½	0.008 (2)
P(2)	2*b*	1.00 (3)	=*x*(Ge2)	=*y*(Ge2)	=*z*(Ge2)	=*B*(Ge2)
S(1)	8*g*	1	0	0.1882 (4)	0.4089 (3)	0.0069 (19)
S(2)	8*g*	1	0	0.2949 (5)	0.0944 (3)	0.0033 (18)
S(3)	8*g*	1	0	0.6993 (4)	0.7912 (3)	0.0015 (18)
Li(1)	16*h*	0.36 (2)	0.2463 (19)	0.276 (2)	0.1799 (18)	0.086
Li(2)	4*d*	1.00 (3)	0	1/2	0.9449 (8)	0.029
Li(3)	8*f*	0.89 (3)	=*y*(Li3)	0.2461 (6)	0	0.097
Li(4)	4*c*	0.78 (5)	0	0	0.2520 (14)	0.060

Atom	U_{11} / Å²	U_{22} / Å²	U_{33} / Å²	U_{12} / Å²	U_{13} / Å²	U_{23} / Å²
Li(1)	0.047 (17)	0.040 (16)	0.17 (2)	0.026 (9)	-0.055 (14)	-0.084 (14)
Li(2)	0.023 (7)	0.054 (9)	0.010 (2)	0	0	0
Li(3)	=U_{22}(Li3)	0.051 (7)	0.188 (14)	-0.029 (6)	=-U_{23}(Li3)	-0.082(5)
Li(4)	0.057 (18)	0.047 (17)	0.075 (18)	0	0	0

Space group $P4_2/nmc$, a = 8.66414 (9) Å, c = 12.5707 (2) Å, R_{wp} = 3.80%, R_p = 3.18%.

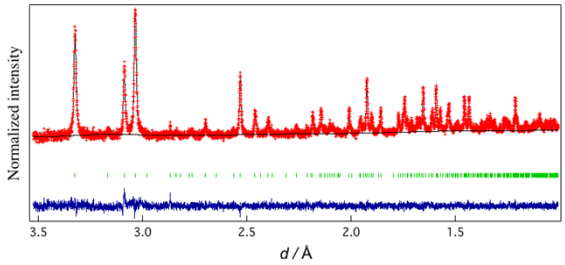

Figure S7. Neutron Rietveld refinement pattern of $Li_{10.05}Ge_{1.05}P_{1.95}S_{12}$ at 135 K. Red: observed intensities; black: calculated intensities; blue: difference plot. The green markers indicate the positions of the diffraction lines.

Table S7. Rietveld refinement results for $Li_{10.05}Ge_{1.05}P_{1.95}S_{12}$ at 135 K. ($Li_{10+\delta}Ge_{1+\delta}P_{2-\delta}S_{12}$, $\delta = 0.05$)

Atom	Site	g	*x*	*y*	*z*	*U* / Å²
Ge(1)	4*d*	0.525 (14)	0	1/2	0.6892 (2)	0.017
P(1)	4*d*	0.475 (14)	=*x*(Ge1)	=*y*(Ge1)	=z(Ge1)	=*B*(Ge1)
Ge(2)	2*b*	0.00 (3)	0	0	½	0.024
P(2)	2*b*	1.00 (3)	=*x*(Ge2)	=*y*(Ge2)	=*z*(Ge2)	=*B*(Ge2)
S(1)	8*g*	1	0	0.1892 (5)	0.4086 (4)	0.025
S(2)	8*g*	1	0	0.2964 (6)	0.0960 (4)	0.017
S(3)	8*g*	1	0	0.6974 (5)	0.7896 (4)	0.017
Li(1)	16*h*	0.37 (2)	0.244 (2)	0.274 (2)	0.179 (2)	0.117
Li(2)	4*d*	1	0	1/2	0.9461 (10)	0.050
Li(3)	8*f*	0.86 (2)	=*y*(Li3)	0.2464 (8)	0	0.110
Li(4)	4*c*	0.81 (2)	0	0	0.2528 (16)	0.087

Atom	U_{11} / Å²	U_{22} / Å²	U_{33} / Å²	U_{12} / Å²	U_{13} / Å²	U_{23} / Å²
Ge(1)	0.022 (2)	0.021 (2)	0.009 (2)	0	0	0
P(1)	=U_{11}(Ge1)	=U_{22}(Ge1)	=U_{33}(Ge1)	=U_{12}(Ge1)	=U_{13}(Ge1)	=U_{23}(Ge1)
Ge(2)	=U_{22}(Ge2)	0.011 (3)	0.051 (5)	0	0	0
P(2)	=U_{11}(Ge2)	=U_{22}(Ge2)	=U_{33}(Ge2)	=U_{12}(Ge2)	=U_{13}(Ge2)	=U_{23}(Ge2)
S(1)	0.031 (4)	0.017 (4)	0.027 (5)	0	0	-0.006 (2)
S(2)	0.014 (4)	0.029 (4)	0.009 (4)	0	0	-0.00009
S(3)	0.029 (4)	0.019 (4)	0.004 (4)	0	0	0.003 (2)
Li(1)	0.059 (2)	0.052 (2)	0.24 (2)	0.038 (2)	-0.071 (2)	-0.100 (2)
Li(2)	0.071 (12)	0.041 (10)	0.039 (10)	0	0	0
Li(3)	=U_{22}(Li3)	0.052 (9)	0.226 (19)	-0.025 (7)	=-U_{23}(Li3)	-0.080 (6)
Li(4)	0.06 (2)	0.11 (2)	0.09 (2)	0	0	0

Space group $P4_2/nmc$, $a = 8.67527$ (9) Å, $c = 12.5828$ (2) Å, $R_{wp} = 3.72\%$, $R_p = 3.14\%$.

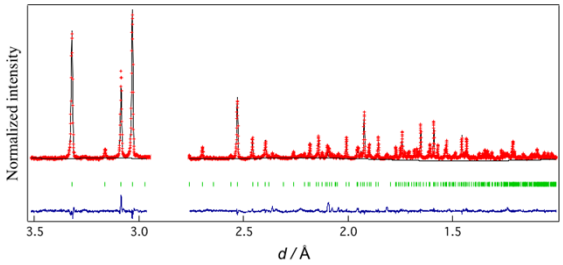

Figure S8. Neutron Rietveld refinement pattern of $Li_{10.05}Ge_{1.05}P_{1.95}S_{12}$ at 300 K. Red: observed intensities; black: calculated intensities; blue: difference plot. The green markers indicate the positions of the diffraction lines.

Table S8. Rietveld refinement results for $Li_{10.05}Ge_{1.05}P_{1.95}S_{12}$ at 300 K. ($Li_{10+\delta}Ge_{1+\delta}P_{2-\delta}S_{12}$, $\delta = 0.05$)

Atom	Site	*g*	*x*	*y*	*z*	*U* / Å²
Ge(1)	4*d*	0.525 (6)	0	1/2	0.6911	0.024
P(1)	4*d*	0.475(6)	=*x*(Ge1)	=*y*(Ge1)	=z(Ge1)	=U_{23}(Ge1)
Ge(2)	2*b*	0.00 (13)	0	0	½	0.028
P(2)	2*b*	1.00 (13)	=*x*(Ge2)	=*y*(Ge2)	=*z*(Ge2)	=U_{23}(Ge2)
S(1)	8*g*	1	0	0.1890 (2)	0.4091 (2)	0.026
S(2)	8*g*	1	0	0.2969 (2)	0.0982 (2)	0.025
S(3)	8*g*	1	0	0.6935 (8)	0.7913 (7)	0.024
Li(1)	16*h*	0.380 (14)	0.2566 (8)	0.2686 (8)	0.1889 (8)	0.105
Li(2)	4*d*	1.00 (2)	0	1/2	0.9468 (4)	0.064
Li(3)	8*f*	0.83 (2)	=*y*(Li3)	0.2430 (4)	0	0.125
Li(4)	4*c*	0.84 (2)	0	0	0.2550 (5)	0.070

Atom	U_{11} / Å²	U_{22} / Å²	U_{33} / Å²	U_{12} / Å²	U_{13} / Å²	U_{23} / Å²
Ge(1)	0.0402 (10)	0.0207 (8)	0.0113 (7)	0	0	0
P(1)	=U_{11}(Ge1)	=U_{22}(Ge1)	=U_{33}(Ge1)	=U_{12}(Ge1)	=U_{13}(Ge1)	=U_{23}(Ge1)
Ge(2)	=U_{22}(Ge2)	0.0240(13)	0.0368 (18)	0	0	0
P(2)	=U_{11}(Ge2)	=U_{22}(Ge2)	=U_{33}(Ge2)	=U_{12}(Ge2)	=U_{13}(Ge2)	=U_{23}(Ge2)
S(1)	0.0450 (15)	0.0128 (15)	0.0200 (16)	0	0	0.0033 (9)
S(2)	0.0229 (16)	0.0272 (14)	0.0259 (17)	0	0	-0.0036 (9)
S(3)	0.0296 (15)	0.0151 (15)	0.0275 (16)	0	0	-0.0023 (10)
Li(1)	0.045 (8)	0.039 (8)	0.230 (15)	0.017 (4)	-0.040 (7)	-0.036 (8)
Li(2)	0.110 (6)	0.059 (4)	0.024 (4)	0	0	0
Li(3)	=U_{22}(Li3)	0.050 (4)	0.274 (10)	-0.007 (3)	=-U_{23}(Li3)	-0.052 (2)
Li(4)	0.019 (6)	0.118 (8)	0.074 (6)	0	0	0

Space group $P4_2/nmc$, a = 8.69440 (2) Å, c = 12.60025 (5) Å, R_{wp} = 2.85%, R_p = 2.09%.

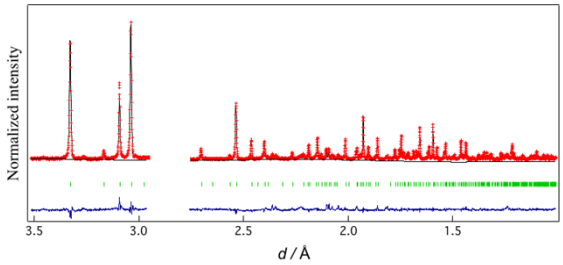

Figure S9. Neutron Rietveld refinement pattern of $Li_{10.05}Ge_{1.05}P_{1.95}S_{12}$ at 450 K. Red: observed intensities; black: calculated intensities; blue: difference plot. The green markers indicate the positions of the diffraction lines.

Table S9. Rietveld refinement results for $Li_{10.05}Ge_{1.05}P_{1.95}S_{12}$ at 450 K. ($Li_{10+\delta}Ge_{1+\delta}P_{2-\delta}S_{12}$, $\delta = 0.05$)

Atom	Site	*g*	*x*	*y*	*z*	*U* / Å²
Ge(1)	4*d*	0.525 (5)	0	1/2	0.6915	0.026
P(1)	4*d*	0.475 (5)	=*x*(Ge1)	=*y*(Ge1)	=z(Ge1)	=U_{23}(Ge1)
Ge(2)	2*b*	0.00 (13)	0	0	½	0.036
P(2)	2*b*	1.00 (13)	=*x*(Ge2)	=*y*(Ge2)	=*z*(Ge2)	=U_{23}(Ge2)
S(1)	8*g*	1	0	0.1886 (2)	0.4081 (13)	0.035
S(2)	8*g*	1	0	0.2990 (2)	0.1032 (13)	0.033
S(3)	8*g*	1	0	0.6949 (2)	0.7900 (13)	0.034
Li(1)	16*h*	0.383 (12)	0.2549 (9)	0.2573 (10)	0.1930 (7)	0.159
Li(2)	4*d*	1.00 (2)	0	1/2	0.9470 (5)	0.113
Li(3)	8*f*	0.81 (2)	=*y*(Li3)	0.2421 (3)	0	0.158
Li(4)	4*c*	0.86 (2)	0	0	0.2535 (4)	0.071

Atom	U_{11} / Å²	U_{22} / Å²	U_{33} / Å²	U_{12} / Å²	U_{13} / Å²	U_{23} / Å²
Ge(1)	0.0351 (8)	0.0318 (8)	0.0115 (5)	0	0	0
P(1)	=U_{11}(Ge1)	=U_{22}(Ge1)	=U_{33}(Ge1)	=U_{12}(Ge1)	=U_{13}(Ge1)	=U_{23}(Ge1)
Ge(2)	=U_{22}(Ge2)	0.0337 (12)	0.0410 (16)	0	0	0
P(2)	=U_{11}(Ge2)	=U_{22}(Ge2)	=U_{33}(Ge2)	=U_{12}(Ge2)	=U_{13}(Ge2)	=U_{23}(Ge2)
S(1)	0.0648 (14)	0.0032 (11)	0.0377 (16)	0	0	0.0046 (8)
S(2)	0.0275 (15)	0.0417 (14)	0.0305 (14)	0	0	-0.0007 (9)
S(3)	0.0310 (15)	0.0283 (14)	0.0416 (16)	0	0	0.0016 (10)
Li(1)	0.064 (8)	0.089 (9)	0.323 (19)	0.057 (4)	-0.065 (9)	-0.141 (12)
Li(2)	0.149 (7)	0.088 (5)	0.103 (5)	0	0	0
Li(3)	=U_{22}(Li3)	0.057 (4)	0.359 (10)	-0.006 (3)	=-U_{23}(Li3)	-0.089 (3)
Li(4)	0.048 (6)	0.125 (7)	0.039 (4)	0	0	0

Space group $P4_2/nmc$, a = 8.71831 (2) Å, c = 12.62836 (4) Å, R_{wp} = 3.84%, R_p = 3.11%.

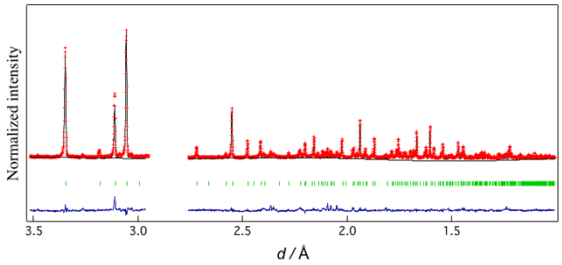

Figure S10. Neutron Rietveld refinement pattern of $Li_{10.05}Ge_{1.05}P_{1.95}S_{12}$ at 750 K. Red: observed intensities; black: calculated intensities; blue: difference plot. The green markers indicate the positions of the diffraction lines.

Table S10. Rietveld refinement results for $Li_{10.05}Ge_{1.05}P_{1.95}S_{12}$ at 750 K. ($Li_{10+\delta}Ge_{1+\delta}P_{2-\delta}S_{12}$, $\delta = 0.05$)

Atom	Site	*g*	*x*	*y*	*z*	*U* / Å²
Ge(1)	4*d*	0.525 (5)	0	1/2	0.6932	0.024
P(1)	4*d*	0.475 (5)	=*x*(Ge1)	=*y*(Ge1)	=z(Ge1)	=U_{23}(Ge1)
Ge(2)	2*b*	0.00 (14)	0	0	1/2	0.040
P(2)	2*b*	1.00 (14)	=*x*(Ge2)	=*y*(Ge2)	=*z*(Ge2)	=U_{23}(Ge2)
S(1)	8*g*	1	0	0.1855 (2)	0.4097 (13)	0.044
S(2)	8*g*	1	0	0.2971 (2)	0.1035 (14)	0.034
S(3)	8*g*	1	0	0.6955 (2)	0.7887 (15)	0.041
Li(1)	16*h*	0.385 (17)	0.2510 (18)	0.2663 (19)	0.1999 (8)	0.175
Li(2)	4*d*	1.000 (6)	0	1/2	0.9533 (4)	0.095
Li(3)	8*f*	0.80 (3)	=*y*(Li3)	0.2491 (5)	0	0.251
Li(4)	4*c*	0.87 (4)	0	0	0.2528 (6)	0.160

Atom	U_{11} / Å²	U_{22} / Å²	U_{33} / Å²	U_{12} / Å²	U_{13} / Å²	U_{23} / Å²
Ge(1)	0.0277 (8)	0.0294 (9)	0.0155 (6)	0	0	0
P(1)	=U_{11}(Ge1)	=U_{22}(Ge1)	=U_{33}(Ge1)	=U_{12}(Ge1)	=U_{13}(Ge1)	=U_{23}(Ge1)
Ge(2)	=U_{22}(Ge2)	0.0410 (13)	0.0370 (18)	0	0	0
P(2)	=U_{11}(Ge2)	=U_{22}(Ge2)	=U_{33}(Ge2)	=U_{12}(Ge2)	=U_{13}(Ge2)	=U_{23}(Ge2)
S(1)	0.0709 (16)	0.0284 (15)	0.0333 (17)	0	0	0.0031 (10)
S(2)	0.0388 (16)	0.0306 (14)	0.0326 (15)	0	0	-0.0251 (9)
S(3)	0.0333 (16)	0.0287 (14)	0.0602 (19)	0	0	0.0068 (12)
Li(1)	0.130 (12)	0.046 (10)	0.35 (3)	-0.011 (5)	0.017 (17)	-0.042 (17)
Li(2)	0.068 (4)	0.147 (6)	0.071 (5)	0	0	0
Li(3)	=U_{22}(Li3)	0.148 (7)	0.456 (19)	-0.029 (5)	=-U_{23}(Li3)	-0.147 (5)
Li(4)	0.160 (10)	0.234 (14)	0.085 (9)	0	0	0

Space group $P4_2/nmc$, $a = 8.76823$ (11) Å, $c = 12.69081$ (3) Å, $R_{wp} = 4.80\%$, $R_p = 3.81\%$.

Table S11. Interatomic distances (l / Å) and bond angles (θ / °) for $Li_{10+\delta}Ge_{1+\delta}P_{2-\delta}S_{12}$

	Polyhedra structure	Bond	δ=0.00	δ=0.05	δ=0.20	δ=0.35	δ=0.50
Interatomic distance (l / Å)	$Ge1S_4$ (Tetrahedra)	$Ge1^a$-$S2^b$	2.122	2.119	2.132	2.109	2.153
		$Ge1^c$-$S3^c$	2.146	2.102	2.139	2.166	2.126
		Average Ge1-S	**2.134**	**2.111**	**2.136**	**2.138**	**2.139**
	$P2S_4$ (Tetrahedra)	$P2^b$-$S1^d$	1.961	2.004	1.991	2.030	2.005
		Average P2-S	**2.005**	**2.004**	**1.991**	**2.030**	**2.005**
	$Li1S_4$ (Tetrahedra)	$Li1^b$-$S1^h$	2.449	2.478	2.467	2.638	2.516
		$Li1^b$-$S2^b$	2.496	2.519	2.517	2.538	2.538
		$Li1^b$-$S3^f$	2.465	2.452	2.475	2.382	2.477
		$Li1^b$-$S3^d$	2.418	2.388	2.381	2.325	2.333
		Average Li1-S	**2.457**	**2.459**	**2.460**	**2.471**	**2.466**
	$Li2S_6$ (Octahedra)	$Li2^e$-$S1^d$	2.779	2.745	2.766	2.738	2.732
		$Li2^a$-$S2^f$	2.577	2.599	2.603	2.568	2.652
		$Li2^a$-$S3^a$	2.592	2.583	2.602	2.718	2.563
		Average Li2-S	**2.649**	**2.642**	**2.657**	**2.675**	**2.649**
	$Li3S_4$ (Tetrahedra)	$Li3^b$-$S1^h$	2.551	2.578	2.580	2.548	2.530
		$Li3^b$-$S2^b$	2.496	2.494	2.494	2.522	2.512
		Average Li3-S	**2.523**	**2.536**	**2.537**	**2.535**	**2.521**
	$Li4S_6$ (Octahedra)	$Li4^b$-$S1^b$		2.544	2.641	2.534	2.776
		$Li4^b$-$S3^c$		2.728	2.680	2.665	2.669
		$Li4^e$-$S2^e$		3.251	3.167	3.273	3.072
		Average Li2-S		**2.841**	**2.829**	**2.824**	**2.839**
Bond angle (θ / °)	$Ge1S_4$ (Tetrahedra)	$S2^b$-$Ge1^a$-$S2^g$	110.763	112.792	113.394	115.052	113.870
		$S2^h$-$Ge1^c$-$S3^c$	109.631	109.373	109.208	108.257	109.121
		$S3^c$-$Ge1^c$-$S3^d$	107.492	106.350	106.378	108.610	106.204
		Average S-Ge1-S	**109.463**	**109.439**	**109.434**	**109.448**	**109.426**
	$P2S_4$ (Tetrahedra)	$S1^h$-$P2^a$-$S1^e$	109.607	110.290	109.748	111.050	110.897
		$S1^d$-$P2^b$-$S1^b$	109.403	109.063	109.333	108.687	108.763
		Average S-P2-S	**109.471**	**109.472**	**109.471**	**109.475**	**109.474**
	$Li2S_6$ (Octahedra)	$S1^b$-$Li2^a$-$S1^g$	162.104	160.076	159.994	156.888	162.328
		$S1^b$-$Li2^a$-$S2^f$	96.567	97.296	97.274	98.306	96.465
		$S1^b$-$Li2^a$-$S3^a$	83.349	82.458	82.486	81.216	83.400
		$S2^f$-$Li2^a$-$S2^a$	85.336	85.541	86.414	87.709	85.722
		$S2^f$-$Li2^a$-$S3^f$	179.203	177.879	177.955	176.479	178.703
		$S2^e$-$Li2^a$-$S3^a$	95.461	96.580	95.631	95.812	95.575
		$S3^e$-$Li2^a$-$S3^a$	83.742	81.299	82.324	80.667	83.128
		Average S-Li2-S	**89.972**	**89.918**	**89.920**	**89.841**	**89.955**
	$Li4S_6$ (Octahedra)	$S1^g$-$Li4^b$-$S1^b$		80.505	76.108	82.685	73.015
		$S1^b$-$Li4^b$-$S2^b$		87.165	87.698	86.707	86.467
		$S1^b$-$Li4^b$-$S2^g$		167.676	163.812	169.395	160.499
		$S1^b$-$Li4^b$-$S3^c$		99.398	97.762	99.645	95.345
		$S2^g$-$Li4^b$-$S2^b$		105.159	108.490	103.898	112.034
		$S2^g$-$Li4^b$-$S3^d$		82.533	84.238	82.069	86.286
		$S3^d$-$Li4^b$-$S3^c$		155.292	160.247	154.156	166.681
		Average S-Li4-S		**90.643**	**90.666**	**90.571**	**90.376**

Symmetry codes: ^{a}-y+1/2, x+1/2, z+1/2, ^{b}x, y, z, ^{c}y, x, -z, ^{d}-y, -x, -z, ^{e}-x+1/2, y+1/2, -z+1/2, ^{f}y+1/2, -x+1/2, z+1/2, ^{g}-x, -y, z, ^{h}x+1/2, -y+1/2, -z+1/2