Supporting Information - Effect of Si substitution on the structural and transport properties of Li-argyrodites

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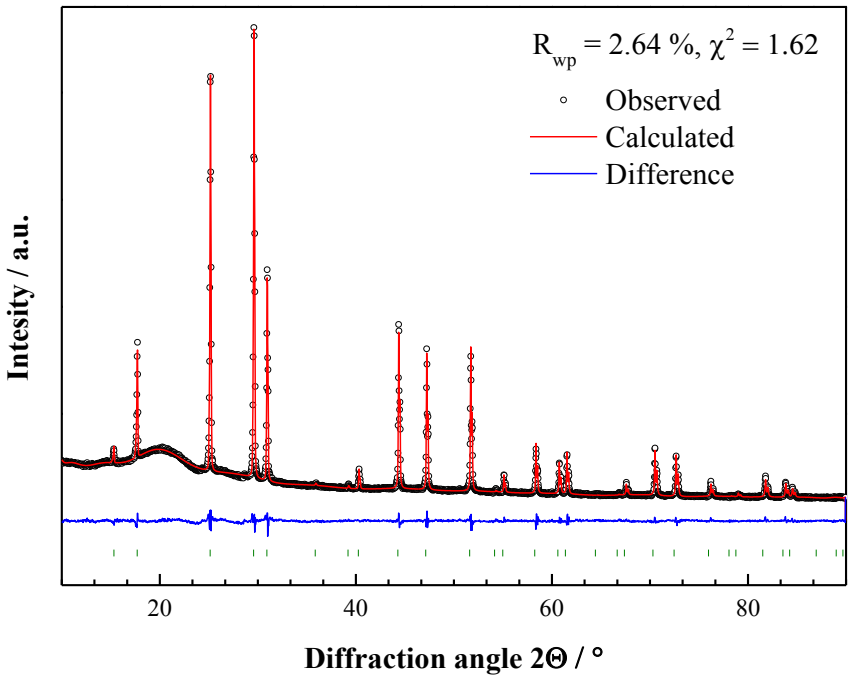

Figure S1. X-ray powder diffraction data for Li_6PS_5Br and the corresponding Rietveld refinements. Shown are the collected data, the profile fit, the profile residuals and the Bragg reflections for the main phase (top).

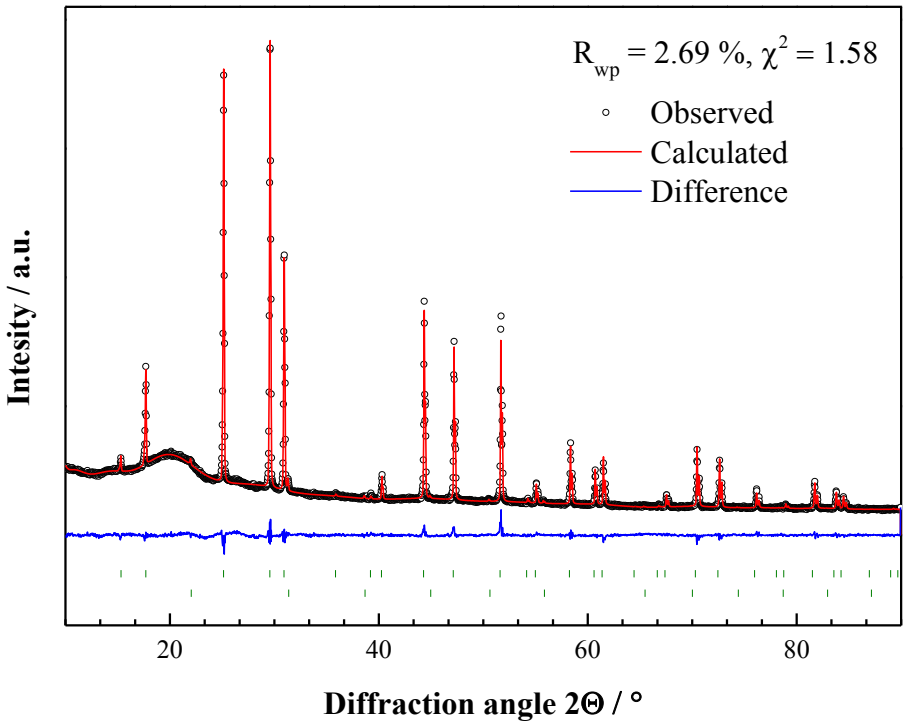

Figure S2. X-ray powder diffraction data for $Li_{6.025}P_{0.975}Si_{0.025}S_5Br$ and the corresponding Rietveld refinements. Shown are the collected data, the profile fit, the profile residuals and the Bragg reflections for the main phase (top).

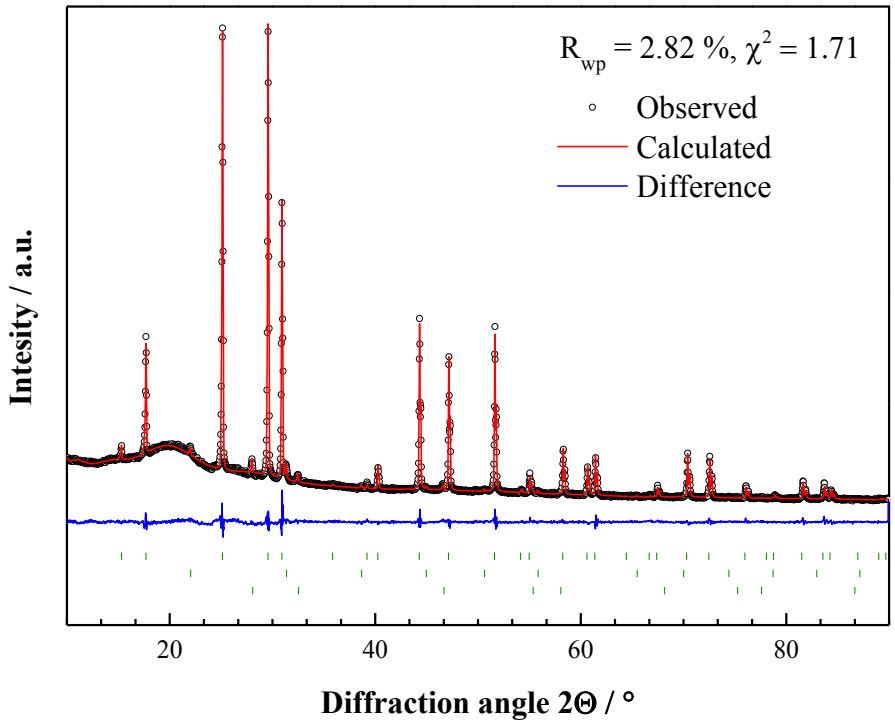

Figure S3. X-ray powder diffraction data for $Li_{6.05}P_{0.95}Si_{0.05}S_5Br$ and the corresponding Rietveld refinements. Shown are the collected data, the profile fit, the profile residuals and the Bragg reflections for the main phase (top).

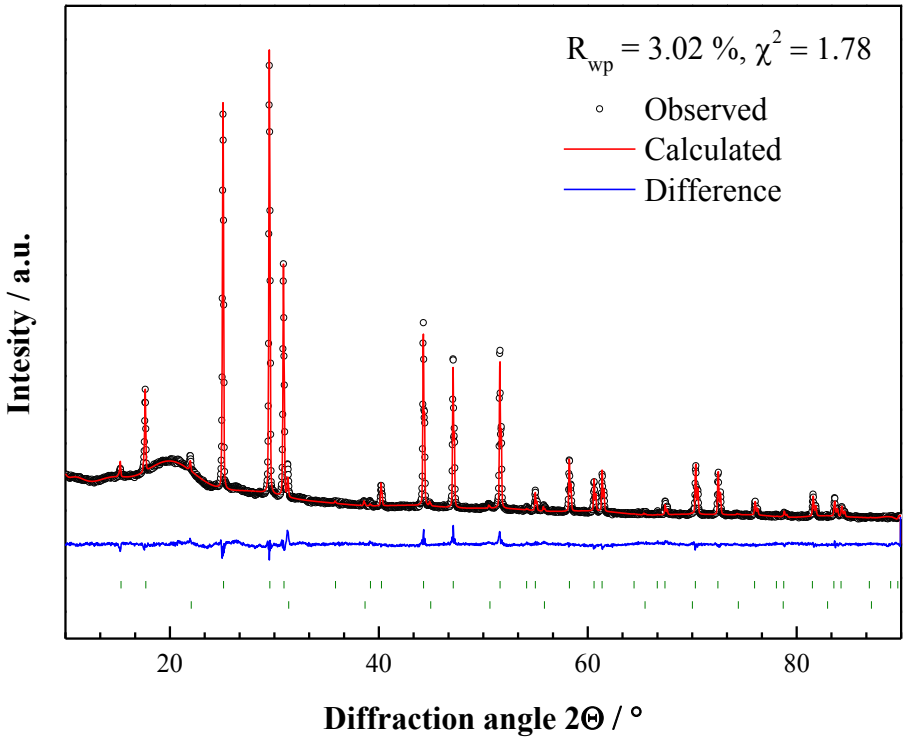

Figure S4. X-ray powder diffraction data for $Li_{6.075}P_{0.925}Si_{0.075}S_5Br$ and the corresponding Rietveld refinements. Shown are the collected data, the profile fit, the profile residuals and the Bragg reflections for the main phase (top).

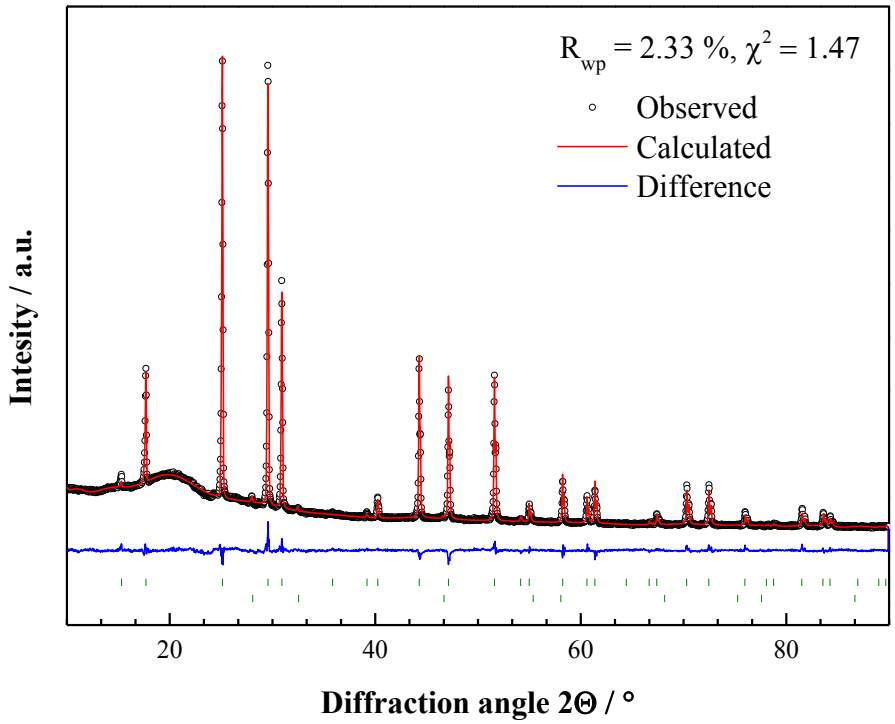

Figure S5. X-ray powder diffraction data for $Li_{6.10}P_{0.90}Si_{0.10}S_5Br$ and the corresponding Rietveld refinements. Shown are the collected data, the profile fit, the profile residuals and the Bragg reflections for the main phase (top).

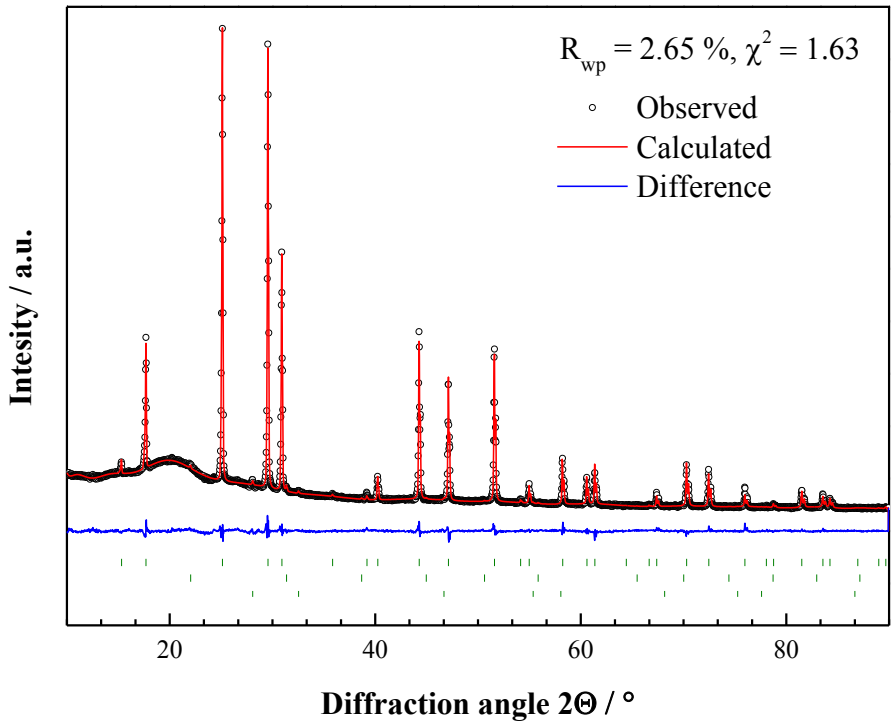

Figure S6. X-ray powder diffraction data for $Li_{6.15}P_{0.85}Si_{0.15}S_5Br$ and the corresponding Rietveld refinements. Shown are the collected data, the profile fit, the profile residuals and the Bragg reflections for the main phase (top).

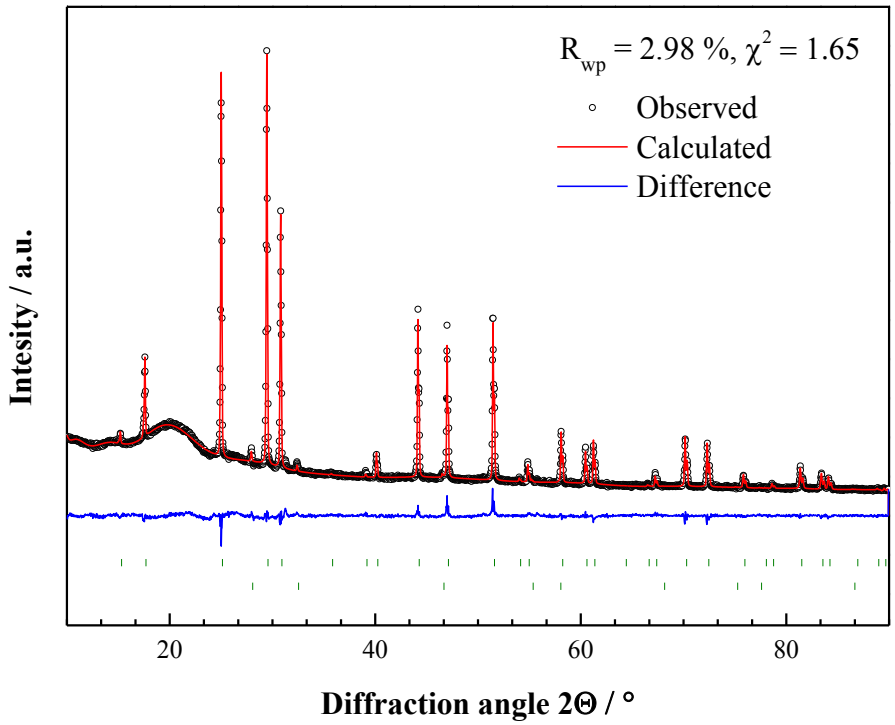

Figure S7. X-ray powder diffraction data for $Li_{6.175}P_{0.825}Si_{0.175}S_5Br$ and the corresponding Rietveld refinements. Shown are the collected data, the profile fit, the profile residuals and the Bragg reflections for the main phase (top).

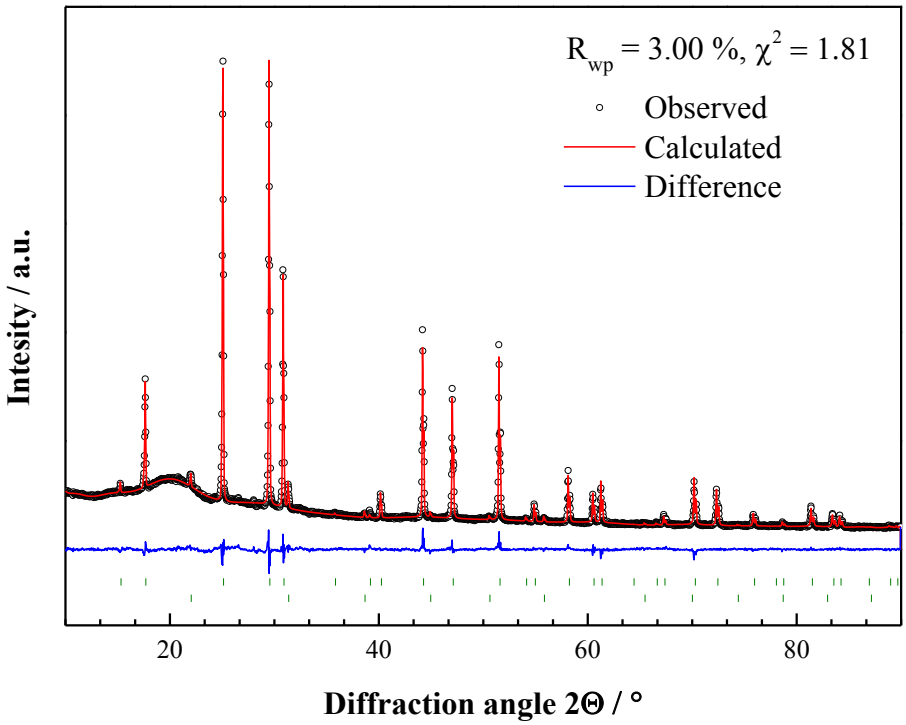

Figure S8. X-ray powder diffraction data for $Li_{6.20}P_{0.80}Si_{0.20}S_5Br$ and the corresponding Rietveld refinements. Shown are the collected data, the profile fit, the profile residuals and the Bragg reflections for the main phase (top).

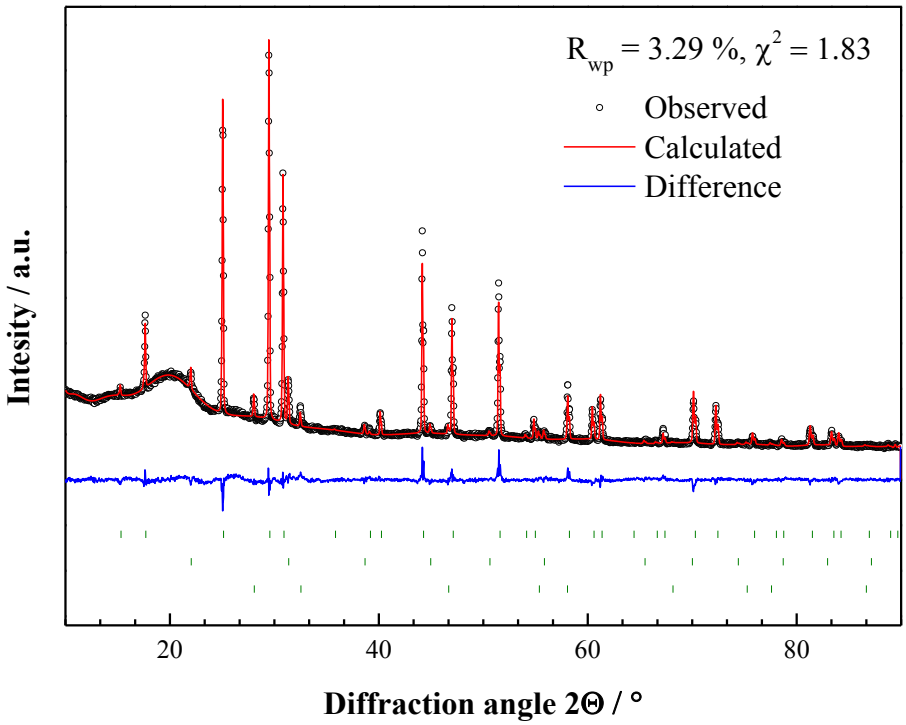

Figure S9. X-ray powder diffraction data for $Li_{6.225}P_{0.775}Si_{0.225}S_5Br$ and the corresponding Rietveld refinements. Shown are the collected data, the profile fit, the profile residuals and the Bragg reflections for the main phase (top).

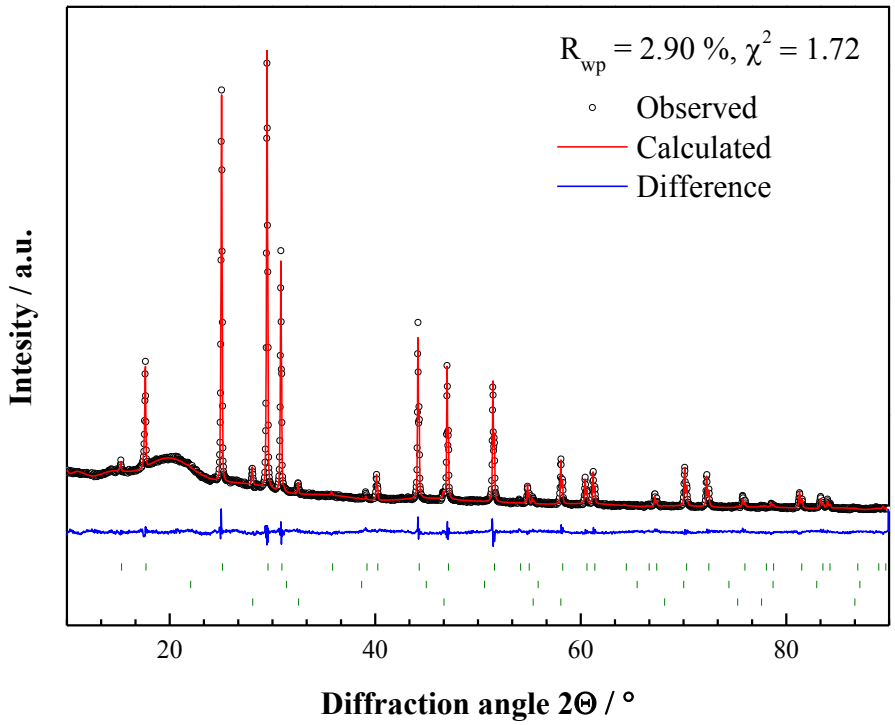

Figure S10. X-ray powder diffraction data for $Li_{6.25}P_{0.75}Si_{0.25}S_5Br$ and the corresponding Rietveld refinements. Shown are the collected data, the profile fit, the profile residuals and the Bragg reflections for the main phase (top).

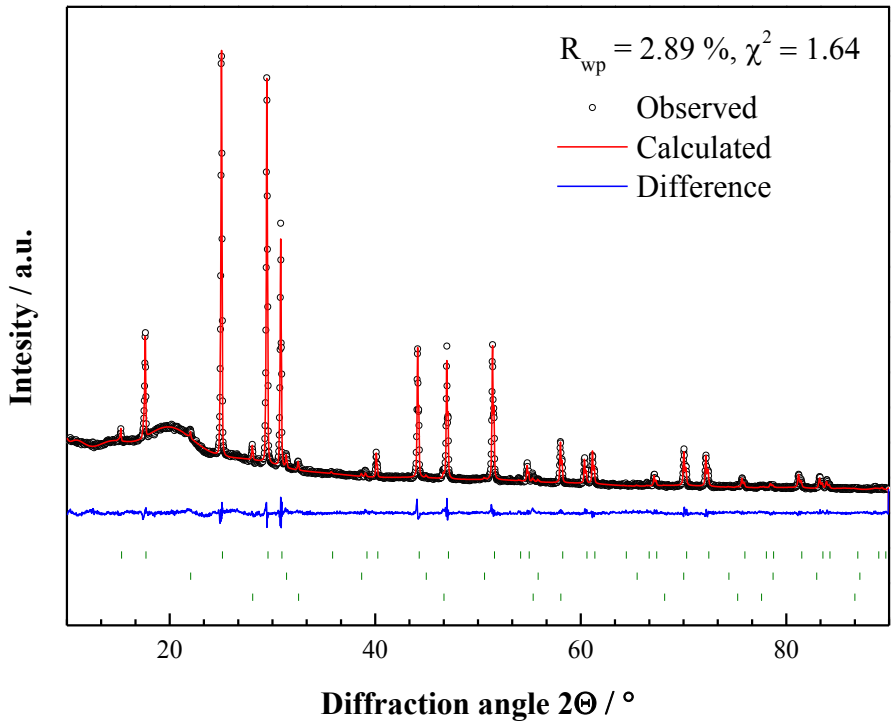

Figure S11. X-ray powder diffraction data for $Li_{6.30}P_{0.70}Si_{0.30}S_5Br$ and the corresponding Rietveld refinements. Shown are the collected data, the profile fit, the profile residuals and the Bragg reflections for the main phase (top).

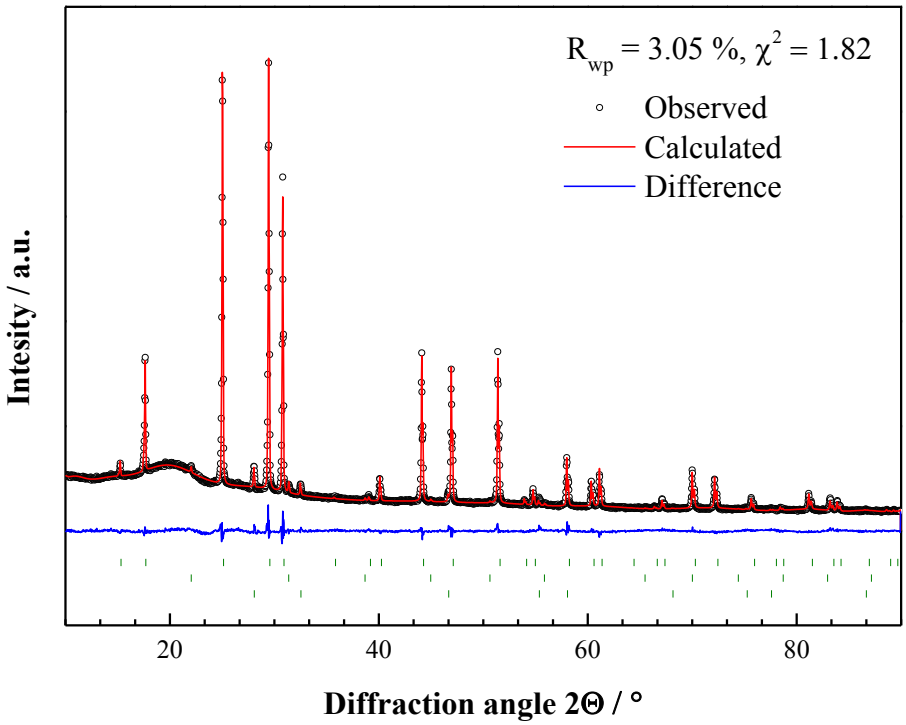

Figure S12. X-ray powder diffraction data for $Li_{6.35}P_{0.65}Si_{0.35}S_5Br$ and the corresponding Rietveld refinements. Shown are the collected data, the profile fit, the profile residuals and the Bragg reflections for the main phase (top).

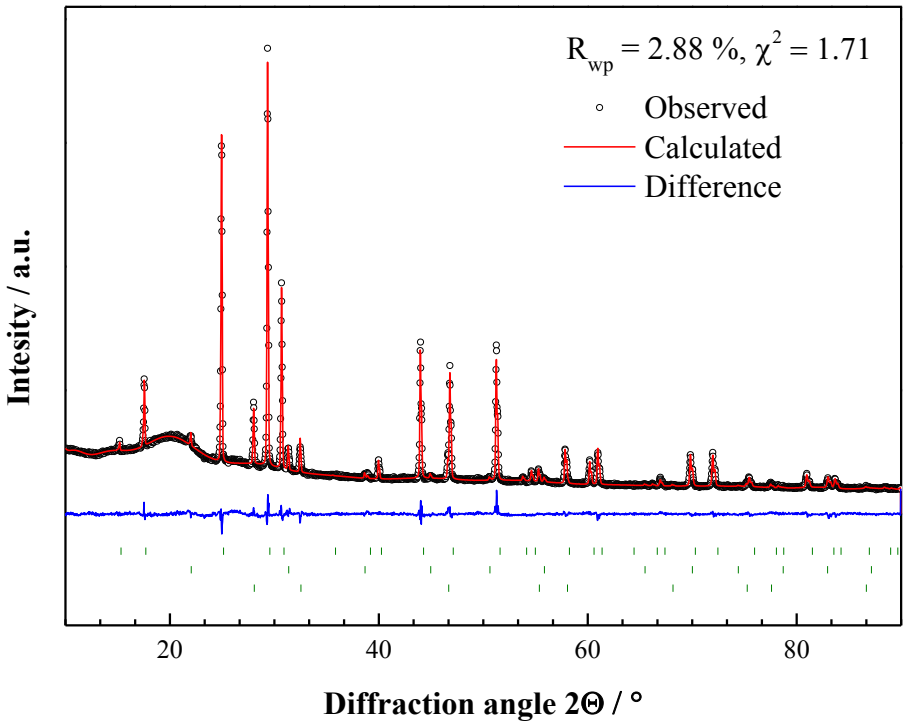

Figure S13. X-ray powder diffraction data for $Li_{6.50}P_{0.50}Si_{0.50}S_5Br$ and the corresponding Rietveld refinements. Shown are the collected data, the profile fit, the profile residuals and the Bragg reflections for the main phase (top).

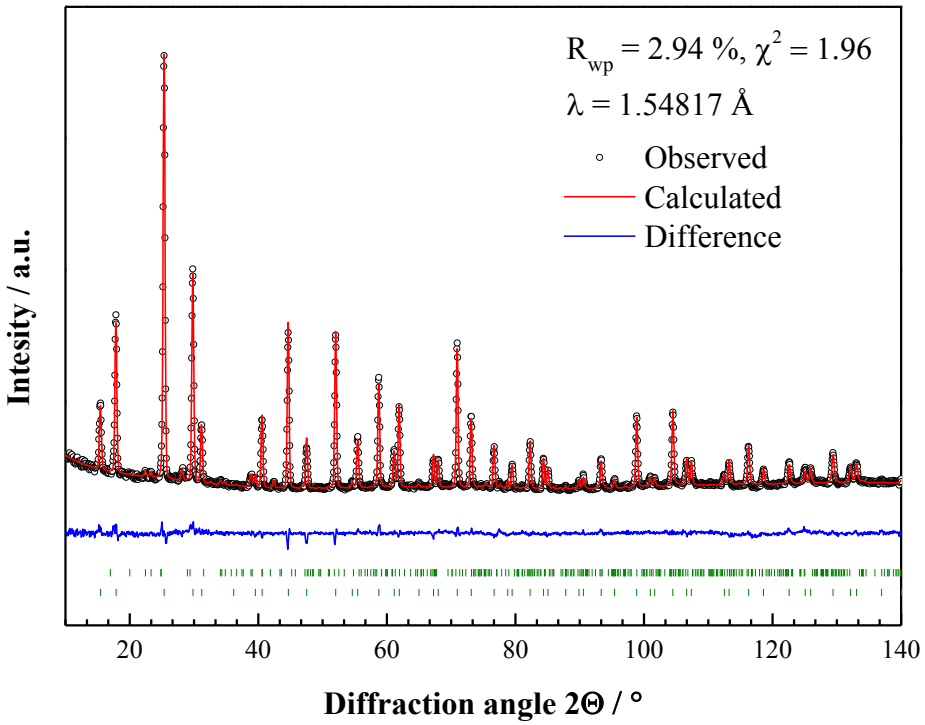

Figure S14. Neutron powder data for Li_6PS_5Br and the corresponding Rietveld refinements. Shown are the collected data, the profile fit, the profile residuals and the Bragg reflections for the main phase (top).

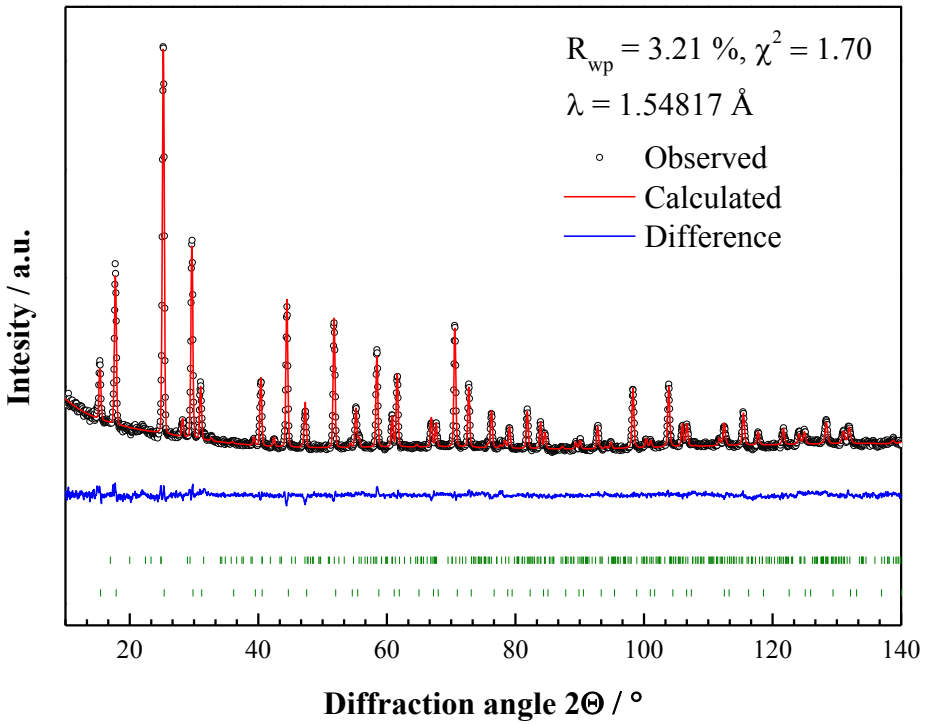

Figure S15. Neutron powder data for $Li_{6.25}P_{0.75}Si_{0.25}S_5Br$ and the corresponding Rietveld refinements. Shown are the collected data, the profile fit, the profile residuals and the Bragg reflections for the main phase (top).

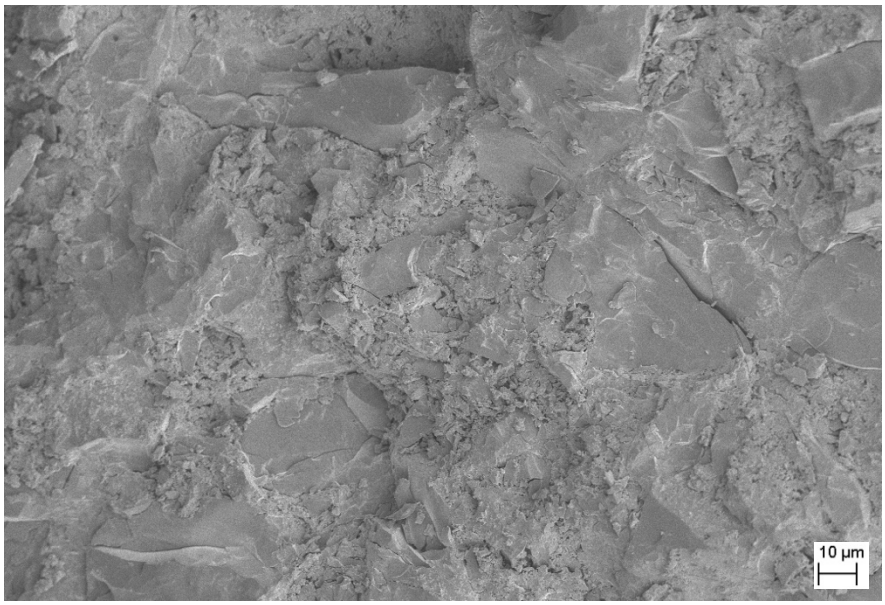

Figure S16: Scanning electron micrograph of Li_6PS_5Br, showing highly dense samples with good grain contact.

Table S1. Crystallographic data (atomic coordinates, occupancy, and U_{iso}) of Li_6PS_5Br, obtained from Rietveld refinement of X-ray diffraction data.

Li_6PS_5Br structure from X-ray diffraction data (space group $F\bar{4}3m$); λ_1 = 1.54051 Å, λ_2 = 1.54433 Å, I(λ_2/λ_1 = 0.5) a = 9.9773(2) Å Fit residuals (R_{wp}, R_{exp}, χ^2): 2.64%, 2.07%, 1.62						
Atom	Wyckoff Site	x/*a*	y/*b*	z/*c*	Occ.	U_{iso} / Å^2
Li1	48*h*	0.3071	0.0251	0.6929	0.44	0.05
Li2	24*g*	0.25	0.017	0.75	0.12	0.05
Br1	4*a*	0.0	0.0	0.0	0.78(1)	0.041(1)
Br2	4*d*	0.75	0.75	0.75	0.22(1)	0.048(1)
P1	4*b*	0.5	0.5	0.5	1.0	0.043(1)
S1	4*d*	0.75	0.75	0.75	0.78(1)	0.048(1)
S2	16*e*	0.1198(1)	-0.1198(1)	0.6198(1)	1.0	0.0431(8)
S3	4*a*	0.0	0.0	1.0	0.22(1)	0.041(1)

Table S2. Crystallographic data (atomic coordinates, occupancy, and U_{iso}) of $Li_{6.025}P_{0.975}Si_{0.025}S_5Br$, obtained from Rietveld refinement of X-ray diffraction data.

$Li_{6.025}P_{0.975}Si_{0.025}S_5Br$ structure from X-ray diffraction data (space group $F\bar{4}3m$); λ_1 = 1.54051 Å, λ_2 = 1.54433 Å, I(λ_2/λ_1 = 0.5) *a* = 9.9819(2) Å; 1.1% Li_3OBr Fit residuals (R_{wp}, R_{exp}, χ^2): 2.69%, 2.14%, 1.58						
Atom	Wyckoff Site	x/*a*	y/*b*	z/*c*	Occ.	U_{iso} / Å^2
Li1	48*h*	0.3071	0.0251	0.6929	0.44	0.05
Li2	24*g*	0.25	0.017	0.75	0.12	0.05
Br1	4*a*	0.0	0.0	0.0	0.80(1)	0.044(1)
Br2	4*d*	0.75	0.75	0.75	0.20(1)	0.036(1)
P1	4*b*	0.5	0.5	0.5	0.975	0.020(1)
Si1	4*b*	0.5	0.5	0.5	0.025	0.020(1)
S1	4*d*	0.75	0.75	0.75	0.80(1)	0.036(1)
S2	16*e*	0.1203(1)	-0.1203(1)	0.6203(1)	1.0	0.0371(7)
S3	4*a*	0.0	0.0	0.0	0.20(1)	0.044(1)

Table S3. Crystallographic data (atomic coordinates, occupancy, and U_{iso}) of $Li_{6.05}P_{0.95}Si_{0.05}S_5Br$, obtained from Rietveld refinement of X-ray diffraction data.

$Li_{6.05}P_{0.95}Si_{0.05}S_5Br$ structure from X-ray diffraction data (space group $F\bar{4}3m$); λ_1 = 1.54051 Å, λ_2 = 1.54433 Å, I(λ_2/λ_1 = 0.5) *a* = 9.9871(2) Å; 1.4% Li_3OBr; 1.0% LiBr Fit residuals (R_{wp}, R_{exp}, χ^2): 2.82%, 2.16%, 1.71						
Atom	Wyckoff Site	x/*a*	y/*b*	z/*c*	Occ.	U_{iso} / Å^2
Li1	48*h*	0.3071	0.0251	0.6929	0.44	0.05
Li2	24*g*	0.25	0.017	0.75	0.12	0.05
Br1	4*a*	0.0	0.0	0.0	0.79(1)	0.049(1)
Br2	4*d*	0.75	0.75	0.75	0.21(1)	0.058(1)
P1	4*b*	0.5	0.5	0.5	0.95	0.038(1)
Si1	4*b*	0.5	0.5	0.5	0.05	0.038(1)
S1	4*d*	0.75	0.75	0.75	0.79(1)	0.058(1)
S2	16*e*	0.1204(1)	-0.1204(1)	0.6204(1)	1.0	0.0456(8)
S3	4*a*	0.0	0.0	0.0	0.21(1)	0.049(1)

Table S4. Crystallographic data (atomic coordinates, occupancy, and U_{iso}) of $Li_{6.075}P_{0.925}Si_{0.075}S_5Br$, obtained from Rietveld refinement of X-ray diffraction data.

$Li_{6.075}P_{0.925}Si_{0.075}S_5Br$ structure from X-ray diffraction data (space group $F\bar{4}3m$); λ_1 = 1.54051 Å, λ_2 = 1.54433 Å, I(λ_2/λ_1 = 0.5) *a* = 9.9938(3) Å; 1.9% Li_3OBr Fit residuals (R_{wp}, R_{exp}, χ^2): 3.02%, 2.26%, 1.78						
Atom	Wyckoff Site	x/*a*	y/*b*	z/*c*	Occ.	U_{iso} / Å^2
Li1	48*h*	0.3071	0.0251	0.6929	0.44	0.05
Li2	24*g*	0.25	0.017	0.75	0.12	0.05
Br1	4*a*	0.0	0.0	0.0	0.77(1)	0.036(1)
Br2	4*d*	0.75	0.75	0.75	0.23(1)	0.047(2)
P1	4*b*	0.5	0.5	0.5	0.925	0.031(2)
Si1	4*b*	0.5	0.5	0.5	0.075	0.031(2)
S1	4*d*	0.75	0.75	0.75	0.77(1)	0.047(2)
S2	16*e*	0.1220(1)	-0.1220(1)	0.6220(1)	1.0	0.042(1)
S3	4*a*	0.0	0.0	0.0	0.23(1)	0.036(1)

Table S5. Crystallographic data (atomic coordinates, occupancy, and U_{iso}) of $Li_{6.10}P_{0.90}Si_{0.10}S_5Br$, obtained from Rietveld refinement of X-ray diffraction data.

$Li_{6.10}P_{0.90}Si_{0.10}S_5Br$ structure from X-ray diffraction data (space group $F\bar{4}3m$); λ_1 = 1.54051 Å, λ_2 = 1.54433 Å, I(λ_2/λ_1 = 0.5) *a* = 10.0024(2) Å; 0.4% LiBr Fit residuals (R_{wp}, R_{exp}, χ^2): 2.33%, 1.92%, 1.47						
Atom	Wyckoff Site	x/*a*	y/*b*	z/*c*	Occ.	U_{iso} / Å^2
Li1	48*h*	0.3071	0.0251	0.6929	0.44	0.05
Li2	24*g*	0.25	0.017	0.75	0.12	0.05
Br1	4*a*	0.0	0.0	0.0	0.79(1)	0.0496(9)
Br2	4*d*	0.75	0.75	0.75	0.21(1)	0.060(1)
P1	4*b*	0.5	0.5	0.5	0.90	0.047(1)
Si1	4*b*	0.5	0.5	0.5	0.10	0.047(1)
S1	4*d*	0.75	0.75	0.75	0.79(1)	0.060(1)
S2	16*e*	0.1193(2)	-0.1193(2)	0.6193(2)	1.0	0.0463(7)
S3	4*a*	0.0	0.0	0.0	0.21(1)	0.0496(9)

Table S6. Crystallographic data (atomic coordinates, occupancy, and U_{iso}) of $Li_{6.125}P_{0.875}Si_{0.125}S_5Br$, obtained from Rietveld refinement of X-ray diffraction data.

$Li_{6.125}P_{0.875}Si_{0.125}S_5Br$ structure from X-ray diffraction data (space group $F\bar{4}3m$); λ_1 = 1.54051 Å, λ_2 = 1.54433 Å, I(λ_2/λ_1 = 0.5) *a* = 10.0098(2) Å; 2.8% Li_3OBr Fit residuals (R_{wp}, R_{exp}, χ^2): 3.02%, 2.24%, 1.82						
Atom	Wyckoff Site	x/*a*	y/*b*	z/*c*	Occ.	U_{iso} / Å^2
Li1	48*h*	0.3071	0.0251	0.6929	0.44	0.05
Li2	24*g*	0.25	0.017	0.75	0.12	0.05
Br1	4*a*	0.0	0.0	0.0	0.82(1)	0.050(1)
Br2	4*d*	0.75	0.75	0.75	0.18(1)	0.041(1)
P1	4*b*	0.5	0.5	0.5	0.875	0.018(1)
Si1	4*b*	0.5	0.5	0.5	0.125	0.018(1)
S1	4*d*	0.75	0.75	0.75	0.82(1)	0.041(1)
S2	16*e*	0.1210(1)	-0.1210(1)	0.6210(1)	1.0	0.0322(8)
S3	4*a*	0.0	0.0	0.0	0.18(1)	0.050(1)

Table S7. Crystallographic data (atomic coordinates, occupancy, and U_{iso}) of $Li_{6.15}P_{0.85}Si_{0.15}S_5Br$, obtained from Rietveld refinement of X-ray diffraction data.

$Li_{6.15}P_{0.85}Si_{0.15}S_5Br$ structure from X-ray diffraction data (space group $F\bar{4}3m$); λ_1 = 1.54051 Å, λ_2 = 1.54433 Å, I(λ_2/λ_1 = 0.5) *a* = 10.0145(2) Å; 0.5% Li_3OBr; 0.3% LiBr Fit residuals (R_{wp}, R_{exp}, χ^2): 2.65%, 2.08%, 1.63						
Atom	Wyckoff Site	x/*a*	y/*b*	z/*c*	Occ.	U_{iso} / Å^2
Li1	48*h*	0.3071	0.0251	0.6929	0.44	0.05
Li2	24*g*	0.25	0.017	0.75	0.12	0.05
Br1	4*a*	0.0	0.0	0.0	0.84(1)	0.056(1)
Br2	4*d*	0.75	0.75	0.75	0.16(1)	0.053(1)
P1	4*b*	0.5	0.5	0.5	0.85	0.030(1)
Si1	4*b*	0.5	0.5	0.5	0.15	0.030(1)
S1	4*d*	0.75	0.75	0.75	0.84(1)	0.053(1)
S2	16*e*	0.1200(1)	-0.1200(1)	0.6200(1)	1.0	0.0449(8)
S3	4*a*	0.0	0.0	0.0	0.16(1)	0.056(1)

Table S8. Crystallographic data (atomic coordinates, occupancy, and U_{iso}) of $Li_{6.175}P_{0.825}Si_{0.175}S_5Br$, obtained from Rietveld refinement of X-ray diffraction data.

$Li_{6.175}P_{0.825}Si_{0.175}S_5Br$ structure from X-ray diffraction data (space group $F\bar{4}3m$); λ_1 = 1.54051 Å, λ_2 = 1.54433 Å, I(λ_2/λ_1 = 0.5) *a* = 10.0193(3) Å; 0.8% LiBr Fit residuals (R_{wp}, R_{exp}, χ^2): 2.98%, 2.32%, 1.65						
Atom	Wyckoff Site	x/*a*	y/*b*	z/*c*	Occ.	U_{iso} / Å^2
Li1	48*h*	0.3071	0.0251	0.6929	0.44	0.05
Li2	24*g*	0.25	0.017	0.75	0.12	0.05
Br1	4*a*	0.0	0.0	0.0	0.79(1)	0.040(1)
Br2	4*d*	0.75	0.75	0.75	0.21(1)	0.041(1)
P1	4*b*	0.5	0.5	0.5	0.825	0.014(2)
Si1	4*b*	0.5	0.5	0.5	0.175	0.014(2)
S1	4*d*	0.75	0.75	0.75	0.79(1)	0.041(1)
S2	16*e*	0.1220(1)	-0.1220(1)	0.6220(1)	1.0	0.0288(9)
S3	4*a*	0.0	0.0	0.0	0.21(1)	0.040(1)

Table S9. Crystallographic data (atomic coordinates, occupancy, and U_{iso}) of $Li_{6.20}P_{0.80}Si_{0.20}S_5Br$, obtained from Rietveld refinement of X-ray diffraction data.

$Li_{6.20}P_{0.80}Si_{0.20}S_5Br$ structure from X-ray diffraction data (space group $F\bar{4}3m$); λ_1 = 1.54051 Å, λ_2 = 1.54433 Å, I(λ_2/λ_1 = 0.5) *a* = 10.0240(2) Å; 2.4% Li_3OBr Fit residuals (R_{wp}, R_{exp}, χ^2): 3.00%, 2.23%, 1.81						
Atom	Wyckoff Site	x/*a*	y/*b*	z/*c*	Occ.	U_{iso} / Å^2
Li1	48*h*	0.3071	0.0251	0.6929	0.44	0.05
Li2	24*g*	0.25	0.017	0.75	0.12	0.05
Br1	4*a*	0.0	0.0	0.0	0.84(1)	0.056(1)
Br2	4*d*	0.75	0.75	0.75	0.16(1)	0.039(1)
P1	4*b*	0.5	0.5	0.5	0.80	0.018(1)
Si1	4*b*	0.5	0.5	0.5	0.20	0.018(1)
S1	4*d*	0.75	0.75	0.75	0.84(1)	0.039(1)
S2	16*e*	0.1216(1)	-0.1216(1)	0.6216(1)	1.0	0.0398(8)
S3	4*a*	0.0	0.0	0.0	0.16(1)	0.056(1)

Table S10. Crystallographic data (atomic coordinates, occupancy, and U_{iso}) of $Li_{6.225}P_{0.775}Si_{0.225}S_5Br$, obtained from Rietveld refinement of X-ray diffraction data.

$Li_{6.225}P_{0.775}Si_{0.225}S_5Br$ structure from X-ray diffraction data (space group $F\bar{4}3m$); λ_1 = 1.54051 Å, λ_2 = 1.54433 Å, I(λ_2/λ_1 = 0.5) *a* = 10.0315(1) Å; 6.1% Li_3OBr; 1.8% LiBr Fit residuals (R_{wp}, R_{exp}, χ^2): 3.29%, 2.43%, 1.83						
Atom	Wyckoff Site	x/*a*	y/*b*	z/*c*	Occ.	U_{iso} / Å^2
Li1	48*h*	0.3071	0.0251	0.6929	0.44	0.05
Li2	24*g*	0.25	0.017	0.75	0.12	0.05
Br1	4*a*	0.0	0.0	0.0	0.83(1)	0.037(1)
Br2	4*d*	0.75	0.75	0.75	0.17(1)	0.036(2)
P1	4*b*	0.5	0.5	0.5	0.775	0.002(1)
Si1	4*b*	0.5	0.5	0.5	0.225	0.002(1)
S1	4*d*	0.75	0.75	0.75	0.83(1)	0.036(2)
S2	16*e*	0.1213(1)	-0.1213(1)	0.6213(1)	1.0	0.025(1)
S3	4*a*	0.0	0.0	0.0	0.17(1)	0.037(1)

Table S11. Crystallographic data (atomic coordinates, occupancy, and U_{iso}) of $Li_{6.25}P_{0.75}Si_{0.25}S_5Br$, obtained from Rietveld refinement of X-ray diffraction data.

$Li_{6.25}P_{0.75}Si_{0.25}S_5Br$ structure from X-ray diffraction data (space group $F\bar{4}3m$); λ_1 = 1.54051 Å, λ_2 = 1.54433 Å, I(λ_2/λ_1 = 0.5) *a* = 10.0365(2) Å; 0.3% Li_3OBr; 1.3% LiBr Fit residuals (R_{wp}, R_{exp}, χ^2): 2.90%, 2.21%, 1.72						
Atom	Wyckoff Site	x/*a*	y/*b*	z/*c*	Occ.	U_{iso} / Å^2
Li1	48*h*	0.3071	0.0251	0.6929	0.44	0.05
Li2	24*g*	0.25	0.017	0.75	0.12	0.05
Br1	4*a*	0.0	0.0	0.0	0.84(1)	0.044(1)
Br2	4*d*	0.75	0.75	0.75	0.16(1)	0.057(2)
P1	4*b*	0.5	0.5	0.5	0.75	0.045(2)
Si1	4*b*	0.5	0.5	0.5	0.25	0.045(2)
S1	4*d*	0.75	0.75	0.75	0.84(1)	0.057(2)
S2	16*e*	0.1208(1)	-0.1208(1)	0.6208(1)	1.0	0.058(2)
S3	4*a*	0.0	0.0	0.0	0.16(1)	0.044(1)

Table S12. Crystallographic data (atomic coordinates, occupancy, and U_{iso}) of $Li_{6.30}P_{0.70}Si_{0.30}S_5Br$, obtained from Rietveld refinement of X-ray diffraction data.

$Li_{6.30}P_{0.70}Si_{0.30}S_5Br$ structure from X-ray diffraction data (space group $F\bar{4}3m$); λ_1 = 1.54051 Å, λ_2 = 1.54433 Å, I(λ_2/λ_1 = 0.5) *a* = 10.0521(3) Å; 1.2% Li_3OBr; 1.1% LiBr Fit residuals (R_{wp}, R_{exp}, χ^2): 2.89%, 2.26%, 1.64						
Atom	Wyckoff Site	x/*a*	y/*b*	z/*c*	Occ.	U_{iso} / Å^2
Li1	48*h*	0.3071	0.0251	0.6929	0.44	0.05
Li2	24*g*	0.25	0.017	0.75	0.12	0.05
Br1	4*a*	0.0	0.0	0.0	0.82(1)	0.043(1)
Br2	4*d*	0.75	0.75	0.75	0.18(1)	0.061(2)
P1	4*b*	0.5	0.5	0.5	0.70	0.044(2)
Si1	4*b*	0.5	0.5	0.5	0.30	0.044(2)
S1	4*d*	0.75	0.75	0.75	0.82(1)	0.061(2)
S2	16*e*	0.1199(2)	-0.1199(2)	0.6199(2)	1.0	0.047(1)
S3	4*a*	0.0	0.0	0.0	0.18(1)	0.043(1)

Table S13. Crystallographic data (atomic coordinates, occupancy, and U_{iso}) of $Li_{6.35}P_{0.65}Si_{0.35}S_5Br$, obtained from Rietveld refinement of X-ray diffraction data.

$Li_{6.35}P_{0.65}Si_{0.35}S_5Br$ structure from X-ray diffraction data (space group $F\bar{4}3m$); λ_1 = 1.54051 Å, λ_2 = 1.54433 Å, I(λ_2/λ_1 = 0.5) *a* = 10.0468(1) Å; 1.0% Li_3OBr; 1.3% LiBr Fit residuals (R_{wp}, R_{exp}, χ^2): 3.05%, 2.26%, 1.82						
Atom	Wyckoff Site	x/*a*	y/*b*	z/*c*	Occ.	U_{iso} / Å^2
Li1	48*h*	0.3071	0.0251	0.6929	0.44	0.05
Li2	24*g*	0.25	0.017	0.75	0.12	0.05
Br1	4*a*	0.0	0.0	0.0	0.83(1)	0.067(1)
Br2	4*d*	0.75	0.75	0.75	0.17(1)	0.052(1)
P1	4*b*	0.5	0.5	0.5	0.65	0.022(1)
Si1	4*b*	0.5	0.5	0.5	0.35	0.022(1)
S1	4*d*	0.75	0.75	0.75	0.83(1)	0.052(1)
S2	16*e*	0.1211(2)	-0.1211(2)	0.6211(2)	1.0	0.0435(8)
S3	4*a*	0.0	0.0	0.0	0.17(1)	0.067(1)

Table S14. Crystallographic data (atomic coordinates, occupancy, and U_{iso}) of $Li_{6.50}P_{0.50}Si_{0.50}S_5Br$, obtained from Rietveld refinement of X-ray diffraction data.

$Li_{6.50}P_{0.50}Si_{0.50}S_5Br$ structure from X-ray diffraction data (space group $F\bar{4}3m$); λ_1 = 1.54051 Å, λ_2 = 1.54433 Å, I(λ_2/λ_1 = 0.5) *a* = 10.0521(2) Å; 2.6% Li_3OBr; 4.8% LiBr Fit residuals (R_{wp}, R_{exp}, χ^2): 2.88%, 2.20%, 1.71						
Atom	Wyckoff Site	x/*a*	y/*b*	z/*c*	Occ.	U_{iso} / Å^2
Li1	48*h*	0.3071	0.0251	0.6929	0.44	0.05
Li2	24*g*	0.25	0.017	0.75	0.12	0.05
Br1	4*a*	0.0	0.0	0.0	0.82(1)	0.055(1)
Br2	4*d*	0.75	0.75	0.75	0.18(1)	0.039(2)
P1	4*b*	0.5	0.5	0.5	0.50	0.021(2)
Si1	4*b*	0.5	0.5	0.5	0.50	0.021(2)
S1	4*d*	0.75	0.75	0.75	0.82(1)	0.052(1)
S2	16*e*	0.1216(1)	-0.1216(1)	0.6216(1)	1.0	0.0435(8)
S3	4*a*	0.0	0.0	0.0	0.18(1)	0.067(1)

Table S15. Crystallographic data (atomic coordinates, occupancy, and U_{iso}) of Li_6PS_5Br, obtained from Rietveld refinement of neutron diffraction data.

Li_6PS_5Br structure from neutron diffraction data (space group $F\bar{4}3m$); λ_1 = 1.54817 Å *a* = 9.9850(3) Å; 1.1% Li_3OBr; 1.0% LiBr Fit residuals (R_{wp}, R_{exp}, χ^2): 2.94%, 2.10%, 1.96						
Atom	Wyckoff Site	x/*a*	y/*b*	z/*c*	Occ.	U_{iso} / Å^2
Li1	48*h*	0.3071(3)	0.0251(5)	0.6929(3)	0.44(1)	0.056(2)
Li2	24*g*	0.25	0.017(3)	0.75	0.12(1)	0.011(4)
Br1	4*a*	0.0	0.0	0.0	0.78(1)	0.0360(6)
Br2	4*d*	0.75	0.75	0.75	0.22(1)	0.0305(7)
P1	4*b*	0.5	0.5	0.5	1.0	0.0200(5)
S1	4*d*	0.75	0.75	0.75	0.78(1)	0.0305(7)
S2	16*e*	0.1181(2)	-0.1181(2)	0.6181(2)	1.0	0.0252(6)
S3	4*a*	0.0	0.0	0.0	0.22(1)	0.0360(6)

Table S16. Crystallographic data (atomic coordinates, occupancy, and U_{iso}) of $Li_{6.125}P_{0.875}Si_{0.125}S_5Br$, obtained from Rietveld refinement of neutron diffraction data.

$Li_{6.125}P_{0.875}Si_{0.125}S_5Br$ structure from neutron diffraction data (space group $F\bar{4}3m$); λ_1 = 1.54817 Å a = 10.0079(1) Å Fit residuals (R_{wp}, R_{exp}, χ^2): 3.22%, 2.53%, 1.63						
Atom	Wyckoff Site	x/*a*	y/*b*	z/*c*	Occ.	U_{iso} / Å^2
Li1	48*h*	0.3079(5)	0.0249(7)	0.6922(5)	0.427(5)	0.044(2)
Li2	24*g*	0.25	0.014(4)	0.75	0.17(1)	0.044(2)
Br1	4*a*	0.0	0.0	0.0	0.82(1)	0.0365(8)
Br2	4*d*	0.75	0.75	0.75	0.18(1)	0.0311(9)
P1	4*b*	0.5	0.5	0.5	0.875	0.0197(7)
Si1	4*b*	0.5	0.5	0.5	0.125	0.0197(7)
S1	4*d*	0.25	0.25	0.75	0.82(1)	0.0311(9)
S2	16*e*	0.1172(2)	-0.1172(2)	0.6172(2)	1.0	0.0247(6)
S3	4*a*	0.0	0.0	0.0	0.18(1)	0.0365(8)

Table S17. Crystallographic data (atomic coordinates, occupancy, and U_{iso}) of $Li_{6.25}P_{0.75}Si_{0.25}S_5Br$, obtained from Rietveld refinement of neutron diffraction data.

$Li_{6.25}P_{0.75}Si_{0.25}S_5Br$ structure from neutron diffraction data (space group $F\bar{4}3m$); λ_1 = 1.54817 Å *a* = 10.0291(1) Å; 1.8% LiBr Fit residuals (R_{wp}, R_{exp}, χ^2): 3.21%, 2.46%, 1.70						
Atom	Wyckoff Site	x/*a*	y/*b*	z/*c*	Occ.	U_{iso} / Å^2
Li1	48*h*	0.3071(4)	0.0246(6)	0.6929(4)	0.418(4)	0.043(2)
Li2	24*g*	0.25	0.017(4)	0.75	0.205(8)	0.043(2)
Br1	4*a*	0.0	0.0	0.0	0.82(1)	0.0392(7)
Br2	4*d*	0.75	0.75	0.75	0.18(1)	0.0316(8)
P1	4*b*	0.5	0.5	0.5	0.75	0.0184(6)
Si1	4*b*	0.5	0.5	0.5	0.25	0.0184(6)
S1	4*d*	0.75	0.75	0.75	0.82(1)	0.0316(8)
S2	16*e*	0.1179(2)	-0.1179(2)	0.6179(2)	1.0	0.0253(5)
S3	4*a*	0.0	0.0	0.0	0.18(1)	0.0392(7)