Supporting Information –

On the competing structural influences in the Li superionic conducting argyrodites $Li_6PS_{5-x}Se_xBr$ ($0 \leq x \leq 1$) upon Se substitution

Tim Bernges,[a] Sean P. Culver,[a] Nicolò Minafra,[a] Raimund Koerver,[a] and Wolfgang G. Zeier*[a,b]

[a]*Institute of Physical Chemistry, Justus-Liebig-University Giessen, Heinrich-Buff-Ring 17, D-35392 Giessen, Germany.*

[b]*Center for Materials Research (LaMa), Justus-Liebig-University Giessen, Heinrich-Buff-Ring 16, D-35392 Giessen, Germany.*

Experimental Methods

Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX). Microstructural images of the solid electrolyte were obtained on a Merlin high-resolution scanning electron microscope (Carl Zeiss AG, Germany). The samples were transferred from a glove box in the analysis chamber under argon atmosphere using a transfer vessel (Leica EM VC500). EDX elemental mapping and compositional analysis were conducted using an XMAX EXTREME EDX detector (Oxford Instruments, United Kingdom). Measurements were carried out with an acceleration voltage of 5 kV and a probing current of 100 pA for SEM and 1000 pA for EDX.

Raman spectroscopy. A Senterra Raman spectrometer (Bruker, USA) with an excitation wavelength of 534 nm was used to collect Raman spectra from 80 to 4450 cm^{-1} using a 20× objective and a power of 0.2 mW. Samples were placed on glass substrates in the glovebox and sealed airtight by a cover glass and silicon vacuum grease.

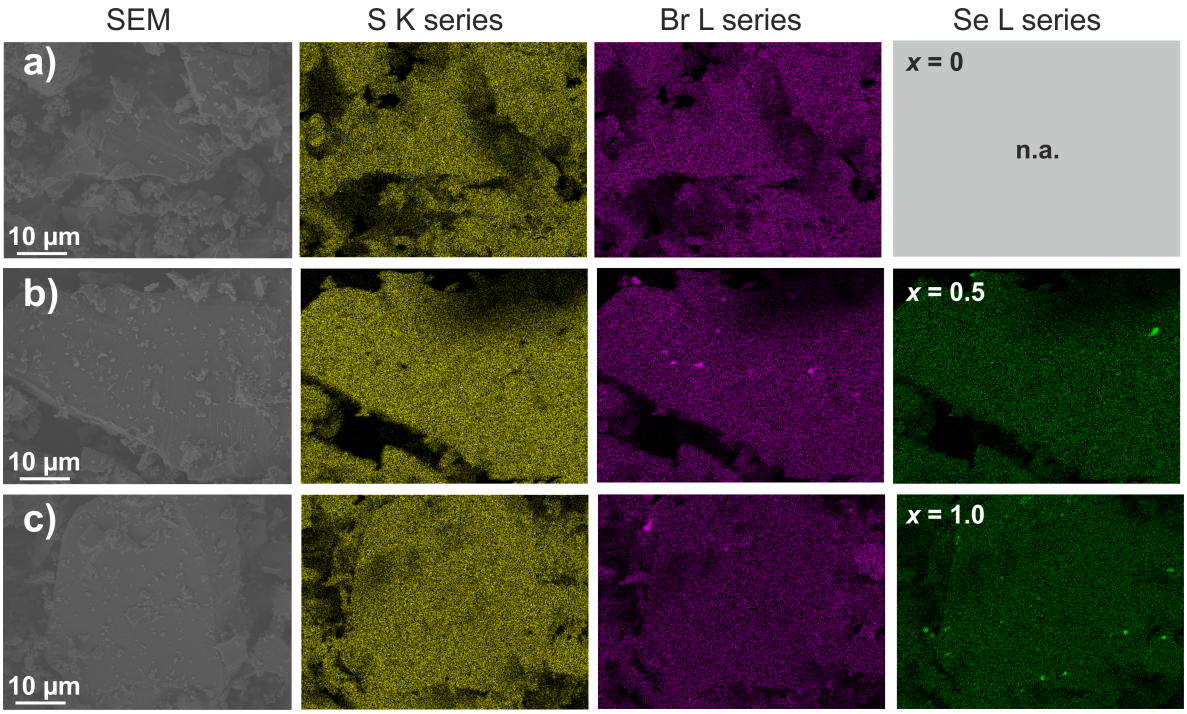

Figure S1: SEM and EDX analysis of $Li_6PS_{5-x}Se_xBr$ showing the excellent elemental homogeneity.

Table S1: Experimental sulfur to selenium ratios extracted from the measured EDX spectra.

$Li_6PS_{5-x}Se_xBr$	S:Se (calculated)	S:Se (experimental)
$x = 0$	5.0 : 0	n.a.
$x = 0.5$	4.5 : 0.5	4.51 : 0.49
$x = 1.0$	4.0 : 1.0	4.00 : 1.00

Table S2: Refined structural parameters for Li_6PS_5Br.

Li_6PS_5Br structure from powder X-ray diffraction data (space group $F\bar{4}3m$); λ = 1.5406 Å *a* = 9.9880(1) Å; 2.6% Li_3OBr; 0.4% LiBr Fit residuals (R_{wp}, R_{exp}, χ^2): 2.83%, 1.12%, 2.54						
Atom	Wyckoff Site	x/*a*	y/*b*	z/*c*	Occ.	B_{eq} / Å^2
Li1	48*h*	0.3071	0.0251	0.6929	0.441	5
Li2	24*g*	0.25	0.017	0.75	0.119	5
Br1	4*a*	0.0	0.0	0.0	0.751(8)	1.9(1)
Br2	4*c*	0.25	0.25	0.25	0.249(8)	3.0(1)
P1	4*b*	0.5	0.5	0.5	1.0	1.7(1)
S1	4*c*	0.25	0.25	0.25	0.751(8)	3.0(1)
S2	16*e*	0.1206(3)	-0.1206(3)	0.6206(3)	1.0	2.25(7)
S3	4*a*	0.0	0.0	0.0	0.249(8)	1.9(1)

Table S3: Refined structural parameters for $Li_6PS_{4.9}Se_{0.1}Br$.

$Li_6PS_{4.9}Se_{0.1}Br$ structure from powder X-ray diffraction data (space group $F\bar{4}3m$); λ = 1.5406 Å *a* = 9.9902(1) Å; 3.4% LiBr Fit residuals (R_{wp}, R_{exp}, χ^2): 3.49%, 1.33%, 2.62						
Atom	Wyckoff Site	x/*a*	y/*b*	z/*c*	Occ.	B_{eq} / Å^2
Li1	48*h*	0.3071	0.0251	0.6929	0.441	5
Li2	24*g*	0.25	0.017	0.75	0.119	5
Br1	4*a*	0.0	0.0	0.0	0.791(8)	2.5(1)
Br2	4*c*	0.25	0.25	0.25	0.208(8)	4.0(2)
P1	4*b*	0.5	0.5	0.5	1.0	1.9(2)
S1	4*c*	0.25	0.25	0.25	0.691(8)	4.0(2)
S2	16*e*	0.1212(3)	-0.1212(3)	0.6212(3)	1.0	1.97(8)
S3	4*a*	0.0	0.0	0.0	0.208(8)	2.5(1)
Se1	4*c*	0.25	0.25	0.25	0.1	4.0(2)

Table S4: Refined structural parameters for $Li_6PS_{4.8}Se_{0.2}Br$.

$Li_6PS_{4.8}Se_{0.2}Br$ structure from powder X-ray diffraction data (space group $F\bar{4}3m$); λ = 1.5406 Å *a* = 9.9946(2) Å; 2.9% Li_3OBr; 1.2% LiBr Fit residuals (R_{wp}, R_{exp}, χ^2): 3.95%, 1.39%, 2.84						
Atom	Wyckoff Site	x/*a*	y/*b*	z/*c*	Occ.	B_{eq} / Å^2
Li1	48*h*	0.3071	0.0251	0.6929	0.441	5
Li2	24*g*	0.25	0.017	0.75	0.119	5
Br1	4*a*	0.0	0.0	0.0	0.897(8)	1.7(2)
Br2	4*c*	0.25	0.25	0.25	0.102(8)	2.4(2)
P1	4*b*	0.5	0.5	0.5	1.0	1.6(2)
S1	4*c*	0.25	0.25	0.25	0.697(8)	2.4(2)
S2	16*e*	0.1210(4)	-0.1210(4)	0.6210(4)	1.0	1.7(1)
S3	4*a*	0.0	0.0	1.0	0.102(8)	1.7(2)
Se1	4*c*	0.25	0.25	0.75	0.2	2.4(2)

Table S5: Refined structural parameters for $Li_6PS_{4.7}Se_{0.3}Br$.

$Li_6PS_{4.7}Se_{0.3}Br$ structure from powder X-ray diffraction data (space group $F\bar{4}3m$); λ = 1.5406 Å *a* = 9.9974(1) Å; 1.0% LiBr Fit residuals (R_{wp}, R_{exp}, χ^2): 3.21%, 1.33%, 2.42						
Atom	Wyckoff Site	x/*a*	y/*b*	z/*c*	Occ.	B_{eq} / Å^2
Li1	48*h*	0.3071	0.0251	0.6929	0.441	5
Li2	24*g*	0.25	0.017	0.75	0.119	5
Br1	4*a*	0.0	0.0	0.0	1.0	2.4(1)
P1	4*b*	0.5	0.5	0.5	1.0	2.8(2)
S1	4*c*	0.25	0.25	0.25	0.825(2)	1.2(1)
S2	16*e*	0.1222(3)	-0.1222(3)	0.6222(3)	0.968(2)	2.08(9)
Se1	4*c*	0.25	0.25	0.25	0.175(2)	1.2(1)
Se2	16e	0.1222(3)	-0.1222(3)	0.6222(3)	0.032(2)	2.08(9)

Table S6: Refined structural parameters for $Li_6PS_{4.6}Se_{0.4}Br$.

$Li_6PS_{4.6}Se_{0.4}Br$ structure from powder X-ray diffraction data (space group $F\bar{4}3m$); λ = 1.5406 Å *a* = 10.0079(1) Å; 1.7% Li_3OBr; 0.7% LiBr Fit residuals (R_{wp}, R_{exp}, χ^2): 3.18%, 1.29%, 2.47						
Atom	Wyckoff Site	x/*a*	y/*b*	z/*c*	Occ.	B_{eq} / Å^2
Li1	48*h*	0.3071	0.0251	0.6929	0.441	5
Li2	24*g*	0.25	0.017	0.75	0.119	5
Br1	4*a*	0.0	0.0	0.0	1.0	3.5(1)
P1	4*b*	0.5	0.5	0.5	1.0	1.1(1)
S1	4*c*	0.25	0.25	0.25	0.729(8)	0.9(1)
S2	16*e*	0.1233(3)	-0.1233(3)	0.6233(3)	0.967(2)	2.22(9)
Se1	4*c*	0.25	0.25	0.25	0.271(8)	0.9(1)
Se2	16e	0.1233(3)	-0.1233(3)	0.6233(3)	0.033(2)	2.22(9)

Table S7: Refined structural parameters for $Li_6PS_{4.5}Se_{0.5}Br$.

$Li_6PS_{4.5}Se_{0.5}Br$ structure from powder X-ray diffraction data (space group $F\bar{4}3m$); λ = 1.5406 Å *a* = 10.0176(1) Å; 2.1% LiBr Fit residuals (R_{wp}, R_{exp}, χ^2): 2.96%, 1.40%, 2.11						
Atom	Wyckoff Site	x/*a*	y/*b*	z/*c*	Occ.	B_{eq} / Å^2
Li1	48*h*	0.3071	0.0251	0.6929	0.441	5
Li2	24*g*	0.25	0.017	0.75	0.119	5
Br1	4*a*	0.0	0.0	0.0	1.0	2.8(1)
P1	4*b*	0.5	0.5	0.5	1.0	1.8(2)
S1	4*c*	0.25	0.25	0.25	0.637(6)	1.0(1)
S2	16*e*	0.1225(3)	-0.1225(3)	0.6225(3)	0.966(2)	2.14(9)
Se1	4*c*	0.25	0.25	0.25	0.363(6)	1.0(1)
Se2	16e	0.1225(3)	-0.1225(3)	0.6225(3)	0.034(2)	2.14(9)

Table S8: Refined structural parameters for $Li_6PS_{4.4}Se_{0.6}Br$.

$Li_6PS_{4.4}Se_{0.6}Br$ structure from powder X-ray diffraction data (space group $F\bar{4}3m$); λ = 1.5406 Å *a* = 10.0259(1) Å; 1.1% Li_3OBr Fit residuals (R_{wp}, R_{exp}, χ^2): 4.29%, 1.33%, 3.22						
Atom	Wyckoff Site	x/*a*	y/*b*	z/*c*	Occ.	B_{eq} / Å^2
Li1	48*h*	0.3071	0.0251	0.6929	0.441	5
Li2	24*g*	0.25	0.017	0.75	0.119	5
Br1	4*a*	0.0	0.0	0.0	1.0	2.8(2)
P1	4*b*	0.5	0.5	0.5	1.0	1.9(3)
S1	4*c*	0.25	0.25	0.25	0.568(8)	1.1(2)
S2	16*e*	0.1224(4)	-0.1224(4)	0.6224(4)	0.957(2)	2.6(1)
Se1	4*c*	0.25	0.25	0.25	0.432(8)	1.1(2)
Se2	16e	0.1224(4)	-0.1224(4)	0.6224(4)	0.043(2)	2.6(1)

Table S9: Refined structural parameters for $Li_6PS_{4.3}Se_{0.7}Br$.

$Li_6PS_{4.3}Se_{0.7}Br$ structure from powder X-ray diffraction data (space group $F\bar{4}3m$); λ = 1.5406 Å *a* = 10.0265(1) Å; 2.7% LiBr; 1.3% Li_3OBr Fit residuals (R_{wp}, R_{exp}, χ^2): 3.24%, 1.27%, 2.56						
Atom	Wyckoff Site	x/*a*	y/*b*	z/*c*	Occ.	B_{eq} / Å^2
Li1	48*h*	0.3071	0.0251	0.6929	0.441	5
Li2	24*g*	0.25	0.017	0.75	0.119	5
Br1	4*a*	0.0	0.0	0.0	1.0	3.0(1)
P1	4*b*	0.5	0.5	0.5	1.0	2.6(2)
S1	4*c*	0.25	0.25	0.25	0.582(6)	1.6(1)
S2	16*e*	0.1235(3)	-0.1235(3)	0.6235(3)	0.929(2)	2.94(9)
Se1	4*c*	0.25	0.25	0.25	0.418(6)	1.6(1)
Se2	16e	0.1235(3)	-0.1235(3)	0.6235(3)	0.071(2)	2.94(9)

Table S10: Refined structural parameters for $Li_6PS_{4.2}Se_{0.8}Br$.

$Li_6PS_{4.2}Se_{0.8}Br$ structure from powder X-ray diffraction data (space group $F\bar{4}3m$); λ = 1.5406 Å *a* = 10.0332(1) Å; 2.9% LiBr; 1.7% Li_3OBr Fit residuals (R_{wp}, R_{exp}, χ^2): 3.40%, 1.28%, 2.66						
Atom	Wyckoff Site	x/*a*	y/*b*	z/*c*	Occ.	B_{eq} / Å^2
Li1	48*h*	0.3071	0.0251	0.6929	0.441	5
Li2	24*g*	0.25	0.017	0.75	0.119	5
Br1	4*a*	0.0	0.0	0.0	1.0	2.9(1)
P1	4*b*	0.5	0.5	0.5	1.0	4.4(2)
S1	4*c*	0.25	0.25	0.25	0.518(7)	2.2(1)
S2	16*e*	0.1217(3)	-0.1217(3)	0.6217(3)	0.920(2)	3.2(1)
Se1	4*c*	0.25	0.25	0.25	0.482(7)	2.2(1)
Se2	16e	0.1217(3)	-0.1217(3)	0.6217(3)	0.080(2)	3.2(1)

Table S11: Refined structural parameters for $Li_6PS_{4.1}Se_{0.9}Br$.

$Li_6PS_{4.1}Se_{0.9}Br$ structure from powder X-ray diffraction data (space group $F\bar{4}3m$); λ = 1.5406 Å *a* = 10.0418(2) Å; 3.0% LiBr Fit residuals (R_{wp}, R_{exp}, χ^2): 3.52%, 1.35%, 2.60						
Atom	Wyckoff Site	x/*a*	y/*b*	z/*c*	Occ.	B_{eq} / Å^2
Li1	48*h*	0.3071	0.0251	0.6929	0.441	5
Li2	24*g*	0.25	0.017	0.75	0.119	5
Br1	4*a*	0.0	0.0	0.0	1.0	2.7(2)
P1	4*b*	0.5	0.5	0.5	1.0	3.1(3)
S1	4*c*	0.25	0.25	0.25	0.515(8)	1.3(2)
S2	16*e*	0.1225(3)	-0.1225(3)	0.6225(3)	0.896(4)	3.3(1)
Se1	4*c*	0.25	0.25	0.25	0.485(8)	1.3(2)
Se2	16e	0.1225(3)	-0.1225(3)	0.6225(3)	0.104(4)	3.3(1)

Table S12: Refined structural parameters for Li_6PS_4SeBr.

Li_6PS_4SeBr structure from powder X-ray diffraction data (space group $F\bar{4}3m$); λ = 1.5406 Å a = 10.0522(1) Å; 1.4% LiBr Fit residuals (R_{wp}, R_{exp}, χ^2): 3.37%, 1.31%, 2.56						
Atom	Wyckoff Site	x/a	y/b	z/c	Occ.	B_{eq} / Å^2
Li1	48h	0.3071	0.0251	0.6929	0.441	5
Li2	24g	0.25	0.017	0.75	0.119	5
Br1	4a	0.0	0.0	0.0	1.0	2.5(2)
P1	4b	0.5	0.5	0.5	1.0	2.1(2)
S1	4c	0.25	0.25	0.25	0.504(2)	1.0(1)
S2	16e	0.1221(3)	-0.1221(3)	0.6221(3)	0.874(2)	3.2(1)
Se1	4c	0.25	0.25	0.25	0.496(2)	1.0(1)
Se2	16e	0.1221(3)	-0.1221(3)	0.6221(3)	0.126(2)	3.2(1)

Table S13: Refined structural parameters for Li_6PS_5Br.

Li_6PS_5Br structure from pair distribution function analysis of neutron diffraction data (space group $F\bar{4}3m$); a = 10.013(5) Å Fit residual R_w: 15.0%						
Atom	Wyckoff Site	x/a	y/b	z/c	Occ.	U_{iso} / Å^2
Li1	48h	0.309(2)	0.025(2)	0.691(2)	0.44(1)	0.060(6)
Li2	24g	0.25	0.005(2)	0.75	0.12(1)	0.021(6)
Br1	4a	0.0	0.0	0.0	0.77(1)	0.042(6)
Br2	4c	0.25	0.25	0.25	0.23(1)	0.026(6)
P1	4b	0.5	0.5	0.5	1.0	0.020(6)
S1	4c	0.25	0.25	0.25	0.77(1)	0.026(6)
S2	16e	0.120(2)	-0.120(2)	0.620(2)	1.0	0.028(6)
S3	4a	0.0	0.0	0.0	0.23(1)	0.042(6)

Table S14: Refined structural parameters for $Li_6PS_{4.5}Se_{0.5}Br$.

$Li_6PS_{4.5}Se_{0.5}Br$ structure from pair distribution function analysis of neutron diffraction data (space group $F\bar{4}3m$); a = 10.040(5) Å Fit residual R_w: 16.3%						
Atom	Wyckoff Site	x/a	y/b	z/c	Occ.	U_{iso} / Å^2
Li1	48h	0.311(2)	0.025(2)	0.689(2)	0.46(1)	0.059(6)
Li2	24g	0.25	0.005(2)	0.75	0.08(1)	0.014(6)
Br1	4a	0.0	0.0	0.0	0.95(1)	0.045(6)
Br2	4c	0.25	0.25	0.25	0.05(1)	0.027(6)
P1	4b	0.5	0.5	0.5	1.0	0.022(6)
S1	4c	0.25	0.25	0.25	0.63(1)	0.027(6)
S2	16e	0.120(2)	-0.120(2)	0.620(2)	0.95(1)	0.033(6)
S3	4a	0.0	0.0	0.0	0.05(1)	0.045(6)
Se1	4c	0.25	0.25	0.25	0.37(1)	0.027(6)
Se2	16e	0.120(2)	-0.120(2)	0.620(2)	0.05(1)	0.033(6)

Table 15: Refined structural parameters for Li_6PS_4SeBr.

Li_6PS_4SeBr structure from pair distribution function analysis of neutron diffraction data (space group $F\bar{4}3m$); a = 10.080(5) Å Fit residual R_w: 14.4%						
Atom	Wyckoff Site	x/*a*	y/*b*	z/*c*	Occ.	U_{iso} / Å^2
Li1	48*h*	0.314(2)	0.021(2)	0.686(2)	0.48(1)	0.062(6)
Li2	24*g*	0.25	0.005(2)	0.75	0.04(1)	0.087(6)
Br1	4*a*	0.0	0.0	0.0	1.0	0.049(6)
P1	4*b*	0.5	0.5	0.5	1.0	0.028(6)
S1	4*c*	0.25	0.25	0.25	0.43(1)	0.022(6)
S2	16*e*	0.121(2)	-0.121(2)	0.621(2)	0.89(1)	0.041(6)
Se1	4*c*	0.25	0.25	0.25	0.57(1)	0.022(6)
Se2	16*e*	0.121(2)	-0.121(2)	0.621(2)	0.11(1)	0.041(6)

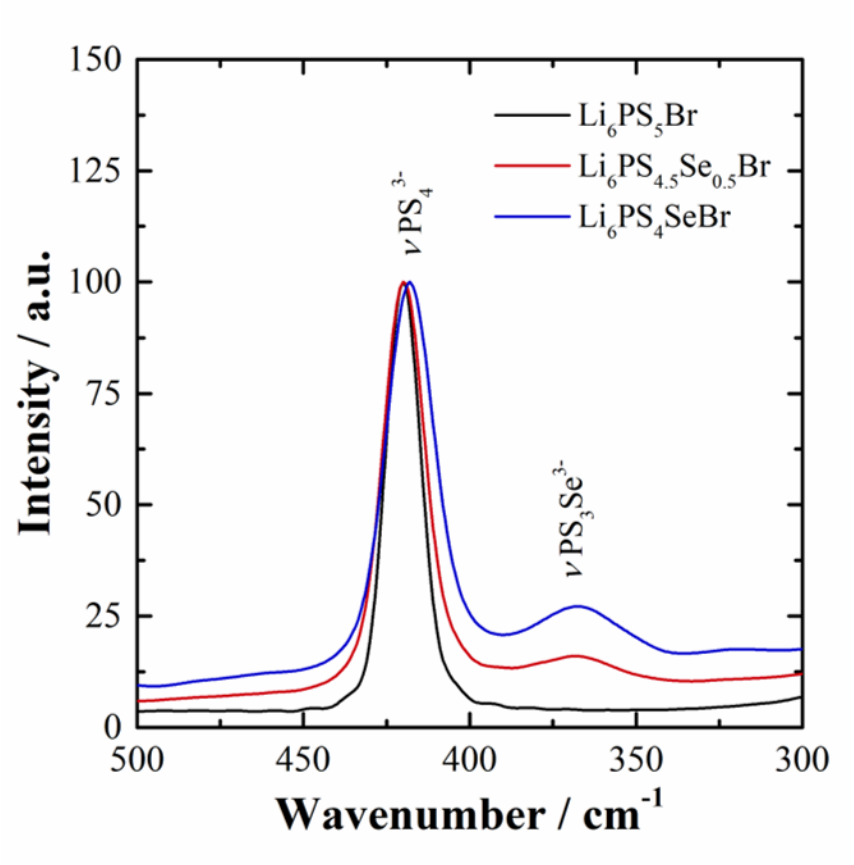

Figure S2: Raman spectra for $Li_6PS_{5-x}Se_xBr$ (x = 0, 0.5 and 1.0) showing the increase in the PS_3Se^{3-} vibrational mode with increasing Se content.

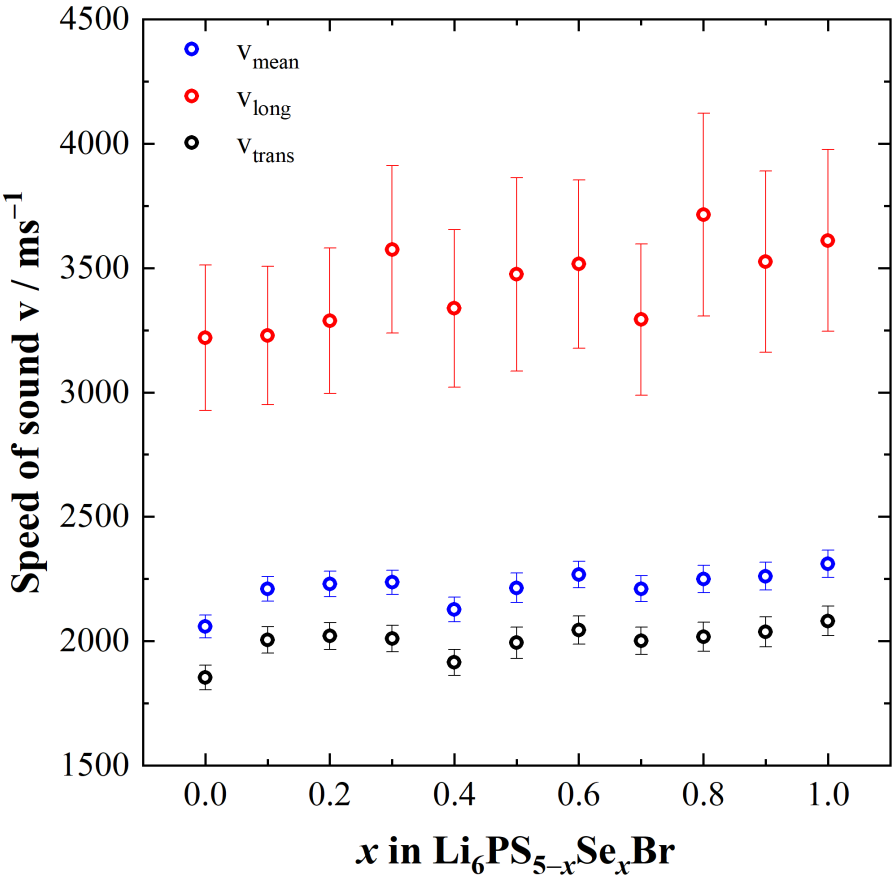

Figure S3: Measured longitudinal, transverse and mean speeds of sound for $Li_6PS_{5-x}Se_xBr$.