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Supporting Information-
On the local charge inhomogeneity and lithium
distribution in the superionic argyrodites $\text{Li}_6\text{PS}_5\text{X}$ ($\text{X} = \text{Cl},$
Br, I)

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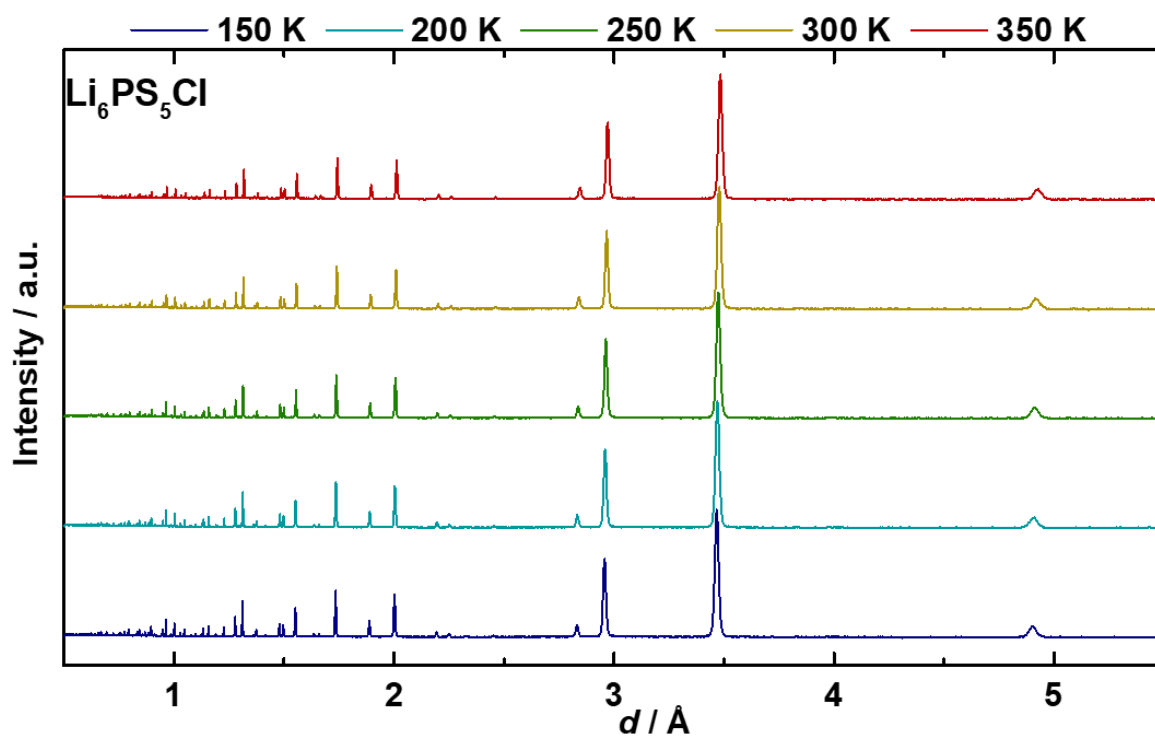


Figure S1: Neutron powder diffraction data of $\text{Li}_6\text{PS}_5\text{Cl}$ measured at different temperatures. The refined structures are available in CIF format.

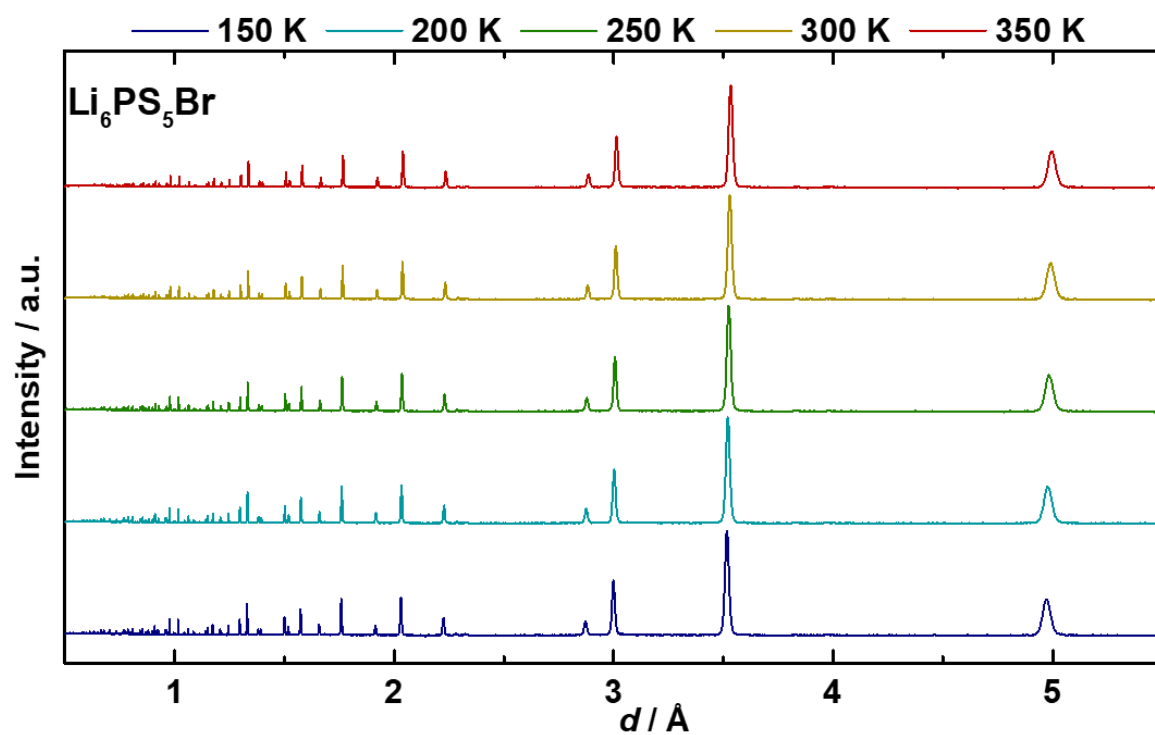


Figure S2: Neutron powder diffraction data of $\text{Li}_6\text{PS}_5\text{Br}$ measured at different temperatures. The refined structures are available in CIF format.

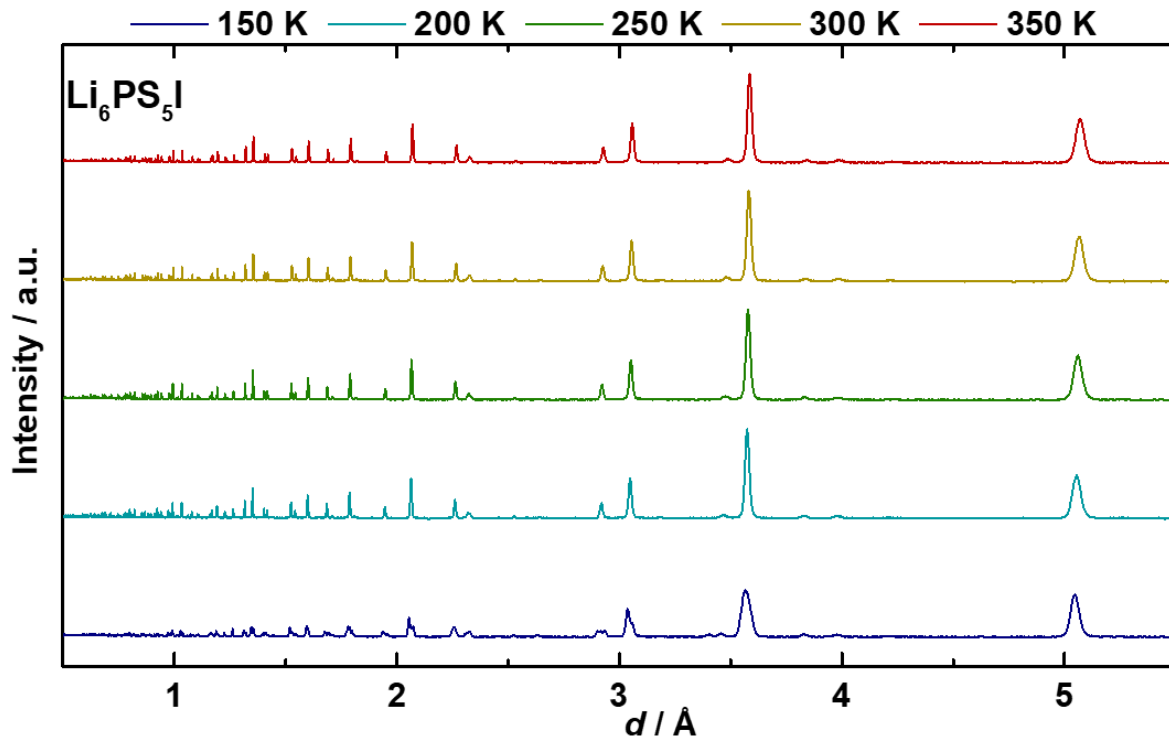


Figure S3: Neutron powder diffraction data of $\text{Li}_6\text{PS}_5\text{I}$ measured at different temperatures. The refined structures are available in CIF format.

Table S1: Coordinates of all possible lithium sites in the $\text{Li}_6\text{PS}_5\text{X}$ structure utilized as starting point for the refinements.

Position	Wyckoff Site	x/a	y/b	z/c
T1	16e	0.9	0.9	0.6
T2	48h	0.25	0.433	0.933
T3	4c	0.25	0.25	0.25
T4	16e	0.15	0.15	0.15
T5	48h	0.304	0.025	0.695
T5a	24g	0.25	0.009	0.75

Table S2: Constraints used to refine the $\text{Li}_6\text{PS}_5\text{Cl}$ structure from powder ToF neutron diffraction data.

Atom	Wyckoff Site	x/a	y/b	z/c	Occ.	$B_{\text{eq}} / \text{\AA}^2$
LiT5	48h	<i>Pos1</i>	<i>Pos2</i>	1- <i>Pos1</i>	<i>Occ1</i>	<i>Var1</i>
LiT2	48h	<i>Pos3</i>	<i>Pos4</i>	0.5+ <i>Pos4</i>	0.5- <i>Occ1</i>	<i>Var2</i>
Cl1	4a	0	0	0	<i>Occ2</i>	<i>Var3</i>
Cl2	4d	0.25	0.25	0.75	1- <i>Occ2</i>	<i>Var4</i>
P1	4b	0	0	0.5	1	<i>Var5</i>
S1	4d	0.25	0.25	0.75	<i>Occ2</i>	<i>Var4</i>
S2	16e	<i>Pos5</i>	- <i>Pos5</i>	0.5+ <i>Pos5</i>	1	<i>Var6</i>
S3	4a	0	0	0	1- <i>Occ2</i>	<i>Var3</i>

Table S3: Constraints used to refine the $\text{Li}_6\text{PS}_5\text{Br}$ structure from powder ToF neutron diffraction data.

Atom	Wyckoff Site	x/a	y/b	z/c	Occ.	$B_{\text{eq}} / \text{\AA}^2$
LiT5	48h	<i>Pos1</i>	<i>Pos2</i>	1- <i>Pos1</i>	<i>Occ1</i>	<i>Var1</i>
LiT2	48h	<i>Pos3</i>	<i>Pos4</i>	0.5+ <i>Pos4</i>	<i>Occ2</i>	<i>Var2</i>
LiT5a	24g	0.25	<i>Pos5</i>	0.75	1-2- <i>Occ1</i> -2- <i>Occ2</i>	<i>Var3</i>
Br1	4a	0	0	0	<i>Occ3</i>	<i>Var4</i>
Br2	4d	0.25	0.25	0.75	1- <i>Occ3</i>	<i>Var5</i>
P1	4b	0	0	0.5	1	<i>Var6</i>
S1	4d	0.25	0.25	0.75	<i>Occ3</i>	<i>Var5</i>
S2	16e	<i>Pos6</i>	- <i>Pos6</i>	0.5+ <i>Pos6</i>	1	<i>Var7</i>
S3	4a	0	0	0	1- <i>Occ3</i>	<i>Var4</i>

Table S4: Constraints used to refine the $\text{Li}_6\text{PS}_5\text{I}$ structure from powder ToF neutron diffraction data.

Atom	Wyckoff Site	x/a	y/b	z/c	Occ.	$B_{\text{eq}} / \text{\AA}^2$
LiT5	48h	$Pos1$	$Pos2$	$1-Pos1$	$Occ1$	$Var1$
LiT5a	24g	0.25	$Pos3$	0.75	$1-2 \cdot Occ1$	$Var2$
I1	4a	0	0	0	1	$Var3$
P1	4b	0	0	0.5	1	$Var4$
S1	4d	0.25	0.25	0.75	1	$Var5$
S2	16e	$Pos4$	$-Pos4$	$0.5+Pos4$	1	$Var6$

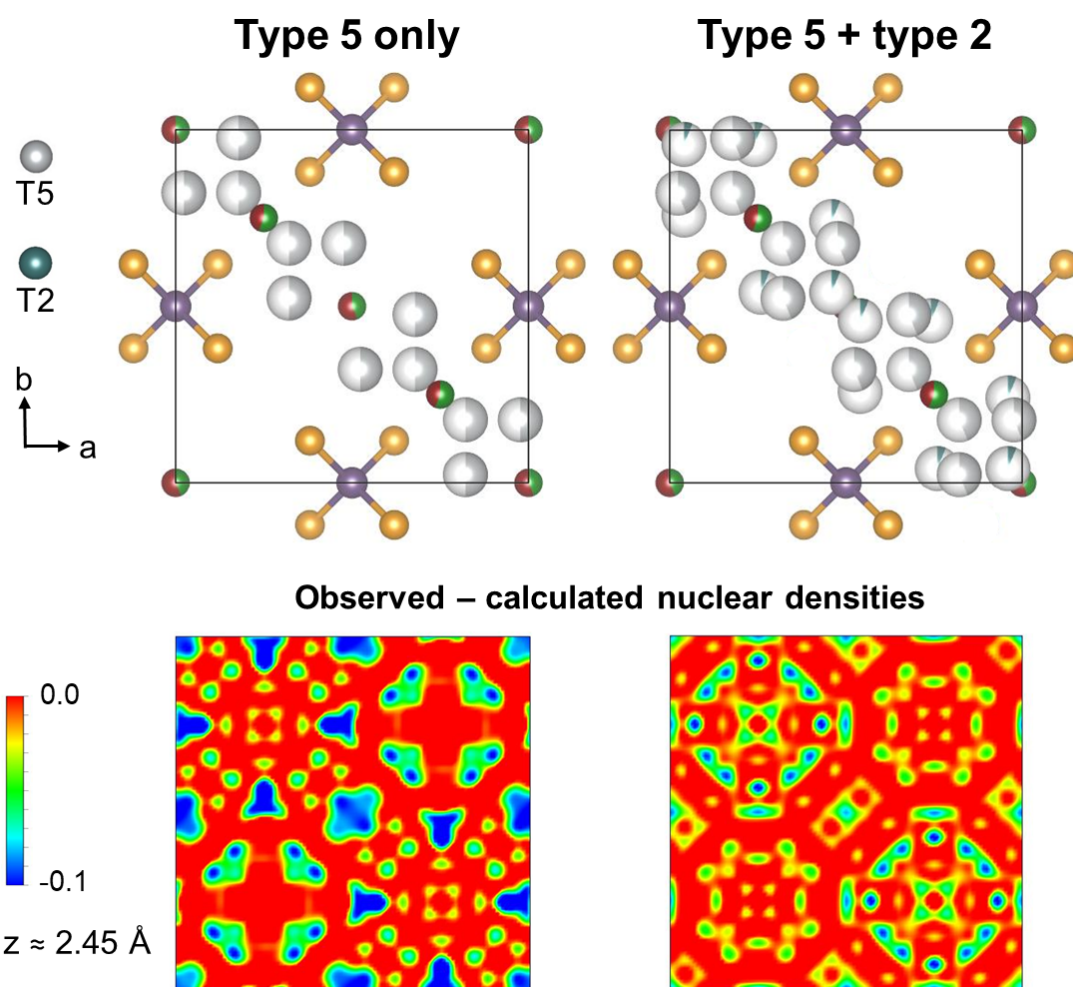


Figure S4: Exemplary difference Fourier maps for $\text{Li}_6\text{PS}_5\text{Cl}$, showing the need to include the type 2 lithium sites in the structural model.

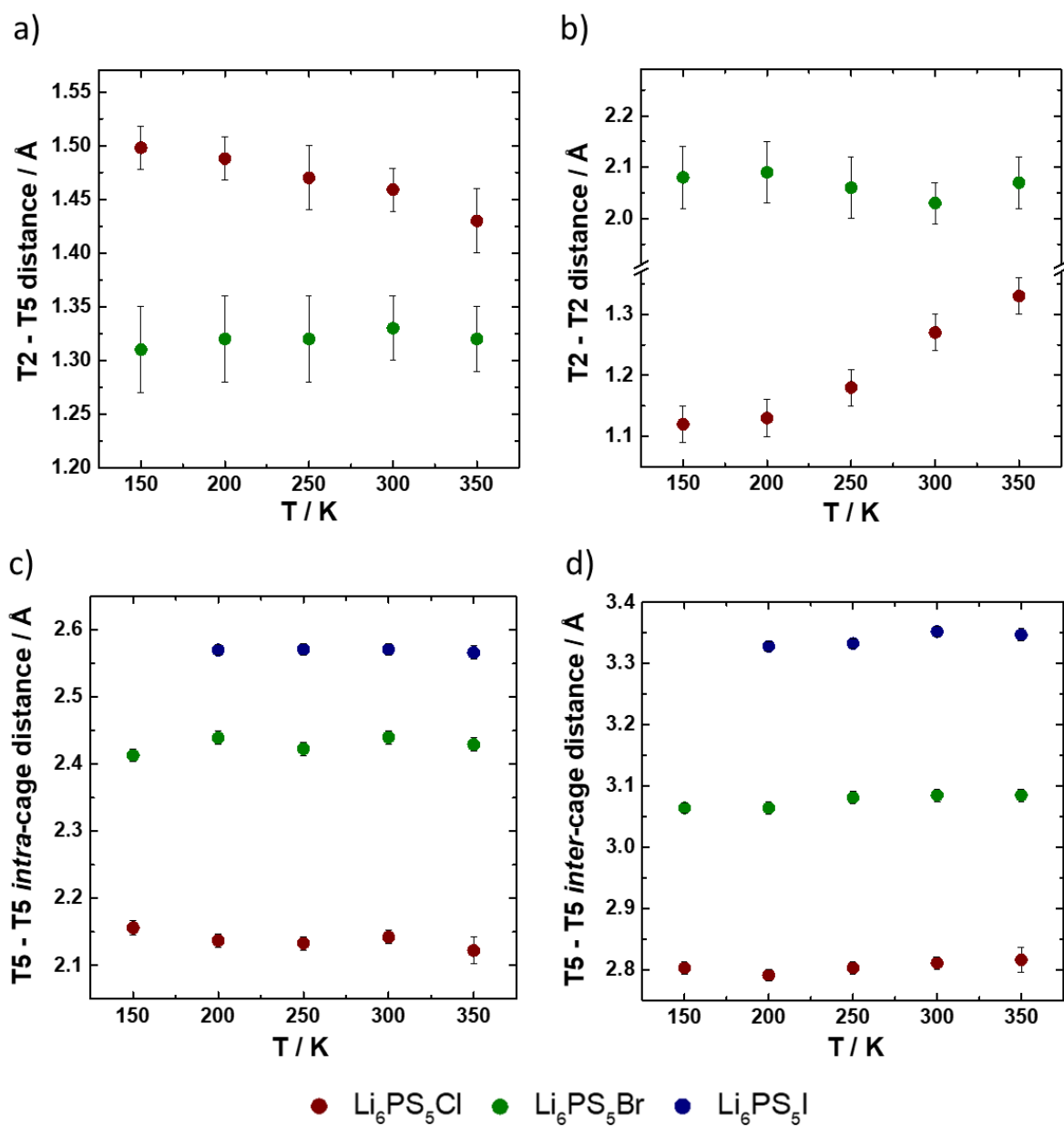


Figure S5: Li – Li distances relative to (a) T2 – T5 and (b) T2 – T2, in comparison to (c) T5 – T5 intra-cage and (d) T5 – T5 inter-cage at different temperatures for $\text{Li}_6\text{PS}_5\text{X}$.