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New Insights into Li Distribution in the Superionic Argyrodite Li_6PS_5Cl

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Experimental Section

Li_6PS_5Cl powder was purchased from NEI Corporation (USA). X-ray diffraction (XRD) patterns were obtained by sealing the powders in boron-rich glass capillaries in an Ar-filled glovebox. Measurements were taken using Cu Kα radiation in a Bruker/Nonius Microstar 592 diffractometer. Scanning electron microscope (SEM) images of the Li_6PS_5Cl powder were obtained with a FEI Scios DualBeam Focused ion beam. The sample was prepared in an Ar-filled glovebox and transferred with an air-tight loader to avoid any atmosphere exposure. Variable temperature (5 K, 300 K, and 550 K) neutron powder diffraction (NPD) data was collected at the beamline of the General Purpose Powder Diffractometer (GPPD) at the China Spallation Neutron Source (CSNS). Rietveld refinements and maximum entropy method (MEM) analysis were carried out using the FullProf Suite software package[1] and Dysnomia software[2], respectively.

For the Rietveld refinements analysis of NPD data, the peak profile shape was described by the function of T.O.F. p-Voigt * B-t-B exponential. During the refinement, the fit indicators R_{wp} was used to assess the quality of the refined structural model. The following parameters were initially refined: (1) scale factor, (2) background (Linear Interpolation between a set background points with refinable heights), (3) shape parameters, and (4) cell parameters. After a suitable fit of the profile was achieved, the structural parameters, including 5) fractional atomic coordinates, (6) isotropic atomic displacement parameters, and (7) atomic occupancies, were then refined. The output atomic displacement parameters (Uiso) were used as indicators for exploring the authenticity of the eventual occupancy. In order to ensure the stability of the refinements, multiple correlated parameters were simultaneously refined over several cycles. The refinement analysis for the various-temperature NPD data were performed in a sequential mode and the consistency of the obtained structural models was corroborated by introducing different starting parameters. Constraints used for the refinement analysis of NPD data are shown in Table S2.

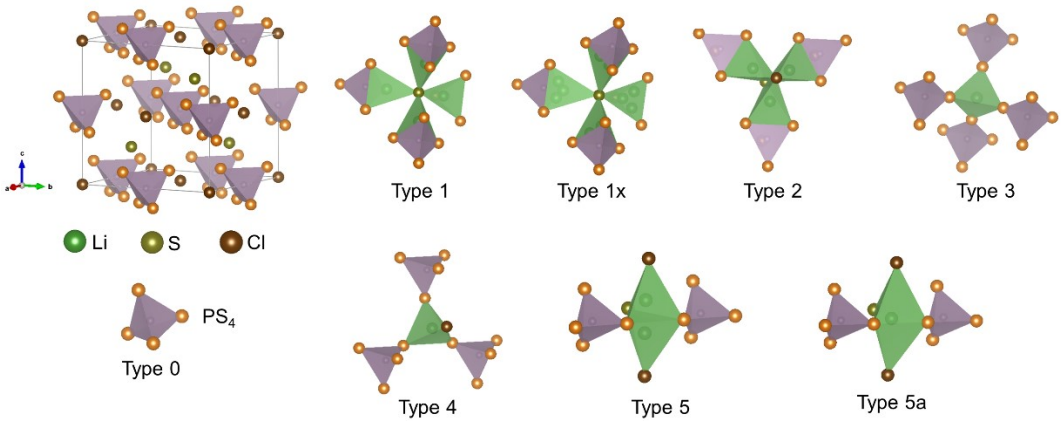

Fig. S1 Crystal structure of the lithium argyrodites Li_6PS_5X (X = Cl, Br, I), with panels showing the typical local coordination of the six types of tetrahedral interstitial sites (type 0-5), alongside the trigonally-coordinated type 5a site and tetrahedrally-coordinated type 1x site.

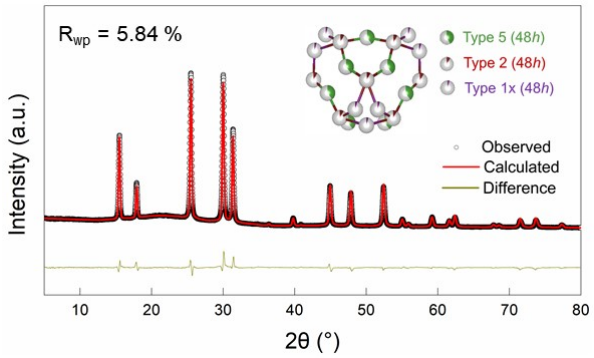

Fig. S2 XRD data of Li_6PS_5Cl compound collected at room temperature and Rietveld refinement results based on the Li sublattice structure model (inset) with type 5, type 2 and type 1x Li positions.

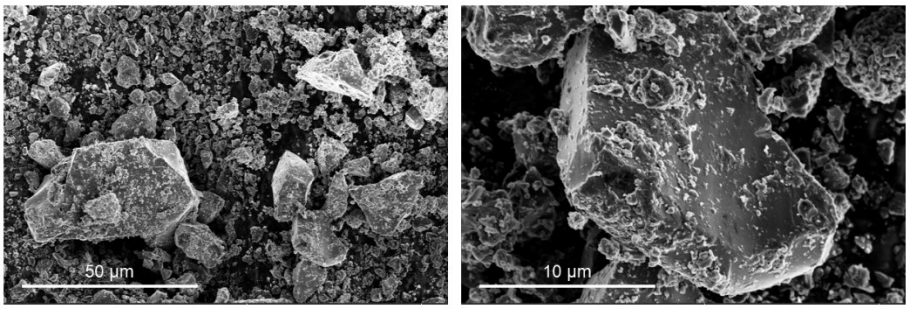

Fig. S3 SEM results of Li_6PS_5Cl powder. It can be seen that the Li_6PS_5Cl particles have irregular shape and the particle size is on the micron scale.

Table S1 Neutron coherent scattering lengths and coherent, incoherent, and absorption cross-sections of Li, P, S and Cl in Li_6PS_5Cl (as obtained from https://www.ncnr.nist.gov/resources/n-lengths/).

Element	Coh b (fm)	Coh xs (barn)	Inc xs (barn)	Abs xs (barn)
Li	-1.90	0.454	0.92	70.5
P	5.13	3.307	0.005	0.172
S	2.847	1.0186	0.007	0.53
Cl	9.5770	11.5257	5.3	33.5

Table S2 Constraints used for the refinement analysis of neutron powder diffraction data of the Li_6PS_5Cl compound.

Atom	Site	x	y	z	Occ.	U_{iso} (Å^2)
P1	4*b*	0	0	0.5	1	*Variation1*
Cl1	4*a*	0	0	1	*Occ1*	*Variation2*
Cl2	4*d*	0.25	0.25	0.75	1- *Occ1*	*Variation3*
Li_{type5}	48*h*	*Site1*	*Site2*	1-*Site1*	*Occ2*	*Variation4*
Li_{type2}	48*h*	0.25	*Site3*	0.5+ *Site3*	*Occ3*	*Variation5*
Li_{type1x}	48*h*	*Site4*	*Site4*	*Site5*	*Occ4*	*Variation6*
Li_{type5a}	24*g*	0.25	*Site6*	0.75	*Occ5*	*Variation7*
S1	4*d*	0.25	0.25	0.75	*Occ1*	*Variation3*
S2	16*e*	*Site7*	-*Site7*	0.5+ *Site7*	1	*Variation8*
S3	4*a*	0	0	1	1- *Occ1*	*Variation2*

Note: *Occ2* + *Occ3* + *Occ4* + 1/2*Occ5* = 0.5

Table S3 The refined crystal structure of Li_6PS_5Cl using neutron powder diffraction data collected at 5 K (in this case, only the type 5 Li Wyckoff site was considered in the refinement structure model).

S.G. F -4 3 m, a = 9.79657(7) Å R_{wp} = 2.56 %

Atom	Site	x	y	z	Occ.	U_{iso} (Å^2)
P1	4*b*	0	0	0.5	1	0.0210(13)
Cl1	4*a*	0	0	1.0	0.447(7)	0.0164(16)
Cl2	4*d*	0.25	0.25	0.75	0.553(7)	0.0198(13)
Li_{type5}	48*h*	0.3170(4)	0.0228(5)	0.6831(4)	0.500(7)	0.0482(19)
S1	4*d*	0.25	0.25	0.75	0.447(7)	0.0198(13)
S2	16*e*	0.1189(2)	-0.1189(2)	0.6189(2)	1	0.0280(10)
S3	4*a*	0	0	1.0	0.553(7)	0.0164(16)

Table S4 The refined crystal structure of Li_6PS_5Cl using neutron powder diffraction data collected at 5 K (in this case, only the type 5 and type 2 Li Wyckoff sites were considered in the refinement structure model).

S.G. F -4 3 m, a = 9.79657(6) Å R_{wp} = 2.26 %						
Atom	Site	x	y	z	Occ.	U_{iso} (Å^2)
P1	4*b*	0	0	0.5	1	0.0194(10)
Cl1	4*a*	0	0	1	0.483(7)	0.0274(15)
Cl2	4*d*	0.25	0.25	0.75	0.517(7)	0.0182(10)
Li_{type5}	48*h*	0.3207(6)	0.0244(6)	0.6794(6)	0.415(6)	0.042(2)
Li_{type2}	48*h*	0.25	0.4474(14)	0.9474(14)	0.085(6)	0.011(8)
S1	4*d*	0.25	0.25	0.75	0.483(7)	0.0182(10)
S2	16*e*	0.1189(2)	-0.1189(2)	0.6189(2)	1	0.0279(9)
S3	4*a*	0	0	1	0.517(7)	0.0274(15)

Table S5 The refined crystal structure of Li_6PS_5Cl using neutron powder diffraction data collected at 300 K (in this case, only the type 5 Li Wyckoff site was considered in the refinement structure model).

S.G. F -4 3 m, a = 9.83664(7) Å R_{wp} = 2.20 %						
Atom	Site	x	y	z	Occ.	U_{iso} (Å^2)
P1	4*b*	0	0	0.5	1	0.0259(11)

Cl1	4*a*	0	0	1	0.460(8)	0.0266(18)
Cl2	4*d*	0.25	0.25	0.75	0.540(8)	0.0279(13)
Li_{type5}	48*h*	0.3145(4)	0.0268(6)	0.6856(4)	0.500(8)	0.078(3)
S1	4*d*	0.25	0.25	0.75	0.460(8)	0.0279(13)
S2	16*e*	0.1194(3)	-0.1194(3)	0.6194(3)	1	0.0368(8)
S3	4*a*	0	0	1	0.540(8)	0.0266(18)

Table S6 The refined crystal structure of Li_6PS_5Cl using neutron powder diffraction data collected at 300 K (in this case, type 5 and type 2 Li Wyckoff sites were considered in the refinement structure model).

S.G. F -4 3 m, a = 9.83667(6) Å R_{wp} = 1.95 %						
Atom	Site	x	y	z	Occ.	U_{iso} (Å^2)
P1	4*b*	0	0	0.5	1	0.0216(9)
Cl1	4*a*	0	0	1.0	0.501(8)	0.0354(16)
Cl2	4*d*	0.25	0.25	0.75	0.499(8)	0.0231(12)
Li_{type5}	48*h*	0.3182(8)	0.0302(8)	0.6819(8)	0.413(7)	0.081(4)
Li_{type2}	48*h*	0.25	0.4458(15)	0.9458(15)	0.087(7)	0.019(11)
S1	4*d*	0.25	0.25	0.75	0.501(8)	0.0231(12)
S2	16*e*	0.1199(3)	-0.1199(3)	0.6199(3)	1	0.0342(7)
S3	4*a*	0	0	1.0	0.499(8)	0.0354(16)

Table S7 The refined crystal structure of Li_6PS_5Cl using neutron powder diffraction data collected at 300 K (in this case, type 5, type 2 and type 1x Li Wyckoff sites were considered in the refinement structure model).

S.G. F -4 3 m, a = 9.83665(6) Å R_{wp} = 1.91 %						
Atom	Site	x	y	z	Occ.	U_{iso} (Å^2)
P1	4*b*	0	0	0.5	1	0.0245(9)
Cl1	4*a*	0	0	1	0.481(8)	0.0321(17)
Cl2	4*d*	0.25	0.25	0.75	0.518(8)	0.0254(12)

Li_{type5}	48*h*	0.3181(7)	0.0289(7)	0.6820(7)	0.387(8)	0.061(3)
Li_{type2}	48*h*	0.25	0.4468(15)	0.9468(15)	0.079(4)	0.014(8)
Li_{type1x}	48*h*	0.59776^	0.59776^	0.515(6)	0.034(4)	0.01297^
S1	4*d*	0.25	0.25	0.75	0.481(8)	0.0254(12)
S2	16*e*	0.1194(3)	-0.1194(3)	0.6195(3)	1	0.0357(7)
S3	4*a*	0	0	1	0.518(8)	0.0321(17)

^ = initially refined then fixed

Table S8 The refined crystal structure of Li_6PS_5Cl using neutron powder diffraction data collected at 550 K (in this case, type 5, type 2 and type 1x Li Wyckoff sites were considered in the refinement structure model).

S.G. F -4 3 m, a = 9.90337(8) Å R_{wp} = 2.05 %						
Atom	Site	x	y	z	Occ.	U_{iso} (Å^2)
P1	4*b*	0	0	0.5	1	0.0323(17)
Cl1	4*a*	0	0	1.0	0.448(11)	0.035(2)
Cl2	4*d*	0.25	0.25	0.75	0.552(11)	0.039(2)
Li_{type5}	48*h*	0.3119(8)	0.0283(9)	0.6882(8)	0.343(11)	0.038(3)
Li_{type2}	48*h*	0.25	0.441(3)	0.941(3)	0.073(5)	0.039(8)
Li_{type1x}	48*h*	0.59317^	0.59317^	0.515(3)	0.084(5)	0.01297^
S1	4*d*	0.25	0.25	0.75	0.448(11)	0.039(2)
S2	16*e*	0.1177(3)	-0.1177(3)	0.6177(3)	1	0.0455(16)
S3	4*a*	0	0	1.0	0.552(11)	0.035(2)

^ = initially refined then fixed

Table S9 The refined crystal structure of Li_6PS_5Cl using neutron powder diffraction data collected at 550 K (in this case, type 5, type 2, type 1x and type 5a Li Wyckoff sites were considered in the refinement structure model).

S.G. F -4 3 m, a = 9.90336(8) Å R_{wp} = 2.01 %						
Atom	Site	x	y	z	Occ.	U_{iso} (Å^2)
P1	4*b*	0	0	0.5	1	0.0313(17)

Cl1	4*a*	0	0	1	0.489(12)	0.049(3)
Cl2	4*d*	0.25	0.25	0.75	0.510(12)	0.0376(19)
Li_{type5}	48*h*	0.3163(11)	0.0322(12)	0.6838(11)	0.334(12)	0.072(4)
Li_{type2}	48*h*	0.25	0.4430(18)	0.9430(18)	0.094(8)	0.027(11)
Li_{type1x}	48*h*	0.59317^	0.59317^	0.516(5)	0.058(8)	0.01297^
Li_{type5a}	24*g*	0.25	0.00922^	0.75	0.029(8)	0.01193^
S1	4*d*	0.25	0.25	0.75	0.489(12)	0.0376(19)
S2	16*e*	0.1185(3)	-0.1185(3)	0.6186(3)	1	0.0454(18)
S3	4*a*	0	0	1	0.510(12)	0.049(3)

^ = initially refined then fixed

Table S10 Concentration of Li ions in the argyrodite lattice based on the refinement results of the temperature-dependent neutron powder diffraction data.

	5 K	300 K	550 K
Type 5	~ 83.0%	~ 77.4%	~ 66.7%
Type 2	~ 17.0%	~ 15.8%	~ 18.8%
Type 1x	0	~ 6.8%	~ 11.6%
Type 5a	0	0	~ 2.9%

Table S11 The summarized bond valence sums (BVS) for Li sites at various temperatures.

Li sites	5 K	300 K	550 K
Type 5	0.93	0.91	0.87
Type 2	1.26	1.21	1.41
Type 1x	--	1.18	0.91
Type 5a	--	--	1.19

Table S12 Summary of the Li-S, Li-Cl and Li-Li bond lengths at various temperatures, which are observed from the refinement results of the neutron diffraction data.

	5 K	300 K	550 K

Li_{T5}-S_{16e} (Å)	2.496	2.515	2.545
Li_{T5}-Cl/S_{4d} (Å)	2.417	2.372	2.348
Li_{T5}-Cl/S_{4a} (Å)	2.496	2.547	2.593
Li_{T5}-Li_{T5} (Å)	2.147	2.129	2.12
Li_{T2}-S_{16e} (Å)	2.212	2.227	2.256
Li_{T2}-Cl/S_{4d} (Å)	2.735	2.738	2.703
Li_{T2}-Cl/S_{4a} (Å)	2.555	2.568	2.601
Li_{T2}-Li_{T2} (Å)	2.73	2.74	2.70
Li_{T1x}-S_{16e} (Å)	--	2.38	2.34
Li_{T1x}-Cl/S_{4d} (Å)	--	3.14	3.19
Li_{T1x}-Li_{T1x} (Å)	--	1.15	1.08
Li_{T5a}-S_{16e} (Å)	--	--	2.234
Li_{T5a}-Cl/S_{4d} (Å)	--	--	2.385
Li_{T5a}-Li_{T5} (Å)	--	--	3.372

Table S13 Coordinates of all possible Li sites in the Li_6PS_5Cl lattice structure utilized as starting point for the refinements[3].

Li sites	Wyckoff Site	x	y	z
Type 1	16*e*	0.9	0.9	0.6
Type 1x	48*h*	0.59	0.59	0.51
Type 2	48*h*	0.25	0.433	0.933
Type 3	4*c*	0.25	0.25	0.25
Type 4	16*e*	0.15	0.15	0.15
Type 5	48*h*	0.304	0.025	0.695
Type 5a	24*g*	0.25	0.009	0.75

Notes: The possible type 1, type 3 as well as type 4 Li positions were tried during the refinement of various-temperature neutron powder diffraction data. The resulted preferred unphysical/negative values of atomic displacement parameters (Uiso) during the refinement indicated that these Li sites are not populated within the compositions and temperature range probed here. These results are moreover consistent with those from literature[3].

References

1 Rodriguez-Carvajal, J., *Physica B.*, 1993, **192**, 55.

2 K. Momma, T. Ikeda, A. A. Belik and F. Izumi, *Powder Diffraction*, 2013, **28**, 184-193.

3 N. Minafra, M. A. Kraft, T. Bernges, C. Li, R. Schlem, B. J. Morgan and W. G. Zeier, *Inorg. Chem.*, 2020, 59, 11009-11019.