Control of ionic conductivity by lithium distribution in the cubic oxide argyrodites

\[ \text{Li}_{6+x}\text{P}_{1-x}\text{Si}_x\text{O}_5\text{Cl} \]

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Table S1: Exact masses of precursors used in the synthesis of Li$_{6+x}$P$_{1-x}$Si$_x$O$_5$Cl

| Precursor   | x = 0.1 | x = 0.3 | x = 0.5 | x = 0.6 | x = 0.7 | x = 0.75 | x = 0.8 | x = 0.85 |
|-------------|---------|---------|---------|---------|---------|----------|---------|----------|
| Li$_2$SiO$_4$ / g | 0.0654  | 0.1899  | 0.3152  | 0.3775  | 0.4394  | 0.4703   | 0.5012  | 0.5319   |
| Li$_3$PO$_4$ / g  | 0.5529  | 0.4282  | 0.3046  | 0.2431  | 0.1820  | 0.1515   | 0.1211  | 0.0907   |
| Li$_2$O / g        | 0.1585  | 0.1579  | 0.1572  | 0.1569  | 0.1565  | 0.1564   | 0.1562  | 0.1560   |
| LiCl / g           | 0.2249  | 0.2240  | 0.2230  | 0.2225  | 0.2221  | 0.2218   | 0.2216  | 0.2214   |

Figure S1: Comparison of XRD patterns and extracted sample purity for powder samples of Li$_{7}$SiO$_{5}$Cl when using (a) hydrated and (b) dehydrated Li$_2$SiO$_4$, Li$_2$O and LiCl precursors.
Table S2. Single crystal data, data collection and structure refinement parameters of Li₇SiO₅Cl.

| **Empirical formula** | Li₇SiO₅Cl |
|-----------------------|-----------|
| **Formula weight**    | 192.12    |
| **Radiation**         | MoKα (λ = 0.71073 Å) | Synchrotron (λ = 0.6889 Å) |
| **Temperature / K**   | 100.0 | 291.2 | 500.0 | 100.0 | 300.0 | 500.0 |
| **Crystal system, Space group** | cubic, P₂₁₃ | cubic, P₂₁₃ | cubic, F₄m | cubic, P₂₁₃ | cubic, P₂₁₃ | cubic, F₄m |
| **a / Å**             | 8.2605(10) | 8.2697(2) | 8.2972(2) | 8.25320(10) | 8.27250(10) | 8.3032(2) |
| **Volume / Å³**       | 563.66(2) | 565.55(4) | 571.21(4) | 562.17(2) | 566.12(2) | 572.45(4) |
| **Z**                 | 4 | 4 | 4 | 4 | 4 | 4 |
| **Reflections collected/Independent reflections** | 16881/439 | 9973/545 | 2705/111 | 10801/726 | 11212/726 | 2730/139 |
| | [Rint = 0.0486] | [Rint = 0.0458] | [Rint = 0.0029] | [Rint = 0.0578] | [Rint = 0.0525] | [Rint = 0.0982] |
| **Crystal size / mm** | 0.11 × 0.07 × 0.07 | 0.03 × 0.02 × 0.02 |
| **Data/restraints/parameters** | 439/0/44 | 545/0/48 | 111/1/20 | 726/0/44 | 726/0/48 | 139/1/20 |
| **Goodness-of-fit on F²** | 1.224 | 1.046 | 1.170 | 1.114 | 1.136 | 1.113 |
Table S3a. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for Li$_7$SiO$_5$Cl at 100 K. $U_{eq}$ is defined as 1/3 of the trace of the orthogonalised $U_{ij}$ tensor.

| Site | wyck. | sof | x     | y     | z     | $U_{eq}$ |
|------|-------|-----|-------|-------|-------|----------|
| Li1  | 12b   | 1   | 7100(4) | 7033(4) | 10342(3) | 15.6(6)  |
| Li2  | 12b   | 1   | 4934(5) | 7630(4) | 7395(4)  | 15.4(6)  |
| Li3  | 4a    | 1   | 8445(4) | 8445(4) | 8445(4)  | 18.3(11) |
| Si1  | 4a    | 1   | 5060(14) | 9939.9(4) | 10060.1(4) | 6.30(17) |
| O1   | 4a    | 1   | 3924.9(12) | 11075.1(12) | 8924.9(12) | 8.5(4)   |
| O2   | 12b   | 1   | 6274.9(12) | 8853.7(14) | 8925.8(13) | 8.7(2)   |
| O3   | 4a    | 1   | 7559.6(13) | 7440.4(13) | 12559.6(13) | 8.0(4)   |
| Cl1  | 4a    | 1   | 5098.5(4) | 4901.5(4) | 9901.5(4) | 9.40(14) |

Table S3b Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for Li$_7$SiO$_5$Cl at 300 K. $U_{eq}$ is defined as 1/3 of the trace of the orthogonalised $U_{ij}$ tensor.

| Site | wyck. | sof | x     | y     | z     | $U_{eq}$ |
|------|-------|-----|-------|-------|-------|----------|
| Li1  | 12b   | 1   | 2839(3) | 4556(4) | 386(4)  | 25.1(7)  |
| Li2  | 12b   | 1   | 2425(6) | 94(4)  | 117(4)  | 24.6(7)  |
| Li3  | 4a    | 0.84(15) | 934(4) | 5934(4) | -934(4) | 20.3(15) |
| Si1  | 4a    | 0.16(15) | 70(20) | 5070(20) | -70(20) | 13(7)    |
| O1   | 4a    | 1   | 2553.7(4) | 7446.3(4) | 2446.3(4) | 9.22(18) |
| O2   | 12b   | 1   | 1419.4(12) | 8581.0(12) | 3581.0(12) | 12.7(4)  |
| O3   | 4a    | 1   | 5055.6(14) | 4944.4(14) | -55.6(14) | 11.9(4)  |
| Cl1  | 4a    | 1   | 2411.4(5) | 2411.4(5) | 2411.4(5) | 16.35(16) |

Table S3c. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for Li$_7$SiO$_5$Cl at 500 K. $U_{eq}$ is defined as 1/3 of the trace of the orthogonalised $U_{ij}$ tensor.

| Site | wyck. | sof | x     | y     | z     | $U_{eq}$ |
|------|-------|-----|-------|-------|-------|----------|
| Li1  | 4d    | 0.443(12) | 7500 | 2500 | 2500 | 14(6)    |
| Li2  | 48h   | 0.4835(1) | 7730(30) | 5180(20) | 2730(20) | 55(9)    |
| Li3  | 16e   | 0.1886(3) | 8460(90) | 3460(90) | 3460(90) | 40(20)   |
| Si1  | 4b    | 1   | 5000 | 5000 | 5000 | 21.2(7)  |
| O1   | 16e   | 1   | 6138(3) | 3862(3) | 3862(3) | 25.9(9)  |
| O2   | 4c    | 1   | 7500 | 7500 | 2500 | 27.1(16) |
| Cl1  | 4a    | 1   | 10000 | 5000 | 5000 | 36.0(8)  |
Table S4a. Anisotropic displacement parameters (Å²×10³) for Li₇SiO₅Cl at 100 K. The anisotropic displacement factor exponent takes the form: -2π²[h²a²U₁₁+2hka*b*U₁₂+…].

| Site | U₁₁  | U₂₂  | U₃₃  | U₂₃  | U₁₃  | U₁₂  |
|------|------|------|------|------|------|------|
| Li₁  | 14.4(12) | 18.7(15) | 13.8(13) | -2.5(11) | -0.7(11) | 2.9(12) |
| Li₂  | 13.1(14) | 19.1(16) | 13.8(14) | -4.2(10) | -1.2(11) | -0.8(10) |
| Li₃  | 18.3(11) | 18.3(11) | 18.3(11) | 2.7(12) | 2.7(12) | 2.7(12) |
| Si₁  | 6.30(17) | 6.30(17) | 6.30(17) | -0.08(15) | 0.08(15) | -0.08(15) |
| O₁  | 8.5(4) | 8.5(4) | 8.5(4) | 0.6(4) | -0.6(4) | 0.6(4) |
| O₂  | 8.6(5) | 8.3(5) | 9.2(5) | 0.1(5) | 0.6(4) | 0.3(4) |
| O₃  | 8.0(4) | 8.0(4) | 8.0(4) | -0.2(3) | 0.2(3) | -0.2(3) |
| Cl₁  | 9.40(14) | 9.40(14) | 9.40(14) | -0.04(17) | 0.04(17) | 0.04(17) |

Table S4b Anisotropic Displacement Parameters (Å²×10³) for Li₇SiO₅Cl at 300 K. The anisotropic displacement factor exponent takes the form: -2π²[h²a²U₁₁+2hka*b*U₁₂+…].

| Site | U₁₁  | U₂₂  | U₃₃  | U₂₃  | U₁₃  | U₁₂  |
|------|------|------|------|------|------|------|
| Li₁  | 18.1(13) | 31.2(16) | 25.9(14) | -6.1(13) | 1.8(12) | -2.2(12) |
| Li₂  | 19.0(15) | 23.9(16) | 31.0(18) | 9.8(11) | -2.5(10) | -1.3(11) |
| Li₃  | 20.3(15) | 20.3(15) | 20.3(15) | -2.4(12) | -2.4(12) | 2.4(12) |
| Li₄  | 13(7) | 13(7) | 13(7) | 5(4) | 5(4) | 5(4) |
| Si₁  | 9.22(18) | 9.22(18) | 9.22(18) | 0.34(16) | -0.34(16) | -0.34(16) |
| O₁  | 12.7(4) | 12.7(4) | 12.7(4) | 0.6(4) | 0.6(4) | 0.6(4) |
| O₂  | 13.5(5) | 12.5(5) | 12.7(5) | -1.1(4) | -1.6(4) | -1.0(4) |
| O₃  | 11.9(4) | 11.9(4) | 11.9(4) | -0.1(3) | 0.1(3) | 0.1(3) |
| Cl₁  | 16.35(16) | 16.35(16) | 16.35(16) | -0.17(18) | -0.17(18) | -0.17(18) |

Table S4c. Anisotropic displacement parameters (Å²×10³) for Li₇SiO₅Cl at 500 K. The anisotropic displacement factor exponent takes the form: -2π²[h²a²U₁₁+2hka*b*U₁₂+…].

| Site | U₁₁  | U₂₂  | U₃₃  | U₂₃  | U₁₃  | U₁₂  |
|------|------|------|------|------|------|------|
| Li₁  | 14(6) | 14(6) | 14(6) | 0 | 0 | 0 |
| Li₂  | 57(12) | 53(9) | 57(12) | 13(7) | 22(14) | 13(7) |
| Li₃  | 40(20) | 40(20) | 40(20) | 7(19) | 7(19) | 7(19) |
| Si₁  | 21.1(7) | 21.1(7) | 21.1(7) | 0 | 0 | 0 |
| O₁  | 25.9(9) | 25.9(9) | 25.9(9) | -2.9(11) | 2.9(11) | 2.9(11) |
| O₂  | 27.0(16) | 27.0(16) | 27.0(16) | 0 | 0 | 0 |
| Cl₁  | 36.0(8) | 36.0(8) | 36.0(8) | 0 | 0 | 0 |
Table S5a. Selected bond lengths (Å) and bond angles (°) for Li₇SiO₅Cl from single crystal X-ray diffraction at 100 K.

| Atoms   | Distance / Å | Atoms   | Angles / ° |
|---------|--------------|---------|------------|
| Li₁—O₂  | 2.042(3)     | O₂—Li₁—O₁ | 97.38(15)  |
| Li₁—O₃  | 2.022(3)     | O₂—Li₁—Cl₁ | 100.90(13) |
| Li₁—Cl₁ | 1.899(3)     |         | 102.79(12) |
| Li₂—O₁  | 2.440(3)     | O₃—Li₁—O₂ | 119.51(17) |
| Li₂—O₂  | 1.929(4)     | O₃—Li₁—Cl₁ | 113.98(14) |
| Li₂—O₃  | 1.961(4)     | Cl₁—O₂   | 97.38(15)  |
| Li₂—Cl₁ | 2.666(3)     |         | 100.90(13) |
| Si₁—O₁  | 1.899(3)     |         | 102.79(12) |
| Si₁—O₂  | 1.6237(18)   |         | 119.51(17) |

Table S5b. Selected bond lengths (Å) and bond angles (°) for Li₇SiO₅Cl from single crystal X-ray diffraction at 300 K.

| Atoms   | Distance / Å | Atoms   | Angles / ° |
|---------|--------------|---------|------------|
| Li₁—O₂  | 2.043(3)     | O₂—Li₁—O₁ | 98.29(15)  |
| Li₁—O₃  | 2.023(3)     | O₂—Li₁—Cl₁ | 100.26(17) |
| Li₁—Cl₁ | 1.897(3)     |         | 102.02(18) |
| Li₂—O₁  | 2.466(4)     | O₃—Li₁—O₂ | 119.65(17) |
| Li₂—O₂  | 1.932(4)     | O₃—Li₁—Cl₁ | 113.05(15) |
| Li₂—O₃  | 1.961(4)     | Cl₁—O₂   | 97.38(15)  |
| Li₂—Cl₁ | 2.666(3)     |         | 100.26(17) |
| Si₁—O₁  | 1.6227(18)   |         | 119.65(17) |
| Si₁—O₂  | 1.63387(13)  |         | 91.41(16)  |

Table S5c. Selected bond lengths (Å) and bond angles (°) for Li₇SiO₅Cl from single crystal X-ray diffraction at 500 K.

| Atoms   | Distance / Å | Atoms   | Angles / ° |
|---------|--------------|---------|------------|
| Li₁—O₁  | 1.959(5)     | O₁—Li₁—O₁ | 98.29(15)  |
| Li₁—O₃  | 1.956(13)    | O₁—Li₁—Cl₁ | 100.26(17) |
| Li₁—Cl₁ | 1.945(19)    |         | 102.02(18) |
| Li₂—O₁  | 2.673(3)     | O₂—Li₂—O₁ | 119.51(17) |
| Li₂—O₂  | 1.999(5)     | O₂—Li₂—O₁ | 102.79(12) |
| Li₂—Cl₁ | 2.211(13)    | Cl₁—O₂   | 97.38(15)  |
| Si₁—O₁  | 1.637(5)     |         | 102.02(18) |
| Si₁—O₂  | 1.63387(13)  |         | 91.41(16)  |
Figure S3: Pawley fits against SXRD data at a) 100 K, b) 300 K and c) 500 K for Li$_7$SiO$_5$Cl; $I_{\text{obs}}$ (black circles), $I_{\text{calc}}$ (red line), $I_{\text{obs}}$--$I_{\text{calc}}$ (grey line) and Bragg reflections (black tick marks for Li$_{6+x}$P$_{1-x}$SixO$_5$Cl, red tick marks for Li$_4$SiO$_4$, orange tick marks for Li$_6$SiO$_4$Cl$_2$ and blue tick marks for LiCl; d) Ordering peaks disappearing as temperature is increased and Li$_7$SiOCl transitions from $P2_1\overline{3}$ to $F\bar{4}3m$. 
Figure S4: a) Lattice parameters as a function of temperature for Li$_7$SiO$_5$Cl b) DSC data collected for Li$_7$SiO$_5$Cl, the peak at 472.1(6) K corresponds to the phase transition from $P2_13$ to $F43m$ in Li$_7$SiO$_5$Cl, the peak is broadened by the presence of the impurity phase of Li$_6$SiO$_4$Cl$_2$ which exhibits a phase transition at a similar temperature.\textsuperscript{1}

Figure S5: $^{29}$Si MAS NMR spectra of Li$_{6+x}$P$_{1-x}$Si$_x$O$_5$Cl ($x$ = 0.3, 0.75, 0.8 and 1). Full-width half maximum values of 350, 330, 250 and 60 Hz were observed for $x$ = 0.3, 0.75, 0.8 and 1, respectively.
Figure S6. $^6$Li MAS NMR spectrum of Li$_7$SiO$_5$Cl. The experimental spectra (full lines), total fit (dashed lines) and spectral deconvolution (dotted lines) of the ordered Li1 (T5a) and Li2 (T5) as well as the mixed occupancy Li3 (T3) and Li4 (T4) environments. The resonances associated with the largest Li$_7$SiO$_5$ impurity (~10 mol%) at 2, 1.2, and -0.7 ppm (red dotted lines)$^2$ as observed in XRD are also shown while the other impurities are below the NMR detection limit or unresolved due to the small shift range of $^6$Li NMR.

Figure S7: Crystal structure of Li$_7$SiO$_5$Cl at 100, 300 and 500 K. Atom and polyhedra colours: SiO$_4$ tetrahedra (dark blue), O (red), Cl (light blue), Li – T5 site (grey), Li – T3 site (purple), Li – T4 site (green), Vacant sites (white); Unit cell at a) 100 K, b) 300 K, c) 500 K; Octahedral Li ion cages and Li–Li distances at d) 100 K, e) 300 K, and f) 500 K.
Figure S9: a) XRD patterns for Li$_{6+2x}$P$_{0.7}$Si$_{0.3}$O$_5$Cl. Black squares denote peaks corresponding to the cubic argyrodite phase and peaks corresponding to Si used as an internal standard are also present in some samples. b) Magnified views of the XRD patterns to highlight peak shift confirming the incorporation of Si and Li into the material.
Figure S10: a) Pawley fit against SXRD data of Li_{6+x}P_{1-x}Si_{x}O_5Cl (Diamond Light Source I11 beam line) with I_{obs} (black circles), I_{calc} (red line), I_{obs}−I_{calc} (grey line) and Bragg reflections (black tick marks for Li_{6+x}P_{1-x}Si_{x}O_5Cl, red tick marks for Li_{3}SiO_{4}, purple tick marks for Li_{3}PO_{4}, light green tick marks for Li_{3}OCl, blue tick marks for LiCl, green tick marks for Li_{2}O, pink tick marks for ZrO_{2} and orange tick marks for Li_{6}SiO_{4}Cl_{2}); a) \( x = 0.1 \); b) \( x = 0.3 \); c) \( x = 0.5 \); d) \( x = 0.6 \); e) \( x = 0.7 \); f) \( x = 0.75 \); g) \( x = 0.8 \); h) \( x = 0.85 \)
Table S6: Empirical formula determined from ICP and SEM-EDX compositional analysis confirming the incorporation of Si and P into the lattice and the increase of Li content with increasing $x$ in Li$_{6+x}$P$_{1-x}$Si$_x$O$_5$Cl

| $x$ in Li$_{6+x}$P$_{1-x}$Si$_x$O$_5$Cl | ICP | SEM - EDX | Empirical formula |
|--------------------------------------|-----|-----------|------------------|
| 0.1                                  | /   | Si$_{0.56(2)}$P$_{0.44(3)}$Cl$_{1.04(13)}$ | / |
| 0.3                                  | Li$_{6.42(5)}$Si$_{0.12(3)}$P$_{0.6767(3)}$Cl$_{1.04(13)}$ | Li$_{6.42(5)}$Si$_{0.12(3)}$P$_{0.6767(3)}$Cl$_{1.04(13)}$ |
| 0.5                                  | Li$_{6.57(2)}$Si$_{0.5138(3)}$P$_{0.4862(5)}$Cl$_{1.04(13)}$ | Li$_{6.57(2)}$Si$_{0.5138(3)}$P$_{0.4862(5)}$Cl$_{1.04(13)}$ |
| 0.6                                  | Li$_{6.66(2)}$Si$_{0.6176(3)}$P$_{0.3824(2)}$Cl$_{1.04(13)}$ | Li$_{6.66(2)}$Si$_{0.6176(3)}$P$_{0.3824(2)}$Cl$_{1.04(13)}$ |
| 0.7                                  | Li$_{6.79(2)}$Si$_{0.6816(2)}$P$_{0.3184(3)}$Cl$_{1.04(13)}$ | Li$_{6.79(2)}$Si$_{0.6816(2)}$P$_{0.3184(3)}$Cl$_{1.04(13)}$ |
| 0.75                                 | Li$_{6.84(2)}$Si$_{0.7665(2)}$P$_{0.2335(5)}$Cl$_{1.04(13)}$ | Li$_{6.84(2)}$Si$_{0.7665(2)}$P$_{0.2335(5)}$Cl$_{1.04(13)}$ |
| 0.8                                  | Li$_{6.89(4)}$Si$_{0.8064(4)}$P$_{0.1935(3)}$Cl$_{1.04(13)}$ | Li$_{6.89(4)}$Si$_{0.8064(4)}$P$_{0.1935(3)}$Cl$_{1.04(13)}$ |
| 0.85                                 | Li$_{6.91(4)}$Si$_{0.8642(4)}$P$_{0.1358(3)}$Cl$_{1.04(13)}$ | Li$_{6.91(4)}$Si$_{0.8642(4)}$P$_{0.1358(3)}$Cl$_{1.04(13)}$ |

Figure S11A: a) Fourier Difference map for $x = 0.7$ when the Li sites are not included in the model. Li atoms contribute ~20% to the total electron count and additional electron density is clearly visible surrounding the T5, T5a and T3 positions, b) $x = 0.7$: Rietveld fit against high resolution data excluding all Li$^+$ sites compared to c) which includes all identified Li$^+$ sites in the model, highlighting the improvement in visual fit quality and $R_{wp}$ from 15.90% (excluding Li$^+$ sites) to 5.60% (including Li$^+$ sites); (black tick marks for Li$_{6.7}P_3Si_0.7O_5Cl$, red tick marks for Li$_6SiO_4$, blue tick marks for LiCl, green tick marks for Li$_2$O and pink tick marks for ZrO$_2$).
Figure S11B: a) Fourier Difference map for $x = 0.7$ highlighting additional electron density surrounding the T3 and T4 positions when these sites are not included in the model. b) $x = 0.7$: Rietveld fit against high resolution data excluding T3 and T4 sites compared to c) including the T3 and T4 sites in the model, highlighting the improvement in visual fit quality and $R_{wp}$ (black tick marks for Li$_6$P$_{0.3}$Si$_{0.7}$O$_5$Cl, red tick marks for Li$_4$SiO$_4$, blue tick marks for LiCl, green tick marks for Li$_2$O and pink tick marks for ZrO$_2$).
Table S7: Structure refinement against powder diffraction data for Li$_{6+x}$P$_{1-x}$Si$_x$O$_5$Cl

| Phase | $x = 0.1$ | $x = 0.3$ | $x = 0.5$ | $x = 0.6$ |
|-------|-----------|-----------|-----------|-----------|
| **Empirical Formula** | Li$_{6.10(3)}$P$_{0.90}$Si$_{0.10}$O | Li$_{6.20(18)}$P$_{0.70}$Si$_{0.30}$O | Li$_{6.45(15)}$P$_{0.45}$Si$_{0.55}$O$_{4.99(4)}$ | Li$_{6.62(2)}$P$_{0.62}$Si$_{0.38}$O$_{4.99(3)}$Cl0.99(7) |
| **Formula Weight (g mol$^{-1}$)** | 188.47 | 189.28 | 190.09 | 190.50 |
| **Space group** | $F\bar{4}3m$ | $F\bar{4}3m$ | $F\bar{4}3m$ | $F\bar{4}3m$ |
| **Z** | 4 | 4 | 4 | 4 |
| **Density (g cm$^{-3}$)** | 1.350 | 1.349 | 1.347 | 1.345 |
| **Temperature (K)** | 293.15 | 293.15 | 293.15 | 293.15 |
| **Wavelength (Å)** | 0.826899 | 0.826899 | 0.826899 | 0.82677 |
| **d – spacing range (Å)** | 0.5716-5.9255 | 0.5716-5.9255 | 0.5716-5.9255 | 0.4298-6.3351 |
| **No. of reflections** | 110 | 110 | 110 | 236 |
| **No. of refined parameters** | 27 | 35 | 28 | 26 |
| **a (Å)** | 8.248176(16) | 8.264610(15) | 8.2677 | 8.273920(16) |
| **Volume (Å$^3$)** | 558.316(3) | 561.143(3) | 564.504(3) | 566.414(3) |
| **$R_p$** | 3.84 | 2.54 | 2.46 | 5.56 |
| **$R_w$** | 5.80 | 3.48 | 3.34 | 8.13 |
| **$R_{exp}$** | 0.85 | 0.75 | 0.87 | 1.70 |
| **$\chi^2$** | 46.64 | 21.53 | 14.74 | 22.86 |

| Phase | $x = 0.7$ | $x = 0.75$ | $x = 0.8$ | $x = 0.85$ |
|-------|-----------|-----------|-----------|-----------|
| **Empirical Formula** | Li$_{6.66(17)}$P$_{0.68}$Si$_{0.32}$O$_{4.98(3)}$Cl | Li$_{6.78(2)}$P$_{0.80}$Si$_{0.20}$O$_{4.98(4)}$Cl0.9902(5) | Li$_{6.85(2)}$P$_{0.85}$Si$_{0.15}$O$_{4.98(7)}$Cl0.98278(5) | Li$_{6.90(2)}$P$_{0.88}$Si$_{0.12}$O$_{4.98(7)}$Cl0.9827(5) |
| **Formula Weight (g mol$^{-1}$)** | 190.90 | 191.105 | 191.308 | 191.511 |
| **Space group** | $F\bar{4}3m$ | $F\bar{4}3m$ | $P\bar{2}1\bar{3}$ | $P\bar{2}1\bar{3}$ |
| **Z** | 4 | 4 | 4 | 4 |
| **Density (g cm$^{-3}$)** | 1.349 | 1.349 | 1.350 | 1.347 |
| **Temperature (K)** | 293.15 | 293.15 | 293.15 | 293.15 |
| **Wavelength (Å)** | 0.82677 | 0.826899 | 0.826899 | 0.826899 |
| **d – spacing range (Å)** | 0.4298-6.3351 | 0.5716-5.9255 | 0.5716-5.9255 | 0.5716-5.9255 |
| **No. of reflections** | 236 | 110 | 627 | 627 |
| **No. of refined parameters** | 28 | 32 | 46 | 43 |
| **a (Å)** | 8.271684(9) | 8.275968(9) | 8.276883(9) | 8.278181(4) |
| **Volume (Å$^3$)** | 565.955(2) | 566.835(2) | 567.023(3) | 567.290(1) |
| **$R_p$** | 4.38 | 2.37 | 2.61 | 2.51 |
| **$R_w$** | 5.60 | 3.27 | 3.79 | 3.55 |
| **$R_{exp}$** | 2.07 | 0.90 | 1.04 | 1.07 |
| **$\chi^2$** | 7.32 | 13.20 | 13.28 | 11.00 |
Table S8: Atomic positions, isotropic atomic displacement parameters (U\textsubscript{iso}, Å\textsuperscript{2}×10\textsuperscript{3}), and site occupancy factors for Li\textsubscript{6+}P\textsubscript{1.8}Si\textsubscript{0.5}O\textsubscript{5}Cl obtained from refinement against powder diffraction data.

| Site   | Wyckoff position | x     | y     | z     | s.o.f. | U\textsubscript{iso} (Å\textsuperscript{2}×10\textsuperscript{3}) |
|--------|------------------|-------|-------|-------|--------|--------------------------------------------------|
| Li1    | 4a               | 0     | 0     | 0     | 1.000(2)| 1.232(7)                                        |
| Si1    | 4b               | 0.5   | 0.5   | 0.5   | 0.1    | 0.18(6)                                         |
| P1     | 4b               | 0.5   | 0.5   | 0.5   | 0.9    | 0.528(7)                                        |
| O1     | 16e              | 0.38962(5) | 0.38962(5) | 0.38962(5) | 1.000(3) | 0.292(9)                                        |
| O2     | 4d               | 0.75  | 0.75  | 0.75  | 1.000(3) | 0.476(15)                                       |
| Li1    | 24g              | 0.51580(3) | 0.25  | 0.25  | 0.841(17) | 1.58(2)                                         |
| Li1a   | 48h              | 0.700(2) | 0.700(2) | 0.986(3) | 0.080(9) | 1.0(4)                                          |
| Li2    | 4c               | 0.25  | 0.25  | 0.25  | 0.1    | 5.00                                            |
| Li1    | 4a               | 0     | 0     | 0     | 1.000(2) | 1.351(6)                                        |
| Si1    | 4b               | 0.5   | 0.5   | 0.5   | 0.3    | 1.81(2)                                         |
| P1     | 4b               | 0.5   | 0.5   | 0.5   | 0.7    | 0.103(5)                                        |
| O1     | 16e              | 0.38862(4) | 0.38862(4) | 0.38862(4) | 0.9837(4) | 0.610(7)                                        |
| O2     | 4d               | 0.75  | 0.75  | 0.75  | 1.000(2) | 0.551(1)                                        |
| Li1    | 24g              | 0.516(5) | 0.25  | 0.25  | 0.521(1) | 0.61(2)                                         |
| Li1a   | 48h              | 0.7123(9) | 0.7123(9) | 0.9814(7) | 0.2353(6) | 0.70(5)                                         |
| Li2    | 4c               | 0.25  | 0.25  | 0.25  | 0.070(5) | 4.6(8)                                          |
| Li3    | 16e              | 0.163(4) | 0.163(4) | 0.163(4) | 0.043(2) | 2.5(6)                                          |
| Li1    | 4a               | 0     | 0     | 0     | 0.9999(5) | 1.402(8)                                        |
| Si1    | 4b               | 0.5   | 0.5   | 0.5   | 0.51   | 1.14(7)                                         |
| P1     | 4b               | 0.5   | 0.5   | 0.5   | 0.49   | 0.33(5)                                         |
| O1     | 16e              | 0.38770(3) | 0.38770(3) | 0.38770(3) | 0.9911(5) | 0.806(13)                                       |
| O2     | 4d               | 0.75  | 0.75  | 0.75  | 1.0000(9) | 0.61(2)                                         |
| Li1    | 24g              | 0.5159(4) | 0.25  | 0.25  | 0.5125(9) | 0.88(8)                                         |
| Li1a   | 48h              | 0.7092(7) | 0.7092(7) | 0.9789(5) | 0.2369(6) | 0.81(1)                                         |
| Li2    | 4c               | 0.25  | 0.25  | 0.25  | 0.159(3) | 1.0(5)                                          |
| Li3    | 16e              | 0.1507(15) | 0.1507(15) | 0.1507(15) | 0.0883(7) | 3.0(6)                                          |
| Li1    | 4a               | 0     | 0     | 0     | 0.9999(7) | 1.678(11)                                       |
| Si1    | 4b               | 0.5   | 0.5   | 0.5   | 0.62   | 0.9(4)                                          |
| P1     | 4b               | 0.5   | 0.5   | 0.5   | 0.38   | 1.0(6)                                          |
| O1     | 16e              | 0.38810(5) | 0.38810(5) | 0.38810(5) | 0.9999(9) | 1.029(15)                                       |
| O2     | 4d               | 0.75  | 0.75  | 0.75  | 1.000(15) | 0.9(3)                                          |
| Li1    | 24g              | 0.5146(7) | 0.25  | 0.25  | 0.4561(14) | 1.18(18)                                        |
| Li1a   | 48h              | 0.7110(16) | 0.7110(16) | 0.9829(11) | 0.2710(9) | 3.3(1)                                          |
| Li2    | 4c               | 0.25  | 0.25  | 0.25  | 0.164(4) | 1.0(5)                                          |
| Li3    | 16e              | 0.1563(9) | 0.1563(9) | 0.1563(9) | 0.117(11) | 0.99(2)                                         |
| Li1    | 4a               | 0     | 0     | 0     | 0.9886(5) | 1.222(5)                                        |
| Si1    | 4b               | 0.5   | 0.5   | 0.5   | 0.68   | 0.538(5)                                        |
| P1     | 4b               | 0.5   | 0.5   | 0.5   | 0.32   | 2.18(2)                                         |
| O1     | 16e              | 0.38743(3) | 0.38743(3) | 0.38743(3) | 0.9965(6) | 0.927(9)                                        |
| O2     | 4d               | 0.75  | 0.75  | 0.75  | 0.9968(10) | 0.871(17)                                       |
| Li1    | 24g              | 0.5166(3) | 0.25  | 0.25  | 0.5125(10) | 1.0(7)                                          |
| Li1a | 48h  | 0.7046(7) | 0.7046(7) | 0.9754(5) | 0.2437(7) | 2.1(1) |
| Li2  | 4c   | 0.25     | 0.25      | 0.25      | 0.284(3)  | 0.61(17) |
| Li3  | 16e  | 0.1420(17) | 0.1420(17) | 0.1420(17) | 0.090(3)  | 4.5(7)  |

| Li3aP2_2_2Si6aO6Cl |
|---------------------|
| C11 4a 0 0 0 0 0.976(2) 1.357(6) |
| Si1 4b 0.5 0.5 0.5 0.75 0.12(1) |
| P1   4b 0.5 0.5 0.5 0.25 3.2(1) |
| O1   16e 0.38744(3) 0.38744(3) 0.38744(3) 0.982(3) 0.84(1) |
| O2   4d 0.75 0.75 0.75 0.9968(19) 0.70(2) |
| Li1 24g 0.5155(3) 0.25 0.25 0.508(15) 0.99(7) |
| Li2a 48h 0.7066(2) 0.7066(2) 0.9733(5) 0.2412(11) 1.74(9) |
| Li2 4c 0.25 0.25 0.25 0.209(2) 0.23(2) |
| Li3 16e 0.1510(9) 0.1510(9) 0.1510(9) 0.1345(7) 3.3(4) |

| Li3aP3_21Si6aO6Cl |
|---------------------|
| C11 4a 0.0011(3) 0.0011(3) 0.0011(3) 0.9901(5) 1.430(7) |
| Si1 4a 0.4989(3) 0.4989(3) 0.4989(3) 0.80 0.50(11) |
| P1   4a 0.4989(3) 0.4989(3) 0.4989(3) 0.20 1.0(5) |
| O1   4a 0.6119(5) 0.6119(5) 0.6119(5) 0.999(9) 1.45(15) |
| O2   12b 0.3842(4) 0.3878(5) 0.6108(5) 0.9990(4) 0.73(3) |
| O3   4a 0.2477(8) 0.2477(8) 0.2477(8) 0.998(1) 0.668(3) |
| Li1 12b 0.01331 0.25000 0.25000 0.5111(17) 1.0(6) |
| Li1a 12b 0.20757 0.20757 0.02923 0.218(2) 0.98(1) |
| Li1b 12b 0.79243 0.20757 0.97077 0.267(2) 2.1(3) |
| Li2 12b 0.48669 0.25000 0.25000 0.4773(18) 1.0(6) |
| Li2a 12b 0.79243 0.79243 0.02923 0.177(3) 1.4(3) |
| Li2b 12b 0.20757 0.79243 0.97077 0.344(2) 1.2(3) |
| Li3 4a 0.7561(14) 0.7561(14) 0.7561(14) 0.224(8) 0.4(2) |
| Li3a 4a 0.8455(11) 0.8455(11) 0.8455(11) 0.23(2) 1.7(2) |
| Li3b 12b 0.150(2) 0.152(2) 0.847(2) 0.114(8) 1.2(2) |

| Li3aP3_12Si6aO6Cl |
|---------------------|
| C11 4a 0.00244(6) 0.00244(6) 0.00244(6) 0.9829(4) 1.349(4) |
| Si1 4a 0.49841(6) 0.49841(6) 0.49841(6) 0.85 0.43(3) |
| P1   4a 0.49841(6) 0.49841(6) 0.49841(6) 0.15 1.3(2) |
| O1   4a 0.6107(2) 0.6107(2) 0.6107(2) 0.999(2) 1.62(6) |
| O2   12b 0.38332(17) 0.38332(17) 0.38332(17) 1.000(3) 0.61(1) |
| O3   4a 0.2487(3) 0.2487(3) 0.2487(3) 0.9939(9) 0.675(9) |
| Li1 12b 0.01331 0.25000 0.25000 0.4874(16) 0.96(3) |
| Li1a 12b 0.20757 0.20757 0.02923 0.213(2) 1.2(2) |
| Li1b 12b 0.79243 0.20757 0.97077 0.291(2) 2.3(2) |
| Li2 12b 0.48669 0.25000 0.25000 0.4696(16) 1.00(3) |
| Li2a 12b 0.79243 0.79243 0.02923 0.176(2) 1.5(2) |
| Li2b 12b 0.20757 0.79243 0.97077 0.355(2) 1.16(12) |
| Li3 4a 0.7544(16) 0.7544(16) 0.7544(16) 0.240(3) 0.51(9) |
| Li3a 4a 0.8456(7) 0.8456(7) 0.8456(7) 0.373(16) 2.0(4) |
| Li3b 12b 0.153(3) 0.154(3) 0.847(3) 0.081(6) 0.56(17) |
Figure S12: a) Rietveld refinements against SXRD of Li$_{6+x}$P$_1$$_x$Si$_x$O$_5$Cl (Diamond Light Source I11 beam line) with $I_{\text{obs}}$ (black circles), $I_{\text{calc}}$ (red line), $I_{\text{obs}}-I_{\text{calc}}$ (grey line) and Bragg reflections (black tick marks for Li$_{6+x}$P$_1$$_x$Si$_x$O$_5$Cl, red tick marks for Li$_3$SiO$_4$, purple tick marks for Li$_3$PO$_4$, light green tick marks for Li$_3$OCl, blue tick marks for LiCl, green tick marks for Li$_2$O, pink tick marks for ZrO$_2$ and orange tick marks for Li$_6$SiO$_4$Cl$_2$); a) $x = 0.3$; b) $x = 0.5$; c) $x = 0.6$; d) $x = 0.75$; e) $x = 0.8$, inset highlights one of the supercell reflections (241)
Figure S13: $^{31}$P MAS NMR spectra of Li$_{6-x}$P$_1$-$x$Si$_x$O$_5$Cl ($x = 0.3$, 0.75 and 0.8). The experimental spectra (full lines), total fit (dashed lines) and spectral deconvolution (dotted lines) of the different $^{31}$P environments arising from differing second coordination spheres due to the site occupancies of neighbouring Li environments. The percentage contributions of each resonance to the overall line shape is available in Table S8. The vertical dashed lines highlight the decrease in chemical shift of the most intense resonance, arising from the increased statistical probability of a greater number of Li atoms in the $^{31}$P second coordination sphere, due to the increasing Li content.
Figure S14: $^{31}$P MAS NMR spectra of Li$_{6.8}$P$_{0.2}$Si$_{0.8}$O$_5$Cl justifying the necessity of a resonance at higher chemical shift (13 ppm) with respect to the main peak (12.5 ppm), where a two-fit model (top) and a three-fit model (bottom) are shown with the residual fits (full green lines). The experimental spectra (full orange lines), total fit (dashed orange lines), spectral deconvolution (dotted orange lines) of the different $^{31}$P environments are also shown.

Figure S15: Relative statistical probability of the different second coordination spheres for Li$_{6.8}$P$_{1-x}$Si$_x$O$_5$Cl ($x = 0.3$, 0.75 and 0.8) from the statistical probability according to the Li site occupancies observed in refinements against SXRD data (Table S7).
Table S9: Summary of the extracted $^{31}\text{P}$ NMR parameters and the tentative assignments for Li$_{6-x}$P$_1x$Si$_x$O$_5$Cl ($x = 0.3, 0.75$ and $0.8$) from the statistical probability according to the Li site occupancies observed in refinements against SXRD data (Table S7).

| $x$ | $^{31}\text{P}$ Chemical shift / ppm | % of overall NMR signal | No of Li atoms in 2nd coordination sphere | % probability according to XRD |
|-----|---------------------------------|-------------------------|------------------------------------------|--------------------------------|
| 0.8 | 13.3 ± 0.8                      | 7 ± 2                   | 7 + 8                                    | 7 ± 1                          |
|     | 12.6 ± 1.5                      | 74 ± 7                  | 9 + 10                                   | 52 ± 14                        |
|     | 11.3 ± 1.5                      | 20 ± 5                  | 11 + 12                                  | 24 ± 6                         |
| 0.75| 13.8 ± 0.6                      | 11 ± 1                  | 4 + 5                                    | 11 ± 1                         |
|     | 13.1 ± 0.9                      | 38 ± 5                  | 6 + 7                                    | 40 ± 2                         |
|     | 11.9 ± 1                        | 34 ± 5                  | 8 + 9                                    | 40 ± 2                         |
|     | 11.0 ± 0.6                      | 8 ± 2                   | 10                                       | 6 ± 1                          |
|     | 9.6 ± 0.7                       | 5 ± 1                   | 11 + 12                                  | 2 ± 1                          |
| 0.3 | 14.3 ± 0.3                      | 6 ± 2                   | 4                                        | 6 ± 1                          |
|     | 13.9 ± 0.5                      | 65 ± 3                  | 5 + 6 + 7                                | 69 ± 5                         |
|     | 11.9 ± 0.9                      | 28 ± 3                  | 8 + 9                                    | 23 ± 2                         |
|     | 10.0 ± 0.4                      | 1.3 ± 3                 | 10 + 11                                  | 1.0 ± 0.1                      |

In order to probe the local phosphorous environments in Li$_{6-x}$P$_1x$Si$_x$O$_5$Cl ($x = 0.3, 0.75$ and $0.8$), $^{31}\text{P}$ MAS NMR spectra were recorded (Figure S12). For all three compositions, multiple contributions to the overall NMR signal are observed and comprised of 3 to 5 resonances while a single average phosphorous environment is modelled in long-range Rietveld structural refinement. As $x$ increases, individual contributions to the NMR signal become more difficult to resolve. In order to analyse the different components to the overall NMR signal, the spectra were deconvoluted with the fewest number of signals (Figure S13) and the relative area fractions of the distinguishable $^{31}\text{P}$ NMR signals were extracted (Figure S14). This analysis reveals a trend towards lower chemical shift for the most intense $^{31}\text{P}$ resonance and an overall decrease in the intensity of signals appearing at higher chemical shift with increasing $x$ content.

These various NMR resonances arise as the $^{31}\text{P}$ nucleus is sensitive to the second coordination sphere, namely the T3, T4 and T5 Li sites. Hence when the site occupancy of these Li sites is less than 1, a statistical distribution of chemical shifts is observed. For example, the likelihood of a $^{31}\text{P}$ nucleus having 0 to 12 Li atoms in its second coordination environment will differ depending on the Li site occupancy of the varying sites. The second coordination sphere of $^{31}\text{P}$ in the three compositions analysed is complex as for all three phases there can be up to 12 second nearest neighbour Li atoms, 8 × T5 and 4 × T3/T4 Li atoms with varying site occupancies (Figure 6). The trend towards lower chemical shift with increasing $x$ content can be explained through the higher concentration of Li atoms on the T3 and T4 position as this provides an increase in electron density in the second coordination sphere of the $^{31}\text{P}$ nucleus and hence an increase in the chemical shielding.
Moreover, the resonances were compared with the expected ratios of the different possible second nearest neighbour environments for phosphorous using the site occupancies of the different lithium sites obtained from structural refinement against SXRD data (Figure S15) and the NMR resonances assigned from the relationship between coordination number and chemical shift (Table S8). The assignment of the different contributions to the overall NMR line shape agrees reasonably well with the expected statistical probabilities obtained from XRD. For example, in $x = 0.75$ according to the Rietveld refinement, 4 or 5 Li atoms are expected within the second coordination sphere 11% of the time while 6 or 7 Li atoms are predicted 40% of the time, the corresponding resonances in the $^{31}$P MAS NMR correspond to 11 and 38% of the overall signal respectively. However due to the small chemical shift change expected when a single Li atom is added or removed from the second coordination sphere (due to the relatively small shielding effects of Li atoms at this atomic distance), coupled with the overlapping signals corresponding to the various different possible configurations, it was not possible to discriminate between all observable NMR signal contributions.

![Figure S16: Comparison of percentage probability of the different second coordination spheres for Li$_{x}$P$_{1-}$xSi$_{x}$O$_{5}$Cl ($x = 0.3, 0.75$ and 0.8) from the statistical probability according to the Li site occupancies observed in structural refinement against SXRD data (filled bars) (Table S7) and integrations of the $^{31}$P MAS resonances (unfilled bars).](image)
Figure S17: SEM Images of Li$_{6.7}$P$_{0.3}$Si$_{0.7}$O$_5$Cl pellets prepared via SPS (a-c) and reactive sintering (d-f).

Figure S18: a) Nyquist plots for Li$_{6+x}$P$_{1-x}$Si$_x$O$_5$Cl; samples prepared via reactive sintering (RS) ($x$ = 0.3, 0.5, 0.6, 0.7, 0.75, 0.8, 0.85) and SPS ($x$ = 0.7, 0.75); b) Arrhenius plots for Li$_{6+x}$P$_{1-x}$Si$_x$O$_5$Cl for samples prepared via reactive sintering (RS) ($x$ = 0.3, 0.5, 0.6, 0.7, 0.8, 0.85) and SPS ($x$ = 0.7, 0.75).
Figure S19: Nyquist plots for Li_{6+x}P_{x}Si_{x}O_{5}Cl; samples prepared via reactive sintering (RS) (x = 0.1, 0.3, 0.5, 0.6, 0.7, 0.8, 0.85) and spark plasma sintering (SPS) (x = 0.7, 0.75, 0.8); a) 0.1 (RS), b) 0.3 (RS), c) 0.5 (RS), d) 0.6 (RS), e) 0.7 (RS), f) 0.75 (SPS), g) 0.75 (SPS), h) 0.8 (RS), i) 0.8 (SPS), j) 0.85 (RS); Data for x = 0.3-0.85 was collected at room temperature, due to the low room temperature ionic conductivity of x = 0.1 data was collected at 425 K.
Figure S20A: a) Bode plots for $\text{Li}_{6-x}\text{P}_{1+2x}\text{Si}_x\text{O}_5\text{Cl}$ measured on pellets produced via a) $x = 0.1$ reactive sintering (RS), b) $x = 0.3$ RS, c) $x = 0.5$ RS, d) $x = 0.6$ RS, e) $x = 0.7$ RS, f) $x = 0.7$ spark plasma sintering (SPS).
Table S10: Extracted total ionic conductivities and activation energies for Li$_{6+x}$P$_{1-x}$Si$_x$O$_5$Cl; samples prepared via reactive sintering (RS) ($x = 0.1, 0.3, .5, 0.6, 0.7, 0.75, 0.8, 0.85$) and spark plasma sintering (SPS) ($x = 0.7, 0.75, 0.8$)

| Composition | Sintering method | Relative density / % | Ionic conductivity / S cm$^{-1}$ | Activation Energy / eV |
|-------------|------------------|----------------------|----------------------------------|------------------------|
| 0.1         | RS               | 73.4                 | $\sim 10^{-9}$                   | 0.687(13)              |
| 0.3         | RS               | 79.0                 | $2.23(1) \times 10^{-7}$         | 0.496(4)               |
| 0.5         | RS               | 74.5                 | $3.53(4) \times 10^{-7}$         | 0.433(4)               |
| 0.6         | RS               | 77.1                 | $4.72(3) \times 10^{-7}$         | 0.502(3)               |
| 0.7         | RS               | 79.7                 | $1.16(4) \times 10^{-6}$         | 0.478(11)              |
| 0.7         | SPS              | 96.0                 | $1.63(4) \times 10^{-6}$         | 0.50(1)                |
| 0.75        | SPS              | 95.1                 | $1.82(1) \times 10^{-6}$         | 0.522(5)               |
| 0.8         | RS               | 85.0                 | $1.54(2) \times 10^{-6}$         | 0.491(7)               |
| 0.8         | SPS              | 96.5                 | $1.42(5) \times 10^{-6}$         | /                      |
| 0.85        | RS               | 78.4                 | $4.93(4) \times 10^{-7}$         | 0.564(8)               |

Figure S20B: a) Bode plots for Li$_{6+x}$P$_{1-x}$Si$_x$O$_5$Cl measured on pellets produced via a) $x = 0.75$ SPS, b) $x = 0.8$ RS, c) 0.8 SPS, d) $x = 0.85$ RS.
Figure S21: DC Polarisation data for $x = 0.7$ pellets produced through a) reactive sintering and b) spark plasma sintering; measurements from $x = 0.8$ pellets produced through c) reactive sintering, and d) spark plasma sintering. The electronic contribution to total conductivity was calculated to be $< 1.5\%$ for all samples.
Figure S22: Static $^7$Li NMR spectra of Li$_{6-x}$P$_{1-x}$Si$_x$O$_5$Cl for $x$ = a) 0.3 b) 0.5 c) 0.75 and d) 1 measured as a function of temperature.
The energy of activation obtained through $^7$Li VT NMR was determined through the correlation of the onset temperature of motional narrowing $T_{\text{onset}}$ and $E_a$:

$$E_a = 1.67 \times 10^{-3} \cdot T_{\text{onset}} \quad \text{(Eq S1)}$$

and the extracted $E_a$ values are summarised in Table S10. The data in Figure S22 was fit to a Boltzmann sigmoid regression curve in order to determine the inflection point of the curve, $T_{\text{inflection}}$, where the Li ions have a jump rate, $\tau^{-1}$ of the order of rigid lattice regime, $(\omega/2\pi)_r$, this expression takes the form of:

$$\frac{\omega(T)}{2\pi} = \left( \frac{(\omega/2\pi)_\infty - (\omega/2\pi)_r}{1 + \exp\left(\frac{T_{\text{inflection}} - T}{a}\right)} \right) \quad \text{(Eq S2)}$$

where $\omega(T)/2\pi$ is the central transition linewidth at temperature $T$, $(\omega/2\pi)_\infty$ is the residual linewidth in the fast motional regime and $a$ is a fitting parameter.
The NMR lithium jump $\tau^{-1}$ values obtained for $x = 0.3, 0.5$ and 0.75 through Equation 2 increase slightly as Li content increases which is to be expected for decreasing inter and intra-cage jumping distances resulting in stronger $^7$Li-$^7$Li homonuclear dipolar coupling and higher density of Li spins. The $T_{\text{inflection}}$ values for the three compositions are largely similar, however as $x$ increases to 1, $T_{\text{inflection}}$ increases significantly, highlighting the reduced Li ion mobility upon the complete ordering of Li sites observed in Li$_7$SiO$_5$Cl.

| Compositions | Jump rate $\tau^{-1}$ / s$^{-1}$ | $T_{\text{inflection}}$ / K | $E_a$ / eV |
|--------------|----------------------------------|-----------------------------|------------|
| 0.3          | $5.7(2) \times 10^4$             | 296(3)                      | 0.39       |
| 0.5          | $6.2(2) \times 10^4$             | 286(3)                      | 0.34       |
| 0.75         | $6.6(1) \times 10^4$             | 290(2)                      | 0.42       |
| 1            | $6.4(1) \times 10^4$             | 345(2)                      | 0.52       |

The NMR lithium jump $\tau^{-1}$ values obtained for $x = 0.3, 0.5$ and 0.75 through Equation 2 increase slightly as Li content increases which is to be expected for decreasing inter and intra-cage jumping distances resulting in stronger $^7$Li-$^7$Li homonuclear dipolar coupling and higher density of Li spins. The $T_{\text{inflection}}$ values for the three compositions are largely similar, however as $x$ increases to 1, $T_{\text{inflection}}$ increases significantly, highlighting the reduced Li ion mobility upon the complete ordering of Li sites observed in Li$_7$SiO$_5$Cl.

Figure S24: a) Li$_6$PS$_5$Cl stability in air for which full decomposition occurs within 1 hour as indicated by the disappearance of cubic argyrodite peaks. b) Li$_{6.7}$P$_{0.3}$Si$_{0.3}$O$_5$Cl exhibits increased stability in air; decomposition starts after $\sim$3h indicated by broadening of cubic argyrodite peaks and the appearance of Li$_2$CO$_3$ impurity peaks.
Table S12: Shortest intra- and inter-cage Li–Li distances in Li_{6+x}P_{1-x}Si_xO_5Cl (x = 0, 0.1, 0.3, 0.5, 0.6, 0.7, 0.75, 0.8, 0.85, 1).

| Intra-cage Distance / Å | 0       | 0.1     | 0.3     | 0.5     | 0.6     | 0.7     | 0.75    | 0.8     | 0.85    | 1       |
|-------------------------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| T5a–T5a                 | 2.728(9)| 2.195(2)| 2.269(2)| 2.196(3)| 2.265(11)| 2.106(2)| 2.101(13)| 2.119(6)| 2.087(2)| 2.721(2)|
| T5–T5                   |         |         |         |         |         |         |         |         |         |         |

| Inter-cage Distance / Å | 0       | 0.1     | 0.3     | 0.5     | 0.6     | 0.7     | 0.75    | 0.8     | 0.85    | 1       |
|-------------------------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| T5a–T5a                 | 3.087(9)| 2.195(2)| 1.588(1)| 1.575(9)| 1.573(4)| 1.561(9)| 1.606(5)| 1.615(8)| 1.624(6)| 2.229(3)|
| T5–T3                   |         |         |         |         |         |         |         |         |         |         |
| T5–T4                   |         |         |         |         |         |         |         |         |         |         |

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