Substitutional disorder: Structure and ion dynamics of the argyrodites Li_6PS_5Cl, Li_6PS_5Br and Li_6PS_5I

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The electronic supporting information contains results from Rietveld analyses (Figs S1, S2) and further information on NMR settings (Table S1); ^{35}Cl, ^{79}Br and ^{127}I MAS NMR spectra are shown in Fig. S3.

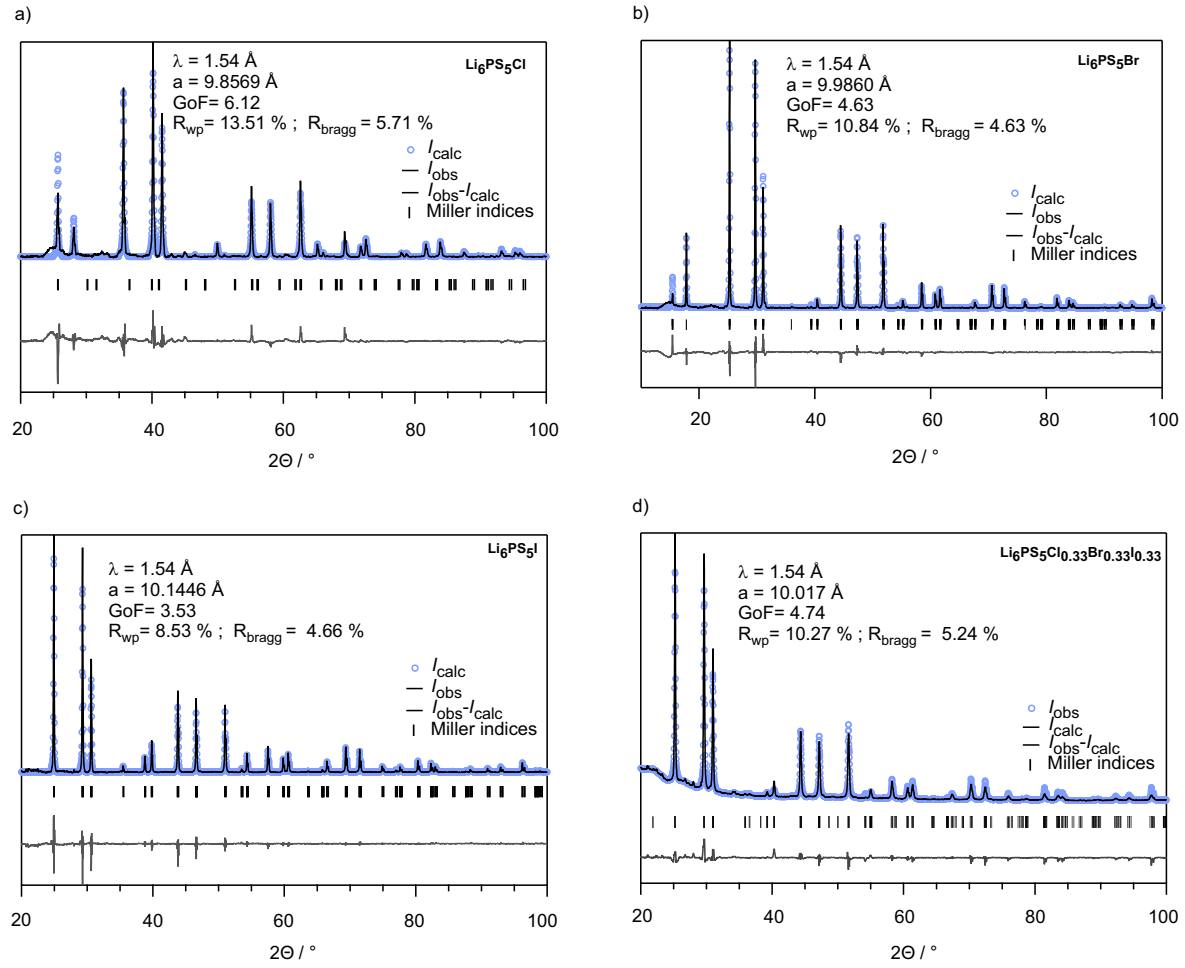

Fig. S1 Crystallographic data of Li_6PS_5Br, Li_6PS_5Cl, Li_6PS_5I, and $Li_6PS_5Cl_{0.50}Br_{0.50}$ obtained from X-ray powder diffraction. GoF means goodness of fit (GoF), the weighted *R*-profile (R_{wp}) and the *R*-Bragg (R_{Bragg}) values are also included. The differential plot as well as the hkl indices are shown, too. The hump at approximately 25° is due to the mercatpo foil, which was used for the measurement

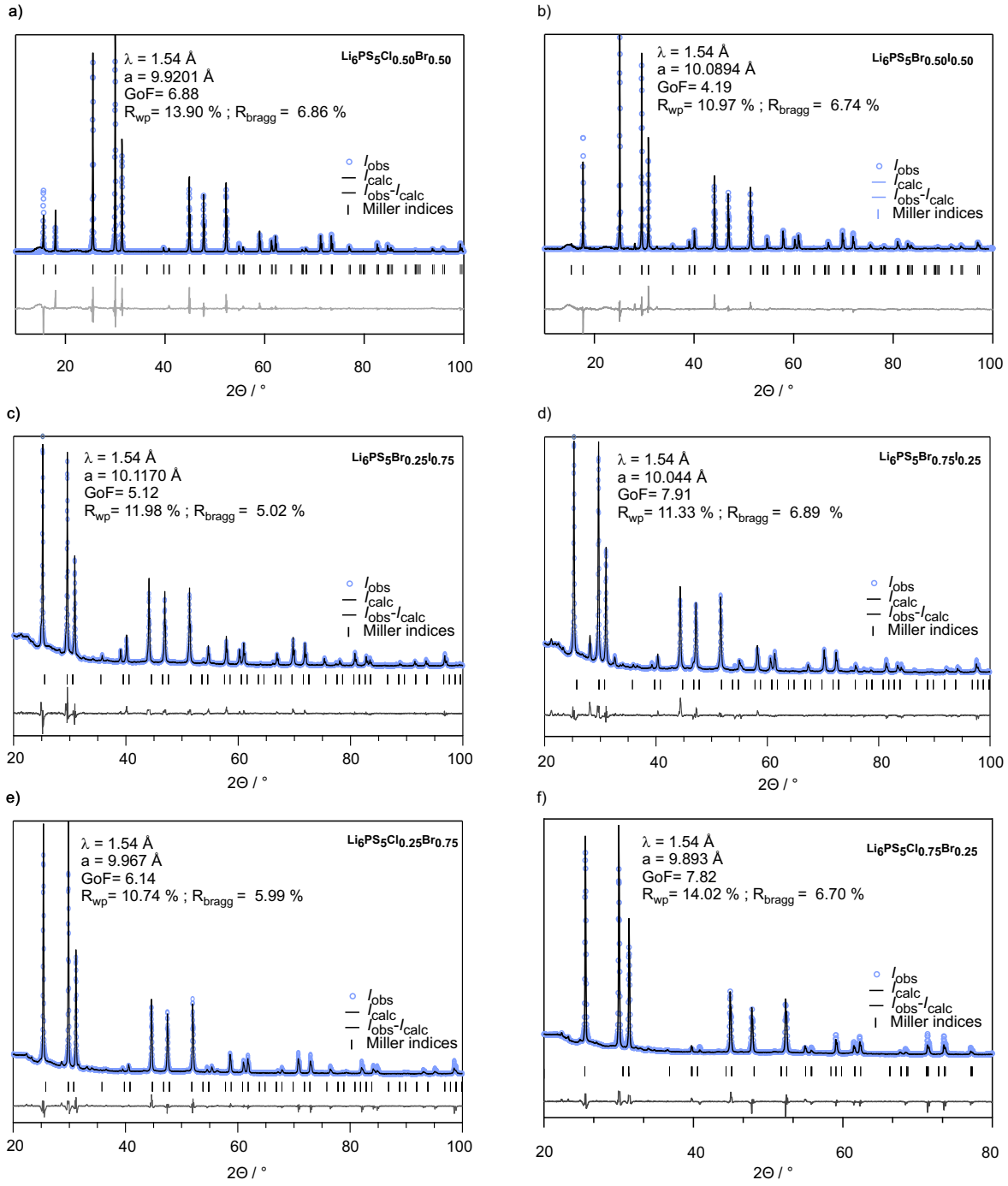

Fig. S2 X-ray powder diffraction patterns and crystallographic data from Rietveld analyses of the Li-argyrodites indicated. As in Fig. S1, GoF means goodness of fit (GoF), the weighted *R*-profile (R_{wp}) and the *R*-Bragg (R_{Bragg}) values are also shown. The differential plot as well as the hkl indices are included, too. The hump at approximately 25° is due to the mercatpo foil, which was used for the measurement

In Table **S1** the experimental settings of the magic angle spinning (MAS) NMR measurements are shown; The table includes pulse lengths and delay times for the ^{6}Li, ^{31}P, ^{35}Cl, ^{79}Br and ^{127}I NMR spectra. In Fig. S1 the corresponding spectra of ^{35}Cl, ^{79}Br and ^{127}I of Li_6PS_5X (X: Cl, Br and I) are presented.

Table S1: Settings to record the MAS NMR spectra of the argyrodites Li_6PS_5Cl, Li_6PS_5Br and Li_6PS_5I, respectively. The pulse length varies from 1 to 4.5 μs and the delay time from 1 s up to 180 s.

sample	measurement	pulse length	delay time
Li_6PS_5Cl	^{6}Li	3.0 μs	10 s
	^{31}P	1.0 μs	10 s
	^{35}Cl	4.5 μs	1 s
Li_6PS_5Br	^{6}Li	3.0 μs	10 s
	^{31}P	1.0 μs	30 s
	^{79}Br	1.3 μs	1.4 s
Li_6PS_5I	^{6}Li	3.0 μs	10 s
	^{31}P	2.0 μs	180 s
	^{127}I	3.0 μs	1 s

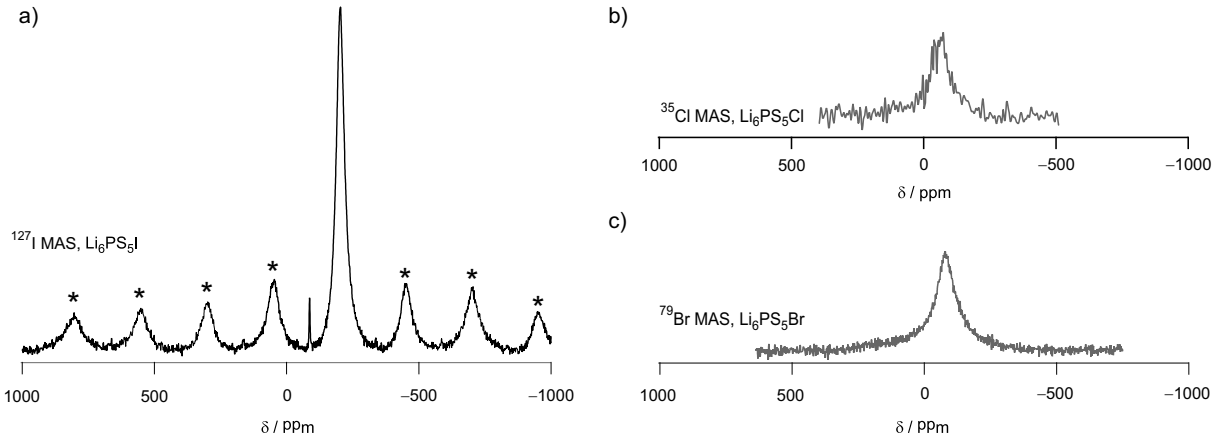

Fig. S3 ^{35}Cl, ^{79}Br and ^{127}I MAS NMR spectra. Asterisks, see the NMR spectrum of Li_6PS_5I, denote spinning sidebands. The narrow line at −86.4 ppm shows a negligible impurity phase.

MAS NMR spectra ere recorded with ambient bearing gas and drive gas pressure. We measured the average temperature of the rotor with external thermocouples in the direct vicinity of the rotor. According to calibration routines using lead nitrate (or KBr), under the conditions described the mean temperature inside the rotor is 34(2)°C.