Supporting information to

Refinement of the Crystal Structure of $Li_4P_2S_6$ using NMR Crystallography

Sven Neuberger[a], Sean P. Culver[b], Hellmut Eckert[c,d], Wolfgang G. Zeier[b], Jörn Schmedt auf der Günne[a]

a. Inorganic Materials Chemistry, University of Siegen, Adolf-Reichwein-Straße 2, 57076 Siegen, Germany

b. Institute of Physical Chemistry, Justus-Liebig-University Giessen, Heinrich-Buff-Ring 17, D-35392 Giessen, Germany

c. Institute of Physics in São Carlos, University of São Paulo, Av. Trabalhador Sãocarlense 400, Sao Carlos, SP 13566-590, Brazil

d. Institute of Physical Chemistry, WWU Münster, Corrensstraße 30, D-48149 Münster, Germany

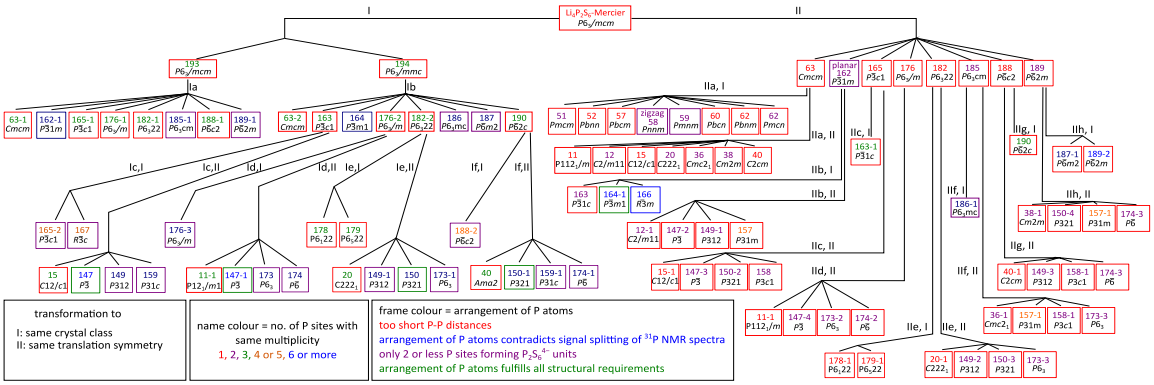


Fig. S1 Group-subgroup diagram starting from the literature structure of $Li_4P_2S_6$ with space group 193.

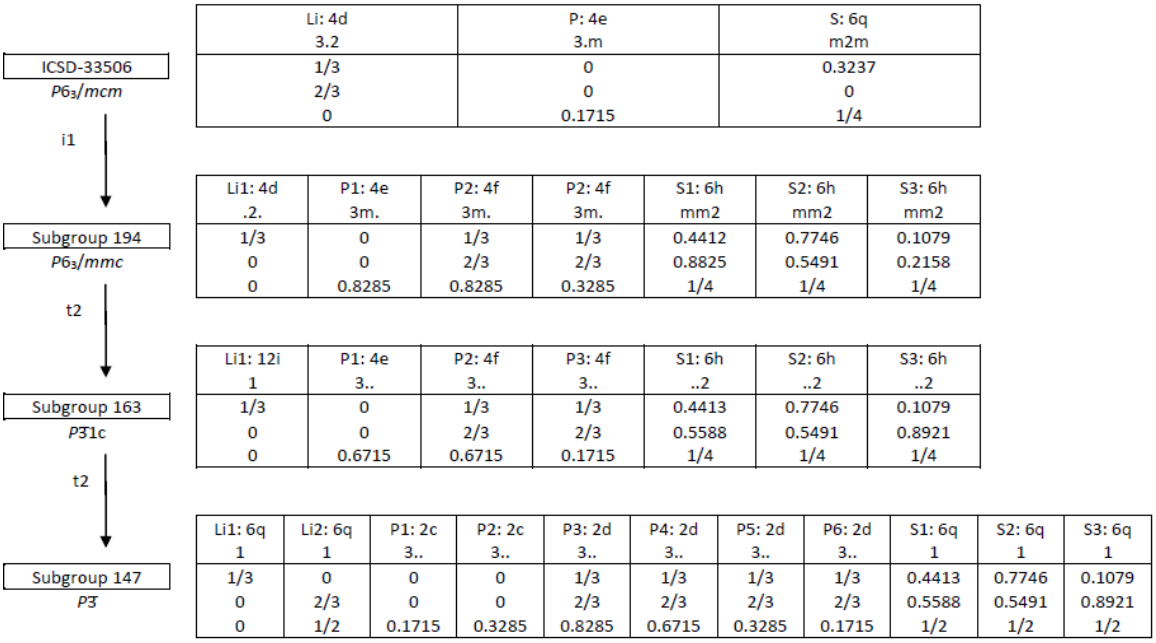
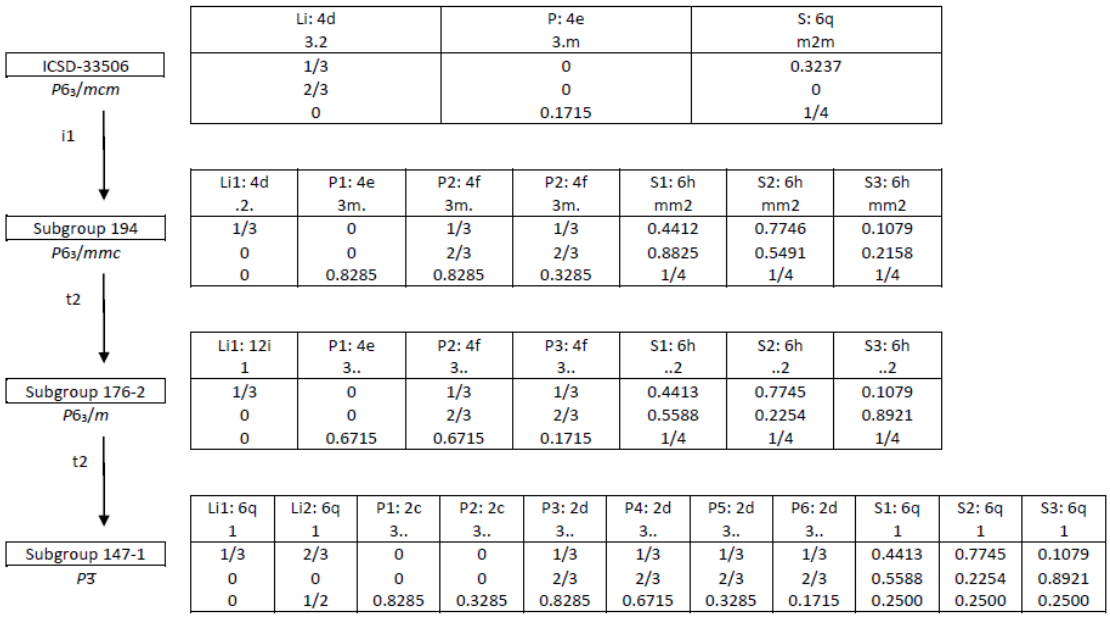


Fig. S2 Tree diagram for the symmetry reduction to structure *P3̄* (147)



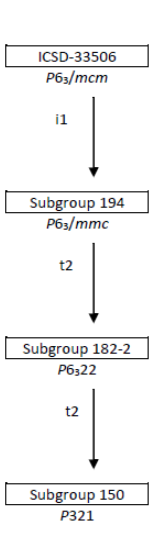
Li: 4d	P: 4e	S: 6q
3.2	3.m	m2m
1/3	0	0.3237
2/3	0	0
0	0.1715	1/4

Li1: 4d	P1: 4e	P2: 4f	P2: 4f	S1: 6h	S2: 6h	S3: 6h
.2.	3m.	3m.	3m.	mm2	mm2	mm2
1/3	0	1/3	1/3	0.4412	0.7746	0.1079
0	0	2/3	2/3	0.8825	0.5491	0.2158
0	0.8285	0.8285	0.3285	1/4	1/4	1/4

Li1: 12i	P1: 4e	P2: 4f	P3: 4f	S1: 6h	S2: 6h	S3: 6h
1	3..	3..	3..	..2	..2	..2
1/3	0	1/3	1/3	0.4413	0.7745	0.1079
0	0	2/3	2/3	0.5588	0.2254	0.8921
0	0.6715	0.6715	0.1715	1/4	1/4	1/4

Li1: 6q	Li2: 6q	P1: 2c	P2: 2c	P3: 2d	P4: 2d	P5: 2d	P6: 2d	S1: 6q	S2: 6q	S3: 6q
1	1	3..	3..	3..	3..	3..	3..	1	1	1
1/3	2/3	0	0	1/3	1/3	1/3	1/3	0.4413	0.7745	0.1079
0	0	0	0	2/3	2/3	2/3	2/3	0.5588	0.2254	0.8921
0	1/2	0.8285	0.3285	0.8285	0.6715	0.3285	0.1715	0.2500	0.2500	0.2500

Fig. S3 Tree diagram for the symmetry reduction to structure *P*3̄ (147-1)



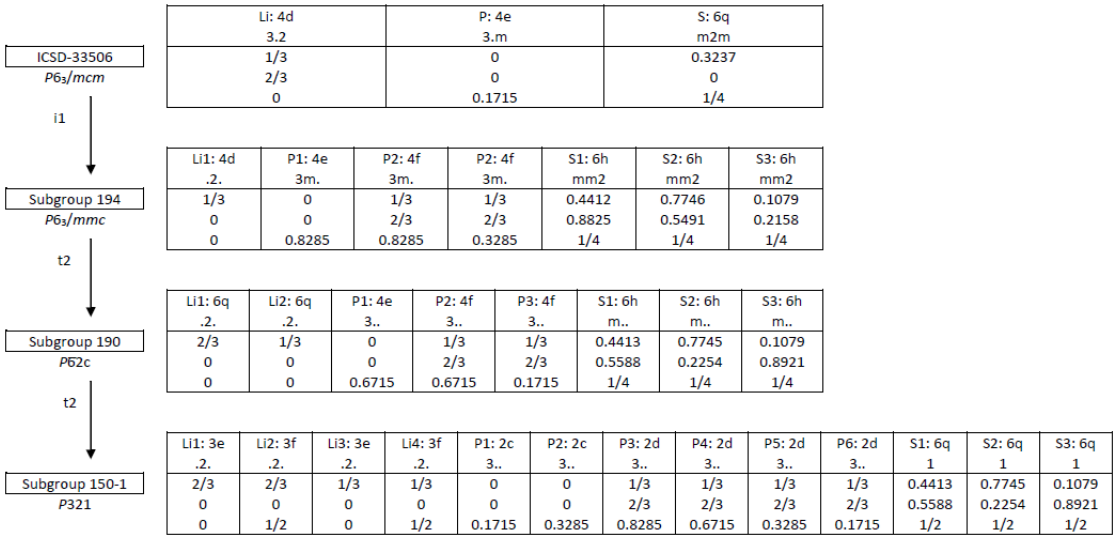
Li: 4d	P: 4e	S: 6q
3.2	3.m	m2m
1/3	0	0.3237
2/3	0	0
0	0.1715	1/4

Li1: 4d	P1: 4e	P2: 4f	P2: 4f	S1: 6h	S2: 6h	S3: 6h
.2.	3m.	3m.	3m.	mm2	mm2	mm2
1/3	0	1/3	1/3	0.4412	0.7746	0.1079
0	0	2/3	2/3	0.8825	0.5491	0.2158
0	0.8285	0.8285	0.3285	1/4	1/4	1/4

Li1: 6q	Li2: 6q	P1: 4e	P2: 4f	P3: 4f	S1: 6h	S2: 6h	S3: 6h
.2.	.2.	3..	3..	3..	..2	..2	..2
2/3	1/3	0	1/3	1/3	0.4412	0.7746	0.1079
0	0	0	2/3	2/3	0.8825	0.5491	0.2158
0	0	0.6715	0.6715	0.1715	1/4	1/4	1/4

Li1: 3e	Li2: 3f	Li3: 3e	Li4: 3f	P1: 2c	P2: 2c	P3: 2d	P4: 2d	P5: 2d	P6: 2d	S1: 6q	S2: 6q	S3: 6q
.2.	.2.	.2.	.2.	3..	3..	3..	3..	3..	3..	1	1	1
2/3	1/3	1/3	2/3	0	0	1/3	1/3	1/3	1/3	0.4412	0.7746	0.1079
0	0	0	0	0	0	2/3	2/3	2/3	2/3	0.8825	0.5491	0.2158
0	1/2	0	1/2	0.8285	0.3285	0.8285	0.6715	0.3285	0.1715	0.2500	0.2500	0.2500

Fig. S4 Tree diagram for the symmetry reduction to structure *P*321 (150)



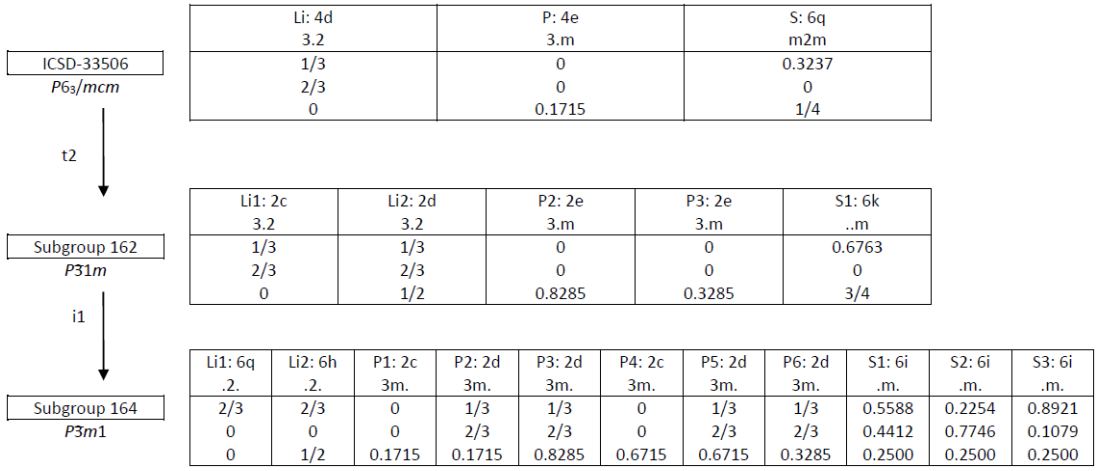
Li: 4d	P: 4e	S: 6q
3.2	3.m	m2m
1/3	0	0.3237
2/3	0	0
0	0.1715	1/4

Li1: 4d	P1: 4e	P2: 4f	P2: 4f	S1: 6h	S2: 6h	S3: 6h
.2.	3m.	3m.	3m.	mm2	mm2	mm2
1/3	0	1/3	1/3	0.4412	0.7746	0.1079
0	0	2/3	2/3	0.8825	0.5491	0.2158
0	0.8285	0.8285	0.3285	1/4	1/4	1/4

Li1: 6q	Li2: 6q	P1: 4e	P2: 4f	P3: 4f	S1: 6h	S2: 6h	S3: 6h
.2.	.2.	3..	3..	3..	m..	m..	m..
2/3	1/3	0	1/3	1/3	0.4413	0.7745	0.1079
0	0	0	2/3	2/3	0.5588	0.2254	0.8921
0	0	0.6715	0.6715	0.1715	1/4	1/4	1/4

Li1: 3e	Li2: 3f	Li3: 3e	Li4: 3f	P1: 2c	P2: 2c	P3: 2d	P4: 2d	P5: 2d	P6: 2d	S1: 6q	S2: 6q	S3: 6q
.2.	.2.	.2.	.2.	3..	3..	3..	3..	3..	3..	1	1	1
2/3	2/3	1/3	1/3	0	0	1/3	1/3	1/3	1/3	0.4413	0.7745	0.1079
0	0	0	0	0	0	2/3	2/3	2/3	2/3	0.5588	0.2254	0.8921
0	1/2	0	1/2	0.1715	0.3285	0.8285	0.6715	0.3285	0.1715	1/2	1/2	1/2

Fig. S5 Tree diagram for the symmetry reduction to structure *P*321 (150-1)



Li: 4d	P: 4e	S: 6q
3.2	3.m	m2m
1/3	0	0.3237
2/3	0	0
0	0.1715	1/4

Li1: 2c	Li2: 2d	P2: 2e	P3: 2e	S1: 6k
3.2	3.2	3.m	3.m	..m
1/3	1/3	0	0	0.6763
2/3	2/3	0	0	0
0	1/2	0.8285	0.3285	3/4

Li1: 6q	Li2: 6h	P1: 2c	P2: 2d	P3: 2d	P4: 2c	P5: 2d	P6: 2d	S1: 6i	S2: 6i	S3: 6i
.2.	.2.	3m.	3m.	3m.	3m.	3m.	3m.	.m.	.m.	.m.
2/3	2/3	0	1/3	1/3	0	1/3	1/3	0.5588	0.2254	0.8921
0	0	0	2/3	2/3	0	2/3	2/3	0.4412	0.7746	0.1079
0	1/2	0.1715	0.1715	0.8285	0.6715	0.6715	0.3285	0.2500	0.2500	0.2500

Fig. S6 Tree diagram for the symmetry reduction to structure *P*$\bar{3}$*m*1 (164)

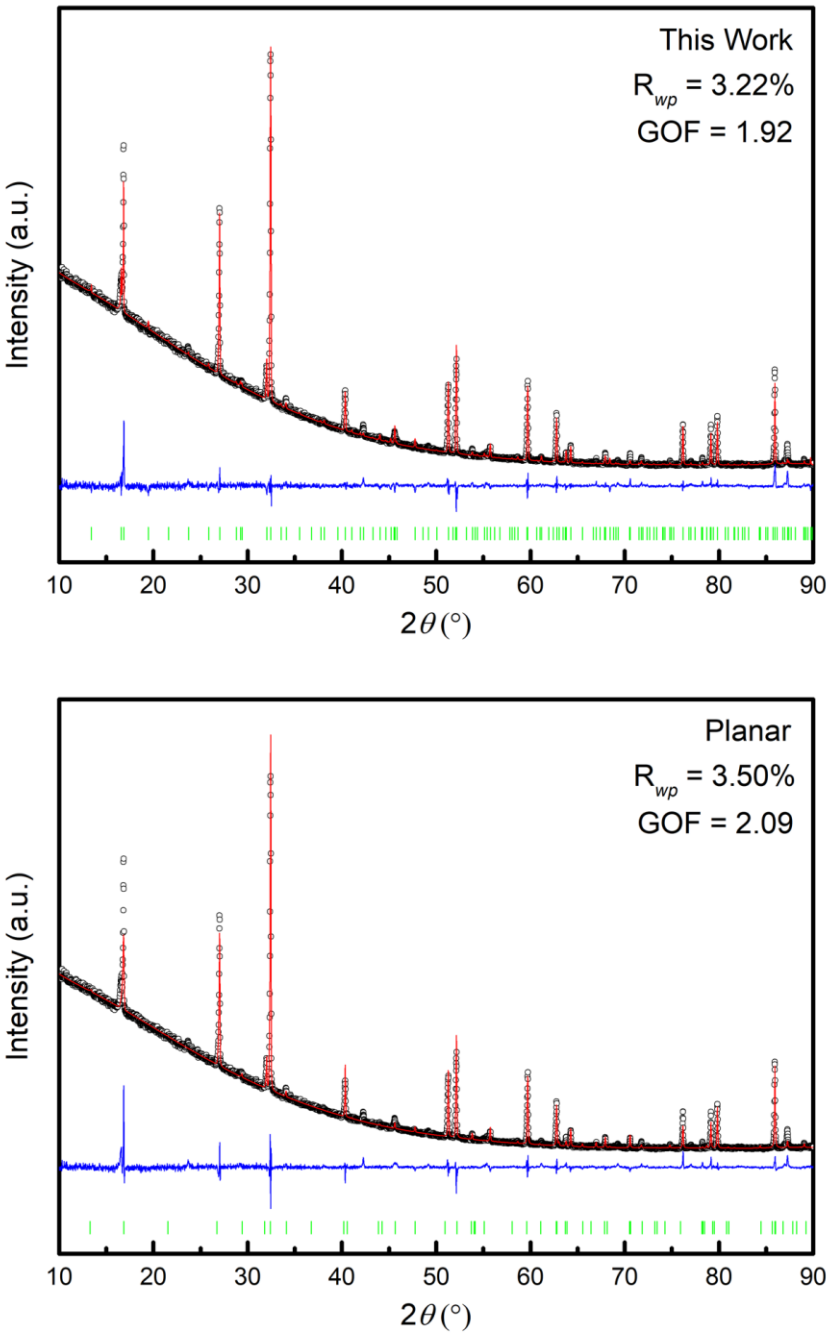


Fig. S7 Rietveld refinement against laboratory X-ray diffraction data of $Li_4P_2S_6$, using the new structural solution as well as the planar structure. The new structure leads to better refinement statistics.

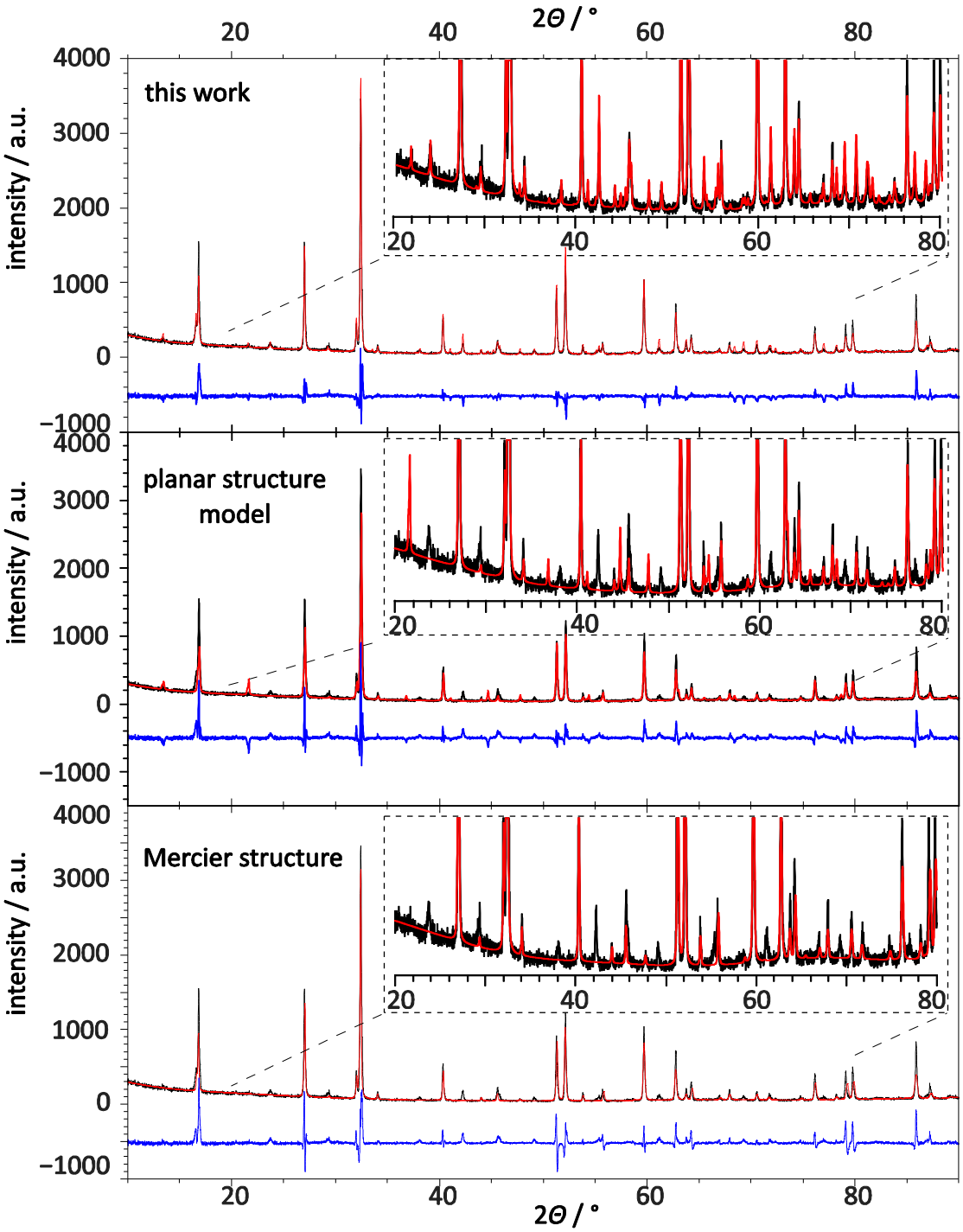


Fig. S8 Comparison of the small intensity reflections and the simulated diffraction patterns of the different structural models

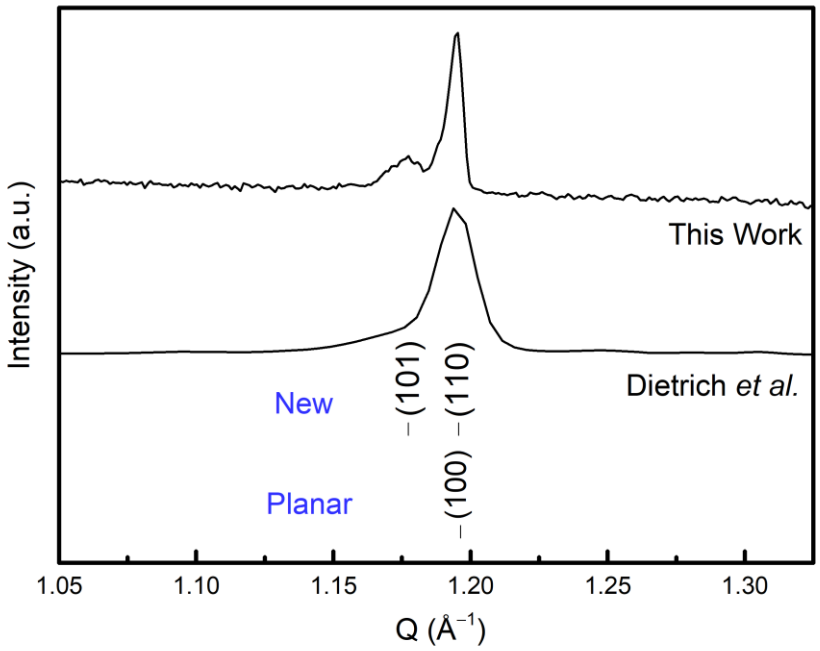


Fig. S9 Zoom in on the low angle reflections of the Lab X-ray and synchrotron diffraction pattern of $Li_4P_2S_6$. While the laboratory X-ray data clearly shows the presence of the (101) Miller reflection that only corresponds to the structure with space group *P*321, the lower crystallinity of $Li_4P_2S_6$ hides this reflection underneath the asymmetry in the synchrotron diffraction pattern.

Simulation formalism and algorithms

Density functional theory (DFT) calculations have been performed using the Quantum ESPRESSO[3] package and projector augmented wave (PAW) pseudopotentials[4] with the Perdew-Burke-Ernzerhof (PBE) functional[5] as exchange-correlation functional. A 10 x 10 x 11 Monkhorst-Pack[6] grid of *k* points was used. The force convergence threshold was set to 10^{-8} Ry/a.u., the convergence threshold for self-consistency to 10^{-10} Ry and the total energy convergence threshold was set to 10^{-10} Ry. The kinetic energy cutoff for wavefunctions was set to 25 Ry.
The calculated results were converted via XCrysDen[7] and VESTA 3[8] into a SHELX file and the symmetry of the calculated structure analysed with KPLOT[9] and normalized in Platon.[10]
VESTA[8] was also used to calculate the Madelung energies per formula unit $Li_4P_2S_6$ in order to compare the stability of the different structural models in a reciprocal space range of 4 $Å^{-1}$. Because the atoms are covalently bonded in the complex anion $P_2S_6^{4-}$, formal charges were used for each atom. VESTA considers site occupancy factors for each atom to calculate the Madelung energies.

Comparison with the calculated structure

The calculated crystal structure also belongs to the space group *P*321. The atom coordinates from the DFT optimization agree with the experimental values within their error limits. The structural parameters of the calculated structure are listed in Table S1.

Table S1: Crystallographic data of $Li_4P_2S_6$ after DFT optimization at 0 K.

$Li_4P_2S_6$ structure from DFT calculation (space group *P*321, No.150) *a* = 10.53662 Å; *c* = 6.56313 Å					
Atom	Wyckoff site	x/*a*	y/*b*	z/*c*	Occ.
Li1	3e	0.64099	0	0	1.0
Li2	3f	0.64236	0	0.5	1.0
Li3	3e	0.31293	0	0	1.0
Li4	3f	0.32632	0	0.5	1.0
P1	2c	0	0	0.17246	1.0
P2	2d	0.33333	0.66667	0.67039	1.0
P3	2d	0.33333	0.66667	0.32468	1.0
S1	6g	0.11404	0.21739	0.24493	1.0
S2	6g	0.11656	0.54755	0.25142	1.0
S3	6g	0.44952	0.22964	0.25780	1.0

The calculated Madelung energies per formula unit $Li_4P_2S_6$ are listed in Table S2. The Madelung energy of the new structural model is a bit lower, which indicates a higher stability of this structure. But in comparison, the deviations of the different energies of all three models are minor. This might be due to the fact that the different structural models only differ in the positions of the P-atoms.

Table S2: Comparison of the Madelung energies of the different structural models per formula unit $Li_4P_2S_6$

Structure model	Madelung energy / MJ · mol^{-1}
Mercier[1]	−5.158
Planar[2]	−5.649
This work	−5.670

References

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