Electronic Supplementary Information

Synthesis of crystalline $Na_2P_2S_6$ via a ball milling route and comparison of its local structure to the amorphous phase

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Table S1: Refined structural parameters obtained from powder diffraction of crystalline $Na_2P_2S_6$ at room temperature compared to those of a single crystal measurement from Ref. [13].

	$Na_2P_2S_6$ synthesized by ballmilling and subsequent thermal annealing	$Na_2P_2S_6$ synthesized by solid state reaction by Lotsch et al. [9]
Space group	$P2_1/m$ (11)	$P2_1/m$ (11)
Lattice parameters		
a / Å	6.6861(3)	6.6752(3)
b / Å	7.8314 (4)	7.7968(4)
c / Å	9.0418 (4)	9.0379(4)
β / °	90.223 (4)	90.151(1)
Cell volume	473.44 (4)	470.38(4)
Atomic coordinates Na		
x	0.2829 (0.0028)	0.2863(2)
y	0.0136 (0.0017)	0.01241(9)
z	0.7130 (0.0016)	0.71003(7)
Structural strain dD/D *10E-4	34.34 (0.12)	-
GOF	2.458	1.090

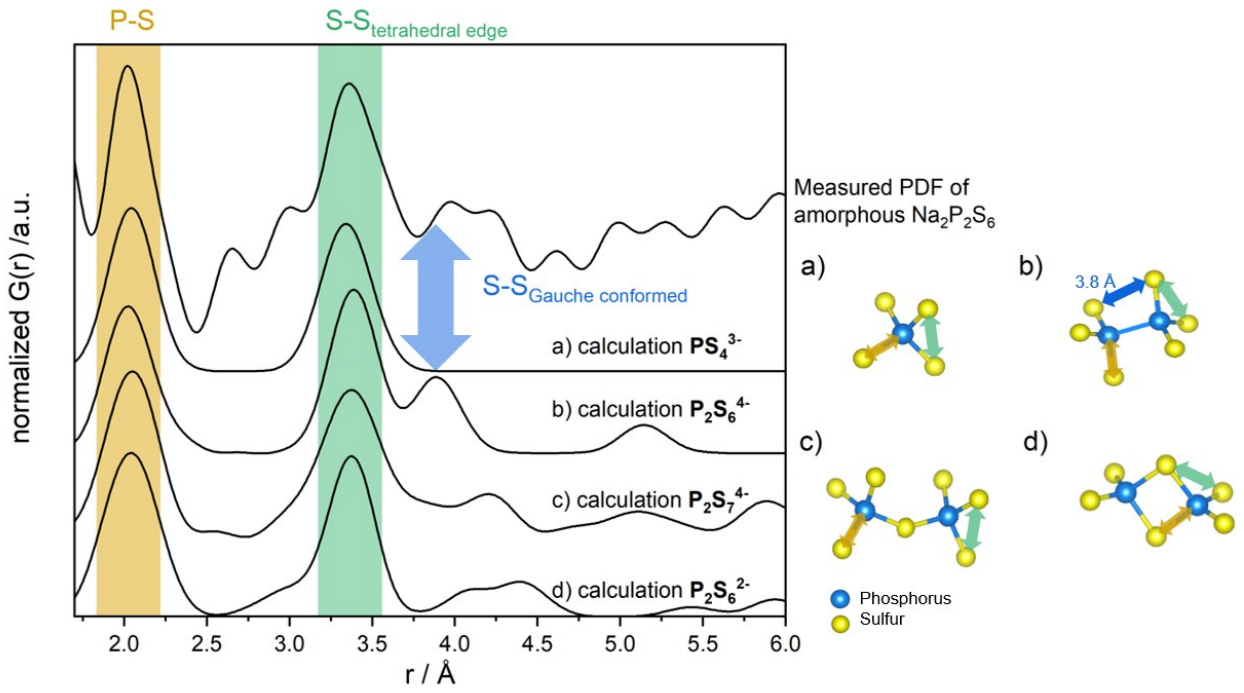

Figure S1: Zoom into the short range region of the pair distribution functions of amorphous $Na_2P_2S_6$ compared with modeled PDFs of single $[PS_4]^{3-}$, $[P_2S_6]^{4-}$, $[P_2S_7]^{4-}$ and $[P_2S_6]^{2-}$ structural building blocks. Atomic distances are marked with yellow, green and blue arrows.

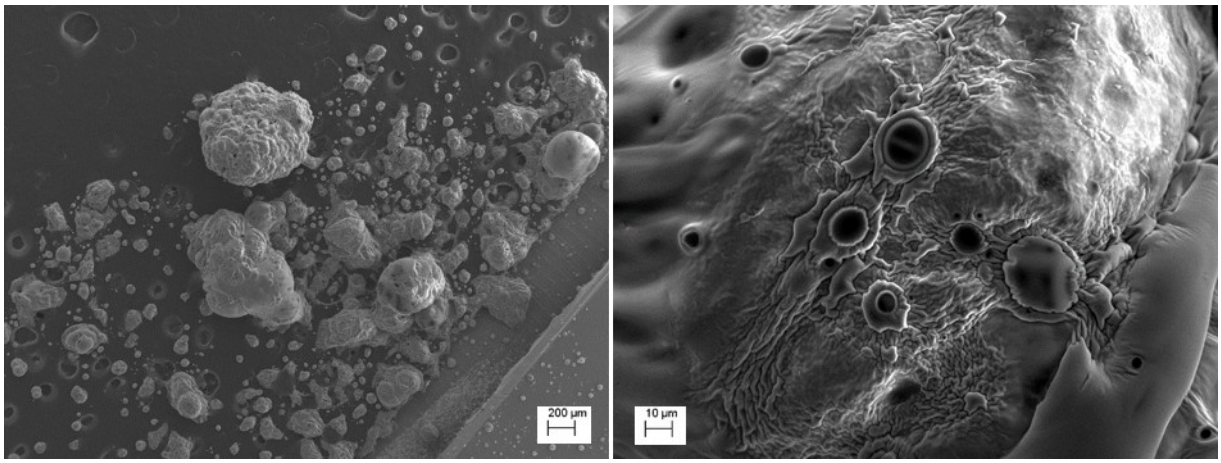

Figure S2: FigureS1-SEM image of amorphous $Na_2P_2S_6$.

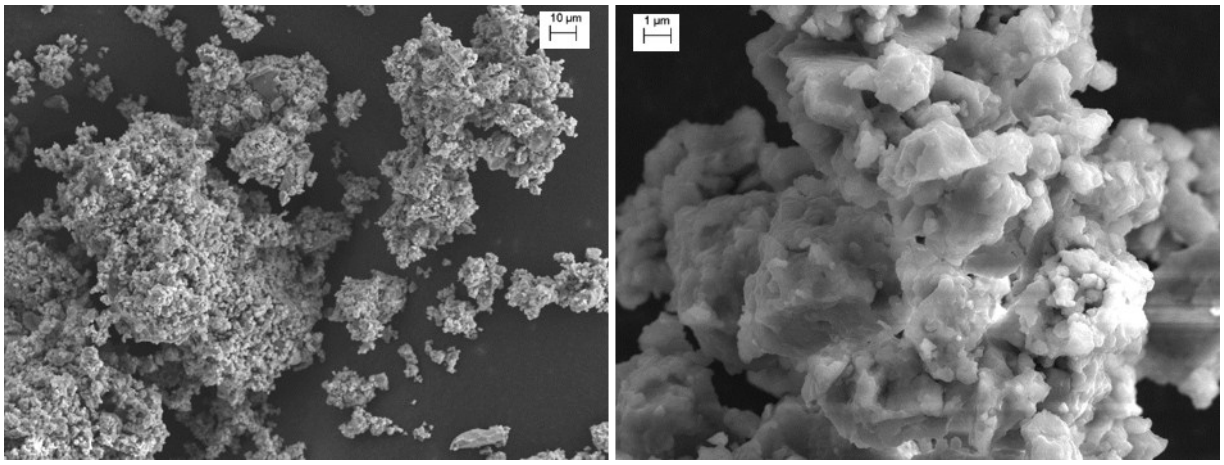

Figure 10: Figure S2-SEM image of crystalline $Na_2P_2S_6$.

Comparison of crystal structures of the same symmetry $P2_1/m$ (No. 11) [unique axis b]

Structure #1

11

6.67893 7.81782 9.05651 90.00000 90.35290 90.00000

8

P	1	2e	0.210080	0.250000	0.390070
P	3	2e	0.322040	0.250000	0.082430
S	1	4f	0.228740	0.448750	0.226260
S	5	2e	0.618980	0.250000	0.043230
S	7	2e	0.447430	0.250000	0.519680
S	9	2e	0.147200	0.250000	0.899310
S	11	2e	0.944070	0.250000	0.486700
Na	1	4f	0.287390	0.990860	0.700950

Structure #2

11

6.68609 7.83137 9.04181 90.0000 90.2232 90.0000

8

P	1	2e	0.786600	0.250000	0.613400

P	2	2e	0.684100	0.250000	0.925800
S	1	4f	0.237800	0.549100	0.225300
S	2	2e	0.385500	0.250000	0.949900
S	3	2e	0.545700	0.250000	0.483800
S	4	2e	0.854600	0.250000	0.089600
S	5	2e	0.046000	0.250000	0.515000
Na	1	4f	0.282900	0.013600	0.713000

Description of Structure #2 in the most similar configuration to Structure #1

011

6.686090 7.831370 9.041810 90.000000 90.223198 90.000000

8

P	1	2e	0.213400	0.250000	0.386600
P	2	2e	0.315900	0.250000	0.074200
S	1	4f	0.237800	0.450900	0.225300
S	2	2e	0.614500	0.250000	0.050100
S	3	2e	0.454300	0.250000	0.516200
S	4	2e	0.145400	0.250000	0.910400
S	5	2e	0.954000	0.250000	0.485000
Na	1	4f	0.282900	0.986400	0.713000

Transformation matrix (**P**, p): **a,b,c** ; 0,1/2,0
Matrix form:

$$(\mathbf{P}, p) = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 1/2 \\ 0 & 0 & 1 & 0 \end{pmatrix}$$

Atom pairings and distances

Atom Mappings					
WP		Atom	Coordinates in S_1	Atom	Coordinates in S_2
2e	(x,1/4,z)	P1	(0.210080,0.250000,0.390070)	P1	(0.213400,0.250000,0.386600)
2e	(x,1/4,z)	P3	(0.322040,0.250000,0.082430)	P2	(0.315900,0.250000,0.074200)
4f	(x,y,z)	S1	(0.228740,0.448750,0.226260)	S1	(0.237800,0.450900,0.225300)

2e	(x,1/4,z)	S5	(0.618980,0.250000,0.043230)	S2	(0.614500,0.250000,0.050100)
2e	(x,1/4,z)	S7	(0.447430,0.250000,0.519680)	S3	(0.454300,0.250000,0.516200)
2e	(x,1/4,z)	S9	(0.147200,0.250000,0.899310)	S4	(0.145400,0.250000,0.910400)
2e	(x,1/4,z)	S11	(0.944070,0.250000,0.486700)	S5	(0.954000,0.250000,0.485000)
4f	(x,y,z)	Na1	(0.287390,0.990860,0.700950)	Na1	(0.282900,0.986400,0.713000)

WP		Atom	Atomic Displacements			
			u_x	u_y	u_z	|u|
2e	(x,1/4,z)	P1	0.0033	0.0000	-0.0035	0.0386
2e	(x,1/4,z)	P3	-0.0061	0.0000	-0.0082	0.0849
4f	(x,y,z)	S1	0.0091	0.0022	-0.0010	0.0635
2e	(x,1/4,z)	S5	-0.0045	0.0000	0.0069	0.0692
2e	(x,1/4,z)	S7	0.0069	0.0000	-0.0035	0.0558
2e	(x,1/4,z)	S9	-0.0018	0.0000	0.0111	0.1012
2e	(x,1/4,z)	S11	0.0099	0.0000	-0.0017	0.0682
4f	(x,y,z)	Na1	-0.0045	-0.0045	0.0120	0.1186

NOTE: u_x, u_y and u_z are given in relative units. |u| is the absolute distance given in Å

Evaluation of the structure similarity

S	$d_{max.}$ (Å)	$d_{av.}$ (Å)	Δ
0.0010	0.1186	0.0782	0.016

- Lattice and atomic position criteria:
    - The degree of lattice distortion (**S**) is the spontaneous strain (sum of the squared eigenvalues of the strain tensor divided by 3). For the given two structures, the **degree of lattice distortion (S)** is **0.0010**.
    - The maximum distance ($\mathbf{d_{max.}}$) shows the maximal displacement between the atomic positions of the paired atoms. The **maximum distance ($\mathbf{d_{max.}}$)** in this case is: **0.1186 Å**
- The arithmetic mean ($\mathbf{d_{av}}$) of the distance. In this case, the **arithmetic mean ($\mathbf{d_{av}}$)** is **0.0782 Å**

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- The measure of similarity (**Δ**) (Bergerhoff *et al.*, 1998) is a function of the differences in atomic positions (weighted by the multiplicities of the sites) and the ratios of the

corresponding lattice parameters of the structures. The **measure of similarity (Δ)** calculated for this case is **0.016**.