Supporting Information

Morphology-dependent Li^+ ion dynamics in X-ray amorphous and crystalline Li_3PS_4 prepared by solvent-assisted synthesis

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Figure S1 shows the X-ray powder diffraction pattern of polycrystalline LPS-170 obtained after annealing at 170 °C. The results from Rietveld refinement are also included.

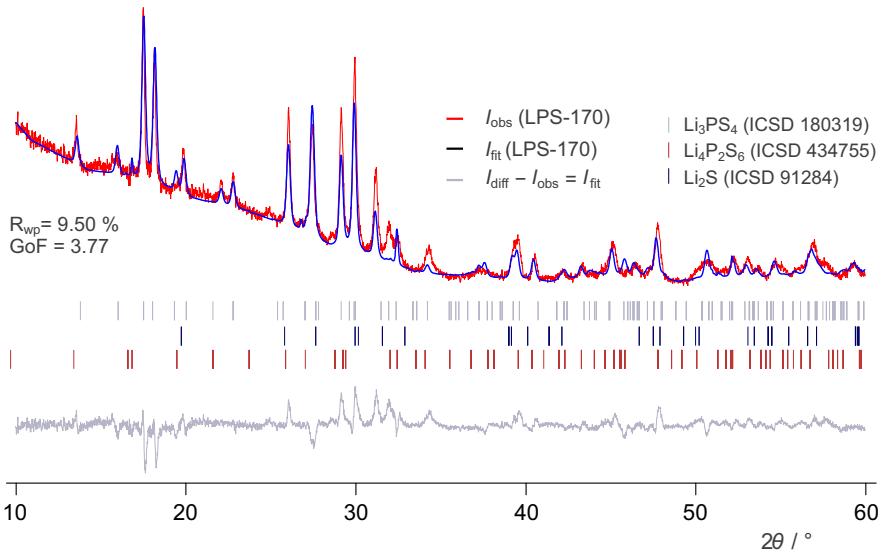

Figure S1: XRD pattern of LPS-170, as shown in Figure 1, together the results from Rietveld refinement (blue line) and the reference patterns of Li_3Ps_4, $Li_4P_2S_{10}$ and Li_2S taken from the ICSD. The grey line at the bottom shows the difference between the refined fit and the observed diffraction pattern. The side phases each represent ≈ 3 % of the sample.

In Figure S2 we compare the conductivity isotherms of the three samples investigated. The isotherms have been recorded at 40 °C; their shapes turn out to be rather similar.

Finally, the rates of mechanosynthesized Li_3PS_4 recorded by Prutsch *et al.*[1] have also been analysed with a relaxation model that takes into account spatially restricted 1D jump diffusion, see Figure S3. The solid line in Figure S3 shows the result obtained with a sum of two $R_1(1/T)$ rate

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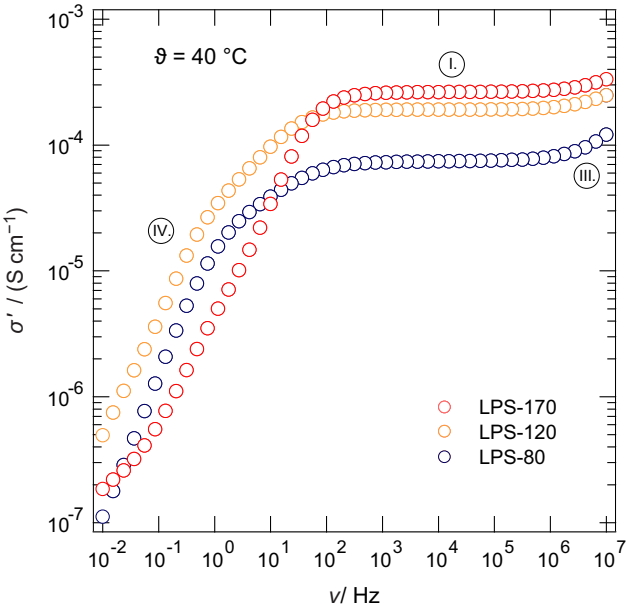

Figure S2: Comparison of the conductivity isotherms $\sigma'(\nu)$ for all samples prepared, that is, LPS-170, LPS-120, and LPS-80; data recorded at $\vartheta = 40\,^{\circ}\mathrm{C}$.

peaks that each use an empirical spectral density function $J(\omega_0)$, which properly reflects the limiting behaviour of $R_1 \equiv 1/T_1$ for $\omega_0\tau \ll 1$, that is, yielding a $\sqrt{\omega_0}$-dependence of T_1 on frequency:[2]

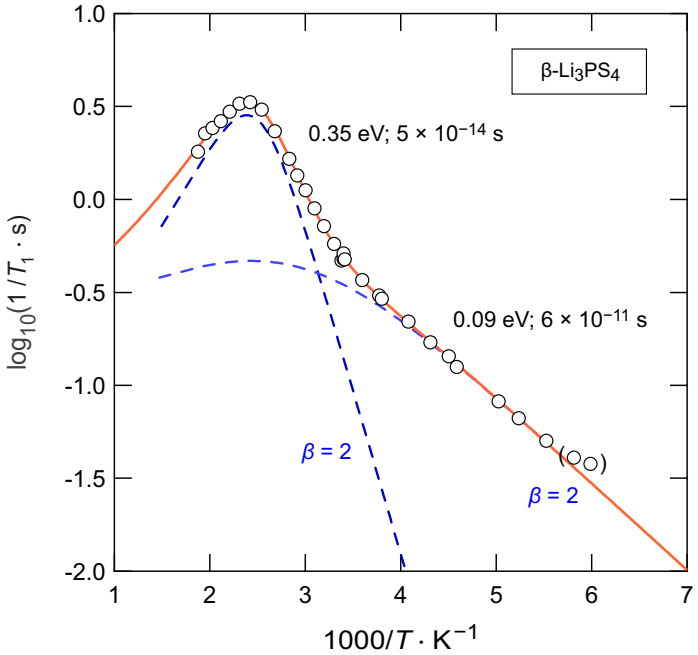

Figure S3: ^{7}Li NMR relaxation rates R_1 of Li_3PS_4 recorded in the laboratory reference frame; the rates are identical with those shown in Figure 5a. Here, the solid line represents a fit with a sum of two rate peaks that take into account a spectral density function $J(\omega_0)$ mirroring the limiting cases for 1D diffusion. The individual peaks are drawn by dashed lines. In both cases, the best fit was obtained with the asymmetry parameter β taking a value of 2, thus following ideal BPP-type behavior for which we expect $R_1 \propto \omega_0^{-\beta}$ in the limit $\omega_0\tau \gg 1$.

$$J(\omega_0, \tau_c)^{1D} \propto \tau_c \frac{(\omega_0 \tau_c)^{-0.5}}{1 + (\omega_0 \tau_c)^{\beta - 0.5}}$$

The relaxation rate $R_1 \propto J(\omega_0, \tau_c)$ is hence controlled by ω_0 and $\tau_c = \tau_{c0} \exp(-E_a/(k_B T))$. The same function has earlier been used to parameterize the NMR relaxation in ramsdellite-type $Li_2Ti_3O_7$.[3] In Figure S3 the values in eV reflect the activation energies E_a referring to the two rate peaks. In the case of $\beta = 2$, which yields the best fits, the slope of the low-T flank directly delivers E_a as no correlation effects ($\beta < 2$) seem to affect the data. The values in s show the Arrhenius pre-exponential factors τ_{c0}, which can be interpreted as attempt frequencies. Values as high as 10^{14} s^{-1} for $1/\tau_{c0}$ are 1 to 1.5 orders of magnitude higher than Debye frequencies, as expected.

References

(1) Prutsch, D.; Gadermaier, B.; Brandstätter, H.; Pregartner, V.; Stanje, B.; Wohlmuth, D.; Epp, V.; Rettenwander, D.; Hanzu, I.; Wilkening, H. M. R. Nuclear Spin Relaxation in Nanocrystalline β-Li_3PS_4 Reveals Low-Dimensional Li Diffusion in an Isotropic Matrix. *Chem. Mater.* **2018**, *30*, 7575–7586.

(2) Heine, J. NMR- und impedanzspektroskopische Untersuchungen an Lithium-Ionenleitern mit eingeschränkter Dimensionalität der Diffusion. Doctoral Thesis, Leibniz University of Hannover, Leibniz University of Hannover, 2020.

(3) Volgmann, K.; Epp, V.; Langer, J.; Stanje, B.; Heine, J.; Nakhal, S.; Lerch, M.; Wilkening, M.; Heitjans, P. Solid-State NMR to Study Translational Li Ion Dynamics in Solids with Low-Dimensional Diffusion Pathways. *Z. Phys. Chem.* **2017**, *231*, 1215–1241.