

**Supplementary Information:**

**$^6\text{Li}$  MAS NMR spectroscopy and first-principles calculations as a combined tool  
for the investigation of  $\text{Li}_2\text{MnSiO}_4$  polymorphs**

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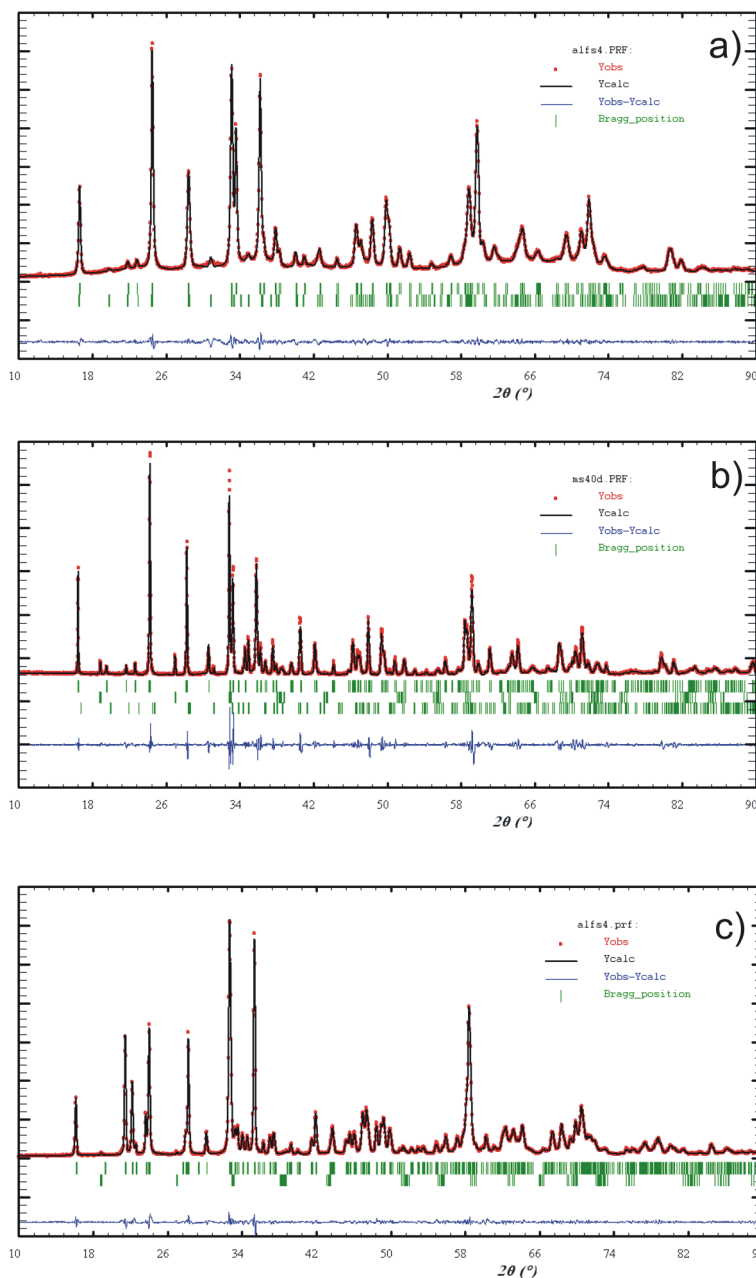
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Hydrothermal synthesis was carried out using one equivalent of  $\text{MnCl}_2 \cdot \text{H}_2\text{O}$  (Aldrich), one equivalent of  $\text{SiO}_2$  (Cab-osil<sup>®</sup> M-5, Riedel-de Haën) and four equivalents of  $\text{LiOH} \cdot \text{H}_2\text{O}$  (Aldrich). Typically half a mol of  $\text{SiO}_2$  was dispersed in 100 ml of oxygen-free mili-Q water in the ultra sound bath within one hour. Then subsequently  $\text{LiOH}$  and  $\text{MnCl}_2$  solutions were added under vigorous stirring in argon atmosphere. The prepared slurry was sealed into Teflon-lined stainless-steel reactor (Berghof) under the overpressure of argon (10 bar) and left there for 6 hours at  $180^\circ\text{C}$ . After the synthesis was completed, the resulting powder was washed with  $\text{LiOH}$  solution and dried at  $100^\circ\text{C}$  in an argon atmosphere. As prepared sample, heated to  $400^\circ\text{C}$  in argon atmosphere, showed equal isotropic NMR shift as high pressure/high temperature treated sample in one of our previous studies [1]. Its X-ray diffraction pattern was also successfully fitted using  $Pmn2_1$  space group (Fig. S1a). The other two samples were prepared by additional thermal treatment. Based on first principle calculations [1] and on the previous work [2]  $\text{Li}_2\text{MnSiO}_4$  polymorph with a  $Pmnb$  space group could be prepared by slow cooling of the sample from  $900^\circ\text{C}$  (Fig. S1b). Thus one part of hydrothermally prepared sample was heated to  $900^\circ\text{C}$  in argon atmosphere, left there for 3 hours, and was then cooled down to room temperature with a rate of  $1^\circ\text{C}/\text{min}$ . The last sample in our study,  $\gamma\text{-Li}_2\text{MnSiO}_4$  polymorph, whose X-ray diffraction pattern can be fitted using  $P2_1/n$  space group, was obtained by thermal treatment of the hydrothermally prepared sample at  $900^\circ\text{C}$  for 6 hours, followed by quenching to room temperature in argon atmosphere (Fig. S1c).

X-ray diffraction patterns of the  $\text{Li}_2\text{MnSiO}_4$  polymorphs were collected at room temperature using Siemens D5000 powder diffractometer in the  $10\text{-}90^\circ 2\theta$  range in steps of  $0.04^\circ$  ( $2\theta$ ) with the constant counting time of 16 s per step. The patterns were analyzed by Rietveld refinement as implemented in the Fullprof program [3]. Refined X-ray diffraction patterns are shown in Figure S1. All three  $\text{Li}_2\text{MnSiO}_4$  samples used in our study contain small amount of impurities identified as  $\text{Mn}_2\text{SiO}_4$  and/or  $\text{Li}_2\text{SiO}_3$ . Cell parameters for each polymorph and the agreements of fits with measurements are given in Table S1.

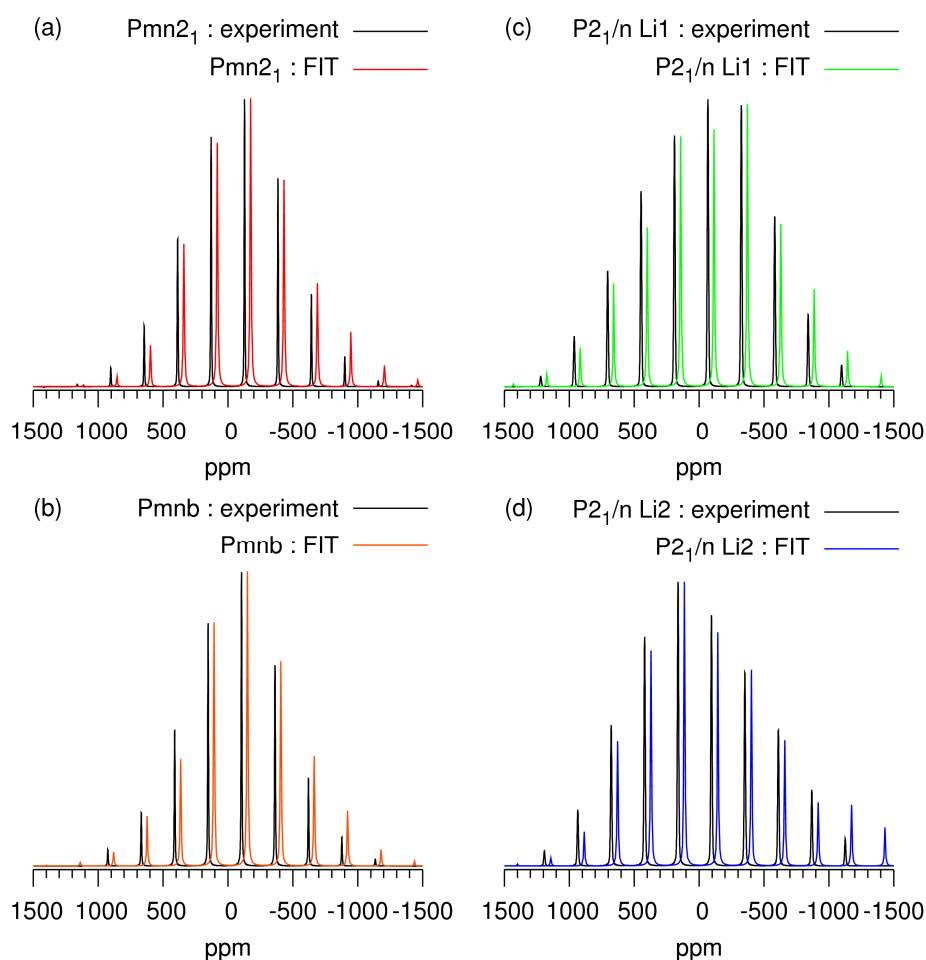
**Table S1:** Refined cell parameters for the  $\text{Li}_2\text{MnSiO}_4$  samples used in our study:

| Space group | $a$ (Å)   | $b$ (Å)    | $c$ (Å)   | $\beta$ (°) | Rwp   | $\chi^2$ |
|-------------|-----------|------------|-----------|-------------|-------|----------|
| $Pmn2_1$    | 6.2762(9) | 5.3355(8)  | 4.9614(9) | /           | 7.93% | 2.27     |
| $Pmnb$      | 6.3148(1) | 10.7742(5) | 5.0138(2) | /           | 11.5% | 7.49     |
| $P2_1/n$    | 6.3435(4) | 10.9208(7) | 5.0818(5) | 90.982(2)   | 8.28% | 4.15     |



**Figure S1:** X-ray diffraction patterns refined using the Rietveld method considering a)  $\text{Li}_2\text{MnSiO}_4$  crystallized in  $Pmn2_1$  space group with  $\text{Li}_2\text{SiO}_3$  as an impurity; b)  $\text{Li}_2\text{MnSiO}_4$  crystallized in  $Pmnb$  space group with  $\text{Li}_2\text{SiO}_3$  and  $\text{Mn}_2\text{SiO}_4$  as impurities; c)  $\text{Li}_2\text{MnSiO}_4$  crystallized in  $P2_1/n$  space group with  $\text{Mn}_2\text{SiO}_4$  as an impurity.

Solid-state  $^6\text{Li}$  magic-angle spinning (MAS) NMR spectra were recorded on a 600 MHz Varian NMR system, operating at  $^6\text{Li}$  Larmor frequency of 88.274 MHz, with rotation synchronized Hahn-echo pulse sequence. Sample rotation frequency was 22.73 kHz, repetition delay between consecutive scans was 0.1 s and number of scans was 15 000. Frequency axis in ppm is reported relative to the lithium signal of 1M solution of LiCl. Spinning-sideband powder patterns were analyzed by Spinevolution simulation package [4]. In addition to electron-nucleus dipolar interaction, which is formally equivalent to chemical shift anisotropy, weak electric quadrupolar interaction was also considered when fitting the spectra of  $^6\text{Li}$  nuclei. Measured and best-fit spectra are shown in Figure S2.



**Figure S2.** Spinning-sideband powder patterns for four different lithium sites in  $\text{Li}_2\text{MnSiO}_4$  polymorphs. The intensities of centerbands and spinning sidebands were first extracted from the measured spectra using ‘dmfit’ software [5]. The intensities were then used for comparison with simulated spectra during a Spinevolution fitting procedure.

First-principles calculations were performed using density functional theory (DFT) in the generalized gradient approximation of Perdew-Burke-Ernzerhof (GGA PBE) [6] with plane wave basis and norm-conserving pseudopotentials. In the first step the structures of  $\text{Li}_2\text{MnSiO}_4$  polymorphs,  $\text{Li}_2\text{MnO}_3$ ,  $\text{Li}_6\text{CoO}_4$ , and  $\text{LiMnPO}_4$  were relaxed and ‘final’ ground state energies were recalculated with the optimized geometries. In all calculations plane-wave cutoff energy was 1100 eV. The reciprocal-space sampling was performed with  $k$ -point grids of  $2 \times 4 \times 4$  points for  $\text{LiMnPO}_4$ ,  $4 \times 4 \times 4$  points for  $\text{Li}_2\text{MnSiO}_4$  polymorphs and for  $\text{Li}_2\text{MnO}_3$ , and  $6 \times 6 \times 4$  points for  $\text{Li}_6\text{CoO}_4$ . All-electron information was reconstructed using the Projector Augmented Wave (PAW) method [7] as implemented in Quantum Espresso’s GIPAW module [8]. The module yielded hyperfine coupling constants, which were then used for quantitative prediction of isotropic shifts.

## References

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