

Supplementary Materials: Mechanochemical Induced Structure Transformations in Lithium Titanates: A Detailed PXRD and ^6Li MAS NMR Study

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Formation of $\alpha\text{-Li}_2\text{TiO}_3$ from LiOH and TiO_2

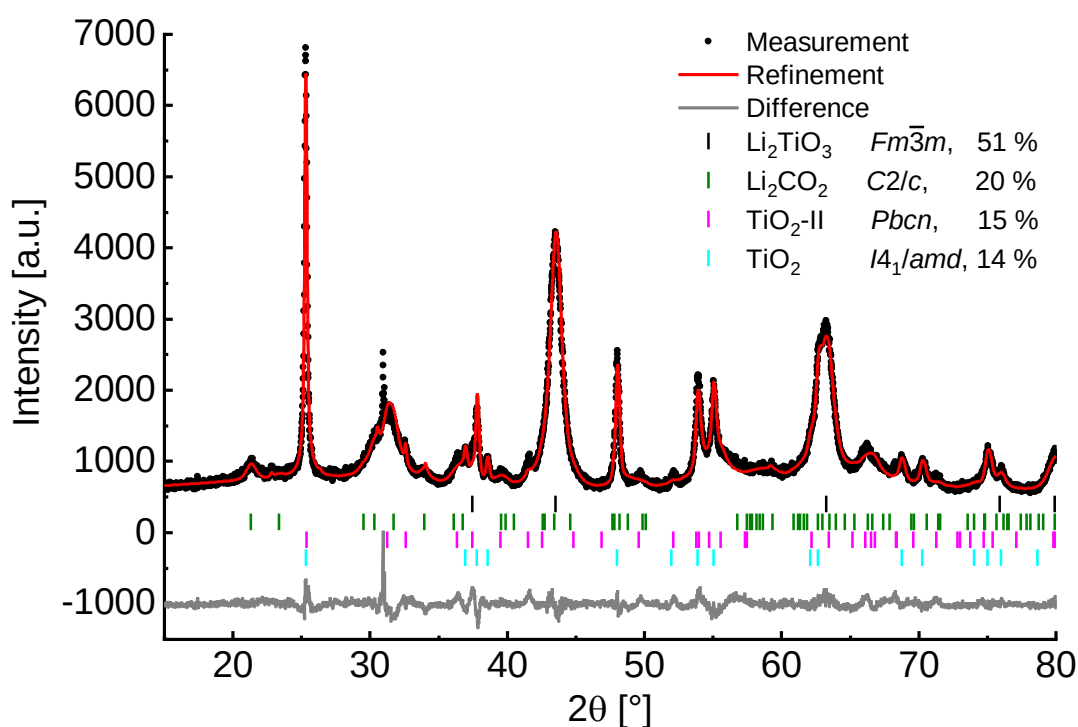


Figure S1: Rietveld refinement of the milling product from LiOH and anatase (ZrO_2 tools, 600 rpm, 6h). Li_2TiO_3 in SG $Fm\bar{3}m$ with $a = 4.1555(2) \text{ \AA}$, $V = 71.76(1) \text{ \AA}^3$, number of reflections = 8 and $R_{\text{Bragg}} = 0.99\%$. Refinement parameters: number of independent parameters = 46, $R_{\text{wp}} = 5.41\%$, $R_{\text{exp}} = 3.30\%$, $GOF = 1.64$.

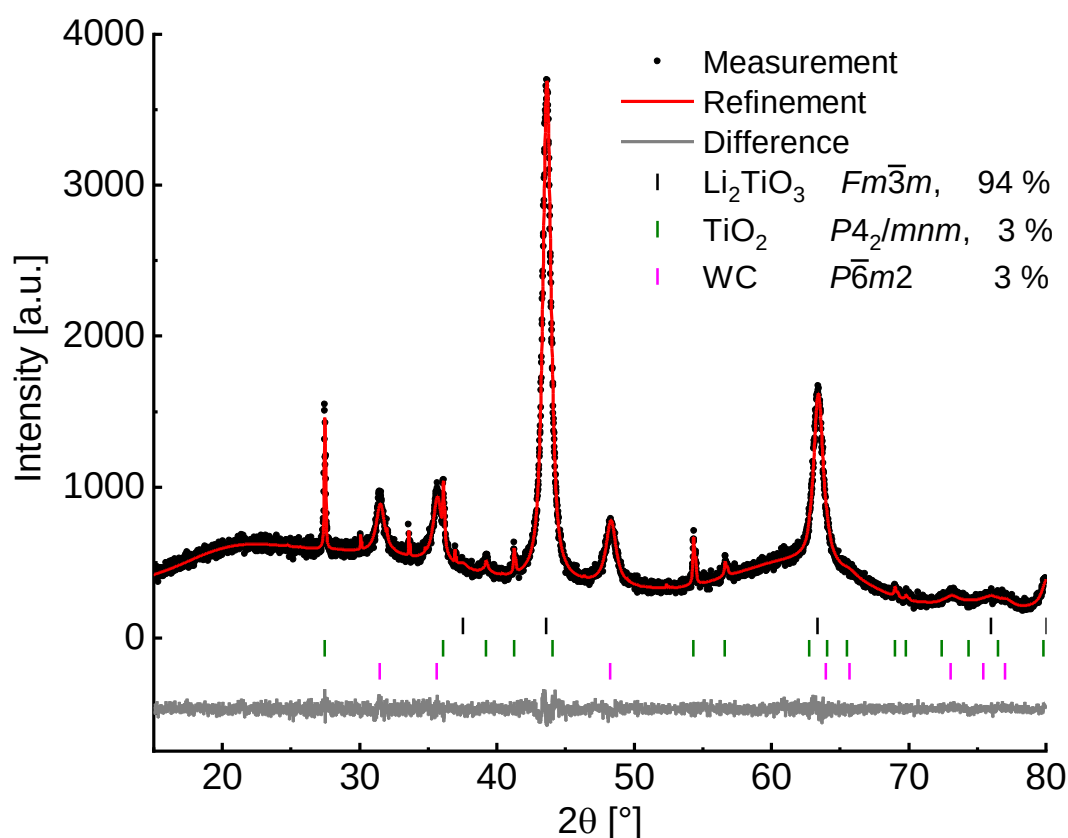


Figure S2: Rietveld refinement of the milling product from LiOH and rutile (WC tools, 600 rpm, 6h) after handling in the glovebox. Measurement was conducted with an air-tight dome sample holder (responsible for the background signal). The small percentage of crystalline TiO_2 is due to a small unreacted residue between milling vial and lid.

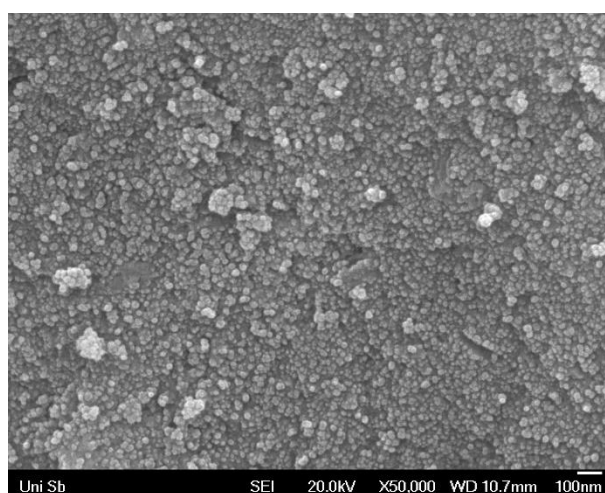


Figure S3: SEM photograph of the milling product from LiOH and rutile in WC tools at 600 rpm and 6h.

Table S1: Refined structure parameters of α -Li₂TiO₃ produced by milling of LiOH and rutile in WC tools at 600 rpm for 6 h. B_{iso} was constrained at the same value for all atoms in the refinement. Global refinement parameters: number of independent parameters = 40, R_{wp} = 3.44%, R_{exp} = 2.60%, GOF = 1.32. WP = Wyckoff position, sof = site occupancy factor.

SG	$Fm\bar{3}m$						
R_{Bragg}	1.17%						
No. of reflections	8						
Wt% Rietveld	68.3(4)						
Cell Mass	150.6(5)						
Cell Volume [$\text{\AA}^3$]	71.93(1)						
Lattice Parameter [$\text{\AA}$]	4.1588(2)						
Crystallite Size L_{vol} -IB [nm]	15.7(4)						
Strain e_0	0.18742						
Lin. Abs. Coeff. [cm^{-1}]	358(4)						
Crystal Density [g/cm^3]	3.48(1)						
Site	WP	x	y	z	Atom	sof	B_{iso}
Li1	$4a$	0	0	0	Li ⁺	0.46(2)	1.34(2)
	$4a$				Ti ⁴⁺	0.39(6)	1.34(2)
O1	$4b$	1/2	1/2	1/2	O ²⁻	1	1.34(2)

Thermogravimetric analysis

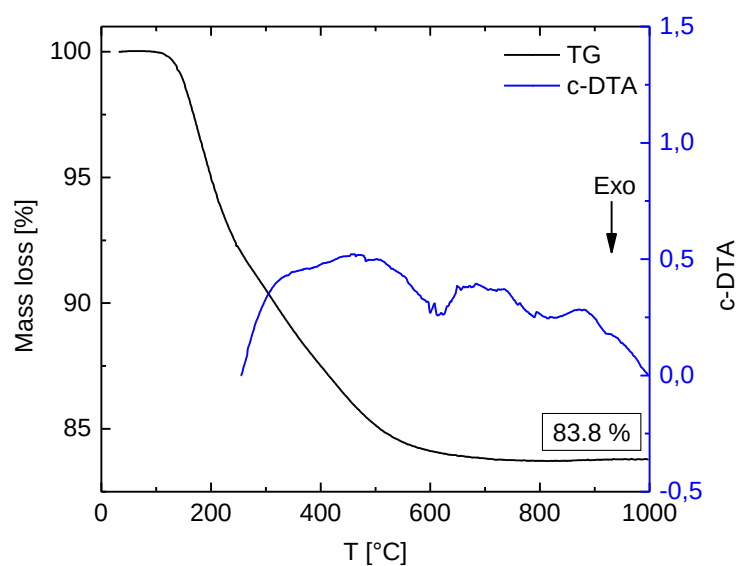


Figure S4: TGA and calculated DTA curve of Li_2TiO_3 from milling of LiOH and rutile in WC tools at 600 rpm for 6 h. Intermediate drying in N_2 atmosphere at 100 °C led to mass loss of 3%.

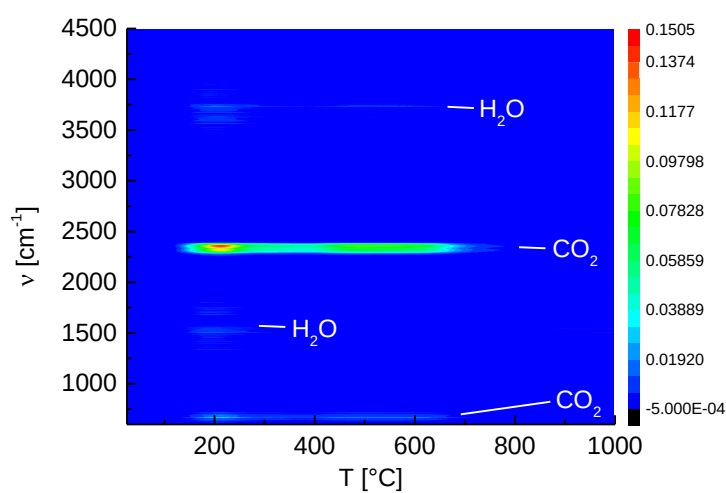


Figure S5: Temperature dependent IR signals from coupling of TGA gas flow to IR detector. Colors indicate intensity of the signals.

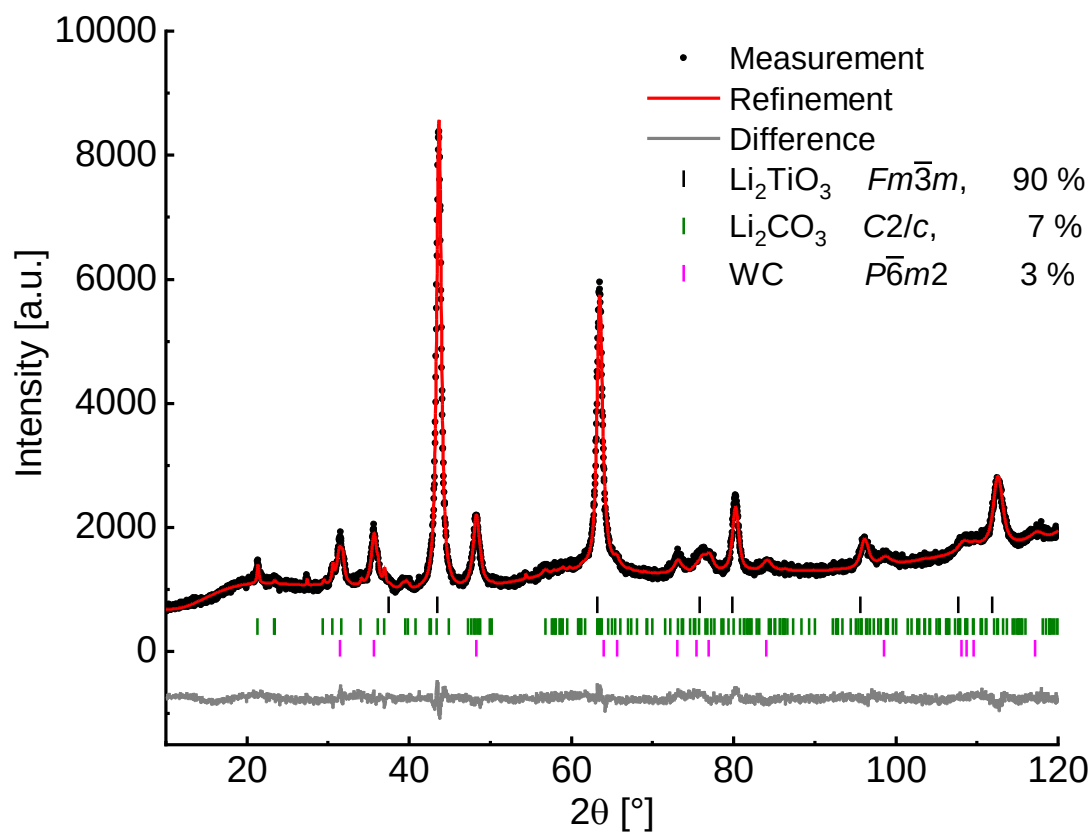
Thermal transformation of α -Li₂TiO₃ to β -Li₂TiO₃

Figure S6: Rietveld refinement of the milling product from LiOH and rutile (WC tools, 600 rpm, 6h) after heating to 200 °C for 1 h. Li₂TiO₃ in SG $Fm\bar{3}m$ with $a = 4.1435(1)$ Å, $V = 71.14(1)$ Å³, number of reflections = 8 and $R_{Bragg} = 1.50\%$. Refinement parameters: number of independent parameters = 48, $R_{wp} = 3.08\%$, $R_{exp} = 2.63\%$, $GOF = 1.17$.

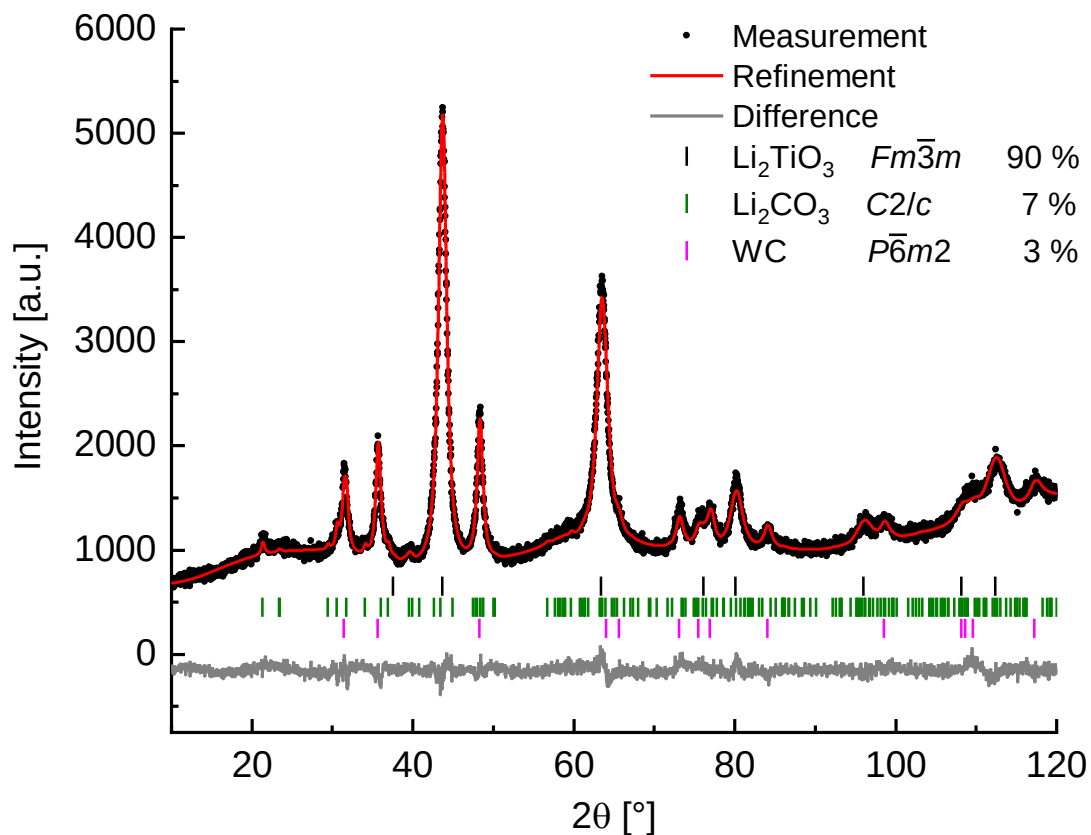
Transformation of β - Li_2TiO_3 and spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ to α - Li_2TiO_3 

Figure S7: Rietveld refinement of β - Li_2TiO_3 after ball milling with WC tools for 6 h at 600 rpm. Li_2TiO_3 in SG $Fm\bar{3}m$ with $a = 4.1463(2) \text{ \AA}$, $V = 71.28(1) \text{ \AA}^3$, number of reflections = 8 and $R_{\text{Bragg}} = 0.60\%$. Refinement parameters: number of independent parameters = 31, $R_{\text{wp}} = 3.60\%$, $R_{\text{exp}} = 2.85\%$, $GOF = 1.26$.

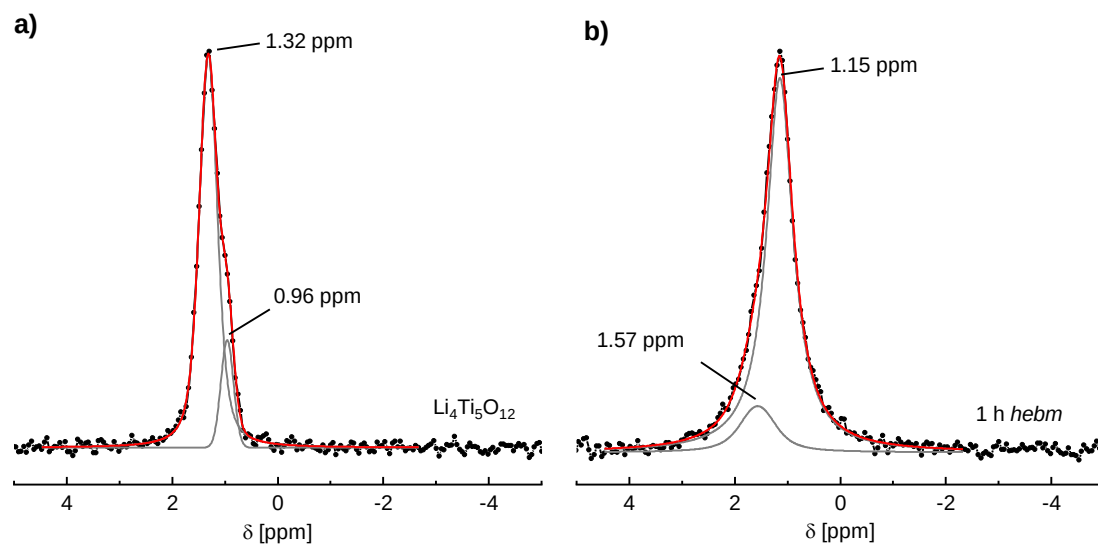
^6Li SPE MAS NMR of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ 

Figure S8: ^6Li SPE MAS NMR spectra of a) spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$, b) after *hebm* for 1 h. The spectra were referenced against solid LiCl and fitted with two independent Voigt functions with $R^2 > 0.99$.