

Supporting Information for

Measuring T_1 relaxation in paramagnetic solids with solid-state NMR: A case study on the milling induced phase transition in Li_6CoO_4

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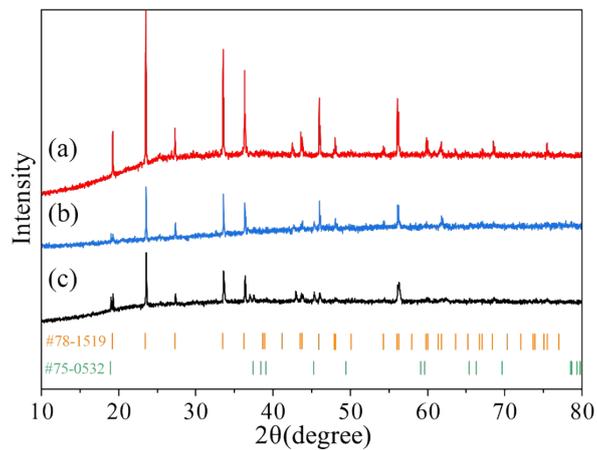


Fig. S1. XRD patterns of Li_6CoO_4 synthesized using sealed quartz tubes with reactants pressed into tablets (a), using sealed quartz tubes with powered reactants (b), and using tubular furnace with reactants pressed into tablets (c). The reference PDF cards for tetragonal Li_6CoO_4 (#78-1519) and trigonal layered LiCoO_2 (#75-0532) are depicted for comparison.

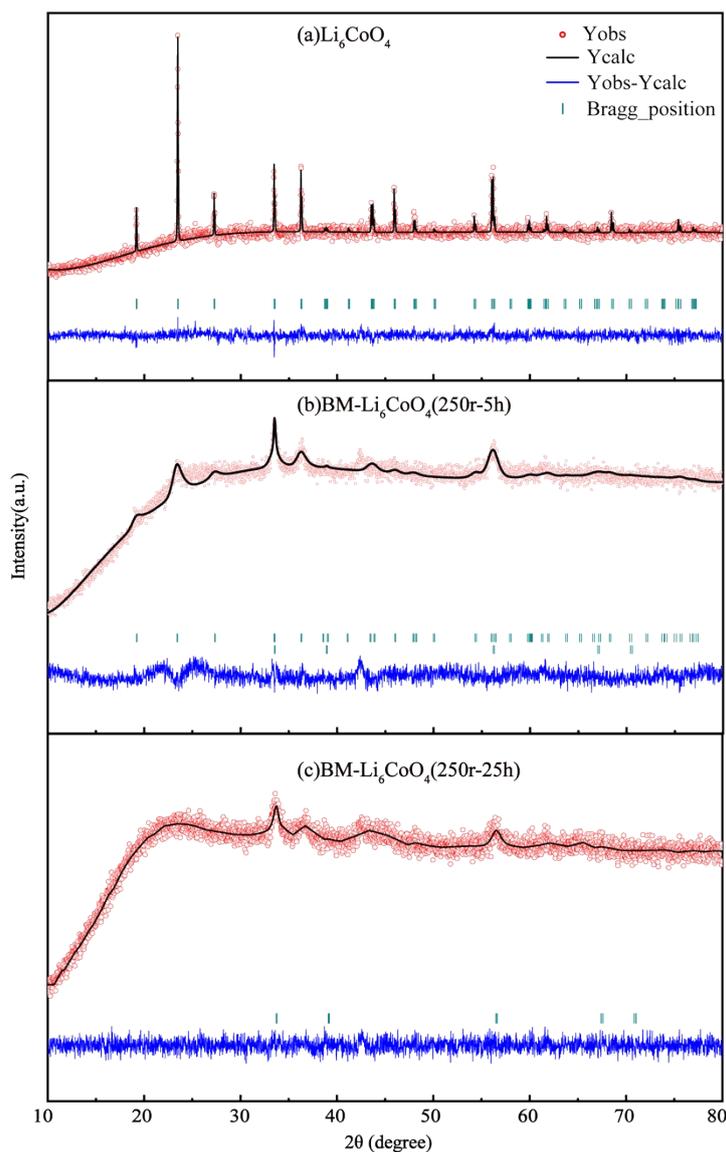


Fig. S2. Rietveld refinement on the laboratory XRD patterns of Li_6CoO_4 (a), $\text{BM-Li}_6\text{CoO}_4(250\text{r-5h})$ (b), and $\text{BM-Li}_6\text{CoO}_4(250\text{r-5h})$ (c). The refined structural parameters are listed in **Table S1** in the following.

Table S1. Results of Rietveld refinement shown in Fig. S2.

sample/phase	space group	lattice parameters (Å)	atom	site	occupancy(g) and atomic coordination	fraction (mol%)
Li_6CoO_4 ordered phase	$P42/nmc$	$a=6.545(1)$ $c=4.651(5)$	Li1	$8f$	$x = 0.020(1)$	100
			Li2	$4d$	$z = 0.283(5)$	
			Co	$2a$		
			O	$8g$	$y = 0.532(1)$	
$R_{wp} = 3.55\%$, $R_p = 2.80\%$, $R_e = 3.27\%$, and $S = 1.09$.						
$\text{Li}_6\text{CoO}_4(\text{BM}250\text{r-5h})$ ordered and disordered phases	$P42/nmc$	$a = 6.528(7)$ $c = 4.669(9)$	Li1	$8f$	$x = -0.009(5)$	63(5)
			Li2	$4d$	$z = 2.764(2)$	
			Co	$2a$		
			O	$8g$	$y = 0.523(1)$ $z = 0.507(8)$	

	$Fm\bar{3}m$	$a=4.616(7)$	Li	$8c$	$g = 0.75$	36(4)
			Co	$8c$	$g = 0.125$	
			O	$4a$		
$R_{wp} = 1.70\%$, $R_p = 1.36\%$, $R_e = 1.15\%$, and $S = 1.48$						
Li_6CoO_4 (BM250r-25h) disordered phase	$Fm\bar{3}m$	$a=4.613(4)$	Li	$8c$	$g = 0.75$	100
			Co	$8c$	$g = 0.125$	
			O	$4a$		
$R_{wp} = 1.40\%$, $R_p = 1.12\%$, $R_e = 1.12\%$, and $S = 1.25$.						

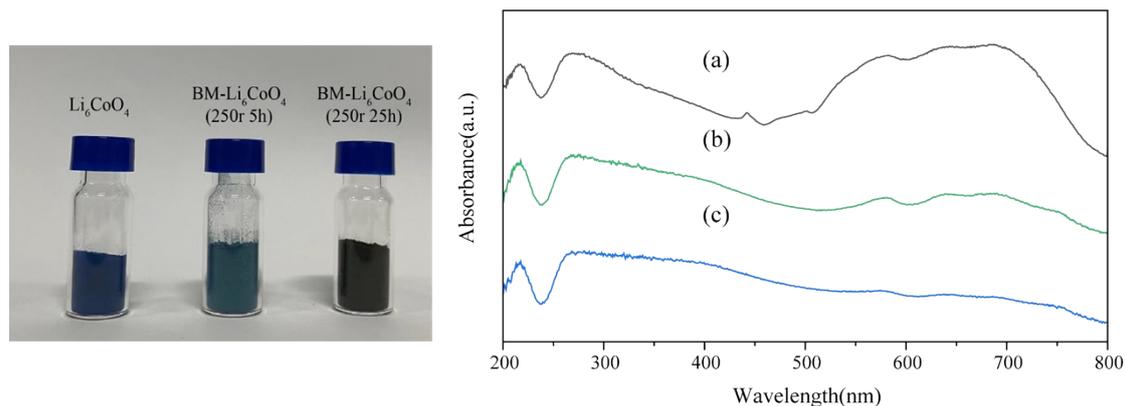


Fig. S3. Photographs of synthesized pristine Li_6CoO_4 and ball-milled samples. The change of color from dark blue to black is in accordance with the UV-Vis spectroscopy results.

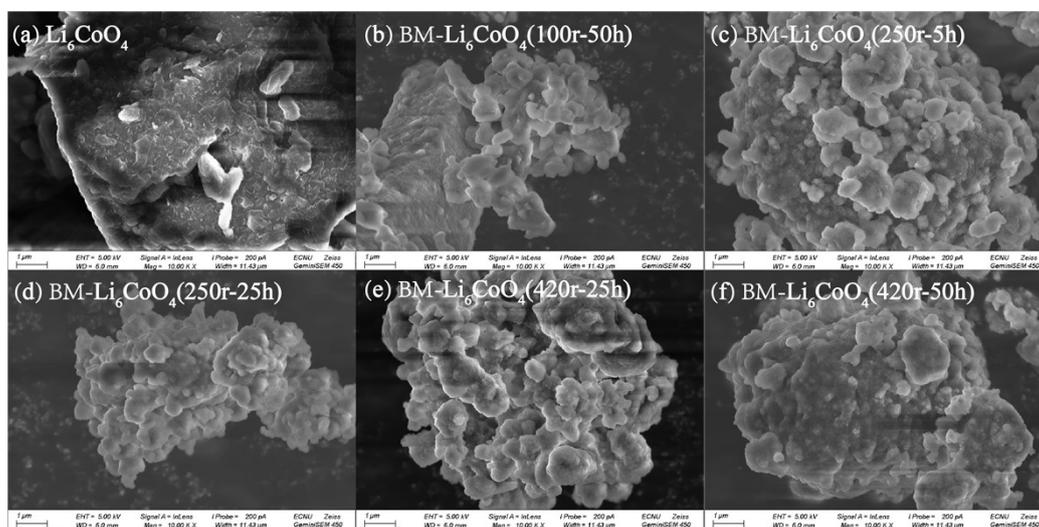


Fig. S4. SEM images of pristine Li_6CoO_4 and ball-milled samples.

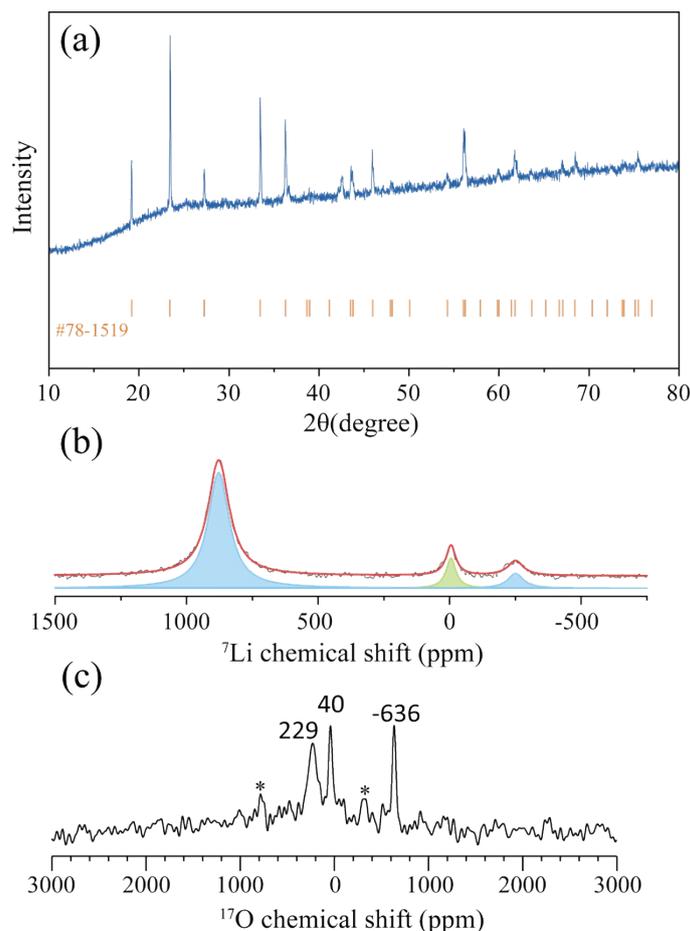


Fig. S5. (a) XRD pattern, (b) ^7Li pjMATPASS projection, and (c) ^{17}O Hahn-echo spectrum of ^{17}O -labelled Li_6CoO_4 . The reference PDF card for tetragonal Li_6CoO_4 (#78-1519) is shown in (a) for comparison.

Although only diffraction peaks from Li_6CoO_4 are shown from XRD results, the ^7Li resonance at 0 ppm and ^{17}O resonance at -636 ppm is a strong signature of LiCoO_2 . We tentatively assign 229 ppm resonance to oxygen atoms in Li_6CoO_4 lattice and the 40 ppm resonance to oxygen atoms in diamagnetic impurity, possibly from Li_2CO_3 .

The synthesis of this sample is based on a low-cost H_2^{17}O -based method, which is similar to others report. (Métro, T.-X.; Gervais, C.; Martinez, A.; Bonhomme, C.; Laurencin, D. Unleashing the Potential of ^{17}O NMR Spectroscopy Using Mechanochemistry. *Angewandte Chemie International Edition* 2017, 56 (24), 6803-6807.) 0.01 mol of Li_2O , 0.01 mol of CoO and 0.5 ml H_2^{17}O (35-40% ^{17}O labelling, Cambridge Isotope) were grounded for 30 minutes in a 45 mL zirconia grinding bowl with two zirconia balls using a SPEX 8000M Mixer/Mill. The mixture was then calcinated at 700 °C with a heating rate of 5 °C/min under argon flow for 12 h in a tube furnace. The product was manually grounded in an agate mortar and stored in an argon-filled glove box.

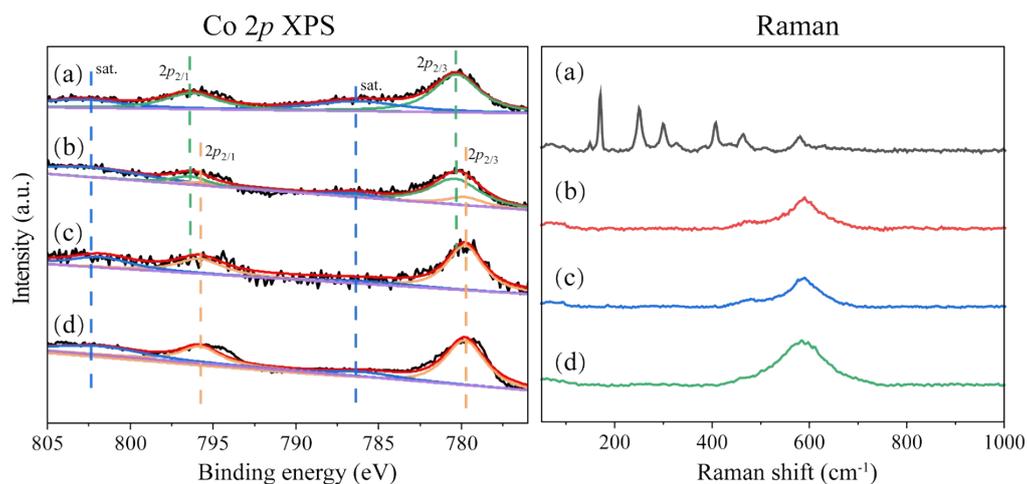


Fig. S6. Co 2p XPS and Raman spectra of pristine Li₆CoO₄ (a) and ball-milled samples: Li₆CoO₄(BM250r-5h) (b), Li₆CoO₄(BM250r-25h) (c), and Li₆CoO₄(BM250r-50h) (d). The Co 2p XPS spectra have two main peaks due to spin-orbit splitting with satellite peaks labelled as 'sat.'.

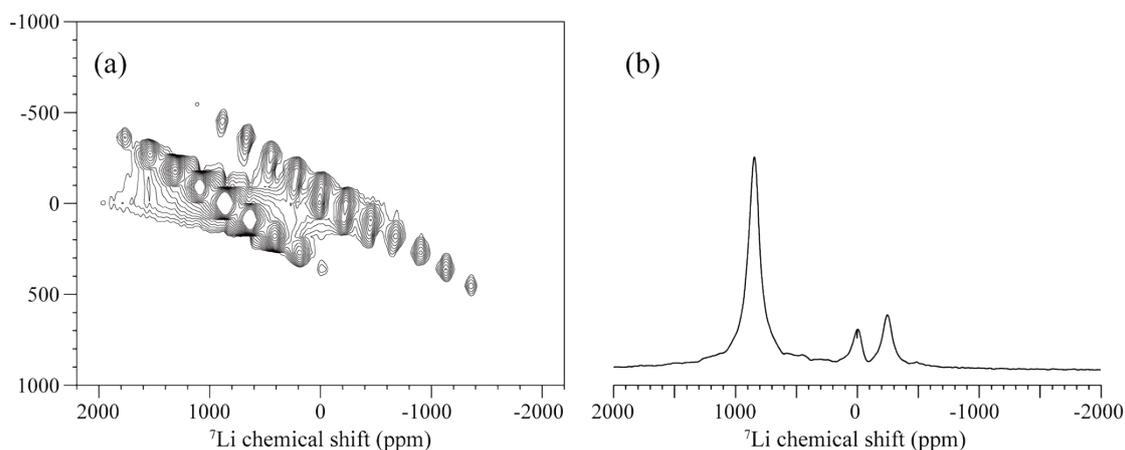


Fig. S7. (a) 2D ⁷Li pj-MATPASS spectrum of Li₆CoO₄ synthesized using tubular furnace with reactants pressed into tablets. (b) ⁷Li 1D projection taken from (a) after shearing transformation. Because this sample is partially oxidized to LiCoO₂ owing to limited air tightness, an additional 0 ppm resonance is shown. The spectrum was recorded with a recycle delay of 0.1 s, which leads to underestimated peak intensity of the LiCoO₂ phase. The XRD pattern of this sample is shown in Fig. S1(c).

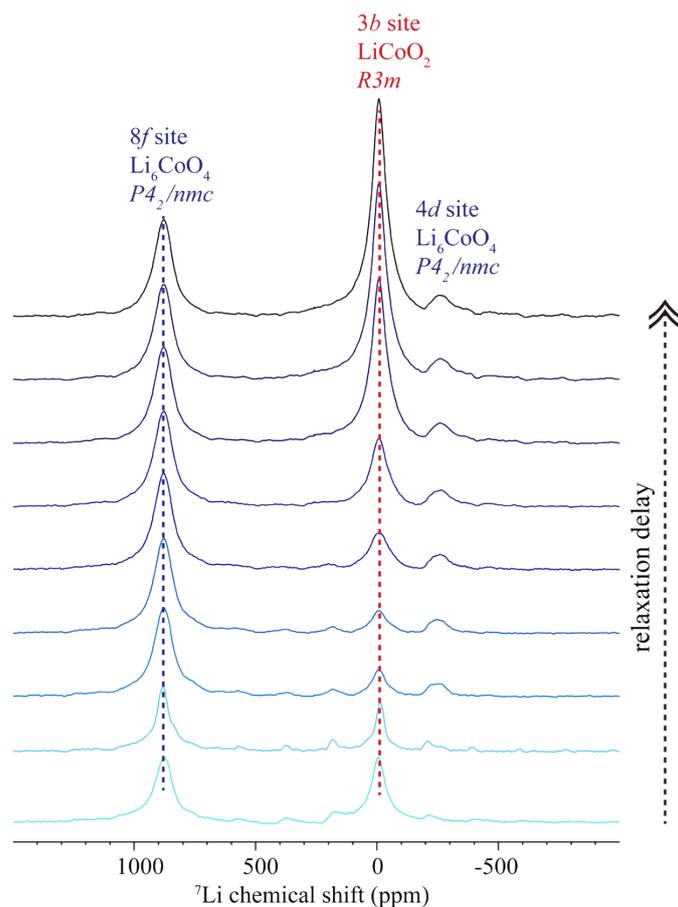


Fig. S8. ^7Li 1D projections extracted from 2D IR-pjMATPASS spectra acquired with incremented relaxation delays. Note that in typical IR experiments, short relaxation delays result in signals with negative intensities. In IR-pjMATPASS, signals are all positive because of the single coherence transfer pathway.

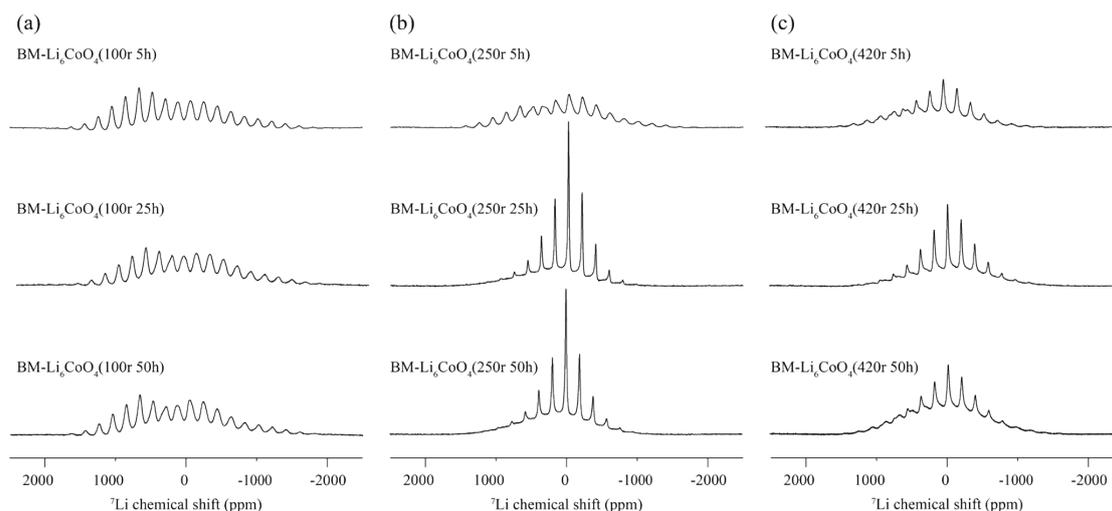


Fig. S9. ^7Li one-dimensional Hahn-echo spectra of ball-milled samples.