

*Supplementary Materials*

# Effects of Non-Stoichiometry on the Ground State of the Frustrated System Li<sub>0.8</sub>Ni<sub>0.6</sub>Sb<sub>0.4</sub>O<sub>2</sub>

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## A. Experimental details

The powder diffraction pattern [1] for the structural refinement was taken in Cu K $\alpha$  radiation using a rotating-anode Rigaku instrument equipped with a secondary-beam graphite monochromator. Structural analysis was performed by the Rietveld method implemented in GSAS+EXPGUI suite [2, 3].

## B. Structural results

The crystal structure was successfully refined with parameters listed in Tables 1, 2, 3 and refinement results are shown in Fig. S1.

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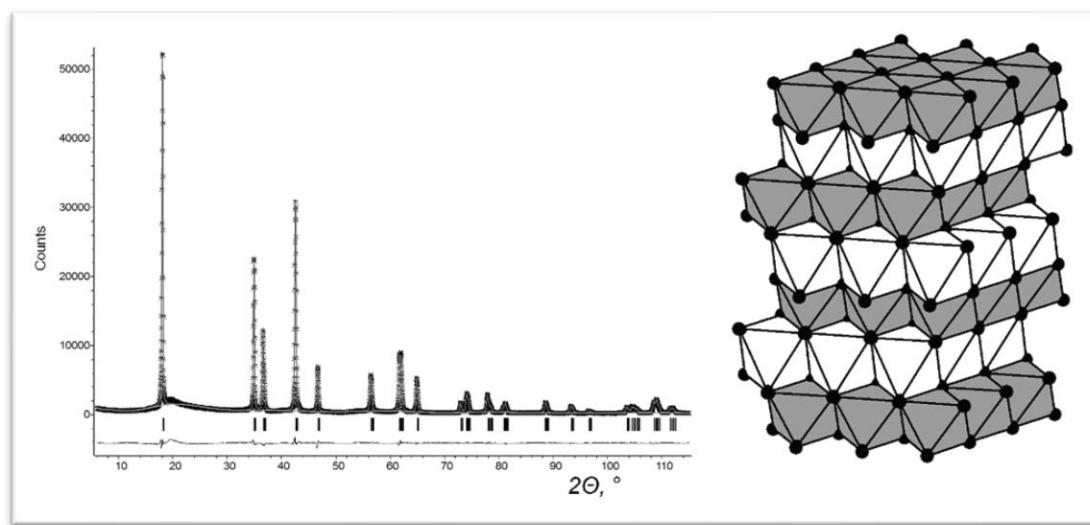
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**Figure S1.** Left: Results of the Rietveld refinement of  $\text{Li}_{0.8}\text{Ni}_{0.6}\text{Sb}_{0.4}\text{O}_2$  XRD profile [1]: asterisks are experimental points; line represents calculated profile; line at the bottom is the difference plot; vertical bars are the Bragg positions. Right: Polyhedral view of the crystal structure [1], where  $(\text{Ni},\text{Sb})\text{O}_6$  octahedra with small admixture of Li are shown in gray and  $\text{LiO}_6$  octahedra, partially occupied with small admixture of Ni are shown in white. See Tables I, II, III for details.

**Table S1.** Crystal structure refinement details for  $\text{Li}_{0.8}\text{Ni}_{0.6}\text{Sb}_{0.4}\text{O}_2$ .

Crystal system	trigonal	Density (calc.)	$5.302 \text{ g/cm}^3$
Space group	$R\bar{3}m$ (no. 166)	Texture parameters (March-Dollase)	axis [001] ratio 0.98967
Lattice constants, Å	$a$ $c$	$2\Theta$ range, ° Step width, °	6.00–115.00 0.02
Cell volume, Å <sup>3</sup>	114.079(2)	No. of data points	5451
Formula weight	121.38	No. of reflections calc. ( $\alpha_1$ only)	32
Z	3	No. of variables	46
Wavelengths, Å	$\alpha_1$ $\alpha_2$ Ratio	Agreement factors $R(F^2)$ $R_p$ $R_{wp}$ $\chi^2$	0.0411 0.0560 0.0785 6.955

**Table S2.** Atomic positions in  $\text{Li}_{0.8}\text{Ni}_{0.6}\text{Sb}_{0.4}\text{O}_2$ .

<i>Symbol</i>	<i>Wyckoff position</i>	<i>Site symmetry</i>	<i>Atom</i>	<i>Occupancy</i>	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U<sub>iso</sub></i>
M1	3a	$\bar{3}m$	Sb	0.40	0	0	0	0.0742(11)
			Ni	0.5159(9)				
			Li	0.0841(9)				
M2	3b	$\bar{3}m$	Li	0.7159(9)	1/3	2/3	1/6	0.0187(13))
			Ni	0.0841(9)				
O	6c	$3m$		1	0	0	0.25723(13)	0.0085(5)

**Table S3.** Bond lengths (Å) and bond angles ( $^{\circ}$ ) in  $\text{Li}_{0.8}\text{Ni}_{0.6}\text{Sb}_{0.4}\text{O}_2$ .

<b>Symbol</b>	<b>M1</b>	<b>M2</b>	<b>M1–O–M1</b>	<b>93.60(6) <math>\times</math> 3</b>
Occupancy	$\text{Sb}_{0.40}\text{Ni}_{0.516}\text{Li}_{0.084}$	$\text{Li}_{0.716}\text{Ni}_{0.084}$	O–M1–O	93.60(6) $\times$ 6
Average radius [4]	0.80	0.89		86.40(6) $\times$ 6
M–O distance	2.0595(10) $\times$ 6	2.1809(12) $\times$ 6		92.99(6) $\times$ 6
Radii sum [4]	2.06	2.15	O–M2–O	87.01(6) $\times$ 6

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