

Supporting Information

Study of Integer Spin $S = 1$ in the Polar Magnet β -Ni(IO₃)₂

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Figure S1. Rietveld fit (black line) of powder XRD pattern of the bulk polycrystalline β -Ni(IO₃)₂ precursor - β -Ni(IO₃)₂/Ni(IO₃)₂·2H₂O mixture (red points) and the blue line is the difference between the measured data and the simulation.

Figure S2. Rietveld fit (black line) of synchrotron XRD pattern of the bulk polycrystalline β -Ni(IO₃)₂ after 6 months in air (red points) and the blue line is the difference between the measured data and the simulation.

Figure S3. (a) Molar heat capacity over temperature (C_p/T) vs. temperature for β -Ni(IO₃)₂. (b) Magnetic entropy change from 2 K to 300 K, ΔS_{mag} ($2 \text{ K} \leq T \leq 300 \text{ K}$) = 3.3(1) J mol⁻¹ K⁻¹ ~ 36 % of expected value for $S = 1$ spins ($R \ln 3$).

Table S1. Crystal structure information and refinement parameters for β -Ni(IO₃)₂ obtained by Rietveld refinement of powder X-ray diffraction patterns.

Table S2. Atomic positions for β -Ni(IO₃)₂ obtained from the single crystal XRD.

Table S3. Bond lengths and bond angles of β -Ni(IO₃)₂.

Table S4: Calculated bond valence sum (V_i) of β -Ni(IO₃)₂.

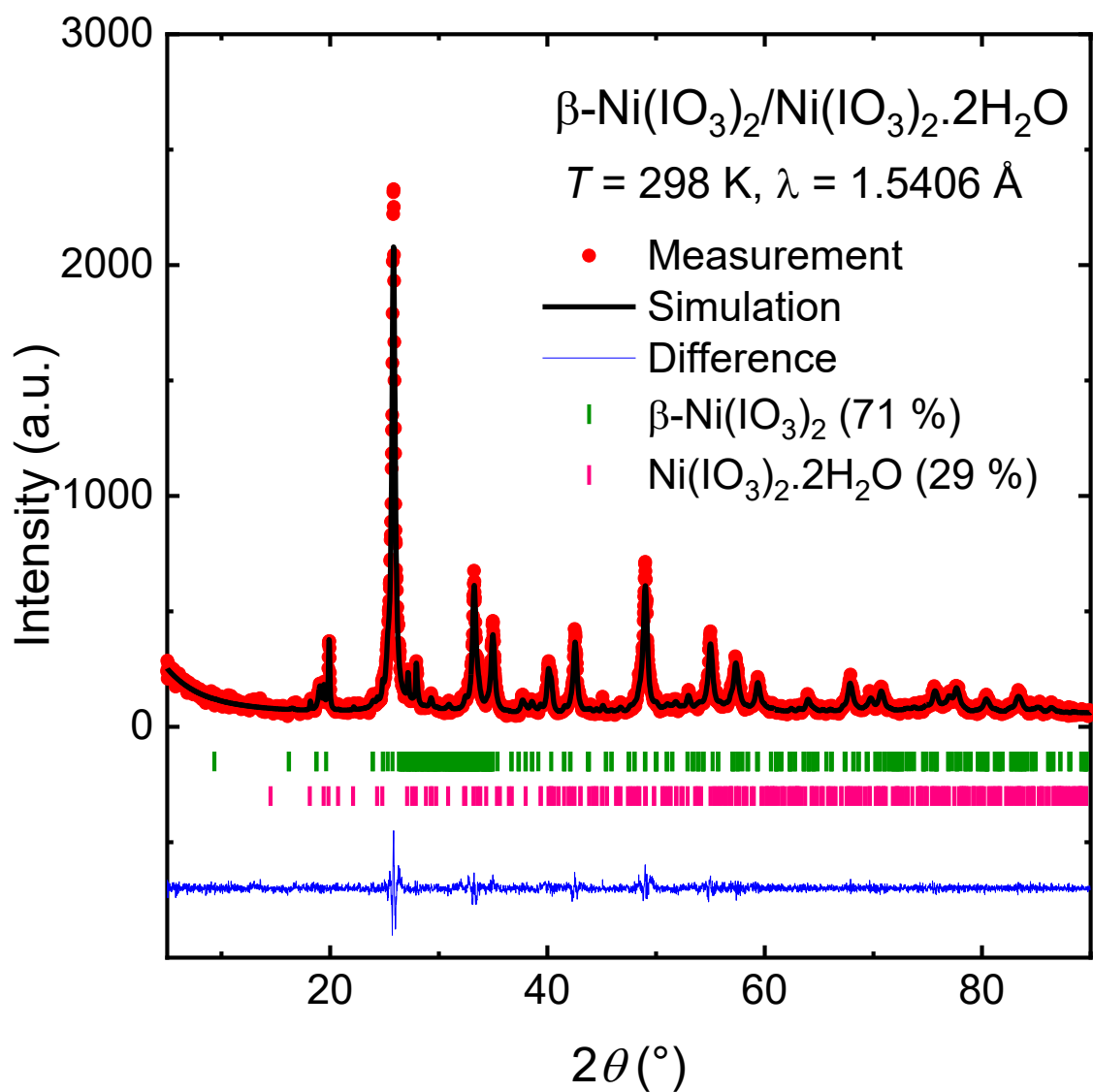


Figure S1. Rietveld fit (black line) of powder XRD pattern of the bulk polycrystalline $\beta\text{-Ni}(\text{IO}_3)_2$ precursor - $\beta\text{-Ni}(\text{IO}_3)_2/\text{Ni}(\text{IO}_3)_2 \cdot 2\text{H}_2\text{O}$ mixture (red points) and the blue line is the difference between the measured data and the simulation.

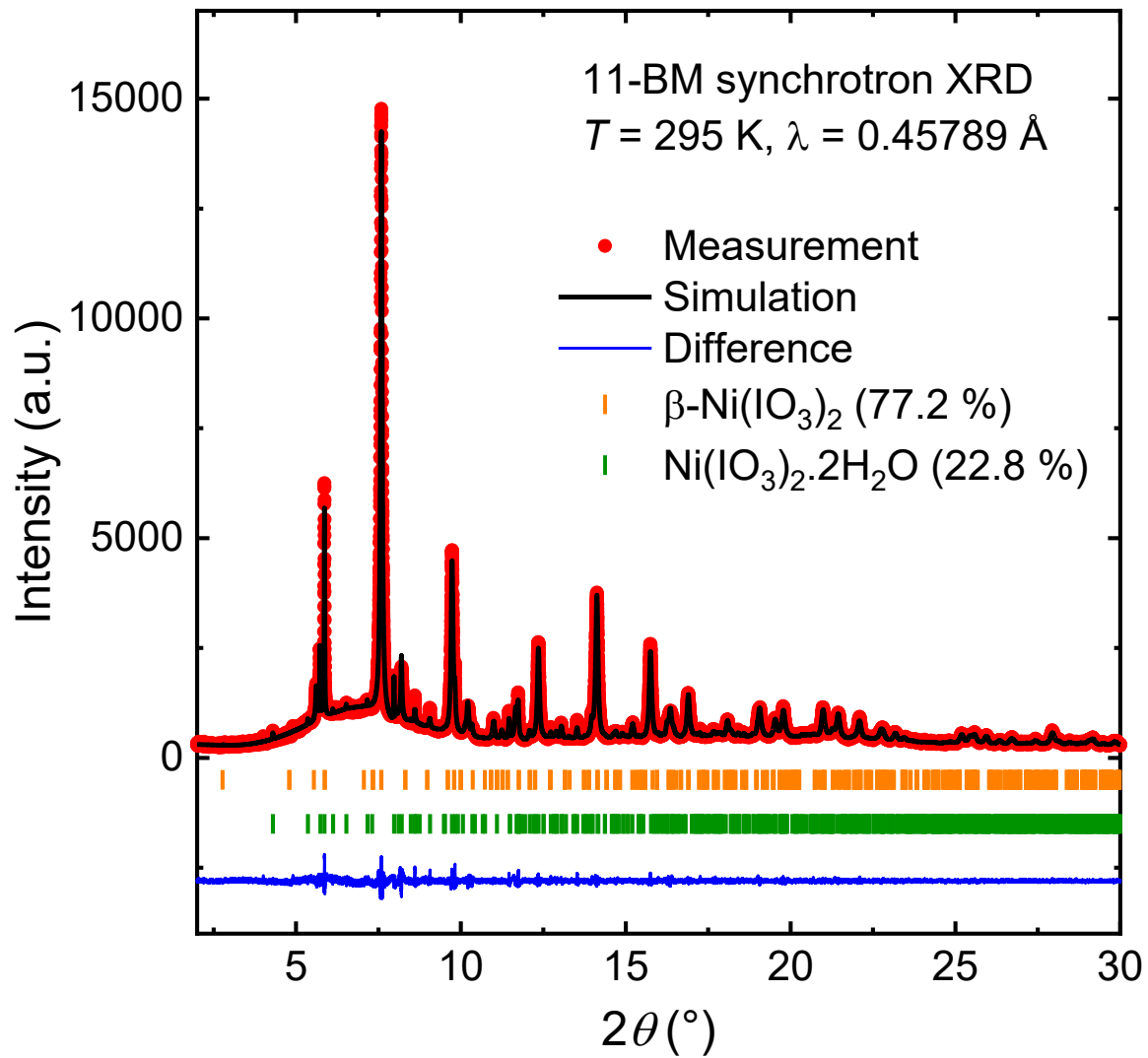


Figure S2. Rietveld fit (black line) of synchrotron XRD pattern of the bulk polycrystalline $\beta\text{-Ni}(\text{IO}_3)_2$ after 6 months in air (red points) and the blue line is the difference between the measured data and the simulation.

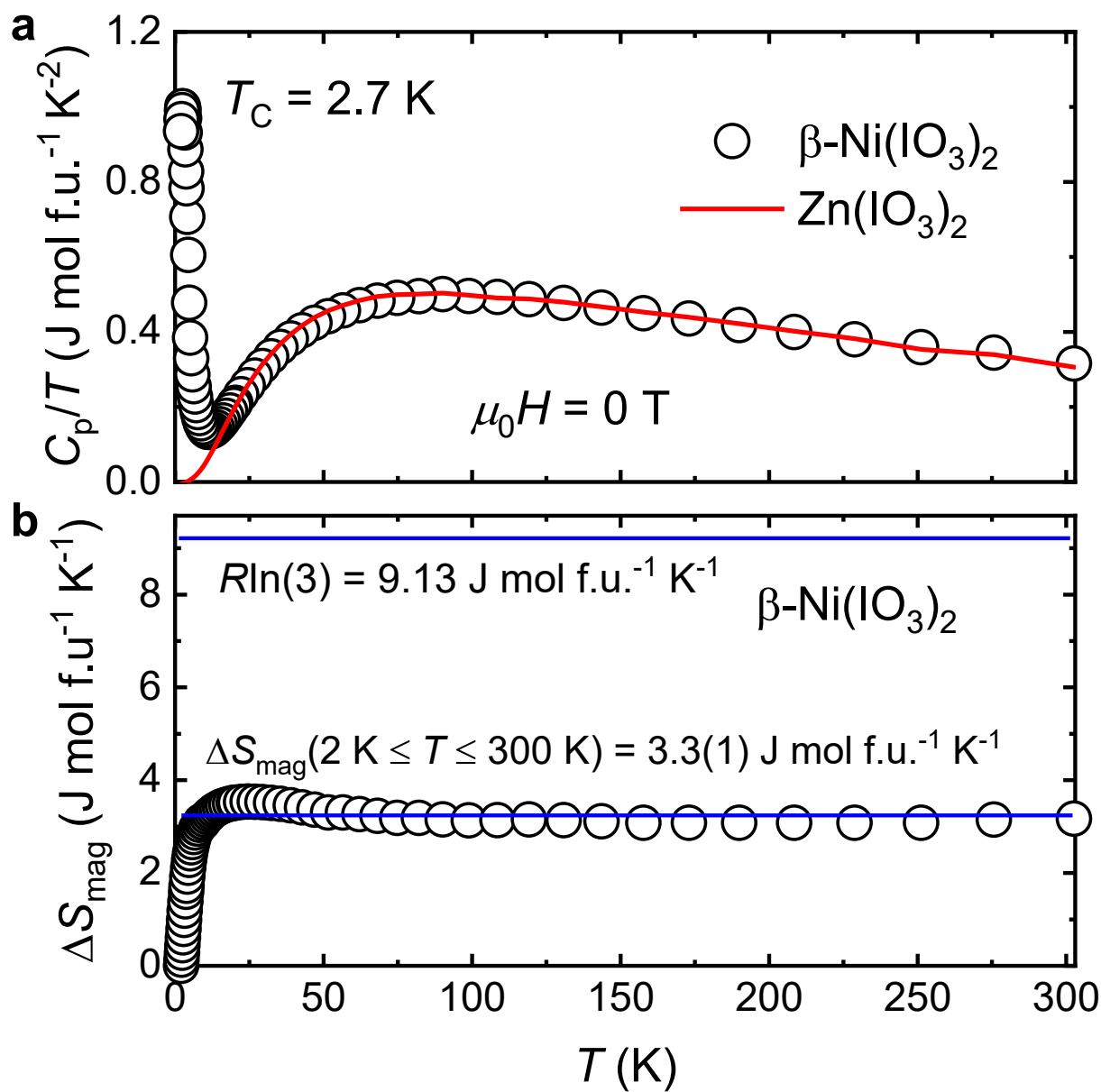


Figure S3. (a) Molar heat capacity over temperature (C_p/T) vs. temperature for $\beta\text{-Ni}(\text{IO}_3)_2$. (b) Magnetic entropy change from 2 K to 300 K, $\Delta S_{\text{mag}}(2 \text{ K} \leq T \leq 300 \text{ K}) = 3.3(1) \text{ J mol}^{-1} \text{K}^{-1} \sim 36\%$ of expected value for $S = 1$ spins ($R \ln 3$).

Table S1. Crystal structure information and refinement parameters for β -Ni(IO₃)₂ obtained by Rietveld refinement of powder X-ray diffraction patterns.

	Powder XRD
Chemical formula	Ni(IO ₃) ₂
Formula weight (g/mol)	408.51
Temperature (K)	298
X-ray radiation	Cu K_{α}
Wavelength (λ , Å)	1.5406
Crystal system	Monoclinic
Space group	$P2_1$
Z	4
a (Å)	10.8059(5)
b (Å)	5.1535(4)
c (Å)	10.7862(6)
$\alpha = \gamma$ (°)	90
β (°)	120.015(6)
V (Å ³)	520.11(4)
ρ_{calc} (g/cm ³)	5.217
2θ (°)	5 – 90
GOF	1.480
R-factor (%)	$R_p^a = 6.61$, $R_{\text{wp}}^b = 9.84$, $R_{\text{exp}}^c = 10.78$

$$^a R_p = \sum_i^n \frac{|Y_i^{\text{obs}} - Y_i^{\text{calc}}|}{\sum_i^n Y_i^{\text{obs}}} \times 100\% \qquad ^b R_p = \sum_i^n \left(\frac{w_i (Y_i^{\text{obs}} - Y_i^{\text{calc}})^2}{\sum_i^n Y_i^{\text{obs}}} \right)^{\frac{1}{2}} \times 100\%$$

$$^c R_{\text{exp}} = \left(\frac{n-p}{\sum_i^n w_i (Y_i^{\text{obs}})^2} \right)^{\frac{1}{2}} \times 100\%$$

Table S2. Atomic positions for β -Ni(IO₃)₂ obtained from the single crystal XRD.

Atomic positions (Single crystal XRD)				
	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (Å ²)
Ni1	0.4950(4)	0.3880(9)	0.2441(4)	0.0089(10)
Ni2	0.0156(6)	0.8942(13)	0.2561(6)	0.0224(12)
I1	0.33846(19)	0.3010(4)	0.43419(18)	0.0081(7)
I2	0.6708(2)	0.8059(4)	0.09926(17)	0.0112(8)
I3	0.8397(2)	0.3150(4)	0.4118(2)	0.0126(8)
I4	0.1725(2)	0.7959(5)	0.0756(3)	0.0168(8)
O1	0.636(3)	0.602(6)	0.212(3)	0.017(5)
O2	0.471(3)	0.104(8)	0.578(4)	0.023(6)
O3	0.321(3)	0.608(5)	0.094(3)	0.015(5)
O4	0.875(4)	0.111(11)	0.292(4)	0.032(9)
O5	0.187(4)	0.108(9)	0.404(6)	0.038(11)
O6	0.839(4)	0.656(7)	0.130(5)	0.032(9)
O7	0.144(4)	0.652(8)	0.214(3)	0.022(6)
O8	0.368(4)	0.169(5)	0.293(4)	0.016(5)
O9	0.550(3)	0.649(5)	-0.070(3)	0.015(5)
O10	0.671(3)	0.158(5)	0.364(3)	0.016(6)
O11	0.029(4)	0.640(7)	-0.076(4)	0.021(6)
O12	0.933(4)	0.150(8)	0.575(3)	0.022(6)

Table S3. Bond lengths and bond angles of β -Ni(IO₃)₂.

β-Ni(IO₃)₂			
Bond lengths (Å)			
Ni1-O8	2.03(3)	I1-O5	1.79(4)
Ni1-O1	2.04(3)	I1-O2	1.81(3)
Ni1-O10	2.05(3)	I1-O8	1.84(3)
Ni1-O3	2.10(3)	I2-O1	1.78(3)
Ni1-O9	2.09(3)	I2-O6	1.84(4)
Ni1-O2	2.09(3)	I2-O9	1.82(3)
Ni2-O5	2.06(4)	I3-O12	1.76(3)
Ni2-O4	2.06(4)	I3-O10	1.82(3)
Ni2-O12	2.07(3)	I3-O4	1.85(4)
Ni2-O7	2.09(4)	I4-O11	1.79(4)
Ni2-O6	2.10(5)	I4-O3	1.79(3)
Ni2-O11	2.16(4)	I4-O7	1.83(3)

Table S4: Calculated bond valence sum (V_i) of β -Ni(IO₃)₂.¹

Ni1		O1	O2	O3	O8	O9	O10	$V_i = \sum S_{ij}$
	R_{ij}	2.04(3)	2.09(3)	2.10(3)	2.03(3)	2.09(3)	2.05(3)	
	S_{ij}	0.30641	0.26498	0.25750	0.31558	0.26498	0.29755	1.7070
Ni2		O4	O5	O6	O7	O11	O12	
	R_{ij}	2.06(4)	2.06(4)	2.10(5)	2.07(4)	2.16(4)	2.07(3)	
	S_{ij}	0.28899	0.28899	0.25750	0.28072	0.21745	0.28072	1.6144
I1		O2	O5	O8				
	R_{ij}	1.81(3)	1.79(4)	1.84(3)				
	S_{ij}	1.8366	1.96321	1.6641				5.4610
I2		O1	O6	O9				
	R_{ij}	1.78(3)	1.84(4)	1.82(3)				
	S_{ij}	2.03033	1.66410	1.77688				5.4713
I3		O4	O10	O12				
	R_{ij}	1.85(4)	1.82(3)	1.76(3)				
	S_{ij}	1.61085	1.77688	2.17275				5.5605
I4		O3	O7	O11				
	R_{ij}	1.79(4)	1.83(3)	1.79(4)				
	S_{ij}	1.96321	1.71941	1.96321				5.6458

The ideal oxidation state of Ni and I are +2 and +5 respectively.

References

1. Altermatt, D.; Brown, I. D., The automatic searching for chemical bonds in inorganic crystal structures. *Acta Crystallogr. B* **1985**, *41* (4), 240-244.