

## Electronic Supplementary Information (ESI)

### Determination of Layered Nickel Hydroxide Phases in Materials Disordered by Stacking Faults and Interstratification

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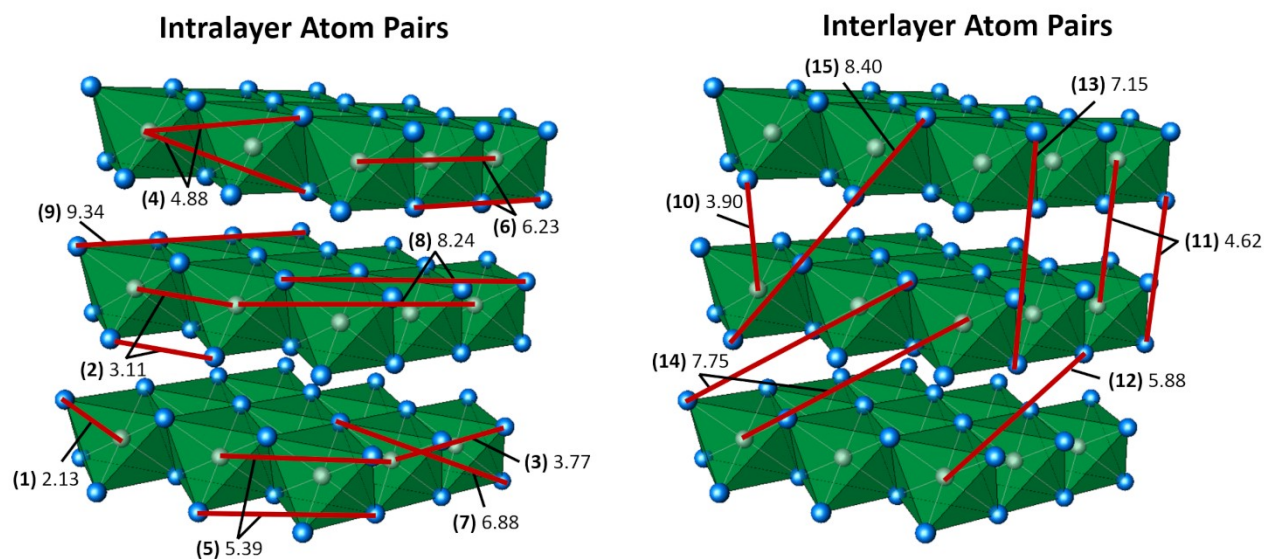
## Extended Experimental Section

### Material Preparation

$\text{Ni}_3(\text{OH})_4(\text{NO}_3)_2$  was prepared by two methods. The first sample was prepared by the precipitation method described by Petrov *et al.*<sup>1</sup> where a sodium hydroxide solution (0.50 M) was added dropwise by burette to a stirred solution of nickel(II) nitrate hexahydrate (3.5 M, 25 mL) heated to >90 °C until the solution pH was 6.0. The addition was performed at less than one drop per second to keep a constant solution volume while heating with care taken to prevent water condensing in the glassware. The final product was washed with water (ca. 250 mL) and dried at 120 °C for 48 h. The second sample was prepared using the thermolysis method described by Biswick *et al.*<sup>2</sup> which involved heating nickel(II) nitrate hexahydrate (5.0 g) in an oven at 220 °C for 2 h with stirring every 15 min. The product was washed with anhydrous ethanol (ca. 500 mL) to remove any nickel(II) nitrate that remained and dried at 120 °C for 48 h.

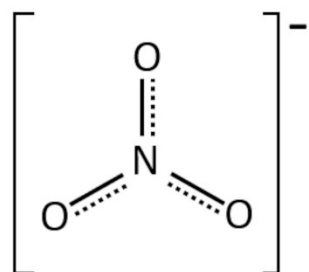
$\text{Ni}(\text{OH})(\text{NO}_3)\cdot\text{H}_2\text{O}$  was prepared by the solid-state mechanochemical synthesis method outlined by Thomas.<sup>3</sup> An agate pestle and mortar was heated in an oven set to 120 °C overnight to which nickel(II) nitrate hexahydrate (2.18 g, 7.5 mmol) and solid sodium hydroxide (0.30 g, 7.5 mmol) were added. The reagents were ground together into a uniform paste (ca. 2 min) to produce a mixture of the hydroxynitrate phase product and sodium nitrate (nitratine). The sodium nitrate was removed by grinding the sample in hot, anhydrous ethanol (ca. 1 L) which was repeatedly decanted with caution taken to prevent the product from drying. The final product was washed with three aliquots of hot propanone (ca. 100 mL) and filtered using a hot sintered glass crucible (grade 4) under vacuum.

## Extended Data Figures

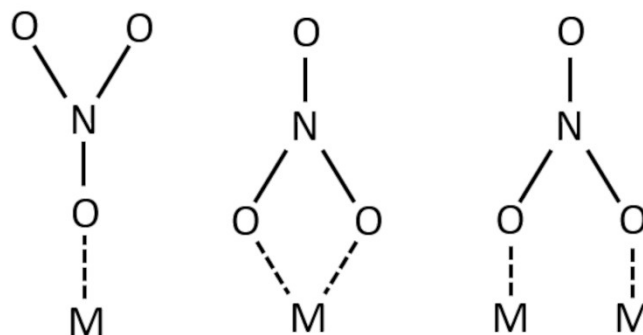


**Figure S1.** Assignment of the intralayer and interlayer atomic pair distances (in Å) to the crystal structure determined for beta-phase nickel hydroxide as the mineral theophrastite.<sup>4</sup>

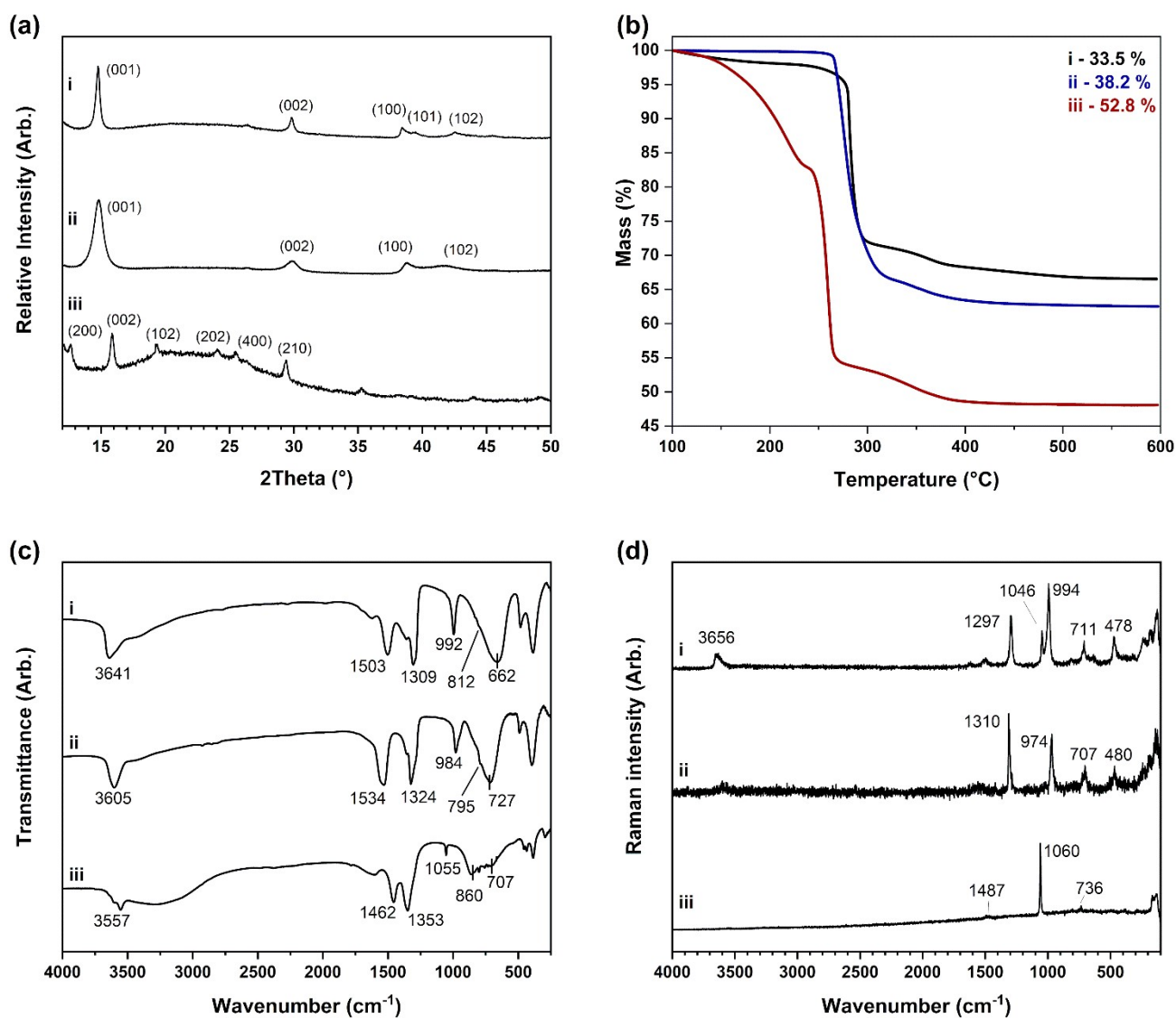
### Unbound Nitrate ( $D_{3h}$ symmetry)



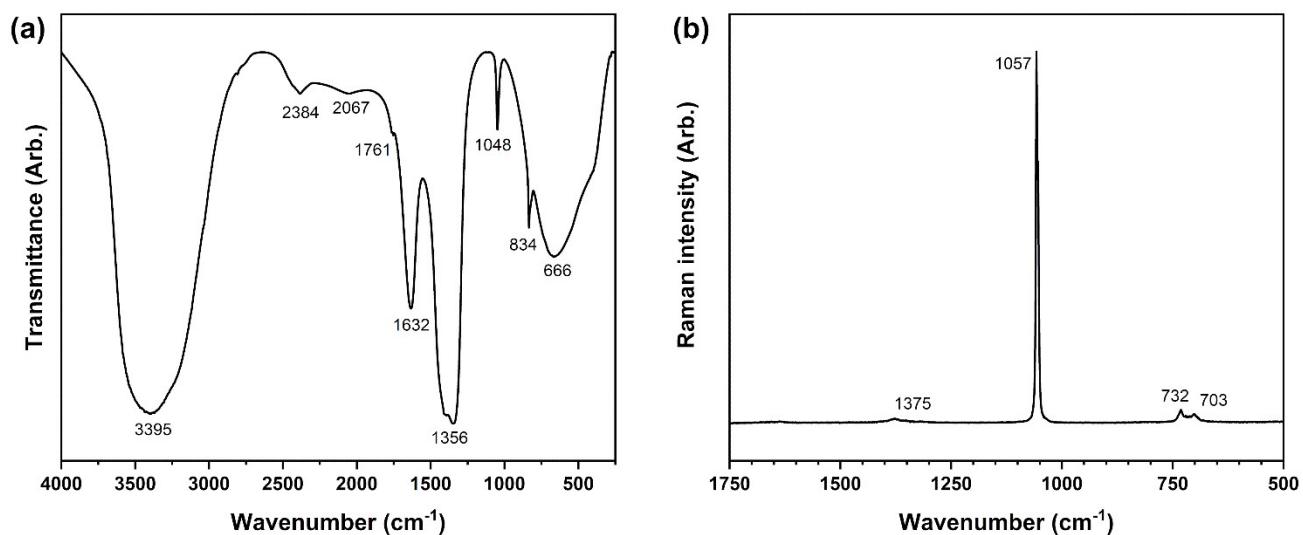
### Cation Bound Nitrate ( $C_{2v}$ symmetry)



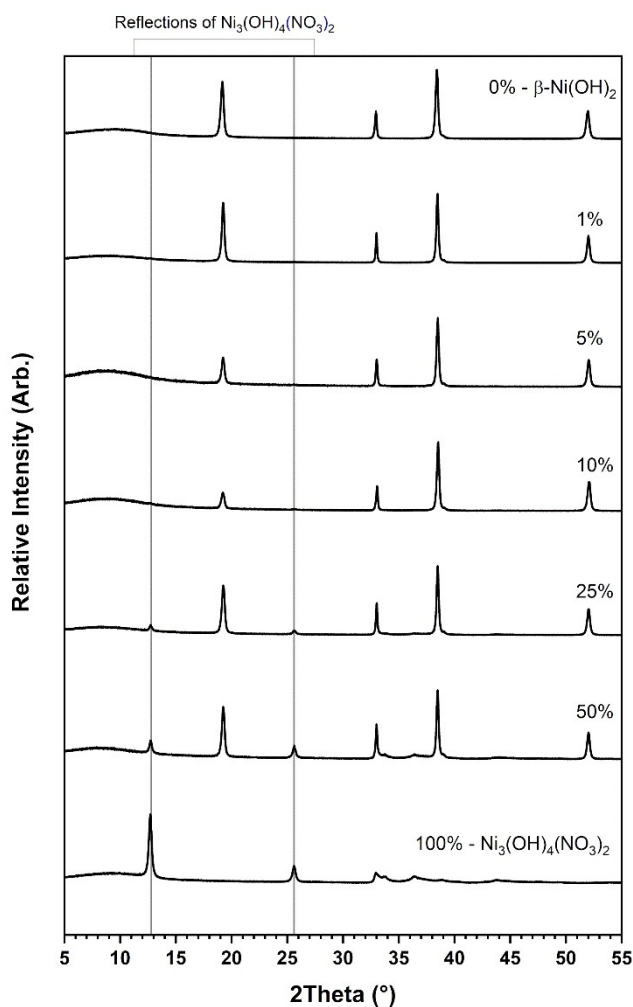
**Figure S2.** The nitrate anion with  $D_{3h}$  symmetry when unbound (left) and with  $C_{2v}$  symmetry when covalently coordinated (right).



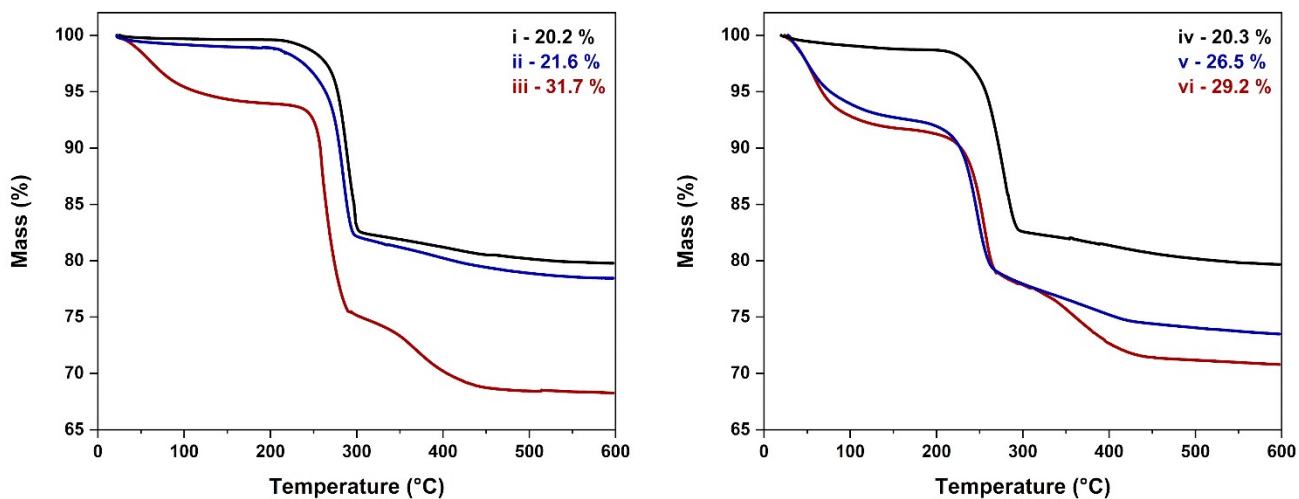
**Figure S3.** Data collected from nickel hydroxynitrates prepared by (i) Petrov precipitation (ii) metal(II) nitrate thermolysis and (iii) mechanochemical synthesis methods. (a) Powder X-ray diffraction patterns collected with Co K<sub>α1</sub> radiation ( $\lambda = 1.7889 \text{ \AA}$ ). The hkl values given are Ni<sub>3</sub>(OH)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub> (ICDD PDF 22-752) and Ni(OH)(NO<sub>3</sub>)·H<sub>2</sub>O (ICDD PDF 27-939). (b) Thermogravimetric weight loss analysis via decomposition of each phase to nickel(II) oxide. (c) Infrared absorption spectra as CsI disks. (d) Raman spectra.



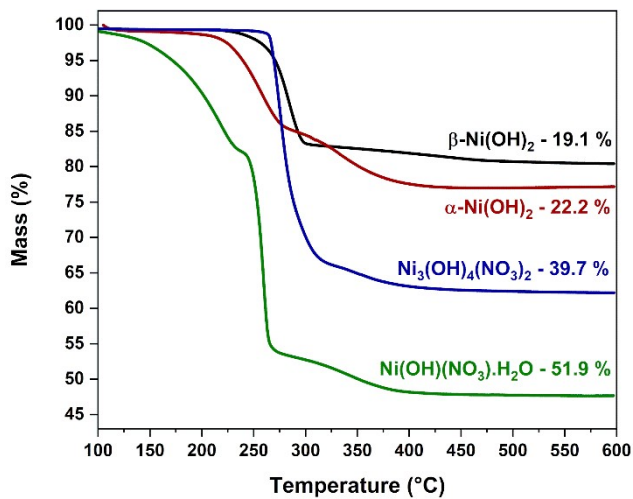
**Figure S4.** (a) Infrared absorption spectra as CsI disks and (b) Raman spectra collected from the nickel(II) nitrate hexahydrate starting reagent.



**Figure S5.** Powder X-ray diffraction patterns collected with Cu K $\alpha_1$  radiation ( $\lambda = 1.5405 \text{ \AA}$ ) on standard mixtures formed between  $\beta$ -Ni(OH)<sub>2</sub> and Ni<sub>3</sub>(OH)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub> at 0, 1, 5, 10, 25, 50 and 100 wt% intervals.



**Figure S6.** Thermogravimetric analysis of the i-vi nickel hydroxide materials showing weight loss profiles by decomposition to nickel(II) oxide.



**Figure S7.** Thermogravimetric analysis data for standard  $\beta$ -Ni(OH)<sub>2</sub>,  $\alpha$ -Ni(OH)<sub>2</sub>, Ni<sub>3</sub>(OH)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub> and Ni(OH)(NO<sub>3</sub>).H<sub>2</sub>O.

## Extended Data Tables

**Table S1.** Preliminary investigations into the preparation of nickel hydroxide materials by the chemical precipitation method using nickel(II) nitrate and potassium hydroxide (1:2 ratio of Ni<sup>2+</sup>:OH<sup>-</sup>) with varying temperatures and chemical ageing durations.

Synthesis Conditions	Material Assigned	PXRD Pattern Reflection Profile	Observed Infrared Bands of Nitrate (cm <sup>-1</sup> )				
			$\nu_1$ (C <sub>2v</sub> )	$\nu_2$ (D <sub>3h</sub> /C <sub>2v</sub> )	$\nu_3$ (D <sub>3h</sub> )	$\nu_3$ (C <sub>2v</sub> )	$\nu_4$ (D <sub>3h</sub> )
5 °C, 1 h	$\beta_{IS}$ -Ni(OH) <sub>2</sub>	Broad / split 001	1046/996	834	1364	1501, 1301	652
5 °C, 6 h	$\beta_{IS}$ -Ni(OH) <sub>2</sub>	Broad / split 001	995	834	1366	1497, 1301	648
5 °C, 1 d	$\beta_{IS}$ -Ni(OH) <sub>2</sub>	Broad / split 001	1055	834	1364	1499, 1301	647
5 °C, 2 d	$\beta_{IS}$ -Ni(OH) <sub>2</sub>	Broad / split 001	1050/995	834	1364	1497, 1302	650
5 °C, 4 d	$\beta_{IS}$ -Ni(OH) <sub>2</sub>	Broad / split 001	998	834	1364	1498, 1302	649
5 °C, 1 w	$\beta_{IS}$ -Ni(OH) <sub>2</sub>	Broad / split 001	996	833	1368	1502, 1302	656
25 °C, 1 h	$\beta_{IS}$ -Ni(OH) <sub>2</sub>	Broad / split 001	994	834	1367	1502, 1302	655
25 °C, 6 h	$\beta_{IS}$ -Ni(OH) <sub>2</sub>	Broad / split 001	994	834	1364	1498, 1301	649
25 °C, 1 d	$\beta_{IS}$ -Ni(OH) <sub>2</sub>	Broad	1050	832	1368	1493, 1300	643
25 °C, 2 d	$\beta_{IS}$ -Ni(OH) <sub>2</sub>	Broad	1050	833	1362	1509, 1298	652
25 °C, 4 d	$\beta/\beta_{IS}$ -Ni(OH) <sub>2</sub>	Crystalline / broad	995	829	1368	1501, 1304	643
25 °C, 1 w	$\beta_{SF}$ -Ni(OH) <sub>2</sub>	Broad	-	833	1372	-	644
50 °C, 1 h	$\beta_{IS}$ -Ni(OH) <sub>2</sub>	Broad	1055	833	1364	1496, 1302	652
50 °C, 6 h	$\beta_{IS}$ -Ni(OH) <sub>2</sub>	Broad	1048	833	1366	1496, 1301	641
50 °C, 1 d	$\beta_{IS}$ -Ni(OH) <sub>2</sub>	Broad	992	833	1366	1501, 1302	642
50 °C, 2 d	$\beta_{SF}$ -Ni(OH) <sub>2</sub>	Broad	-	833	1374	-	648
50 °C, 4 d	$\beta/\beta_{SF}$ -Ni(OH) <sub>2</sub>	Crystalline	-	-	1363	-	-
50 °C, 1 w	$\beta/\beta_{SF}$ -Ni(OH) <sub>2</sub>	Crystalline	-	-	1371	-	-
75 °C, 1 h	$\beta_{IS}$ -Ni(OH) <sub>2</sub>	Broad	1049/993	834	1364	1496, 1302	649
75 °C, 6 h	$\beta_{SF}$ -Ni(OH) <sub>2</sub>	Broad	-	833	1371	-	635
75 °C, 1 d	$\beta_{SF}$ -Ni(OH) <sub>2</sub>	Broad	-	833	1367	-	637
75 °C, 2 d	$\beta$ -Ni(OH) <sub>2</sub>	Highly crystalline	-	-	-	-	-
75 °C, 4 d	$\beta/\beta_{SF}$ -Ni(OH) <sub>2</sub>	Crystalline	-	-	1366	-	-
75 °C, 1 w	$\beta/\beta_{SF}$ -Ni(OH) <sub>2</sub>	Crystalline	-	-	1368	-	-
95 °C, 1 h	$\beta_{IS}$ -Ni(OH) <sub>2</sub>	Broad	998	833	1365	1496, 1301	636
95 °C, 6 h	$\beta/\beta_{SF}$ -Ni(OH) <sub>2</sub>	Crystalline	-	-	1369	-	-
95 °C, 1 d	$\beta$ -Ni(OH) <sub>2</sub>	Highly crystalline	-	-	-	-	-
95 °C, 2 d	$\beta$ -Ni(OH) <sub>2</sub>	Crystalline	-	-	-	-	-
95 °C, 4 d	$\beta/\beta_{SF}$ -Ni(OH) <sub>2</sub>	Crystalline	-	-	1374	-	-
95 °C, 1 w	$\beta$ -Ni(OH) <sub>2</sub>	Highly crystalline	-	-	-	-	-

**Table S2.** Preliminary investigations into the preparation of nickel hydroxide materials by the chemical precipitation method using nickel(II) nitrate and potassium hydroxide with varying temperatures, chemical ageing durations and stoichiometric ratios of nickel(II) to hydroxide anions.

Synthesis Conditions	Ni <sup>2+</sup> :OH <sup>-</sup> Ratio	Material Assigned	PXRD Pattern Reflection Profile	Observed Infrared Bands of Nitrate (cm <sup>-1</sup> )				
				$\nu_1$ (C <sub>2v</sub> )	$\nu_2$ (D <sub>3h</sub> /C <sub>2v</sub> )	$\nu_3$ (D <sub>3h</sub> )	$\nu_3$ (C <sub>2v</sub> )	$\nu_4$ (D <sub>3h</sub> )
5 °C, 1 w	1:1	$\beta_{1S}$ -Ni(OH) <sub>2</sub>	Broad / split 001	997	832	1364	1503, 1303	659
50 °C, 2 d	1:1	$\beta_{SF}$ -Ni(OH) <sub>2</sub>	Broad	-	805	1364	-	527
95 °C, 1 w	1:1	$\beta$ -Ni(OH) <sub>2</sub>	Highly crystalline	-	-	-	-	-
5 °C, 1 w	1:2	$\beta_{1S}$ -Ni(OH) <sub>2</sub>	Broad / split 001	996	833	1368	1502, 1302	656
50 °C, 2 d	1:2	$\beta_{SF}$ -Ni(OH) <sub>2</sub>	Broad	-	833	1374	-	648
95 °C, 1 w	1:2	$\beta$ -Ni(OH) <sub>2</sub>	Highly crystalline	-	-	-	-	-
5 °C, 1 w	1:3	$\beta_{SF}$ -Ni(OH) <sub>2</sub>	Broad	-	833	1377	-	648
50 °C, 2 d	1:3	$\beta_{SF}$ -Ni(OH) <sub>2</sub>	Broad	-	838	1368	-	635
95 °C, 1 w	1:3	$\beta_{SF}$ -Ni(OH) <sub>2</sub>	Broad	-	832	1369	-	521
5 °C, 1 w	1:4	$\beta_{SF}$ -Ni(OH) <sub>2</sub>	Broad	-	848	1379	-	649
50 °C, 2 d	1:4	$\beta_{SF}$ -Ni(OH) <sub>2</sub>	Broad	-	837	1364	-	524
95 °C, 1 w	1:4	$\beta_{SF}$ -Ni(OH) <sub>2</sub>	Broad	-	831	1363	-	515

## References

- 1 L. Markov, K. Petrov and V. Petkov, *Thermochim. Acta*, 1986, **106**, 283–292.
- 2 T. Biswick, W. Jones, A. Pacuła and E. Serwicka, *J. Solid State Chem.*, 2006, **179**, 49–55.
- 3 N. Thomas, *Mater. Res. Bull.*, 2012, **47**, 3568–3572.
- 4 R. W. Cairns and E. Ott, *J. Am. Chem. Soc.*, 1933, **55**, 527–533.