

Supporting Information

Synthesis and Spectroscopic Identification of Nickel and Cobalt Layered Hydroxides and Hydroxynitrates

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Extended Experimental

Cobalt gravimetric analysis

Cobalt(II) content in cobalt hydroxide/hydroxynitrate phases was determined by the selective precipitation method with benzimidazole as described by Upadhyaya with minor alterations.¹ A cobalt hydroxynitrate sample (to equate to ca. 20 mg of Co) was placed directly into a 400 ml beaker and dissolved in a minimum quantity of concentrated hydrochloric acid. Benzimidazole solution (20 ml, 0.04M) was added and the mixture was diluted to approximately 150 ml. The solution was then heated to near boiling with the solution pH raised slowly by dropwise addition of 1 M aqueous ammonia solution with constant stirring until the pH exceeded 8.2 and no further precipitate was formed. The mixture was then heated below boiling for 15 min and filtered through a porosity G4 sintered-class crucible. The resulting purple precipitate of $\text{Co}(\text{C}_7\text{H}_5\text{N}_2)_2$ was washed with 0.4 mM benzimidazole solution, then three times with distilled water (100 mL) and once with 50% ethanol solution (ca. 30 mL). The pre-weighed crucible and stir bar were dried to constant weight at 110 °C overnight and weighed. The conversion factor used in the calculations of $\text{Co}(\text{C}_7\text{H}_5\text{N}_2)_2$ to Co(II) is 0.2010.

Extended Data Figures

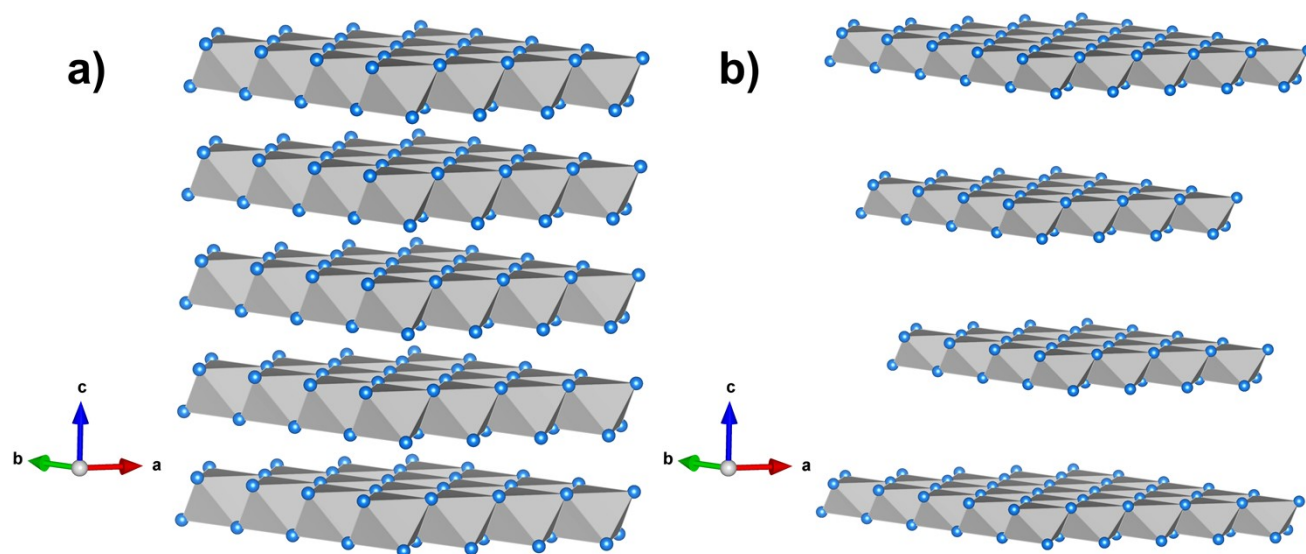


Figure S1. Crystal structures of (a) β -Mg(OH)₂ and (b) α -Ni(OH)₂ with ideal layer stacking adapted from crystallographic data of the minerals brucite and jamborite, respectively.^{2,3} M(II) cations form octahedra (grey) with oxygen atoms (blue) arranged into layers that extend over the *a* and *b* directions. Hydrogen atoms are excluded for clarity. Brucite has an interlayer spacing of 4.7 Å compared to 7.7 Å for jamborite. β -Mg(OH)₂ crystallises in the space group $P\bar{3}m1$ where $a = b = 3.14$ Å and $c = 4.77$ Å with $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$, when α -Ni(OH)₂ has an ideal layer stacking it crystallises in the space group $R\bar{3}m$ where $a = b = 3.07$ Å and $c = 23.2$ Å whilst with $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$. The inclusion of hydrated anions in the alpha-phase structure are excluded in this instance for clarity.

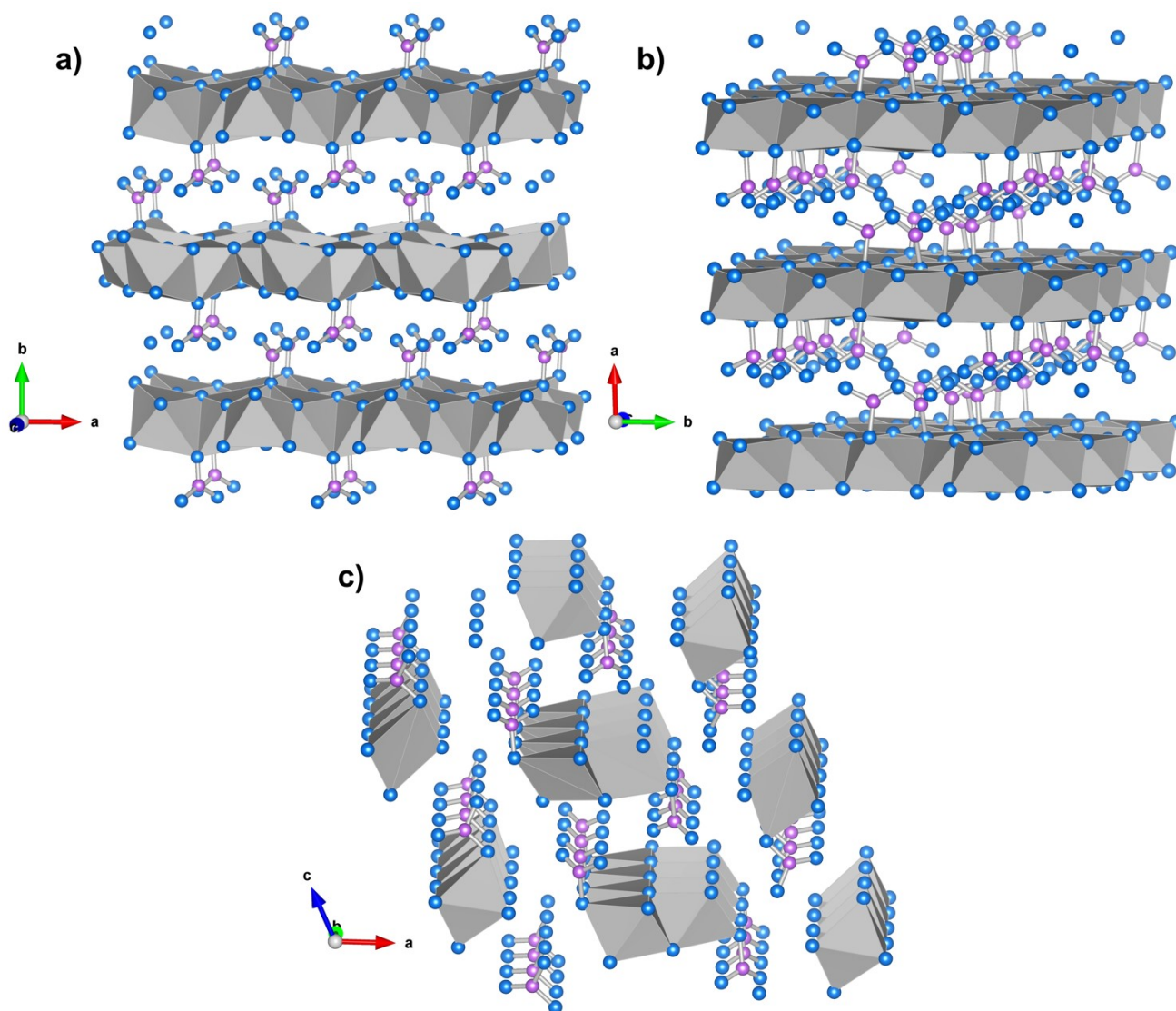


Figure S2. Crystal structures of the three studied layered hydroxynitrate phases (a) $\text{Cu}_2(\text{OH})_3(\text{NO}_3)$ where $x = 0.5$ (mineral gerhardtite), (b) $\text{Zn}_3(\text{OH})_4(\text{NO}_3)_2$ where $x = 0.67$ and (c) $\text{Zn}(\text{OH})(\text{NO}_3) \cdot \text{H}_2\text{O}$ where $x = 1$.^{4–6} M(II) cations form octahedra (grey) with oxygen atoms (blue) arranged into layers that extend over the *a* and *b* directions. Nitrate anions (nitrogen atoms shown in purple) substitute for the hydroxyl group to varying extents depending on the value of x and are coordinated directly to the metal cation.

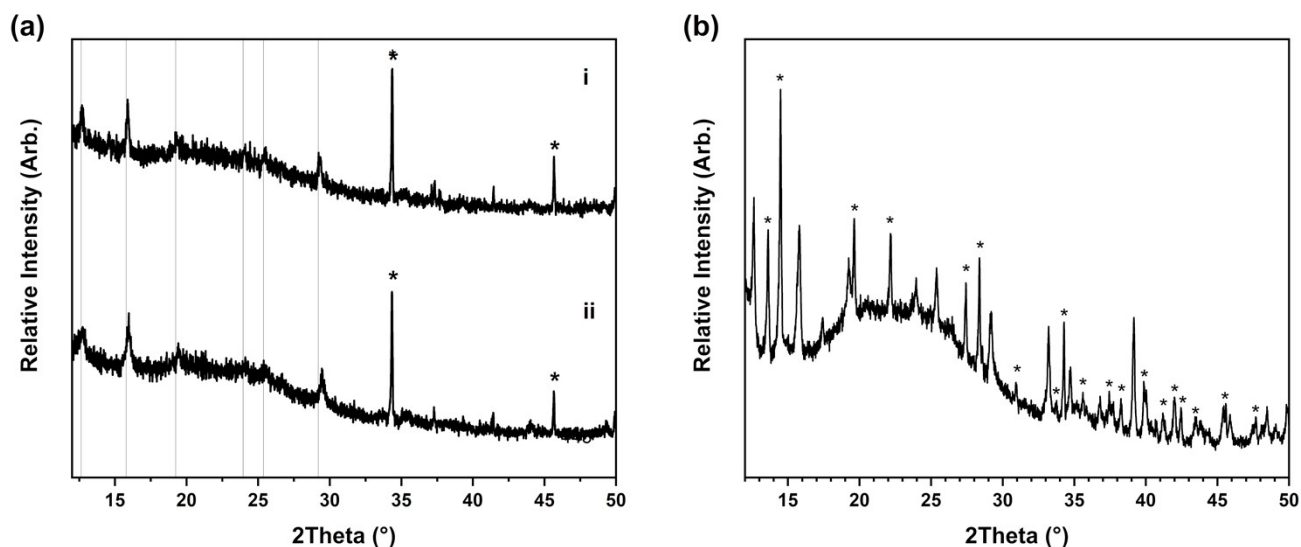


Figure S3. Powder X-ray diffraction patterns collected with Co $K_{\alpha 1}$ radiation ($\lambda = 1.7889 \text{ \AA}$) (a) of (i) $\text{Ni}(\text{OH})(\text{NO}_3) \cdot \text{H}_2\text{O}$ and (ii) $\text{Co}(\text{OH})(\text{NO}_3) \cdot \text{H}_2\text{O}$ prepared by the mechanochemical method before washing was performed to remove the sodium nitrate (NaNO_3) impurity. The vertical lines indicate the reflections of hydroxynitrate phases whilst the reflections marked with an asterisk indicate the presence of sodium nitrate (ICDD PDF 36-1474).⁷ (b) $\text{Co}(\text{OH})(\text{NO}_3) \cdot \text{H}_2\text{O}$ prepared by the mechanochemical method after the washing step was performed. The reflections marked with an asterisk indicate the presence of an unassigned impurity phase.

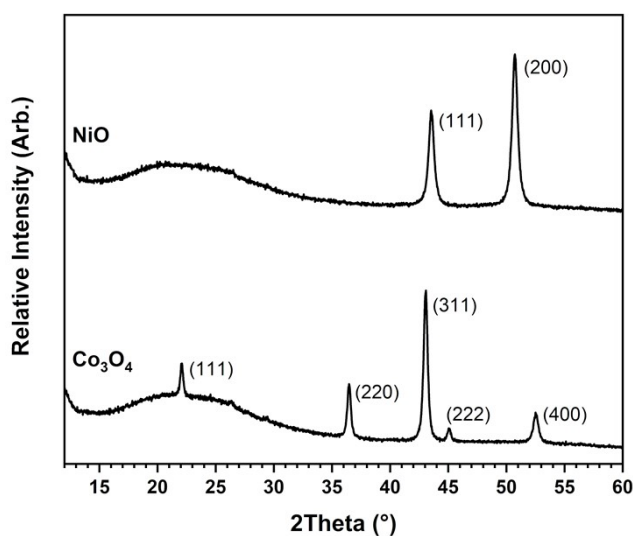


Figure S4. Powder X-ray diffraction patterns collected with Co $K_{\alpha 1}$ radiation ($\lambda = 1.7889 \text{ \AA}$) of the nickel and cobalt oxide products obtained after thermogravimetric analysis of the nickel and cobalt hydroxide phases. The hkl assignments are given for the reflections of nickel(II) oxide (ICDD PDF 47-1049)⁸ and cobalt(II, III) oxide (ICDD PDF 42-1467).⁹

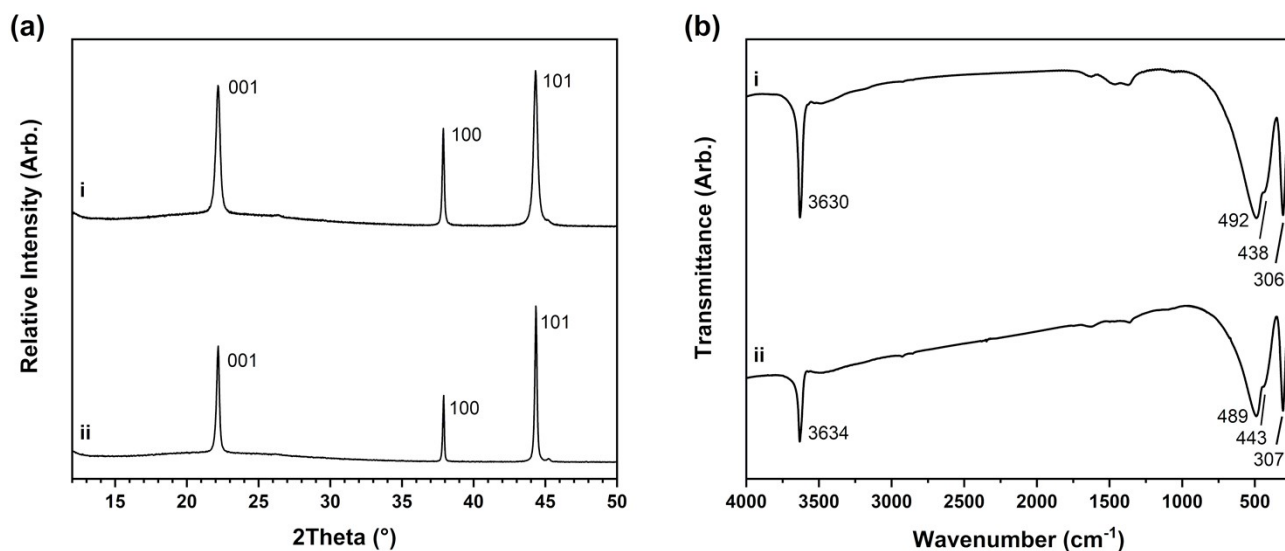


Figure S5. (a) Powder X-ray Diffraction patterns collected with Co K α_1 radiation ($\lambda = 1.7889 \text{ \AA}$) and (b) Infrared absorption spectra as CsI disks of β -Co(OH)₂ (i) prepared by the precipitation method and (ii) a commercial reagent. The hkl assignments are given for the reflections of cobalt hydroxide (ICDD PDF 30-0443).¹⁰

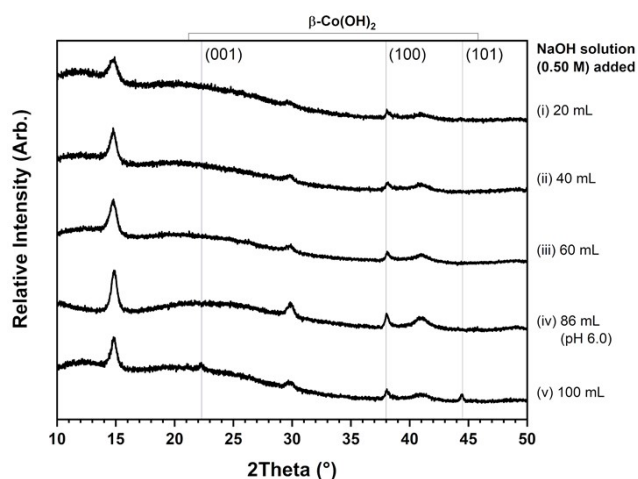


Figure S6. Powder X-ray diffraction patterns collected with Co K α_1 radiation ($\lambda = 1.7889 \text{ \AA}$) of Co₃(OH)₄(NO₃)₂ prepared by the Petrov precipitation method at different volumes of base added. The hkl assignments are given for the reflections of β -Co(OH)₂ (ICDD PDF 30-0443)¹⁰ which were detected when the solution increased beyond pH 6.0.

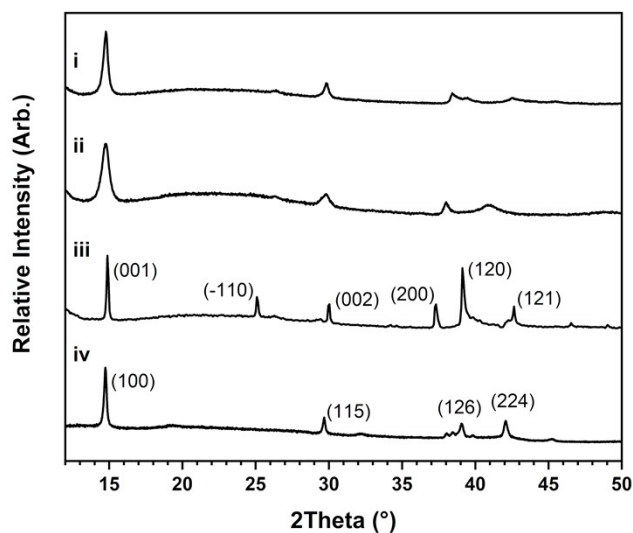


Figure S7. Powder X-ray diffraction patterns collected with Co $K_{\alpha 1}$ radiation ($\lambda = 1.7889 \text{ \AA}$) of (i) $\text{Ni}_3(\text{OH})_4(\text{NO}_3)_2$ prepared by the thermolysis method and (ii) $\text{Co}_3(\text{OH})_4(\text{NO}_3)_2$ prepared by the Petrov precipitation method as well as (iii) $\text{Cu}_2(\text{OH})_3(\text{NO}_3)$ where $x=0.5$ and (iv) $\text{Mg}_3(\text{OH})_4(\text{NO}_3)_2$ where $x=0.67$. The hkl assignments are given for the reflections of $\text{Cu}_2(\text{OH})_3(\text{NO}_3)$ (ICDD PDF 15-14)¹¹ and $\text{Mg}_3(\text{OH})_4(\text{NO}_3)_2$ (ICDD PDF 26-1221).¹²

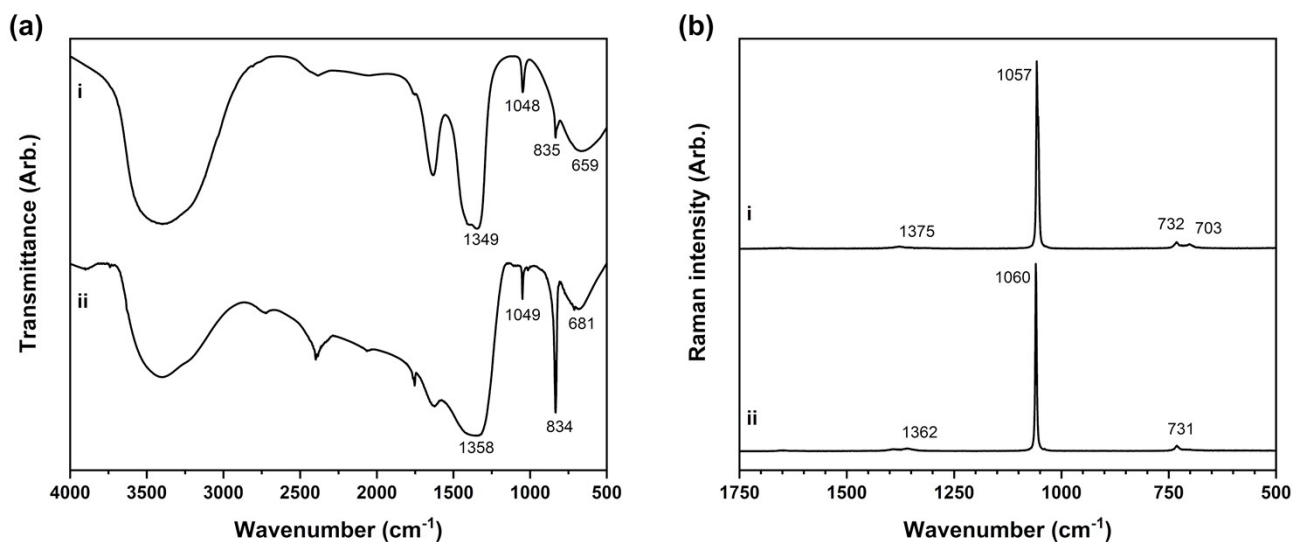


Figure S8. (a) Infrared absorption spectra as CsI disks and (b) Raman spectra of (i) $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and (ii) $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$.

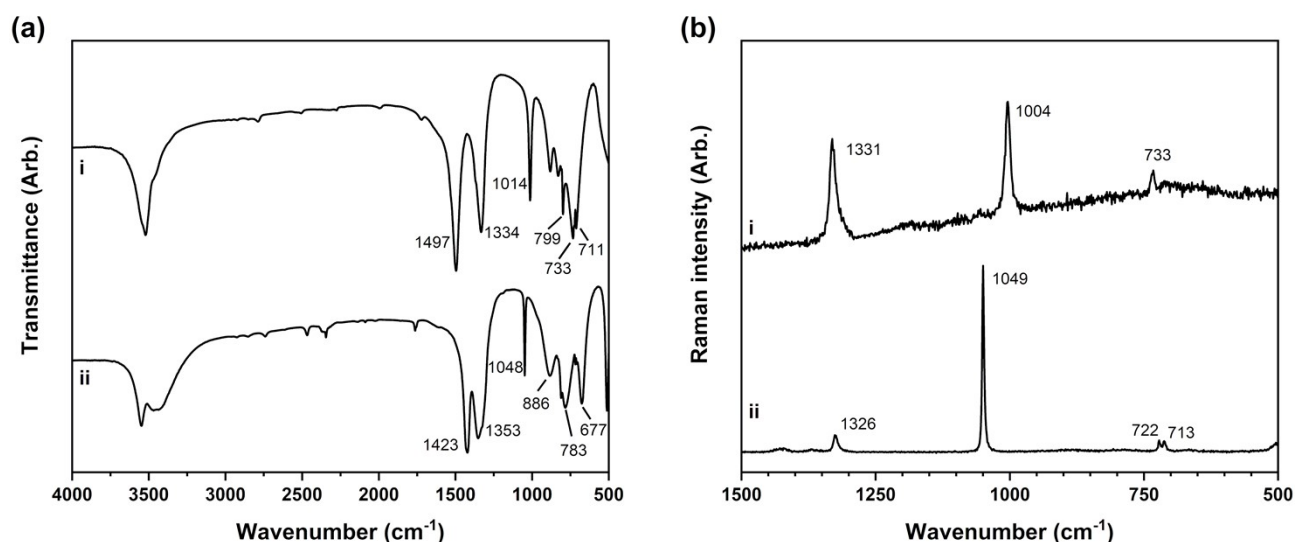


Figure S9. (a) Infrared absorption spectra as CsI disks and (b) Raman spectra of (i) Mg₃(OH)₄(NO₃)₂ and (ii) Cu₂(OH)₃(NO₃) prepared by the thermolysis method.

Extended Data Tables

Table S1. Cobalt gravimetric analysis carried out for the three studied cobalt phases and compared to a cobalt sulfate standard. These data show a systematic error is observed when carrying out this method for determination of the cobalt content.

	Cobalt content (diff. %)	ESD (±%)
Co(SO ₄).6H ₂ O	-3.9	0.6
Co ₃ (OH) ₄ (NO ₃) ₂	-3.7	0.9
Co(OH)(NO ₃).H ₂ O	-4.3	1.9
Co(OH) ₂	-2.4	2.3

References

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