

## Electronic Supplementary Information

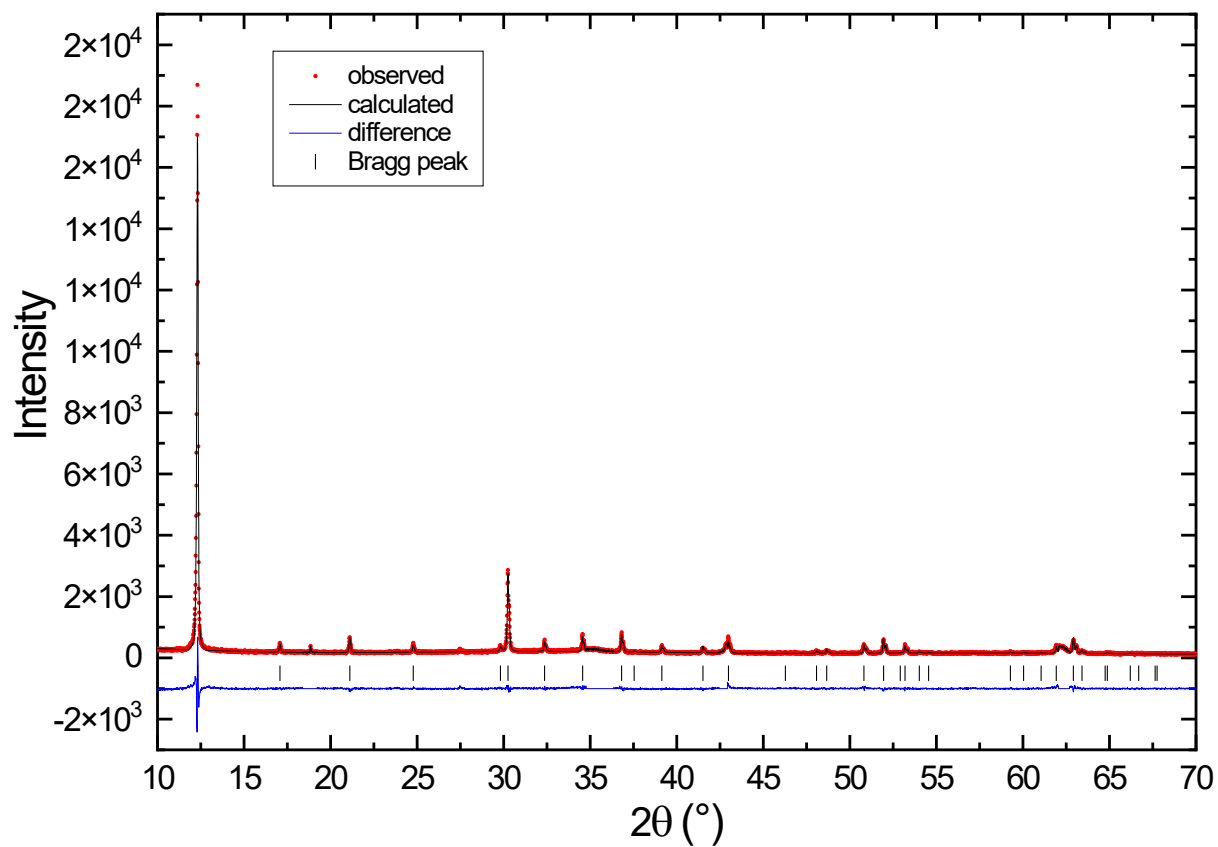
### Microstructured layered-kagome $\text{BaCo}_3(\text{VO}_4)_2(\text{OH})_2$ with variable crystallite size: alternative synthetic route and comparison with nanostructured samples

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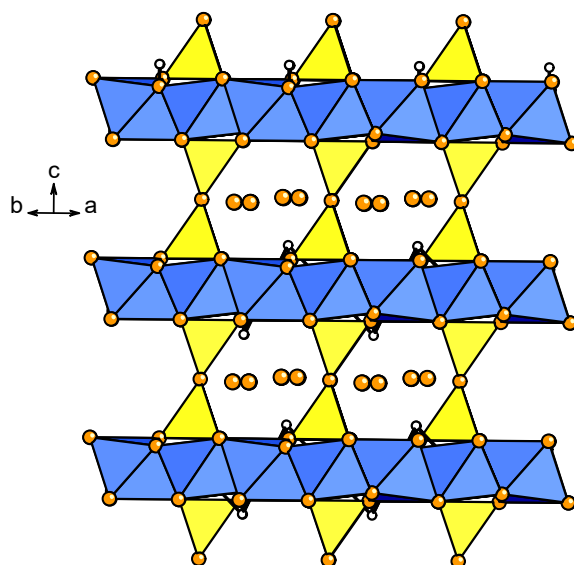
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**Figure S1.** Rietveld refinement plot for  $\text{Co}_3\text{V}_2\text{O}_7(\text{OH})_2 \cdot 2\text{H}_2\text{O}$  showing observed, calculated and difference patterns. The high-level noisy pattern is due to cobalt fluorescence.



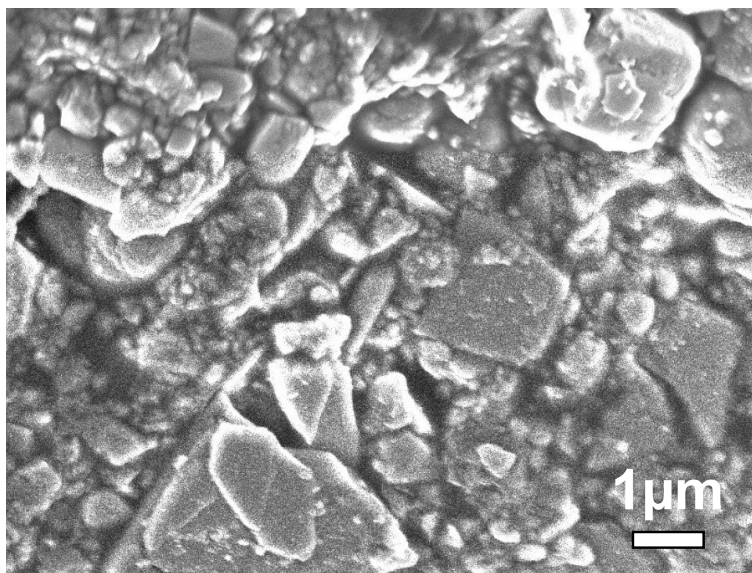
**Figure S2.** Crystal structure of  $\text{Co}_3\text{V}_2\text{O}_7(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ . Blue octahedra:  $\text{CoO}_6$ , yellow tetrahedra:  $\text{VO}_4$ , orange sphere: oxygen, white sphere: hydrogen.

**Table S1.** Structural parameters and crystallite size of  $\text{Co}_3\text{V}_2\text{O}_7(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ .

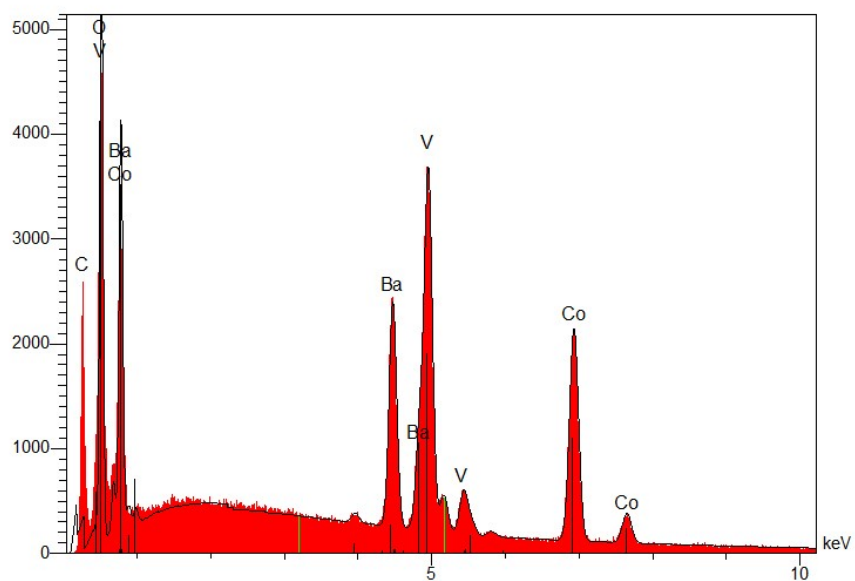
SG $P\bar{3}m$ : $a=5.9886(3)$ Å, $c=7.1804(4)$ Å, Cryst. size= $217(5)$ nm $\perp$ [001]						
Atom	x	y	z	SOF		$U_{\text{iso}}$ Equiv (Å <sup>2</sup> )
Co <sub>1</sub>	0.5	0	0	1		0.019(7)
V <sub>1</sub>	0	0	0.2494(16)	1		0.034(7)
O <sub>1</sub>	0.6667	0.3333	0.874(5)	1		0.000(7)
O <sub>2</sub>	0.155(3)	0.311 (5)	0.829 (2)	1		0.000
O <sub>3</sub>	0	0	0.5	1		0.000
O <sub>4</sub>	0.7548(13)	0.374(6)	0.482(12)	1		0.000
H <sub>1</sub>	0.6667	0.3333	0.75*	1		0.02*
GOF= 1.41, Rwp= 9.49, Rp= 7.43						

Aniso. ADP (Å <sup>2</sup> )	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Co <sub>1</sub>	0.013(9)	0.002(10)	0.039(6)	0.001(5)	0.014(11)	0.03(2)
V <sub>1</sub>	0.032(10)	0.032	0.037(9)	0.0216(5)	0	0

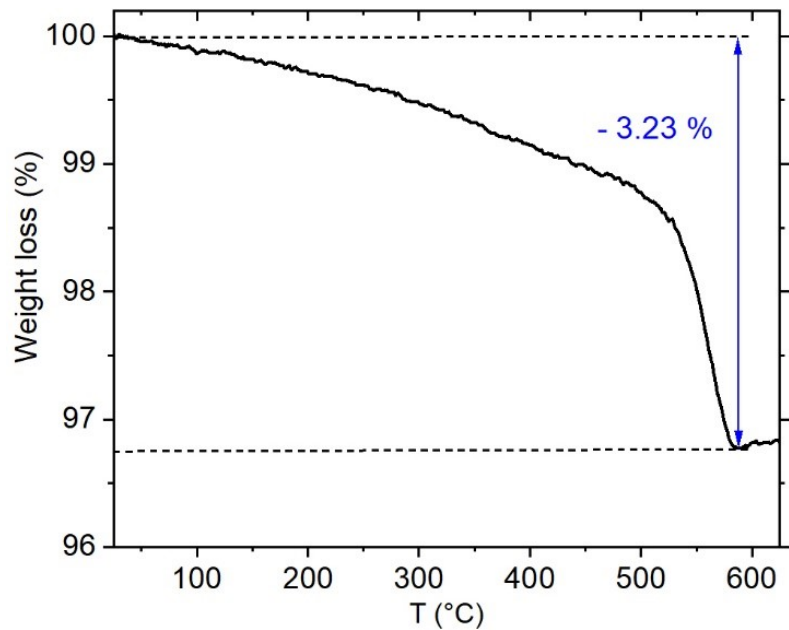
\*not refined



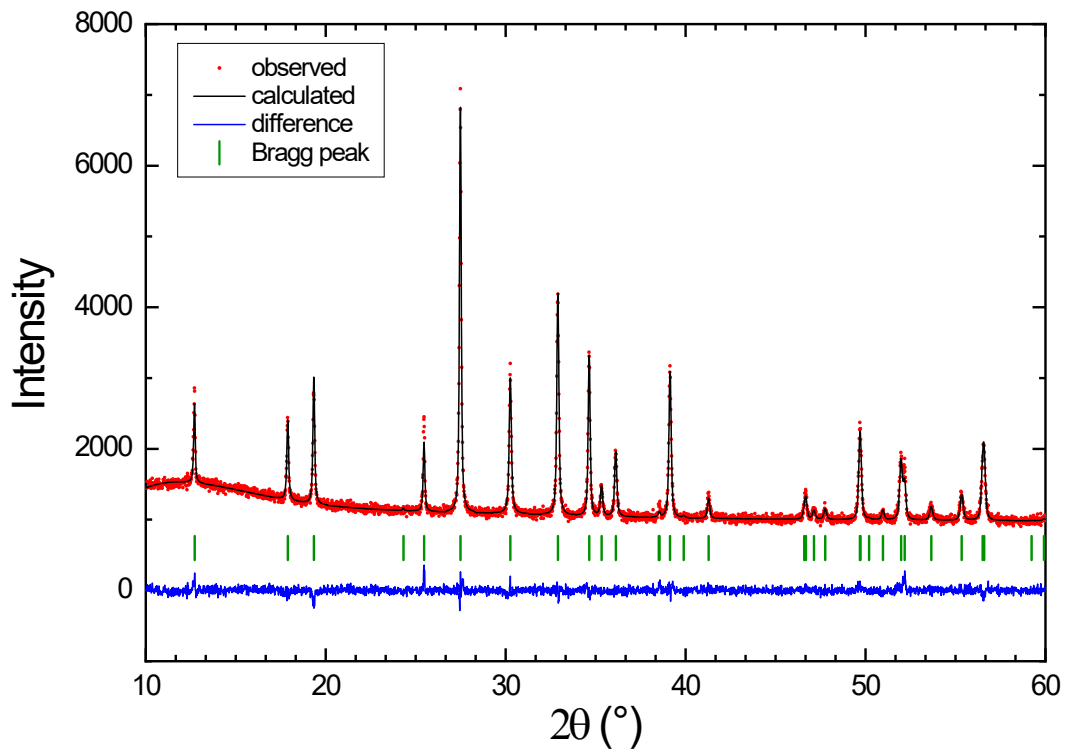
**Figure S3.** SEM image of  $\text{Co}_3\text{V}_2\text{O}_7(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ .



**Figure S4.** EDS spectrum acquired on micrometric particles of  $\text{BaCo}_3\text{-A}$  (a similar spectrum has been obtained for  $\text{BaCo}_3\text{-B}$ ).



**Figure S5.** Thermogravimetric curve of microstructured  $\text{BaCo}_3\text{-B}$  recorded in air.



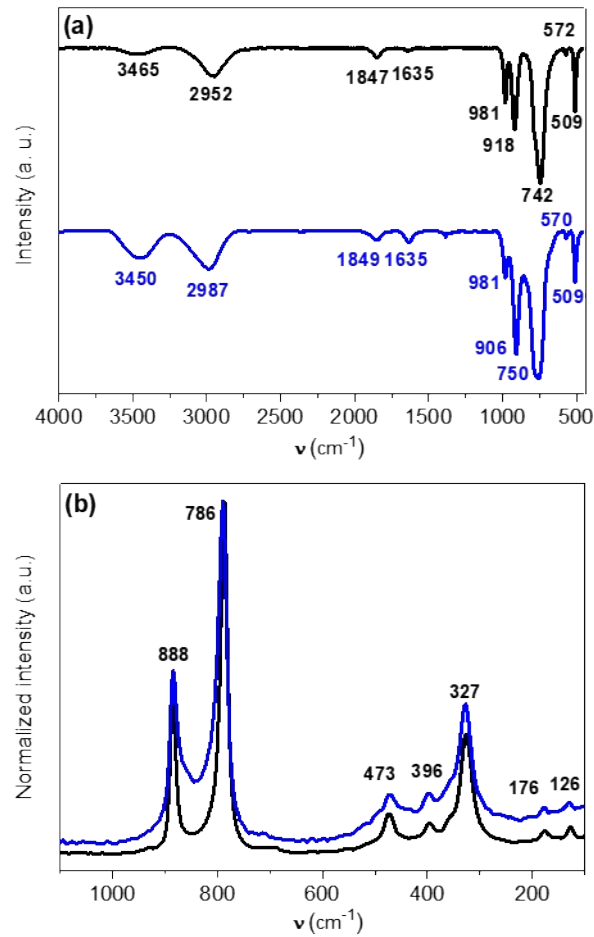
**Figure S6.** Rietveld refinement plot for microstructured  $\text{BaCo}_3\text{-B}$  showing observed, calculated and difference patterns. The high-level noisy pattern is due to cobalt fluorescence.

**Table S2.** Structural parameters and crystallite size of **BaCo<sub>3</sub>-B**.

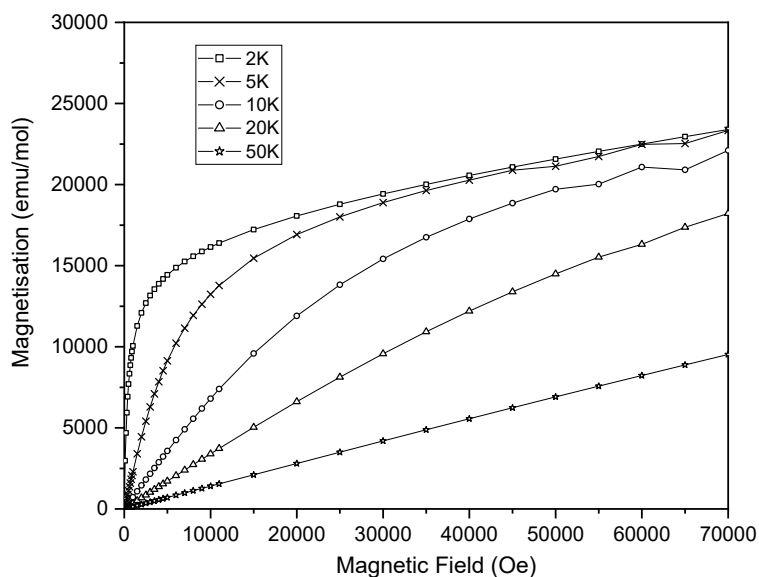
SG $R^{3m}$ : $a=5.9238(2)$ Å, $c=21.0609(9)$ Å, Cryst. size= $92(3)$ nm $\perp$ [001], $47(5)$ nm // [001]					
Atom	x	y	z	SOF	$U_{iso}$ Equiv (Å <sup>2</sup> )
Ba <sub>1</sub>	0.6667	0.3333	0.8333	1	0.033(2)
Co <sub>1</sub>	0.8333	0.6667	0.6667	1	0.013(2)
V <sub>1</sub>	0.3333	0.6667	0.7527(3)	1	0.015(3)
O <sub>1</sub>	0.3333	0.6667	0.832(8)	1	0.005(3)
O <sub>2</sub>	0.4930(9)	0.5070(10)	0.7275(4)	1	0.005
O <sub>3</sub>	0	0	0.7030(10)	1	0.005
H <sub>1</sub>	0	0	0.7494*	1	0.008*

GOF= 1.11, Rwp= 3.32, Rp= 2.62

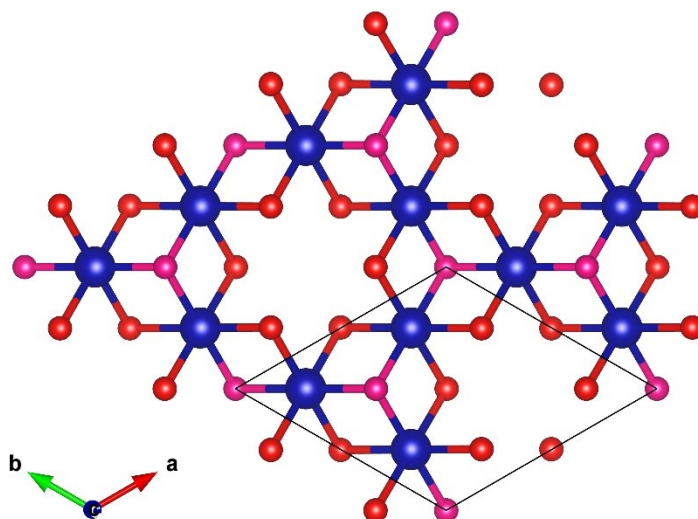
\*not refined



**Figure S7.** Comparison of (a) FT-IR and (b) Raman spectra of microstructured **BaCo<sub>3</sub>-B** (black line) and **BaCo<sub>3</sub>(VO<sub>4</sub>)<sub>2</sub>(OH)<sub>2</sub> nanoparticles<sup>S1</sup> (NPs)** (blue line).



**Figure S8.** Magnetic field dependence of magnetisation measured at several temperatures for  $\text{BaCo}_3\text{-B}$ .



**Figure S9.** Fragment of a kagome layer in the  $\text{BaCo}_3(\text{VO}_4)_2(\text{OH})_2$  crystal structure (projection along  $[001]$  direction). Blue, red, and pink spheres represent Co, O<sub>2</sub>, and O<sub>3</sub> atoms (see Tables 1 and S2), respectively. Barium, vanadium, and hydrogen atoms have been removed for clarity. Each kagome layer is formed from compressed  $\text{Co}(\text{O}_2)_4(\text{O}_3)_2$  octahedra with  $d_{\text{Co-O}_2} = 2.176(4)$  Å and  $d_{\text{Co-O}_3} = 1.9407(6)$  Å.

## References

[S1] R. Dessapt, L. Lajaunie, J. J. Calvino, P. Deniard, I. Trenque and C. Payen, *J. Mater. Chem. C*, 2022, **10**, 3287-3291.