

## Electronic Supplementary Information

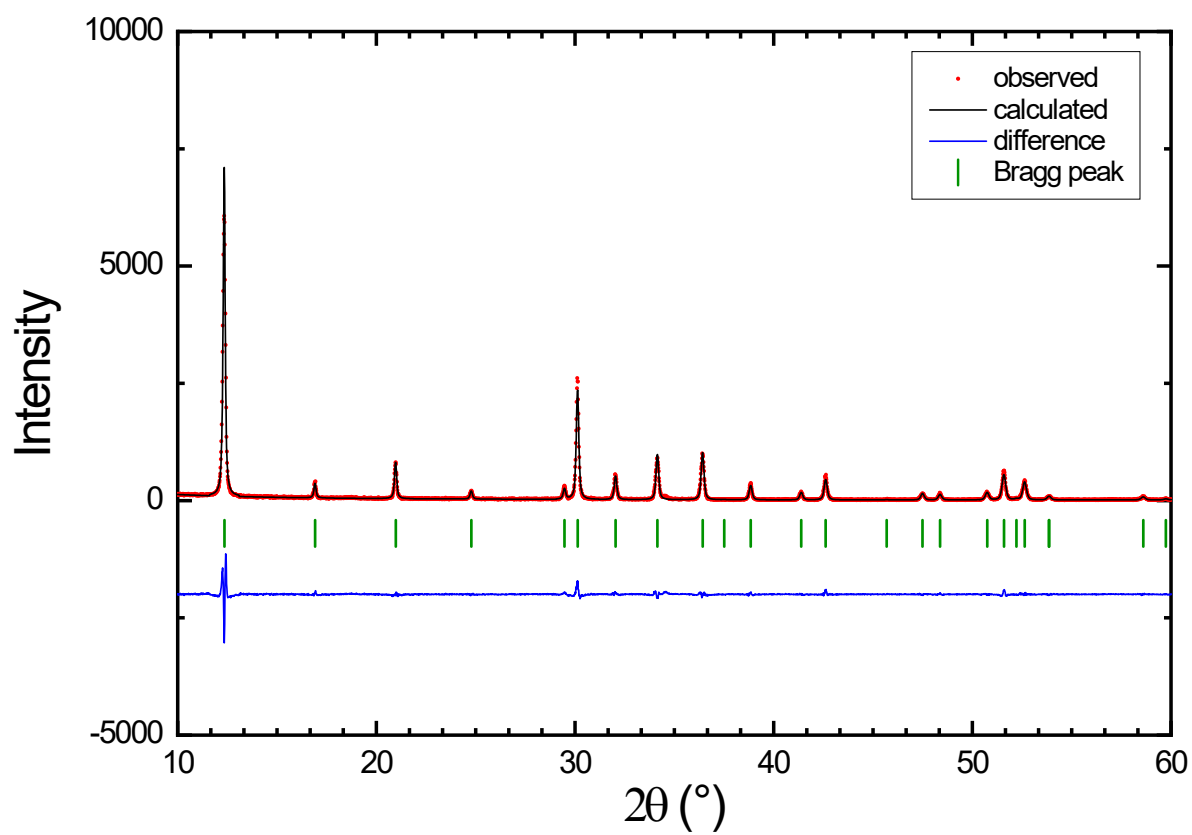
### Micro- and nanostructured layered-kagome zinc orthovanadate $\text{BaZn}_3(\text{VO}_4)_2(\text{OH})_2$

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**Figure S1.** Portion of the Rietveld refinement plot for  $\text{Zn}_3\text{V}_2\text{O}_7(\text{OH})_2 \cdot 2\text{H}_2\text{O}$  showing observed, calculated and difference patterns. Data were taken and refined from  $2\theta = 10^\circ$  to  $2\theta = 90^\circ$ .

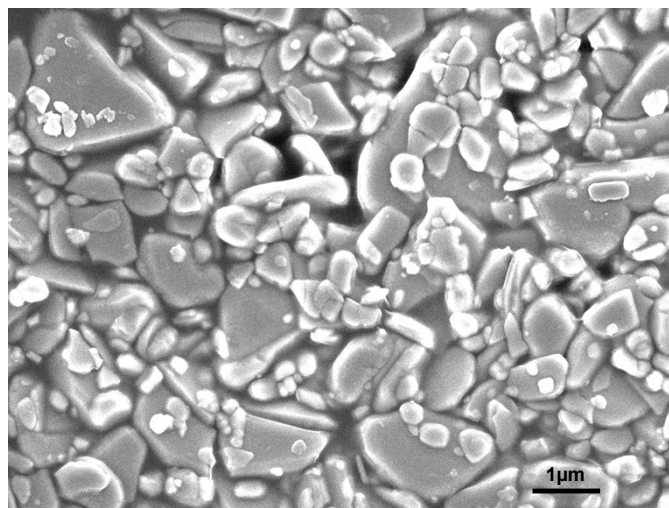
**Table S1.** Structural parameters, crystallite size, and final agreement factors for  $\text{Zn}_3\text{V}_2\text{O}_7(\text{OH})_2 \cdot 2\text{H}_2\text{O}$  derived from our Rietveld refinement.

S.G ( $P3m$ ): $a$ (Å) = 6.0698(2), $c$ (Å) = 7.1986(5), Cryst. Size = 109(2) nm					
Atom	x	y	z	SOF	$U_{\text{iso}}$ Equiv (Å <sup>2</sup> )
Zn <sub>1</sub>	1/2	0	0	1	0.031(2)
V <sub>1</sub>	0	0	0.2506(8)	1	0.019(2)
O <sub>1</sub>	2/3	1/3	0.878(3)	1	0.023(4)
O <sub>2</sub>	0.1533(13)	0.307(3)	0.826 (2)	1	0.023
O <sub>3</sub>	0	0	1/2	1	0.023
O <sub>4</sub>	0.733(6)	0.367(3)	0.498(11)	0.333	0.023
H <sub>1</sub>	2/3	1/3	0.75*	1	0.07599*
GOF = 1.4, Rwp = 15.73, and Rp = 11.73					

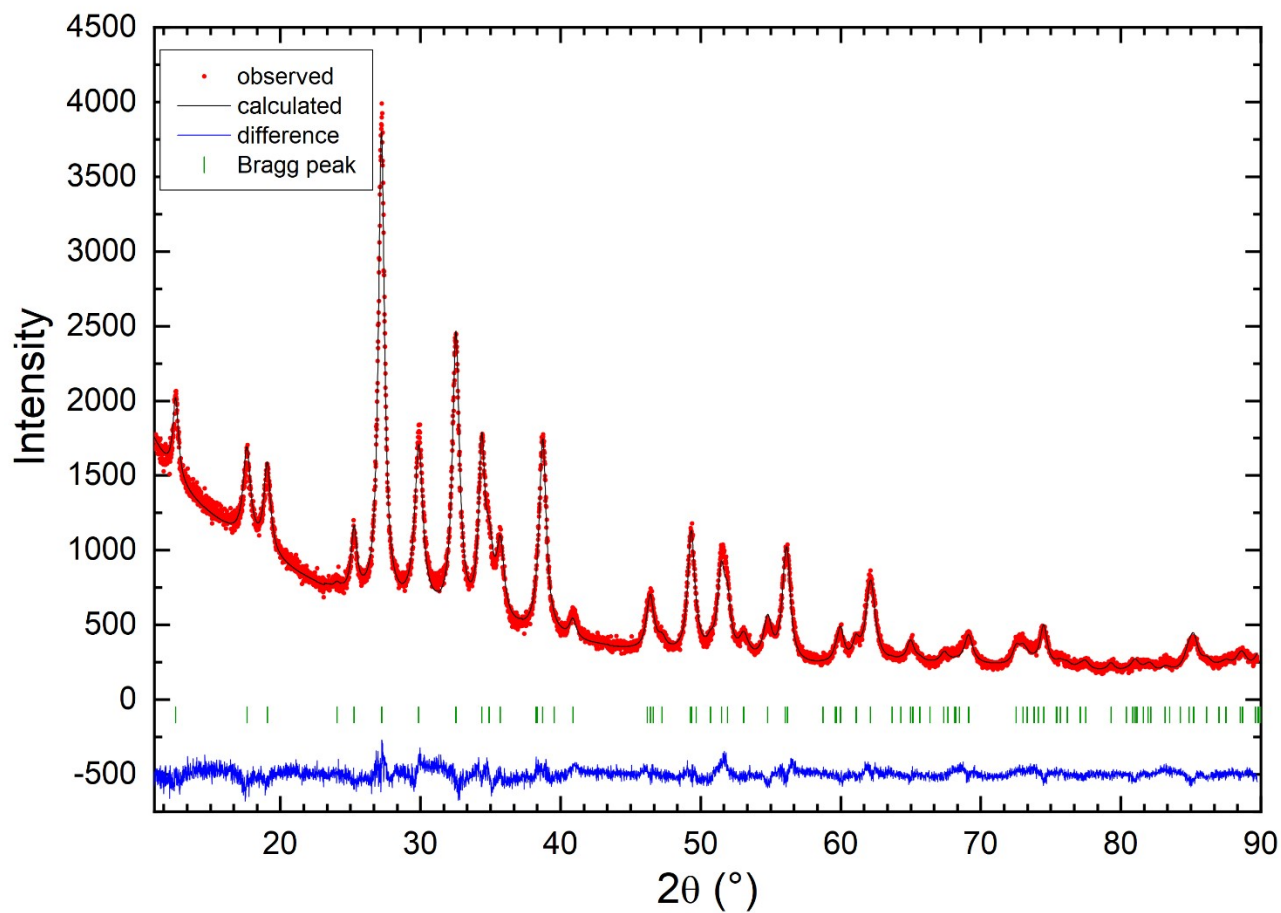
\*not refined

ADP harmonic parameters

Aniso. ADP (Å <sup>2</sup> )	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Zn <sub>1</sub>	0.031(3)	0.025(4)	0.035(3)	0.012(2)	0.008(4)	0.016(8)
V <sub>1</sub>	0.020(3)	0.020	0.017(4)	0.010(2)	0	0



**Figure S2.** SEM image of  $\text{Zn}_3\text{V}_2\text{O}_7(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ .



**Figure S3.** Rietveld refinement plot for **BaZn<sub>3</sub> NPs-25min** showing observed, calculated and difference patterns.

**Table S2.** Structural parameters, crystallite sizes, and final agreement factors for **BaZn<sub>3</sub> NPs-7h**.

S.G ( $R\bar{3}m$ ): a (Å) = 5.9608(5), c (Å) = 21.062(2), Cryst. Size = 26.0(8) nm // [001], 37(2) nm $\perp$ [001]					
	x	y	z	SOF	$U_{iso}$
Ba <sub>1</sub>	2/3	1/3	5/6	1	0.042(3)
Zn <sub>1</sub>	5/6	2/3	2/3	1	0.040(4)
V <sub>1</sub>	1/3	2/3	0.7561(4)	1	0.011(4)
O <sub>1</sub>	1/3	2/3	0.8347(12)	1	0.007(4)
O <sub>2</sub>	0.493(2)	0.507(2)	0.7322(6)	1	0.007
O <sub>3</sub>	1	1	0.704(2)	1	0.007
H <sub>1</sub>	1	1	0.7494*	1	0.008*
GOF = 2.28, Rwp = 4.05, and Rp = 2.73					

\*not refined

## ADP harmonic parameters

	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Ba <sub>1</sub>	0.051(4)	0.051	0.023(5)	0.026(2)	0	0
Zn <sub>1</sub>	0.044(4)	0.053(5)	0.026(6)	0.027(2)	0.004(2)	0.008(4)
V <sub>1</sub>	0.005(4)	0.005	0.023(7)	0.003(2)	0	0

**Table S3.** Structural parameters, crystallite sizes, and final agreement factors for **BaZn<sub>3</sub> NPs-25 min.**

S.G ( $R\bar{3}m$ ): a (Å) = 5.9675(10), c (Å) = 21.100(4), Cryst. Size = 13.1(4) nm // [001], 19.3(1) nm $\perp$ [001]					
	x	y	z	SOF	$U_{iso}$
Ba <sub>1</sub>	2/3	1/3	5/6	1	0.069(4)
Zn <sub>1</sub>	5/6	2/3	2/3	1	0.070(4)
V <sub>1</sub>	1/3	2/3	0.7574(5)	1	0.016(4)
O <sub>1</sub>	1/3	2/3	0.8411(13)	1	0.019(4)
O <sub>2</sub>	0.490(2)	0.510(2)	0.7324(7)	1	0.019
O <sub>3</sub>	1	1	0.709(2)	1	0.019
H <sub>1</sub>	1	1	0.7494*	1	0.008*
GOF = 1.38, Rwp = 4.86, and Rp = 3.58					

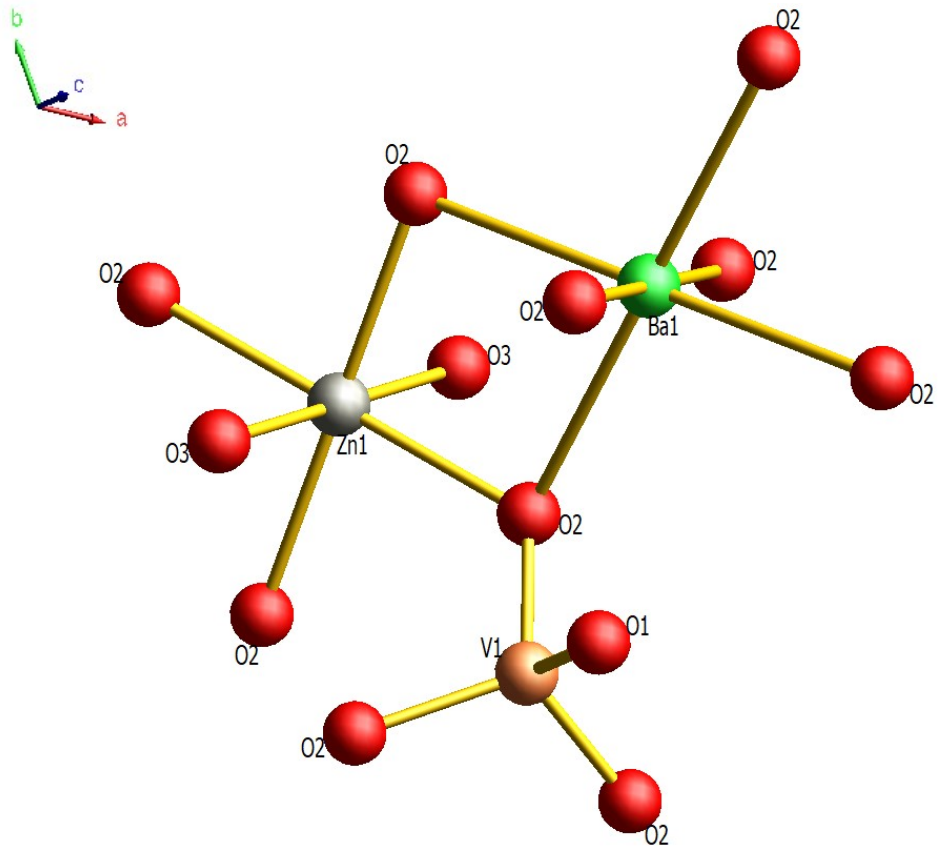
\*not refined

ADP harmonic parameters

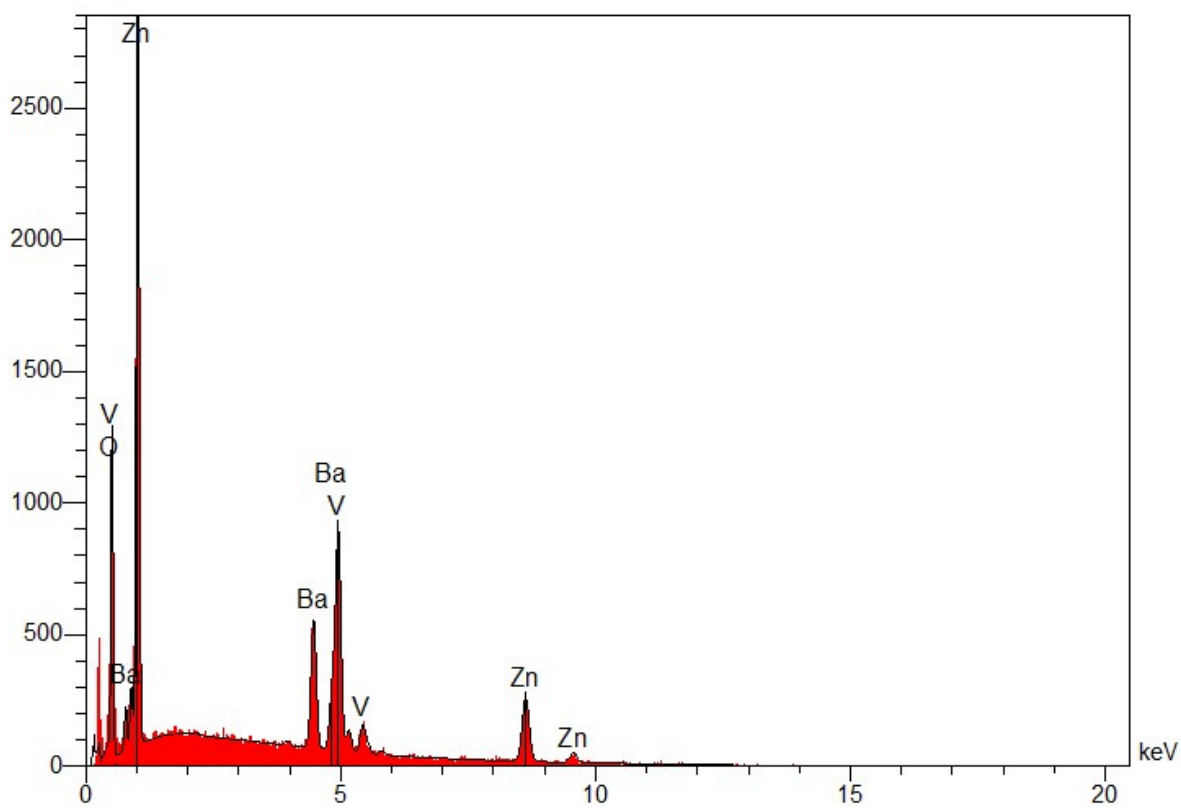
	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Ba <sub>1</sub>	0.094(6)	0.094	0.021(6)	0.047(3)	0	0
Zn <sub>1</sub>	0.075(5)	0.099(6)	0.044(8)	0.049(3)	0.014(3)	0.028(5)
V <sub>1</sub>	0.004(5)	0.004	0.039(9)	0.002(2)	0	0

**Table S4.** Main M-O (M = Ba, Zn, and V) bond distances (Å) and O-V-O angles for **BaZn<sub>3</sub> MPs, BaZn<sub>3</sub> NPs-7h and BaZn<sub>3</sub> NPs-25min.**

BaZn <sub>3</sub> MPs	BaZn <sub>3</sub> NPs-25min	BaZn <sub>3</sub> NPs-7h
Ba1—O2 (x 6): 2.811(10) Ba1—O1 (x 4): 3.4488(3) Ba1—O1 (x 2): 3.4488(2) Mean: 3.13±0.02	Ba1—O2 (x 6): 2.81(2) Ba1—O1 (x 4): 3.449(2) Ba1—O1 (x 2): 3.4492(14) Mean: 3.13±0.03	Ba1—O2 (x 6): 2.786(12) Ba1—O1 (x 4): 3.4416(9) Ba1—O1 (x 2): 3.4416(4) Mean: 3.11±0.02
Zn1—O2 (x 2): 2.233(8) Zn1—O2 (x 2): 2.233(12) Zn1—O3 (x 2): 1.948(11) Mean: 2.14 ± 0.03	Zn1—O2 (x 2): 2.26(2) Zn1—O2 (x 2): 2.255(12) Zn1—O3 (x 2): 1.94(2) Mean: 2.15 ± 0.05	Zn1—O2 (x 2): 2.235(10) Zn1—O2 (x 2): 2.235(13) Zn1—O3 (x 2): 1.893(13) Mean: 2.12 ± 0.04
V1—O1: 1.67(2) V1—O2 (x 3): 1.706(11) Mean: 1.70 ± 0.04 Angles: O1—V1—O2 (x 3): 107.5(4)° O2—V1—O2 (x 3): 111.4(6)°	V1—O1: 1.77(3) V1—O2 (x 3): 1.701(14) Mean: 1.72 ± 0.05 Angles: O1—V1—O2 (x 3): 108.0(6)° O2—V1—O2 (x 3): 110.9(7)°	V1—O1: 1.65(3) V1—O2 (x 3): 1.722(11) Mean: 1.70 ± 0.05 Angles: O1—V1—O2 (x 3): 107.0(5)° O2—V1—O2 (x 3): 111.8(5)°

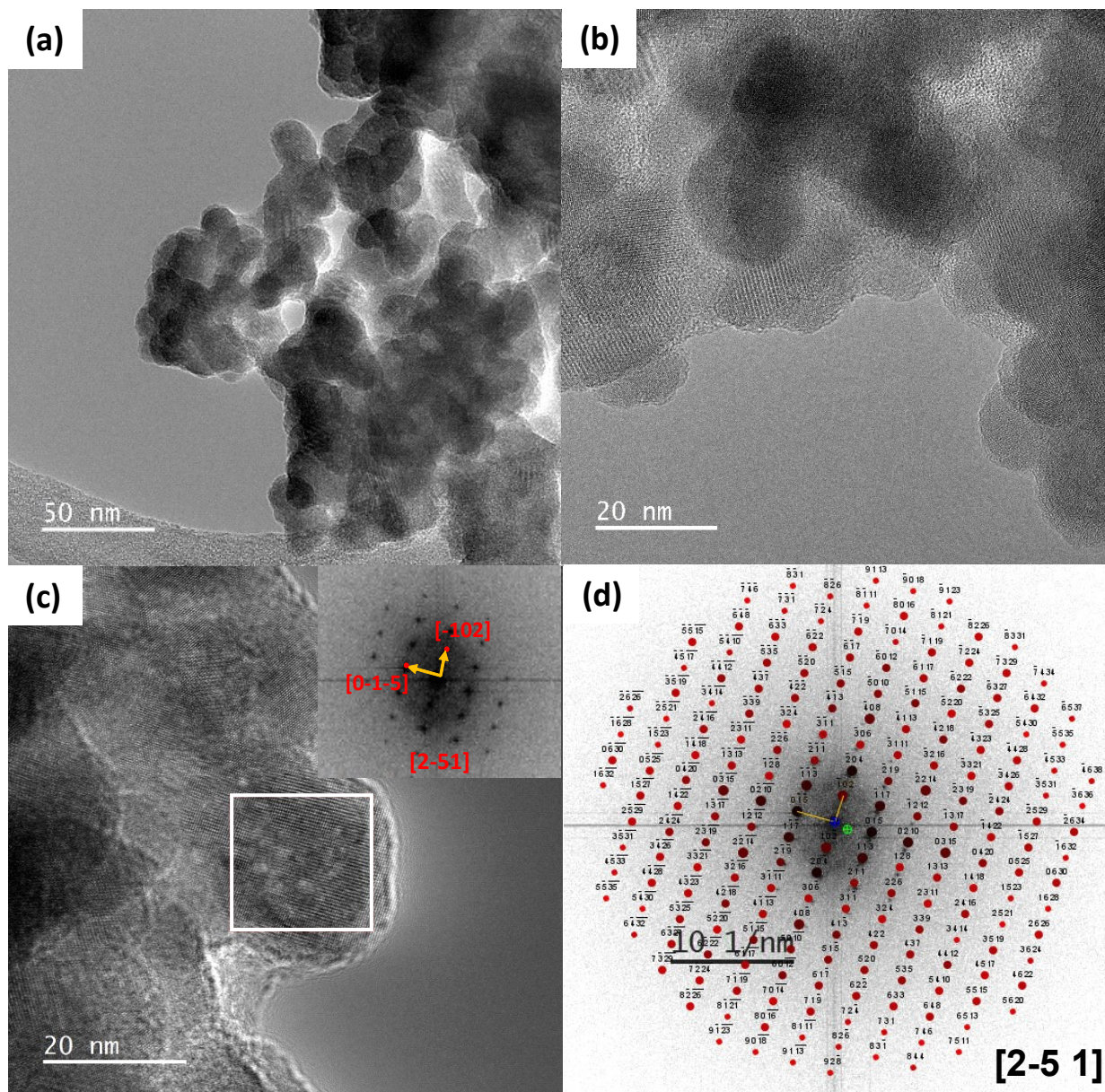


**Figure S4.** Ball and stick model showing  $\text{MO}_x$  polyhedra ( $M = \text{Ba}, \text{Zn}, \text{and V}$ ) in the crystal structure of  $\text{BaZn}_3(\text{VO}_4)_2(\text{OH})_2$ . The six long  $\text{Ba—O}$  distances are not visualized for the sake of clarity.

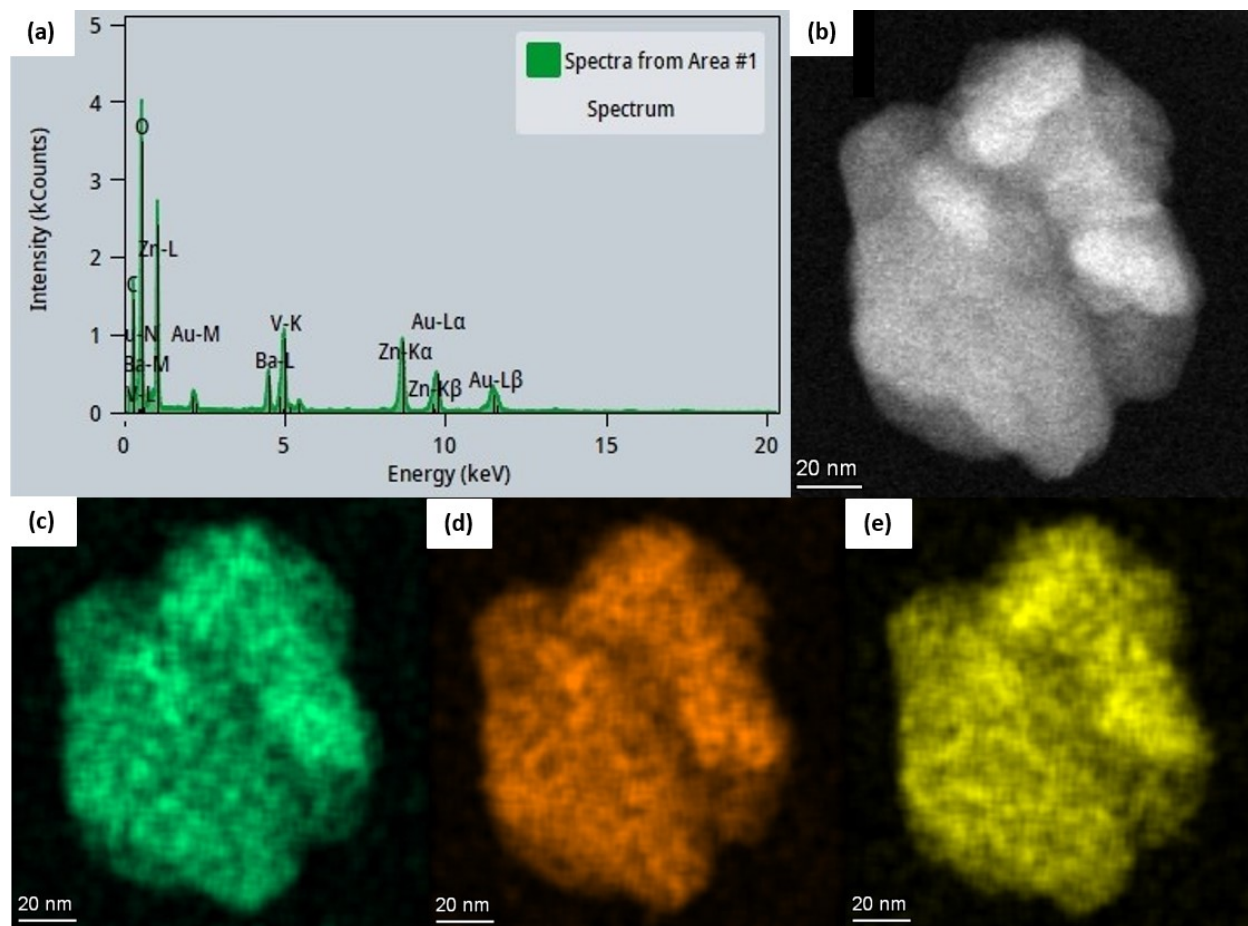


**Figure S5.** SEM-EDS spectrum acquired on  $\text{BaZn}_3$  MPs.

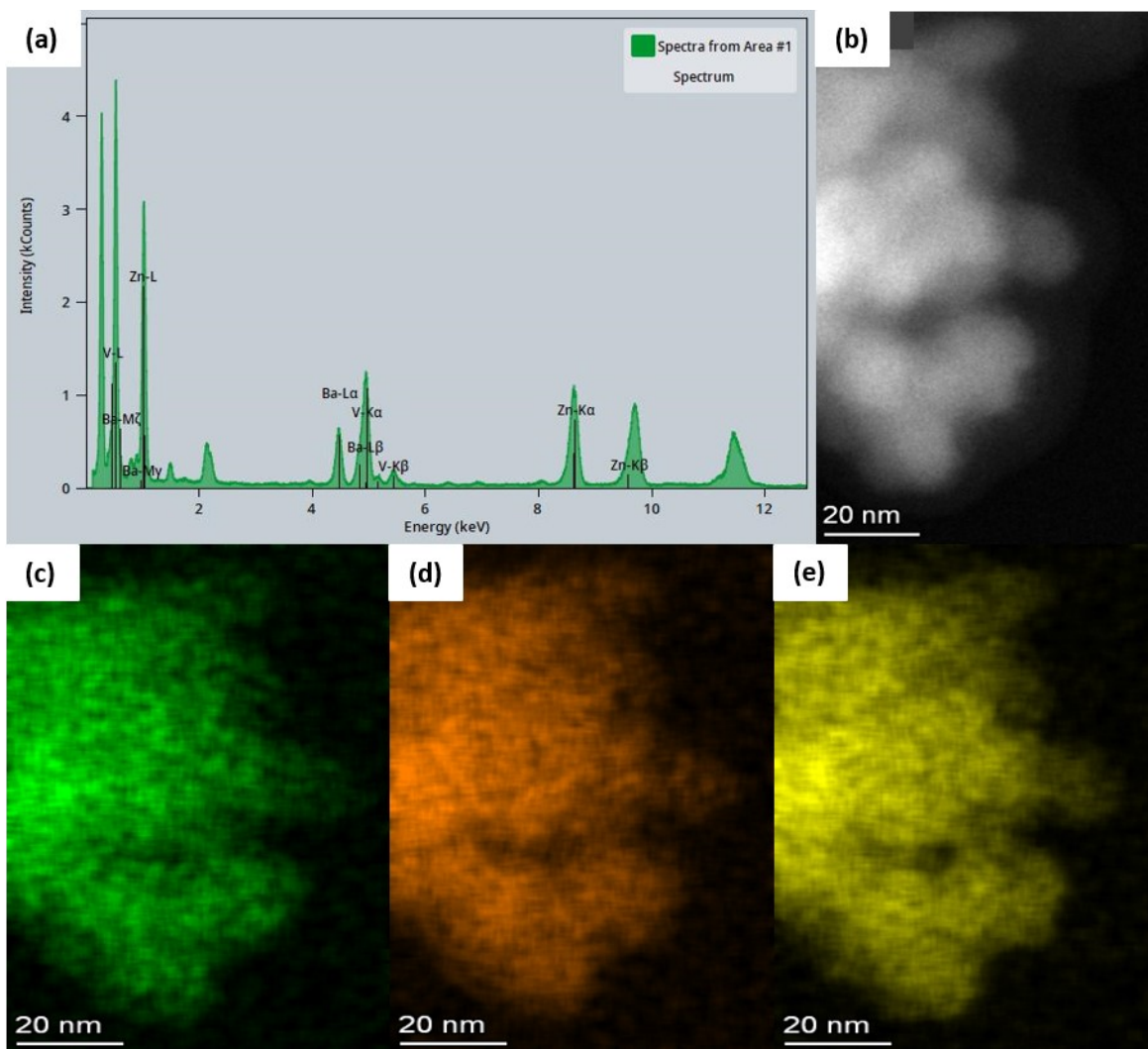




**Figure S6.** (a, b) TEM images of representative **BaZn<sub>3</sub> NPs-25min** at different magnifications. Reticular planes are visible in (b). (c, d) FFT diffraction pattern along the [2-51] zone axis from the region marked out by the white rectangle in (c). Global indexing in (d) was obtained using the structural model deduced from XRD (Table S3).



**Figure S7.** (a) EDS spectrum of the chosen particle of **BaZn<sub>3</sub> NPs-7h** displayed in (b). (c,d,e) EDS mapping analysis of Ba, Zn and V elements, respectively.



**Figure S8.** (a) EDS spectrum of the chosen particle of **BaZn<sub>3</sub> NPs-25min** displayed in (b). (c,d,e) EDS mapping analysis of Ba, Zn and V elements, respectively.