Uniaxial thermal expansion behaviors and ionic conduction in a layered $(NH_4)_2V_3O_8$

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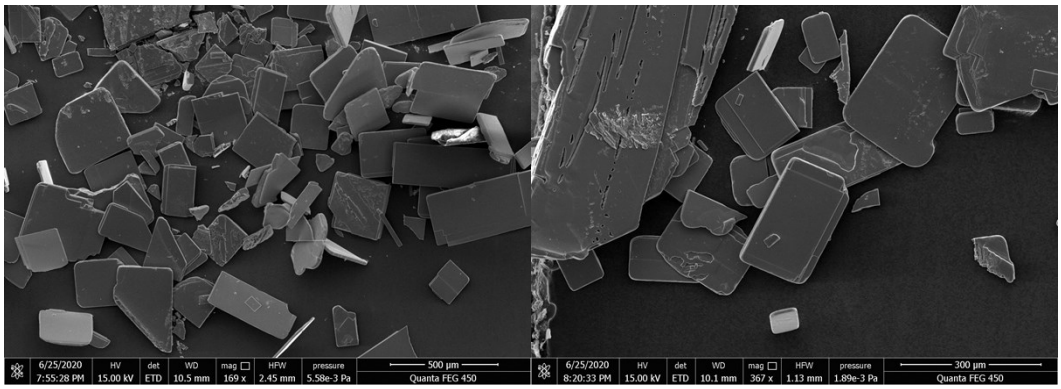

Fig. S1: SEM images with different magnifications for the lamellar crystals of $(NH_4)_2V_3O_8$.

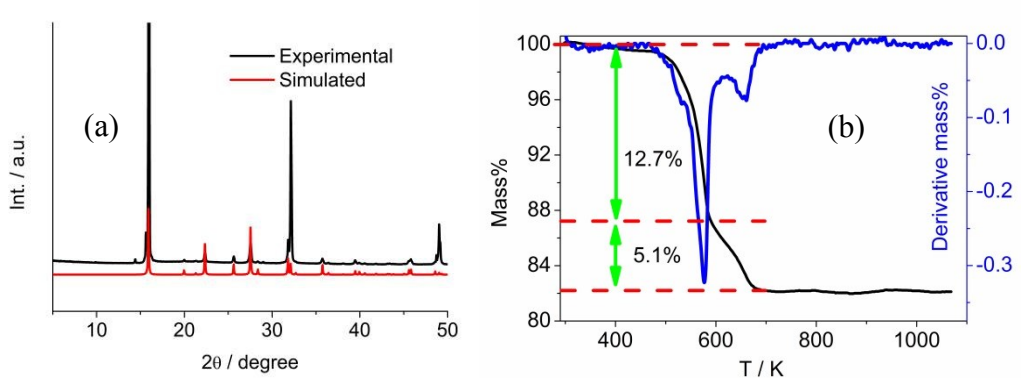

Fig. S2: (a) PXRD patterns of $(NH_4)_2V_3O_8$ at ambient temperature (b) TG and its derivative region of $(NH_4)_2V_3O_8$ in 303-1073 K.

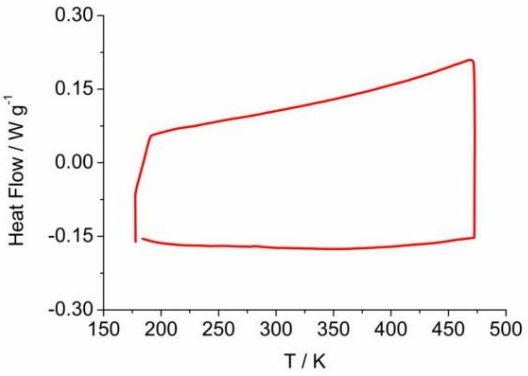

Fig. S3: DSC plots of $(NH_4)_2V_3O_8$ in 173-473 K.

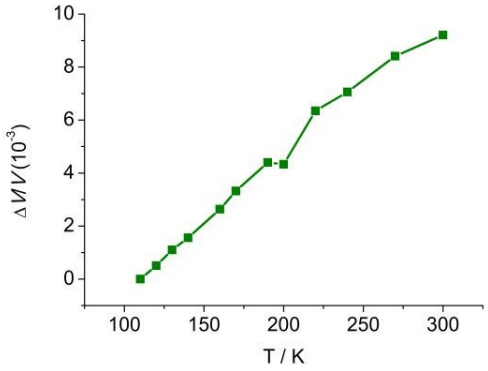

Fig. S4: Plots of relative cell parameters of $\Delta V/V$ against temperature in the range of 110-300 K for $(NH_4)_2V_3O_8$.

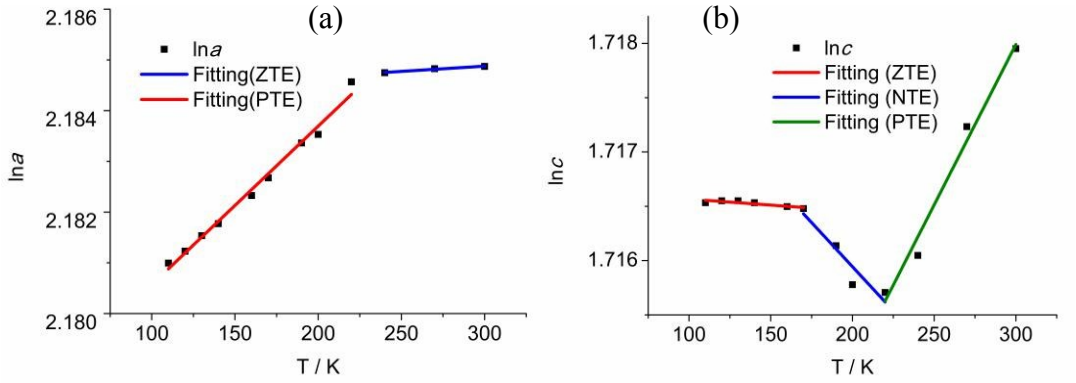

Fig. S5: Plots of lattice parameters (*a* and *c*) as a function of temperature in the form of natural logarithm for $(NH_4)_2V_3O_8$. Herein, the linear fitting is performed for *a* in the temperature ranges of 110-220 K and 240-300 K; for *c* in the temperature ranges of 110-170 K, 170-220 K and 240-300 K, respectively. The coefficient of thermal expansion of lattice is given by

$$\alpha_L = \frac{1}{L}\left(\frac{\partial L}{\partial T}\right)_p$$

In which L represents the lattice parameters *a*- and *c*-axes. In the plot of ln*L* vs. T, the slope $\frac{1}{L}\left(\frac{\partial L}{\partial T}\right)_p$ corresponds to the lattice coefficient of thermal expansion.

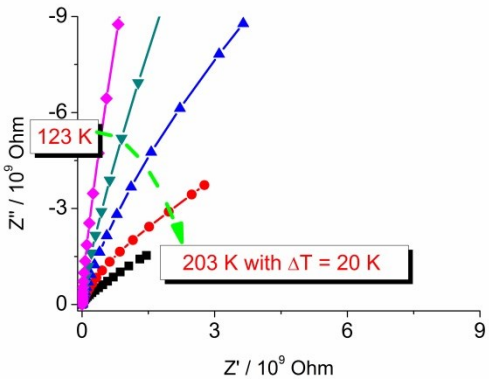

Fig. S6: Impedance plots of $(NH_4)_2V_3O_8$ at selected temperature from 123-203 K.

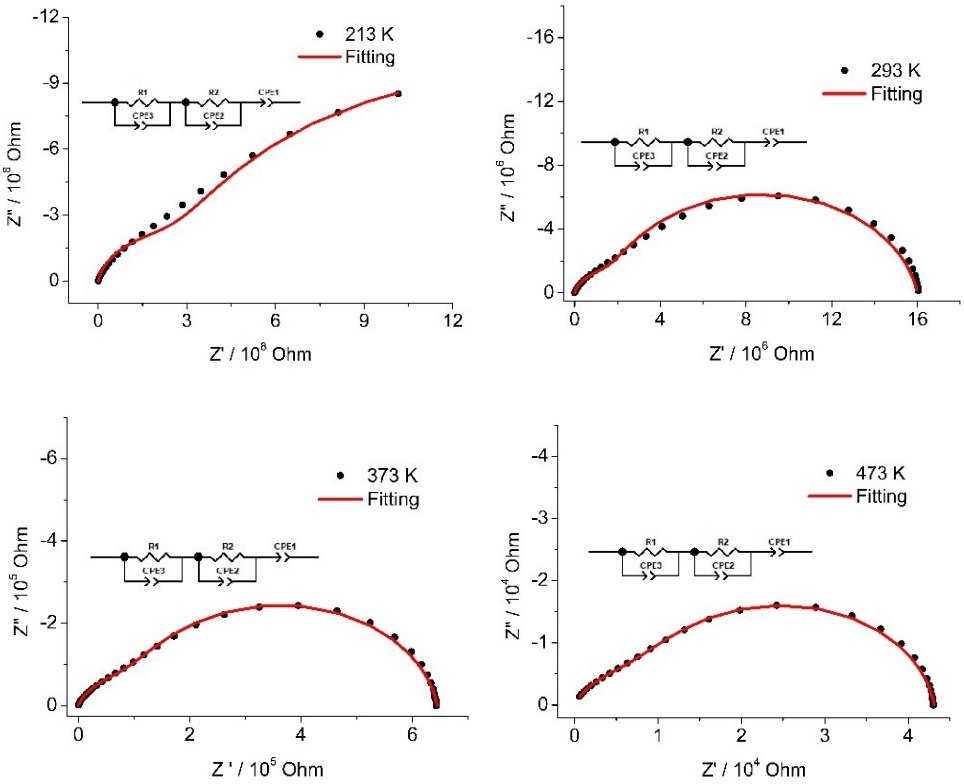

Fig. S7: Experimental and fitted impedance spectra of $(NH_4)_2V_3O_8$ at the selected temperatures (Inset: the equivalent circuit).

Table S1: Selected bond lengths and bond valence sum (BVS) for calculation of V at 110, 190 and 300K

T/K	Space group	V atom	V-O bond	Distance r /Å	bond-valence parameter r_0	Valence state (s value)
110	*P4bm*	V1	V1-O1	1.602(9)	1.784	3.96
			V1-O2	1.985(4)		
			V1-O2#1	1.985(4)		
			V1-O2#2	1.985(4)		
			V1-O2#3	1.985(4)		
		V2	V2-O4	1.637(6)	1.803	5.23
			V2-O2	1.703(4)		
			V2-O2#4	1.703(4)		
			V2-O3	1.786(3)		
Symmetry codes: #1 = -1-x, 1+y, z; #2 = -x, -2-y, z; #3 = -1+x, -1-y, z; #4 = -0.5+x, 0.5+y, z						
190	*P4bm*	V1	V1-O1	1.600(8)	1.784	4.11
			V1-O2	1.962(4)		
			V1-O2#1	1.962(4)		
			V1-O2#2	1.962(4)		
			V1-O2#3	1.962(4)		
		V2	V2-O4	1.641(5)	1.803	5.18
			V2-O2	1.706(4)		
			V2-O2#4	1.706(4)		
			V2-O3	1.792(3)		
Symmetry codes: #1= -x, -y, z; #2 = x, -y, z; #3 = -x, y, z; #4 = -x-0.5, -y-0.5, z						
300	*P4bm*	V1	V1-O1	1.599(9)	1.784	4.11
			V1-O2	1.963(4)		
			V1-O2#1	1.963(4)		
			V1-O2#2	1.963(4)		
			V1-O2#3	1.963(4)		
		V2	V2-O4	1.634(6)	1.803	5.19
			V2-O2	1.707(4)		
			V2-O2#4	1.707(4)		
			V2-O3	1.796(3)		
Symmetry codes: #1= -x+2, -y, z; #2 = x-1, -y+1, z; #3 = -x+1, y+1, z; #4 = x-0.5, y+0.5, z						

The relationship between the bond length (r) and the bond valence (s) is described below,

$$s = exp(\frac{r_0 - r}{B})$$

where B is empirically determined parameter[1] with the value of 0.37.

Table S2: Crystallographic data and structural refinements for $(NH_4)_2V_3O_8$ at the selected temperatures

Temperature (K)	110	120	130	140
Formula	$H_8N_2O_8V_3$	$H_8N_2O_8V_3$	$H_8N_2O_8V_3$	$H_8N_2O_8V_3$
Formula weight	316.90	316.90	316.90	316.90
CCDC	2004615	2004673	2005049	2004617
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	tetragonal	tetragonal	tetragonal	tetragonal
Space group	*P4bm*	*P4bm*	*P4bm*	*P4bm*
a / Å	8.8551(3)	8.8572(3)	8.8599(4)	8.8620(4)
b / Å	8.8551(3)	8.8572(3)	8.8599(4)	8.8620(4)
c / Å	5.5652(5)	5.5653(5)	5.5653(6)	5.5652(6)
α/ (°)	90	90	90	90
β / (°)	90	90	90	90
γ/ (°)	90	90	90	90
V / Å³	436.38(5)	436.60(5)	436.86(6)	437.06(6)
Z	2	2	2	2
F(000)	310	310	310	310
$\theta_{min,max}$/°	3.254-27.575	3.253-27.574	3.252-27.574	3.251-27.574
GOF	1.145	1.182	1.168	1.165
R_1[a], wR_2[b] *[I >2σ(I)]*	0.0335, 0.0671	0.0335, 0.0680	0.0318, 0.0651	0.0311, 0.0635

[a] $R_1 = \sum||F_o| - |F_c|/\sum|Fo|$. [b] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$

Continue

Temperature (K)	160	170	190	200
Formula	$H_8N_2O_8V_3$	$H_8N_2O_8V_3$	$H_8N_2O_8V_3$	$H_8N_2O_8V_3$
Formula weight	316.90	316.90	316.90	316.90
CCDC	2004936	2005050	2004937	2005052
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	tetragonal	tetragonal	tetragonal	tetragonal
Space group	*P4bm*	*P4bm*	*P4bm*	*P4bm*
a / Å	8.8669(4)	8.8700(4)	8.8761(4)	8.8776(4)
b / Å	8.8669(4)	8.8700(4)	8.8761(4)	8.8776(4)
c / Å	5.5650(6)	5.5649(6)	5.5632(6)	5.5610(6)
α/ (°)	90	90	90	90
β / (°)	90	90	90	90
γ/ (°)	90	90	90	90
V / Å³	437.53(6)	437.83(6)	438.30(6)	438.27(6)
Z	2	2	2	2
F(000)	310	310	310	310
$\theta_{min,max}$/°	3.249-27.574	3.248-27.573	3.246-27.581	3.245-27.591
GOF	1.159	1.168	1.147	1.143
R_1[a], wR_2[b] $[I > 2\sigma(I)]$	0.0316, 0.0653	0.0316, 0.0652	0.0283, 0.0589	0.0288, 0.0604

[a] $R_1 = \sum||F_o| - |F_c|/\sum|Fo|$. [b] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$

Continue

Temperature (K)	220	240	270	300
Formula	$H_8N_2O_8V_3$	$H_8N_2O_8V_3$	$H_8N_2O_8V_3$	$H_8N_2O_8V_3$
Formula weight	316.90	316.90	316.90	316.90
CCDC number	2004952	2005051	2004953	2004938
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	tetragonal	tetragonal	tetragonal	tetragonal
Space group	*P4bm*	*P4bm*	*P4bm*	*P4bm*
a / Å	8.8868(3)	8.8884(3)	8.8891(3)	8.8895(4)
b / Å	8.8868(3)	8.8884(3)	8.8891(3)	8.8895(4)
c / Å	5.5606(5)	5.5625(5)	5.5691(5)	5.5731(6)
α/ (°)	90	90	90	90
β / (°)	90	90	90	90
γ/ (°)	90	90	90	90
V / Å³	439.15(5)	439.46(5)	440.05(5)	440.40(6)
Z	2	2	2	2
F(000)	310	310	310	310
$\theta_{min,max}$/°	3.242-27.479	3.241-27.470	3.241-27.436	3.241-27.416
GOF	1.110	1.130	1.104	1.113
R_1[a], wR_2[b] *[I >2σ(I)]*	0.0269, 0.0547	0.0279, 0.0576	0.0325, 0.0680	0.0338, 0.0702

[a] $R_1 = \sum||F_o| - |F_c|/\sum|Fo|$. [b] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$

Continue

Temperature (K)	295 (In literature)[2]
Formula	$H_8N_2O_8V_3$
Formula weight	316.90
CCDC number	1997397
Wavelength (Å)	0.71073
Crystal system	tetragonal
Space group	*P4bm*
a / Å	8.9062 (4)
b / Å	8.9062 (3)
c / Å	5.5784(5)
α/ (°)	90
β / (°)	90
γ/ (°)	90
V / Å³	442.48(5)
Z	2
F(000)	310
$\theta_{min,max}$/°	2.552-27.488
GOF	0.866
R_1[a], wR_2[b] *[I >2σ(I)]*	0.0163, 0.0296

[a] $R_1 = \sum||F_o| - |F_c|/\sum|Fo|$. [b] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$

References

1. I. D. Brown and D. Altermatt, *Acta Cryst.*, 1985, **B41**, 244−247.
2. A. Perez-Benitez and S. Bernes, *IUCrData*, 2020, **5**, x200488.