Supporting information:

Structure, phase transition and negative thermal expansion in the ammoniated ZrW_2O_8

Weigang Cao,[a] Qingzhen Huang,[b] Yangchun Rong,[a] You Wang,[a] Jinxia Deng,[a] Jun Chen[a] and Xianran Xing*[a]

[a]Department of Physical Chemistry, University of Science and Technology Beijing, Beijing 100083, China

[b]NIST Center for Neutron Research, National Institute of Standards and Technology (NIST), Gaithersburg, Maryland 20899-6102, United States

In order to compare with the the ammoniated ZrW_2O_8, we also collected the data of the pristine ZrW_2O_8, and refined it. In Fig. S1, the calculated diffraction is in agreement well with the observed.

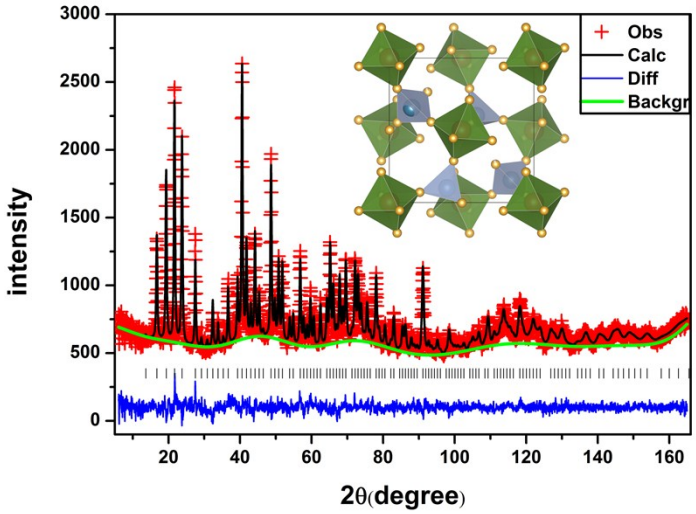

Fig. S1 Rietveld refinement of the neutron diffraction pattern of the pristine ZrW_2O_8

Table S1. Crystallographic data of ZrW_2O_8 and the ammoniated ZrW_2O_8 Refined from NPD at Room Temperature

	ZrW_2O_8	ammoniated ZrW_2O_8
R_p	3.14	1.88
R_{wp}	3.79	2.23
χ^2	1.005	1.001
space group	$P2_13$	$P2_13$
lattice constant	9.1501	9.1738
N occupancy	0	0.64

Table S2 The selected bond distances and angles of the pristine ZrW_2O_8 and the ammoniated ZrW_2O_8 from the refinement at Room Temperature.

bond	distance（Å）		bond angle	size(degree)	
	ZrW2O8	$ZrW_2O_{7.91}·0.64NH_3$		ZrW_2O_8	$ZrW_2O_{7.91}·0.64NH_3$
Zr1-O1	2.055(6)	2.045(6)	O1-Zr1-O1	92.9(2)	92.5(3)
Zr1-O2	2.100(5)	2.095(7)	O1-Zr1-O2	86.3(2)	87.0(3)
W1-O1	1.781(6)	1.810(7)	O1-Zr1-O2	90.3(2)	90.5(3)
W1-O4	1.729(13)	1.59(2)	O2-Zr1-O2	90.6(2)	90.0(3)
W2-O2	1.792(6)	1.786(7)	O1-W1-O1	116.3(2)	115.4(2)
W2-O3	1.63(2)	1.744(18)	O1-W1-O4	101.3(3)	102.6(3)
W1-O3	2.43(2)	2.44(2)	O2-W2-O2	109.5(3)	116.0(2)
W2-N		2.383(14)	O2-W2-O3	109.4(3)	101.7(3)
N-H		0.98(3)	Zr-O1-W1	154.1(4)	152.7(4)
			Zr-O2-W2	170.6(4)	172.9(4)

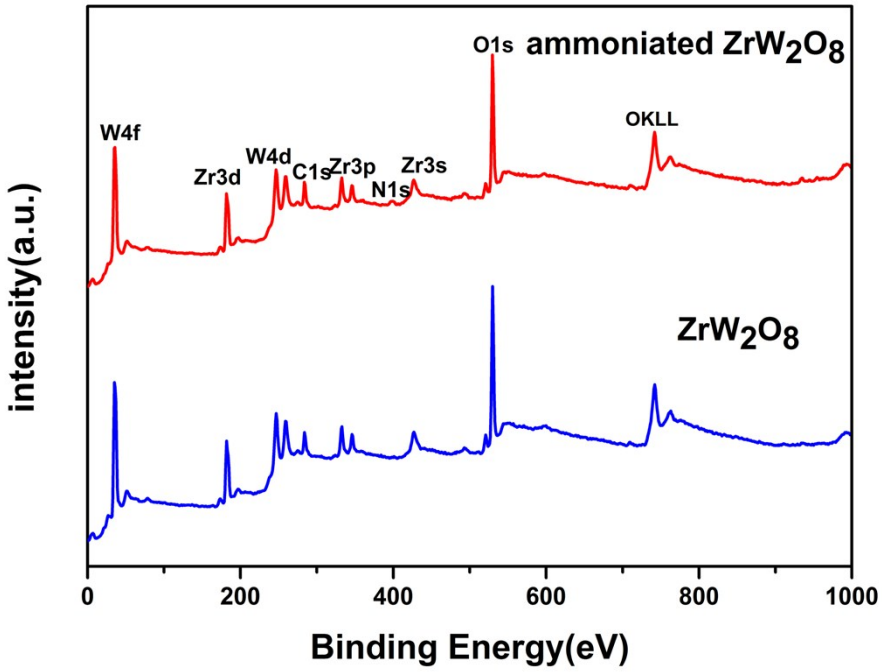

Fig. S2 The XPS spectra of the pristine ZrW_2O_8 and the ammoniated ZrW_2O_8.

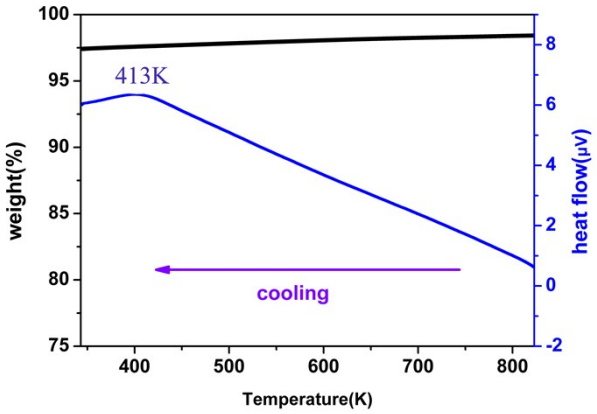

Fig. S3 The TG-DSC curves of the ammoniated ZrW_2O_8 on cooling.

The Fig. S3 is the TG-DSC curves of the ammoniated ZrW_2O_8 on cooling. The measuring process is that the ammoniated ZrW_2O_8 is heated up to 823K, then measured on cooling with 10K/min. This figure is just to illustrate the ammoniated ZrW_2O_8 is more like pristine ZrW_2O_8 after the heat treatment. The temperature of the phase transition is 413K。

Table S3 The cell parameters of ZrW_2O_8

Temperature(K)	Cell parameter(Å)	R_{wp}(%)
	ZrW_2O_8	ZrW_2O_8
173	9.15631(8)	6.11
198	9.15453(18)	5.8
223	9.15329(18)	6.27
248	9.15182(18)	6.31
273	9.14951(17)	5.69
298	9.14876(18)	6.12
323	9.14581(8)	5.86
348	9.14382(18)	5.39
373	9.14235(18)	5.4
398	9.14030(20)	6.53

Table S4 The cell parameters of the ammoniated ZrW_2O_8

Temperature(K)	Cell parameter(Å)		R_{wp}(%)	
	heating	cooling	heating	cooling
173	9.17533(20)	9.17477(21)	6.73	6.84
198	9.17515(20)	9.17421(23)	6.54	7.71
223	9.17428(20）	9.17378(20)	6.66	6.61
248	9.17380(20)	9.17338(20)	6.52	6.49
273	9.17288(20)	9.17375(20)	6.57	6.61
298	9.17300(21)	9.17259(20)	6.41	6.26
323	9.17218(21)	9.17199(20)	6.61	6.15
348	9.17185(21)	9.17139(20)	6.23	6.24
373	9.17168(23)	9.17109(21)	7.86	6.39
398	9.17105(22)	9.17085(20)	6.9	6.23