Electronic Supplementary Information

A new 3-D open-framework Li-rich vanadoborate and its high ionic conductivity after transformed into glasses

Xinxin Liu, Dan Zhang, He Li, Lingyun Li and Hongming Yuan*

State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, P.R. China.
E-mail: hmyuan@jlu.edu.cn; Fax: +86-0431-85168318

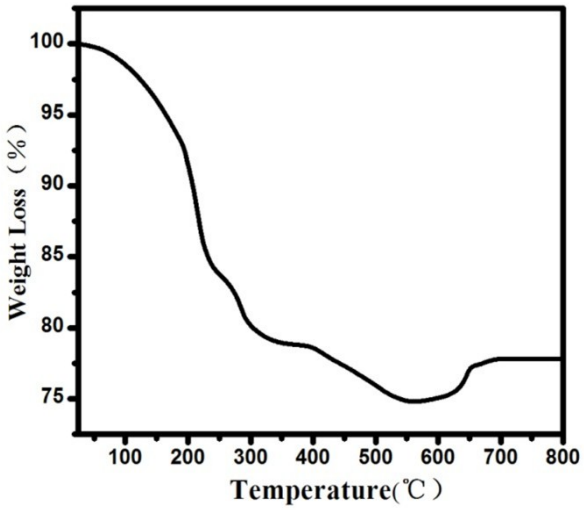

Fig. S1. TG curve of **1** in air.

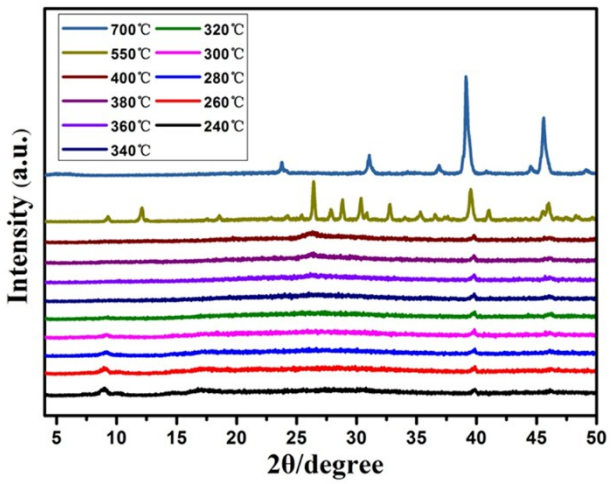

Fig. S2. In-situ PXRD patterns were collected in air from240 °C to 700 °C

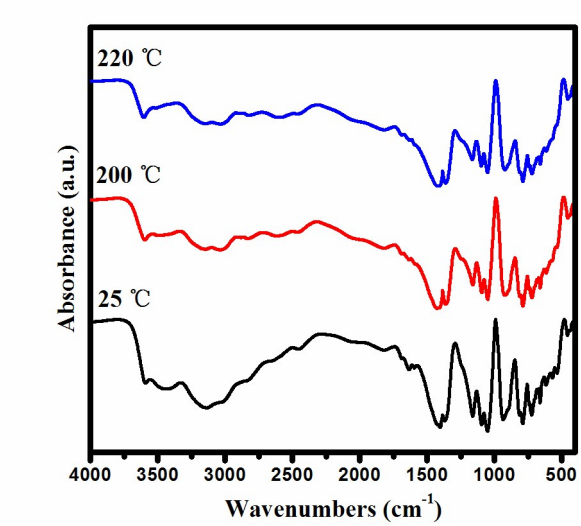

Fig. S3. The FT-IR spectra of **1**, **1** calcined at 200 °C and 220 °C

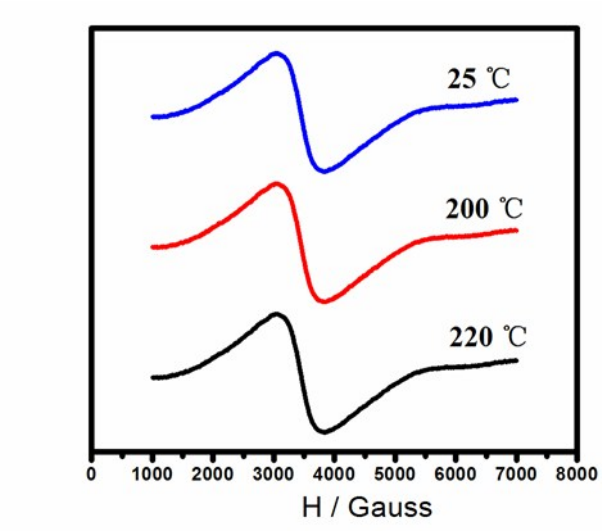

Fig. S4. EPR spectra of **1**, **1** calcined at 200 °C and 220 °C

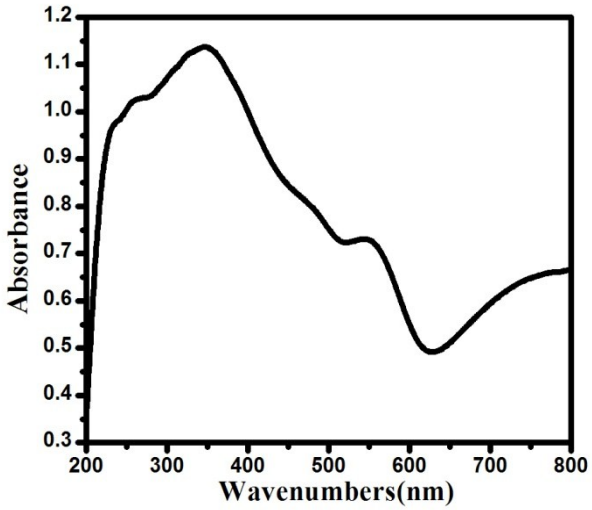

Fig. S5. UV-Vis-NIR diffuse reflectance spectrum of **1**.

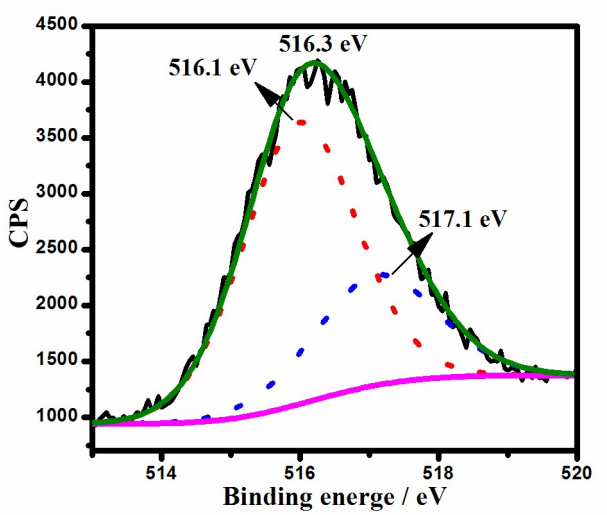

Fig. S6. XPS spectrum of vanadium in $Li_{10}[V_{12}B_{18}O_{60}H_6]\cdot 28H_2O$

The peak at 516.1 eV is attributed to V^{4+} and a shoulder at about 517.1 eV is assigned to for V^{5+}

Table S1. Bond lengths [Å] for **1**.

B(1)-O(2)	1.363(6)
B(1)-O(3)	1.364(6)
B(1)-O(1)	1.372(6)
B(2)-O(5)	1.431(6)
B(2)-O(4)	1.468(6)
B(2)-O(3)	1.493(6)
B(2)-O(6)#1	1.517(6)
B(3)-O(5)	1.417(6)
B(3)-O(7)	1.479(6)
B(3)-O(2)#2	1.492(5)
B(3)-O(6)	1.520(6)
O(1)-H(1)	0.82(8)
O(2)-B(3)#1	1.492(5)
O(4)-V(1)	1.943(3)
O(4)-V(2)#1	1.965(3)
O(6)-B(2)#2	1.517(6)
O(6)-V(1)	2.009(3)
O(7)-V(2)	1.945(3)
O(7)-V(1)#1	1.949(3)
O(8)-V(2)#3	1.932(3)
O(8)-V(2)	1.934(3)
O(8)-V(1)#1	1.943(3)
O(9)-V(2)	1.637(4)
O(10)-V(1)	1.629(4)
V(1)-O(8)#2	1.943(3)
V(1)-O(7)#2	1.949(3)
V(1)-V(2)#1	3.0116(11)
V(1)-V(2)#2	3.0170(11)
V(2)-O(8)#4	1.932(3)
V(2)-O(4)#2	1.965(3)

Table S1. Bond angles [deg] for **1**.

O(2)-B(1)-O(3)	122.1(4)
O(2)-B(1)-O(1)	117.4(4)
O(3)-B(1)-O(1)	120.6(4)
O(5)-B(2)-O(4)	112.3(4)
O(5)-B(2)-O(3)	103.6(3)
O(4)-B(2)-O(3)	111.0(4)
O(5)-B(2)-O(6)#1	113.5(4)
O(4)-B(2)-O(6)#1	108.1(3)
O(3)-B(2)-O(6)#1	108.4(3)
O(5)-B(3)-O(7)	110.8(4)
O(5)-B(3)-O(2)#2	107.5(4)
O(7)-B(3)-O(2)#2	109.8(4)
O(5)-B(3)-O(6)	112.7(4)
O(7)-B(3)-O(6)	108.2(3)
O(2)#2-B(3)-O(6)	107.7(3)
B(1)-O(1)-H(1)	109(6)
B(1)-O(2)-B(3)#1	122.8(4)
B(1)-O(3)-B(2)	120.8(4)
B(2)-O(4)-V(1)	129.3(3)
B(2)-O(4)-V(2)#1	129.8(3)
V(1)-O(4)-V(2)#1	100.80(15)
B(3)-O(5)-B(2)	120.1(3)
B(2)#2-O(6)-B(3)	114.0(3)
B(2)#2-O(6)-V(1)	121.4(3)
B(3)-O(6)-V(1)	122.4(3)
B(3)-O(7)-V(2)	128.5(3)
B(3)-O(7)-V(1)#1	129.9(3)
V(2)-O(7)-V(1)#1	101.57(15)
V(2)#3-O(8)-V(2)	146.35(19)
V(2)#3-O(8)-V(1)#1	102.00(15)
V(2)-O(8)-V(1)#1	102.18(15)
O(10)-V(1)-O(4)	107.38(17)
O(10)-V(1)-O(8)#2	109.30(18)
O(4)-V(1)-O(8)#2	78.60(14)
O(10)-V(1)-O(7)#2	110.10(16)
O(4)-V(1)-O(7)#2	140.52(14)
O(8)#2-V(1)-O(7)#2	77.82(14)
O(10)-V(1)-O(6)	106.14(17)
O(4)-V(1)-O(6)	90.63(13)
O(8)#2-V(1)-O(6)	144.57(14)
O(7)#2-V(1)-O(6)	90.59(13)
O(9)-V(2)-O(8)#4	107.81(18)

O(9)-V(2)-O(8)	108.33(18)
O(8)#4-V(2)-O(8)	92.95(19)
O(9)-V(2)-O(7)	108.73(18)
O(8)#4-V(2)-O(7)	143.37(15)
O(8)-V(2)-O(7)	78.14(14)
O(9)-V(2)-O(4)#2	108.04(18)
O(8)#4-V(2)-O(4)#2	78.33(14)
O(8)-V(2)-O(4)#2	143.54(15)
O(7)-V(2)-O(4)#2	87.99(14)

Symmetry transformations used to generate equivalent atoms:

#1 z+1/2,-x+2,y-1/2 #2 -y+2,z+1/2,x-1/2

#3 y,-z+3/2,-x+3/2 #4 -z+3/2,x,-y+3/2

#5 -x+3/2,-y+3/2,z #6 x,-y+3/2,-z+1/2

Table S2. Ionic Conductivities (*ó*) and Activation Energies (*E*) for lithium glasses conductors

Compound	*ó*(S cm^{-1})	*E* (eV)	Ref.
LAGP	0.61	4.22×10^{-3}	[34]
Ag_2O-P_2O_5-(15%)LiCl	0.47	4.16×10^{-3}	[35]
LGPA10	0.548	8.29×10^{-4}	[36]