Electronic Supplementary Information

$K_{11}RbB_{28}O_{48}$: A New Triple-layered Borate with an Unprecedented $[B_{28}O_{57}]$ Fundamental Building Block

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Experimental section

Synthesis

Single crystals of $K_{11}RbB_{28}O_{48}$ were prepared using the high-temperature solution method. A mixture of K_2CO_3, Rb_2CO_3, and H_3BO_3 was weighed with the stoichiometric molar ratio of 11:1:56. The mixture was thoroughly grinded in an agate mortar and then placed into a platinum crucible. In the beginning, the mixture was heated slowly in a vertical programmable temperature electric furnace in order to release H_2O and CO_2, and then the mixture was heated to 800 °C to guarantee the complete fusion of the mixture. This temperature was kept for 10 h aiming to the homogeneous mixing. The mixture was cooled slowly to 700 °C at a rate of 1 °C/h. At this time the mixture was solidified and was directly taken out from the furnace in order to the rapid cooling. The surface crystals were separated using mechanical ways. Thus colorless and transparent single crystals were acquired for the structure determination.

Polycrystalline samples of $K_{11}RbB_{28}O_{48}$ were obtained by the identical method of single crystal preparation. After several repetitions, the millimeter-level single crystals were thoroughly grinded to form powder samples.

Structure determination

The crystal structure of $K_{11}RbB_{28}O_{48}$ were determined by single-crystal X-ray diffraction on an APEX II CCD diffractometer at 296(2) K using monochromatic Mo-Kα radiation (λ = 0.71073 Å) and integrated with the SAINT program.[1] Multi-scan absorption corrections were performed on the SCALE program for area detector.[1] All calculations were performed with programs from the SHELXTL crystallographic software package.[2] The positions of all atoms were refined using full matrix least-squares techniques with anisotropic thermal parameters. Final least-squares refinement is on F_o^2 with data having $F_o^2 \geq 2\sigma(F_o^2)$. The structure of $K_{11}RbB_{28}O_{48}$ was checked for missing symmetry elements with the program Platon.[3] Crystal data and structure refinement information of $K_{11}RbB_{28}O_{48}$ are shown in Table S1. Relevant atomic coordinates and equivalent isotropic displacement parameters are presented in Table S2. Selected interatomic distances and angles are listed in Tables S3.

Powder X-ray diffraction (PXRD)

The PXRD pattern of $K_{11}RbB_{28}O_{48}$ was obtained at room temperature on a Bruker D2 PHASER diffractometer, which is equipped with an incident beam monochromator with Cu-Kα radiation (λ = 1.5418 Å). The angular range is from 5° to 70° with a scan step of 0.02° and a fixed counting time of 1 s/step.

Thermal behavior analysis

Heating and cooling curves were acquired during the thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) of $K_{11}RbB_{28}O_{48}$ on a NETZSCH STA 449F3 simultaneous analyzer. The sample was placed in platinum crucibles using Al_2O_3 as the reference heating from room temperature to 1000 °C and then cooling down to room temperature under the flowing N_2 gas at a rate of 5 °C/min.

UV-Vis-NIR diffuse reflectance spectroscopy

The diffuse reflectance data for the powder sample of $K_{11}RbB_{28}O_{48}$ were acquired at room temperature with a Shimadzu SolidSpec-3700DUV spectrophotometer. The wavelength range is from 250 to 2600nm.

Infrared (IR) spectroscopy

The IR spectroscopy was obtained using a Shimadzu IR Affinity-1 Fourier transform IR spectrometer

ranging from 400 to 4000 cm^{-1} with a resolution of 2 cm^{-1}. 6 mg of the sample was thoroughly mixed with 600 mg of dried KBr and then pressed into a disc.

Calculation details

To further comprehend the nature of chemical bonding of $K_{11}RbB_{28}O_{48}$, the first-principles calculations on its electronic structures were performed by using the density functional theory (DFT) with the CASTEP package.[4] The exchange-correlation functional was the Perdew-Burke-Emzerhof (PBE) functional within the generalized gradient approximation (GGA).[5-7] The Monkhorst-Pack *k*-points within the Brillouin zone were chosen as 4 × 2 × 1. [8] The plane wave cut-off energy was set at 830 eV. The valence electrons of the elements in $K_{11}RbB_{28}O_{48}$ were calculated as follows: K $3s^2 3p^6 4s^1$, Rb $4s^2 4p^6 5s^1$, B $2s^2 2p^1$, and O $2s^2 2p^4$, respectively.

Table S1. Crystal data and structure refinement for $K_{11}RbB_{28}O_{48}$.

Empirical formula	$K_{11}RbB_{28}O_{48}$
Formula weight	1586.25
Temperature	296(2) K
Crystal system	Triclinic
Space group, Z	$P\bar{1}$ (No.2), 2
Calculated density	2.451 g·cm^{-3}
Unit cell dimensions	a = 6.6231(2) Å
	b = 11.3213(3) Å
	c = 28.7010(9) Å
	α = 92.208(2)°
	β = 91.584(2)°
	γ = 90.200(2)°
Volume	2149.62(11) Å^3
Absorption coefficient	2.363 mm^{-1}
F(000)	1540
The range for data collection	1.421 - 27.556°
Limiting indices	-8 ≤ h ≤ 8
	-14 ≤ k ≤ 14
	-36 ≤ l ≤ 37
Reflections collected / unique	26849 / 9738
R(int)	0.0869
Completeness	99.7 %
Data / restraints / parameters	9738 / 0 / 793
GOF on F^2	1.049
Final R indices [$F_o^2 > 2\sigma(F_o^2)$][a]	R_1 = 0.0719
	wR_2 = 0.1805
R indices (all data)[a]	R_1 = 0.1361
	wR_2 = 0.2200
Largest diff peak and hole	1.851 and -2.685 e·Å^{-3}

[a] $R_1 = \mathbf{\Sigma}||F_o| - |F_c||/\mathbf{\Sigma}|F_o|$ and $wR_2 = [\mathbf{\Sigma}w(F_o^2 - F_c^2)^2/\mathbf{\Sigma}wF_o^4]^{1/2}$ for $F_o^2 > 2\sigma(F_o^2)$.

Table S2. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for $K_{11}RbB_{28}O_{48}$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atoms	*x/a*	*y/b*	*z/c*	U_{eq}	BVS
Rb(1)	-5552(2)	-1532(1)	1379(1)	57(1)	0.98
K(1)	4538(2)	1455(1)	4797(1)	22(1)	1.17
K(2)	1130(2)	2973(2)	1602(1)	22(1)	0.88
K(3)	4001(3)	4327(2)	2999(1)	23(1)	1.24
K(4)	-289(3)	3520(1)	263(1)	22(1)	1.16
K(5)	6233(3)	1576(2)	3420(1)	26(1)	1.16
K(6)	-687(3)	-233(2)	1892(1)	32(1)	1.13
K(7)	10661(3)	-715(2)	3075(1)	25(1)	1.20
K(8)	-14235(3)	-5077(2)	1801(1)	26(1)	0.98
K(9)	478(3)	3486(2)	5311(1)	28(1)	1.11
K(10)	187(4)	3608(2)	6403(1)	40(1)	0.80
K(11)	-5681(3)	-1502(2)	252(1)	26(1)	1.20
B(1)	968(13)	2364(7)	3546(3)	18(2)	3.10
B(2)	5602(12)	2057(7)	5902(3)	17(2)	3.03
B(3)	-10620(12)	-3294(7)	814(3)	16(2)	3.07
B(4)	-2499(12)	4443(7)	-906(3)	18(2)	3.03
B(5)	-2607(12)	594(7)	795(3)	14(2)	3.06
B(6)	6948(12)	2411(7)	2347(3)	16(2)	3.11
B(7)	-713(12)	3952(7)	2649(3)	15(2)	3.05
B(8)	3861(12)	7021(7)	2474(3)	17(2)	3.02
B(9)	317(11)	5999(7)	2466(3)	15(2)	3.09
B(10)	3375(12)	5798(7)	5686(3)	16(2)	3.07
B(11)	5896(13)	4315(8)	5846(3)	21(2)	3.08
B(12)	8605(13)	781(7)	5690(3)	16(2)	3.04
B(13)	3101(12)	3530(7)	4096(3)	18(2)	3.03
B(14)	9076(12)	801(7)	4472(3)	17(2)	3.01
B(15)	10413(12)	1892(7)	2657(3)	16(2)	3.07
B(16)	-9751(12)	-4030(7)	1574(3)	18(2)	3.05
B(17)	4998(12)	-909(7)	2500(3)	14(2)	3.04
B(18)	3825(11)	1125(7)	2363(3)	12(2)	3.02
B(19)	-5213(12)	3950(7)	637(3)	16(2)	3.08
B(20)	-5680(12)	1773(7)	758(3)	18(2)	3.07
B(21)	-10228(12)	-1065(8)	795(3)	18(2)	3.05
B(22)	-4013(13)	5963(7)	620(3)	18(2)	3.04
B(23)	6381(14)	1912(8)	1463(3)	25(2)	3.04
B(24)	824(13)	919(7)	620(3)	19(2)	3.10
B(25)	-2541(13)	-2542(8)	2517(3)	21(2)	3.06
B(26)	4589(13)	1071(7)	6610(3)	20(2)	3.05
B(27)	2267(12)	1053(7)	5920(3)	18(2)	3.02

B(28)	-275(12)	2905(7)	4322(3)	19(2)	3.06
O(1)	-279(7)	5107(4)	2797(2)	14(1)	2.05
O(2)	4878(7)	2119(4)	2462(2)	21(1)	2.10
O(3)	-1185(7)	1967(4)	4607(2)	18(1)	1.97
O(4)	818(7)	3170(4)	2600(2)	19(1)	2.13
O(5)	3909(8)	4616(4)	5720(2)	29(1)	2.06
O(6)	-5276(7)	81(4)	2196(2)	16(1)	1.95
O(7)	-696(7)	4226(4)	-639(2)	16(1)	2.01
O(8)	-11182(8)	-3529(5)	1300(2)	24(1)	1.85
O(9)	-4713(7)	2809(4)	539(2)	17(1)	2.03
O(10)	3087(8)	4313(4)	834(2)	22(1)	2.14
O(11)	-8704(7)	-202(4)	791(2)	21(1)	2.04
O(12)	3474(7)	1993(4)	5761(2)	15(1)	1.93
O(13)	2185(7)	1762(4)	613(2)	21(1)	2.18
O(14)	1805(7)	3103(4)	4444(2)	15(1)	2.10
O(15)	-2189(7)	-694(4)	837(2)	21(1)	2.05
O(16)	2527(7)	6127(4)	2509(2)	19(1)	2.09
O(17)	7336(7)	3615(4)	2574(2)	16(1)	2.11
O(18)	119(7)	1438(4)	5901(2)	17(1)	2.10
O(19)	1405(7)	5982(4)	5568(2)	21(1)	2.00
O(20)	-9561(8)	-2164(4)	792(2)	24(1)	2.12
O(21)	-2953(7)	-1404(4)	2435(2)	21(1)	2.22
O(22)	-10323(8)	-4399(5)	2003(2)	23(1)	2.05
O(23)	1764(7)	1118(4)	2390(2)	19(1)	2.22
O(24)	-6534(7)	-1849(4)	2373(2)	20(1)	2.01
O(25)	-2233(8)	1185(5)	1255(2)	25(1)	2.07
O(26)	7500(7)	91(4)	4343(2)	23(1)	2.03
O(27)	8375(7)	1574(4)	2499(2)	27(1)	1.99
O(28)	6675(7)	1144(4)	5628(2)	21(1)	2.04
O(29)	-4642(7)	722(4)	625(2)	16(1)	2.15
O(30)	5958(8)	1787(5)	6403(2)	23(1)	1.81
O(31)	-5796(7)	-3653(4)	792(2)	21(1)	2.06
O(32)	4783(8)	-522(4)	2986(2)	20(1)	2.09
O(33)	5881(7)	6657(4)	2549(2)	24(1)	2.04
O(34)	-585(8)	2534(5)	3831(2)	24(1)	2.04
O(35)	2805(8)	2866(5)	3646(2)	24(1)	2.19
O(36)	6558(7)	3212(4)	5833(2)	22(1)	2.10
O(37)	4493(8)	2021(5)	1275(2)	25(1)	1.99
O(38)	2785(8)	4814(4)	4011(2)	25(1)	1.94
O(39)	-3727(8)	4766(4)	528(2)	28(1)	2.06
O(40)	2143(8)	5732(5)	1422(2)	24(1)	1.96
O(41)	-1122(7)	1094(4)	475(2)	20(1)	1.98
O(42)	7036(9)	2611(5)	1839(2)	32(1)	2.06
O(43)	4748(7)	6662(4)	5763(2)	24(1)	2.06

O(44)	8982(8)	-354(4)	5521(2)	30(1)	2.12
O(45)	-12521(7)	-3263(4)	532(2)	19(1)	1.99
O(46)	685(10)	1639(5)	3154(2)	31(1)	2.07
O(47)	-592(7)	7153(4)	2601(2)	22(1)	2.02
O(48)	7227(7)	-815(5)	3578(2)	23(1)	2.15

Table S3. Selected bond lengths (Å) and angles (deg.) for $K_{11}RbB_{28}O_{48}$.

Rb(1)-O(6)	2.917(5)	K(7)-O(46)#3	2.666(6)	B(9)-O(16)	1.472(9)
Rb(1)-O(11)	3.081(5)	K(7)-O(47)#11	2.834(6)	B(9)-O(22)#6	1.441(10)
Rb(1)-O(15)	2.928(5)	K(7)-O(48)	2.732(5)	B(9)-O(47)	1.482(9)
Rb(1)-O(20)	3.170(5)	K(8)-O(8)	3.092(6)	B(10)-O(5)	1.392(9)
Rb(1)-O(21)	3.441(6)	K(8)-O(10)#13	3.301(6)	B(10)-O(19)	1.358(9)
Rb(1)-O(24)	2.978(5)	K(8)-O(16)#13	3.261(5)	B(10)-O(43)	1.340(10)
Rb(1)-O(29)	3.471(5)	K(8)-O(17)#13	2.886(5)	B(11)-O(5)	1.402(10)
Rb(1)-O(31)	2.881(5)	K(8)-O(22)	2.740(5)	B(11)-O(36)	1.325(10)
Rb(1)-O(40)#2	3.456(6)	K(8)-O(33)#13	2.852(6)	B(11)-O(38)#5	1.359(10)
K(1)-O(3)#3	2.959(5)	K(8)-O(40)#13	2.779(5)	B(12)-O(18)#3	1.362(9)
K(1)-O(12)	2.916(5)	K(8)-O(42)#13	2.757(6)	B(12)-O(28)	1.353(9)
K(1)-O(14)	2.802(5)	K(9)-O(3)	2.802(6)	B(12)-O(44)	1.383(10)
K(1)-O(26)#4	3.387(6)	K(9)-O(5)	2.810(6)	B(13)-O(14)	1.432(10)
K(1)-O(26)	2.818(5)	K(9)-O(12)	2.917(5)	B(13)-O(35)	1.479(10)
K(1)-O(28)#4	3.231(5)	K(9)-O(14)	2.681(5)	B(13)-O(38)	1.498(9)
K(1)-O(28)	2.773(5)	K(9)-O(18)	2.936(5)	B(13)-O(43)#5	1.489(9)
K(1)-O(43)#5	2.767(5)	K(9)-O(19)#14	2.870(6)	B(14)-O(3)#3	1.374(9)
K(1)-O(44)#4	2.756(6)	K(9)-O(19)	2.951(5)	B(14)-O(26)	1.351(10)
K(2)-O(4)	2.876(6)	K(9)-O(36)#1	3.055(5)	B(14)-O(44)#9	1.384(9)
K(2)-O(10)	3.041(5)	K(10)-O(1)#14	2.668(5)	B(15)-O(4)#3	1.487(9)
K(2)-O(13)	3.199(6)	K(10)-O(5)	3.412(6)	B(15)-O(23)#3	1.466(9)
K(2)-O(22)#6	3.304(6)	K(10)-O(12)	3.387(5)	B(15)-O(27)	1.452(9)
K(2)-O(23)	3.164(5)	K(10)-O(18)	2.799(5)	B(15)-O(46)#3	1.472(10)
K(2)-O(25)	3.121(6)	K(10)-O(36)#1	2.894(6)	B(16)-O(8)	1.355(9)
K(2)-O(37)	2.657(5)	K(10)-O(38)#14	2.922(5)	B(16)-O(22)	1.377(10)
K(2)-O(40)	3.256(6)	K(10)-O(47)#14	3.020(6)	B(16)-O(40)#2	1.364(9)
K(2)-O(42)#1	2.846(6)	K(11)-O(9)#7	2.681(5)	B(17)-O(6)#3	1.454(9)
K(3)-O(1)	3.019(5)	K(11)-O(11)	2.930(5)	B(17)-O(21)#3	1.484(9)
K(3)-O(2)	2.953(5)	K(11)-O(15)	2.942(6)	B(17)-O(24)#3	1.496(9)
K(3)-O(4)	2.684(5)	K(11)-O(20)	3.139(6)	B(17)-O(32)	1.459(10)
K(3)-O(16)	2.690(5)	K(11)-O(29)#7	2.715(5)	B(18)-O(2)	1.339(9)
K(3)-O(17)	2.665(5)	K(11)-O(29)	2.775(5)	B(18)-O(6)#3	1.400(9)
K(3)-O(33)	3.240(5)	K(11)-O(31)	2.937(5)	B(18)-O(23)	1.369(9)
K(3)-O(35)	2.668(5)	K(11)-O(41)#7	2.982(5)	B(19)-O(9)	1.357(9)
K(3)-O(38)	3.066(6)	K(11)-O(45)#3	3.010(5)	B(19)-O(10)#1	1.332(9)
K(4)-O(7)#8	2.801(5)	B(1)-O(34)	1.342(10)	B(19)-O(39)	1.398(10)
K(4)-O(7)	2.745(5)	B(1)-O(35)	1.359(10)	B(20)-O(9)	1.501(9)
K(4)-O(9)	3.166(5)	B(1)-O(46)	1.375(11)	B(20)-O(13)#1	1.462(9)
K(4)-O(10)	2.857(6)	B(2)-O(12)	1.456(9)	B(20)-O(29)	1.420(9)
K(4)-O(13)	2.783(5)	B(2)-O(28)	1.472(10)	B(20)-O(37)#1	1.501(11)
K(4)-O(20)#7	3.339(6)	B(2)-O(30)	1.495(10)	B(21)-O(11)	1.403(10)
K(4)-O(39)	2.791(5)	B(2)-O(36)	1.473(9)	B(21)-O(15)#1	1.374(9)

K(4)-O(41)	2.891(5)	B(3)-O(7)#7	1.453(9)	B(21)-O(20)	1.322(10)
K(4)-O(45)#7	2.990(5)	B(3)-O(8)	1.488(10)	B(22)-O(31)#16	1.358(10)
K(5)-O(2)	2.955(6)	B(3)-O(20)	1.460(9)	B(22)-O(39)	1.386(10)
K(5)-O(26)	3.284(6)	B(3)-O(45)	1.478(10)	B(22)-O(45)#6	1.354(10)
K(5)-O(27)	3.032(6)	B(4)-O(7)	1.428(9)	B(23)-O(25)#3	1.369(11)
K(5)-O(32)	2.793(6)	B(4)-O(10)#8	1.470(9)	B(23)-O(37)	1.356(11)
K(5)-O(34)#3	2.601(6)	B(4)-O(31)#7	1.490(10)	B(23)-O(42)	1.375(11)
K(5)-O(35)	2.782(5)	B(4)-O(40)#8	1.512(10)	B(24)-O(11)#3	1.411(9)
K(5)-O(43)#5	3.104(6)	B(5)-O(15)	1.493(9)	B(24)-O(13)	1.311(10)
K(5)-O(46)#3	3.067(7)	B(5)-O(25)	1.472(10)	B(24)-O(41)	1.361(10)
K(5)-O(48)	2.839(5)	B(5)-O(29)	1.431(9)	B(25)-O(21)	1.346(9)
K(6)-O(6)	3.203(5)	B(5)-O(41)	1.489(9)	B(25)-O(33)#2	1.389(10)
K(6)-O(15)	3.184(6)	B(6)-O(2)	1.459(9)	B(25)-O(47)#15	1.356(10)
K(6)-O(21)	2.591(5)	B(6)-O(17)	1.505(9)	B(26)-O(30)	1.376(10)
K(6)-O(23)	2.589(5)	B(6)-O(27)	1.413(9)	B(26)-O(32)#4	1.390(10)
K(6)-O(25)	2.664(6)	B(6)-O(42)	1.487(10)	B(26)-O(48)#4	1.331(10)
K(6)-O(27)#1	2.722(6)	B(7)-O(1)	1.386(9)	B(27)-O(12)	1.426(9)
K(7)-O(18)#4	3.137(5)	B(7)-O(4)	1.356(9)	B(27)-O(18)	1.490(9)
K(7)-O(21)#3	3.057(6)	B(7)-O(17)#1	1.355(9)	B(27)-O(26)#4	1.484(10)
K(7)-O(23)#3	3.014(5)	B(8)-O(16)	1.350(9)	B(27)-O(48)#4	1.505(10)
K(7)-O(24)#10	3.029(5)	B(8)-O(24)#6	1.347(9)	B(28)-O(3)	1.500(10)
K(7)-O(30)#9	2.950(5)	B(8)-O(33)	1.414(9)	B(28)-O(14)	1.427(9)
K(7)-O(32)#3	2.757(5)	B(9)-O(1)	1.473(9)	B(28)-O(19)#14	1.495(9)
B(28)-O(34)	1.464(11)				

O(34)-B(1)-O(35)	121.3(7)	O(1)-B(9)-O(47)	109.5(6)	O(23)-B(18)-O(6)#3	116.7(6)
O(34)-B(1)-O(46)	118.6(7)	O(16)-B(9)-O(47)	108.0(6)	O(9)-B(19)-O(39)	114.0(6)
O(35)-B(1)-O(46)	120.1(7)	O(22)#6-B(9)-O(1)	108.7(6)	O(10)#1-B(19)-O(9)	125.6(7)
O(12)-B(2)-O(28)	107.8(6)	O(22)#6-B(9)-O(16)	111.6(6)	O(10)#1-B(19)-O(39)	120.5(6)
O(12)-B(2)-O(30)	112.6(6)	O(22)#6-B(9)-O(47)	111.8(6)	O(13)#1-B(20)-O(9)	107.3(6)
O(12)-B(2)-O(36)	114.3(6)	O(19)-B(10)-O(5)	114.7(7)	O(13)#1-B(20)-O(37)#1	109.0(6)
O(28)-B(2)-O(30)	106.4(6)	O(43)-B(10)-O(5)	120.9(6)	O(29)-B(20)-O(9)	109.4(6)
O(28)-B(2)-O(36)	108.8(6)	O(43)-B(10)-O(19)	124.4(6)	O(29)-B(20)-O(13)#1	113.6(6)
O(36)-B(2)-O(30)	106.7(6)	O(36)-B(11)-O(5)	122.9(8)	O(29)-B(20)-O(37)#1	111.3(6)
O(7)#7-B(3)-O(8)	109.7(6)	O(36)-B(11)-O(38)#5	118.0(7)	O(37)#1-B(20)-O(9)	105.9(6)
O(7)#7-B(3)-O(20)	108.5(6)	O(38)#5-B(11)-O(5)	119.1(7)	O(15)#1-B(21)-O(11)	118.0(7)
O(7)#7-B(3)-O(45)	110.9(7)	O(18)#3-B(12)-O(44)	120.1(7)	O(20)-B(21)-O(11)	114.4(6)
O(20)-B(3)-O(8)	111.2(7)	O(28)-B(12)-O(18)#3	125.2(7)	O(20)-B(21)-O(15)#1	127.3(7)
O(20)-B(3)-O(45)	109.7(6)	O(28)-B(12)-O(44)	114.8(7)	O(31)#16-B(22)-O(39)	119.7(7)
O(45)-B(3)-O(8)	106.9(6)	O(14)-B(13)-O(35)	111.7(6)	O(45)#6-B(22)-O(31)#16	120.8(7)
O(7)-B(4)-O(10)#8	109.4(6)	O(14)-B(13)-O(38)	112.6(6)	O(45)#6-B(22)-O(39)	119.5(7)
O(7)-B(4)-O(31)#7	113.0(6)	O(14)-B(13)-O(43)#5	110.0(6)	O(25)#3-B(23)-O(42)	117.4(8)
O(7)-B(4)-O(40)#8	110.8(6)	O(35)-B(13)-O(38)	107.8(6)	O(37)-B(23)-O(25)#3	120.9(8)
O(10)#8-B(4)-O(31)#7	110.0(6)	O(35)-B(13)-O(43)#5	105.3(6)	O(37)-B(23)-O(42)	121.3(8)

O(10)#8-B(4)-O(40)#8	106.1(6)	O(43)#5-B(13)-O(38)	109.2(6)	O(13)-B(24)-O(11)#3	121.5(7)
O(31)#7-B(4)-O(40)#8	107.3(6)	O(3)#3-B(14)-O(44)#9	118.1(7)	O(13)-B(24)-O(41)	121.6(7)
O(15)-B(5)-O(41)	108.6(6)	O(26)-B(14)-O(3)#3	121.9(6)	O(41)-B(24)-O(11)#3	116.8(7)
O(25)-B(5)-O(15)	108.2(6)	O(26)-B(14)-O(44)#9	120.0(7)	O(21)-B(25)-O(33)#2	119.5(7)
O(25)-B(5)-O(41)	106.6(6)	O(23)#3-B(15)-O(4)#3	113.2(6)	O(21)-B(25)-O(47)#15	118.3(7)
O(29)-B(5)-O(15)	108.3(6)	O(27)-B(15)-O(4)#3	111.2(6)	O(47)#15-B(25)-O(33)#2	122.0(7)
O(29)-B(5)-O(25)	112.9(6)	O(27)-B(15)-O(23)#3	106.1(6)	O(30)-B(26)-O(32)#4	117.6(7)
O(29)-B(5)-O(41)	112.0(6)	O(27)-B(15)-O(46)#3	109.6(6)	O(48)#4-B(26)-O(30)	123.0(7)
O(2)-B(6)-O(17)	105.0(6)	O(46)#3-B(15)-O(4)#3	108.5(6)	O(48)#4-B(26)-O(32)#4	119.2(7)
O(2)-B(6)-O(42)	109.1(6)	O(46)#3-B(15)-O(23)#3	108.2(6)	O(12)-B(27)-O(18)	107.8(6)
O(27)-B(6)-O(2)	113.3(6)	O(8)-B(16)-O(22)	117.5(7)	O(12)-B(27)-O(26)#4	114.6(7)
O(27)-B(6)-O(17)	111.8(6)	O(8)-B(16)-O(40)#2	122.3(7)	O(12)-B(27)-O(48)#4	110.9(6)
O(27)-B(6)-O(42)	112.8(6)	O(40)#2-B(16)-O(22)	119.9(7)	O(18)-B(27)-O(48)#4	106.6(6)
O(42)-B(6)-O(17)	104.1(6)	O(6)#3-B(17)-O(21)#3	108.8(6)	O(26)#4-B(27)-O(18)	110.4(6)
O(4)-B(7)-O(1)	119.3(6)	O(6)#3-B(17)-O(24)#3	109.8(6)	O(26)#4-B(27)-O(48)#4	106.2(6)
O(17)#1-B(7)-O(1)	119.4(6)	O(6)#3-B(17)-O(32)	110.5(6)	O(14)-B(28)-O(3)	111.8(6)
O(17)#1-B(7)-O(4)	121.3(7)	O(21)#3-B(17)-O(24)#3	108.8(6)	O(14)-B(28)-O(19)#14	108.3(6)
O(16)-B(8)-O(24)#6	127.7(7)	O(32)-B(17)-O(21)#3	109.5(6)	O(14)-B(28)-O(34)	112.4(7)
O(16)-B(8)-O(33)	112.4(6)	O(32)-B(17)-O(24)#3	109.5(6)	O(19)#14-B(28)-O(3)	106.5(6)
O(24)#6-B(8)-O(33)	119.9(7)	O(2)-B(18)-O(6)#3	122.7(6)	O(34)-B(28)-O(3)	107.1(6)
O(1)-B(9)-O(16)	107.2(5)	O(2)-B(18)-O(23)	120.4(7)	O(34)-B(28)-O(19)#14	110.7(6)

Symmetry transformations used to generate equivalent atoms:

#1 x-1,y,z	#2 x-1,y-1,z	#3 x+1,y,z	#4 -x+1,-y,-z+1	#5 -x+1,-y+1,-z+1
#6 x+1,y+1,z	#7 -x-1,-y,-z	#8 -x,-y+1,-z	#9 -x+2,-y,-z+1	#10 x+2,y,z
#11 x+1,y-1,z	#12 -x-2,-y,-z	#13 x-2,y-1,z	#14 -x,-y+1,-z+1	#15 x,y-1,z
#16 x,y+1,z	#17 x+2,y+1,z	#18 x-2,y,z	#19 x-1,y+1,z	

Figure S1. The PXRD patterns. The blue curve is the calculated pattern of $K_{11}RbB_{28}O_{48}$. The black one is the experimental pattern of $K_{11}RbB_{28}O_{48}$. The red one is the pattern of the residual sample after heating to 600 °C.

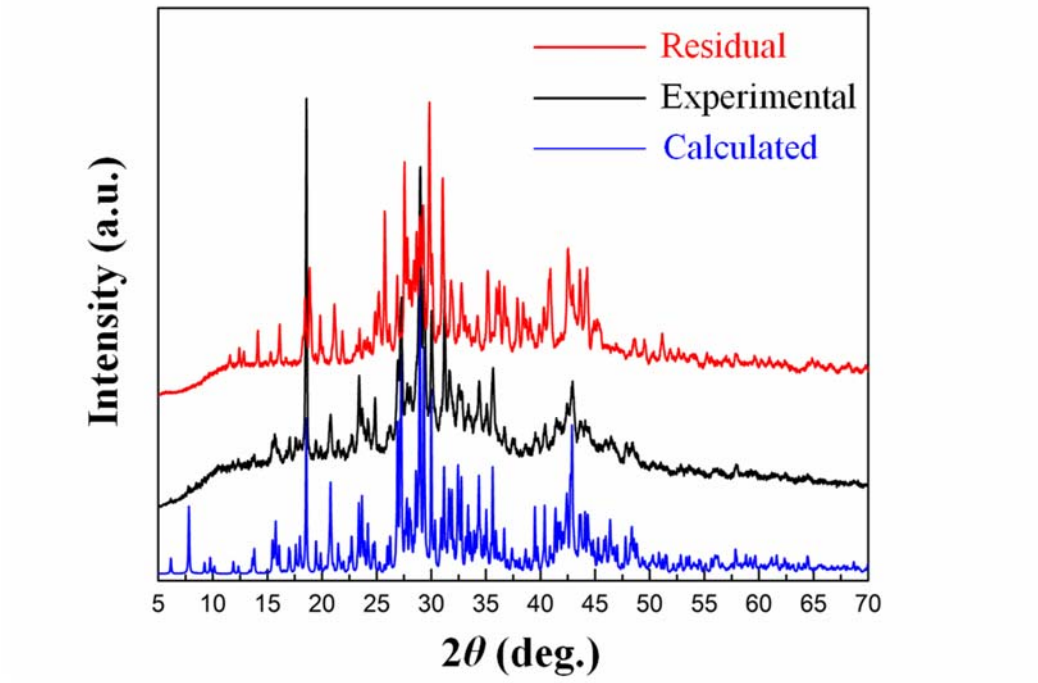


Figure S2. TG-DSC curves of $K_{11}RbB_{28}O_{48}$. On the DSC curve (black solid line), only one endothermic peak during the heating process at about 742 °C is observed. The TG curve (blue solid line) shows no obvious weight loss during the process.

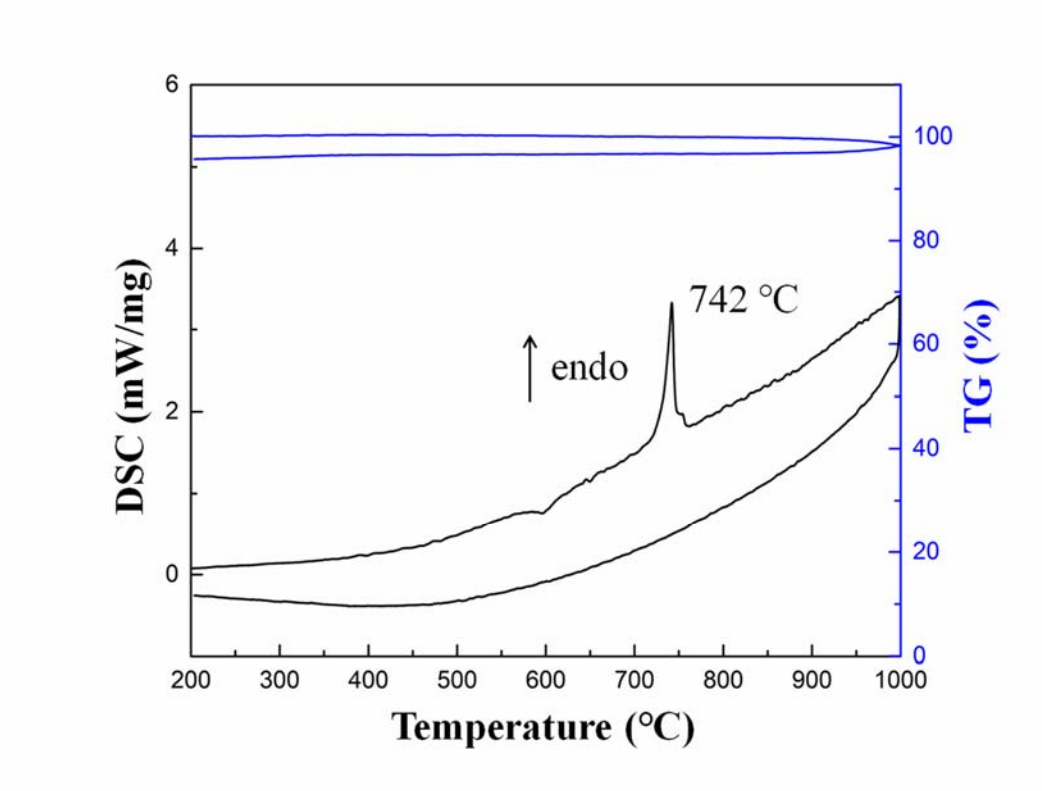
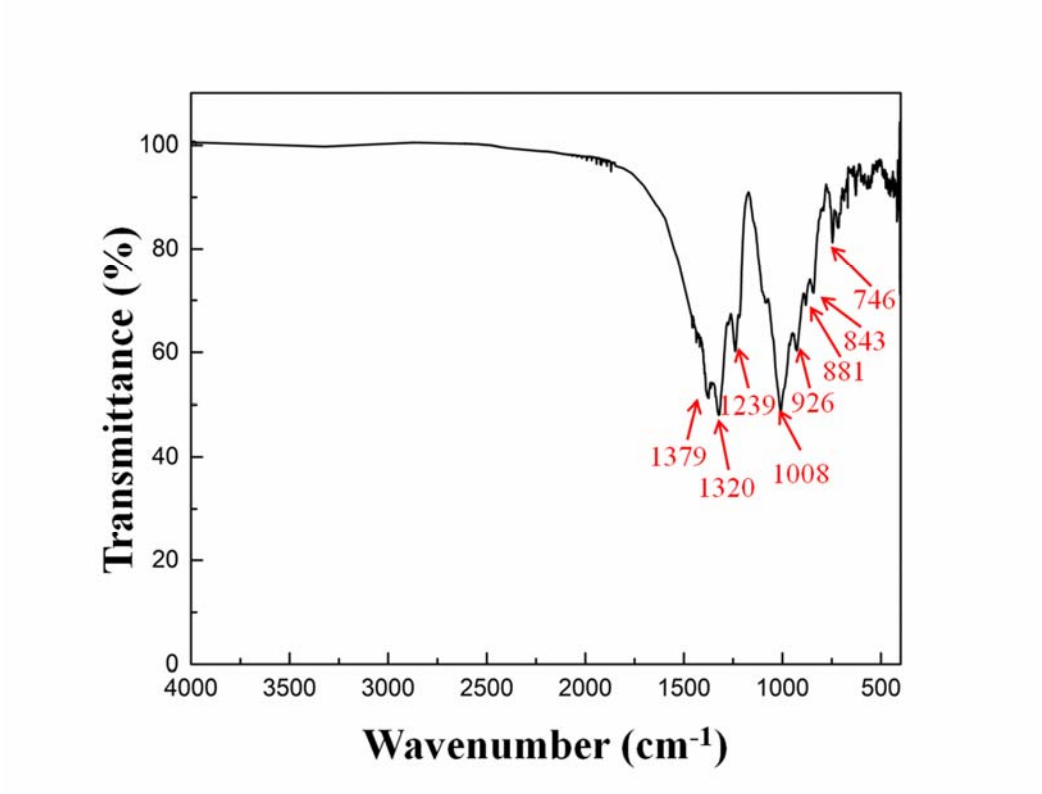


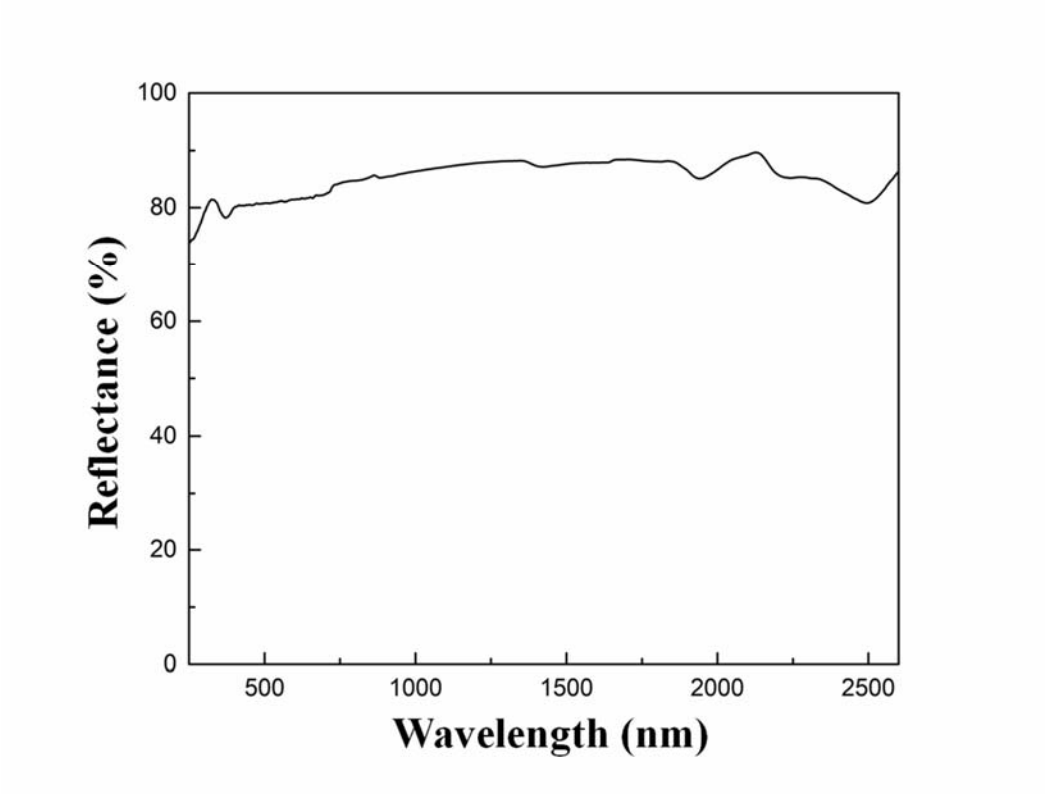
Figure S3. The IR spectrum of $K_{11}RbB_{28}O_{48}$.



Assignment of the absorption bands observed in the IR spectrum of $K_{11}RbB_{28}O_{48}$:

Mode description	Absorption bands (cm^{-1}) for $K_{11}RbB_{28}O_{48}$
asymmetric stretching of B-O bonds in the $[BO_3]$	1379, 1320, 1239
asymmetric stretching of B-O bonds in the $[BO_4]$	1008
symmetric stretching of B-O bonds in $[BO_3]$ and $[BO_4]$	926, 881, 843, 746

Figure S4. The UV-Vis-NIR diffuse reflectance spectrum of $K_{11}RbB_{28}O_{48}$.



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