Electronic Supporting Information (ESI)

A bifunctional primitive strategy induces enhancements of large second harmonic generation and wide UV transmittance in rare-earth borates containing [B_5O_{10}] groups

Shuaifeng Li,[a] Weiming Li,[a] Xiang Li,[a] Guangsai Yang,[a] Ning Ye,[a] Zhanggui Hu,[a] Yicheng Wu [a] and Conggang Li *[a, b]

[a]Tianjin Key Laboratory of Functional Crystal Materials, Institute of Functional Crystal, Tianjin University of Technology, Tianjin 300384, China.

[b]State Key Laboratory of Crystal Materials, Shandong University, Jinan, 250100, China.

***Corresponding author**, E-mail address: cgli@email.tjut.edu.cn

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Experimental Section

Compounds preparation. Polycrystalline samples of $K_7BaSc_2B_{15}O_{30}$ and $Rb_{21}Sr_{3.8}Sc_{5.2}B_{45}O_{90}$ were prepared by using solid-state techniques with a stoichiometric ratio of K_2CO_3/Rb_2CO_3, $BaCO_3$/$SrCO_3$, Sc_2O_3, and H_3BO_3. The mixtures were gradually heated up to 700-750°C for both compounds with several intermediate grindings and mixings, followed by a duration of 72 hours at 700-750°C to ensure complete reactions. Subsequently, the mixtures were cooled to room temperature at a rate of 10°C. Ultimately, the reaction products were synthesized. The purities of the two products were proved by the powder X-ray diffraction texts. Single crystals of $K_7BaSc_2B_{15}O_{30}$ and $Rb_{21}Sr_{3.8}Sc_{5.2}B_{45}O_{90}$ were prepared by the high-temperature solution method, by utilizing K_2CO_3/Rb_2CO_3-H_3BO_3 as a flux.

Powder X-ray diffraction (PXRD). The PXRD measurements of the $K_7BaSc_2B_{15}O_{30}$ and $Rb_{21}Sr_{3.8}Sc_{5.2}B_{45}O_{90}$ compounds were conducted utilizing a Rigaku SmartLab 9kW diffractometer equipped with a diffracted monochromator setting for Cu Kα radiation (λ =1.5418 Å). The experimental data were characterized at ambient temperature within the 2θ range of 10−70°, at a step size of 0.01° and a step time of 2 s.

Thermal Analysis. Thermal gravimetric analysis (TG) and differential scanning calorimetry (DSC) for the $K_7BaSc_2B_{15}O_{30}$ and $Rb_{21}Sr_{3.8}Sc_{5.2}B_{45}O_{90}$ compounds were measured on a HITACHI STA200 TG/DSC analyzer. The polycrystalline samples were placed in an alumina crucible and heated up to 1000 °C at a rate of 10 °C/ min in the N_2 atmosphere.

Single-Crystal X-ray Diffraction. The crystallographic data of $K_7BaSc_2B_{15}O_{30}$ and $Rb_{21}Sr_{3.8}Sc_{5.2}B_{45}O_{90}$ crystals were recorded on a Bruker SMART APEX II 4K CCD diffractometer Mo Kα radiation (λ = 0.71073 Å) at 298(2) K. The APEX III software with multiple scan models was applied to carry out the data integration and absorption corrections. The preliminary crystal models were solved by direct methods and refined via the SHELXTL system.[1-2] The structural symmetry was determined by using the PLATON program for eliminating symmetry elements to ensure the high degree of symmetry in the crystal structure.[3] The extended structural data including the values of the bond valence sum (BVS), equivalent isotropic displacement parameters, and the selected bond distances (Å) and angles (deg.) are available in Tables S3 and S4.

Transmission Spectrum. The UV−vis−NIR diffuse reflectance spectra for $K_7BaSc_2B_{15}O_{30}$ and $Rb_{21}Sr_{3.8}Sc_{5.2}B_{45}O_{90}$ were performed using a Hitachi UH4150 spectrophotometer with a wavelength range from 190 to 2000 nm at room temperature. Barium sulfate was utilized as the reference standard for the diffuse reflectance measurements. The experimental band gaps of the title compounds can be determined based on the Kubelka−Munk function: $F(R) = (1-R)^2/2R =$ K/S, where R represents reflectance, K represents absorption, and S represents scattering.[4] In addition, the infrared spectrum of the two compounds were available at room temperature by using a STA6000-TL9000 FTIR spectrometer in the measured range of 400−4000 cm^{-1}. To prepare the test samples, the two compounds were completely mixed with KBr at a mass ratio of about 1 : 150, respectively.

Second harmonic generation (SHG) measurement. The powder SHG tests of the title compounds were performed by the Kurtz−Perry method using a Q-switched Nd:YAG laser with a wavelength of 1064 nm.[5] The different particle size ranges (50−75, 75−108, 108−120, 120−150, 150−180, and 180−215 μm) were available through grinding and filtering polycrystalline samples of the two compounds. Meanwhile commercial KH_2PO_4 (KDP) single crystals were sieved into the consistent particle size ranges as the reference sample.

Computational details. The band structures, the density of states (DOS) as well as partial density of states (PDOS) were calculated by the density functional theory (DFT) method, as implemented in the CASTEP package.[6] To accurately capture the electronic and structural properties, the Perdew−Burke−Ernzerhof (PBE) functional, formulated within the framework of generalized gradient approximation (GGA), was employed to account for the exchange-correlation energy.[7-8] The kinetic energy cutoffs of 750 and 810 eV were chosen for $K_7BaSc_2B_{15}O_{30}$ and $Rb_{21}Sr_{3.8}Sc_{5.2}B_{45}O_{90}$, respectively. The numerical integration of the Brillouin zone was performed using Monkhorst-Pack k-point sampling of 3 × 3 × 3 and 4 × 4 × 4 for $K_7BaSc_2B_{15}O_{30}$ and $Rb_{21}Sr_{3.8}Sc_{5.2}B_{45}O_{90}$, respectively. [9] Under the norm-conserving pseudopotential (NCP), the following orbital electrons were treated as valence electrons: K $4s^1$, Rb $5s^1$, Ba $6s^2$, Sr $5s^2$, Sc $3d^1 4s^2$, B $2s^2$ $2p^1$, and O $2s^2$ $2p^4$.

Table S1 Crystallographic data and structural refinement for KBSBO and RSSBO.

Empirical formula	$K_7BaSc_2B_{15}O_{30}$	$Rb_{21}Sr_{3.8}Sc_{5.2}B_{45}O_{90}$
formula weight	13717.30	4288.08
temperature (K)	273(2)	273(2)
wavelength (Å)	0.71073	0.71073
crystal system	trigonal	trigonal
space group	*R32*	*R32*
a (Å)	13.0897(10)	13.367 (3)
b (Å)	13.0897(10)	13.367 (3)
c (Å)	60.7234 (7)	14.906 (3)
β(°)	90°	90°
γ(°)	120°	120°
Volume (Å^3)	9010.4(2)	2306.4 (14)
Z	1	1
density (g/cm^3)	2.528	3.087
F(000)	6552	1976
R(int)	0.0427	0.0336
Completeness (%)	99.7	99.6
GOF on (F^2)	1.053	1.088
Final *R* indices $[I > 2\sigma(I)]^a$	R_1=0.0251, wR_2=0.0571	R_1=0.0167, wR_2=0.0378
R indices (all data)^a	R_1=0.0311, wR_2=0.0600	R_1=0.0189, wR_2=0.0385
CCDC	2335307	2335374

$^aR_1=\Sigma||F_o|-|F_c||/\Sigma|F_o|$ and $wR_2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

Table S2 The final atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2×10^3) for $K_7BaSc_2B_{15}O_{30}$, U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor, and the bond valence sum (BVS) for each atom in asymmetric unit.

Atom	x	y	z	U_{eq}	BVS
Ba(1)	10000	10000	4325(1)	15(1)	2.14
Ba(2)	6667	3333	4601(1)	32(1)	1.95
Sc(1)	6667	3333	5193(1)	8(1)	2.99
Sc(2)	3333	-3333	5986(1)	8(1)	2.87
Sc(3)	0	0	6257(1)	9(1)	3.05
Sc(4)	6667	3333	6559(1)	8(1)	2.94
K(1)	11337(1)	7898(1)	4572(1)	31(1)	0.94
O(1)	9357(2)	7971(2)	4494(1)	20(1)	1.06
K(2)	8440(1)	6655(1)	4139(1)	33(1)	0.97
K(3)	10000	10000	5000	26(1)	1.42
K(4)	4902(2)	4902(2)	5000	40(1)	0.76
K(5)	6667	3333	5840(1)	22(1)	1.33
K(6)	5392(1)	-10(1)	6264(1)	22(1)	1.04
K(7)	3333	-3333	6667	22(1)	1.32
K(8)	3333	1789(1)	6667	27(1)	1.12
O(2)	8305(3)	8071(3)	4806(1)	23(1)	1.52
O(3)	7399(3)	6384(3)	5050(1)	26(1)	1.56
O(4)	7591(2)	4725(2)	4963(1)	22(1)	1.12
O(5)	8328(5)	6315(3)	4722(1)	54(1)	1.58
O(6)	691(3)	-660(3)	6507(1)	16(1)	1.10
O(7)	2280(2)	-711(3)	6674(1)	17(1)	1.55
O(8)	3338(2)	-1488(2)	6471(1)	15(1)	1.56
O(9)	2372(2)	-2747(2)	6166(1)	15(1)	1.11
O(10)	1521(3)	-1732(3)	6338(1)	22(1)	1.57
O(11)	5962(3)	1753(2)	5369(1)	20(1)	1.10

O(12)	4736(3)	1483(2)	5676(1)	18(1)	1.56
O(13)	4004(3)	-290(2)	5892(1)	19(1)	1.54
O(14)	5021(4)	-86(2)	5554(1)	25(1)	1.55
O(15)	4135(3)	-1898(2)	5751(1)	20(1)	1.09
O(16)	1424(2)	910(3)	6054(1)	18(1)	1.11
O(17)	2956(2)	768(3)	5879(1)	23(1)	1.51
O(18)	4857(2)	1585(2)	6068(1)	16(1)	1.53
O(19)	5163(2)	2792(2)	6385(1)	14(1)	1.10
O(20)	3341(2)	1905(3)	6206(1)	23(1)	1.59
B(1)	2546(4)	1181(5)	6046(1)	14(1)	3.05
B(2)	1488(4)	-1023(4)	6506(1)	13(1)	3.03
B(3)	4372(4)	-789(4)	5734(1)	14(1)	3.01
B(4)	8690(6)	7495(4)	4669(1)	19(1)	3.05
B(5)	3333	-839(5)	6667	14(1)	3.08
B(6)	7764(5)	5787(4)	4918(1)	19(1)	3.12
B(7)	4130(4)	879(4)	5877(1)	17(1)	3.08
B(8)	7544(6)	7544(6)	5000	20(2)	3.07
B(9)	4497(4)	2098(4)	6220(1)	14(1)	3.03
B(10)	2436(4)	-2002(4)	6321(1)	12(1)	3.02
B(11)	5252(4)	1079(4)	5529(1)	15(1)	3.01

Table S3 The final atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2×10^3) for $Rb_{21}Sr_{3.8}Sc_{5.2}B_{45}O_{90}$, U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor, and the bond valence sum (BVS) for each atom in asymmetric unit.

Atom	x	y	z	U_{eq}	BVS
Sr(1)/ Sc(1)	6667	3333	6084(1)	13(1)	3.19/2.40
Sr(2)/ Sc(2)	10000	10000	5000	16(1)	2.33/3.18
Rb(1)	10000	4578(1)	5000	25(1)	1.21
Rb(2)	6667	3333	3333	30(1)	1.2
Rb(3)	8098(1)	6667	6667	30(1)	1.06
O(1)	8602(2)	5284(2)	4129(2)	23(1)	1.58
O(2)	9371(3)	7070(2)	3294(2)	31(1)	1.54
O(3)/O(6)	9218(9)	8622(7)	3739(6)	23(1)	0.95/1.08
	9284(10)	8600(8)	4120(6)	23(1)	
O(4)/O(7)	8266(10)	6749(7)	4662(13)	31(2)	1.52/1.71
	8120(30)	6760(20)	4370(20)	31(2)	
O(5)	7283(3)	4938(3)	5309(2)	36(1)	1.07
B(1)	9246(5)	5913(5)	3333	20(1)	3.1
B(2)	8028(4)	5622(4)	4690(3)	25(1)	3.15/2.80
B(3)	8966(4)	7501(4)	3935(4)	34(1)	3.48/2.77

Table S4 Selected bond lengths (Å) and angles (deg.) for $K_7BaSc_2B_{15}O_{30}$.

Ba(1)-O(1)	2.565(3)	Sc(4)-O(19)	2.022(3)
Ba(1)-O(1)#1	2.565(3)	Sc(4)-O(6)#17	2.233(2)
Ba(1)-O(1)#2	2.565(3)	Sc(4)-O(6)#18	2.233(2)
Ba(1)-O(16)#3	2.820(2)	Sc(4)-O(6)#19	2.233(2)
Ba(1)-O(16)#4	2.820(2)	K(1)-O(12)#3	2.680(3)
Ba(1)-O(16)#5	2.820(2)	K(1)-O(1)	2.684(3)
Ba(2)-O(15)#6	2.691(2)	K(1)-O(3)#20	2.770(3)
Ba(2)-O(15)#7	2.691(2)	K(1)-O(11)#7	2.869(4)
Ba(2)-O(15)#5	2.691(2)	K(1)-O(2)#1	3.098(3)
Ba(2)-O(4)#8	2.723(3)	K(1)-O(17)#3	3.141(3)
Ba(2)-O(4)#9	2.723(3)	K(1)-O(14)#7	3.351(4)
Ba(2)-O(4)	2.723(3)	O(1)-B(4)	1.320(5)
Sc(1)-O(11)#8	2.088(2)	O(1)-K(2)	2.642(3)
Sc(1)-O(11)#9	2.088(2)	K(2)-O(9)#5	2.738(3)
Sc(1)-O(11)	2.088(2)	K(2)-O(13)#5	2.800(3)
Sc(1)-O(4)#8	2.127(3)	K(2)-O(10)#5	2.897(3)
Sc(1)-O(4)	2.127(3)	K(2)-O(17)#5	2.901(3)
Sc(1)-O(4)#9	2.127(3)	K(2)-O(15)#7	3.171(4)
Sc(2)-O(9)	2.083(2)	K(2)-O(16)#3	3.201(3)
Sc(2)-O(9)#11	2.083(3)	K(3)-O(2)#21	2.662(3)
Sc(2)-O(9)#12	2.083(3)	K(3)-O(2)#20	2.662(3)
Sc(2)-O(15)	2.165(2)	K(3)-O(2)#22	2.662(3)
Sc(2)-O(15)#12	2.165(2)	K(3)-O(2)#1	2.662(3)
Sc(2)-O(15)#11	2.165(2)	K(3)-O(2)#2	2.662(3)
Sc(3)-O(16)	2.049(3)	K(3)-O(2)	2.662(3)
Sc(3)-O(16)#14	2.049(3)	K(4)-O(3)	2.863(4)
Sc(3)-O(16)#15	2.049(3)	K(4)-O(3)#22	2.863(4)
Sc(3)-O(6)	2.157(2)	K(4)-O(4)#8	2.948(3)
Sc(3)-O(6)#14	2.157(2)	K(4)-O(4)#23	2.948(3)
Sc(3)-O(6)#15	2.157(2)	K(4)-O(11)#5	2.994(3)
Sc(4)-O(19)#8	2.022(3)	K(4)-O(11)#9	2.994(3)
Sc(4)-O(19)#9	2.022(3)	K(4)-O(14)#9	3.368(3)

K(4)-O(14)#5	3.368(3)	O(5)-B(6)	1.386(5)
K(5)-O(12)#8	2.669(3)	O(5)-B(4)	1.408(5)
K(5)-O(12)#9	2.669(3)	O(6)-B(2)	1.345(5)
K(5)-O(12)	2.669(3)	O(7)-B(2)	1.363(5)
K(5)-O(18)#8	2.709(3)	O(7)-B(5)	1.471(5)
K(5)-O(18)#9	2.709(3)	O(8)-B(10)	1.370(5)
K(5)-O(18)	2.709(3)	O(8)-B(5)	1.464(5)
K(6)-O(8)	2.709(3)	O(9)-B(10)	1.328(5)
K(6)-O(18)	2.782(3)	O(10)-B(2)	1.397(5)
K(6)-O(13)	2.806(3)	O(10)-B(10)	1.411(5)
K(6)-O(9)#11	2.879(3)	O(11)-B(11)	1.330(5)
K(6)-O(7)#18	2.881(3)	O(12)-B(11)	1.375(5)
K(6)-O(19)#8	2.914(3)	O(12)-B(7)	1.455(5)
K(6)-O(20)#8	3.086(3)	O(13)-B(3)	1.378(5)
K(6)-O(10)#11	3.280(4)	O(13)-B(7)	1.457(5)
K(7)-O(8)	2.691(3)	O(14)-B(11)	1.406(5)
K(7)-O(8)#12	2.691(3)	O(14)-B(3)	1.408(5)
K(7)-O(8)#11	2.691(3)	O(15)-B(3)	1.327(5)
K(7)-O(8)#24	2.691(3)	O(16)-B(1)	1.329(5)
K(7)-O(8)#25	2.691(3)	O(17)-B(1)	1.375(6)
K(7)-O(8)#18	2.691(3)	O(17)-B(7)	1.470(5)
K(8)-O(19)	2.690(3)	O(18)-B(9)	1.359(5)
K(8)-O(19)#18	2.690(3)	O(18)-B(7)	1.492(5)
K(8)-O(20)	2.798(3)	O(19)-B(9)	1.341(5)
K(8)-O(20)#18	2.798(3)	O(20)-B(1)	1.396(5)
K(8)-O(7)#18	2.846(3)	O(20)-B(9)	1.406(5)
K(8)-O(7)	2.846(3)	O(1)-Ba(1)-O(1)#1	105.05(7)
K(8)-O(6)#14	3.392(4)	O(1)-Ba(1)-O(1)#2	105.05(7)
K(8)-O(6)#19	3.392(4)	O(1)#1-Ba(1)-O(1)#2	105.05(7)
O(2)-B(4)	1.374(6)	O(1)-Ba(1)-O(16)#3	85.01(8)
O(2)-B(8)	1.473(5)	O(1)#1-Ba(1)-O(16)#3	104.10(9)
O(3)-B(6)	1.364(6)	O(1)#2-Ba(1)-O(16)#3	145.27(8)
O(3)-B(8)	1.465(5)	O(1)-Ba(1)-O(16)#4	145.27(8)
O(4)-B(6)	1.321(5)	O(1)#1-Ba(1)-O(16)#4	85.02(9)

O(1)#2-Ba(1)-O(16)#4	104.10(9)	O(11)-Sc(1)-O(4)#9	83.22(12)
O(16)#3-Ba(1)-O(16)#4	60.26(8)	O(4)#8-Sc(1)-O(4)#9	81.69(12)
O(1)-Ba(1)-O(16)#5	104.10(9)	O(4)-Sc(1)-O(4)#9	81.69(12)
O(1)#1-Ba(1)-O(16)#5	145.27(9)	O(9)-Sc(2)-O(9)#11	94.83(10)
O(1)#2-Ba(1)-O(16)#5	85.02(9)	O(9)-Sc(2)-O(9)#12	94.83(10)
O(16)#3-Ba(1)-O(16)#5	60.26(8)	O(9)#11-Sc(2)-O(9)#12	94.83(10)
O(16)#4-Ba(1)-O(16)#5	60.26(8)	O(9)-Sc(2)-O(15)	98.41(12)
O(15)#6-Ba(2)-O(15)#7	63.34(8)	O(9)#11-Sc(2)-O(15)	85.34(12)
O(15)#6-Ba(2)-O(15)#5	63.34(8)	O(9)#12-Sc(2)-O(15)	166.70(12)
O(15)#7-Ba(2)-O(15)#5	63.34(8)	O(9)-Sc(2)-O(15)#12	85.34(12)
O(15)#6-Ba(2)-O(4)#8	123.17(10)	O(9)#11-Sc(2)-O(15)#12	166.70(13)
O(15)#7-Ba(2)-O(4)#8	171.22(11)	O(9)#12-Sc(2)-O(15)#12	98.41(13)
O(15)#5-Ba(2)-O(4)#8	113.03(9)	O(15)-Sc(2)-O(15)#12	81.49(10)
O(15)#6-Ba(2)-O(4)#9	113.03(9)	O(9)-Sc(2)-O(15)#11	166.70(12)
O(15)#7-Ba(2)-O(4)#9	123.17(9)	O(9)#11-Sc(2)-O(15)#11	98.41(13)
O(15)#5-Ba(2)-O(4)#9	171.22(11)	O(9)#12-Sc(2)-O(15)#11	85.34(12)
O(4)#8-Ba(2)-O(4)#9	61.43(9)	O(15)-Sc(2)-O(15)#11	81.49(10)
O(15)#6-Ba(2)-O(4)	171.22(11)	O(15)#12-Sc(2)-O(15)#11	81.49(10)
O(15)#7-Ba(2)-O(4)	113.03(9)	O(16)-Sc(3)-O(16)#14	87.38(10)
O(15)#5-Ba(2)-O(4)	123.17(9)	O(16)-Sc(3)-O(16)#15	87.38(10)
O(4)#8-Ba(2)-O(4)	61.43(9)	O(16)#14-Sc(3)-O(16)#15	87.38(10)
O(4)#9-Ba(2)-O(4)	61.43(9)	O(16)-Sc(3)-O(6)	102.44(12)
O(11)#8-Sc(1)-O(11)#9	96.21(10)	O(16)#14-Sc(3)-O(6)	170.11(12)
O(11)#8-Sc(1)-O(11)	96.20(10)	O(16)#15-Sc(3)-O(6)	94.17(11)
O(11)#9-Sc(1)-O(11)	96.20(10)	O(16)-Sc(3)-O(6)#14	94.16(12)
O(11)#8-Sc(1)-O(4)#8	164.59(13)	O(16)#14-Sc(3)-O(6)#14	102.45(12)
O(11)#9-Sc(1)-O(4)#8	83.22(12)	O(16)#15-Sc(3)-O(6)#14	170.10(12)
O(11)-Sc(1)-O(4)#8	99.17(13)	O(6)-Sc(3)-O(6)#14	75.95(9)
O(11)#8-Sc(1)-O(4)	83.22(12)	O(16)-Sc(3)-O(6)#15	170.10(12)
O(11)#9-Sc(1)-O(4)	99.16(13)	O(16)#14-Sc(3)-O(6)#15	94.17(11)
O(11)-Sc(1)-O(4)	164.60(13)	O(16)#15-Sc(3)-O(6)#15	102.44(12)
O(4)#8-Sc(1)-O(4)	81.69(12)	O(6)-Sc(3)-O(6)#15	75.95(9)
O(11)#8-Sc(1)-O(4)#9	99.16(12)	O(6)#14-Sc(3)-O(6)#15	75.95(9)
O(11)#9-Sc(1)-O(4)#9	164.60(13)	O(19)#8-Sc(4)-O(19)#9	95.38(10)

O(19)#8-Sc(4)-O(19)	95.38(10)	O(17)#3-K(1)-O(14)#7	105.54(8)
O(19)#9-Sc(4)-O(19)	95.38(10)	O(1)-K(2)-O(9)#5	164.29(10)
O(19)#8-Sc(4)-O(6)#17	99.40(12)	O(1)-K(2)-O(13)#5	113.01(9)
O(19)#9-Sc(4)-O(6)#17	90.83(12)	O(9)#5-K(2)-O(13)#5	72.79(8)
O(19)-Sc(4)-O(6)#17	163.37(11)	O(1)-K(2)-O(10)#5	142.63(9)
O(19)#8-Sc(4)-O(6)#18	90.83(11)	O(9)#5-K(2)-O(10)#5	49.44(7)
O(19)#9-Sc(4)-O(6)#18	163.37(11)	O(13)#5-K(2)-O(10)#5	86.66(10)
O(19)-Sc(4)-O(6)#18	99.40(12)	O(1)-K(2)-O(17)#5	83.71(9)
O(6)#17-Sc(4)-O(6)#18	72.91(9)	O(9)#5-K(2)-O(17)#5	109.73(9)
O(19)#8-Sc(4)-O(6)#19	163.37(11)	O(13)#5-K(2)-O(17)#5	49.48(8)
O(19)#9-Sc(4)-O(6)#19	99.40(12)	O(10)#5-K(2)-O(17)#5	86.66(10)
O(19)-Sc(4)-O(6)#19	90.83(11)	O(1)-K(2)-O(15)#7	106.80(8)
O(6)#17-Sc(4)-O(6)#19	72.91(9)	O(9)#5-K(2)-O(15)#7	57.77(7)
O(6)#18-Sc(4)-O(6)#19	72.91(9)	O(13)#5-K(2)-O(15)#7	91.10(8)
O(12)#3-K(1)-O(1)	131.59(9)	O(10)#5-K(2)-O(15)#7	104.09(8)
O(12)#3-K(1)-O(3)#20	94.68(9)	O(17)#5-K(2)-O(15)#7	138.98(8)
O(1)-K(1)-O(3)#20	117.91(10)	O(1)-K(2)-O(16)#3	76.49(8)
O(12)#3-K(1)-O(11)#7	77.00(8)	O(9)#5-K(2)-O(16)#3	111.93(8)
O(1)-K(1)-O(11)#7	131.87(9)	O(13)#5-K(2)-O(16)#3	128.90(8)
O(3)#20-K(1)-O(11)#7	91.25(9)	O(10)#5-K(2)-O(16)#3	66.70(7)
O(12)#3-K(1)-O(2)#1	102.96(9)	O(17)#5-K(2)-O(16)#3	84.70(8)
O(1)-K(1)-O(2)#1	79.36(9)	O(15)#7-K(2)-O(16)#3	136.08(8)
O(3)#20-K(1)-O(2)#1	47.39(8)	O(2)#21-K(3)-O(2)#20	101.89(7)
O(11)#7-K(1)-O(2)#1	138.63(8)	O(2)#21-K(3)-O(2)#22	101.89(7)
O(12)#3-K(1)-O(17)#3	47.38(8)	O(2)#20-K(3)-O(2)#22	101.89(7)
O(1)-K(1)-O(17)#3	84.59(8)	O(2)#21-K(3)-O(2)#1	115.74(13)
O(3)#20-K(1)-O(17)#3	118.84(9)	O(2)#20-K(3)-O(2)#1	53.97(12)
O(11)#7-K(1)-O(17)#3	115.41(8)	O(2)#22-K(3)-O(2)#1	137.89(13)
O(2)#1-K(1)-O(17)#3	90.38(8)	O(2)#21-K(3)-O(2)#2	53.97(12)
O(12)#3-K(1)-O(14)#7	96.95(8)	O(2)#20-K(3)-O(2)#2	137.89(13)
O(1)-K(1)-O(14)#7	89.75(9)	O(2)#22-K(3)-O(2)#2	115.74(13)
O(3)#20-K(1)-O(14)#7	128.41(9)	O(2)#1-K(3)-O(2)#2	101.89(7)
O(11)#7-K(1)-O(14)#7	43.97(7)	O(2)#21-K(3)-O(2)	137.89(13)
O(2)#1-K(1)-O(14)#7	159.86(8)	O(2)#20-K(3)-O(2)	115.74(13)

O(2)#22-K(3)-O(2)	53.98(12)	O(12)#8-K(5)-O(18)#8	52.63(8)
O(2)#1-K(3)-O(2)	101.89(7)	O(12)#9-K(5)-O(18)#8	125.76(9)
O(2)#2-K(3)-O(2)	101.89(7)	O(12)-K(5)-O(18)#8	126.47(9)
O(3)-K(4)-O(3)#22	49.10(13)	O(12)#8-K(5)-O(18)#9	126.47(9)
O(3)-K(4)-O(4)#8	88.37(8)	O(12)#9-K(5)-O(18)#9	52.63(8)
O(3)#22-K(4)-O(4)#8	134.42(10)	O(12)-K(5)-O(18)#9	125.76(9)
O(3)-K(4)-O(4)#23	134.42(10)	O(18)#8-K(5)-O(18)#9	96.25(8)
O(3)#22-K(4)-O(4)#23	88.37(8)	O(12)#8-K(5)-O(18)	125.76(9)
O(4)#8-K(4)-O(4)#23	136.68(13)	O(12)#9-K(5)-O(18)	126.47(9)
O(3)-K(4)-O(11)#5	109.92(11)	O(12)-K(5)-O(18)	52.63(8)
O(3)#22-K(4)-O(11)#5	69.43(10)	O(18)#8-K(5)-O(18)	96.25(8)
O(4)#8-K(4)-O(11)#5	124.10(8)	O(18)#9-K(5)-O(18)	96.25(8)
O(4)#23-K(4)-O(11)#5	56.20(8)	O(8)-K(6)-O(18)	101.63(9)
O(3)-K(4)-O(11)#9	69.43(10)	O(8)-K(6)-O(13)	86.09(8)
O(3)#22-K(4)-O(11)#9	109.92(11)	O(18)-K(6)-O(13)	50.40(8)
O(4)#8-K(4)-O(11)#9	56.20(8)	O(8)-K(6)-O(9)#11	73.40(8)
O(4)#23-K(4)-O(11)#9	124.10(8)	O(18)-K(6)-O(9)#11	134.94(8)
O(11)#5-K(4)-O(11)#9	179.33(19)	O(13)-K(6)-O(9)#11	84.58(8)
O(3)-K(4)-O(14)#9	83.87(10)	O(8)-K(6)-O(7)#18	50.18(8)
O(3)#22-K(4)-O(14)#9	94.71(11)	O(18)-K(6)-O(7)#18	85.97(8)
O(4)#8-K(4)-O(14)#9	96.16(8)	O(13)-K(6)-O(7)#18	111.84(9)
O(4)#23-K(4)-O(14)#9	84.41(7)	O(9)#11-K(6)-O(7)#18	117.70(8)
O(11)#5-K(4)-O(14)#9	136.73(6)	O(8)-K(6)-O(19)#8	129.35(8)
O(11)#9-K(4)-O(14)#9	43.26(6)	O(18)-K(6)-O(19)#8	71.45(8)
O(3)-K(4)-O(14)#5	94.71(11)	O(13)-K(6)-O(19)#8	118.09(8)
O(3)#22-K(4)-O(14)#5	83.87(10)	O(9)#11-K(6)-O(19)#8	145.91(8)
O(4)#8-K(4)-O(14)#5	84.41(7)	O(7)#18-K(6)-O(19)#8	79.17(8)
O(4)#23-K(4)-O(14)#5	96.16(8)	O(8)-K(6)-O(20)#8	156.16(8)
O(11)#5-K(4)-O(14)#5	43.26(6)	O(18)-K(6)-O(20)#8	97.59(8)
O(11)#9-K(4)-O(14)#5	136.73(6)	O(13)-K(6)-O(20)#8	117.24(8)
O(14)#9-K(4)-O(14)#5	178.45(19)	O(9)#11-K(6)-O(20)#8	102.44(8)
O(12)#8-K(5)-O(12)#9	106.92(7)	O(7)#18-K(6)-O(20)#8	118.14(8)
O(12)#8-K(5)-O(12)	106.91(7)	O(19)#8-K(6)-O(20)#8	45.65(7)
O(12)#9-K(5)-O(12)	106.91(7)	O(8)-K(6)-O(10)#11	98.62(8)

O(18)-K(6)-O(10)#11	157.77(8)	O(20)-K(8)-O(7)	93.74(9)
O(13)-K(6)-O(10)#11	122.76(8)	O(20)#18-K(8)-O(7)	91.72(9)
O(9)#11-K(6)-O(10)#11	44.49(7)	O(7)#18-K(8)-O(7)	49.67(11)
O(7)#18-K(6)-O(10)#11	114.33(8)	O(19)-K(8)-O(6)#14	119.50(7)
O(19)#8-K(6)-O(10)#11	102.30(8)	O(19)#18-K(8)-O(6)#14	58.51(7)
O(20)#8-K(6)-O(10)#11	65.55(7)	O(20)-K(8)-O(6)#14	72.51(7)
O(8)-K(7)-O(8)#12	101.91(7)	O(20)#18-K(8)-O(6)#14	105.31(7)
O(8)-K(7)-O(8)#11	101.91(7)	O(7)#18-K(8)-O(6)#14	133.25(8)
O(8)#12-K(7)-O(8)#11	101.91(7)	O(7)-K(8)-O(6)#14	86.83(7)
O(8)-K(7)-O(8)#24	126.50(12)	O(19)-K(8)-O(6)#19	58.51(7)
O(8)#12-K(7)-O(8)#24	126.94(11)	O(19)#18-K(8)-O(6)#19	119.50(7)
O(8)#11-K(7)-O(8)#24	52.52(11)	O(20)-K(8)-O(6)#19	105.32(7)
O(8)-K(7)-O(8)#25	126.93(12)	O(20)#18-K(8)-O(6)#19	72.51(7)
O(8)#12-K(7)-O(8)#25	52.52(11)	O(7)#18-K(8)-O(6)#19	86.83(7)
O(8)#11-K(7)-O(8)#25	126.50(11)	O(7)-K(8)-O(6)#19	133.25(8)
O(8)#24-K(7)-O(8)#25	101.91(7)	O(6)#14-K(8)-O(6)#19	139.39(10)
O(8)-K(7)-O(8)#18	52.52(11)	O(16)-B(1)-O(17)	121.3(4)
O(8)#12-K(7)-O(8)#18	126.50(11)	O(16)-B(1)-O(20)	120.4(4)
O(8)#11-K(7)-O(8)#18	126.94(12)	O(17)-B(1)-O(20)	118.4(3)
O(8)#24-K(7)-O(8)#18	101.91(7)	O(6)-B(2)-O(7)	119.9(4)
O(8)#25-K(7)-O(8)#18	101.91(7)	O(6)-B(2)-O(10)	121.6(4)
O(8)-K(7)-B(5)	26.25(5)	O(7)-B(2)-O(10)	118.5(3)
O(19)-K(8)-O(19)#18	175.05(14)	O(15)-B(3)-O(13)	121.3(4)
O(19)-K(8)-O(20)	50.28(8)	O(15)-B(3)-O(14)	120.6(4)
O(19)#18-K(8)-O(20)	129.39(8)	O(13)-B(3)-O(14)	118.1(3)
O(19)-K(8)-O(20)#18	129.39(8)	O(1)-B(4)-O(2)	124.4(4)
O(19)#18-K(8)-O(20)#18	50.27(8)	O(1)-B(4)-O(5)	118.8(5)
O(20)-K(8)-O(20)#18	173.99(15)	O(2)-B(4)-O(5)	116.8(4)
O(19)-K(8)-O(7)#18	72.86(8)	O(8)-B(5)-O(8)#18	108.8(5)
O(19)#18-K(8)-O(7)#18	111.90(9)	O(8)-B(5)-O(7)	111.58(15)
O(20)-K(8)-O(7)#18	91.72(9)	O(8)#18-B(5)-O(7)	108.10(16)
O(20)#18-K(8)-O(7)#18	93.73(9)	O(8)-B(5)-O(7)#18	108.12(16)
O(19)-K(8)-O(7)	111.91(9)	O(8)#18-B(5)-O(7)#18	111.57(15)
O(19)#18-K(8)-O(7)	72.86(8)	O(7)-B(5)-O(7)#18	108.7(5)

O(4)-B(6)-O(3)	123.6(4)	O(3)-B(8)-O(2)	110.99(16)
O(4)-B(6)-O(5)	118.2(4)	O(3)#22-B(8)-O(2)	108.00(17)
O(3)-B(6)-O(5)	118.1(4)	O(2)#22-B(8)-O(2)	110.3(5)
O(12)-B(7)-O(13)	111.8(3)	O(19)-B(9)-O(18)	125.1(4)
O(12)-B(7)-O(17)	108.7(3)	O(19)-B(9)-O(20)	116.3(4)
O(13)-B(7)-O(17)	109.4(4)	O(18)-B(9)-O(20)	118.6(4)
O(12)-B(7)-O(18)	108.0(3)	O(9)-B(10)-O(8)	123.5(4)
O(13)-B(7)-O(18)	107.6(3)	O(9)-B(10)-O(10)	119.0(3)
O(17)-B(7)-O(18)	111.4(3)	O(8)-B(10)-O(10)	117.4(3)
O(3)-B(8)-O(3)#22	108.6(5)	O(11)-B(11)-O(12)	122.2(4)
O(3)-B(8)-O(2)#22	108.01(17)	O(11)-B(11)-O(14)	120.0(4)
O(3)#22-B(8)-O(2)#22	110.99(16)	O(12)-B(11)-O(14)	117.7(4)

Symmetry transformations used to generate equivalent atoms:

#1 -y+2,x-y+1,z #2 -x+y+1,-x+2,z #3 x-y+1,-y+1,-z+1
#4 y+1,x+1,-z+1 #5 -x+1,-x+y+1,-z+1 #6 x-y,-y,-z+1
#7 y+1,x,-z+1 #8 -y+1,x-y,z #9 -x+y+1,-x+1,z
#10 y,x-1,-z+1 #11 -x+y+1,-x,z #12 -y,x-y-1,z
#13 -x+1,-x+y,-z+1 #14 -y,x-y,z #15 -x+y,-x,z
#16 y-1/3,x-2/3,-z+4/3 #17 x-y+2/3,-y+1/3,-z+4/3
#18 -x+2/3,-x+y+1/3,-z+4/3 #19 y+2/3,x+1/3,-z+4/3
#20 -x+2,-x+y+1,-z+1 #21 x-y+1,-y+2,-z+1 #22 y,x,-z+1
#23 x-y,-y+1,-z+1 #24 y+2/3,x-2/3,-z+4/3 #25 x-y-1/3,-y-2/3,-z+4/3
#26 y-1,x-1,-z+1

Table S5 Selected bond lengths (Å) and angles (deg.) for $Rb_{21}Sr_{3.8}Sc_{5.2}B_{45}O_{90}$.

Sc(1)-O(3)#1	2.175(9)	Rb(2)-O(1)	2.855(3)
Sc(1)-O(3)#2	2.175(9)	Rb(2)-O(1)#4	2.855(3)
Sc(1)-O(3)#3	2.175(9)	Rb(2)-O(1)#5	2.855(3)
Sr (1)-O(5)	2.202(3)	Rb(2)-O(1)#12	2.855(3)
Sr (1)-O(5)#4	2.202(3)	Rb(2)-O(1)#14	2.855(3)
Sr (1)-O(5)#5	2.202(3)	Rb(3)-O(5)	2.847(3)
Sr (1)-O(6)#1	2.606(9)	Rb(3)-O(5)#15	2.847(3)
Sr(1)-O(6)#2	2.606(9)	Rb(3)-O(2)#1	2.947(3)
Sr(1)-O(6)#3	2.606(9)	Rb(3)-O(2)#7	2.947(3)
Sc(2)-O(6)#6	2.084(9)	Rb(3)-O(4)	2.994(19)
Sc(2)-O(6)#7	2.084(9)	Rb(3)-O(4)#15	2.994(19)
Sc(2)-O(6)#8	2.084(9)	Rb(3)-O(3)#3	3.177(11)
Sc(2)-O(6)#9	2.084(9)	Rb(3)-O(3)#9	3.177(11)
Sc(2)-O(6)#10	2.084(9)	Rb(3)-O(7)	3.42(3)
Sc(2)-O(6)	2.084(9)	Rb(3)-O(7)#15	3.42(3)
Sr(2)-O(3)	2.468(8)	O(1)-B(2)	1.357(5)
Sr(2)-O(3)#6	2.468(8)	O(1)-B(1)	1.459(4)
Sr(2)-O(3)#7	2.468(8)	O(2)-B(3)	1.359(6)
Sr(2)-O(3)#8	2.468(8)	O(2)-B(1)	1.472(4)
Sr(2)-O(3)#9	2.468(8)	O(3)-B(3)	1.393(10)
Sr(2)-O(3)#10	2.468(8)	O(4)-B(2)	1.375(10)
Rb(1)-O(1)#7	2.798(3)	O(4)-B(3)	1.457(15)
Rb(1)-O(1)	2.798(3)	O(5)-B(2)	1.329(6)
Rb(1)-O(5)#4	2.902(4)	O(6)-B(3)	1.339(10)
Rb(1)-O(5)#11	2.902(4)	O(7)-B(3)	1.26(3)
Rb(1)-O(2)#12	2.989(3)	O(7)-B(2)	1.53(3)
Rb(1)-O(2)#1	2.989(3)	O(3)#1-Sr(1)-O(3)#2	79.1(3)
Rb(1)-O(7)#4	3.26(3)	O(3)#1-Sr(1)-O(3)#3	79.1(3)
Rb(1)-O(7)#11	3.26(3)	O(3)#2-Sr(1)-O(3)#3	79.1(3)
Rb(1)-O(4)#4	3.333(10)	O(3)#1-Sr(1)-O(5)	99.4(3)
Rb(1)-O(4)#11	3.333(10)	O(3)#2-Sr(1)-O(5)	165.4(3)
Rb(2)-O(1)#13	2.855(3)	O(3)#3-Sr(1)-O(5)	86.3(3)

O(3)#1-Sr(1)-O(5)#4	86.3(3)	O(6)#7-Sr(2)-O(6)#9	84.6(4)
O(3)#2-Sr(1)-O(5)#4	99.4(3)	O(6)#8-Sr(2)-O(6)#9	96.2(6)
O(3)#3-Sr(1)-O(5)#4	165.4(3)	O(6)#6-Sr(2)-O(6)#10	96.2(6)
O(5)-Sr(1)-O(5)#4	94.96(10)	O(6)#7-Sr(2)-O(6)#10	94.6(6)
O(3)#1-Sr(1)-O(5)#5	165.4(3)	O(6)#8-Sr(2)-O(6)#10	84.6(4)
O(3)#2-Sr(1)-O(5)#5	86.3(3)	O(6)#9-Sr(2)-O(6)#10	178.8(7)
O(3)#3-Sr(1)-O(5)#5	99.4(3)	O(6)#6-Sr(2)-O(6)	178.8(7)
O(5)-Sr(1)-O(5)#5	94.96(10)	O(6)#7-Sr(2)-O(6)	96.2(6)
O(5)#4-Sr(1)-O(5)#5	94.96(10)	O(6)#8-Sr(2)-O(6)	84.6(4)
O(3)#1-Sr(1)-O(6)#1	9.3(3)	O(6)#9-Sr(2)-O(6)	94.6(6)
O(3)#2-Sr(1)-O(6)#1	73.9(4)	O(6)#10-Sr(2)-O(6)	84.6(4)
O(3)#3-Sr(1)-O(6)#1	70.9(4)	O(6)#6-Sr(2)-O(3)	168.7(3)
O(5)-Sr(1)-O(6)#1	102.5(3)	O(6)#7-Sr(2)-O(3)	105.5(3)
O(5)#4-Sr(1)-O(6)#1	94.7(3)	O(6)#8-Sr(2)-O(3)	75.2(4)
O(5)#5-Sr(1)-O(6)#1	159.2(2)	O(6)#9-Sr(2)-O(3)	100.8(3)
O(3)#1-Sr(1)-O(6)#2	70.9(4)	O(6)#10-Sr(2)-O(3)	78.5(4)
O(3)#2-Sr(1)-O(6)#2	9.3(3)	O(6)-Sr(2)-O(3)	10.9(3)
O(3)#3-Sr(1)-O(6)#2	73.9(4)	O(6)#6-Sr(2)-O(3)#6	10.9(3)
O(5)-Sr(1)-O(6)#2	159.2(2)	O(6)#7-Sr(2)-O(3)#6	78.5(4)
O(5)#4-Sr(1)-O(6)#2	102.5(3)	O(6)#8-Sr(2)-O(3)#6	100.8(3)
O(5)#5-Sr(1)-O(6)#2	94.7(3)	O(6)#9-Sr(2)-O(3)#6	75.2(4)
O(6)#1-Sr(1)-O(6)#2	65.2(3)	O(6)#10-Sr(2)-O(3)#6	105.5(3)
O(3)#1-Sr(1)-O(6)#3	73.9(4)	O(6)-Sr(2)-O(3)#6	168.7(3)
O(3)#2-Sr(1)-O(6)#3	70.9(4)	O(3)-Sr(2)-O(3)#6	174.2(5)
O(3)#3-Sr(1)-O(6)#3	9.3(3)	O(6)#6-Sr(2)-O(3)#7	75.2(4)
O(5)-Sr(1)-O(6)#3	94.7(3)	O(6)#7-Sr(2)-O(3)#7	10.9(3)
O(5)#4-Sr(1)-O(6)#3	159.2(2)	O(6)#8-Sr(2)-O(3)#7	168.7(3)
O(5)#5-Sr(1)-O(6)#3	102.5(3)	O(6)#9-Sr(2)-O(3)#7	78.5(4)
O(6)#1-Sr(1)-O(6)#3	65.2(3)	O(6)#10-Sr(2)-O(3)#7	100.8(3)
O(6)#2-Sr(1)-O(6)#3	65.2(3)	O(6)-Sr(2)-O(3)#7	105.5(3)
O(6)#6-Sr(2)-O(6)#7	84.6(4)	O(3)-Sr(2)-O(3)#7	115.4(4)
O(6)#6-Sr(2)-O(6)#8	94.6(6)	O(3)#6-Sr(2)-O(3)#7	68.3(3)
O(6)#7-Sr(2)-O(6)#8	178.8(7)	O(6)#6-Sr(2)-O(3)#8	100.8(3)
O(6)#6-Sr(2)-O(6)#9	84.6(4)	O(6)#7-Sr(2)-O(3)#8	168.7(3)

O(6)#8-Sr(2)-O(3)#8	10.9(3)	O(1)#7-Rb(1)-O(2)#12	84.75(8)
O(6)#9-Sr(2)-O(3)#8	105.5(3)	O(1)-Rb(1)-O(2)#12	48.40(7)
O(6)#10-Sr(2)-O(3)#8	75.2(4)	O(5)#4-Rb(1)-O(2)#12	116.95(8)
O(6)-Sr(2)-O(3)#8	78.5(4)	O(5)#11-Rb(1)-O(2)#12	84.45(8)
O(3)-Sr(2)-O(3)#8	68.3(3)	O(1)#7-Rb(1)-O(2)#1	48.40(7)
O(3)#6-Sr(2)-O(3)#8	108.4(5)	O(1)-Rb(1)-O(2)#1	84.75(8)
O(3)#7-Sr(2)-O(3)#8	174.2(5)	O(5)#4-Rb(1)-O(2)#1	84.46(8)
O(6)#6-Sr(2)-O(3)#9	78.5(4)	O(5)#11-Rb(1)-O(2)#1	116.95(8)
O(6)#7-Sr(2)-O(3)#9	75.2(4)	O(2)#12-Rb(1)-O(2)#1	111.51(11)
O(6)#8-Sr(2)-O(3)#9	105.5(3)	O(1)#7-Rb(1)-O(7)#4	165.4(5)
O(6)#9-Sr(2)-O(3)#9	10.9(3)	O(1)-Rb(1)-O(7)#4	98.2(5)
O(6)#10-Sr(2)-O(3)#9	168.7(3)	O(5)#4-Rb(1)-O(7)#4	48.0(6)
O(6)-Sr(2)-O(3)#9	100.8(3)	O(5)#11-Rb(1)-O(7)#4	98.4(5)
O(3)-Sr(2)-O(3)#9	108.4(5)	O(2)#12-Rb(1)-O(7)#4	108.0(6)
O(3)#6-Sr(2)-O(3)#9	68.3(3)	O(2)#1-Rb(1)-O(7)#4	128.5(6)
O(3)#7-Sr(2)-O(3)#9	68.3(3)	O(1)#7-Rb(1)-O(7)#11	98.2(5)
O(3)#8-Sr(2)-O(3)#9	115.4(4)	O(1)-Rb(1)-O(7)#11	165.4(5)
O(6)#6-Sr(2)-O(3)#10	105.5(3)	O(5)#4-Rb(1)-O(7)#11	98.4(5)
O(6)#7-Sr(2)-O(3)#10	100.8(3)	O(5)#11-Rb(1)-O(7)#11	48.0(6)
O(6)#8-Sr(2)-O(3)#10	78.5(4)	O(2)#12-Rb(1)-O(7)#11	128.5(6)
O(6)#9-Sr(2)-O(3)#10	168.7(3)	O(2)#1-Rb(1)-O(7)#11	108.0(6)
O(6)#10-Sr(2)-O(3)#10	10.9(3)	O(7)#4-Rb(1)-O(7)#11	68.5(9)
O(6)-Sr(2)-O(3)#10	75.2(4)	O(1)#7-Rb(1)-O(4)#4	159.4(3)
O(3)-Sr(2)-O(3)#10	68.3(3)	O(1)-Rb(1)-O(4)#4	100.74(18)
O(3)#6-Sr(2)-O(3)#10	115.4(4)	O(5)#4-Rb(1)-O(4)#4	42.8(2)
O(3)#7-Sr(2)-O(3)#10	108.4(5)	O(5)#11-Rb(1)-O(4)#4	101.8(2)
O(3)#8-Sr(2)-O(3)#10	68.3(3)	O(2)#12-Rb(1)-O(4)#4	115.5(3)
O(3)#9-Sr(2)-O(3)#10	174.2(5)	O(2)#1-Rb(1)-O(4)#4	120.7(3)
O(1)#7-Rb(1)-O(1)	95.70(12)	O(7)#4-Rb(1)-O(4)#4	8.2(4)
O(1)#7-Rb(1)-O(5)#4	132.83(8)	O(7)#11-Rb(1)-O(4)#4	66.9(4)
O(1)-Rb(1)-O(5)#4	75.25(8)	O(1)#7-Rb(1)-O(4)#11	100.74(18)
O(1)#7-Rb(1)-O(5)#11	75.25(8)	O(1)-Rb(1)-O(4)#11	159.4(3)
O(1)-Rb(1)-O(5)#11	132.83(8)	O(5)#4-Rb(1)-O(4)#11	101.8(2)
O(5)#4-Rb(1)-O(5)#11	143.06(12)	O(5)#11-Rb(1)-O(4)#11	42.8(2)

O(2)#12-Rb(1)-O(4)#11	120.7(3)	O(4)-Rb(3)-O(4)#15	173.5(5)
O(2)#1-Rb(1)-O(4)#11	115.5(3)	O(5)-Rb(3)-O(3)#3	59.30(16)
O(7)#4-Rb(1)-O(4)#11	66.9(3)	O(5)#15-Rb(3)-O(3)#3	121.68(17)
O(7)#11-Rb(1)-O(4)#11	8.2(4)	O(2)#1-Rb(3)-O(3)#3	85.15(16)
O(4)#4-Rb(1)-O(4)#11	66.5(3)	O(2)#7-Rb(3)-O(3)#3	131.44(16)
O(1)#13-Rb(2)-O(1)	125.23(10)	O(4)-Rb(3)-O(3)#3	103.7(2)
O(1)#13-Rb(2)-O(1)#4	126.56(10)	O(4)#15-Rb(3)-O(3)#3	78.4(2)
O(1)-Rb(2)-O(1)#4	103.96(6)	O(5)-Rb(3)-O(3)#9	121.68(17)
O(1)#13-Rb(2)-O(1)#5	49.09(10)	O(5)#15-Rb(3)-O(3)#9	59.30(16)
O(1)-Rb(2)-O(1)#5	103.96(6)	O(2)#1-Rb(3)-O(3)#9	131.44(16)
O(1)#4-Rb(2)-O(1)#5	103.96(6)	O(2)#7-Rb(3)-O(3)#9	85.15(16)
O(1)#13-Rb(2)-O(1)#12	103.96(6)	O(4)-Rb(3)-O(3)#9	78.4(2)
O(1)-Rb(2)-O(1)#12	49.09(10)	O(4)#15-Rb(3)-O(3)#9	103.7(2)
O(1)#4-Rb(2)-O(1)#12	125.23(10)	O(3)#3-Rb(3)-O(3)#9	143.2(3)
O(1)#5-Rb(2)-O(1)#12	126.56(10)	O(5)-Rb(3)-O(7)	46.4(4)
O(1)#13-Rb(2)-O(1)#14	103.96(6)	O(5)#15-Rb(3)-O(7)	133.6(5)
O(1)-Rb(2)-O(1)#14	126.55(10)	O(2)#1-Rb(3)-O(7)	90.1(5)
O(1)#4-Rb(2)-O(1)#14	49.09(10)	O(2)#7-Rb(3)-O(7)	90.9(5)
O(1)#5-Rb(2)-O(1)#14	125.23(10)	O(4)-Rb(3)-O(7)	3.8(6)
O(1)#12-Rb(2)-O(1)#14	103.96(6)	O(4)#15-Rb(3)-O(7)	177.3(6)
O(5)-Rb(3)-O(5)#15	177.34(14)	O(3)#3-Rb(3)-O(7)	102.4(5)
O(5)-Rb(3)-O(2)#1	71.32(9)	O(3)#9-Rb(3)-O(7)	77.2(5)
O(5)#15-Rb(3)-O(2)#1	106.14(9)	O(5)-Rb(3)-O(7)#15	133.6(5)
O(5)-Rb(3)-O(2)#7	106.14(9)	O(5)#15-Rb(3)-O(7)#15	46.4(4)
O(5)#15-Rb(3)-O(2)#7	71.32(9)	O(2)#1-Rb(3)-O(7)#15	90.9(5)
O(2)#1-Rb(3)-O(2)#7	47.91(11)	O(2)#7-Rb(3)-O(7)#15	90.1(5)
O(5)-Rb(3)-O(4)	46.49(17)	O(4)-Rb(3)-O(7)#15	177.3(6)
O(5)#15-Rb(3)-O(4)	133.30(17)	O(4)#15-Rb(3)-O(7)#15	3.8(6)
O(2)#1-Rb(3)-O(4)	86.6(2)	O(3)#3-Rb(3)-O(7)#15	77.2(5)
O(2)#7-Rb(3)-O(4)	87.4(3)	O(3)#9-Rb(3)-O(7)#15	102.4(5)
O(5)-Rb(3)-O(4)#15	133.30(17)	O(7)-Rb(3)-O(7)#15	178.9(11)
O(5)#15-Rb(3)-O(4)#15	46.49(17)	O(1)-B(1)-O(1)#12	108.7(5)
O(2)#1-Rb(3)-O(4)#15	87.4(2)	O(1)-B(1)-O(2)	111.23(16)
O(2)#7-Rb(3)-O(4)#15	86.6(2)	O(1)#12-B(1)-O(2)	108.47(15)

O(1)-B(1)-O(2)#12	108.47(15)	O(7)-B(3)-O(2)	115.0(12)
O(1)#12-B(1)-O(2)#12	111.23(16)	O(6)-B(3)-O(2)	129.4(7)
O(2)-B(1)-O(2)#12	108.8(5)	O(7)-B(3)-O(3)	126.8(14)
O(5)-B(2)-O(1)	123.6(4)	O(6)-B(3)-O(3)	24.3(3)
O(5)-B(2)-O(4)	117.2(6)	O(2)-B(3)-O(3)	112.1(6)
O(1)-B(2)-O(4)	119.1(6)	O(7)-B(3)-O(4)	18.4(12)
O(5)-B(2)-O(7)	123.6(11)	O(6)-B(3)-O(4)	110.2(7)
O(1)-B(2)-O(7)	111.2(11)	O(2)-B(3)-O(4)	119.0(5)
O(4)-B(2)-O(7)	17.8(8)	O(3)-B(3)-O(4)	128.7(7)
O(7)-B(3)-O(6)	115.3(14)		

Symmetry transformations used to generate equivalent atoms:

#1 -y+5/3,x-y+1/3,z+1/3 #2 x-1/3,y-2/3,z+1/3 #3 -x+y+2/3,-x+4/3,z+1/3

#4 -x+y+1,-x+1,z #5 -y+1,x-y,z #6 x-y+1,-y+2,-z+1

#7 -x+2,-x+y+1,-z+1 #8 -x+y+1,-x+2,z #9 y,x,-z+1

#10 -y+2,x-y+1,z #11 x-y+1,-y+1,-z+1 #12 y+1/3,x-1/3,-z+2/3

#13 -x+4/3,-x+y+2/3,-z+2/3 #14 x-y+1/3,-y+2/3,-z+2/3

#15 x-y+2/3,-y+4/3,-z+4/3 #16 -x+y+4/3,-x+5/3,z-1/3 #17 x+1/3,y+2/3,z-1/3

#18 -y+4/3,x-y+2/3,z-1/3

Table S6 Direction and magnitude of the dipole moments in $K_7BaSc_2B_{15}O_{30}$ and $Rb_{21}Sr_{3.8}Sc_{5.2}B_{45}O_{90}$ compounds.

Compounds	Species	Dipole moment (Debye)			Dipole moment
		x	y	z	(Debye)
$K_7BaSc_2B_{15}O_{30}$	$Ba_{(1)}O_6$	-0.0016	-0.0007	5.6541	5.6541
	$Ba_{(2)}O_6$	-0.0002	0.0004	0.3257	0.3257
	$Sc_{(1)}O_6$	-0.0014	0.0002	4.9072	4.9072
	$Sc_{(2)}O_6$	-0.0050	0.0024	3.9639	3.9639
	$Sc_{(3)}O_6$	-0.0069	0.0058	2.8012	2.8012
	$Sc_{(4)}O_6$	-0.0016	0.0016	-5.7993	5.7993
	$B_{(1)}O_3$	-0.7501	0.4855	0.0355	0.8942
	$B_{(2)}O_3$	0.0560	0.6326	0.0137	0.6353
	$B_{(3)}O_3$	-0.7798	0.5130	0.1746	0.9496
	$B_{(4)}O_3$	-0.9343	0.7944	0.8115	1.4705
	$B_{(5)}O_4$	0.0234	-0.0402	-0.0009	0.0466
	$B_{(6)}O_3$	-0.3946	0.2110	1.0869	1.1754
	$B_{(7)}O_4$	-0.0989	0.3559	-0.3518	0.5101
	$B_{(8)}O_4$	0.1409	0.2437	-0.0001	0.2815
	$B_{(9)}O_3$	-0.7252	1.2098	-0.0495	1.4114
	$B_{(10)}O_3$	-0.6999	0.7551	0.5551	1.1697
	$B_{(11)}O_3$	-0.5195	0.4620	0.5269	0.8723
$Rb_{21}Sr_{3.8}Sc_{5.2}B_{45}O_{90}$	$Sc_{(1)}/Sr_{(1)}O_6$	0.0001	-0.0015	-3.9248	3.9248
		0.0001	-0.0026	-2.5963	2.5963
	$Sc_{(2)}/Sr_{(2)}O_6$	-0.0008	-0.0003	0.0008	0.0011
		0.0000	0.0000	0.0000	0.0000
	$B_{(1)}O_4$	-0.0786	0.1596	-0.0005	0.1778
	$B_{(2)}O_3$	-0.8827	0.7159	-0.6337	1.3013
		-0.9967	-1.1379	3.5073	3.8196
	$B_{(3)}O_3$	0.5257	0.1915	-2.0814	2.1553
		0.5378	2.2801	-0.0886	2.3443

Table S7 Distortion direction and eccentricity degree (Δd) of the dipole moments in the Ba/SrO_6 and ScO_6 octahedra.

compounds	type of octahedron	distortion direction	Δd
$K_7BaSc_2B_{15}O_{30}$	$Ba_{(1)}O_6$	C3	0.9327
	$Ba_{(2)}O_6$	C3	0.0977
	$Sc_{(1)}O_6$	C3	0.1201
	$Sc_{(2)}O_6$	C3	0.2521
	$Sc_{(3)}O_6$	C3	0.3277
	$Sc_{(4)}O_6$	C3	0.6511
$Rb_{21}Sr_{3.8}Sc_{5.2}B_{45}O_{90}$	$Sc_{(1)}$ /$Sr_{(1)}O_6$	C3	0.0846
		C3	1.2455
	$Sc_{(2)}$/$Sr_{(2)}O_6$	undistorted	0
		undistorted	0

The magnitude of the out-of-center distortion: $\Delta d = |(A–O1) – (A–O4)|/|\cos\theta 1| + |(A–O2) – (A–O5)|/ |\cos\theta 2| + |(A–O3) – (A–O6)|/|\cos\theta 3|$.

Table S8 The investigation of B-O bond lengths in BO_3 units for the inorganic metal borates.

No.	Compounds	space groups	range of B-O bond lengths
1	KBBF[10]	*R*32	1.37
2	*β*-BBO[11]	$R\bar{3}c$	1.32-1.41
3	LBO[12]	$Pna2_1$	1.35-1.4
4	CsB_3O_5[13]	$P2_12_12_1$	1.35-1.4
5	*β*-$Rb_2Al_2B_2O_7$[14]	*P*321	1.317
6	$Sr_2Be_2B_2O_7$[15]	$P\bar{6}c2$	1.38
7	Bi_3TeBO_9[16]	$P6_3$	1.378
8	$Pb_2Ba_3(BO_3)_3Cl$[17]	$C222_1$	1.378-1.393
9	$Ba_3La_4O_4(BO_3)_3Cl$[18]	$P6_3$	1.373-1.403
10	$Mg_3B_7O_{13}Cl$[19]	$Pca2_1$	1.371
11	$K_5Mg_2La_3(BO_3)_6$[20]	$P3_1m$	1.364-1.377
12	$KNa_2La_2(BO_3)_3$[21]	*Amm*2	1.361-1.41
13	$CsLiB_6O_{10}$[22]	$I\bar{4}2d$	1.36-1.4
14	Pb_2BO_3I[23]	*P*321	1.357
15	$Sr_2B_{10}O_{14}F_6$[24]	$Cmc2_1$	1.354-1.379
16	$Ca_2B_{10}O_{14}F_6$[24]	$Cmc2_1$	1.353-1.371
17	$Li_4Sr(BO_3)_2$[25]	*Cc*	1.35-1.396
18	$Ba_3Mg_3(BO_3)_3F_3$[26]	$P\bar{6}2m$	1.349-1.381
19	$CsKB_8O_{12}F_2$[27]	*P*321	1.343-1.391
20	$Rb_3Al_3B_3O_{10}F$[28]	*P*31*c*	1.305-1.405
21	BiB_3O_6[29]	*C*2	1.34-1.4
22	$CsAlB_3O_6F$[30]	$Pna2_1$	1.339-1.391
23	$K_7PbGd_2B_{15}O_{30}$[31]	*R*32	1.337-1.398
24	$NaRb_6CaY_2B_{15}O_{30}$[32]	*R*32	1.335-1.398
25	$K_{7.5}Gd_{2.5}B_{15}O_{30}$[33]	*R*32	1.332-1.398
26	$Cs_2La_2B_{10}O_{17}Cl_4$[34]	*Cm*	1.336-1.385
27	$Rb_3B_{11}P_2O_{23}$[35]	*P*1	1.335-1.399
28	$K_7Pb_{0.23}Zn_{0.77}Lu_2B_{15}O_{30}$[31]	*R*32	1.332-1.405
29	$K_7Cd_{0.85}Pb_{0.15}Lu_2B_{15}O_{30}$[31]	*R*32	1.332-1.41
30	$K_7CdGd_2B_{15}O_{30}$[31]	*R*32	1.329-1.393
31	$Rb_7CaY_2B_{15}O_{30}$[32]	*R*32	1.328-1.419
32	$K_7CdY_2B_{15}O_{30}$[31]	*R*32	1.326-1.41
33	$K_7BaY_2B_{15}O_{30}$[33]	*R*32	1.326-1.41
34	$K_{7.5}Y_{2.5}B_{15}O_{30}$[33]	*R*32	1.324-1.388
35	$K_7BaLu_2B_{15}O_{30}$[33]	*R*32	1.322-1.424
36	$K_7ZnSc_2B_{15}O_{30}$[31]	*R*32	1.321-1.405
37	$K_7SrY_2B_{15}O_{30}$[33]	*R*32	1.321-1.399

38	$K_7CaLu_2B_{15}O_{30}$[33]	*R*32	1.321-1.406
39	$K_7CdSc_2B_{15}O_{30}$[31]	*R*32	1.32-1.413
40	$K_7Pb_{0.31}Zn_{0.69}Gd_2B_{15}O_{30}$[31]	*R*32	1.32-1.399
41	$K_7CaY_2B_{15}O_{30}$[33]	*R*32	1.32-1.396
42	$LiRb_6CaY_2B_{15}O_{30}$[32]	*R*32	1.32-1.421
43	$K_7PbBi_2B_{15}O_{30}$[33]	*R*32	1.319-1.432
44	$K_7SrBi_2B_{15}O_{30}$[33]	*R*32	1.318-1.393
45	$K_7CaGd_2B_{15}O_{30}$[33]	*R*32	1.317-1.4
46	$K_7PbY_2B_{15}O_{30}$[31]	*R*32	1.315-1.4
47	$K_7SrGd_2B_{15}O_{30}$[33]	*R*32	1.315-1.4
48	$Li_4Rb_3B_7O_{14}$[36]	$P3_121$	1.315-1.435
49	$K_7SrLu_2B_{15}O_{30}$[33]	*R*32	1.314-1.403
50	$Li_2B_6O_9F_2$[37]	*Cc*	1.314-1.41
51	$K_7Pb_{0.11}Cd_{0.89}Lu_2B_{15}O_{30}$[17]	*R*32	1.312-1.409
52	$K_7CdLu_2B_{15}O_{30}$[31]	*R*32	1.303-1.42
53	$K_7PbSc_2B_{15}O_{30}$[31]	*R*32	1.3-1.4
54	$Cs_3Zn_6B_9O_{21}$[38]	$Cmc2_1$	1.284-1.407
this work	KBSBO	*R*32	1.32-1.411
this work	RSSBO	*R*32	1.26-1.53

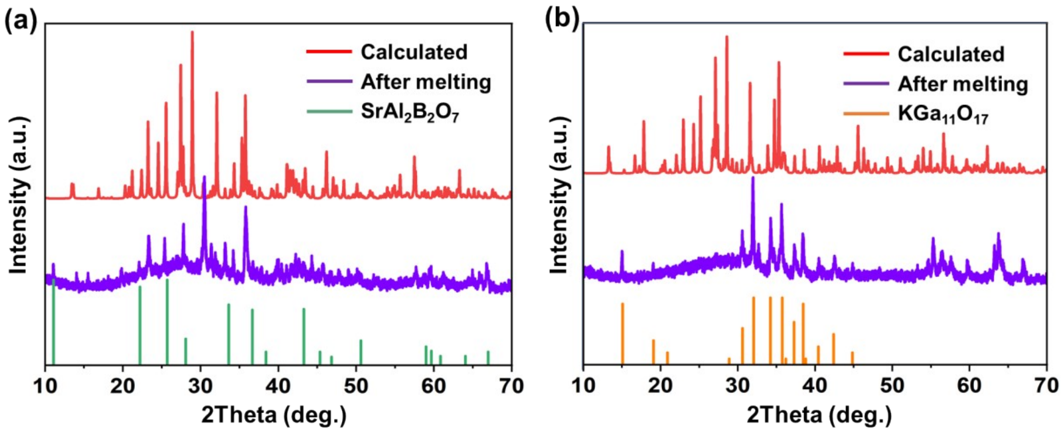

Fig. S1 (a-b) Powder X-ray diffraction patterns results for melted $K_7BaSc_2B_{15}O_{30}$ and $Rb_{21}Sr_{3.8}Sc_{5.2}B_{45}O_{90}$, respectively.

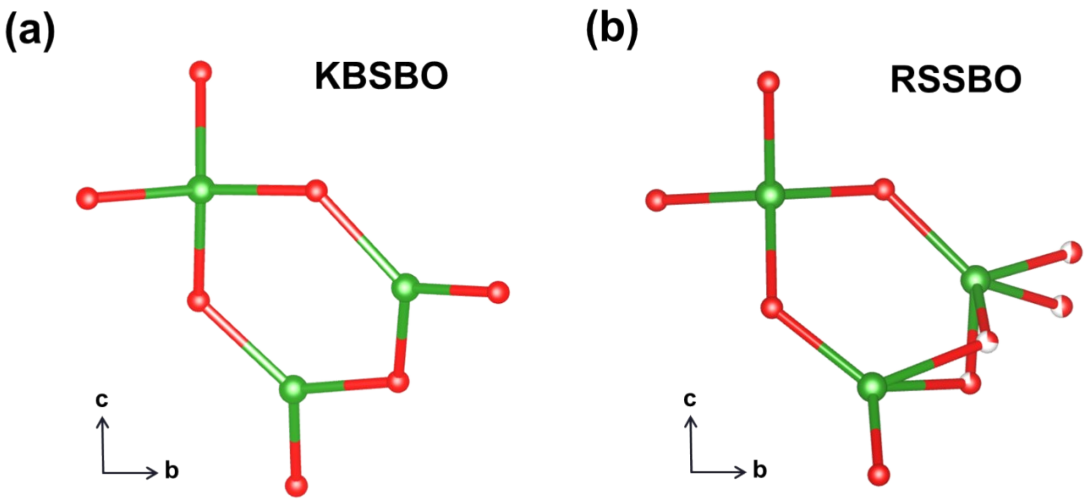

Fig. S2 (a-b) The partial enlargement of B_5O_{10} units in KBSBO and RSSBO, respectively.

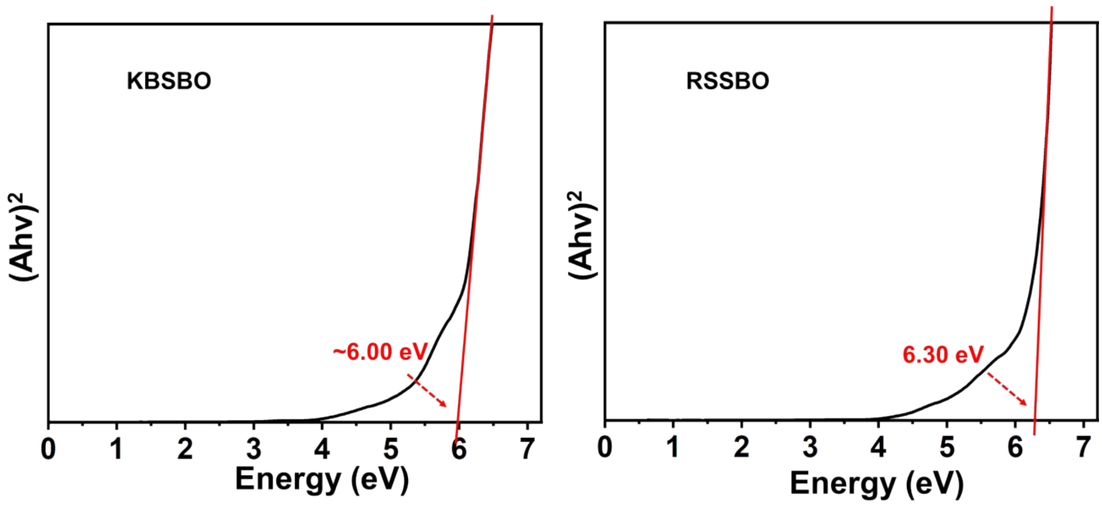

Fig. S3 (a-b) The optical band gap values for KBSBO and RSSBO by Tauc plots absorption spectrometry, respectively.

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