Supporting Information

Designing Rare Earth Borates as UV Nonlinear Optical crystals exhibiting strong second-harmonic generation responses

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EXPERIMENTAL SECTION

Reagents.

Without further purification, raw ingredients including K_2CO_3 (Sinopharm, 99.9%), Rb_2CO_3(Sinopharm, 99.9%), Na_2CO_3 (Sinopharm, 99.9%), $SrCO_3$ (Sinopharm, 99.9%),$BaCO_3$(Sinopharm, 99.9%), Y_2O_3 (Sinopharm, 99.9%), Lu_2O_3(Sinopharm, 99.9%), B_2O_3 (Sinopharm, 99.9%) and NaF_2 (Sinopharm, 99.9%)，were of analytical grade pure phase and obtained from commercial sources.

Crystal Synthesis.

Polycrystalline samples of KNSYBO and RBLBO were synthesized by employing solid-state techniques with a stoichiometric ratio of K_2CO_3, Rb_2CO_3 Na_2CO_3, $SrCO_3$, $BaCO_3$, Y_2O_3/Lu_2O_3, and B_2O_3. The mixtures were gradually heated up to 750 °C and 850 °C for both compounds with several intermediate grindings and mixings, followed by a duration of 72 hours to ensure complete reactions. Subsequently, the mixtures were cooled to room temperature at a rate of 3-5 °C. Finally, the reaction products were obtained. The purities of the two polycrystalline samples were verified by the powder X-ray diffraction texts. Single crystals of KNSYBO and RBLBO were prepared via the high-temperature solution method, utilizing Na_2CO_3 as a flux with spontaneous crystallization technique.

Single-Crystal Structure Determination.

To determine the structure of the title compound, single crystal with good quality was selected to characterize its structure. The single-crystal X-ray diffraction data of KNSYBO and RBLBO were collected and processed via the Bruker SMART APEX III CCD single crystal diffractometer in the ω-scanning mode using Mo Kα radiation (λ = 0.71073 Å) at 298(2) K.[1] The collected diffraction data was directly integrated and absorbed by utilizing the SAINT-Plus program, and then, which then enabled single crystal data processing, analysis, and refinement utilizing SHELXTL software.[2-3] Subsequently, by utilizing the full-matrix least-squares on F^2 and the PLATON program,[4] the structure and symmetry was detected, respectively, and the existence of space group was confirmed without higher symmetry was confirmed. The crystallographic information and detailed structural data of KNSYBO and RBLBO are shown in Table S1; equivalent isotropic displacement parameters, and the selected bond distances (Å) and angles (deg.) are available in Tables S2 -S5, respectively.

Powder X-ray diffraction.

The polycrystalline powder XRD test of title compound was performed at room temperature by utilizing a Rigaku Smart-Lab 9kW X-ray diffractometer with Cu *K*α radiation (λ =1.5418 Å). The scanning angle range (2θ) for the test was from 5 to70°, the scan step width and rate were 0.01° and 2s/step, respectively.

Thermal Analysis.

The thermodynamic behavior of KNYBO and RBLBO polycrystalline powders was characterized by differential scanning calorimetry (DSC) and thermogravimetric (TG) analysis utilizing NETZSCH STA 449C thermal analyzer. The polycrystalline samples were placed in a platinum pot and heated from room temperature to 1000 °C at a rate of 10 °C/min in a nitrogen filled environment.

Elemental Analysis.

To further substantiate the elemental composition and validate the rationality of the crystal structure for the two compounds, microprobe elemental analyses and elemental distribution maps were carried out using electron microscopy in a field-emission scanning electron mode (FESEM, Quanta FEG 250).

Optical Spectrum Measurements.

To determine the ultraviolet cutoff edge of KNSYBO and RBLBO polycrystalline powder, the UV-vis-NIR diffuse reflectance spectra for KNSYBO and RBLBO were measured using a Hitachi UH4150 spectrophotometer with a wavelength range from 190 to 2000 nm at room temperature. Barium sulfate served as the reference standard for diffuse reflectance. The experimental band gaps of these two compounds were determined based on the Kubelka−Munk function: $F(R) = (1-R)^2/2R = K/S$,[5] where *R* represents reflectance, K represents absorption, and S represents scattering. In addition, infrared spectrum of the two compounds were performed at room temperature by using a Nicolet iS50 FT-IR spectrometer in the measured range of 200-1200 cm^{-1}.

Powder Second Harmonic Generation (SHG) Measurements.

The title compound crystallizes in the *R*32 NSC space group, which confirms that it has second-order nonlinear optical effects. Based on Kurtz-Perry powder frequency doubling method, with wavelength of 1064 nm,[6] pulse width of 10 ns and pulse repetition rate of 5 Hz, a Q-switched Nd: YAG laser was used to measure KNSYBO polycrystalline powders with different particle sizes, and then the measured

frequency doubling signal is compared with the standard sample (KH_2PO_4) under the same particle size condition, so that the relative intensity of the second order frequency doubling effect of the title compound can be obtained.

Theoretical Calculation Details.

Crystallographic data of the KNSYBO and RBLBO crystals were used for the theoretical calculations. The electronic structures and optical properties were calculated based on the density functional theory (DFT) method, as implemented in the CASTEP package.[7] Under the norm-conserving pseudopotential (NCP), the following orbital electrons were treated as valence electrons: K $4s^1$, Na$3s^1$, Sr $5s^2$, Rb $5s^1$, Ba $6s^2$, Y$4d^1$$5s^2$, Lu $5d^1$$6s^2$, B $2s^2$ $2p^1$, and O $2s^2$ $2p^4$. To accurately capture the electronic and structural properties, the Perdew-Burke-Ernzerhof (PBE) functional,[8] formulated within the framework of generalized gradient approximation (GGA), was employed to account for the exchange-correlation energy.[9] The kinetic energy cutoffs of 450 and 800 eV were chosen for KNSYBO and RBLBO, respectively. The numerical integration of the Brillouin zone was performed using Monkhorst-Pack k-point sampling of $1 \times 1 \times 1$ and $2 \times 2 \times 2$ for KNSYBO and RBLBO, respectively.

Table S1 Crystallographic data and structural refinement for $K_6NaSrY_2B_{15}O_{30}$ and $Rb_7BaLu_2B_{15}O_{30}$

empirical formula	$K_6NaSrY_2B_{15}O_{30}$	$Rb_7BaLu_2B_{15}O_{30}$
formula weight	3495.54	287.95
temperature	297 K	297 K
crystal system	Trigonal	Trigonal
space group	*R*32	*R32*
a (Å)	12.974(3)	13.5347(8)
b (Å)	12.974(3)	13.5347(8)
c (Å)	15.367(3)	15.7190(13
Z	1	3
V (Å^3)	2240.1(11)	2493.7(4)
Density (g/cm^3)	2.2591	3.451
F (000)	1668	2316
R (int)	0.0459	0.0483
GOF (F^2)	1.118	1.051
final R indices [I>2σ (I)][a]	R_1=0.0504, wR_2=0.1372	R_1=0.0433, wR_2=0.1126
R indices (all data)	R_1 = 0.0620, wR_2 = 0.1478	R_1 = 0.0482, wR_2 = 0.1157
absolute structure parameter	0.035(13)	0.21(6)
CCDC number	2391659	2391660

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

Table S2. Atomic coordinates equivalent isotropic displacement parameters for $K_6NaSrY_2B_{15}O_{30}$. Ueq is defined as one-third of the trace of the orthogonalized Uij tensor.

Atom	*x*	*y*	*z*	Ueq	BVS
Y(1)	6667	3333	6091(1)	16(1)	3.26
Sr(1)	0	0	5000	40(1)	2.21
K(1)	3333	1963(4)	1667	56(2)	1.10
K(2)	3333	1704(7)	6667	70(1)	0.83
Na(1)	6667	3333	3333	27(2)	1.13
O(1)	3223(7)	1750(14)	4580(5)	54(3)	1.92
O(2)	1462(7)	777(17)	3786(5)	66(3)	2.06
O(3)	3195(8)	915(10)	3210(6)	47(3)	2.13
O(4)	4974(7)	1774(7)	4094(5)	33(2)	2.16
O(5)	4981(7)	2764(7)	5397(5)	34(2)	1.92
B(1)	4388(14)	1054(14)	3333	33(4)	3.10
B(2)	4441(9)	2121(16)	4692(7)	30(3)	3.04
B(3)	2607(11)	1139(19)	3835(8)	44(5)	3.16

Table S3. Atomic coordinates equivalent isotropic displacement parameters for $Rb_7BaLu_2B_{15}O_{30}$. Ueq is defined as one-third of the trace of the orthogonalized Uij tensor.

Atom	*x*	*y*	*z*	Ueq
Lu(1)	3333	6667	9310(1)	23(1)
Ba(1)	0	0	5000	38(1)
Rb(1)	3333	6667	6667	32(1)
Rb(2)	1311(2)	3333	8333	27(1)
Rb(3)	3333	1478(2)	6667	54(1)
O(1)	4402(15)	6012(13)	8556(8)	53(4)
O(2)	3396(11)	4748(11)	7427(8)	35(3)
O(3)	5210(20)	5090(20)	7870(13)	75(6)
O(4)	2320(13)	2947(10)	6717(9)	43(3)
O(5)	570(20)	1451(17)	6285(18)	107(8)
B(1)	4323(18)	5309(18)	7921(14)	34(5)
B(2)	3333	4080(20)	6667	31(6)
B(3)	1440(30)	2545(18)	6191(18)	50(6)

Table S4. Bond lengths (Å) and angles (deg.) for $K_6NaSrY_2B_{15}O_{30}$

Y(1)-O(5)	2.202(7)	O(3)#11-K(1)-O(4)#14	50.3(3)
Y(1)-O(5)#1	2.202(7)	O(3)-K(1)-O(4)#14	97.4(3)
Y(1)-O(5)#2	2.202(7)	O(5)#12-K(1)-O(4)#14	72.5(2)
Y(1)-O(2)#3	2.281(7)	O(5)#13-K(1)-O(4)#14	136.2(2)
Y(1)-O(2)#4	2.281(7)	O(3)#11-K(1)-O(4)#15	97.4(3)
Y(1)-O(2)#5	2.281(7)	O(3)-K(1)-O(4)#15	50.3(3)
Sr(1)-O(2)	2.486(8)	O(5)#12-K(1)-O(4)#15	136.2(2)
Sr(1)-O(2)#6	2.486(8)	O(5)#13-K(1)-O(4)#15	72.5(2)
Sr(1)-O(2)#7	2.486(8)	O(4)#14-K(1)-O(4)#15	114.3(4)
Sr(1)-O(2)#8	2.486(8)	O(3)#11-K(1)-O(1)#13	122.7(3)
Sr(1)-O(2)#9	2.486(8)	O(3)-K(1)-O(1)#13	105.1(3)
Sr(1)-O(2)#10	2.486(8)	O(5)#12-K(1)-O(1)#13	93.8(3)
K(1)-O(3)#11	2.694(11)	O(5)#13-K(1)-O(1)#13	43.4(2)
K(1)-O(3)	2.694(11)	O(4)#14-K(1)-O(1)#13	152.9(2)
K(1)-O(5)#12	2.783(9)	O(4)#15-K(1)-O(1)#13	91.8(2)
K(1)-O(5)#13	2.783(9)	O(3)#11-K(1)-O(1)#12	105.1(3)
K(1)-O(4)#14	2.893(9)	O(3)-K(1)-O(1)#12	122.7(3)
K(1)-O(4)#15	2.893(9)	O(5)#12-K(1)-O(1)#12	43.4(2)
K(1)-O(1)#13	3.382(16)	O(5)#13-K(1)-O(1)#12	93.8(3)
K(1)-O(1)#12	3.382(16)	O(4)#14-K(1)-O(1)#12	91.8(2)
K(2)-O(5)	2.706(9)	O(4)#15-K(1)-O(1)#12	152.9(2)
K(2)-O(5)#16	2.706(9)	O(1)#13-K(1)-O(1)#12	63.4(3)
K(2)-O(3)#3	2.967(13)	O(5)-K(2)-O(5)#16	167.0(5)
K(2)-O(3)#9	2.967(13)	O(5)-K(2)-O(3)#3	77.6(3)
K(2)-O(1)#16	3.212(9)	O(5)#16-K(2)-O(3)#3	115.0(3)

K(2)-O(1)	3.212(9)	O(5)-K(2)-O(3)#9	115.0(3)
K(2)-O(2)#6	3.25(2)	O(5)#16-K(2)-O(3)#9	77.6(3)
K(2)-O(2)#5	3.25(2)	O(3)#3-K(2)-O(3)#9	47.6(4)
Na(1)-O(4)#13	2.417(8)	O(5)-K(2)-O(1)#16	133.5(2)
Na(1)-O(4)#1	2.417(8)	O(5)#16-K(2)-O(1)#16	45.7(2)
Na(1)-O(4)	2.417(8)	O(3)#3-K(2)-O(1)#16	94.9(3)
Na(1)-O(4)#2	2.417(8)	O(3)#9-K(2)-O(1)#16	89.4(3)
Na(1)-O(4)#15	2.417(8)	O(5)-K(2)-O(1)	45.7(2)
Na(1)-O(4)#17	2.417(8)	O(5)#16-K(2)-O(1)	133.5(2)
O(1)-B(3)	1.394(16)	O(3)#3-K(2)-O(1)	89.4(3)
O(1)-B(2)	1.413(13)	O(3)#9-K(2)-O(1)	94.9(4)
O(2)-B(3)	1.317(15)	O(1)#16-K(2)-O(1)	175.3(6)
O(3)-B(3)	1.347(19)	O(5)-K(2)-O(2)#6	113.8(3)
O(3)-B(1)	1.477(14)	O(5)#16-K(2)-O(2)#6	60.2(2)
O(4)-B(2)	1.354(17)	O(3)#3-K(2)-O(2)#6	135.9(3)
O(4)-B(1)	1.452(13)	O(3)#9-K(2)-O(2)#6	92.3(2)
O(5)-B(2)	1.333(15)	O(1)#16-K(2)-O(2)#6	103.4(2)
O(5)-Y(1)-O(5)#1	98.5(3)	O(1)-K(2)-O(2)#6	74.6(2)
O(5)-Y(1)-O(5)#2	98.5(3)	O(5)-K(2)-O(2)#5	60.2(2)
O(5)#1-Y(1)-O(5)#2	98.5(3)	O(5)#16-K(2)-O(2)#5	113.8(3)
O(5)-Y(1)-O(2)#3	98.5(5)	O(3)#3-K(2)-O(2)#5	92.3(2)
O(5)#1-Y(1)-O(2)#3	84.7(4)	O(3)#9-K(2)-O(2)#5	135.9(3)
O(5)#2-Y(1)-O(2)#3	162.0(4)	O(1)#16-K(2)-O(2)#5	74.6(2)
O(5)-Y(1)-O(2)#4	161.9(4)	O(1)-K(2)-O(2)#5	103.4(3)
O(5)#1-Y(1)-O(2)#4	98.5(5)	O(2)#6-K(2)-O(2)#5	131.1(4)
O(5)#2-Y(1)-O(2)#4	84.7(4)	O(4)#13-Na(1)-O(4)#1	135.0(4)
O(2)#3-Y(1)-O(2)#4	77.2(3)	O(4)#13-Na(1)-O(4)	121.3(4)

O(5)-Y(1)-O(2)#5	84.7(4)	O(4)#1-Na(1)-O(4)	98.6(2)
O(5)#1-Y(1)-O(2)#5	162.0(4)	O(4)#13-Na(1)-O(4)#2	58.4(4)
O(5)#2-Y(1)-O(2)#5	98.5(5)	O(4)#1-Na(1)-O(4)#2	98.6(2)
O(2)#3-Y(1)-O(2)#5	77.2(3)	O(4)-Na(1)-O(4)#2	98.6(2)
O(2)#4-Y(1)-O(2)#5	77.2(3)	O(4)#13-Na(1)-O(4)#15	98.6(2)
O(2)-Sr(1)-O(2)#6	108.5(7)	O(4)#1-Na(1)-O(4)#15	121.3(4)
O(2)-Sr(1)-O(2)#7	69.9(3)	O(4)-Na(1)-O(4)#15	58.4(4)
O(2)#6-Sr(1)-O(2)#7	177.2(10)	O(4)#2-Na(1)-O(4)#15	135.0(4)
O(2)-Sr(1)-O(2)#8	69.9(3)	O(4)#13-Na(1)-O(4)#17	98.5(2)
O(2)#6-Sr(1)-O(2)#8	111.9(6)	O(4)#1-Na(1)-O(4)#17	58.4(4)
O(2)#7-Sr(1)-O(2)#8	69.9(3)	O(4)-Na(1)-O(4)#17	135.0(4)
O(2)-Sr(1)-O(2)#9	111.9(6)	O(4)#2-Na(1)-O(4)#17	121.3(4)
O(2)#6-Sr(1)-O(2)#9	69.9(3)	O(4)#15-Na(1)-O(4)#17	98.5(2)
O(2)#7-Sr(1)-O(2)#9	108.5(7)	O(4)-B(1)-O(4)#15	108.6(14)
O(2)#8-Sr(1)-O(2)#9	177.2(10)	O(4)-B(1)-O(3)	111.2(5)
O(2)-Sr(1)-O(2)#10	177.2(10)	O(4)#15-B(1)-O(3)	108.7(5)
O(2)#6-Sr(1)-O(2)#10	69.9(3)	O(4)-B(1)-O(3)#15	108.7(5)
O(2)#7-Sr(1)-O(2)#10	111.9(6)	O(4)#15-B(1)-O(3)#15	111.2(5)
O(2)#8-Sr(1)-O(2)#10	108.5(7)	O(3)-B(1)-O(3)#15	108.4(15)
O(2)#9-Sr(1)-O(2)#10	69.9(3)	O(5)-B(2)-O(4)	124.3(9)
O(3)#11-K(1)-O(3)	123.7(5)	O(5)-B(2)-O(1)	117.4(12)
O(3)#11-K(1)-O(5)#12	115.3(3)	O(4)-B(2)-O(1)	118.3(11)
O(3)-K(1)-O(5)#12	86.5(2)	O(2)-B(3)-O(3)	122.8(13)
O(3)#11-K(1)-O(5)#13	86.5(2)	O(2)-B(3)-O(1)	118.3(13)
O(3)-K(1)-O(5)#13	115.3(3)	O(3)-B(3)-O(1)	118.9(11)
O(5)#12-K(1)-O(5)#13	134.4(4)		

Symmetry transformations used to generate equivalent atoms:

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

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

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

#7 -x+y,-x,z #8 -y,x-y,z

#9 x-y,-y,-z+1 #10 -x,-x+y,-z+1

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

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

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

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

Table S5. Bond lengths (Å) and angles (deg.) for $Rb_7BaLu_2B_{15}O_{30}$

Lu(1)-O(1)	2.358(17)	O(2)#19-Rb(1)-O(2)#2	123.0(5)
Lu(1)-O(1)#1	2.358(17)	O(2)#17-Rb(1)-O(2)	48.8(5)
Lu(1)-O(1)#2	2.358(17)	O(2)#18-Rb(1)-O(2)	123.0(5)
Lu(1)-O(5)#3	2.40(3)	O(2)#19-Rb(1)-O(2)	128.6(5)
Lu(1)-O(5)#4	2.40(3)	O(2)#2-Rb(1)-O(2)	104.2(3)
Lu(1)-O(5)#5	2.40(3)	O(2)#17-Rb(1)-O(2)#1	123.0(5)
Ba(1)-O(5)#10	2.65(2)	O(2)#18-Rb(1)-O(2)#1	128.6(5)
Ba(1)-O(5)#11	2.65(2)	O(2)#19-Rb(1)-O(2)#1	48.8(5)
Ba(1)-O(5)#12	2.65(2)	O(2)#2-Rb(1)-O(2)#1	104.2(3)
Ba(1)-O(5)	2.65(2)	O(2)-Rb(1)-O(2)#1	104.2(3)
Ba(1)-O(5)#13	2.65(2)	O(2)-Rb(2)-O(2)#4	99.1(5)
Ba(1)-O(5)#14	2.65(2)	O(2)-Rb(2)-O(1)#1	77.5(4)
Rb(1)-O(2)#17	2.897(14)	O(2)#4-Rb(2)-O(1)#1	136.0(4)
Rb(1)-O(2)#18	2.898(14)	O(2)-Rb(2)-O(1)#20	136.0(4)
Rb(1)-O(2)#19	2.898(14)	O(2)#4-Rb(2)-O(1)#20	77.5(4)
Rb(1)-O(2)#2	2.898(14)	O(1)#1-Rb(2)-O(1)#20	134.3(7)
Rb(1)-O(2)	2.898(14)	O(2)-Rb(2)-O(4)#4	88.9(4)
Rb(1)-O(2)#1	2.898(14)	O(2)#4-Rb(2)-O(4)#4	47.7(3)
Rb(2)-O(2)	2.873(13)	O(1)#1-Rb(2)-O(4)#4	88.3(4)
Rb(2)-O(2)#4	2.873(13)	O(1)#20-Rb(2)-O(4)#4	116.3(4)
Rb(2)-O(1)#1	2.906(16)	O(2)-Rb(2)-O(4)	47.7(3)
Rb(2)-O(1)#20	2.906(16)	O(2)#4-Rb(2)-O(4)	88.9(4)
Rb(2)-O(4)#4	3.051(15)	O(1)#1-Rb(2)-O(4)	116.3(4)
Rb(2)-O(4)	3.051(15)	O(1)#20-Rb(2)-O(4)	88.3(4)
Rb(2)-O(3)#20	3.46(3)	O(4)#4-Rb(2)-O(4)	115.5(6)
Rb(2)-O(3)#1	3.47(3)	O(2)-Rb(2)-O(3)#20	159.5(4)
Rb(3)-O(4)	2.927(15)	O(2)#4-Rb(2)-O(3)#20	99.2(4)
Rb(3)-O(4)#17	2.927(15)	O(1)#1-Rb(2)-O(3)#20	95.6(5)

Rb(3)-O(1)#4	2.953(16)	O(1)#20-Rb(2)-O(3)#20	41.2(5)
Rb(3)-O(1)#15	2.953(16)	O(4)#4-Rb(2)-O(3)#20	110.4(4)
Rb(3)-O(5)#13	3.14(3)	O(4)-Rb(2)-O(3)#20	123.5(5)
Rb(3)-O(5)#21	3.14(3)	O(2)-Rb(2)-O(3)#1	99.2(4)
Rb(3)-O(3)#4	3.35(2)	O(2)#4-Rb(2)-O(3)#1	159.5(4)
Rb(3)-O(3)#15	3.35(2)	O(1)#1-Rb(2)-O(3)#1	41.2(5)
O(1)-B(1)	1.35(3)	O(1)#20-Rb(2)-O(3)#1	95.6(5)
O(2)-B(1)	1.34(2)	O(4)#4-Rb(2)-O(3)#1	123.5(5)
O(2)-B(2)	1.471(19)	O(4)-Rb(2)-O(3)#1	110.4(4)
O(3)-B(1)	1.38(3)	O(3)#20-Rb(2)-O(3)#1	64.8(6)
O(3)-B(3)#17	1.45(3)	O(4)-Rb(3)-O(4)#17	48.0(5)
O(4)-B(3)	1.32(3)	O(4)-Rb(3)-O(1)#4	74.2(4)
O(4)-B(2)	1.47(2)	O(4)#17-Rb(3)-O(1)#4	106.7(4)
O(5)-B(3)	1.36(3)	O(4)-Rb(3)-O(1)#15	106.7(4)
O(1)-Lu(1)-O(1)#1	96.9(5)	O(4)#17-Rb(3)-O(1)#15	74.2(4)
O(1)-Lu(1)-O(1)#2	96.9(5)	O(1)#4-Rb(3)-O(1)#15	179.0(6)
O(1)#1-Lu(1)-O(1)#2	96.9(5)	O(4)-Rb(3)-O(5)#13	87.6(4)
O(1)-Lu(1)-O(5)#3	161.5(7)	O(4)#17-Rb(3)-O(5)#13	133.6(4)
O(1)#1-Lu(1)-O(5)#3	101.0(8)	O(1)#4-Rb(3)-O(5)#13	63.8(6)
O(1)#2-Lu(1)-O(5)#3	85.3(8)	O(1)#15-Rb(3)-O(5)#13	115.8(7)
O(1)-Lu(1)-O(5)#4	101.0(8)	O(4)-Rb(3)-O(5)#21	133.6(4)
O(1)#1-Lu(1)-O(5)#4	85.3(8)	O(4)#17-Rb(3)-O(5)#21	87.6(4)
O(1)#2-Lu(1)-O(5)#4	161.5(7)	O(1)#4-Rb(3)-O(5)#21	115.8(6)
O(5)#3-Lu(1)-O(5)#4	76.2(9)	O(1)#15-Rb(3)-O(5)#21	63.8(6)
O(1)-Lu(1)-O(5)#5	85.3(8)	O(5)#13-Rb(3)-O(5)#21	138.5(7)
O(1)#1-Lu(1)-O(5)#5	161.5(7)	O(4)-Rb(3)-O(3)#4	88.6(5)
O(1)#2-Lu(1)-O(5)#5	101.0(8)	O(4)#17-Rb(3)-O(3)#4	89.7(5)
O(5)#3-Lu(1)-O(5)#5	76.2(9)	O(1)#4-Rb(3)-O(3)#4	42.2(4)
O(5)#4-Lu(1)-O(5)#5	76.2(9)	O(1)#15-Rb(3)-O(3)#4	137.8(4)

O(5)#10-Ba(1)-O(5)#11	68.1(9)	O(5)#13-Rb(3)-O(3)#4	103.6(6)
O(5)#10-Ba(1)-O(5)#12	171.1(13)	O(5)#21-Rb(3)-O(3)#4	77.0(6)
O(5)#11-Ba(1)-O(5)#12	107.0(13)	O(4)-Rb(3)-O(3)#15	89.7(5)
O(5)#10-Ba(1)-O(5)	117.7(11)	O(4)#17-Rb(3)-O(3)#15	88.6(5)
O(5)#11-Ba(1)-O(5)	171.1(13)	O(1)#4-Rb(3)-O(3)#15	137.8(4)
O(5)#12-Ba(1)-O(5)	68.1(9)	O(1)#15-Rb(3)-O(3)#15	42.2(4)
O(5)#10-Ba(1)-O(5)#13	107.0(13)	O(5)#13-Rb(3)-O(3)#15	77.0(6)
O(5)#11-Ba(1)-O(5)#13	117.7(11)	O(5)#21-Rb(3)-O(3)#15	103.6(6)
O(5)#12-Ba(1)-O(5)#13	68.1(9)	O(3)#4-Rb(3)-O(3)#15	178.2(9)
O(5)-Ba(1)-O(5)#13	68.1(9)	O(2)-B(1)-O(1)	123.3(18)
O(5)#10-Ba(1)-O(5)#14	68.1(9)	O(2)-B(1)-O(3)	120.9(19)
O(5)#11-Ba(1)-O(5)#14	68.1(9)	O(1)-B(1)-O(3)	115.3(19)
O(5)#12-Ba(1)-O(5)#14	117.7(11)	O(4)#17-B(2)-O(4)	109(2)
O(5)-Ba(1)-O(5)#14	107.0(13)	O(4)#17-B(2)-O(2)	110.0(8)
O(5)#13-Ba(1)-O(5)#14	171.1(14)	O(4)-B(2)-O(2)	109.6(8)
O(2)#17-Rb(1)-O(2)#18	104.2(3)	O(4)#17-B(2)-O(2)#17	109.6(8)
O(2)#17-Rb(1)-O(2)#19	104.2(3)	O(4)-B(2)-O(2)#17	110.0(8)
O(2)#18-Rb(1)-O(2)#19	104.2(3)	O(2)-B(2)-O(2)#17	109(2)
O(2)#17-Rb(1)-O(2)#2	128.6(5)	O(4)-B(3)-O(5)	119(2)
O(2)#18-Rb(1)-O(2)#2	48.8(5)	O(4)-B(3)-O(3)#17	120.4(19)
		O(5)-B(3)-O(3)#17	120(3)

Symmetry transformations used to generate equivalent atoms:

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

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

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

#7 -x+y,-x,z #8 -y,x-y,z

#9 x-y,-y,-z+1 #10 -x,-x+y,-z+1

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

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

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

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

Table S6 Direction and magnitude of the dipole moments in $K_6NaSrY_2B_{15}O_{30}$

compounds	**species**	**dipole moment (debye)**			**dipolemoment**
		x	y	z	**(debye)**
$K_6NaSrY_2B_{15}O_{30}$	YO_6	0.0000	-0.0001	5.6103	5.6103
	$B_{(1)}O_4$	0.1233	-0.1498	0.0000	0.1940
	$B_{(2)}O_3$	-1.4099	1.2450	-1.2550	2.2612
	$B_{(3)}O_3$	-1.1393	1.3257	-1.2342	2.1398

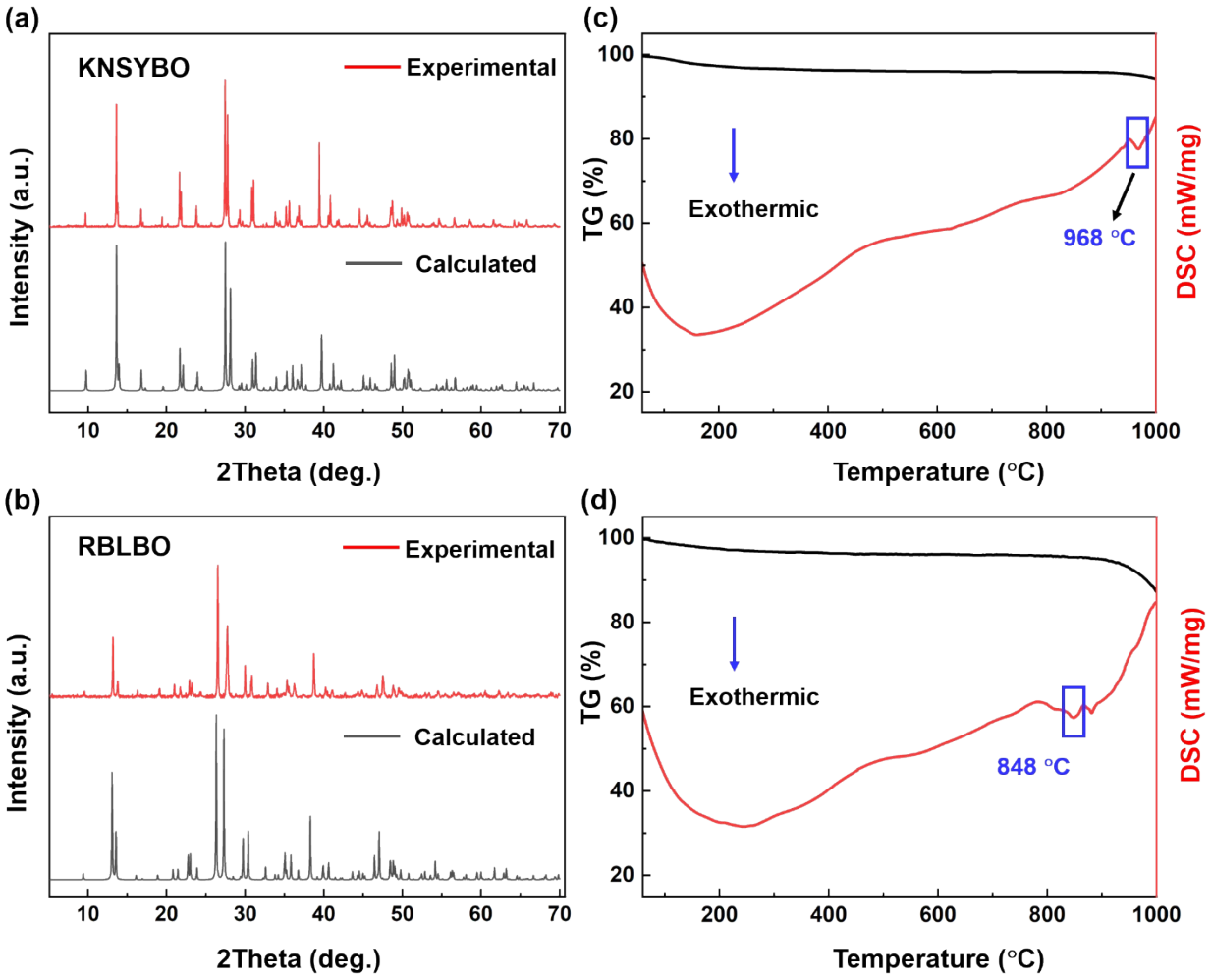

Figure S1. Comparation of experimental and calculated PXRD curves of KNSYBO and RBLBO, respectively. (c-d) TG-DSC curves for the KNSYBO and RBLBO polycrystalline, respectively.

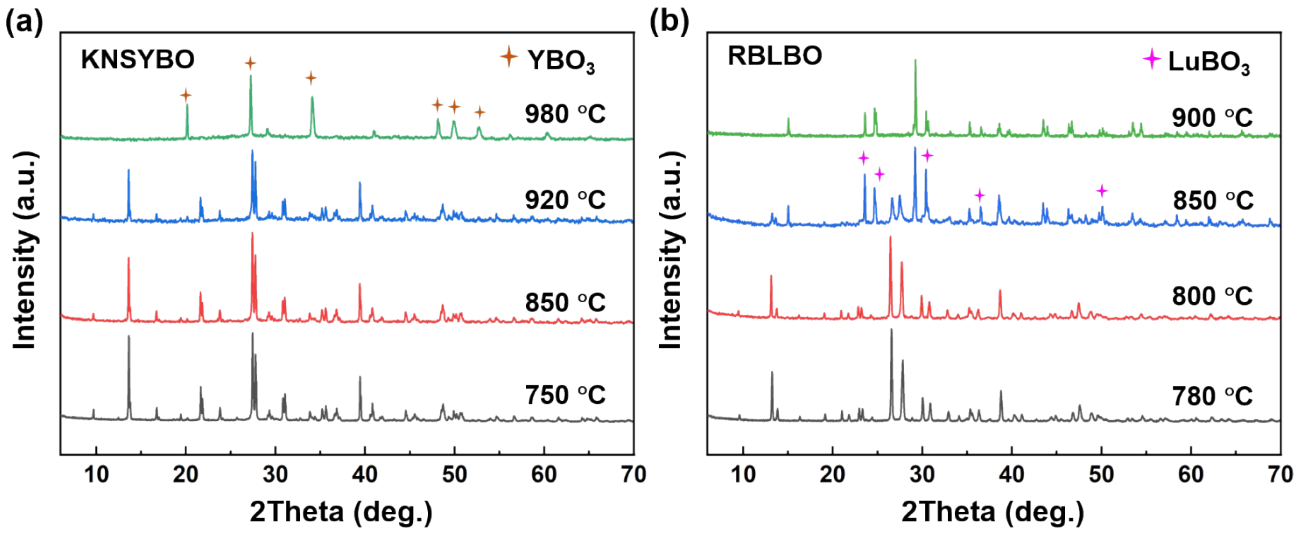

Figure S2. (a-b) The PXRD patterns evolution of KNSYBO and RBLBO polycrystalline pure phases under elevated temperature conditions.

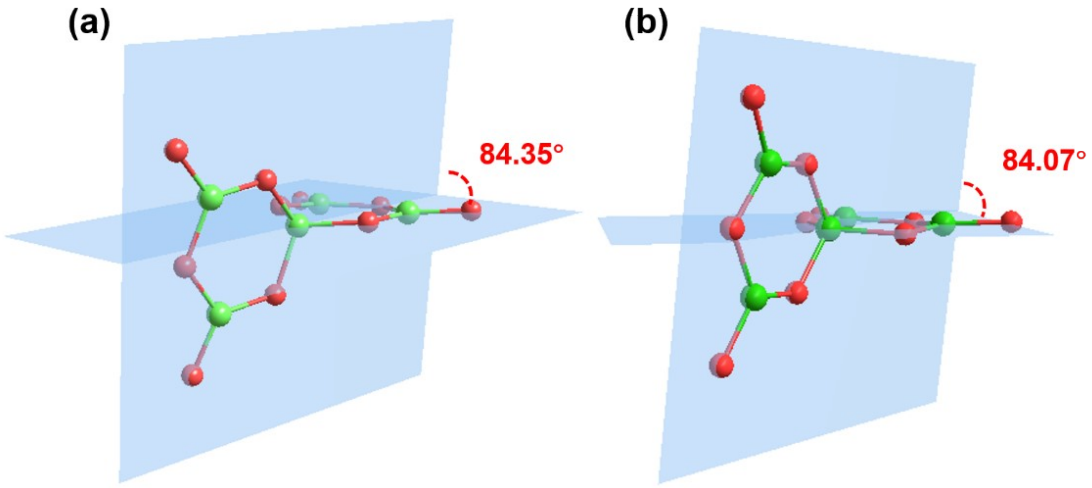

Figure S3 The dihedral angles of B_5O_{10} groups in (a) KNSYBO, (b) RBLBO, respectively.

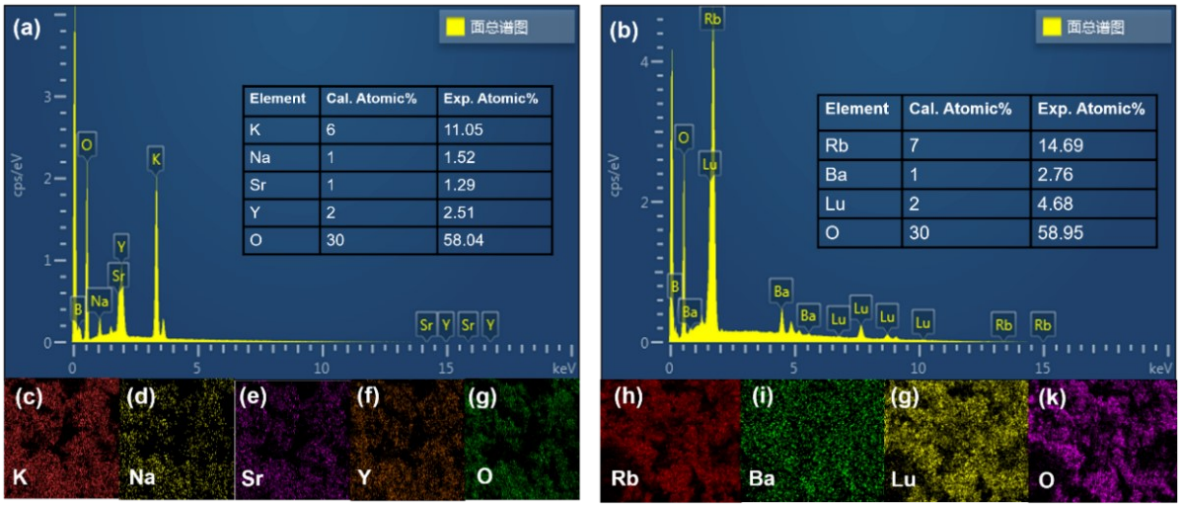

Figure S4. EDS of the two compounds. (a) Atomic ratio of various elements for $K_6NaSrY_2B_{15}O_{30}$, (b) Atomic ratio of various elements for $Rb_7BaLu_2B_{15}O_{30}$, (c-g) K, Na, Sr, Y and O elements mapping results, respectively. (h-k) Rb, Ba, Lu, and O elements mapping results, respectively.

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