Electronic Supplementary Information:

$Li_7SrScB_{12}O_{24}$ and $Li_7Ba_{0.6}Ca_{0.4}ScB_{12}O_{24}$: Two new quaternary rare-earth borates with short UV cutoff edges

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Experimental section

Reagents

All raw materials including K_2CO_3, Li_2CO_3, $M^{II}CO_3$ (M^{II} = Sr, $Ba_{0.6}Ca_{0.4}$), Sc_2O_3, and B_2O_3 were purchased from Shanghai Aladdin Chemical Industry Co., Ltd, as, M^{II}, Sc, and B-based reactants for the expected $Li_7M^{II}ScB_{12}O_{24}$ (M^{II} = Sr, $Ba_{0.6}Ca_{0.4}$).

Single crystal preparation

Single crystals of $Li_7SrScB_{12}O_{24}$ and $Li_7Ba_{0.6}Ca_{0.4}ScB_{12}O_{24}$ were synthesized by a high-temperature solution reaction with a spontaneous nucleation technique. The $Li_7SrScB_{12}O_{24}$ crystal was obtained from a mixture of Li_2CO_3, K_2CO_3, $SrCO_3$, Sc_2O_3, and B_2O_3 at a molar ratio of 9:1:1:2:15. The starting materials were thoroughly ground in an agate mortar and transferred to a Pt crucible, and then placed in the center of a programmable temperature furnace. The mixture was melted into solution at 800 ℃ and kept for 20 h to ensure the solution melt completely and homogeneously. Then the homogenized solution was slowly cooled to 700 ℃ at a rate of 1℃/h, and finally cooled to room temperature (RT) at a rate of 1.5 ℃/h. The colorless, block crystals were observed on the surface of the platinum crucible. For $Li_7Ba_{0.6}Ca_{0.4}ScB_{12}O_{24}$, raw materials of Li_2CO_3, K_2CO_3, $BaCO_3$, $CaCO_3$, Sc_2O_3, and B_2O_3 at a molar ratio of 9:1:1:1:2:15 was adopted using the same heating procedure. Small crystals were mechanically selected from the reaction products under a microscope and further characterized by single crystal X-ray diffraction measurement.

Solid-state synthesis

The polycrystalline sample of $Li_7SrScB_{12}O_{24}$ was obtained by traditional high temperature solid-state reaction. The raw materials of Li_2CO_3 (Aladdin, 99.5 %), $SrCO_3$ (Aladdin, 99 %), Sc_2O_3 (99.0 %), and B_2O_3 (Aladdin, 98 %) were carefully weighed according to the stoichiometric ratio 3.5:1:1:6 and packed into a corundum crucible after mixed in an agate mortar. First, the raw materials were fully ground and preheated at 500 °C for 24 h. Second, the sample was fully ground again and then heated to 760 °C and kept at this temperature for 4 days with several mixing and grinding during this process. Finally, the polycrystalline sample of $Li_7SrScB_{12}O_{24}$ was obtained and its purity was verified by powder X-ray diffraction (PXRD) analysis.

The pure phase of $Li_7Ba_{0.6}Ca_{0.4}ScB_{12}O_{24}$ was failed to obtained even if we have tried several different methods, such as changing synthetic methods (two-stage chemical synthesis method, molten salt and sol-gel method), replacing different raw materials, adjusting the molar ratio of the raw materials, etc.

Powder X-ray diffraction

PXRD measurement on the thoroughly ground polycrystalline powder of $Li_7SrScB_{12}O_{24}$ was carried out with a Bruker D2 Phaser diffractometer equipped with an incident beam monochromator set for Cu Kα radiation (λ = 1.5418 Å). Diffraction patterns were taken from 10 to 70 ° with a scan step width of 0.02 ° and a fixed counting time of 1 s per step. The XRD patterns of the powder sample of the title compound agree well with the calculated results (Figure.S1).

Structure determination

The crystal structure of $Li_7SrScB_{12}O_{24}$ was determined at room temperature using a Bruker D8 Venture single-crystal X-ray diffractometer with Mo-Kα radiation (λ = 0.71073 Å). The Bruker suite of software packages was used for the reduction of the diffraction data. Numerical absorption corrections were performed using the SCALE program[1] for area detection and integrated with the SAINT program. The structure was solved with Olex2 and SHELXTL by direct methods.[2-3] All atoms were refined with anisotropic displacement parameters. The program PLATON was used for verifying possible missing symmetry elements, but no higher symmetries were found.[4] The integrity and consistency of the crystal structure determination were checked using the check CIF tool (http://checkcif. iucr.org). Detailed information on the structural data is given in Table S1, and the redefined atomic positions, equivalent isotropic displacement parameters and bond valence are listed in Table S2. The information of selected bond lengths and angles is given in Table S3 in the ESI.

UV-Vis-NIR diffuse reflectance spectroscopy

The UV–Vis–NIR diffuse-reflectance spectroscopy data in a wavelength range of 200–2600 nm was recorded at room temperature using the powder samples of $Li_7SrScB_{12}O_{24}$ on a Shimadzu SolidSpec-3700DUV spectrophotometer. Tetrafluoroethylene was used as a diffuse reflectance standard.

Infrared spectroscopy

Infrared (IR) spectra were recorded on a Shimadzu IR Affinity-11 Fourier transform IR spectrometer in a range from 400 to 4000 cm^{-1} with a resolution of 1 cm^{-1}. The sample was mixed thoroughly with 500 mg of dried KBr.

Thermal analysis

Thermal gravimetry (TG) and differential scanning calorimetry (DSC) were carried out to examine the thermal stability of $Li_7SrScB_{12}O_{24}$ on a simultaneous NETZSCH STA 449 F3 thermal analyzer instrument under a flowing N_2 atmosphere. The sample was placed in a Pt crucible and heated from 40 to 1000 °C at a rate of 5 °C·min^{-1}.

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Table S1 Crystal data and structure refinement for $Li_7SrScB_{12}O_{24}$ and $Li_7Ba_{0.6}Ca_{0.4}ScB_{12}O_{24}$.

Empirical formula	$Li_7SrScB_{12}O_{24}$	$Li_7Ba_{0.6}Ca_{0.4}ScB_{12}O_{24}$
Formula weight	694.88	704.08
Temperature	339.00 K	295.00 K
Wavelength	0.71073 Å	0.71073 Å
Crystal system, space group	Trigonal, $R\bar{3}$	Trigonal, $R\bar{3}$
Unit cell dimensions	a = 14.8742(11) (Å) α = 90 ° b = 14.8742(11) (Å) β = 90 ° c = 6.5524(9) (Å) γ = 120 °	a = 14.9000(6) (Å) α = 90 ° b = 14.9000(6) (Å) β = 90 ° c = 6.5867(5) (Å) γ = 120 °
Volume	1255.4(3) $Å^3$	1266.4(14) $Å^3$
Z	3	3
Calculated density	2.757 $g·cm^{-3}$	2.770 $g·cm^{-3}$
Absorption coefficient	3.736 mm^{-1}	2.038 mm^{-1}
F (000)	996	1005
Crystal size	0.22 × 0.12 × 0.05 mm^3	0.12 × 0.1 × 0.08 mm^3
Theta range for data collection	3.488 to 27.439 °	3.473 to 27.485 °
Limiting indices	$-19 \le h \le 18$, $-18 \le k \le 18$, $-8 \le l \le 8$	$-19 \le h \le 19$, $-18 \le k \le 13$, $-8 \le l \le 8$
Reflections collected/unique	3114/635 [$R_{(int)}$ = 0.0706]	2362/631 [$R_{(int)}$ = 0.0403]
Completeness to theta	98.1%	96.1%
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.121	1.101
Data / restraints / parameters	635 / 6 / 77	631 / 6 / 78
Final R indices [F_o^2 >	R_1 = 0.0413, wR_2 = 0.0883	R_1 = 0.0253, wR_2 = 0.0645

$2\sigma(F_o^2)]$[a]		
R indices (all data)	R_1 = 0.0480, wR_2 = 0.0924	R_1 = 0.0270, wR_2 = 0.0655
Largest diff. peak and hole	0.509 and -0.697 e·Å^{-3}	0.458 and -0.306 e·Å^{-3}

Table S2. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for $Li_7SrScB_{12}O_{24}$ and $Li_7Ba_{0.6}Ca_{0.4}ScB_{12}O_{24}$. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.[a,b]

Atom	x	y	z	U(eq)	BVS
Li(1)	1240(30)	4100(30)	10500(60)	9(6)	1.23
Li(2)	1024(7)	4995(6)	9297(14)	32(2)	0.93
Sr(1)	3333	6667	6667	22(1)	1.94
Sc(1)	3333	6667	1667	5(1)	3.24
B(1)	559(3)	3614(3)	5904(6)	8(1)	2.99
B(2)	1331(3)	5199(3)	3679(6)	8(1)	3.03
O(1)	379(2)	3694(2)	8035(4)	7(1)	2.07
O(2)	1455(2)	4617(2)	5180(4)	11(1)	2.16
O(3)	2060(2)	6218(2)	3561(4)	8(1)	1.96
O(4)	525(2)	4741(2)	2302(4)	10(1)	1.82

Atom	x	y	z	U(eq)	BVS
Li(1)	1023(4)	4988(4)	9302(8)	39(1)	0.92
Li(2)	1245(16)	4082(16)	10450(30)	12(4)	1.23
Ba(1)/Ca(1)	3333	6667	6667	17(1)	2.21
Sc(1)	3333	6667	1667	12(1)	3.28
B(1)	554(2)	3613(2)	5862(3)	13(1)	3.03
B(2)	1324(2)	5192(2)	3636(4)	14(1)	2.99
O(1)	373(1)	3696(1)	7990(2)	12(1)	2.05
O(2)	1445(1)	4613(1)	5142(2)	17(1)	1.81
O(3)	519(1)	4738(1)	2270(2)	16(1)	1.96
O(4)	2047(1)	6210(1)	3503(2)	17(1)	2.21

[a] Bond valences calculated with the program Bond Valence Calculator Version 2.00, Hormillosa, C., Healy, S., Stephen, T. McMaster University (1993).

[b] Valence sums calculated with the formula: $S_i = \exp[(R_0-R_i)/B]$, where S_i = valence of

bond “*i*” and B = 0.37.

Table S3. Selected bond lengths [Å] and angles [deg.] for $Li_7SrScB_{12}O_{24}$.

Li(1)-O(1)	1.96(4)	Sr(1)-O(3)#3	2.629(2)
Li(1)-O(1)#12	1.88(4)	Sr(1)-O(3)#2	2.629(2)
Li(1)-O(3)#4	1.96(4)	Sr(1)-O(2)	2.914(2)
Li(1)-O(4)#4	2.04(3)	Sr(1)-O(2)#1	2.914(2)
Li(1)-O(4)#10	2.10(4)	Sr(1)-O(2)#2	2.914(2)
Li(2)-O(1)	1.868(8)	Sr(1)-O(4)#1	2.558(2)
Li(2)-O(2)#3	2.198(9)	Sc(1)-O(3)	2.076(2)
Li(2)-O(3)#4	2.004(9)	Sc(1)-O(3)#1	2.076(2)
Li(2)-O(4)#10	2.072(9)	Sc(1)-O(3)#6	2.076(2)
Sr(1)-O(2)#1	3.087(2)	Sc(1)-O(3)#7	2.076(2)
Sr(1)-O(2)#2	3.087(3)	Sc(1)-O(3)#5	2.076(2)
Sr(1)-O(2)#3	3.087(2)	Sc(1)-O(3)#8	2.076(2)
Sr(1)-O(2)#4	3.087(2)	B(1)-O(1)	1.438(5)
Sr(1)-O(2)	3.087(3)	B(1)-O(1)#11	1.454(4)
Sr(1)-O(2)#5	3.087(2)	B(1)-O(2)	1.496(4)
Sr(1)-O(3)	2.629(2)	B(1)-O(4)#12	1.507(4)
Sr(1)-O(3)#1	2.629(2)	B(2)-O(2)	1.382(5)
Sr(1)-O(3)#4	2.629(2)	B(2)-O(3)	1.356(4)
Sr(1)-O(3)#5	2.629(2)	B(2)-O(4)	1.378(5)
O(1)#11-Li(1)-O(1)	76.7(13)	O(2)#3-Sr(1)-O(2)	69.47(4)
O(1)-Li(1)-O(3)#3	105.2(17)	O(2)#3-Sr(1)-O(2)#2	110.54(4)
O(1)#11-Li(1)-O(3)#3	174(2)	O(2)#2-Sr(1)-O(2)	180.00(8)
O(1)-Li(1)-O(4)#3	125.6(18)	O(2)#1-Sr(1)-O(2)#4	69.47(4)
O(1)-Li(1)-O(4)#16	101.8(15)	O(2)#4-Sr(1)-O(2)#5	180.0
O(1)#11-Li(1)-O(4)#3	110.6(17)	O(3)#4-Sr(1)-O(2)	112.93(7)
O(1)#11-Li(1)-O(4)#16	75.2(13)	O(3)#4-Sr(1)-O(2)#2	67.06(7)
O(1)-Li(2)-O(2)#4	129.7(5)	O(3)#1-Sr(1)-O(2)#5	67.07(7)
O(1)-Li(2)-O(3)#3	107.2(4)	O(3)#1-Sr(1)-O(2)	109.47(7)
O(1)-Li(2)-O(4)#16	106.3(4)	O(3)#3-Sr(1)-O(2)#3	47.46(7)
O(3)#3-Li(2)-O(2)#4	98.3(4)	O(3)#3-Sr(1)-O(2)#1	132.54(7)
O(3)#3-Li(2)-O(4)#16	98.5(4)	O(3)#5-Sr(1)-O(2)#3	70.54(7)
O(4)#16-Li(2)-O(2)#4	112.0(4)	O(3)#2-Sr(1)-O(2)	132.55(7)
O(2)#1-Sr(1)-O(2)#3	180.0	O(3)#3-Sr(1)-O(2)	70.53(7)
O(2)#2-Sr(1)-O(2)#4	110.53(4)	O(3)#5-Sr(1)-O(2)	67.07(7)
O(2)#2-Sr(1)-O(2)#5	69.47(4)	O(3)#1-Sr(1)-O(2)#1	47.45(7)
O(2)#3-Sr(1)-O(2)#4	110.53(4)	O(2)#3-Sr(1)-O(2)	69.47(4)

O(2)#1-Sr(1)-O(2)#5	110.53(4)	O(3)#2-Sr(1)-O(2)#2	47.46(7)
O(2)#3-Sr(1)-O(2)#5	69.47(4)	O(3)-Sr(1)-O(2)#3	112.93(7)
O(2)-Sr(1)-O(2)#5	110.53(4)	O(3)#2-Sr(1)-O(2)#5	70.54(7)
O(2)#1-Sr(1)-O(2)#2	69.46(4)	O(3)-Sr(1)-O(2)#4	70.53(7)
O(2)#1-Sr(1)-O(2)	110.53(4)	O(3)#5-Sr(1)-O(2)#2	112.94(7)
O(2)-Sr(1)-O(2)#4	69.47(4)	O(3)#4-Sr(1)-O(2)#4	47.45(7)
O(2)-Sr(1)-O(2)#5	110.53(4)	O(3)#3-Sr(1)-O(2)#4	67.07(7)
O(2)#1-Sr(1)-O(2)#2	69.46(4)	O(3)#5-Sr(1)-O(2)#4	132.55(7)
O(2)#1-Sr(1)-O(2)	110.53(4)	O(3)#4-Sr(1)-O(2)#1	70.53(7)
O(2)-Sr(1)-O(2)#4	69.47(4)	O(3)#5-Sr(1)-O(2)#1	109.47(7)
O(2)#3-Sr(1)-O(2)	69.47(4)	O(3)#1-Sr(1)-O(3)#3	180.0
O(2)#3-Sr(1)-O(2)#2	110.54(4)	O(3)#2-Sr(1)-O(3)#5	113.52(8)
O(2)#2-Sr(1)-O(2)	180.00(8)	O(3)#4-Sr(1)-O(3)#5	180.0
O(2)#1-Sr(1)-O(2)#4	69.47(4)	O(3)#3-Sr(1)-O(3)#5	113.52(8)
O(2)#4-Sr(1)-O(2)#5	180.0	O(3)#4-Sr(1)-O(3)#1	113.52(8)
O(3)#4-Sr(1)-O(2)	112.93(7)	O(3)-Sr(1)-O(3)#3	113.52(8)
O(3)#4-Sr(1)-O(2)#2	67.06(7)	O(3)#1-Sr(1)-O(3)#2	113.52(8)
O(3)#1-Sr(1)-O(2)#5	67.07(7)	O(3)-Sr(1)-O(3)#2	180.0
O(3)#1-Sr(1)-O(2)	109.47(7)	O(3)#3-Sr(1)-O(3)#2	66.48(8)
O(3)#3-Sr(1)-O(2)#3	47.46(7)	O(3)-Sr(1)-O(3)#4	113.51(8)
O(3)#3-Sr(1)-O(2)#1	132.54(7)	O(3)-Sr(1)-O(2)#5	109.47(7)
O(3)#5-Sr(1)-O(2)#3	70.54(7)	O(3)#2-Sr(1)-O(2)#3	67.07(7)
O(3)#1-Sr(1)-O(2)	109.47(7)	O(3)#3-Sr(1)-O(2)#2	109.47(7)
O(3)#3-Sr(1)-O(2)#3	47.46(7)	O(3)#4-Sr(1)-O(2)#5	132.55(7)
O(3)#3-Sr(1)-O(2)#1	132.54(7)	O(3)#4-Sr(1)-O(2)#3	109.47(7)
O(3)#5-Sr(1)-O(2)#3	70.54(7)	O(3)#3-Sr(1)-O(2)#5	112.93(7)
O(3)#2-Sr(1)-O(2)	132.55(7)	O(3)#1-Sc(1)-O(3)#5	87.92(10)
O(3)#3-Sr(1)-O(2)	70.53(7)	O(3)#1-Sc(1)-O(3)#7	180.0
O(3)#5-Sr(1)-O(2)	67.07(7)	O(3)#8-Sc(1)-O(3)#6	87.92(10)
O(3)#1-Sr(1)-O(2)#1	47.45(7)	O(1)-B(1)-O(1)#12	111.0(3)
O(3)#2-Sr(1)-O(2)#1	112.93(7)	O(1)#12-B(1)-O(2)	110.2(3)
O(3)#5-Sr(1)-O(2)#5	47.46(7)	O(1)-B(1)-O(2)	109.6(3)
O(3)-Sr(1)-O(2)#1	67.07(7)	O(1)#12-B(1)-O(4)#11	110.8(3)
O(3)#1-Sr(1)-O(2)#4	112.93(7)	O(1)-B(1)-O(4)#11	109.1(3)
O(3)#1-Sr(1)-O(2)#2	70.53(7)	O(2)-B(1)-O(4)#11	106.0(3)
O(3)#2-Sr(1)-O(2)#4	109.46(7)	O(3)-B(2)-O(2)	117.3(3)
O(3)-Sr(1)-O(2)#2	132.54(7)	O(3)-B(2)-O(4)	121.8(3)

O(3)#1-Sr(1)-O(2)#3	132.55(7)	O(4)-B(2)-O(2)	120.8(3)
O(3)#7-Sc(1)-O(3)#6	87.93(10)		
O(3)#8-Sc(1)-O(3)#7	87.92(10)		
O(3)-Sc(1)-O(3)#8	92.08(10)		
O(3)-Sc(1)-O(3)#7	92.08(10)		
O(3)-Sc(1)-O(3)#6	180.00(10)		
O(3)-Sc(1)-O(3)#5	87.92(10)		
O(3)#6-Sc(1)-O(3)#5	92.08(10)		
O(3)#8-Sc(1)-O(3)#5	180.0		
O(3)#1-Sc(1)-O(3)	87.92(10)		
O(3)#1-Sc(1)-O(3)#6	92.08(10)		
O(3)#1-Sc(1)-O(3)#8	92.08(10)		
O(3)#7-Sc(1)-O(3)#5	92.08(10)		

Symmetry transformations used to generate equivalent atoms:

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

#4 y-1/3,-x+y+1/3,-z+4/3 #5 -y+1,x-y+1,z #6 -x+2/3,-y+4/3,-z+1/3

#7 x-y+2/3,x+1/3,-z+1/3 #8 y-1/3,-x+y+1/3,-z+1/3

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

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

#14 x-y+2/3,x+1/3,-z+7/3 #15 -x,-y+1,-z+2 #16 x,y,z+1

#17 -y+1/3,x-y+2/3,z+2/3 #18 y-1/3,-x+y+1/3,-z+7/3

Table S4. Basic information of anhydrous borates with B_6O_{14} groups.

No.	Chemical Formula	Space Group	B-O Clusters	Unit Cell Dimensions	Refer-ence
1	$Ba_6Al_4B_{14}O_{33}$	$P\bar{1}$	$[B_6O_{14}]$	a = 7.0070(14) (Å) α = 86.48 ° b = 13.880(3) (Å) β = 88.99 ° c = 14.702(3) (Å) γ = 83.46 °	5
2	$Ba_3B_6O_{11}F_2$	$P2_1$	$[B_6O_{14}]$	*a* = 6.5672(4) (Å) α = 90 ° *b* = 8.5035(6) (Å) β = 101.351 ° *c* = 9.6637(6) (Å) γ = 90 °	6
3	$Pb_6O(B_6O_{14})$	$P\bar{1}$	$[B_6O_{14}]$	a = 6.9567 (Å) α = 97.275 ° b = 7.7849 (Å) β = 100.442 ° c = 14.0825 (Å) γ = 103.024 °	7
4	$Ba_2B_6O_{11}$	$P2_1/c$	$[B_6O_{14}]$	*a* = 9.115(1) (Å) α = 90 ° b = 7.773(1) (Å) β =100.325 ° c = 12.696(2) (Å) γ = 90 °	8
5	$Pb_3B_6O_{11}F_2$	$P2_1$	$[B_6O_{14}]$	*a* = 6.414(4) (Å) α = 90 ° *b* = 8.310(6) (Å) β = 101.284 ° *c* = 9.470(6) (Å) γ = 120 °	9
6	$Li_7BaAlB_{12}O_{24}$	$R\bar{3}$	$[B_6O_{14}]$	*a* = 18.0600(9) (Å) α = 90 ° *b* = 6.9728(6) (Å) β = 90 ° *c* = 6.9728(6) (Å) γ = 120 °	10
7	$Li_7SrAlB_{12}O_{24}$	$R\bar{3}$	$[B_6O_{14}]$	*a* = 14.6943(14) (Å) α = 90 ° *b* = 6.6971(8) (Å) β = 90 ° *c* = 6.6971(8) (Å) γ = 120 °	10
8	$Li_7CaAlB_{12}O_{24}$	$R\bar{3}$	$[B_6O_{14}]$	*a* = 14.5702(14) (Å) α = 90 ° *b* = 6.5040(8) (Å) β = 90 ° *c* = 6.5040(8) (Å) γ = 120 °	10
9	$Sr_3B_6O_{11}F_2$	$P2_1$	$[B_6O_{14}]$	*a* = 6.4093(13) (Å) α = 90 ° *b* = 8.2898(17) (Å) β = 101.51 ° *c* = 9.3656(6) (Å) γ = 90 °	11

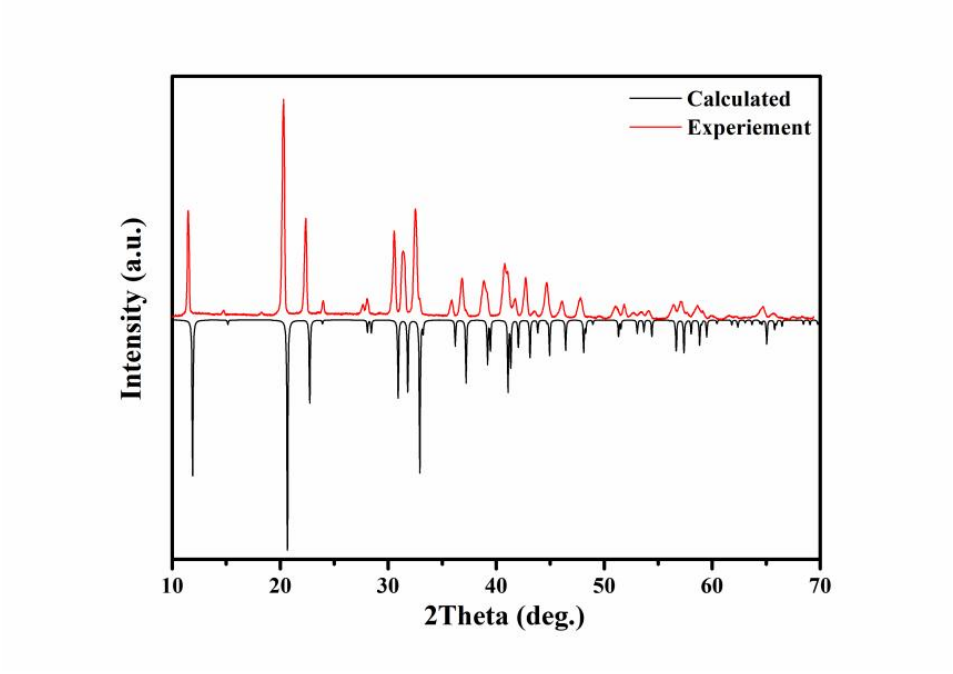

Figure S1. Calculated and experimental powder-XRD patterns of $Li_7SrScB_{12}O_{24}$.

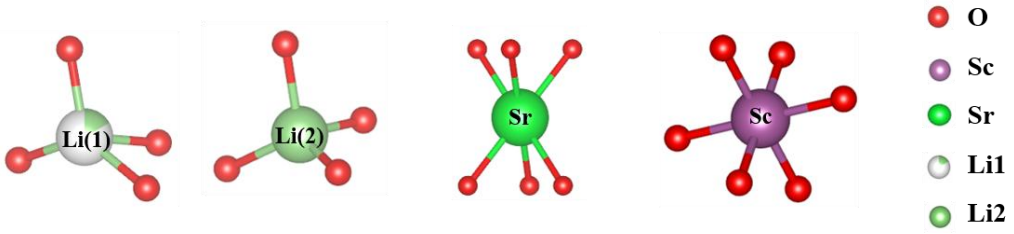

Figure S2. Coordination environments of the Li, Sr and Sc atoms.

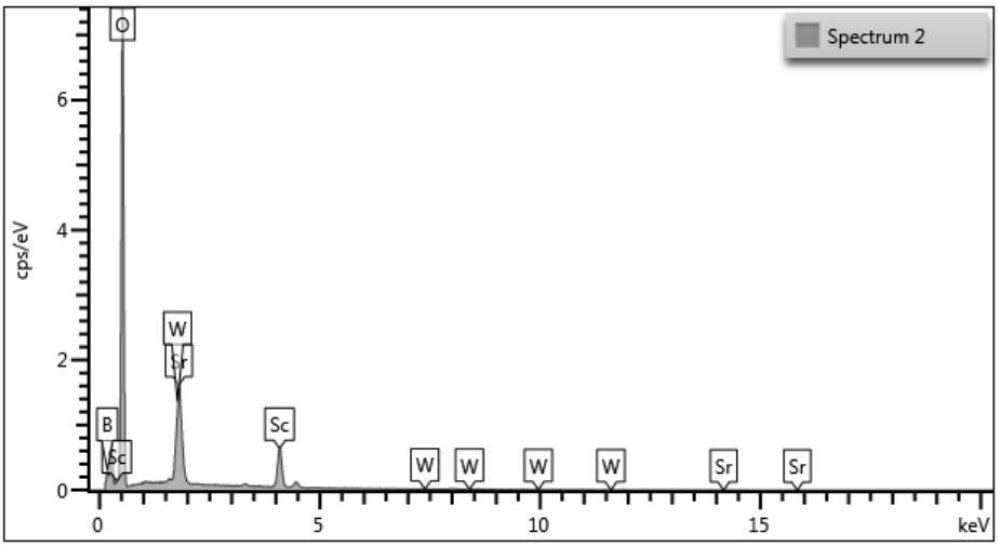

Figure S3. Elemental analysis of $Li_7SrScB_{12}O_{24}$. Energy dispersive X-ray spectroscope (EDS) was performed to verify the presence of the Sr atom.

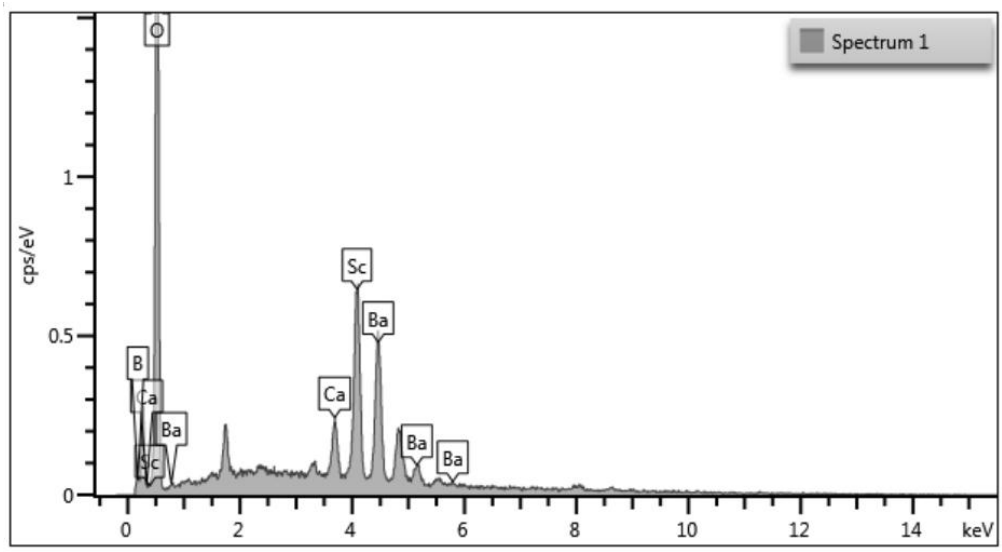

Figure S4. Elemental analysis of $Li_7Ba_{0.6}Ca_{0.4}ScB_{12}O_{24}$. Energy dispersive X-ray spectroscope (EDS) was performed to verify the presence of the Ba and Ca atoms.

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