Supporting Information

$Rb_3MgB_5O_{10}$ and $LiBaAl(BO_3)_2$: Covalent Tetrahedra MO_4-Containing Borates with Deep-ultraviolet Cutoff Edges

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Experimental Procedures

Reagents. Rb_2CO_3 (99 %), $Mg(OH)_2$ (99 %), H_3BO_3 (≥99.5 %), $BaCO_3$ (≥99.5 %), Al_2O_3 (99.9 %), LiF (≥99.5 %), and NaF (≥99.5 %) were purchased from Aladdin and used as received.

Synthesis.

$Rb_3MgB_5O_{10}$

Single crystals of $Rb_3MgB_5O_{10}$ were grown via spontaneous crystallization. A mixture of Rb_2CO_3 (3 mmol, 0.693 g), MgO (2 mmol, 0.081 g) and H_3BO_3 (10 mmol, 0.618 g) was thoroughly ground. The mixture was then packed into a platinum crucible that was placed into a vertical, programmable temperature furnace. The crucible was gradually heated to 750 °C and held for 6 h. The temperature was slowly cooled down to 650 °C at a rate of 1.5 °C·h^{-1}, then cooled down to 550 °C at a rate of 2 °C·h^{-1}, and then cooled down to 450 °C at a rate of 3 °C·h^{-1}, followed by rapidly cooling to room temperature. Millimeter-sized crystals were selected from the products for single crystal data testing.

The polycrystalline sample of $Rb_3MgB_5O_{10}$ was obtained by a two-step method. In the first step, the polycrystalline powder of MgB_4O_7 was preferentially prepared as follows: a mixture of $Mg(OH)_2$ and H_3BO_3 with a molar ratio of 1:3 was thoroughly ground, and then slowly heated to 690 °C and held at this temperature for 48 h with several intermediate grindings. In the second step, a mixture of MgB_4O_7, Rb_2CO_3, and H_3BO_3 with a molar ratio of 1:1.5:1 was thoroughly ground, and then slowly heated to 700 °C and held at this temperature for 48 h with several intermediate grindings. The purity of the sample was checked by powder XRD diffraction.

$LiBaAl(BO_3)_2$

Single crystals of $LiBaAl(BO_3)_2$ were also grown via spontaneous crystallization. A mixture of $BaCO_3$ (4 mmol, 0.789 g), Al_2O_3 (2 mmol, 0.204 g), LiF (10 mmol, 0.259 g), NaF (1.2 mmol, 0.05 g), and H_3BO_3 (12 mmol, 0.742 g) was thoroughly ground. The mixture was then packed into a platinum crucible that was placed into a vertical, programmable temperature furnace. The crucible was gradually heated to 1000 °C for 20 h and held for 10 h. The temperature was slowly cooled down to 900°C at a rate of 3 °C·h^{-1}, then cooled down to 700 °C at a rate of 2 °C·h^{-1}, and then cooled down to 600°C at a rate of 3 °C·h^{-1}, and finally cooled to room temperature by switching off the furnace. The colorless block crystals were obtained for structure determination.

We tried to use direct solid-state reactions under an open system and a two-step method to synthesize polycrystalline samples of $LiBaAl(BO_3)_2$. For the direct solid-state reactions, Li_2CO_3, $BaCO_3$, Al (OH_3), and H_3BO_3 were mixed in a stoichiometric ratio, slowly heated to 300 °C for presenting, and then slowly heated to 600 °C, the phase of $Li_2Ba_4B_{10}O_{20}$ began to appear. Continue to heat up until dissolution and no $LiBaAl(BO_3)_2$ phase appears. For the two-step method, $BaAlBO_4$ was first synthesized according to the methods mentioned in relevant literature, and then $BaAlBO_4$, Li_2CO_3, and H_3BO_3 were uniformly mixed in a ratio of 2:1:2. After pre-burning at 300 °C, the $Li_2Ba_4B_{10}O_{20}$ phase began to appear at 620 °C. Continue heating until it melted and there was no $LiBaAl(BO_3)_2$ phase presented. We finally attempted to spontaneously crystallize using the method of obtaining single crystals and obtained the sample containing $LiBaAl(BO_3)_2$ phase. The XRD pattern is shown in Figure S1. After comparison with Jade 6 software, it was found that the main impurities are Li_2AlBO_4 and $Li_6Ba_2B_4O_{11}$, while no compounds corresponding to the impurity peak at 11.8 ° were found yet.

Structure Determination. The colorless, transparent bulk single crystals of the title compounds were selected under an optical microscope for structural determination. The single-crystal XRD data

were collected on a Bruker D8 Venture diffractometer assembled with monochromatic Mo-Kα (λ = 0.71073 Å) as the radiation source at room temperature and then integrated by using the SAINT program.[1] All the structures were solved by direct methods and refined through the full-matrix least-squares fitting on F_2 with the OLEX2 software.[2] The crystal structures were solved using the direct method and refined using the SHELXL least-squares refinement package.[3] The structures were checked for possible higher symmetry using the ADDSYM algorithm from the program PLATON.[4] Crystal data and structure refinements of $Rb_3MgB_5O_{10}$ and $LiBaAl(BO_3)_2$ are listed in Tables S1 and S4, respectively. The atomic coordinates and equivalent isotropic displacement parameters selected bond distances and angles of $Rb_3MgB_5O_{10}$ and $LiBaAl(BO_3)_2$ are given in Tables S2-S3 and S5-S6, respectively.

Powder X-ray Diffraction. Powder XRD data were collected at room temperature with a Bruker D2 PHASER diffractometer equipped with Cu Kα radiation (λ = 1.5418 Å). Data were collected in the angular (2θ) ranging from 5 to 70 ° for $Rb_3MgB_5O_{10}$ and 10 to 70 ° for $LiBaAl(BO_3)_2$ with a scan step width and a fixed counting time of 0.02 ° and 1 s/step, respectively.

Infrared (IR) Spectroscopy. IR spectroscopy of $Rb_3MgB_5O_{10}$ was inspected with a Shimadzu IR Affinity1 spectrometer at room temperature, and the wavelength ranges from 400 to 4000 cm^{-1}. The test was carried out by thoroughly mixing the sample and dried KBr (5 mg of the sample and 500 mg of KBr).

UV-Vis NIR Diffuse Reflectance Spectroscopy. The diffuse reflectance spectra were measured by using a Shimadzu Solid Spec-3700 DUV spectrophotometer in the wavelength range of 200–2600 nm at room temperature.

Computational Methods. The band structures, partial density of state (PDOS), and optical properties of $Rb_3MgB_5O_{10}$ and $LiBaAl(BO_3)_2$ were calculated by utilizing the CASTEP program.[5] Under the norm-conserving pseudopotentials (NCPs),[6] the following orbital electrons were treated as valence electrons. The functional developed by Perdew-Burke-Ernzerhof (PBE) in generalized gradient approximation (GGA) form was used to describe the exchange-correlation energy. A kinetic energy cutoff of 750 eV is chosen with Monkhorst-Pack k-point meshes spanning less than 0.035/Å in the Brillouin zone.

Results and Discussion

Table S1. Crystal data and structure refinement for $Rb_3MgB_5O_{10}$.

Empirical formula	**$Rb_3MgB_5O_{10}$**
Formula weight	494.77
Temperature	293.15 K
Wavelength	0.71073 Å^3
Crystal system, space group	Monoclinic, $P2_1/c$
Unit cell dimensions	a = 10.557(9) Å, α = 90°
	b = 9.449(8) Å, β = 122.72(5)°
	c = 13.336(9) Å, γ = 90°
Volume	1119.2(16) Å^3
Z	4
Calculated density	2.936 g·cm^{-3}
Absorption coefficient	13.160 mm^{-1}
F (000)	912
Crystal size	0.257 × 0.13 × 0.099 mm^3
Theta range for data collection	2.293 to 27.546°
Limiting indices	-13 ≤ h ≤ 13, -10 ≤ k ≤ 12, -17 ≤ l ≤ 17
Reflections collected / unique	10474 / 2562 [R(int) = 0.0864]
Completeness	100.0 %
Data/ restraints/ parameters	2562 / 0 / 173
Goodness-of-fit on F^2	1.046
Final R indices [$F_o^2 > 2\sigma(F_o^2)$] [a]	R_1 = 0.0501, wR_2 = 0.0943
R indices (all data) [a]	R_1 = 0.0885, wR_2 = 0.1081
Largest diff. peak and hole	2.315 and -1.401 e·Å^{-3}

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

Table S2. Fractional atomic coordinates ($\times 10^4$), equivalent isotropic displacement parameters ($Å^2 \times 10^3$), and bond valence sum (BVS) for $Rb_3MgB_5O_{10}$. $U(eq)$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atoms	Wyck.	*x*	*y*	*z*	$U_{(eq)}$	S.O.F.	BVS
			$Rb_3MgB_5O_{10}$				
Rb(1)	2i	-127(1)	-4314(1)	-1626(1)	45(1)	1	1.06
Rb(2)	2i	2970(1)	-5659(1)	-2103(1)	25(1)	1	1.15
Rb(3)	2i	4488(1)	-1702(1)	-1115(1)	28(1)	1	0.91
Mg(1)	2i	-6839(3)	-1965(3)	-9386(2)	19(1)	1	1.97
B(1)	2i	-3268(9)	49(9)	-5475(7)	21(2)	1	3.01
B(2)	2i	-3852(9)	-1152(9)	-7321(7)	18(2)	1	3.05
B(3)	2i	760(9)	-3065(9)	-3954(7)	20(2)	1	2.99
B(4)	2i	-1418(9)	-4554(8)	-4397(7)	18(2)	1	3.07
B(5)	2i	-1880(9)	-2178(9)	-5334(8)	23(2)	1	3.06
O(1)	2i	-4750(5)	-1323(5)	-8478(4)	25(1)	1	1.97
O(2)	2i	-4163(5)	-86(5)	-6728(4)	23(1)	1	2.03
O(3)	2i	-3287(6)	1231(5)	-4942(4)	24(1)	1	1.92
O(4)	2i	-2421(6)	-1099(6)	-4835(4)	24(1)	1	2.11
O(5)	2i	-2568(6)	-1920(5)	-6623(4)	24(1)	1	2.25
O(6)	2i	-2350(5)	-3567(5)	-5203(5)	30(1)	1	2.08
O(7)	2i	-244(5)	-2060(5)	-4729(4)	24(1)	1	2.04
O(8)	2i	2235(5)	-2968(5)	-3457(4)	22(1)	1	1.93
O(9)	2i	119(5)	-4216(5)	-3701(4)	23(1)	1	2.15
O(10)	2i	-1899(5)	-5771(5)	-4224(4)	24(1)	1	1.79

Table S3. Selected bond lengths (Å) and angles (°) for $Rb_3MgB_5O_{10}$.

Rb(1)-O(3)#1	3.080(6)	O(4)#1-Rb(1)-O(9)	97.55(15)
Rb(1)-O(4)#1	2.866(6)	O(4)#1-Rb(1)-O(10)	105.38(15)
Rb(1)-O(5)#2	2.830(6)	O(5)#2-Rb(1)-O(3)#1	131.52(15)
Rb(1)-O(7)#1	3.065(6)	O(5)#2-Rb(1)-O(4)#1	139.65(15)
Rb(1)-O(7)#2	2.905(6)	O(5)#2-Rb(1)-O(7)#2	49.28(14)
Rb(1)-O(9)	2.917(6)	O(5)#2-Rb(1)-O(7)#1	100.03(15)
Rb(1)-O(10)	3.224(5)	O(5)#2-Rb(1)-O(9)	122.44(14)
Rb(2)-O(1)#4	3.270(6)	O(5)#2-Rb(1)-O(10)	100.24(15)
Rb(2)-O(2)#3	2.876(6)	O(7)#2-Rb(1)-O(3)#1	85.36(15)
Rb(2)-O(3)#1	3.122(5)	O(7)#1-Rb(1)-O(3)#1	90.66(13)
Rb(2)-O(4)#1	2.968(6)	O(7)#2-Rb(1)-O(7)#1	85.23(15)
Rb(2)-O(5)#4	2.742(5)	O(7)#2-Rb(1)-O(9)	151.57(15)
Rb(2)-O(6)#4	3.367(6)	O(7)#1-Rb(1)-O(10)	94.98(14)
Rb(2)-O(8)	2.969(5)	O(7)#2-Rb(1)-O(10)	148.64(14)
Rb(2)-O(9)	2.920(5)	O(9)-Rb(1)-O(3)#1	88.10(15)
Rb(3)-O(1)#6	2.951(6)	O(9)-Rb(1)-O(7)#1	122.53(15)
Rb(3)-O(1)#5	3.176(6)	O(9)-Rb(1)-O(10)	44.90(14)
Rb(3)-O(2)#6	3.192(6)	O(1)#4-Rb(2)-O(6)#4	79.53(13)
Rb(3)-O(3)#1	3.055(5)	O(2)#3-Rb(2)-O(1)#4	75.88(14)
Rb(3)-O(4)#3	3.443(6)	O(2)#3-Rb(2)-O(3)#1	95.85(15)
Rb(3)-O(6)#3	2.881(6)	O(2)#3-Rb(2)-O(4)#1	124.43(14)
Rb(3)-O(8)	2.969(5)	O(2)#3-Rb(2)-O(6)#4	79.52(14)
Rb(3)-O(10)#7	3.128(6)	O(2)#3-Rb(2)-O(8)	78.50(14)
		O(2)#3-Rb(2)-O(9)	125.82(15)
Mg(1)-O(1)	1.952(6)	O(3)#1-Rb(2)-O(1)#4	121.04(14)
Mg(1)-O(3)#8	1.964(6)	O(3)#1-Rb(2)-O(6)#4	157.46(13)
Mg(1)-O(8)#9	1.950(6)	O(4)#1-Rb(2)-O(1)#4	91.69(15)
Mg(1)-O(10)#10	1.953(5)	O(4)#1-Rb(2)-O(3)#1	45.49(14)
		O(4)#1-Rb(2)-O(6)#4	151.91(13)
B(1)-O(2)	1.412(9)	O(4)#1-Rb(2)-O(8)	122.68(15)
B(1)-O(3)	1.330(10)	O(5)#4-Rb(2)-O(1)#4	45.23(14)
B(1)-O(4)	1.371(10)	O(5)#4-Rb(2)-O(2)#3	96.19(16)
B(2)-O(1)	1.313(9)	O(5)#4-Rb(2)-O(3)#1	157.79(15)
B(2)-O(2)	1.425(10)	O(5)#4-Rb(2)-O(4)#1	112.64(16)
B(2)-O(5)	1.366(9)	O(5)#4-Rb(2)-O(6)#4	44.09(14)
B(3)-O(7)	1.381(9)	O(5)#4-Rb(2)-O(8)	115.82(15)
B(3)-O(8)	1.326(9)	O(5)#4-Rb(2)-O(9)	100.62(15)
B(3)-O(9)	1.415(10)	O(8)-Rb(2)-O(1)#4	144.96(14)
B(4)-O(6)	1.360(9)	O(8)-Rb(2)-O(3)#1	84.88(15)
B(4)-O(9)	1.403(9)	O(8)-Rb(2)-O(6)#4	72.58(14)
B(4)-O(10)	1.326(9)	O(9)-Rb(2)-O(1)#4	144.49(13)
B(5)-O(4)	1.488(10)	O(9)-Rb(2)-O(3)#1	87.25(15)
B(5)-O(5)	1.482(10)	O(9)-Rb(2)-O(4)#1	95.26(16)
B(5)-O(6)	1.446(10)	O(9)-Rb(2)-O(6)#4	78.08(15)
B(5)-O(7)	1.464(9)	O(9)-Rb(2)-O(8)	47.82(13)
		O(1)#6-Rb(3)-O(1)#5	95.86(14)
O(3)#1-Rb(1)-O(10)	125.96(14)	O(1)#6-Rb(3)-O(2)#6	45.24(13)
O(4)#1-Rb(1)-O(3)#1	46.58(14)	O(1)#5-Rb(3)-O(2)#6	141.09(14)
O(4)#1-Rb(1)-O(7)#1	47.67(14)	O(1)#6-Rb(3)-O(3)#1	143.90(15)
O(4)#1-Rb(1)-O(7)#2	97.86(15)	O(1)#5-Rb(3)-O(4)#3	85.10(13)

O(1)#6-Rb(3)-O(4)#3	121.15(14)	O(1)-Mg(1)-O(10)#10	111.8(3)
O(1)#6-Rb(3)-O(8)	107.34(14)	O(8)#9-Mg(1)-O(1)	113.7(2)
O(1)#6-Rb(3)-O(10)#7	86.03(15)	O(8)#9-Mg(1)-O(3)#8	116.3(3)
O(2)#6-Rb(3)-O(4)#3	112.17(14)	O(8)#9-Mg(1)-O(10)#10	107.6(2)
O(3)#1-Rb(3)-O(1)#5	58.76(14)	O(10)#10-Mg(1)-O(3)#8	104.3(2)
O(3)#1-Rb(3)-O(2)#6	152.25(13)		
O(3)#1-Rb(3)-O(4)#3	84.50(14)	O(3)-B(1)-O(2)	121.0(7)
O(3)#1-Rb(3)-O(10)#7	60.04(15)	O(3)-B(1)-O(4)	121.7(7)
O(6)#3-Rb(3)-O(1)#6	77.84(14)	O(4)-B(1)-O(2)	117.3(7)
O(6)#3-Rb(3)-O(1)#5	88.88(16)	O(1)-B(2)-O(2)	120.2(6)
O(6)#3-Rb(3)-O(2)#6	82.49(15)	O(1)-B(2)-O(5)	123.8(7)
O(6)#3-Rb(3)-O(3)#1	122.45(15)	O(5)-B(2)-O(2)	116.0(6)
O(6)#3-Rb(3)-O(4)#3	43.31(14)	O(7)-B(3)-O(9)	115.8(6)
O(6)#3-Rb(3)-O(8)	124.48(16)	O(8)-B(3)-O(7)	123.1(7)
O(6)#3-Rb(3)-O(10)#7	144.88(15)	O(8)-B(3)-O(9)	121.1(7)
O(8)-Rb(3)-O(1)#5	142.18(14)	O(6)-B(4)-O(9)	116.7(6)
O(8)-Rb(3)-O(2)#6	68.30(14)	O(10)-B(4)-O(6)	123.4(7)
O(8)-Rb(3)-O(3)#1	86.07(15)	O(10)-B(4)-O(9)	119.8(6)
O(8)-Rb(3)-O(4)#3	106.49(14)	O(5)-B(5)-O(4)	109.9(6)
O(8)-Rb(3)-O(10)#7	89.98(14)	O(6)-B(5)-O(4)	109.2(7)
O(10)#7-Rb(3)-O(1)#5	61.73(13)	O(6)-B(5)-O(5)	107.7(6)
O(10)#7-Rb(3)-O(2)#6	107.74(14)	O(6)-B(5)-O(7)	112.4(6)
O(10)#7-Rb(3)-O(4)#3	140.02(13)	O(7)-B(5)-O(4)	109.0(6)
		O(7)-B(5)-O(5)	108.6(7)
O(1)-Mg(1)-O(3)#8	102.7(2)		

Symmetry transformations used to generate equivalent atoms:

#1 -x, y-1/2, -z-1/2; #2 x, -y-1/2, z+1/2; #3 x+1, -y-1/2, z+1/2; #4 -x, -y-1, -z-1; #5 x+1, y, z+1; #6 -x, -y, -z-1; #7 -x, y+1/2, -z-1/2; #8 -x-1, y-1/2, -z-3/2; #9 x-1, -y-1/2, z-1/2; #10 -x-1, y+1/2, -z-3/2; #11 x-1, y, z-1; #12 x, -y-1/2, z-1/2.

Table S4. Crystal data and structure refinement for $LiBaAl(BO_3)_2$.

Empirical formula	**$LiBaAl(BO_3)_2$**
Formula weight	288.88
Temperature	293.15 K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, *P*21/*c*
Unit cell dimensions	a = 4.91610(10) Å, α = 90°
	b = 8.7222(2) Å, β = 108.2900(10)°
	c = 13.2280(3) Å, γ = 90°
Volume	538.55(2) Å^3
Z	4
Calculated density	3.563 g·cm^{-3}
Absorption coefficient	7.494 mm^{-1}
F (000)	520
Crystal size	0.205 × 0.092 × 0.062 mm^3
Theta range for data collection	2.843 to 27.504°
Limiting indices	-6 ≤ h ≤ 6, -10 ≤ k ≤ 11, -17 ≤ l ≤ 17
Reflections collected / unique	8775 / 1233 [R(int) = 0.0310]
Completeness	99.5 %
Data/ restraints/ parameters	1233 / 0 / 101
Goodness-of-fit on F^2	1.120
Final R indices [$F_o^2 > 2\sigma(F_o^2)$] [a]	R_1 = 0.0109, wR_2 = 0.0257
R indices (all data) [a]	R_1 = 0.0116, wR_2 = 0.0259
Largest diff. peak and hole	0.382 and -0.337 e·Å^{-3}

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

Table S5. Fractional atomic coordinates ($\times 10^4$), equivalent isotropic displacement parameters ($Å^2 \times 10^3$), and bond valence sum (BVS) for $LiBaAl(BO_3)_2$. $U(eq)$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atoms	Wyck.	*x*	*y*	*z*	$U_{(eq)}$	S.O.F.	BVS
			$LiBaAl(BO_3)_2$				
Li(1)	2i	652(7)	-475(4)	-6123(3)	14(1)	1	1.11
Ba(1)	2i	1624(1)	-710(1)	-1372(1)	11(1)	1	1.88
Al(1)	2i	4297(1)	-1635(1)	-3932(1)	8(1)	1	2.8
B(1)	2i	-1607(4)	-2377(2)	-4927(2)	10(1)	1	2.96
B(2)	2i	5448(4)	1062(2)	-2666(2)	10(1)	1	3.00
O(1)	2i	3525(3)	-87(1)	-3214(1)	12(1)	1	1.98
O(2)	2i	7954(3)	1309(2)	-2825(1)	14(1)	1	1.91
O(3)	2i	1126(3)	-1988(1)	-4978(1)	10(1)	1	2.11
O(4)	2i	7155(3)	-1312(2)	-4427(1)	12(1)	1	1.97
O(5)	2i	-2818(3)	-3701(2)	-5345(1)	14(1)	1	1.85
O(6)	2i	4554(3)	1808(2)	-1912(1)	17(1)	1	1.95

Table S6. Selected bond lengths (Å) and angles (°) for $LiBaAl(BO_3)_2$.

Li(1)-O(1)#1	2.024(4)	O(2)#5-Ba(1)-O(6)	67.06(4)
Li(1)-O(2)#3	1.880(4)	O(3)#4-Ba(1)-O(1)	143.41(3)
Li(1)-O(3)	1.967(3)		
Li(1)-O(4)#3	1.905(4)	O(3)#4-Ba(1)-O(2)#6	67.66(4)
		O(3)#4-Ba(1)-O(2)#5	137.19(4)
Ba(1)-O(1)	2.9202(13)	O(3)#4-Ba(1)-O(5)#4	48.71(3)
Ba(1)-O(2)#5	2.8053(13)	O(3)#4-Ba(1)-O(6)	151.71(4)
Ba(1)-O(2)#6	2.8413(13)	O(5)#7-Ba(1)-O(1)	121.56(4)
Ba(1)-O(3)#4	2.7891(12)	O(5)#8-Ba(1)-O(1)	85.22(4)
Ba(1)-O(5)#7	2.7821(14)	O(5)#8-Ba(1)-O(2)#6	80.34(4)
Ba(1)-O(5)#4	2.9566(13)	O(5)#7-Ba(1)-O(2)#5	95.14(4)
Ba(1)-O(5)#8	2.6916(13)	O(5)#8-Ba(1)-O(2)#5	142.97(4)
Ba(1)-O(6)	2.8380(13)	O(5)#7-Ba(1)-O(2)#6	149.36(4)
		O(5)#7-Ba(1)-O(3)#4	87.32(4)
Al(1)-O(1)	1.7597(14)	O(5)#8-Ba(1)-O(3)#4	79.32(4)
Al(1)-O(3)	1.7569(14)	O(5)#7-Ba(1)-O(5)#4	74.41(4)
Al(1)-O(4)	1.7495(13)	O(5)#8-Ba(1)-O(5)#7	77.74(4)
Al(1)-O(6)#6	1.7358(14)	O(5)#8-Ba(1)-O(5)#4	120.93(5)
B(1)-O(3)	1.408(2)	O(5)#8-Ba(1)-O(6)	76.11(4)
B(1)-O(4)#5	1.387(2)	O(5)#7-Ba(1)-O(6)	74.02(4)
B(1)-O(5)	1.337(2)	O(6)-Ba(1)-O(1)	47.59(4)
B(2)-O(1)	1.412(2)	O(6)-Ba(1)-O(2)#6	120.79(4)
B(2)-O(2)	1.331(2)	O(6)-Ba(1)-O(5)#4	139.18(4)
B(2)-O(6)	1.372(2)		
		O(3)-Al(1)-O(1)	105.74(6)
O(2)#3-Li(1)-O(1)#1	109.19(17)	O(4)-Al(1)-O(1)	114.41(7)
O(2)#3-Li(1)-O(3)	109.15(17)	O(4)-Al(1)-O(3)	110.56(7)
O(2)#3-Li(1)-O(4)#3	107.77(17)	O(6)#6-Al(1)-O(1)	109.56(7)
O(3)-Li(1)-O(1)#1	110.81(16)	O(6)#6-Al(1)-O(3)	113.52(7)
O(4)#3-Li(1)-O(1)#1	110.07(16)	O(6)#6-Al(1)-O(4)	103.28(7)
O(4)#3-Li(1)-O(3)	109.78(17)		
		O(4)#5-B(1)-O(3)	115.44(16)
O(1)-Ba(1)-O(5)#4	153.04(4)	O(5)-B(1)-O(3)	119.76(17)
O(2)#5-Ba(1)-O(1)	67.51(4)	O(5)-B(1)-O(4)#5	124.80(17)
O(2)#6-Ba(1)-O(1)	77.20(4)	O(2)-B(2)-O(1)	122.51(17)
O(2)#5-Ba(1)-O(2)#6	115.153(17)	O(2)-B(2)-O(6)	124.15(17)
O(2)#6-Ba(1)-O(5)#4	99.42(4)	O(6)-B(2)-O(1)	113.19(16)
O(2)#5-Ba(1)-O(5)#4	90.84(4)		

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y,-z-1; #2 x,-y-1/2,z-1/2; #3 -x+1,-y,-z-1; #4 x,-y-1/2,z+1/2; #5 x-1,y,z; #6 -x+1,y-1/2,-z-1/2; #7 -x,y+1/2,-z-1/2; #8 x+1,-y-1/2,z+1/2; #9 -x,y-1/2,-z-1/2; #10 x+1,y,z; #11 -x+1,y+1/2,-z-1/2; #12 x-1,-y-1/2,z-1/2.

Table S7. Investigation of the reported disorder-free borate containing isolated [MgO_4] groups.

No.	Formula	Space group	Symmetry	B-O basic units	Mg-O groups	Ref.
1	$Na_3MgB_5O_{10}$	*Pbca*	CS	[BO_3]+[BO_4]	isolated [MgO_4]	49
2	$Cs_4Mg_4(BO_3)_4$	$P2_1/c$	CS	[BO_3]	isolated [MgO_4]	50
3	$Rb_3MgB_5O_{10}$	$P2_1/c$	CS	[BO_3]+[BO_4]	isolated [MgO_4]	This work
4	$Rb_{18}Mg_6(B_5O_{10})_3(B_7O_{14})_2F$	*C*2/*c*	CS	[BO_3]+[BO_4]	isolated [MgO_4]	51
5	$Cs_{18}Mg_6(B_5O_{10})_3(B_7O_{14})_2F$	*C*2/*c*	CS	[BO_3]+[BO_4]	isolated [MgO_4]	51
6	$Ca_{16}Mg(B_{13}O_{17}(OH)_{12})_4Cl_6(H_2O)_{28}$	*Pba*2	NCS	[BO_3]+[BO_4]	isolated [MgO_4]	52

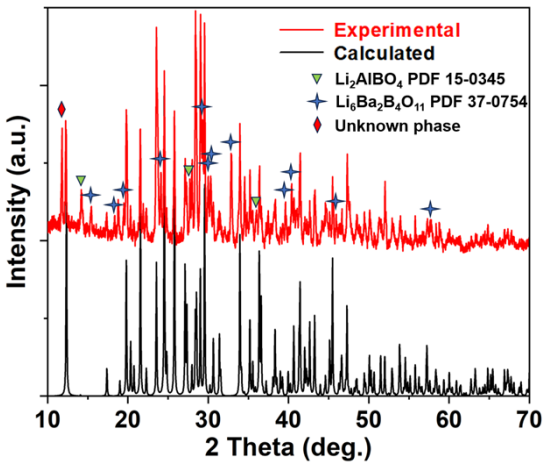

Figure S1. Comparison of XRD patterns of $LiBaAl(BO_3)_2$ samples obtained by spontaneous crystallization method with theoretical results.

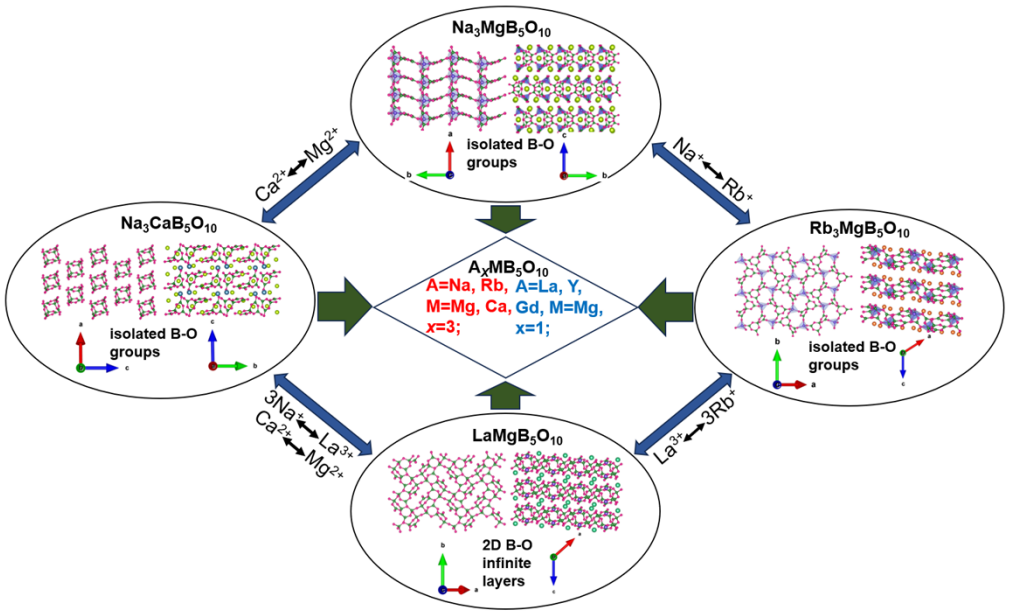

Figure S2. The structural transformation between $A_XMB_5O_{10}$ (A=Na, Rb, M=Mg, Ca, x=3; A=La, Y, Gd, M=Mg, x=1).

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