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# $Li_3Ba_4Sc_3(BO_3)_4(B_2O_5)_2$: featuring the coexistence of isolated $BO_3$ and $B_2O_5$ units

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## Experiment section

### Reagents

All of the starting reagents, i.e., $Li_2CO_3$, $BaCO_3$, $Sc_2O_3$, LiF, NaF and $B_2O_3$, were of analytical grade and used without further purification.

### Synthesis of Polycrystalline

$Li_2CO_3$, $BaCO_3$, $Sc_2O_3$, and $B_2O_3$ were fully mixed and grind with a molar ratio of $Li_2CO_3$: $BaCO_3$: $Sc_2O_3$: $B_2O_3$=1.5: 4:1.5:4. Then, the mixture was gradually heated to 723K at the rate of 50K/h from room temperature with several intermediate grindings and continued to heat up to 1053K in 24h and sintered at that temperature for 12h.

### Crystal Growth

Colorless rod-like single crystals of LBSBO were successfully obtained from LiF-NaF-$B_2O_3$ flux with molar ratio of LBSBO: LiF: NaF: $B_2O_3$=1:3:2:2. After weighing the corresponding reactants according to the above proportion, the mixture was ground in a mortar and then transferred to a ϕ10×20 platinum crucible. Afterward, the platinum crucible was heated in a crystal growth furnace at a rate of 50K/h from room temperature to 1223K and hold at this temperature for 24h. After that, the high-temperature melt was cooled to 923K at a cooling rate of 1K/h, followed by rapid cooling to room temperature at a rate of 25K/h.

### Powder X-ray Diffraction (PXRD)

PXRD data of LBSBO was collected on Bruker D8 Focus diffractometer equipped with Cu Kα radiation (λ=1.5418Å) in the 2θ range of 5-70° at room temperature.

### Single-Crystal Structure Determination

The diffraction data were collected on a Rigaku Oxford Diffraction single-crystal diffractometer equipped with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 293 K. The crystal structures were solved by direct methods with the program SHELXS-97 and refined by full-matrix least squares on $F^2$ by SHELXL-97 programs.[1] The structures were verified using the ADDSYM algorithm from the program PLATON, and no higher symmetry was discovered. The relevant crystallographic data are presented in **Table S1**. Additional crystallographic information is provided in **Table S2-S4.**

**Thermal analysis.**

The different scanning calorimetry (DSC) analysis was performed on NETZSCH STA 409 CD thermal analyzer under $N_2$ flow with a sample heating rate of 20 °C/min from room temperature to 1000 °C.

**UV-Vis-Near-IR (NIR) Diffuse-Reflectance Spectrum.**

The reflectance spectra were measured in the range of 200-2000 nm by Cary 7000 UV-VIS-NIR Universal Measurement Spectrophotometer. BaSO4 was employed as the 100% reflectance standard.

**Infrared spectra**

Infrared spectroscopy of LBSBO were collected on a Varian Excalibur 3100 spectrometer in air from 400 $cm^{-1}$ to 1500 $cm^{-1}$ to clarify the coordination environment of the boron atoms.

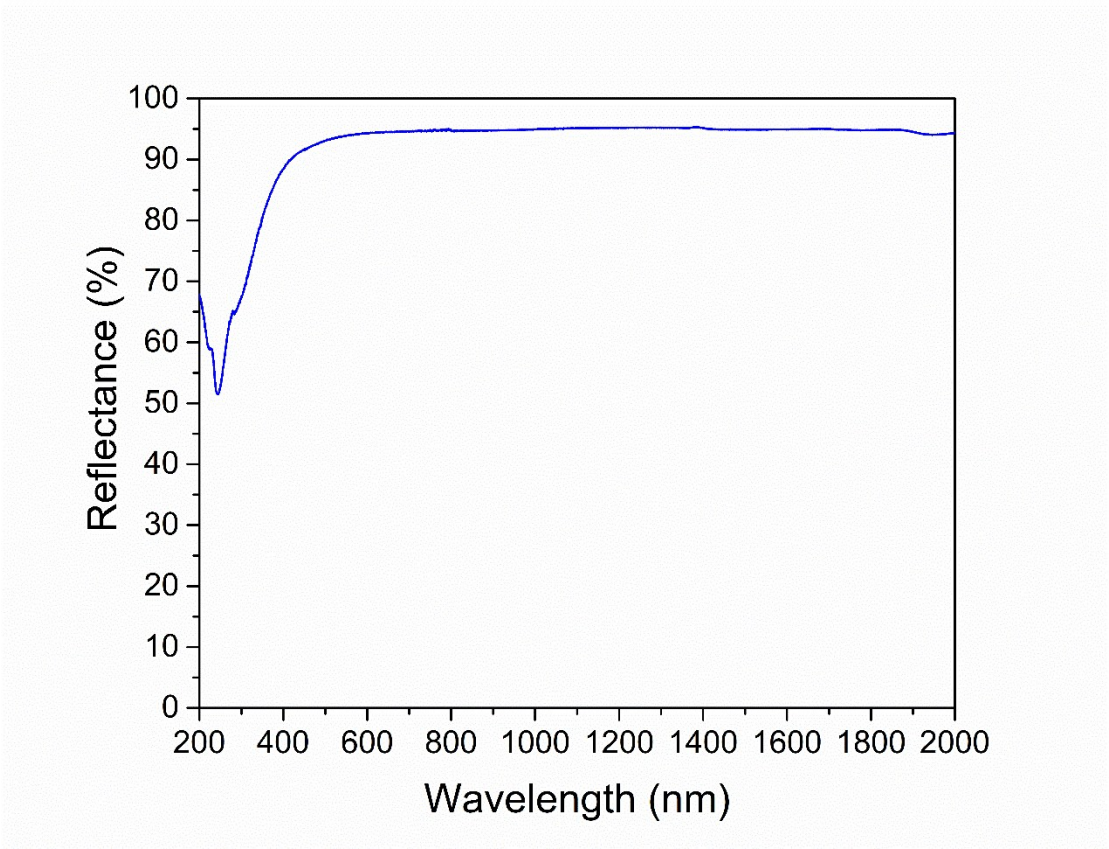


Figure S1. The UV-vis NIR diffuse reflectance spectrum of **LBSBO**.

Table 1. Crystal data and structure refinement for **LBSBO**.

| | |
|---|---|
| Formula | $Li_3Ba_4Sc_3B_8O_{22}$ |
| Weight | 1143.4735 |
| Temperature/K | 293(2) |
| Crystal system | triclinic |
| Space group | $P\bar{1}$ |
| a/Å | 9.7959(3) |
| b/Å | 10.2519(2) |
| c/Å | 11.5878(3) |
| α/° | 85.069(2) |
| β/° | 68.734(2) |
| γ/° | 62.795(2) |
| Volume/Å$^3$ | 960.02(5) |
| Z | 2 |
| $\rho_{calc}$g/cm$^3$ | 3.956 |
| μ/mm$^{-1}$ | 9.178 |
| F(000) | 1024.0 |
| Independent reflections | 3921 [$R_{int}$ = 0.0404] |
| Data/restraints/parameters | 3921/0/361 |
| Goodness-of-fit on $F^2$ | 1.066 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0196, $wR_2$ = 0.0490 |
| Final R indexes [all data] | $R_1$ = 0.0229, $wR_2$ = 0.0509 |

Table 2 Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters($Å^2×10^3$) for **LBSBO**.

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| Ba1 | 0.12594 (2) | 0.80760 (2) | −0.14850 (2) | 8.45(6) |
| Ba2 | 0.37961 (2) | 0.69832 (2) | 1.14932 (2) | 8.47(6) |
| Ba3 | 0.32855 (3) | 0.35721 (2) | 0.55353 (2) | 8.93(6) |
| Ba4 | 0.19285 (3) | 1.12431 (2) | 0.43844 (2) | 9.55(6) |
| Sc1 | 0.23857 (7) | 0.74789 (6) | 0.50868 (5) | 6.59(14) |
| Sc2 | 0.57523 (8) | 0.70243 (7) | 0.79199 (6) | 5.34(13) |
| Sc3 | −0.07211 (8) | 0.78925 (7) | 0.21299 (6) | 5.63(13) |
| O1 | 0.3537 (3) | 0.4507 (3) | 0.0847 (2) | 12.9(5) |
| O2 | 0.1586 (3) | 1.0539 (3) | 0.9051 (2) | 15.9(6) |
| O3 | −0.0219 (3) | 1.1239 (3) | 0.3434 (2) | 9.4(5) |
| O4 | 0.1492 (3) | 0.8881 (3) | 0.3883 (2) | 13.6(6) |
| O5 | 0.5115 (3) | 0.8513 (3) | 0.6578 (2) | 11.0(5) |
| O6 | 0.0391 (3) | 0.9084 (3) | 0.2328 (2) | 11.5(5) |
| O7 | 0.3076 (3) | 1.0871 (3) | 0.6404 (2) | 9.9(5) |
| O8 | 0.3509 (3) | 0.8725 (3) | 0.5364 (2) | 13.7(5) |
| O9 | 0.3707 (3) | 0.8399 (3) | 0.9412 (2) | 10.4(5) |
| O10 | 0.5457 (3) | 0.3772 (3) | 0.6408 (2) | 12.2(5) |
| O11 | 0.7968 (3) | 0.5804 (3) | 0.6400 (2) | 10.9(5) |
| O12 | 0.4570 (3) | 0.5905 (3) | 0.7696 (2) | 11.8(5) |
| O13 | 0.1316 (3) | 0.6650 (3) | 0.0608 (2) | 10.2(5) |

| | | | | |
|---|---|---|---|---|
| O14 | −0.0166 (3) | 0.6490 (3) | 0.3530 (2) | 12.9(5) |
| O15 | 0.3279 (3) | 0.6035 (3) | 0.6288 (2) | 15.1(6) |
| O16 | 0.1152 (3) | 0.6255 (3) | 0.4985 (2) | 15.4(6) |
| O17 | 0.7234 (3) | 0.7923 (3) | 0.8095 (2) | 11.5(5) |
| O18 | 0.2088 (3) | 0.3138 (3) | −0.1955 (2) | 12.8(5) |
| O19 | 0.5808 (3) | 1.0559 (3) | 0.8212 (2) | 17.9(6) |
| O20 | 0.0418 (3) | 0.5761 (3) | −0.1523 (2) | 15.0(6) |
| O21 | 0.2489 (3) | 1.0770 (3) | 1.0568 (2) | 12.4(5) |
| O22 | 0.2478 (3) | 0.4322 (3) | −0.0591 (2) | 11.5(5) |
| B1 | 0.0538 (4) | 0.9727 (4) | 0.3221 (3) | 5.5(7) |
| B2 | 0.3876 (5) | 0.9362 (4) | 0.6134 (3) | 7.2(8) |
| B3 | 0.2656 (5) | 0.9840 (4) | 0.9643 (4) | 8.2(8) |
| B4 | 0.2392 (5) | 0.5214 (4) | 0.0320 (4) | 7.5(8) |
| B5 | 0.4448 (5) | 0.5251 (4) | 0.6785 (3) | 6.8(8) |
| B6 | 0.1570 (5) | 0.4475 (4) | −0.1372 (3) | 7.5(8) |
| B7 | 0.1012 (5) | 0.5670 (4) | 0.4030 (4) | 7.6(8) |
| B8 | 0.6739 (5) | 0.9325 (4) | 0.8562 (3) | 9.8(8) |
| Li1 | −0.1855 (9) | 0.7123 (8) | −0.0482 (7) | 27.9(17) |
| Li2 | 0.4030 (9) | 1.1079 (9) | 0.7685 (7) | 29.1(17) |
| Li3 | −0.0604 (11) | 0.6012 (9) | −0.2768 (8) | 39(2) |

Table 3. Atomic displacement parameters of **LBSBO** (Å$^2$).

| atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|
| Ba1 | 0.00922 (11) | 0.00696 (11) | 0.00831 (11) | −0.00242 (9) | −0.00401 (8) | 0.00086 (8) |
| Ba2 | 0.00947 (11) | 0.00654 (11) | 0.00788 (11) | −0.00213 (9) | −0.00359 (8) | 0.00064 (8) |
| Ba3 | 0.01014 (11) | 0.00846 (11) | 0.01011 (11) | −0.00477 (9) | −0.00506 (8) | 0.00100 (8) |
| Ba4 | 0.01111 (11) | 0.01063 (11) | 0.01016 (11) | −0.00642 (9) | −0.00557 (8) | 0.00172 (8) |
| Sc1 | 0.0065 (3) | 0.0041 (3) | 0.0089 (3) | −0.0002 (3) | −0.0053 (3) | −0.0012 (2) |
| Sc2 | 0.0057 (3) | 0.0045 (3) | 0.0060 (3) | −0.0018 (3) | −0.0029 (2) | −0.0002 (2) |
| Sc3 | 0.0057 (3) | 0.0046 (3) | 0.0068 (3) | −0.0016 (3) | −0.0032 (2) | −0.0005 (2) |
| O1 | 0.0162 (13) | 0.0102 (12) | 0.0137 (12) | −0.0043 (11) | −0.0094 (11) | 0.0019 (10) |
| O2 | 0.0206 (14) | 0.0102 (13) | 0.0184 (13) | −0.0030 (11) | −0.0139 (11) | 0.0014 (10) |
| O3 | 0.0097 (12) | 0.0077 (12) | 0.0092 (11) | −0.0018 (10) | −0.0047 (10) | 0.0005 (9) |
| O4 | 0.0176 (14) | 0.0104 (12) | 0.0130 (12) | −0.0027 (11) | −0.0107 (11) | 0.0016 (10) |
| O5 | 0.0087 (12) | 0.0115 (12) | 0.0120 (12) | −0.0022 (10) | −0.0063 (10) | 0.0021 (10) |
| O6 | 0.0122 (13) | 0.0098 (12) | 0.0153 (12) | −0.0048 (10) | −0.0076 (10) | −0.0021 (10) |
| O7 | 0.0096 (12) | 0.0062 (12) | 0.0103 (11) | −0.0010 (10) | −0.0027 (10) | −0.0015 (9) |
| O8 | 0.0131 (13) | 0.0091 (12) | 0.0216 (13) | −0.0045 (11) | −0.0096 (11) | −0.0002 (10) |
| O9 | 0.0113 (12) | 0.0065 (12) | 0.0084 (11) | −0.0010 (10) | −0.0024 (10) | 0.0007 (9) |
| O10 | 0.0130 (13) | 0.0087 (12) | 0.0114 (12) | 0.0001 (10) | −0.0065 (10) | −0.0024 (9) |
| O11 | 0.0085 (12) | 0.0079 (12) | 0.0103 (11) | 0.0013 (10) | −0.0027 (10) | −0.0040 (9) |
| O12 | 0.0129 (13) | 0.0106 (12) | 0.0165 (13) | −0.0057 (11) | −0.0097 (11) | 0.0000 (10) |
| O13 | 0.0098 (12) | 0.0072 (12) | 0.0080 (11) | −0.0011 (10) | −0.0006 (10) | −0.0010 (9) |

| | | | | | | |
|---|---|---|---|---|---|---|
| O14 | 0.0131 (13) | 0.0115 (13) | 0.0135 (12) | −0.0041 (11) | −0.0070 (10) | 0.0047 (10) |
| O15 | 0.0183 (14) | 0.0095 (12) | 0.0185 (13) | −0.0006 (11) | −0.0148 (11) | −0.0010 (10) |
| O16 | 0.0169 (14) | 0.0062 (12) | 0.0291 (15) | −0.0028 (11) | −0.0173 (12) | −0.0020 (11) |
| O17 | 0.0126 (13) | 0.0130 (13) | 0.0124 (12) | −0.0075 (11) | −0.0056 (10) | −0.0016 (10) |
| O18 | 0.0111 (13) | 0.0126 (13) | 0.0157 (12) | −0.0047 (11) | −0.0058 (10) | −0.0031 (10) |
| O19 | 0.0260 (15) | 0.0129 (13) | 0.0275 (15) | −0.0117 (12) | −0.0210 (13) | 0.0080 (11) |
| O20 | 0.0185 (14) | 0.0107 (13) | 0.0227 (14) | −0.0075 (11) | −0.0143 (11) | 0.0043 (10) |
| O21 | 0.0140 (13) | 0.0102 (12) | 0.0153 (12) | −0.0029 (11) | −0.0108 (11) | −0.0014 (10) |
| O22 | 0.0107 (13) | 0.0095 (12) | 0.0132 (12) | −0.0006 (10) | −0.0074 (10) | −0.0046 (10) |
| B1 | 0.0031 (17) | 0.0073 (18) | 0.0065 (17) | −0.0042 (15) | −0.0001 (14) | 0.0023 (14) |
| B2 | 0.0063 (18) | 0.0047 (17) | 0.0090 (18) | −0.0025 (15) | −0.0007 (15) | −0.0012 (14) |
| B3 | 0.0090 (19) | 0.0081 (18) | 0.0078 (17) | −0.0047 (16) | −0.0023 (15) | 0.0013 (14) |
| B4 | 0.0089 (19) | 0.0059 (18) | 0.0082 (18) | −0.0057 (16) | −0.0007 (15) | 0.0012 (14) |
| B5 | 0.0079 (19) | 0.0053 (18) | 0.0058 (17) | −0.0039 (15) | 0.0000 (14) | 0.0000 (14) |
| B6 | 0.0088 (19) | 0.0094 (18) | 0.0078 (17) | −0.0074 (16) | −0.0029 (15) | 0.0038 (14) |
| B7 | 0.0066 (18) | 0.0069 (18) | 0.0090 (18) | −0.0046 (15) | −0.0010 (14) | 0.0031 (14) |
| B8 | 0.0112 (19) | 0.015 (2) | 0.0067 (17) | −0.0087 (17) | −0.0026 (15) | −0.0003 (15) |
| Li1 | 0.029 (4) | 0.018 (4) | 0.046 (4) | −0.013 (3) | −0.024 (4) | 0.015 (3) |
| Li2 | 0.022 (4) | 0.033 (4) | 0.032 (4) | −0.009 (3) | −0.016 (3) | 0.005 (3) |
| Li3 | 0.032 (5) | 0.026 (4) | 0.055 (5) | 0.006 (4) | −0.034 (4) | −0.009 (4) |

Table 4. Bond lengths and bond angles of **LBSBO**.

| | | | |
|---|---|---|---|
| Ba1—O3$^{i}$ | 2.716 (2) | Li1—O17$^{xv}$ | 2.085 (8) |
| Ba1—O13 | 2.727 (2) | Li1—O20 | 1.965 (8) |
| Ba1—O12$^{ii}$ | 2.811 (2) | Li2-O2 | 2.618 |
| Ba1—O2$^{ii}$ | 2.831 (3) | Li2—O18$^{xvi}$ | 2.038 (8) |
| Ba1—O20 | 2.854 (3) | Li2—O7 | 2.089 (8) |
| Ba1—O15$^{ii}$ | 2.897 (3) | Li2—O19 | 1.886 (8) |
| Ba1—O6$^{i}$ | 2.897 (2) | Li2—O5 | 2.595 (9) |
| Ba1—O2$^{iii}$ | 3.018 (3) | Li3—O11$^{xv}$ | 2.054 (9) |
| Ba1—O21$^{iii}$ | 3.070 (3) | Li3—O17$^{xv}$ | 2.081 (8) |
| Ba1—O9$^{ii}$ | 3.088 (3) | Li3—O14$^{xii}$ | 2.463 (9) |
| Ba2—O9 | 2.714 (2) | Li3—O20 | 1.975 (8) |
| Ba2—O10$^{iv}$ | 2.738 (2) | B1—O3 | 1.377 (4) |
| Ba2—O19$^{v}$ | 2.785 (3) | B1—O4 | 1.371 (4) |
| Ba2—O1$^{vi}$ | 2.850 (3) | B1—O6 | 1.356 (5) |
| Ba2—O6$^{vi}$ | 2.855 (2) | B2—O5 | 1.380 (4) |
| Ba2—O1$^{vii}$ | 2.904 (3) | B2—O8 | 1.378 (5) |
| Ba2—O12$^{iv}$ | 2.914 (2) | B3—O2 | 1.354 (5) |
| Ba2—O4$^{vi}$ | 2.988 (2) | B3—O9 | 1.338 (5) |
| Ba2—O22$^{vii}$ | 3.035 (2) | B3—O21 | 1.412 (5) |
| Ba2—O13$^{vi}$ | 3.114 (3) | B4—O1 | 1.354 (5) |
| Ba3—O15 | 2.737 (3) | B4—O13 | 1.341 (5) |
| Ba3—O10 | 2.754 (3) | B4—O22 | 1.410 (5) |
| Ba3—O16 | 2.784 (2) | B5—O10 | 1.377 (4) |
| Ba3—O8$^{vii}$ | 2.789 (3) | B5—O12 | 1.365 (5) |
| Ba3—O18$^{vi}$ | 2.795 (2) | B5—O15 | 1.359 (5) |
| Ba3—O11$^{vii}$ | 2.824 (2) | B6—O18 | 1.366 (5) |
| Ba3—O5$^{vii}$ | 2.841 (2) | B6—O20 | 1.336 (5) |
| Ba3—O14$^{viii}$ | 2.878 (3) | B6—O22 | 1.438 (5) |
| Ba3—O7$^{ix}$ | 2.935 (2) | B7—O11$^{vii}$ | 1.385 (5) |
| Ba4—O3 | 2.707 (3) | B7—O14 | 1.375 (5) |
| Ba4—O8 | 2.733 (2) | B7—O14 | 1.375 (5) |
| Ba4—O4 | 2.784 (3) | B7—O16 | 1.378 (5) |
| Ba4—O16$^{iii}$ | 2.804 (3) | B8—O17 | 1.377 (5) |
| Ba4—O5$^{x}$ | 2.823 (3) | B8—O19 | 1.312 (5) |
| Ba4—O17$^{x}$ | 2.858 (2) | B8—O21$^{v}$ | 1.438 (5) |
| Ba4—O7 | 2.872 (2) | O6—B1—O4 | 120.3 (3) |
| Ba4—O14$^{iii}$ | 2.914 (3) | O6—B1—O3 | 120.1 (3) |
| Ba4—O11$^{x}$ | 3.121 (2) | O4—B1—O3 | 119.6 (3) |
| Ba4—O19$^{x}$ | 3.123 (3) | O8—B2—O7 | 120.0 (3) |
| Sc1—O4 | 2.041 (2) | O8—B2—O5 | 120.6 (3) |
| Sc1—O15 | 2.059 (2) | O7—B2—O5 | 119.3 (3) |
| Sc1—O10$^{vii}$ | 2.088 (2) | O9—B3—O2 | 123.3 (3) |

| | | | |
|---|---|---|---|
| Sc1—O3$^{iii}$ | 2.090 (2) | O9—B3—O21 | 123.6 (3) |
| Sc1—O8 | 2.135 (3) | O2—B3—O21 | 113.1 (3) |
| Sc1—O16 | 2.137 (3) | O13—B4—O1 | 122.7 (3) |
| Sc2—O12 | 2.052 (3) | O13—B4—O22 | 123.2 (3) |
| Sc2—O9 | 2.078 (2) | O1—B4—O22 | 114.0 (3) |
| Sc2—O1$^{vii}$ | 2.080 (2) | O15—B5—O12 | 120.3 (3) |
| Sc2—O17 | 2.114 (3) | O15—B5—O10 | 119.5 (3) |
| Sc2—O11 | 2.122 (2) | O12—B5—O10 | 120.1 (3) |
| Sc2—O5 | 2.136 (2) | O20—B6—O18 | 125.6 (3) |
| Sc3—O6 | 2.044 (3) | O20—B6—O22 | 123.9 (3) |
| Sc3—O13 | 2.055 (2) | O18—B6—O22 | 110.5 (3) |
| Sc3—O2$^{iii}$ | 2.096 (2) | O14—B7—O16 | 121.9 (3) |
| Sc3—O18$^{xii}$ | 2.116 (3) | O14—B7—O11$^{vii}$ | 118.8 (3) |
| Sc3—O14 | 2.126 (2) | O16—B7—O11$^{vii}$ | 119.3 (3) |
| Sc3—O7$^{iii}$ | 2.161 (2) | O19—B8—O17 | 126.1 (3) |
| Li1—O21$^{iii}$ | 1.960 (7) | O19—B8—O21$^{v}$ | 124.7 (3) |
| Li1—O22$^{xii}$ | 2.018 (7) | O17—B8—O21$^{v}$ | 109.1 (3) |

Symmetry codes: (i) −*x*, −*y*+2, −*z*; (ii) *x*, *y*, *z*−1; (iii) −*x*, −*y*+2, −*z*+1; (iv) −*x*+1, −*y*+1, −*z*+2; (v) −*x*+1, −*y*+2, −*z*+2; (vi) *x*, *y*, *z*+1; (vii) −*x*+1, −*y*+1, −*z*+1; (viii) −*x*, −*y*+1, −*z*+1; (ix) *x*, *y*−1, *z*; (x) −*x*+1, −*y*+2, −*z*+1; (xi) *x*+1, *y*, *z*+1; (xii) −*x*, −*y*+1, −*z*; (xiii) *x*, *y*+1, *z*; (xiv) *x*, *y*−1, *z*−1; (xv) *x*−1, *y*, *z*−1; (xvi) *x*, *y*+1, *z*+1.

Table S5. The BVS of **LBSBO**.

| Atom | BVS | Atom | BVS |
|---|---|---|---|
| Ba1 | 2.116 | O3 | 2.1571 |
| Ba2 | 2.1181 | O4 | 2.0915 |
| Ba3 | 2.2361 | O5 | 1.959 |
| Ba4 | 2.2289 | O6 | 2.0527 |
| Li1 | 0.9499 | O7 | 1.9913 |
| Li2 | 0.7799 | O8 | 2.0162 |
| Li3 | 0.7731 | O9 | 2.0746 |
| Sc1 | 3.1501 | O10 | 2.1029 |
| Sc2 | 3.101 | O11 | 2.001 |
| Sc3 | 3.0876 | O12 | 2.0342 |
| B1 | 3.025 | O13 | 2.0813 |
| B2 | 2.9365 | O14 | 1.9318 |
| B3 | 3.0349 | O15 | 2.1029 |
| B4 | 3.031 | O16 | 2.0108 |
| B5 | 3.0329 | O17 | 2.0796 |
| B6 | 2.9475 | O18 | 1.979 |
| B7 | 2.9342 | O19 | 1.8702 |
| B8 | 2.991 | O20 | 1.8392 |
| O1 | 2.0031 | O21 | 2.1233 |
| O2 | 1.9872 | 022 | 2.1019 |

## References

(1) Sheldrick, G. SHELXS-97, Program for crystal structure solution; *University of Göttingen: Göttingen, Germany,* 1997.