Electronic Supplementary Material (ESI) for Chemical Communications.

Electronic Supplementary Information (ESI)

$Sr[B(OH)_4](IO_3)$ and $Li_4Sr_5[B_{12}O_{22}(OH)_4](IO_3)_2$: Two Unprecedented Metal Borate-Iodates Showing Subtle Balance of Enlarged Band Gap and Birefringence†

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Methods

Crystals Growth

$LiBO_2$ (99%), I_2O_5 (99%), HIO_3 (99%), and $Sr(OH)_2 \cdot 8H_2O$ (>99%) were all purchased from Taitan and used as received. Both the crystals were synthesized under traditional subcritical hydrothermal condition. A mixture of $LiBO_2$ (0.015 mol, 0.746 g), I_2O_5 (0.005 mol, 1.669 g), $Sr(OH)_2 \cdot 8H_2O$ (0.01 mol, 2.656 g) and H_2O (10 mL) were sealed in an autoclave equipped with a Teflon liner (23 mL) and heated at 220 ^oC for 5 days, followed by slow cooling to room temperature at a rate of 3 $^oC \cdot h^{-1}$. The reaction product was washed with deionized water and ethanol, and then dried in air. Large amount of octahedral colorless crystal were obtained and determined to be $Li_4Sr_5[B_{12}O_{22}(OH)_4](IO_3)_2$ (LSBIO). Under the same experimental conditions and operating procedures, when I_2O_5 was changed to be HIO_3 (0.01 mol, 1.759 g) or $NaIO_3$ (0.005 mol, 0.99g), the $Sr[B(OH)_4](IO_3)$ (SBIO) crystal was synthesized. The largest yields of LSBIO and SBIO were about 70% according to Sr.

Physical Measurements

Powder XRD analysis was carried out on a Miniflex-600 diffractometer with Cu Kα radiation (λ = 1.54059 Å) at room temperature in the angular range of 2θ=5−75° with a scan step width of 0.02° and a fixed time of 0.2 s. Single crystal X-ray diffraction data for SBIO and LSBIO were collected at room temperature on a Rigaku Mercury CCD diffractometer equipped with graphite-monochromatic Mo Kα radiation (λ = 0.71073 Å). The hemisphere of data was corrected using a narrow-frame method with ω-scan mode. By using the CrystalClear program, all data were integrated, and the intensities were corrected for Lorentz polarization, air absorption, and absorption attributable to the variation in the path length through the detector faceplate. Absorption corrections were also applied based on the Multiscan technique. The crystal structures were determined by the direct methods and refined by full-matrix least-squares fitting on F^2 using SHELXL.[1,2] All the atoms were refined with anisotropic displacement parameters. All the thermal parameters were satisfying. The PLATON program[3] was used to check the correctness of the structures and no higher symmetry was found. The thermogravimetric analysis (TGA) and differential thermal analysis (DTA) for SBIO and LSBIO were conducted on a Netzsch STA449F3 simultaneous analyzer. Reference (Al_2O_3) and crystal samples (5−10 mg) were enclosed in Al_2O_3 crucibles and heated from 30 to 1100 ^oC at a rate of 10 $^oC \cdot min^{-1}$ under a constant flow of nitrogen gas. The UV−vis-NIR diffuse reflections were measured at room temperature in the range of 190−2500 nm with $BaSO_4$ as the standard of 100% reflectance. All the data were collected on a PerkinElmer Lamda-950 ultraviolet/visible/near-infrared spectrophotometer. The reflectance values were converted to absorbance using the Kubelka-Munk function $F(R) = (1-R)^2/(2R) = K/S$ (R is the reflectance, K is the absorption, and S is the scattering).[4,5] The birefringence were measured on a Nikon ECLIPSE LV100 POL polarizing microscope with the wavelength of the light source in 589.6 nm. The formula for the calculation of birefringence can be expressed as follows: $\Delta R(\text{retardation}) = \Delta n \times T$, where ΔR represents the optical path difference, Δn denotes the birefringence, and T denotes the thickness of the crystal. The positive and negative rotation of compensatory can determine the retardation. The crystals were ground into micron fragment for the measurement of the maximum birefringence. The retardation of LSBIO and SBIO were 850 and 579 nm, respectively. The thickness of LSBIO and SBIO were 20.72 and 10.8 μm.

Computional methods

The electronic structure for all compounds were accomplished by using CASTEP, a plane-wave pseudopotential total energy package based on density functional theory (DFT).[6,7] The functional developed by Perdew-Burke-Emzerhoff (PBE) functional within the generalized gradient approximation (GGA)[8] form were adopted to describe the exchange-correlation energy. Interaction of the electrons with ion cores was represented by the norm-conserving pseudopotentials, and the valence electrons were treated as H: $1s^1$, Li: $2s^1$, B: $2s^22p^1$, O: $2s^22p^4$, Sr: $4s^24P^65S^2$, I: $5s^25p^5$. The k-point of first Brillouin zone for SBIO and LSBIO were sampled as 2 × 2 × 2 and 1 × 1 × 2 Monkhorst–Pack scheme, respectively.[9] The energy cut-off and convergence criteria were set to 340 and 750 eV for SBIO and LSBIO. The self-consistent convergence of the total energy was 1.0×10^{-6} eV per atom for the two compounds. Because of the commonly underestimate of band gap by DFT, the scissor operator was adopted to make the calculated band gaps consistent with the experimental values.[10] Based on the scissor-corrected electron band structure, the imaginary part of the dielectric function was calculated according to the electron transition from the valence bands (VB) to conduction band (CB). Consequently, the real part of the dielectric function is obtained by the Kramers-Kronig[11] transform and the calculated refractive index is determined.

Table S1. Crystal data and structural refinement for SBIO and LSBIO

formula	$Sr[B(OH)_4](IO_3)$	$Li_4Sr_5[B_{12}O_{22}(OH)_4](IO_3)_2$
formula mass (amu)	341.36	1365.41
temperature (K)	293(2)	293(2)
λ(Å)	0.71073	0.71073
crystal system	Triclinic	Monoclinic
space group	P	C2/m
a (Å)	6.595(17)	14.245(8)
b(Å)	6.868(16)	11.239(5)
c (Å)	7.120(19)	9.215(5)
α (deg)	96.73(3)	90
β (deg)	108.18(2)	123.625(7)
γ (deg)	92.37(4)	90
V (Å^3)	303.3(13)	1228.5(11)
Z	2	2
ρ(calcd) (g/cm^3)	3.738	3.691
μ (mm^{-1})	13.959	13.446
F(000)	312	1256
ϑ (deg)	2.997-27.514	2.869-27.480
index range	$-8 \le h \le 7$, $-8 \le k \le 8$, $-9 \le l \le 9$	$-18 \le h \le 18$, $-14 \le k \le 14$, $-11 \le l \le 11$
Reflections collected / unique	3550/1384	4900/1472
R_{int}	0.0594	0.0316
Completeness to θ = 27.42° (%)	99.6	99.6
GOF on F^2	1.102	1.098
R_1/wR_2 $[F_o^2 > 2\sigma(F_o^2)]^a$	0.0395/0.0715	0.0220/0.0504
R_1/wR_2 (all data)	0.0462/0.0757	0.0248/0.0513
Extinction coefficient	0.0052(10)	n/a

$^aR_1(F) = \sum||F_o| - |F_c||/\sum|F_o|$, $wR_2(F_o^2) = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

Table S2. Atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2×10^3) for SBIO

Atom	x	y	z	U(eq)
I(1)	11963(1)	8998(1)	8954(1)	10(1)
Sr(1)	8883(1)	3538(1)	6932(1)	11(1)
O(1)	3099(7)	2824(7)	8634(7)	16(1)
O(2)	5413(7)	5103(7)	7626(7)	13(1)
O(3)	2036(7)	3563(7)	5283(7)	14(1)
O(4)	12783(7)	8289(7)	6785(7)	15(1)
O(5)	9383(7)	9898(7)	7776(7)	15(1)
O(6)	10979(7)	6646(7)	9320(7)	14(1)
O(7)	5258(7)	1774(7)	6527(8)	16(1)
B(1)	3931(13)	3320(12)	6948(12)	15(2)

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table S3. Selected bond lengths (Å) and angles (degrees) for SBIO

I(1)-O(6)	1.794(6)	O(2)-B(1)	1.469(10)
I(1)-O(4)	1.811(6)	O(3)-B(1)	1.460(9)
I(1)-O(5)	1.816(5)	O(7)-B(1)	1.466(9)
Sr(1)-O(7)	2.552(7)	O(6)-I(1)-O(4)	100.2(2)
Sr(1)-O(6)	2.607(6)	O(6)-I(1)-O(5)	97.4(2)
Sr(1)-O(5)#3	2.649(7)	O(4)-I(1)-O(5)	100.3(3)
Sr(1)-O(3)#4	2.657(7)	O(3)-B(1)-O(7)	115.2(7)
Sr(1)-O(6)#1	2.660(9)	O(3)-B(1)-O(2)	112.5(6)
Sr(1)-O(4)#5	2.661(8)	O(7)-B(1)-O(2)	104.2(6)
Sr(1)-O(3)#6	2.689(7)	O(3)-B(1)-O(1)	105.9(6)
Sr(1)-O(2)	2.724(7)	O(7)-B(1)-O(1)	109.0(6)
Sr(1)-O(1)#6	2.755(8)	O(2)-B(1)-O(1)	110.0(6)
O(1)-B(1)	1.532(10)		

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y+1,-z+2 #2 x,y+1,z #3 x,y-1,z #4 -x+1,-y+1,-z+1
#5 -x+2,-y+1,-z+1 #6 x+1,y,z #7 x-1,y,z

Table S4. Anisotropic displacement parameters (Å^2×10^3) for SBIO

The anisotropic displacement factor exponent takes the form: $-2\pi^2$ [$h^2 a^{*2}$ U11 + ... + 2hka* b*U12]

	U11	U22	U33	U23	U13	U12
I(1)	11(1)	11(1)	9(1)	4(1)	2(1)	2(1)
Sr(1)	12(1)	13(1)	9(1)	5(1)	3(1)	2(1)
O(1)	13(3)	21(3)	14(3)	4(2)	4(2)	-5(2)
O(2)	13(3)	11(3)	14(3)	8(2)	2(2)	3(2)
O(3)	14(3)	7(3)	17(3)	0(2)	-2(2)	3(2)
O(4)	16(1)	15(1)	14(1)	1(1)	6(1)	1(1)
O(5)	12(3)	19(3)	13(3)	9(2)	-1(2)	7(2)
O(6)	20(3)	10(3)	11(3)	4(2)	3(2)	0(2)
O(7)	15(3)	14(3)	22(3)	7(2)	9(2)	4(2)
B(1)	14(4)	16(5)	15(5)	4(4)	3(4)	3(4)

Table S5. Hydrogen coordinates (×10^4) and isotropic displacement parameters (Å^2×10^3) for SBIO

	x	y	z	U(eq)
H(1)	4510(20)	2770(110)	9300(40)	24
H(2)	4650(40)	6090(30)	7550(80)	19
H(3)	1890(110)	2460(60)	4560(100)	22
H(7)	4550(50)	660(20)	6350(110)	24

Table S6. Atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2×10^3) for LSBIO

Atom	x	y	z	U(eq)
Sr(1)	2136(1)	2024(1)	7374(1)	8(1)
Sr(2)	5000	0	5000	12(1)
I(1)	2208(1)	0	4209(1)	5(1)
B(1)	3957(3)	1121(4)	11219(5)	7(1)
B(2)	2095(4)	0	9974(7)	5(1)
B(3)	5000	2148(5)	10000	7(1)
B(4)	-288(3)	-2146(4)	7139(5)	7(1)
O(1)	523(2)	2962(2)	7372(3)	7(1)
O(2)	2694(3)	0	6503(4)	7(1)
O(3)	2746(2)	1090(2)	10529(3)	8(1)
O(4)	1360(3)	0	7958(4)	7(1)
O(5)	-1292(3)	0	9485(4)	8(1)
O(6)	4531(3)	0	12024(4)	7(1)
O(7)	4097(2)	1409(2)	9802(3)	9(1)
O(8)	3143(2)	1186(2)	4405(3)	12(1)
O(9)	-518(2)	-2089(2)	8425(3)	8(1)
O(10)	-772(2)	-1383(2)	5787(3)	9(1)
Li(1)	4196(7)	0	8402(11)	9(2)
Li(2)	0	0	5000	37(4)
Li(3)	0	787(17)	10000	16(4)

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table S7. Selected bond lengths (Å) and angles (degrees) for LSBIO

Sr(1)-O(8)#1	2.484(3)	B(4)-O(1)#7	1.395(4)
Sr(1)-O(7)	2.523(3)	B(4)-O(9)	1.397(5)
Sr(1)-O(1)	2.527(3)	O(2)-Li(1)	1.869(9)
Sr(1)-O(10)#2	2.552(3)	O(4)-Li(2)	2.309(3)
Sr(1)-O(2)	2.676(2)	O(5)-Li(3)	1.852(9)
Sr(1)-O(4)	2.710(2)	O(5)-Li(3)#15	1.852(9)
Sr(1)-O(3)	2.741(3)	O(6)-Li(1)#5	2.058(9)
Sr(1)-O(3)#3	2.810(3)	O(7)-Li(1)	2.095(6)
Sr(1)-O(9)#4	3.084(3)	O(7)-Li(1)#5	2.589(7)
Sr(2)-O(6)#5	2.437(4)	O(9)-Li(3)#15	1.899(15)
Sr(2)-O(6)#6	2.437(4)	O(10)-Li(2)	2.244(2)
Sr(2)-O(8)	2.733(3)	O(8)-I(1)-O(8)#7	94.08(17)
Sr(2)-O(8)#7	2.733(3)	O(8)-I(1)-O(2)	95.59(10)
Sr(2)-O(8)#8	2.733(3)	O(8)#7-I(1)-O(2)	95.59(10)
Sr(2)-O(8)#9	2.733(3)	O(6)-B(1)-O(7)	109.2(3)
Sr(2)-O(1)#10	2.962(3)	O(6)-B(1)-O(3)	113.0(3)
Sr(2)-O(1)#11	2.962(3)	O(7)-B(1)-O(3)	109.1(3)
Sr(2)-O(1)#1	2.962(3)	O(6)-B(1)-O(1)#3	106.5(3)
Sr(2)-O(1)#12	2.962(3)	O(7)-B(1)-O(1)#3	112.1(3)
I(1)-O(8)	1.822(2)	O(3)-B(1)-O(1)#3	106.9(3)
I(1)-O(8)#7	1.822(2)	O(3)#7-B(2)-O(3)	115.5(4)
I(1)-O(2)	1.823(3)	O(3)#7-B(2)-O(5)#15	110.2(3)
B(1)-O(6)	1.461(4)	O(3)-B(2)-O(5)#15	110.2(3)
B(1)-O(7)	1.463(5)	O(3)#7-B(2)-O(4)	107.4(3)
B(1)-O(3)	1.471(4)	O(3)-B(2)-O(4)	107.4(3)
B(1)-O(1)#3	1.493(5)	O(5)#15-B(2)-O(4)	105.6(4)
B(2)-O(3)#7	1.449(4)	O(7)-B(3)-O(7)#14	110.4(4)
B(2)-O(3)	1.449(4)	O(7)-B(3)-O(9)#16	112.31(13)
B(2)-O(5)#15	1.479(6)	O(7)#14-B(3)-O(9)#16	106.29(13)
B(2)-O(4)	1.547(6)	O(7)-B(3)-O(9)#4	106.29(13)
B(3)-O(7)	1.454(4)	O(7)#14-B(3)-O(9)#4	112.31(13)
B(3)-O(7)#14	1.454(4)	O(9)#16-B(3)-O(9)#4	109.3(4)
B(3)-O(9)#16	1.483(4)	O(10)-B(4)-O(1)#7	121.2(3)
B(3)-O(9)#4	1.483(4)	O(10)-B(4)-O(9)	121.0(3)
B(4)-O(10)	1.346(5)	O(1)#7-B(4)-O(9)	117.6(3)

Symmetry transformations used to generate equivalent atoms:

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

Table S8. Anisotropic displacement parameters (Å²×10³) for LSBIO

The anisotropic displacement factor exponent takes the form: -2π² [h² a*² U11 + ... + 2hka* b*U12]

	U11	U22	U33	U23	U13	U12
Sr(1)	10(1)	6(1)	7(1)	1(1)	5(1)	2(1)
Sr(2)	9(1)	20(1)	7(1)	0	5(1)	0
I(1)	5(1)	5(1)	5(1)	0	3(1)	0
B(1)	6(2)	9(2)	9(2)	-1(2)	5(2)	0(2)
B(2)	2(2)	8(3)	3(3)	0	1(2)	0
B(3)	12(3)	5(3)	6(3)	0	6(2)	0
B(4)	5(2)	6(2)	10(2)	-3(2)	3(2)	-4(1)
O(1)	9(1)	9(1)	5(1)	-2(1)	4(1)	-3(1)
O(2)	8(2)	10(2)	2(2)	0	3(1)	0
O(3)	6(1)	5(1)	12(1)	0(1)	5(1)	0(1)
O(4)	6(2)	9(2)	6(2)	0	3(1)	0
O(5)	10(2)	10(2)	9(2)	0	7(2)	0
O(6)	6(2)	6(2)	6(2)	0	1(1)	0
O(7)	9(1)	12(1)	4(1)	-3(1)	4(1)	-6(1)
O(8)	9(1)	12(1)	14(1)	1(1)	7(1)	-7(1)
O(9)	12(1)	7(1)	9(1)	4(1)	8(1)	4(1)
O(10)	12(1)	7(1)	9(1)	2(1)	6(1)	2(1)
Li(1)	12(4)	6(4)	11(4)	0	8(4)	0
Li(2)	22(8)	66(13)	19(8)	0	8(7)	0
Li(3)	23(10)	14(10)	18(10)	0	16(9)	0

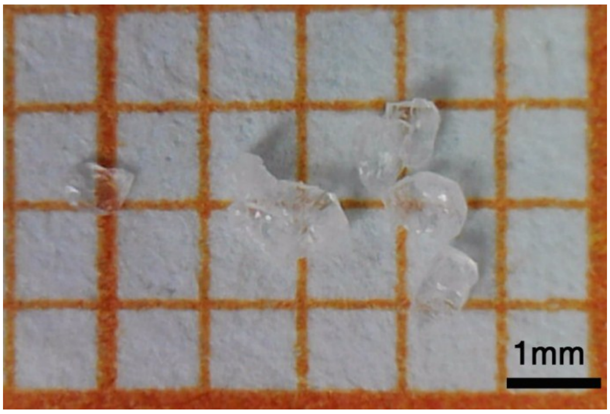

Figure S1. Crystal picture of SBIO.

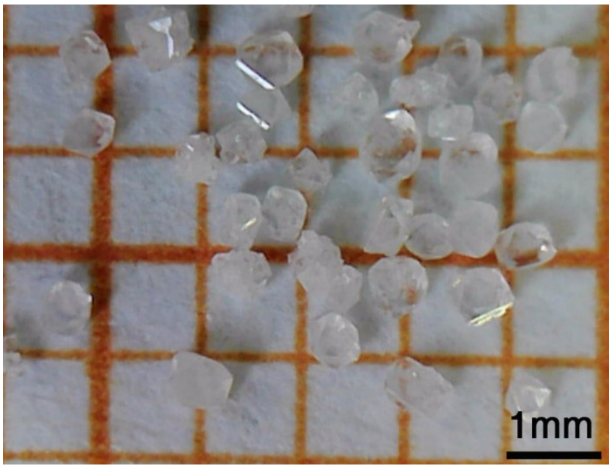

Figure S2. Crystal picture of LSBIO.

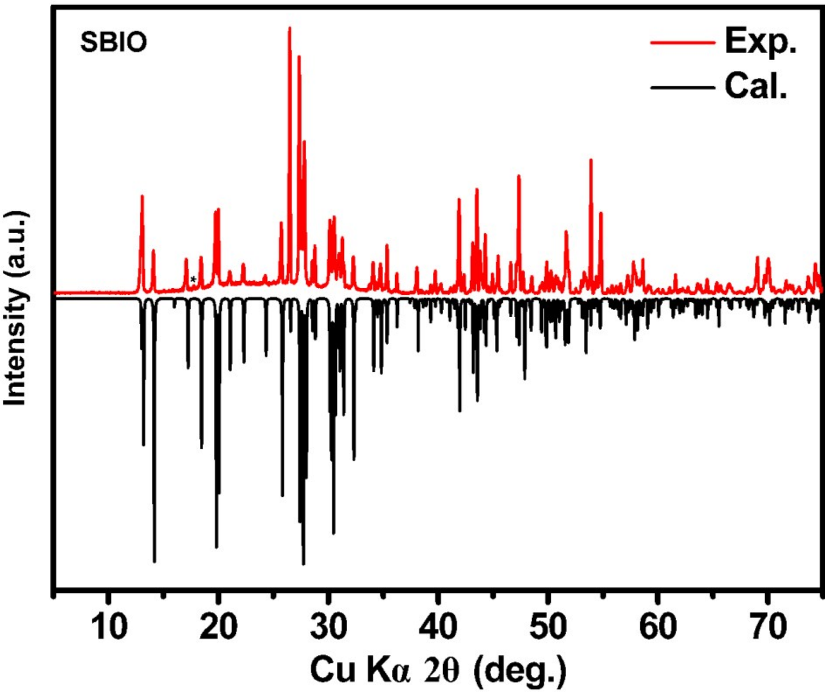

Figure S3. Calculated and experimental powder X-ray diffraction patterns of SBIO. The reflections marked with an asterisk may result from $Sr(OH)_2$ (PDF-27-0847).

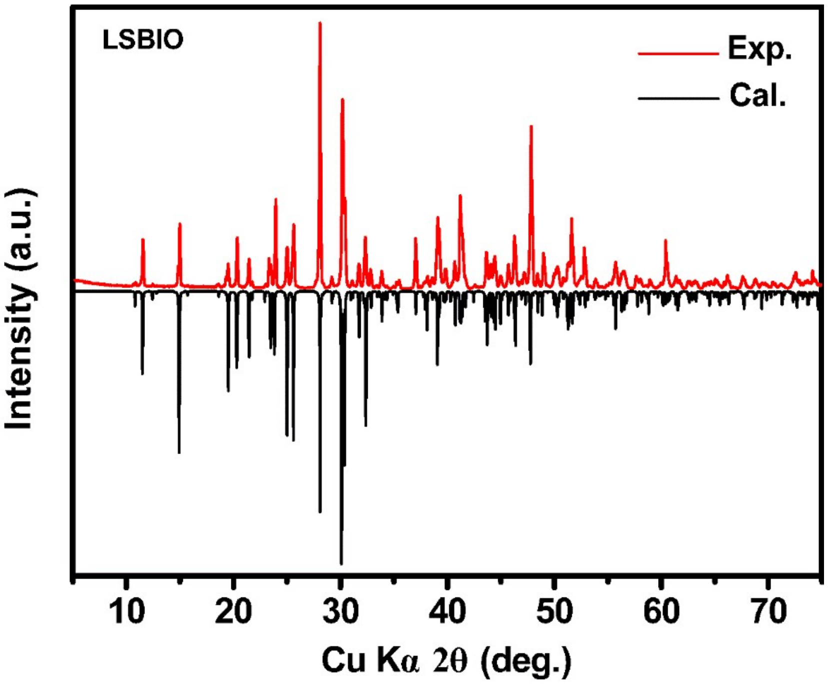

Figure S4. Calculated and experimental powder X-ray diffraction patterns of LSBIO

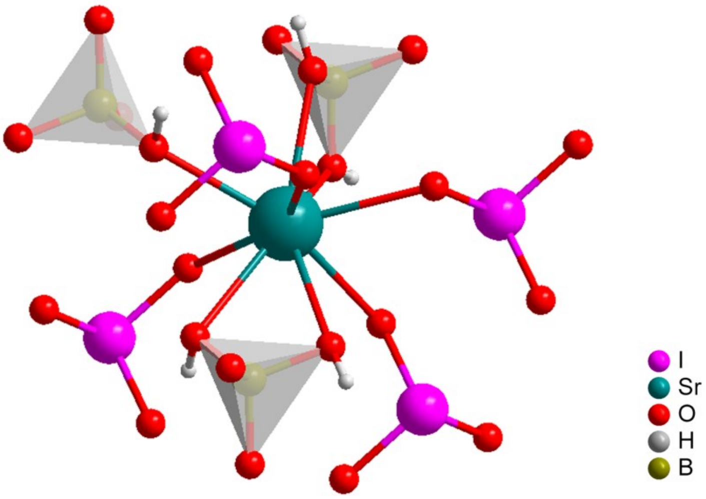

Figure S5. Coordination mode of a Sr^{2+} in SBIO

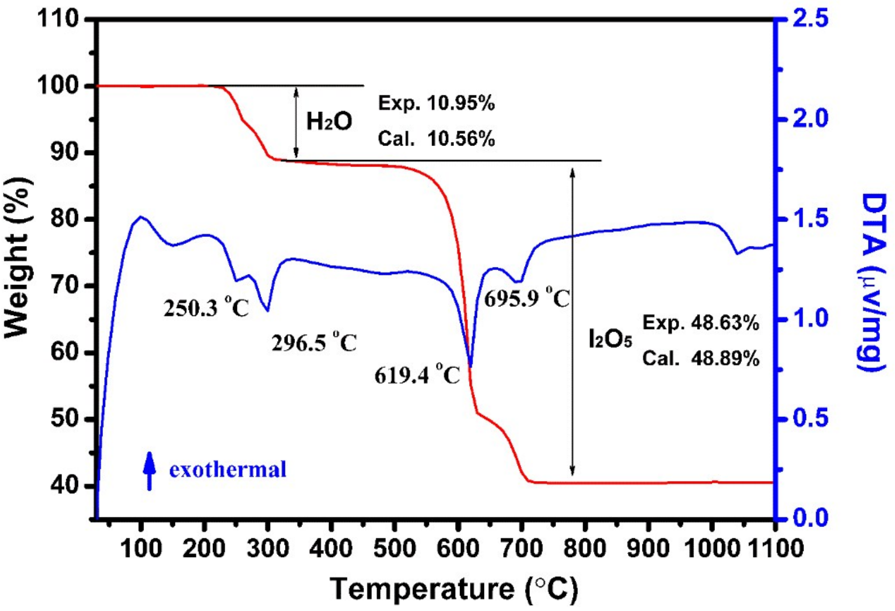

Figure S6. TGA and DTA curves of SBIO

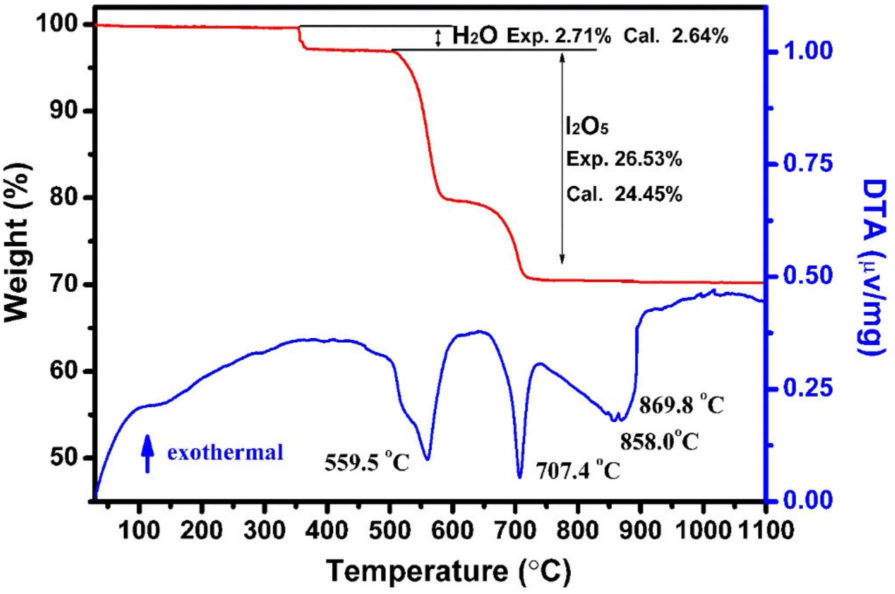

Figure S7. TGA and DTA curves of LSBIO

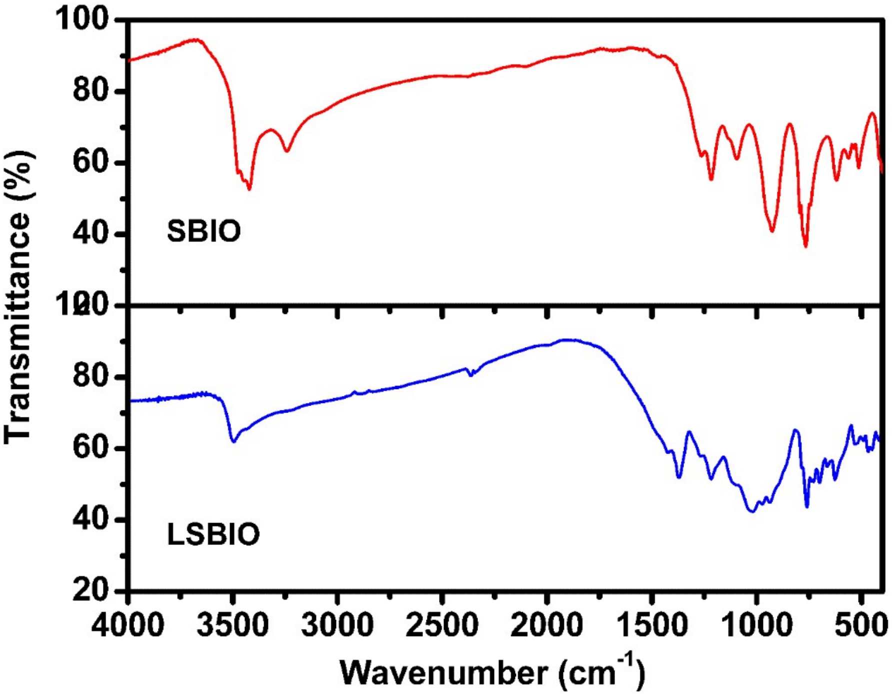

Figure S8. IR absorption spectra of SBIO and LSBIO

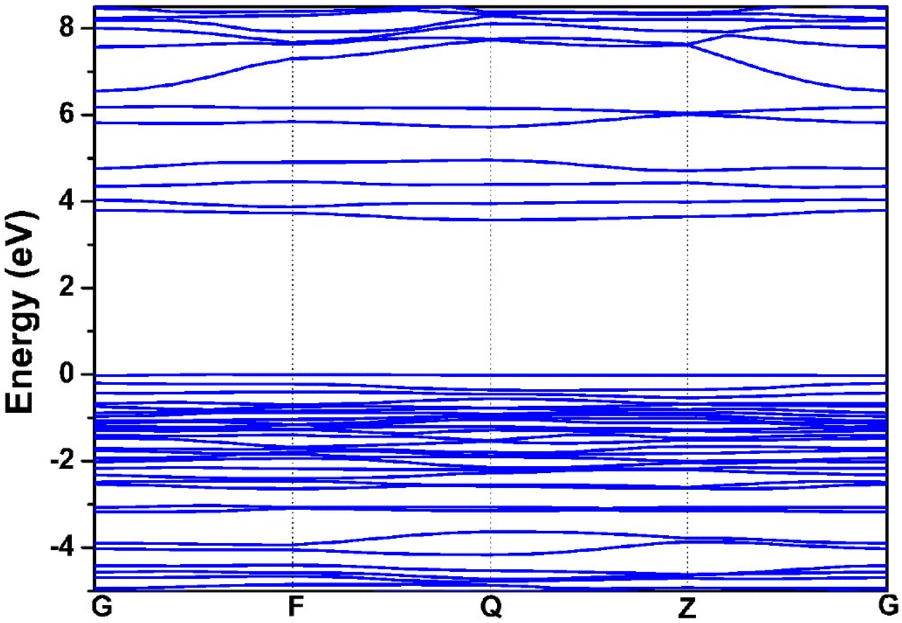

Figure S9. Calculated electronic band structure for SBIO

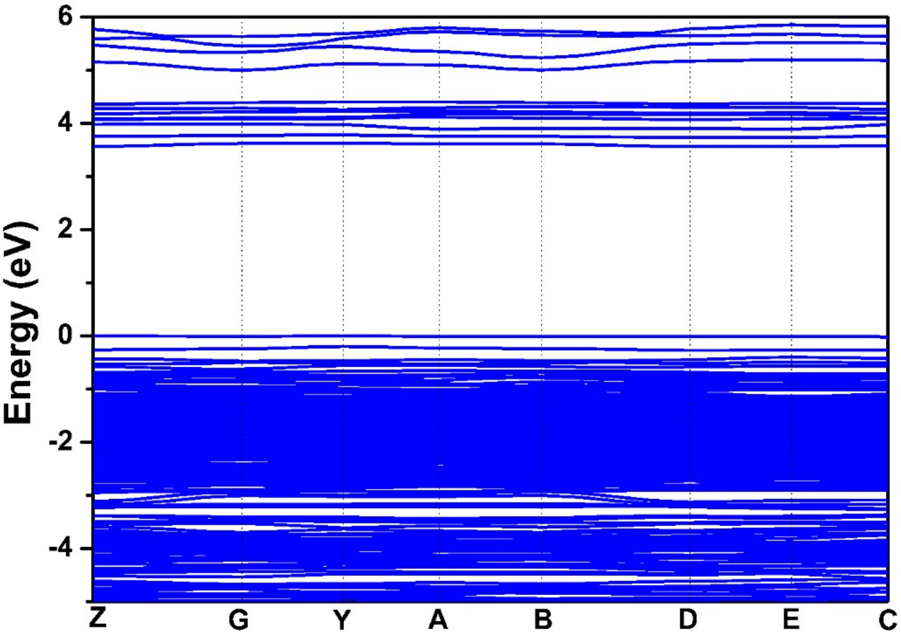

Figure S10. Calculated electronic band structure for LSBIO

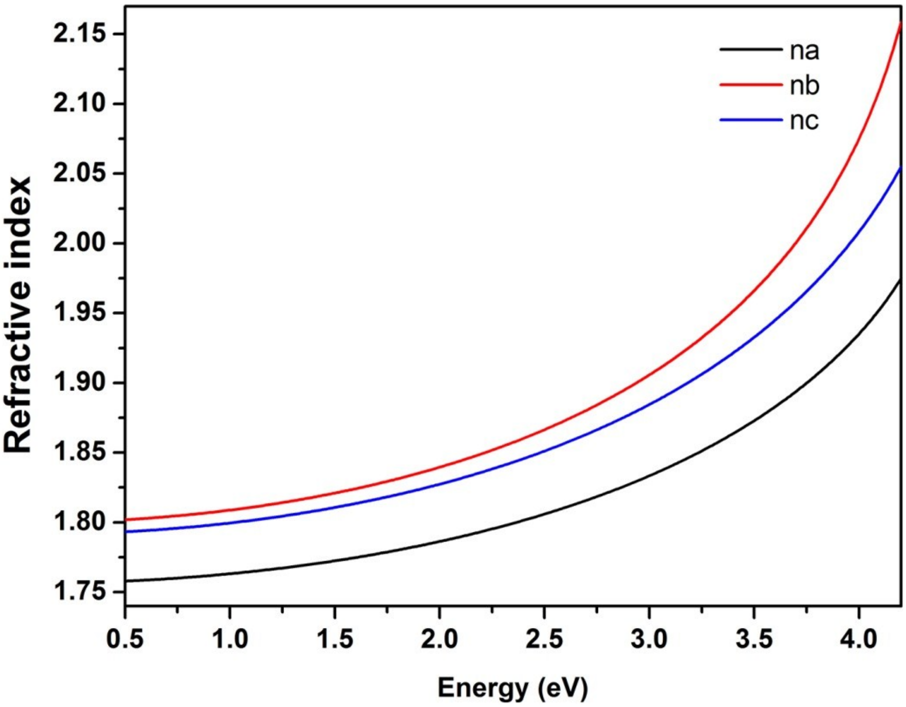

Figure S11. Calculated refractive index dispersion curves for SBIO

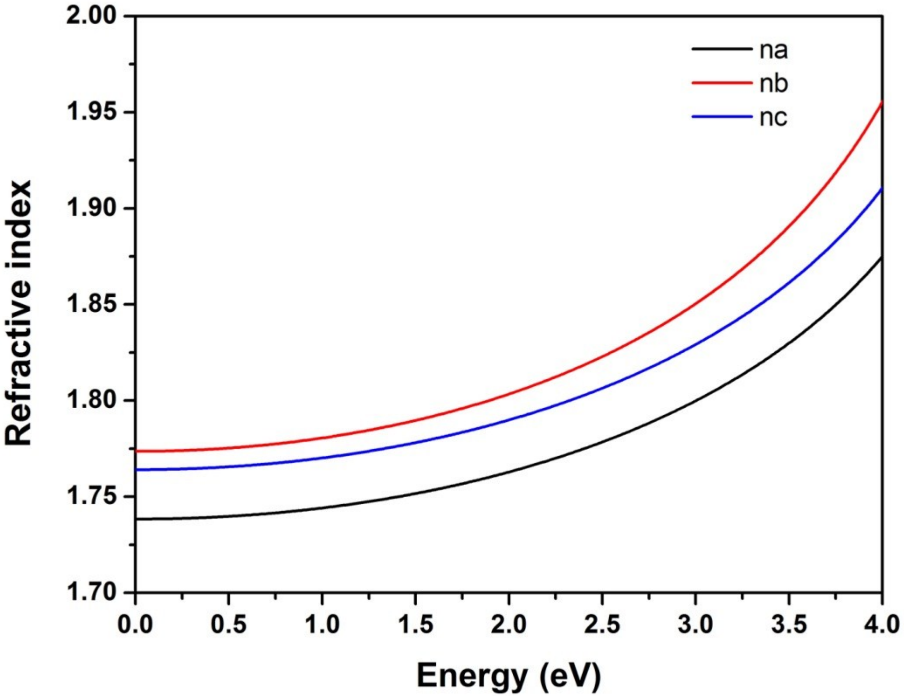

Figure S12. Calculated refractive index dispersion curves for LSBIO

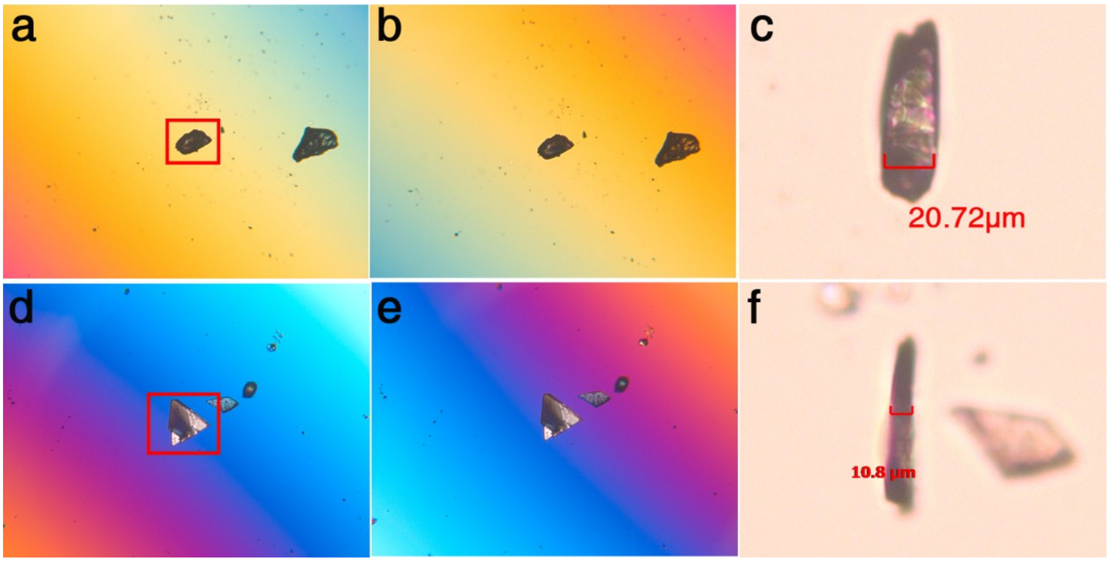

Figure S13. Photograph of LSBIO (a-c) and SBIO (d-f) for the measurement of birefringence

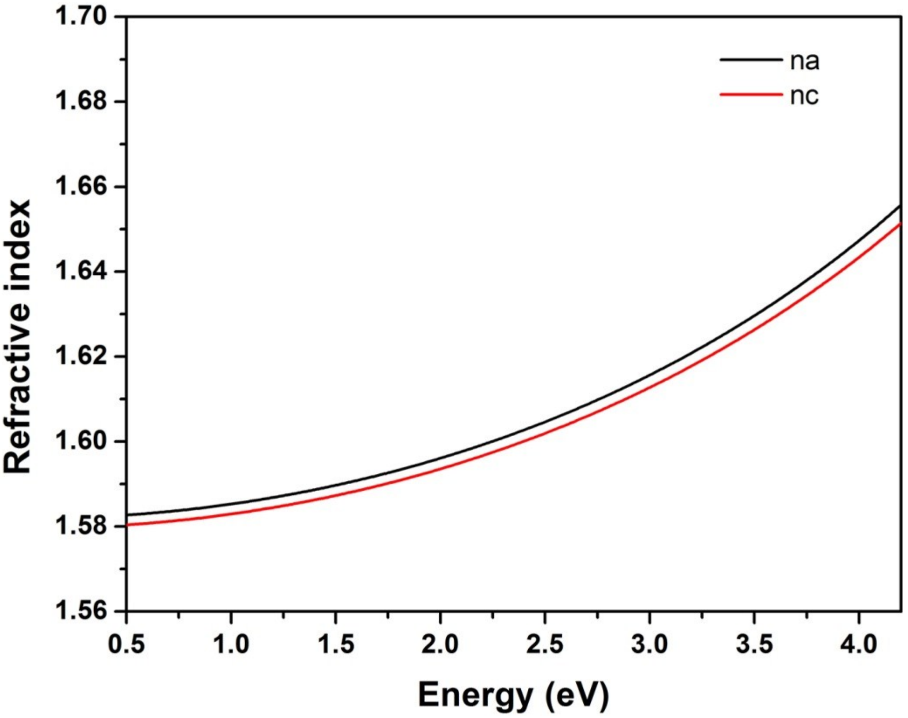

Figure S14. Calculated refractive index dispersion curves for $Li_3KB_4O_8$

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