Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

$Pb_{2.28}Ba_{1.72}B_{10}O_{19}$ Featuring Three-dimensional B-O Anionic Network with Edge-Sharing [BO_4] Obtained under Ambient Pressure

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Table S1. Crystallographic data for $Pb_{2.28}Ba_{1.72}B_{10}O_{19}$.

Empirical formula	$Pb_{2.28}Ba_{1.72}B_{10}O_{19}$
Temperature	297(2) K
Crystal system, space group	Monoclinic, *C*2/*c*
Unit cell dimensions	a = 11.912(8) Å
	b = 6.616(5) Å , β = 99.406(3)°
	c = 18.238(10) Å
Volume	1418.0(16) Å^3
Z, Calculated density	4, 5.250 Mg/m^3
Absorption coefficient	31.823 mm^{-1}
F (000)	1941
Crystal size	0.104× 0.069 × 0.047 mm^3
Theta range for data collection	2.264 to 27.506°
Limiting indices	$-15 \le h \le 15$, $-7 \le k \le 8$, $-23 \le l \le 23$
Reflections collected / unique	6639 / 1619 [R(int) = 0.0828]
Completeness to theta = 27.506°	99.70 %
Goodness-of-fit on F^2	1.023
Final R indices [$F_o^2 > 2\sigma(F_o^2)$][a]	R_1 = 0.0329, wR_2 = 0.0541
R indices (all data) [a]	R_1 = 0.0470, wR_2 = 0.0585
Largest diff. peak and hole	1.806 and -1.637 e·Å^{-3}

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

Table S2. Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) and BVS for $Pb_{2.28}Ba_{1.72}B_{10}O_{19}$. $U_{(eq)}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atoms	*x*	*y*	*z*	$U_{eq}(Å^2)$	S.O.F.	BVS	
Pb(1)	0.5881(1)	1.2825(1)	0.4888(1)	0.010(1)	1	2.19	
Ba(1A)	0.3006(1)	-0.1107(1)	0.6919(1)	0.010(1)	0.86	2.51	2.38
Pb(1A)	0.3006(1)	-0.1107(1)	0.6919(1)	0.010(1)	0.14	1.58	
B(1)	0.3409(12)	0.3370(20)	0.6267(7)	0.009(3)	1	2.98	
B(2)	0.6286(11)	0.8890(20)	0.6261(7)	0.008(3)	1	3.03	
B(3)	0.7057(11)	0.8960(20)	0.4989(7)	0.007(2)	1	2.93	
B(4)	0.5406(11)	0.2270(20)	0.6669(7)	0.008(3)	1	3.02	
B(5)	0.4975(11)	0.5990(20)	0.6758(7)	0.006(2)	1	3.05	
O(1)	0.3823(6)	0.5448(12)	0.6386(4)	0.006(1)	1	2.07	
O(2)	0.5000	0.6847(17)	0.7500	0.006(2)	1	2.10	
O(3)	0.2377(7)	0.2922(12)	0.6573(4)	0.006(2)	1	1.96	
O(4)	0.8157(6)	0.8099(12)	0.5424(4)	0.006(2)	1	1.97	
O(5)	0.6237(7)	0.9417(13)	0.5476(4)	0.009(2)	1	2.04	
O(6)	0.5767(7)	0.4250(13)	0.6775(4)	0.009(2)	1	2.08	
O(7)	0.6248(7)	0.0858(13)	0.6683(4)	0.010(2)	1	2.06	
O(8)	0.4278(7)	0.1856(13)	0.6551(4)	0.012(2)	1	2.22	
O(9)	0.7192(7)	0.10680(14)	0.4546(4)	0.008(2)	1	2.20	
O(10)	0.5311(7)	0.7619(13)	0.6298(4)	0.008(1)	1	2.05	

Table S3. Selected bond lengths (Å) and angles (°) for $Pb_{2.28}Ba_{1.72}B_{10}O_{19}$.

Bond lengths			
Pb(1)-O(9)	2.271(8)	B(1)-O(8)	1.472(17)
Pb(1)-O(10)#1	2.404(8)	B(1)-O(4)#6	1.528(15)
Pb(1)-O(5)	2.503(8)	B(2)-O(10)	1.443(16)
Pb(1)-O(9)#2	2.557(8)	B(2)-O(5)	1.465(15)
Pb(1)-O(1)#1	2.663(8)	B(2)-O(3)#10	1.476(15)
Pb(1)-O(5)#1	2.904(6)	B(2)-O(7)#11	1.519(16)
Pb(1)-O(4)#2	3.020(8)	B(3)-O(9)	1.421(15)
Ba/Pb(1A)-O(8)	2.631(9)	B(3)-O(5)	1.456(14)
Ba/Pb(1A)-O(6)#6	2.648(8)	B(3)-O(4)	1.526(14)
Ba/Pb(1A)-O(9)#4	2.658(7)	B(3)-O(4)#12	1.556(15)
Ba/Pb(1A)-O(1)#7	2.719(8)	B(4)-O(8)	1.353(16)
Ba/Pb(1A)-O(2)#7	2.788(6)	B(4)-O(7)	1.368(16)
Ba/Pb(1A)-O(3)	2.813(8)	B(4)-O(6)	1.383(15)
Ba/Pb(1A)-O(7)#8	2.870(8)	B(5)-O(10)	1.461(15)
Ba/Pb(1A)-O(7)#6	2.883(8)	B(5)-O(2)	1.464(13)
Ba/Pb(1A)-O(3)#9	2.932(7)	B(5)-O(1)	1.473(14)
B(1)-O(3)	1.460(16)	B(5)-O(6)	1.485(15)
B(1)-O(1)	1.466(16)		
Bond angles			
O(9)-Pb(1)-O(10)#1	90.5(3)	O(6)#6- Ba/Pb(1A)-O(9)#4	88.2(2)
O(9)-Pb(1)-O(5)#1	103.2(3)	O(8)- Ba/Pb(1A)-O(1)#7	106.2(3)
O(9)-Pb(1)-O(5)	58.6(3)	O(6)#6- Ba/Pb(1A)-O(1)#7	116.9(2)
O(10)#1-Pb(1)-O(5)	108.0(3)	O(9)#4- Ba/Pb(1A)-O(1)#7	73.0(2)
O(10)#1-Pb(1)-O(5)#1	50.9(2)	O(8)- Ba/Pb(1A)-O(2)#7	88.2(3)
O(10)#1-Pb(1)-O(4)	97.3(2)	O(6)#6- Ba/Pb(1A)-O(2)#7	149.6(2)
O(9)-Pb(1)-O(9)#2	75.0(3)	O(9)#4- Ba/Pb(1A)-O(2)#7	111.34(18)
O(10)#1-Pb(1)-O(9)#2	140.4(3)	O(1)#7- Ba/Pb(1A)-O(2)#7	52.9(2)
O(5)-Pb(1)-O(5)#2	73.6(3)	O(8)- Ba/Pb(1A)-O(3)	51.7(2)
O(5)-Pb(1)-O(9)#2	95.6(3)	O(6)#6- Ba/Pb(1A)-O(3)	70.5(2)
O(9)-Pb(1)-O(4)	102.0(3)	O(9)#4- Ba/Pb(1A)-O(3)	72.4(2)
O(9)-Pb(1)-O(1)#1	80.4(3)	O(1)#7- Ba/Pb(1A)-O(3)	144.3(2)
O(10)#1-Pb(1)-O(1)#1	53.9(3)	O(2)#7- Ba/Pb(1A)-O(3)	136.4(3)
O(5)-Pb(1)-O(4)	147.4(2)	O(8)- Ba/Pb(1A)-O(7)#8	77.4(2)
O(5)-Pb(1)-O(1)#1	136.3(3)	O(6)#6- Ba/Pb(1A)-O(7)#8	102.0(2)
O(9)#2-Pb(1)-O(1)#1	87.0(2)	O(3)-B(1)-O(1)	114.7(10)
O(9)#2-Pb(1)-O(4)	52.2(2)	O(3)-B(1)-O(8)	108.4(10)
O(5)#1-Pb(1)-O(1)#1	104.7(2)	O(1)-B(1)-O(8)	112.7(10)
O(5)#1-Pb(1)-O(9)#2	167.8(3)	O(3)-B(1)-O(4)#6	108.7(9)
O(5)#1-Pb(1)-O(4)	138.9(2)	O(1)-B(1)-O(4)#6	105.3(10)
O(1)#1-Pb(1)-O(4)	49.0(2)	O(8)-B(1)-O(4)#6	106.6(10)

O(9)#4- Ba/Pb(1A)-O(7)#8	143.9(3)	O(10)-B(2)-O(5)	106.3(9)
O(1)#7- Ba/Pb(1A)-O(7)#8	128.3(2)	O(10)-B(2)-O(3)#10	113.3(11)
O(2)#7- Ba/Pb(1A)-O(7)#8	76.2(2)	O(5)-B(2)-O(3)#10	111.8(10)
O(3)- Ba/Pb(1A)-O(7)#8	78.6(2)	O(10)-B(2)-O(7)#11	112.6(10)
O(8)- Ba/Pb(1A)-O(7)#6	156.3(2)	O(5)-B(2)-O(7)#11	106.9(10)
O(6)#6- Ba/Pb(1A)-O(7)#6	49.6(2)	O(3)#10-B(2)-O(7)#11	105.9(9)
O(9)#4- Ba/Pb(1A)-O(7)#6	88.9(2)	O(9)-B(3)-O(5)	109.2(10)
O(1)#7- Ba/Pb(1A)-O(7)#6	69.9(2)	O(9)-B(3)-O(4)	115.3(10)
O(2)#7- Ba/Pb(1A)-O(7)#6	105.8(3)	O(5)-B(3)-O(4)	111.4(9)
O(3)- Ba/Pb(1A)-O(7)#6	117.8(2)	O(9)-B(3)-O(4)#12	116.8(9)
O(7)#8- Ba/Pb(1A)-O(7)#6	124.05(14)	O(5)-B(3)-O(4)#12	113.9(9)
O(8)- Ba/Pb(1A)-O(3)#9	125.9(2)	O(4)-B(3)-O(4)#12	89.1(8)
O(6)#6- Ba/Pb(1A)-O(3)#9	78.7(2)	O(8)-B(4)-O(7)	124.8(12)
O(9)#4- Ba/Pb(1A)-O(3)#9	164.6(2)	O(8)-B(4)-O(6)	119.5(11)
O(1)#7- Ba/Pb(1A)-O(3)#9	105.8(2)	O(7)-B(4)-O(6)	115.7(11)
O(2)#7- Ba/Pb(1A)-O(3)#9	77.92(16)	O(10)-B(5)-O(2)	106.2(10)
O(3)- Ba/Pb(1A)-O(3)#9	110.0(2)	O(10)-B(5)-O(1)	103.7(9)
O(7)#8- Ba/Pb(1A)-O(3)#9	48.6(2)	O(2)-B(5)-O(1)	113.4(9)
O(7)#6- Ba/Pb(1A)-O(3)#9	76.5(2)	O(10)-B(5)-O(6)	110.6(10)
O(8)- Ba/Pb(1A)-O(6)#6	121.4(3)	O(2)-B(5)-O(6)	111.3(9)
O(8)- Ba/Pb(1A)-O(9)#4	68.0(2)	O(1)-B(5)-O(6)	111.3(9)

Symmetry transformations used to generate equivalent atoms:

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

#5 x+1/2,y+3/2,z #6 x-1/2,y-1/2,z #7 x,y-1,z #8 -x+1,y,-z+3/2 #9 -x+1/2,y-1/2,-z+3/2

#10 x+1/2,y+1/2,z #11 x,y+1,z #12 -x+3/2,-y+3/2,-z+1 #13 -x+1,y+1,-z+3/2

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

Table S4. The geometric features and synthesis conditions of the edge-sharing [BO_4] in previously reported borates.

	Compounds	Inside O – B – O angles (°)	Outside O – B – O angles (°)	B·····B interatomic distance（Å）	A/B	Synthesis conditions
0 D	$Ba_4Na_2Zn_4(B_3O_6)_2(B_{12}O_{24})$	95.482	111.565	2.000	0.56	Ambient pressure
	$Li_4Na_2CsB_7O_{14}$	94.621	110.599	2.026	1.00	Ambient pressure
	$BaAlBO_4$	94.062	110.944	2.098	2.00	Ambient pressure
	$KZnB_3O_6$	92.013	113.972	2.079	0.67	Ambient pressure
	LT-$K_3Sb_4BO_{13}$	86.833	110.9	2.288	7.00	Ambient pressure (crystallize at 200 K)
3 D	$Pb_{2.28}Ba_{1.72}B_{10}O_{19}$	89.066	109.299	2.199	0.40	Ambient pressure
2 D	$Ho_4B_6O_{15}$	94.375	109.722	2.071	0.67	8 GPa, 1000 °C
	HP-NiB_2O_4	93.559	114.688	2.086	0.50	7.5 GPa, 680 °C
	β-FeB_2O_4	93.359	113.835	2.083	0.50	8 GPa, 1030 °C
	HP-CoB_2O_4	93.305	114.179	2.090	0.50	6.5 GPa, 950 °C
	$Dy_4B_6O_{15}$	92.959	109.490	2.098	0.67	8 GPa, 1000 °C
	$La_3B_6O_{13}(OH)$-B3	92.720	112.613	2.077	0.50	6 GPa, 1400 °C
	$La_3B_6O_{13}(OH)$-B6	92.559	113.266	2.077		
	β-CsB_9O_{14}	89.272	114.877	2.169	0.11	Vacuum sealed
3 D	α-$Ho_2B_4O_9$	94.270	114.184	2.040	0.50	10 GPa, 1050 °C
	α-$Gd_2B_4O_9$	93.971	113.592	2.034	0.50	10 GPa, 1150 °C
	α-$Eu_2B_4O_9$	93.627	113.499	2.054	0.50	10 GPa, 1150 °C
	α-$Tb_2B_4O_9$	93.150	114.275	2.059	0.50	10 GPa, 1150 °C
	α-$Sm_2B_4O_9$	92.730	113.614	2.071	0.50	7.5 GPa, 1050 °C
	$Co_7B_{24}O_{42}(OH)_2 \cdot 2H_2O$	90.613	110.891	2.148	0.29	6 GPa, 880 °C
	α-$Ba_3[B_{10}O_{17}(OH)_2]$	89.966	115.207	2.169	0.30	1000 bar, 500 °C
	HP-CsB_5O_8	88.798	115.745	2.182	0.20	6 GPa, 900 °C
	HP-KB_3O_5	87.349	114.838	2.215	0.33	3 GPa, 600 °C
	HP-TlB_3O_5	87.175	113.890	2.211	0.33	6 GPa, 1400 °C
	HP-$(NH_4)B_3O_5$	87.070	113.806	2.215	0.33	3 GPa, 600 °C
	HP-RbB_3O_5	86.781	113.942	2.231	0.33	6 GPa, 1000 °C

Table S5.The molecular formulas or FBBs contain ten boron atoms in anhydrous borates.

Compounds		Space Group	FBBs	B-O configurations
Ternary	$Cu_{15}(B_2O_5)_2(BO_3)_6O_2$	$P\bar{1}$	BO_3+B_2O_5	0D
	$Ba_2(B_{10}O_{17})$	$P\bar{1}$	$B_{10}O_{23}$	3D
	$La_4B_{10}O_{21}$	$P2_1/n$	$B_{10}O_{26}$	3D
	$Pr_4(B_{10}O_{21})$	$P2_1/n$	$B_{10}O_{26}$	3D
	$Pb_6B_{10}O_{21}$	$P\bar{1}$	$B_{10}O_{21}$	0D
	δ - CsB_5O_8	$Pccn$	$B_{10}O_{19}$	3D
Quaternary	$Cs_2Na_2(B_{10}O_{17})$	$C2/c$	$B_{10}O_{21}$	2D
	$Cs_2K_2(B_{10}O_{17})$	$C2/c$	$B_{10}O_{21}$	2D
	$Na_2Tl_2(B_{10}O_{17})$	$C2/c$	$B_{10}O_{21}$	2D
	$Pb_4Zn_2B_{10}O_{21}$	$Pbcn$	$B_{10}O_{24}$	2D
	$Ba_3B_{10}O_{17}Br_2$	$C2/c$	B_5O_{11}	2D
	$Ca_2B_{10}O_{14}F_6$	$Cmc2_1$	$B_5O_9F_3$	2D
	$Sr_2B_{10}O_{14}F_6$	$Cmc2_1$	$B_5O_9F_3$	2D
	$La_2CaB_{10}O_{19}$	$C2$	B_5O_{12}	2D
	$Li_2Sr_4B_{12}O_{23}$	$P2_1/c$	$B_{10}O_{18}$+B_2O_5	3D
Hexameric	$NaBa_4B_{10}O_{18}BrF_2$	$P2_1/n$	B_5O_{12}	3D
Heptameric	$Cd_3LiNa_4Be_4B_{10}O_{24}F$	$R\bar{3}H$	$B_{12}O_{24}$+BO_3	0D
	$Sr_3LiNa_4Be_4B_{10}O_{24}F$	$R\bar{3}H$	$B_{12}O_{24}$+BO_3	0D
	$Ca_3Na_4LiBe_4B_{10}O_{24}F$	$R\bar{3}H$	$B_{12}O_{24}$+BO_3	0D
	$Li_4NaKAl_4Be_3B_{10}O_{27}$	$P\bar{4}3m$	$(B/Be)_3O_9$	3D

Figure S1. The B-O configurations in $Pb_4Zn_2B_{10}O_{21}$ and $Pb_{2.28}Ba_{1.72}B_{10}O_{19}$. (a) $[B_{10}O_{24}]$ FBB; (b) $^2_\infty[B_{10}O_{21}]$ layers in $Pb_4Zn_2B_{10}O_{21}$. (c) $[B_{10}O_{24}]$ FBB; (d) $^3_\infty[B_{10}O_{19}]$ network in $Pb_{2.28}Ba_{1.72}B_{10}O_{19}$.

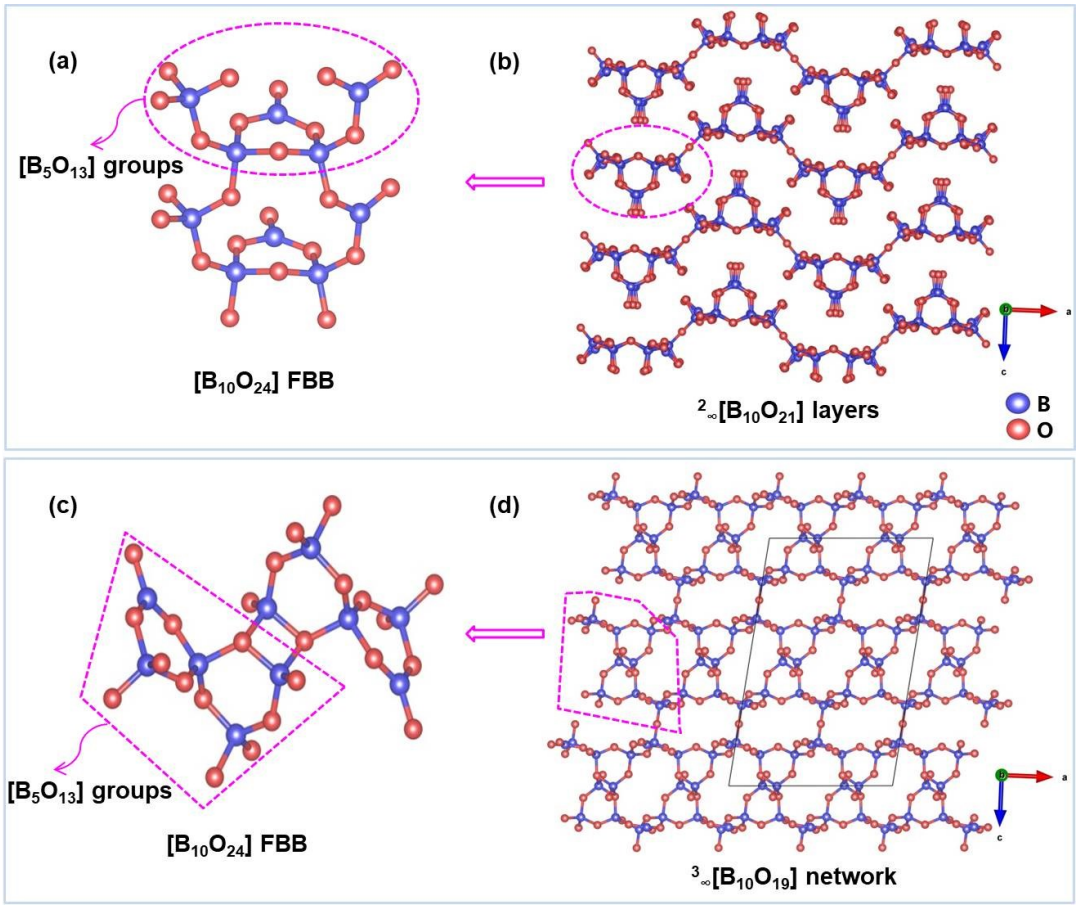

Figure S2. The UV-vis-NIR diffuse reflectance spectrum of $Pb_{2.28}Ba_{1.72}B_{10}O_{19}$.

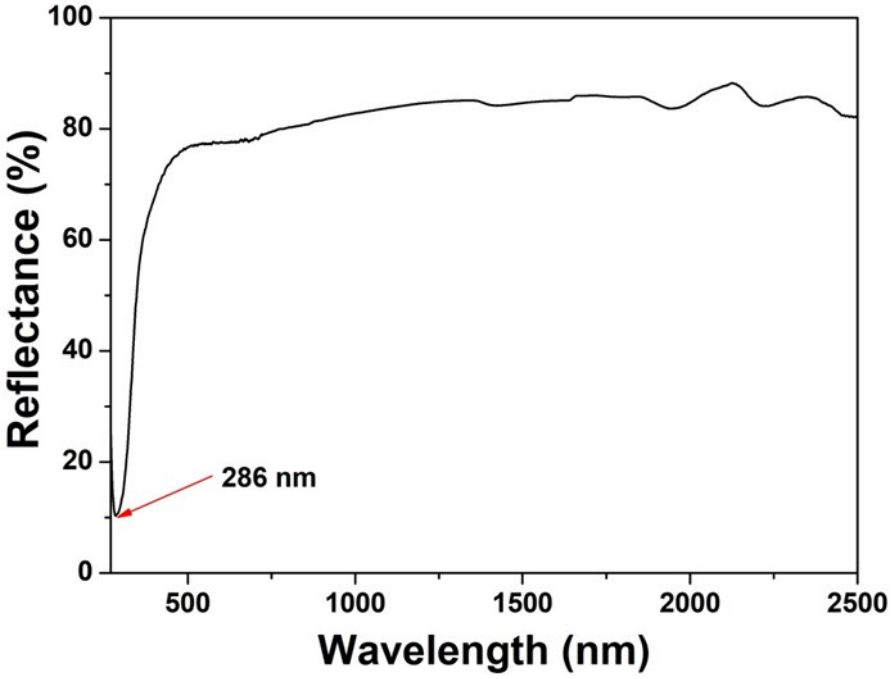

Figure S3. The TG-DSC curves of $Pb_{2.28}Ba_{1.72}B_{10}O_{19}$.

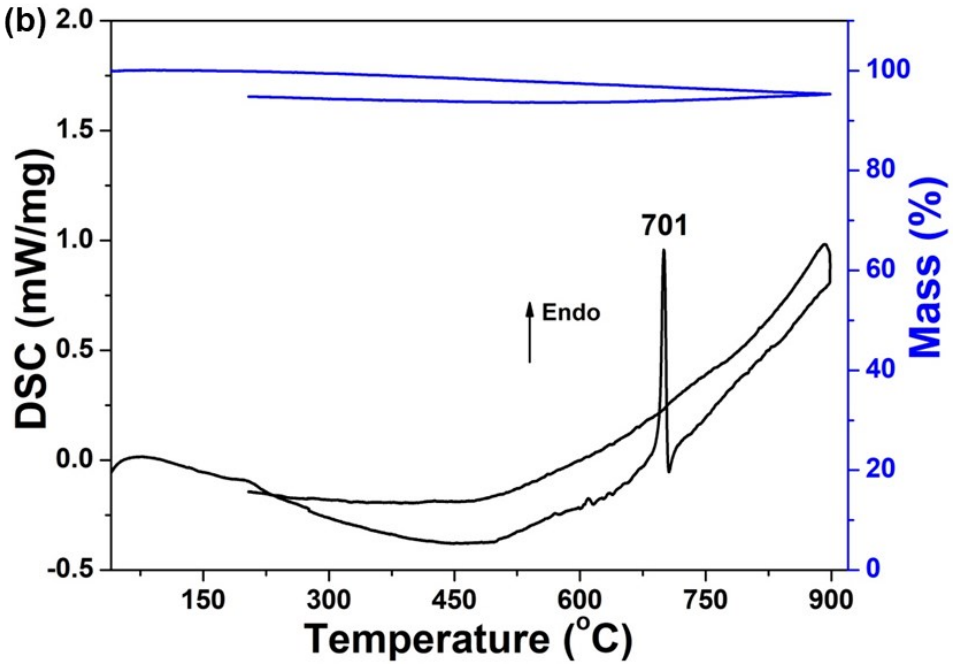

Figure S4. The powder X-ray diffraction patterns of $Pb_{2.28}Ba_{1.72}B_{10}O_{19}$.

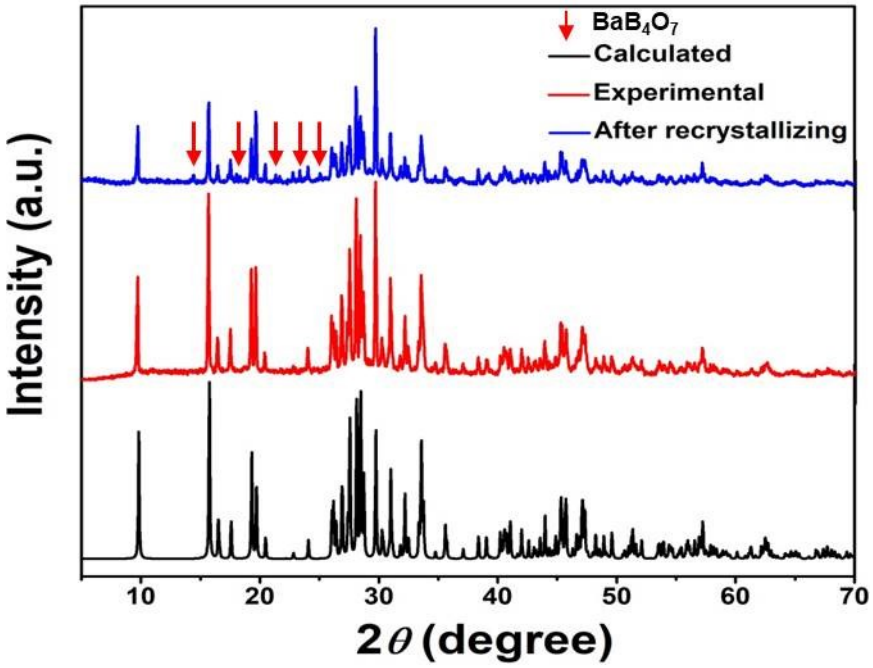

Figure S5. The electronic band structure of the model of $Pb_{2.28}Ba_{1.72}B_{10}O_{19}$.

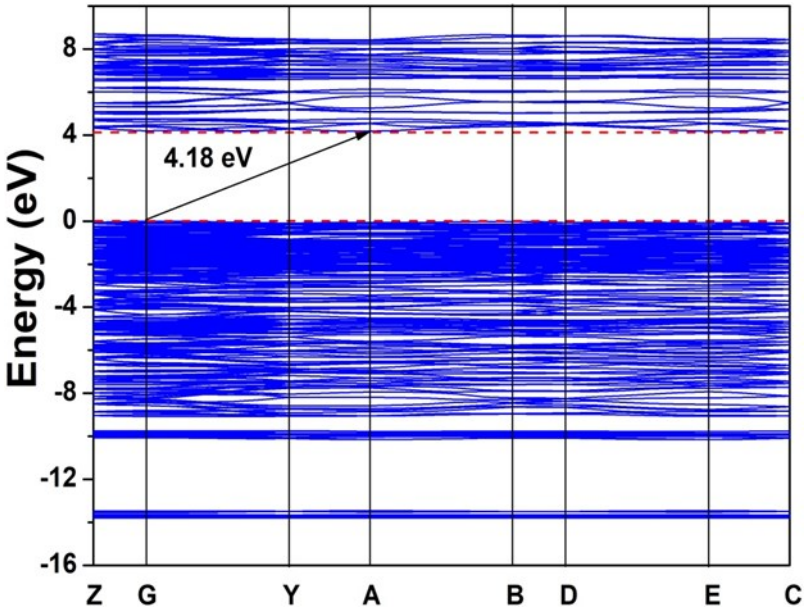

Figure S6. The calculated birefringence of the model of $Pb_{2.28}Ba_{1.72}B_{10}O_{19}$.