Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

$Ba_2Zn_2B_6O_{13}$: Coplanar [B_2O_5] in Unnoted U-Shaped [B_6O_{13}] Groups Achieving Large Birefringence

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Experimental Section

Compound Synthesis

BaF_2 (Shanghai Aladdin Bio-Chem Technology Co., Ltd.,99%), $BaCO_3$ (Tianjin Baishi Chemical Reagent Co., Ltd., 99.9%), ZnF_2 (Shanghai Aladdin Bio-Chem Technology Co., Ltd., 99.9%), $Zn(NO_3)_2 \cdot 6H_2O$ (Shanghai Aladdin Bio-Chem Technology Co., Ltd., 99.99%) and B_2O_3 (Shanghai Aladdin Bio-Chem Technology Co., Ltd., 99.9%) are analytical grade and obtained from commercial sources without further purification.

The title crystal was obtained from the high-temperature solution in the open system. First, the mixture of BaF_2, ZnF_2, and B_2O_3 was placed in the platinum crucible with a molar ratio of 1 : 2 : 3 (about 3g of total). The temperature was slowly increased from room temperature to 800 °C, and kept at this temperature for 30 h. Then the furnace was cooled down to 600 °C at a rate of 2 °C/h, then lowered to 400 °C at a rate of 5 °C/h, and finally cooled to room temperature using 30 h. Colorless crystals were separated from the crucible for structural characterization.

Polycrystalline sample of $Ba_2Zn_2B_6O_{13}$ is synthesized by solid-state reaction technique. All reagents are commercially available in analytical purity. A mixture of $BaCO_3$, $Zn(NO_3)_2 \cdot 6H_2O$, and B_2O_3 in the molar ratio of 2 : 2 : 3 was ground and loaded into a platinum crucible. The mixture was preheated at 500 °C for 10 h. Then the temperature was raised to 680 °C and held at that temperature for 20 days with several intermediate grindings and mixings.

Single Crystal X-ray Diffraction

$Ba_2Zn_2B_6O_{13}$ was used for single crystal data collection using a Bruker D8 Venture diffractometer with Mo Kα radiation (λ = 0.71073 Å) and integrated with a SAINT program.[1] The OLEX2 system was used to solve and refine the crystal structure.[2] The structure was solved by direct methods, and all of the atoms were refined using full-matrix least-squares techniques with an-isotropic thermal parameters and finally converged for $F_o^2 \geq 2\sigma(F_o^2)$. The structure was checked for missing symmetry element with PLATON.[3] The information including crystal data and structural refinements is summarized in Table S1, the atomic coordinates and the equivalent isotropic displacement parameters are given in Table S2 in the Supporting Information (SI).

Powder X-ray Diffraction

Powder XRD data of polycrystalline samples were obtained on a Bruker D2 PHASER diffractometer with Cu Kα radiation (λ = 1.5418 Å) at room temperature. The 2θ range was 10-70° with a step size of 0.02° and a fixed counting time of 1s/step. The diffraction patterns are in good agreementwith the calculated ones, except for a slight amount ofimpurities in $Ba_2Zn_2B_6O_{13}$ (Figure S3).

Thermal Analysis.

The circular thermal gravimetric (TG) and differential scanning calorimetry (DSC) analyses of $Ba_2Zn_2B_6O_{13}$ were investigated using a simultaneous Netzsch STA 449C

thermal analyzer instrument at a heating rate of 5 °C min^{-1} in an atmosphere of flowing N_2 from 40 to 1000 °C.

Infrared Spectroscopy

IR spectroscopy was carried out on a Shimadzu IR Affinity-1 spectrometer in the 500-4000 cm^{-1} range. The sample was mixed thoroughly with dried KBr.

UV-vis-NIR Diffuse-Reflectance Spectroscopy

UV-vis-NIR diffuse-reflectance data were collected with a SolidSpec-3700 DUV spectrophotometer in the wavelength range from 190 to 2600 nm. And the reflectance spectrum was converted to absorbance with the Kubelka-Munk remission function.[4]

Theoretical Calculations

First-principles density generalized function theory (DFT) electronic structure calculations of $Ba_2Zn_2B_6O_{13}$ were performed with the total energy code CASTEP.[5,6] The exchange-correlation functional and pseudopotential were the GGA with the Perdew-Burke-Ernzerhof (PBE) functional and norm-conserving pseudopotential (NCP).[7,8] The valence electrons of the involved elements were O-$2s^2 2p^4$, B-$2s^2 2p^1$, Zn-$3d^{10} 4s^2$, and Ba-$5s^2 5p^6 6s^2$. The plane-wave cutoff energy was set to 750 eV.The Monkhorst-Pack *k*-point was sampled with a separation of 0.05 $Å^{-1}$ for self-consistent field: 3 × 3 × 2 for $Ba_2Zn_2B_6O_{13}$.[9] We kept the default values of the CASTEP code on the aspect of the other calculation parameters and convergent criteria. The phonon dispersions were calculated using the linear response method.

Thermal Analysis

As shown in Figure S4a, the TG curve of $Ba_2Zn_2B_6O_{13}$ shows no significant change in mass throughout the heating process. There are two obvious heat absorption peaks at 790 and 827°C, suggesting that $Ba_2Zn_2B_6O_{13}$maybe an incongruent compound. To further verify the melting behavior of $Ba_2Zn_2B_6O_{13}$, we placed the powder of $Ba_2Zn_2B_6O_{13}$ into a platinum crucible and heated it to 820 °C for 20 h; then it was slowly cooled to room temperature. The powder XRD pattern of the recrystallized powder was different from the calculated one (Figure S4b), which further indicates that $Ba_2Zn_2B_6O_{13}$ is an incongruent melting compound.

Table S1. Crystal data and structure refinement for $Ba_2Zn_2B_6O_{13}$.

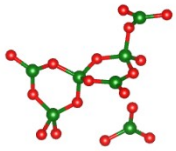
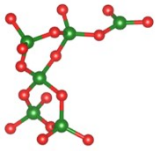
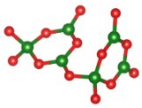
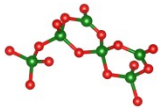
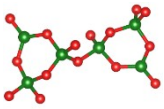
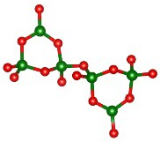
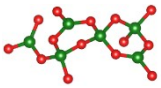
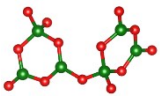
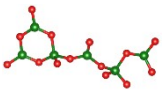
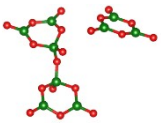
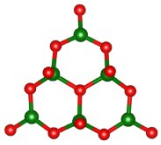
Empirical formula	$Ba_2Zn_2B_6O_{13}$
Formula weight	678.28
Crystal system, space group	triclinic, $P\bar{1}$
a (Å)	6.9742 (4), α = 93.645(2)
b (Å)	7.0347 (4), β = 99.323(2)
c (Å)	13.2993(8), γ = 119.262(2)
Volume (Å^3)	553.92(6)
Z, Calculated density	2, 4.067 g/cm^3
F(000)	612.0
Theta range for data collection	3.14 to 55.02
Index ranges	-9 ≤ h ≤ 9, -9 ≤ k ≤ 9, -17 ≤ I ≤ 17
Reflections collected / unique	20701
Independent reflections	2529 [R_{int} = 0.0569, R_{sigma}= 0.0301]
Data / restraints / parameters	2529/0/209
Goodness-of-fit on F_o^2	1.04
Final *R* indices [$F_o^2 > 2\sigma(F_o^2)$][a]	R_1=0.024, wR_2=0.079
Final *R* indices (all data)	R_1=0.025, wR_2=0.0797

[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 ($\times 10^4$) and equivalent isotropic displacement parameters ($Å \times 10^3$) for $Ba_2Zn_2B_6O_{13}$. U_{eq} is defined as one-third of the trace the orthogonalisedU_{ij} tensor.

Atom	x	y	Z	U_{eq}	BVS
Ba(1)	4052.0(4)	409.8(4)	6534.2(2)	11.96(12)	1.93
Ba(2)	1729.6(5)	4192.2(5)	8450.1(2)	16.88(12)	1.90
Zn(1)	401.7(9)	3549.5(9)	5586.1(4)	11.00(14)	2.05
Zn(2)	5817.3(9)	1228.4(9)	9231.5(4)	10.70(14)	2.09
B(1)	10851(9)	8033(9)	8693(4)	11.3(9)	3.04
B(2)	9331(8)	6830(8)	6670(4)	9.1(9)	3.03
B(3)	8034(9)	9248(8)	8512(4)	10.6(9)	2.96
B(4)	6921(9)	5494(9)	8800(4)	13.7(10)	3.04
B(5)	5134(9)	5382(8)	6401(4)	11.6(9)	2.99
B(6)	7590(9)	9083(8)	6043(4)	10.6(9)	3.03
O(1)	12976(6)	8643(5)	9334(2)	12.5(6)	2.08
O(2)	7438(6)	10757(5)	8258(3)	12.8(6)	2.01
O(3)	9110(5)	6054(5)	9057(3)	13.1(6)	1.93
O(4)	5435(6)	7309(6)	6043(3)	15.1(7)	2.05
O(5)	10133(6)	6151(5)	5872(2)	12.4(6)	2.09
O(6)	10936(5)	7337(5)	7637(2)	11.2(6)	2.00
O(7)	9426(5)	8930(5)	6429(3)	12.5(6)	1.96
O(8)	10227(6)	9776(5)	8709(3)	12.3(6)	1.99
O(9)	6958(5)	5119(5)	6701(3)	12.0(6)	1.89
O(10)	6343(5)	7091(5)	8555(3)	14.1(7)	2.05
O(11)	3056(6)	3751(5)	6433(3)	14.8(7)	2.00
O(12)	7657(6)	10836(6)	5668(3)	15.3(7)	2.02
O(13)	5206(6)	3493(7)	8837(4)	28.9(10)	1.99

Table S3. The inorganic borates without hydroxyl group, whose FBB contains six B atoms.

Compound	Space Group	B-O framework	ICSD Code	FBB
$Ba_6Al_4B_{14}O_{33}$	$P\bar{1}$	0D $[B_6O_{14}]$ and $[BO_3]$ groups	242282	
$Bi_3B_6O_{13}(OH)$	$P1$	3D network formed by $[B_6O_{16}]$	172482	
CaB_6O_{10}	$P2_1/c$	3D network formed by $[B_6O_{13}]$	161320	
$Ca_2B_6O_{11}$	$P2_1/c$	3D network formed by $[B_6O_{15}]$	23032	
$(Pb_4O)Pb_2B_6O_{14}$-I	$P1$	1D chain formed by $[B_6O_{15}]$	239790	
$(Pb_4O)Pb_2B_6O_{14}$-II	$P\bar{1}$	1D chain formed by $[B_6O_{15}]$	431518	
$Pb_4B_6O_{13}$	Cc	2D layer formed by $[B_6O_{14}]$	13422	
$Na_2ZnB_6O_{11}$	Cc	2D layer formed by $[B_6O_{13}]$	167333	
$Na_2Co_2B_{12}O_{21}$	$I2/a$	3D network formed by $[B_6O_{14}]$	281706	
$Ba_2KZn_3(B_3O_6)(B_6O_{13})$	$P\bar{1}$	0D $[B_6O_{13}]$ and $[B_3O_6]$ groups	404485	
$NH_4NaB_6O_{10}$	$Pa\bar{3}$	3D network formed by $[B_6O_{13}]$	427197	

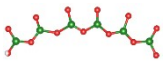
$K_3(B_6O_{10})Cl$ series	*R*3m	3D network formed by $[B_6O_{13}]$	262005	
$Fe_5O_5(B_6O_{10}(OH)_3)(H_2O)_{0.5}$	*P*2/c	1D short chain formed by $[B_6O_{13}]$	249979	

Table S4. Selected bond distances (Å) and angles (deg.) for $Ba_2Zn_2B_6O_{13}$.

Ba(1)-O(2) #1	2.916(3)	Zn(2)-O(2)#1	1.962(3)
Ba(1)-O(4)#1	2.863(3)	Zn(2)-O(13)	1.921(4)
Ba(1)-O(5)#2	2.846(3)	B(1)-O(1)	1.425(6)
Ba(1)-O(6)#2	2.896(3)	B(1)-O(3)	1.507(6)
Ba(1)-O(7)#2	2.840(3)	B(1)-O(6)	1.478(6)
Ba(1)-O(9)	2.886(3)	B(1)-O(8)	1.488(6)
Ba(1)-O(11)	2.763(3)	B(2)-O(5)	1.434(6)
Ba(1)-O(12)#1	2.825(3)	B(2)-O(6)	1.456(6)
Ba(1)-O(12)#3	2.879(3)	B(2)-O(7)	1.507(6)
Ba(2)-O(1)#4	2.912(3)	B(2)-O(9)	1.501(6)
Ba(2)-O(2)#2	2.733(3)	B(3)-O(2)	1.357(6)
Ba(2)-O(3)#4	2.896(3)	B(3)-O(8)	1.360(6)
Ba(2)-O(6)#4	2.771(3)	B(3)-O(10)	1.407(6)
Ba(2)-O(8)#2	2.818(3)	B(4)-O(3)	1.357(6)
Ba(2)-O(10)	2.816(3)	B(4)-O(10)	1.406(6)
Ba(2)-O(11)	3.021(3)	B(4)-O(13)	1.345(7)
Ba(2)-O(13)	2.679(3)	B(5)-O(4)	1.398(6)
Zn(1)-O(5)#3	1.958(3)	B(5)-O(9)	1.373(6)
Zn(1)-O(5)#4	1.949(3)	B(5)-O(11)	1.349(6)
Zn(1)-O(11)	1.940(3)	B(6)-O(4)	1.407(6)
Zn(1)-O(12)#2	1.960(3)	B(6)-O(7)	1.355(6)
Zn(2)-O(1)#10	1.934(3)	B(6)-O(12)	1.342(6)
Zn(2)-O(1)#2	1.962(3)		
O(4)#1-Ba(1)-O(2)#1	69.89(10)	O(8)#2-Ba(2)-O(1)#4	148.50(9)
O(4)#1-Ba(1)-O(6)#2	89.92(10)	O(8)#2-Ba(2)-O(3)#4	116.24(10)
O(4)#1-Ba(1)-O(9)	122.66(10)	O(8)#2-Ba(2)-O(11)	94.89(9)
O(4)#1-Ba(1)-O(12)#3	78.09(10)	O(10)-Ba(2)-O(1)#4	70.43(9)
O(5)#2-Ba(1)-O(2)#1	115.91(9)	O(10)-Ba(2)-O(3)#4	118.00(10)
O(5)#2-Ba(1)-O(4)#1	71.66(10)	O(10)-Ba(2)-O(8)#2	119.41(9)
O(5)#2-Ba(1)-O(6)#2	47.68(9)	O(10)-Ba(2)-O(11)	67.47(10)
O(5)#2-Ba(1)-O(9)	158.61(9)	O(13)-Ba(2)-O(1)#4	112.08(12)
O(5)#2-Ba(1)-O(12)#3	64.89(9)	O(13)-Ba(2)-O(2)#2	119.74(11)
O(6)#2-Ba(1)-O(2)#1	83.25(9)	O(13)-Ba(2)-O(3)#4	151.68(13)
O(7)#2-Ba(1)-O(2)#1	128.91(9)	O(13)-Ba(2)-O(6)#4	136.55(11)
O(7)#2-Ba(1)-O(4)#1	120.20(10)	O(13)-Ba(2)-O(8)#2	69.30(11)
O(7)#2-Ba(1)-O(5)#2	48.66(9)	O(13)-Ba(2)-O(10)	50.14(10)
O(7)#2-Ba(1)-O(6)#2	49.55(9)	O(13)-Ba(2)-O(11)	72.01(12)
O(7)#2-Ba(1)-O(9)	115.73(9)	O(5)#4-Zn(1)-O(5)#3	86.10(14)
O(7)#2-Ba(1)-O(12)#3	79.98(10)	O(5)#4-Zn(1)-O(12)#2	111.53(15)
O(9)-Ba(1)-O(2)#1	85.13(9)	O(5)#3-Zn(1)-O(12)#2	103.31(15)
O(9)-Ba(1)-O(6)#2	138.57(9)	O(11)-Zn(1)-O(5)#3	128.29(15)

O(11)-Ba(1)-O(2)#1	120.07(10)	O(11)-Zn(1)-O(5)#4	113.68(14)
O(11)-Ba(1)-O(4)#1	162.17(10)	O(11)-Zn(1)-O(12)#2	111.29(14)
O(11)-Ba(1)-O(5)#2	112.04(10)	O(1)#10-Zn(2)-O(1)#2	88.88(14)
O(11)-Ba(1)-O(6)#2	105.45(10)	O(1)#10-Zn(2)-O(2)#1	114.84(14)
O(11)-Ba(1)-O(7)#2	66.80(9)	O(1)#2-Zn(2)-O(2)#1	116.40(14)
O(11)-Ba(1)-O(9)	49.20(9)	O(13)-Zn(2)-O(1)#2	108.40(15)
O(11)-Ba(1)-O(2)#1	117.24(10)	O(13)-Zn(2)-O(1)#10	119.59(18)
O(11)-Ba(1)-O(12)#3	87.71(10)	O(13)-Zn(2)-O(2)#1	107.86(16)
O(12)#1-Ba(1)-O(2)#1	74.49(9)	O(1)-B(1)-O(3)	106.3(4)
O(12)#3-Ba(1)-O(2)#1	144.77(9)	O(1)-B(1)-O(6)	106.1(4)
O(12)#1-Ba(1)-O(4)#1	48.39(10)	O(1)-B(1)-O(8)	115.5(4)
O(12)#1-Ba(1)-O(5)#2	112.09(10)	O(6)-B(1)-O(3)	108.4(4)
O(12)#3-Ba(1)-O(6)#2	111.58(9)	O(6)-B(1)-O(8)	111.2(4)
O(12)#1-Ba(1)-O(6)#2	137.27(9)	O(8)-B(1)-O(3)	109.0(4)
O(12)#1-Ba(1)-O(7)#1	152.68(10)	O(5)-B(2)-O(6)	107.1(4)
O(12)#3-Ba(1)-O(9)	100.61(9)	O(5)-B(2)-O(7)	105.5(4)
O(12)#1-Ba(1)-O(9)	75.86(10)	O(5)-B(2)-O(9)	112.8(4)
O(12)#1-Ba(1)-O(12)#3	73.39(11)	O(6)-B(2)-O(7)	108.3(4)
O(1)#4-Ba(2)-O(11)	115.82(9)	O(6)-B(2)-O(9)	112.6(4)
O(2)#2-Ba(2)-O(1)#4	120.38(9)	O(9)-B(2)-O(7)	110.2(3)
O(2)#2-Ba(2)-O(3)#4	72.94(10)	O(2)-B(3)-O(8)	121.2(4)
O(2)#2-Ba(2)-O(6)#4	101.37(10)	O(2)-B(3)-O(10)	119.5(4)
O(2)#2-Ba(2)-O(8)#2	50.53(9)	O(8)-B(3)-O(10)	119.4(4)
O(2)#2-Ba(2)-O(10)	168.99(10)	O(3)-B(4)-O(10)	120.5(4)
O(2)#2-Ba(2)-O(11)	106.75(10)	O(13)-B(4)-O(3)	123.2(4)
O(3)#4-Ba(2)-O(1)#4	47.72(9)	O(13)-B(4)-O(10)	116.0(4)
O(3)#4-Ba(2)-O(11)	131.56(9)	O(9)-B(5)-O(4)	119.7(4)
O(6)#4-Ba(2)-O(1)#4	48.10(9)	O(11)-B(5)-O(4)	120.4(4)
O(6)#4-Ba(2)-O(3)#4	50.56(9)	O(11)-B(5)-O(5)	119.9(4)
O(6)#4-Ba(2)-O(8)#2	150.35(10)	O(7)-B(6)-O(4)	119.1(4)
O(6)#4-Ba(2)-O(10)	87.55(10)	O(12)-B(6)-O(4)	115.9(4)
O(6)#4-Ba(2)-O(11)	83.84(9)	O(12)-B(6)-O(7)	125.0(4)

Symmetry transformations used to generate equivalent atoms:

#1 +X,-1+Y,+Z	#2 -1+X,-1+Y,+Z
#3 1-X,1-Y,1-Z	#4 -1+X,+Y,+Z
#10 2-X,1-Y,2-Z	

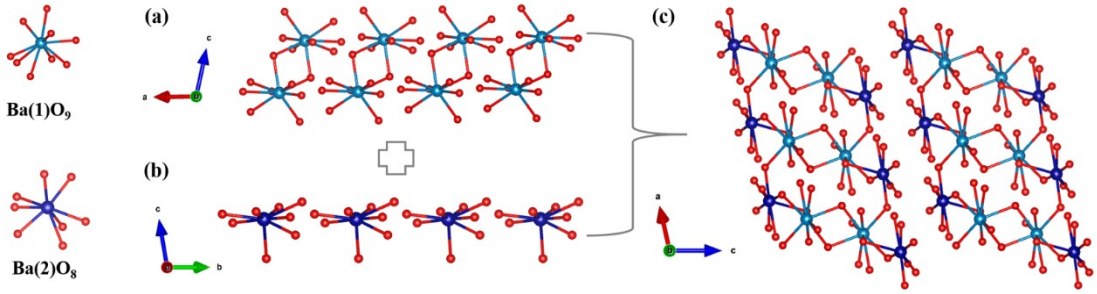


Figure S1. (a) The$[Ba(1)_2O_{16}]$ dimers; (b) isolated $[Ba(2)O_8]$ polyhedra; (c) the $[Ba_2O_{16}]$ layers in $Ba_2Zn_2B_6O_{13}$.

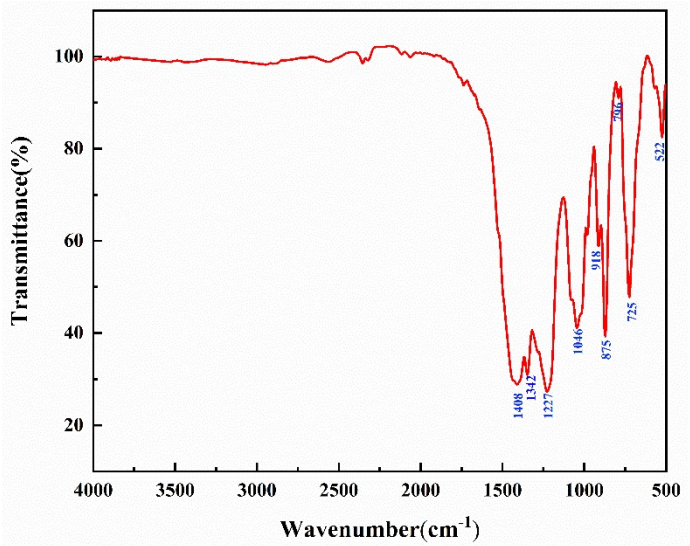


Figure S2. The IR spectrum of $Ba_2Zn_2B_6O_{13}$.

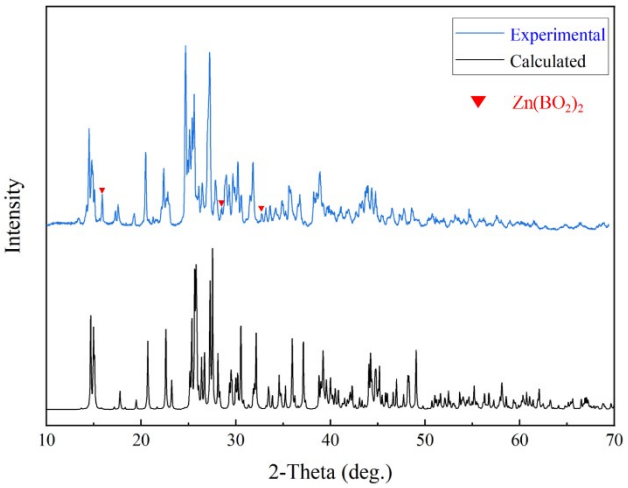


Figure S3. Experimental powder XRD pattern and calculated XRD pattern for $Ba_2Zn_2B_6O_{13}$.

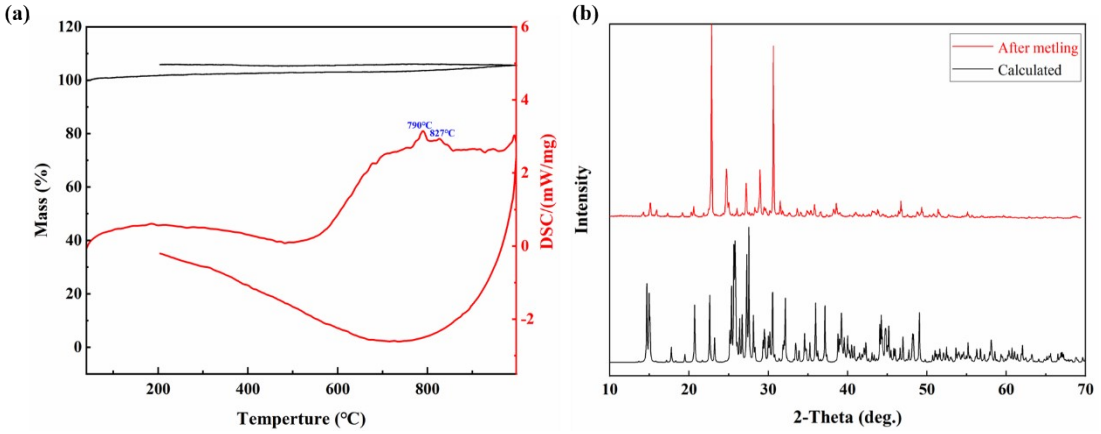


Figure S4. (a) The TG and DSC curves of$Ba_2Zn_2B_6O_{13}$; (b)XRD patterns of $Ba_2Zn_2B_6O_{13}$ powder after melting.

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