Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Discovery of $SrZn_2B_6O_{12}$ with an Unprecedented Quadruple-layered Configuration

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Experimental Section

Crystal Growth. Single crystals of $SrZn_2B_6O_{12}$ were obtained by high-temperature spontaneous crystallization in the open air. All raw materials were purchased through commercial channels. SrF_2, $SrCO_3$, ZnF_2, $Zn(BF_4)_2$ and H_3BO_3 were weighed at the molar ratio of 2:3:10:1:30; Then ground in a mortar, and poured into a platinum crucible for heating. The mixture was slowly heated to 800 °C in 20 h and held for 10 h. Then, the mixture was cooled to 700, 500, 300 °C, and room temperature in 16, 130, 65, and 10 h, respectively.

Compounds Synthesis. Polycrystalline powders of $SrZn_2B_6O_{12}$ simple was synthesized via a solid-state reaction in air. We first mixed ZnO (3.26 g) and $SrCO_3$ (2.95 g) in alcohol (95%) and then ground them fully mixed (four times). The mixture was pressed into tablets, and then heated to 500 °C for 8 h. Then, mixed the as prepared-mixture with B_2O_3 (4.18 g), followed with wet ground with alcohol by four times. The final mixture was pressed into tablets, and then heated to 750 °C for 8 h. With this, the polycrystalline samples of $SrZn_2B_6O_{12}$ were obtained (Figure S1). Although the sample has been calcined many times, there are still some extra peaks that are from the raw and intermediate materials of SrB_2O_4 and ZnB_2O_4.

Single Crystal Structure Data Collection. The single crystal diffraction data were collected on a Bruker D8 Venture Single Crystal X-ray Diffractometer (Mo Kα radiation with λ = 0.71073 Å) at 300 K. Data integration, cell refinement and absorption corrections of the data were completed by utilizing SAINT program.[1] The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques using the program suite SHELXL.[2] No missed symmetry was proved using PLATON program.[3]

Powder X-ray Diffraction Powder XRD patterns of polycrystalline materials were obtained on a Bruker D2 PHASER diffractometer with Cu Kα radiation (λ = 1.5418 Å) at room temperature. The 2θ range was 5–70° with a step size of 0.02° and a fixed counting time of 1 s per step.

Thermal and Optical Performance Characterization. TG and DSC analyses were carried out on a simultaneous NETZSCH STA 449 F3 thermal analyzer instrument in a flowing N_2 atmosphere. The powder sample of $SrZn_2B_6O_{12}$ was placed in the Pt crucible, and heated from 40 to 1000 °C at a rate of 5 °C min^{-1}. The infrared spectroscopy was measured on a Shimadzu IR Affinity-1 Fourier transform infrared spectrometer in the 4000-400 cm^{-1} range. The UV-Vis-NIR diffuse-reflectance spectroscopy data were recorded at 25 °C using a powder sample of $SrZn_2B_6O_{12}$ on a Shimadzu SolidSpec-3700DUV spectrophotometer.

Computational Methods. The electronic structure and optical properties of $SrZn_2B_6O_{12}$ are performed by using the DFT method implemented in the CASTEP module.[4] The exchange-correlation potential is set to local density approximation (LDA), and the norm conservation pseudo potential (NCP) is used for all chemical elements.[5] The valence electron configurations for diverse electron orbital pseudopotentials were Sr $4s^2$ $4p^6$ $5s^2$, Zn $3d^{10}$ $4s^2$, B $2s^2$ $2p^1$ and O $2s^2$ $2p^4$. The plane-wave energy cutoff was set at 830 eV. The Monkhorst-Pack k-point was sampled with a separation of less than 0.025 $Å^{-1}$, which was 7×7×4 for the Brillouin Zone (BZ). Other parameters and convergent criteria were set by the default values of the CASTEP code.

Table S1. Crystal data and structure refinement for $SrZn_2B_6O_{12}$

Formula	**$SrZn_2B_6O_{12}$**
Formula weight	475.22
Temperature (K)	273.15
Wavelength (Å)	0.71073
Crystal system	triclinic
Space group	*P*-1
Unit cell dimension (Å, °)	a = 6.5206(4) b = 6.5408(4) c = 11.4026(7) α = 79.290(2) β = 83.151(2) γ = 61.048(2)
Volume ($Å^3$)	417.89(5)
Z	2
Density (calcd) (g/cm^3)	3.777
Absorption coefficient (mm^{-1})	12.132
***F* (000)**	448.0
The range for data collection (°)	3.638 to 54.928
Index ranges	$-7 \le h \le 8$, $-8 \le k \le 8$, $-14 \le l \le 14$
Reflections collected/unique	5598 / 1907 [R_{int} = 0.0456]
Completeness (%)	98.6
Refinement method	Full-matrix least-squares on F^2
Data/restrains/parameters	1907/0/191
Goodness-of-fit on F^2	1.104
Final *R* indices [$F_o^2 > 2\sigma(F_o^2)$][a]	R_1 = 0.0359, wR_2 = 0.0778
***R* indices (all data)**[a]	R_1 = 0.0439, wR_2 = 0.0828

[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 ($\times 10^4$), equivalent isotropic displacement parameters ($Å^2 \times 10^3$) and BVS results for $SrZn_2B_6O_{12}$. U_{eq} is defined as 1/3 of the trace of the orthogonalised U tensor.

Atom	x	y	z	U(eq)	BVS
Sr1	-3240.6(9)	7100.2(8)	9083.3(4)	9.66(16)	2.30
Zn1	10146.3(11)	-2212.3(11)	4243.6(5)	10.67(18)	2.01
Zn2	4962.1(11)	-2849.8(11)	6025.7(5)	11.09(18)	1.83
B1	12487(11)	4408(10)	6293(6)	11.9(12)	3.03
B2	7265(11)	-174(11)	6261(6)	13.1(12)	2.96
B3	1594(11)	8472(10)	8778(5)	7.8(11)	3.04
B4	10852(11)	2597(10)	8142(5)	9.9(12)	3.11
B5	3325(11)	4371(10)	8357(5)	6.8(11)	3.02
B6	7692(10)	1478(10)	8176(5)	8.5(12)	3.11
O1	5374(6)	2117(6)	8653(3)	8.3(7)	1.96
O2	2375(7)	10089(6)	8538(3)	12.5(8)	2.08
O3	13329(7)	5307(6)	7000(3)	9.4(7)	1.97
O4	11252(6)	4125(6)	8706(3)	8.7(7)	2.12
O5	12621(7)	4908(6)	5077(3)	11.7(8)	1.98
O6	3307(7)	6152(6)	8986(3)	9.9(8)	2.17
O7	8423(7)	3189(6)	8217(3)	10.2(8)	2.00
O8	-741(7)	9128(6)	8797(3)	11.7(8)	2.12
O9	7521(7)	230(6)	5019(3)	11.4(8)	1.91
O10	6539(7)	-1700(6)	6837(3)	13.1(8)	1.96
O11	11498(7)	3021(6)	6791(3)	11.9(8)	2.11
O12	7896(7)	1122(6)	6849(3)	11.7(8)	2.03

Table S3. Bond lengths for $SrZn_2B_6O_{12}$.

Atom 1	Atom 2	Bond length	Atom 1	Atom 2	Bond length
Sr1	O1[2]	2.794(3)	B1	O11	1.359(7)
Sr1	O1[3]	2.909(3)	B2	O9	1.396(7)
Sr1	O2[1]	2.635(4)	B2	O10	1.338(7)
Sr1	O4[4]	2.775(4)	B2	O12	1.398(8)
Sr1	O4[1]	2.654(4)	B3	O2	1.354(7)
Sr1	O6[1]	2.627(4)	B3	O6	1.377(7)
Sr1	O6[2]	2.774(4)	B3	O8	1.366(7)
Sr1	O7[1]	2.587(4)	B4	O2[9]	1.462(7)
Sr1	O8	2.516(4)	B4	O4	1.418(7)
Sr1	O10[3]	2.535(4)	B4	O7	1.433(7)
Zn1	O5[5]	1.953(4)	B4	O11	1.558(7)
Zn1	O9	1.945(4)	B5	O1	1.445(7)
Zn1	O11[6]	1.976(4)	B5	O3[1]	1.555(6)
Zn1	O12[6]	1.965(4)	B5	O4[1]	1.439(7)
Zn2	O3[7]	2.070(4)	B5	O6	1.472(7)
Zn2	O5[6]	1.995(4)	B6	O1	1.425(7)
Zn2	O9[8]	1.998(4)	B6	O7	1.423(7)
Zn2	O10	1.927(4)	B6	O8[9]	1.468(7)
B1	O3	1.375(8)	B6	O12	1.553(7)
B1	O5	1.366(7)			

Table S4. The O-B-O Angles for $SrZn_2B_6O_{12}$.

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
O11	B1	O5	119.0(6)	O1	B5	O3[2]	111.2(4)
O9	B2	O12	113.6(5)	O1	B5	O6	110.3(5)
O10	B2	O9	123.3(6)	O4[2]	B5	O1	109.2(4)
O10	B2	O12	123.0(5)	O4[2]	B5	O3[2]	110.4(4)
O2	B3	O6	115.5(5)	O4[2]	B5	O6	109.3(4)
O2	B3	O8	121.5(5)	O6	B5	O3[2]	106.5(4)
O8	B3	O6	123.0(5)	O1	B6	O8[8]	107.6(4)
O2[8]	B4	O11	105.3(4)	O1	B6	O12	110.7(5)
O4	B4	O2[8]	113.8(5)	O7	B6	O1	113.5(4)
O4	B4	O7	111.5(4)	O7	B6	O8[8]	113.1(5)
O4	B4	O11	106.7(4)	O7	B6	O12	107.1(4)
O7	B4	O2[8]	112.3(4)	O8[8]	B6	O12	104.3(4)
O7	B4	O11	106.6(4)				

[1]-1+X,1-Y,2-Z; [2]-1+X,+Y,+Z; [3]-1+X,1+Y,+Z; [4]1-X,1-Y,2-Z; [5]+X,-1+Y,+Z; [6]2-X,-Y,1-Z; [7]-1+X,-1+Y,+Z; [8]1+X,-1+Y,+Z; [9]1-X,-Y,1-Z; [10]1+X,+Y,+Z; [11]1+X,1+Y,+Z; [12]+X,1+Y,+Z

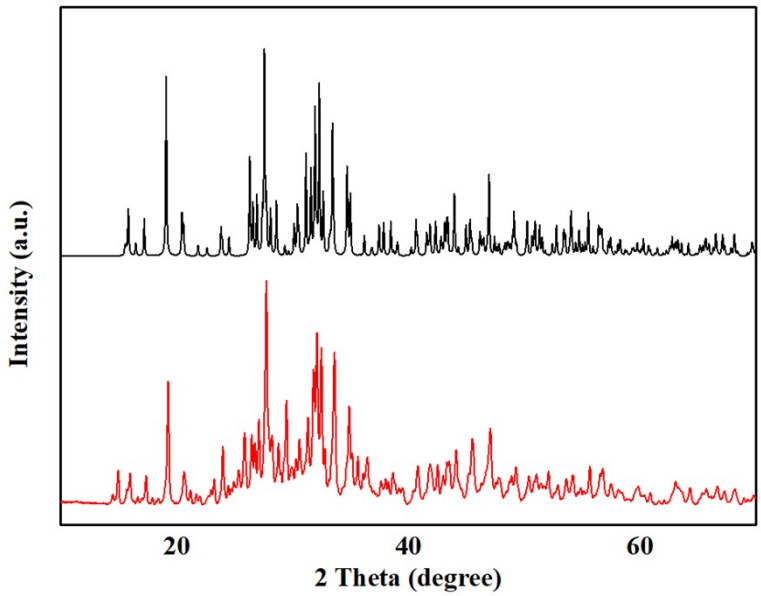

Figure S1. Experimental (red), calculated (black) XRD patterns of $SrZn_2B_6O_{12}$

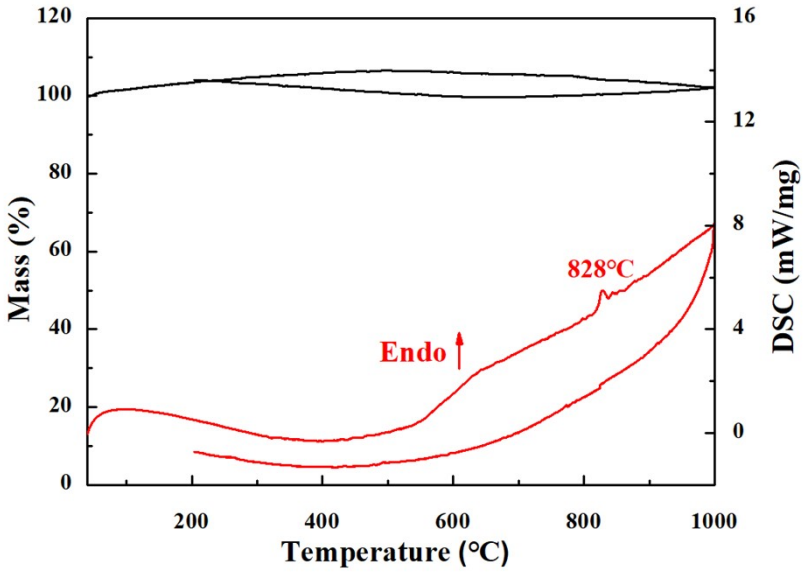

Figure S2. TG–DSC curves of $SrZn_2B_6O_{12}$.

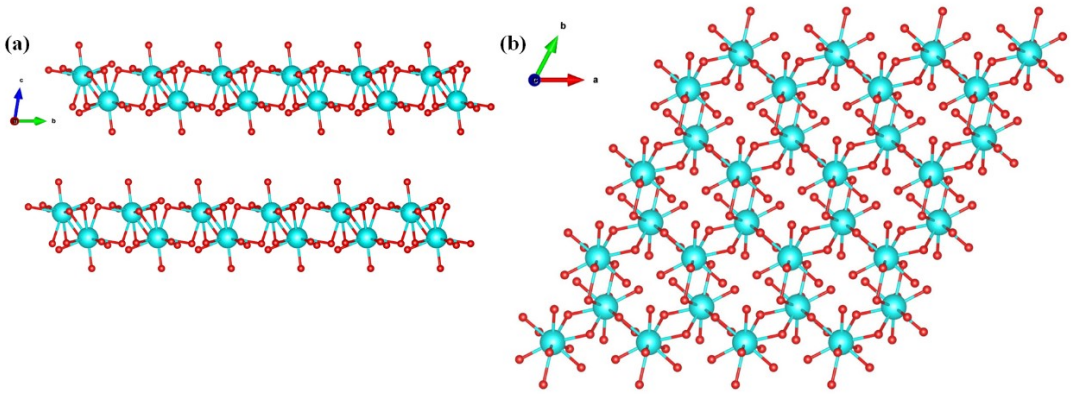

Figure S3. The layers composed of Sr-based polyhedra in $SrZn_2B_6O_{12}$.

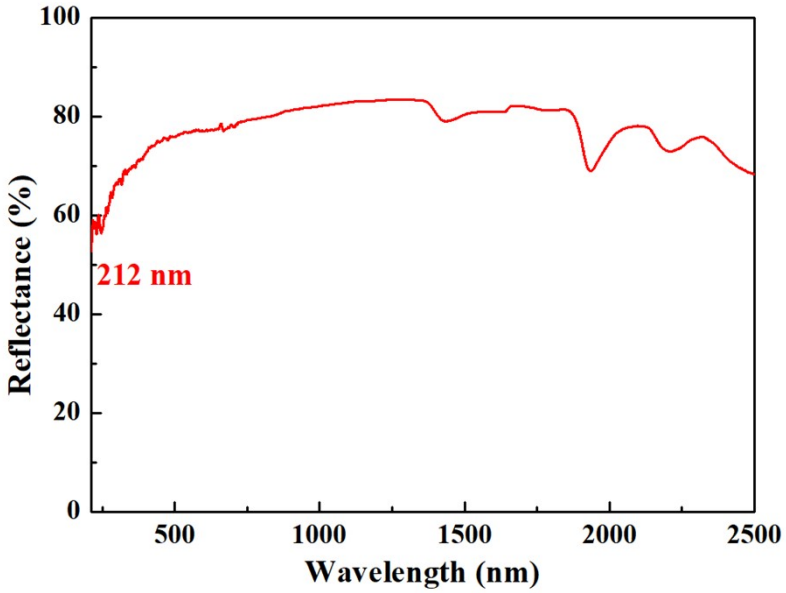

Figure S4. The UV-Vis-NIR diffuse reflectance spectrum of $SrZn_2B_6O_{12}$.

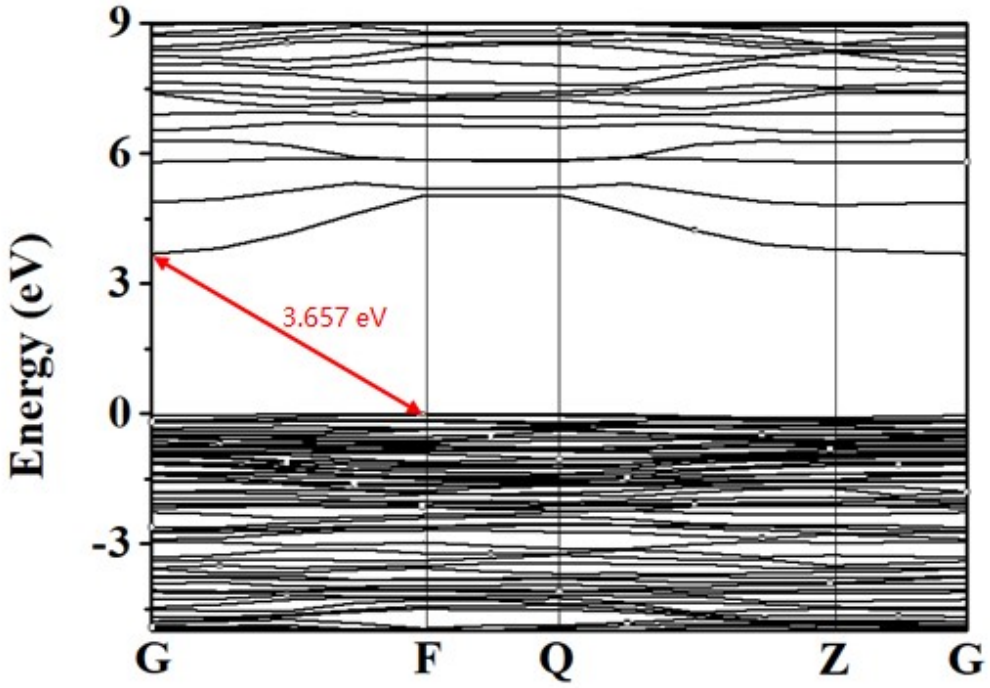

Figure S5. Electronic band structure of $SrZn_2B_6O_{12}$ based on the results of GGA method.

References and Notes

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5. (a) A. M. Rappe, K. M. Rabe, E. Kaxiras, J. D. Joannopoulos, *Phys. Rev. B*, 1990, **41**, 1227; (b) J. S. Lin, A. Qteish, M. C. Payne, V. Heine, *Phys. Rev. B*, 1993, **47**, 4174; (c) M. H. Lee, PhD. Thesis, The University of Cambridge 1996.