Supporting Information

Cation regulation achieves symmetry breaking: from centrosymmetric $M_2Cs_2B_{10}O_{17}$（M = Na, K）to noncentrosymmetric $Na_3CsB_{10}O_{17}$

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Experimental Section

Synthesis.

The raw materials include NaOH (Aladdin Chemical Industry Co., Ltd. 98 %), $NaNO_3$ (Aladdin Chemical Industry Co., Ltd. 99 %), KNO_3 (Aladdin Chemical Industry Co., Ltd. 99%), Cs_2CO_3 (Aladdin Chemical Industry Co., Ltd. 99.99 %), CsF (Aladdin Chemical Industry Co., Ltd. 98 %), B_2O_3 (Aladdin Chemical Industry Co., Ltd. 98 %). All reagents were of analytical grade from commercial sources without purification.

The crystals of $K_2Cs_2B_{10}O_{17}$ and $Na_2Cs_2B_{10}O_{17}$ were obtained by spontaneous crystallization in an open environment. The raw mixture (KNO_3 : Cs_2CO_3 : B_2O_3 = 2 : 1 : 5 for $K_2Cs_2B_{10}O_{17}$) and ($NaNO_3$: Cs_2CO_3 : B_2O_3 = 2 : 1 : 5 for $Na_2Cs_2B_{10}O_{17}$) was thoroughly mixed and placed into a platinum crucible, heated to 750 °C and held for one day, then lowered to 650 °C at a rate of 1 °C/h, and further lowered to room temperature at a rate of 5.5 °C/h. Finally, single crystals of $K_2Cs_2B_{10}O_{17}$ and $Na_2Cs_2B_{10}O_{17}$ were obtained. Polycrystalline samples of $K_2Cs_2B_{10}O_{17}$ and $Na_2Cs_2B_{10}O_{17}$ were obtained by stoichiometric ratio. The raw mixture (KNO_3 : Cs_2CO_3 : B_2O_3 = 2 : 1 : 5 for $K_2Cs_2B_{10}O_{17}$) and ($NaNO_3$: Cs_2CO_3 : B_2O_3 = 2 : 1 : 5 for $Na_2Cs_2B_{10}O_{17}$) were completely mixed. The thoroughly mixed raw materials were put into a platinum crucible, using the YR-SYL-K model miniature intelligent temperature-controlled laboratory furnace, heated at a rate of 1°C/min to 700°C, and held for 80h to obtain polycrystalline samples, which were confirmed by powder XRD measurement, as depicted in Fig. S8 a and b.

The precursor CsB_4O_6F was first obtained through the solid-state method using CsF and B_2O_3 in a ratio of 1 : 2. Then, NaOH, CsB_4O_6F, and B_2O_3 were thoroughly mixed in a ratio of 2.5 : 0.5 : 3, placed into a platinum crucible, using the YR-SYL-K model miniature intelligent temperature-controlled laboratory furnace, heated at a rate of 1°C/min to 750°C and held for one day, then lowered to 600 °C at a rate of 1.5 °C/h, and further lowered to room temperature at a rate of 5.5 °C/h. Finally, single crystals of $Na_3CsB_{10}O_{17}$ were obtained. The polycrystalline sample of $Na_3CsB_{10}O_{17}$ was prepared by thoroughly mixing NaOH, CsB_4O_6F, and B_2O_3 in a ratio of 3 : 1 : 3, then placing it into a platinum crucible. The crucible was heated to 750 °C and held for 48 hours, after which it was cooled to 600 °C at a rate of 1 °C/h, and then to room temperature at a rate of 5 °C/h, finally the polycrystalline sample was obtained, which was confirmed by powder XRD measurement, as depicted in Fig. S8 c.

Powder X-ray diffraction.

The powder XRD patterns of $K_2Cs_2B_{10}O_{17}$, $Na_2Cs_2B_{10}O_{17}$ and $Na_3CsB_{10}O_{17}$ were carried out using a Bruker D2 PHASER X-ray diffractometer equipped with Cu Kα radiation (λ = 1.5418 Å). The 2θ range was 5-70°, the fixed counting time and scan step width were 1 s/step and 0.02°, respectively.

Structural Determination.

The structural data were collected at 296 K and 170 K using a Bruker SMART APEX II CCD diffractometer with Mo Kα radiation (λ = 0.71073 Å). The SAINT-Plus and SADABS programs were used for the collection and integration of diffraction data, as well as for the indexing of reflections or digital absorption corrections, respectively. The analysis and refinement of the crystal structure data were carried out using the SHELXTL and Olex software packages, the positions of heavy atoms and hydrogen atoms were determined through direct methods or difference Fourier synthesis in the SHELXTL program.[1-3] Subsequently, all atomic coordinates and anisotropic displacement parameters were refined using the full matrix least squares

method until convergence was achieved. The PLATON program was utilized to verify whether the crystal structure has a higher symmetry space group, and the rationality and completeness of the CIF format structure file were evaluated through the online network of the International Union of Crystallography (http://checkcif.iucr.org/) to ensure the accuracy and reliability of the crystal structure data.[4] Relevant atomic coordinates, equivalent isotropic displacement parameters, and selected interatomic distances and angles are listed in Tables S1-S4 of the SI.

UV−vis−NIR Diffuse Reflectance Spectroscopy.

The optical diffuse reflectance spectra of $K_2Cs_2B_{10}O_{17}$, $Na_2Cs_2B_{10}O_{17}$ and $Na_3CsB_{10}O_{17}$ were measured by a Shimadzu SolidSpec-3700 DUV spectrophotometer in the wavelength range of 190-2600 nm at room temperature.

IR Spectroscopy.

The IR spectra of $K_2Cs_2B_{10}O_{17,}$ $Na_2Cs_2B_{10}O_{17}$ and $Na_3CsB_{10}O_{17}$ were inspected by Shimadzu IR Affinity-1 Fourier transform IR spectrometer over 500-4000 cm^{-1}. During the measurement, the sample was mixed thoroughly and pressed into discs with dried KBr (1 mg of the sample and 100 mg of KBr).

Birefringence measurements.

The refractive index difference of $Na_2Cs_2B_{10}O_{17}$ and $Na_3CsB_{10}O_{17}$ were characterized using the polarizing microscope equipped (ZEISS Axio Scope. A1) with Berek compensator with a wavelength of 546 nm. The birefringence was obtained by the equation, $R = |N_g - N_p| \times d = \Delta n \times d$, where R, N_g, N_p, d, and Δn are corresponding to optical path difference, refractive index of fast light, refractive index of slow light, thickness of crystal, and birefringence, respectively.[5]

Elemental Analysis.

A field-emission scanning electron microscope (SEM, SUPRA 55 VP) equipped with an energy dispersive X-ray spectroscope (BRUKER X-flash-Sdd-5010) was used to acquire the EDS data, as depicted in Fig. S9.

Computational Methods.

The CASTEP package was used to calculate electronic structure, linear and nonlinear optical properties of $K_2Cs_2B_{10}O_{17}$, $Na_2Cs_2B_{10}O_{17}$ and $Na_3CsB_{10}O_{17}$.[6] In the functional, the same setting as in the structural optimization, the plane wave interception, is used. The breaking energy is 750 eV, and the grid density at k points is set to 5×5×3. In the pseudopotential selection, the modulo conservation pseudopotential is selected, and the valence electron configurations involved are as follows: Na-$2p^6$ $3s^1$, K-$3p^6$ $4s^1$, Cs-$5p^6$ $6s^1$, B-$2s^2$ $2p^1$, O-$2s^2$ $2p^4$. The phonon dispersion curve is calculated using the finite displacement method to determine the dynamic stability of the structure, and the default values in the CASTEP code are used for other calculation parameters and convergence criteria. To achieve the convergence of the optical properties, the number of empty bands is set to three times the number of valence bands. In addition, in order to balance the computational efficiency and accuracy of the optical properties under high-density k-point grids, HSEO6 hybrid functional and PBEO functional calculations in PWmat were used to obtain more accurate bandgap values (Eg^{HSE06}, Eg^{PBE0}), which were corrected by scissor operators the calculated refractive index and SHG coefficient.[7,8] The scissor operator is set to the difference between the bandgap calculated by HSE06 and the GGA method. The scissor operators for $K_2Cs_2B_{10}O_{17}$, $Na_2Cs_2B_{10}O_{17}$ and $Na_3CsB_{10}O_{17}$ are 1.42, 1.50, and 1.39 eV, respectively.

We conducted multiple single-crystal data collections and analyses on the $Na_3CsB_{10}O_{17}$ crystal, revealing Cs positional disorder within the compound. The Cs1A occupancy fluctuates within the range of 0.8–0.9, with the Cs1B occupancy fluctuating between 0.1 and 0.2. Due to limitations in our computational model, and for computational convenience, all theoretical calculations for $Na_3CsB_{10}O_{17}$ were based on removing Cs1B and setting the Cs1A occupancy to 1. The results were obtained after optimising the structure. The reliability of these theoretical calculations was subsequently validated experimentally.Calculations yield a maximum second-harmonic generation coefficient for $Na_3CsB_{10}O_{17}$ of d_{15} = 0.083 pm/V, approximately 0.21×KDP. The polycrystalline powder sample exhibits faint green light under laser irradiation; however, owing to operational sensitivity and operator variability, no discernible second-harmonic generation signal was observed during testing with 1064 nm and 532 nm lasers.

Table S1. Crystallographic data for $K_2Cs_2B_{10}O_{17}$, $Na_2Cs_2B_{10}O_{17}$ and $Na_3CsB_{10}O_{17}$.

Empirical formula	$K_2Cs_2B_{10}O_{17}$	$Na_2Cs_2B_{10}O_{17}$	$Na_3CsB_{10}O_{17}$
Formula weight	724.12	691.90	581.98
Temperature/K	296	296	170
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	*C*2/*c*	*C*2/*c*	*Pc*
a/Å	22.6022(11)	21.723(9)	11.3848(5)
b/Å	6.5992(2)	6.566(3)	6.4819(3)
c/Å	11.2991(6)	11.082(5)	11.3125(5)
β/°	103.460(2)	105.557(17)	113.466(2)
Volume/Å^3	1639.04(13)	1522.6(12)	765.77(6)
Z	4	4	2
ρ_{calcg}/cm3	2.934	3.018	2.524
μ/mm^{-1}	5.047	4.942	2.598
F(000)	1336.0	1272.0	548.0
Radiation		MoKα (λ = 0.71073)	
2θ range for data collection/°	6.446 to 52.728	3.892 to 54.966	6.286 to 55.814
Index ranges	-28≤*h*≤28, -8≤*k*≤8, -14≤*l*≤14	-27≤*h*≤28, -8≤*k*≤8, -14≤*l*≤14	-14≤*h*≤14, -8≤*k*≤8, -14≤*l*≤14
Reflections collected	24985	14648	20890
Independent reflections	1682 [*R*(int) = 0.0686]	1737 [*R*(int) = 0.0644]	3639 [*R*(int) = 0.0590]
Data/restraints/parameters	1682 / 0 / 141	1737/0/141	3639/2/291
Goodness-of-fit on F^2	1.094	1.062	1.181
Final *R* indexes [*I*>=2σ (*I*)] [a]	R_1 = 0.0264, wR_2 = 0.0757	R_1 = 0.0298, wR_2 = 0.0676	R_1 = 0.0351, wR_2 = 0.0801
Final R indexes [all data] [a]	R_1 = 0.0294, wR_2 = 0.0772	R_1 = 0.0342, wR_2 = 0.0697	R_1 = 0.0363, wR_2 = 0.0809
Largest diff. peak/hole (e/Å^3)	1.20/-0.94	0.84/-0.88	0.92/-0.81
Flack parameter	/	/	0.49(2)
Hooft	/	/	-0.017(6)

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$ for $F_o^2 > 2\sigma(F_o^2)$

Table S2. Atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2×10^3) and bond valence sum (BVS)* calculations for $K_2Cs_2B_{10}O_{17}$, $Na_2Cs_2B_{10}O_{17}$ and $Na_3CsB_{10}O_{17}$. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

$K_2Cs_2B_{10}O_{17}$						
Atoms	Wyck.	x	y	z	U(eq)	BVS
K1	8f	2286.5(4)	5831.8(13)	6743.0(8)	18.3(2)	1.20
Cs1	8f	4455.7(2)	1912.6(4)	9063.0(3)	30.02(13)	0.95
B1	8f	4486.9(19)	6752(6)	7666(4)	12.1(8)	3.06
B2	8f	3650.2(19)	6821(6)	8718(4)	9.1(7)	3.04
B3	8f	3553.0(19)	8479(6)	6634(3)	9.2(7)	3.05
B4	8f	3325.7(19)	5580(6)	5153(4)	11.2(8)	3.04
B5	8f	3493.1(19)	2079(6)	5753(4)	10.5(8)	3.05
O1	4e	5000	5741(6)	7500	19.4(8)	2.02
O2	8f	4278.3(12)	6295(4)	8663(2)	15.3(5)	2.11
O3	8f	4217.7(12)	8122(4)	6822(3)	16.6(6)	1.93
O4	8f	3313.1(11)	7676(4)	7601(2)	8.1(5)	2.21
O5	8f	3257.7(13)	7549(4)	5440(2)	13.6(5)	2.04
O6	8f	3358.4(12)	5096(4)	3999(2)	11.5(5)	1.96
O7	8f	3345.0(15)	4069(4)	6008(2)	20.0(6)	2.00
O8	8f	3680.1(13)	1688(4)	4721(2)	13.2(5)	2.02
O9	8f	3433.7(13)	684(4)	6581(2)	12.8(5)	2.10

$Na_2Cs_2B_{10}O_{17}$						
Atoms	Wyck.	x	y	z	U(eq)	BVS
Na1	8f	2327.5(8)	9518(2)	6837.9(15)	21.2(4)	1.08
Cs1	8f	4417.8(2)	13070.7(4)	9038.6(3)	27.18(11)	0.97
B1	8f	3197(2)	-731(6)	4964(4)	11.7(8)	3.00
B2	8f	3339(2)	2778(6)	5634(4)	12.6(8)	3.01
B3	8f	3448(2)	6373(6)	6512(4)	10.0(8)	3.00
B4	8f	4451(2)	8052(6)	7632(4)	14.1(8)	3.04
B5	8f	3547(2)	8219(6)	8592(4)	12.5(8)	3.04
O1	8f	3188.1(14)	-2738(4)	5243(2)	13.7(6)	2.00
O2	8f	3259.0(13)	-190(4)	3811(2)	12.7(5)	2.02
O3	8f	3169.4(15)	771(4)	5833(2)	18.7(6)	2.01

O4	8f	3561.2(14)	3228(4)	4634(2)	16.4(6)	1.99
O5	8f	3292.8(13)	4177(4)	6502(2)	13.5(5)	2.02
O6	8f	4163.1(14)	6608(4)	6799(3)	16.8(6)	1.92
O7	8f	3189.6(12)	7324(4)	7441(2)	10.7(5)	2.13
O8	8f	4221.0(13)	8657(4)	8599(3)	16.8(6)	2.04
O9	4e	5000	9001(6)	7500	22.9(9)	2.00

$Na_3CsB_{10}O_{17}$

Atoms	Wyck.	x	y	z	U(eq)	BVS
Na1	2a	1468(3)	5887(5)	1674(3)	21.1(6)	1.02
Na2	2a	627(3)	9(5)	2596(3)	16.6(5)	1.37
Na3	2a	9337(6)	6080(5)	8312(4)	60.8(16)	1.04
Cs1A	2a	5125.9(6)	-3326.7(8)	2958.0(6)	24.84(15)	0.65
Cs1B	2a	6244(6)	3406(7)	2298(5)	71(2)	0.64
B1	2a	9149(7)	10670(11)	4844(6)	11.5(13)	3.04
B2	2a	8717(7)	7145(11)	5199(7)	12.9(14)	3.04
B3	2a	8502(7)	1767(12)	7995(7)	13.9(13)	3.04
B4	2a	8674(7)	3515(11)	6041(7)	12.5(14)	3.06
B5	2a	6753(7)	1648(12)	5867(7)	14.6(14)	3.06
B6	2a	4505(7)	1640(12)	4262(7)	16.4(14)	3.05
B7	2a	2589(7)	3507(11)	4130(7)	13.3(13)	3.05
B8	2a	2713(7)	1785(10)	2164(7)	12.0(13)	3.04
B9	2a	2106(7)	692(11)	5355(7)	12.7(14)	2.99
B10	2a	2514(8)	-2861(12)	4962(7)	12.4(14)	3.04
O1	2a	9373(4)	12652(7)	5268(4)	12.0(9)	2.12
O2	2a	9185(4)	10153(7)	3692(4)	11.5(9)	2.08
O3	2a	8949(5)	9193(7)	5621(4)	16.0(10)	2.13
O4	2a	8400(5)	6722(8)	3943(4)	17.8(11)	2.18
O5	2a	8887(5)	5747(7)	6139(4)	15.8(9)	2.08
O6	2a	7316(5)	3011(7)	5358(5)	13.7(9)	2.03
O7	2a	9229(4)	2696(7)	7341(4)	11.0(8)	2.07
O8	2a	7221(4)	1152(7)	7139(4)	16.3(10)	2.11
O9	2a	5634(5)	693(7)	5055(5)	19.9(9)	2.04
O10	2a	3999(4)	1127(7)	2996(4)	14.7(9)	2.07

O11	2a	3956(5)	3029(7)	4783(5)	16.9(9)	1.93
O12	2a	2006(4)	2687(7)	2836(4)	11.1(9)	1.86
O13	2a	1907(5)	2700(7)	4920(4)	15.1(10)	1.90
O14	2a	2017(4)	122(7)	6460(4)	13.7(9)	2.04
O15	2a	2315(4)	-784(7)	4563(4)	13.6(9)	2.07
O16	2a	2757(5)	-3323(7)	6196(5)	15.4(9)	2.08
O17	2a	2405(5)	-4220(7)	4022(4)	15.6(9)	2.01

(BVS)*: The bond valence sums were calculated using the formula $V_i = \sum S_{ij} = \sum \exp[(r_0 - r_{ij}) / B]$, where S_{ij} is the bond valence associated with bond length r_{ij}, and r_0 and B (usually 0.37) are empirically determined parameters.

Table S3. Selected bond distances (Å) for $K_2Cs_2B_{10}O_{17}$, $Na_2Cs_2B_{10}O_{17}$ and $Na_3CsB_{10}O_{17}$.

$K_2Cs_2B_{10}O_{17}$					
Atom	Atom	Length/Å	Atom	Atom	Length/Å
K1	$O4^1$	2.682(3)	B1	O2	1.353(5)
K1	O4	2.600(3)	B1	O3	1.351(5)
K1	$O5^2$	2.706(3)	B2	O2	1.476(5)
K1	$O6^2$	3.079(3)	B2	O4	1.429(4)
K1	O7	2.948(3)	B2	$O6^3$	1.494(4)
K1	$O8^4$	2.931(3)	B2	$O8^3$	1.491(4)
K1	$O9^5$	2.771(3)	B3	O3	1.486(5)
Cs1	O1	3.468(3)	B3	O4	1.430(5)
Cs1	$O2^6$	3.573(3)	B3	O5	1.492(4)
Cs1	O2	2.940(3)	B3	$O9^9$	1.478(4)
Cs1	$O3^3$	3.285(3)	B4	O5	1.357(5)
Cs1	$O3^7$	3.510(3)	B4	O6	1.362(5)
Cs1	$O5^3$	3.441(3)	B4	O7	1.381(5)
Cs1	$O6^3$	3.158(3)	B5	O7	1.401(5)
Cs1	$O8^8$	3.143(3)	B5	O8	1.354(5)
Cs1	O9	3.293(3)	B5	O9	1.342(5)
B1	O1	1.388(5)			

Symmetry transformations used to generate equivalent atoms:

#1 1/2-X,-1/2+Y,3/2-Z; #2 1/2-X,3/2-Y,1-Z; #3 +X,1-Y,1/2+Z; #4 1/2-X,1/2-Y,1-Z;
#5 1/2-X,1/2+Y,3/2-Z; #6 1-X,1-Y,2-Z; #7 +X,-1+Y,+Z; #8 +X,-Y,1/2+Z;
#9 +X,1+Y,+Z

$Na_2Cs_2B_{10}O_{17}$					
Atom	Atom	Length/Å	Atom	Atom	Length/Å
Na1	$O1^4$	2.559(3)	B1	O2	1.367(5)
Na1	$O2^5$	2.588(3)	B1	O3	1.392(5)
Na1	$O3^3$	2.521(3)	B2	O3	1.401(5)
Na1	$O4^6$	2.625(3)	B2	O4	1.355(5)
Na1	$O5^2$	2.565(3)	B2	O5	1.352(5)
Na1	$O7^2$	2.403(3)	B3	$O1^3$	1.488(5)
Na1	O7	2.315(3)	B3	O5	1.480(5)
Cs1	$O1^5$	3.298(3)	B3	O6	1.507(5)

Cs1	$O2^{5}$	3.104(3)	B3	O7	1.440(5)
Cs1	$O4^{7}$	3.235(3)	B4	O6	1.353(5)
Cs1	$O5^{3}$	3.273(3)	B4	O8	1.357(5)
Cs1	$O6^{3}$	3.335(3)	B4	O9	1.389(5)
Cs1	$O6^{7}$	3.258(3)	B5	$O2^{5}$	1.485(5)
Cs1	O8	2.951(3)	B5	$O4^{5}$	1.490(5)
Cs1	$O8^{8}$	3.568(3)	B5	O7	1.430(5)
Cs1	O9	3.578(3)	B5	O8	1.489(5)
B1	O1	1.355(5)			

Symmetry transformations used to generate equivalent atoms:

#1 1/2-X,-1/2+Y,3/2-Z #2 1/2-X,1/2+Y,3/2-Z #3 +X,1+Y,+Z #4 1/2-X,1/2-Y,1-Z
#5 +X,1-Y,1/2+Z # 6 1/2-X,3/2-Y,1-Z #7 +X,2-Y,1/2+Z #8 1-X,2-Y,2-Z

$Na_3CsB_{10}O_{17}$

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Na1	$O1^{4}$	2.468(5)	Cs1B	$O5^{3}$	3.770(7)
Na1	O12	2.401(5)	B1	O1	1.359(8)
Na1	$O13^{3}$	2.411(5)	B1	O2	1.362(8)
Na1	$O14^{3}$	2.695(6)	B1	O3	1.379(8)
Na1	$O16^{5}$	2.416(6)	B2	O3	1.400(8)
Na1	$O17^{1}$	2.438(6)	B2	O4	1.347(8)
Na2	$O2^{7}$	2.422(6)	B2	O5	1.351(8)
Na2	$O3^{2}$	2.347(5)	B3	$O2^{8}$	1.512(8)
Na2	$O7^{6}$	2.308(5)	B3	$O4^{8}$	1.491(9)
Na2	O12	2.283(5)	B3	O7	1.443(8)
Na2	$O14^{5}$	2.404(5)	B3	O8	1.449(8)
Na2	O15	2.346(5)	B4	$O1^{11}$	1.505(8)
Na3	$O1^{9}$	2.346(5)	B4	O5	1.463(8)
Na3	$O2^{9}$	2.497(6)	B4	O6	1.463(9)
Na3	$O4^{8}$	2.356(6)	B4	O7	1.450(8)
Na3	O5	2.313(6)	B5	O6	1.349(9)
Na3	O7	2.434(6)	B5	O8	1.359(8)
Cs1A	$O4^{11}$	3.440(5)	B5	O9	1.385(9)
Cs1A	$O6^{11}$	3.719(5)	B6	O9	1.384(9)

Cs1A	$O8^{5}$	3.209(5)	B6	O10	1.355(9)
Cs1A	O9	3.415(5)	B6	O11	1.356(9)
Cs1A	O10	3.166(5)	B7	O11	1.466(9)
Cs1A	$O11^{11}$	3.715(5)	B7	O12	1.447(8)
Cs1A	$O11^{5}$	3.302(5)	B7	O13	1.493(8)
Cs1A	$O16^{12}$	3.418(5)	B7	$O17^{1}$	1.486(8)
Cs1A	O17	3.788(5)	B8	O10	1.454(8)
Cs1A	$O10^{11}$	3.823(5)	B8	O12	1.433(8)
Cs1B	O4	3.236(7)	B8	$O14^{5}$	1.513(8)
Cs1B	O6	3.190(7)	B8	$O16^{5}$	1.496(8)
Cs1B	$O6^{3}$	3.719(7)	B9	O13	1.378(9)
Cs1B	$O8^{3}$	3.724(6)	B9	O14	1.346(9)
Cs1B	$O8^{5}$	3.187(7)	B9	O15	1.395(8)
Cs1B	$O9^{5}$	3.546(7)	B10	O15	1.409(9)
Cs1B	O10	3.308(7)	B10	O16	1.345(8)
Cs1B	$O16^{5}$	3.658(8)	B10	O17	1.348(9)
Cs1B	$O2^{11}$	3.734(8)			

Symmetry transformations used to generate equivalent atoms:

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

Table S4. Selected angles (deg) for $K_2Cs_2B_{10}O_{17}$, $Na_2Cs_2B_{10}O_{17}$ and $Na_3CsB_{10}O_{17}$.

$K_2Cs_2B_{10}O_{17}$							
Atom	**Atom**	**Atom**	**Angle/˚**	**Atom**	**Atom**	**Atom**	**Angle/˚**
O4	K1	O4^{1}	136.48(6)	O5^{3}	Cs1	O3^{7}	113.27(6)
O4	K1	O5^{2}	109.39(8)	O6^{3}	Cs1	O1	84.41(6)
O4^{1}	K1	O5^{2}	114.00(8)	O6^{3}	Cs1	O2^{6}	107.64(6)
O4	K1	O6^{2}	91.03(8)	O6^{3}	Cs1	O3^{3}	74.04(7)
O4^{1}	K1	O6^{2}	121.03(8)	O6^{3}	Cs1	O3^{7}	116.18(6)
O4^{1}	K1	O7	105.47(8)	O6^{3}	Cs1	O5^{3}	41.34(6)
O4	K1	O7	65.00(8)	O6^{3}	Cs1	O9	75.09(6)
O4^{1}	K1	O8^{4}	50.00(7)	O8^{8}	Cs1	O1	162.69(5)
O4	K1	O8^{4}	163.61(8)	O8^{8}	Cs1	O2^{6}	118.53(6)
O4	K1	O9^{5}	112.14(8)	O8^{8}	Cs1	O3^{3}	63.04(7)
O4^{1}	K1	O9^{5}	50.86(7)	O8^{8}	Cs1	O3^{7}	68.39(6)
O5^{2}	K1	O6^{2}	47.27(7)	O8^{8}	Cs1	O5^{3}	55.26(6)
O5^{2}	K1	O7	97.21(8)	O8^{8}	Cs1	O6^{3}	89.98(7)
O5^{2}	K1	O8^{4}	65.71(8)	O8^{8}	Cs1	O9	72.30(7)
O5^{2}	K1	O9^{5}	114.95(9)	O9	Cs1	O1	90.42(5)
O7	K1	O6^{2}	129.16(7)	O9	Cs1	O2^{6}	168.41(6)
O8^{4}	K1	O6^{2}	95.63(7)	O9	Cs1	O3^{7}	41.49(6)
O8^{4}	K1	O7	99.45(8)	O9	Cs1	O5^{3}	86.59(6)
O9^{5}	K1	O6^{2}	84.29(7)	O2	B1	O1	118.0(3)
O9^{5}	K1	O7	145.37(8)	O3	B1	O1	118.7(3)
O9^{5}	K1	O8^{4}	83.48(8)	O3	B1	O2	123.3(4)
O1	Cs1	O2^{6}	78.78(5)	O2	B2	O6^{3}	106.6(3)
O1	Cs1	O3^{7}	99.49(6)	O2	B2	O8^{3}	108.2(3)
O2	Cs1	O1	42.01(7)	O4	B2	O2	112.1(3)
O2	Cs1	O2^{6}	80.95(7)	O4	B2	O6^{3}	110.5(3)
O2	Cs1	O3^{3}	96.08(7)	O4	B2	O8^{3}	109.3(3)
O2	Cs1	O3^{7}	126.70(7)	O8^{3}	B2	O6^{3}	110.0(3)
O2	Cs1	O5^{3}	82.78(7)	O3	B3	O5	106.8(3)
O2	Cs1	O6^{3}	45.82(7)	O4	B3	O3	112.5(3)
O2	Cs1	O8^{8}	135.74(7)	O4	B3	O5	111.7(3)
O2	Cs1	O9	93.89(7)	O4	B3	O9^{9}	107.3(3)
O3^{3}	Cs1	O1	130.11(6)	O9^{9}	B3	O3	109.3(3)
O3^{7}	Cs1	O2^{6}	135.82(6)	O9^{9}	B3	O5	109.2(3)
O3^{3}	Cs1	O2^{6}	66.45(6)	O5	B4	O6	119.2(3)
O3^{3}	Cs1	O3^{7}	130.40(5)	O5	B4	O7	120.8(3)
O3^{3}	Cs1	O5^{3}	41.56(6)	O6	B4	O7	120.0(3)
O3^{3}	Cs1	O9	124.70(7)	O8	B5	O7	119.6(3)

O5[3]	Cs1	O1	124.38(6)	O9	B5	O7	115.6(3)
O5[3]	Cs1	O2[6]	102.92(6)	O9	B5	O8	124.8(3)

Symmetry transformations used to generate equivalent atoms:

#1 1/2-X,-1/2+Y,3/2-Z; #2 1/2-X,3/2-Y,1-Z; #3 +X,1-Y,1/2+Z; #41/2-X,1/2-Y,1-Z;
#5 1/2-X,1/2+Y,3/2-Z; #6 1-X,1-Y,2-Z; #7 +X,-1+Y,+Z; #8 +X,-Y,1/2+Z;
#9 +X,1+Y,+Z; #10 +X,1-Y,-1/2+Z; #11 1-X,+Y,3/2-Z; #12 +X,-Y,-1/2+Z

$Na_2Cs_2B_{10}O_{17}$

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
O1[4]	Na1	O2[5]	153.26(11)	O5[1]	Na1	O2[5]	81.43(10)
O1[4]	Na1	O4[6]	68.06(10)	O5[1]	Na1	O4[6]	93.14(10)
O1[4]	Na1	O5[1]	114.78(11)	O7	Na1	O1[4]	95.77(11)
O1	B1	O2	118.5(3)	O7[1]	Na1	O1[4]	121.27(11)
O1	B1	O3	121.7(3)	O7	B3	O6	112.5(3)
O2	B1	O3	119.7(3)	O6	B4	O8	122.9(4)
O4	B2	O3	120.0(3)	O6	B4	O9	119.7(3)
O5	B2	O3	117.0(3)	O8	B4	O9	117.4(4)
O5	B2	O4	123.0(3)	O7	Na1	O2[5]	58.23(9)
O2[5]	Na1	O4[6]	135.00(10)	O7[1]	Na1	O2[5]	85.27(10)
O3[3]	Na1	O1[4]	86.86(10)	O7	Na1	O3[3]	72.77(10)
O3[3]	Na1	O2[5]	79.75(10)	O7[1]	Na1	O3[3]	110.85(11)
O3[3]	Na1	O4[6]	92.36(11)	O7	Na1	O4[6]	159.00(11)
O3[3]	Na1	O5[1]	158.16(11)	O7[1]	Na1	O4[6]	56.16(9)
O1[3]	B3	O6	105.6(3)	O7[1]	Na1	O5[1]	56.36(9)
O5	B3	O1[3]	110.3(3)	O7	Na1	O5[1]	106.19(11)
O5	B3	O6	108.8(3)	O7	Na1	O7[1]	142.67(9)
O7	B3	O1[3]	112.5(3)	O1[5]	Cs1	O6[3]	110.88(7)
O7	B3	O5	107.2(3)	O1[5]	Cs1	O8[7]	106.49(7)
O2[5]	B5	O4[5]	110.5(3)	O4[8]	Cs1	O9	162.64(5)
O2[5]	B5	O8	106.7(3)	O5[3]	Cs1	O1[5]	82.12(7)
O7	B5	O2[5]	110.6(3)	O5[3]	Cs1	O6[3]	43.11(7)
O7	B5	O4[5]	108.8(3)	O5[3]	Cs1	O8[7]	168.95(6)
O7	B5	O8	112.5(3)	O5[3]	Cs1	O9	91.97(5)
O8	B5	O4[5]	107.7(3)	O6[8]	Cs1	O1[5]	42.65(7)
O1[5]	Cs1	O9	124.86(6)	O6[8]	Cs1	O5[3]	121.08(7)
O2[5]	Cs1	O1[5]	42.72(6)	O6[8]	Cs1	O6[3]	128.13(5)
O2[5]	Cs1	O4[8]	88.63(8)	O6[3]	Cs1	O8[7]	134.98(7)
O2[5]	Cs1	O5[3]	70.31(7)	O6[8]	Cs1	O8[7]	69.37(7)
O2[5]	Cs1	O6[3]	113.26(7)	O6[3]	Cs1	O9	100.06(7)
O2[5]	Cs1	O6[8]	77.15(7)	O6[8]	Cs1	O9	131.80(6)

$O2^{5}$	Cs1	$O8^{7}$	111.11(7)	O8	Cs1	$O1^{5}$	84.53(7)
$O2^{5}$	Cs1	O9	83.62(6)	O8	Cs1	$O2^{5}$	46.35(7)
$O4^{8}$	Cs1	$O1^{5}$	52.73(7)	O8	Cs1	$O4^{8}$	134.89(8)
$O4^{8}$	Cs1	$O5^{3}$	70.77(7)	O8	Cs1	$O5^{3}$	91.96(7)
$O4^{8}$	Cs1	$O6^{8}$	60.53(7)	O8	Cs1	$O6^{3}$	124.97(7)
$O4^{8}$	Cs1	$O6^{3}$	68.83(7)	O8	Cs1	$O6^{8}$	99.51(7)
$O4^{8}$	Cs1	$O8^{7}$	119.87(7)	O8	Cs1	$O8^{7}$	82.18(7)
O8	Cs1	O9	40.71(7)	$O8^{7}$	Cs1	O9	77.47(5)

Symmetry transformations used to generate equivalent atoms:

#1 1/2-X,1/2+Y,3/2-Z #2 1/2-X,-1/2+Y,3/2-Z #3 +X,1+Y,+Z #4 1/2-X,1/2-Y,1-Z
#5 +X,1-Y,1/2+Z #6 1/2-X,3/2-Y,1-Z #7 1-X,2-Y,2-Z #8 +X,2-Y,1/2+Z
#9 +X,-1+Y,+Z #10 +X,1-Y,-1/2+Z #11 +X,2-Y,-1/2+Z #12 1-X,+Y,3/2-Z

$Na_3CsB_{10}O_{17}$

Atom	**Atom**	**Atom**	**Angle/˚**	**Atom**	**Atom**	**Atom**	**Angle/˚**
$O1^{4}$	Na1	$O14^{3}$	76.88(17)	$O9^{5}$	Cs1B	$O16^{5}$	82.43(15)
O12	Na1	$O13^{3}$	133.4(2)	O10	Cs1B	$O2^{12}$	107.15(17)
O12	Na1	$O14^{3}$	149.4(2)	O10	Cs1B	$O6^{3}$	152.4(2)
O12	Na1	$O16^{5}$	58.86(17)	O10	Cs1B	$O8^{3}$	135.1(2)
$O13^{3}$	Na1	$O14^{3}$	55.25(16)	O10	Cs1B	$O9^{5}$	83.47(15)
$O13^{3}$	Na1	$O16^{5}$	74.57(17)	O10	Cs1B	$O16^{5}$	40.34(13)
$O16^{5}$	Na1	$O14^{3}$	117.19(19)	$O16^{5}$	Cs1B	$O2^{12}$	143.58(16)
$O7^{6}$	Na2	$O2^{7}$	61.22(16)	$O16^{5}$	Cs1B	$O6^{3}$	112.03(18)
$O7^{6}$	Na2	$O14^{5}$	118.3(2)	$O16^{5}$	Cs1B	$O8^{3}$	107.59(18)
$O7^{6}$	Na2	O15	102.47(19)	O1	B1	O2	119.8(6)
O12	Na2	$O2^{7}$	118.9(2)	O1	B1	O3	119.2(5)
O12	Na2	$O7^{6}$	179.7(2)	O2	B1	O3	121.0(6)
O12	Na2	$O14^{5}$	61.51(17)	O4	B2	O3	119.2(6)
O12	Na2	O15	77.83(18)	O4	B2	O5	126.0(6)
$O14^{5}$	Na2	$O2^{7}$	178.7(2)	O5	B2	O3	114.8(6)
O15	Na2	$O2^{7}$	89.37(18)	$O4^{10}$	B3	$O2^{10}$	109.7(5)
O15	Na2	$O14^{5}$	91.97(18)	O7	B3	$O2^{10}$	109.3(5)
O5	Na3	O7	59.08(17)	O7	B3	$O4^{10}$	108.6(5)
$O8^{5}$	Cs1A	O9	85.74(12)	O7	B3	O8	113.7(5)
$O8^{5}$	Cs1A	$O11^{5}$	71.60(12)	O8	B3	$O2^{10}$	107.1(5)
O10	Cs1A	$O8^{5}$	87.43(12)	O8	B3	$O4^{10}$	108.4(6)
O10	Cs1A	O9	41.60(11)	O5	B4	$O1^{12}$	107.5(5)
O10	Cs1A	$O11^{5}$	88.36(11)	O5	B4	O6	111.7(5)
$O11^{5}$	Cs1A	O9	126.48(12)	O6	B4	$O1^{12}$	107.6(5)

O4	Cs1B	O2[12]	77.57(17)	O7	B4	O1[12]	109.6(5)
O4	Cs1B	O6[3]	64.71(14)	O7	B4	O5	107.0(5)
O4	Cs1B	O8[3]	39.28(12)	O7	B4	O6	113.3(5)
O4	Cs1B	O9[5]	142.8(2)	O6	B5	O8	123.7(6)
O4	Cs1B	O10	129.81(19)	O6	B5	O9	118.6(6)
O4	Cs1B	O16[5]	132.7(2)	O8	B5	O9	117.8(6)
O6	Cs1B	O2[12]	66.72(16)	O10	B6	O9	118.1(7)
O6[3]	Cs1B	O2[12]	98.75(17)	O10	B6	O11	123.1(6)
O6	Cs1B	O4	63.52(15)	O11	B6	O9	118.8(6)
O6	Cs1B	O6[3]	128.09(19)	O11	B7	O13	109.0(5)
O6[3]	Cs1B	O8[3]	37.41(11)	O11	B7	O17[2]	109.7(5)
O6	Cs1B	O8[3]	97.81(16)	O12	B7	O11	113.5(5)
O6	Cs1B	O9[5]	126.7(2)	O12	B7	O13	109.8(5)
O6	Cs1B	O10	72.73(15)	O12	B7	O17[2]	106.7(5)
O6	Cs1B	O16[5]	105.24(17)	O17[2]	B7	O13	107.9(5)
O8[3]	Cs1B	O2[12]	108.69(17)	O10	B8	O14[5]	106.4(5)
O8[5]	Cs1B	O2[12]	39.27(13)	O10	B8	O16[5]	110.5(5)
O8[5]	Cs1B	O4	116.5(2)	O12	B8	O10	114.2(5)
O8[5]	Cs1B	O6[3]	109.98(18)	O12	B8	O14[5]	109.0(5)
O8[5]	Cs1B	O6	89.73(19)	O12	B8	O16[5]	107.8(5)
O8[5]	Cs1B	O8[3]	139.2(2)	O16[5]	B8	O14[5]	108.8(5)
O8[5]	Cs1B	O9[5]	40.40(12)	O13	B9	O15	117.7(6)
O8[5]	Cs1B	O10	85.39(16)	O14	B9	O13	121.9(6)
O8[5]	Cs1B	O16[5]	108.85(16)	O14	B9	O15	120.3(6)
O9[5]	Cs1B	O2[12]	76.49(15)	O16	B10	O15	119.1(6)
O9[5]	Cs1B	O6[3]	93.59(16)	O16	B10	O17	126.1(7)
O9[5]	Cs1B	O8[3]	130.73(18)	O17	B10	O15	114.8(6)

Symmetry transformations used to generate equivalent atoms:

#1 -1+X,1-Y,-1/2+Z; #2 +X,1+Y,+Z; #3 +X,1-Y,-1/2+Z; #4 -1+X,2-Y,-1/2+Z;
#5 +X,-Y,-1/2+Z; # 6 -1+X,-Y,-1/2+Z; #7 -1+X,-1+Y,+Z; # 8 1+X,1-Y,1/2+Z;
#9 1+X,+Y,1+Z; #10 +X,-Y,1/2+Z; #11 +X,2-Y,1/2+Z; #12 +X,1-Y,1/2+Z;
#13 +X,-1+Y,+Z; # 14 +X,-1-Y,-1/2+Z; #15 +X,-2+Y,+Z; #16 +X,2+Y,+Z;
#17 +X,2-Y,-1/2+Z; #18 1+X,-Y,1/2+Z; #19 +X,-1-Y,1/2+Z; #20 1+X,2-Y,1/2+Z;
#21 1+X,1+Y,+Z

Table S5. 2D layered borates with $[B_5O_{11}]$ FBB.

Compounds	Space groups	B-O configuration	Symmetry	Reference
$Na_3CsB_{10}O_{17}$	*Pc*	2D double layer	Non-centrosymmetric	this work
$K_2Cs_2B_{10}O_{17}$	*C*2/*c*	2D double layer	Centrosymmetric	9
$Na_2Cs_2B_{10}O_{17}$	*C*2/*c*	2D double layer	Centrosymmetric	9
$Ba_3B_{10}O_{17}Br_2$	*C*2/*c*	2D double layer	Centrosymmetric	10
$Na_2B_{10}O_{17}\cdot H_2en$	*C*2/*c*	2D double layer	Centrosymmetric	11
$Rb_5Ba_2(B_{10}O_{17})_2(BO_2)$	$P\bar{1}$	2D double layer	Centrosymmetric	12
$Rb_4Ba_{2.5}B_{20}O_{34}Cl$	$P\bar{1}$	2D double layer	Centrosymmetric	13
$Rb_4Ba_{2.5}B_{20}O_{34}Br$	$P\bar{1}$	2D double layer	Centrosymmetric	13
$Rb_2Ba_4B_{20}O_{34}Br_2$	$P2_1/m$	2D double layer	Centrosymmetric	13
$KBaB_5O_9$- Ⅰ	$P2_1/c$	2D single layer	Centrosymmetric	13
$KBaB_5O_9$- Ⅱ	$P2_1/c$	2D single layer	Centrosymmetric	14
$NaPbB_5O_9$	$P2_1/c$	2D single layer	Centrosymmetric	15
$NaCaB_5O_9$	$P2_1/c$	2D single layer	Centrosymmetric	16
$NaSrB_5O_9$	$P2_1/c$	2D single layer	Centrosymmetric	17
$NaBaB_5O_9$	$P2_1/c$	2D single layer	Centrosymmetric	14
SbB_5O_9	$P2_1/c$	2D single layer	Centrosymmetric	18
$Ca_3V_2B_{10}O_{23}$	$P\bar{1}$	2D single layer	Centrosymmetric	19
$Sr_3V_2B_{10}O_{23}$	$P\bar{1}$	2D single layer	Centrosymmetric	19

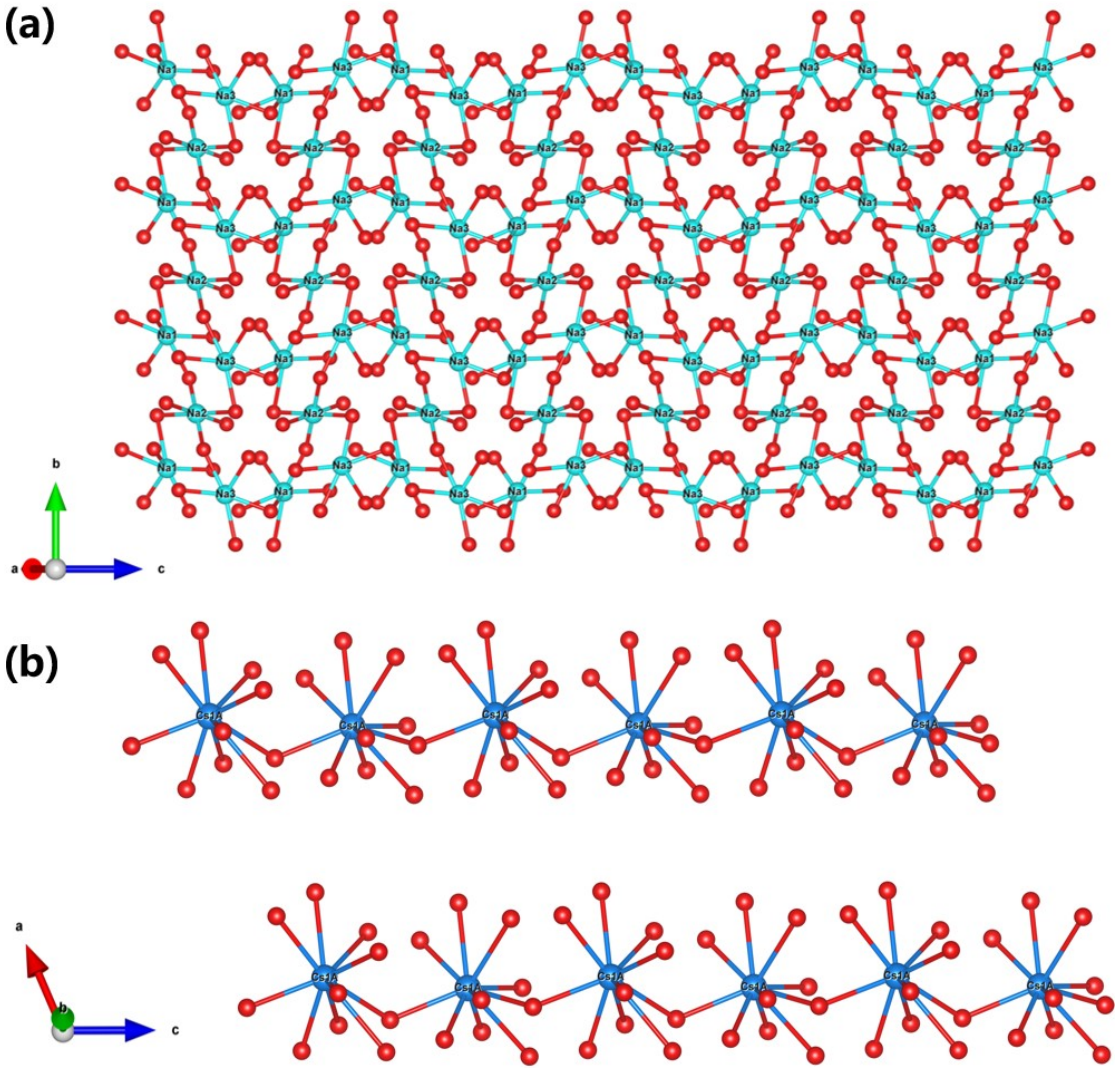


Fig. S1 (a) 2D Na-O-Na layer in $Na_3CsB_{10}O_{17}$; (b) 1D $^1[CsO_9]_\infty$ chains in $Na_3CsB_{10}O_{17}$.

The Cs1 site is not required; two possible sites exist, Cs1A and Cs1B. The probability of Cs1 appearing at the Cs1B site is only 0.17. In the main text and Supplementary Information, for the sake of simplicity in illustration, we have omitted Cs1B. Coordination diagrams and structural diagrams are depicted solely for the Cs1A site. Descriptions of the structure in the main text are also based on Cs occupying the Cs1A site.

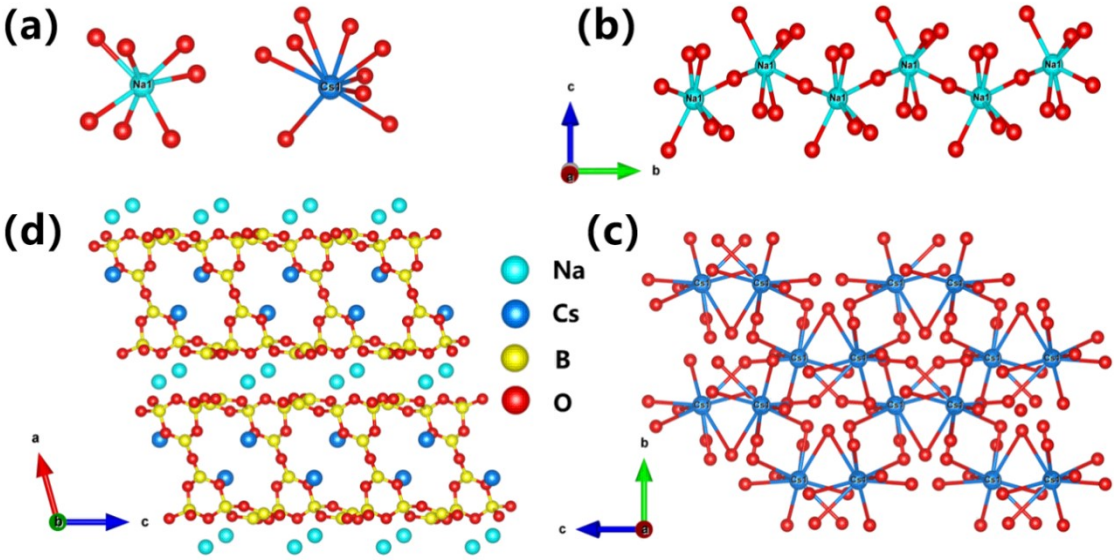


Fig. S2 (a) Coordination environment of cations Na and Cs; (b) 1D $^{1}[NaO_6]_{\infty}$ chains composed by $[NaO_7]$ polyhedra; (c) 2D Cs-O-Cs layer composed by $[CsO_9]$ polyhedra in $Na_2Cs_2B_{10}O_{17}$.

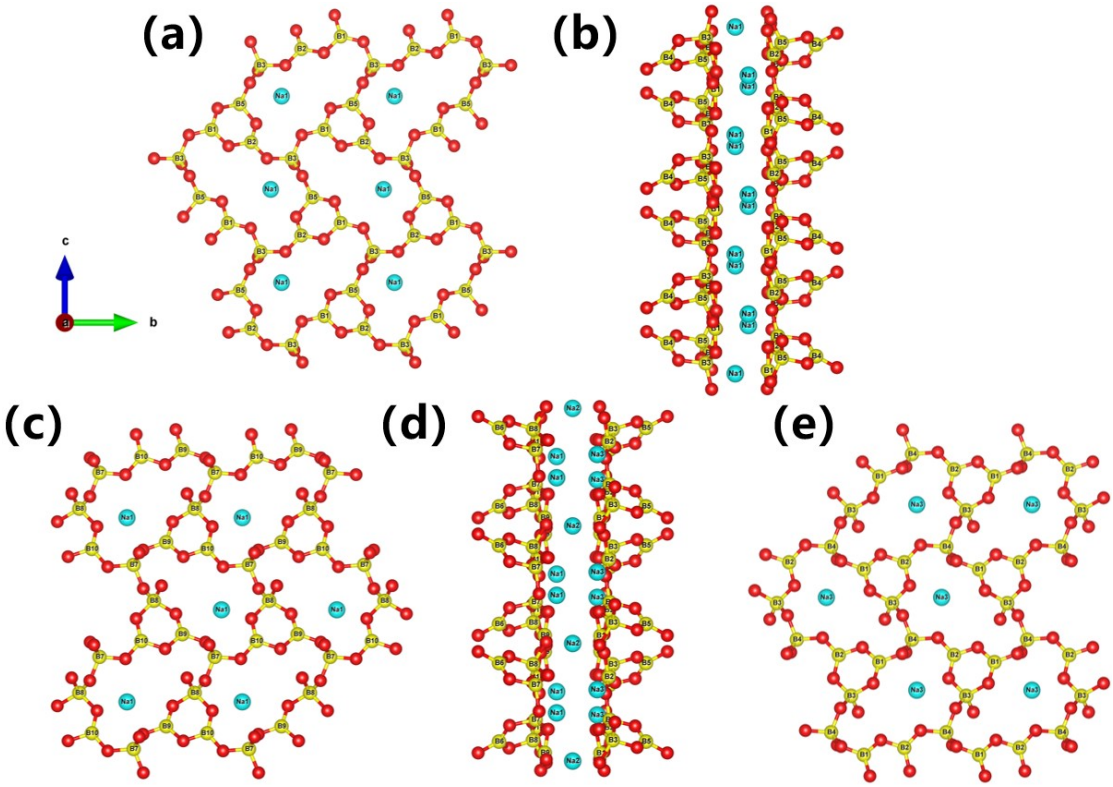


Fig. S3 (a) The 18-membered ring of $Na_2Cs_2B_{10}O_{17}$; (b) Interlayer distribution of Na^+ in $Na_2Cs_2B_{10}O_{17}$; (c) (e) The 18-membered ring of $Na_3CsB_{10}O_{17}$; (d) Interlayer distribution of Na^+ in $Na_3CsB_{10}O_{17}$;

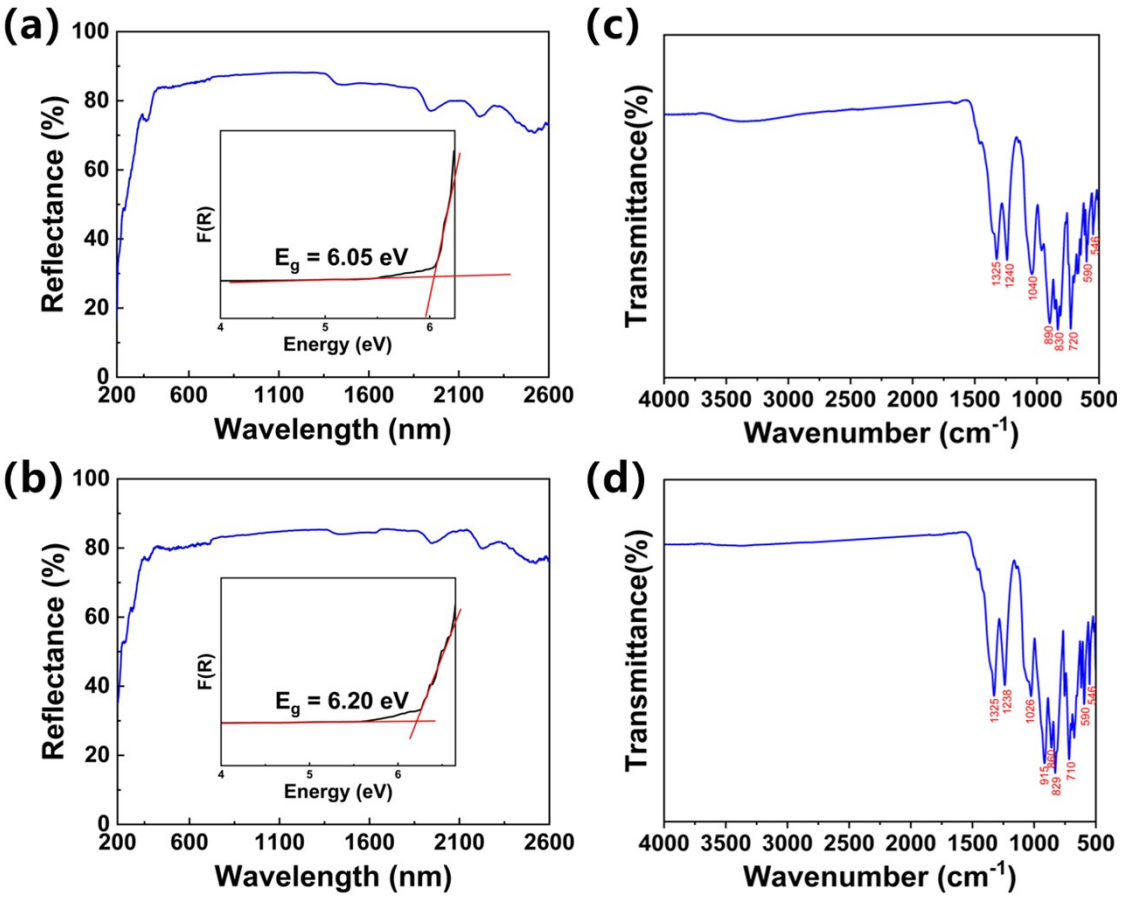


Fig. S4 (a) (c) The diffuse reflectance spectra, experimental bandgap and IR spectra for $K_2Cs_2B_{10}O_{17}$; (b) (d) The diffuse reflectance spectra, experimental bandgap and IR spectra for $Na_2Cs_2B_{10}O_{17}$.

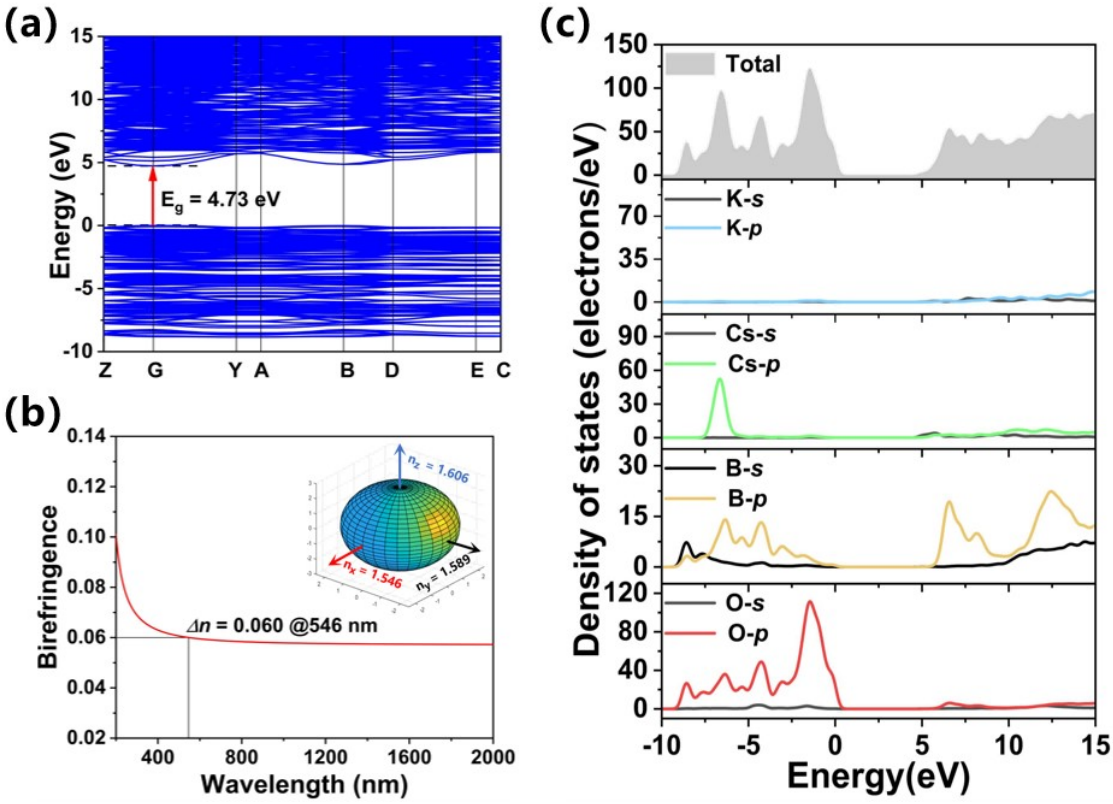


Fig. S5 (a) Electronic band structure using GGA method, (b) calculated birefringence and (c) partial and total density of states of $K_2Cs_2B_{10}O_{17}$.

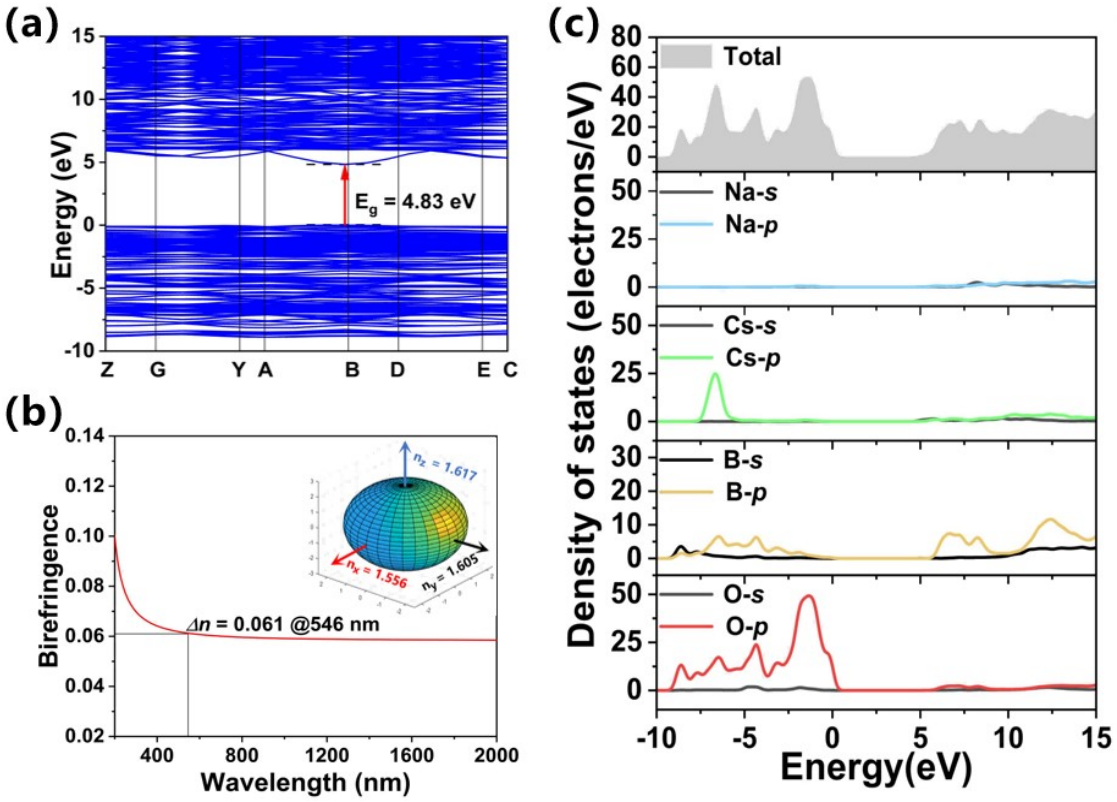


Fig. S6 (a) Electronic band structure using GGA method, (b) calculated birefringence and (c) partial and total density of states of $Na_2Cs_2B_{10}O_{17}$.

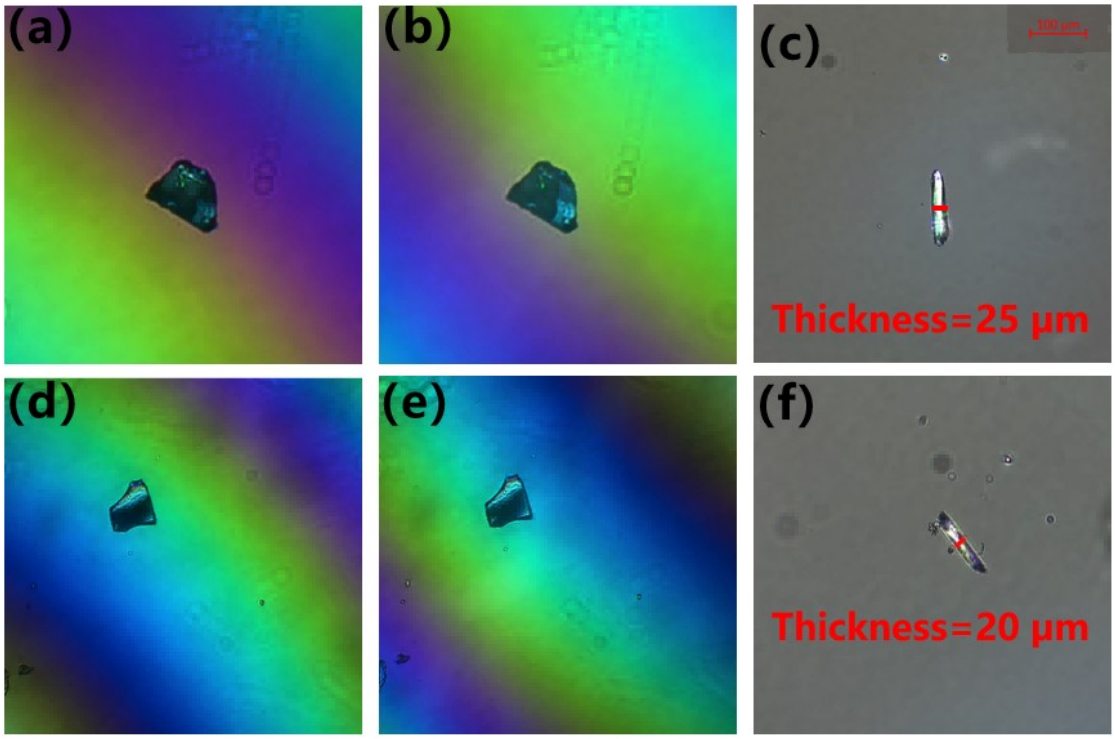


Fig. S7 Birefringence measurement of $Na_3CsB_{10}O_{17}$ (a, b, c) and $Na_2Cs_2B_{10}O_{17}$ (d, e, f) using a polarizing microscope. The view of the crystal achieving extinction at the negative (a, d) and positive (b, e) rotation of the compensator, respectively; the thickness (c, f) of the crystal for measurement. Based on measurements using a Berek compensator, the optical path differences (OPD) for $Na_3CsB_{10}O_{17}$ and $Na_2Cs_2B_{10}O_{17}$ were determined to be 1179.15 nm and 1001.68 nm, respectively.

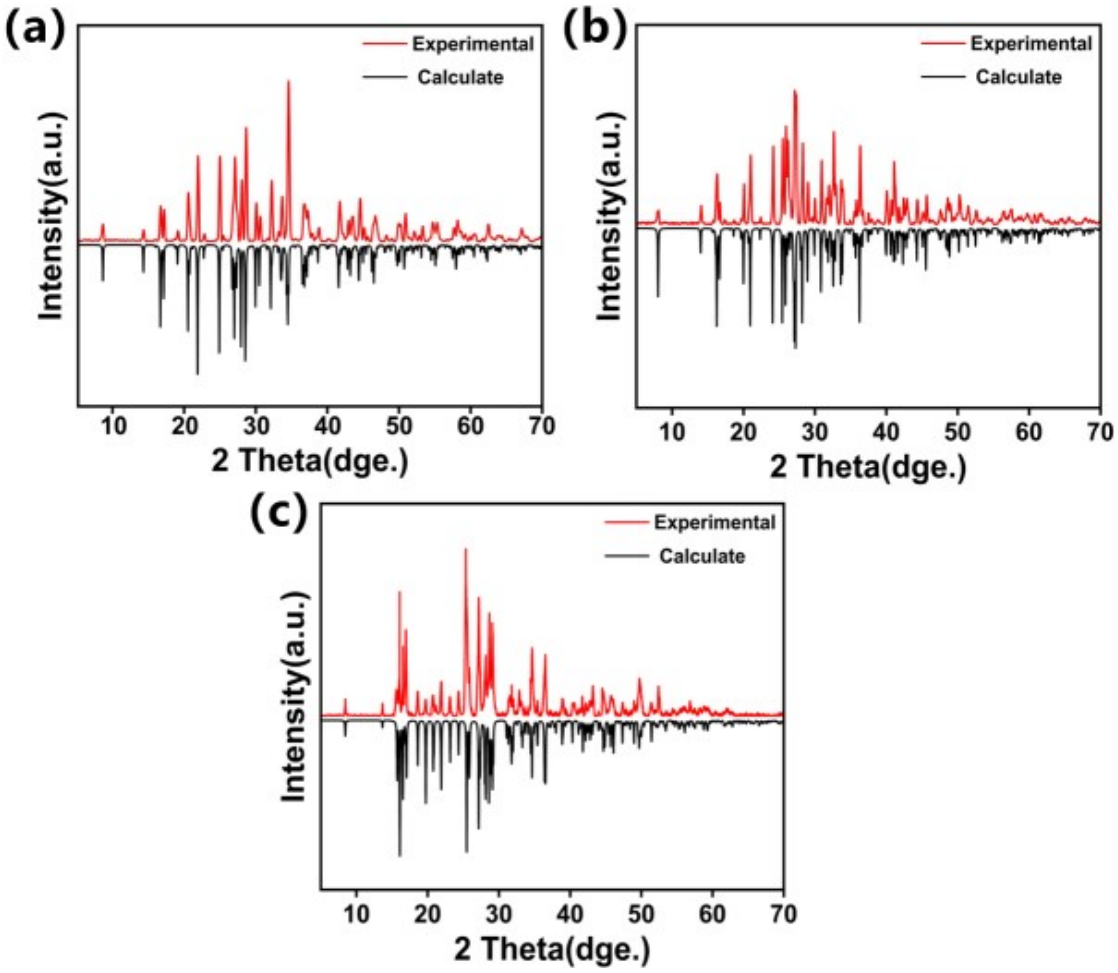
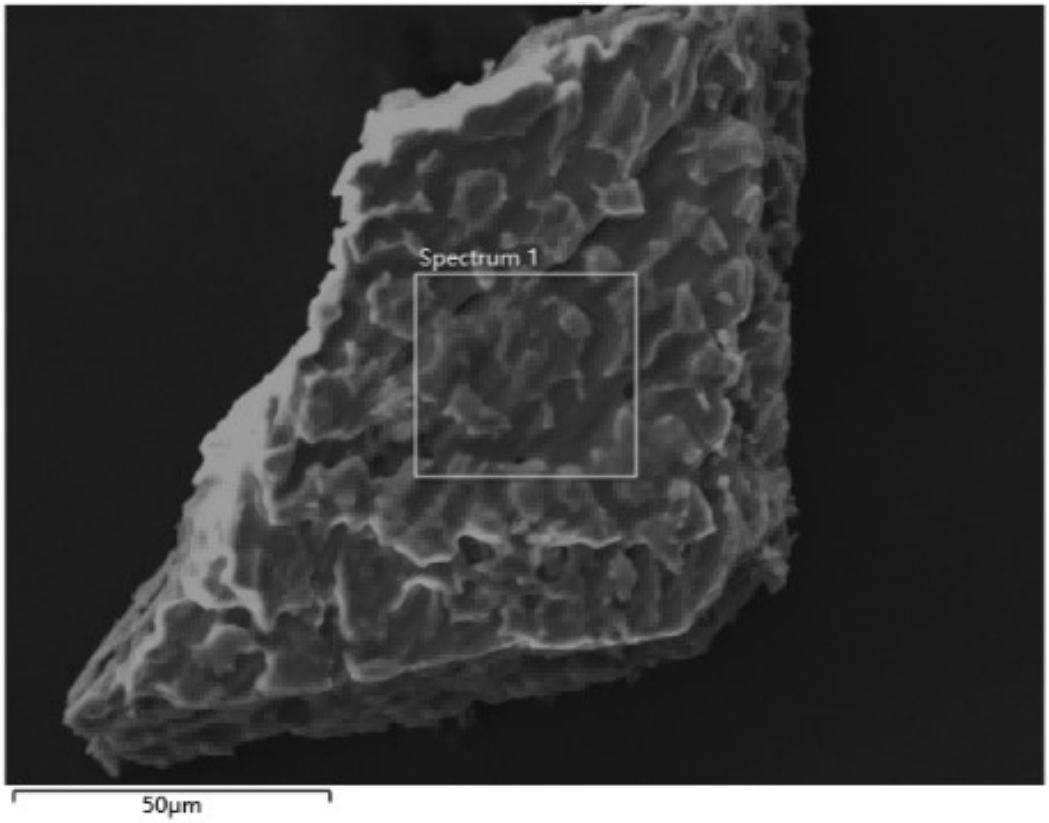


Fig. S8. (a), (b) and (c) Experimental and calculated powder XRD patterns for $K_2Cs_2B_{10}O_{17}$, $Na_2Cs_2B_{10}O_{17}$ and $Na_3CsB_{10}O_{17}$.



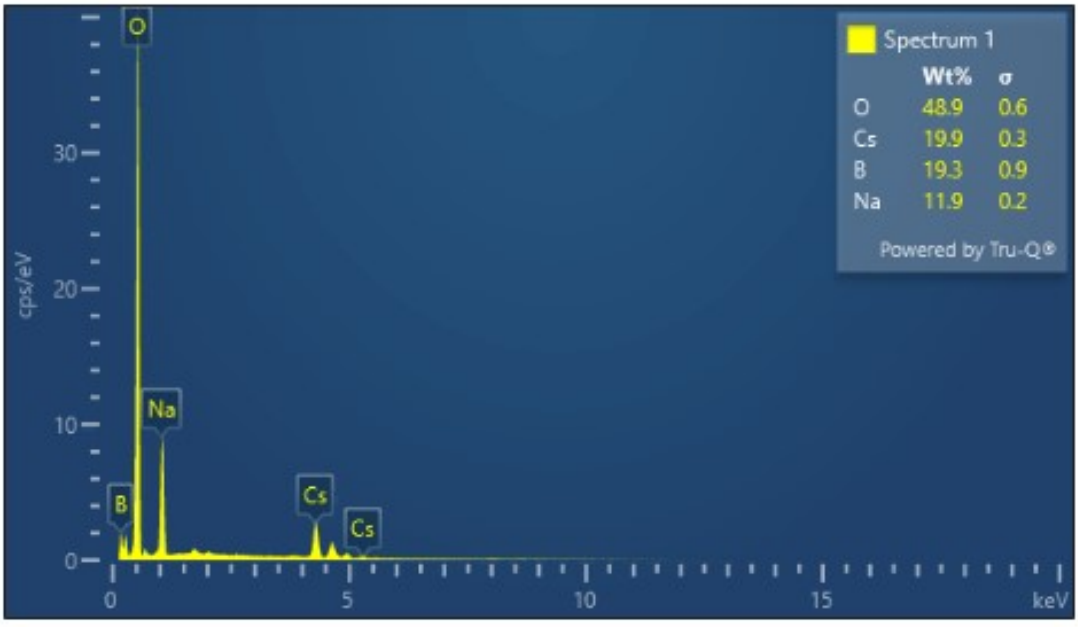


Fig. S9. EDS analysis diagram of $Na_3CsB_{10}O_{17}$.

The EDS analysis results shown in the figure confirm the presence of constituent elements in $Na_3CsB_{10}O_{17}$. Although EDS is a semi-quantitative analysis with certain errors in the measured elemental percentages, the atomic percentages of these elements generally align with the expected stoichiometric ratios. This further supports the overall validity of the $Na_3CsB_{10}O_{17}$ structure.

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