

Electronic Supplementary Information

**Cs₂AlB₅O₁₀: A Short-wavelength Nonlinear Optical Crystal with Moderate
Second Harmonic Generation Response**

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Experimental section

Synthesis

Crystal Growth. Crystals of $\text{Cs}_2\text{AlB}_5\text{O}_{10}$ were synthesized via the spontaneous nucleation method in open air by melting the high purity (purity $\geq 99.5\%$) commercial grade reagents of CsF, AlF_3 , PbO and H_3BO_3 with a molar ratio: 2 : 1 : 1 : 5. The weighed mixture was transferred into a platinum crucible which was placed inside the vertical electric furnace, after the furnace was heated to 820 °C in 12 hours, and the furnace temperature was held for 6 hours to ensure the homogeneity of the solution. Subsequently, with the steady rate of 1.5 °C/h, the temperature was decreased to 480 °C; finally, the furnace was cooled to room temperature by switching off. Dozens of small crystals were removed from the crucible for single crystal XRD investigation.

Compound Synthesis. Polycrystalline sample of $\text{Cs}_2\text{AlB}_5\text{O}_{10}$ was obtained via solid state sintering method with stoichiometric amounts of Cs_2CO_3 , Al_2O_3 , and H_3BO_3 . The weighed materials were thoroughly mixed in an agate mortar by grinding and preheated at 350 and 550 °C for 12 hours, respectively. Then the mixture was transferred into a platinum crucible and gradually heated to 675 °C and maintained at this temperature for 15 days. During the sintering process, the furnace was switched off for several times and the sample was thoroughly ground. As displayed in Figure S1, powder sample of $\text{Cs}_2\text{AlB}_5\text{O}_{10}$ was obtained without impurities.

Single Crystal Structure Data Collection. Single-crystal X-ray diffraction data collection for $\text{Cs}_2\text{AlB}_5\text{O}_{10}$ was carried out with APEX II CCD X-ray diffractometer with monochromatic Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) under the room temperature (25 °C). The collected data were integrated with the SAINT program,¹ numerical absorption corrections were implemented by the SCALE program for the area detector. The crystal structure model was identified with the SHELXTL crystallographic suite.² The atomic position refinements were implemented with full matrix least-squares techniques, final least squares refinement is on F_o^2 with data having $F_o^2 \geq 2\sigma(F_o^2)$. The resolved structure's symmetry accuracy was validated with PLATON program.³ The crystal information and final structure refinements data are briefly listed in Table S1, and the parameters for atomic position coordinates are offered in Table S2 in the SI.

Powder XRD Measurement. Powder XRD pattern data of $\text{Cs}_2\text{AlB}_5\text{O}_{10}$ was collected at room temperature with a Bruker D2 PHASER diffractometer equipped with Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$). Instrument basic constants including the angular range, and the fixed scanning step were kept constant value of $2\theta = 10\text{-}70^\circ$, and 1 s/step, respectively.

Optical Spectroscopic Studies. To specify the nature of the covalent bonding in the

structure, the IR performance of $\text{Cs}_2\text{AlB}_5\text{O}_{10}$ was tested in the $450\text{--}4000\text{ cm}^{-1}$ wavenumber region by Shimadzu IR Affinity1 spectrometer at $25\text{ }^\circ\text{C}$. About 4 mg powder sample was thoroughly mixed with about 400 mg dried KBr (99.9 % purity) and compressed into thin semi-transparent cylindrical plates. The diffuse reflectance performance over the wavelength region $180\text{--}2500\text{ nm}$ was tested with Shimadzu SolidSpec-3700DUV spectrophotometer at $25\text{ }^\circ\text{C}$. The reflectance spectrum data was converted into absorbance under the Kubelka–Munk function.⁴

Thermal Property Investigation. Thermal stability of $\text{Cs}_2\text{AlB}_5\text{O}_{10}$ was checked by a NETZSCH STA 449C thermal analysis instrument. About 10 mg portions of powders of the compounds were filled in Pt crucibles and heated from 50 to $830\text{ }^\circ\text{C}$ at a constant speed of $10\text{ }^\circ\text{C}/\text{min}$ under a flowing N_2 atmosphere. Meanwhile, to achieve reliable measurement results, prepared polycrystalline powder sample was melted again and recrystallized for polycrystalline XRD inspection.

SHG Measurement. Powder SHG measurement was carried out with the aid of Kurtz-Perry method,⁵ under the fundamental laser beam ($\lambda=1064\text{ nm}$) emitted from a Q-switched Nd:YAG laser. As the SHG efficiency strongly correlates with particle size, solidified polycrystalline sample of $\text{Cs}_2\text{AlB}_5\text{O}_{10}$ was ground and standardized into below particle size ranges: $38\text{--}55$, $55\text{--}88$, $88\text{--}105$, $105\text{--}155$, and $155\text{--}200\text{ }\mu\text{m}$. Polycrystalline KH_2PO_4 (KDP) samples of above sizes were employed as the standard materials.

Numerical Computation Methods. A numerical computations based on the first principles density functional theory (DFT) were applied to understand and explain the reliance of electronic properties to the atomic and molecular configuration of the structure. The plane-wave pseudopotential method was applied within the CASTEP,⁶ program package. During the computation, the generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof functional (PBE)⁷ was employed, energy convergence was ensured with norm-conserving pseudopotential (NCP).⁸ The kinetic energy cut-off value was set as 750 V , and Monkhorst-Pack K-point mesh was adjusted to $4\times 4\times 4$ in the Brillouin zone of the unit cell. The convergent conditions and other parameters applied during the computation were in line with the CASTEP's default parameters.

Table S1. Crystal data and structure refinements for Cs₂AlB₅O₁₀.

Empirical formula	Cs ₂ AlB ₅ O ₁₀
Formula weight	506.85
Crystal system	Trigonal
Space group, Z	<i>P</i> 3 ₁ 21, 3
Unit cell dimensions (Å)	<i>a</i> = 7.051(9) <i>c</i> = 21.042(5)
Volume (Å ³)	906.2(3)
Density (calc.) (g/cm ³)	2.786
θ range for data collection	2.90-27.35
Limiting indices	-9 ≤ <i>h</i> ≤ 8, -8 ≤ <i>k</i> ≤ 9, -17 ≤ <i>l</i> ≤ 27
Reflections collected/unique	5602/1363 [<i>R</i> (int) = 0.0517]
Completeness to θ (%)	99.4
Goodness of fit on <i>F</i> ²	1.064
Final <i>R</i> indices [<i>F</i> _o ² > 2δ(<i>F</i> _o ²)] ^a	<i>R</i> ₁ = 0.0493, <i>wR</i> ₂ = 0.1261
<i>R</i> indices (all data) ^a	<i>R</i> ₁ = 0.0672, <i>wR</i> ₂ = 0.1407
Largest diff. peak and hole	2.048 and -1.163
Absolute structure parameter	0.00(8)

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

Table S2(a). The final Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for Cs₂AlB₅O₁₀, U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor, and the Bond Valence Sum (BVS) for each atom in asymmetric unit.

Atom	x	y	z	U(eq)	BVS
Cs(1)	3264(1)	9396(1)	526(1)	60(1)	0.692
Al(1)	0	3951(5)	1667	29(1)	3.016
B(1)	7522(16)	5038(18)	878(5)	35(2)	3.054
B(2)	3886(15)	4240(16)	1112(5)	30(2)	3.067
B(3)	5380(40)	5380(40)	0	66(4)	3.202
O(3)	9417(10)	5106(12)	1032(3)	50(2)	1.820
O(1)	2279(9)	3687(11)	1545(3)	38(2)	1.877
O(2)	3591(12)	4601(18)	485(3)	73(3)	1.845
O(4)	5850(9)	4486(9)	1291(3)	33(1)	2.148
O(5)	7336(13)	5629(16)	261(3)	75(2)	1.863

Table S2(b). Selected bond distances (Å) and angles (deg) for Cs₂AlB₅O₁₀.

Cs(1)-O(3)#1	3.075(6)	O(4)#3-Cs(1)-O(3)#2	142.19(14)
Cs(1)-O(5)#2	3.167(7)	O(2)#4-Cs(1)-O(3)#2	57.93(16)
Cs(1)-O(4)#3	3.344(6)	O(4)#5-Cs(1)-O(3)#2	115.02(14)
Cs(1)-O(2)#4	3.369(7)	O(2)#4-Cs(1)-O(2)	134.96(13)
Cs(1)-B(2)#5	3.454(10)	O(4)#5-Cs(1)-O(2)	138.53(15)
Cs(1)-O(4)#5	3.503(6)	O(3)#2-Cs(1)-O(2)	77.22(15)
Cs(1)-O(3)#2	3.518(7)	O(3)#1-Cs(1)-O(2)#5	126.33(17)
Cs(1)-O(2)	3.501(11)	O(5)#2-Cs(1)-O(2)#5	133.1(2)
Cs(1)-O(2)#5	3.563(11)	O(4)#3-Cs(1)-O(2)#5	105.47(15)
Cs(1)-O(5)#1	3.709(9)	O(2)#4-Cs(1)-O(2)#5	40.2(2)
Al(1)-O(3)#1	1.721(6)	O(4)#5-Cs(1)-O(2)#5	39.01(14)
Al(1)-O(3)#3	1.721(6)	O(3)#2-Cs(1)-O(2)#5	98.11(15)
Al(1)-O(1)#6	1.728(7)	O(2)-Cs(1)-O(2)#5	173.1(2)
Al(1)-O(1)	1.728(6)	O(3)#1-Cs(1)-O(5)#1	38.82(16)
B(1)-O(5)	1.382(12)	O(5)#2-Cs(1)-O(5)#1	104.7(2)
B(1)-O(3)	1.344(11)	O(4)#3-Cs(1)-O(5)#1	105.21(14)
B(1)-O(4)	1.368(11)	O(2)#4-Cs(1)-O(5)#1	104.8(2)
B(2)-O(4)	1.368(11)	O(4)#5-Cs(1)-O(5)#1	128.87(16)
B(2)-O(1)	1.346(11)	O(3)#2-Cs(1)-O(5)#1	98.23(15)
B(2)-O(2)	1.375(12)	O(2)-Cs(1)-O(5)#1	84.10(18)
B(3)-O(5)	1.414(17)	O(2)#5-Cs(1)-O(5)#1	101.74(17)
B(3)-O(5)#2	1.414(17)	O(3)#1-Al(1)-O(3)#3	107.4(5)
B(3)-O(2)	1.498(18)	O(3)#1-Al(1)-O(1)#6	106.6(3)
B(3)-O(2)#2	1.498(18)	O(3)#3-Al(1)-O(1)#6	113.0(3)
		O(3)#1-Al(1)-O(1)	113.0(3)
O(3)#1-Cs(1)-O(5)#2	97.8(2)	O(3)#3-Al(1)-O(1)	106.6(3)
O(3)#1-Cs(1)-O(4)#3	69.94(16)	O(1)#6-Al(1)-O(1)	110.3(5)
O(5)#2-Cs(1)-O(4)#3	103.99(15)	O(5)-B(1)-O(3)	117.7(8)
O(3)#1-Cs(1)-O(2)#4	143.4(2)	O(5)-B(1)-O(4)	118.9(8)
O(5)#2-Cs(1)-O(2)#4	95.3(2)	O(3)-B(1)-O(4)	123.4(9)
O(4)#3-Cs(1)-O(2)#4	138.56(18)	O(4)-B(2)-O(1)	119.9(8)
O(3)#1-Cs(1)-O(4)#5	127.01(16)	O(4)-B(2)-O(2)	118.7(8)
O(5)#2-Cs(1)-O(4)#5	125.95(19)	O(1)-B(2)-O(2)	121.4(8)
O(4)#3-Cs(1)-O(4)#5	71.45(9)	O(5)-B(3)-O(5)#2	113(2)
O(2)#4-Cs(1)-O(4)#5	67.53(15)	O(5)-B(3)-O(2)	112.0(4)
O(3)#1-Cs(1)-O(3)#2	117.8(2)	O(5)#2-B(3)-O(2)	106.8(5)
O(5)#2-Cs(1)-O(3)#2	40.42(16)	O(5)-B(3)-O(2)#2	106.8(5)
O(3)#1-Cs(1)-O(2)	60.59(18)	O(5)#2-B(3)-O(2)#2	112.0(4)
O(5)#2-Cs(1)-O(2)	40.67(19)	O(2)-B(3)-O(2)#2	105.8(19)
O(4)#3-Cs(1)-O(2)	76.19(15)		

Symmetry transformations used to generate equivalent atoms:

#1 x-1,y,z #2 y,x,-z #3 -x+1,-x+y+1,-z+1/3 #4 y,x+1,-z #5 x,y+1,z
#6 -x,-x+y,-z+1/3 #7 x,y-1,z #8 x+1,y,z #9 -x+1,-x+y,-z+1/3 #10 y-1,x,-z

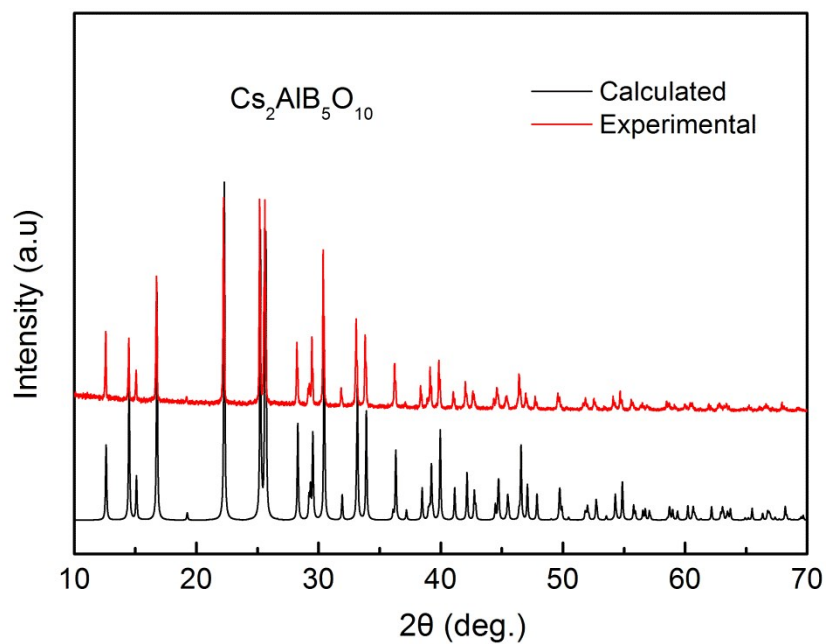


Figure S1. Simulated and experimental powder XRD patterns of $\text{Cs}_2\text{AlB}_5\text{O}_{10}$.

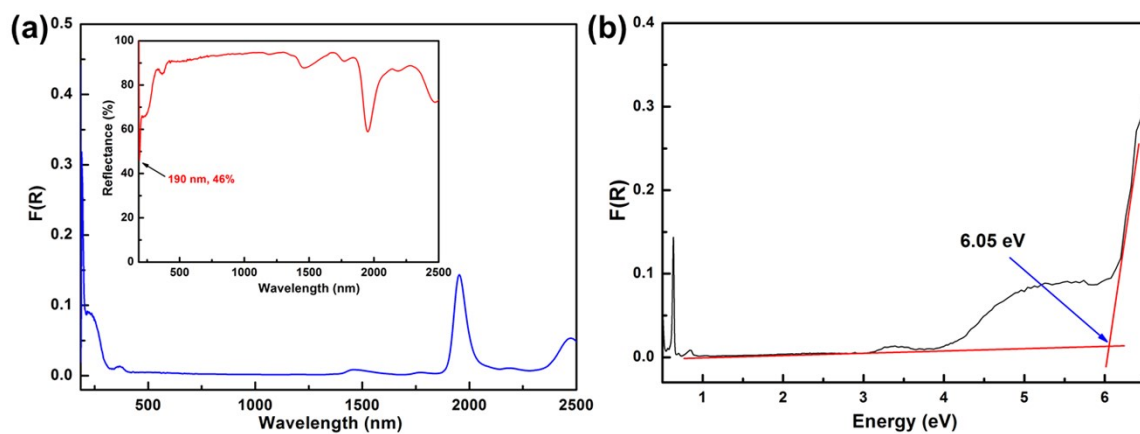


Figure S2. (a) UV-Vis-NIR diffuse reflectance spectrum; (b) the experimental band gap of $\text{Cs}_2\text{AlB}_5\text{O}_{10}$.

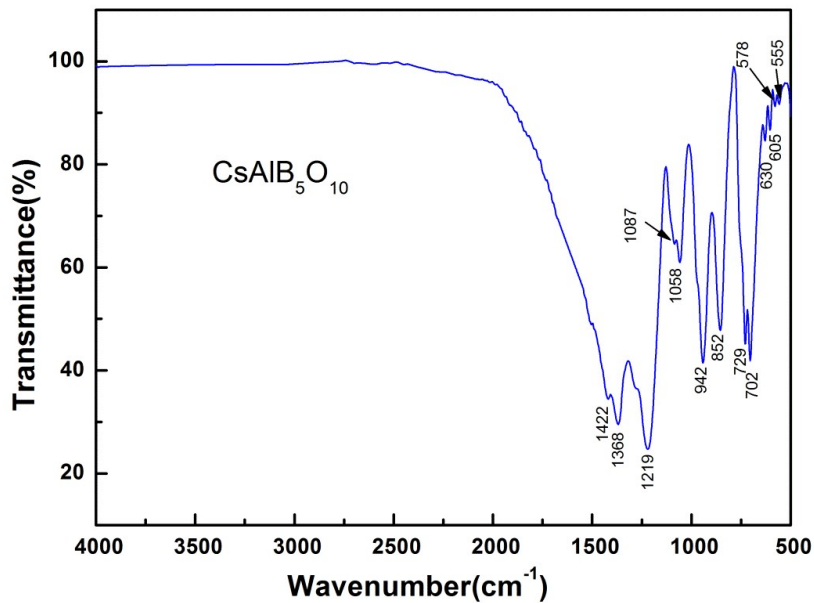


Figure S3. The IR spectrum of $\text{Cs}_2\text{AlB}_5\text{O}_{10}$.

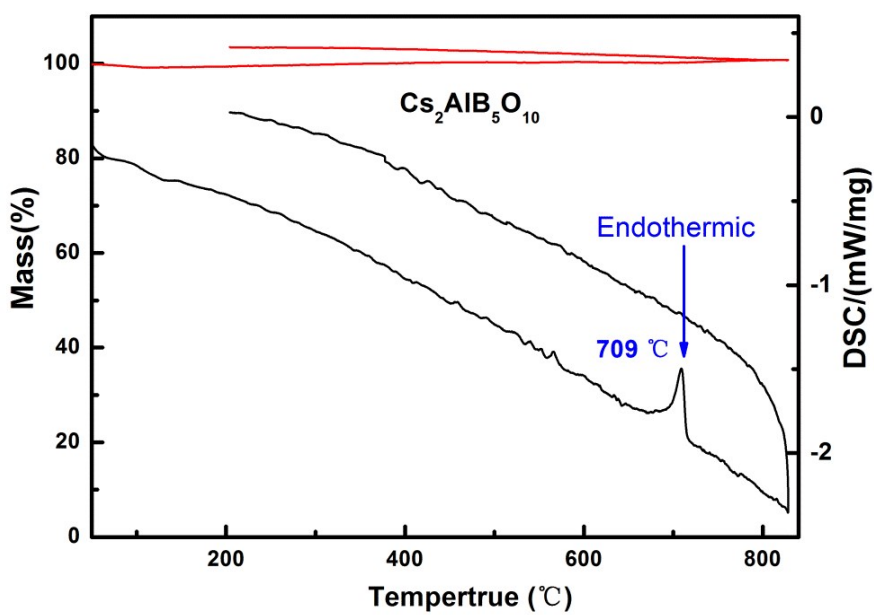


Figure S4. The TG-DSC curves of polycrystalline samples of $\text{Cs}_2\text{AlB}_5\text{O}_{10}$.

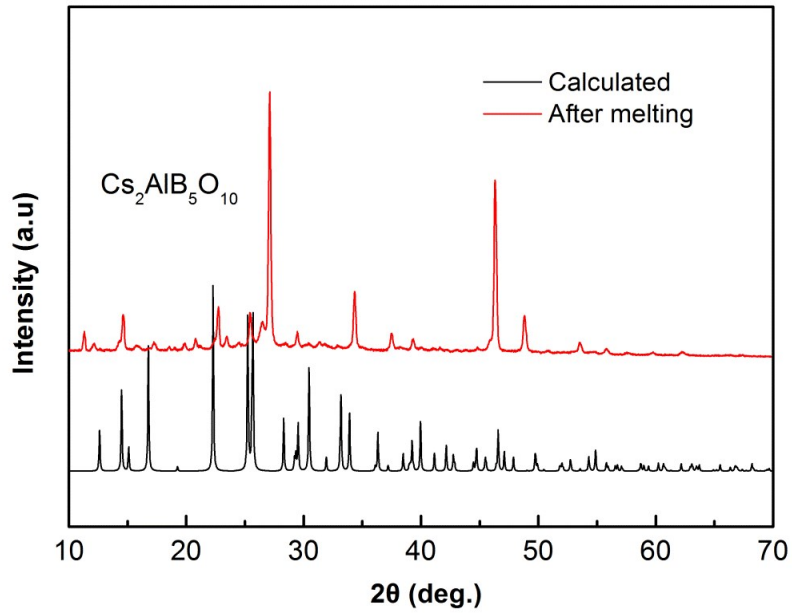


Figure S5. Simulated, and after melting powder XRD patterns of $\text{Cs}_2\text{AlB}_5\text{O}_{10}$.

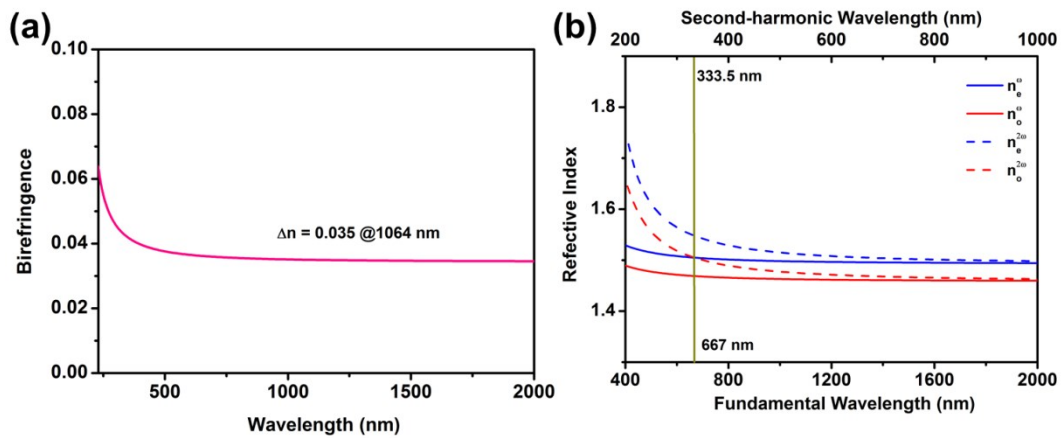


Figure S6. (a) The calculated birefringence curve, and (b) Dispersion curves of refractive index of $\text{Cs}_2\text{AlB}_5\text{O}_{10}$.

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