Electronic Supplementary Information

$CsAlB_3O_6Cl$: The rational construction of a KBBF-type structure with aligned $^{2}{}_{\infty}[AlB_3O_6Cl]$ layers via introducing unprecedented $[AlO_3Cl]$ tetrahedra

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Experimental Section

1. Single crystals and polycrystalline. $CsAlB_3O_6Cl$ crystals can be obtained by the high-temperature solution method in a closed system. CsCl (99.5 %), Al_2O_3 (99.99 %), and B_2O_3 (99.99 %) were purchased from Aladdin Chemical Industry Co., Ltd. The reactants CsCl, Al_2O_3, and B_2O_3 were weighed according to the molar ratio of 1: 0.5: 1.5, and then loaded into a quartz tube of Φ10 mm × 120 mm after grinding uniformly, and then vacuumed with a vacuum pump to make the vacuum inside the tube 1×10^{-3} Pa, and then sealed with a high-temperature flame gun on the quartz tube. The encapsulated quartz tube was placed into a high-temperature muffle furnace, which was raised to 700 °C for 10 h and held for 15 h. The temperature was lowered to 650 °C at a rate of 1.0 °C/h, then to 600 °C at a rate of 0.5 °C/h, and then to 500 °C at a rate of 1 °C/h. The muffle furnace was closed, and the crystals inside the quartz tube were taken out for structural determination when the temperature was lowered to room temperature. The polycrystalline powder sample of the compound $CsAlB_3O_6Cl$ was obtained by direct grinding of the sample inside the quartz tube, and the purity of the sample was examined by powder X-ray diffraction (XRD), which reveals the presence of a small amount of unreacted CsCl impurity phase.

2. Characterization. Powder XRD data were collected with a Bruker D2 PHASER diffractometer (Cu Kα radiation with $\lambda = 1.5418$ Å, $2\theta = 10$ to 70 °, scan step width = 0.02 °, and counting time = 1 s/step). The single-crystal XRD data were collected on a Bruker D8 Venture diffractometer using Mo Kα radiation ($\lambda = 0.71073$ Å) at room temperature. The intensity, reduction, and cell refinement were carried out on Bruker SAINT.[1] All the structures were solved by direct method and refined through the full-matrix least-squares fitting on F^2 with OLEX2 software.[2] These structures were verified by virtue of the ADDSYM algorithm from PLATON.[3] The Cs(2) atom has an occupancy of 0.167, which is located not only on the threefold inversion axis but also at the center of symmetry, with the disorder existing to satisfy the bond valence equilibrium.

Infrared spectroscopy was carried out on a Shimadzu IR Affinity-1 Fourier transform infrared spectrometer in the 400-4000 cm^{-1} range. UV−vis−NIR diffuse-reflectance spectroscopy data in the wavelength range of 175-2600 nm were recorded at room temperature using a powder sample of $CsAlB_3O_6Cl$ on a Shimadzu SolidSpec-3700 DUV spectrophotometer. Energy Dispersive X-ray Spectroscope (EDS) was measured on a SUPRA 55VP field emission scanning electron microscope equipped with a BRUKER X-ray Flash-SDD-5010 energy-dispersive X-ray spectroscope. As crystals are preserved in dimethyl-silicon oil, small amounts of C elements are present. We have measured the experimental birefringence of $CsAlB_3O_6Cl$ by using polarizing microscopy. The $CsAlB_3O_6Cl$ crystal with a thickness of 15.679 μm and retardation value of 854.79 nm can be obtained from the tables of the Berek compensator specification. Furthermore, the difference between refractive indices values of the crystal plane is 0.055 at 546.1 nm. This measured refractive index difference is smaller than the actual birefringence since the direction of the natural growth plane of the crystals is always not along a specific optical principal axis, which verifies the reasonableness of the theoretical calculations.

3. Calculation details

The electronic structure and optical properties were calculated by using the DFT method implemented in the CASTEP package.[4] During the calculation, the generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) functional was adopted.[5a] Under the norm-conserving pseudopotential (NCP), due to discontinuities in the exchange-correlation energies, the GGA usually underestimates the bandgap. Therefore the Heyd-Scuseria-Ernzerhof (HSE06) hybrid function was chosen to provide a more accurate bandgap value. Therefore, the bandgap difference between the GGA and the experimental value or the HSE06 method was used as the scissor operation to calculate the optical properties. The cutoff energy of the plane wave was set to 850 eV for the self-consistent field (SCF) calculations, the convergence criterion for the total energy was 10^{-6} eV/atom. In the Brillouin zone, the *k*-point separation was set to 0.07 $Å^{-1}$ for each material, resulting in a corresponding Monkhorst-Pack *k*-point grid. The linear optical properties are obtained from the dielectric function: $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$. where $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ are the real and imaginary parts of the dielectric function, respectively. The imaginary part ε_2 of the dielectric function can be calculated from the electronic structure, while the real part can be obtained from the Cramers-Kronig transform, which allows the calculation of the refractive index and birefringence (Δn). To clarify the contribution of different units to the birefringence of $CsAlB_3O_6Cl$, the bonding electron density difference ($\Delta\rho$) of $[B_3O_6]$, $[AlO_3Cl]$, $[CsO_{12}]$, and $[CsCl_6]$ was calculated using the REDA method. were calculated using the REDA method.[5b]

Table S1. Crystallographic data and structural refinement parameters of $CsAlB_3O_6Cl$.

Compound	$CsAlB_3O_6Cl$
Formula weight	323.77
Temperature(K)	293(2)
Crystal system	Trigonal
Space group	$P\bar{3}c1$
a (Å)	7.0716(4)
c (Å)	18.0458(19)
V (Å^3)	781.52(12)
Z	4
d_{cal} (g/cm^3)	2.752
μ (mm^{-1})	5.170
F(000)	592
Crystal size (mm^3)	0.252 × 0.172 × 0.080
Theta range for data collection	2.257 to 27.451°
Limiting indices	$-9\leq h\leq 9$, $-9\leq k\leq 8$, $-23\leq l\leq 23$
Reflections collected / unique	3595/606 [R(int) = 0.0447]
Completeness	100.0 %
Data / restraints / parameters	606 / 0 / 45
Goodness-of-fit on F^2	1.252
R_1 (I>2sigma(I)])[a]	0.0317
wR_2 (I >2sigma(I)])[a]	0.0771
R_1 (all data)[a]	0.0399
wR_2 (all data)[a]	0.0802
Largest diff. peak and hole e.Å^{-3}	0.577 and -0.439

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

Table S2. Atomic coordinates (× 10^4), equivalent isotropic displacement parameters (Å^2 × 10^3), and the bond valence sum for $CsAlB_3O_6Cl$.

Atoms	*x*	*y*	*z*	$U_{(eq)}$	S.O.F.	BVS
Cs(1)	0	0	2500	25(1)		1.26
Cs(2)	530(40)	480(50)	4833(2)	88(2)	0.167	/
Al(1)	6667	3333	3696(1)	21(1)		3.02
B(1)	4941(7)	6090(8)	3396(3)	24(1)		3.07
O(1)	2753(5)	4500(5)	3386(2)	27(1)		2.13
O(2)	6509(4)	5572(5)	3414(2)	34(1)		2.03
Cl(1)	6667	3333	4888(1)	78(1)		1.13

Table S3. Selected bond lengths (Å) and angles (°) for CsAlB$_3$O$_6$Cl.

Bond	Length	Bond	Length
Cs(1)-O(1)#1	3.206(3)	Cs(2)-Cl(1)	3.76(3)
Cs(1)-O(1)#2	3.206(3)	Cs(2)-Cl(1)#16	3.83(3)
Cs(1)-O(1)#3	3.206(3)	Cs(2)-O(1)	3.592(19)
Cs(1)-O(1)#4	3.206(3)	Cs(2)-O(2)#9	3.79(4)
Cs(1)-O(1)#5	3.206(3)	Cs(2)-O(2)#11	3.66(3)
Cs(1)-O(1)	3.206(3)		
Cs(1)-O(2)#6	3.300(3)	Al(1)-O(2)#11	1.719(3)
Cs(1)-O(2)#7	3.300(3)	Al(1)-O(2)	1.719(3)
Cs(1)-O(2)#8	3.300(3)	Al(1)-O(2)#18	1.719(3)
Cs(1)-O(2)#9	3.300(3)	Al(1)-Cl(1)	2.150(3)
Cs(1)-O(2)#10	3.300(3)		
Cs(1)-O(2)#11	3.300(3)	B(1)-O(1)#9	1.376(6)
		B(1)-O(1)	1.385(5)
		B(2)-O(1)	1.331(5)

Type	Angle	Type	Angle
O(2)#11-Al(1)-O(2)	111.60(12)	O(1)#23-B(1)-O(1)	119.1(4)
O(2)#18-Al(1)-O(2)	111.60(12)	O(2)-B(1)-O(1)#23	119.4(4)
O(2)#18-Al(1)-O(2)#11	111.60(12)	O(2)-B(1)-O(1)	121.5(4)
O(2)#18-Al(1)-Cl(1)	107.25(13)		
O(2)#11-Al(1)-Cl(1)	107.25(13)		
O(2)-Al(1)-Cl(1)	107.25(13)		

Symmetry transformations used to generate equivalent atoms:

#1 x-y,-y,-z+1/2 #2 -y,x-y,z #3 -x+y,-x,z
#4 -x,-x+y,-z+1/2 #5 y,x,-z+1/2 #6 y-1,x-1,-z+1/2
#7 -x+1,-x+y,-z+1/2 #8 x-y,-y+1,-z+1/2 #9 -x+y,-x+1,z
#10 x-1,y-1,z #11 -y+1,x-y,z #12 x-y,x,-z+1
#13 -x,-y,-z+1 #14 y,-x+y,-z+1 #15 -x+1,-y,-z+1
#16 -x+1,-y+1,-z+1 #17 x-1,y,z #18 -x+y+1,-x+1,z
#19 x+1,y,z #20 x-y+1,x,-z+1 #21 y+1,-x+y+1,-z+1
#22 x+1,y+1,z #23 -y+1,x-y+1,z

Table S4. Bonding electron density difference ($\Delta\rho$) and contribution percent *w* (%) of different units in $CsAlB_3O_6Cl$ calculated by the REDA method.

Units	**$\Delta\rho$ ($\times10^4$)**	***w* (%)**
$[B_3O_6]$	234.5	92.70
$[AlO_3Cl]$	5.7	2.26
$[Cs(1)O_{12}]$	8.1	3.23
$[Cs(2)Cl_6]$	4.5	1.81

Figure S1. The structures of CsB_4O_6F (a), $CsAlB_3O_6F$ (b), $CsKB_8O_{12}F_2$ (c), and $CsAlB_3O_6Cl$ (d).

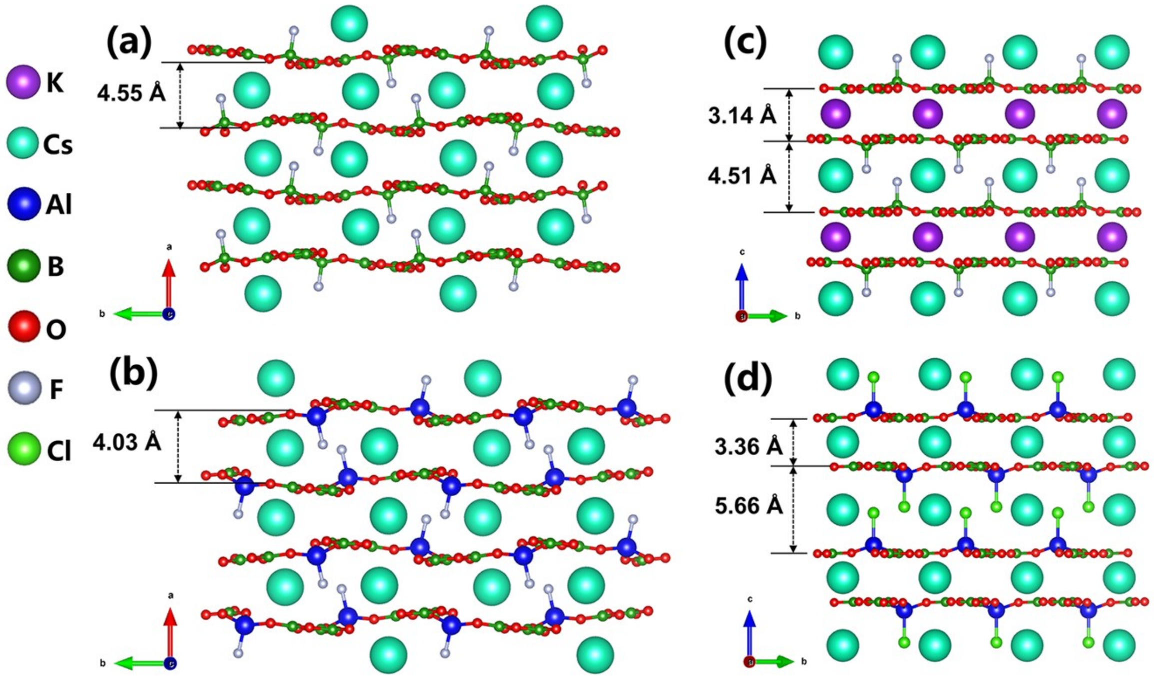


Figure S2. Powder X-ray diffraction patterns of experimental and calculated results for $CsAlB_3O_6Cl$.

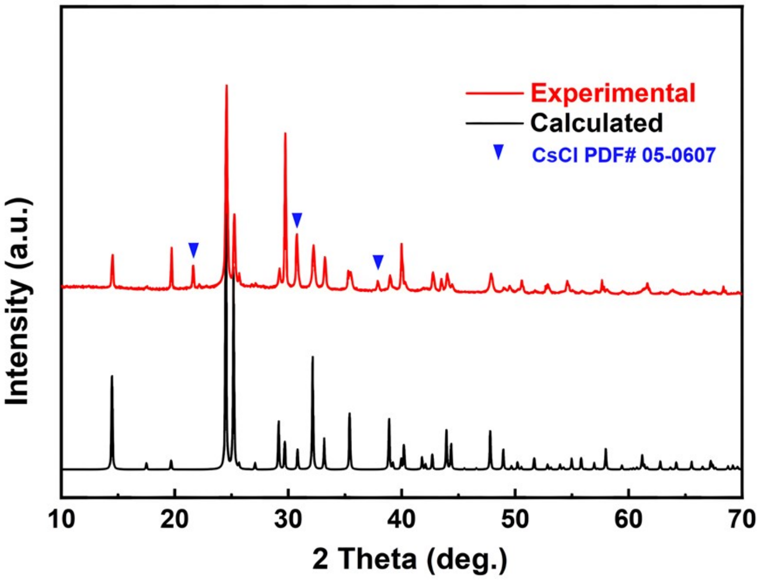


Figure S3. (a) The experimental and calculated XRD patterns of $CsAlB_3O_6Cl$ at different temperatures. (b) The TG-DSC curves of $CsAlB_3O_6Cl$.

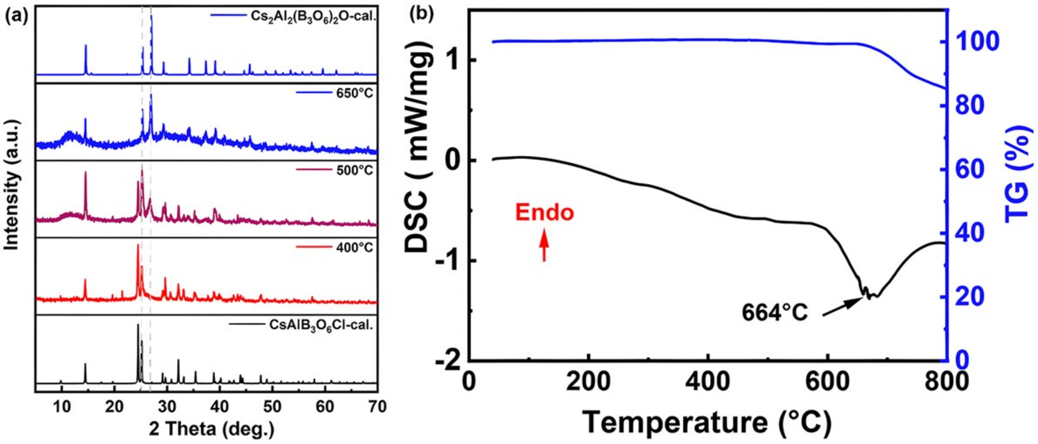


Figure S4. The energy dispersive X-ray spectrum of $CsAlB_3O_6Cl$.

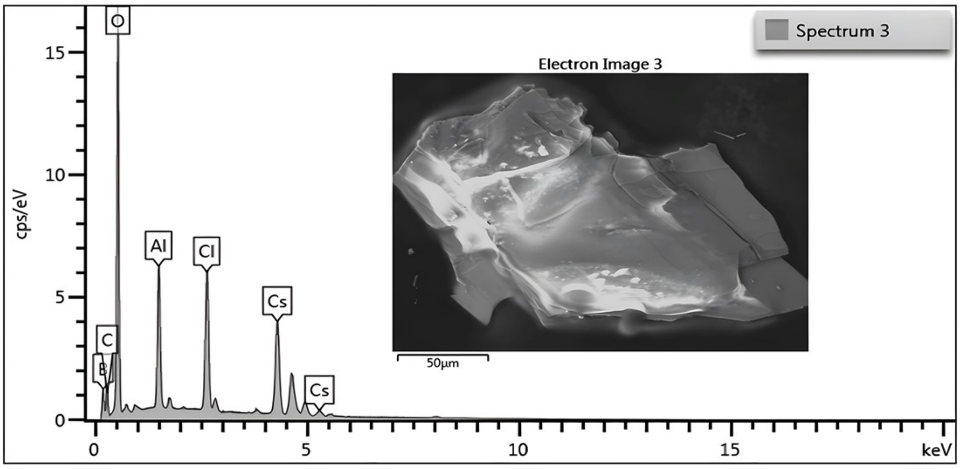


Figure S5. The IR spectrum of $CsAlB_3O_6Cl$. (a) The experimental and calculated IR spectrum of $CsAlB_3O_6Cl$. (b)-(c) Vibrations at 819.74 cm^{-1} (b) and 898,84 cm^{-1} in calculated IR spectrum.

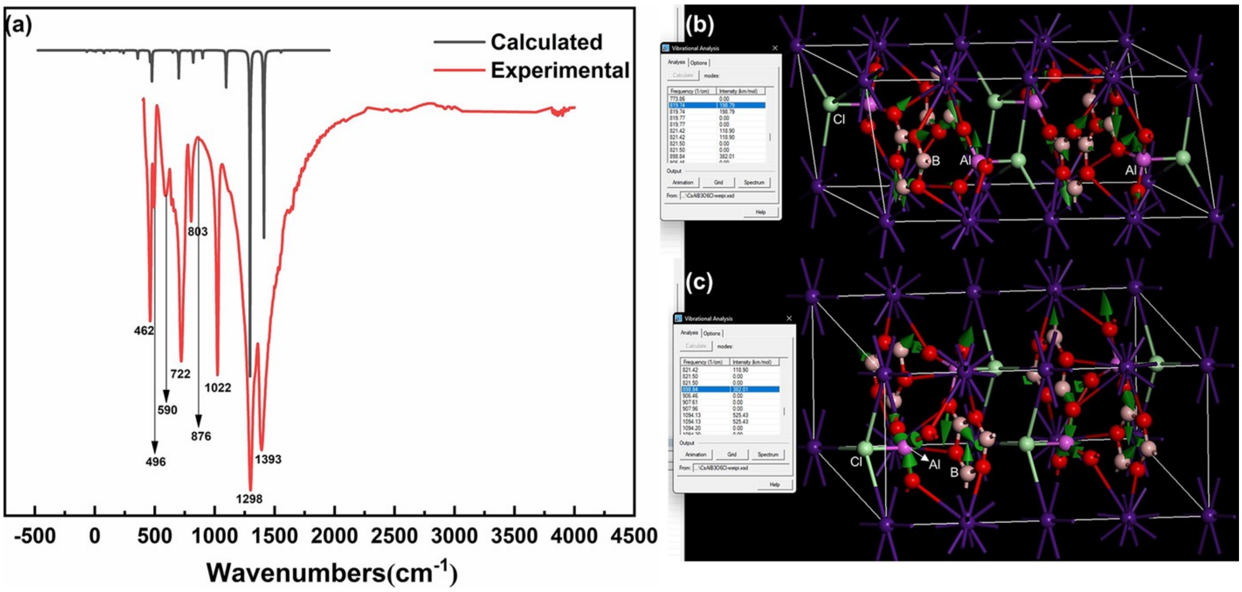


Figure S6. The UV-VIS-NIR reflection spectrum of $CsAlB_3O_6Cl$.

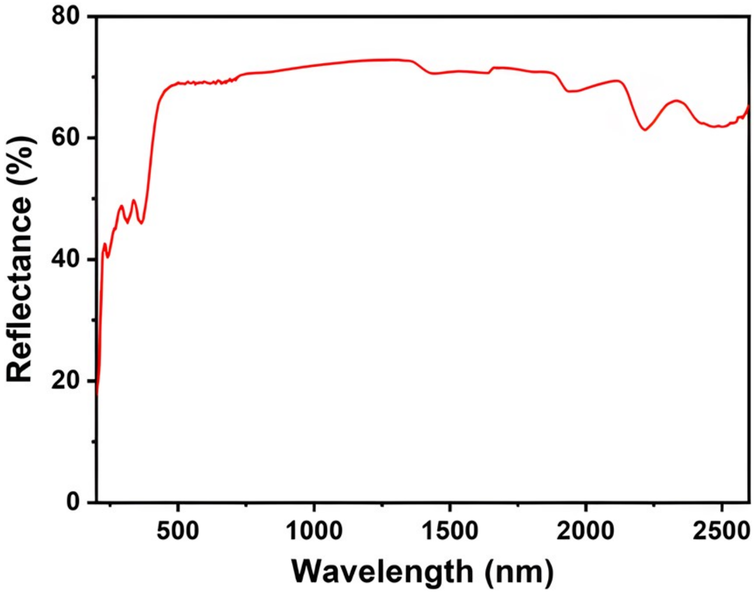


Figure S7. The electronic structure of $CsAlB_3O_6Cl$ based on GGA method.

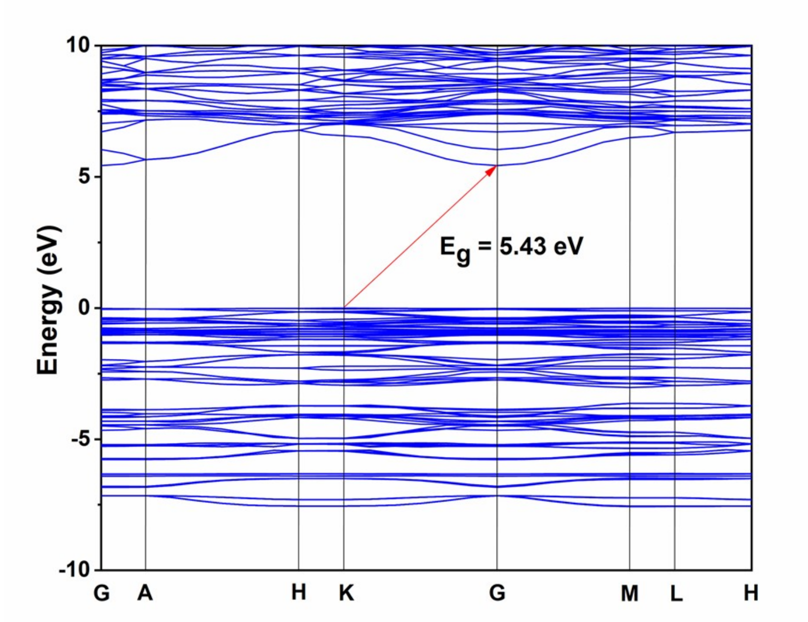


Figure S8. The density of states of $CsAlB_3O_6Cl$.

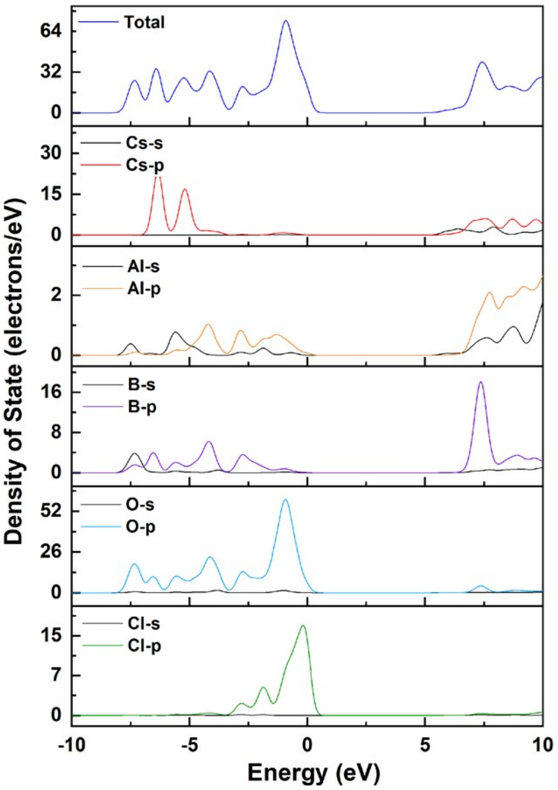
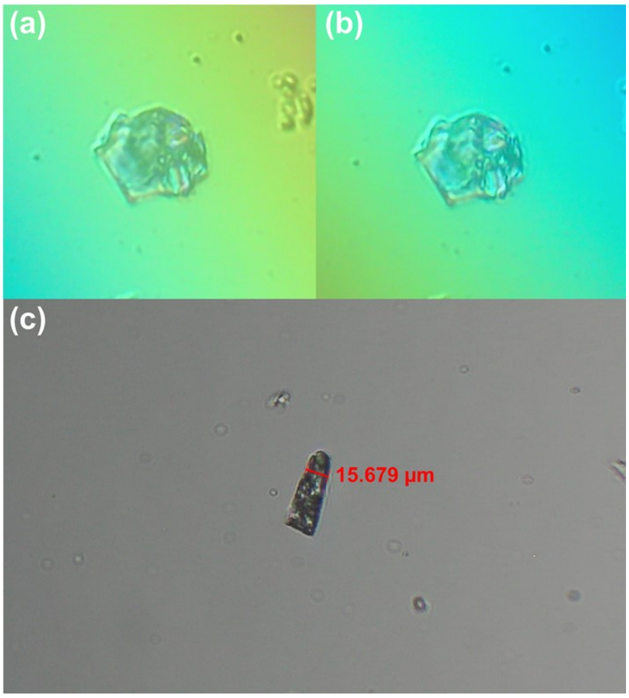


Figure S9. Birefringence measurements on the $CsAlB_3O_6Cl$ crystal. (a)-(b) The photograph of $CsAlB_3O_6Cl$ crystal under the polarizing microscope, and the (c) thickness of $CsAlB_3O_6Cl$ crystal.



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5. (a) J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865; (b) B. H. Lei, Z. H. Yang and S. L. Pan, *Chem. Commun.*, 2017, **53**, 2818-2821.