Supporting Information for

$Na_3B_7O_{11}F_2$: A new sodium-rich fluorooxoborate with a unique $[B_{14}O_{24}F_4]$ ring and a short ultraviolet absorption edge

Changcheng Tang,[a,b] XingXing Jiang,[a] Wenlong Yin,[c] Lijuan Liu,[a] Mingjun Xia,[a] Qian Huang,[d] Gaomin Song,[a,b] Xiaoyang Wang,*[a],Zheshuai Lin,[a,b] and Chuangtian Chen[a]

a. Beijing Center for Crystal Research and Development, Key Laboratory of Functional Crystals and Laser Technology of Chinese Academy of Sciences, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, China.

b. University of Chinese Academy of Sciences, Beijing 100049, China

c. Institute of Chemical Materials, China Academy of Engineering Physics, Mianyang 621900, China

d. Institute of Engineering Thermophysics, Chinese Academy of Sciences, Beijing 100190, China.

Content

1. Experimental and Computational Methods

Before experiment, X-ray powder diffraction was used to confirm the purity of NaF and B_2O_3.

Synthesis. First, 0.840g (20 mmol) NaF (AR, 99%, purchased from Tianjin Fengchuan Chemical Reagent Co., Ltd) and 0.696g (10 mmol) B_2O_3(AR, 98%, purchased from Macklin) were totally ground in a molar ratio of 2:1 and then placed in a platinum crucible. Second, the crucible was heated at 473 K for two days to dry up. Then this mixture was sealed in a 10 ml quart tube with high vacuity (10^{-5} pa). Finally, the quart tube was heated to 673 K following a special temperature control process: 24 hours heated from room temperature to 673 K, held for 480 hours; cooled during 192 hours to 623 K, cooled during 96 hours to room temperature. The single crystals were obtained.

Single crystal X-ray diffraction. A colorless block crystal of $Na_3B_7O_{11}F_2$ was selected for single crystal data analysis. The diffraction data collection was carried on a Bruker APEX II single crystal X-ray diffractometer with a graphite-monochromator Mo Kα radiation (λ = 0.71073Å) and Bruker APEX-II CCD equipment at 153 K. Then diffraction data, unit cell refinement and diffraction data reductionism were gathered by the CrystalClear program. Finally, the crystal structure was worked out directly by program SHELXS-97 and refined by the full matrix least squares on F^2 by SHELXL-97, respectively.[1] Crystallographic record and structural refinement information are given in **Table S1**. The Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters, atomic displacement parameters, selected geometric parameters were listed in **Table S2-4** in supporting information respectively. The CCDC number of summary data is 1840310.

Powder X-ray diffraction. The powder crystals was analyzed on an automated Bruker D8 ADVANCE X-ray diffractometer utilizing Cu *Kα* radiation (*λ*= 1.5418 Å) at room temperature in the range 2θ = 5-80° with a 0.2s / step time and a 0.02° scan step width.

Infrared (IR) spectroscopy. 5 mg $Na_3B_7O_{11}F_2$ crystal was ground totally with 500 mg dried KBr, the mixture was pressed to be a thin wafer. The wafer was tested on an Excalibur 3100 Fourier transform infrared spectrometer at 293 K. The IR spectrum was recorded in the 400-4000 cm^{-1} range with a resolution of 4 cm^{-1}.

UV-vis-IR diffuse reflectance spectroscopy. 600 mg pure and clean $Na_3B_7O_{11}F_2$ crystal-powder pressed in a special aperture was tested on a Cary 7000 UV-vis-NIR spectrophotometer in the 200-2500 nm wavelength range with a resolution of 1 nm at room temperature. The UV-vis-NIR diffuse reflectance spectrum was converted to optical absorption spectrum through the Kubeka Munk function,[2] $F(R) = (1-R)^2/2R = k/s = Ac/s$, where k is absorption coefficients, s is scattering coefficient, c is concentration of the absorbing species, A is absorbance and R is the reflectance.

Elemental analysis. Several $Na_3B_7O_{11}F_2$ crystals were chosen for elements analysis on a HITACHI S-4300 SEM with Energy Dispersive X-ray Detector (EDX). The testing results gave that the molar ratio of elements Na:B:O:F is 3:7.8:13:3.2 (**Table S5**), which is close to the theoretical ratio 3:7:11:2. The elements analysis picture is in Figure S3.

First-principles calculation. The first-principles electronic structure calculation of

$Na_3B_7O_{11}F_2$ was carried out by plane-wave pseudopotential method[3] implemented in CASTEP package[4] based on density function theory[5]. The functionals developped by Perdew-Burke-Ernzerhof (PBE)[6] in generalized gradient approximation (GGA) form were adoptted to describe the exchange-correlation terms in the Hamiltonian. The effective ion-electron interactions were modeled by the optimized normal-conserving pseudopotentials for all elements[7] (with the Na $2s^22p^63s^1$, B $2s^22p^1$, O $2s^22p^4$ and F $2s^22p^5$ treated as valence electrons), which allow a relatively small plane-wave basis set without compromising the computational accuracy. The kinetic enrgy cuttoff of 940 eV and intensive Monkhorst-Pack[8] k-point meshes of $2\times1\times2/Å^{-3}$ spaning less than $0.015/Å^3$ in Brillouin zone were choosen.

The band gaps calculated by PBE functionals in standard DFT framework are usually smaller than observed values for borates with wide band gaps, due to the discontinunity of exchange-correlation energy. The band gap of $Na_3B_7O_{11}F_2$ was predicted by hybridized PBE0 functionals,[9] by which the relative error of the calculated band gaps is less than 5% as demonstrated in our previous study. According to the electron band structure, the dielectric function $\varepsilon(\omega)=\varepsilon_1(\omega)+i\varepsilon_2(\omega)$, the imaginary part $\varepsilon_2(\omega)$ was calculated by the electron transition between the valence bands (VB) and conduction band (CB). The real part $\varepsilon_1(\omega)$, i.e., refractive index, was calculated by the imaginary part $\varepsilon_2(\omega)$ by the Kramers-Kronig relations[10]:

$$\varepsilon_1(\omega) = \frac{P}{\pi}\int_{-\infty}^{\infty}\frac{\varepsilon_2(\omega')}{\omega' - \omega}d\omega'$$

Where P is the Cauchy principal value. So the real and imaginary parts can be reconstructed given just one of them. Consequently, the real and imaginary parts was obtained and then the refractive index and birefringence Δn is determined.

2. Tables and figures

Table S1. Crystallographic record and structural refinement information.

Empirical formula	$Na_3B_7O_{11}F_2$
Formula weight(g/mol)	717.28
Temperature(K)	153.15
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	*Pnma*
a(Å)	9.2659(1)
b(Å)	16.3431(2)
c(Å)	6.6326(5)
Volume(Å ^{3})	1004.40 (2)
Z	2
Density (g cm^{-3})	2.372
μ (mm^{-1})	0.34
F(000)	696
R1,wR2 [I>2σ(I)][a]	0.0389,0.1105
R1,wR2[all data][a]	0.0517,0.1212

[a] $R_1 = \sum \big| \, |F_o| - |F_c| \, \big| / \sum |F_o|$; $wR_2 = \{(\sum [w(F_o^2 - F_c^2)^2] / \sum wF_o^4 \}^{1/2}$

Table S2. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	Wyck.	x/a	y/b	z/c	Ueq [Å^2]	BVS
Na1	4c	1.05858 (1)	0.75	1.25115 (1)	0.0221 (3)	1.1720
Na2	8d	1.05872 (9)	0.62907 (5)	0.75319 (1)	0.0270 (3)	1.0167
B1	8d	0.4360 (2)	0.55475 (1)	0.1891 (3)	0.0159 (4)	3.0700
B2	8d	0.6823 (2)	0.55239 (1)	0.3145 (3)	0.0168 (5)	3.0585
B3	4c	0.8093 (3)	0.7500	0.8045 (4)	0.0162 (6)	3.1160
B4	8d	0.8079 (2)	0.67208 (1)	0.4763 (3)	0.0153 (5)	3.0594
O1	4c	0.80456 (19)	0.7500	0.3792 (2)	0.0178 (5)	2.0474
O2	8d	0.67658 (13)	0.62421 (8)	0.41104 (2)	0.0173 (4)	2.1915
O3	8d	0.55836 (13)	0.51363 (8)	0.25025 (2)	0.0194 (4)	2.0813
O4	8d	0.44091 (14)	0.62677 (8)	0.09423 (2)	0.0181 (4)	2.2110
O5	8d	0.31010 (13)	0.51300 (9)	0.2273 (2)	0.0226 (4)	2.0830
O6	8d	0.81014 (14)	0.67592 (8)	0.69328 (2)	0.0204 (4)	2.0395
F7	4c	0.68188 (18)	0.7500	0.9331 (2)	0.0314 (5)	0.9031
F8	4c	0.93387 (19)	0.7500	0.9374 (2)	0.0320 (5)	0.9141

Table S3. Selected geometric parameters (Å, º).

Na1—F8	2.3804 (2)	B3—F8	1.452 (3)
Na1—F7^{i}	2.3856 (2)	B3—F7	1.456 (3)
Na1—O1^{ii}	2.438 (2)	B4—O1	1.427 (2)
Na1—O1^{iii}	2.502 (2)	B4—O6	1.440 (2)
Na1—O4^{ii}	2.5093 (1)	B4—O2	1.510 (2)
Na1—O4^{iv}	2.5093 (1)	B4—O4^{vi}	1.512 (2)
Na1—O2^{ii}	2.5651 (1)	O4—B1—O5	123.59 (2)
Na1—O2^{iv}	2.5651 (1)	O4—B1—O3	122.69 (2)
Na2—O6	2.4595 (2)	O5—B1—O3	113.67 (2)
Na2—O6^{ii}	2.4779 (2)	O2—B2—O5^{vi}	122.75 (2)
Na2—O2^{ii}	2.4817 (1)	O2—B2—O3	121.18 (2)
Na2—O4^{vi}	2.5500 (1)	O5^{vi}—B2—O3	116.07 (2)
Na2—O3^{vii}	2.5722 (2)	O6—B3—O6^{ix}	117.3 (2)
Na2—F8	2.5956 (2)	O6—B3—F8	108.15 (1)
Na2—F7^{ii}	2.5952 (2)	O6^{ix}—B3—F8	108.15 (1)
Na2—O5^{vii}	2.6264 (2)	O6—B3—F7	108.01 (1)
B1—O4	1.335 (2)	O6^{ix}—B3—F7	108.01 (1)
B1—O5	1.375 (2)	F8—B3—F7	106.8 (2)
B1—O3	1.379 (2)	O1—B4—O6	114.35 (2)
B2—O2	1.338 (2)	O1—B4—O2	108.39 (2)
B2—O5^{vi}	1.376 (2)	O6—B4—O2	108.71 (1)
B2—O3	1.379 (2)	O1—B4—O4^{vi}	108.35 (2)
B3—O6	1.418 (2)	O6—B4—O4^{vi}	108.58 (1)
B3—O6^{ix}	1.418 (2)	O2—B4—O4^{vi}	108.31 (1)

Symmetry codes:

(i) x+1/2, y, -z+5/2 (ii) x+1/2, y, -z+3/2 (iii) x, y, z+1

(iv) x+1/2, -y+3/2, -z+3/2 (v) x, -y+3/2, z+1 (vi) x+1/2,y, -z+1/2

(vii) -x+3/2, -y+1, z+1/2 (viii) -x+3/2, -y+1, z-1/2 (ix) x, -y+3/2, z

(x) x-1/2, y, -z+3/2 (xi) x-1/2, -y+3/2, -z+3/2 (xii)x, y, z-1

(xiii) x-1/2, y, -z+1/2 (xiv) x-1/2, y, -z+5/2.

Table S4. Atomic displacement parameters (Å^2×10^2).

Atom	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Na1	2.41 (7)	2.42 (6)	1.82 (6)	0	0.31 (4)	0
Na2	2.83 (6)	2.60 (5)	2.68 (5)	−0.02 (4)	−0.81 (3)	−0.08 (3)
B1	1.42 (1)	1.68 (9)	1.68 (9)	0.01 (8)	0.02 (8)	−0.29 (8)
B2	1.87 (1)	1.56 (1)	1.61 (9)	0.09 (8)	−0.11 (8)	0.20 (8)
B3	1.88 (2)	1.84 (2)	1.15 (1)	0	−0.13 (1)	0
B4	1.76 (1)	1.54 (1)	1.30 (9)	0.03 (8)	0.05 (8)	−0.03 (8)
O1	2.72 (1)	1.49 (9)	1.14 (8)	0	−0.12 (7)	0
O2	1.42 (7)	1.81 (7)	1.97 (7)	−0.01 (5)	0.08 (5)	−0.24 (5)
O3	1.39 (7)	1.53 (7)	2.90 (8)	−0.03 (5)	−0.30 (5)	−0.16 (5)
O4	1.49 (7)	1.91 (7)	2.04 (7)	−0.17 (5)	0.02 (5)	0.17 (5)
O5	1.57 (7)	2.01 (7)	3.21 (8)	0.01 (6)	−0.04 (5)	0.87 (6)
O6	3.19 (8)	1.67 (7)	1.27 (6)	−0.08 (5)	0.03 (5)	0.12 (5)
F7	3.35 (1)	3.61 (1)	2.46 (9)	0	1.37 (7)	0
F8	3.26 (1)	3.63 (1)	2.73 (9)	0	−1.30 (8)	0

Table S5. Elements analysis of $Na_3B_7O_{11}F_2$.

Element	Mass (%)	Molar (%)
B K	19.88	28.75
O K	49.49	48.36
F K	14.43	11.87
Na K	16.20	11.02
Total	100.00	100.00

Table S6. The calculated refractive indices n and the birefringence Δn of $Na_3B_7O_{11}F_2$.

wavelength(nm)	n_x	n_y	n_z	Δn
1059.338	1.432	1.433	1.371	0.061
592.692	1.438	1.438	1.376	0.062
268.513	1.475	1.476	1.407	0.070
200.382	1.524	1.527	1.446	0.081
192.933	1.534	1.538	1.454	0.083
177.822	1.563	1.568	1.478	0.091
167.957	1.591	1.599	1.501	0.099
161.247	1.618	1.630	1.524	0.106

Table S7. The comparison between common DUV birefringence crystals and $Na_3B_7O_{11}F_2$.

Crystal	Transmission range (nm)	Transmittance at 193 nm	Birefringence at 193 nm
α-BBO	189 - 3000	< 10%	0.20
BNBF	186 - 3000	45%	0.18
$Ca_3(BO_3)_2$	180 - 3000	60%	0.15
MgF_2	110 - 8500	> 90%	0.012
BMBO	177 - 3000	65%	0.20
BCBO	178 - 3000	75%	0.21
$Na_3B_7O_{11}F_2$*	161 - 2500	> 90%	0.083

$Na_3B_7O_{11}F_2$*: data from the first principle calculation.

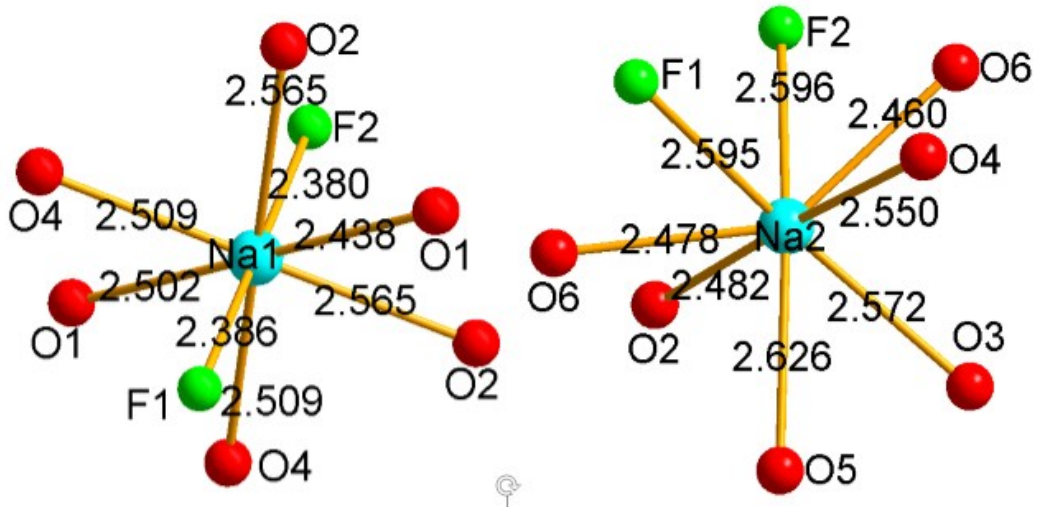

Figure S1. The coordination environment of Na atoms.

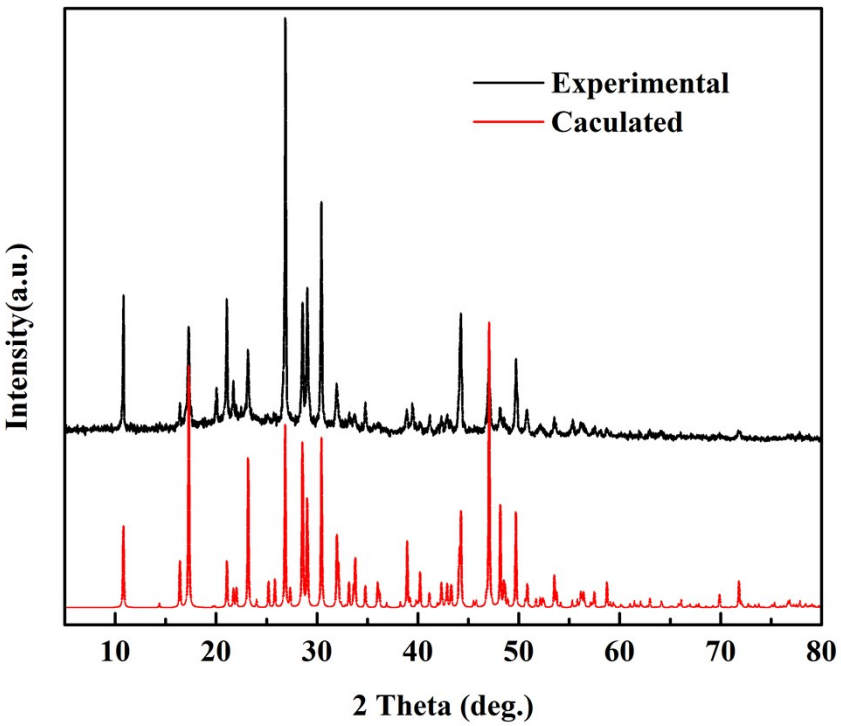

Figure S2. Comparison powder XRD of $Na_3B_7O_{11}F_2$.

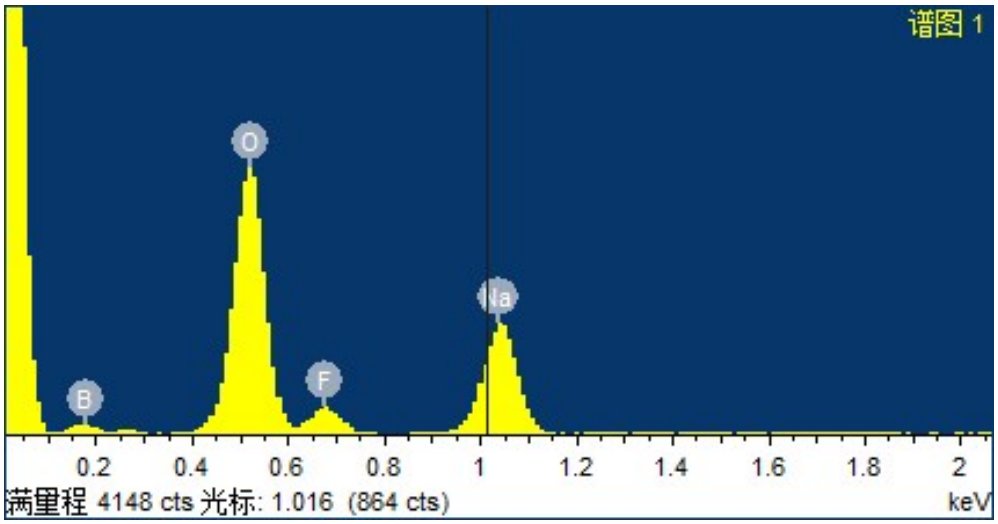

Figure S3. Elemental analysis by EDX.

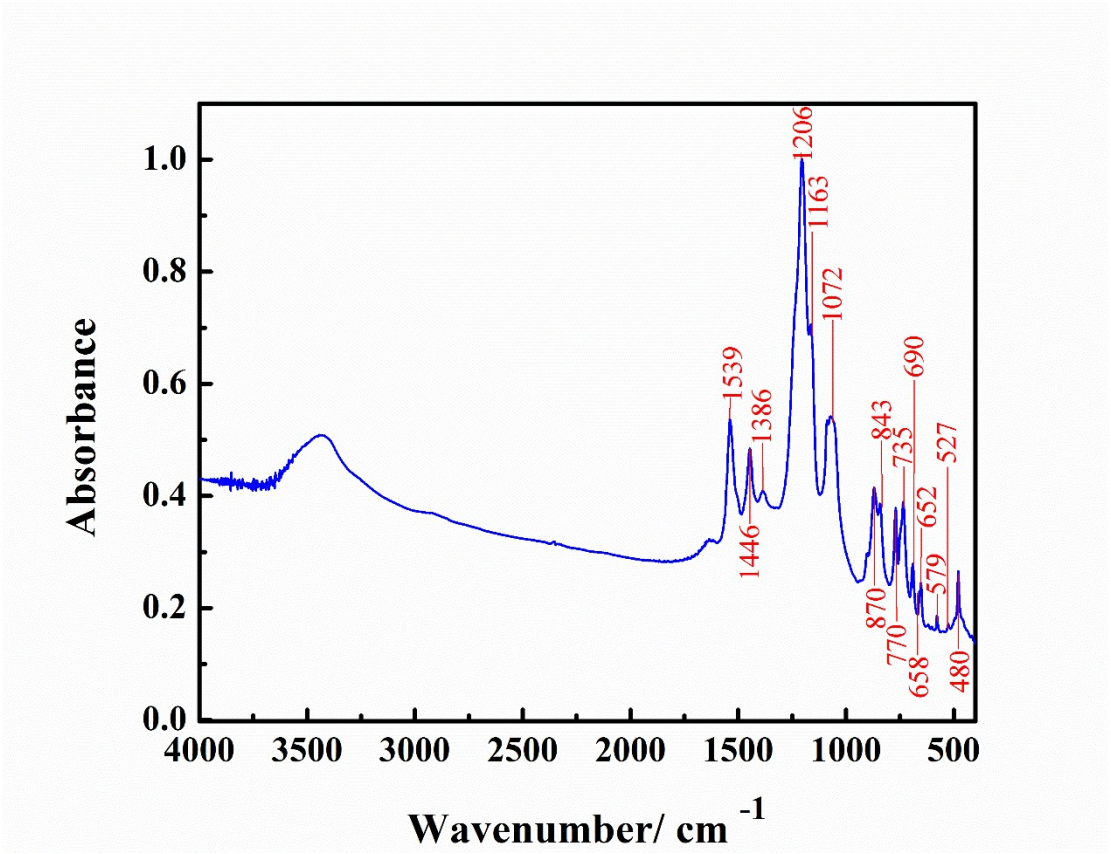

Figure S4. IR spectroscopy of $Na_3B_7O_{11}F_2$.

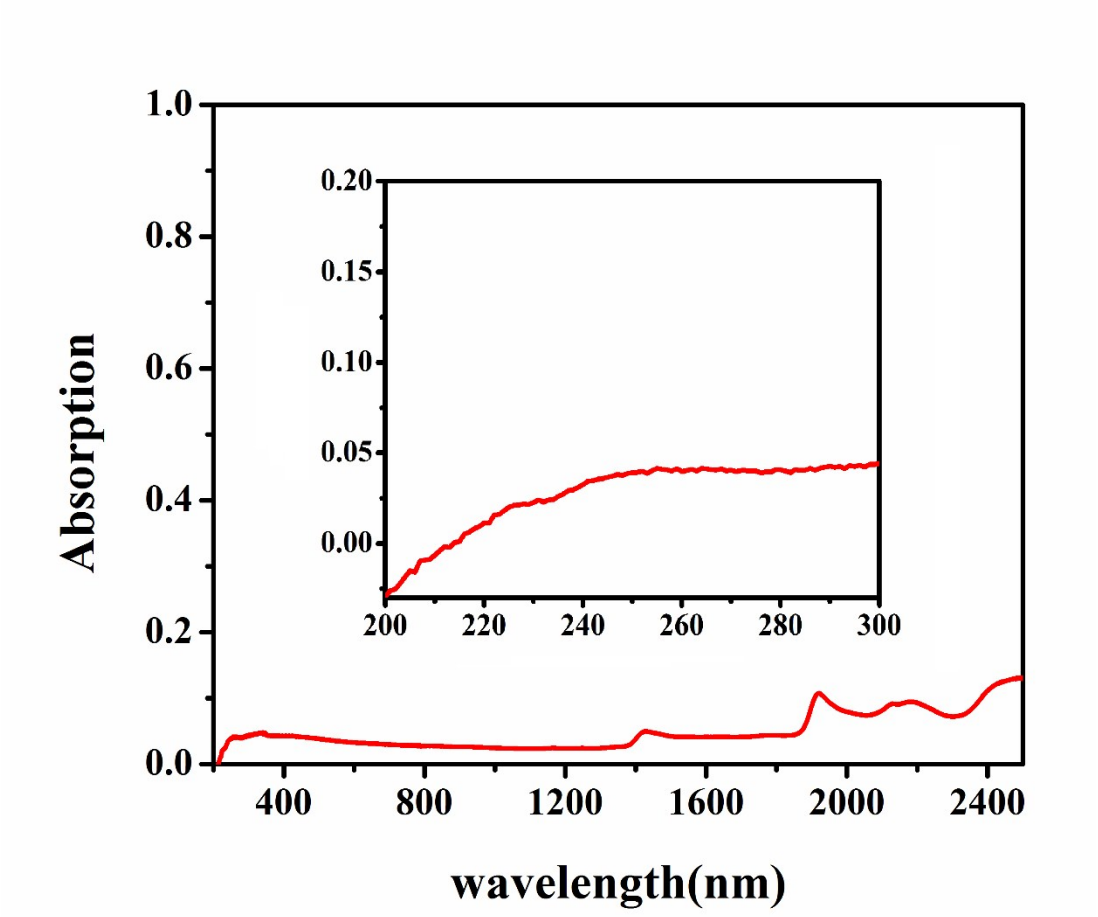

Figure S5. UV-vis-IR diffuse reflectance spectroscopy of $Na_3B_7O_{11}F_2$.

3. References

1 *G. Sheldrick, SHELXS97, Progr. Solut. Cryst. Struct. Univ. Göttingen Göttingen, Ger. (1997).*

2 W. B. Schevciw, O.; White, *Mater. Res. Bull.*, 1983, **18(9)**, 1059–1068.

3 M. C. Payne, M. P. Teter, D. C. Allan, T. A. Arias and J. D. Joannopoulos, *Rev. Mod. Phys.*, 1992, **64**, 1045–1097.

4 Z. K. S. J. Clark, M. D. Segall, C. J. Pickard, P. J. Hasnip, M. I. Probert, K. Refson and M. C. Payne, *Cryst. Mater*, 2005, **220**, 567–570.

5 W. Kohn and L. J. Sham, *Phys. Rev.*, 1965, **140**, 1133.

6 J. P. Perdew and Y. Wang, *Phys. Rev. B*, 1992, 45, 13244–13249.

7 A. M. Rappe, K. M. Rabe, E. Kaxiras and J. D. Joannopoulos, *Phys. Rev. B*, 1990, **41**, 1227–1230.

8 Hendrik J. Monkhorst and James D. Pack, *Phys. Rev. B*, 1977, **16**, 1748–1749.

9 C. Adamo and V. Barone, *J. Chem. Phys.*, 1999, **110**, 6158–6170.

10 E. D. Palik and E. J. Prucha, *Handbook of optical constants of solids*, Academic Press, 1985.