# NaB(OH)$_3$CH$_3$: A Deep-Ultraviolet Optical Crystal with Unprecedented Methyl-modification [B(OH)$_3$CH$_3$] Units

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EXPERIMENTAL METHODOLOGY

1. Synthesis.

Colorless and transparent $NaB(OH)_3CH_3$ crystals were readily grown from the solution through slow evaporation. The raw materials $B(OH)_2CH_3$, and NaOH at a molar ratio of 1:1 were placed in a 100 mL erlenmeyer flask wrapped in plastic wrap and mixed with a small amount of deionized water (20 mL). They were put in a water bath and heated to 70 °C for a week. With this process, the colorless crystals of $NaB(OH)_3CH_3$ were obtained. The polycrystalline powder sample was obtained directly from grinding the as-grown crystals, and its purity was checked by X-ray diffraction patterns.[1]

2. Characterizations.

High-quality crystals were picked under an optical microscope (OM) and applied

for the measurements of single-crystal X-ray diffraction. The experiments were carried out at room temperature on a Bruker D8 Venture diffractometer with monochromatic Cu K$\alpha$ radiation ($\lambda$ =1.54056 Å). The diffraction data were integrated using the SAINT program. Meanwhile, multiscan-type absorption corrections were performed using the SADABS program. To determine the space groups, the XPREP program in the SHELXTL package was used.[2] The crystal structures of

NaB(OH)$_3$CH$_3$ were solved by the direct method, and refined using F$^2$ full matrix least squares. Then, the structures were checked by the PLATON program.[3, 4]

UV-vis-NIR diffuse-reflectance spectroscopy data was recorded using a Shimadzu 3700DUV spectrophotometer in the wavelength range from 190-2600 nm at room temperature. The bandgap can be calculated as follows：Eg(eV)=(h/k)×(c/λ). (Planck's constant h approximately equal 6.6260693×10$^{-34}$ J·s; k=1.6×10$^{-19}$ eV; c is the speed of light; λ is the wavelength) To facilitate the calculation: Eg(eV)=1240/λ (nm).

The data of thermal behavior of NaB(OH)$_3$CH$_3$ was collected by NETZSCH STA 449C simultaneous analyzer instrument under flowing nitrogen gas and the sample and Al$_2$O$_3$ reference were put in closed platinum crucibles with a temperature from 40 to 600 ℃ at a heating rate of 10 ℃/ min.

3. Calculations

The theoretical calculations of NaB(OH)$_3$CH$_3$ are performed using the plane wave density functional theory (DFT) package CASTEP.[5, 6] The exchange-correlation functional was treated by the generalized gradient approximation (GGA) in the formulation of Perdew-Burke-Emzerhoff (PBE) functional, and core-valence interactions were described by norm-conserving pseudopotentials (NCP).[7, 8] Because GGA usually

underestimates the bandgap owing to the discontinuity of exchange-correlation energy, the HeydScuseria-Ernzerhof (HSE06) mixed function and PBE0 function implemented in PWmat code[9-10] were chosen to provide more accurate bandgap values. Therefore, the bandgap difference between the GGA and experimental value was used as the operation of a scissor to calculate optical properties. The cutoff energy of the plane wave was set to 800 eV. Self-consistent field (SCF) calculations were performed with a convergence criterion of $5\times10^{-7}$ eV/atom on the total energy. The $k$-point separation for each material was set as 0.04 $\text{Å}^{-1}$ in the Brillouin zone, resulting in the corresponding Monkhorst-Pack $k$-point meshes. The linear optical properties were obtained based on 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 of the dielectric function $\varepsilon_2$ can be calculated based on the electronic structures and the real part is obtained by the Kramers-Kronig transformation, accordingly, the refractive indices and the birefringence ($\Delta n$) can be calculated. Finally, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the $[B(OH)_3CH_3]$ group were calculated using the Gaussian 09 package under the conditions of the 6-31G basis set.
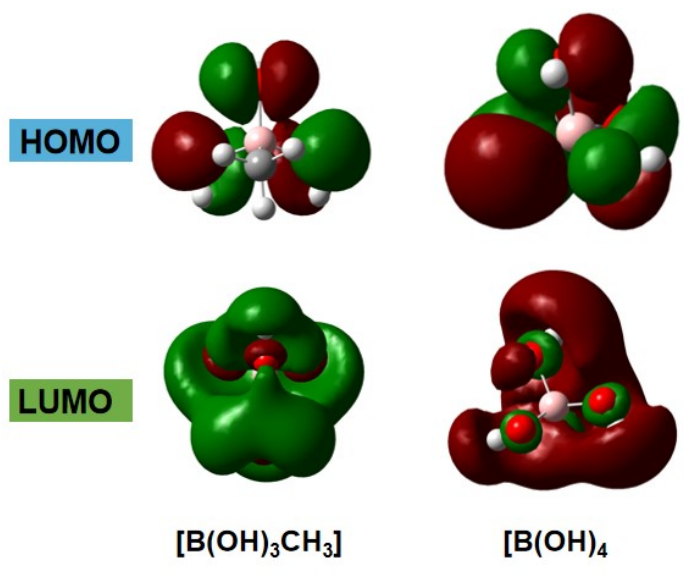
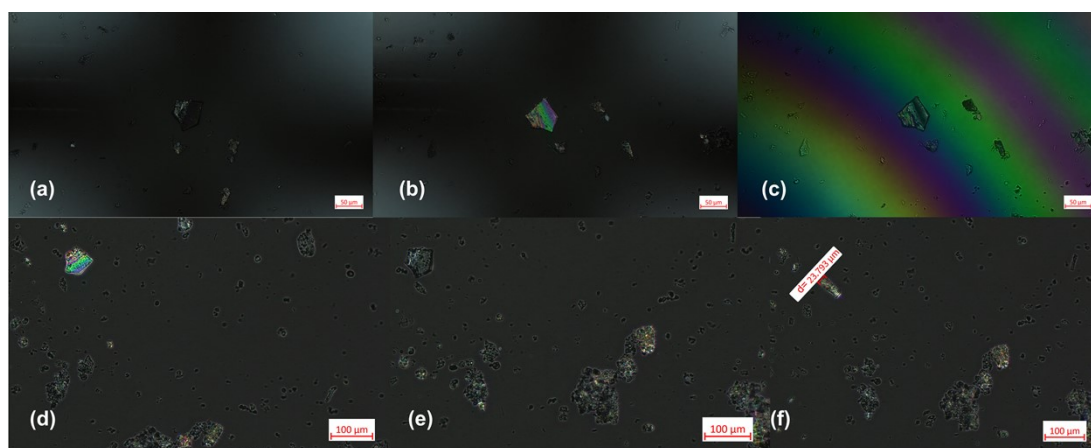**Figure S1**. The HOMO-LUMO GAP of NaB(OH)$_3$CH$_3$ crystal.

**Figure S2**. (a) and (b) $NaB(OH)_3CH_3$ single crystals under the polarizing microscope. (c) Extinction of the measurement of refractive index difference. (d), (e), and (f) Thickness of the selected crystal.
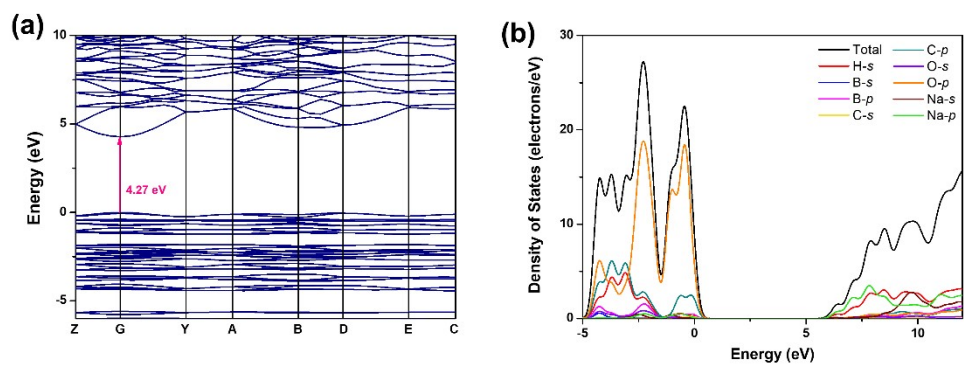
**Figure S3**. (a) The calculated electronic band structures of NaB(OH)$_3$CH$_3$.

(b) The total and partial density of states of NaB(OH)$_3$CH$_3$.

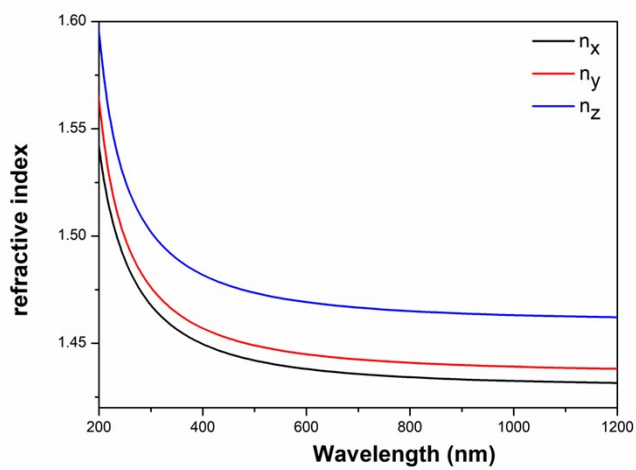**Figure S4**. The refractive index of $NaB(OH)_3CH_3$.

**Table S1**. Crystal data and structure refinements for $NaB(OH)_3CH_3$.

| | |
|---|---|
| Empirical formula | $NaB(OH)_3$ |
| Temperature (K) | 300(2) |
| Wavelength (Å) | 1.54178 |
| Crystal system | monoclinic |
| Space group | $P2_1/n$ |
| Formula weight | 99.86 |
| $a$ (Å) | 9.0897(2) |
| $b$ (Å) | 5.60850(10 |
| $c$ (Å) | 9.6007(2) |
| $\beta$ (º) | 115.5310(1 |
| $Z$, Volume (Å$^3$) | 4, |
| $\rho_{Calcd}$ (mg/m$^3$) | 1.502 |
| $\mu$(/mm) | 1.981 |
| $F(000)$ | 208 |
| $R$(int) | 0.0631 |
| Goodness-of-fit on $F^2$ | 1.098 |
| Final $R$ indices $[F_o^2 > 2\sigma(F_o^2)]^a$ | $R_1 =$ 0.0266, $wR_2 =$ 0.0676 |
| $R$ indices (all data)$^a$ | $R_1 =$ 0.0309, $wR_2 =$ 0.0698 |
| Largest diff. peak and hole (e·Å$^{-3}$) | 0.236/-0.181 |

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

**Table S2**. Fractional atomic Coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for $NaB(OH)_3CH_3$. Ueq is defined as 1/3 of the trace of the orthogonalised $U_{ij}$ tensor.

| Atom | x | y | z | $U$(eq) |
|------|------|------|------|------|
| Na(1) | 6366(1) | 6489(1) | 6742(1) | 30(1) |
| B(1) | 6959(2) | 1255(3) | 4804(2) | 24(1) |
| C(1) | 8169(2) | 2761(3) | 4303(2) | 40(1) |
| O(1) | 6326(1) | 2737(2) | 5684(1) | 26(1) |
| O(2) | 5488(1) | 385(2) | 3421(1) | 30(1) |
| O(3) | 7800(1) | -805(2) | 5827(1) | 31(1) |

**Table S3**. Bond lengths for NaB(OH)$_3$CH$_3$.

| Atom | Length/Å |
|------|----------|
| Na(1)-O(1) | 2.3304(11) |
| Na(1)-O(1)#3 | 2.5552(11) |
| Na(1)-O(1)#1 | 2.5861(11) |
| Na(1)-O(1) | 2.3304(11) |
| Na(1)-O(1)#3 | 2.5552(11) |
| Na(1)-O(1)#1 | 2.5861(11) |
| Na(1)-O(2)#1 | 2.3900(12) |
| Na(1)-O(3)#3 | 2.4808(12) |
| Na(1)-O(3)#4 | 2.3999(12) |
| B(1)-O(1) | 1.4677(19) |
| B(1)-O(2) | 1.5033(19) |
| B(1)-O(3) | 1.495(2) |
| B(1)-C(1) | 1.616(2) |
| O(1)-H(4) | 0.76(2) |
| O(3)-H(6) | 0.958(10) |
| C(1)-H(2) | 0.9600 |
| C(1)-H(3) | 0.9600 |
| C(1)-H(1) | 0.9600 |
| C(1)-H(2) | 0.9600 |
| C(1)-H(3) | 0.9600 |
| C(1)-H(1) | 0.9600 |

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1   #2 -x+3/2,y-1/2,-z+3/2   #3 -x+3/2,y+1/2,-z+3/2

#4 x,y+1,z   #5 x,y-1,z

**Table S4**. Bond angles for NaB(OH)$_3$CH$_3$.

| Atom | Angle/° |
| --- | --- |
| O(1)-Na(1)-O(1)#3 | 121.39(4) |
| O(1)#3-Na(1)-O(1)#1 | 152.73(3) |
| O(1)-Na(1)-O(1)#1 | 85.88(4) |
| O(1)-Na(1)-O(2)#1 | 139.11(4) |
| O(1)-Na(1)-O(3)#3 | 83.26(4) |
| O(1)-Na(1)-O(3)#4 | 108.68(4) |
| O(2)#1-Na(1)-O(1)#1 | 56.71(3) |
| O(2)#1-Na(1)-O(1)#3 | 97.14(4) |
| O(2)#1-Na(1)-O(3)#4 | 89.50(4) |
| O(2)#1-Na(1)-O(3)#3 | 111.29(4) |
| O(3)#3-Na(1)-O(1)#3 | 56.04(3) |
| O(3)#3-Na(1)-O(1)#1 | 136.16(4) |
| O(3)#4-Na(1)-O(1)#3 | 80.33(4) |
| O(3)#4-Na(1)-O(1)#1 | 90.95(4) |
| O(3)#4-Na(1)- | 132.72(3) |

O(3)#3

| | |
|---|---|
| O(1)-B(1)-O(2) | 105.80(12) |
| O(1)-B(1)-O(3) | 106.03(11) |
| O(1)-B(1)-C(1) | 111.17(13) |
| O(2)-B(1)-C(1) | 111.52(12) |
| O(3)-B(1)-O(2) | 109.72(12) |
| O(3)-B(1)-C(1) | 112.27(13) |

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1    #2 -x+3/2,y-1/2,-z+3/2    #3 -x+3/2,y+1/2,-z+3/2

#4 x,y+1,z    #5 x,y-1,z

**Table S5.** Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters ( x $10^3$) for $NaB(OH)_3CH_3$.

| Atom | x | y | z | $U$(eq) |
|---|---|---|---|---|
| H(1) | 8503 | 1787 | 3669 | 60 |
| H(2) | 9111 | 3245 | 5209 | 60 |
| H(3) | 7611 | 4148 | 3733 | 60 |
| H(4) | 5800(20) | 1960(30) | 5940(20) | 29(5) |
| H(5) | 5772 | -136 | 2776 | 44 |
| H(6) | 8530(30) | -1590(40) | 5490(30) | 84(8) |

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The explanation for alert level B found from the CHECKCIF report for NaB(OH)$_3$CH$_3$: Although the crystal data are good (*Rint* = 0.0631) and the structure solution parameters ($R_1$ = 0.0266, $wR_2$ = 0.0698, *GOF* = 1.098) are reasonable, there is no suitable receptor in the surrounding environment.