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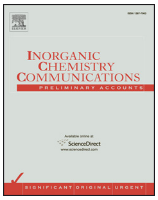

Short communication

Synthesis, structure and electronic calculation of alkali metals borate $Li_2Na[B_5O_8(OH)_2]$

Qian Wang [a], Li Wang [a,*], Dan-Dan Zheng [a], Bing-Bing Zhang [b], Zulipiya Abulizi [a], Shi-Lie Pan [b], Tao Yang [c,*]

[a] College of Chemistry and Chemical Engineering, Xinjiang Normal University, Urumqi 830054, PR China
[b] Xinjiang Technical Institute of Physics & Chemistry of CAS, Urumqi 830011, PR China
[c] College of Chemistry and Chemical Engineering, Hubei University, Wuhan 430062, PR China

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ABSTRACT

A new alkali metals borate complex, $Li_2Na[B_5O_8(OH)_2]$, has been successfully synthesized by a facile hydrothermal method. Single-crystal X-ray diffraction analysis reveals that it crystallizes in orthorhombic space group *Pbcn* with $a = 8.919(3)$ Å, $b = 9.181(3)$ Å, $c = 8.416(2)$ Å, Z = 4. The crystal structure is constructed of two dimensional (2D) $[(B_5O_8)(OH)_2]_\infty$ layers, while stacking along *b* axis and then connected by Li^+ and Na^+ cations to extend to 3D framework $Li_2Na[B_5O_8(OH)_2]$. UV-vis-NIR spectrum shows that $Li_2Na[B_5O_8(OH)_2]$ possesses a wide range of transparency and a UV cut-off edge below 190 nm which indicates that it may be applied in the deep ultraviolet region. The calculated band structures and the density of states indicate that $Li_2Na[B_5O_8(OH)_2]$ is a direct band gap compound with a band gap of 5.68 eV. In addition, IR spectroscopy, thermal stability and theoretical calculations of $Li_2Na[B_5O_8(OH)_2]$ are also reported in this work.

Materials capable of generating coherent deep ultraviolet (UV) light, which wavelengths below 200 nm ($E_g > 6.2$ eV), are of intense interest from both an academic and technological standpoint. Technologically, these materials are used in semiconductor manufacturing, photolithography, laser systems, atto-second pulse generation, and advanced instrument development [1–9]. During the past several decades, continuous efforts have led to significant discoveries of a number of important borate compounds, such as β-BaB_2O_4 (β-BBO), LiB_3O_5 (LBO), CsB_3O_5 (CBO), $CsLiB_6O_{10}$ (CLBO). Among these materials, the UV cut-off edge of BBO and CLBO are 185 and 180, respectively. Furthermore, Coherent light could be achieved at range of close and even deep UV. In addition, according to the orbital energies of boron oxygen groups calculated by Chen et al. [10], if the dangling bond or terminal oxygen of borates were removed, the energy gap could be increased. Therefore, in order to obtain a shorter cut-off edge, we adopted hydrothermal method, in which produced crystals with hydrogen atoms always connect the terminal oxygen atoms of borates. This could be attributed to the high-temperature and high-pressure in the 'black' box. Alkali metal cations shows the cut-off edge shift to the UV region, due to their closed d or f orbits contribute negative influences on the energy band gap.

Based on the discussions above, we investigate the Li_2O-Na_2O-H_3BO_3 system to explore novel compounds of alkali metals borate. In this system, some other borates have also been reported, such as $Na_4Li_5B_3O_9$ [11], $NaLi_2BO_3$ [12], $LiNaB_4O_7$ [13], $LiNaB_8O_{13}$ and $LiNa_4B_{15}O_{25}$ [14], in which $LiNaB_4O_7$ has a short cut-off edge (below 180 nm) and weak SHG responses, ~0.15 times that of the KDP standard with a similar grain size. Herein, we report the synthesis, crystal structure, thermal stability, IR spectrum, UV–vis-NIR spectrum and theoretical calculations of $Li_2Na[B_5O_8(OH)_2]$.

Single crystal sample of $Li_2Na[B_5O_8(OH)_2]$ was synthesized by the hydrothermal reaction. A mixture of $Na_2B_4O_7\cdot 10H_2O$ (4.5764 g, 12 mmol), $LiOH\cdot H_2O$ (0.1677 g, 4 mmol) $Sr(OH)_2\cdot 8H_2O$ (0.2658 g, 1 mmol), KOH (0.1120 g, 2 mmol), and distilled water (3 mL) were placed into a 23 mL autoclave with a Teflon liner. The autoclave was heated at 180 °C for 24 h and then cooled to room temperature. Large quantities of colorless block crystals were recovered by filtration. The crystals were dried in a vacuum drying oven after washing with deionized water. Yield: 90% (based on sodium). The EDS spectral suggest the absence of Sr and K element. Elemental analysis of lithium and sodium element was conducted on America Thermo Simultaneous ICAP-QC. The crystal samples were nitrated in nitric acid under heating condition for 1 h. Element analysis of $Li_2Na[B_5O_8(OH)_2]$: Calcd.(%) Li, 5.49; Na, 9.09; Found (%): Li, 5.20; Na, 9.41.The phase purity of the crystalline solid was confirmed by the powder X-ray diffraction (Fig. S1).

Single-crystal X-ray diffraction data of $Li_2Na[B_5O_8(OH)_2]$ was collected using an APEX II CCD diffractometer equipped with monochromatic Mo *Kα* radiation ($\lambda = 0.71073$ Å) at 143 K [15].The data are integrated using the SAINT program [16]. The structures were solved using ShelXS. The structural solutions were found by Direct Methods and refined using the ShelXL package by least squares minimization.

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* Corresponding authors.
E-mail addresses: wangliresearch@163.com (L. Wang), yt01_1986@163.com (T. Yang).

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Table 1
Crystal data and structure refinements for $Li_2Na[B_5O_8(OH)_2]$.

	$Li_2Na[B_5O_8(OH)_2]$
Formula	$B_5H_2Li_2NaO_{10}$
Formula weight	252.94
Temperature (K)	293(2)
Crystal system	Orthorhombic
Space group	*Pbcn*
a (Å)	8.919(3)
b (Å)	9.181(3)
c (Å)	8.416(2)
V (Å^3)	689.2(4)
Z	4
D_c ($g \cdot cm^{-3}$)	2.438
F (000)	496
μ (mm^{-1})	0.279
Reflection collected	3721
Unique reflection	795
R_{int}	0.1062
R_1[a], wR_2[b] [$I > 2\sigma(I)$]	0.1119/0.2585
R_1, wR_2 (all data)	0.1127/0.2588
GOF	1.252
$\Delta\rho_{max}$, $\Delta\rho_{min}$, (e Å^{-3})	0.662, −1.060

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

The positions of non-hydrogen atoms were refined with anisotropic displacements parameters. Na1 located in a special position, and its chemical occupancy is 0.5, half of 1 Na atom with disorder refinement. The final structures were examined using the Addsym subroutine of PLATON to assure that no additional symmetry could be applied to the models [17]. The supplementary crystallographic data can be found in the Supporting Information or can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif. The CCDC reference number is 1535497. Crystal data for $Li_2Na[B_5O_8(OH)_2]$ are summarized in Table 1. Relevant atomic coordinates, occupancies and anisotropic displacement parameters were listed in the Table S1. The selected bond distances and bond angles were listed in Table S2.

$Li_2Na[B_5O_8(OH)_2]$ crystallizes in space group *Pbcn* (No. 60). In the asymmetric unit, there are one Li atom, half of Na atom, two and half B atoms, five unique O atoms and 1 H atom. It is noted that B atoms possesses two different coordination modes in the structure of $Li_2Na[B_5O_8(OH)_2]$, one is triangle (Δ) BO_3 (Fig. 1a, B1) and the other is tetrahedral (T) BO_4 (Fig. 1a, B2 and B3). One triangle B and two tetrahedral B atoms connect together with O, lead to 6-member B_3O_3 ring, which is the basic building unit (Fig. 1a). B_3O_3 ring connect together to form a layer (6, 3) net (Fig. 1b). View along *b* axis, layer and layer stacking by ABAB mode. And then Li and Na atoms insert between the layers to build three dimensional (3D) frameworks. According to the suggestion by Burns et al. [18], the layer also could be considered as $[(B_5O_8)(OH)_2]_\infty$, in which B_5O_{10} is the basic building unit. B_5O_{10} could be written as 5: (2Δ + 3T). This kind of layer is the same as the anion layer contained in the $Li_3B_5O_8(OH)_2$ [19]. The different connecting way between layers lead to $Li_3B_5O_8(OH)_2$ crystallize in different space group. As shown in Fig. 2a, in the structure of $Li_2Na[B_5O_8(OH)_2]$, two 5-coordinated Li(1) atoms are located in 20-member ring of $B_{10}O_{10}$, while 8-coordinated Na(1) atoms are located in a dense cage (Fig. 2b), in which half is B_5O_6 11-member ring and the other half is boat-like $(BO_2)Li_2(BO)_2$.

In the crystal structure of $Li_2Na[B_5O_8(OH)_2]$, the anion layer is composed by the B—O units. The B—O bonds lengths vary from 1.345(9)–

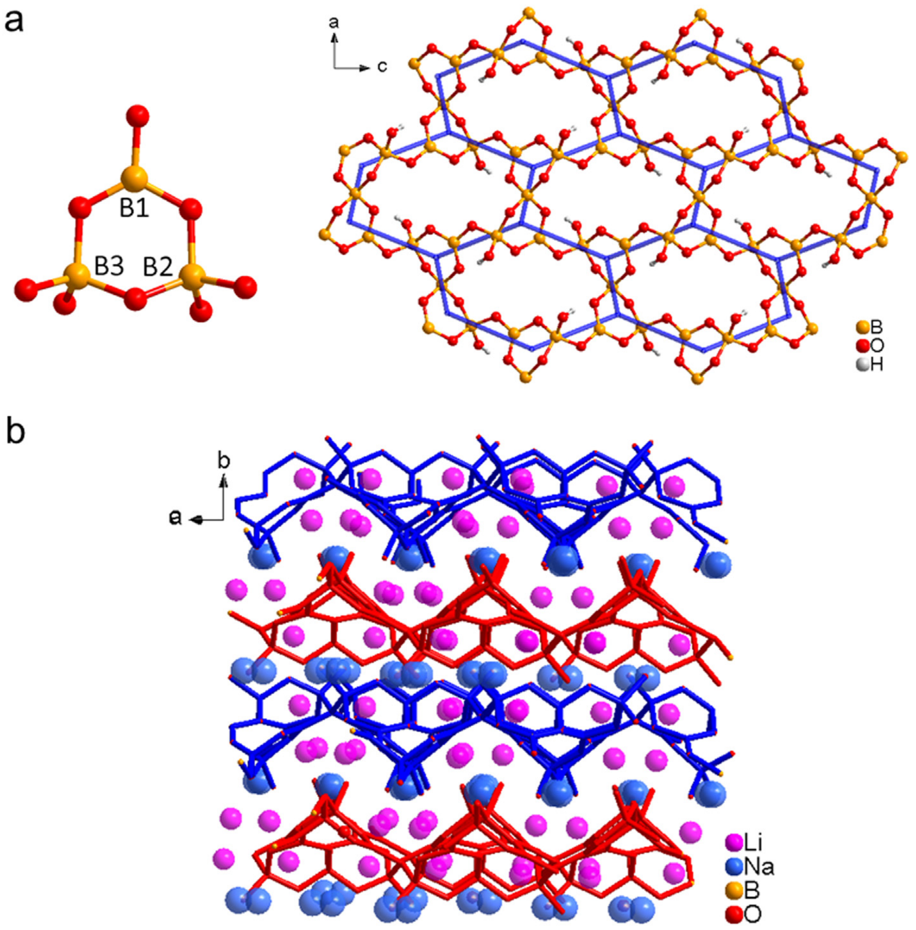

Fig. 1. (a) B_3O_3 6-member ring with triangle and tetrahedral coordination B atoms (left) and (6, 3) net (b) ABAB stacking mode and Li and atom insert between the layers.