

Synthesis and crystal structure of a novel hexaborate, Na₂ZnB₆O₁₁

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A novel hexaborate, Na₂ZnB₆O₁₁, has been successfully synthesized by solid-state reaction and *ab initio* crystal-structure analysis has been completed using powder X-ray diffraction data. The compound crystallizes in the monoclinic space group *Cc* with lattice parameters $a = 10.7329(2)$ Å, $b = 7.4080(3)$ Å, $c = 11.4822(2)$ Å, and $\beta = 112.16(2)^\circ$. The number of chemical formula per unit cell is $Z = 4$ and the calculated density is $2.768(3)$ g/cm³. It represents a new structure type in which double-bridge-ring [B₆O₁₁]⁴⁻ groups were found as fundamental building units. The infrared spectrum confirms the presence of both [BO₃]³⁻ groups and [BO₄]⁵⁻ groups. © 2010 International Centre for Diffraction Data. [DOI: 10.1154/1.3309719]

Key words: Na₂ZnB₆O₁₁, crystal structure, powder diffraction, hexaborate, synthesis

I. INTRODUCTION

ZnO is a II-VI semiconductor with a wide band gap of 3.4 eV and a large exciton binding energy of 60 meV (Look, 2001; Norton *et al.*, 2004). Wide band gap ZnO has important applications in many ways such as transparent conducting films, gas sensors, piezoelectric transducers, varistors, and surface acoustic wave devices (Look, 2001). Owing to its excellent properties, the growth of bulk ZnO single crystals is strongly desired. ZnO crystals can be grown by hydrothermal, vapor transport, and flux methods. The flux method, which can grow crystals at atmospheric pressure, is promising to obtain high-quality single crystals. However, the melting point of ZnO is 1975 °C; as a consequence, the growth of ZnO crystal at high temperatures is accompanied by serious volatilizations of ZnO. Therefore, the growth of ZnO crystals at low temperatures by aid of a suitable flux is desired. Using a group-IA oxide as flux, *p*-type ZnO might be obtained via the substitution of the Zn²⁺ ion by an IA metal ion. Since the melting point of B₂O₃ is relatively low (about 450 °C), it is useful to study phase relations of the ternary system ZnO-A₂O (A=Li, Na, K)-B₂O₃ and to explore a suitable flux for the growth of ZnO crystals. According to the literature reports, only one compound Na₃ZnB₅O₁₀ has been structurally characterized (Chen *et al.*, 2007). During our study of phase relations and flux research for zinc oxide crystal growth in the ZnO-Na₂O-B₂O₃ system, we discovered the existence of another new compound Na₂ZnB₆O₁₁. In this paper, we report the synthesis and the study of the crystal structure of the title compound by *ab initio* using powder diffraction method.

II. EXPERIMENTAL

A. Solid-state synthesis

The polycrystalline Na₂ZnB₆O₁₁ sample was prepared by sintering through solid-state reactions. All reagents were of analytical grades. The powders in the appropriate compo-

sition of raw materials Na₂CO₃, ZnO, and H₃BO₃ were mixed and ground in an agate mortar, then heated at 300 °C for 10 h after slowly elevating to the specified temperature to avoid the loss of components caused by the volatilization of H₂O and CO₂. After being pressed into a pellet of 12 mm in diameter and 1 to 2 mm in thickness, the sample was sintered at 650 °C for 1 week in a stove. The sintered sample was ground into powders and repeatedly pressed into a pellet and sintered for several times. Then pure Na₂ZnB₆O₁₁ powders were obtained and characterized by powder X-ray diffraction method (XRD).

TABLE I. Crystallographic data, experimental details for powder XRD, and Rietveld refinement for Na₂ZnB₆O₁₁.^a

Chemical formula	Na ₂ ZnB ₆ O ₁₁
Formula weight	352.24
Crystal system	Monoclinic
Space group	<i>Cc</i>
a (Å)	10.7329(2)
b (Å)	7.4080(3)
c (Å)	11.4822(2)
B (°)	112.16(2)
V (Å ³)	845.52(1)
Z	4
d_c (g/cm ³)	2.768(3)
Diffractometer	D/Max 2500, Rigaku
Radiation type	Cu $K\alpha$
Profile range (°)	14–120
Step width (2θ , deg)	0.02
Number of observation	5301
Number of reflection lines	624
Number of profile parameters	16
Number of structure parameters	80
R_p (%)	12.26
R_{WP} (%)	15.02
R_{exp} (%)	5.75
S	2.61

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^a $R_p = \sum |Y_{io} - Y_{ic}| / \sum Y_{io}$, $R_{WP} = \{ \sum w_i (Y_{io} - Y_{ic})^2 / \sum w_i Y_{io}^2 \}^{1/2}$, $R_{exp} = [(N - P) / \sum w_i Y_{io}^2]^{1/2}$, and $s = R_{WP} / R_{exp}$.

TABLE II. XRD diffraction data for Na₂ZnB₆O₁₁.^{a,b}

<i>hkl</i>	<i>d</i> _{obs} (Å)	<i>d</i> _{cal} (Å)	Δ <i>d</i> (Å)	2 <i>θ</i> _{obs} (°) ^c	2 <i>θ</i> _{cal} (°)	Δ2 <i>θ</i> (°)	<i>I</i> _{obs} (%)	<i>I</i> _{cal} (%)
110	5.9263	5.9342	0.0080	14.937	14.916	-0.020	53.2	54.7
-111	5.7596	5.7613	0.0017	15.371	15.367	-0.004	4.2	4.7
002	5.3067	5.3118	0.0050	16.692	16.676	-0.016	22.8	22.6
200	4.9623	4.9643	0.0021	17.860	17.852	-0.008	9.7	10.0
-112	4.4893	4.4911	0.0018	19.759	19.752	-0.008	22.1	27.0
020	3.6985	3.7009	0.0024	24.042	24.026	-0.016	2.8	3.5
112	3.5759	3.5783	0.0024	24.879	24.862	-0.017	53.2	70.6
021	3.4935	3.4949	0.0014	25.475	25.465	-0.010	9.9	11.5
-311	3.2098	3.2105	0.0006	27.770	27.765	-0.006	100	100
-312	3.1282	3.1279	-0.0004	28.510	28.513	0.003	17.9	21.8
202	3.0904	3.0929	0.0025	28.867	28.843	-0.024	11.9	15.5
-221	3.0394	3.0403	0.0009	29.361	29.353	-0.009	53.3	53.1
220	2.9666	2.9671	0.0005	30.099	30.093	-0.005	45.2	47.7
-204	2.8255	2.8250	-0.0005	31.641	31.646	0.005	20.3	25.3
113	2.7768	2.7785	0.0017	32.210	32.190	-0.020	2.8	3.7
004	2.6562	2.6559	-0.0003	33.715	33.719	0.004	23.0	22.9
023	2.5588	2.5586	-0.0002	35.039	35.042	0.003	4.5	5.4
400	2.4818	2.4822	0.0004	36.163	36.158	-0.006	2.3	2.9
131	2.2913	2.2917	0.0004	39.287	39.281	-0.006	5.8	6.3
-132	2.2614	2.2611	-0.0003	39.830	39.835	0.005	6.6	6.4
114	2.2435	2.2435	0.0000	40.161	40.162	0.001	12.4	12.4
-422	2.1633	2.1631	-0.0002	41.717	41.722	0.004	12.8	13.0
-315	2.1127	2.1124	-0.0003	42.766	42.772	0.007	4.4	4.9
-512	2.0583	2.0585	0.0002	43.954	43.950	-0.004	7.6	7.5
-511	2.0207	2.0200	-0.0007	44.816	44.831	0.016	8.9	7.7
-332	2.0068	2.0071	0.0003	45.143	45.136	-0.008	7.3	5.7
330	1.9794	1.9781	-0.0014	45.802	45.835	0.033	16.5	15.7
-225	1.9471	1.9470	-0.0001	46.607	46.610	0.003	17.7	15.2
-333	1.9194	1.9204	0.0010	47.319	47.294	-0.026	16.6	17.3
331	1.8704	1.8705	0.0001	48.640	48.637	-0.002	6.3	6.7
025	1.8421	1.8426	0.0006	49.436	49.421	-0.016	2.8	2.7
041	1.8224	1.8230	0.0006	50.006	49.989	-0.016	3.0	2.8

^aThe *I*_{obs} < 1.0 and Cu *Kα* 2*θ* > 50° are not shown in the table.

^b*I*_{cal} are obtained by using the structural parameters from the Rietveld refinement.

^cThe values of 2*θ*_{obs} determined by peak search were used in the second derivative method.

B. X-ray powder diffraction analysis

The XRD data of Na₂ZnB₆O₁₁ used for structure determination and Rietveld refinement were collected at room temperature by a step scan mode on a Rigaku D/Max-2500 diffractometer with a graphite monochromator. The step width and the sampling time were set as 2*θ*=0.02° and 2 s per step, respectively. The angular range was set from 2*θ* = 14° to 2*θ*=120°. Additional technical details are listed in Table I.

C. Vibration spectrum

The infrared absorption spectrum of the sample was measured at room temperature in KBr disks using a SPECORD-751R infrared spectrophotometer in the frequency range of 400 to 4000 cm⁻¹. Wave-number accuracy is within ±2 cm⁻¹ for narrow bands.

III. RESULTS AND DISCUSSION

A. Automatic indexing of X-ray diffraction data

The powder diffraction peaks were listed as the standard of phase identification (Table II). The diffraction pattern of

Na₂ZnB₆O₁₁ was indexed using the DICVOL program (Boultif and Louër, 2004). It belongs to a monoclinic unit cell with *a*=10.715(1) Å, *b*=7.402(2) Å, *c*=11.465(4) Å, and β = 112.088(5)°. The systematic absence rules are the following: *hkl* with *h+k*=2*n*+1, *h0l* with *l*=2*n*+1 (*h*=2*n*+1), and *0k0* with *k*=2*n*+1; the possible space groups are *Cc* and *C2/c*. Since the measured density was about 2.75 ± 0.25 g cm⁻³, it is easy to derive that the number of chemical formula per unit cell, *Z*, is 4. In other words, a Na₂ZnB₆O₁₁ unit cell contains 8 Na, 4 Zn, 24 B, and 44 O atoms.

B. Vibrational spectrum analysis

The purpose of infrared-spectrum analysis is to obtain the structural information on boron coordination. We can see from Figure 1 that the strongest bonds in the range 1254 to 1464 cm⁻¹ are attributed to the three-coordinated [BO₃]³⁻ group and those near 853 and 1020 cm⁻¹ are mainly attributed to the four-coordinated [BO₄]⁵⁻ group. The bonds associated with [BO₃]³⁻ groups and [BO₄]⁵⁻ groups bending modes are overlapped and located below 760 cm⁻¹. The vibrational spectrum shows that the existence of both [BO₃]³⁻

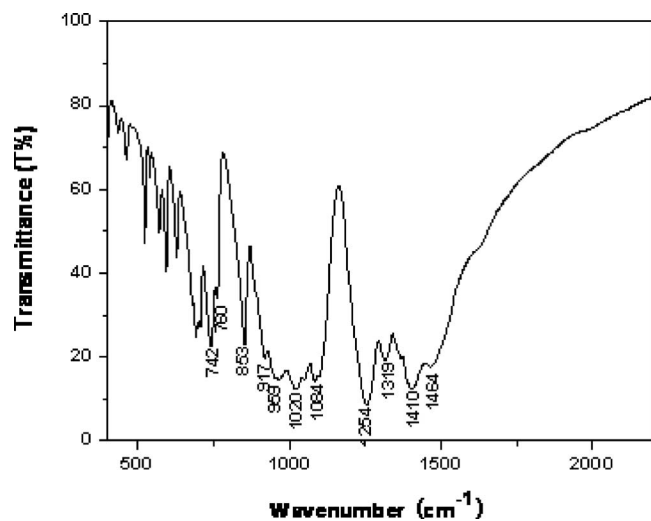


Figure 1. Infrared spectrum of $\text{Na}_2\text{ZnB}_6\text{O}_{11}$.

groups and $[\text{BO}_4]^{5-}$ groups and the content of $[\text{BO}_3]^{3-}$ groups are considerably greater than that of $[\text{BO}_4]^{5-}$ groups.

C. *Ab initio* crystal-structure determination

The correct decomposition of X-ray diffraction profiles is the key to successfully determine crystal structure from powder diffraction data using the single-crystal structure determination method. The profile decomposition was carried out on the experimental X-ray powder diffraction pattern of $\text{Na}_2\text{ZnB}_6\text{O}_{11}$ using the FULLPROF program (Rodríguez-Carvajal *et al.*, 1991) based on the Le Bail method (Le Bail *et al.*, 1988) with the possible space group *Cc*. The final agreement factors converged to $R_p=10.83\%$, $R_{wp}=13.42\%$, and $R_{exp}=5.74\%$. Structure factors for 624 reflections were extracted in the diffraction range $2\theta=14^\circ$ to 120° and put into the direct methods program SHELXL-97 (Sheldrick, 1997). Based on the extracted structure factors, an E map (electronic density map) was obtained. According to the atom distances, six peaks listed in the E map probably corresponded to the correct positions of the atoms, among which one was assigned to the Zn atom, two were assigned to Na atoms, and the other three were assigned to O atoms. Other O and B atoms were located by using difference Fourier synthesis. In this course, once an atom was located, it would be used for the next run of difference Fourier synthesis. Owing to the scattering factor of B is smaller, we failed to reveal all B atoms by the difference Fourier syntheses. However, because the positions of Zn, Na, and O have been determined initially, possible equilibrium positions of B atoms can be analyzed by reported data of bonds and angles of $[\text{BO}_3]^{3-}$ groups and $[\text{BO}_4]^{5-}$ groups. Finally, we determined the positions of B by three parameter equations (two distance equations and one angle equation). So far, all the atomic positions of $\text{Na}_2\text{ZnB}_6\text{O}_{11}$ have been determined initially. The structural model is used to calculate the X-ray diffraction data by the LAZY program (Klaus *et al.*, 1977); the first six peaks agree well with the experimental data. Then the structure was refined using the Rietveld method (Rietveld, 1967, 1969) of the FULLPROF program. There is a total of 96 parameters including 16 profile parameters (five peak-shape pa-

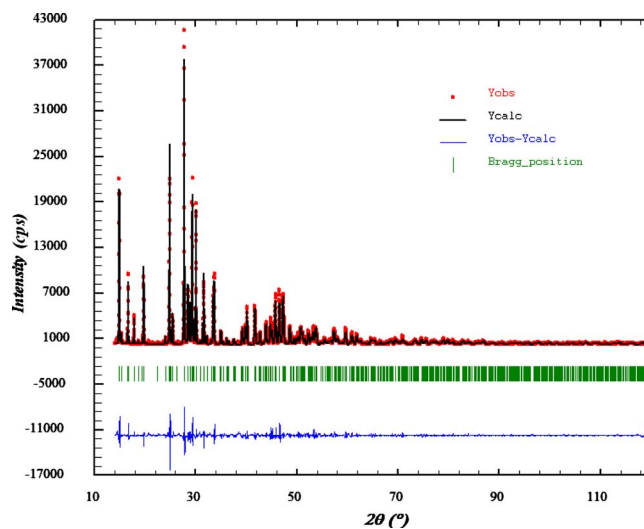


Figure 2. (Color online) Rietveld refinement plots of $\text{Na}_2\text{ZnB}_6\text{O}_{11}$. Small circles correspond to experimental values, and the solid curve, the calculated pattern. Vertical bars indicate the positions of the Bragg peaks. The bottom curve depicts the difference between the experimental and calculated intensity values.

rameters, three background parameters, four lattice parameters, one asymmetrical parameter, one scale parameter, one zero parameter, and one preference parameter). The March–Dollase model, $P_K=(G_1^2 \cos^2 \delta + (1/G_1) \sin^2 \delta)^{-3/2}$, was used to refine the preference parameter (G_1 is the refinable parameter and its value is 0.9937) and 80 structural parameters (including 20 temperature factors). The final residual factors converged to $R_p=12.26\%$, $R_{wp}=15.02\%$, and $R_{exp}=5.75\%$. Values of R_p and R_{wp} are slightly large, probably because of crystal imperfection and minor impurities produced during crystal growth by the solid-state reaction process. The refined lattice parameters are $a=10.7329(2)$ Å, $b=7.4080(3)$ Å, $c=11.4822(2)$ Å, and $\beta=112.16(2)^\circ$. The final result was put into the PLATON program (Spek, 2003) and no additional symmetry was found. Then the final space group was determined as *Cc*. The Rietveld refinement results are given in Figure 2. The crystallographic data, fractional atomic coordinates, and the thermal parameters (B) are listed in Tables I and III.

D. Description on crystal structure

The $\text{Na}_2\text{ZnB}_6\text{O}_{11}$ compound crystallizes in the space group *Cc*. The structure perspective of $\text{Na}_2\text{ZnB}_6\text{O}_{11}$ is shown in Figure 3. The basic structural unit is a double hexagonal ring $[\text{B}_6\text{O}_{11}]^{4-}$ consisting of two BO_4 tetrahedrons and four BO_3 triangles and they are connected by one O atom (see Figure 4), which is consistent with the results obtained from the vibrational spectrum. According to Yuan and Xue (2007), it belongs to double-bridge-ring fundamental building blocks (FBBs) and its topology was also given in Figure 4. In this unit, two hexagonal rings formed a certain angle, which is defined by B4, O11, B5, O5, B1, and O1 and by B3, O2, B2, O4, B6, and O8. Values of B–O bonds in the tetrahedral coordination range from 1.406(5) Å to 1.547(1) Å and O–B–O angles from $101.20(4)^\circ$ to $117.45(4)^\circ$; in the triangle coordination the respective ranges are 1.296(4) to 1.438(2) Å

TABLE III. Atomic coordinates and equivalent isotropic displacement parameters for Na₂ZnB₆O₁₁.

Atom	Site	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i> (Å ²)	BVS ^a
Zn	4a	0.903 25(3)	0.133 30(2)	0.620 26(1)	1.21(3)	1.80
Na1	4a	0.040 17(4)	0.406 83(3)	0.394 84(2)	1.64(3)	0.98
Na2	4a	0.255 70(3)	0.081 53(2)	0.327 68(3)	0.75(3)	1.21
O1	4a	0.114 54(2)	0.958 81(3)	0.626 20(2)	1.30(5)	2.06
O2	4a	0.808 59(2)	0.699 22(2)	0.756 79(4)	1.48(6)	1.98
O3	4a	0.210 41(3)	0.155 62(2)	0.526 50(1)	1.10(6)	1.94
O4	4a	0.719 67(2)	0.947 54(3)	0.830 54(1)	1.49(4)	2.18
O5	4a	0.074 81(3)	0.948 08(4)	0.398 18(2)	1.71(4)	2.09
O6	4a	0.894 50(2)	0.868 21(3)	0.628 05(4)	1.82(4)	2.04
O7	4a	0.866 88(1)	0.268 88(2)	0.466 47(1)	1.39(1)	1.95
O8	4a	0.195 70(1)	0.448 80(2)	0.620 33(3)	1.47(3)	2.07
O9	4a	0.083 01(1)	0.683 46(2)	0.708 38(4)	1.65(2)	1.82
O10	4a	0.910 51(2)	0.253 75(3)	0.764 05(2)	2.01(4)	2.14
O11	4a	0.975 09(3)	0.715 51(4)	0.480 85(1)	1.44(3)	1.80
B1	4a	0.126 18(2)	0.018 97(1)	0.514 57(3)	1.97(4)	3.09
B2	4a	0.785 26(3)	0.784 55(3)	0.856 23(2)	1.85(4)	3.06
B3	4a	0.284 87(2)	0.293 30(1)	0.633 72(1)	1.79(4)	3.09
B4	4a	0.017 66(1)	0.809 41(2)	0.610 93(3)	1.54(4)	2.93
B5	4a	0.971 20(3)	0.181 01(2)	0.873 63(1)	1.61(5)	2.95
B6	4a	0.663 46(2)	0.018 55(4)	0.715 38(3)	1.83(5)	2.85

^aValues of BVS are calculated using Eq. (2).

and 113.10(2) to 129.61(4)°. Values of Na–O, B–O, and Zn–O distances as well as O–B–O angles are listed in Table IV.

The Zn atom is coordinated with four O atoms to form a distorted tetrahedron, as illustrated in Figure 5(a). The ZnO₄ tetrahedron is linked to four different [B₆O₁₁]⁴⁻ groups. Zn–O distances vary from 1.852(2) Å to 2.589(3) Å and O–Zn–O angles between 63.73° and 124.14° suggesting that the tetrahedron is highly distorted.

The coordination surroundings of the Na1 and Na2 atoms are shown in Figures 5(b) and 5(c). Each Na1 is strongly bonded to five O atoms with distances of 2.447(0) to 2.549(0) Å and also weakly bonded to three other O at distances of 2.647(3) to 2.990(5) Å. Taking all these eight bonds into account, the bond valence sum is equal to 0.98 which is close to the normal bond valence of Na. However, if the O atoms with a longer distance from Na1 are not considered, the BVSs for Na1, O3, and O11 will have a larger deviation from the normal values. Each Na2 is surrounded by seven O

atoms forming an irregular polyhedron. The Na–O distances are 2.447(0) to 2.990(5) Å (average 2.609 Å) for Na1 and 2.258(5) to 2.567(4) Å (average 2.464 Å) for Na2 (Table IV).

As for the 11 unique O atoms, four are three-coordinated, bonded to two B atoms, one Na atom for O4, O5, and O8 or two B atoms, one Zn atom for O6; seven are

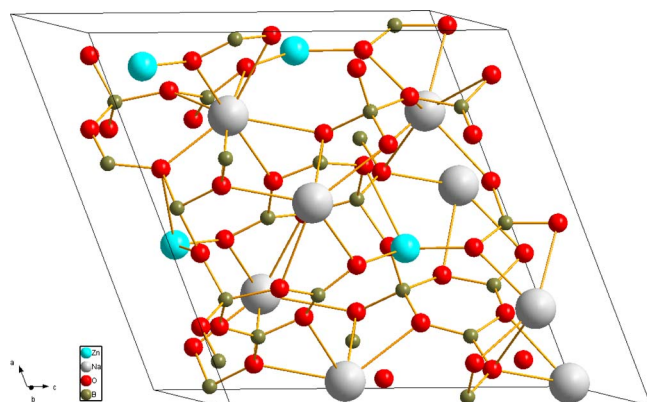
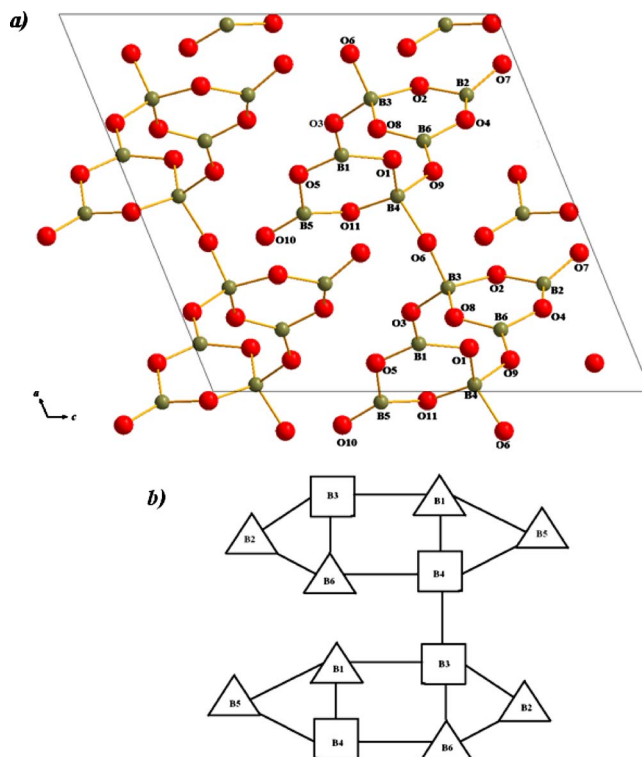
Figure 3. (Color online) Structure perspective of Na₂ZnB₆O₁₁.Figure 4. (Color online) (a) Projection of the [B₆O₁₁]⁴⁻ onto the *ac* plane. (b) Topology of [B₆O₁₁]⁴⁻.

TABLE IV. Selected bond lengths (\AA) and angles ($^\circ$) for $\text{Na}_2\text{ZnB}_6\text{O}_{11}$. (The v_{ij} is the bond valence of a bond between atoms i and j ; the r_{ij} is the corresponding bond distance between the two atoms.)

Atom i - j	r_{ij} (\AA)	v_{ij}	Atom i - j	r_{ij}	v_{ij}
Na1-O9 ^b	2.447(0)	0.175	B2-O7 ^b	1.300(4)	1.210
Na1-O8 ^a	2.516(2)	0.146	B2-O4 ^a	1.373(0)	0.947
Na1-O7 ^a	2.518(5)	0.145	B2-O2 ^a	1.408(0)	0.905
Na1-O2 ^b	2.518(2)	0.145	Mean	1.36	
Na1-O4 ^d	2.549(0)	0.133	B3-O8 ^a	1.406(5)	0.911
Na1-O3 ^a	2.647(3)	0.102	B3-O6 ^c	1.423(1)	0.869
Na1-O11 ^a	2.686(3)	0.092	B3-O2 ^c	1.493(0)	0.719
Na1-O10 ^b	2.990(5)	0.04	B3-O3 ^a	1.547(1)	0.596
Mean	2.609		Mean	1.47	
Na2-O1 ^b	2.258(5)	0.292	B4-O9 ^a	1.472(3)	0.760
Na2-O2 ^d	2.380(5)	0.210	B4-O1 ^a	1.474(1)	0.757
Na2-O10 ^d	2.388(0)	0.206	B4-O11 ^a	1.485(4)	0.736
Na2-O9 ^b	2.536(2)	0.138	B4-O6 ^a	1.514(2)	0.680
Na2-O11 ^c	2.550(4)	0.133	Mean	1.48	
Na2-O3 ^a	2.567(0)	0.127	B5-O10 ^a	1.296(4)	1.223
Na2-O5 ^a	2.567(4)	0.126	B5-O5 ^b	1.413(4)	0.894
Mean	2.464		B5-O11 ^b	1.438(2)	0.835
Zn-O10 ^a	1.852(2)	0.670	Mean	1.38	
Zn-O7 ^a	1.939(40)	0.530	B6-O4 ^a	1.337(3)	1.095
Zn-O6 ^a	1.970(2)	0.487	B6-O8 ^c	1.365(1)	1.016
Zn-O1 ^a	2.589(3)	0.100	B6-O9 ^c	1.481(0)	0.743
Mean	2.088		Mean	1.38	
B1-O3 ^a	1.330(1)	1.117			
B1-O5 ^a	1.346(2)	1.070			
B1-O1 ^a	1.407(3)	0.908			
Mean	1.36				
O3-B1-O5	114.06(2)		O9-B4-O1	104.26(3)	
O3-B1-O1	115.98(1)		O9-B4-O11	111.09(4)	
O5-B1-O1	129.61(4)		O9-B4-O6	102.37(2)	
Mean	119.88		O1-B4-O11	117.45(4)	
O7-B2-O4	125.44(0)		O1-B4-O6	111.11(3)	
O7-B2-O2	113.10(2)		O11-B4-O6	109.42(4)	
O4-B2-O2	117.03(2)		Mean	109.28	
Mean	118.52		O10-B5-O5	123.03(0)	
O8-B3-O6	101.20(4)		O10-B5-O11	116.83(1)	
O8-B3-O2	114.03(3)		O5-B5-O11	115.07(3)	
O8-B3-O3	112.52(5)		Mean	118.31	
O6-B3-O2	108.94(1)		O4-B6-O8	119.07(4)	
O6-B3-O3	111.19(3)		O4-B6-O9	114.51(3)	
O2-B3-O2	108.76(3)		O8-B6-O9	125.98(1)	
Mean	109.44		Mean	119.85	

^a x, y, z .

^b $x, -y, 1/2+z$.

^c $x+1/2, y+1/2, z$.

^d $x+1/2, -y+1/2, z+1/2$.

four-coordinated, bonded to two B atoms, two Na atoms for O2, O3, O9, O11 or one B atom, one Zn atom, two Na atoms for O7, O10, O11.

The bond valence sum V_i is useful for checking the reliability of a determined crystal structure. The bond valence and the bond valence sum are defined as follows (Brown and Altermatt, 1985; O'Keeffe and Brese, 1991):

$$v_{ij} = \exp[(r_0 - r_{ij})/0.37], \quad (1)$$

$$V_i = \sum_j v_{ij} = \sum_j \exp[(r_0 - r_{ij})/0.37]. \quad (2)$$

The v_{ij} is the bond valence of a bond between atoms i and j ;

the r_{ij} is the corresponding bond distance between the two atoms. The bond valence parameter, r_0 , for Na–O, Zn–O, and B–O ion pairs are 1.803, 1.704, and 1.731, respectively (Brown and Altermatt, 1985). The bond valence v_{ij} between cations and oxygen is listed in Table IV and their sums (BVS) listed in Table III. It shows that the BVS of Na⁺, Zn²⁺, and B³⁺ cations are close to their chemical valences. The BVS for individual O atoms vary from 1.80 to 2.14, which is close to its chemical valence.

Up to now, only hydrate hexaborates were reported in the literature such as $\text{Ca}_2\text{B}_6\text{O}_{11} \cdot x\text{H}_2\text{O}$ (Clark and Christ, 1957) which crystallizes in the triclinic and $\text{Mg}_2\text{B}_6\text{O}_{11} \cdot x\text{H}_2\text{O}$ (Rumanova and Ashirov, 1963) which crystallizes in the tri-

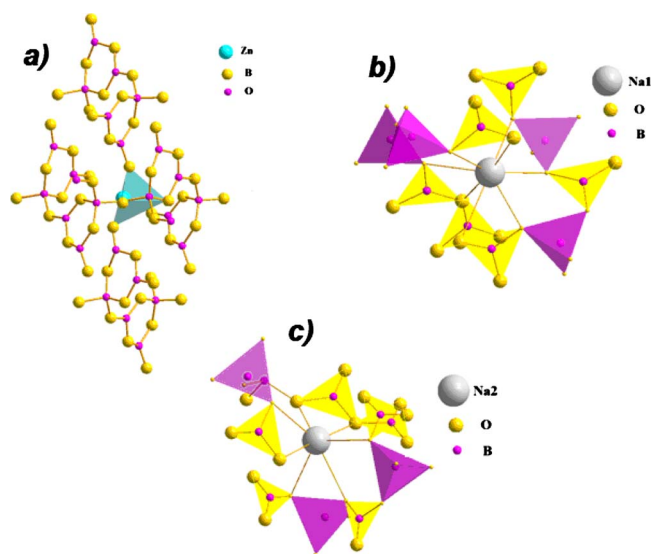


Figure 5. (Color online) (a) Coordination environments of Zn in $\text{Na}_2\text{ZnB}_6\text{O}_{11}$. The tetrahedrons are ZnO_4 . (b) Coordination environments of Na1 in $\text{Na}_2\text{ZnB}_6\text{O}_{11}$. The tetrahedrons are BO_4 and triangles are $[\text{BO}_3]^{3-}$ groups. (c) Coordination environments of Na2 in $\text{Na}_2\text{ZnB}_6\text{O}_{11}$. The tetrahedrons are BO_4 and triangles are $[\text{BO}_3]^{3-}$ groups.

clinic and monoclinic. Since there is no reported in the literature for the dehydrated hexaborate, $\text{Na}_2\text{ZnB}_6\text{O}_{11}$ is a new compound with a new structure type.

IV. CONCLUSIONS

A novel hexaborate with the composition $\text{Na}_2\text{ZnB}_6\text{O}_{11}$ has been synthesized by solid-state reaction and its crystal structure was successfully determined from powder XRD data. It crystallizes in the monoclinic space group Cc . The final residual factors converged to $R_p=12.26\%$, $R_{WP}=15.02\%$, and $R_{\text{exp}}=5.75\%$. The refined lattice parameters are $a=10.7329(2)$ Å, $b=7.4080(3)$ Å, $c=11.4822(2)$ Å, and $\beta=112.16(2)^\circ$. Double-bridge-ring $[\text{B}_6\text{O}_{11}]^{4-}$ groups

were found as fundamental building units, which are linked by a ZnO_4 tetrahedron. The structure model is reasonable based on the BVS analysis.

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