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Synthesis and crystal structure of a novel pentaborate, $Na_3ZnB_5O_{10}$

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Abstract

A novel ternary borate, trisodium zinc pentaborate, $Na_3ZnB_5O_{10}$, has been prepared by solid-state reaction at temperature below 750 °C. The single-crystal X-ray structural analysis showed that $Na_3ZnB_5O_{10}$ crystallizes in the monoclinic space group $P2_1/n$ with $a = 6.6725(7)$ Å, $b = 18.1730(10)$ Å, $c = 7.8656(9)$ Å, $\beta = 114.604(6)°$, $Z = 4$. It represents a new structure type in which double ring $[B_5O_{10}]^{5-}$ building units are bridged by ZnO_4 tetrahedra through common O atoms to form a two-dimensional $^2_\infty[ZnB_5O_{10}]^{3-}$-layer that affords one-dimensional channels running parallel to the [101] direction. *Symmetry-center* related $^2_\infty[ZnB_5O_{10}]^{3-}$ layers are stacked along the b-axis, with the interlayer void spaces and intralayer open channels filled by Na^+ cations to balance charge. The IR spectrum further confirms the presence of both BO_3 and BO_4 groups and UV–vis diffuse reflectance spectrum shows a band gap of about 3.2 eV.
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Keywords: $Na_3ZnB_5O_{10}$; Borate; Synthesis; Crystal structure

1. Introduction

Borates have attracted considerable interest because they have important practical applications in second harmonic generation (SHG). For example, β-BaB_2O_4, LiB_3O_5, and $YCa_4(BO_3)_3O$ are all well-known nonlinear optical (NLO) crystals [1]. Zinc-containing borates have been previously studied due to their potential value as catalysis and optical materials [2,3]. In the ternary systems of A_2O–ZnO–B_2O_3 (A = alkali-metal atoms), only four compounds have been structurally characterized including $AZn_4(BO_3)_3$ (A = K, Rb, Cs) [4] and $LiZnBO_3$ [5,6]. Among them, $AZn_4(BO_3)_3$ (A = K, Rb, Cs) are isomorphous series of compounds characterized by a three-dimensional (3D) framework built up from corner-sharing ZnO_4 tetratahedra and BO_3 triangles. The framework affords rectangular channels that are occupied by alkali metal atoms. $LiZnBO_3$ was reported to exist in two forms: the triclinic phase in the space group $P\bar{1}$ [5] and the monoclinic phase in the group $C2/c$ [6]. The crystal structure of the triclinic $LiZnBO_3$ polymorph is also composed of tetrahedral ZnO_4 and triangular BO_3 groups that are arranged into a 3D network by sharing O vertices.

However, this framework is different from those observed in $AZn_4(BO_3)_3$. In addition, Li and Zn atoms are disordered over the available tetrahedral sites. The monoclinic modification of $LiZnBO_3$ contains a 3D framework of vertex-sharing ZnO_5 trigonal bipyramids and BO_3 triangles, which isolates Li^+ ions in channels. Insofar as we know, no sodium zinc borates have been reported in the literature, even in powder form.

In an attempt to synthesize *non*-centrosymmetric compounds that are potentially applicable as NLO materials, we have obtained a new phase, $Na_3ZnB_5O_{10}$, which is the first ternary borate to be discovered in the Na_2O–ZnO–B_2O_3 system and crystallizes in a new unique structure type never observed for any of the known borates. Herein we report its synthesis and crystal structure.

2. Experimental

2.1. Sample preparation and general characterization

The title compound was synthesized by employing a conventional solid-state reaction method. All reagents were of analytical grade. A powder mixture of 2.160 g Na_2CO_3, 3.320 g ZnO, 2.520 g H_3BO_3, 7.772 g $Na_2B_4O_7 \cdot 10H_2O$ (the

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$Na_2CO_3/ZnO/H_3BO_3/Na_2B_4O_7$ molar ratio = 1:2:2:1) was transferred to a Pt crucible. The sample was gradually heated to $750\,°C$, where it was kept for 1 day, then cooled down to $730\,°C$ at a rate of $1\,°C/h$, and further to $720\,°C$ at $0.5\,°C/h$, followed by cooling to room temperature at a rate of $20\,°C/h$. The colorless, prismatic crystals of $Na_3ZnB_5O_{10}$ with dimensions of up to $0.3 \times 0.4 \times 1.2\,mm^3$ were embedded in a borate matrix. Several small crystals could be isolated mechanically from the reaction product for the further characterization by single-crystal X-ray diffraction measurements. Subsequently, direct reaction of a stoichiometric mixture of Na_2CO_3, ZnO, and H_3BO_3 at $600\,°C$ for 2 weeks with an intermediate grinding yielded a single-phase polycrystalline sample of $Na_3ZnB_5O_{10}$ that was confirmed by powder X-ray diffraction analysis using the monochromatized CuKα radiation of a Bruker D8 ADVANCE diffractometer. The compound appears to be relatively stable in air and water, but soluble in hot diluted HNO_3 solution.

2.2. Structure determination

Single-crystal X-ray intensity data were collected at room temperature (290 K) on an automated Rigaku AFC7R four-circle diffractometer using monochromatized MoKα radiation. Cell dimensions were obtained from a least-square refinement with 25 automatically centered reflections in the range $38.02° \leqslant 2\theta \leqslant 44.34°$. Three standard reflections were re-measured after every 150 reflections. No decay was observed except the statistic fluctuation in a range of $\pm 1.27\%$. The raw intensity data were corrected for Lorentz and polarization effects, and for absorption by empirical method based on ψ-scan data.

The crystal structure was solved by a direct method and refined in SHELX-97 system [7] by full-matrix least-squares methods on F_o^2. After introduction of anisotropic displacement parameters for all atoms the refinement of 173 parameters with 2149 observed reflections [$I \geqslant 2\sigma(I)$] resulted in the residuals of $R1/wR2 = 0.0363/0.0978$. The final difference electron density maps were featureless, with the highest electron density of $0.919\,e\text{Å}^{-3}$ at a position that is very close to the heavy atomic site (Zn). Details of crystal parameters, data collection and structure refinements are given in Table 1 and the atomic coordinates and the equivalent isotropic displacement parameters are summarized in Table 2. Listings of the anisotropic displacement parameters and the structure factors are available from the authors.

3. Results and discussion

$Na_3ZnB_5O_{10}$ represents a new structure type (Pearson symbol *mP76*) and the basic structural unit is a double ring $[B_5O_{10}]^{5-}$ consisting of one BO_4 tetrahedron ($\square$) and four BO_3 triangles (Δ) (Fig. 1), which can be written as $4\Delta 1\square$: $\langle 2\Delta\square\rangle$-$\langle 2\Delta\square\rangle$ according to the definition given by Burns et al. [8]. In this unit, two hexagonal rings are almost

Table 1
Crystallographic data for $Na_3ZnB_5O_{10}$

Formula	$Na_3ZnB_5O_{10}$
Formula weight	348.39
Space group	$P2_1/n$ (No.14)
a (Å)	6.6725(7)
b (Å)	18.1730(10)
c (Å)	7.8656(9)
β	114.604(6)°
V (Å^3), Z	867.18(14), 4
d_{calc} (g/cm^3)	2.668
λMoKα (Å)	0.71073
μ (mm^{-1})	3.029
$2\theta_{max}$	59.96°
Unique reflection	2520
Observed [$I \geqslant 2\sigma(I)$]	2149
No. of variables	173
GOF on F_o^2	1.087
$R1/wR2$ [$I \geqslant 2\sigma(I)$]	0.0363/0.0978
$R1/wR2$ (all data)	0.0461/0.1032

Table 2
Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for $Na_3ZnB_5O_{10}$

Atoms	X	Y	Z	U_{eq}	BVS
Na1	0.2832(2)	0.07978(7)	0.6144(2)	0.0253(3)	0.96
Na2	0.6261(2)	0.24295(7)	0.41948(16)	0.0214(3)	1.09
Na3	0.3004(2)	0.43014(7)	0.66044(18)	0.0226(3)	0.96
Zn	0.34460(5)	0.096489(17)	0.19384(4)	0.01438(12)	1.96
B1	0.1351(5)	0.20291(17)	0.3319(4)	0.0147(5)	3.00
B2	0.0517(5)	0.30331(17)	0.4984(4)	0.0165(6)	3.02
B3	0.2110(5)	0.33445(16)	0.2720(4)	0.0147(5)	3.07
B4	0.2048(5)	0.42834(17)	0.0336(4)	0.0145(5)	2.99
B5	0.5188(5)	0.42328(17)	0.3387(4)	0.0157(5)	3.02
O1	0.1452(3)	0.13048(11)	0.3054(3)	0.0155(4)	1.99
O2	0.2082(3)	0.25475(11)	0.2435(3)	0.0167(4)	2.10
O3	0.0541(4)	0.22789(12)	0.4597(3)	0.0252(5)	1.91
O4	0.0831(4)	0.35384(11)	0.3801(3)	0.0201(4)	2.01
O5	0.0146(4)	0.32363(12)	0.6439(3)	0.0228(5)	2.02
O6	0.1129(3)	0.36994(11)	0.0883(3)	0.0159(4)	2.08
O7	0.4398(4)	0.35865(11)	0.3764(3)	0.0204(4)	1.98
O8	0.4109(4)	0.45496(12)	0.1596(3)	0.0208(4)	1.96
O9	0.1066(3)	0.45917(11)	−0.1351(3)	0.0177(4)	1.99
O10	0.7020(4)	0.45532(12)	0.4588(3)	0.0220(4)	1.93

Note: U_{eq} is defined as one third of the trace of the orthogonalized **U** tensor.

perpendicular to each other, the angle between the planes defined by B1, O2, B3, O4, B2, O3 and by B3, O6, B4, O8, B5, O7 being $81.83(8)°$. The four terminal O atoms lie close to the corresponding hexagonal ring planes, with the maximum deviation of $0.389(4)\,\text{Å}$ at O5 and $0.243(4)\,\text{Å}$ at O10, respectively.

Each $[B_5O_{10}]^{5-}$ group is linked to four different ZnO_4 tetrahedra through its terminal O atoms and likewise each ZnO_4 tetrahedron shares its four vertices with four neighboring $[B_5O_{10}]^{5-}$ groups to form a two-dimensional (2D) infinite $_\infty^2[ZnB_5O_{10}]^{3-}$ layer extending in the (010) plane (Fig. 2). The zinc borate anionic layer is severely
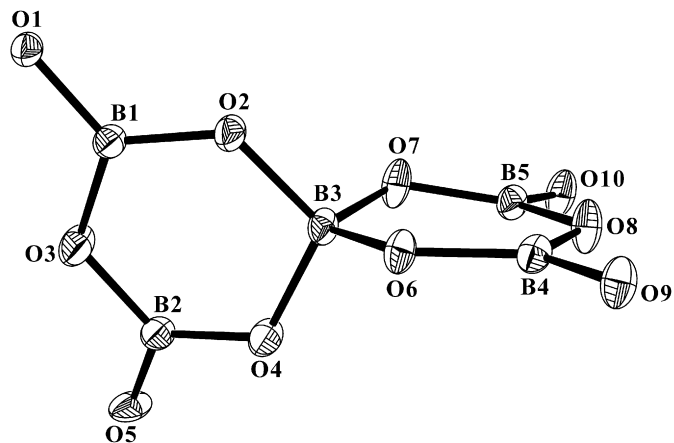
Fig. 1. An ORTEP representation of the $[B_5O_{10}]^{5-}$ structural building unit to show the atomic labeling scheme. Displacement ellipsoids are drawn at the 50% probability level.
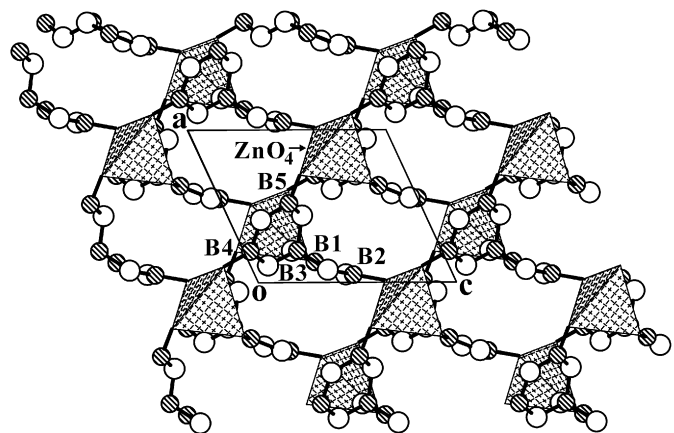

Fig. 2. The single $^2_\infty[ZnB_5O_{10}]^{3-}$ layer parallel to the (010) plane. B atoms: circles with parallel lines; O atoms: open circles; ZnO_4 groups: tetrahedra filled by crosses.
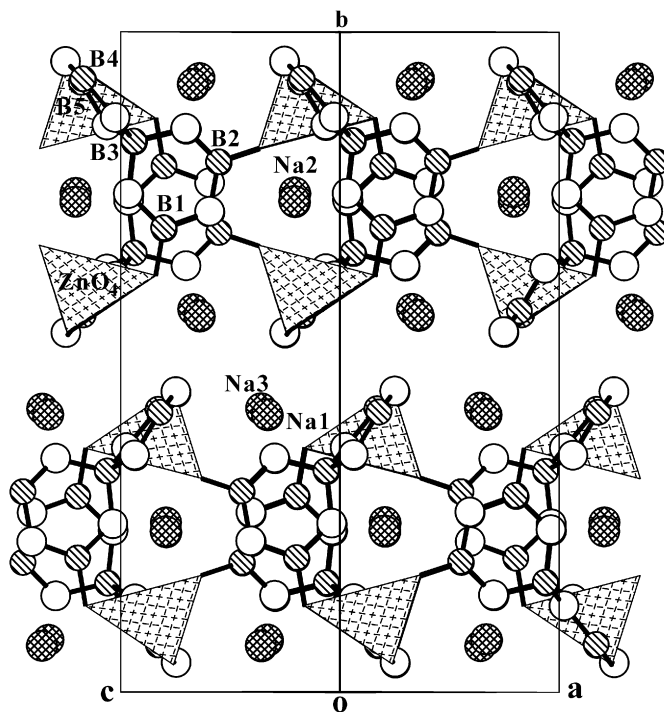

Fig. 3. The crystal structure of $Na_3ZnB_5O_{10}$ projected along the [101] direction. Na atoms: circles with grid lines; B atoms: circles with parallel lines; O atoms: open circles; ZnO_4 groups: tetrahedra filled by crosses.
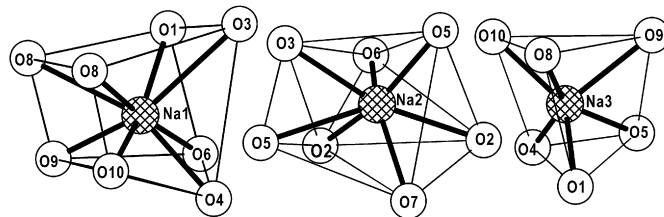

Fig. 4. The local coordination geometries of Na atoms in $Na_3ZnB_5O_{10}$.

puckered, with ZnO_4 tetrahedra appearing on both sides of each $^2_\infty[ZnB_5O_{10}]^{3-}$ sheet due to the presence of n-glide planes perpendicular to the b-axis direction. Applying the *inversion* operations at the cell origin and center to the layer at $y = 1/4$ produces adjacent equivalent layers along the [010] direction. $Na1^+$ and $Na3^+$ cations are located between these layers to balance charge and also to hold the layers together through coordination with oxygen atoms (Fig. 3). The $^2_\infty[ZnB_5O_{10}]^{3-}$ layer also affords one-dimensional (1D) open channels running parallel to the [101] direction where $Na2^+$ cations reside.

Each Na1 is strongly bonded to five O atoms at distances of 2.296(2)–2.727(3) Å and also weakly bonded to three more oxygens at distances of 3.024(3)–3.084(3) Å. Taking all these eight bonds into account, the concept of bond valence [9] allows us to calculate a valence sum equal to 0.96 for Na1 which proves that the long bonds indeed participate in the metal coordination scheme. The eight-fold coordination around Na1 can be described as a highly distorted square prism. Each Na2 is surrounded by seven O

atoms forming an irregular polyhedron, and Na3 coordinated to six O atoms giving rise to a distorted trigonal prismatic arrangement, as depicted in Fig. 4. The Na–O distances of 2.296(2)–3.084(3) Å (average 2.695 Å) for Na1, 2.318(2)–2.859(3) Å (average 2.531 Å) for Na2, and 2.280(2)–2.794(2) Å (average 2.521 Å) for Na3 (Table 3) are very reasonable when compared with the ranges 2.254(3)–2.925(4) Å (average 2.561 Å, CN = 8) in $Na_2B_8O_{13}$ [10], 2.332(4)–2.795(4) Å (average 2.486 Å, CN = 6) in $Na_4Li_5(BO_3)_3$ [11], and 2.409(3)–2.606(3) Å (average 2.505 Å, CN = 7) in $NaLi_2BO_3$ [12]. Bond valence sum (BVS) calculations also gave reasonable values of 1.09 and 0.96 for Na2 and Na3 atoms, respectively (see Table 2).

In this structure, the zinc atom occupies one crystallographically distinct site, adopting typical tetrahedral oxygen coordination geometry. Zn–O distances vary from 1.935(2) to 1.982(2) Å and O–Zn–O angles cover the range between 95.31(10) and 115.16(8)°, which are closely comparable to those found in $BaZn_2(BO_3)_2$, $Ba_2Zn(BO_3)_2$,

Table 3
Selected bond lengths (Å) and angles (°) for $Na_3ZnB_5O_{10}$

Na1–O9	2.296(2)	Zn–O10	1.935(2)
Na1–O1	2.396(2)	Zn–O1	1.9733(19)
Na1–O6	2.468(3)	Zn–O5	1.980(2)
Na1–O4	2.519(3)	Zn–O9	1.982(2)
Na1–O8	2.727(3)	Mean	1.968
Na1–O8	3.024(3)	B1–O1	1.339(4)
Na1–O10	3.044(3)	B1–O2	1.375(3)
Na1–O3	3.084(3)	B1–O3	1.400(4)
Mean	2.695	Mean	1.371
Na2–O5	2.318(2)	B2–O5	1.320(4)
Na2–O2	2.374(2)	B2–O4	1.384(4)
Na2–O7	2.394(3)	B2–O3	1.405(4)
Na2–O2	2.465(2)	Mean	1.370
Na2–O2	2.554(3)	B3–O2	1.465(3)
Na2–O3	2.753(3)	B3–O6	1.465(3)
Na2–O5	2.859(3)	B3–O7	1.468(4)
Mean	2.531	B3–O4	1.477(4)
Na3–O10	2.280(2)	Mean	1.469
Na3–O1	2.371(2)	B4–O9	1.334(3)
Na3–O4	2.495(3)	B4–O6	1.381(4)
Na3–O9	2.503(3)	B4–O8	1.404(4)
Na3–O5	2.682(3)	Mean	1.373
Na3–O8	2.794(2)	B5–O10	1.328(4)
Mean	2.521	B5–O7	1.370(4)
		B5–O8	1.411(3)
		Mean	1.370
O5–Zn–O9	95.31(10)	O2–B3–O6	108.2(2)
O10–Zn–O1	115.00(9)	O2–B3–O7	109.0(2)
O10–Zn–O5	105.18(10)	O6–B3–O7	110.7(2)
O1–Zn–O5	114.01(9)	O2–B3–O4	110.5(2)
O10–Zn–O9	110.12(9)	O6–B3–O4	109.6(2)
O1–Zn–O9	115.16(8)	O7–B3–O4	108.8(2)
Mean	109.13	Mean	109.47
O1–B1–O2	122.9(3)	O9–B4–O6	122.3(3)
O1–B1–O3	119.3(3)	O9–B4–O8	119.3(2)
O2–B1–O3	117.7(2)	O6–B4–O8	118.4(2)
Mean	119.97	Mean	120.0
O5–B2–O4	122.2(3)	O10–B5–O7	123.0(3)
O5–B2–O3	118.9(3)	O10–B5–O8	117.9(3)
O4–B2–O3	118.9(2)	O7–B5–O8	118.9(3)
Mean	120.0	Mean	119.93

and $Pb_2Zn(BO_3)_2$, all featuring tetrahedrally coordinated Zn^{2+} [3,13,14]. A BVS of 1.96 can be computed for the Zn atom, in good agreement with its expected formal valence.

There are five crystallographically independent B atoms in the asymmetric unit, of which B3 is in tetrahedral coordination and the other B atoms in triangular coordination (Fig. 1). The B–O bond lengths in the tetrahedra range from 1.465(3) to 1.477(4) Å, and the O–B–O angles from 108.2(2)° to 110.7(2)°; in the triangles the respective ranges are 1.320(4)–1.411(3) Å and 117.7(2)–123.0(3)° (Table 3). These geometric parameters compare well with those observed in $Na_3CaB_5O_{10}$ containing similar $[B_5O_{10}]^{5-}$ units [15]. BVS values for B atoms are also reasonable, lying in the range 2.99–3.07. Average Zn–O and B–O distances as well as O–Zn–O and O–B–O angles are listed in Table 3. It is clear that ZnO_4 tetrahedra are slightly distorted, while BO_4 tetrahedra and BO_3

triangles are relatively regular, judged from the deviations of interatomic angles from the ideal tetrahedral or triangular values (109.5° and 120°, respectively).

Of the ten unique oxygen atoms, three are three-coordinate, binding to 2B and 1Na (for O3 and O7) or 1B, 1Zn, and 1Na (for O10) centers in a trigonal pyramidal manner, as indicated by interatomic angles (79.8(2)–138.9(1)°); six are four-coordinate, being bonded to 2B and 2Na (for O2, O4, O6, and O8) or 1B, 1Zn, and 2Na (for O1 and O9) centers to constitute distorted O-centered tetrahedra [the tetrahedral angles are in the range 76.43(7)–151.8(2)°]; the remaining one (O5) is five-coordinate, being centered in a trigonal bipyramidal geometry with three Na atoms in equatorial positions and one Zn and one B atom in the axial positions. Despite the fact that each O5 is surrounded by more nearest-neighbours, a bond valence analysis produced a BVS value of 2.02, very close to those for the other O atoms (1.93–2.10).

Note that a hydroxylated version of $[B_5O_{10}]^{5-}$ anion ($[B_5O_6(OH)_4]^-$) is very common, as found (in an isolated form or as the basic structural unit) in many natural minerals or synthetic hydrated borates, e.g., $K[B_5O_6(OH)_4] \cdot 2H_2O$ [16], larderellite $NH_4[B_5O_7(OH)_2] \cdot H_2O$ [17], ammonioborite $(NH_4)_3[B_{15}O_{20}(OH)_8] \cdot 4H_2O$ [18], and $(NH_4)_2[B_{10}O_{14}(OH)_4] \cdot H_2O$ [19] etc. The anhydrous $[B_5O_{10}]^{5-}$ groups have also been observed in a number of polyborates such as $Na_3CaB_5O_{10}$ [15], MB_5O_8 (M = K, Rb, Cs, Tl) [20–22], $Ag_2CsB_{15}O_{24}$ [23], and $Li_2AlB_5O_{10}$ [24]. Among them, $Na_3CaB_5O_{10}$ is closely related to the title compound in stoichiometry but differs in the structure. The former crystallizes in the triclinic space group $P\bar{1}$ [15] and the crystal structure consists of discrete $[B_5O_{10}]^{5-}$ anions separated by six-coordinate Ca^{2+} as well as five- and six-coordinate Na^+ cations. It is the variation in the coordination environments as well as chemical bond nature around metal cations that is mainly responsible for the structural difference between $Na_3ZnB_5O_{10}$ and its calcium analog. All the MB_5O_8 compounds (M = K, Rb, Cs, Tl, $Ag_{2/3}$ $Cs_{1/3}$) [20–23] contain $[B_5O_{10}]^{5-}$ building units which are interconnected through sharing the four terminal O atoms resulting in a 2D infinite corrugated $^2_\infty[B_5O_8]^-$ layer in α-CsB_5O_8 and 3D $^3_\infty[B_5O_8]^-$ networks in the others. Their structures differ in the mutual arrangement of the pentaborate groups. $Li_2AlB_5O_{10}$ is known to have a 3D network composed of $[B_5O_{10}]^{5-}$ groups linked by AlO_4 tetrahedra [24]. The title compound, to the best of our knowledge, is the first 2D compound consisting of $[B_5O_{10}]^{5-}$ groups bridged by MO_4 tetrahedra (M = tetrahedrally co-ordinated cations).

Several other polyborates such as $Bi_3B_5O_{12}$ [25], $NaCaB_5O_9$ [26], $KSrB_5O_9$ [27], and $Cs_2M_2B_{10}O_{17}$ (M = Na, K) [28], also contain pentaborate groups as the fundamental building blocks. However, these pentaborate groups $(3\Delta 2\square : \langle \Delta 2\square \rangle - \langle 2\Delta \square \rangle)$ are double ring $[B_5O_{11}]^{7-}$ units, each consisting of two BO_4 tetrahedra and three BO_3 triangles. An isolated $[B_5O_{11}]^{7-}$ group contains six bridging and five terminal O atoms, as found in $Bi_3B_5O_{12}$ [25]. The condensation of $[B_5O_{11}]^{7-}$ groups

through sharing four or five terminal O atoms will result in the layered $NaCaB_5O_9$ and $KSrB_5O_9$ or $Cs_2M_2B_{10}O_{17}$ (M = Na, K) structures [26–28]. Moreover, several rare-earth layered materials including $LaCoB_5O_{10}$, $La_2CaB_{10}O_{19}$, and analogs [29,30] have the third type of the pentaborate group $(2\Delta3\square:<\Delta2\square>-<\Delta2\square>)$, $[B_5O_{12}]^{9-}$, as the basic structural unit, which is a double ring unit formed by three BO_4 tetrahedra and two BO_3 triangles with shared O atoms. As an isolated unit, the $[B_5O_{12}]^{9-}$ group contains six terminal O atoms, but four of them in the $LaCoB_5O_{10}$ and five of them in the $La_2CaB_{10}O_{19}$ structure, respectively, are shared with like units.

The cadmium atoms are known to form distorted CdO_4 tetrahedra in CdB_4O_7 [31] and CdO_6 octahedra in both $Cd_3(BO_3)_2$ and $Cd_2B_2O_5$ [32,33]. The coordination configuration is similar to that observed for Zn and Ca in $Na_3ZnB_5O_{10}$ and $Na_3CaB_5O_{10}$, respectively. Our attempts to prepare the corresponding Cd analog, "$Na_3CdB_5O_{10}$" with a similar synthesis procedure have so far been unsuccessful. The reaction always resulted in the formation of $Cd_2B_2O_5$ [33] with cell dimensions of about $a = 9.929(4)$ Å, $b = 6.349(3)$ Å, $c = 3.442(2)$ Å, $\alpha = 91.95(5)°$, $\beta = 90.77(5)°$, $\gamma = 105.48(3)°$, $V = 208.9(2)$ Å^3. In the ternary $Na_2O–ZnO–B_2O_3$ system, two hypothetical compounds, "$NaZnBO_3$" and "$NaZnB_5O_9$", have also been tried by us via solid state reactions of stoichiometric mixtures of Na_2CO_3, ZnO, and H_3BO_3 powders. The samples were slowly heated in stages up to $600\,°C$ with several intermediate re-mixings and the resultant products were identified by powder X-ray diffraction analysis. For the composition of "$NaZnBO_3$", no new phase except for $NaBO_2$ [34] along with the unreacted ZnO has been obtained. In the case of "$NaZnB_5O_9$", only a mixture of $Zn_4O(BO_2)_6$, $Na_2B_8O_{13}$, and $Na_2B_6O_{10}$ [35–37] was formed.

The infrared spectrum of $Na_3ZnB_5O_{10}$ was recorded on a Perkin Elmer 1730 FT-IR spectrometer from KBr pellets. As can be seen from Fig. 5, the strong bands in the range $1201–1441\,cm^{-1}$ arise from BO_3 antisymmetric stretching vibrations and those near 939 and $1027\,cm^{-1}$ are mainly attributed to BO_4 antisymmetric stretch. The bands associated with BO_3 and BO_4 bending modes are overlaped and located below $777\,cm^{-1}$. The IR spectrum confirms the existence of both trigonally and tetrahedrally coordinated boron atoms, consistent with the results obtained from the single-crystal X-ray structural analysis.

The optical properties of $Na_3ZnB_5O_{10}$ were examined by analyzing its diffuse reflectance data measured with a Shimadzu UV-3101PC double-beam, double-monochromator spectrophotometer. It is clear from Fig. 6 that the compound is basically transparent to approximately $3.1\,eV$. A steep absorption edge was observed, confirming the semiconducting nature as predicted by the electron precise nature of the chemical formula. The optical band gap obtained by extrapolation of a linear portion of the band edge is roughly $3.2\,eV$. Plots of absorbance^2 vs. energy and absorbance$^{1/2}$ vs. energy at the absorption edge both show nearly linear dependence with R values of 0.958
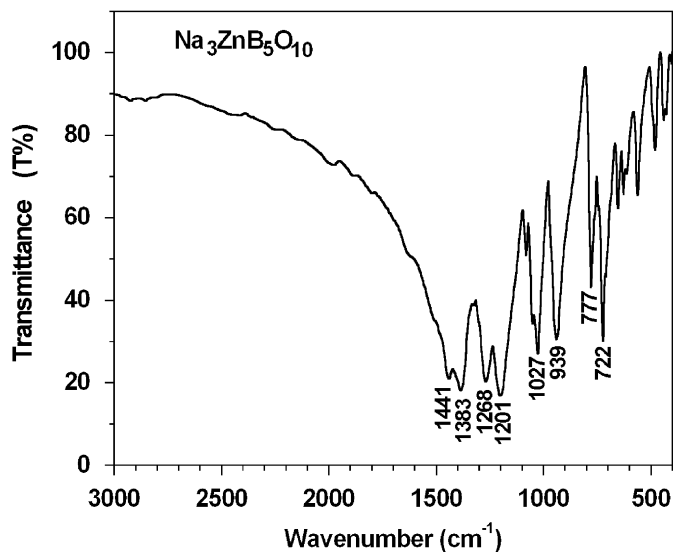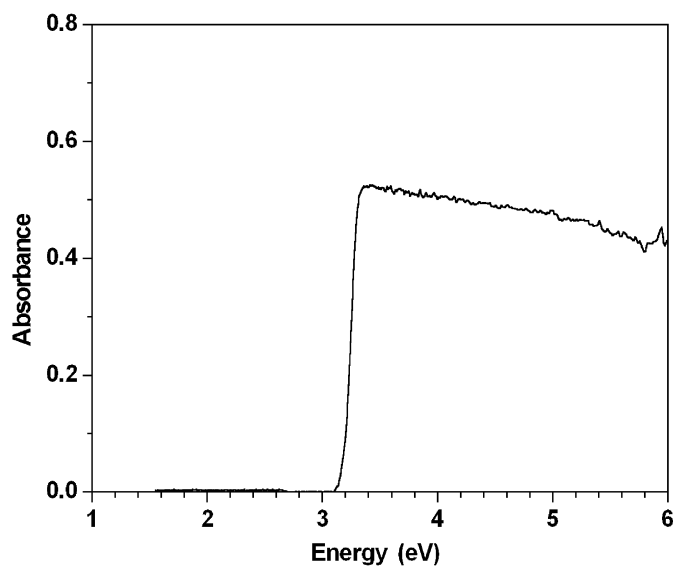

Fig. 5. Infrared spectrum of $Na_3ZnB_5O_{10}$.

Fig. 6. Optical absorption spectrum of $Na_3ZnB_5O_{10}$.

and 0.995, respectively. Therefore, it is unclear whether the band gap is direct or indirect in character.

4. Conclusions

A new sodium zinc pentaborate with the composition $Na_3ZnB_5O_{10}$ has been synthesized and the crystal structure has been studied. It has an original layered structure consisting of $[B_5O_{10}]^{5-}$ groups bridged by ZnO_4 tetrahedra. This structure differs from that of $Na_3CaB_5O_{10}$ due to the difference in the coordination environments as well as chemical bond nature around metal cations. Although cadmium and zinc belong to the same group elements in the Periodic Table, the isostructural Cd analog, "$Na_3CdB_5O_{10}$" could not be synthesized and a more stable binary

phase $Cd_2B_2O_5$ formed instead. Attempts to prepare two hypothetical compounds, "NaZnBO$_3$" and "NaZnB$_5$O$_9$", have also been unsuccessful. The reactions resulted in the formation of $NaBO_2$ together with the unreacted ZnO for the former and a mixture of $Zn_4O(BO_2)_6$, $Na_2B_8O_{13}$, and $Na_2B_6O_{10}$ for the latter.

Auxiliary Material: Further details of the crystal structure investigation may be obtained from the Fachinformationzentrum Karlsruhe, D-76344 Eggenstein- Leopoldshafen, Germany (Fax: +49 7247 808 666; E-mail: crysdata@fiz-karlsruhe.de) on quoting depository numbers CSD417848.

Acknowledgments

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