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Solid-State Structures

Stable Oxoborate with Edge-Sharing BO_4 Tetrahedra Synthesized under Ambient Pressure**

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Analysis of an atom's coordination and the linkage of polyhedra is of vital importance for understanding crystal structures,[1] especially considering our general inability to forecast structure types for new systems of elements.[2] As a general rule, the presence of shared edges or faces of polyhedra in a coordinated structure is common for large cations, but scarcely seen for high-valence low coordinated small cations. This conclusion is the main thrust of the Pauling's third and fourth rules[3,4] and is especially strict for compounds such as borates,[5,6] silicates,[7] and phosphates.[8] Until now, edge-sharing of those cation–oxygen (cation = B, Si, P) polyhedra was considered impossible except under extreme conditions.[9]

Unlike silicon and carbon, boron has the ability to bind to either three or four oxygen atoms to form a BO_3 triangle or a BO_4 tetrahedron. Polymerization of those B−O blocks can give omnifarious types of anion groups (the BO_3 and BO_4 groups can occur isolated or linked in the form of rings, chains, layers, or networks) and endow over 1000 borate compounds with amazing structural diversity from triclinic symmetry to cubic symmetry.[10,11] On the basis of the borate structures discovered, Ross and Edwards in 1967 postulated that B−O groups can only link to each other through common corners, not by edge-sharing or face-sharing.[12] This hypothesis reduced the number of possible fundamental building blocks (FBB, the repeat B−O block of the structure) greatly, making it possible for subsequent researchers to develop concise theories and clearer nomenclature for the unique borate structural chemistry.[13–17] The hypothesis is valid except under extreme conditions. In 2002, Huppertz and van der Eltz[18] claimed first violation of this hypothesis as they synthesized $Dy_4B_6O_{15}$ under high pressure (HP) (8 GPa, 1000 K). Since then, several more edge-sharing HP borates have been synthesized under high-pressure/high-temperature conditions; thus, the appearance of edge-sharing BO_4 is a significant phenomenon for distinguished HP borates.[18–20] Herein, we present a novel borate $KZnB_3O_6$ synthesized under ambient pressure which is built from edge-sharing BO_4 tetrahedra and is stable up to its melting point. Our work demonstrates that high pressure is not an indispensable prerequisite for the formation of edge-sharing BO_4 polyhedra, and that the original hypothesis should be reexamined.

$KZnB_3O_6$ was synthesized through solid-state reaction in air with K_2CO_3, H_3BO_3, and ZnO powders as the starting materials. The compound thus obtained is air- and water-stable. The crystal structure was solved and refined on the basis of single-crystal data,[21] which confirms the title compound to be the first ambient pressure borate with the edge-sharing BO_4 tetrahedra. Figure 1 shows the structure, in which the metal–borate framework is built up from corner-sharing B_6O_{12} and Zn_2O_6 blocks, and weakly bonded K ions are

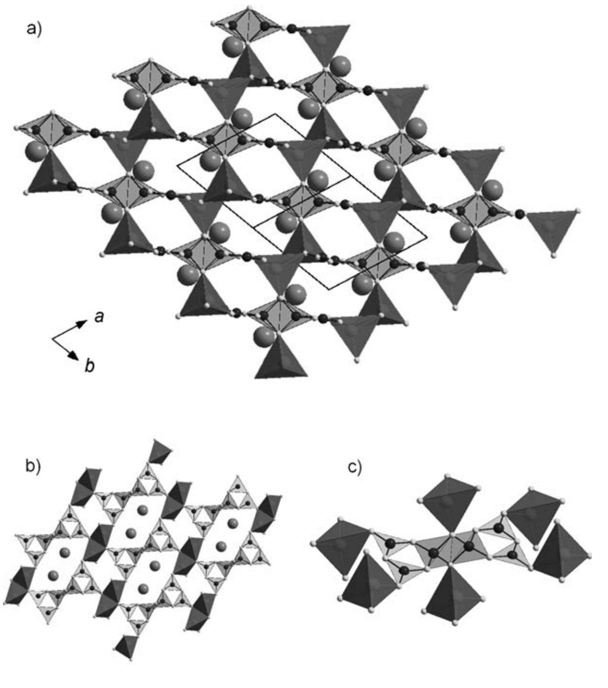

Figure 1. a) Polyhedral view of the $KZnB_3O_6$ crystal structure projected along the [01$\bar{1}$] direction. ZnO_4 tetrahedra shown in dark gray and triangular BO_3 and tetrahedral BO_4 units in light gray (BO_3 triangle is nearly perpendicular). The metaborate network also affords two types of tunnels along this direction, with the bigger one filled with K ions (light color spheres). b) Connection details of B_6O_{12} and Zn_2O_6 blocks in the ($\bar{1}$11) plane. Two more connections can be found perpendicular to the plane. c) B_6O_{12} and its coordination environment.

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interspersed. Examination of the network revealed that each B_6O_{12} and Zn_2O_6 block is sixfold coordinated to each other, so in view of the building blocks, the metaborate network is a NaCl analogue except that the lattice is titled. Meanwhile, the network also afford two types of tunnels running along the $[1\bar{1}0]$ direction; the larger one is filled with K cations and the smaller one is virtually vacant. The single crystallographically independent K ion is coordinated by nine oxygen atoms in a very asymmetric way; they filled the bigger channel in a zigzag fashion, in a similar way to Na ions filling the channels of $Na_2Co_2B_{12}O_{21}$.[11]

In detail, the B_6O_{12} block consists of two BO_4 tetrahedra and four BO_3 triangles. The BO_4 tetrahedra are edge shared to each other and further corner-shared by BO_3 triangles in their outer vertex. The appearance of BO_3 triangles distinguished the current structure from those edge-sharing structures obtained under high pressure. Using the descriptor proposed by Huppertz,[22] this FBB could be described as 4△2□: <2△⧄> = <⧄2△>.[14]

Although the synthesis conditions and coordination environment of the B–O groups are very different for previously reported HP borates and the title compound, the geometry of those edge-sharing tetrahedral is highly consistent (Figure 2). As a common feature, the like-charges repulsion will push higher valence ions apart in the edge-sharing polyhedra to minimize the electrostatic potential, thus the O-B-O angle within the B_2O_2 ring is remarkably reduced and the B–O bond within the ring elongated. In comparison with the slight fluctuation of B–O bond length shown in Figure 2, the major narrowing of the O-B-O angle within the planar B_2O_2 ring (∢in) is the factor most responsible for the significant expansion of the B···B interatomic distances—the values of ∢in for those edge-sharing compounds is reduced into the range of 92.0(2)–94.4(4)° (from the ideal value of 109.4°). Two edge-sharing B–O bonds (d_{BO1} and d_{BO2}) slightly exceed the typical B–O bond length, while the two B–O bonds outside the ring (d_{BO3} and d_{BO4}) are typically shorter. It seems that the B···B interatomic distance of 2.040(17)–2.098(13) Å is essential to compromise between the electrostatic potential and the edge-sharing geometry. The O-B-O bond angles of two bonds outside the B_2O_2 ring ∢out vary between 109.5(7) and 114.3(4)°. It is clear the geometry of edge-sharing B–O tetrahedra is well defined, either because of the covalent bonding character or because the deliberate balance of B–O edge sharing cannot tolerate further variation. Meanwhile, Zn–O bonds are in the range 1.887(3)–2.048(3) Å and show a slightly wider distribution relative to similar compounds such as $KZn_4(BO_3)_3$ (1.901(3)–1.985(3) Å).[23] Bond-valence sum (BVS) calculation confirms that all the atoms in the compound adopted normal valance states (see Table S1 in the Supporting Information).[24]

Figure 3 gives the deformation charge density (DCD) map of this compound obtained by DFT calculations.[25] From the DCD map we found bonding details of the compound that

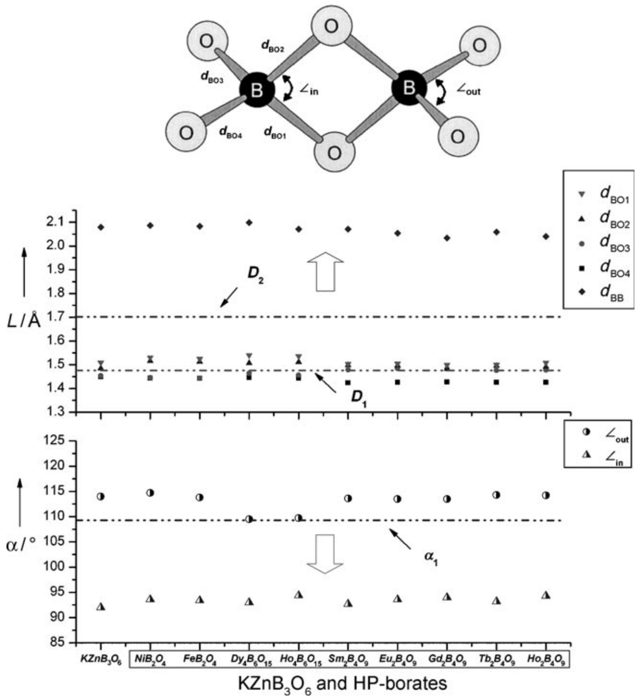

Figure 2. Graph of the bond lengths, interatomic distances, and bond angles inside the edge-sharing tetrahedra of $KZnB_3O_6$ and currently available edge-sharing HP borates (d_{BO1} and d_{BO2} represent the B–O bond lengths inside the B_2O_2 ring, d_{BO3} and d_{BO4} are the bond lengths of two B–O bonds outside the B_2O_2 ring, d_{BB} is the shortest B···B interatomic distances, ∢in and ∢out are O-B-O angles within and opposite the B_2O_2 ring, respectively. α_1 and D_1 represent ideal bond angle and statically averaged bond length of a BO_4 tetrahedra, D_2 is the ideal B···B interatomic distances of two undeformed edge-sharing BO_4 tetrahedra).

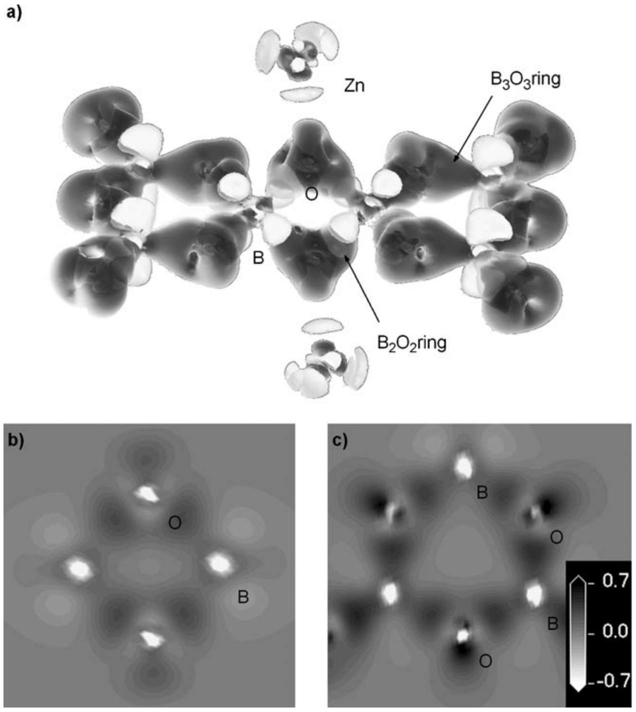

Figure 3. a) Isosurface plot of deformation electron density (DED) for B_6O_{12} blocks and Zn atoms at a level of 0.1 e Å^{-3} (negative values shown in light gray and positive value in dark gray). b) Bonding details of the B_2O_2 ring by DED slice across the square plane. c) DED slice across the mean plane B_3O_3 ring (legend for DED maps in e Å^{-3}).

features in strong covalent B–O bonds (significant DCD value in the bonding zone), invisible ionic K–O bonds, and the partial covalent Zn–O bonds. The B-O-B bonds within B_2O_2 and B_3O_3 rings look similar: both of them comprise two covalence σ bonds between B–O atoms; the B_3O_3 ring has an remarkable electron segregation in the antibonding region, which is characteristic of p atomic orbital in forming the bond, whereas for the B_2O_2 ring antibonding segregation is replaced by one extra bond with the Zn atom (partial covalence) in the same position. The bond strength of the B_2O_2 ring is significantly weaker than that of the B_3O_3 ring (Figure 3b,c), indicating latent instability in the edge-sharing region. DCD map slices (see Figure S1 in the Supporting Information) evidenced considerable electrons transference from nearby Zn atoms to the B_2O_2 ring, and an obvious polarization effect was observed from K cations to the B_2O_2 ring.

In contrast to those HP metastable edge-sharing borates, the title compound is the only stable edge-sharing borate that can survive up to its melting point in ambient pressure. The thermal behavior of the compound was examined with a combined differential scanning calorimetry/thermogravimetric analysis (DSC/TGA) thermobalance. No obvious endo- or exothermic peak was observed until the melting point of the compound was reached near 800 °C (as shown in Figure 4a), indicating that congruent melting. Furthermore, low-temperature in situ powder diffraction data (Figure 4b) show that the crystal structure is well preserved from room temperature down to 30 K; only unit cell shrinkage was detected during the process (see Table S2 in the Supporting Information).

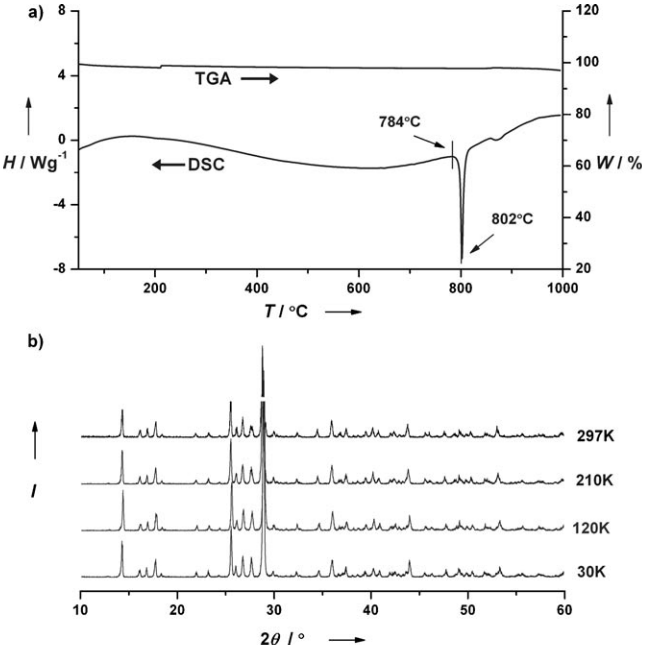

Figure 4. a) DSC/TGA curves of $KZnB_3O_6$, indicating that the crystal melts congruently near 800 °C. b) Low-temperature in situ powder diffraction pattern of the title compound at 30 K, 120 K, 210 K, and 297 K.

In the HP borate cases, Huppertz and co-workers presumably attributed two ranges as the Raman-active modes of the edge-sharing BO_4 tetrahedra,[20] but only one of them weakly shows up in the current case, which could be due to lower symmetry of the title compound. Raman and IR spectra for the title compound (Figure S2 in the Supporting Information) confirm well that both the BO_3 and BO_4 polyhedra are present in the title compound.

Element substitution experiments in the form $X'Y'B_3O_6$ (X' = Li, Na, K, Rb, Cs and Y' = Zn, Cd, respectively) were performed to test the tolerance of this unique structure, but no isostructure was found. The only identified compound is $KCdB_3O_6$ with a corner-sharing structure (FBB = $3\triangle$: $<3\triangle>$, SG = $C2/c$).[26] Through the geometry optimization and total energy calculation for the two available structures, we found that it is energetically more favorable for the title compound to retain its novelty rather than take the common corner-sharing $KCdB_3O_6$ structure (see Table S3 in the Supporting Information). Although replacing the B_6O_{12} with two B_3O_6 triangles seems to be beneficial to ease the instability caused by edge-sharing, it also makes the Zn structure poorly coordinated (see Figure S3b), thus leading to an unstable structure. The lack of strong corner-sharing competitors could be the key factor that allows this edge-sharing compound to prevail.

Interestingly, the indispensable K cations within the tunnels are mobile and partially exchangeable while preserving the original crystal morphology. Ion exchange was facilitated by heating the compound in a large excess of molten $NaNO_3$ and $LiNO_3$ for a few days (corresponding results are presented in Figure S4). Elemental analysis of K ion and (Li, Na) ions reveals that more than half of the K ions is exchangeable with Li ions without ruining the borate network. Excess ion exchange will result in the appearance of $Li_2B_4O_7$ and some unknown phase in the diffraction pattern. However, Na ion is barely exchangeable in this way, so it is probable that the smaller vacant channel mentioned above functioned as a diffusion path way for small Li ions.

The existence of BO_3 and BO_4 and their exclusive corner-sharing linkage form the foundation of the traditional borate structural chemistry. However, the compound described herein demonstrates that compounds with edge-sharing BO_4 polyhedra can be obtained and be very stable even at ambient pressure. High pressure is not an indispensable condition to synthesis such compounds. After that, the fundamental linkage rule governing over 1000 borates is challenged to the core. So now is a good time to consider incorporating the edge-sharing configuration into our traditional borate chemistry, after all, borate structure is proved to be more flexible than we expected.[29]

Experimental Section

The title material was prepared by grinding a stoichiometric mixture of K_2CO_3 (A.R.), ZnO (A.R.), and H_3BO_3 (99.99 %) to a fine powder, and then heating at 500 °C for 12 h to decompose the salt. The sample was reground and annealed at 750 °C for 24 h, and a single-phase white powder was readily obtained. The sample purity was verified by X-ray powder diffraction. Transparent colorless single crystals were obtained by spontaneous nucleation by melting the obtained pure phase powder at 820 °C, then slowly cooling the melt to 600 °C at a rate of 1 °C h^{-1}.

Deformation charge density calculations were performed by using the GGA (PEB) functional method implemented with the DMol3 package.[25] All-electron calculations with scalar relativistic core corrections were used together with the numerical DND basis set to ensure the calculation accuracy. The total energy calculation was performed using the CASTEP (Cambridge Serial Total energy Package) computer code using the GGA (PEB) functional method.[27] All the calculations performed herein were to ultrafine accuracy. The total energy of the title compound was obtained after fully relaxing the experimental structure (through geometry optimization implemented within the code). The suppositional lattice type was initiated from the experimentally derived structure of $KCdB_3O_6$ by replacing Cd to Zn atoms and then relaxed with the cell unfixed. The geometry optimization performed thenceforth was quite time-consuming but converged well with the total energy being larger than that of the title compound after normalization.

The DSC/TGA experiment was performed on a SDT Q600 (V20.9 Build 20) instrument. The sample was put into an alumina crucible and was heated in air at 10 °C min^{-1} from room temperature to a final temperature of 1000 °C.

Temperature-dependent in situ X-ray diffractometry was performed on a Mac Science M18AHF powder diffractometer ($Cu_{K\alpha1}$; 1.54056 Å) equipped with a PID-controlled low-temperature accessory. The room-temperature diffraction pattern was firstly obtained as a standard, and then the sample was cooled to 30 K and slowly heated up. Each diffraction pattern was obtained 10 min after the required temperature was reached. Unit-cell information was calculated by using the pattern indexing software Dicvol04.[28]

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[1] U. Müller, *Inorganic Structural Chemistry*, 2nd ed., Wiley, **2006**, pp. 2–10.

[2] K. Sanderson, *Nature* **2007**, *450*, 771–771.

[3] L. Pauling, *J. Am. Chem. Soc.* **1929**, *51*, 1010–1026.

[4] J. K. Burdett, T. J. McLarnan, *Am. Mineral.* **1984**, *69*, 601–621.

[5] G. Heller, *Top. Curr. Chem.* **1986**, *131*, 42–98.

[6] S. K. Filatov, R. S. Bubnova, *Phys. Chem. Glasses* **2000**, *41*, 216–224.

[7] W. K. Li, G. D. Zhou, T. Mak, *Advanced Structural Inorganic Chemistry*, Oxford University Press, New York **2008**, pp. 543–544.

[8] M. T. Averbuch, P. A. Durif, *Topics in Phosphate Chemistry*, World Scientific, London, **1996**, pp. 11–18.

[9] H. Huppertz, W. Schnick, *Chem. Eur. J.* **1997**, *3*, 249–252.

[10] a) W. H. Zachariasen, *Z. Kristallogr. Kristallgeom. Kristallphys. Kristallchem.* **1931**, *76*, 289; b) W. H. Zachariasen, G. E. Ziegler, *Z. Kristallogr. Kristallgeom. Kristallphys. Kristallchem.* **1932**, *83*, 354; c) W. H. Zachariasen, *Z. Kristallogr. Kristallgeom. Kristallphys. Kristallchem.* **1937**, *98*, 266.

[11] a) J. P. Attfield, A. M. T. Bell, L. M. Rodriguez-Martinez, J. M. Greneche, R. J. Cernik, J. F. Clarke, D. A. Perkins, *Nature* **1998**, *396*, 655–658; b) J. L. C. Rowsell, N. J. Taylor, L. F. Nazar, *J. Am. Chem. Soc.* **2002**, *124*, 6522–6523; c) J. Ju, J. Lin, G. Li, T. Yang, H. Li, F. Liao, C. K. Loong, L. You, *Angew. Chem.* **2003**, *115*, 5765–5768; *Angew. Chem. Int. Ed.* **2003**, *42*, 5607–5610; d) L. Wu, X. L. Chen, Y. P. Xu, Y. P. Sun, *Inorg. Chem.* **2006**, *45*, 3042–3047.

[12] a) J. O. Edwards, V. F. Ross, *J. Inorg. Nucl. Chem.* **1960**, *15*, 329–337; b) C. L. Christ, *Am. Mineral.* **1960**, *45*, 334–340; c) C. Tennyson, *Fortschr. Mineral.* **1963**, *41*, 64–91; d) V. F. Ross, J. O. Edwards, *The Structural Chemistry of the Borates in The Chemistry of Boron and its Compounds* (Eds.: E. L. Muetterties), Wiley, New York, **1967**; e) G. Heller, *Fortschr. Chem. Forsch.* **1970**, *15*, 206–280.

[13] C. L. Christ, J. R. Clark, *Phys. Chem. Miner.* **1977**, *2*, 59–87.

[14] a) P. C. Burns, J. D. Grice, F. C. Hawthorne, *Can. Mineral.* **1995**, *33*, 1131–1151; b) J. D. Grice, P. C. Burns, F. C. Hawthorne, *Can. Mineral.* **1999**, *37*, 731–762.

[15] P. Becker, *Z. Kristallogr.* **2001**, *216*, 523–533.

[16] M. Touboul, N. Penin, G. Nowogrocki, *Solid State Sci.* **2003**, *5*, 1327–1342.

[17] G. H. Yuan, D. F. Xue, *Acta Crystallogr. Sect. B* **2007**, *63*, 353–362.

[18] H. Huppertz, B. von der Eltz, *J. Am. Chem. Soc.* **2002**, *124*, 9376–9377.

[19] a) H. Emme, H. Huppertz, *Z. Anorg. Allg. Chem.* **2002**, *628*, 2165; b) H. Huppertz, *Z. Naturforsch. B* **2003**, *58*, 278; c) H. Emme, H. Huppertz, *Chem. Eur. J.* **2003**, *9*, 3623; d) H. Huppertz, H. Emme, *J. Phys. Condens. Matter* **2004**, *16*, S 1283; e) H. Emme, H. Huppertz, *Acta Crystallogr. Sect. C* **2005**, *61*, i 29; f) S. C. Neumair, R. Glaum, H. Huppertz, *Z. Naturforsch. B* **2009**, *64*, 883.

[20] J. S. Knyrim, F. Roessner, S. Jakob, D. Johrendt, I. Kinski, R. Glaum, H. Huppertz, *Angew. Chem.* **2007**, *119*, 9256–9259; *Angew. Chem. Int. Ed.* **2007**, *46*, 9097–9100.

[21] Crystal structure analysis of $KZnB_3O_6$: MW = 232.90 g mol^{-1}, colorless block, $0.8 \times 0.2 \times 0.05$ mm^3, triclinic, space group: $P\bar{1}$, $a = 6.753(6)$, $b = 6.911(6)$, $c = 7.045(7)$ Å, $\alpha = 63.39(5)$, $\beta = 72.58(4)$, $\gamma = 69.13(5)°$, $V = 270.8(5)$ $Å^3$, $Z = 2$, $\rho_{calcd} = 2.856$ g cm^{-3}, Bruker SMART APEX-CCD, Mo radiation ($\lambda = 0.71073$ Å), graphite monochromator, $F(000) = 224$, $\mu = 5.262$ mm^{-1}, $T = 298(2)$ K, multiscan, 1581 measured reflections in the range $3.27° < 2\theta < 30.49°$, 1524 unique reflections with $I > 2\sigma(I)$, numerical absorption correction (SAINT), $R_{int} = 0.0234$; the crystal structure was solved by direct methods (SHELXS-97) and anisotropically refined by a least-squares procedure against F^2 with all data, 100 refined parameters, $R_1 = 0.0227$ and $wR_2 = 0.0617$ for $F_o^2 > 2\sigma(F_o^2)$; $R_1 = 0.0234$ and $wR_2 = 0.0621$ for all F_o^2, residual electron density between -0.698 and 0.554 e$Å^{-3}$, GOF = 1.074. Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe (FIZ, 76344 Eggenstein-Leopoldshafen (Germany); tel.: (+49) 7247-808-205, fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-421311.

[22] H. Huppertz, *Z. Naturforsch. B* **2003**, *58*, 278–290.

[23] R. W. Smith, J. L. Luce, D. A. Keszler, *Inorg. Chem.* **1992**, *31*, 4679–4682.

[24] R. Hoppe, S. Voigt, H. Glaum, J. Kissel, H. P. Müller, K. J. Bernet, *J. Less-Common Met.* **1989**, *156*, 105–122.

[25] B. Delley, *J. Chem. Phys.* **2000**, *113*, 7756–7764.

[26] S. F. Jin, G. M. Cai, J. Liu, W. Y. Wang, X. L. Chen, *Acta Crystallogr. Sect. C* **2009**, *65*, i42–i44.

[27] M. D. Segall, P. J.D. Lindan, M. J. Probert, C. J. Pickard, P. J. Hasnip, S. J. Clark, M. C. Payne, *J. Phys.: Condens. Matter* **2002**, *14*, 2717–2744.

[28] A. Boultif, D. Louër, *J. Appl. Crystallogr.* **2004**, *37*, 724–731.

[29] Note added in proof (May 19, 2010): After the submission of this manuscript we learnt of a related paper on potassium zinc borate ($KZnB_3O_6$) that should be cited: Y. Wu, J.-Y. Yao, J.-X. Zhang, P.-Z. Fu, Y.-C. Wu, *Acta Crystallogr. Sect. E*, **2010**, *66*, i45.