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Some Experimental Evidence that $Zn_4O(BO_3)_2$ is $Zn_6O(OH)(BO_3)_3$

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Oxides exhibiting a disordered arrangement of oxygen vacancies are of potential interest as oxygen-ion conductors. In this respect, our attention has recently been drawn by the crystal structure of $Zn_4O(BO_3)_2$ in which one of the oxygen sites is not fully occupied, leading to an overall composition $Zn_{12}B_6O_{21}\square$ per rhombohedral unit cell.[1] However, on detailed examination of the structure data, some surprising features appear:

- The oxygen site that is only 5/6 occupied (O(2) in ref.[1]), belongs to the three-fold coordination of boron. That a BO_3 group, which can be considered as a polyanion, could exhibit an oxygen vacancy is unlikely and, to our knowledge, has never been reported to date.
- Bond valence sums calculations for the three oxygen sites show that, for O(3), this sum is anomalously low ($\Sigma O(3) = 1.49$ v.u.) compared to the expected value of 2 ($\Sigma O(1) = 1.97$ and $\Sigma O(2) = 2.00$ v.u.).[2,3] In addition, considering that O(3) is bonded to Zn only, the O(3)···O(3) distance is abnormally short (2.543(9) Å) for a distance between oxygen atoms from different ZnO_4 tetrahedra.

The first feature suggests that there is no oxygen vacancy in the structure and that, accordingly, two missing positive charges per unit cell have to be found to maintain charge balance in the formula. By taking into account both this preliminary conclusion and the second feature, the presence of a hydrogen atom between pairs of O(3) atoms becomes a reasonable assumption, because it would both induce an increase of the bond valence sum for O(3) and explain the constriction of the O(3)···O(3) distance by the straddling of a O−H···O bridge, that is, the formation of a strong hydrogen bond.

We describe herein some experiments which demonstrate that "$Zn_4O(BO_3)_2$" is in fact $Zn_6O(OH)(BO_3)_3$ (**1**) and we give a more accurate description of its structure thanks to a new determination from single-crystal X-ray diffraction data.

A slightly modified version of the hydrothermal reaction described in ref. [1] yielded small ($0.02 \leq$ max. dimension ≤ 0.06 mm), colorless, single crystals in the shape of faceted rhombohedra. The phase purity of the product was checked by comparison of the observed powder X-ray diffraction (XRD) pattern with that reported for "$Zn_4O(BO_3)_2$". The first support for our assumption was obtained by a difference thermoanalytical/thermogravimetric analysis coupled with an analysis of released gases by mass spectrometry (Setaram TG-DSC 111 system equipped with a Leybold Mass Spectrometer, heating rate 5 K min^{-1}, dry Argon stream) showing that the phase undergoes a water loss of 1.49 % in weight (the expected value for **1** is 1.50 %) at 670 °C. This temperature indicates a remarkable stability of the compound. The decomposition products were identified from the XRD pattern (at room temperature) of the sample heated at 750 °C, as ZnO and $Zn_3(BO_3)_2$, suggesting that the dehydration process occurs according to the hypothetical reaction given in Equation (1).

$$2\,Zn_6O(OH)(BO_3)_3 \rightarrow 3\,ZnO + 3\,Zn_3(BO_3)_2 + H_2O \tag{1}$$

The measured density ($\rho = 3.99(2)$ g cm^{-3}, AccuPyc 1330 system, He pressure, sample mass = 1.2605 g), is in better agreement with that calculated for **1** ($\rho = 3.98$ g cm^{-3}) than for "$Zn_4O(BO_3)_2$" ($\rho = 3.92$ g cm^{-3}).

Structural analysis of **1** by single-crystal XRD revealed the three-dimensional framework of vertex-sharing ZnO_4 tetrahedra and triangular BO_3 groups described in ref. [1] with however, and as expected, a better precision in the atomic coordinates (Table 1). This improvement leads to more regular oxygen environments for both Zn and B atoms, as can be appreciated from bond lengths given in Table 2, and to an O(3)···O(3) distance even shorter (2.456(4) Å) than that inferred from the previous study.

This strong overlapping of O(3) atoms, coming close to the critical O···O distance (2.42 Å) for which symmetric hydrogen bonds could theoretically be observed, is the signature of a very strong hydrogen bonding implying a linear or nearly linear O−H···O bridge.[4,5] Accordingly, the acid hydrogen atom (H(1)) was introduced in a statistically disordered (half-occupied) 4c site between pairs of O(3) atoms; it

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Table 1: Atomic coordinates and isotropic temperature factors for $Zn_6O(OH)(BO_3)_3$. Values from ref. [1] are given in italics for comparison.

Atom	W[a]	τ[b]	*x*	*y*	*z*	U_{eq}/U_{iso} [Å^2]
Zn(1)	12f	1.0	0.64005(5)	0.69493(5)	0.07925(5)	0.0087(3)
			0.6408(2)	*0.6925(2)*	*0.0794(2)*	*0.007(1)*
B(1)	6e	1.0	0.7276(6)	0.7724	0.25	0.008(3)
			0.728(2)	*0.772*	*0.25*	*0.005*[c]
O(1)	12f	1.0	0.5892(3)	0.8031(3)	0.2222(3)	0.0114(18)
			0.5854(8)	*0.8045(7)*	*0.2181(8)*	*0.007(2)*
O(2)	6e	1.0	0.3958(3)	0.75	0.1042	0.012(2)
		5/6	*0.396(2)*	*0.75*	*0.104*	*0.018(4)*
O(3)	4c	1.0	0.79695(12)	0.79695	0.79695	0.0097(15)
			0.7986(4)	*0.7986*	0.7986	*0.013(4)*
H(1)	4c	0.5	0.767(3)	0.767	0.767	0.02(4)[d]

[a] Wyckoff-site notation. [b] Occupancy. [c] Not refined in ref. [1]. [d] Isotropic thermal parameter; U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 2: Selected bond lengths [Å], bond valences (BV) [v.u.], and bond valence sums for $Zn_6O(OH)(BO_3)_3$.

	This work		From ref. [1]		
	Bond length [Å]	BV [v.u.]	Bond length [Å]	BV [v.u.]	
Zn(1)-O(1)	1.939(4)	0.530	1.906(5)	0.579	
Zn(1)-O(1)[a]	1.9581(17)	0.503	1.926(5)	0.549	
Zn(1)-O(2)	1.965(4)	0.494	1.962(5)	0.498	
Zn(1)-O(3)[b]	1.9632(8)	0.496	1.962(2)	0.498	
	ΣZn = 2.023		ΣZn =		2.124
B(1)-O(1)	1.374(7)	0.992	1.435	0.841	
B(1)-O(1)[c]	1.374(7)	0.992	1.435	0.841	
B(1)-O(2)[a]	1.372(4)	0.997	1.367	1.011	
	ΣB = 2.981		ΣB = 2.693		
O(3)-H(1)	0.78(5)[e]	0.63[f]			
O(3)-H(1)[d]	1.67(5)[e]	0.37[f]			
	ΣO(1) = 2.025		ΣO(1) = 1.969		
	ΣO(2) = 1.985		ΣO(2) = 2.007		
	ΣO(3) = 1.988		ΣO(3) = 1.494		
O(3)···O(3)	2.456(4)		2.543(9)		

[a] 1−z,1−x,1−y ; [b] −x,−y,−1−z; [c] 13/6−y,11/6−x,5/6−z ; [d] 3/2−z,3/2−y,3/2−x. [e] The H atom being closer to the O atom than it actually is, the bond valences marked [f] were determined from Figure 2 in ref. [3] with the use of the O(3)···O(3) distance.

was refined satisfactorily along with its isotropic thermal parameter (Table 1). However, since X-ray diffraction locates the centroid of the electron density rather than the position of the nucleus, the hydrogen atom appears to be closer to the oxygen atom than it actually is (Table 2). The O−H···O bridge straddles the small cavity centered on the 2a site and delimited by six ZnO_4 tetrahedra (Figure 1).

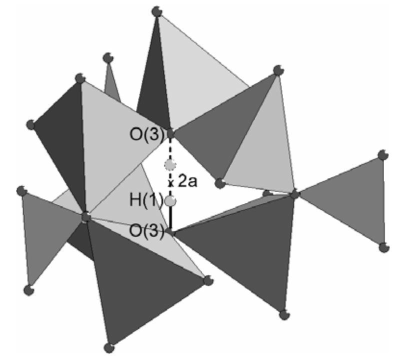

Figure 1. Perspective view of the cavity centered on the 2a site and straddled by the O−H···O bridge along the [111] axis (both statistically half-occupied H positions are represented).

The ^1H magic-angle spinning (MAS) NMR spectrum (Bruker "Avance" 500 MHz spectrometer, TMS reference, MAS rate 14 kHz, 1000 s repetition time) shows a single resonance at $\delta = 14.5$ ppm. This important downfield chemical shift is in fair agreement with the value ($\delta \approx 16$ ppm) that can be expected from the O(3)···O(3) distance.[6] It confirms that the hydrogen bond is strong.

The validity of the asymmetric versus symmetric hydrogen-bond model, arising from a statistical disorder between two positions on either side of the 2a site, was evaluated by means of density functional theory (DFT). The computation results show that the asymmetric configuration is more stable with an energy difference of 6 meV per formula unit. This low, but significant, activation energy barrier (≈ 70 K) agrees perfectly with the dynamic disorder observed at room temperature. Furthermore; the O−H (1.10 Å) and H···O (1.36 Å) optimized bond lengths fit rather well with those expected from the chemical shift.[7]

In summary, some experiments aimed at characterizing protons in solids, have shown that the so-called zincoborate "$Zn_4O(BO_3)_2$" is in fact a zinc oxyhydroxyborate. As expected, the introduction of the H atom into the structure now brings the bond-valence sum of O(3) to a more reasonable value of 1.988 and it rules out the hypothesis of oxygen vacancies in the environment of boron.

Experimental Section

Synthesis: 50-mL Teflon vessels were filled with the same amount of borax ($Na_2B_4O_7 \cdot 10H_2O$, 3.814 g), $Zn(NO_3)_2$ (6.43 g) and water (10 mL) as in the previous study,[1] and decreasing amounts of 4 M NaOH (from 3.44 g to 1.72 g) so as to decrease the starting pH value of the mixture down to ≈7. These vessels were placed in stainless steel bombs and heated as indicated previously (200 °C, 4 days). The preparation with the lowest starting pH value yielded the desired product in the form of small single crystals.

Crystal structure determination: The cell parameters (Table 3) were refined from the powder XRD pattern (INEL CPS 120 diffractometer, quartz monochromator, $Cu_{K\alpha 1}$, $\lambda = 1.540598$ Å) using the program FULLPROF in the full pattern matching mode,[8] and its interface : the program WinPLOTR.[9] The single-crystal data collection was carried out on a Bruker-Nonius Kappa CCD diffractometer (graphite monochromated MoK-$L_{2,3}$ radiation, 600 s exposure time per frame). Intensity integration and standard Lorentz-polarization correction were performed with the Bruker-Nonius Eval-CCD program package. On account of both the shape and the

Table 3: Crystallographic data for $Zn_6O(OH)(BO_3)_3$.

Empirical formula	$Zn_6O_{11}B_3H$
Formula weight	601.65
Crystal system	Rhombohedral
Space group	$R\bar{3}c$ (No. 167)
$a=b=c$ [Å]	9.9120(4)[a]
$\alpha=\beta=\gamma$ [°]	48.609(2)[a]
V [Å^3]	502.81(4)
Z	2
ρ_{calcd} [g cm^{-3}]	3.98
ρ_{meas} [g cm^{-3}]	3.99(2)
Absorption coefficient [mm^{-1}]	14.1
Crystal size [mm]	$0.04\times0.04\times0.05$
Data range	$6.56\leq\theta\leq35.06$
Reflections collected	3859
Independent reflections	737
Reflections with $I>3\sigma(I)$ (obs.)	610
Number of variables	35
$R(F)$[b]/$R_w(F)$[c] (obs. refl.)	0.0296/0.0220
$R(F)$[b]/$R_w(F)$[c] (all refl.)	0.0472/0.0229
$\Delta\rho_{max}/\Delta\rho_{min}$ [e$^-$ Å^{-3}] (all refl.)	1.50/−1.64
Extinction method	Lorentzian type I isotropic.[12]
Extinction coefficient	0.027(6)

[a] Refined from powder data. [b] $R(F)=\Sigma||F_o|-|F_c||/\Sigma|F_o|$.[c] $R_w(F)=[\Sigma w(|F_o|-|F_c|)^2/\Sigma w F_o^2]^{1/2}$ with $w=1/[\sigma^2(F_o)]$

very small size of the crystal an absorption correction was not deemed necessary. All other structure calculations were conducted with the Jana2000 program suite.[10] The structure was refined with anisotropic atomic displacement parameters for all non-H atoms. Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-415925.

Electronic band structure calculations: Calculations were carried out with the VASP package,[11] within the DFT framework and using the PBE96 exchange and correlation potential. Complete structural optimizations were performed by calculating the Hellmann–Feynman (HF) forces on the atoms and HF stresses on the unit cell. As usually observed, the optimized cell parameters ($a=10.031$ Å (+1.2%), $\alpha=48.74°$) and average distances (Zn–O$_{av}=1.985$ Å (+1.4%), B–O$_{av}=1.386$ Å (+0.9%)) are slightly overestimated.

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