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$Cd_{1.17}Zn_{0.83}B_2O_5$, a new cadmium zinc diborate

Xin Yuan,* Ru-Ji Wang, De-Zhong Shen, Xiao-Qing Wang and Guang-Qiu Shen

Department of Chemistry, Tsinghua University, Beijing 100084, People's Republic of China

Correspondence e-mail:
yuanx02@mails.tsinghua.edu.cn

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Crystals of cadmium zinc diborate, $Cd_{1.17}Zn_{0.83}B_2O_5$, have been obtained by spontaneous nucleation in a platinum crucible at 1072 K. The crystal structure exhibits diborate groups, $B_2O_5^{4-}$, sharing O atoms with considerably distorted $M1O_6$ octahedra and $M2O_4$ tetrahedra. Both metal centers are disordered in the proportion Cd:Zn = 0.92:0.08 on the $M1$ site and Cd:Zn = 0.25:0.75 on the $M2$ site. A strong second-harmonic generation has been observed for the title compound when excited with an Nd:YAG laser (λ = 1064 nm).

Key indicators

Single-crystal X-ray study
T = 296 K
Mean σ(O–B) = 0.011 Å
Disorder in main residue
R factor = 0.032
wR factor = 0.079
Data-to-parameter ratio = 13.0

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Inorganic borates continue to be an active area of research, with the aim of finding new compounds with interesting optical properties. In the CdO–ZnO–B_2O_3 pseudo-ternary system, four compounds, *viz*. $Cd_2ZnB_4O_9$ (Harrison & Hummel, 1959), $CdZn_2B_2O_6$ (Harrison & Hummel, 1959), $Cd_{0.5}Zn_{0.5}B_4O_7$ (Laureiro *et al.*, 1988) and $Cd_3Zn_3B_4O_{12}$ (Whitaker & Channell, 1993), have been reported. The crystal structure of $Cd_3Zn_3B_4O_{12}$ was determined from single-crystal X-ray data (Sun *et al.*, 2003), whereas for the others only X-ray powder data were published. In the present work, a new cadmium zinc diborate with the formula $Cd_{1.17}Zn_{0.83}B_2O_5$ has been synthesized and its structure determined from single-crystal data.

The structure of $Cd_{1.17}Zn_{0.83}B_2O_5$ represents a new structure type. It is based on a three-dimensional framework built

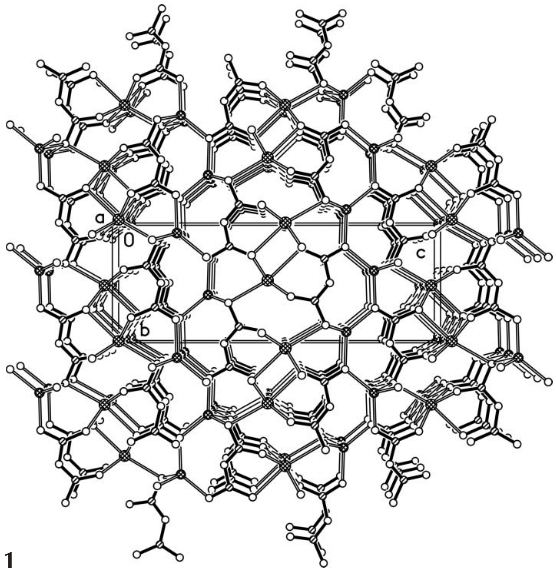

Figure 1
A view of the crystal structure along the *a* direction. Small shaded circles represent B atoms, small open circles represent O atoms, while large hatched circles represent Cd and Zn atoms on $M1$ and $M2$ sites, respectively.

of B_2O_5 units sharing O atoms with considerably distorted $M1O_6$ octahedra and $M2O_4$ tetrahedra (Fig. 1). Both metal centers are disordered in the proportion Cd:Zn = 0.92:0.08 on the octahedral *M*1 site and Cd:Zn = 0.25:0.75 on the tetrahedral *M*2 site. The $B_2O_5^{4-}$ anion is composed of two BO_3 groups, both of which are slightly distorted from the ideal triangular geometry. The bridging B–O–B angle of the diborate anion is 132.0 (6)° (Fig. 2). Each O atom, except the bridging O1 atom of the B_2O_5 group, belongs to a BO_3 group and an $M1O_6$ octahedron or an $M2O_4$ tetrahedron.

The coordination environments of the metal sites in $Cd_{1.17}Zn_{0.83}B_2O_5$ are different from those of $Cd_3Zn_3B_4O_{12}$ (Sun *et al.*, 2003). In the diborate compound, the coordination around *M*1 is considerably distorted octahedral, which is augmented by having an additional long bond with 2.695 (6) Å. Site *M*2 is surrounded by four O atoms with an average bond length of 2.049 Å. However, there are two other longer *M*2–O bonds, with distances of 2.712 (5) Å and 2.907 (6) Å, respectively. In $Cd_3Zn_3B_4O_{12}$, the metal center of the MO_4 tetrahedron is statistically occupied by Cd and Zn in the proportion 1:1. The average *M*—O bond length of 2.064 (4) Å is slightly longer than that of the $M1O_4$ group of the title compound, owing to the higher proportion of Cd at this site.

From the viewpoint of the crystal structure, both the $B_2O_5^{4-}$ groups, which are composed of nearly planar BO_3 groups, and the distorted MO_x polyhedra are favorable for superposition of microscopic second-order NLO susceptibilities. In fact, a strong second-harmonic generation (SHG) was observed for $Cd_{1.17}Zn_{0.83}B_2O_5$ single crystals when excited with Nd:YAG laser radiation (λ = 1064 nm). The powder SHG is over two times as large as that of KH_2PO_4 (KDP) crystals.

Experimental

Crystals of the title compound were grown by spontaneous nucleation in a platinum crucible using a vertical cylindrical electric furnace. Starting materials were prepared from a mixture of CdO (35.2 wt%), ZnO (22.3 wt%) and H_3BO_3 (42.5 wt%). Crystal growth was carried out at 1072 K in air. A large quantity of colorless needle-shaped crystals with size of up to 10 × 1.5 × 1 mm were obtained from the melt.

Crystal data

$Cd_{1.17}Zn_{0.83}B_2O_5$
M_r = 287.46
Orthorhombic, $P2_12_12_1$
a = 3.4147 (4) Å
b = 6.5060 (7) Å
c = 17.8263 (19) Å
V = 396.03 (8) Å^3
Z = 4
D_x = 4.686 Mg m^{-3}

Mo *Kα* radiation
Cell parameters from 3098 reflections
θ = 2.3–30.0°
μ = 11.33 mm^{-1}
T = 296 (2) K
Needle, colorless
0.22 × 0.10 × 0.10 mm

Data collection

Bruker SMART APEX CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1997)
T_{min} = 0.090, T_{max} = 0.322
2308 measured reflections

1101 independent reflections
1100 reflections with $I > 2\sigma(I)$
R_{int} = 0.028
θ_{max} = 30.0°
h = −4 → 4
k = −5 → 9
l = −23 → 24

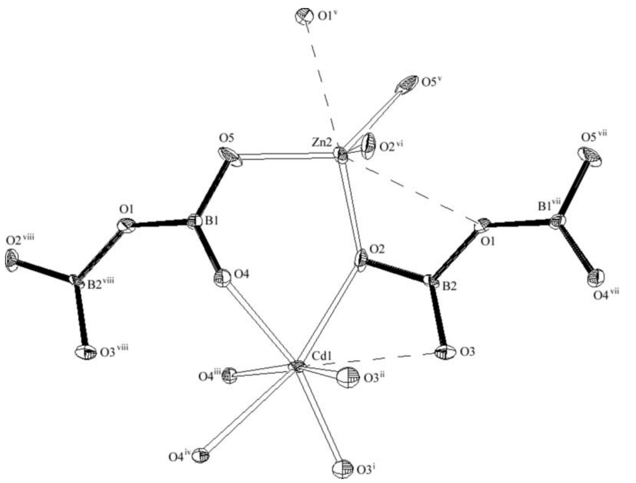

Figure 2
A view of the title compound, with 50% probability displacement ellipsoids, showing the atomic numbering scheme. [Symmetry codes: (i) $\frac{1}{2} + x, \frac{3}{2} - y, 1 - z$; (ii) $-\frac{1}{2} + x, \frac{3}{2} - y, 1 - z$; (iii) $1 + x, y, z$; (iv) $\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$; (v) $-x, \frac{1}{2} + y, \frac{1}{2} - z$; (vi) $-1 + x, y, z$; (vii) $x, 1 + y, z$; (viii) $x, -1 + y, z$.]

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.079
S = 1.04
1101 reflections
85 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0118P)^2 + 10.0237P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 2.83 e Å^{-3}
$\Delta\rho_{min}$ = −2.07 e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.040 (2)
Absolute structure: Flack (1983), 380 Friedel pairs
Flack parameter: 0.13 (5)

Table 1
Selected geometric parameters (Å, °).

$M1-O3^{i}$	2.231 (6)	$M2-O2^{vi}$	2.108 (7)
$M1-O4$	2.260 (6)	$M2-O1^{v}$	2.712 (5)
$M1-O3^{ii}$	2.283 (6)	$M2-O1^{vii}$	2.907 (6)
$M1-O4^{iii}$	2.339 (6)	$O1-B2^{viii}$	1.387 (10)
$M1-O4^{iv}$	2.428 (6)	$O1-B1$	1.396 (10)
$M1-O2$	2.432 (6)	$O2-B2$	1.389 (10)
$M1-O3$	2.695 (6)	$O3-B2$	1.346 (10)
$M2-O5$	1.997 (7)	$O4-B1$	1.365 (10)
$M2-O5^{v}$	1.997 (7)	$O5-B1$	1.360 (10)
$M2-O2$	2.092 (7)		
$O3^{i}-M1-O4$	164.5 (2)	$O5-M2-O2$	100.7 (3)
$O3^{i}-M1-O3^{ii}$	98.3 (2)	$O5^{v}-M2-O2$	111.3 (3)
$O4-M1-O3^{ii}$	81.2 (2)	$O5-M2-O2^{vi}$	99.6 (3)
$O3^{i}-M1-O4^{iii}$	80.6 (2)	$O5^{v}-M2-O2^{vi}$	104.1 (3)
$O4-M1-O4^{iii}$	95.9 (2)	$O2-M2-O2^{vi}$	108.8 (3)
$O3^{ii}-M1-O4^{iii}$	165.0 (2)	$O5-M2-O1^{v}$	77.4 (2)
$O3^{i}-M1-O4^{iv}$	81.5 (2)	$O5^{v}-M2-O1^{v}$	55.9 (2)
$O4-M1-O4^{iv}$	83.0 (2)	$O2-M2-O1^{v}$	149.4 (2)
$O3^{ii}-M1-O4^{iv}$	83.6 (2)	$O2^{vi}-M2-O1^{v}$	101.6 (2)
$O4^{iii}-M1-O4^{iv}$	81.4 (2)	$O5-M2-O1^{vii}$	152.6 (2)
$O3^{i}-M1-O2$	112.7 (2)	$O5^{v}-M2-O1^{vii}$	72.6 (2)
$O4-M1-O2$	82.5 (2)	$O2-M2-O1^{vii}$	52.82 (19)
$O3^{ii}-M1-O2$	99.9 (2)	$O2^{vi}-M2-O1^{vii}$	85.3 (2)
$O4^{iii}-M1-O2$	94.2 (2)	$O1^{v}-M2-O1^{vii}$	128.32 (19)
$O4^{iv}-M1-O2$	164.4 (2)	$B2^{viii}-O1-B1$	132.0 (6)
$O3^{i}-M1-O3$	72.00 (18)	$O5-B1-O4$	123.7 (8)
$O4-M1-O3$	121.8 (2)	$O5-B1-O1$	112.8 (7)
$O3^{ii}-M1-O3$	71.28 (19)	$O4-B1-O1$	123.4 (7)
$O4^{iii}-M1-O3$	121.8 (2)	$O3-B2-O1^{vii}$	125.1 (7)
$O4^{iv}-M1-O3$	139.81 (17)	$O3-B2-O2$	119.8 (7)
$O2-M1-O3$	54.67 (18)	$O1^{vii}-B2-O2$	115.0 (7)
$O5-M2-O5^{v}$	130.67 (18)		

Symmetry codes: (i) $x + \frac{1}{2}, -y + \frac{3}{2}, -z + 1$; (ii) $x - \frac{1}{2}, -y + \frac{3}{2}, -z + 1$; (iii) $x + 1, y, z$; (iv) $x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; (v) $-x, y + \frac{1}{2}, -z + \frac{1}{2}$; (vi) $x - 1, y, z$; (vii) $x, y + 1, z$; (viii) $x, y - 1, z$.

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The crystal of $Cd_{1.17}Zn_{0.83}B_2O_5$ proved to be a partial inversion twin. The occupancies of Cd and Zn on the two metal sites, *M*1 and *M*2, were refined in the final refinement cycles. The results showed that *M*1 is occupied by 0.924 Cd + 0.076 Zn, and *M*2 by 0.247 Cd + 0.753 Zn. These results were confirmed by ICP–AES elemental analysis of selected crystals, which gave an overall ratio of Cd:Zn = 1.45:1. The highest peak and the deepest hole in the final Fourier map are both located 0.83 Å from the *M*1 site.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *XP* in *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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References

Bruker (1997). *SHELXTL*, *SMART*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Harrison, D. E. & Hummel, F. A. (1959). *J. Electrochem. Soc.* **106**, 24–26.

Laureiro, Y., Camps, M. D., Veiga, M. L., Jerez, A. & Pico, C. (1988). *Eur. J. Solid State Inorg. Chem.* **25**, 381–386.

Sun, T., Pan, F., Wang, R., Shen, G., Wang, X. & Shen, D. (2003). *Acta Cryst.* C**59**, i107–i108.

Whitaker, A. & Channell, A. D. (1993). *J. Mater. Sci.* **28**, 2489–2493.

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