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A non-linear optical crystal, $Cd_3Zn_3(BO_3)_4$

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The title compound, tricadmium trizinc tetraborate, $Cd_3Zn_3(BO_3)_4$, is a new non-linear optical (NLO) crystal and its structure has been determined by single-crystal X-ray diffraction. This compound is composed of planar $[BO_3]^{3-}$ groups sharing O atoms with CdO_4 or ZnO_4 tetrahedra. The BO_3 triangles are located on threefold axes and are arranged with nearly the same orientation. The Cd and Zn atoms are disordered on the same site in the proportion 1:1. A strong second harmonic generation of Nd:YAG laser radiation (λ = 1064 nm) has been observed for a crystal of the title compound.

Comment

To date, many promising borate materials have been discovered and studied for harmonic generation of laser radiation to produce new laser sources in the visible and UV spectroscopic ranges, such as β-$Ba_2B_2O_4$ (BBO; Chen *et al.*, 1985), LiB_3O_5 (LBO; Chen *et al.*, 1989), $CsLiB_6O_{10}$ (CLBO; Mori *et al.*, 1995), $KBe_2BO_3F_2$ (KBBF; Mei *et al.*, 1995), $Sr_2Be_2B_2O_7$ (SBBO; Chen *et al.*, 1995) and $K_2Al_2B_2O_7$ (KAB; Hu *et al.*, 1998). Few borate non-linear optical (NLO) materials incorporating transition metal elements have been studied, except for $BaZn_2(BO_3)_2$ (Smith & Keszler, 1992), $Ba_2Zn(BO_3)_2$ (Smith & Keszler, 1994) and $RECa_4O(BO_3)_3$ (RE is Y or Gd; Iwai *et al.*, 1997). Whitaker & Channell (1993) investigated the ternary system CdO–ZnO–B_2O_3 at 1123 K and a new phase, $Cd_3Zn_3B_4O_{12}$, was postulated for the first time. Based on their study, we have grown single crystals of $Cd_3Zn_3(BO_3)_4$ (abbreviated to CZBO). To the best of our knowledge, CZBO has not previously been grown as a single crystal.

The crystal structure of trigonal CZBO is characterized by a three-dimensional framework built from corner-sharing BO_3 triangles with CdO_4 or ZnO_4 tetrahedra (Fig. 1). In this configuration, each O atom belongs to two tetrahedra and a triangle. All $[BO_3]^{3-}$ trigonal groups are almost perfectly planar and perpendicular to the *c* axis. The BO_3 triangles in the different layers are orientated in nearly the same direction and are only slightly rotated around the threefold axis. The B1—O and B2—O bond lengths are nearly equal [1.377 (3) and 1.374 (4) Å, respectively] and the O—B—O bond angles are very close to 120°.

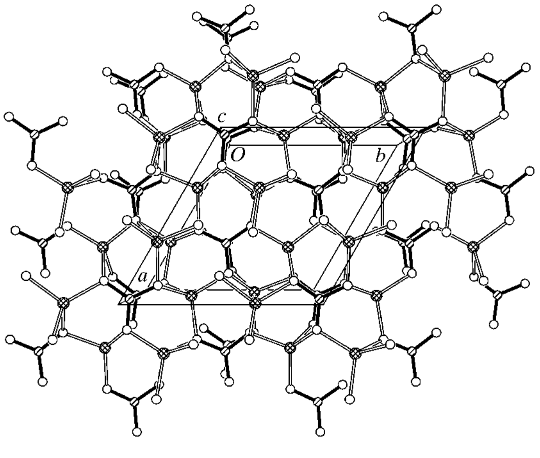

Figure 1
A view of the molecular packing in CZBO along the [001] direction. Small shaded circles represent B atoms, small open circles represent O atoms and large hatched circles depict Cd or Zn atoms.

The Cd^{2+} and Zn^{2+} cations in CZBO share the same site in the unit cell and are disordered. The occupancy of the metal position was assigned to be 0.5 Cd + 0.5 Zn, according to the result of an ICP–AES analysis. The Cd/ZnO_4 moiety is distorted from an ideal tetrahedron and the four O atoms connect to different B atoms (Fig. 2). The Cd/Zn—O distances lie between 2.014 (3) and 2.131 (4) Å, and the O—Cd/Zn—O angles are in the range 92.04 (14)–128.39 (11)°. CdB_4O_7 (Ihara & Krogh-Moe, 1966) and $Zn_3B_2O_6$ (Baur & Tillmanns, 1970) also contain $[CdO_4]^{6-}$ and $[ZnO_4]^{6-}$ groups, respectively, with similar bond lengths and angles. The average Cd/Zn—O bond length in CZBO is shorter than the average of the Cd—O bonds in $Cd_3B_2O_6$ (Laureiro *et al.*, 1991), because the ionic radius of Zn^{2+} is smaller than that of Cd^{2+}, and also because

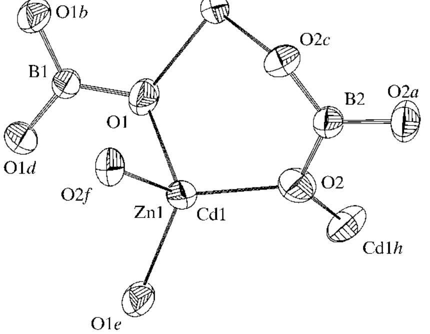

Figure 2
A view of the molecule of CZBO with 50% probability displacement ellipsoids, showing the atomic numbering scheme. Cd and Zn share the same site. [Symmetry codes: (*a*) $1 - y, 1 + x - y, z$; (*b*) $2 - y, 2 + x - y, z$; (*c*) $y - x, 1 - x, z$; (*d*) $y - x, 2 - x, z$; (*e*) $\frac{4}{3} - y, \frac{5}{3} - x, \frac{1}{6} + z$; (*f*) $\frac{1}{3} + x, \frac{5}{3} + x - y, \frac{1}{6} + z$; (*g*) $\frac{5}{3} - y, \frac{4}{3} - x, z - \frac{1}{6}$; (*h*) $x - \frac{1}{3}, \frac{4}{3} + x - y, z - \frac{1}{6}$.]

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Cd is coordinated by six O atoms in the structure of $Cd_3B_2O_6$.

Chen *et al.* (1990) classified known NLO borate crystals by their coordinated anionic groups and succeeded in predicting second-order NLO susceptibilities. According to their classification, the NLO-active clusters in CZBO should be the anionic groups, *viz.* $[BO_3]^{3-}$. It is favourable for the superposition of microscopic second-order NLO susceptibilities if the planar $[BO_3]^{3-}$ groups are arranged with the same orientation in the structure of CZBO. In addition, the presence of distorted Cd/ZnO_4 tetrahedra sharing vertices with BO_3 triangles may not only enhance the NLO effect, but also make CZBO easier to grow, because of strong bonding between the layered structural units. The structural features indicated above show that CZBO is a potential NLO crystal. In fact, a strong second harmonic generation (SHG) of Nd:YAG laser radiation (λ = 1064 nm) was observed on the as-grown single 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 43.9 wt% CdO, 27.9 wt% ZnO and 28.2 wt% H_3BO_3. Crystal growth was carried out at 1170 K in air. A clear colourless single crystal of CZBO, with a size of 3 × 1.5 × 1 mm, was obtained.

Crystal data

$Cd_3Zn_3(BO_3)_4$
$M_r = 768.64$
Trigonal, *R*3*c*
$a = 8.364\ (6)$ Å
$c = 12.286\ (10)$ Å
$V = 744.3\ (10)$ Å^3
$Z = 3$
$D_x = 5.145$ Mg m^{-3}
Mo *K*α radiation
Cell parameters from 21
reflections
$\theta = 4.8$–$14.7°$
$\mu = 13.52$ mm^{-1}
$T = 293\ (2)$ K
Block, colourless
0.12 × 0.10 × 0.10 mm

Data collection

Bruker *P*4 diffractometer
ω scans
Absorption correction: ψ scan
(North *et al.*, 1968)
$T_{min} = 0.195$, $T_{max} = 0.260$
3235 measured reflections
607 independent reflections
526 reflections with $I > 2\sigma(I)$
$R_{int} = 0.094$
$\theta_{max} = 32.5°$
$h = -12 \rightarrow 12$
$k = -12 \rightarrow 12$
$l = -18 \rightarrow 18$
3 standard reflections
every 100 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.052$
$wR(F^2) = 0.121$
$S = 1.07$
607 reflections
35 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0013P)^2 + 35.8548P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.031$
$\Delta\rho_{max} = 1.59$ e Å^{-3}
$\Delta\rho_{min} = -1.38$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.01004 (19)
Absolute structure: Flack (1983),
300 Friedel pairs
Flack parameter = −0.11 (16)

Table 1
Selected geometric parameters (Å, °).

Cd1—O2	2.014 (3)	Zn1—O1^{i}	2.016 (4)
Cd1—O1^{i}	2.016 (4)	Zn1—O2^{ii}	2.095 (4)
Cd1—O2^{ii}	2.095 (4)	Zn1—O1	2.131 (4)
Cd1—O1	2.131 (4)	B1—O1	1.377 (3)
Zn1—O2	2.014 (3)	B2—O2	1.374 (4)
O2—Cd1—O1^{i}	115.23 (12)	O2—B2—O2^{v}	119.994 (12)
O2—Cd1—O2^{ii}	128.39 (11)	O2—B2—O2^{vi}	119.994 (12)
O1^{i}—Cd1—O2^{ii}	99.95 (14)	O2^{v}—B2—O2^{vi}	119.994 (11)
O2—Cd1—O1	101.80 (15)	B1—O1—Cd1^{vii}	120.0 (2)
O1^{i}—Cd1—O1	118.55 (17)	B1—O1—Cd1	120.0 (3)
O2^{ii}—Cd1—O1	92.04 (14)	Cd1^{vii}—O1—Cd1	107.49 (14)
O1^{iii}—B1—O1	119.999 (6)	B2—O2—Cd1	115.39 (19)
O1^{iii}—B1—O1^{iv}	119.998 (8)	B2—O2—Cd1^{viii}	118.9 (3)
O1—B1—O1^{iv}	119.999 (8)	Cd1—O2—Cd1^{viii}	115.94 (18)

Symmetry codes: (i) $\frac{4}{3} - y, \frac{5}{3} - x, z + \frac{7}{6} - 1$; (ii) $\frac{1}{3} + x, \frac{5}{3} + x - y, z + \frac{7}{6} - 1$; (iii) $2 - y, 2 + x - y, z$; (iv) $-x + y, 2 - x, z$; (v) $-x + y, 1 - x, z$; (vi) $1 - y, 1 + x - y, z$; (vii) $\frac{5}{3} - y, \frac{4}{3} - x, z - \frac{1}{6}$; (viii) $x - \frac{1}{3}, \frac{4}{3} + x - y, z - \frac{1}{6}$.

The systematic absences of *hkl* with $-h + k + l = 3n$, $hh2(-h)l$ with $l = 3n$, $h(-h)0l$ with $2h + l = 3n$ and $l = 2n$ showed that the space group should be $R\bar{3}c$ or *R*3*c*. However, the NLO properties of the crystal suggested that the space group must be the non-centrosymmetric space group *R*3*c*. The metal ions, Cd^{2+} and Zn^{2+}, share the same site. According to the results of an ICP–AES analysis and occupancy refinement, the occupancy of the metal site was assigned as 0.5 Cd + 0.5 Zn in the final refinement.

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

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1661). Services for accessing these data are described at the back of the journal.

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