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The Noncentrosymmetric Orthoborate $BaZn_2(BO_3)_2$

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The new orthoborate $BaZn_2(BO_3)_2$ has been synthesized and its structure determined by single-crystal X-ray methods. It crystallizes in an orthorhombic cell with dimensions a = 9.305(3), b = 12.128(1), and c = 4.9255(8) Å; the space group is $P2_12_12_1$. The structure was determined from 876 independent reflections and refined to the final residuals R = 0.024 and R_w = 0.034. It exhibits a three-dimensional framework of vertex-sharing ZnO_4 tetrahedra and BO_3 triangles that isolates Ba atoms in channels extending along the c axis. The optical second harmonic signal generated from a 1064-nm fundamental and microcrystalline sample is approximately 10% of that observed from the frequency converter potassium dihydrogen phosphate (KDP). This result is consistent with the magnitude of the nonlinearity computed on the basis of the anionic group model. © 1992 Academic Press, Inc.

Introduction

In this report, we describe the synthesis, structure, and optical second-order nonlinear characteristics of the new material $BaZn_2(BO_3)_2$. This compound has resulted from our continuing studies of borates having the formula $XY_2(BO_3)_2$, where X and Y are different cations with +2 formal charges (*1*).

Borates containing Zn in combination with Cu have been reported to catalyze oxidative dehydrogenation of a variety of organic molecules and to be effective in the conversion of synthesis gas to alcohols (*2*). Because of their wide transparency windows, new noncentrosymmetric zinc borates could also well afford desirable nonlinear optical characteristics similar to those of the materials BaB_2O_4 (*3*) and LiB_3O_5 (*4*). In the title compound, the presence of simple orthoborate groups only and their poor alignment, however, affords a small harmonic conversion efficiency.

Experimental

Powders of $BaZn_2(BO_3)_2$ were prepared by grinding stoichiometric ratios of $Ba(NO_3)_2$ (99.999%, Johnson Matthey), $Zn(NO_3)_2 \cdot 6H_2O$ (99.999%, Johnson Matthey), and B_2O_3 (99.99%, Morton Thiokol) under hexane followed by heating in Pt crucibles at 600°C for 30 min and at 800°C for 18 hr with several intermittent grindings. Samples were single phase as determined from analysis of X-ray powder diffractograms obtained with an automated Philips diffractometer. Single crystals were grown from the melt by heating a sample to 980°C, cooling to 860°C at 1.5°C/hr, then air-quenching.

A rod-shaped crystal having dimensions 0.25 × 0.12 × 0.10 mm was physically sepa-

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TABLE I

CRYSTAL DATA AND EXPERIMENTAL CONDITIONS FOR $BaZn_2(BO_3)_2$

Diffractometer	Rigaku AFC6R
Radiation	Graphite-monochromated Mo $K\alpha$ (λ = 0.70926 Å)
Formula wt. (amu)	385.71
a (Å)	9.305(3)
b (Å)	12.128(1)
c (Å)	4.926(1)
V (Å^3)	555.9(2)
Space group	$P2_12_12_1$
D_{calc} (g cm^{-3})	4.61
$F(000)$	696
Z	4
Linear abs. coeff. (cm^{-1})	157.58
p factor	0.05
No. unique data with $F_o^2 > 3\sigma(F_o^2)$	876
R_{int}	0.033
$R(F_o)$	0.024
$R_w(F_o)$	0.034
Error in observation of unit wt. (e^2)	1.03

rated from the crucible for structure analysis. Lattice parameters were refined from 10 reflections in the range $26° < 2\theta < 31°$ that were automatically centered on a Rigaku AFC6R diffractometer equipped with Mo $K\alpha$ radiation. Intensity data covering the range of indices $0 \leq h \leq 13$, $0 \leq k \leq 17$, and $-6 \leq l \leq 6$ were collected with the ω-2θ scan technique at a scan speed of 16°/min in ω and a scan width $\Delta\omega = (1.50 + 0.30 \tan \theta)°$. From 1756 reflections measured to $2\theta = 60°$, 876 unique data having $F_o^2 \geq 3\sigma(F_o^2)$ were obtained.

All calculations were performed on a μVax II computer with programs from the TEXSAN crystallographic software package (*5*). The systematic absences $h00$ ($h = 2n + 1$), $0k0$ ($k = 2n + 1$), and $00l$ ($l = 2n + 1$) unambiguously define the noncentrosymmetric space group $P2_12_12_1$. Ba and Zn positional parameters were determined with the computer program SHELXS (*6*), and the B and O positions were found from subsequent analyses of difference electron density maps. Following refinement with isotropic thermal parameters the data were corrected for absorption with the computer program DIFABS (*7*) and averaged. Minimization of the function $\Sigma w(|F_0| - |F_c|)^2$ with data having $F_o^2 \geq 3\sigma(F_o^2)$ and anisotropic temperature factors on each atom resulted in the residuals $R = 0.024$ and $R_w = 0.034$; weights were assigned as the reciprocal of the variance for each observation, and atomic form factors were taken from "International Tables for X-ray Crystallography" (*8*). The final difference electron density map is featureless with the largest peak corresponding to 0.40% of a Ba atom. Crystal data and final atomic parameters are listed in Tables I and II, respectively.

Unit cell parameters were also refined from powder X-ray data. A sample was ground under hexane, sieved with a 200 mesh wire screen, and annealed at 700°C for 2 hr. Eleven intense reflections in the range $19° < 2\theta < 45°$ were measured and their Bragg angles corrected with Si (NIST Reference Material 640b) as the internal standard. Least-squares refinement of the cell parameters afforded the values a = 9.332(3),

TABLE II

FINAL ATOMIC COORDINATES AND TEMPERATURE FACTORS FOR $BaZn_2(BO_3)_2$

Atom	x	y	z	B_{eq}[a]
Ba	0.39607(5)	0.22892(3)	0.0310(1)	1.04(2)
Zn1	0.36945(8)	0.89488(6)	0.0452(2)	0.89(3)
Zn2	0.6588(1)	0.03145(7)	0.9474(2)	0.99(3)
B1	0.4098(8)	0.0059(6)	0.558(2)	0.7(2)
B2	0.6663(8)	0.1669(6)	0.464(2)	0.9(3)
O1	0.5931(6)	0.2475(4)	0.595(1)	1.3(2)
O2	0.3335(5)	0.0932(4)	0.460(1)	1.3(2)
O3	0.2513(6)	0.4061(5)	0.380(1)	1.1(2)
O4	0.4602(6)	0.0113(5)	0.827(1)	1.2(2)
O5	0.5653(7)	0.4128(5)	0.086(1)	1.9(2)
O6	0.6683(6)	0.1569(5)	0.192(1)	1.1(2)

[a] $B_{eq} = (8\pi^2/3) \Sigma_i \Sigma_j U_{ij} a_i^* a_j^* a_i a_j$.

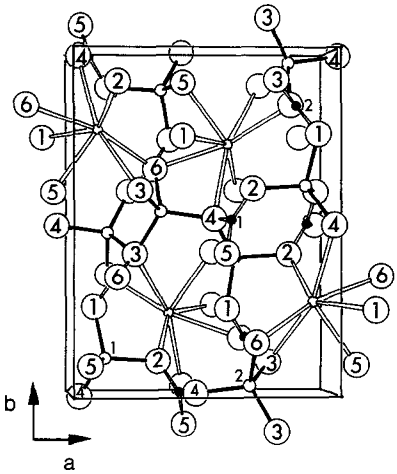

FIG. 1. Labeled sketch of the unit cell of the compound $BaZn_2(BO_3)_2$ as viewed along the *c* axis. Small filled circles represent B atoms, small open circles with shaded bonds Zn atoms, small open circles with open bonds Ba atoms, and large open circles O atoms, here, and in subsequent figures.

b = 12.121(5), and c = 4.922(2) Å, which compare well to those from the single-crystal data (cf. Table I).

An optical second-harmonic test was performed by the Kurtz–Perry method (9). The 1064-nm line of a Nd^{3+} : YAG laser served as the fundamental. Visible light was filtered from the incident beam with a Corning 1-75 filter having a transmittance of 87% at 1064 nm and 0% at 532 nm. The microcrystalline solid was placed on a quartz plate inside the sample chamber. Infrared radiation was filtered from the output beam with a Corning 7-57 filter having a transmittance of 88% at 532 nm and 1% at 1064 nm. The intensity of the second harmonic was monitored with a photomultiplier tube attached to a Tektronix oscilloscope. Microcrystalline KDP served as a standard for the measurement.

Results and Discussion

A labeled sketch of the contents of the unit cell appears as Fig. 1. The structure is a new type exhibiting a framework of ZnO_4 tetrahedra and BO_3 triangles that share vertices; a portion of the framework is depicted in Fig. 2. Two crystallographically distinct types of Zn atoms are present in the structure. Zn2-centered distorted tetrahedra share vertices O3 to form zig-zag strings that extend in the *c* direction. Vertices of adjacent tetrahedra are additionally bridged by atom B2. The B2-centered triangle also serves as a bridge to atom Zn1. The tetrahedra centered by atom Zn1 are isolated from one another, but are bridged through vertices O4 and O5 by atom B1. Application of the 2_1 screw axis along b to the fragment of Fig. 2 completes the framework. By sharing O4 atoms, fused ZnO_4 groups afford the one-dimensional zinc oxide matrix sketched in Fig. 3.

The framework may also be described as a condensation of the six- and eight-membered rings illustrated in Fig. 4. The six-membered ring is composed of two Zn2 atoms, one B2 atom, two O3 atoms, and

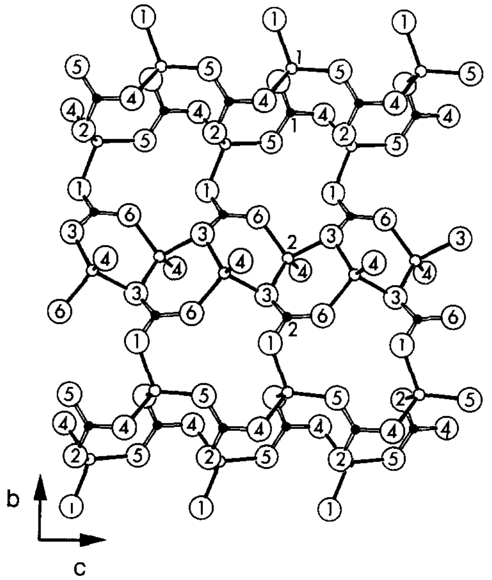

FIG. 2. Sketch of the zinc borate framework as viewed along the *a* axis.

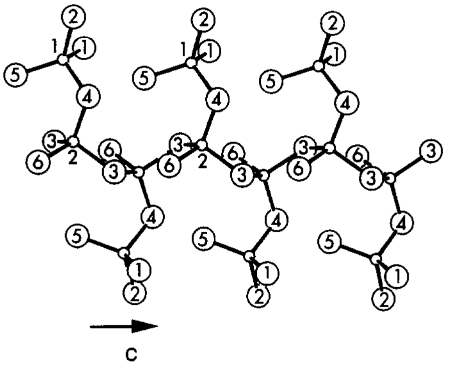

FIG. 3. One-dimensional zinc oxide portion of structure.

TABLE III

SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) IN BaZn$_2$(BO$_3$)$_2$

	Distance		Angle
Ba–O1	2.831(5)	O1–Ba–O4	71.0(1)
Ba–O2	2.740(5)	O1–Ba–O5	68.8(2)
Ba–O3	3.063(6)	O1–Ba–O6	69.7(2)
Ba–O4	2.887(6)	O1–Ba–O6	99.0(2)
Ba–O5	2.744(6)	O3–Ba–O2	84.0(2)
Ba–O6	2.759(6)	O3–Ba–O5	68.1(2)
Ba–O6	2.794(6)	O3–Ba–O6	62.2(2)
		O3–Ba–O6	117.3(2)
		O5–Ba–O6	94.1(2)
		O5–Ba–O6	72.9(2)
		O2–Ba–O4	76.3(2)
Zn1–O1	1.949(5)	O1–Zn1–O2	99.5(2)
Zn1–O2	1.940(5)	O1–Zn1–O4	112.8(2)
Zn1–O4	1.966(6)	O1–Zn1–O5	112.5(3)
Zn1–O5	1.926(6)	O2–Zn1–O4	104.2(2)
		O2–Zn1–O5	120.2(3)
		O4–Zn1–O5	107.4(3)
Zn2–O3	1.977(6)	O3–Zn2–O3	118.1(2)
Zn2–O3	1.933(6)	O3–Zn2–O4	102.3(2)
Zn2–O4	1.956(5)	O3–Zn2–O6	100.7(2)
Zn2–O6	1.942(5)	O3–Zn2–O4	116.4(2)
		O3–Zn2–O6	108.8(2)
		O4–Zn2–O6	109.2(2)
B1–O2	1.36(1)	O2–B1–O4	118.2(7)
B1–O4	1.41(1)	O4–B1–O5	118.4(6)
B1–O5	1.35(1)	O5–B1–O2	123.3(7)
B2–O1	1.35(1)	O1–B2–O3	118.3(8)
B2–O3	1.41(1)	O3–B2–O6	118.4(7)
B2–O6	1.35(1)	O6–B2–O1	123.1(7)

one O6 atom. The rings are fused through vertices O3 and O6 to form a chain that extends in the *c* direction (Fig. 2). The eight-membered ring is composed of two Zn1 atoms, two B1 atoms, two O2 atoms, one O4 atom, and one O5 atom. The rings are fused by sharing terminal vertices O4 and O5 to again form a chain that extends in the *c* direction. The full three-dimensional framework is realized by connecting the chains through vertices O4. Within this construction, Ba atoms occupy sites in tunnels that extend along the *c* axis (Fig. 1).

Interatomic distances and angles are listed in Table III. The average Ba–O distance, 2.8(1) Å, derived from the seven nearest O neighbors, is comparable to the expected value of 2.77 Å calculated from crystal radii (*10*). Average distances for Zn–O and B–O interactions are normal. The average Zn–O distance 1.95(2) Å compares well to the value reported in Zn$_3$(BO$_3$)$_2$, 1.97 Å (*11*). Mild deviations from tetrahedral angles in the Zn environments are observed with the largest excursions represented by O1–Zn1–O2, 99.5(2)°, and O3–Zn2–O6, 100.7(2)°. The average B–O distance 1.37(3) Å in the orthoborate triangles is consistent

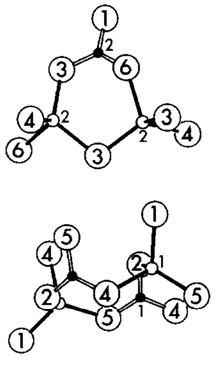

FIG. 4. Sketches of (top) 6-membered Zn$_2$BO$_8$ ring and (bottom) 8-membered Zn$_2$B$_2$O$_9$ ring.

with the expected value, 1.365 Å (*12*). Each triangle, however, contains one interaction that is longer than the other two. In each case, the O atoms associated with the longer distances bridge two Zn atoms, while the O atoms associated with the shorter distances bind to only one Zn atom. The BO_3 triangles exhibit jejune deviations from the ideal O–B–O angle of 120°. Atoms O1, O2, and O5 are three-coordinate and atoms O3, O4, and O6 are four-coordinate.

The intensity of light produced by SHG from the 1064-nm line of a Nd^{3+} : YAG laser and a microcrystalline sample of $BaZn_2(BO_3)_2$ was found to be approximately 10% of that produced from a sample of KDP. We have computed an approximate nonlinearity of the material by application of the anionic group theory (*13*). In this computation, we assume that the BO_3 groups are the principal chromophores contributing to the nonlinearity and fix their symmetry as D_{3h}. The extended zinc oxide submatrix, which could contribute to the efficiency of harmonic conversion, has not been included in the present model. The components of the hyperpolarizability tensor of an individual BO_3 group are summed from (1) with the orientation of each group in the crystal structure; the density of the groups is

$$\chi_{IJK}^{(2\omega)} \approx \sum_{ijk} R_{I_i} R_{J_j} R_{K_k} \beta_{ijk}(\omega, \omega), \qquad (1)$$

also important in determining the magnitude of the nonlinear response. For a BO_3 group having D_{3h} symmetry, the only nonzero components in the hyperpolarizability tensor are given by the relationship $\beta_{111} = -\beta_{122}$. We use the value $\beta_{111} = 0.641 \times 10^{-31}$ esu as reported by Chen, Wu, and Li (*14*). With this value, we compute for the title compound the coefficient $d_{14} = 0.02$ pm/V.

To appreciate this result and the contribution of the relative orientations of the BO_3 groups, we can consider the magnitude of the maximum nonlinearity that could be observed for a collection of BO_3 groups having a density equal to that of $BaZn_2(BO_3)_2$. That is, we consider a collection of eight BO_3 groups, each having B–O vectors aligned in the same directions. The maximum nonlinear coefficient d_{11} that could be observed for such a collection of groups would be proportional to $8 \times \beta_{111} \times (\text{unit cell volume})^{-1} = 0.39$ pm/V. The result calculated for the compound is only 4% of this value.

The small magnitude of the coefficient d_{14} is determined by a poor alignment of the BO_3 groups. The two types of crystallographically distinct BO_3 groups are displayed in Fig. 1; a unit cell contains four groups of each kind that are related to one another by the three 2_1 screw operations along the crystallographic axes. The β_{123} coefficients for each type of group sum constructively, but the signs of the coefficients for the different types are opposite, affording a nearly complete cancellation of the hyperpolarizability-tensor components and a small magnitude for the coefficient d_{14}. We will discuss in greater detail the structural contributions to the magnitudes of the *d* coefficients in a forthcoming paper on harmonic generation with compounds containing triangular oxoanions.

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