February, 1994] © 1994 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 67, 379—382(1994) 379

Crystal Structure of Barium Tetrahydroxo Borate ($Ba[B(OH)_4]_2$)

Koichi WATANABE* and Shoichi SATO†
Department of Materials Chemistry, Faculty of Engineering, Gunma University, Kiryu, Gunma 376
† X-Ray Research Institute, Rigaku Co., Matsubara-cho, Akishima, Tokyo 196

(Received June 8, 1993)

The crystal structure as well as the chemical and physical properties of a new compound, barium tetrahydroxoborate ($Ba[B(OH)_4]_2$), are described. The compound is prepared by the chemical reaction of $BaCl_2+2NaBO_2+4H_2O=Ba[B(OH)_4]_2+2NaCl$ in an aqueous solution. The crystal is monoclinic, space group $P2_1/n$ with cell constants $a=8.332(2)$, $b=16.522(3)$, $c=10.216(3)$ Å, $\beta=106.63(2)°$, $V=1347.51(6)$ Å^3, $Z=8$, $D_m=2.90(1)$, $D_c=2.85(4)$ g cm^{-3}. Melting point=ca. 1075 °C; Transition point (γ- to β-form)=ca. 532 °C. Refraction indexes: $\alpha=1.567(6)$, $\beta=1.547(6)$, and $\gamma=1.517(8)$.

In the barium metaborate compound (BaB_2O_4) there are three modifications: α (high temperature phase), β, and γ (low temperature phases). Its melting point is ca. 1095 °C.[1] The α-phase reversibly transform to the β-phase at ca. 925 °C; the γ-phase,[2] however, transforms irreversibly to the β-phase at ca. 600 °C. The β-BaB_2O_4 crystal[3] is an excellent new nonlinear optical material with good pyroelectric properties. As a second-harmonic generation (SHG) crystal, it possesses many attractively useful characteristics, such as large effective SHG coefficients, a wide transparent waveband, a high damage threshold, a large birefringence, low dispersion, good chemical stability, and good optical homogeneity. Bulky single crystals of β-BaB_2O_4 have been successfully grown by top-seeded growth[4] and the pulling growth technique.[5] Single-crystal fibers have also been grown by the laser-heated pedestal growth method.[6] When applied as an optoelectronic material crystals of high quality are highly demanded. Moreover, starting materials of sufficiently high purity must be prepared to obtain such crystals without defects, inclusions or impurities. The compound BaB_2O_4 as a starting material of optoelectronics is currently being prepared from chemical reagents of $BaCO_3$ and B_2O_3 by a normal solid-state reaction method. The result, however, has not been satisfactory.

The purpose of the present study was to prepare a new barium borate compound of high quality which would be useful as the starting material of optoelectronics by the precipitation method from an aqueous solution, to examine its thermal and optical properties, and to determine the crystal structure.

Experimental

Preparation of Crystals. Small and colorless crystals with monoclinic prism-form were prepared from an aqueous solution in the pH range of 1.2—13.5 at 20 °C according to the following chemical reaction: $BaCl_2$ (aq)+$2NaBO_2$ (aq)=$Ba[B(OH)_4]_2$+2NaCl. The details concerning the preparation method were described in a separate paper.[7] Large single crystals which were adequate for an X-ray structure analysis were grown by recrystallization from an aqueous solution.

Chemical and Physical Properties. A chemical analysis of the precipitated crystals was performed by the inductively coupled plasma (ICP) method. The refractive indexes of the crystals were measured by the immersion method with the d-line (5889.97 Å) of a Na-lamp under a polarizing microscope. The density was determined using a pycnometer and by the float-sink method with 1,1,2,2-tetrabromoethane ($d=2.9673$ g cm^{-3}) of higher density and ethanol ($d=0.7893$) of lower density; as standard-density samples AlF_3 ($d=2.882$), SiO_2 ($d=2.20$), $CaCO_3$ ($d=2.711$), and B_2O_3 ($d=2.46$) were used. The phase transitions of the crystal upon heating were measured by the differential thermal analysis (DTA) technique at a heating rate of 5 °C min^{-1}; they were also confirmed based on changes in the X-ray powder diffraction pattern of samples quenched in a small Pt capsule. The melting point of the crystal was measured directly under an optical microscope with a hot stage. The infrared spectrum was recorded on a Hitachi 270-50 type IR spectrophotometer in the 4000—250 cm^{-1} region as KBr pellets. The Raman spectrum of the powder sample was taken on a JRS-400T (Ar-laser) spectrometer at room temperature in the 1800—30 cm^{-1} region.

X-Ray Crystal Structure Analysis. The structure of precipitated crystals was determined. A crystal shaped like a sphere with a diameter of about 0.4 mm was used for the intensity measurement on a Rigaku AFC5R four-circle diffractometer with graphite monochromate Mo $K\alpha$ radiation ($\lambda=0.71073$ Å). The intensity data were collected at 23±1 °C using the ω–2θ scan technique in a 2θ range from 3° to 55°, $\Delta\omega=(1.73+0.30\tan\theta)°$, scan speed 16.0° min^{-1} in ω. The ranges of the indexes were $0\leqq h\leqq 11$, $0\leqq k\leqq 22$, $-13\leqq l\leqq 13$. The weak reflections ($I<10.0\sigma(I)$) were rescanned (maximum of 2 rescans). Stationary background counts were recorded on each side of the reflection; the ratio of the peak to the background counting times was 2:1. The intensities of three standard reflections monitored every 150 reflections showed no significant fluctuation, indicating crystal and electronic stability throughout the data collection. A total of 3439 reflections were collected; 3230 were unique ($R_{\text{int}}=0.023$), of which 2661 reflections with $I_{\text{obsd}}>3\sigma(I_{\text{obsd}})$ were used for the structure determination. The applied corrections were Lp and absorption. The linear absorption coefficient for Mo $K\alpha$ is 58.91 cm^{-1}. The lattice parameters were obtained from the least squares of 2θ values of 25 independent reflections in the range $44.7°<2\theta<45.0°$. The structure was solved by a direct method.[8] The non-hydrogen atoms were refined anisotropically by full-matrix least squares. The function minimized

Table 1. Crystal Data and Some Physicochemical Properties for $Ba[B(OH)_4]_2$

Chemical formula	$Ba[B(OH)_4]_2$
Formula weight	294.9
Crystal system	Monoclinic
Space group	$P2_1/n$
Systematic absences	$h0l$: $h+l=2n+1$ $0k0$: $k=2n+1$
Lattice constants a/Å	8.332(2)
b/Å	16.522(3)
c/Å	10.216(3)
β(°)	106.63(2)
Volume V/Å^3	1347.5(6)
D_m/g cm^{-3}	2.85
D_c/g cm^{-3}	2.91
Z	8
μ(Mo $K\alpha$)/cm^{-1}	58.91
Crystal shape	Monoclinic prism
Crystal size	Sphere of 0.4 mm in diameter
Crystal color	Colorless
Refractive indexes α	1.567(6)
β	1.547(6)
γ	1.517(8)
Melting point/°C	1075
Transition point/°C	532 ($\gamma\rightarrow\beta$-phase)
Dehydration temperature/°C	102 ($\rightarrow\gamma$-phase)

Table 2. Selected Positional Parameters and B_{eq}[a] (Å^2) for $Ba[B(OH)_4]_2$

Atom	x	y	z	B_{eq}
Ba(1)	0.27611(2)	0.15618(1)	0.28973(2)	0.918(6)
Ba(2)	0.25407(2)	0.09746(1)	0.71845(2)	0.956(6)
B(1)	0.1965(4)	−0.0143(2)	0.4373(4)	1.0(1)
B(2)	0.3250(4)	0.2709(2)	0.5708(4)	1.1(1)
B(3)	0.3110(5)	0.0064(2)	0.0655(4)	1.2(1)
B(4)	0.2140(4)	0.2464(2)	0.9363(4)	1.0(1)
O(1)	0.1158(3)	0.0656(2)	0.4324(3)	1.20(8)
O(2)	0.3540(3)	0.0005(2)	0.4025(2)	1.29(8)
O(3)	0.2225(3)	−0.0443(2)	0.5755(2)	1.22(8)
O(4)	0.0921(3)	−0.0726(2)	0.3393(3)	1.47(9)
O(5)	0.4143(3)	0.1928(2)	0.5803(3)	1.30(9)
O(6)	0.1686(3)	0.2534(2)	0.6040(2)	1.31(8)
O(7)	0.2910(3)	0.3015(2)	0.4299(3)	1.34(9)
O(8)	0.4290(3)	0.3261(2)	0.6733(3)	1.5(1)
O(9)	0.4276(3)	0.0771(2)	0.1041(3)	1.52(9)
O(10)	0.1513(3)	0.0314(2)	0.0907(3)	2.1(1)
O(11)	0.3907(3)	−0.0591(2)	0.1598(3)	1.35(8)
O(12)	0.2763(3)	−0.0174(2)	−0.0770(3)	1.5(1)
O(13)	0.1179(3)	0.1703(2)	0.9143(3)	1.6(1)
O(14)	0.3725(3)	0.2294(2)	0.9020(3)	1.36(9)
O(15)	0.1185(3)	0.3103(1)	0.8476(2)	1.15(8)
O(16)	0.2460(3)	0.2696(2)	1.0796(2)	1.28(8)
H(1)	0.044(5)	0.066(3)	0.418(4)	1.0(9)
H(2)	0.37(1)	−0.029(7)	0.33(1)	15(4)
H(3)	0.266(4)	−0.078(2)	0.595(4)	0.3(7)
H(4)	0.077(6)	−0.069(3)	0.271(5)	4(1)
H(5)	0.486(5)	0.197(3)	0.591(4)	2(1)
H(6)	0.089(6)	0.257(3)	0.543(5)	3(1)
H(7)	0.26(1)	0.333(4)	0.426(8)	8(2)
H(8)	0.411(5)	0.360(3)	0.656(5)	2(1)
H(9)	0.404(6)	0.106(3)	0.043(5)	3(1)
H(10)	0.090(8)	0.054(4)	0.034(6)	7(2)
H(11)	0.44(1)	−0.087(6)	0.16(1)	16(4)
H(12)	0.345(6)	−0.035(3)	−0.079(5)	3(1)
H(13)	0.133(8)	0.153(4)	0.961(7)	6(2)
H(14)	0.383(7)	0.260(3)	0.861(6)	4(1)
H(15)	0.123(5)	0.301(3)	0.776(5)	2(1)
H(16)	0.291(6)	0.305(3)	1.091(5)	3(1)

a) $B_{\mathrm{eq}}=(8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\boldsymbol{a}_i\cdot\boldsymbol{a}_j$.

was $\Sigma w(|F_o|-|F_c|)^2$, $w=4(\mathrm{Lp})^2\cdot F_o^2/[\sigma^2_{\mathrm{count}}(F_o^2)+(\mathrm{p}F_o^2)^2]$. Hydrogen atoms were located based on difference Fourier maps, and were included isotropically in the refinement. A correction for isotropic secondary extinction was applied (coefficient$=0.99338\times10^{-6}$). The refinement for 264 variable parameters converged to $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|=0.019$, $R_w=[(\Sigma w(|F_o|-|F_c|)^2/\Sigma wF_o^2)]^{1/2}=0.023$, and $s=2.33$. The weighting scheme was based on counting statistics and included a factor of P (=0.01), which was used to downweight the intense reflections. Plots of $\Sigma w(|F_o|-|F_c|)^2$ versus $|F_o|$, the reflection order in the data collection, $\sin\theta/\lambda$, and various classes of indexes showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map were 1.39 and −1.39 e/Å^3, respectively. Neutral atom scattering factors were taken from Cromer and Waber;[9] anomalous dispersion corrections were those by Cromer.[10] All of the calculations were performed using the TEXSAN[11] crystallographic software package.

Results and Discussion

Small and colorless crystals were used in order to collect the data concerning the chemical and physical properties. The density of the crystals was 2.85(4) g cm^{-3}, and the refractive indexes were $\alpha=1.567(6)$, $\beta=1.547(6)$, and $\gamma=1.517(8)$, respectively. In the TG curve of the thermal analysis a drastic weight loss of ca. 25%, probably caused by the reaction of dehydration, was observed at approximately 102 °C. Thus, the water included in the crystals was evaluated to be 4 mole in a chemical unit. From a chemical analysis using the ICP method, moreover, it was determined that the concentrations of barium, boron, oxygen, and hydrogen contained in the crystals were 46.55, 7.33, 43.39, and 2.73 in wt%, respectively. Consequently, the crystals were found to be a new compound with a chemical composition of $BaB_2O_8H_8$. In the DTA curve two comparatively large endothermal peaks were observed at positions of about 102 and 1075 °C, and a small exothermal one at about 532 °C. It was believed that the former two peaks were caused by the phenomena of dehydration and melting. After dehydration at 102 °C the crystal phase ($BaB_2O_8H_8$) transformed to the γ-phase of BaB_2O_4. However, the latter one might correspond to a transition from the γ-phase to the β-phase in the BaB_2O_4 compound. The IR spectrum showed a moderate absorption band at 1200 cm^{-1}, a very strong band at 941 cm^{-1} (ν_3), and weak bands at 741 cm^{-1} (ν_1) and 535 cm^{-1} (ν_4), respectively.[12,13] The Raman spectrum showed a strong, but somewhat broad, band

Table 3. Bond Distances (Å) and Angles (°) for $\mathrm{Ba[B(OH)_4]_2}$ (Estimated Standard Deviations in the Last Significant Figure Are Given in Parentheses.)

$\mathrm{Ba^{2+}}$–O coordination		O(7)–O(8)	2.456(4)
Ba(1)–O(1)	2.695(3)	O(7)–O(11)	2.764(4)
Ba(1)–O(2)	2.817(3)	O(7)–O(13)	2.812(4)
Ba(1)–O(5)	2.924(3)	O(8)–O(12)	3.100(4)
Ba(1)–O(7)	2.781(3)	O(8)–O(14)	2.978(4)
Ba(1)–O(8)	2.810(3)	O(9)–O(10)	2.389(4)
Ba(1)–O(9)	2.875(3)	O(9)–O(11)	2.363(4)
Ba(1)–O(10)	2.873(3)	O(9)–O(12)	2.474(4)
Ba(1)–O(15)	2.798(3)	O(9)–O(12)	2.743(4)
Ba(1)–O(16)	2.807(3)	O(9)–O(13)	3.150(4)
Ba(2)–O(1)	2.867(3)	O(10)–O(10)	2.864(5)
Ba(2)–O(3)	2.733(3)	O(10)–O(11)	2.430(4)
Ba(2)–O(4)	2.804(3)	O(10)–O(12)	2.386(4)
Ba(2)–O(5)	2.708(3)	O(10)–O(13)	2.881(4)
Ba(2)–O(6)	2.834(3)	O(11)–O(12)	2.432(4)
Ba(2)–O(11)	2.933(3)	O(13)–O(14)	2.371(4)
Ba(2)–O(12)	2.790(3)	O(13)–O(15)	2.413(4)
Ba(2)–O(13)	2.835(3)	O(13)–O(16)	2.378(4)
Ba(2)–O(14)	2.860(3)	O(14)–O(15)	2.430(3)
$\mathrm{[B(OH)_4]^-}$ units		O(14)–O(16)	2.437(4)
B(1)–O(1)	1.476(5)	O(15)–O(16)	2.400(3)
B(1)–O(2)	1.475(4)	Bond angles	
B(1)–O(3)	1.453(4)	O(3)–B(1)–O(2)	113.3(3)
B(1)–O(4)	1.479(4)	O(3)–B(1)–O(1)	106.1(3)
B(2)–O(5)	1.478(5)	O(3)–B(1)–O(4)	109.4(3)
B(2)–O(6)	1.466(4)	O(2)–B(1)–O(1)	105.7(3)
B(2)–O(7)	1.475(5)	O(2)–B(1)–O(4)	109.7(3)
B(2)–O(8)	1.470(4)	O(1)–B(1)–O(4)	112.7(3)
B(3)–O(9)	1.498(5)	O(6)–B(2)–O(8)	109.8(3)
B(3)–O(10)	1.484(5)	O(6)–B(2)–O(7)	111.0(3)
B(3)–O(11)	1.474(5)	O(6)–B(2)–O(5)	106.1(3)
B(3)–O(12)	1.455(5)	O(8)–B(2)–O(7)	113.0(3)
B(4)–O(13)	1.473(5)	O(8)–B(2)–O(5)	108.2(3)
B(4)–O(14)	1.487(4)	O(7)–B(2)–O(5)	108.5(3)
B(4)–O(15)	1.469(4)	O(12)–B(3)–O(11)	112.2(3)
B(4)–O(16)	1.463(4)	O(12)–B(3)–O(10)	108.5(3)
O(1)–O(2)	2.353(4)	O(12)–B(3)–O(9)	113.8(3)
O(1)–O(3)	2.341(4)	O(11)–B(3)–O(10)	110.5(3)
O(1)–O(3)	2.819(4)	O(11)–B(3)–O(9)	105.3(3)
O(1)–O(4)	2.459(4)	O(10)–B(3)–O(9)	106.4(3)
O(2)–O(2)	2.667(5)	O(16)–B(4)–O(15)	109.9(3)
O(2)–O(3)	2.445(4)	O(16)–B(4)–O(13)	108.2(3)
O(2)–O(4)	2.415(3)	O(16)–B(4)–O(14)	111.4(3)
O(2)–O(10)	3.190(4)	O(15)–B(4)–O(13)	110.2(3)
O(2)–O(11)	2.765(4)	O(15)–B(4)–O(14)	110.6(3)
O(3)–O(4)	2.392(4)	O(13)–B(4)–O(14)	106.5(3)
O(3)–O(15)	2.747(4)	Intermolecular distances (<3.19 Å)	
O(4)–O(13)	3.128(4)	O(3)–O(15^{i})	2.747(4)
O(4)–O(16)	2.944(4)	O(4)–O(16^{i})	2.944(4)
O(5)–O(6)	2.352(4)	O(7)–O(11^{ii})	2.764(4)
O(5)–O(7)	2.396(4)	O(8)–O(12^{ii})	3.100(4)
O(5)–O(8)	2.388(4)	O(9)–O(12^{iii})	2.743(4)
O(5)–O(16)	2.835(4)	O(10)–O(10^{iv})	2.864(5)
O(6)–O(7)	2.424(4)	Symmetry operators:	
O(6)–O(8)	2.403(4)	(i) $1/2-x,\ -1/2+y,\ 3/2-z$	
O(6)–O(14)	3.059(4)	(ii) $1/2-x,\ 1/2+y,\ 1/2-z$	
O(6)–O(14)	2.740(3)	(iii) $1-x,\ -y,\ -z$	
O(6)–O(15)	2.801(4)	(iv) $-x,\ -y,\ -z$	

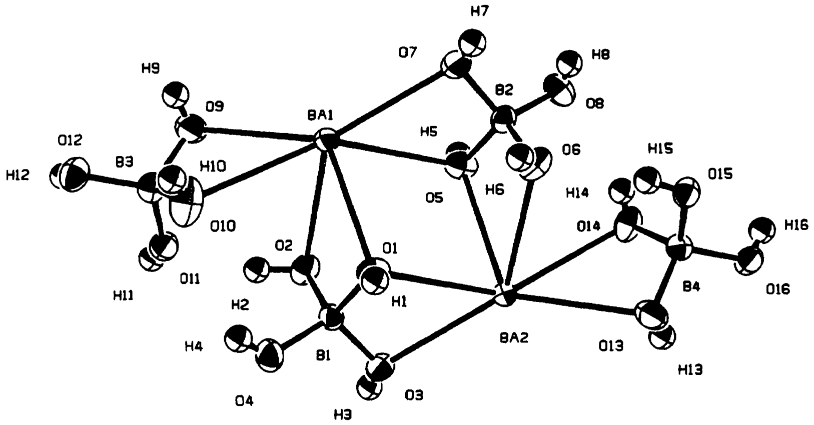

Fig. 1. Perspective view of $Ba[B(OH)_4]_2$ crystal consisting of two unit cells, showing the atom-numbering scheme.

at 740 cm^{-1} and a weak, broad band at 535 cm^{-1}. The strong band is assignable to the mononuclear tetrahedral $B(OH)_4^-$ ion in the solid.[14]

Structural details concerning the crystals are described below. The crystal data and some physicochemical properties are given in Table 1.[#] The formula unit comprises one Ba^{2+} cation and two $[B(OH)_4]^-$ anions. The asymmetric unit contains two formula units. A perspective view of the asymmetric unit, along with the atom-numbering scheme, is presented in Fig. 1. Table 2 shows selected atomic positional parameters and B_{eq} for $Ba[B(OH)_4]_2$. The relevalent bond distances and angles are summarized in Table 3. The structure is pseudo-centrosymmetric around the midpoint between the Ba(1) and Ba(2) atoms, 4.541(1) Å distant from each other. The Ba(1)–O(1)–Ba(2) angle is 109.41(8)° and the Ba(1)–O(5)–Ba(2) 107.35(8)°. The geometries of the BO_4 groups are close to tetrahedral with B–O bonds ranging over 1.454(4)—1.498(5) Å (mean 1.474(2) Å) and O–B–O angles 105.0(3)—113.7(3)° (mean 109.5(5)°); these values resemble to those reported for a double salt $LiBa_2B_5O_{10}$.[15] Each Ba atom is irregularly surrounded by nine O atoms. The B atoms are also surrounded by oxygen atoms with tetrahedral geometry. Two oxygen atoms, O(1) and O(2), directly bridge the two Ba atoms. The Ba atoms are infinitely bonded through BO_4^- anions to form a three-dimensional network.

Based on the structural data and Raman spectrum, we concluded that the crystals prepared from the aqueous solutions of barium chloride and sodium metaborate at 20 °C were $Ba[B(OH)_4]_2$, which belongs to the monoclinic system, space group $P2_1/n$; we also determined the crystal structure.

One (K. W) of the authors is indebted to Professor Mitsuo Sato of Gunma University for his helpful discussion concerning the X-ray crystallographic data, and also to Dr. Shoudou Kobayashi (Gunma University) for the Raman spectrum.

References

1) D. Guiqin, W. Lin, A. Zheng, Q. Hung, and J. Liang, *J. Am. Ceram. Soc.*, **73**, 2526 (1990).

2) P. Yamaguchi, et al., *Ceramurgia*, **1980**, 6, 103 (Ref. ASTM-card 35-181).

3) A. Jinang, F. Cheng, Q. Lin, Z. Cheng, and Y. Zheng, *J. Crystal Growth*, **79**, 963 (1986).

4) S. Kimura and K. Kitamura, *J. Ceram. Soc. Jpn.*, **101**, 22 (1993).

5) L. K. Cheng, W. Bosenberg, and C. L. Tang, *J. Crystal Growth*, **89**, 553 (1988).

6) D. Y. Tang, R. K. Route, and R. S. Feigelson, *J. Crystal Growth*, **91**, 81 (1988).

7) K. Watanabe, M. Ichikawa, and S. Sato, *Chem. Lett.*, **1993**, 1247.

8) C. J. Gilmore, *J. Appl. Cryst.*, **17**, 42 (1984).

9) D. T. Cromer and J. T. Waber, "International Tables for X-Ray Crystallography," Kynoch, Birmingham (1974), Vol. IV, Table 2.2 A.

10) D. T. Cromer, "International Tables for X-Ray Crystallography," Kynoch, Birmingham (1974), Vol. IV, Table 2.3.1.

11) "TEXRAY Structure Analysis Package," Molecular Structure Corp., (1985).

12) J. E. Edwards, G. C. Morrison, V. F. Ross, and J. W. Schultz, *J. Am. Chem. Soc.*, **77**, 266 (1955).

13) S. D. Ross, "Inorganic Infrared and Raman Spectra," McGraw, London (1972), pp. 190—230.

14) V. G. Kessler and H. A. Lehmann, *Z. Anorg. Allog. Chem.*, **339**, 87 (1965).

15) Q. Huang, S. Lu, G. Dai, and J. Liang, *Acta Crystallogr., Sect. C*, **C48**, 1576 (1992).

[#] Tables of anisotropic thermal parameters and structure factors are deposited as Document No. 67010 at the Office of the Editor of Bull. Chem. Soc. Jpn.