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Strontium Barium Metaborate, $Sr_{1.36}Ba_{1.64}(B_3O_6)_2$

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Abstract

Single crystals of strontium barium metaborate, $Sr_{1.36}Ba_{1.64}(B_3O_6)_2$, were grown for the first time by the high-temperature-solution-growth technique, and a detailed structure analysis was carried out with the space group $R\bar{3}c$. The metaborate $(B_3O_6)^{3-}$ anion planar groups in the title compound form infinite layers parallel to (001) plane, and Sr and Ba atoms are alternatively placed between the layers and are octahedrally coordinated by six O(2) atoms in the neighbouring anion rings.

要 約

Strontium barium metaborate, $Sr_{1.36}Ba_{1.64}(B_3O_6)_2$의 單結晶은 高溫 溶液 成長 方法을 使用하여 成長되었고, 上記의 構造解析은 空間群 $R\bar{3}c$에서 遂行되었다. 表題 化合物내의 Metaborate $(B_3O_6)^{3-}$ 陰ion 平面 group은 (001)面에 平行한 無限한 層들을 形成하고 있고, Sr과 Ba 原子는 그 層사이에 交代로 位置하고 있으며, 이웃하고 있는 陰ion ring內의 O(2) 原子에 依해 六配位 八面體 構造를 갖는다.

1. Introduction

Nonlinear optical crystals that enable to generate third and fourth harmonic generation of 1.064 μm wavelength of an Nd : YAG laser become very important in providing UV light sources for the fabrication of very large scale integrated circuits by lithographic technique. For this purpose, much effort has been paid to develop borate crystals[1] because the borates that are composed of BO_3 or BO_4 units are not only highly transparent in the UV spectral region, but also possess relatively large second-order nonlinear optical coefficients. A metaborate crystal containing $(B_3O_6)^{3-}$ anion rings is one of such borates and is expected to show large second- and third-order nonlinear optical effects because of high nonlinearity of $(B_3O_6)^{3-}$ rings. However no crystal apart from β-BaB_2O_4[2] has been reported in this family. This work forms a part of elaboration in search for new borate nonlinear optical crystals.

2. Experimetal Section

Synthesis. The high-temperature-solution-growth-

technique was used to grow a strontium barium metaborate ($Sr_{1.36}Ba_{1.64}B_4O_8$) crystal. The starting materials, $BaCO_3$, SrO, and B_2O_3, were mixed in the molar ratio of 1 : 1 : 2, and KBF_4 was used as a flux. The materials were melted at 1000°C for 10 h with an efficient agitation and then cooled to 900°C. The crystal was grown in the temperature range of 900~890°C with a cooling rate of 0.1°C/h.

Table 1. Crystal data and structure refinement for compound

Color/shape	colorless/block
Empirical formula	$Ba_{0.82}Sr_{0.68}B_3O_6$
Formula weight	300.54
Temperature	293(2) K
Wavelength	0.71069 Å
Crystal system	Trigonal
Space group	$R\bar{3}c$
Unit cell dimensions	a = 7.1584(9) Å α = 90°
	b = 7.1584(9) Å β = 90°
	c = 36.995(4) Å γ = 120°
Volume	1641.8(3) Å^3
Z, Calculated density	12, 3.648 Mg/m^3
Absorption coefficient	12.506 mm^{-1}
F(000)	1617
Crystal size	0.429×0.33×0.231 mm
θ range for data collection	3.30 to 29.96°
Index ranges	$-10 <= h <= 8$, $0 <= k <= 10$, $0 <= l <= 51$
Reflections collected/unique	1503/538 (R_{int} = 0.0491)
Completeness to θ = 29.96	100.0%
Absorption correction	Empirical (φ-scan)
Max. and min. transmission	0.1392 and 0.0466
Refinement method	Full-matrix least-squares on F^2
Data/restraints/ parameters	538/0/36
Goodness-of-fit on F^2	1.041
Final R indices [$I > 2\sigma(I)$]	R1[a] = 0.0185, wR2[b] = 0.0399
R indices (all data)	R1[a] = 0.0289, wR2[b] = 0.0433
Weight	$w = 1/[\sigma^2(F_o^2) + (0.0176P)^2 + 0.0000P]$ where $P = (F_o^2 + 2F_c^2)/3$
Extinction coefficient	0.00402(17)
Largest diff. peak and hole	1.007 and −1.362 e · Å^{-3}

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[b] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2/\Sigma[w(F_o^2)^2]]^{1/2}$.

Table 2. Atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2×10^3)

	x	y	z	U(eq)
Sr	6667	3333	833	8(1)
Ba	6667	3333	−186(1)	6(1)
Sr'	6667	3333	−186	27(5)
O(1)	7926(3)	9641(3)	418(1)	15(1)
O(2)	6574(3)	5886(3)	378(1)	13(1)
B	8224(6)	7838(5)	404(1)	11(1)

U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

X-ray Crystallography. Transparent crystals of about 3×4×3 mm^3 size were grown on a Pt wire that was placed in the melt. A crystal was mounted and aligned on an Enraf-Nonius CAD4 diffactometer.[3] The accurate trigonal unit-cell parameters and an orientation matrix for data collection were obtained by least-squares refinement of the setting angles of 25 reflections. X-ray data were collected using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å), by the ω-2θ scan technique. The intensity data were corrected for Lorentz and polarization effects, and an empirical absorption correction based on φ-scan was applied. The structure was solved by direct methods and refined by full-matrix least-squares on F^2.[10-11] All atoms were refined anisotropically, and the occupancy factors for Ba^{2+} and Sr^{2+} placed together at a Wyckoff letter 12(c) site were also refined. The most suitable stabilization was reached with $0.82Ba^{2+} + 0.18Sr^{2+}$, and the highest peak and the deepest hole in the final difference density map were 1.01 eÅ^{-3} at 1.87 Å from O2 and −1.36 eÅ^{-3} at 0.66 Å from Ba atom. A summary of the data collection and details of the structure refinement is listed in Table 1. Final atomic coordinates and equivalent isotropic displacement parameters are given in Table 2.

3. Result and Discussion

An asymmetric unit of the title complex is composed of five atoms: one strontium at the Wyckoff

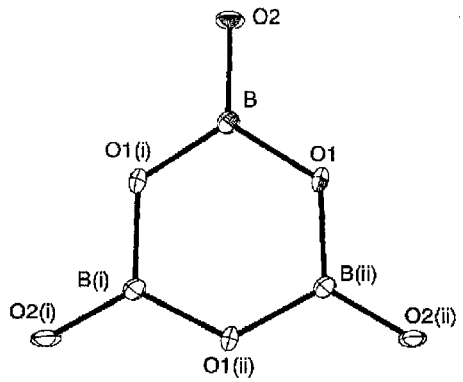

Fig. 1. ORTEP diagram of the $(B_3O_6)^{3-}$ anion ring with atom-labelling scheme. The atoms in an asymmetric unit are expressed with ellipsoids with octant shading and ellipsoids with only enveloping ellipses are the equivalent atoms related by 3-fold symmetry. The displacement ellipsoids are drawn at the 50% probability level. Symmetry Code; (i) $-y+2, x-y+1, z$ (ii) $-x+y+1, -x+2, z$.

letter 6(a) site, one atom named barium consisting of Ba^{2+} and Sr^{2+} in the ratio 0.82 : 0.18 at the Wyckoff letter 12(c) site, and two oxygen atoms and a boron atom at general positions. A metaborate molecule, $(B_3O_6)^{3-}$ anion ring, is completed by three BO_2 groups related by 3-fold rotation symmetry along the *c*-axis perpendicularly passing through the center of the molecular plane (Fig. 1). The ring plane is planar within 0.078(3) Å with O1-B = 1.410(4) Å, O1-B^{ix} = 1.397(4) Å, and O2-B = 1.306(4) Å showing double bond character (Table 3), whose geometry is very similar to that of $Sr_xBa_{3-x}(B_3O_6)_2$.[9] Strontium atom is octahedrally coordinated by O2 atoms in the anion groups with a Sr...O2 = 2.5100(18) Å, and barium atom is also octahedrally coordinated by the same O2 atoms but with two different coordination bond lengths Ba...O2 = 2.7964(19) Å and Ba...$O2^{vi}$ = 2.738(2) Å so that the O2 atoms are participating in three coordinations with Sr...O2...Ba = 90.39(5)°, Sr...O2...Ba^{viii} = 131.05(7)°, Ba...O2...Ba^{viii} = 103.81(6)°. The 6-fold coordination bond lengths of Sr...O2 and Ba...O2 are very close to the respective 2.5801 Å and 2.76 Å shown in International Tables for X-Ray Crystallography Vol. III.[7] Therefore three-dimensional infinite molecular network is formed by the O2 atom in the $(B_3O_6)^{3-}$ anion ring which

Table 3. Selected Bond Distances (Å) and Angles (°)

Sr-$O2^{i}$	2.5099(18)	Ba-$O2^{viii}$	2.7377(17)
Sr-$O2^{ii}$	2.5100(18)	Ba-$O2^{v}$	2.7964(19)
Sr-$O2^{iii}$	2.5100(18)	Ba-$O2^{iv}$	2.7964(19)
Sr-$O2^{iv}$	2.5100(18)	Ba-O2	2.7964(19)
Sr-$O2^{v}$	2.5100(18)	O1-B^{ix}	1.397(4)
Sr-O2	2.5100(18)	O1-B	1.410(4)
Ba-$O2^{vi}$	2.7377(17)	O2-B	1.306(4)
Ba-$O2^{vii}$	2.7377(17)		
$O2^{i}$-Sr-$O2^{ii}$	79.93(7)	$O2^{vi}$-Ba-$O2^{vii}$	113.49(4)
$O2^{i}$-Sr-$O2^{iii}$	79.93(7)	$O2^{vi}$-Ba-$O2^{viii}$	113.49(4)
$O2^{ii}$-Sr-$O2^{iii}$	79.93(7)	$O2^{vii}$-Ba-$O2^{viii}$	113.49(4)
$O2^{i}$-Sr-$O2^{iv}$	138.93(7)	$O2^{vi}$-Ba-$O2^{v}$	89.74(7)
$O2^{ii}$-Sr-$O2^{iv}$	84.31(9)	$O2^{vii}$-Ba-$O2^{v}$	76.19(6)
$O2^{iii}$-Sr-$O2^{iv}$	134.02(8)	$O2^{viii}$-Ba-$O2^{v}$	145.30(4)
$O2^{i}$-Sr-$O2^{v}$	134.02(8)	$O2^{vi}$-Ba-$O2^{iv}$	76.19(6)
$O2^{ii}$-Sr-$O2^{v}$	138.93(7)	$O2^{vii}$-Ba-$O2^{iv}$	145.30(4)
$O2^{iii}$-Sr-$O2^{v}$	84.31(9)	$O2^{viii}$-Ba-$O2^{iv}$	89.94(7)
$O2^{iv}$-Sr-$O2^{v}$	79.93(7)	$O2^{v}$-Ba-$O2^{iv}$	70.42(6)
$O2^{i}$-Sr-O2	84.31(9)	$O2^{vi}$-Ba-O2	145.30(4)
$O2^{ii}$-Sr-O2	134.02(8)	$O2^{vii}$-Ba-O2	89.94(7)
$O2^{iii}$-Sr-O2	138.93(8)	$O2^{viii}$-Ba-O2	76.19(6)
$O2^{iv}$-Sr-O2	79.93(7)	$O2^{v}$-Ba-O2	70.42(6)
$O2^{v}$-Sr-O2	79.93(7)	$O2^{iv}$-Ba-O2	70.42(6)

Symmetry code: (i) $-x+4/3, -x+y+2/3, -z+1/6$; (ii) $x-y+1/3, -y+2/3, -z+1/6$; (iii) $y+1/3, x-1/3, -z+1/6$; (iv) $-y+1, x-y, z$; (v) $-x+y+1, -x+1, z$; (vi) $y, -x+y, -z$; (vii) $x-y+1, x, -z$; (viii) $-x+1, -y+1, -z$; (ix) $-x+y+1, -x+2, z$.

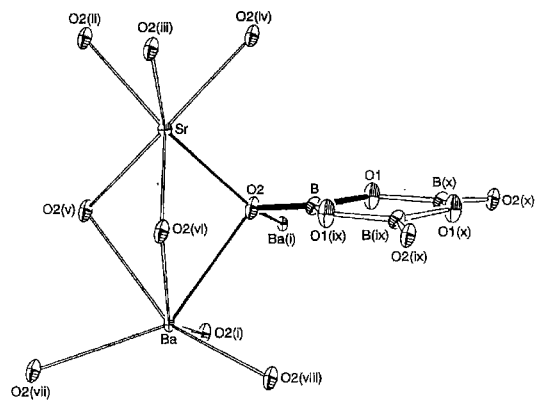

Fig. 2. The relationship between the $(B_3O_6)^{3-}$ anion rings and the cations Sr^{2+} and Ba^{2+}, where Ba^{2+} atom is made up of $0.82Ba^{2+}$ and $0.18Sr^{2+}$ atoms statistically. Symmetry Code; (i) $-x+1, -y+1, -z$ (ii) $x-y+1/3, -y+2/3, -z+1/6$ (iii) $y+1/3, x-1/3, -z+1/6$; (iv) $-x+4/3, -x+y+1/6, -z+1/6$ (v) $-y+1, x-y, z$ (vi) $-x+y+1, 1-x, z$ (vii) $y, -x+y, -z$ (viii) $1+x-y, x, -z$; (ix) $-y+2, x-y+1, z$ (x) $-x+y+1, -x+2, z$.

plays a bridging role among Sr, Ba atoms, and the metaborate molecule (Fig. 2).

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