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Flux Growth and Crystal Structure Refinement of Calcite Type Borate GaBO₃

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Academic Editor: Glen Deacon

Abstract: A single crystal of gallium borate, $GaBO_3$, $4 \times 4 \times 0.2$ mm^3 in size has been grown by spontaneous crystallization with a molten flux based on a Bi_2O_3-$3B_2O_3$ solvent. From single crystal X-ray diffraction measurement, $GaBO_3$ was found to crystallize in the trigonal calcite type, space group R-3c, with cell dimensions $a = 4.56590(10)$ and $c = 14.1764(4)$ Å, $Z = 6$. Layers of distorted $[GaO_6]$ octahedra are interleaved by layers of triangular planar $[BO_3]$ unites. The transmission spectrum on a single crystal indicated that the band gap of $GaBO_3$ is 3.62 eV.

Keywords: borates; gallium borate; calcite type; crystal growth; flux

1. Introduction

Calcium carbonate, $CaCO_3$, exists in three different polymorphs: The calcite, vaterite, and aragonite structures [1]. Triangle planar BO_3^{3-} groups can replace CO_3^{2-} to form metal orthoborates with the nominal formula $A^{III}BO_3$ which have been determined to be isostructural with different forms of $CaCO_3$. Usually, small cations of A^{3+} lead to the crystallization of $A^{III}BO_3$ in a calcite type structure which belongs to the trigonal space group R-3c. The A^{3+} caions occupy octahedral positions and can be substituted by Al^{3+}, In^{3+}, Fe^{3+} and Sc^{3+} [2–6]. These compounds have attracted attention because of their

potential applications as photoluminescence materials, laser media, scintillating materials and magnetic materials [7,8].

Gallium borate, $GaBO_3$, has been well studied with respect to luminescence properties [9–11], thermal behavior [12,13] and thermochemistry [14,15] in phase equilibria in the Ga_2O_3-B_2O_3 system. Gallium borate melts incongruently, decomposes to β-Ga_2O_3 above 918 °C, and crystallizes in the calcite-type structure with the unit cell $a = 4.568$ Å and $c = 14.182$ Å by powder X-ray diffraction [16]. Single crystal of calcite-type borates usually are grown by the hydrothermal method [4], high pressure solid state reaction [16] or in a flux. The B_2O_3 [13], Li_2O-B_2O_3 [5,6], B_2O_3-PbO-PbF_2 [17] systems have been proved to be suitable flux for growing calcite-type borates. Recently, Vitzthum *et al.* have also reported the structure of $GaBO_3$ determined from crystals synthesized under high pressure [18]. We report a flux-based crystal growth procedure under ambient pressures to grow crystals up to $4 \times 4 \times 0.2$ mm^3 in size. In this contribution, the flux-based crystal growth procedure, crystal structure, and optical properties of $GaBO_3$ are reported.

2. Results and Discussion

2.1. Crystal Growth

According to a previous study [12] of the thermochemistry of $GaBO_3$ and phase equilibria in the Ga_2O_3-B_2O_3 system, the compound $GaBO_3$ melts incongruently and decomposes to β-Ga_2O_3 above 918 °C. Thus, a flux must be used to grow single crystals. Here, transparent and light yellowish $GaBO_3$ crystals have been grown by spontaneous crystallization in a molten flux based on the Bi_2O_3-$3B_2O_3$ solvent, which has a low melting temperature (708 °C) [19] and good solubility for the calcite type borates [2]. There are two key experimental considerations in order to obtain phase pure $GaBO_3$: (1) The ratio of $GaBO_3$ and Bi_2O_3-$3B_2O_3$; and (2) Annealing procedure. Without enough flux or annealing procedure, single crystals of β-Ga_2O_3 will be obtained as a secondary phase. Simultaneously, too much flux will lead to the formation of a glass because of the high viscosity of B_2O_3. As shown in Figure 1, the $GaBO_3$ crystals have the typical morphology of the calcite type showing forms of well-formed hexagonal plates elongated along the *c*-axis, with sizes up to $4 \times 4 \times 0.2$ mm^3. They are chemically stable with respect to hot water and strong acid.
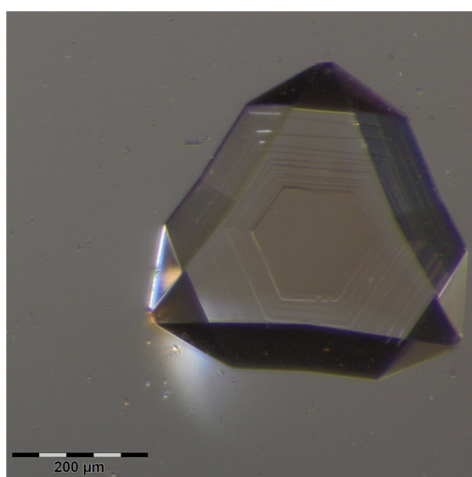
Figure 1. As-grown $GaBO_3$ crystal.

2.2. Structural Analysis

GaBO$_3$ is isostructural with the mineral calcite CaCO$_3$ and other calcite type borates, such as AlBO$_3$, InBO$_3$, FeBO$_3$ and ScBO$_3$. The cell dimensions of GaBO$_3$ (a = 4.56590(10) and c = 14.1764(4) Å) are larger than AlBO$_3$ (a = 4.4638(3) and c = 13.745(1) Å) [4] and smaller than InBO$_3$ (a = 4.8217(8) and c = 15.438(1) Å) [6]. The structure of GaBO$_3$ is illustrated in Figure 2.
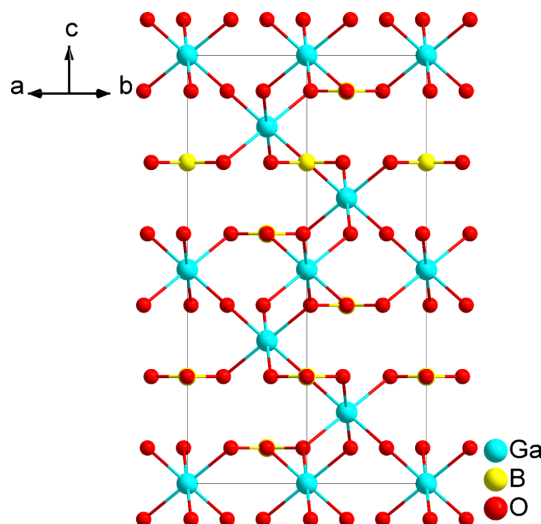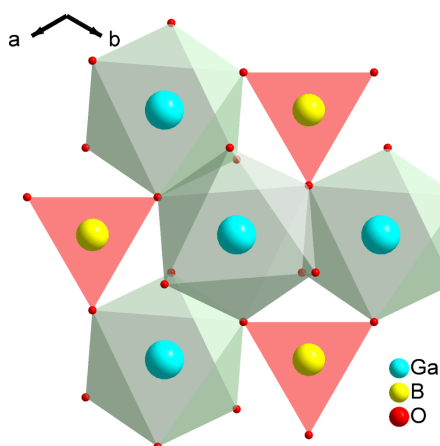

Figure 2. Crystal structure of GaBO$_3$.

GaBO$_3$ crystallizes in the centrosymmetric trigonal space group *R*-3*c*. In the asymmetric unit of GaBO$_3$, Ga, B, and O occupy only one crystallographically unique positions, respectively. The bond length and bond angles are listed in Table 1. It is worthwhile to note that our crystal structure (cell constants, bond distances and angles) agrees very closely with those reported by Vitzthum *et al*. [18].

Table 1. Bond lengths and bond angles for GaBO$_3$ (Å, °)

| Bond lengths (Å)		Bond angles (°)	
Ga–O	1.9875(2)	O–Ga–O	180.00(3)
		O–Ga–O	91.718(7)
		O–Ga–O	91.719(8)
		B–O–Ga	117.055(14)
		O–B–O	120
B–O	1.3789(5)	O–Ga–O	180
		O–Ga–O	88.282(7)
		O–Ga–O	88.281(8)
		Ga–O–Ga	125.89(3)

The B atoms are coordinated to three O atoms to form planar [BO$_3$] triangles with B–O bond lengths 1.3789(5) Å and O–B–O bond angles 120°. The Ga atoms are bound to six O atoms to form distorted [GaO$_6$] octahedra with Ga–O bond lengths 1.9875(2) Å and O–Ga–O bond angles from 88.281(8)° to 180.00(3)°. Each O atom is threefold coordinated with two Ga atoms and one B atom. The compound adopts the classical calcite structure type with Ga-centered distorted octahedra connected by sharing vertices with the isolated [BO$_3$] triangles that extend parallel to the *ab* plane. The [BO$_3$] borate groups

are distributed in layers so that the [BO₃] triangles present reversed orientations in alternating layers, while each [GaO₆] octahedron share only vertices with other six [GaO₆] octahedra (Figure 3), three from the upper layer and three from the lower layer, resulting in the final 3D framework.

Figure 3. The connection of the polyhedra in the structure of GaBO₃ shown along the *c*-axis.

As shown in Figure 4, the powder X-ray diffraction patterns of GaBO₃, as-grown crystals and the theoretical simulations from single crystal structures match each other very well. The differences in peak intensity for the same crystallographic index between the two patterns are believed to be caused by the preferred orientation of the powder samples. The powder patterns also confirmed the presence of small amount of β-Ga₂O₃ as a secondary phase.
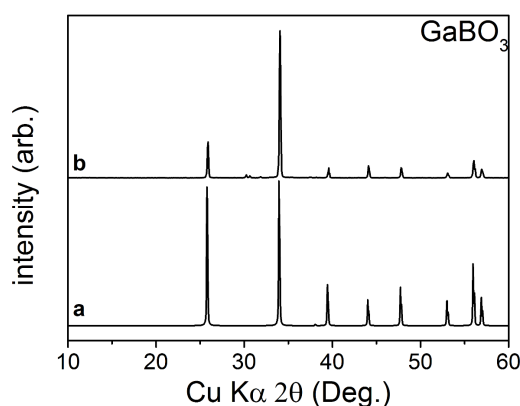

Figure 4. X-ray powder diffraction patterns of (**a**) simulation results, and (**b**) crystal sample.

The result of ICP elemental analysis of GaBO₃ is calculated on the basis of one B atom and three O atoms in each formula unit. The result of $Ga_{0.94}BO_3$ is consistent with the compositions determined from the single crystal X-ray analysis.

2.3. Optical Properties

To confirm the band gap of GaBO₃, transmittance (*T*) and reflectance (*R*) spectra were recorded from single crystals. From *T* and *R*, the absorption coefficient (α) can be determined as a function of incident photon energy. As shown in Figure 5, a linear fit to α^2 *versus* energy gives a band gap 3.62 eV for GaBO₃ crystal.
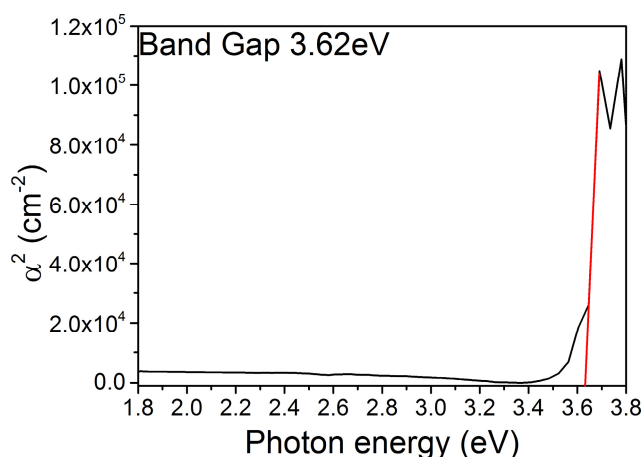
Figure 5. Square of absorption coefficient *vs.* photon energy of a GaBO₃ sample. The optical band gap of the sample was estimated to be 3.62 eV.

3. Experimental Section

3.1. Growth

Single crystals of $GaBO_3$ were grown from a high temperature solution by using Bi_2O_3-$3B_2O_3$ as a flux. This solution was prepared in a platinum crucible with an Al_2O_3 lid by melting a reagent-grade mixture of Bi_2O_3 (99.999%, Alfa-Aesar, Ward Hill, MA, USA), Ga_2O_3 (99.99%, Alfa-Aesar) and B_2O_3 (99.999%, Alfa-Aesar) in a molar ratio of Ga_2O_3:Bi_2O_3:B_2O_3 = 3:4:15. The mixture was heated in a programmable temperature electric furnace at 1000 °C, and held for one day until the melt became transparent and clear. The homogenized melt solution was then cooled rapidly (50 °C/h) to the initial temperature of crystallization 850 °C, and then cooled slowly to the final crystallization temperature 700 °C at the rate of 3 °C/h. After annealing for three days at 700 °C, the melt was allowed to cool to room temperature by turning off the power of the furnace. The flux attached to the crystal was readily dissolved in nitric acid and hot water.

3.2. Elemental Analysis

Elemental analysis of the crystals was performed using a Jobin Yvon Ultima2 inductively coupled plasma optical emission spectrometer (ICP-OES) with Sepex Certiprep standards. The crystal samples were dissolved in a mixture of nitric acid (2 mL), phosphoric acid (3 mL) and hydrochloric acid (5 mL) by microwave digestion at 220 °C for 2 h.

3.3. X-ray Measurements

X-ray diffraction patterns of polycrystalline materials were obtained on a Rigaku Ulitma powder X-ray diffractometer (Rigaku Americas, Woodlands, TX, USA) by using Cu Kα radiation (λ = 1.540598 Å) at room temperature in the angular range of 2θ = 5°–65° with a scan step width of 0.05° and a dwell step of 2 s.

Single crystal X-ray diffraction data were collected at 100 K on a Bruker Kappa APEX II CCD diffractometer (Bruker AXS Inc., Madison, WI, USA) with monochromatic Mo Kα radiation

(λ = 0.71073 Å). A transparent crystal block was mounted on a glass fiber with epoxy for structure determination. The data were integrated using the SAINT program (Bruker AXS Inc., Madison, WI, USA). Absorption corrections based on the Multi-scan technique were applied with SADABS (Bruker AXS Inc., Madison, WI, USA). The structure was solved by direct methods using SHELXS-97 [20] and then refined by full-matrix least-squares refinement on F^2 with SHELXL-97 [20] found in the software suite WinGX v2013.3 [21]. The structure was verified using ADDSYM algorithm from the program PLATON [22], and no higher symmetries were found. Relevant crystallographic data and details of the experimental conditions are summarized in Table 2. Atomic coordinates and isotropic displacement coefficients are listed in Table 3. The Cif document could be found in supplementary information.

Table 2. Crystal data and structure refinement for $GaBO_3$.

Parameter	Data
Formula mass (amu)	128.53
Crystal system	Trigonal
Space group	*R*-3*c*
a (Å)	4.56590(10)
c (Å)	14.1764(4)
V(Å^3)	255.946(11)
Z	6
Crystal size (mm)	0.15 × 0.11 × 0.07
ρ(calcd) (g/cm^3)	5.003
F(000)	360
μ (mm^{-1})	15.716
Absorption correction	Multi-scan
Temperature (K)	100(2)
Wavelength (Å)	0.71073
θ (deg)	5.91–45.16
Index range	$-8 \leq h \leq 9$
	$-8 \leq k \leq 9$
	$-26 \leq l \leq 28$
R_{int}	0.0353
Reflections collected	6025
Independent reflections	242
Reflections ($I > 2\sigma(I)$)	237
Completeness	100%
Data/Restraints/Parameters	242/0/11
R/*wR* ($I > 2\sigma$ (*I*))	0.0153/0.0432
R/*wR* (all data)	0.0155/0.0433
GOF on F^2	1.172
Largest diff. peak and hole (e/Å^{-3})	1.504 and −1.156

Notes: $R(\text{F}) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR(F_o^2) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Table 3. Atomic positions and isotropic displacement factors for $GaBO_3$.

Atom	x	y	z	Wyckoff	$U_{eq}(\text{Å}^2)$	Occupancy
Ga	0	0	0	6b	0.00262(8)	1
B	0	0	1/4	6a	0.0043(3)	1
O	0.30201(12)	0	1/4	18e	0.00391(11)	1

3.4. Optical Measurements

The optical transmission and reflection spectra of single crystal samples were measured with a PerkinElmer Lambda 1050 UV/Vis/NIR spectrometer over the range of 180–860 nm with a photomultiplier tube (PMT). In the transmission configuration, the transmittance T, reflectivity R, and absorption coefficient α are related by the expression

$$\alpha = \frac{1}{d} \ln \left[\frac{(1-R)^2}{2T} + \sqrt{\frac{(1-R)^4}{4T^2} + R^2} \right]$$

where d is the thickness of the sample ($d = 0.2$ mm). The reflectivity was obtained by normalizing the reflectance of the sample to that of a silicon reference, which has a reflectivity of 0.3 at the wavelength regime > 1300 nm. The band gap energy is determined by plotting the square of absorption coefficient, α^2, *versus* photon energy. Extrapolating the linear part of the curve to zero and finding the point of interception with the E axis gives the corresponding band gap energy.

4. Conclusions

Transparent and yellowish calcite type borate $GaBO_3$ crystals have been grown using Bi_2O_3-B_2O_3 as a flux by spontaneous crystallization for the first time. The crystal structure of $GaBO_3$ is refined by single crystal X-ray diffraction. It crystallizes in space group *R*-3c with cell dimensions $a = 4.56590(10)$ and $c = 14.1764(4)$ Å. The transmission spectrum results indicated that band gap of $GaBO_3$ compound is 3.62 eV.

Acknowledgments

Author Contributions

Shichao Wang and Ning Ye conceived the project, Shichao Wang performed the experiments and analyzed the data under the direction of Ning Ye and Kenneth R. Poeppelmeier, and all authors contributed in the manuscript preparation.

Conflicts of Interest

The authors declare no conflict of interest.

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