Ab Initio Structure Determination of a New Compound, β-SrGaBO₄, from Powder X-Ray Diffraction Data

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A new compound, β-SrGaBO₄, has been attained through solid phase transition from α-SrGaBO₄ at high temperatures. Its crystal structure has been determined from powder X-ray diffraction data by direct methods. The refinement was carried out using the Rietveld method and the final refinement converged with $Rp = 11.42\%$ and $Rwp = 15.16\%$. It has an orthorhombic $P2_12_12$ space group with cell parameters $a = 15.3706(2)$ Å, $b = 8.9921(1)$ Å, $c = 5.9191(1)$ Å, and $Z = 8$. The structure of β-SrGaBO₄ is built up from Ga_2BO_8 units formed by two GaO_4 tetrahedra and one BO_3 triangle, and Sr_2O_{12} units formed by two SrO_7 groups. Tetrahedra $[GaO_4]$ are linked by shared $O(3)$ and $O(7)$ atoms to form infinite chains along the c axis. © 2002 Elsevier Science (USA)

Key Words: β-SrGaBO₄; borate; structure determination; X-ray powder diffraction.

1. INTRODUCTION

Alkaline earth borates and rare earth alkaline earth borates, which are used as the hosts of laser materials and nonlinear optical materials, have been studied widely (1, 2). A series of important nonlinear optical materials and laser materials, such β-BaB₂O₄ (BBO)(1) and Ca₄YO(BO₃)₃ (2), have been discovered in these systems. The excellent nonlinear optical properties of borate crystals mainly come from the anionic groups. Based on theoretical work on nonlinear optical susceptibility in crystals (3), the larger the distortions in oxygen polyhedra and the more inhomogeneous the electron density distribution on the bonds in these groups, the higher the values of the second-order microscopic susceptibility. The Ga^{3+} and B^{3+} ions have similar outer electronic structure, and both can be bonded to oxygen tetrahedraly. The ionic radius of the Ga^{3+} ion,

however, is much larger than that of B^{3+} and the bond strength of $Ga^{3+}-O^{2-}$ is much weaker than that of $B^{3+}-O^{2-}$. So the BO_n^{m-} group or complex anionic group in gallium borate or gallium alkaline earth borate may present greater distortion and lead to a bigger second-order microscopic susceptibility. In order to search new ternary compounds with good laser and /or nonlinear optical properties, we investigated the phase relations in $MO-Ga_2O_3-B_2O_3$ (M = Mg, Ca, Sr, Ba), and found some new ternary compounds (4, 5). In this paper, we reported the crystal structure of β-SrGaBO₄, which is a modification of α-SrGaBO₄, solved by direct methods from powder X-ray diffraction data.

2. EXPERIMENTAL PROCEDURE

The specimens were prepared by solid state reaction at high temperatures. The mixtures of SrCO₃ (A.R.), Ga₂O₃ (99.99%), and H₃BO₃ (A.R.) were first heated at 750°C for 5 h to decompose H₃BO₃ and SrCO₃, and then reground and reheated at 910°C for three weeks to obtain α-SrGaBO₄. Finally, β-SrGaBO₄ was obtained by annealing α-SrGaBO₄ at 930°C for a few days. We attempted to grow single crystals using B₂O₃ or LiBO₂ as flux, and no suitable single crystals for structure determination were obtained. All X-ray powder diffraction data were recorded on a Rigaku Rint 2500 X-ray diffractometer with $CuK\alpha$ radiation from a rotating anode. Infrared spectrum was performed with Perkin–Elmer 983G infrared spectrophotometer. A powder second-harmonic generation test was carried out on the β-SrGaBO₄ sample by means of the method of Kurtz and Perry (6). Fundamental 1064-nm light was generated with a Q-switched Nd:YAG laser. Microcrystalline KDP (KH₂PO₄) was used as reference material.

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3. RESULTS AND DISCUSSION

The powder X-ray diffractogram of β-SrGaBO$_4$ could be indexed based on an orthorhombic cell with lattice parameters $a = 15.3706(2)$ Å, $b = 8.9921(1)$ Å, and $c = 5.9191(1)$ Å. One unit cell should contain eight formula. Systematic absences of $h00$ with $h = 2n + 1$; $0k0$ with $k = 2n + 1$ suggest that its space group is $P2_12_12$.

Due to the lack of suitable single crystals and similar structure model, the crystal structure of β-SrGaBO$_4$ was determined using powder X-ray diffraction techniques. The powder X-ray diffraction data were collected in a 2θ range of $10°$ to $135°$. In order to establish the structure model of β-SrGaBO$_4$, a full-pattern decomposition program EXTRA (7) was used to extract integrated intensities from the powder diffractogram. By refining the lattice constants, the background and the profile parameters, a total of 574 individual reflection intensities (227 nonoverlapping) were obtained in a 2θ range of $10°$ to $105°$.

The structure was solved by direct methods with the program SIRPOW92 (8). Some possible space groups, for example, $Pbam$, $Pba2$, and $P2_12_12_1$, were ever employed in the course of establishing structure model of beta phase by direct methods from powder X-ray diffraction data. As $Pba2$ or $Pbam$ was employed, the atomic positions were floating along the c axis. Because the diffraction peaks of $(00l)$ are not observed, so the space group, $P2_12_12_1$, also was employed, but some atomic positions were not found. Finally, we selected $P2_12_12$ as its right space group. Twelve independent atomic positions (two Sr, two Ga, seven O, and one B) were located from the E-map. The last two
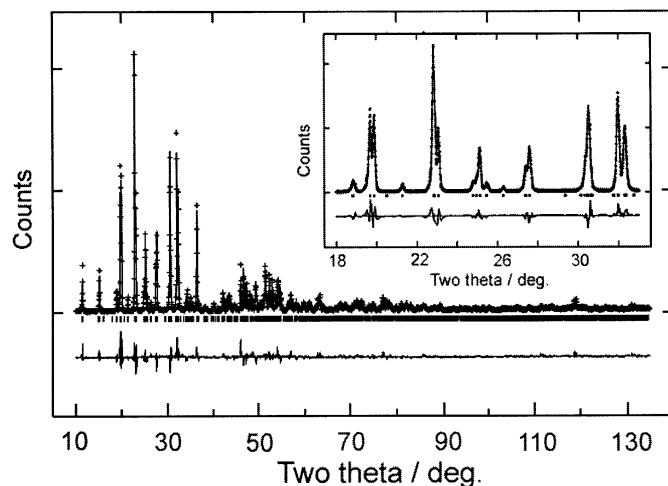
independent atomic positions, one O, and one B, were found by difference Fourier map using the program GSAS (9). The crystal structure obtained by using direct methods was refined with the Rietveld method by the program GSAS (9). All atomic positions were refined isotropically

TABLE 1
Crystal Data and Structure Refinement for β-SrGaBO$_4$

Molecular formula	β-SrGaBO$_4$
Formula weight	232.15
Crystal system	Orthorhombic
Space group	$P2_12_12$ (No. 18)
Unit cell dimensions (Å)	$a = 15.3706(2)$, $b = 8.9921(1)$, $c = 5.9191(1)$
Volume (Å^3)	$v = 818.11(2)$
Z	8
Density (cal., g/cm^3)	3.770
	Data collection
Diffractometer used	Rigaku Rint 2500
Monochrometer	Graphite
Temperature	Room temperature
Radiation	Cu$K\alpha$
2θ range for data collection	10 to 135°
	Data extraction
Program used	EXTRA
Profile function	Lorentzian
2θ range for extraction	10 to 105°
Step size (2θ)	0.01°
Step scan time (s)	1
Reflections	574
Independent reflections	227
	Structure determination
Solution	Direct method
System used	SIRPOW 92
Refinement	Rietveld method
Program used	GSAS
Final R indices	Rp = 11.42%, Rwp = 15.16%, and Rexp = 5.97

FIG. 1. Rietveld refinement of powder X-ray diffractogram of β-SrGaBO$_4$. The cross symbols (+) are observed data, the continuous line corresponds to the calculated spectrum, and vertical bars (|) indicate the positions of Bragg peaks. The bottom trace depicts the difference between the experimental and calculated intensity values.

TABLE 2
Atomic Coordinates for β-SrGaBO$_4$

Atom	x	y	z	B^a/Å^2
Sr1	0.1218(1)	−0.0716(2)	0.5001(21)	1.0
Sr2	0.5220(1)	0.2863(2)	0.0076(17)	1.0
Ga1	0.3498(3)	0.0341(6)	0.7571(18)	1.0
Ga2	0.3412(3)	0.0428(6)	0.2499(19)	1.0
O1	0.0981(6)	−0.0364(11)	−0.003(11)	1.0
O2	0.4015(14)	−0.1264(22)	0.272(6)	1.0
*O3	0.3671	0.1505	0.5041	1.0
O4	0.5941(14)	0.1461(22)	0.683(6)	1.0
O5	0.2323(12)	−0.0386(19)	0.198(5)	1.0
O6	0.2278(13)	−0.0007(20)	0.795(5)	1.0
*O7	0.3950	0.1300	0.0080	1.0
O8	0.0306(6)	0.1794(12)	0.478(7)	1.0
*B1	0.1850	−0.0317	0.0050	1.0
*B2	0.0850	0.2950	0.5300	1.0
$a = 15.3707(2)$ Å, $b = 8.9921(1)$ Å, $c = 5.9191(1)$ Å, $v = 818.11(2)$ Å^3				

^{a}Not refined.

TABLE 3
Selected Inter-atomic Distances and Angles in β-SrGaBO$_4$

Distances (Å)

B(1)–O(1)	1.337(10)	Ga(1)–O(3)	1.847(9)	Sr(1)–O(1b)	3.02(6)
B(1)–O(5)	1.353(28)	Ga(1)–O(4)	1.887(20)	Sr(1)–O(1a)	2.98(6)
B(1)–O(6)	1.433(29)	Ga(1)–O(6)	1.913(20)	Sr(1)–O(3)	2.505(2)
		Ga(1)–O(7)	1.853(9)	Sr(1)–O(5)	2.486(26)
				Sr(1)–O(6)	2.472(27)
				Sr(1)–O(8b)	2.661(11)
				Sr(1)–O(8a)	2.539(10)
Mean		Mean		Mean	
B(1)–(O)	1.374	Ga(1)–(O)	1.875	Sr(1)–(O)	2.666
B(2)–O(2)	1.386(27)	Ga(2)–O(2)	1.787(20)	Sr(2)–O(1b)	2.536(10)
B(2)–O(4)	1.373(30)	Ga(2)–O(3)	1.833(9)	Sr(2)–O(1a)	2.439(10)
B(2)–O(8)	1.369(14)	Ga(2)–O(5)	1.852(19)	Sr(2)–O(2)	2.428(30)
		Ga(2)–O(7)	1.830(9)	Sr(2)–O(4)	2.553(32)
				Sr(2)–O(7)	2.405(2)
				Sr(2)–O(8a)	2.89(4)
				Sr(2)–O(8b)	3.06(4)
Mean		Mean		Mean	
B(2)–(O)	1.376	Ga(2)–(O)	1.826	Sr(2)-(O)	2.615

Angles (°)

O(1)–B(1)–O(5)	124.5(31)	O(3)–Ga(1)–O(4)	103.4(11)	O(8a)–Sr(1)–O(8b)	80.5(4)
O(1)–B(1)–O(6)	115.6(30)	O(3)–Ga(1)–O(6)	109.2(8)	O(8a)–Sr(1)–O(3)	71.4(3)
O(5)–B(1)–O(6)	119.5(6)	O(3)–Ga(1)–O(7)	109.4(3)	O(8a)–Sr(1)–O(1a)	88.8(9)
		O(4)–Ga(1)–O(6)	109.6(9)	O(8a)–Sr(1)–O(1b)	83.9(9)
		O(4)–Ga(1)–O(7)	114.5(9)	O(5)–Sr(1)–O(6)	91.6(4)
		O(6)–Ga(1)–O(7)	110.5(10)	O(5)–Sr(1)–O(3)	93.8(5)
				O(5)–Sr(1)–O(1b)	50.1(6)
				O(5)–Sr(1)–O(8b)	102.9(8)
				O(6)–Sr(1)–O(3)	102.7(5)
				O(6)–Sr(1)–O(1a)	49.9(7)
				O(6)–Sr(1)–O(8b)	99.4(8)
				O(3)–Sr(1)–O(1b)	95.9(4)
				O(3)–Sr(1)–O(1a)	97.1(4)
				O(1a)–Sr(1)–O(8b)	83.0(9)
				O(8b)–Sr(1)–O(1b)	78.4(9)
O(2)–B(2)–O(4)	124.4(6)	O(2)–Ga(2)–O(3)	106.1(11)	O(1b)–Sr(2)–O(1a)	76.6(6)
O(2)–B(2)–O(8)	132.0(20)	O(2)–Ga(2)–O(5)	98.3(9)	O(1b)–Sr(2)–O(8b)	84.3(4)
O(4)–B(2)–O(8)	98.6(20)	O(2)–Ga(2) –O(7)	100.8(9)	O(1b)–Sr(2)–O(2)	108.0(9)
		O(3)–Ga(2)–O(5)	122.8(9)	O(1b)–Sr(2)–O(4)	103.3(8)
		O(3)–Ga(2)–O(7)	108.5(3)	O(1b)–Sr(2)–O(8a)	82.7(4)
		O(5)–Ga(2)–O(7)	116.5(10)	O(7)–Sr(2)–O(1a)	76.5(7)
				O(7)–Sr(2)–O(8b)	95.3(4)
				O(7)–Sr(2)–O(2)	92.7(5)
				O(7)–Sr(2)–O(4)	93.7(5)
				O(7)–Sr(2)–O(8a)	95.7(6)
				O(1a)–Sr(2)–O(8b)	88.7(4)
				O(8b)–Sr(2)–O(2)	53.0(1)
				O(2)–Sr(2)–O(4)	89.0(4)
				O(4)–Sr(2)–O(8a)	44.3(4)
				O(8a)–Sr(2)–O(1a)	87.3(4)

and their thermal parameters are set to be 1 Å^2. The final position of boron atom is adjusted based on the requirement of both the B–O bond length and the shape of a BO$_3$ triangle. During refinement process, we found that the positions of O(3) and O(7) that link Ga(1)O$_4$ and Ga(2)O$_4$ tetrahedra are not reasonable. The bond length of Ga(1, 2)–

O(3, 7) is longer (or shorter) than that of Ga(2, 1)–O(3, 7). Considering the reasonable bond length range of Ga–O in GaO$_4$ tetrahedra, the final positions of O(3) and O(7) were also adjusted. In the course of last refinement, the bond lengths of B–O in BO$_3$ and Ga–O3 (O7) in GaO$_4$ were restricted; i.e., the atomic positions of B in BO$_3$ triangles
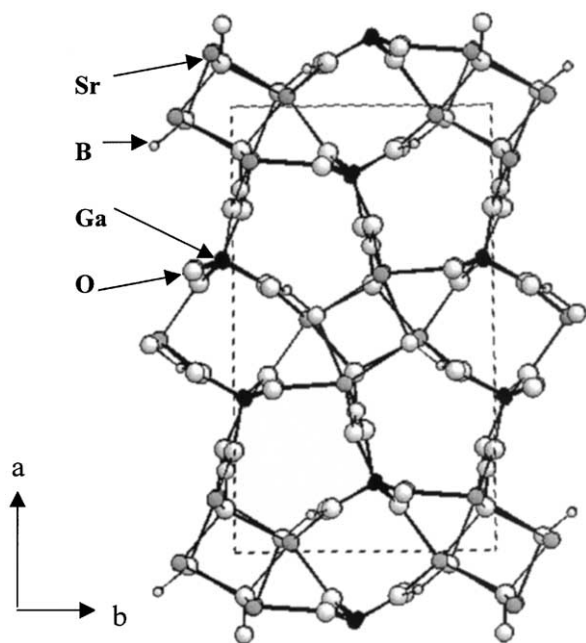
FIG. 2. Projection of the structure of β-SrGaBO$_4$ along [001].

The unit cell of β-SrGaBO$_4$ consists of 8 Sr, 8 Ga, 8 B, and 32 O atoms, all are located on the general Wyckoff positions. Figure 2 shows the projection of the structure of β-SrGaBO$_4$ along the c axis. The structure contains infinite

and O3 (O7) in GaO$_4$ tetrahedra were fixed. The final residual factors of the refinement are Rp = 11.42% and Rwp = 15.16%. In Fig. 1, we show the refined powder X-ray diffractogram. Experimental detail and crystallographic detail are summarized in Table 1. The final atomic coordinates are listed in Table 2. Some selected bond lengths and angles are given in Table 3.
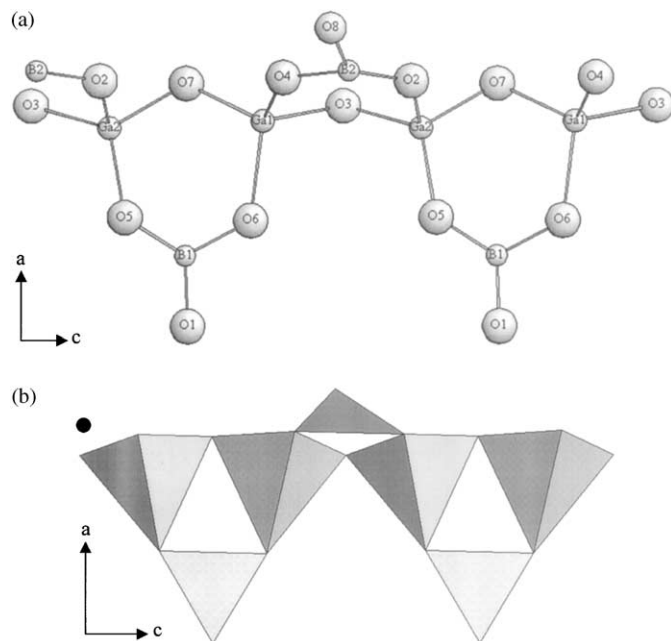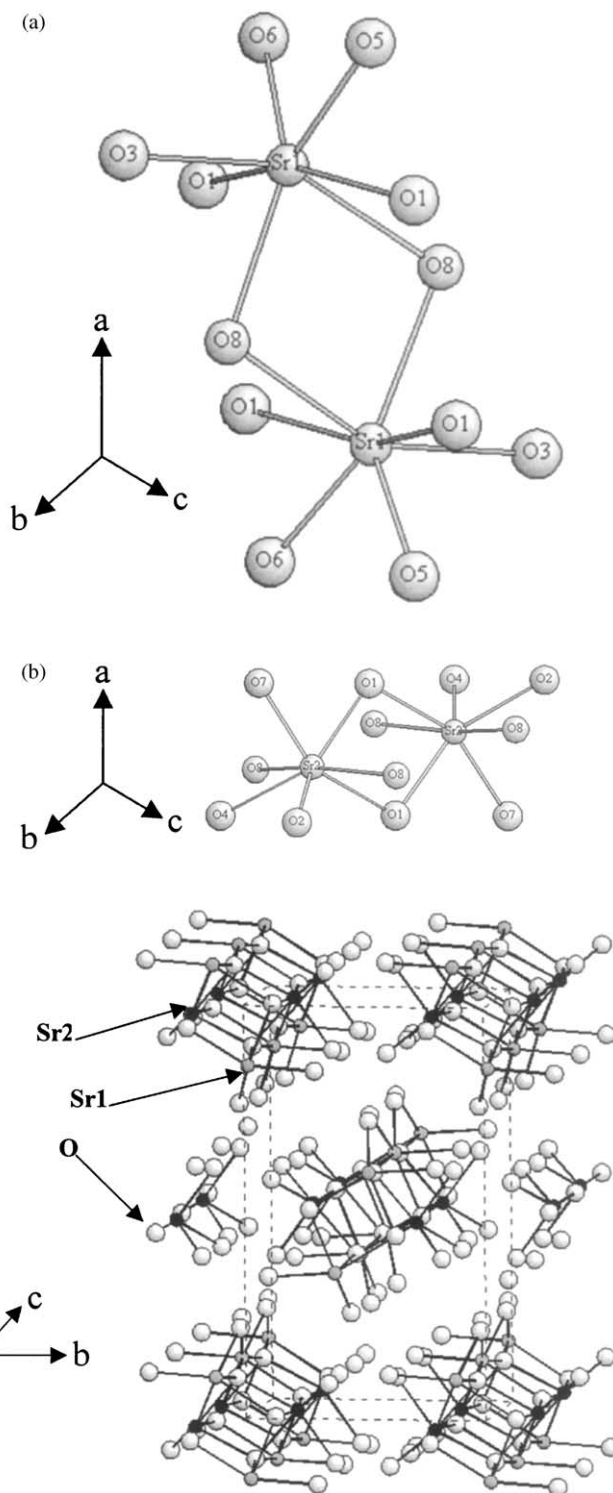

FIG. 3. The Ga$_2$BO$_8$ group.

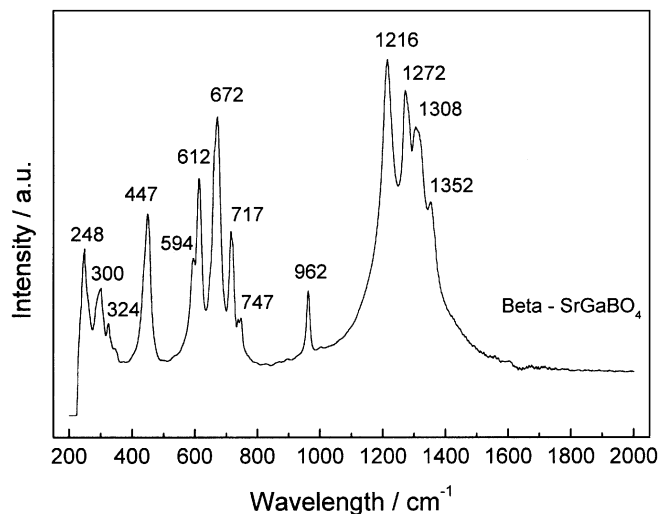**FIG. 4.** Coordination surroundings of Sr with O atoms.

FIG. 5. IR spectrum of β-SrGaBO$_4$ at room temperature.

chains built up from Ga(1)O$_4$ and Ga(2)O$_4$ tetrahedra by shared O(3) and O(7) atoms along the c axis (Fig. 3). Both Ga$_2$B(1)O$_8$ and Ga$_2$B(2)O$_8$ groups are formed by two GaO$_4$ tetrahedra and one BO$_3$ triangle with shared O atoms (Fig. 3). In Ga$_2$B(1)O$_8$ group, O(7) is shared with Ga(1)O$_4$ and Ga(2)O$_4$ tetrahedra, while O(5) and O(6) atoms are shared with two GaO$_4$ tetrahedra and one B(1)O$_3$ triangle. In another Ga$_2$B(2)O$_8$ group, O(3) atom is shared with Ga(1)O$_4$ and Ga(2)O$_4$ tetrahedra; however, O(4) and O(2) atoms are shared with two GaO$_4$ tetrahedra and B(2)O$_3$ triangle. In this structure, the Sr atoms occupy two cation sites. Each Sr atom is surrounded by seven O atoms. Pentacoordinated Sr atoms are characterized by two longer Sr–O distances (between 2.89 and 3.02 Å) and five shorter ones (between 2.405 and 2.553 Å) (see Table 3). Two Sr(2)O$_7$ groups are linked by O(1a) and O(1b) atoms to form a Sr$_2$(2)O$_{12}$ group. In the same way, two Sr(1)O$_7$ groups are also linked by O(8a) and O(8b) atoms to form a Sr$_2$(1)O$_{12}$ group. Sr$_2$(1)O$_{12}$ and Sr$_2$(2)O$_{12}$ groups are arrayed alternately by shared O(1) and O(8) atoms along the c axis (Fig. 4c). The coordination environments of Sr, Ga, and B atoms by O atoms are presented in Figs. 3 and 4.

In order to confirm the coordination surroundings of B–O in β-SrGaBO$_4$ structure, IR spectrum of β-SrGaBO$_4$ was measured at room temperature and given in Fig. 5. The IR absorption at wavenumbers smaller than 800 cm^{-1} originate mainly from the lattice dynamic modes and will not be considered duo to its complexity. According to previous work (10), the observed frequencies at $\sim$1300 cm^{-1} are characteristic of triangle BO$_3$ units.

The rationality of this structure is examined by the bond valence theory. The bond valence calculations were performed using the Brown–Altermatt empirical expression (11): with $B = 0.37$ Å. We have used 2.118, 1.730, and 1.371 Å for the Sr^{2+}, Ga^{3+}, and B^{3+} R_0 values respectively (11). The bond valence calculations V are listed in Table 4. The bond valence sum of each cation is in agreement with the formal oxidation state, indicating this structure is reasonable.

Ga has been introduced successfully into six-membered [B$_3$O$_8$]$^{7-}$ rings, as the properties of the Ga atom are very much different from those of B. The bond length of Ga–O in GaO$_4$ tetrahedra is more than 1.8 Å, while that of B–O in BO$_4$ tetrahedra is less than 1.5 Å, so the distribution of electron density on the [Ga$_2$BO$_8$]$^{7-}$ ring will be expected to be more inhomogeneous than that on the [B$_3$O$_8$]$^{7-}$ ring, and will lead to a higher second-order microscopic susceptibility. The powder SHG measurement confirmed that the structure of β-SrGaBO$_4$ is noncentrosymmetric. However, β-SrGaBO$_4$ was found to have SGH effect about 1/2 compared with that of KDP.

4. CONCLUSION

In this work a new compound, β-SrGaBO$_4$, has been synthesized by solid state reaction and the crystal structure has been studied by means of powder X-ray diffraction techniques. The structure of β-SrGaBO$_4$ is built up from Ga$_2$BO$_8$ units formed by both two GaO$_4$ tetrahedra and one BO$_3$ triangle, and Sr$_2$O$_{12}$ units formed by two SrO$_7$ groups. The Ga$_2$BO$_8$ unit can be characterized as a B$_2$BO$_8$ unit with the tetracoordinated B replaced by two Ga atoms. The similar units Ga$_2$BO$_8$ and Al$_2$BO$_8$ could be

TABLE 4
Ga–O, Sr–O and B–O Bond Valences in β-SrGaBO$_4$

	C.N.	O1	O2	O3	O4	O5	O6	O7	O8	V
Sr1	7	0.097 + 0.087		0.351		0.370	0.384		0.321 + 0.230	1.840
Sr2	7	0.420 + 0.323	0.433		0.309			0.460	0.124 + 0.078	2.147
Ga1	4		0.729	0.654			0.610	0.717		2.710
Ga2	4		0.857	0.757		0.719		0.763		3.096
B1	3	1.096				1.050	0.846			2.992
B2	3		0.960		0.995			1.005		2.960
V		2.023	2.250	1.837	1.958	2.139	1.840	1.940	1.758	

separated from the structures of $CaGaBO_4$ (5) and $CaAlBO_4$ (12), respectively. These complex units are arrayed alternately by shared O atoms to form infinite chains along the c axis.

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