A New Lanthanum and Calcium Borate $La_2CaB_{10}O_{19}$

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A new lanthanum calcium borate with the composition $La_2CaB_{10}O_{19}$ has been synthesized. Single crystals have been grown from a melt close to the stoichiometric composition. The compound crystallizes in the monoclinic system, space group *C*2, with $a = 11.043(3)$ Å, $b = 6.563(2)$ Å, $c = 9.129(2)$ Å, $\alpha = \gamma = 90°$, $\beta = 91.47°$, and two formula units per cell. The crystal structure contains B_5O_{12} double-ring pentaborate groups, which are linked together to form an infinite two-dimensional double layer. The layer runs almost perpendicular to the *c* axis of the crystal. The La atoms are located in layers, while the Ca atoms are located between two layers. $La_2CaB_{10}O_{19}$ exhibits an optical second-harmonic generation effect about twice as large as that of KDP (KH_2PO_4).

Introduction

In the past few years several new rare-earth (R) calcium borates such as $RCa_4O(BO_3)_3$, $R_2CaO(BO_3)_2$, and $RCaB_7O_{13}$ have been synthesized[1−3] in the ternary system $R_2O_3-CaO-B_2O_3$. Among them, $RCa_4O(BO_3)_3$ has attracted considerable interest as a potential material for nonlinear optical (NLO) applications because it exhibits a relatively large second-harmonic generation (SHG) effect,[4] and the single crystal is easily grown.[5] Recently, we discovered a new class of rare-earth borates of composition $R_2CaB_{10}O_{19}$ with a powder SHG effect as large as that of $RCa_4O(BO_3)_3$.[6] In this paper, we describe the synthesis, crystal growth, structure, and nonlinear optical properties of $La_2CaB_{10}O_{19}$ (LCB), one member of the $R_2CaB_{10}O_{19}$ family.

Experimental Section

Synthesis and Crystal Growth. A powder sample of $La_2CaB_{10}O_{19}$ was prepared by using solid-state reaction techniques and then examined by X-ray powder diffraction analysis. A stoichiometric ratio of La_2O_3, $CaCO_3$, and H_3BO_3 (all of analytical grade) was mixed thoroughly. The mixture was heated at 450 °C for 10 h and again at 930 °C for 24 h at least twice. The material was ground between all heatings. A single-phase powder of $La_2CaB_{10}O_{19}$ was obtained when repeated heat treatment caused no further changes in the X-ray powder diffraction pattern. LCB crystal was grown from the melt with a 30 mol % excess of CaB_4O_7 compared to the stoichiometric composition under a temperature of 1043 °C. The temperature of the melt was slowly reduced at a rate of 0.5 °C/day. The experiments were carried out in a resistance-heated furnace. To prepare large single crystals, seeded growth was used. The seed crystal of LCB was obtained by means of spontaneous crystallization from the melt.

Differential Thermal Analysis. The melting behavior of LCB was investigated by differential thermal analysis (DTA) performed on a Shimadzu DTA-50 differential thermal analyzer in a N_2 atmosphere at a heating rate of 10 °C/min.

Density Measurement. The LCB crystal density was determined at 28 °C by using a JN-A torsion balance.

Element Content Determination. The La, Ca, and B contents in the crystal were determined by using an ICP-6500 plasma spectrometer.

X-ray Crystallography. X-ray powder diffraction analysis for LCB was performed with a Bruker D8 ADVANCE X-ray diffractometer with Cu $K\alpha_1$ radiation. Table 1 presents the X-ray powder diffraction pattern of $La_2CaB_{10}O_{19}$. The crystal structure of LCB was investigated by using a Rigaku AFC5R automatic diffractometer (graphite monochromator, Mo $K\alpha$ radiation). The experimental parameters for data collection and refinement are given in Table 2. Lorentz and polarizing effect corrections were performed before the refinement of the structure. An empirical absorption correction from the ψ-scan data was applied. The structure was solved with Shelxs-86 by the Patterson method and refined with Shelxl-93 by full-matrix least-squares techniques with anisotropic thermal parameters for all atoms. The Flack absolute structure parameter[7] was estimated in the final structure factor summation. The final refined atomic positions and isotropic thermal parameters are given in Table 3. The main interatomic distances are listed in Table 4.

Second-Harmonic Generation Measurement. A powder second-harmonic generation test was carried out on the LCB

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Table 1. X-ray Powder Diffraction Pattern of $La_2CaB_{10}O_{19}$

h	*k*	*l*	d_{calc}	d_{obs}	I/I_0	*h*	*k*	*l*	d_{calc}	d_{obs}	I/I_0
0	0	1	9.1260	9.11252	51.3	1	1	$\bar{4}$	2.1248	2.12111	7.0
1	1	0	5.6413	5.63636	37.3	4	2	0	2.1122	2.10990	10.6
1	1	$\bar{1}$	4.8269	4.81887	53.7	1	1	4	2.1055	2.10080	12.1
1	1	1	4.7707	4.75408	10.6	2	0	$\bar{4}$	2.0896	2.08856	28.3
2	0	1	4.6702	4.66248	12.5	2	2	$\bar{3}$	2.0820	2.07838	10.6
0	0	$\bar{2}$	4.5630	4.55179	10.0	4	2	$\bar{1}$	2.0667	2.06525	27.9
2	0	$\bar{2}$	3.5620	3.56507	54.7	4	2	1	2.0489	2.04764	10.4
1	1	2	3.5252	3.51959	25.7	5	1	1	2.0290	2.02714	9.4
0	2	0	3.2815	3.27801	25.7	1	3	2	1.9382	1.93616	16.2
3	1	0	3.2097	3.20636	30.3	4	2	2	1.9026	1.90017	8.2
3	1	$\bar{1}$	3.0493	3.04812	5.3	3	3	0	1.8804	1.88059	8.7
0	0	3	3.0420	3.03607	100.0	0	2	4	1.8732	1.87260	7.2
3	1	1	3.0069	3.00361	6.1	6	0	0	1.8399	1.83855	9.8
2	2	0	2.8207	2.81884	40.9	4	0	$\bar{4}$	1.7810	1.77946	7.6
2	2	$\bar{1}$	2.7049	2.70262	11.4	1	1	$\bar{5}$	1.7433	1.74221	4.2
2	2	1	2.6850	2.67988	10.6	2	0	5	1.7198	1.71789	4.7
3	1	$\bar{2}$	2.6534	2.65702	22.8	0	4	0	1.6408	1.64017	4.5
2	2	$\bar{2}$	2.4135	2.41147	8.8	6	2	0	1.6048	1.60467	2.2
2	2	2	2.3853	2.38268	15.4	3	3	3	1.5902	1.58981	3.0
4	0	2	2.3351	2.33187	8.6	2	4	0	1.5727	1.57305	2.9
0	0	4	2.2815	2.27665	15.3	2	4	1	1.5480	1.54849	1.1
0	2	3	2.2309	2.22891	11.2	0	0	6	1.5210	1.52041	4.8
3	1	3	2.1837	2.17922	1.5	2	4	$\bar{2}$	1.4903	1.49013	5.2
1	3	0	2.1459	2.14520	6.9						

Table 2. Crystal Data and Structure Refinement

formula	$La_2CaB_{10}O_{19}$
temperature	20 °C
wavelength	0.71069 Å
space group	*C*2
a	11.043(3) Å
b	6.563(2) Å
c	9.129(2) Å
β	91.47°
volume	661.4(3) Å^3
Z	2
density (calculated)	3.665 g/cm^3
absorption coefficient	6.886/mm
max./min. transmission	0.4248/0.2318
crystal size	0.15 × 0.2 × 0.3 mm
θ range for data collection	2.23°−39.98°
index ranges	$-19 \le h \le 19$, $0 \le k \le 11$, $0 \le 1 \le 16$
reflections collected	2139
independent reflections	2139
refinement method	full-matrix least-squares on F^2
data/restraints/params	2084/0/148
goodness-of-fit on F^2	0.816
final *R* indices [$I > 2\sigma(I)$]	R1=0.0389 wR2=0.0798
R indices (all data)	R1=0.0389, wR2=0.0917
absolute structure param.	0.01(3)
extinction coefficient	0.194(7)
largest diff. peak and hole	2.339 and −5.965 e Å^{-3}

sample by means of the method of Kurtz and Perry.[8] Fundamental 1064-nm light was generated with a Q-switched Nd:YAG laser. Microcrystalline KDP (KH_2PO_4) served as the standard.

Results and Discussion

The differential thermal curve for LCB (Figure 1) shows a sharp endothermal peak associated with the melting of LCB at 1043 °C followed by a wide and flat endothermal effect beginning at about 1062 °C. The latter is associated with the dissolution of a higher melting product of a peritectic decomposition due to incongruent melting behavior.

The crystal of LCB can be easily grown. The typical size of a single crystal obtained from the melt at a pulling rate of 0.5−1 mm/h is ϕ 14 × 25 mm. The crystal is clear and colorless. It is chemically stable and not hygroscopic. The hardness of the crystal is 6.5 Mohs, close to that of quartz. The element content determination suggests that the ratio of La to Ca to B atoms in the crystal is 2 (±0.04) to 1.06 (±0.02) to 9.9 (±0.20),

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Table 3. Final Refined Atomic Positions (×10^4) and U_{eq} (×10^3)

atom	*x*	*y*	*z*	U_{eq}
La(1)	1624(1)	0	1405(1)	6(1)
Ca(1)	0	−1855(2)	5000	7(1)
O(1)	0	−2350(9)	0	6(1)
O(2)	3884(3)	−231(6)	1124(4)	6(1)
O(3)	3218(3)	3112(6)	1359(4)	7(1)
O(4)	−714(3)	1234(6)	1319(4)	7(1)
O(5)	2158(3)	−3745(6)	1790(4)	5(1)
O(6)	722(3)	3528(6)	2213(5)	9(1)
O(7)	157(3)	−2905(6)	2537(4)	6(1)
O(8)	1939(3)	−4(12)	3903(3)	11(1)
O(9)	−1482(3)	−4464(7)	5732(4)	8(1)
O(10)	1456(3)	−8(15)	6372(3)	9(1)
B(1)	4326(5)	1919(10)	1249(6)	7(1)
B(2)	−397(5)	3219(9)	1608(6)	6(1)
B(3)	3272(4)	−4884(14)	2072(5)	6(1)
B(4)	1142(4)	−4406(9)	2688(6)	6(1)
B(5)	2327(5)	212(12)	5289(5)	8(1)

Table 4. Selected Bond Distances (Å)

atoms	distance	atoms	distance
La(1)−O(8)	2.297(3)	Ca(1)−O(10)	2.349(5)
La(1)−O(2)	2.520(4)	Ca(1)−O(10)#3	2.349(5)
La(1)−O(5)	2.550(4)	Ca(1)−O(7)	2.362(3)
La(1)−O(6)	2.633(4)	Ca(1)−O(7)#3	2.362(3)
La(1)−O(1)	2.669(3)	Ca(1)−O(9)	2.472(4)
La(1)−O(4)	2.705(4)	Ca(1)−O(9)#3	2.472(4)
La(1)−O(3)	2.698(4)	Ca(1)−O(8)	2.678(5)
La(1)−O(7)	2.722(4)	Ca(1)−O(8)#3	2.678(5)
La(1)−O(4)#1	2.779(4)		
La(1)−O(3)#2	2.821(4)		
B(1)−O(1)#4	1.459(6)	B(4)−O(7)	1.471(6)
B(1)−O(3)	1.457(7)	B(4)−O(5)	1.472(6)
B(1)−O(7)#4	1.478(7)	B(4)−O(6)#7	1.494(7)
B(1)−O(2)	1.497(8)	B(4)−O(9)#3	1.481(6)
B(2)−O(2)#5	1.358(7)	B(5)−O(8)	1.333(6)
B(2)−O(6)	1.356(7)	B(5)−O(9)#4	1.383(7)
B(2)−O(4)	1.372(8)	B(5)−O(10)	1.404(6)
B(3)−O(10)#6	1.447(5)		
B(3)−O(3)#7	1.468(9)		
B(3)−O(5)	1.456(7)		
B(3)−O(4)#8	1.518(7)		

[a] Note. Symmetry transformations used to generate equivalent atoms: (#1) $-x, y, -z$; (#2) $-x + 1/2, y - 1/2, -z$; (#3) $-x, y, -z + 1$; (#4) $x + 1/2, y + 1/2, z$; (#5) $x - 1/2, y + 1/2, z$; (#6) $-x + 1/2, y - 1/2, -z + 1$; (#7) $x, y - 1, z$; (#8) $x + 1/2, y - 1/2, z$; (#9) $x - 1/2, y - 1/2, z$; (#10) $x, y + 1, z$; (#11) $-x + 1/2, y + 1/2, -z$; (#12) $-x + 1/2, y + 1/2, -z + 1$.

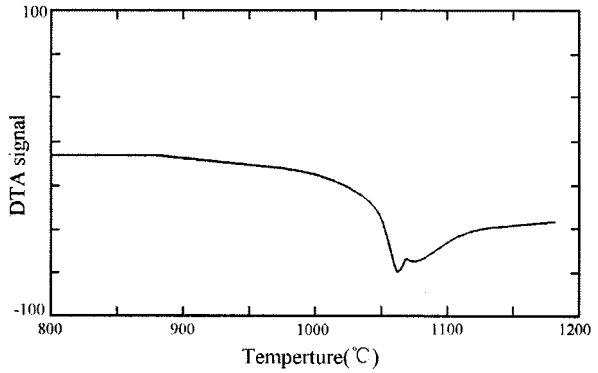

Figure 1. Differential thermal curve for $La_2CaB_{10}O_{19}$.

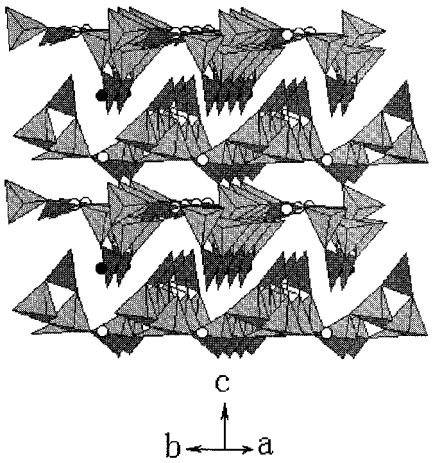

Figure 2. Polyhedral representation of the $La_2CaB_{10}O_{19}$ structure. The structure contains the infinite two-dimensional double layers running almost perpendicular to the *c* axis of the crystal. The La atoms are located in layers, while the Ca atoms are located between two layers. The open circles represent La atoms, and the filled circles represent Ca atoms.

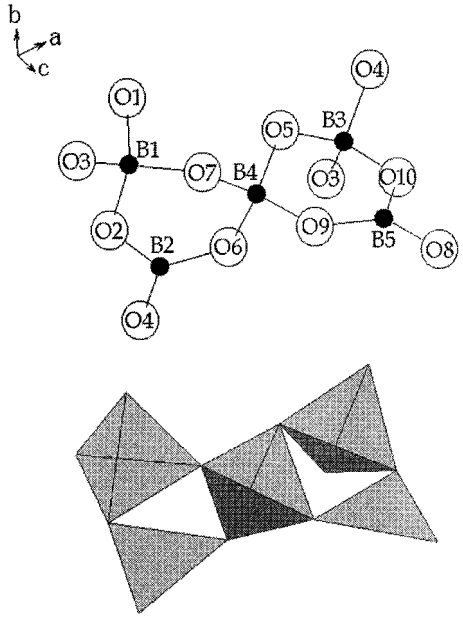

Figure 3. The B_5O_{12} group.

which agrees with the composition of the compound, $La_2CaB_{10}O_{19}$, confirmed by determining the crystal structure within experimental error. The experimental value for the density of the crystal is 3.65 g/cm^3, which is in good agreement with the calculated value 3.665 g/cm^3.

Figure 2 represents a view of the structure of LCB. The structure contains layers built up from B_5O_{12} double-ring pentaborate groups. The B_5O_{12} group is formed by three BO_4 tetrahedra and two BO_3 triangles with shared O atoms (Figure 3). In this group, O(5) and O(7) atoms are shared with other BO_4 tetrahedra, while O(2), O(6), O(9), and O(10) atoms are shared with BO_4 tetrahedra and BO_3 triangles. B_5O_{12} groups are linked together to form an infinite two-dimensional double layer by sharing O(3) and O(4) atoms with one another. In this layer, upper and lower networks are connected by shared O(1) atoms. The layer runs almost perpendicular to the *c* axis of the crystal. The La atoms are located in layers, while the Ca atoms are located between two layers. The coordination environments of La and Ca atoms by O atoms are shown in Figure 4. The La atom is surrounded by ten O atoms. It is linked to the O(8) atom at a significantly shorter distance of 2.297(3) Å and to the other nine O atoms at longer distances from 2.520(4) to 2.821(4) Å. On the other hand, the Ca atom is coordinated by eight O atoms, that is, O(10), O(7), O(9), and O(8). The distance between Ca and O(10) is 2.349(5) Å. Those between Ca and O(7), O(9), and O(8) are 2.362(3), 2.472(4), and 2.678(5) Å, respectively. The infinite two-dimensional layers built up from B_5O_{12} double-ring pentaborate groups have previously been reported in the structures of rare earth borate $CoLa[B_5O_{10}]$ and analogues.[9] As an isolated unit, the B_5O_{12} group contains six terminal O atoms, but four of them in the $CoLa[B_5O_{10}]$ structure and five of them in the $La_2CaB_{10}O_{19}$ structure, respectively, are shared with like units.

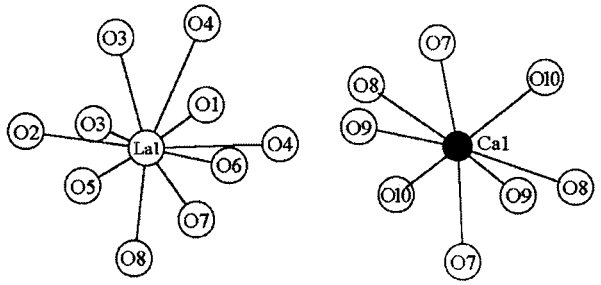

Figure 4. Oxygen coordination to the La and Ca atoms.

The compound crystallizes in a noncentrosymmetric space group, a basic condition for a potential harmonic generation material. According to the anionic group theory,[10] the nonlinearity of a borate crystal originates in the boron−oxygen groups, so borates containing BO_3 groups or more complex groups made of BO_3 triangles such as B_3O_7, B_3O_8, and B_5O_{12} groups could be expected to possess a SHG effect 2−3 times larger than that of KDP. In fact, LCB was found to have a powder SHG effect about twice as large as that of KDP.

In conclusion, a new borate of lanthanum and calcium $La_2CaB_{10}O_{19}$ has been synthesized and the crystal structure has been studied. The crystal can be easily grown from a melt reasonably close to the stoichiometeric composition and exhibits a SHG effect about twice as large as that of KDP. These advantages make it attractive for continued research and development as a NLO material.

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Supporting Information Available: Tables of structure factors, anisotropic displacement factors, and bond lengths and angles for $La_2CaB_{10}O_{19}$ (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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