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Ab initio structure determination of new compound $Li_4CaB_2O_6$

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Abstract

A new compound, $Li_4CaB_2O_6$, has been synthesized by solid-state reaction and its structure has been determined from powder X-ray diffraction data by direct methods. The refinement was carried out using the Rietveld methods and the final refinement converged with $R_p = 10.4\%$, $R_{wp} = 14.2\%$, $R_{exp} = 4.97\%$. This compound belongs to the orthorhombic space group *Pnnm*, with lattice parameters $a = 9.24036(9)$ Å, $b = 8.09482(7)$ Å, and $c = 3.48162(4)$ Å. Fundamental building units are isolated $[BO_3]^{3-}$ anionic groups, which are all parallel to the $a-b$ plane stacked along the *c*-axis. The Ca atoms are six-coordinated by the O atoms to form octahedral coordination polyhedra, which are joined together through edges along the *c*-axis, forming infinitely long three-dimensional chains. The Li atoms have a four-fold and a five-fold coordination with O atoms that lead to complex Li–O–Li chains that also extend along the *c*-axis. The infrared spectrum of $Li_4CaB_2O_6$ was also studied, which is consistent with the crystallographic study.

Keywords: $Li_4CaB_2O_6$; Structure determination; X-ray powder diffraction

1. Introduction

It is well known that the boron atom can be coordinated by oxygen atoms to form a variety of atomic groups, which are considered to be a dominant factor for the physical properties, in particular, the optical properties of the borates. The ultraviolet-transparent range of borate materials is determined mainly by the energy gap of the anionic groups if the cations are alkali or alkaline-earth metals. Absorption in $[BO_3]^{3-}$ group occurs at 173 nm [1]. On the other hand, the anisotropy of polarizability of planar $[BO_3]^{3-}$ groups indicates that some borates are likely to be good candidates for future birefringent materials if their $[BO_3]^{3-}$ groups are in suitable configuration, as for $[CO_3]^{2-}$ in $CaCO_3$.

In the past decades, much research interest has been focused on the synthesis and characterization of inorganic borates for the exploration of nonlinear optical materials. Many borates, Such as β-BaB_2O_4 [2], LiB_3O_5 [3], $Sr_2Be_2B_2O_7$ [1] and $K_2Al_2B_2O_7$ [4], have been synthesized and structurally characterized as successful examples of new optical materials.

Recently, the demand for birefringent crystals and the nonlinear optical crystals in the deep UV band is soaring with the development of optical communications and the semiconductor large-scale integrated circuit. In the search for new useful optical crystals, a series of work have been done [5–7]. We investigated the phase relations in Li_2O–CaO–B_2O_3, and found several new ternary compounds [8], one of them is $Li_4CaB_2O_6$, which is synthesized through a solid-state reaction. Here, we report the synthesis, structure determination, and infrared spectra of this new compound.

2. Experimental

Polycrystalline $Li_4CaB_2O_6$ were prepared by a solid-state reaction. The starting compounds, high-purity Li_2CO_3(A.R.), $CaCO_3$(A.R.), H_3BO_3($>$99.99%) were mixed homogeneously in the original molar ratios 3:1:3 and fired at 630°C for 72 h with intermediate grindings. The process was repeated until its diffraction pattern had no further changes. The nominal formula was

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Table 1
Experimental details of X-ray powder diffraction and Rietveld refinement

Diffractometer	Rigaku D/Max-2400
Radiation type	Cu*K*α
Wavelength (Å)	1.5418
Profile range (°2θ)	10–135
Step size (°2θ)	0.02
Step scan time per step (s)	1
Number of observation (N)	6251
Number of contributing reflections	563 ($K\alpha_1 + K\alpha_2$)
Number of structure parameters (P_1)	19
Number of profile parameters (P_2)	17
R_p (%)	10.4
R_{wp} (%)	14.2
R_{exp} (%)	4.97
R_B (%)	6.56

Note: $R_p = \sum|y_{io} - y_{ic}|/\sum|y_{io}|$, $R_{wp} = [\sum w_i(y_{io} - y_{ic})^2/\sum w_i y_{io}^2]^{1/2}$, $R_{exp} = [(N - P_1 - P_2)/\sum w_i y_{io}^2]^{1/2}$, $S = \sum[w_i(y_{io} - y_{ic})^2/(N - P_1 - P_2)]^{1/2}$.

Table 2
Crystallographic data

Chemical formula	$Li_4CaB_2O_6$
Symmetry	Orthorhombic
Space group	*Pnnm*
a (Å)	9.24036(9)
b (Å)	8.09482(7)
c (V)	3.48162(4)
Volume (Å^3)	260.422(7)
Z	2
D_m (g cm^{-3})	2.46
D_x (g cm^{-3})	2.364

Table 3
Positional, thermal, and occupancy parameters for $Li_4CaB_2O_6$

Atom	Site	x	y	z	B (Å^2)
Ca	2*c*	0.0000	0.5000	0.0000	1.83(3)
O(1)	4*g*	0.1423(3)	0.2473(3)	0.0000	1.89(7)
O(2)	4*g*	0.3786(3)	0.1366(4)	0.0000	1.83(7)
O(3)	4*g*	0.3510(3)	0.4293(3)	0.0000	1.84(7)
B	4*g*	0.2888(6)	0.2776(7)	0.0000	1.5(1)
Li(1)	4*g*	0.1923(9)	0.0049(14)	0.0000	2.8(2)
Li(2)	4*g*	0.5479(8)	0.3263(9)	0.0000	1.4(2)

determined as $Li_6CaB_3O_{8.5}$ originally [8]; however, a chemical analysis showed that the loss of Li and B was substantial during the course of the solid-state reaction, and the final stoichiometric proportion was 2:1:2.

X-ray powder diffraction data were collected on an X-ray Rigaku diffractometer D/Max-2400 with Cu*K*α radiation (40 kV, 140 mA) working in the step scanning mode and equipped with a graphite monochromator, see Table 1.

Infrared spectrum was recorded with a Perkin-Elmer 983 infrared spectrophotometer in the 300–1500 cm^{-1} wavenumber range using KBr pellets.

3. Results and discussion

The unit cell of the title compound was determined from the powder diffraction pattern using the Dicvol91 program [9]. All the reflections before 80° in 2θ can be indexed based on an orthorhombic unit cell with lattice parameters $a = 9.24036(9)$ Å, $b = 8.09482(7)$ Å, and $c = 3.48162(4)$ Å. According to the systematic absence of $0\,k\,l$ with $k + l = 2n + 1$ and $h\,0\,l$ with $h + l = 2n + 1$, we determined its possible space group as *Pnn2* [8] or *Pnnm*.

Because the space group *Pnnm* possesses a higher symmetry, it is tested firstly. The symmetry information, the unit cell dimensions, and the data were input to the Fullprof program [10] to decompose the pattern. Totally, 230 unique $|F_{obs}|$ were extracted. The agreement indices converged to the values $R_p = 8.29\%$, $R_{wp} = 12.4\%$, $R_{exp} = 6.14\%$.

The density of the samples was measured to be 2.46 g cm^{-3}. According to this result and the symmetry information, it is determined that there are two $Li_4CaB_2O_6$ molecules in one unit cell.

Direct methods were applied with *SHELXL97* program package [11] to the extracted $|F_{obs}|$. According to the known values of bond length and the site occupation factor, two of the eight peaks listed in the E-map were likely to correspond to the correct positions of atoms, one was assigned to Ca, and the other O(1). The other atoms were located by using difference-Fourier synthesis and approximate $|F_{obs}|$ values derived by the pattern decomposition method. In this course, once an atom was located, it would be used for the next run of difference-Fourier synthesis.

Rough structure obtained by using direct methods and difference-Fourier synthesis was then input to the Fullprof program to be refined with the Rietveld method. All atoms were refined isotropically. The final refinement converged with $R_B = 6.56\%$, $R_p = 10.4\%$, $R_{wp} = 14.2\%$, and $R_{exp} = 4.97\%$. The space group *Pnn2* was also tested to refine the approximate structure, but the final atom positions changed little. Therefore, the structure of $Li_4CaB_2O_6$ was centrosymmetric and belongs to space group *Pnnm*.

Crystallographic data are summarized in Table 2. The final positional parameters are listed in Table 3. A list of selected bond lengths and angles is given in Table 4. Final refinement results are presented in Fig. 1.

The projection structure of the compound $Li_4CaB_2O_6$ along the [001] direction was shown in Fig. 2. Isolated BO_3 triangles are parallel to the a–b plane and distributed layer upon layer along the c-axis. The B–O distance varies from 1.355(6) to 1.411(6) Å with an average value of 1.381 Å, and the O–B–O angles are

Table 4
Selected interatomic distances (Å) and angles (deg)

Li(1)–O1	2.016(12)		
Li(1)–O2	2.025(9)		
Li(1)–O3^{ix}	1.888(9)		
Li(1)–O3^{x}	1.888(9)		
		Ca–O1	2.432(3)
Li(2)–O1^{i}	2.036(4)	Ca–O1^{iii}	2.432(3)
Li(2)–O1^{ii}	2.036(4)	Ca–O2^{iv}	2.347(2)
Li(2)–O2	2.192(8)	Ca–O2^{v}	2.347(2)
Li(2)–O3	2.001(8)	Ca–O2^{vi}	2.347(2)
Li(2)–O3^{viii}	2.188(8)	Ca–O2^{vii}	2.347(2)
B–O1	1.376(6)	O1–B–O2	115.72(5)
B–O2	1.411(6)	O1–B–O3	125.36(5)
B–O3	1.355(6)	O2–B–O3	118.92(5)

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

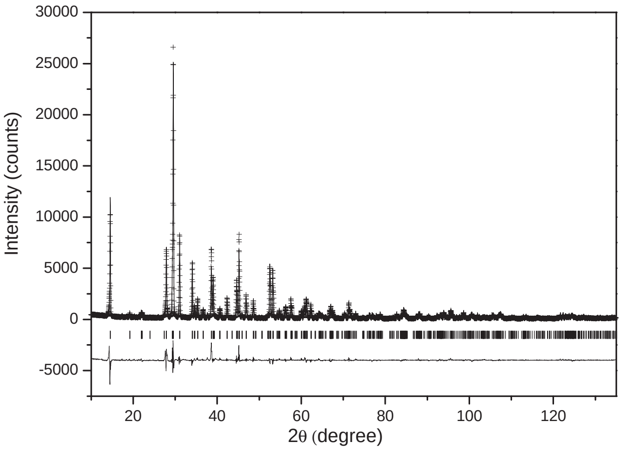

Fig. 1. The final Rietveld refinement plot of the $Li_4CaB_2O_6$. Small crosses (+) correspond to experimental values and the continuous lines the calculated pattern; and vertical bars (|) indicate the positions of Bragg peaks. The bottom trace depicts the difference between the experimental and the calculated intensity values.

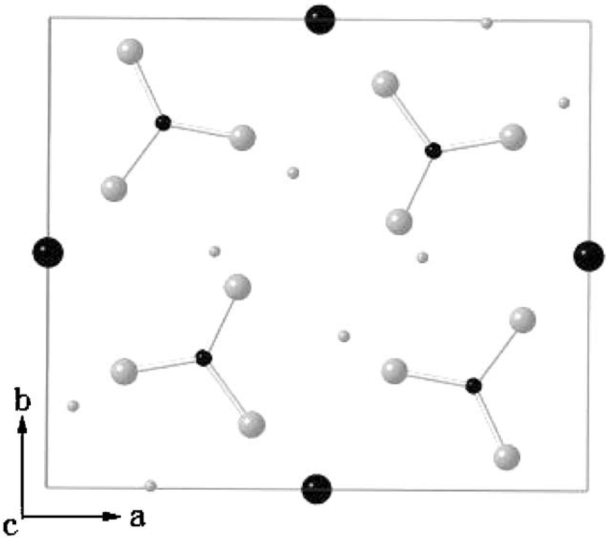

Fig. 2. The structure projection of $Li_4CaB_2O_6$ along [001]; big black balls stand for Ca atoms, and small ones for B atoms. Big gray balls represent O atoms, and small ones Li atoms.

between 115.72(5)° and 125.36(5)°. These values are normal in a BO_3 plane triangle. The Ca atomes are six-coordinated by the oxygen atoms with two kinds of distances, 2.347(2) and 2.432(3) Å, forming octahedral polyhedra, which is shown in Fig. 3(a). The edge-sharing CaO_6 octahedra extend along the *c* direction to form a series of infinitely long chains, and the adjacent chains are connected by BO_3 triangles through corners. The coordination environments of Li atoms are presented in Fig. 3(b), from which we can see that there are two kinds of coordination manners in the Li atoms. The Li(1) atoms are coordinated with four oxygen atoms, forming a distorted tetrahedron. The Li(2) atoms are coordinated with five oxygen atoms, forming a distorted trigonal bipyramid. Every LiO_4 tetrahedron jointed with two LiO_5 polyhedra to form a $[Li_3O_{10}]$ group, and those LiO_4 tetrahedra share corners with each other along the [001] direction, so do the LiO_5 polyhedra. As a result, the $[Li_3O_{10}]$ groups form a lot of complex chains along the *c*-axis, and the chains are joined together by bridging O(2) atoms. In the $[Li_3O_{10}]$ groups, two LiO_5 share O(3)–O(3) edge with each other, and one LiO_5 share O(1)–O(3) edge with LiO_4, while the other LiO_5 share O(3) with the LiO_4. BO_3 triangles are distributed between those chains, and share one of the three edges with LiO_4, while another with LiO_5.

Another known lithium borate $Li_3AlB_2O_6$ had been synthesized and structure determined by M. He et al. [12]. Although the isolated BO_3 groups exist in the two compounds, their structures are very different from each other. They belong to different crystal system and space group; moreover, in $Li_3AlB_2O_6$, not all BO_3 plane triangles run parallel to each other, and the AlO_4 groups jointed the adjacent four BO_3 groups through corners, forming infinite $[Al_2(BO_3)_4]^{6-}$ complex chains that run parallel to the *a*-axis and separated by tetra-coordinated Li atoms.

To provide a check on the consistency of the structure solution, the bond valences have been calculated according to the Brown and Altermatt parameters [13] for the structure of the title compound, and are listed in Table 5. It can be seen that in our structure the bond valence sums are very reasonable for both cations and oxygens.

In order to testify the coordination surrounding of B–O in $Li_4CaB_2O_6$, its IR spectrum was measured at room temperature and given in Fig. 4. Those vibrational frequencies observed above 1200 cm^{-1} should be ascribed to the stretching modes of triangular BO_3

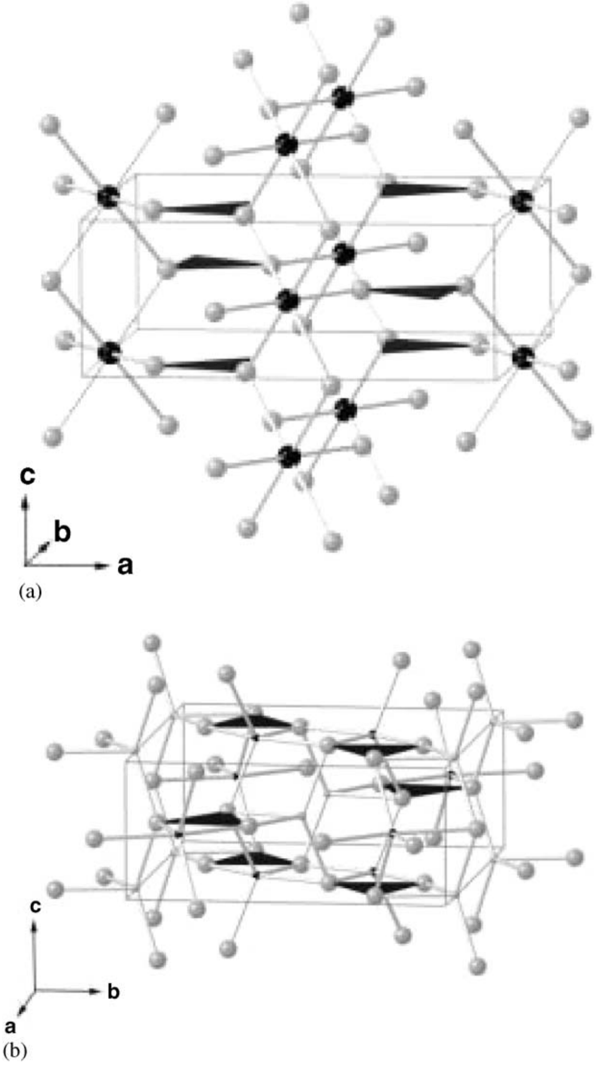

Fig. 3. (a) The coordination around Ca with O atoms; and (b) the coordination around Li with O atoms. Big black balls stand for Ca atoms, and small ones for Li(2) atoms. Big gray ones depict O atoms, and small ones Li(1) atoms. The black triangles are BO_3.

Table 5
Li–O, Ca–O, and B–O bond valence in $Li_4CaB_2O_6$

	O(1)	O(2)	O(3)	$\sum S$
Li(1)	0.226	0.221	0.319 0.319	1.085
Li(2)	0.214 0.214	0.140	0.236 0.142	0.946
Ca	0.285 0.285	0.357 0.357 0.357 0.357		1.998
B	0.985	0.897	1.044	2.926
$\sum S$	1.924	1.972	2.060	

Note: The summaries of bond valence for O(1) only account for one “0.285”, and for O(2) only account for two “0.357”, according to their coordination numbers.

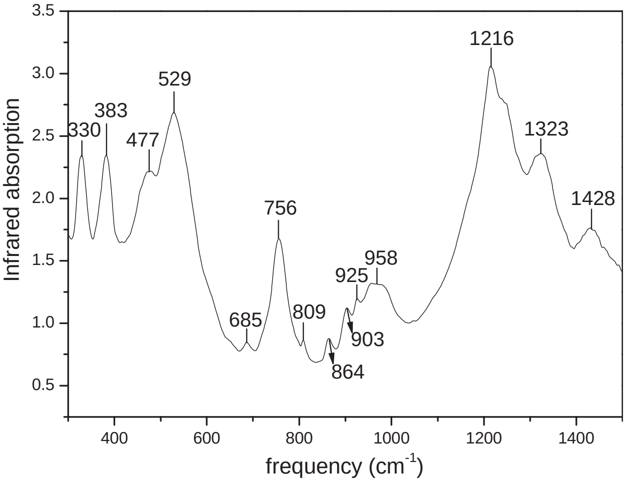

Fig. 4. Infrared spectrum of $Li_4CaB_2O_6$.

groups, which confirm the existence of isolated BO_3 triangles [14].

4. Conclusion

In this work, a new compound, $Li_4CaB_2O_6$, has been synthesized by solid-state reactions. The crystal structure has been solved from powder X-ray diffraction data, and was further refined by the Rietveld method. It is composed of three coordinated boron atoms, six-fold coordinated calcium atoms, partially four-fold and partially five-fold coordinated lithium atoms. The isolated BO_3 triangles parallel to each other and distributed layer upon layer along the *c*-axis. The Ca atoms are coordinated by six O atoms to form octahedron coordination polyhedra, which are joined together through edges along the *c*-axis, forming infinitely long three-dimensional chains. The Li atoms have a four-fold and five-fold coordination with O atoms that lead to complex Li–O–Li chains that also extend along the *c*-axis. The infrared spectrum also reported here is consistent with the crystallographic study.

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