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Structure determination of a new compound $LiCaBO_3$

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Abstract

A new compound, $LiCaBO_3$, has been identified in the system Li_2O–CaO–B_2O_3 and high-quality single crystals were obtained by the flux method. Its structure has been solved and refined from single crystal and powder X-ray diffraction data, respectively. This compound crystallizes in an orthorhombic unit cell (space group *Pbca*) with lattice parameters $a = 13.227(13)$ Å, $b = 6.1675(6)$ Å, and $c = 6.0620(6)$ Å. There are 8 formulas per unit cell and 6 unique atoms sites in the unit. Its structure is stacked alternately with [LiBO] and [CaO] layers along the [100] direction. In the [LiBO] layers, the isolated $[BO_3]^{3-}$ anionic groups, distributed along two directions, [011] and $[0\bar{1}1]$, are almost perpendicular to each other. The differences among the structures of the four compounds, $LiCaBO_3$, $LiMgBO_3$, $LiSrBO_3$ and $LiBaBO_3$ have been discussed, and the infrared spectra of $LiCaBO_3$ has also been researched, which is consistent with the crystallographic study.

Keywords: $LiCaBO_3$; Structure determination; Single-crystal diffraction; X-ray powder diffraction

1. Introduction

It is well known that boron atom can be coordinated by oxygen atoms to form a variety of atomic groups, which are considered to be a dominant factor for physical properties, in particular, optical properties of 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, as $[CO_3]^{2-}$ in $CaCO_3$, 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.

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 exploring 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 integrate circuit. To find new useful optical crystals, a series of works have been done [5–7]. We investigated the phase relations in Li_2O–CaO–B_2O_3, and found several new ternary compounds, $LiCaBO_3$, $Li_6CaB_3O_{8.5}$, and $0.83LiO_{0.5} \cdot 0.005CaO \cdot 0.165BO_{1.5}$ [8]. They were synthesized through solid-state reaction. Here, we report the synthesis, structure determination, and infrared spectra of $LiCaBO_3$.

2. Experimental

We obtained this new compound by 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 appropriate molar ratios and roasted at 790°C for 72 h, producing the raw $LiCaBO_3$ material. The raw material was heated to 950°C in a platinum crucible and kept at this temperature for 24 h, then was cooled from 950°C to 650°C at a rate of $1°C\,h^{-1}$. Finally, it was cooled to 300°C at a rate of $10°C\,h^{-1}$ and the furnace was

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switched off. The crucible was removed from the furnace after it had cooled to room temperature. It was found that the compound crystallized as transparent irregular grains.

Table 1
Experimental details of single-crystal data collection and refinement

Molecular formula	$LiCaBO_3$
Molecular weight	105.83
Crystal system	Orthorhombic
Space group	*Pbca*
Unit cell dimensions (Å)	$a = 13.227(13)$, $b = 6.1675(6)$, $c = 6.0620(6)$
Volume (Å^3)	494.5(14)
Z	8
Density (g cm^{-3})	2.842
Color	Colorless
Diffractometer	Bruker SMART APEX CCD area-detector diffractometer
Radiation, temperature (K)	Mo$K\alpha$, 293(2)
Wavelength (Å)	0.71073
Absorption correction	SADABS-Bruker/Siemens area detector absorption and other corrections-V2.03
Reflections for refined cell parameters	3279
Scan mode	φ and ω scans
Measured reflections	4573
Independent reflections with $I > 2\sigma(I)$	1112
Data collection range (deg)	$6.167 < 2\theta < 66.628$
Reflections used in the last refinement	924
Weighting scheme	$W = 1/[\sigma^2(F_o^2) + (0.0228P)^2 + 0.16P]$ where $P = (F_o^2 + 2F_c^2)/3$
Number of refined parameters	56
Reliability factor R_1; w$R_2(F_o > 4\sigma(F_o))$	0.0189, 0.0567
Goodness of fit	1.237
$\Delta\rho_{max}$ (e Å^{-3})	0.37
$\Delta\rho_{min}$ (e Å^{-3})	−0.55

Table 2
Experimental details of X-ray powder diffraction and rietveld refinement

Diffractometer used	Rigaku D/Max-2500
Radiation type	Cu$K\alpha$
Wavelength	1.5418
Profile range	10° to 130°
Step size (2θ)	0.02°
Step scan time (s)	15
Number of observation (N)	6001
Number of contributing reflections	843($K\alpha1$+$K\alpha2$)
Number of structure parameters (P_1)	18
Number of profile parameters (P_2)	13
R_p (%)	8.75
R_{wp} (%)	10.99
R_{exp} (%)	6.84
S	1.61

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

Single-crystal diffraction data were collected with a Bruker SMART APEX CCD area-detector diffractometer. The crystal used for collecting the data (about $0.1 \times 0.1 \times 0.1\,mm^3$ in size) was selected from the product of the flux method. Additional technical details are given in Table 1.

X-ray powder diffraction measurement were performed with an automated Rigaku D/Max-2500 diffractometer working in the step scanning mode and equipped with a graphite monochromator. Since the sample exhibited a strong tendency of preferred orientation along the [011] direction, the diffraction data with transmission mode were collected in a capillary sample holder. More technical details can be found in Table 2.

Infrared spectra were 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 first 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 $a = 6.1799(3)$ Å, $b = 13.2537(6)$ Å, $c = 6.0746(3)$ Å. According to the systematic absence of $0\,k\,l$ with $k + l = 2n + 1$ and $h\,k\,0$ with $h = 2n + 1$, we determined its possible space group as *Pnma* at first [8]. However, we failed to solve the structure from X-ray powder diffraction data collected in a capillary with this space group, because of the low intensity of the diffraction pattern with the high background, no reliable $|F_{obs}|$ can be extracted by Fullprof program [10]. The single-crystal analysis gave almost the same unit cell with lattice parameters $a = 13.227(13)$ Å, $b = 6.1675(6)$ Å, and $c = 6.0620(6)$ Å (after the order of the three lattice parameters of the former are changed). The systematic absence of $0\,k\,l$ with $k = 2n + 1$, $h\,0\,l$ with $l = 2n + 1$, and $h\,k\,0$ with $h = 2n + 1$ suggests that the possible space group is *Pbca*, which has some difference with the former. We believe that the indexed reflections of powder diffraction

Table 3
Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)

	Site	x	y	z	U_{eq}
Ca	8*c*	0.42968(2)	0.50948(3)	0.25121(2)	0.0074(1)
O1	8*c*	0.25085(6)	0.5343(1)	0.2344(1)	0.0107(2)
O2	8*c*	0.40484(5)	0.8733(1)	0.1179(1)	0.0089(1)
O3	8*c*	0.40485(5)	0.1449(1)	0.3985(1)	0.0092(1)
B	8*c*	0.1478(1)	0.5174(2)	0.2500(1)	0.0079(2)
Li	8*c*	0.2519(1)	0.7086(3)	0.5150(3)	0.0150(3)

pattern were inaccurate because of some overlapped peaks. The structure was solved using the direct methods and refined by full matrix least-squares techniques with isotropic or anisotropic thermal parameters for all atoms, using the *SHELXL*97 program package [11]. The reliability factors converged to $R_1 = 0.0189$, and $wR_2 = 0.0567$. Table 1 lists the crystallographic data. The fractional atomic coordinates and equivalent isotropic displacement parameters are reported in Table 3. Anisotropic displacement parameters and some important geometric parameters are listed in Tables 4 and 5, respectively.

Table 4
Anisotropic displacement parameters (Å^2)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ca	0.0069(1)	0.0074(1)	0.0078(1)	−0.00001(5)	0.00003(4)	0.00015(5)
O1	0.0061(3)	0.0129(3)	0.0130(3)	−0.0030(2)	0.0003(2)	−0.0006(2)
O2	0.0086(3)	0.0083(3)	0.0098(3)	0.0000(2)	0.0013(2)	0.0014(2)
O3	0.0093(3)	0.0089(3)	0.0095(3)	0.0003(2)	−0.0013(2)	−0.0016(2)
B	0.0073(5)	0.0078(4)	0.0087(5)	0.0012(2)	−0.0002(2)	0.0004(3)
Li	0.0153(9)	0.0140(7)	0.0157(8)	−0.0022(5)	0.0012(6)	−0.0003(5)

Table 5
Selected interatomic distances (Å) and angles (deg)

Li–O1^{i}	2.004(2)	Ca–O1	2.3726(9)
Li–O1	2.012(2)	Ca–O2	2.4076(7)
Li–O1^{iv}	2.070(2)	Ca–O2^{ii}	2.4750(7)
Li–O2^{iv}	2.176(2)	Ca–O2^{iv}	2.3606(7)
Li–O3^{v}	2.226(2)	Ca–O3^{ii}	2.5122(7)
		Ca–O3^{iii}	2.3637(7)
		Ca–O3^{vi}	2.4412(7)
B–O1	1.3699(15)	O1–B–O3^{v}	120.19(8)
B–O2^{v}	1.3844(12)	O1–B–O2^{v}	120.62(8)
B–O3^{v}	1.3835(12)	O2^{v}–B–O3^{v}	119.19(11)

Note. Symmetry codes: (i)$-x+1/2$, $-y+1$, $z+1/2$; (ii) $-x+1$, $y-1/2$, $-z+1/2$; (iii) x, $-y+3/2$, $z-1/2$; (iv) x, $-y+3/2$, $z+1/2$; (v) $-x+1/2$, $y-1/2$, z; (vi) x, $y-1$, z.

To prove that the single crystal used in the structure analysis was indeed the bulk material, a Rietveld refinement was performed on the X-ray powder diffraction data using a DBW9411 program [12]. The high background intensities from 20° to 38° were attributed to the influence of the capillary tube. Thermal parameters were set to be the same with those values obtained in the single-crystal data analysis and were not refined. A total of 18 structural parameters and 13 profile parameters were refined. The refinement finally converged to agreement factors of $R_p = 8.75\%$, and $R_{wp} = 10.99\%$ with $R_{exp} = 6.84\%$. The details of the Rietveld refinement are presented in Table 2 and the final refinement pattern is given in Fig. 1. Lattice constants were refined to $a = 13.2552(1)$ Å, $b = 6.1808(0)$ Å, $c = 6.0754(0)$ Å. The positional parameters obtained by the Rietveld refinement gave essentially the same result with the single-crystal structure refinement.

Drawings of the contents of the unit cells of the title compound are shown in Figs. 2 and 3. It is found that the structure can be constructed from a stack of [LiBO] and [CaO] layers along the [100] direction, distributed alternately. In the [LiBO] layers, the isolated $[BO_3]^{3-}$ anionic groups distribute along two directions, some of them run parallel with the [011] direction, while the

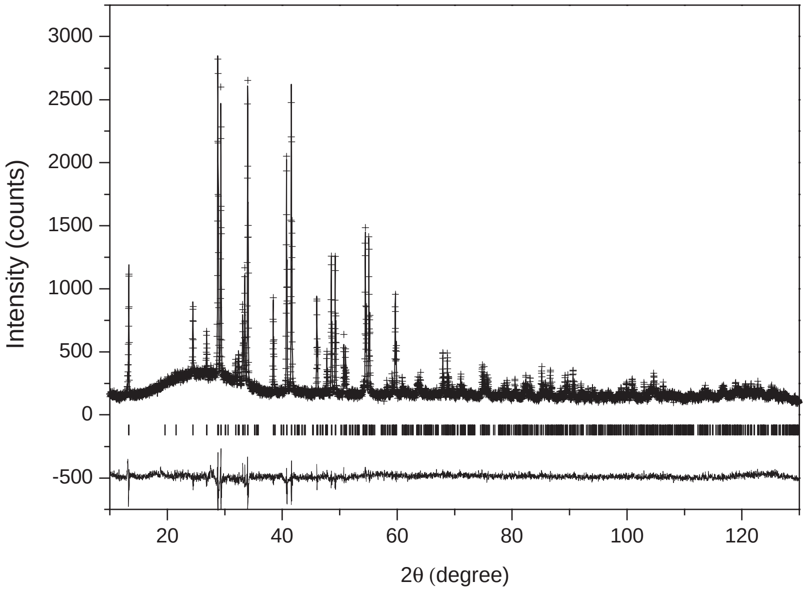

Fig. 1. The final Rietveld refinement plots of the $LiCaBO_3$. Small crosses (+) correspond to experimental values and the continuous lines the calculated pattern; vertical bars (|) indicate the positions of Bragg peaks. The bottom trace depicts the difference between the experimental and the calculated intensity values.

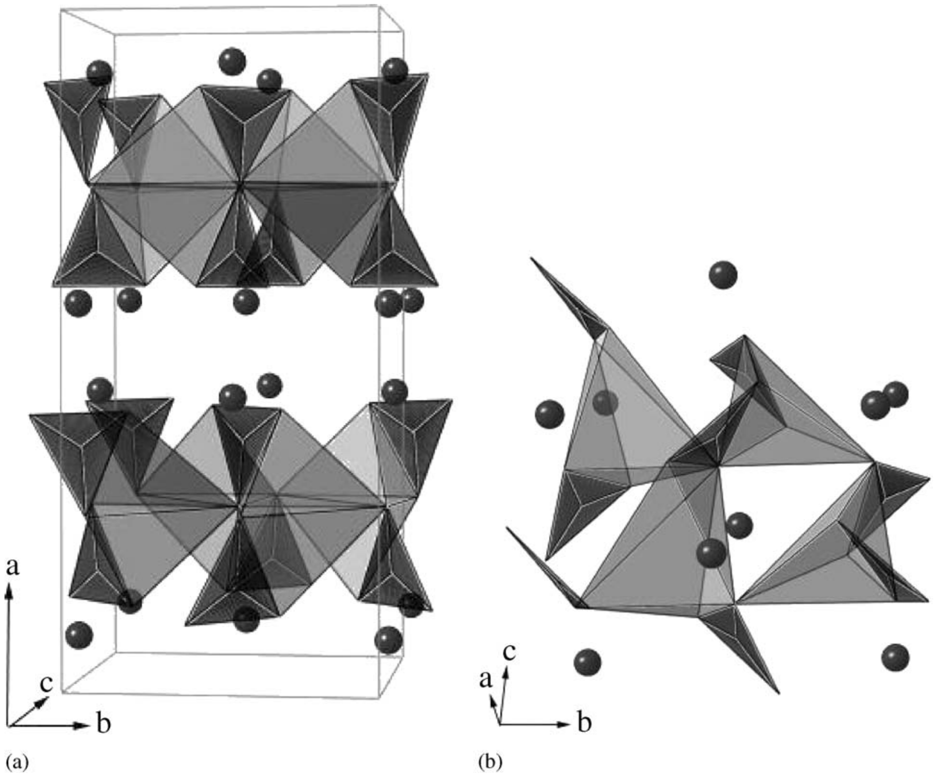

Fig. 2. Crystal structure stacked from the LiO_5 polyhedra and BO_3 triangles viewed along [001] (a), and viewed along [100] (b). Big black balls stand for Ca atoms. The grayish polyhedra are LiO_5 bipyramids, and the black triangles are BO_3 triangles.

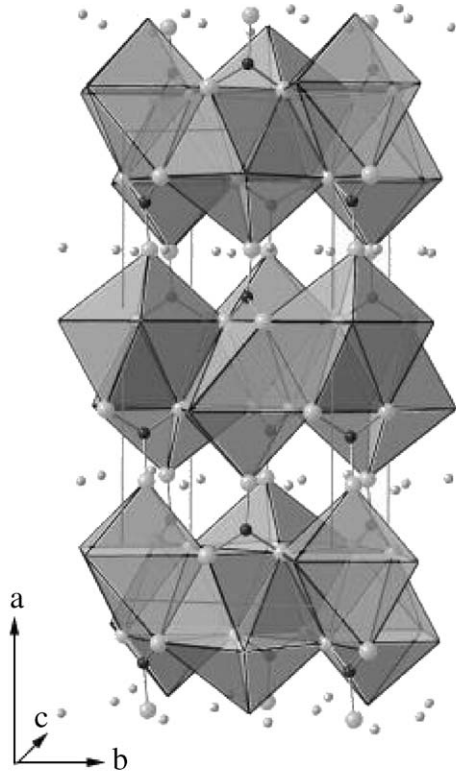

Fig. 3. Crystal structure stacked from the CaO_7 polyhedra and BO_3 triangles viewed along the [001]. Big grayish balls stand for O atoms, and small ones Li atoms, while black balls depict B atoms. The grayish polyhedra are CaO_7 polyhedra.

Table 6
Li–O, Ca–O, and B–O bond valence in $LiCaBO_3$

	O1	O2	O3	Σs
Li	0.234 0.229 0.196	0.147	0.128	0.934
Ca	0.334	0.345 0.304 0.253	0.342 0.278 0.229	2.085
B	1.003	0.964	0.967	2.934
Σs	1.996	2.013	1.944	

others run parallel to the $[0\bar{1}1]$ direction. So they are almost perpendicular to each other. The B–O distance varies from 1.3699(15) to 1.3844(12) Å with an average value of 1.379 Å, and the O–B–O angles are between 119.19(11)° and 120.62(8)°. These values are normal in a BO_3 plane triangle. The Li atoms are coordinated with five oxygen atoms, forming distorted trigonal bipyramids. Those LiO_5 polyhedra share corners with each other via bridging-oxygen atoms, and locate in the intersections of [011] and $[0\bar{1}1]$ as a bridging role, joining the adjacent BO_3 triangles. In the [CaO] layers, the Ca atoms are coordinated with seven oxygen atoms, forming mono-capped distorted trigonal prisms, sharing edges with each other. From Fig. 3 we can find that the adjacent [CaO] layers are connected with BO_3 plane triangles.

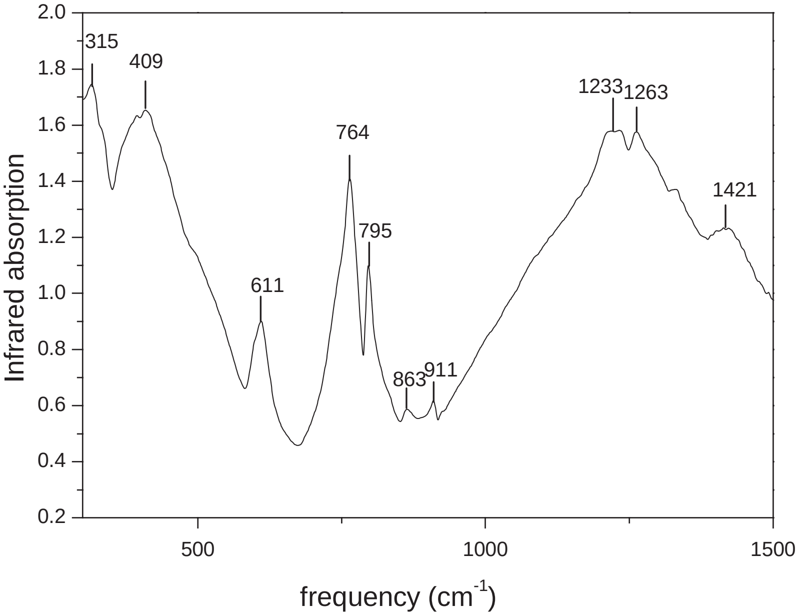

Fig. 4. Infrared spectra of $LiCaBO_3$.

The structure of $LiCaBO_3$ is very different from the other three alkaline-earth metal compounds, $LiMgBO_3$ [13], $LiSrBO_3$ [14] and $LiBaBO_3$ [14,15], though they have similar chemical formula. The other three compounds all belong to monoclinic crystal system. In $LiMgBO_3$, all the BO_3 plane triangles are parallel to each other, while they are neither parallel nor perpendicular to each other in $LiSrBO_3$ and $LiBaBO_3$. The Mg atoms are five-coordinated by O atoms to form roughly trigonal bipyramidal coordination polyhedra, and are linked together by sharing edges. The Sr atoms are coordinated by seven O atoms, forming mono-capped distorted trigonal prisms, and sharing edges with each other, which seemed very like the coordination surrounding of Ca atoms in the title compound. The Ba atoms are nine-coordinated, and the BaO_9 polyhedron is described as a mono-capped distorted square anti-prism. Some of the polyhedra share plane, while others share edge with each other. In the four compounds, the only similar structural unit is the LiO_5 polyhedron, which is described as different distorted trigonal bipyramid.

The bond valences have also been calculated according to the Brown and Altermatt parameters [16] for the structure of the title compound, and are listed in Table 6. It can be seen that in our structure the bond valence sums are very reasonable for both cations and oxygens.

The infrared spectra of this structure are given in Fig. 4. The vibrational frequencies observed above $1200\,cm^{-1}$ should be ascribed to the stretching modes of triangular $[BO_3]^{3-}$ groups, and those below $800\,cm^{-1}$ are the bending modes of them. As to the vibrational frequencies below $450\,cm^{-1}$, they should be attributed to lattice vibrations [17].

4. Conclusion

In this work we have synthesized a new compound $LiCaBO_3$, by solid-state reaction and solved its structure from single-crystal diffraction data. The structure was further verified by Rietveld refinement on the powder diffraction data. It was found that this structure was built up from an alternate stack of [LiBO] and [CaO] layers along the [100] direction. In the [LiBO] layers, isolated BO_3 triangles distribute along two directions, one is [011], and the other is $[0\bar{1}1]$. The LiO_5 polyhedra locate in the intersections of [011] and $[0\bar{1}1]$, connecting the adjacent perpendicular BO_3 triangles. The CaO_7 polyhedra share edges with each other, forming layers parallel to the *bc* plane. The adjacent [CaO] layers are joined with BO_3 triangles. Moreover, we analyzed the differences among the structures of the four compounds, $LiCaBO_3$, $LiMgBO_3$, $LiSrBO_3$, $LiBaBO_3$, and found some distinct differences. Finally, we also detected the Infrared spectra of the title compound, and found it was consistent with the crystallographic study.

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