Synthesis, structure, and properties of $Li_2Pb_2CuB_4O_{10}$ with isolated $[CuB_4O_{10}]^{6-}$ units

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ABSTRACT

The copper borate $Li_2Pb_2CuB_4O_{10}$ has been synthesized in air by the standard solid-state reaction at temperature in the range 550–650 °C and the structure of $Li_2Pb_2CuB_4O_{10}$ was determined by single-crystal X-ray diffraction. $Li_2Pb_2CuB_4O_{10}$ crystallizes in the monoclinic space group $C2/c$ (no. 15) with $a = 16.8419(12)$, $b = 4.7895(4)$, $c = 13.8976(10)$ Å, and $\beta = 125.3620(10)°$, $V = 914.22(12)$ Å^3, and $Z = 4$, as determined by single-crystal X-ray diffraction. The $Li_2Pb_2CuB_4O_{10}$ structure exhibits isolated units of stoichiometry $[CuB_4O_{10}]^{6-}$ that are built from CuO_4 distorted square planes and triangular BO_3 groups. The IR spectroscopy and thermal analysis investigations of $Li_2Pb_2CuB_4O_{10}$ are also presented.

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1. Introduction

The advent of new crystalline materials is of perpetual interest in solid-state chemistry, primarily for the potential of unearthing novel optical, electronic, or magnetic properties. Borate materials have attracted considerable attention in the past decades due to their rich structural chemistry and potential applications [1–10]. From the perspective of structure, a boron atom will link with either three oxygen atoms to form a triangle BO_3 or four oxygen atoms to form a tetrahedron. BO_4 groups are generally polymerized to form polynuclear anions, including isolated rings, infinite chains, infinite sheets and frameworks [11–15]. Most ternary M–B–O systems have been thoroughly examined wherein certain motifs dominate, including isolated BO_3 triangles, isolated BO_4 tetrahedra, and extended networks containing BO_3 and BO_4. Because the Li_2O–PbO–CuO–B_2O_3 system largely has been unexplored [16–18], new phases can provide interesting stoichiometries, structures, and properties. Our own search for new metal borate phases has led us to the new compounds $Li_2Pb_2CuB_4O_{10}$. In this report the synthesis, crystal structure, IR, and thermal properties of $Li_2Pb_2CuB_4O_{10}$ are described.

2. Experimental

2.1. Solid-state syntheses

The $Li_2Pb_2CuB_4O_{10}$ compound was discovered during the survey of the Li_2CO_3–PbO–CuO–B_2O_3 system. Samples were synthesized via solid-state reactions from powder mixtures (99%, Sigma–Aldrich), PbO (99.99%, Alfa-Aesar), CuO (99%, Sigma–Aldrich), and H_3BO_3 (99.99%, Alfa-Aesar). The mixtures were heated to 550–650 °C for 2–3 days in several stages separated by intermediate stirring. In all cases, care was taken to avoid any partial melting of the samples. The sample purity was verified using X-ray powder diffraction.

X-ray powder diffraction analysis of $Li_2Pb_2CuB_4O_{10}$ was performed at room temperature in the angular range of $2\theta = 10–70°$ with a scan step width of 0.02° and a fixed counting time of 1 s/step using an automated Rigaku X-ray diffractometer equipped with a diffracted-beamed monochromator set for Cu Kα ($\lambda = 1.5418$ Å) radiation.

2.2. Single-crystal growth

Small single crystals of $Li_2Pb_2CuB_4O_{10}$ were successfully grown in air. A mixture with stoichiometric molar composition for $Li_2Pb_2CuB_4O_{10}$ was melted at 800–1000 °C in a covered platinum crucible with a vertical, programmable temperature Molysili furnace, held within that temperature range for 24 h, slowly cooled to 550–600 °C at a rate of 0.05 °C/min, and finally cooled to room temperature at a rate of 10 °C/min. Clear, sub-millimeter size, blue tabular crystals were separated from the melt for $Li_2Pb_2CuB_4O_{10}$. Crystals of suitable quality for X-ray diffraction work were selected under an optical microscope.

2.3. X-ray crystallographic studies

The crystal structure of $Li_2Pb_2CuB_4O_{10}$ was determined by single-crystal X-ray diffraction on a Bruker SMART-1000 CCD diffractometer using monochromatic Mo Kα radiation ($\lambda = 0.71073$ Å) and integrated with the SAINT-Plus program [19].

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Table 1
Crystal data and structure refinement for $Li_2Pb_2CuB_4O_{10}$.

Empirical formula	$Li_2Pb_2CuB_4O_{10}$
Temperature	153(2) K
Formula weight	695.04
Crystal system	Monoclinic
Space group	$C2/c$
Unit cell dimensions	$a = 16.8419(12)$ Å, $\alpha = 90°$
	$b = 4.7895(4)$ Å, $\beta = 125.3620(10)°$
	$c = 13.8976(10)$ Å, $\gamma = 90°$
Volume	$914.22(12)$ Å^3
Z	4
Density (calculated)	5.050 g/cm^3
Absorption coefficient	39.087/mm
$F(000)$	1196
Crystal size	0.06 mm $\times$ 0.09 mm $\times$ 0.26 mm
Theta range for data collection	$3.06–28.52°$
Index ranges	$-21 \leq h \leq 21, -6 \leq k \leq 6, -17 \leq l \leq 18$
Reflections collected/unique	$3122/994$ [$R(int) = 0.0423$]
Completeness to theta	85.2%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	994/0/89
Goodness-of-fit on F^2	1.093
Final R indices [$F_0^2 > 2\sigma(F_0^2)$][a]	$R_1 = 0.0438$, $wR_2 = 0.1189$
R indices (all data) [a]	$R_1 = 0.0454$, $wR_2 = 0.1205$
Maximum and minimum transmission	0.00489, 0.15283
Largest diff. peak and hole	4.704 and -5.405 e Å^{-3}

[a] $R_1 = \Sigma ||F_0| - |F_c||/\Sigma |F_0|$ and $wR_2 = [\Sigma w(F_0^2 - F_c^2)^2/\Sigma wF_0^4]^{1/2}$ for $F_0^2 > 2\sigma(F_0^2)$.

All calculations were performed with programs from the SHELXTL crystallographic software package [20]. The space group $C2/c$ is unambiguously determined from the systematic absences. The structure was solved by direct methods. A face-indexed absorption correction was performed using the XPREP program, followed by the SADABS program [21]; equivalent reflections were then averaged. Final least-squares refinement is on F_0^2 with data having $F_0^2 \geq 2\sigma(F_0^2)$. The final difference Fourier synthesis revealed maximum and minimum peaks at 4.70 (0.84 Å from Pb(1)) and -5.40 e Å^{-3} (0.86 Å from Pb(1)), respectively. The structure was checked for missing symmetry elements with PLATON [22]. Crystal data and structure refinement information are summarized in Table 1.

Final atomic coordinates and equivalent isotropic displacement parameters of the title compounds are listed in Table 2. Selected interatomic distances and angles for $Li_2Pb_2CuB_4O_{10}$ are given in Table 3.

2.4. Vibrational spectroscopy

IR spectroscopy was carried out with the objective of specifying the coordination of boron in $Li_2Pb_2CuB_4O_{10}$. The mid-infrared spectrum was obtained at room temperature via a Bio-Rad FTS-60 FTIR spectrometer. The sample was thoroughly mixed with dried KBr (5 mg of the sample, 500 mg of KBr). The spectrum was collected in a range from 400 to 4000 cm^{-1} with a resolution of 1 cm^{-1}.

2.5. Thermal analysis

The thermal stability of $Li_2Pb_2CuB_4O_{10}$ was examined under static air with a TA Instruments, Inc. differential thermal analyzer 1600-2910 DSC. The sample and reference (Al_2O_3) were enclosed in Pt crucibles, heated, and then cooled at a rate of 10 °C/min.

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) for $Li_2Pb_2CuB_4O_{10}$. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Atom	Wyckoff position	x	y	z	U_{eq}
Li(1)	8f	1864(17)	3100(30)	1370(20)	12(5)
Pb(1)	8f	320(1)	6800(1)	1386(1)	7(1)
Cu(1)	4c	2500	2500	0	7(1)
B(1)	8f	1529(9)	1885(19)	3191(10)	6(2)
B(2)	8f	1257(9)	2060(20)	4804(11)	9(2)
O(1)	8f	1270(7)	3117(12)	2158(8)	12(2)
O(2)	8f	2955(5)	4480(14)	1435(6)	8(1)
O(3)	8f	1673(5)	357(14)	290(6)	8(1)
O(4)	8f	1187(7)	3172(12)	3795(9)	9(2)
O(5)	8f	794(5)	6206(14)	152(7)	9(1)

Table 3
Selected bond lengths (Å) and angles (°) for $Li_2Pb_2CuB_4O_{10}$.

Atoms	Distances	Atoms	Angle
Li(1)–O(1)#1	1.86(2)	O(1)–Li(1)–O(3)	125.0(10)
Li(1)–O(3)	1.88(2)	O(1)–Li(1)–O(2)	143.5(13)
Li(1)–O(2)	1.91(2)	O(3)–Li(1)–O(2)	89.6(9)
Li(1)–O(5)#1	2.19(2)	O(1)–Li(1)–O(5)	88.3(9)
		O(3)–Li(1)–O(5)	99.8(11)
		O(2)–Li(1)–O(5)	97.9(9)
Pb(1)–O(1)	2.200(7)	O(1)–Pb(1)–O(5)	78.1(3)
Pb(1)–O(5)	2.290(7)	O(1)–Pb(1)–O(5)#1	85.7(3)
Pb(1)–O(5)#4	2.350(7)	O(5)–Pb(1)–O(5)#1	71.5(3)
Cu(1)–O(2)	1.922(7)	O(2)–Cu(1)–O(2)#4	180.0(3)
Cu(1)–O(2)#6	1.922(7)	O(2)–Cu(1)–O(3)#4	93.0(3)
Cu(1)–O(3)#6	1.952(6)	O(2)–Cu(1)–O(3)	87.0(3)
Cu(1)–O(3)	1.952(6)	O(2)#4–Cu(1)–O(3)#4	87.0(3)
		O(2)#4–Cu(1)–O(3)	93.0(3)
		O(3)–Cu(1)–O(3)#4	180.0(4)
B(1)–O(2)	1.353(12)	O(2)–B(1)–O(1)	120.9(9)
B(1)–O(1)	1.369(13)	O(2)–B(1)–O(4)	122.5(9)
B(1)–O(4)	1.407(13)	O(1)–B(1)–O(4)	116.5(9)
B(2)–O(3)	1.318(12)	O(3)–B(2)–O(5)#7	125.3(10)
B(2)–O(5)#7	1.404(13)	O(3)–B(2)–O(4)#6	123.0(9)
B(2)–O(4)#6	1.439(15)	O(5)#7–B(2)–O(4)#6	111.6(8)

Note: Symmetry transformations used to generate equivalent atoms: #1 $-x, -y+1, -z$; #2 $x+1/2, y+1/2, -z+1/2$; #3 $-x+1/2, y-1/2, -z+1/2$; #4 $-x+1/2, -y+1/2, -z$; #5 $x, -y, z+1/2$; #6 $x, -y+1, z+1/2$; #7 $x, -y, z-1/2$; #8 $x, -y+1, z-1/2$.

3. Results and discussion

3.1. Crystal structure of $Li_2Pb_2CuB_4O_{10}$

The $Li_2Pb_2CuB_4O_{10}$ compound crystallizes in the space group $C2/c$. The structure is shown in Fig. 1. One unique lithium atom, one unique lead atom, one unique copper atom, two unique boron atoms, and five unique oxygen atoms are in the asymmetric unit (Table 2). The basic building units of the $Li_2Pb_2CuB_4O_{10}$ are corner shared BO_3 polyhedra that form isolated pyroborate (B_2O_5) units, and therefore $Li_2Pb_2CuB_4O_{10}$ can be written as $Li_2Pb_2Cu(B_2O_5)_2$. The extended framework of the structure can be described as isolated $[CuB_4O_{10}]^{6-}$ units that are linked by LiO_4 polyhedra and PbO_3 polyhedra. The isolated $[CuB_4O_{10}]^{6-}$ units are depicted in Fig. 2 (the distance of the nearest neighbor Cu pairs is 4.7895 Å), and are later
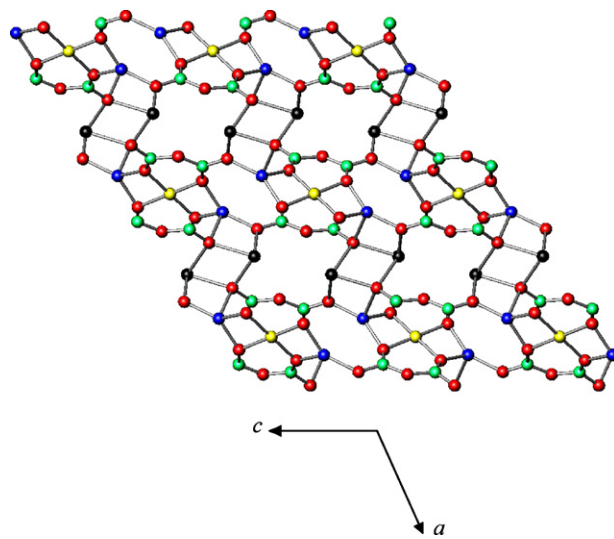
Fig. 1. A drawing of the structure of $Li_2Pb_2CuB_4O_{10}$ as viewed down the b-axis. The blue balls are Li; the black balls are Pb; the yellow balls are Cu; the green balls are B, the red balls are O atoms, the green balls are B atoms. (For interpretation of the references to color in the figure caption, the reader is referred to the web version of the article.)
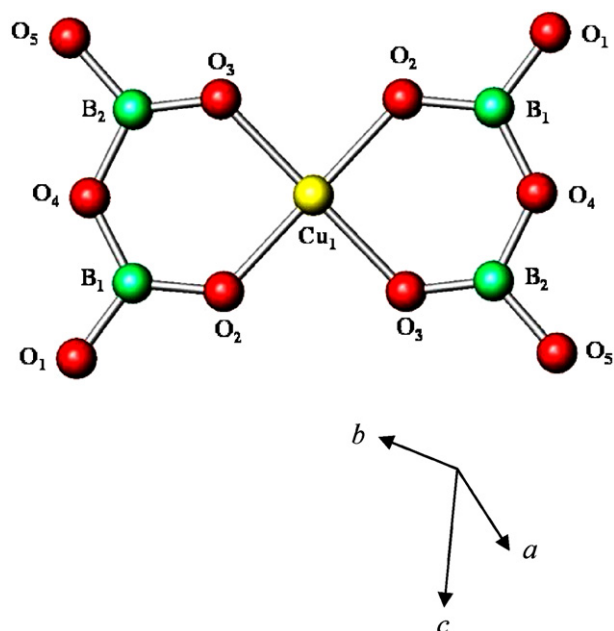
Fig. 2. Structural unit $[CuB_4O_{10}]^{6-}$ in $Li_2Pb_2CuB_4O_{10}$.

described. The CuO_4 polyhedra are nearly square planar, and the Cu–O bonds range from 1.922(7) to 1.952(6) Å. The CuO_4 polyhedra share four oxygen atoms with four boron atoms within two different B_2O_5 pyroborate groups (Fig. 2).

The Li coordination is a distorted LiO_4 tetrahedron with the Li atom position almost in the center of one face. The Li–O bond lengths and angles are given in Table 3. The coordination of Pb is a PbO_3 trigonal pyramid with the Pb atom at the vertex of the pyramid. Furthermore, two PbO_3 trigonal pyramids share one edge forming Pb_2O_4 dimers that are depicted in Fig. 3. Within the dimer, all four oxygen atoms are positioned in the same plane. The two Pb atoms and the two shared oxygens are also positioned in the
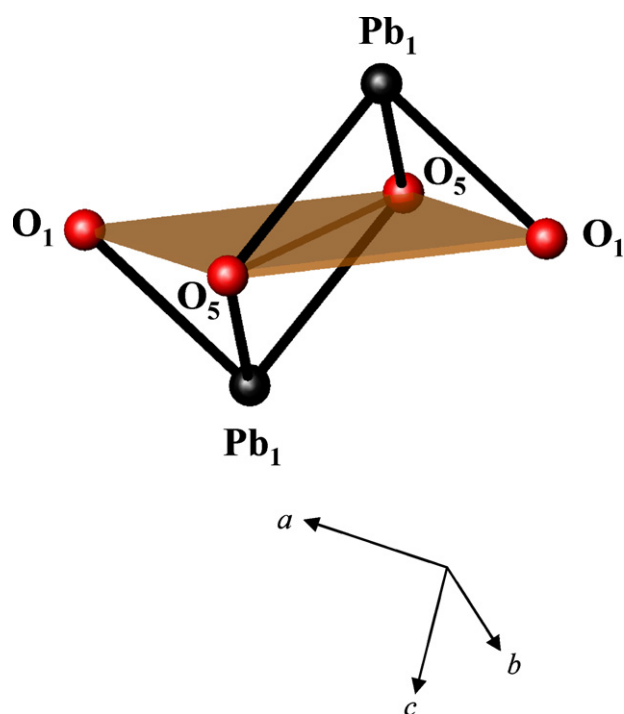

Fig. 3. Pb_2O_4 polyhedra in $Li_2Pb_2CuB_4O_{10}$.

Table 4
Bond valence analysis of the $Li_2Pb_2CuB_4O_{10}$.[a,b]

Atom	O1	O2	O3	O4	O5	$\sum_{cations}$
Li1	0.345	0.301	0.327		0.141	1.114
Pb1	0.788				0.618 + 0.526	1.932
Cu1		0.519[×2]	0.478[×2]			1.994
B1	1.005	1.050		0.907		2.962
B2			1.154	0.832	0.915	2.901
$\sum_{anions}$	2.138	1.870	1.959	1.739	2.200	

[a] Bond valences calculated with the program Bond Valence Calculator Version 2.00, Hormillosa, C., Healy, S., Stephen, T., McMaster University (1993).
[b] Valence sums calculated with the formula: $S_i = \exp[(R_0 - R_i)/B]$, where S_i = valence of bond "i" and $B = 0.37$. Left and right subscripts indicate the number of equivalent bonds for anions and cations, respectively.

same plane. Cu is surrounded by four oxygen atoms forming a CuO_4 rectangular plane. Both B(1) and B(2) show BO_3 trigonal planar oxygen coordination, furthermore, $B(1)O_3$ and $B(2)O_3$ share one corner forming $[B_2O_5]$ dimers.

The Li–O bond distances of the distorted tetrahedra vary 1.86(2)–2.19(2) Å with an average of 1.96(2) Å. This average Li–O bond distance in $Li_2Pb_2CuB_4O_{10}$ is consistent with the average Li–O distances of 1.999 Å in $Li_6CuB_4O_{10}$ [18]. The average Pb–O distance in $Li_2Pb_2CuB_4O_{10}$ is consistent with the average Pb–O distances in $K_2Pb_2O_3$ [23], and in $Pb_2Cu_3B_4O_{11}$ [24]. Likewise, the average Cu(1)–O distance for the square planar polyhedron in $Li_2Pb_2CuB_4O_{10}$ is 1.937(7) Å as compared to 1.932 Å in $Pb_2CuB_2O_6$, and $CuSe_2O_5$ [25,26]. For the $B(1)O_3$ and $B(2)O_3$ groups, the mean B–O distances of each polyhedra are similar to values observed in other BO_3 groups [27,28]. The long B(1)–O(4) and B(2)–O(4) distances of 1.407(13) Å and 1.439(15) Å structure of $Li_2Pb_2CuB_4O_{10}$, respectively, are due to constraints imposed by corner sharing, and are similar to those found in other compounds with B_2O_5 units such as $Mg_2(B_2O_5)$ [29] and $Bi_2ZnO(B_2O_6)$ [30].

For further clarification, the bond valence sums of each atom in $Li_2Pb_2CuB_4O_{10}$ were calculated [31,32] and are listed in Table 4. These valence sums agree with the expected oxidation states.

3.2. Vibrational spectroscopic characterization

Figure S1 shows the section from 400 to 4000 cm^{-1} of the infrared spectrum of $Li_2Pb_2CuB_4O_{10}$. The IR spectrum of the synthetic samples exhibited the following absorptions which were assigned referring to literature [33–35]. The main infrared absorption region between about 1100 and 1400 cm^{-1} reveals several absorption bands owing to asymmetric stretching of trigonal BO_3 (1372, 1335 and 1170 cm^{-1}) groups. The bands at 700, 688 and 663 cm^{-1} are the out-of-plane bending of B–O in BO_3. In the long-wavelength part of the spectrum there are weak bands at 508 and 531 cm^{-1}, which correspond to the deformation vibrations of trigonal BO_3 groups.

3.3. Thermal analysis

The $Li_2Pb_2CuB_4O_{10}$ compound was shown to be one peak at 663.3 °C, on the heating curve in Figure S2. For borate compounds, the viscosity is very high, which can cause the melt to supercool, so from only the DTA curve, it is difficult to determine if $Li_2Pb_2CuB_4O_{10}$ melts congruently. In order to verify whether $Li_2Pb_2CuB_4O_{10}$ melts congruently, 0.6 g of $Li_2Pb_2CuB_4O_{10}$ powder was heated to 700 °C, in a box furnace, and rapidly cooled to room temperature. Analysis of the powder XRD pattern of the frozen melt revealed that the diffraction patterns are the same as that of the initial $Li_2Pb_2CuB_4O_{10}$ powder, which further demonstrates that $Li_2Pb_2CuB_4O_{10}$ is a congruently melting compound.

4. Conclusions

In summary, $Li_2Pb_2CuB_4O_{10}$ has been synthesized and their structures have been determined by single crystal X-ray diffraction. It crystallizes in the space group $C2/c$ and exhibits isolated units of stoichiometry $[CuB_4O_{10}]^{6-}$ that are built from CuO_4 distorted square planes and triangular BO_3 groups. Thermal analysis shows that $Li_2Pb_2CuB_4O_{10}$ melts congruently. Our future research efforts will be devoted to the exploration of its magnetic properties.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jallcom.2010.11.206.

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