



Preparation and Structure of the Non-centrosymmetric Hydrated Borate: $K_2Ca[B_4O_5(OH)_4]_2 \cdot 8H_2O$

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Single crystal of hydrated borate $K_2Ca[B_4O_5(OH)_4]_2 \cdot 8H_2O$ (KCB) has been grown with sizes up to 30 mm × 10 mm × 5 mm under the condition of water solution. The structure is determined by X-ray diffraction, IR and SEM. It crystallizes in the orthorhombic space group $P2_12_12_1$, with $a = 16.59700(\text{Å})$, $b = 12.46900(\text{Å})$, $c = 11.56900(\text{Å})$, $z = 4$. In the structure, Ca and K atoms are disordered on different 4a sites. The fundamental building units are K-O polyhedra, Ca-O polyhedral and $[B_4O_5(OH)_4]^{2-}$ polyborate anions, with the new coordination number of K_1^+ , K_2^+ and Ca^{2+} is 9, 7, 6. And we fit the crystal structure and ideal shape integrally.

Key Words: Crystal structure, Preparation, Hydrated borate, Characterization.

INTRODUCTION

Many large compounds are mainly composed of boron atoms so that they own the unique structural characteristics of boron-oxygen group, with planar BO_3 and tetrahedral BO_4 groups as the basic structures. These BO_3 triangles and BO_4 tetrahedral can further link together *via* common oxygen atoms to form isolated rings or cages, or polymerize into infinite chains (1D), sheets (2D) or networks (3D).

Generally, borates include single metal and double metal borates. The later is composed of alkaline earth metals and alkali metals mostly. Alkali metal and alkaline-earth metal borates have produced a large family of compounds with outstanding physical properties. For instance, Ca-B-O and K-B-O ternary system, especially more excellent new borates, have been found, such as $KB_5O_8 \cdot 4H_2O$ ¹, $K_2B_4O_7 \cdot 7H_2O$ ², $K(B_5O_6(OH)_4) \cdot 2H_2O$ ², $K_4[B_{10}O_{15}(OH)_4]^{3-}$, $CaB_8O_{11}(OH)_4$ ⁴, $Ca[B_5O_8(OH)] \cdot H_2O$ ⁵, $xCaO \cdot 5B_2O_3 \cdot yH_2O$ ($x = 2$ and 4 , $y = 5$ and 7)⁶, $Ca(B_3O_5(OH))$ ⁷, $Ca_4(B_5O_7(OH)_5) \cdot 2H_2O$ ⁷ and $Ca_2(B_5O_7(OH)_5) \cdot 2H_2O$ ⁷, which have been importantly applied in optical materials, glass materials and communication materials. $K_2Ca[B_4O_5(OH)_4]_2 \cdot 8H_2O$ (KCB) as a kind of potassium and calcium borates, has been applied in manufacturing colour ceramic, porcelain glazes and glass preparation. Its composition and structure has been studied by Solans and Altaba⁸, and Jia *et al.*⁹. It is found that KCB has 8, 6, 7 or 5, 5, 6 coordination number of K_1^+ , K_2^+ and Ca^{2+} , respectively. But, to the structural description of KCB, it is imperfect. In this paper, we report on the syntheses and structural characteristics

of the hydrated borates $K_2Ca[B_4O_5(OH)_4]_2 \cdot 8H_2O$ (KCB) with different coordination number of K_1^+ , K_2^+ and Ca^{2+} . And we fit the crystal structure integrally.

EXPERIMENTAL

Preparation: At 35 °C, a mass ratio of 25:50:7.43 of KOH, H_3BO_3 and $CaCl_2 \cdot 2H_2O$ were mixed with stirring speed 400 rpm, in a 500 mL three-neck flask. Under the rate of drop temperature- 2 °C/day from 35 °C, the single crystals of KCB began to generate after 3 days. Characterization crystallization existed in 15 days at room temperature. Then, the colourless block crystals were physically separated from the matrix. All reagents were analytical grade.

Characterization: The crystallographic information of KCB was obtained by X-ray powder diffraction and FT-IR spectroscopy recorded over the 4000-400 cm^{-1} region on a Nicolet 470 spectrometer with KBr pellets at room temperature. Its diffraction patterns were collected using a D8 Advance X-ray diffractometer, operating in the Bragg configuration using $CuK_{\alpha}1$ radiation ($\lambda = 1.54 \text{ Å}$) from 10-50° at a scanning rate of 0.2°/min for the identification of crystal phases. The morphology of the products was observed with a scanning electron microscope.

Determination of crystal structure: A colourless and transparent crystal of KCB with the dimension 30 mm × 10 mm × 5 mm, was carefully selected under an optical microscope. The crystal structure was investigated by single-crystal X-ray diffraction on an automated Bruker Smart-1000 CCD

automatic four-circle diffractometer with graphite-monochromatized MoK_{α} ($\lambda = 0.71073 \text{ \AA}$) radiation. All calculations were performed with programs from the SHELXTL crystallographic software package. Final least-squares refinement was on F_o^2 with data having $F_o^2 \geq 2\sigma(F_o^2)$.

RESULTS AND DISCUSSION

FT-IR spectra: The IR spectra was measured at room temperature and shown in Fig. 1. According to the reference¹⁰, stretching vibration absorption peaks of O-H situate $3612\text{--}3204 \text{ cm}^{-1}$ and H-O-H bending modes exist at 1685 and 1635 cm^{-1} , the peaks at 1455 , 1399 and 1345 cm^{-1} ascribing to B(3)-O asymmetric stretching, the two peaks at 1296 and 1165 cm^{-1} assigned to B-O-H bending modes, the three peaks at 1072 , 1037 and 1002 cm^{-1} assigned to B(4)-O asymmetric stretching, the peak at 946 cm^{-1} assigned to B(3)-O symmetric stretching, the peak at 834 cm^{-1} assigned to B(4)-O symmetric stretching and the three peaks at 709 , 658 and 532 cm^{-1} assigned to B(3)-O bending modes, the peak at 591 cm^{-1} assigned to symmetrical pulse vibration of B(4)-O, the peak at 463 cm^{-1} assigned to bending vibration peak of B(4)-O.

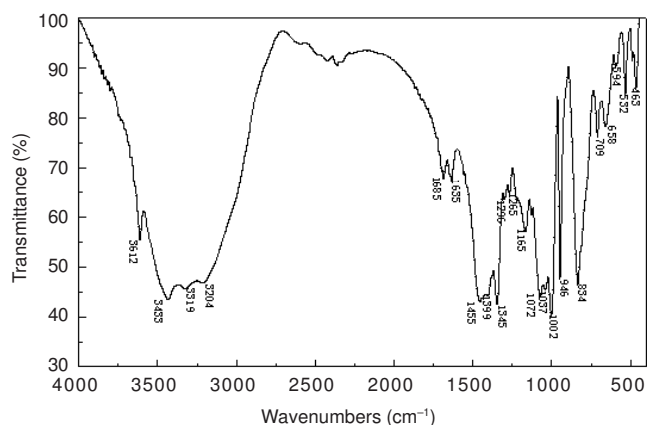


Fig. 1. FT-IR spectrum of the KCB

SEM Photograph: The SEM photograph of KCB crystal is shown in Fig. 2, which clearly reveals the hexagonal structure as a single crystal, 30 mm long.

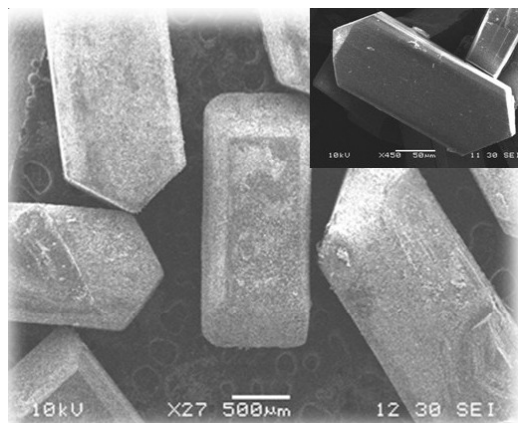


Fig. 2. SEM photograph of KCB crystals

X-Ray diffraction analysis: A colourless and transparent crystal of KCB with the dimension $30 \text{ mm} \times 10 \text{ mm} \times 5 \text{ mm}$

is selected for the crystal structure measurements. Fig. 3 shows the XRD pattern of KCB and the simulated single-crystal structure (JCPDS (76-1013)). The diffraction peaks on the patterns correspond well in position, indicating the phase purity of the as-synthesized sample. It crystallizes in the orthorhombic space group $P2_12_12_1$, with $a = 16.59700 \text{ (\AA)}$, $b = 12.46900 \text{ (\AA)}$, $c = 11.56900 \text{ (\AA)}$, $z = 4$.

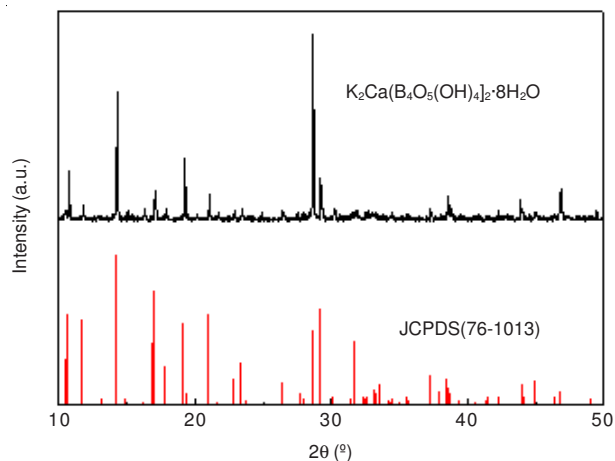


Fig. 3. X-Ray powder diffraction patterns of the as-synthesized KCB and the simulated

Cation and anion coordination: There are eight independent B atoms in the structure of KCB. B1, B3, B7 and B8 atoms coordinate with three O atoms in a triangular arrangement (Fig. 4(a)) while B2, B5, B4 and B6 atoms are tetrahedral coordinated with four O atoms each [Fig. 4(b)]. The mean $\langle B-O \rangle$ distances of BO_3 and BO_4 groups are 1.360 and 1.511 \AA , respectively. The O-B-O angles range from $106.97\text{--}123.45^\circ$ while its average value is 112.971° .

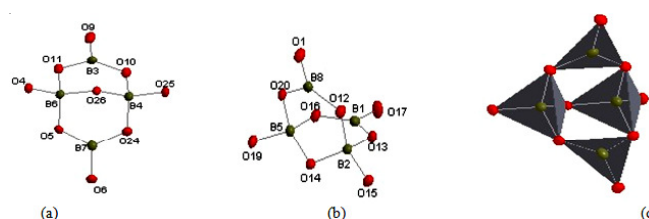


Fig. 4. Coordination environment of BO_3 (a), BO_4 (b), Ca^{2+} (c) and K^+ (d) (e) cations

One Ca atom site coordinates with seven oxygen atoms and the mean distance of Ca-O waves in range of $2.3479\text{--}2.479 \text{ \AA}$ [Fig. 4(c)]. But the reported average (Ca-O) bond length is 2.409 \AA . In Fig. 4, there are two kinds of coordinated forms for K^+ ions in the structure. One is one K^+ ion coordinated by nine O atoms [Fig. 4(d)]. The other is one K^+ ion coordinated by seven O atoms in Fig. 4(e). In the K(1)O9 polyhedron, nine short bond lengths vary from $2.975\text{--}3.369 \text{ \AA}$, with $\langle K-O \rangle = 3.109 \text{ \AA}$. In the K(2)O7 polyhedron, seven short bond lengths are in the range of $2.738\text{--}3.365 \text{ \AA}$, with $\langle K-O \rangle = 3.361 \text{ \AA}$.

Structure of the borate anion: Using the diamond software, we analyze the structure of KCB. The $BO_2(OH)$ and $BO_3(OH)$ polyhedra share their corners to form $[B_4O_5(OH)_4]^{2-}$ polyborate anions (Fig. 5). The two $[B_4O_5(OH)_4]^{2-}$ consist of

two eight-membered rings in which one consists of B1, B2, B5 and B8 and another includes B3, B4, B6 and B7. Every two B atoms are connected by one O atom. The structural unit in KCB can be described as $2\Delta 2\square:(2\Delta 2\square)$, where Δ and \square refer to BO_3 or $\text{BO}_2(\text{OH})$ and BO_4 or $\text{BO}_3(\text{OH})$ polyhedra, respectively [(Fig. 5(c)), according to the notation given by Burns *et al.*¹¹. Anionic group $[\text{B}_4\text{O}_5(\text{OH})_4]^{2-}$ can be as a group of independent unit processes, because the strength of $[\text{B}_4\text{O}_5(\text{OH})_4]^{2-}$ anionic covalent bond is big and the ion in tetraborate anion can maintain connections in crystal and solution. The $[\text{B}_4\text{O}_5(\text{OH})_4]^{2-}$ units are linked together through four exocyclic oxygen atoms ((a): O4, O6, O25, O9 and (b): O1, O19, O15, O17) to neighboring units respectively.

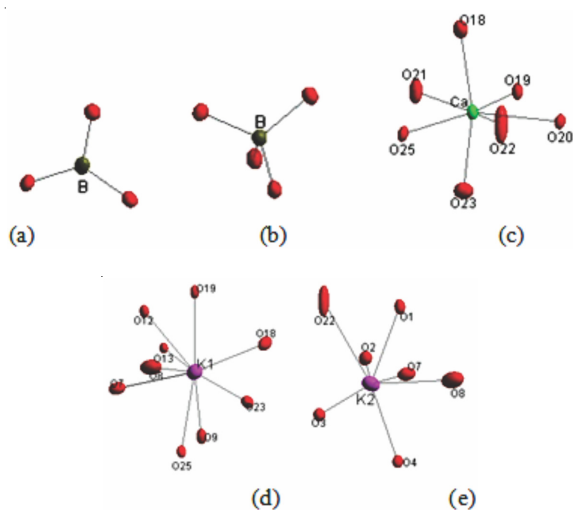


Fig. 5. Coordination environment of $[\text{B}_4\text{O}_5(\text{OH})_4]^{2-}$ ((a), (b), (c))

Structure description: Crystallographic analysis reveals that KCB belongs to the space group $\text{P}2_12_12_1$. Crystal data and structural refinement information are summarized in Table-1. Atomic coordinates parameters and the main bond lengths and angles for KCB can be seen in Tables 2 and 3. The K, Ca and

TABLE-1 CRYSTAL DATA AND STRUCTURE REFINEMENT FOR KCB	
Empirical	$\text{K}_2\text{Ca}[\text{B}_4\text{O}_5(\text{OH})_4]_2 \cdot 8\text{H}_2\text{O}$
Formula weight	620.747 g/mol
Temperature	289(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	$\text{P}2_12_12_1(19)$
Unit cell dimensions	a = 11.5801(10) Å b = 12.4030(11) Å c = 16.5597(14) Å
Volume	2378.44(40) Å ³
Z	4
Density (calculated)	1.73343 g/cm ³
Crystal size	30 mm × 10 mm × 5 mm
θ range for data collection	8.901- 89.993°
R _{All}	0.049
Index ranges	0 ≤ h ≤ 8, 0 ≤ k ≤ 7, 0 ≤ l ≤ 6

B atoms lie in four different 4a sites. All of the cations are located in the anionic $[\text{B}_4\text{O}_5(\text{OH})_4]^{2-}$ framework and compensate its negative charge, shown in Fig. 6(a). It can be described as including $[\text{B}_4\text{O}_5(\text{OH})_4]^{2-}$ and the coordination environment of K^+ and Ca^{2+} cations. The Ca atom shares an edge with one $[\text{B}_4\text{O}_5(\text{OH})_4]^{2-}$ and K1 atom, meanwhile, connects a corner with another $[\text{B}_4\text{O}_5(\text{OH})_4]^{2-}$ and K2 atom. The two K^+ ions connecting one $[\text{B}_4\text{O}_5(\text{OH})_4]^{2-}$, respectively, share one O-O ridge each other [Fig. 6(b-d)].

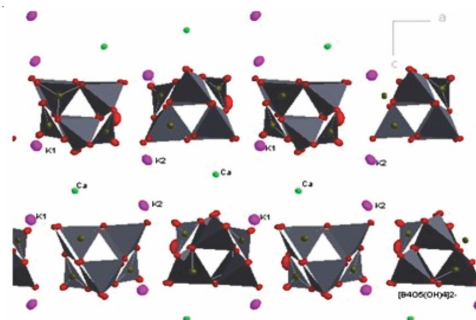


TABLE-2
ATOMIC COORDINATES PARAMETERS FOR KCB

Atom	x	y	z	Atom	x	y	z
B1	0.8255(3)	0.4181(3)	0.0747(2)	O9	0.3905(2)	0.7007(2)	0.09826(14)
B2	0.7137(3)	0.2519(3)	0.0801(2)	O10	0.28823(19)	0.7303(2)	-0.02349(14)
B3	0.2873(3)	0.7128(3)	0.0576(2)	O11	0.1878(2)	0.7080(2)	0.10147(14)
B4	0.3220(3)	0.2552(3)	0.4313(2)	O12	0.6075(2)	0.2754(2)	0.03056(14)
B5	0.3234(3)	0.2147(3)	0.0395(2)	O13	0.7524(2)	0.3539(2)	0.11818(14)
B6	0.5746(3)	0.7827(3)	-0.0571(2)	O14	0.80308(19)	0.2107(2)	0.02628(14)
B7	0.5686(3)	0.9212(3)	0.0508(2)	O15	0.6819(2)	0.1775(2)	0.14406(14)
B8	0.6132(3)	0.2939(3)	-0.0511(2)	O16	0.8580(2)	0.3919(2)	-0.00265(14)
Ca1	0.31515(6)	0.22174(6)	0.22155(4)	O17	0.8632(2)	0.5118(2)	0.10998(15)
K2	0.51272(9)	0.47512(8)	0.12186(6)	O18	0.3254(3)	0.4149(2)	0.24151(16)
K3	0.50771(8)	0.51546(8)	-0.17107(6)	O19	0.4077(2)	0.2499(2)	0.09717(14)
O1	0.5162(2)	0.3013(2)	-0.09766(15)	O20	0.2172(2)	0.1996(2)	0.08945(14)
O2	0.3305(2)	0.4165(2)	-0.25482(16)	O21	0.5175(2)	0.2514(3)	0.25249(16)
O3	0.7031(2)	0.6213(2)	-0.22000(16)	O22	0.1123(3)	0.2171(4)	0.24593(17)
O4	0.4906(2)	0.74079(19)	-0.11169(14)	O23	0.3707(2)	0.0332(2)	0.21685(17)
O5	0.5396(2)	0.8918(2)	-0.02584(14)	O24	0.3610(2)	0.3611(2)	0.40037(14)
O6	0.5268(2)	1.0159(2)	0.08400(15)	O25	0.3030(2)	0.1842(2)	0.36224(14)
O7	0.6390(3)	0.5127(2)	-0.03201(18)	O26	0.40954(18)	0.2125(2)	0.48634(14)
O8	0.3644(3)	0.5008(3)	-0.0279(2)	—	—	—	—

Symmetry codes: (1) x, y, z; (2) 0.5-x, -y, 0.5+z; (3) 0.5+x, 0.5-y, -z; (4) -x, 0.5+y, 0.5-z.

TABLE-3
MAIN BOND LENGTHS AND ANGLES

Bond	Distance	Bond	Distance	Bond	Distance
B1-O13	1.367(4)	B7-O5	1.362(4)	K2-O13	3.157(3)
B1-O17	1.372(4)	B7-O24iii	1.369(4)	K2-O9	3.160(3)
B1-O16	1.373(4)	B7-O6	1.384(4)	K2-O25iii	3.369(3)
B2-O15	1.453(4)	B8-O20v	1.364(4)	K2-Ca1iii	4.477(2)
B2-O14	1.458(4)	B8-O1	1.366(4)	K3-O3	2.738(3)
B2-O13	1.483(4)	B8-O12	1.374(4)	K3-O7	2.760(4)
B2-O12	1.506(4)	Ca1-O19	2.349(2)	K3-O2	2.764(3)
B3-O10	1.360(4)	Ca1-O25	2.378(2)	K3-O8	2.900(4)
B3-O11	1.364(4)	Ca1-O22	2.383(4)	K3-O1	2.923(3)
B3-O9	1.380(4)	Ca1-O18	2.422(3)	K3-O4	2.969(3)
B4-O25	1.461(4)	Ca1-O23	2.426(3)	K3-O22v	3.365(5)
B4-O26	1.462(4)	Ca1-O21	2.427(3)	K3-Ca1v	4.693(2)
B4-O24	1.480(4)	Ca1-O20	2.479(2)	O10-B4vii	1.490(4)
B4-O10i	1.490(4)	Ca1-K2	4.224(2)	O11-B6viii	1.507(4)
B5-O19	1.434(4)	Ca1-K2vi	4.477(2)	O14-B5v	1.449(4)
B5-O14ii	1.449(4)	Ca1-K3ii	4.693(2)	O16-B5v	1.511(4)
B5-O20	1.494(4)	K2-O7	2.975(4)	O20-B8ii	1.364(4)
B5-O16ii	1.511(4)	K2-O18	3.031(4)	O22-K3iii	3.365(5)
B6-O4	1.426(4)	K2-O8	3.034(4)	O23-K2vi	3.078(3)
B6-O26iii	1.472(4)	K2-O19	3.074(3)	O24-B7vi	1.369(4)
B6-O5	1.505(4)	K2-O23iii	3.078(3)	O25-K2vi	3.369(3)
B6-O11iv	1.507(4)	K2-O12	3.103(3)	O26-B6vi	1.472(4)

Bond	Angle	Bond	Angle	Bond	Angle	Bond	Angle
O19-Ca1-O25	156.16(6)	O22-Ca1-K3ii	42.92(9)	O23-Ca1-O20	89.19(9)	B1-O13-B2	117.37(27)
O19-Ca1-O22	126.98(10)	O18-Ca1-K3ii	132.99(7)	O21-Ca1-O20	130.12(8)	B1-O13-K2	106.10(19)
O25-Ca1-O22	76.82(10)	O23-Ca1-K3ii	65.88(6)	O19-Ca1-K2	45.49(5)	B2-O13-K2	98.55(18)
O19-Ca1-O18	87.11(10)	O21-Ca1-K3ii	149.90(6)	O25-Ca1-K2	124.06(5)	B5v-O14-B2	110.54(22)
O25-Ca1-O18	93.62(10)	O20-Ca1-K3ii	55.01(5)	O22-Ca1-K2	128.14(9)	B1-O16-B5v	120.76(24)
O22-Ca1-O18	92.82(15)	K2-Ca1-K3ii	143.87(3)	O18-Ca1-K2	44.78(6)	Ca1-O18-K2	100.96(9)
O19-Ca1-O23	89.63(9)	K2vi-Ca1-K3ii	90.73(2)	O23-Ca1-K2	124.09(6)	B5-O19-Ca1	103.20(16)
O25-Ca1-O23	81.91(10)	O7-K2-O18	161.85(10)	O21-Ca1-K2	56.38(6)	B5-O19-K2	129.39(19)
O22-Ca1-O23	104.12(12)	B8-O1-K3	108.89(20)	O20-Ca1-K2	89.15(6)	Ca1-O19-K2	101.49(8)
O18-Ca1-O23	160.88(9)	B6-O4-K3	120.50(18)	O19-Ca1-K2vi	113.96(5)	B8ii-O20-B5	117.44(25)
O19-Ca1-O21	73.82(9)	B7-O5-B6	119.68(24)	O25-Ca1-K2vi	47.63(5)	B8ii-O20-Ca1	143.94(18)
O25-Ca1-O21	83.12(9)	K3-O7-K2	116.49(12)	O22-Ca1-K2vi	108.95(9)	B5-O20-Ca1	95.67(15)
O22-Ca1-O21	156.86(11)	K3-O8-K2	110.57(11)	O18-Ca1-K2vi	125.11(6)	Ca1-O22-K3ii	108.24(13)
O18-Ca1-O21	76.91(12)	B3-O9-K2	122.99(19)	O23-Ca1-K2vi	40.76(6)	Ca1-O23-K2vi	108.27(9)
O23-Ca1-O21	84.08(10)	B3-O10-B4vii	120.56(23)	O21-Ca1-K2vi	63.36(7)	B7vi-O24-B4	117.45(27)
O19-Ca1-O20	56.72(6)	B3-O11-B6viii	118.13(25)	O20-Ca1-K2vi	129.71(5)	B4-O25-Ca1	129.80(16)
O25-Ca1-O20	144.61(6)	B8-O12-B2	121.93(23)	K2-Ca1-K2vi	119.56(2)	B4-O25-K2vi	107.91(18)
O22-Ca1-O20	72.29(10)	B8-O12-K2	111.32(17)	O19-Ca1-K3ii	106.46(6)	Ca1-O25-K2vi	100.94(7)
O18-Ca1-O20	104.60(9)	B2-O12-K2	100.26(18)	O25-Ca1-K3ii	90.41(6)	B4-O26-B6vi	111.63(22)

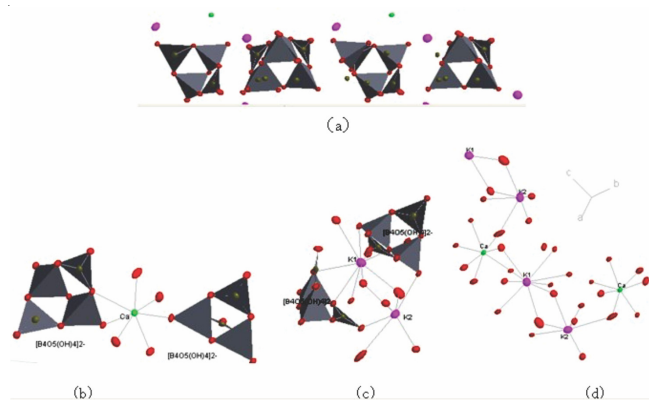
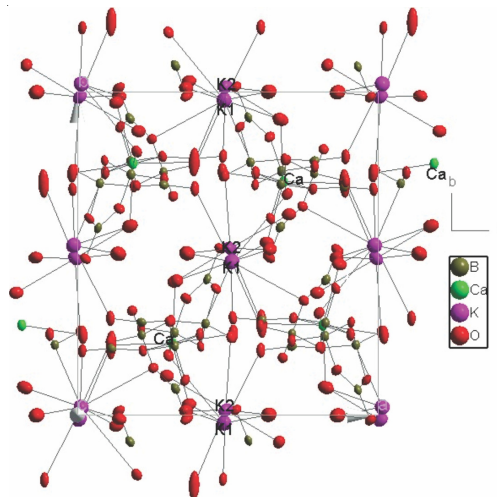
Symmetry codes: (1) x, y, z ; (2) $0.5-x, -y, 0.5+z$; (3) $0.5+x, 0.5-y, -z$; (4) $-x, 0.5+y, 0.5-z$.

Fig. 6. Form of cations existed in KCB [(a), (b), (c), (d)]

Fig. 7. View of the structure of KCB along c axisCrystal structure is chain arranged in parallel along the c axis (Fig. 7). Adjacent chains are further linked *via* H-bonding

interaction into stratiform structure. K and Ca atoms between chains compensate the negative charge of borate chains and hold the layers together into the 3D structure through bonding with oxygen atoms of chains.

Crystal shape prediction: In the above work, we have researched the structure of KCB crystal, which is asymmetric and helical, parallel to the c axis (Fig. 7). These parallel helical chains infinite link to boric acid salt layer through the hydrogen bond in Fig. 8. In structure, K-O bond is easily broken because its bond energy is smaller than Ca-O and B-O. So the crystal fracture position is at 1, 2, 3, 4 dotted line positions. Fig. 9 shows ideal shape of KCB crystal which mark the axis direction of crystal and symbols of main display surface. The ideal shape is anastomotic with photograph of KCB crystals.

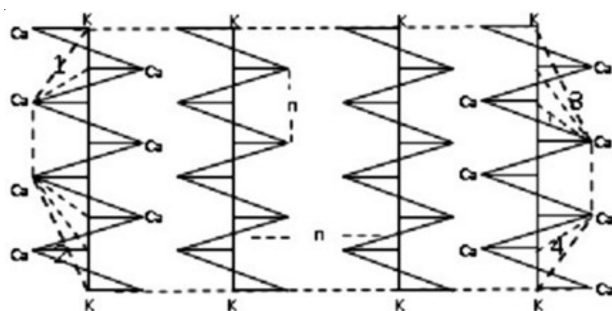


Fig. 8. Structure fitting plan along c axis of KCB

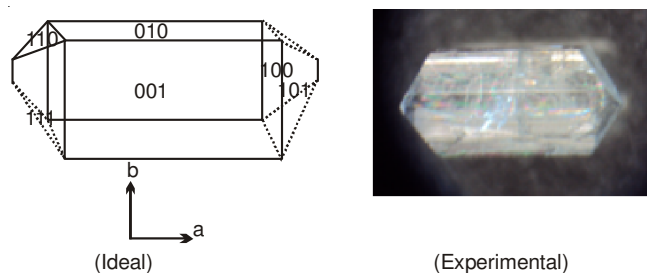


Fig. 9. Ideal and experimental shape of KCB crystal

Conclusion

In summary, 30 mm × 10 mm × 5 mm KCB crystals are synthesized by water solution method and its structure is consistent with the simulated crystal, fitting the crystal structure and ideal shape integrally. The fundamental building block in the structure is the eight-membered ring $[B_4O_5(OH)_4]^{2-}$. Calcium ion has six-fold coordination, while potassium ions have nine-fold and sevenfold coordination. They compensate the negative charge of borate chains and hold the layers together into the 3D structure. The presence of OH^- in the lattice is not desired because of their tendency to dehydrate upon heating. Further structural exploratory work need to do with change of OH^- group.

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