Electronic Supplementary Material (ESI) for Dalton Transactions.

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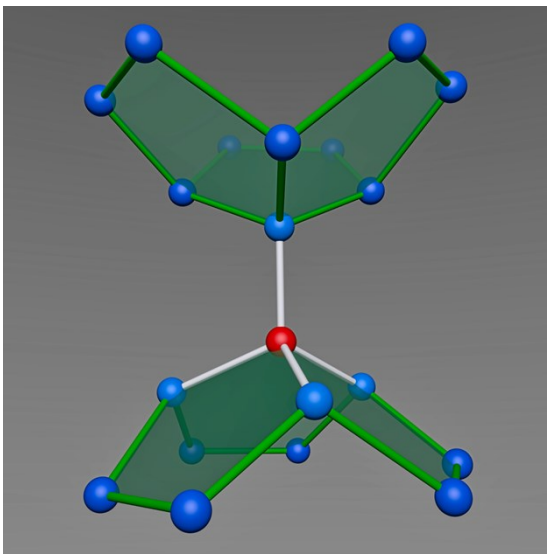
The Impact of Boron Atoms on Clathrate-I Silicides: Composition Range of the Borosilicide $K_{8-x}B_ySi_{46-y}$

Walter Jung, Bodo Böhme, Julia M. Hübner, Ulrich Burkhardt, Horst Borrmann, Matej Bobnar, Hong Duong Nguyen, Ingo Pantenburg, Martin Etter, Ulrich Schwarz, Yuri Grin, and Michael Baitinger



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1. Crystallographic determination of the boron content

The crystal structure refinement was conducted for a binary model $K_{8-x}Si_{46-y}$. In this model, the refinement reveals for site Si2 at Wyckoff position 16*i* and Si3 at Wyckoff position Si3 a deficiency in silicon. After the refinement, we have calculated the number of boron atoms assuming no vacancies in the framework. As explained in the main text, there are two 16*i* split-positions for Si2. Site Si21 is occupied by boron and silicon atoms, site Si22 by silicon atoms only (Fig. S1).

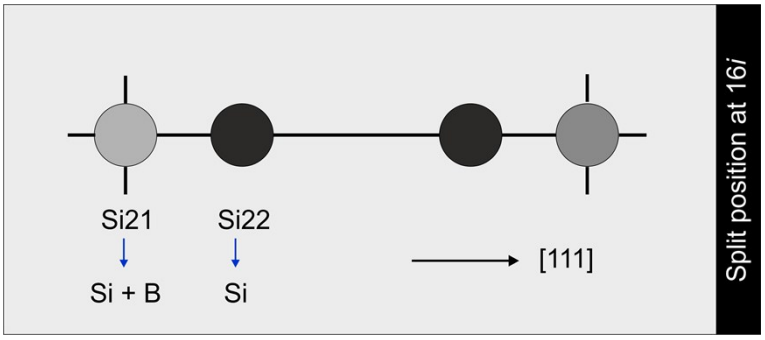

Fig. S1: The split positions Si21 and Si22 at Wyckoff position 16i.

From the crystal structure refinement of the binary model, the occupancy values *occ*(Si21) and *occ*(Si22) are experimentally obtained. As the 16*i* split-position Si22 is occupied by Si atoms only, the number of Si atoms is

$$n(Si_{22}) = 16\ occ(Si22)$$

The number of electrons $n_e(Si22)$ amounts to:

$$n_e(Si22) = 14\ *\ 16\ occ(Si22)$$

The 16*i* split-position Si21 is mixed occupied by Si21 and B21 atoms. As Si21 and Si22 are alternatively occupied, the total number of atoms at Si21 amounts to:

$$n(B21,Si21) = 16 -\ n(Si22)$$

The overall number of electrons at $n_e(B21,Si21)$ is derived from *occ*(*Si21*):

$$n_e(B21,Si21) = 14\ *\ 16\ occ(Si21)$$

Alternatively, n_e(*B/Si21*) corresponds to:

$$n_e(B21/Si21) = 5\,n(B21) + 14 * n(Si21)$$

With 16 atoms on both split positions:

$$n(Si21) = 16 - 16\,occ(Si22) - n(B21)$$

and thus:

$$n_e(B21/Si21) = 5\,n(B21) + 14 * [16 - 16\,occ(Si22) - n(B21)]$$

By equating both formulas for n_e(*B21, Si21*), the number *n*(B21) is calculated as follows:

$$14 * 16 * occ(Si21) = 5\,n(B21) + 14 * [16 - 16\,occ(Si22) - n(B21)]$$

$$9\,n(B21) = 14 * 16 - 14 * 16occ(Si22) - 14 * 16occ(Si21)$$

$$n(B21) = \frac{14 * 16}{9}[1 - occ(Si21) - occ(Si22)]$$

Remarkably, the formula does not depend on the actual distribution of boron atoms over Si21 and Si22 and provides the total number of boron atoms at position 16*i*.

In similar way, the overall boron content is calculated for Si3, which is represented by the split positions 24*k* and 48*l*. However, the deficiency of Si3 in the binary model is small and the calculated boron content is thus obtained with a high standard deviation.

$$14 * 24 * occ(Si31) + 14 * 48 * occ(Si32) = 5\,n(B3) + 14 * n(Si3)$$

$$14 * 24 * occ(Si31) + 14 * 48 * occ(Si32) = 5\,n(B3) + 14\,(24 - n(B3))$$

$$n(B_3) = \frac{14 * 24}{9}[1 - occ(Si31) - 2\,occ(Si32)]$$

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2. Crystallographic data for crystal 1: $K_{7.18(2)}B_{7.2(5)}Si_{38.8(5)}$

Table S-1a. Experimental details for the single-crystal XRD measurement of **crystal 1**.

Chemical formula	$K_{7.18(2)}B_{7.2(5)}Si_{38.8(5)}$
Space group	$Pm\bar{3}n$
a	9.9366(3) Å
Calculated density	2.4424(2) g/cm^3
Data collection Radiation; λ / Å Temperature	Rigaku Saturn724+, CCD detector MoKα radiation; λ =0.71073 Å 293 K
Reflections: measured unique Reflections with *F*(hkl) > 4 σ(F(hkl)) 2θ and sinθ/λ (max)	 14944 267 259 58.56; 0.688
Refined parameters	29
R(sig); R(eq)	0.0110; 0.0672
Goodness of fit	1.100
R_f; R_w	0.0372; 0.0413

Table S-1b. Atomic coordinates and isotropic displacement parameter (in Å^2) for **crystal 1**.

Atom	**Wyckoff Site**	***x/a***	***y/a***	***z/a***	**s.o.f.**	B_{iso}/B_{eq}*
K1	2*a*	0	0	0	0.59(1)	2.40(9)
K2	6*d*	1/4	1/2	0	1	2.91(5)
Si1	6*c*	1/4	0	1/2	1	2.07(4)
Si21	16*i*	0.1857(10)	*x*	*x*	0.494(7)	2.03(6)
Si22	16*i*	0.202(2)	*x*	*x*	0.244(6)	2.09(6)
Si31	24*k*	0	0.307(2)	0.1146(14)	0.344(7)	1.96(6)
Si32	48*l*	0.0149(9)	0.2909(10)	0.1267(8)	0.319(4)	1.82(5)

* $B_{eq} = 1/3[B_{11}\, a^{*2}\, a^2 + ... \, 2\, B_{23}\, b^*\, c^*\, b\, c \cos\alpha]$

Table S-1c. Anisotropic atomic displacement parameters (in Å^2) for **crystal 1**.

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
K1	2.4(2)	B_{11}	B_{11}	0	0	0
K2	2.40(10)	3.17(8)	B_{22}	0	0	0
Si1	2.17(10)	2.02(6)	B_{22}	0	0	0

Table S-1d. Interatomic distances for **crystal 1** (in Å).

K1	8	6.0	Si21/B	3.195(10)
		2.0	Si22	3.47(2)
	12	4.2	Si31	3.26(2)
		7.8	$Si32_1$	3.156(9)
			$Si32_2$	
K2	4		Si1	3.5131(1)
	8	2.8	Si31	3.336(12)
		5.2	$Si32_1$	3.370(9)
			$Si32_2$	3.582(9)
	8	6.0	Si21/B	3.684(10)
		2.0	Si22	3.61(2)
	4	1.2	Si31	3.872(14)
		2.8	$Si32_1$	3.735(8)
			$Si32_2$	
Si1	4	1.4	Si31	2.34(2)
		2.6	$Si32_1$	2.417(9)
			$Si32_2$	
Si21/B	1	0.2	Si22	1.94(2)
		0.8	Si21/B	2.215(14)
	3	1.1	Si31	2.316(14)
		1.9	$Si32_1$	2.078(13)
			$Si32_2$	2.326(13)
Si22	1	0	Si22	1.67(3)
		1	B	1.94(2)
	3	1.1	Si31	2.42(2)
		1.9	$Si32_1$	2.19(2)
			$Si32_2$	2.44(2)
Si31	2	1.5	Si21/B	2.316(14)
		0.5	Si22	2.42(2)
	1		Si1	2.34(2)
	1	0.4	Si31	2.28(2)
		0.6	$Si32_1$	2.41(2)
			$Si32_2$	
$Si32_{1,2}$	2	1.5	Si21/B	2.078(13)
				2.326(13)
		0.5	Si22	2.19(2)
				2.44(2)
	1		Si1	2.417(9)
	1	0.4	Si31	2.41(2)
		0.6	Si32	2.517(11)
				2.535(11)

3. Crystallographic data for crystal 2: $K_{7.12(4)}B_{7.1(6)}Si_{38.9(6)}$

Table S-2a. Experimental details for the single-crystal XRD measurement of **crystal 2**.

Chemical formula	**$K_{7.12(4)}B_{7.1(6)}Si_{38.9(6)}$**
Space group	$Pm\bar{3}n$
a	9.9393(2) Å
Calculated density	2.4380(2) g/cm^3
Data collection Radiation; λ / Å Temperature	Rigaku Saturn724+, CCD detector MoKα radiation; λ =0.71073 Å 293 K
Reflections: measured unique Reflections with *F*(hkl) > 4 σ(F(hkl)) 2θ and sinθ/λ (max)	 4457 415 339 69.94; 0.806
Refined parameters	29
R(sig); R(eq)	0.0410; 0.0861
Goodness of fit	1.110
R_f; R_w	0.0446; 0.0489

Table S-2b. Atomic coordinates and isotropic displacement parameter (in Å^2) for **crystal 2**.

Atom	**Wyckoff Site**	***x/a***	***y/a***	***z/a***	**s.o.f.**	***B_{iso}/B_{eq}****
K1	2*a*	0	0	0	0.56(2)	0.95(8)
K2	6*d*	1/4	1/2	0	1	1.74(5)
Si1	6*c*	1/4	0	1/2	1	0.82(4)
Si21	16*i*	0.1857(8)	*x*	*x*	0.491(8)	0.78(6)
Si22	16*i*	0.2019(15)	*x*	*x*	0.240(7)	0.69(8)
Si31	24*k*	0	0.309(3)	0.113(2)	0.228(8)	0.69(9)
Si32	48*l*	0.0141(7)	0.2926(8)	0.1254(7)	0.380(6)	0.69(6)

* $B_{eq} = 1/3[B_{11}\, a^{*2}\, a^2 + ... \, 2\, B_{23}\, b^*\, c^*\, b\, c \cos\alpha]$

Table S-2c. Anisotropic atomic displacement parameters (in Å^2) for **crystal 2**.

Atom	***B_{11}***	***B_{22}***	***B_{33}***	***B_{12}***	***B_{13}***	***B_{23}***
K1	0.95(13)	B_{11}	B_{11}	0	0	0
K2	1.15(8)	2.04(7)	B_{22}	0	0	0
Si1	0.77(9)	0.84(7)	B_{22}	0	0	0

Table S-2d. Interatomic distances for **crystal 2** (in Å).

K1	8	6.1	Si21/B	3.197(8)
		1.9	Si22	3.476(15)
	12	2.8	Si31	3.28(3)
		9.2	$Si32_1$	3.167(8)
			$Si32_2$	
K2	4		Si1	3.5141(1)
	8	1.8	Si31	3.32(2)
		6.2	$Si32_1$	3.362(8)
			$Si32_2$	3.563(7)
	8	6.1	Si21/B	3.684(8)
		1.9	Si22	3.610(15)
	4	0.9	Si31	3.89(2)
		3.1	$Si32_1$	3.750(6)
			$Si32_2$	
Si1	4	0.9	Si31	2.33(2)
		3.1	$Si32_1$	2.409(8)
			$Si32_2$	
Si21/B	1	0.2	Si22	1.93(2)
		0.8	Si21/B	2.214(11)
	3	0.7	Si31	2.33(2)
		2.3	$Si32_1$	2.097(11)
			$Si32_2$	2.330(11)
Si22	1	0	Si22	1.66(2)
		1	B	1.93(2)
	3	0.7	Si31	2.44(2)
		2.3	$Si32_1$	2.21(2)
			$Si32_2$	2.45(2)
Si31	2	1.5	Si21/B	2.33(2)
		0.5	Si22	2.44(2)
	1		Si1	2.33(2)
	1	0.2	Si31	2.25(3)
		0.8	$Si32_1$	2.38(2)
			$Si32_2$	
$Si32_{1,2}$	2	1.5	Si21/B	2.097(11)
				2.330(11)
		0.5	Si22	2.21(2)
				2.45(2)
	1		Si1	2.409(8)
	1	0.2	Si31	2.38(2)
		0.8	Si32	2.493(9)
				2.509(9)

4. Crystallographic data for crystal 3: $K_{6.98(4)}B_{6.4(5)}Si_{39.6(5)}$

Table S-3a. Experimental details for the single-crystal XRD measurement of **crystal 3**.

Chemical formula	$K_{6.98(4)}B_{6.4(5)}Si_{39.6(5)}$
Space group	$Pm\bar{3}n$
a	9.9470(2) Å
Calculated density	2.4470(2) g/cm^3
Data collection Radiation; λ / Å Temperature	Rigaku Saturn724+, CCD detector MoKα radiation; λ =0.71073 Å 293 K
Reflections: measured unique Reflections with *F*(hkl) > 4 σ(F(hkl)) 2θ and sinθ/λ (max)	 19861 341 259 64.32; 0.749
Refined parameters	29
R(sig); R(eq)	0.0110; 0.0641
Goodness of fit	1.100
R_f; R_w	0.0473; 0.0513

Table S-3b. Atomic coordinates and isotropic displacement parameter (in Å^2) for **crystal 3**.

Atom	**Wyckoff Site**	***x/a***	***y/a***	***z/a***	**s.o.f.**	B_{iso}/B_{eq}*
K1	2*a*	0	0	0	0.49(2)	1.04(8)
K2	6*d*	1/4	1/2	0	1	1.89(4)
Si1	6*c*	1/4	0	1/2	1	1.00(4)
Si21	16*i*	0.1836(3)	*x*	*x*	0.397(8)	1.20(5)
Si22	16*i*	0.1976(3)	*x*	*x*	0.352(7)	1.01(5)
Si31	24*k*	0	0.3070(5)	0.1160(5)	0.371(7)	0.87(5)
Si32	48*l*	0.0154(3)	0.2906(3)	0.1264(4)	0.313(5)	0.96(4)

* $B_{eq} = 1/3[B_{11}\, a^{*2}\, a^2 + ... \, 2\, B_{23}\, b^*\, c^*\, b\, c \cos\alpha]$

Table S-3c. Anisotropic atomic displacement parameters (in Å^2) for **crystal 3**.

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
K1	1.04(14)	B_{11}	B_{11}	0	0	0
K2	1.40(8)	2.13(6)	B_{22}	0	0	0
Si1	1.03(8)	0.98(6)	B_{22}	0	0	0

Table S-3d. Interatomic distances for **crystal 3** (in Å).

K1	8	5.2	Si21/B	3.164(3)
		2.8	Si22	3.404(3)
	12	4.5	Si31	3.264(5)
		7.5	$Si32_1$	3.156(3)
			$Si32_2$	
K2	4		Si1	3.5168(1)
	8	3.0	Si31	3.347(3)
		5.0	$Si32_1$	3.371(3)
			$Si32_2$	3.590(3)
	8	5.2	Si21/B	3.698(3)
		2.8	Si22	3.631(3)
	4	1.5	Si31	3.861(5)
		2.5	$Si32_1$	3.741(3)
			$Si32_2$	
Si1	4	1.5	Si31	2.337(5)
		2.5	$Si32_1$	2.423(3)
			$Si32_2$	
Si21/B	1	0.4	Si22	2.046(4)
		0.6	Si21/B	2.287(4)
	3	1.1	Si31	2.301(4)
		1.9	$Si32_1$	2.063(4)
			$Si32_2$	2.319(4)
Si22	1	0	Si22	1.806(4)
		1	B	2.046(4)
	3	1.1	Si31	2.388(4)
		1.9	$Si32_1$	2.154(4)
			$Si32_2$	2.418(4)
Si31	2	1.3	Si21/B	2.301(4)
		0.7	Si22	2.388(4)
	1		Si1	2.337(5)
	1	0.4	Si31	2.308(7)
		0.6	$Si32_1$	2.422(6)
			$Si32_2$	
$Si32_{1,2}$	2	1.3	Si21/B	2.063(4)
				2.319(4)
		0.7	Si22	2.154(4)
				2.418(4)
	1		Si1	2.423(3)
	1	0.4	Si31	2.422(6)
		0.6	Si32	2.515(5)
				2.533(5)

5. Crystallographic data for crystal 4: $K_{7.08(1)}B_{6.8(3)}Si_{39.2(3)}$

Table S-4a. Experimental details for the single-crystal XRD measurement of **crystal 4**.

Chemical formula	$K_{7.08(1)}B_{6.8(3)}Si_{39.2(3)}$
Space group	$Pm\bar{3}n$
a	9.952(1) Å
Calculated density	2.4368(8) g/cm^3
Data collection Radiation; λ / Å Temperature	Rigaku Spider AgKα radiation; λ = 0.56087 Å 293 K
Reflections: measured unique Reflections with *F*(hkl) > 4 σ(F(hkl)) 2θ and sinθ/λ (max)	 18587 2001 872 101.88; 1.388
Refined parameters	32
R(sig); R(eq)	0.0330
Goodness of fit	1.050
R_f; R_w	0.0317; 0.0367

Table S-4b. Atomic coordinates and isotropic displacement parameter (in Å^2) for **crystal 4**.

Atom	**Wyckoff Site**	***x/a***	***y/a***	***z/a***	**s.o.f.**	B_{eq}*
K1	2*a*	0	0	0	0.538(7)	0.683(8)
K2	6*d*	1/4	1/2	0	1	1.501(9)
Si1	6*c*	1/4	0	1/2	1	0.596(8)
Si21	16*i*	0.18286(7)	*x*	*x*	0.356(9)	0.640(7)
Si22	16*i*	0.19668(7)	*x*	*x*	0.384(9)	0.580(6)
Si31	24*k*	0	0.30357(8)	0.11802(8)	0.513(2)	0.69(1)
Si32	48*l*	0.0160(1)	0.28996(10)	0.1267(1)	0.239(1)	0.50(2)

* $B_{eq} = 1/3[B_{11}\, a^{*2}\, a^2 + ... \, 2\, B_{23}\, b^*\, c^*\, b\, c \cos\alpha]$

Table S-4c. Anisotropic atomic displacement parameters (in Å^2) for **crystal 4**.

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
K1	0.68(2)	B_{11}	B_{11}	0	0	0
K2	1.04(2)	1.73(2)	B_{22}	0	0	0
Si1	0.63(2)	0.58(1)	B_{22}	0	0	0
Si21	0.64(1)	B_{11}	B_{11}	0.03(2)	B_{12}	B_{12}
Si22	0.58(1)	B_{11}	B_{11}	0.07(1)	B_{12}	B_{12}
Si31	0.79(2)	0.61(2)	0.67(2)	0	0	–0.05(2)
Si32	0.46(5)	0.57(2)	0.48(2)	0.17(2)	–0.14(2)	–0.03(2)

Table S-4d. Interatomic distances for **crystal 4** (in Å).

K1	8	4.9	Si21/B	3.1520(8)
		3.1	Si22	3.3901(7)
	12	6.2	Si31	3.2413(8)
		5.8	$Si32_1$	3.153(1)
			$Si32_2$	
K2	4		Si1	3.5186(2)
	8	4.1	Si31	3.3751(5)
		3.9	$Si32_1$	3.374(1)
			$Si32_2$	3.601(1)
	8	4.9	Si21/B	3.7040(8)
		3.1	Si22	3.6367(7)
	4	2.1	Si31	3.8387(8)
		1.9	$Si32_1$	3.739(1)
			$Si32_2$	
Si1	4	2.1	Si31	2.3552(8)
		1.9	$Si32_1$	2.429(1)
			$Si32_2$	
Si21/B	1	0.4	Si22	2.077(1)
		0.6	Si21/B	2.315(1)
	3	1.6	Si31	2.2740(9)
		1.4	$Si32_1$	2.051(1)
			$Si32_2$	2.316(1)
Si22	1	0	Si22	1.838(1)
		1	B	2.077(1)
	3	1.6	Si31	2.3612(8)
		1.4	$Si32_1$	2.140(1)
			$Si32_2$	2.414(1)
Si31	2	1.2	Si21/B	2.2740(9)
		0.8	Si22	2.3612(8)
	1		Si1	2.3552(8)
	1	0.5	Si31	2.349(1)
		0.5	$Si32_1$	2.445(1)
			$Si32_2$	
$Si32_{1,2}$	2	1.2	Si21/B	2.051(1)
				2.316(1)
		0.8	Si22	2.140(1)
				2.414(1)
	1		Si1	2.429(1)
	1	0.5	Si31	2.445(1)
		0.5	Si32	2.522(1)
				2.543(1)

6. Crystallographic data for crystal 5: $K_{6.80(2)}B_{6.4(5)}Si_{39.6(5)}$

Table S-5a. Experimental details for the single-crystal XRD measurement of **crystal 5**.

Chemical formula	$K_{6.80(2)}B_{6.4(5)}Si_{39.6(5)}$
Space group	$Pm\bar{3}n$
a	9.968(1) Å
Calculated density	2.4192(8) g/cm^3
Data collection Radiation; λ / Å Temperature	Rigaku Saturn724+, CCD detector MoKα radiation; λ =0.71073 Å 293 K
Reflections: measured unique Reflections with *F*(hkl) > 4 σ(F(hkl)) 2θ and sinθ/λ (max)	 15714 267 263 58.35; 0.686
Refined parameters	29
R(sig); R(eq)	0.0120; 0.0767
Goodness of fit	1.100
R_f; R_w	0.0380; 0.0416

Table S-5b. Atomic coordinates and isotropic displacement parameter (in Å^2) for **crystal 5**.

Atom	**Wyckoff Site**	***x/a***	***y/a***	***z/a***	**s.o.f.**	B_{eq}*
K1	2*a*	0	0	0	0.40(1)	1.43(12)
K2	6*d*	1/4	1/2	0	1	2.16(5)
Si1	6*c*	1/4	0	1/2	1	1.29(5)
Si21	16*i*	0.18286(7)	*x*	*x*	0.507(7)	1.16(6)
Si22	16*i*	0.199(2)	*x*	*x*	0.256(7)	1.25(7)
Si31	24*k*	0	0.309(2)	0.1137(15)	0.309(7)	1.21(7)
Si32	48*l*	0.0147(8)	0.2926(10)	0.1253(7)	0.339(4)	1.12(6)

* $B_{eq} = 1/3[B_{11}\, a^{*2}\, a^2 + ... \, 2\, B_{23}\, b^*\, c^*\, b\, c \cos\alpha]$

Table S-5c. Anisotropic atomic displacement parameters (in Å^2) for **crystal 5**.

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
K1	1.4(2)	B_{11}	B_{11}	0	0	0
K2	1.61(9)	2.43(7)	B_{22}	0	0	0
Si1	1.33(10)	1.27(7)	B_{22}	0	0	0

Table S-5d. Interatomic distances for **crystal 5** (in Å).

K1	8	6.0	Si21/B	3.184(10)
		2.0	Si22	3.44(2)
	12	3.8	Si31	3.28(2)
		8.2	$Si32_1$	3.176(9)
			$Si32_2$	
K2	4		Si1	3.5242(2)
	8	2.5	Si31	3.333(13)
		5.5	$Si32_1$	3.367(9)
			$Si32_2$	3.577(9)
	8	6.0	Si21/B	3.702(10)
		2.0	Si22	3.63(2)
	4	1.3	Si31	3.896(15)
		2.7	$Si32_1$	3.762(7)
			$Si32_2$	
Si1	4	1.3	Si31	2.34(2)
		2.7	$Si32_1$	2.417(9)
			$Si32_2$	
Si21/B	1	0.3	Si22	2.01(2)
		0.7	Si21/B	2.265(14)
	3	0.9	Si31	2.329(15)
		2.1	$Si32_1$	2.091(13)
			$Si32_2$	2.334(13)
Si22	1	0	Si22	1.75(3)
		1	B	2.01(2)
	3	0.9	Si31	2.42(2)
		2.1	$Si32_1$	2.19(2)
			$Si32_2$	2.44(2)
Si31	2	0.5	Si21/B	2.329(15)
		1.5	Si22	2.42(2)
	1		Si1	2.34(2)
	1	0.3	Si31	2.27(2)
		0.7	$Si32_1$	2.39(2)
			$Si32_2$	
$Si32_{1,2}$	2	0.5	Si21/B	2.091(13)
				2.334(13)
		1.5	Si22	2.19(2)
				2.44(2)
	1		Si1	2.417(9)
	1	0.3	Si31	2.39(2)
		0.7	Si32	2.498(10)
				2.515(10)

7. Crystallographic data for the high-pressure prepared $K_{7.85(2)}B_{7.8(1)}Si_{38.2(1)}$

Table S-6a. Experimental details for the XRPD measurement.

Chemical formula	**$K_{7.85(2)}B_{7.8(1)}Si_{38.2(1)}$**
Space group	$Pm\bar{3}n$
a	9.9050(2) Å
Calculated density	2.5018(2) g/cm^3
Data collection Radiation; λ / Å Temperature	 Synchrotron radiation; λ =0.20720 Å 293 K
Reflections: Reflections used 2θ and sinθ/λ (max)	 145 13.31; 0.559
Refined parameters	15
Berar's factor:	3.16
R_I; R_p	0.0230; 0.0731

Table S-6b. Atomic coordinates and isotropic displacement parameter (in Å^2) for $K_{7.85(2)}B_{7.8(1)}Si_{38.2(1)}$.

Atom	**Wyckoff Site**	***x/a***	***y/a***	***z/a***	**s.o.f.**	***B*$_{eq}$***
K1	2*a*	0	0	0	1	1.04(3)
K2	6*d*	1/4	1/2	0	0.976(3)	1.67(4)
Si1	6*c*	1/4	0	1/2	1	1.33(5)
Si2 B2	16*i*	0.1898(1)	*x*	*x*	0.581(5) 0.419(5)	1.29(3)
Si3 B3	24*k*	0	0.2981(1)	0.1228(1)	0.954(4) 0.046(4)	1.53(3)

* $B_{eq} = 1/3[B_{11}\, a^{*2}\, a^2 + ... \, 2\, B_{23}\, b^*\, c^*\, b\, c \cos\alpha]$

Table S-6c. Anisotropic atomic displacement parameters in (in Å^2) for $K_{7.85(2)}B_{7.8(1)}Si_{38.2(1)}$.

Atom	***B*$_{11}$**	***B*$_{22}$**	***B*$_{33}$**	***B*$_{12}$**	***B*$_{13}$**	***B*$_{23}$**
K1	1.04(5)	B_{11}	B_{11}	0	0	0
K2	1.43(9)	1.79(6)	B_{22}	0	0	0
Si1	1.10(11)	1.44(7)	B_{22}	0	0	0
Si2/B2	1.29(4)	B_{11}	B_{11}	0.28(5)	B_{12}	B_{12}
Si3/B3	1.91(6)	1.38(6)	1.30(6)	0	0	–0.15(6)

Table S-6d. Interatomic distances (in Å) for $K_{7.85(2)}B_{7.8(1)}Si_{38.2(1)}$.

K1	8	4.6	Si2	3.257(1)
		3.4	B2	
	12	11.4	Si3	3.193(1)
		0.6	B3	
K2	4		Si1	3.5019(1)
	8	7.6	Si3	3.4072(8)
		0.4	B3	
	8	4.6	Si2	3.651(1)
		3.4	B2	
	4	3.8	Si3	3.767(1)
		0.2	B3	
Si1	4	3.8	Si3	2.364(1)
		0.2	B3	
Si2/B2	1	0.6	Si2	2.065(2)
		0.4	B2	
	3	2.9	Si3	2.264(1)
		0.1	B3	
Si3/B3	2	1.2	Si2	2.264(1)
		0.8	B2	
	1		Si1	2.364(1)
	1	0.95	Si3	2.432(2)
		0.05	B3	

8. Crystal structure models for quantum chemical calculations

Table S-7a. Model 1 with composition $K_8B_8Si_{38}$ (space group $P4\bar{3}n$; a = 9.963 Å)

Atom	Wyckoff Site	*x/a*	*y/a*	*z/a*
K1	2*a*	0	0	0
K2	6*d*	1/4	0	1/2
Si1	6*c*	1/4	1/2	0
Si2	8*e*	0.19666	0.19666	0.19666
B2	8*e*	0.31711	0.31711	0.31711
Si3	24*i*	0.298	0	0.123

Table S-7b. Model 2 with composition $K_8B_8Si_{38}$ (space group $P4\bar{3}n$; a = 9.963 Å)

Atom	Wyckoff Site	*x/a*	*y/a*	*z/a*
K1	2*a*	0	0	0
K2	6*d*	1/4	0	1/2
Si1	6*c*	1/4	1/2	0
B2	8*e*	0.19666	0.19666	0.19666
Si2	8*e*	0.31711	0.31711	0.31711
Si3	24*i*	0.298	0	0.123

The calculations have revealed that the energy of model 1 is lower than for than model 2.

9. Quantitative evaluation of the ^{11}B NMR signals

Table S-8. Boron mass fraction in the clathrate $K_{8-x}B_ySi_{46-y}$ determined by structure refinement and by quantitative evaluation of the ^{11}B NMR signals. The sample number is related to table 1 (main text).

	Crystal structure refinement			^{11}B NMR
No(i)	composition	w(B) in %	w_i(B)/w_1(B)	w_i(B)/w_1(B)
1	$K_{7.18(2)}B_{7.2(5)}Si_{38.8(5)}$	5.37	1	1
3	$K_{6.98(4)}B_{6.4(5)}Si_{39.6(5)}$	4.68	0.87	1.13
5	$K_{6.80(2)}B_{6.4(5)}Si_{39.6(5)}$	4.78	0.89	0.87

10. Magnetic susceptibility

Table S-9. Comparison of the diamagnetic contributions to the measured magnetic susceptibility χ_0 and the sum of diamagnetic increments ΣχDia for the refined clathrate compositions. The sample number is related to table 1 (main text).

No	composition	χ_0 / emu mol^{-1}	$\Sigma\chi_{Dia,}$ / emu mol^{-1}
1	$K_{7.18(2)}B_{7.2(5)}Si_{38.8(5)}$	-3.18×10^{-4}	-3.48×10^{-4}
3	$K_{6.98(4)}B_{6.4(5)}Si_{39.6(5)}$	-3.65×10^{-4}	-3.42×10^{-4}
5	$K_{6.80(2)}B_{6.4(5)}Si_{39.6(5)}$	-1.55×10^{-4}	-3.48×10^{-4}