Chemical control of electronic structure and superconductivity in layered borides and borocarbides -
understanding the absence of superconductivity in Li_xBC

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Supporting Information

Figure S1 Variation of a , c and V with refined Li content in Li_xBC at 5 K.

Figure S2 Variation of a , c and V with refined Li content in Li_xBC at 973 K.

Figure S3 The observed, calculated and difference patterns from the Rietveld refinement of sample XI ($\text{Li}_{0.16(1)}\text{BC}$ - 73 % $\text{Li}_{0.21(1)}\text{B}_{0.73(1)}\text{C}_{1.27(1)}$ + 27 % B_{13}C_2) in the $\text{P6}_3/\text{mmc}$ space group. Data were collected on Station 9.1 of the U.K. Synchrotron Radiation Source, Daresbury Laboratory at a wavelength of 0.8 Å. The upper set of vertical ticks marks the position of the $\text{Li}_{0.10}\text{BC}$ peak and the lower set of ticks marks the positions of the B_{13}C_2 peaks. Inset: Very low calculated intensity at $21.76^\circ 2\theta$ where the (101) reflection of $\text{Li}_{0.10}\text{BC}$ should be observed.

(i)

(ii)

Figure S4 (i) EELS data from sample X, (ii) EELS data from sample comparable to sample III and (iii) deconvoluted EELS data for (a) sample comparable to sample III and (b) sample X (86 % $\text{Li}_{0.24(1)}\text{B}_{0.87(1)}\text{C}_{1.13(1)}$ + 14 % B_{13}C_2).

(i)

(ii)

Figure S5 Plot of (i) $U_{\text{iso}}(\text{Li})$ for the Li_xBC phases ($\text{Li}_{0.40}\text{BC}$ (VI, $\bullet$), $\text{Li}_{0.41}\text{BC}$ (IV, $\bullet$), $\text{Li}_{0.56}\text{BC}$ (III, $\bullet$), $\text{Li}_{0.90}\text{BC}$ (III, $\bullet$), $\text{Li}_{0.95}\text{BC}$ (VI, $\bullet$), LiBC (IV, $\bullet$)) and (ii) $U_{\text{iso}}(\text{Li})$ for the $\text{Li}_x\text{B}_{1-y}\text{C}_{1+y}$ phases (LiBC (IV, $\bullet$), $\text{Li}_{0.50}\text{BC}$ (VIII, $\bullet$) and $\text{Li}_{0.45}\text{BC}$ (IX, $\bullet$)).

Figure S6 Plot of (i) $U_{11}(B/C)$ for the Li_xBC phases ($\text{Li}_{0.40}\text{BC}$ (VI, $\bullet$), $\text{Li}_{0.41}\text{BC}$ (IV, $\bullet$), $\text{Li}_{0.56}\text{BC}$ (III, $\bullet$), $\text{Li}_{0.90}\text{BC}$ (III, $\bullet$), $\text{Li}_{0.95}\text{BC}$ (VI, $\bullet$), LiBC (IV, $\bullet$)) and (ii) $U_{11}(B/C)$ for the $\text{Li}_x\text{B}_{1-y}\text{C}_{1+y}$ phases (LiBC (IV, $\bullet$), $\text{Li}_{0.50}\text{BC}$ (VIII, $\bullet$) and $\text{Li}_{0.45}\text{BC}$ (IX, $\bullet$)).

Refinement Figures

SAMPLE I

Figure S7 The observed, calculated and difference patterns from the Rietveld refinement of sample I ($\text{Li}_{1.00(1)}\text{BC}$ – black tick marks; lithium acetylide – red tick marks; lithium oxide - blue tick marks; lithium - green tick marks)

SAMPLE II

Figure S8 The observed, calculated and difference patterns from the Rietveld refinement of sample II (overall composition $\text{Li}_{0.90(2)}\text{BC}$: 38% $\text{Li}_{0.83(2)}\text{BC}$ (lower tick marks) + 62% $\text{Li}_{0.95(2)}\text{BC}$).

SAMPLE III

Figure S9 The observed, calculated and difference patterns from the Rietveld refinement of sample III (overall composition $\text{Li}_{0.79(1)}\text{BC}$: 33% $\text{Li}_{0.56(2)}\text{BC}$ (lower tick marks) + 67% $\text{Li}_{0.904(8)}\text{BC}$).

SAMPLE IV

Figure S10 The observed, calculated and difference patterns from the Rietveld refinement of sample IV (overall composition $\text{Li}_{0.70(1)}\text{BC}$: 51% $\text{Li}_{0.41(2)}\text{BC}$ (upper tick marks) + 49% $\text{Li}_{1.000(5)}\text{BC}$).

SAMPLE V

Figure S11 The observed, calculated and difference patterns from the Rietveld refinement of sample V (overall composition $\text{Li}_{0.67(4)}\text{BC}$: 51% $\text{Li}_{0.38(5)}\text{BC}$ (upper tick marks) + 49% $\text{Li}_{0.97(3)}\text{BC}$).

SAMPLE VI

Figure S12 The observed, calculated and difference patterns from the Rietveld refinement of sample VI (overall composition $\text{Li}_{0.67(1)}\text{BC}$: 51% $\text{Li}_{0.40(1)}\text{BC}$ (upper tick marks) + 49% $\text{Li}_{0.95(1)}\text{BC}$).

SAMPLE VII

Figure S13 The observed, calculated and difference patterns from the Rietveld refinement of sample VII (overall composition $\text{Li}_{0.59(2)}\text{BC}$: 70% $\text{Li}_{0.43(1)}\text{BC}$ (lower tick marks) + 30% $\text{Li}_{0.96(3)}\text{BC}$).

SAMPLE VIII

Figure S14 The observed, calculated and difference patterns from the Rietveld refinement of sample VIII (overall composition $\text{Li}_{0.36(2)}\text{BC}$: 75% $\text{Li}_{0.50(2)}\text{B}_{0.70(1)}\text{C}_{1.30(1)}$ (lower tick marks) + 25% B_{13}C_2).

SAMPLE IX

Figure S15 The observed, calculated and difference patterns from the Rietveld refinement of sample IX (overall composition $\text{Li}_{0.27(2)}\text{BC}$: 63% $\text{Li}_{0.45(2)}\text{B}_{0.49(1)}\text{C}_{1.51(1)}$ (lower tick marks) + 37% B_{13}C_2).

SAMPLE X

Figure S16 The observed, calculated and difference patterns from the Rietveld refinement of sample X (overall composition $\text{Li}_{0.22(2)}\text{BC}$: 86 % $\text{Li}_{0.24(1)}\text{B}_{0.87(1)}\text{C}_{1.13(1)}$ + 14 % B_{13}C_2).

SAMPLE XI

Figure S17 The observed, calculated and difference patterns from the Rietveld refinement of sample X (overall composition $\text{Li}_{0.16(1)}\text{BC}$: 73% $\text{Li}_{0.21(1)}\text{B}_{0.73(1)}\text{C}_{1.27(1)}$ (lower tick marks) + 27% B_{13}C_2).

Table S1 Elemental analysis data for samples I (LiBC), VI ($\text{Li}_{0.67(1)}\text{BC}$, 51 % $\text{Li}_{0.40(1)}\text{BC}$ + 49 % $\text{Li}_{0.95(1)}\text{BC}$) and IX ($\text{Li}_{0.27(2)}\text{BC}$, 63 % $\text{Li}_{0.45(2)}\text{B}_{0.49(1)}\text{C}_{1.51(1)}$ + 37 % B_{13}C_2).

Sample	Element	Theoretical (%)	Experimental (%)
I	Li	23.37	13.92
	B	36.67	21.93
Li:B = 1.00:1.01 (refined Li:B = 1.00:1.00)			
VI	Li	16.96	12.81
	B	39.73	23.32
Li:B = 0.86:1.00 (refined Li:B = 0.67:1.00)			
IX	Li	7.61	6.18
	B	44.21	32.18
Li:B = 0.30:1.00 (refined Li:B = 0.27:1.00)			

Table S2 Effect of time at 1500 °C on the Li content of the resulting sample.

Sample	Overall Li_mBC sample Composition	Li_xBC Phase Compositions and Weight Fractions within sample [§]	Amounts of starting material used (g)			Time at 500°C (hrs)	Time at 1500°C (hrs)
			Li	B	C		
I	$\text{Li}_{1.00(1)}\text{BC}$	$\text{Li}_{1.00(1)}\text{BC}$	0.3225	0.18	0.185	2	1
II	$\text{Li}_{0.90(2)}\text{BC}$	38 % $\text{Li}_{0.83(2)}\text{BC}$ + 62 % $\text{Li}_{0.95(2)}\text{BC}$	0.3225	0.18	0.185	2	6
III	$\text{Li}_{0.79(1)}\text{BC}$	33 % $\text{Li}_{0.56(2)}\text{BC}$ + 67 % $\text{Li}_{0.904(8)}\text{BC}$	0.3225	0.18	0.185	2	24

Table S3 Effect of the initial amount of starting materials on the Li content of the resulting sample.

Sample	Overall Li_mBC sample Composition	Li_xBC Phase Compositions and Weight Fractions within sample [§]	Amounts of starting material used (g)			Time at 500°C (hrs)	Time at 1500°C (hrs)
			Li	B	C		
II	$\text{Li}_{0.90(2)}\text{BC}$	38 % $\text{Li}_{0.83(2)}\text{BC}$ + 62 % $\text{Li}_{0.95(2)}\text{BC}$	0.3225	0.18	0.185	2	6
VI	$\text{Li}_{0.67(1)}\text{BC}$	51 % $\text{Li}_{0.40(1)}\text{BC}$ + 49 % $\text{Li}_{0.95(1)}\text{BC}$	0.1075	0.06	0.0617	2	6
IX	$\text{Li}_{0.27(2)}\text{BC}$	63 % $\text{Li}_{0.45(2)}\text{B}_{0.49(1)}\text{C}_{1.51(1)}$ + 37 % B_{13}C_2	0.0537	0.03	0.0308	2	6

Table S4 Comparison of selected refined parameters for sample XI ($\text{Li}_{0.16(1)}\text{BC}$ - 73 % $\text{Li}_{0.21(1)}\text{B}_{0.73(1)}\text{C}_{1.27(1)}$ + 27 % B_{13}C_2) in the space groups P6/mmm and P6₃/mmc.

	P6/mmm	P6 ₃ /mmc
a (Å)	2.5376(2)	2.5378(2)
c (Å)	3.7929(1)	7.5857(2)
V (Å ³)	21.152(2)	42.309(5)
f _{Li}	0.21 (1)	0.21(1)
χ^2	3.833	3.824
R _{F2}	0.1017	0.0877