Supporting Information

Table S1 Selected bond distances (Å) and angles (deg) for $K_6Li_3Sc_2B_{15}O_{30}$

K1—O3^{i}	2.688(3)	Sc—O2^{vii}	2.056(3)
K1—O3^{ii}	2.688(3)	Sc—O2^{ix}	2.056(3)
K1—O2^{iii}	2.851(3)	Sc—O2^{x}	2.057(3)
K1—O2^{iv}	2.851(3)	Sc—O1^{xi}	2.151(3)
K1—O5^{v}	2.930(3)	Sc—O1	2.151(3)
K1—O5^{vi}	2.930(3)	Sc—O1^{iii}	2.151(3)
K2—O2^{iv}	2.612(2)	B1—O2	1.331(5)
K2—O2^{vii}	2.612(2)	B1—O5	1.374(5)
K2—O3	2.888(3)	B1—O4	1.407(5)
K2—O3^{viii}	2.888(3)	B2—O5	1.459(4)
K2—O4^{iv}	2.934(3)	B2—O5^{viii}	1.460(4)
K2—O4^{vii}	2.934(3)	B2—O3^{viii}	1.471(5)
Li1—O5^{xviii}	2.207(3)	B2—O3	1.471(5)
Li1—O5^{ix}	2.207(3)	B3—O1	1.324(5)
Li1—O5^{xix}	2.207(3)	B3—O3	1.378(5)
Li1—O5^{vii}	2.207(3)	B3—O4	1.407(5)
Li1—O5^{x}	2.207(3)	O2—B1—O5	124.4(4)
Li1—O5^{xx}	2.207(3)	O2—B1—O4	117.4(4)
Li2—O1	2.297(3)	O5—B1—O4	118.2(3)
Li2—O1^{xii}	2.297(3)	O5—B2—O5^{viii}	107.7(4)
Li2—O1^{xiii}	2.297(3)	O5—B2—O3^{viii}	108.96(15)
Li2—O1^{xi}	2.297(3)	O5^{viii}—B2—O3^{viii}	112.38(15)
Li2—O1^{iii}	2.297(3)	O5—B2—O3	112.38(15)
Li2—O1^{iv}	2.297(3)	O5^{viii}—B2—O3	108.95(15)
Li3—O1^{xiii}	1.92(3)	O3^{viii}—B2—O3	106.5(4)
Li3—O1	2.00(2)	O1—B3—O3	122.7(4)
Li3—O1^{iv}	2.03(3)	O1—B3—O4	120.0(4)
Li3—O4	2.43(3)	O3—B3—O4	117.3(4)

Symmetry code: (i) 1/3+x-y, 5/3-y, 5/3-z; (ii) -1/3+x, 1/3+y, 1/3+z; (iii) 1-x+y, 2-x, z; (iv) y, x, 2-z; (v) 1-x, 1-x+y, 2-z; (vi) 1-y, 1+x-y, z; (vii) 4/3-y, 2/3+x-y, -1/3+z; (viii) 4/3-x, 2/3-x+y, 5/3-z; (ix) 1/3+x, 2/3+y, -1/3+z; (x) 4/3-x+y, 5/3-x, -1/3+z; (xi) 2-y, 1+x-y, z; (xii) 1+x-y, 2-y, 2-z; (xiii) 2-x, 1-x+y, 2-z; (xiv) 2/3-x+y, 4/3-x, 1/3+z; (xv) -x+y, 1-x, z; (xvi) -1/3+x, -2/3+y, 1/3+z; (xvii) 1/3+x, -1/3+y, -1/3+z; (xviii) 2/3+y, 1/3+x, 4/3-z; (xix) 2/3+x-y, 4/3-y, 4/3-z; (xx) 5/3-x, 4/3-x+y, 4/3-z.

Table S2 Anisotropic displacement parameters ($Å^2$) of $K_6Li_3Sc_2B_{15}O_{30}$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
K1	0.0175(4)	0.0126(6)	0.0147(5)	0.0063(3)	0.0005(2)	0.0011(5)
K2	0.0343(8)	0.0219(5)	0.0808(11)	0.0171(4)	0.0399(8)	0.0199(4)
Sc	0.0096(3)	0.0096(3)	0.0093(5)	0.00479(16)	0.00000	0.00000
B1	0.014(2)	0.0149(18)	0.015(2)	0.0090(17)	0.0018(17)	0.0003(16)
B2	0.014(3)	0.0108(19)	0.010(3)	0.0071(13)	-0.005(2)	-0.0027(11)
B3	0.015(2)	0.016(2)	0.0124(19)	0.0049(17)	0.0030(16)	-0.0010(15)
Li1	0.023(6)	0.023(6)	0.052(13)	0.011(3)	0.00000	0.00000
Li2	0.024(15)	0.024(15)	0.02(2)	0.012(7)	0.00000	0.00000
Li3	0.020(14)	0.022(13)	0.016(12)	0.016(12)	-0.009(10)	-0.001(9)
O1	0.039(2)	0.0123(13)	0.0126(13)	-0.0006(15)	-0.0028(15)	0.0032(10)
O2	0.0138(14)	0.0117(12)	0.0163(13)	0.0060(11)	-0.0006(10)	0.0007(10)
O3	0.0229(15)	0.0117(13)	0.0118(12)	0.0072(12)	-0.0001(11)	0.0007(11)
O4	0.0199(16)	0.0125(13)	0.0188(12)	-0.0023(12)	-0.0063(12)	0.0063(10)
O5	0.0124(13)	0.0084(13)	0.0203(15)	0.0023(11)	-0.0041(11)	0.0031(11)

Fig.S1 XRD patterns before and after melting.

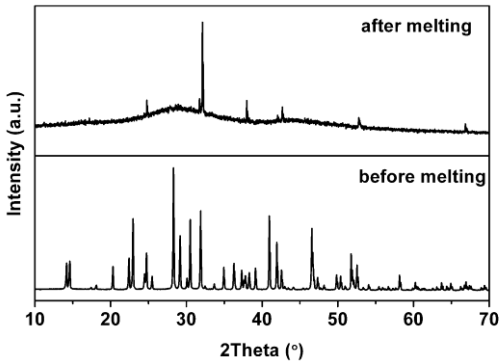

Fig.S2 The $K_6Li_3Sc_2B_{15}O_{30}$ crystal with the $K_2O–Li_2O–B_2O_3$ self-flux

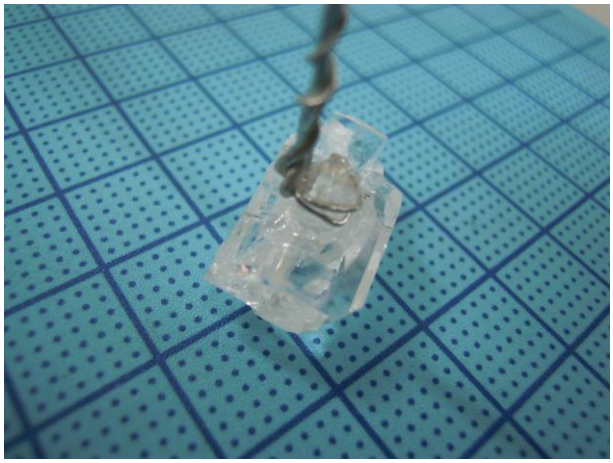

Fig.S3 View of the linkages of B_5O_{10} groups and ScO_6 octahedra.

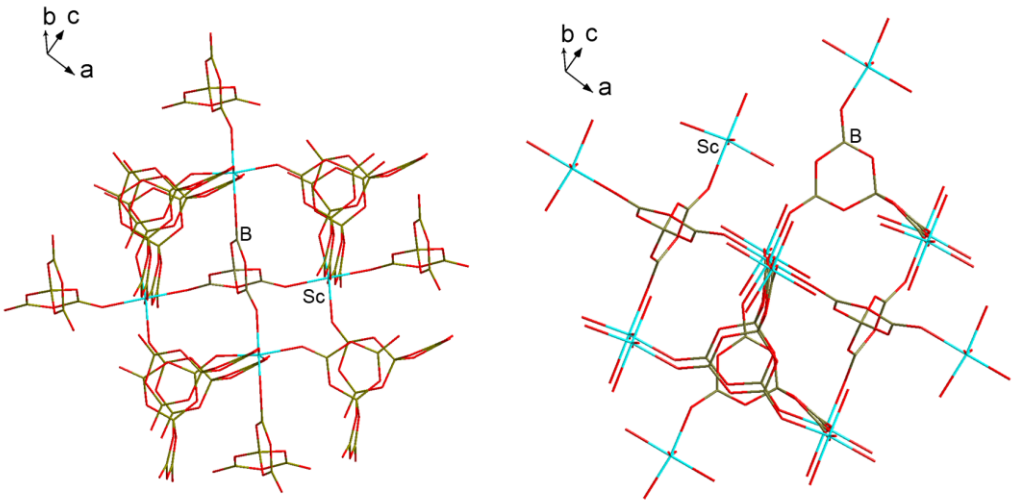

Fig.S4 View of the 8-membered rings composed of four BO_3 triangles, two BO_4 tetrahedra and two ScO_6 octahedra.

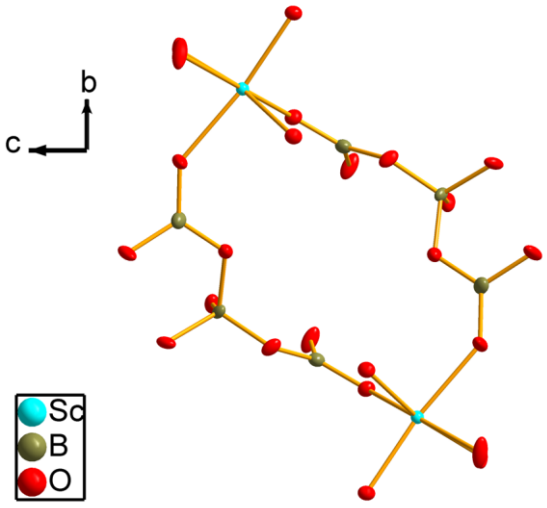

Fig.S5 Coordination environments of K atoms

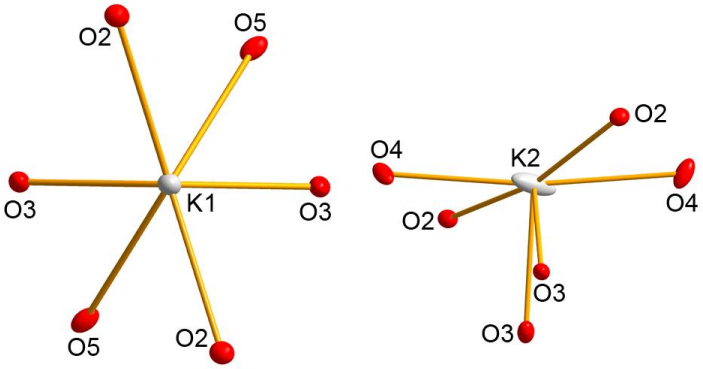

Fig.S6 Coordination environments of Li atoms

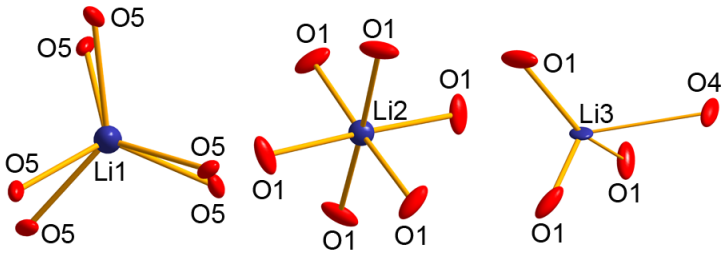

Fig.S7 SHG measurements on the ground $K_6Li_3Sc_2B_{15}O_{30}$ crystals