

# Supplementary Materials: Borates—Crystal Structures of Prospective Nonlinear Optical Materials: High Anisotropy of The Thermal Expansion Caused by Anharmonic Atomic Vibrations

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Table S1. Experimental details of  $\beta$ -BaB<sub>2</sub>O<sub>4</sub> measurements

Chemical formula	BaB <sub>2</sub> O <sub>4</sub>							
<i>M<sub>r</sub></i>	223							
Crystal system,	Trigonal, <i>R</i> 3c							
space group								
Temperature (K)	98	123	173	223	298	323	293	693
<i>a</i> (Å)	12.5761(3)	12.5868(18)	12.5828(15)	12.5820(15)	12.5685(14)	12.5806(14)	12.5269(3)	12.552(2)
<i>c</i> (Å)	12.6453 (9)	12.709 (2)	12.7291 (18)	12.7519 (19)	12.7714 (18)	12.7947 (18)	12.7181(3)	12.985(3)
<i>V</i> (Å <sup>3</sup> )	1732.02 (14)	1743.7 (4)	1745.4 (4)	1748.3 (4)	1747.2 (4)	1753.7 (4)	1728.38(7)	1771.7(5)
<i>Z</i>	18							
Radiation type	Mo <i>K</i> α							
$\mu$ (mm <sup>-1</sup> )	10.18	10.11	10.1	10.08	10.09	10.05	10.20	9.95
Crystal size (mm)	0.10 × 0.12 × 0.20						0.05	0.2 × 0.4 × 0.5
							× 0.10 × 0.22	
Absorption correction	Based on crystal shape							
No. of measured, independent and observed [ <i>I</i> > 3σ( <i>I</i> )] reflections	5068, 1021, 1017	5100, 1033, 1027	5121, 1036, 1032	5084, 1040, 1032	5177, 1041, 1030	5166, 1043, 1028	30297, 3517, 3046	–, 914, 809
<i>R</i> <sub>int</sub>	0.090	0.079	0.078	0.079	0.082	0.082	0.078	–
( <i>sin</i> θ/λ) <sub>max</sub> (Å <sup>-1</sup> )	0.685	0.686	0.686	0.686	0.685	0.686	1.034	1.087
<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )]	0.034,	0.025,	0.029,	0.024,	0.024,	0.029,	0.031,	0.037,
<i>wR</i> ( <i>F</i> <sup>2</sup> )	0.045,	0.032,	0.039,	0.030,	0.031,	0.038,	0.035,	0.043,
<i>S</i>	4.02	2.84	3.49	2.54	2.66	3.28	1.17	1.26
No. of reflections	1021	1033	1036	1040	1041	1043	3517	914
No. of parameters	65							
Δρ <sub>max</sub> , Δρ <sub>min</sub> (e Å <sup>-3</sup> )	1.03, –1.27	0.90, –0.94	0.95, –0.86	0.86, –0.68	0.79, –0.79	0.92, –0.78	2.50, –0.89	–
Absolute structure	504	509	513	516	516	516	1743	–
No. of Friedel pairs used in the refinement								

Table S2. Atomic coordinates, displacement parameters (Å<sup>2</sup>) and site-occupancy factors (SOFs) in the structure of  $\beta$ -BaB<sub>2</sub>O<sub>4</sub> modifications at different temperatures.

AtomOcc.	<i>x</i>	<i>y</i>	<i>z</i>	U iso/eq	
98 K					
B1	1	0.0216(7)	–0.1017(7)	0.2434(7)	0.008(3)
B2	1	0.0423(8)	–0.0876(8)	0.5043(7)	0.009(3)
Ba1	1	0.36142(3)	0.35836(3)	0.37990(2)	0.00635(19)
O1	1	–0.0410(5)	0.0834(5)	0.5013(4)	0.0104(19)
O2	1	0.1642(5)	0.2499(5)	0.5091(5)	0.0099(19)
O3	1	0.1186(5)	0.0211(5)	0.2444(5)	0.011(2)
O4	1	0.0451(5)	0.2382(5)	0.7349(5)	0.0095(19)
123 K					
B1	1	0.0210(5)	–0.1016(5)	0.2428(5)	0.0085(19)
B2	1	0.0428(5)	–0.0872(5)	0.5039(4)	0.0100(18)
Ba1	1	0.36136(2)	0.35829(2)	0.379896(14)	0.00751(13)

O1	1	-0.0412(4)	0.0833(4)	0.5014(3)	0.0113(13)
O2	1	0.1638(4)	0.2497(4)	0.5094(3)	0.0117(13)
O3	1	0.1185(3)	0.0210(3)	0.2445(3)	0.0117(13)
O4	1	0.0452(3)	0.2383(3)	0.7349(3)	0.0101(13)
173 K					
B1	1	0.0213(6)	-0.1018(6)	0.2430(6)	0.011(2)
B2	1	0.0425(7)	-0.0872(7)	0.5035(6)	0.012(2)
Ba1	1	0.36122(3)	0.35814(3)	0.379909(18)	0.00934(17)
O1	1	-0.0410(5)	0.0833(5)	0.5015(4)	0.0145(17)
O2	1	0.1639(5)	0.2497(5)	0.5090(4)	0.0145(17)
O3	1	0.1184(4)	0.0211(4)	0.2442(4)	0.0145(17)
O4	1	0.0456(4)	0.2383(4)	0.7349(4)	0.0127(16)
223 K					
B1	1	0.0211(5)	-0.1016(5)	0.2426(5)	0.0117(19)
B2	1	0.0429(5)	-0.0872(6)	0.5034(5)	0.0136(19)
Ba1	1	0.36104(2)	0.35797(2)	0.379931(14)	0.01105(13)
O1	1	-0.0415(4)	0.0826(4)	0.5009(3)	0.0170(14)
O2	1	0.1638(4)	0.2496(4)	0.5088(3)	0.0170(14)
O3	1	0.1185(3)	0.0211(4)	0.2441(3)	0.0170(14)
O4	1	0.0455(3)	0.2380(3)	0.7348(3)	0.0152(13)
298 K					
B1	1	0.0210(5)	-0.1015(5)	0.2422(5)	0.0154(19)
B2	1	0.0421(6)	-0.0873(6)	0.5031(5)	0.017(2)
Ba1	1	0.36080(2)	0.35774(2)	0.379938(15)	0.01445(13)
O1	1	-0.0410(4)	0.0829(4)	0.5008(4)	0.0223(15)
O2	1	0.1636(4)	0.2493(4)	0.5088(4)	0.0216(14)
O3	1	0.1182(3)	0.0210(4)	0.2440(4)	0.0215(14)
O4	1	0.0460(4)	0.2383(3)	0.7350(3)	0.0191(14)
323 K					
B1	1	0.0214(7)	-0.1014(7)	0.2425(6)	0.017(3)
B2	1	0.0422(7)	-0.0874(7)	0.5030(6)	0.019(3)
Ba1	1	0.36073(3)	0.35763(3)	0.37993(2)	0.01553(17)
O1	1	-0.0410(5)	0.0830(5)	0.5007(5)	0.024(2)
O2	1	0.1636(5)	0.2494(5)	0.5091(5)	0.0238(19)
O3	1	0.1183(5)	0.0214(5)	0.2441(5)	0.024(2)
O4	1	0.0457(5)	0.2380(4)	0.7349(4)	0.0212(18)
693 K					
B1	1	0.0228	-0.1005	0.2426	0.029632
B2	1	0.0427	-0.0866	0.5021	0.02952
Ba1	1	0.3587	0.3558	0.3799	0.031132
O1	1	-0.0411	0.0818	0.501	0.046695
O2	1	0.1639	0.25	0.5093	0.046491
O3	1	0.1175	0.0204	0.2438	0.045029
O4	1	0.0463	0.2369	0.7354	0.041366

Table S3. Anisotropic parameters of atomic displacements in  $\beta$ -BaB<sub>2</sub>O<sub>4</sub> at different temperatures.

Atom	U <sub>11</sub>	U <sub>22</sub>	U <sub>33</sub>	U <sub>12</sub>	U <sub>13</sub>	U <sub>23</sub>
98 K						
B1	0.003(4)	0.008(3)	0.012(4)	0.002(3)	0.003(3)	0.001(3)
B2	0.003(3)	0.007(3)	0.013(3)	-0.001(3)	-0.001(3)	-0.003(3)
Ba1	0.0045(2)	0.0045(3)	0.0102(2)	0.00235(15)	-0.00008(19)	0.0001(2)
O1	0.007(2)	0.004(2)	0.018(3)	0.0019(19)	0.001(2)	0.000(2)
O2	0.011(2)	0.006(2)	0.013(2)	0.0043(19)	0.003(2)	0.0022(19)
O3	0.005(2)	0.005(3)	0.024(3)	0.003(2)	0.000(2)	-0.001(2)
O4	0.010(2)	0.004(2)	0.015(2)	0.004(2)	0.0026(19)	0.0012(19)
123 K						
B1	0.007(2)	0.008(2)	0.011(2)	0.0040(19)	-0.0018(18)	0.0003(18)
B2	0.005(2)	0.009(2)	0.013(2)	0.0014(19)	-0.0010(19)	-0.0015(19)
Ba1	0.00546(17)	0.00543(18)	0.01174(17)	0.00280(10)	-0.00026(13)	0.00001(13)
O1	0.0061(16)	0.0072(16)	0.0210(18)	0.0035(13)	-0.0004(14)	0.0005(14)
O2	0.0106(16)	0.0076(16)	0.0172(18)	0.0048(13)	0.0036(14)	0.0017(13)
O3	0.0075(15)	0.0044(17)	0.0253(19)	0.0046(14)	0.0018(13)	0.0012(14)
O4	0.0093(15)	0.0073(16)	0.0124(15)	0.0031(14)	0.0012(12)	-0.0017(13)
173 K						

B1	0.008(3)	0.009(3)	0.015(3)	0.004(2)	0.001(2)	0.002(2)
B2	0.009(3)	0.010(3)	0.014(3)	0.004(2)	−0.002(2)	−0.003(2)
Ba1	0.0068(2)	0.0069(2)	0.0144(2)	0.00351(13)	−0.00026(16)	0.00007(17)
O1	0.010(2)	0.008(2)	0.027(3)	0.0055(17)	−0.0011(19)	−0.0010(18)
O2	0.012(2)	0.010(2)	0.021(2)	0.0054(17)	0.0042(18)	0.0022(17)
O3	0.0071(19)	0.007(2)	0.031(3)	0.0042(18)	0.0009(17)	0.0002(18)
O4	0.013(2)	0.009(2)	0.016(2)	0.0047(18)	0.0019(16)	−0.0017(17)
223 K						
B1	0.010(3)	0.009(2)	0.016(2)	0.005(2)	−0.0009(19)	0.0000(19)
B2	0.007(2)	0.011(2)	0.021(3)	0.0030(19)	−0.001(2)	−0.002(2)
Ba1	0.00800(16)	0.00829(18)	0.01698(16)	0.00417(10)	−0.00034(14)	0.00009(15)
O1	0.0087(17)	0.0099(17)	0.032(2)	0.0047(14)	0.0000(15)	0.0000(15)
O2	0.0140(17)	0.0111(17)	0.0258(19)	0.0063(14)	0.0062(15)	0.0030(14)
O3	0.0068(16)	0.0073(18)	0.037(2)	0.0034(14)	0.0009(15)	0.0007(15)
O4	0.0145(16)	0.0099(17)	0.0205(17)	0.0056(14)	0.0024(13)	−0.0008(14)
298 K						
B1	0.011(3)	0.014(2)	0.021(2)	0.005(2)	0.0024(19)	0.0027(19)
B2	0.012(2)	0.015(2)	0.024(2)	0.006(2)	−0.001(2)	−0.003(2)
Ba1	0.01057(17)	0.01107(19)	0.02176(17)	0.00545(10)	−0.00051(14)	−0.00003(15)
O1	0.0129(18)	0.0125(17)	0.043(2)	0.0071(14)	0.0000(16)	0.0010(16)
O2	0.0159(17)	0.0144(17)	0.034(2)	0.0074(14)	0.0071(16)	0.0029(15)
O3	0.0108(16)	0.0091(18)	0.045(2)	0.0054(14)	0.0000(15)	−0.0001(15)
O4	0.0177(17)	0.0118(17)	0.0264(17)	0.0064(15)	0.0022(14)	−0.0017(14)
323 K						
B1	0.014(3)	0.015(3)	0.022(3)	0.008(3)	0.001(3)	0.003(3)
B2	0.014(3)	0.016(3)	0.026(3)	0.007(3)	−0.002(3)	−0.005(3)
Ba1	0.0114(2)	0.0120(2)	0.0233(2)	0.00596(13)	−0.00061(19)	−0.0001(2)
O1	0.015(2)	0.013(2)	0.047(3)	0.0087(19)	0.001(2)	0.001(2)
O2	0.018(2)	0.014(2)	0.039(3)	0.0076(18)	0.007(2)	0.003(2)
O3	0.011(2)	0.012(2)	0.048(3)	0.0060(19)	0.000(2)	−0.001(2)
O4	0.020(2)	0.013(2)	0.029(2)	0.0078(19)	0.0020(18)	−0.0020(19)
693 K						
B1	0.029132	0.024383	0.035821	0.013708	0.006579	−0.00062
B2	0.028114	0.019196	0.042228	0.012561	−0.0035	−0.00715
Ba1	0.02248	0.025255	0.045892	0.012108	−0.00164	−0.00053
O1	0.021963	0.023858	0.090028	0.008278	0.005192	0.005021
O2	0.030928	0.024383	0.076939	0.008411	0.01479	0.00708
O3	0.025328	0.025108	0.086573	0.014051	−0.00571	0.000103
O4	0.045314	0.027815	0.055099	0.02138	0.001681	−0.00037

Table S4. Anharmonic thermal parameters ( $\times 10^{-4}$ ) of the third and fourth order for barium atoms in the structure of  $\beta$ -BaB<sub>2</sub>O<sub>4</sub> at 298 K obtained using Gram–CharLie model.

C <sub>111</sub>	C <sub>112</sub>	C <sub>113</sub>	C <sub>122</sub>	C <sub>123</sub>	C <sub>133</sub>	C <sub>222</sub>	C <sub>223</sub>	C <sub>233</sub>	C <sub>333</sub>					
0.0002.3(7)	0.0000.5(3)	1.0(5)	−0.8(4)	0.6(3)	0.59(8)	−2.7(7)	1.2(5)	−0.57(9)	−2.8(9)					
D <sub>1111</sub>	D <sub>1112</sub>	D <sub>1113</sub>	D <sub>1122</sub>	D <sub>1123</sub>	D <sub>1133</sub>	D <sub>1222</sub>	D <sub>1223</sub>	D <sub>1233</sub>	D <sub>1333</sub>	D <sub>2222</sub>	D <sub>2223</sub>	D <sub>2333</sub>	D <sub>3333</sub>	
0.25(18)	0.17(9)	0.18(8)	0.09(7)	0.15(6)	−0.34(4)	0.09(11)	0.03(6)	−0.12(2)	−0.06(6)	−0.1(2)	−0.01(8)	−0.38(4)	−0.09(6)	−1.66(7)

Table S5. B–O (Å) bond lengths and O–B–O (°) angles in the  $\beta$ -BaB<sub>2</sub>O<sub>4</sub> structure at different temperatures.

T / K	98	123	173	223	298	323	693	$\Delta$ (98–693 K)
B1–O3	1.410(8)	1.412(6)	1.413(7)	1.413(6)	1.408(6)	1.410(8)	1.3833(6)	−0.027
B1–O3 <sup>i</sup>	1.404(13)	1.398(9)	1.399(12)	1.397(9)	1.393(9)	1.395(13)	1.4102(5)	0.006
B1–O4 <sup>ii</sup>	1.327(14)	1.335(10)	1.328(12)	1.328(10)	1.329(10)	1.327(13)	1.3072(3)	−0.020
B2–O1 <sup>iii</sup>	1.409(12)	1.413(8)	1.409(10)	1.405(8)	1.400(9)	1.404(11)	1.3924(5)	−0.017
B2–O1 <sup>i</sup>	1.419(10)	1.417(6)	1.415(8)	1.419(7)	1.415(7)	1.417(9)	1.4032(6)	−0.016
B2–O2 <sup>i</sup>	1.324(15)	1.323(10)	1.327(13)	1.321(11)	1.323(11)	1.323(15)	1.3328(2)	0.009
O3–B1–O3 <sup>i</sup>	116.1(8)	116.4(6)	115.9(7)	116.3(6)	116.2(6)	116.1(8)	115.578(12)	−0.5
O3–B1–O4 <sup>ii</sup>	120.2(8)	119.7(5)	119.9(7)	119.6(5)	119.5(5)	120.0(7)	120.610(13)	0.4
O3 <sup>i</sup> –B1–O4 <sup>ii</sup>	123.6(6)	123.8(4)	124.1(5)	123.9(4)	124.3(4)	123.9(6)	123.725(10)	0.1
O1 <sup>iii</sup> –B2–O1 <sup>i</sup>	115.6(10)	115.6(7)	115.7(9)	115.2(7)	115.5(7)	115.5(9)	114.885(11)	−0.7
O1 <sup>iii</sup> –B2–O2 <sup>i</sup>	124.4(7)	124.1(5)	124.2(6)	124.1(5)	124.6(5)	124.5(7)	124.264(11)	−0.1
O1 <sup>i</sup> –B2–O2 <sup>i</sup>	120.1(8)	120.3(6)	120.1(7)	120.7(6)	119.9(6)	120.0(8)	120.755(13)	0.7

Symmetry codes: (i)  $-x+y, -x, z$ ; (ii)  $x, x-y, z-1/2$ ; (iii)  $-y, x-y, z$

Table S6. Ba–O (Å) bond lengths and O–Ba–O (°) angles in the  $\beta$ -BaB<sub>2</sub>O<sub>4</sub> structure at different temperatures.

T / K	98	123	173	223	298	323	693	$\Delta(98-693\text{ K})$
Ba1–O1 <sup>i</sup>	2.755(7)	2.759(5)	2.760(6)	2.769(5)	2.766(5)	2.768(7)	2.7923(9)	0.037
Ba1–O2	2.701(6)	2.713(4)	2.709(5)	2.708(4)	2.708(4)	2.712(6)	2.7058(8)	0.005
Ba1–O2 <sup>ii</sup>	3.027(6)	3.038(4)	3.045(5)	3.053(4)	3.058(5)	3.060(6)	3.0969(10)	0.070
Ba1–O2 <sup>i</sup>	2.834(8)	2.832(5)	2.833(7)	2.833(6)	2.828(6)	2.830(8)	2.8161(6)	−0.018
Ba1–O3 <sup>iii</sup>	2.775(7)	2.779(5)	2.781(6)	2.780(5)	2.781(5)	2.786(7)	2.7888(6)	0.014
Ba1–O4 <sup>ii</sup>	2.910(5)	2.913(4)	2.909(5)	2.911(4)	2.906(4)	2.913(5)	2.9204(13)	0.010
Ba1–O4 <sup>i</sup>	2.811(6)	2.822(4)	2.827(5)	2.830(4)	2.837(4)	2.839(6)	2.8843(9)	0.073
Ba1–O4 <sup>iv</sup>	2.632(6)	2.638(4)	2.642(5)	2.646(4)	2.643(4)	2.648(6)	2.6549(8)	0.023
O1 <sup>i</sup> –Ba1–O2	143.4(2)	143.41(14)	143.41(18)	143.57(15)	143.55(15)	143.5(2)	143.554(7)	0.2
O1 <sup>i</sup> –Ba1–O2 <sup>ii</sup>	81.3(2)	81.23(16)	81.2(2)	81.03(16)	80.99(17)	80.9(2)	80.301(5)	−1.0
O1 <sup>i</sup> –Ba1–O2 <sup>i</sup>	50.32(16)	50.30(11)	50.27(14)	50.31(11)	50.12(12)	50.14(15)	50.188(9)	−0.1
O1 <sup>i</sup> –Ba1–O3 <sup>iii</sup>	128.27(16)	128.19(11)	128.17(14)	128.00(11)	127.96(11)	128.00(15)	126.903(10)	−1.4
O1 <sup>i</sup> –Ba1–O4 <sup>ii</sup>	79.4(2)	79.35(15)	79.38(19)	79.31(15)	79.35(16)	79.4(2)	79.112(12)	−0.3
O1 <sup>i</sup> –Ba1–O4 <sup>i</sup>	75.38(17)	75.51(12)	75.48(16)	75.57(13)	75.69(13)	75.70(17)	75.649(8)	0.3
O1 <sup>i</sup> –Ba1–O4 <sup>iv</sup>	113.0(2)	112.98(15)	113.01(19)	112.90(15)	112.87(16)	112.7(2)	112.712(12)	−0.3
O2–Ba1–O2 <sup>ii</sup>	134.6(2)	134.74(17)	134.8(2)	134.78(17)	134.84(17)	134.9(2)	135.748(6)	1.1
O2–Ba1–O2 <sup>i</sup>	103.07(19)	103.13(13)	103.23(17)	103.32(13)	103.45(14)	103.43(18)	104.163(11)	1.1
O2–Ba1–O3 <sup>iii</sup>	78.78(19)	78.76(13)	78.79(17)	78.83(14)	78.93(14)	78.84(18)	79.009(11)	0.2
O2–Ba1–O4 <sup>ii</sup>	118.0(2)	117.94(14)	117.91(17)	117.89(14)	117.83(14)	117.76(19)	116.777(10)	−1.2
O2–Ba1–O4 <sup>i</sup>	70.91(18)	70.72(13)	70.73(16)	70.80(13)	70.67(14)	70.65(18)	70.366(12)	−0.5
O2–Ba1–O4 <sup>iv</sup>	81.93(18)	82.19(13)	82.23(16)	82.31(13)	82.41(14)	82.59(18)	83.920(17)	2.0
O2 <sup>ii</sup> –Ba1–O2 <sup>i</sup>	105.9(2)	105.93(14)	105.74(18)	105.63(15)	105.55(15)	105.6(2)	105.010(9)	−0.9
O2 <sup>ii</sup> –Ba1–O3 <sup>iii</sup>	72.3(2)	72.33(14)	72.35(18)	72.36(15)	72.29(15)	72.3(2)	72.515(9)	0.2
O2 <sup>ii</sup> –Ba1–O4 <sup>ii</sup>	65.05(15)	65.07(11)	65.14(13)	65.14(11)	65.21(11)	65.14(15)	65.371(9)	0.3
O2 <sup>ii</sup> –Ba1–O4 <sup>i</sup>	152.99(18)	153.02(13)	153.03(16)	152.94(13)	152.99(13)	152.89(17)	152.144(8)	−0.8
O2 <sup>ii</sup> –Ba1–O4 <sup>iv</sup>	68.43(16)	68.32(11)	68.19(14)	68.13(11)	68.04(12)	68.04(15)	67.685(15)	−0.7
O2 <sup>i</sup> –Ba1–O3 <sup>iii</sup>	178.09(16)	178.08(11)	177.93(14)	177.80(11)	177.59(12)	177.71(15)	176.816(4)	−1.3
O2 <sup>i</sup> –Ba1–O4 <sup>ii</sup>	129.5(2)	129.41(14)	129.41(18)	129.39(15)	129.22(15)	129.3(2)	129.038(12)	−0.5
O2 <sup>i</sup> –Ba1–O4 <sup>i</sup>	68.90(18)	68.98(13)	69.04(16)	69.13(13)	69.19(14)	69.16(18)	69.580(8)	0.7
O2 <sup>i</sup> –Ba1–O4 <sup>iv</sup>	82.3(2)	82.39(15)	82.41(19)	82.38(15)	82.57(16)	82.5(2)	82.789(10)	0.5
O3 <sup>iii</sup> –Ba1–O4 <sup>ii</sup>	49.3(2)	49.26(14)	49.22(18)	49.13(15)	49.09(15)	49.1(2)	48.269(12)	−1.0
O3 <sup>iii</sup> –Ba1–O4 <sup>i</sup>	112.35(19)	112.17(13)	112.26(17)	112.24(13)	112.22(14)	112.14(18)	111.613(7)	−0.7
O3 <sup>iii</sup> –Ba1–O4 <sup>iv</sup>	97.5(2)	97.60(15)	97.49(19)	97.54(15)	97.44(16)	97.5(2)	97.929(9)	0.4
O4 <sup>ii</sup> –Ba1–O4 <sup>i</sup>	97.02(17)	96.93(11)	96.97(14)	96.92(12)	96.85(12)	96.81(16)	96.100(8)	−0.9
O4 <sup>ii</sup> –Ba1–O4 <sup>iv</sup>	129.03(19)	128.98(13)	128.87(17)	128.81(13)	128.76(14)	128.72(18)	128.439(7)	−0.6
O4 <sup>i</sup> –Ba1–O4 <sup>iv</sup>	133.73(15)	133.87(11)	133.94(13)	134.06(11)	134.17(11)	134.26(14)	135.264(10)	1.5

Symmetry codes: (i)  $-y+2/3, -x+1/3, z-1/6$ ; (ii)  $-x+y+1/3, -x+2/3, z-1/3$ ; (iii)  $-y+1/3, -x+2/3, z+7/6$ ; (iv)  $-x+y, y, z-1/2$ Table S7. B–O–B (°) angles in the  $\beta$ -BaB<sub>2</sub>O<sub>4</sub> structure at different temperatures.

	98	123	173	223	298	323	693	$\Delta(98-693\text{ K})$
B2 <sup>i</sup> –O1–B2 <sup>ii</sup>	124.3(10)	124.3(7)	124.2(9)	124.8(7)	124.4(7)	124.5(10)	125.094(10)	0.8
B1–O3–B1 <sup>i</sup>	123.9(7)	123.5(5)	124.0(6)	123.6(5)	123.8(5)	123.9(7)	124.395(13)	0.5

Symmetry codes: (i)  $-y, x-y, z$ ; (ii)  $-x+y, -x, z$ ; (iii)  $x, x-y, z+1/2$ Table S8. O–O–O (°) angles in the  $\beta$ -BaB<sub>2</sub>O<sub>4</sub> structure at different temperatures.

T / K	98	123	173	223	298	323	693	$\Delta(98-693\text{ K})$
O1–O2–O1 <sup>ii</sup>	59.9(3)	59.9(2)	59.8(3)	59.7(2)	59.7(2)	59.8(3)	58.957(11)	−0.9
O3 <sup>i</sup> –O3–O4 <sup>iii</sup>	59.4(3)	59.3(2)	59.3(3)	59.3(2)	59.2(2)	59.4(3)	58.812(11)	−0.6
O2–O1–O2 <sup>i</sup>	175.3(3)	175.1(2)	175.4(3)	175.2(2)	175.1(3)	174.8(4)	174.7351(19)	−0.6
O3 <sup>ii</sup> –O3–O4 <sup>iii</sup>	119.3(4)	119.2(3)	119.3(4)	119.2(3)	119.2(3)	119.4(4)	118.743(11)	−0.6
O3 <sup>v</sup> –O4–O3 <sup>vi</sup>	59.9(3)	59.9(2)	59.8(3)	60.0(2)	59.8(2)	59.8(3)	59.887(13)	0.0
O1 <sup>i</sup> –O1–O1 <sup>ii</sup>	60.0(3)	60.00(19)	60.0(2)	60.0(2)	60.00(11)	60.0(3)	60.000(11)	0.0
O3 <sup>i</sup> –O3–O3 <sup>ii</sup>	60.0(3)	60.0(2)	60.0(3)	60.0(2)	60.00(11)	60.0(3)	60.000(13)	0.0
O1 <sup>ii</sup> –O1–O2	60.9(3)	60.88(19)	60.9(2)	60.7(2)	61.0(2)	61.0(3)	61.171(13)	0.3
O1 <sup>i</sup> –O1–O2	120.8(4)	120.8(3)	120.9(4)	120.7(3)	120.9(3)	120.9(4)	121.103(11)	0.3
O4 <sup>iii</sup> –O3–O4 <sup>iv</sup>	174.2(4)	174.2(2)	174.3(3)	174.3(3)	174.5(3)	174.3(3)	174.7211(15)	0.5
O3 <sup>ii</sup> –O3–O4 <sup>iv</sup>	60.7(3)	60.81(19)	60.9(2)	60.8(2)	61.0(2)	60.8(3)	61.301(11)	0.6
O1 <sup>ii</sup> –O1–O2 <sup>i</sup>	119.2(4)	119.1(3)	119.2(3)	119.5(3)	119.2(3)	119.2(4)	119.806(13)	0.6
O3 <sup>i</sup> –O3–O4 <sup>iv</sup>	120.6(3)	120.7(2)	120.8(3)	120.7(2)	120.9(2)	120.7(3)	121.229(11)	0.6
O1 <sup>i</sup> –O1–O2 <sup>i</sup>	59.2(3)	59.2(2)	59.2(3)	59.6(2)	59.3(2)	59.3(3)	59.872(11)	0.7

Symmetry codes: (i)  $-y, x-y, z$ ; (ii)  $-x+y, -x, z$ ; (iii)  $-x+y, y, z-1/2$ ; (iv)  $x, x-y, z-1/2$ ; (v)  $-x+y, y, z+1/2$ ; (vi)  $x, x-y, z+1/2$ .

Table S9. Experimental details of  $\alpha$ -BaB<sub>2</sub>O<sub>4</sub> measurements.

Chemical formula	BaB <sub>2</sub> O <sub>4</sub>		
<i>M<sub>r</sub></i>	223		
Crystal system, space group	Trigonal, <i>R</i> -3 <i>c</i>		
Temperature (K)	298	673	
<i>a</i> , <i>c</i> (Å)	7.227 (6), 39.031 (2)	7.242 (6), 39.250 (2)	
<i>V</i> (Å <sup>3</sup> )	1765 (2)	1783 (2)	
<i>Z</i>	18		
Radiation type	Mo K $\alpha$		
<i>m</i> (mm <sup>-1</sup> )	29.96	29.67	
Crystal size (mm)	0.11×0.14×0.21		
Absorption correction	Based on crystal shape		
No. of independent and observed reflections	1729,1558	760, 696	
( <i>sin</i> $\theta$ / $\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	1.26	1.26	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.036, 0.041	0.037, 0.032	
No. of parameters	33		

Table S10. Atomic coordinates displacement parameters (Å<sup>2</sup>) and site-occupancy factors (SOFs) in the structure of  $\alpha$ -BaB<sub>2</sub>O<sub>4</sub> modifications at different temperatures.

Atom	Occ.	<i>x</i>	<i>y</i>	<i>z</i>	U iso/eq
298 K					
O1	1	-0.1610(15)	-0.4630(10)	0.3733(9)	0.018854
O2	1	-0.2620(15)	-0.2722(10)	0.7031(9)	0.015128
B1	1	-0.368(2)	-0.4882(14)	0.3720(14)	0.012173
Ba1	1	0.000000(7)	0.000000(13)	0.349970(7)	0.0132
Ba2	1	0	0	0.25	0.013496
673 K					
O1	1	-0.1601(15)	-0.4649(10)	0.3743(9)	0.047535
O2	1	-0.2641(15)	-0.2737(10)	0.7031(9)	0.043081
B1	1	-0.371(2)	-0.4900(14)	0.3722(14)	0.03548
Ba1	1	0.000000(7)	0.000000(13)	0.350400(7)	0.036046
Ba2	1	0	0	0.25	0.035099

Table S11. Anisotropic parameters of atomic displacements in  $\alpha$ -BaB<sub>2</sub>O<sub>4</sub> at different temperatures.

Atom	U <sub>11</sub>	U <sub>22</sub>	U <sub>33</sub>	U <sub>12</sub>	U <sub>13</sub>	U <sub>23</sub>
298 K						
O1	0.008509	0.010578	0.037283	0.004628	0.001711	-0.00095
O2	0.010085	0.013932	0.021441	0.00606	-0.00205	-0.00345
B1	0.008895	0.011101	0.017575	0.005697	0.001717	0.001291
Ba1	0.010803	0.010803	0.017992	0.005401	0	0
Ba2	0.013309	0.013309	0.01387	0.006654	0	0
673 K						
O1	0.021903	0.018677	0.098787	0.007716	0.008057	-8.3E-05
O2	0.026548	0.039643	0.063948	0.01722	-0.00345	-0.00617
B1	0.025524	0.03252	0.046966	0.013439	0.004543	0.002894
Ba1	0.028984	0.028984	0.05017	0.014492	0	0
Ba2	0.034579	0.034579	0.036138	0.017289	0	0

Table S12. B–O (Å) bond lengths and O–B–O (°) angles in the  $\alpha$ -BaB<sub>2</sub>O<sub>4</sub> structure at different temperatures.

	293	673	$\Delta$ (293–673 K)
B1–O1	1.42(2)	1.45(2)	0.030
B1–O1 <sup>i</sup>	1.393(13)	1.365(13)	-0.028
B1–O2 <sup>ii</sup>	1.30(2)	1.30(2)	0.000
O1–B1–O1 <sup>i</sup>	115.7(12)	115.1(12)	-0.6
O1–B1–O2 <sup>ii</sup>	120.9(8)	120.1(8)	-0.8
O1 <sup>i</sup> –B1–O2 <sup>ii</sup>	123.4(14)	124.7(14)	1.3

Symmetry codes: (i)  $-y-1, x-y-1, z$ ; (ii)  $-y-2/3, x-y-1/3, z-1/3$

Table S13. Ba–O (Å) bond lengths and O–Ba–O (°) angles in the  $\alpha$ -BaB<sub>2</sub>O<sub>4</sub> structure at different temperatures.

	293	673	$\Delta(293-673\text{ K})$
Ba1–O1	3.080(14)	3.107(14)	0.027
Ba1–O2 <sup>iii</sup>	2.742(14)	2.739(14)	−0.003
Ba1–O2 <sup>vi</sup>	2.83(3)	2.86(3)	0.03
Ba2–O2	2.66(3)	2/68(3)	0.02
O1–Ba1–O2 <sup>iv</sup>	47.5(4)	47.5(4)	0
O1–Ba1–O2 <sup>v</sup>	66.9(3)	66.9(3)	0
O1–Ba1–O2 <sup>viii</sup>	67.1(8)	67.5(8)	0.4
O2 <sup>vi</sup> –Ba1–O2 <sup>vii</sup>	72.4(6)	72.2(6)	−0.2
O2 <sup>iii</sup> –Ba1–O2 <sup>vi</sup>	76.8(7)	76.8(7)	0
O2 <sup>vi</sup> –Ba2–O2 <sup>vii</sup>	77.9(7)	78.0(7)	0.1
O2 <sup>vi</sup> –Ba2–O2 <sup>ix</sup>	87.0(8)	86.9(8)	−0.1
O2 <sup>iii</sup> –Ba1–O2 <sup>vii</sup>	90.0(7)	89.6(7)	−0.4
O1–Ba1–O2 <sup>vii</sup>	107.9(5)	108.4(5)	0.5
O1–Ba1–O1 <sup>i</sup>	111.7(5)	111.3(5)	−0.4
O2 <sup>iii</sup> –Ba1–O2 <sup>iv</sup>	112.4(6)	112.6(6)	0.2
O2 <sup>vi</sup> –Ba2–O2 <sup>xi</sup>	134.9(5)	135.0(5)	0.1
O2 <sup>vi</sup> –Ba2–O2 <sup>x</sup>	140.0(5)	139.8(5)	−0.2
O1–Ba1–O2 <sup>iii</sup>	145.0(10)	144.8(10)	−0.2
O2 <sup>iii</sup> –Ba1–O2 <sup>viii</sup>	147.9(9)	147.6(9)	−0.3

Symmetry codes: (i)  $-y, x-y, z$ ; (ii)  $-x+y, -x, z$ ; (iii)  $x+1/3, y+2/3, z-1/3$ ; (iv)  $-y-2/3, x-y-1/3, z-1/3$ ; (v)  $-x+y+1/3, -x-1/3, z-1/3$ ; (vi)  $-x, -y, -z+1$ ; (vii)  $y, -x+y, -z+1$ ; (viii)  $x-y, x, -z+1$ ; (ix)  $-y, -x, z-1/2$ ; (x)  $-x+y, y, z-1/2$ ; (xi)  $x, x-y, z-1/2$

Table S14. O–O–O (°) angles in the  $\alpha$ -BaB<sub>2</sub>O<sub>4</sub> structure at different temperatures.

	293	673	$\Delta(293-673\text{ K})$
O1 <sup>i</sup> –O1–O1 <sup>ii</sup>	60.0(5)	60.0(5)	0
O1 <sup>i</sup> –O1–O2 <sup>iii</sup>	119.6(5)	120.1(5)	0.5
O1 <sup>i</sup> –O1–O2 <sup>iv</sup>	60.0(5)	59.5(5)	−0.5
O1 <sup>ii</sup> –O1–O2 <sup>iii</sup>	59.7(4)	60.3(4)	0.6
O1 <sup>ii</sup> –O1–O2 <sup>iv</sup>	119.9(5)	119.4(5)	−0.5
O2 <sup>iii</sup> –O1–O2 <sup>iv</sup>	173(2)	171(2)	−2
O1 <sup>v</sup> –O2–O1 <sup>vi</sup>	60.3(5)	60.1(5)	−0.2

Symmetry codes: (i)  $-y-1, x-y-1, z$ ; (ii)  $-x+y, -x-1, z$ ; (iii)  $x+1/3, y-1/3, z-1/3$ ; (iv)  $-y-2/3, x-y-1/3, z-1/3$ ; (v)  $x-1/3, y+1/3, z+1/3$ ; (vi)  $-x+y-1/3, -x-2/3, z+1/3$

Table S15. Experimental details of LiB<sub>3</sub>O<sub>5</sub> measurements.

Chemical formula	LiB <sub>3</sub> O <sub>5</sub>								
<i>M<sub>r</sub></i>	119.4								
Crystal system, space group	Orthorhombic, <i>Pna</i> 2 <sub>1</sub>								
Temperature (K)	98	123	148	173	198	223	248	273	298
<i>a</i> (Å)	8.478(5)	8.4386(11)	8.4524(12)	8.437(13)	8.5010(12)	8.4460(11)	8.4605(11)	8.4453(10)	8.5109(11)
<i>b</i> (Å)	7.398(4)	7.3725(16)	7.3868(18)	7.3770(19)	7.4043(18)	7.3749(17)	7.3809(16)	7.3653(15)	7.4112(17)
<i>c</i> (Å)	5.220(3)	5.1954(19)	5.202(2)	5.189(2)	5.211(2)	5.175(2)	5.1703(19)	5.1564(19)	5.173(2)
<i>V</i> (Å <sup>3</sup> )	327.4(3)	323.22(14)	324.78(17)	323.22(17)	328.02(17)	322.32(15)	322.87(14)	320.74(14)	326.27(16)
<i>Z</i>	4								
Radiation type	Mo <i>K</i> α								
$\mu$ (mm <sup>−1</sup> )	0.23								
Crystal size (mm)	0.09×0.19×0.27								
Diffractometer	IPDS Stoe								
Absorption correction	Based on crystal shape								
No. of measured, independent and observed [ <i>I</i> > 3σ( <i>I</i> )] reflections	1907, 760, 617	1898, 750, 638	1884, 751, 608	1893, 756, 614	1884, 750, 607	1874, 745, 606	1874, 745, 586	1859, 743, 590	1903, 755, 586
<i>R</i> <sub>int</sub>	0.044	0.032	0.046	0.041	0.039	0.049	0.065	0.076	0.064
( <i>sin</i> θ/ <i>λ</i> ) <sub>max</sub> (Å <sup>−1</sup> )	0.688	0.687	0.688	0.693	0.686	0.685	0.688	0.686	0.686
<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )]	0.029,	0.025,	0.029,	0.026,	0.026,	0.027,	0.035,	0.037,	0.032,
<i>wR</i> ( <i>F</i> <sup>2</sup> )	0.029,	0.025,	0.030,	0.027,	0.025,	0.027,	0.035,	0.040,	0.034,
$\Sigma$	1.39	1.26	1.40	1.30	1.14	1.25	1.54	1.77	1.46

No. of reflections	760	750	751	756	750	745	745	743	755
No. of parameters	83	83	83	83	83	83	78	83	83
$\Delta\rho_{\max}, \Delta\rho_{\min}$ (e Å <sup>-3</sup> )	0.20,	0.15,	0.20,	0.26,	0.17,	0.22,	0.21,	0.31,	0.19,
	-0.22	-0.17	-0.18	-0.24	-0.16	-0.23	-0.24	-0.30	-0.19
No. Friedel pairs used in the refinement	268	267	266	267	264	264	263	262	266

Table S16. Atomic coordinates, displacement parameters (Å<sup>2</sup>) and site-occupancy factors (SOFs) in the structure of LiB<sub>3</sub>O<sub>5</sub> at different temperatures.

Atom Occ.	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> iso/eq
98 K				
Li1 1	0.4160(4)	0.5677(6)	-0.0073(9)	0.0115(11)
B1 1	0.5094(3)	0.8357(3)	0.3530(5)	0.0067(7)
B2 1	0.6949(3)	0.0578(4)	0.5492(6)	0.0065(7)
B3 1	0.6575(2)	0.7510(3)	0.7317(6)	0.0067(7)
O1 1	0.58596(14)	0.9970(2)	0.3466(3)	0.0063(4)
O2 1	0.38335(15)	0.7943(2)	0.1974(3)	0.0065(4)
O3 1	0.55842(15)	0.7014(2)	0.5272(3)	0.0071(4)
O4 1	0.74019(16)	0.90979(19)	0.7321(3)	0.0059(4)
O5 1	0.65948(16)	0.6263(2)	0.9270(3)	0.0062(4)
123 K				
Li1 1	0.4154(3)	0.5676(4)	-0.0065(8)	0.0132(9)
B1 1	0.5096(2)	0.8353(3)	0.3534(4)	0.0069(5)
B2 1	0.6949(2)	0.0575(3)	0.5504(4)	0.0063(6)
B3 1	0.6573(2)	0.7514(3)	0.7328(4)	0.0068(5)
O1 1	0.58576(12)	0.99648(17)	0.3466(3)	0.0065(3)
O2 1	0.38337(13)	0.79419(17)	0.1971(3)	0.0065(3)
O3 1	0.55845(12)	0.70169(18)	0.5277(3)	0.0073(4)
O4 1	0.74037(13)	0.90971(16)	0.7322(3)	0.0064(3)
O5 1	0.65972(13)	0.62602(18)	0.9272(2)	0.0069(3)
148 K				
Li1 1	0.4145(4)	0.5674(6)	-0.0068(10)	0.0132(12)
B1 1	0.5093(3)	0.8358(4)	0.3540(6)	0.0067(7)
B2 1	0.6947(3)	0.0572(4)	0.5499(6)	0.0067(7)
B3 1	0.6569(2)	0.7507(3)	0.7331(6)	0.0064(7)
O1 1	0.58588(15)	0.9965(2)	0.3469(3)	0.0068(4)
O2 1	0.38360(16)	0.7944(2)	0.1968(3)	0.0067(5)
O3 1	0.55836(15)	0.7013(2)	0.5276(3)	0.0073(5)
O4 1	0.73999(17)	0.9099(2)	0.7321(3)	0.0066(4)
O5 1	0.65974(17)	0.6261(2)	0.9273(3)	0.0072(5)
173 K				
Li1 1	0.4150(4)	0.5669(5)	-0.0046(9)	0.0149(11)
B1 1	0.5093(2)	0.8356(3)	0.3535(5)	0.0076(6)
B2 1	0.6947(2)	0.0574(3)	0.5505(5)	0.0070(6)
B3 1	0.6574(2)	0.7515(3)	0.7333(5)	0.0073(6)
O1 1	0.58579(13)	0.9965(2)	0.3465(3)	0.0084(4)
O2 1	0.38333(14)	0.79470(19)	0.1970(3)	0.0084(4)
O3 1	0.55835(13)	0.7015(2)	0.5276(3)	0.0086(4)
O4 1	0.73984(15)	0.90982(18)	0.7322(3)	0.0074(4)
O5 1	0.65972(15)	0.6259(2)	0.9270(3)	0.0084(4)
198 K				
Li1 1	0.4142(4)	0.5677(5)	-0.0054(9)	0.0155(10)
B1 1	0.5094(2)	0.8358(3)	0.3530(5)	0.0083(6)
B2 1	0.6942(2)	0.0571(3)	0.5503(5)	0.0071(6)
B3 1	0.6574(2)	0.7513(3)	0.7331(5)	0.0078(6)
O1 1	0.58609(12)	0.99649(19)	0.3462(3)	0.0079(4)
O2 1	0.38339(13)	0.79463(18)	0.1970(3)	0.0080(4)
O3 1	0.55826(13)	0.70187(20)	0.5280(3)	0.0085(4)
O4 1	0.73967(14)	0.90981(17)	0.7325(3)	0.0074(4)
O5 1	0.65982(14)	0.62579(19)	0.9271(3)	0.0081(4)
223 K				
Li1 1	0.4129(4)	0.5673(5)	-0.0061(10)	0.0167(12)
B1 1	0.5099(2)	0.8359(3)	0.3539(5)	0.0086(7)

B2	1	0.6942(2)	0.0567(3)	0.5509(5)	0.0068(7)
B3	1	0.6574(2)	0.7512(3)	0.7331(5)	0.0077(6)
O1	1	0.58631(14)	0.9960(2)	0.3459(3)	0.0088(4)
O2	1	0.38369(15)	0.7950(2)	0.1969(3)	0.0083(4)
O3	1	0.55818(14)	0.7017(2)	0.5277(3)	0.0091(4)
O4	1	0.73946(16)	0.90956(19)	0.7329(3)	0.0075(4)
O5	1	0.66029(15)	0.6260(2)	0.9268(3)	0.0084(4)
248 K					
Li1	1	0.4129(6)	0.5672(8)	-0.0059(14)	0.0193(17)
B1	1	0.5099(3)	0.8365(5)	0.3533(7)	0.0087(9)
B2	1	0.6938(3)	0.0565(5)	0.5499(7)	0.0061(9)
B3	1	0.6569(3)	0.7513(4)	0.7340(7)	0.0070(6)
O1	1	0.58614(18)	0.9960(3)	0.3458(4)	0.0083(5)
O2	1	0.3836(2)	0.7949(3)	0.1965(4)	0.0084(6)
O3	1	0.55823(19)	0.7020(3)	0.5280(4)	0.0095(6)
O4	1	0.7392(2)	0.9099(3)	0.7333(4)	0.0072(5)
O5	1	0.6604(2)	0.6256(3)	0.9269(4)	0.0076(6)
273 K					
Li1	1	0.4119(7)	0.5677(9)	-0.0041(16)	0.0209(19)
B1	1	0.5103(4)	0.8359(5)	0.3543(8)	0.0092(10)
B2	1	0.6942(4)	0.0567(5)	0.5504(8)	0.0075(10)
B3	1	0.6572(4)	0.7509(5)	0.7341(9)	0.0085(10)
O1	1	0.5864(2)	0.9962(3)	0.3450(5)	0.0097(6)
O2	1	0.3835(2)	0.7950(3)	0.1965(5)	0.0090(7)
O3	1	0.5577(2)	0.7024(3)	0.5284(5)	0.0106(7)
O4	1	0.7391(2)	0.9093(3)	0.7332(5)	0.0090(6)
O5	1	0.6609(2)	0.6260(3)	0.9266(4)	0.0094(6)
298 K					
Li1	1	0.4114(6)	0.5668(8)	-0.0046(14)	0.0225(17)
B1	1	0.5099(3)	0.8363(4)	0.3532(7)	0.0091(9)
B2	1	0.6935(3)	0.0565(4)	0.5502(7)	0.0065(9)
B3	1	0.6574(3)	0.7507(4)	0.7346(7)	0.0082(8)
O1	1	0.58655(18)	0.9956(3)	0.3447(4)	0.0094(5)
O2	1	0.38380(19)	0.7951(3)	0.1966(4)	0.0092(6)
O3	1	0.55813(19)	0.7021(3)	0.5284(4)	0.0108(6)
O4	1	0.7387(2)	0.9096(2)	0.7337(4)	0.0081(5)
O5	1	0.6611(2)	0.6252(3)	0.9266(4)	0.0088(6)

Table S17. Anisotropic parameters of atomic displacements in LiB<sub>3</sub>O<sub>5</sub> at different temperatures.

Atom	U <sub>11</sub>	U <sub>22</sub>	U <sub>33</sub>	U <sub>12</sub>	U <sub>13</sub>	U <sub>23</sub>
98 K						
Li1	0.0134(17)	0.0082(18)	0.013(2)	0.0000(15)	-0.0049(16)	0.0021(18)
B1	0.0087(10)	0.0057(13)	0.0056(12)	0.0022(9)	0.0041(10)	-0.0010(11)
B2	0.0075(11)	0.0045(12)	0.0075(14)	0.0003(9)	0.0005(10)	0.0003(11)
B3	0.0050(9)	0.0062(11)	0.0088(14)	0.0027(7)	0.0022(10)	-0.0026(13)
O1	0.0080(6)	0.0050(7)	0.0057(8)	-0.0001(5)	-0.0017(7)	0.0002(7)
O2	0.0071(6)	0.0038(7)	0.0084(9)	0.0000(6)	-0.0011(7)	0.0005(8)
O3	0.0081(7)	0.0062(7)	0.0068(8)	-0.0010(6)	-0.0009(6)	0.0001(8)
O4	0.0068(6)	0.0046(7)	0.0064(8)	-0.0004(5)	0.0000(7)	0.0012(8)
O5	0.0061(6)	0.0062(8)	0.0064(8)	-0.0004(5)	-0.0012(6)	-0.0004(7)
123 K						
Li1	0.0174(14)	0.0075(14)	0.0148(20)	-0.0007(12)	-0.0031(13)	-0.0009(15)
B1	0.0072(8)	0.0061(10)	0.0074(10)	0.0027(7)	0.0034(8)	-0.0014(9)
B2	0.0074(9)	0.0050(9)	0.0066(11)	-0.0008(7)	-0.0004(8)	-0.0001(9)
B3	0.0062(7)	0.0053(9)	0.0091(11)	0.0023(6)	0.0017(8)	-0.0022(10)
O1	0.0076(5)	0.0055(6)	0.0064(6)	-0.0007(4)	-0.0011(5)	0.0009(6)
O2	0.0073(5)	0.0045(6)	0.0077(7)	0.0001(5)	0.0000(5)	0.0013(7)
O3	0.0091(6)	0.0056(6)	0.0072(7)	-0.0001(5)	-0.0014(5)	0.0002(6)
O4	0.0080(5)	0.0051(6)	0.0061(6)	-0.0004(4)	-0.0006(5)	0.0014(7)
O5	0.0060(5)	0.0065(6)	0.0083(6)	-0.0005(4)	-0.0006(5)	0.0007(6)
148 K						
Li1	0.0151(18)	0.010(2)	0.015(3)	-0.0020(16)	-0.0024(17)	-0.001(2)
B1	0.0082(10)	0.0051(14)	0.0067(13)	0.0032(9)	0.0037(11)	-0.0017(12)
B2	0.0086(12)	0.0059(13)	0.0055(14)	-0.0015(9)	0.0002(11)	0.0011(12)



B3	0.0038(9)	0.0053(12)	0.0100(15)	0.0025(7)	0.0012(10)	-0.0044(14)
O1	0.0082(6)	0.0056(8)	0.0065(8)	-0.0005(6)	-0.0028(7)	0.0007(8)
O2	0.0071(7)	0.0050(8)	0.0081(9)	0.0003(6)	-0.0009(7)	0.0014(9)
O3	0.0071(7)	0.0069(8)	0.0078(9)	0.0006(7)	-0.0010(7)	0.0007(8)
O4	0.0083(7)	0.0053(8)	0.0062(8)	-0.0005(6)	-0.0007(7)	0.0030(9)
O5	0.0068(7)	0.0071(8)	0.0076(8)	-0.0005(6)	-0.0011(6)	0.0010(8)
173 K						
Li1	0.0168(16)	0.0096(17)	0.018(2)	0.0000(13)	-0.0040(15)	0.0026(18)
B1	0.0086(9)	0.0068(11)	0.0075(11)	0.0018(8)	0.0025(9)	0.0001(10)
B2	0.0065(10)	0.0070(11)	0.0076(12)	-0.0006(8)	-0.0001(9)	0.0004(10)
B3	0.0061(8)	0.0059(10)	0.0098(13)	0.0014(7)	0.0022(9)	-0.0035(12)
O1	0.0098(5)	0.0073(7)	0.0082(7)	-0.0002(5)	-0.0009(6)	0.0011(7)
O2	0.0088(6)	0.0066(7)	0.0099(8)	0.0003(5)	-0.0012(6)	-0.0009(8)
O3	0.0104(7)	0.0069(7)	0.0085(8)	0.0001(6)	-0.0019(6)	-0.0002(7)
O4	0.0083(6)	0.0066(7)	0.0072(7)	-0.0013(5)	0.0006(6)	0.0015(8)
O5	0.0075(6)	0.0078(7)	0.0099(7)	-0.0009(5)	-0.0011(5)	0.0009(7)
198 K						
Li1	0.0178(15)	0.0096(16)	0.019(2)	0.0001(13)	-0.0027(15)	-0.0013(17)
B1	0.0091(9)	0.0079(12)	0.0078(11)	0.0024(8)	0.0038(9)	-0.0028(10)
B2	0.0092(10)	0.0053(10)	0.0067(12)	-0.0003(8)	-0.0003(9)	0.0001(10)
B3	0.0060(8)	0.0065(10)	0.0108(12)	0.0028(6)	0.0013(9)	-0.0032(12)
O1	0.0097(5)	0.0062(6)	0.0079(7)	-0.0006(5)	-0.0026(6)	0.0014(6)
O2	0.0085(6)	0.0059(6)	0.0096(8)	-0.0002(5)	-0.0011(6)	0.0009(7)
O3	0.0100(6)	0.0071(6)	0.0083(8)	-0.0002(5)	-0.0012(6)	0.0001(7)
O4	0.0090(5)	0.0054(6)	0.0078(7)	-0.0011(5)	-0.0006(6)	0.0028(7)
O5	0.0071(5)	0.0080(7)	0.0094(7)	-0.0006(5)	-0.0014(5)	0.0012(6)
223 K						
Li1	0.0215(18)	0.0087(18)	0.020(2)	0.0006(15)	-0.0050(17)	-0.0007(19)
B1	0.0100(10)	0.0080(13)	0.0080(12)	0.0021(8)	0.0029(10)	-0.0021(11)
B2	0.0085(10)	0.0060(11)	0.0059(12)	-0.0006(8)	-0.0011(10)	0.0009(10)
B3	0.0061(8)	0.0076(11)	0.0094(13)	0.0017(7)	0.0023(9)	-0.0030(12)
O1	0.0101(6)	0.0070(7)	0.0092(8)	-0.0005(5)	-0.0011(7)	0.0013(7)
O2	0.0093(6)	0.0063(7)	0.0092(8)	0.0004(5)	-0.0014(6)	0.0011(8)
O3	0.0104(7)	0.0071(7)	0.0099(8)	-0.0004(6)	-0.0020(6)	0.0013(8)
O4	0.0085(6)	0.0058(7)	0.0080(8)	-0.0008(5)	-0.0004(6)	0.0019(8)
O5	0.0076(6)	0.0075(8)	0.0100(8)	-0.0008(5)	-0.0018(6)	0.0009(7)
248 K						
Li1	0.021(2)	0.010(3)	0.027(4)	-0.001(2)	-0.010(2)	0.000(3)
B1	0.0084(13)	0.0081(17)	0.0096(17)	0.0029(11)	0.0028(13)	-0.0026(15)
B2	0.0089(14)	0.0048(15)	0.0044(16)	0.0004(11)	-0.0013(13)	0.0006(14)
O1	0.0083(7)	0.0069(10)	0.0096(11)	-0.0016(7)	-0.0012(9)	0.0015(10)
O2	0.0079(8)	0.0066(10)	0.0108(12)	-0.0009(7)	-0.0012(9)	0.0001(11)
O3	0.0094(9)	0.0073(10)	0.0119(12)	-0.0007(8)	-0.0013(9)	0.0006(11)
O4	0.0077(8)	0.0064(10)	0.0075(10)	-0.0009(7)	-0.0003(8)	0.0014(11)
O5	0.0064(8)	0.0076(10)	0.0088(10)	-0.0003(7)	-0.0021(7)	0.0008(9)
Li1	0.021(2)	0.010(3)	0.027(4)	-0.001(2)	-0.010(2)	0.000(3)
273 K						
Li1	0.025(3)	0.012(3)	0.025(4)	-0.001(2)	-0.009(3)	-0.001(3)
B1	0.0103(15)	0.0075(19)	0.0097(19)	0.0018(13)	0.0026(15)	-0.0019(17)
B2	0.0102(16)	0.0054(17)	0.007(2)	-0.0012(13)	0.0014(15)	0.0018(16)
B3	0.0077(13)	0.0059(16)	0.012(2)	0.0034(11)	0.0004(15)	-0.0032(20)
O1	0.0103(9)	0.0081(11)	0.0108(12)	-0.0018(8)	-0.0021(11)	0.0025(11)
O2	0.0089(9)	0.0062(11)	0.0120(14)	-0.0006(8)	-0.0018(10)	0.0006(13)
O3	0.0108(11)	0.0092(11)	0.0116(13)	-0.0002(9)	-0.0039(10)	0.0013(12)
O4	0.0080(9)	0.0091(11)	0.0100(12)	-0.0011(8)	-0.0010(10)	0.0036(13)
O5	0.0060(9)	0.0101(12)	0.0120(12)	-0.0007(8)	-0.0022(9)	0.0022(11)
298 K						
Li1	0.027(3)	0.011(3)	0.029(4)	0.000(2)	-0.010(3)	0.001(3)
B1	0.0096(13)	0.0083(17)	0.0094(16)	0.0038(11)	0.0036(13)	-0.0007(15)
B2	0.0091(14)	0.0057(15)	0.0046(16)	0.0003(11)	0.0000(13)	0.0009(14)
B3	0.0070(11)	0.0055(14)	0.0121(18)	0.0024(9)	0.0024(13)	-0.0048(17)
O1	0.0120(8)	0.0070(10)	0.0094(10)	-0.0019(7)	-0.0032(9)	0.0025(9)
O2	0.0098(8)	0.0067(9)	0.0110(12)	-0.0002(7)	-0.0019(9)	0.0000(11)
O3	0.0116(9)	0.0080(9)	0.0128(12)	-0.0005(8)	-0.0034(9)	0.0007(11)
O4	0.0101(8)	0.0057(9)	0.0084(10)	-0.0018(7)	-0.0011(8)	0.0027(11)
O5	0.0067(8)	0.0091(10)	0.0106(10)	-0.0009(7)	-0.0023(7)	0.0018(9)

Table S18. Li–O (Å) bond lengths and O–Li–O (°) angles in the LiB<sub>3</sub>O<sub>5</sub> structure at different temperatures.

T / K	98	123	148	173	198	223	248	273	298	500	650	Δ(98–650 K)
Li1–O2	2.007(5)	1.995(4)	2.001(5)	1.998(4)	2.001(4)	1.996(5)	1.996(6)	1.98 (1)	2.000(6)	1.968(3)	1.953(4)	−0.054
Li1–O3 <sup>i</sup>	2.011(5)	2.006(4)	2.006(5)	2.000(4)	2.017(4)	2.006(4)	2.009(6)	2.01(1)	2.017(6)	2.023(3)	2.049(4)	0.038
Li1–O4 <sup>ii</sup>	2.025(5)	2.013(4)	2.012(5)	2.021(4)	2.024(4)	2.000(5)	2.002(6)	2.00(1)	2.006(6)	2.004(4)	1.998(6)	−0.027
Li1–O5 <sup>iii</sup>	2.137(4)	2.134(3)	2.146(4)	2.141(4)	2.161(3)	2.162(4)	2.166(5)	2.18(1)	2.198(5)	2.382(4)	2.576(7)	0.439
Li1–O5 <sup>i</sup>	2.759(5)	2.741(4)	2.745(5)	2.727(5)	2.744(5)	2.726(5)	2.723(7)	2.71(1)	2.717(7)	2.571(4)	2.469(6)	−0.290
O2–Li1–O3 <sup>i</sup>	142.6(3)	142.8(2)	142.8(3)	143.5(3)	143.2(2)	143.2(3)	143.3(4)	143.8(5)	143.8(4)	148.8(1)	150.6(2)	8.0
O2–Li1–O4 <sup>ii</sup>	100.8 (2)	100.9(2)	101.1(2)	100.6(2)	101.0(2)	101.1(2)	101.0(2)	101.2(3)	101.0(2)	101.6(1)	102.8(2)	2.0
O2–Li1–O5 <sup>iii</sup>	92.82(17)	92.72(14)	92.35(18)	92.58(15)	92.58(15)	92.04(16)	92.1(2)	92.0(3)	91.8(2)	89.44(11)	86.3(2)	−6.5
O2–Li1–O5 <sup>i</sup>	87.99(18)	88.22(15)	88.34(19)	88.72(17)	88.61(16)	88.81(18)	88.9(3)	89.4(3)	89.4(3)	94.43(11)	98.8(2)	10.9
O3 <sup>i</sup> –Li1–O4 <sup>ii</sup>	102.8(2)	102.9(2)	103.1(2)	102.9(2)	103.0(2)	103.5(2)	103.4(3)	103.5(3)	103.8(3)	104.6(1)	105.6(2)	2.8
O3 <sup>i</sup> –Li1–O5 <sup>iii</sup>	96.37(16)	96.18(13)	95.95(17)	96.13(15)	95.66(14)	95.42(16)	95.4(2)	94.9(3)	94.8(2)	90.51(11)	86.3(2)	−10.1
O3 <sup>i</sup> –Li1–O5 <sup>i</sup>	55.68(12)	55.74(10)	55.78(13)	56.00(11)	55.88(11)	55.88(12)	55.9(2)	56.0(2)	56.1(2)	58.44(11)	60.0(2)	4.3
O4 <sup>ii</sup> –Li1–O5 <sup>iii</sup>	125.9(2)	125.7(2)	125.7(3)	125.2(2)	125.6(2)	125.6(2)	125.8(3)	125.3(4)	125.6(3)	122.57(12)	119.5(2)	−6.4
O4 <sup>ii</sup> –Li1–O5 <sup>i</sup>	115.10(16)	115.34(14)	115.54(17)	115.46(15)	115.44(15)	115.69(17)	115.5(2)	115.7(3)	115.7(2)	117.35(15)	120.1(2)	5.0
O5 <sup>iii</sup> –Li1–O5 <sup>i</sup>	117.48(18)	117.45(15)	117.22(19)	117.75(17)	117.34(16)	117.12(18)	117.1(3)	117.3(3)	117.1(3)	117.66(12)	117.1(2)	−0.4

Symmetry codes: (i)  $-x+1, -y+1, z-1/2$ ; (ii)  $x-1/2, -y+3/2, z-1$ ; (iii)  $x, y, z-1$ .Table S19. B–O (Å) bond lengths and O–B–O (°) angles in the LiB<sub>3</sub>O<sub>5</sub> structure at different temperatures.

T / K	98	123	148	173	198	223	248	273	298	500	650	Δ(98–650 K)
B1–O1	1.359(3)	1.351(2)	1.352(3)	1.352(3)	1.357(3)	1.346(3)	1.343(4)	1.345(4)	1.349(4)	1.3474(16)	1.349(2)	−0.010
B1–O2	1.377(3)	1.373(2)	1.375(3)	1.372(3)	1.379(3)	1.374(3)	1.376(4)	1.378(4)	1.379(4)	1.363(3)	1.364(4)	−0.013
B1–O3	1.409(3)	1.400(3)	1.405(3)	1.402(3)	1.410(3)	1.398(3)	1.403(4)	1.391(5)	1.407(4)	1.394(3)	1.395(5)	−0.014
B2–O1 <sup>i</sup>	1.475(3)	1.474(2)	1.471(3)	1.473(3)	1.475(3)	1.469(3)	1.464(4)	1.466(4)	1.471(4)	1.458(4)	1.454(5)	−0.021
B2–O2 <sup>ii</sup>	1.495(3)	1.487(2)	1.491(3)	1.484(3)	1.492(3)	1.483(3)	1.485(4)	1.480(4)	1.489(4)	1.484(3)	1.483(4)	−0.012
B2–O4 <sup>i</sup>	1.503(3)	1.492(3)	1.493(3)	1.489(3)	1.497(3)	1.487(3)	1.489(4)	1.487(5)	1.495(4)	1.488(3)	1.489(5)	−0.014
B2–O5 <sup>iii</sup>	1.479(3)	1.473(2)	1.477(3)	1.476(2)	1.487(2)	1.477(3)	1.479(4)	1.471(4)	1.483(3)	1.457(3)	1.457(4)	−0.022
B3–O3	1.407(3)	1.402(2)	1.404(3)	1.405(3)	1.409(3)	1.402(3)	1.402(4)	1.399(5)	1.408(4)	1.392(4)	1.390(6)	−0.017
B3–O4	1.368(3)	1.362(2)	1.370(3)	1.360(2)	1.366(2)	1.358(3)	1.362(4)	1.357(4)	1.365(3)	1.3556(16)	1.3567(19)	−0.011
B3–O5	1.375(3)	1.369(3)	1.367(3)	1.367(3)	1.373(3)	1.363(3)	1.362(4)	1.353(5)	1.361(4)	1.365(4)	1.363(5)	−0.012
O1–B1–O2	123.5(2)	123.22(17)	123.3(2)	123.2(2)	123.49(19)	123.1(2)	123.5(3)	122.9(3)	123.4(3)	123.1(2)	122.8(3)	−0.7
O1–B1–O3	119.6(2)	119.70(16)	119.8(2)	119.69(18)	119.45(17)	120.04(19)	120.0(3)	120.4(3)	119.9(3)	119.7(2)	119.8(3)	0.2
O2–B1–O3	116.91(19)	117.08(16)	116.9(2)	117.11(18)	117.07(17)	116.83(19)	116.6(3)	116.7(3)	116.7(2)	117.14(10)	117.39(13)	0.5
O1 <sup>i</sup> –B2–O2 <sup>ii</sup>	108.44(16)	108.36(13)	108.36(17)	108.37(14)	108.50(14)	108.50(15)	108.6(2)	108.4(2)	108.7(2)	108.99(11)	109.34(16)	0.9
O1 <sup>i</sup> –B2–O4 <sup>i</sup>	113.16(19)	113.10(15)	113.2(2)	113.07(17)	113.36(16)	113.24(18)	113.5(2)	113.2(3)	113.2(2)	112.47(10)	111.92(15)	−1.2
O1 <sup>i</sup> –B2–O5 <sup>iii</sup>	108.5(2)	108.22(16)	108.4(2)	108.22(18)	108.24(17)	107.91(19)	108.3(3)	108.0(3)	108.1(2)	108.3(3)	108.4(4)	−0.1
O2 <sup>ii</sup> –B2–O4 <sup>i</sup>	108.5(2)	109.08(16)	108.9(2)	109.06(18)	108.98(17)	109.24(19)	109.0(3)	109.2(3)	109.2(2)	109.0(3)	109.3(4)	0.8
O2 <sup>ii</sup> –B2–O5 <sup>iii</sup>	110.07(19)	109.91(15)	109.74(19)	109.89(17)	109.78(16)	109.60(17)	109.4(2)	109.5(3)	109.6(2)	109.85(9)	109.75(12)	−0.3
O4 <sup>i</sup> –B2–O5 <sup>iii</sup>	108.10(16)	108.14(13)	108.15(17)	108.21(14)	107.94(14)	108.31(15)	108.0(2)	108.4(2)	108.0(2)	108.29(10)	108.08(14)	0.0
O3–B3–O4	122.1(2)	121.90(18)	121.6(2)	121.8(2)	121.81(19)	121.9(2)	121.7(3)	121.6(3)	121.5(3)	122.5(2)	122.4(3)	0.3
O3–B3–O5	113.26(18)	113.14(15)	113.48(19)	112.91(16)	113.06(16)	113.05(18)	113.1(2)	113.4(3)	113.1(2)	112.55(11)	112.44(16)	−0.8
O4–B3–O5	124.7(2)	124.95(17)	124.9(2)	125.3(2)	125.13(19)	125.0(2)	125.2(3)	125.1(3)	125.5(3)	125.0(3)	125.2(4)	0.5

Symmetry codes: (i)  $x, y-1, z$ ; (ii)  $-x+1, -y+1, z+1/2$ ; (iii)  $-x+3/2, y-1/2, z-1/2$ .Table S20. B–O–B (°) angles in the LiB<sub>3</sub>O<sub>5</sub> structure at different temperatures.

T / K	98	123	148	173	198	223	248	273	298	500	650	Δ(98–650 K)
B1–O1–B2 <sup>i</sup>	123.33(19)	123.16(16)	123.2(2)	123.16(18)	123.18(17)	122.86(19)	123.0(3)	122.6(3)	123.0(2)	123.4(3)	123.6(4)	0.3
B1–O2–B2 <sup>ii</sup>	119.15(18)	119.01(14)	118.96(19)	119.07(16)	118.89(16)	118.91(17)	118.6(2)	118.9(3)	118.7(2)	119.47(8)	119.56(11)	0.4
B1–O3–B3	118.79(18)	118.87(15)	118.74(19)	118.71(17)	118.97(16)	118.54(18)	118.6(2)	118.8(3)	118.9(2)	118.46(10)	118.32(14)	−0.5
B2 <sup>i</sup> –O4–B3	119.60(18)	119.69(14)	119.77(18)	119.98(16)	119.69(15)	119.81(17)	119.6(2)	120.0(3)	120.0(2)	120.2(2)	120.8(3)	1.2
B2 <sup>iii</sup> –O5–B3	124.04(17)	124.37(13)	124.46(17)	124.30(15)	124.19(14)	124.64(16)	124.6(2)	125.0(2)	124.6(2)	126.48(12)	127.82(16)	3.8

Symmetry codes: (i)  $x, y+1, z$  (ii)  $-x+1, -y+1, z-1/2$  (iii)  $-x+3/2, y+1/2, z+1/2$ Table S21. O–O–O (°) angles in the LiB<sub>3</sub>O<sub>5</sub> structure at different temperatures.

T / K	98	123	148	173	198	223	248	273	298	500	650	Δ(98–650 K)
O1 <sup>v</sup> –O5–O4	91.01(7)	91.11(6)	91.23(7)	91.23(6)	91.17(6)	91.53(7)	91.56(9)	91.67(10)	91.82(9)	94.18(8)	95.98(10)	5.0
O2 <sup>i</sup> –O4–O5	133.4(1)	133.4(1)	133.52(8)	133.6 (1)	133.6(1)	133.8(1)	134.0(1)	134.1(1)	134.3(1)	136.6 (1)	138.3(1)	4.9
O1 <sup>v</sup> –O5–O3	105.7(1)	105.8(1)	105.76(8)	105.84(7)	105.92(7)	106.01(8)	106.12(10)	106.30(12)	106.38(10)	108.44(16)	110.2(2)	4.5
O2–O3–O5	162.0(1)	162.1(1)	162.15(9)	162.12(8)	162.24(7)	162.36(8)	162.43(11)	162.76(12)	162.67(11)	164.39(13)	165.95(18)	4.0
O2–O1–O5 <sup>ii</sup>	161.2(1)	161.2(1)	161.22(9)	161.28(8)	161.36(8)	161.61(8)	161.53(11)	161.73(13)	161.87(11)	163.44(9)	164.18(13)	3.0
O3–O5–O4 <sup>v</sup>	151.8(1)	151.9(1)	151.81(10)	151.93(8)	152.08(8)	151.98(9)	152.20(12)	152.11(14)	152.36(12)	153.63(10)	154.19(14)	2.4

O4–O5–O4 <sup>v</sup>	138.6(1)	138.7(1)	138.70(8)	138.64(7)	138.56(7)	138.75(8)	138.66(10)	138.89(12)	138.75(10)	139.53(8)	140.29(12)	1.7
O1–O2–O4 <sup>iii</sup>	73.92(8)	73.89(5)	73.89(7)	73.91(6)	74.04(6)	74.02(6)	73.98(9)	73.95(10)	74.11(9)	74.89(6)	75.22(8)	1.3
O3–O1–O5 <sup>ii</sup>	112.6(1)	112.5(1)	112.63(8)	112.58(7)	112.56(7)	112.80(7)	112.68(10)	112.83(11)	112.76(10)	113.36(10)	113.64(14)	1.1
O2 <sup>vi</sup> –O5–O3	138.6(1)	138.5(1)	138.50(9)	138.51(8)	138.47(7)	138.63(8)	138.47(11)	138.75(13)	138.54(11)	139.03(9)	139.59(13)	1.0
O3–O4–O5 <sup>ii</sup>	110.7(1)	110.8(1)	110.88(9)	110.88(8)	110.87(7)	110.83(8)	110.85(11)	110.86(12)	110.93(11)	111.10(17)	111.6(2)	0.9
O1–O4–O5	114.5(1)	114.4(2)	114.52(8)	114.50(7)	114.51(7)	114.58(7)	114.50(10)	114.70(11)	114.58(9)	114.88(9)	115.16(12)	0.6
O2 <sup>vi</sup> –O5–O4 <sup>v</sup>	60.21(7)	60.39(5)	60.33(7)	60.26(6)	60.22(5)	60.29(6)	60.30(8)	60.38(9)	60.36(8)	60.60(8)	60.82(12)	0.6
O1 <sup>v</sup> –O5–O2 <sup>vi</sup>	59.77(7)	59.87(5)	59.79(7)	59.78(6)	59.72(5)	59.86(6)	59.78(8)	59.92(9)	59.88(8)	60.27(9)	60.37(13)	0.6
O2 <sup>i</sup> –O1–O4	59.60(7)	59.68(5)	59.71(7)	59.64(6)	59.62(6)	59.70(6)	59.69(8)	59.72(9)	59.74(8)	59.91(10)	60.16(14)	0.6
O1–O3–O5	122.4(1)	122.6(1)	122.46(9)	122.57(8)	122.67(7)	122.55(8)	122.70(11)	122.66(13)	122.81(11)	122.97(10)	122.99(14)	0.6
O1–O4–O2 <sup>i</sup>	58.65(6)	58.66(5)	58.66(7)	58.68(6)	58.65(5)	58.68(6)	58.63(8)	58.59(9)	58.68(8)	58.93(9)	59.05(13)	0.4
O4–O3–O5	61.44(7)	61.56(5)	61.55(7)	61.60(6)	61.58(6)	61.49(6)	61.60(9)	61.42(10)	61.61(8)	61.70(10)	61.82(13)	0.4
O2 <sup>vi</sup> –O5–O4	79.36(7)	79.26(6)	79.33(7)	79.33(6)	79.27(6)	79.36(7)	79.22(9)	79.38(10)	79.20(9)	79.37(8)	79.74(11)	0.4
O1–O4–O3	58.27(7)	58.21(5)	58.31(7)	58.31(6)	58.25(6)	58.29(6)	58.27(8)	58.31(10)	58.32(8)	58.41(9)	58.64(13)	0.4
O2 <sup>i</sup> –O1–O3	107.3(1)	107.3(1)	107.43(9)	107.36(8)	107.22(8)	107.32(8)	107.37(11)	107.19(13)	107.28(11)	107.45(17)	107.6(2)	0.4
O3–O1–O4	59.67(6)	59.66(5)	59.74(6)	59.69(6)	59.67(5)	59.69(6)	59.70(8)	59.57(9)	59.64(8)	59.93(9)	60.01(12)	0.3
O1 <sup>iii</sup> –O2–O3	132.0(8)	131.9(1)	132.08(8)	131.96(7)	131.96(7)	132.15(7)	132.00(10)	132.07(11)	132.04(10)	132.33(5)	132.32(7)	0.3
O4–O1–O5 <sup>ii</sup>	59.22(6)	59.15(5)	59.22(6)	59.22(5)	59.18(5)	59.36(6)	59.27(8)	59.40(9)	59.32(8)	59.47(9)	59.54(13)	0.3
O1–O2–O5 <sup>iv</sup>	126.3(1)	126.3(1)	126.36(9)	126.38(8)	126.45(7)	126.50(8)	126.44(11)	126.45(13)	126.43(11)	126.59(7)	126.65(10)	0.3
O2 <sup>i</sup> –O4–O3	105.4(1)	105.3(1)	105.45(8)	105.48(7)	105.32(6)	105.39(7)	105.38(10)	105.28(11)	105.38(9)	105.46(9)	105.67(12)	0.3
O3–O2–O4 <sup>iii</sup>	118.4(1)	118.3(1)	118.33(9)	118.36(8)	118.25(8)	118.32(8)	118.18(11)	118.08(13)	118.21(11)	118.54(14)	118.6(2)	0.2
O2–O1–O4	118.4(1)	118.5(1)	118.54(9)	118.50(8)	118.51(7)	118.45(8)	118.50(11)	118.30(12)	118.39(11)	118.42(10)	118.55(15)	0.2
O2–O1–O3	59.27(7)	59.39(5)	59.36(7)	59.38(6)	59.41(6)	59.35(6)	59.39(8)	59.31(9)	59.37(8)	59.30(8)	59.43(11)	0.2
O3–O5–O4	61.40(7)	61.32(5)	61.35(7)	61.35(6)	61.33(6)	61.42(6)	61.39(9)	61.45(10)	61.42(8)	61.50(9)	61.50(13)	0.1
O1–O2–O3	60.01(7)	59.94(5)	60.02(7)	60.01(6)	59.87(6)	60.03(6)	59.95(8)	59.98(10)	59.96(8)	60.08(8)	60.10(12)	0.1
O1–O4–O5 <sup>ii</sup>	58.58(7)	58.62(5)	58.66(6)	58.68(6)	58.69(5)	58.54(6)	58.63(8)	58.45(9)	58.58(8)	58.45(9)	58.61(13)	0.0
O3–O2–O5 <sup>iv</sup>	167.5(1)	167.5(1)	167.32(9)	167.45(8)	167.40(7)	167.36(8)	167.33(11)	167.33(13)	167.38(11)	167.51(14)	167.5(2)	0.0
O2 <sup>i</sup> –O1–O5 <sup>ii</sup>	60.93(6)	60.82(5)	60.86(6)	60.83(6)	60.90(5)	60.84(6)	60.82(8)	60.75(9)	60.81(8)	60.79(9)	60.70(12)	–0.2
O4 <sup>iii</sup> –O2–O5 <sup>iv</sup>	59.42(6)	59.34(5)	59.38(7)	59.44(6)	59.40(5)	59.51(6)	59.48(8)	59.61(9)	59.45(8)	59.30(8)	59.18(11)	–0.2
O1–O3–O2	60.72(6)	60.67(5)	60.62(7)	60.61(6)	60.72(6)	60.62(6)	60.66(8)	60.71(10)	60.67(8)	60.62(8)	60.47(11)	–0.3
O1 <sup>v</sup> –O5–O4 <sup>v</sup>	62.20(7)	62.23(5)	62.12(7)	62.11(6)	62.13(6)	62.10(6)	62.10(8)	62.16(10)	62.10(8)	62.08(9)	61.85(13)	–0.4
O1 <sup>iii</sup> –O2–O5 <sup>iv</sup>	59.30(6)	59.31(5)	59.35(6)	59.39(6)	59.39(5)	59.30(6)	59.40(8)	59.34(9)	59.30(8)	58.93(8)	58.93(12)	–0.4
O2 <sup>i</sup> –O4–O5 <sup>ii</sup>	60.37(7)	60.27(5)	60.29(7)	60.30(6)	60.38(5)	60.20(6)	60.22(8)	60.02(9)	60.19(8)	60.10(8)	60.00(11)	–0.4
O3–O4–O5	57.16(7)	57.12(5)	57.09(7)	57.06(6)	57.10(6)	57.09(6)	57.02(8)	57.14(9)	56.97(8)	56.80(10)	56.68(14)	–0.5
O1–O3–O4	62.06(7)	62.13(5)	61.95(7)	62.00(6)	62.08(6)	62.02(6)	62.03(8)	62.12(10)	62.04(8)	61.66(9)	61.35(13)	–0.7
O1–O2–O1 <sup>iii</sup>	76.70(7)	76.62(6)	76.70(7)	76.64(7)	76.68(6)	76.69(7)	76.60(9)	76.57(10)	76.53(9)	76.30(10)	75.99(13)	–0.7
O1 <sup>iii</sup> –O2–O4 <sup>iii</sup>	61.75(7)	61.67(5)	61.64(7)	61.68(6)	61.73(6)	61.63(6)	61.68(9)	61.68(10)	61.57(8)	61.17(10)	60.79(14)	–1.0
O2–O3–O4	122.2(1)	122.2(1)	121.97(9)	122.00(8)	122.18(8)	122.00(8)	122.05(11)	122.20(13)	122.04(11)	121.41(8)	120.90(10)	–1.3
O2–O1–O2 <sup>i</sup>	136.2(1)	136.3(1)	136.31(8)	136.25(7)	136.08(7)	135.95(8)	136.04(10)	135.88(12)	135.69(10)	134.26(12)	133.75(16)	–2.4
O5–O4–O5 <sup>ii</sup>	161.5(1)	161.5(1)	161.51(9)	161.41(8)	161.33(8)	161.28(8)	161.06(12)	161.20(13)	160.88(11)	158.93(15)	157.7(2)	–3.8

Symmetry codes: (i)  $-x+1, -y+2, z+1/2$ ; (ii)  $-x+3/2, y+1/2, z-1/2$ ; (iii)  $-x+1, -y+2, z-1/2$ ; (iv)  $x-1/2, -y+3/2, z-1$ ; (v)  $-x+3/2, y-1/2, z+1/2$ ; (vi)  $x+1/2, -y+3/2, z+1$ .

Table S22. Experimental details of  $K_2Al_2B_2O_7$  measurements.

Crystal data							
Chemical formula	$K_2Al_2B_2O_7$						
$M_r$	265.8	265.8	265.8	265.8	265.8	265.8	265.8
Crystal system, space group	Trigonal, $P321$						
Temperature (K)	98	123	173	223	298	348	
$a$ (Å)	8.5550 (12),	8.5592 (12),	8.5852 (13),	8.5683 (12),	8.5843 (9),	8.5987 (13),	
$c$ (Å)	8.4430 (13)	8.4485 (13)	8.4855 (14)	8.4633 (13)	8.486 (2)	8.5052 (15)	
$V$ (Å <sup>3</sup> )	535.14 (13)	536.01 (13)	541.64 (15)	538.10 (13)	541.56 (15)	544.60 (15)	
$Z$	3						
Radiation type	Mo $K\alpha$						
$\mu$ (mm <sup>-1</sup> )	1.57	1.57	1.55	1.56	1.55	1.54	
Crystal size (mm)	0.1×0.2×0.4						
Data collection							
Diffractionmeter	IPDS Stoe						
Absorption correction	Based on crystal shape						
No. of measured, independent and observed [ $I > 3\sigma(I)$ ] reflections	5079, 970, 895	5022, 962, 872	5171, 993, 914	5097, 982, 896	5153, 993, 896	5176, 998, 877	
$R_{int}$	0.043	0.048	0.041	0.043	0.043	0.047	

$(\sin \theta/\lambda)_{\max}$ ( $\text{\AA}^{-1}$ )	0.686	0.684	0.689	0.687	0.686	0.687
Refinement						
$R[F^2 > 2\sigma(F^2)]$ , $wR(F^2)$ , $S$	0.023, 0.026,	0.023, 0.024,	0.022, 0.023,	0.021, 0.022,	0.023, 0.024,	0.025, 0.024,
	1.52	1.34	1.31	1.22	1.27	1.19
No. of reflections	970	962	993	982	993	998
No. of parameters	63	63	63	63	63	63
$\Delta\rho_{\max}$ , $\Delta\rho_{\min}$ ( $e \text{\AA}^{-3}$ )	0.30, −0.27	0.23, −0.20	0.23, −0.25	0.16, −0.17	0.18, −0.21	0.19, −0.26
Absolute structure	390	388	402	395	401	405
No. of Friedel pairs used in the refinement						

Table S23. Atomic coordinates, displacement parameters ( $\text{\AA}^2$ ) and site-occupancy factors (SOFs) in the structure of  $\text{K}_2\text{Al}_2\text{B}_2\text{O}_7$  at different temperatures.

Atom	Occ.	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> iso/eq
98 K					
K1	1	0.30811(12)	0	0	0.0224(3)
K2	1	0.35912(12)	0	0.5	0.0228(3)
Al1	1	0	0	0.29952(18)	0.0128(4)
Al2	1	0.3333	0.6667	0.18217(17)	0.0108(4)
Al3	1	0.6667	0.3333	0.22148(16)	0.0116(4)
O1	1	0.1572(3)	0.2132(3)	0.2261(3)	0.0212(9)
O2	1	0.3971(3)	0.5149(3)	0.2512(3)	0.0209(9)
O3	1	0.4526(3)	0.2743(3)	0.2925(3)	0.0198(9)
O4	1	0	0	0.5	0.0404(19)
O5	1	0.6667	0.3333	0.0193(4)	0.0335(11)
B1	1	0.3355(5)	0.3344(5)	0.2583(4)	0.0123(12)
123 K					
K1	1	0.31102(12)	0	0	0.0097(3)
K2	1	0.35750(11)	0	0.5	0.0095(3)
Al1	1	0	0	0.29786(19)	0.0069(4)
Al2	1	0.3333	0.6667	0.18327(18)	0.0053(4)
Al3	1	0.6667	0.3333	0.22292(17)	0.0048(4)
O1	1	0.1568(3)	0.2145(3)	0.2249(2)	0.0100(9)
O2	1	0.4010(3)	0.5168(3)	0.2523(2)	0.0091(8)
O3	1	0.4511(3)	0.2719(3)	0.2944(2)	0.0096(8)
O4	1	0	0	0.5	0.0175(14)
O5	1	0.6667	0.3333	0.0205(4)	0.0149(9)
B1	1	0.3356(6)	0.3339(6)	0.2577(5)	0.0075(13)
173 K					
K1	1	0.31053(10)	0	0	0.0131(2)
K2	1	0.35789(9)	0	0.5	0.0130(2)
Al1	1	0	0	0.29834(16)	0.0082(3)
Al2	1	0.3333	0.6667	0.18306(15)	0.0072(3)
Al3	1	0.6667	0.3333	0.22287(15)	0.0077(3)
O1	1	0.1568(3)	0.2146(3)	0.2253(2)	0.0135(8)
O2	1	0.3999(3)	0.5162(3)	0.2523(2)	0.0124(7)
O3	1	0.4513(3)	0.2721(2)	0.2942(2)	0.0118(7)
O4	1	0	0	0.5	0.0231(13)
O5	1	0.6667	0.3333	0.0198(4)	0.0196(8)
B1	1	0.3349(5)	0.3339(4)	0.2583(4)	0.0086(11)
223 K					
K1	1	0.30978(10)	0	0	0.0161(3)
K2	1	0.35844(10)	0	0.5	0.0158(3)
Al1	1	0	0	0.29866(16)	0.0102(3)
Al2	1	0.3333	0.6667	0.18263(15)	0.0083(3)
Al3	1	0.6667	0.3333	0.22243(14)	0.0087(3)
O1	1	0.1570(3)	0.2143(3)	0.2257(2)	0.0156(8)
O2	1	0.3989(3)	0.5160(3)	0.2520(2)	0.0153(7)
O3	1	0.4515(3)	0.2728(2)	0.2938(2)	0.0149(7)
O4	1	0	0	0.5	0.0283(14)
O5	1	0.6667	0.3333	0.0194(4)	0.0244(9)
B1	1	0.3343(5)	0.3334(5)	0.2579(4)	0.0102(11)
298 K					

K1	1	0.30894(11)	0	0	0.0206(3)
K2	1	0.35876(11)	0	0.5	0.0207(3)
Al1	1	0	0	0.29908(17)	0.0125(3)
Al2	1	0.3333	0.6667	0.18258(16)	0.0107(4)
Al3	1	0.6667	0.3333	0.22179(15)	0.0109(4)
O1	1	0.1578(3)	0.2140(3)	0.2262(2)	0.0203(8)
O2	1	0.3981(3)	0.5158(3)	0.2518(2)	0.0195(8)
O3	1	0.4518(3)	0.2733(3)	0.2932(2)	0.0183(8)
O4	1	0	0	0.5	0.0350(17)
O5	1	0.6667	0.3333	0.0197(4)	0.0311(10)
B1	1	0.3345(5)	0.3342(5)	0.2580(4)	0.0128(12)
348 K					
K1	1	0.30811(12)	0	0	0.0224(3)
K2	1	0.35912(12)	0	0.5	0.0228(3)
Al1	1	0	0	0.29952(18)	0.0128(4)
Al2	1	0.3333	0.6667	0.18217(17)	0.0108(4)
Al3	1	0.6667	0.3333	0.22148(16)	0.0116(4)
O1	1	0.1572(3)	0.2132(3)	0.2261(3)	0.0212(9)
O2	1	0.3971(3)	0.5149(3)	0.2512(3)	0.0209(9)
O3	1	0.4526(3)	0.2743(3)	0.2925(3)	0.0198(9)
O4	1	0	0	0.5	0.0404(19)
O5	1	0.6667	0.3333	0.0193(4)	0.0335(11)
B1	1	0.3355(5)	0.3344(5)	0.2583(4)	0.0123(12)

Table S24. Anisotropic parameters of atomic displacements in  $K_2Al_2B_2O_7$  at different temperatures.

Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
98 K						
K1	0.0086(3)	0.0072(4)	0.0098(4)	0.00361(19)	0.00098(16)	0.0020(3)
K2	0.0085(3)	0.0078(4)	0.0100(4)	0.00392(19)	0.00109(17)	0.0022(3)
Al1	0.0062(4)	0.0062(4)	0.0068(7)	0.0031(2)	0	0
Al2	0.0045(5)	0.0045(5)	0.0058(7)	0.0022(2)	0	0
Al3	0.0045(5)	0.0045(5)	0.0070(7)	0.0022(2)	0	0
O1	0.0068(10)	0.0064(12)	0.0142(10)	0.0025(9)	-0.0014(8)	0.0013(8)
O2	0.0075(9)	0.0068(11)	0.0127(9)	0.0039(10)	-0.0013(7)	0.0009(7)
O3	0.0071(11)	0.0073(10)	0.0134(9)	0.0043(9)	0.0003(8)	0.0027(7)
O4	0.0190(17)	0.0190(17)	0.006(2)	0.0095(9)	0	0
O5	0.0171(12)	0.0171(12)	0.0088(14)	0.0085(6)	0	0
B1	0.0066(16)	0.0086(18)	0.0048(12)	0.0040(14)	0.0007(8)	0.0002(9)
123 K						
K1	0.0095(3)	0.0079(4)	0.0112(5)	0.00393(19)	0.00125(16)	0.0025(3)
K2	0.0096(3)	0.0085(4)	0.0099(5)	0.0043(2)	0.00129(17)	0.0026(3)
Al1	0.0063(5)	0.0063(5)	0.0081(7)	0.0031(2)	0	0
Al2	0.0048(5)	0.0048(5)	0.0063(7)	0.0024(2)	0	0
Al3	0.0042(5)	0.0042(5)	0.0059(7)	0.0021(2)	0	0
O1	0.0065(10)	0.0062(12)	0.0160(11)	0.0021(9)	-0.0015(8)	0.0020(8)
O2	0.0069(9)	0.0056(11)	0.0149(9)	0.0032(9)	-0.0014(7)	0.0011(7)
O3	0.0071(11)	0.0085(10)	0.0140(9)	0.0047(9)	0.0003(8)	0.0018(7)
O4	0.0226(18)	0.0226(18)	0.007(2)	0.0113(9)	0	0
O5	0.0175(12)	0.0175(12)	0.0098(14)	0.0088(6)	0	0
B1	0.0075(16)	0.0095(18)	0.0062(12)	0.0048(15)	0.0016(9)	0.0012(10)
173 K						
K1	0.0128(3)	0.0118(3)	0.0144(4)	0.00588(17)	0.00170(14)	0.0034(3)
K2	0.0127(3)	0.0123(3)	0.0139(4)	0.00616(17)	0.00187(16)	0.0037(3)
Al1	0.0073(4)	0.0073(4)	0.0101(6)	0.00363(19)	0	0
Al2	0.0065(4)	0.0065(4)	0.0086(6)	0.0032(2)	0	0
Al3	0.0065(4)	0.0065(4)	0.0101(6)	0.0033(2)	0	0
O1	0.0078(9)	0.0080(10)	0.0217(10)	0.0019(8)	-0.0027(7)	0.0018(7)
O2	0.0100(8)	0.0075(9)	0.0204(8)	0.0049(8)	-0.0031(7)	0.0007(7)
O3	0.0083(9)	0.0095(9)	0.0184(8)	0.0050(8)	0.0017(7)	0.0036(6)
O4	0.0294(17)	0.0294(17)	0.010(2)	0.0147(9)	0	0
O5	0.0235(11)	0.0235(11)	0.0116(12)	0.0118(5)	0	0
B1	0.0086(14)	0.0099(15)	0.0079(10)	0.0051(12)	0.0020(7)	0.0006(8)
223 K						
K1	0.0155(3)	0.0141(3)	0.0181(4)	0.00706(17)	0.00215(15)	0.0043(3)

K2	0.0155(3)	0.0156(4)	0.0165(4)	0.00779(18)	0.00220(16)	0.0044(3)
Al1	0.0089(4)	0.0089(4)	0.0128(6)	0.00447(19)	0	0
Al2	0.0075(4)	0.0075(4)	0.0099(6)	0.0038(2)	0	0
Al3	0.0076(4)	0.0076(4)	0.0108(6)	0.0038(2)	0	0
O1	0.0087(9)	0.0083(10)	0.0262(10)	0.0015(8)	−0.0030(7)	0.0034(7)
O2	0.0111(8)	0.0093(10)	0.0262(9)	0.0056(8)	−0.0034(7)	0.0008(7)
O3	0.0098(10)	0.0111(9)	0.0252(8)	0.0063(8)	0.0023(7)	0.0048(7)
O4	0.0354(18)	0.0354(18)	0.014(2)	0.0177(9)	0	0
O5	0.0293(12)	0.0293(12)	0.0147(13)	0.0147(6)	0	0
B1	0.0078(13)	0.0112(15)	0.0113(10)	0.0046(12)	0.0015(7)	0.0010(8)
298 K						
K1	0.0202(3)	0.0186(4)	0.0225(5)	0.00928(19)	0.00264(17)	0.0053(3)
K2	0.0201(3)	0.0206(4)	0.0217(5)	0.0103(2)	0.00294(18)	0.0059(4)
Al1	0.0109(4)	0.0109(4)	0.0158(6)	0.0055(2)	0	0
Al2	0.0092(4)	0.0092(4)	0.0138(6)	0.0046(2)	0	0
Al3	0.0094(4)	0.0094(4)	0.0139(6)	0.0047(2)	0	0
O1	0.0119(10)	0.0117(11)	0.0333(11)	0.0030(9)	−0.0042(8)	0.0040(8)
O2	0.0151(9)	0.0105(10)	0.0334(10)	0.0068(9)	−0.0038(8)	0.0017(7)
O3	0.0117(10)	0.0148(9)	0.0306(10)	0.0083(9)	0.0040(8)	0.0073(7)
O4	0.044(2)	0.044(2)	0.018(2)	0.0219(11)	0	0
O5	0.0388(14)	0.0388(14)	0.0158(14)	0.0194(7)	0	0
B1	0.0109(14)	0.0135(16)	0.0147(10)	0.0066(13)	0.0013(8)	0.0016(9)
323 K						
K1	0.0222(3)	0.0205(4)	0.0239(5)	0.0103(2)	0.00303(19)	0.0061(4)
K2	0.0222(3)	0.0228(5)	0.0237(5)	0.0114(2)	0.0033(2)	0.0066(4)
Al1	0.0112(4)	0.0112(4)	0.0159(7)	0.0056(2)	0	0
Al2	0.0096(5)	0.0096(5)	0.0132(6)	0.0048(2)	0	0
Al3	0.0095(5)	0.0095(5)	0.0157(7)	0.0047(2)	0	0
O1	0.0113(11)	0.0122(12)	0.0357(12)	0.0024(9)	−0.0046(8)	0.0047(9)
O2	0.0146(10)	0.0107(11)	0.0381(11)	0.0068(10)	−0.0058(8)	0.0001(8)
O3	0.0134(11)	0.0159(10)	0.0320(10)	0.0088(9)	0.0028(9)	0.0074(8)
O4	0.053(3)	0.053(3)	0.016(3)	0.0264(13)	0	0
O5	0.0420(15)	0.0420(15)	0.0166(15)	0.0210(8)	0	0
B1	0.0090(14)	0.0125(17)	0.0144(10)	0.0046(14)	0.0025(8)	0.0013(10)

Table S25. K–O (Å) bond lengths and O–K–O (°) angles in the  $K_2Al_2B_2O_7$  structure at different temperatures.

T / K	98	123	173	223	298	348	$\Delta(98-348\text{ K})$
K1–O1	3.344(3)	3.339(3)	3.350(3)	3.337(3)	3.335(3)	3.335(3)	−0.009
K1–O1 <sup>i</sup>	2.680(3)	2.684(3)	2.693(2)	2.689(2)	2.700(3)	2.701(3)	0.021
K1–O1 <sup>iii</sup>	3.344(3)	3.339(3)	3.350(3)	3.337(3)	3.335(3)	3.335(3)	−0.009
K1–O2 <sup>iv</sup>	3.020(3)	3.026(3)	3.046(3)	3.046(3)	3.061(3)	3.074(3)	0.054
K1–O3	3.198(2)	3.201(2)	3.213(2)	3.207(2)	3.213(2)	3.219(2)	0.021
K1–O5	2.9537(14)	2.9583(14)	2.9692(14)	2.9667(13)	2.9764(11)	2.9851(15)	0.031
K2–O1 <sup>i</sup>	3.212(3)	3.216(3)	3.228(3)	3.223(3)	3.235(3)	3.244(3)	0.032
K2–O2 <sup>iv</sup>	2.751(3)	2.754(3)	2.768(3)	2.766(3)	2.775(3)	2.788(3)	0.037
K2–O3	2.679(2)	2.686(2)	2.698(2)	2.698(2)	2.710(2)	2.726(2)	0.047
K2–O3 <sup>iv</sup>	3.252(2)	3.251(2)	3.259(2)	3.246(2)	3.250(2)	3.251(3)	−0.001
K2–O3 <sup>ix</sup>	2.679(2)	2.686(2)	2.6979(19)	2.6980(19)	2.710(2)	2.726(2)	0.047
K2–O3 <sup>viii</sup>	3.252(3)	3.251(3)	3.259(3)	3.246(3)	3.250(3)	3.251(3)	−0.001
K2–O4	3.0580(12)	3.0599(13)	3.0725(12)	3.0712(12)	3.0797(11)	3.0880(14)	0.03
O1 <sup>i</sup> –K1–O1 <sup>ii</sup>	112.21(10)	112.20(10)	112.47(9)	112.65(9)	112.88(10)	112.93(11)	0.72
O1 <sup>i</sup> –K1–O1 <sup>iii</sup>	79.63(7)	79.80(7)	80.04(7)	80.23(7)	80.49(7)	80.64(8)	1.01
O1 <sup>i</sup> –K1–O2 <sup>iv</sup>	74.90(9)	75.01(9)	74.97(8)	75.05(8)	75.07(9)	75.28(9)	0.38
O1 <sup>i</sup> –K1–O2 <sup>v</sup>	169.94(11)	169.89(11)	169.82(10)	169.73(10)	169.56(10)	169.46(11)	−0.48
O1 <sup>i</sup> –K1–O3	74.16(6)	74.26(6)	74.23(5)	74.36(5)	74.53(6)	74.68(6)	0.52
O1 <sup>i</sup> –K1–O3 <sup>iii</sup>	106.44(7)	106.46(7)	106.60(6)	106.58(6)	106.56(6)	106.60(7)	0.16
O1 <sup>i</sup> –K1–O5	128.78(8)	128.70(8)	128.73(7)	128.81(7)	128.79(8)	128.80(8)	0.02
O1 <sup>i</sup> –K1–O5 <sup>vi</sup>	88.98(9)	89.12(9)	89.04(8)	89.00(8)	89.01(9)	89.09(9)	0.11
O1 <sup>ii</sup> –K1–O1 <sup>iii</sup>	55.34(6)	55.21(6)	55.20(6)	55.24(5)	55.31(6)	55.18(6)	−0.16
O1 <sup>iii</sup> –K1–O2 <sup>iv</sup>	134.45(7)	134.59(7)	134.60(6)	134.56(6)	134.56(7)	134.67(7)	0.22
O1 <sup>iii</sup> –K1–O2 <sup>v</sup>	99.86(6)	99.80(6)	99.81(6)	99.90(6)	99.82(6)	99.97(7)	0.11
O1 <sup>iii</sup> –K1–O3	138.34(9)	138.53(9)	138.72(7)	138.95(7)	139.32(8)	139.51(9)	1.17
O1 <sup>iii</sup> –K1–O3 <sup>iii</sup>	42.70(9)	42.72(9)	42.71(8)	42.68(8)	42.58(9)	42.72(9)	0.02

O1 <sup>iii</sup> -K1-O5	142.91(7)	142.90(7)	142.78(6)	142.70(7)	142.70(7)	142.62(7)	-0.29
O1 <sup>iii</sup> -K1-O5 <sup>vi</sup>	86.26(7)	86.29(7)	86.37(6)	86.43(6)	86.37(7)	86.52(7)	0.26
O1-K1-O1 <sup>i</sup>	55.34(8)	55.21(8)	55.20(7)	55.24(7)	55.31(7)	55.18(8)	-0.16
O1-K1-O1 <sup>ii</sup>	79.63(8)	79.80(8)	80.04(7)	80.23(7)	80.49(7)	80.64(8)	1.01
O1-K1-O1 <sup>iii</sup>	95.67(8)	95.83(8)	96.03(7)	96.29(7)	96.75(8)	96.79(8)	1.12
O1-K1-O2 <sup>iv</sup>	99.86(8)	99.80(8)	99.81(7)	99.90(7)	99.82(7)	99.97(8)	0.11
O1-K1-O2 <sup>v</sup>	134.45(8)	134.59(8)	134.60(7)	134.56(7)	134.56(8)	134.67(8)	0.22
O1-K1-O3	42.70(7)	42.72(7)	42.71(6)	42.68(6)	42.58(6)	42.72(6)	0.02
O1-K1-O3 <sup>iii</sup>	138.34(8)	138.53(8)	138.72(7)	138.95(7)	139.32(8)	139.51(8)	1.17
O1-K1-O5	86.26(5)	86.29(5)	86.37(5)	86.43(5)	86.37(5)	86.52(5)	0.26
O1-K1-O5 <sup>vi</sup>	142.91(7)	142.90(7)	142.78(6)	142.70(7)	142.70(7)	142.62(7)	-0.29
O2 <sup>iv</sup> -K1-O2 <sup>v</sup>	99.03(8)	98.80(8)	98.58(7)	98.22(7)	97.93(8)	97.43(9)	-1.6
O2 <sup>iv</sup> -K1-O3	67.91(8)	67.93(8)	67.96(7)	68.15(7)	68.23(8)	68.35(8)	0.44
O2 <sup>iv</sup> -K1-O3 <sup>iii</sup>	111.36(9)	111.20(9)	111.04(8)	110.70(8)	110.44(8)	110.07(9)	-1.29
O2 <sup>iv</sup> -K1-O5	80.97(7)	80.77(7)	80.79(6)	80.77(6)	80.61(7)	80.46(7)	-0.51
O2 <sup>iv</sup> -K1-O5 <sup>vi</sup>	56.54(9)	56.54(9)	56.32(8)	56.02(8)	55.91(9)	55.69(9)	-0.85
O3-K1-O3 <sup>iii</sup>	178.95(9)	178.75(9)	178.57(8)	178.37(8)	178.10(8)	177.77(9)	-1.18
O3-K1-O5	54.91(8)	54.73(8)	54.81(7)	54.77(7)	54.61(7)	54.48(7)	-0.43
O3-K1-O5 <sup>vi</sup>	124.40(8)	124.43(9)	124.24(7)	124.14(7)	124.11(8)	124.02(8)	-0.38
O1 <sup>i</sup> -K2-O1 <sup>vii</sup>	108.05(8)	107.80(9)	107.71(7)	107.40(7)	107.16(8)	106.96(9)	-1.09
O1 <sup>i</sup> -K2-O2 <sup>iv</sup>	70.85(9)	71.01(9)	71.05(7)	71.18(7)	71.28(8)	71.38(9)	0.53
O1 <sup>i</sup> -K2-O2 <sup>viii</sup>	176.33(7)	176.28(6)	176.32(6)	176.28(6)	176.17(6)	176.19(6)	-0.14
O1 <sup>i</sup> -K2-O3	73.95(6)	73.99(6)	73.93(5)	73.98(5)	74.03(6)	73.94(6)	-0.01
O1 <sup>i</sup> -K2-O3 <sup>iv</sup>	101.38(6)	101.38(6)	101.32(6)	101.38(6)	101.38(6)	101.20(7)	-0.18
O1 <sup>i</sup> -K2-O3 <sup>ix</sup>	96.74(7)	96.69(7)	96.70(6)	96.49(6)	96.38(7)	96.46(7)	-0.28
O1 <sup>i</sup> -K2-O3 <sup>viii</sup>	132.30(8)	132.42(8)	132.47(7)	132.54(7)	132.59(7)	132.79(7)	0.49
O1 <sup>i</sup> -K2-O4	54.03(7)	53.90(7)	53.86(6)	53.70(6)	53.58(6)	53.48(7)	-0.55
O2 <sup>iv</sup> -K2-O2 <sup>viii</sup>	110.47(10)	110.41(10)	110.39(8)	110.45(8)	110.50(9)	110.48(10)	0.01
O2 <sup>iv</sup> -K2-O3	79.60(9)	79.59(9)	79.64(8)	79.83(8)	79.84(9)	79.81(9)	0.21
O2 <sup>iv</sup> -K2-O3 <sup>iv</sup>	45.57(7)	45.49(7)	45.50(6)	45.55(6)	45.53(7)	45.41(7)	-0.16
O2 <sup>iv</sup> -K2-O3 <sup>ix</sup>	109.57(9)	109.56(9)	109.56(8)	109.48(8)	109.50(9)	109.53(10)	-0.04
O2 <sup>iv</sup> -K2-O3 <sup>viii</sup>	81.67(9)	81.76(9)	81.81(8)	81.89(8)	82.04(8)	82.25(9)	0.58
O2 <sup>iv</sup> -K2-O4	124.77(6)	124.80(6)	124.80(5)	124.77(5)	124.75(6)	124.76(6)	-0.01
O3 <sup>iv</sup> -K2-O3 <sup>viii</sup>	84.41(7)	84.55(7)	84.76(6)	84.94(6)	85.20(7)	85.58(7)	1.17
O3 <sup>iv</sup> -K2-O4	137.80(6)	137.72(6)	137.62(5)	137.53(5)	137.40(6)	137.21(6)	-0.59
O3-K2-O3 <sup>iv</sup>	56.54(9)	56.47(9)	56.42(7)	56.45(7)	56.37(8)	56.20(9)	-0.34
O3-K2-O3 <sup>ix</sup>	164.43(11)	164.47(11)	164.39(9)	164.18(9)	164.11(10)	164.14(11)	-0.29
O3-K2-O3 <sup>viii</sup>	138.76(7)	138.79(7)	138.92(6)	139.08(6)	139.22(7)	139.36(7)	0.6
O3-K2-O4	82.22(6)	82.23(6)	82.19(5)	82.09(5)	82.06(6)	82.07(6)	-0.15
O5-K1-O5 <sup>vi</sup>	113.87(3)	113.71(3)	113.56(3)	113.35(3)	113.12(3)	112.89(4)	-0.98

Symmetry codes: (i)  $-x+y,-x,z$ ;(ii)  $y,x,-z$ ;(iii)  $x-y,-y,-z$ ;(iv)  $-y+1,x-y,z$ ;(v)  $-x+1,-x+y,-z$ ;(vi)  $y,x-1,-z$ ;(vii)  $y,x,-z+1$ ;(viii)  $-x+1,-x+y,-z+1$ ;(ix)  $x-y,-y,-z+1$

Table S26. T–O (Å) bond lengths and O–T–O (°) angles, T = Al, B in the K<sub>2</sub>Al<sub>2</sub>B<sub>2</sub>O<sub>7</sub> structure at different temperatures.

T / K	98	123	173	223	298	348	Δ(98–348 K)
Al1–O1	1.762(2)	1.757(2)	1.764(2)	1.7585(19)	1.762(2)	1.761(2)	-0.001
Al1–O4	1.7063(16)	1.7078(17)	1.7112(14)	1.7040(14)	1.7050(16)	1.7051(17)	-0.001
Al2–O2	1.749(3)	1.751(3)	1.754(3)	1.747(3)	1.747(3)	1.750(3)	0.001
Al2–O5 <sup>v</sup>	1.717(4)	1.722(4)	1.721(4)	1.709(4)	1.717(4)	1.714(4)	-0.003
Al3–O3	1.755(3)	1.754(3)	1.758(2)	1.754(2)	1.756(2)	1.754(3)	-0.001
Al3–O5	1.715(4)	1.710(4)	1.723(4)	1.719(4)	1.715(4)	1.719(4)	0.004
B1–O1	1.380(4)	1.378(4)	1.378(4)	1.368(4)	1.369(4)	1.383(4)	0.003
B1–O2	1.374(5)	1.374(5)	1.375(4)	1.376(4)	1.371(5)	1.368(5)	-0.006
B1–O3	1.369(6)	1.371(6)	1.379(5)	1.375(5)	1.379(6)	1.373(6)	0.004
O1–Al1–O1 <sup>i</sup>	108.38(15)	108.40(15)	108.34(13)	108.37(13)	108.37(14)	108.13(15)	-0.3
O1–Al1–O4	110.54(8)	110.52(8)	110.58(7)	110.55(7)	110.55(8)	110.78(9)	0.2
O2–Al2–O5 <sup>v</sup>	109.46(9)	109.46(9)	109.56(8)	109.64(8)	109.65(8)	109.61(9)	0.2
O2 <sup>iii</sup> –Al2–O2 <sup>iv</sup>	109.48(14)	109.48(14)	109.38(12)	109.31(12)	109.29(13)	109.33(14)	-0.2
O3–Al3–O3 <sup>vi</sup>	108.83(12)	108.81(12)	108.81(10)	108.78(10)	108.75(11)	108.80(12)	0
O3–Al3–O5	110.10(8)	110.13(8)	110.13(7)	110.16(7)	110.19(8)	110.13(8)	0
O1–B1–O2	120.0(4)	120.5(4)	120.4(4)	120.4(4)	120.7(4)	120.1(4)	0.1
O1–B1–O3	120.4(3)	120.4(4)	120.4(3)	120.7(3)	120.0(3)	120.2(3)	-0.2
O2–B1–O3	119.6(3)	119.1(3)	119.1(2)	118.9(2)	119.2(3)	119.7(3)	0.1

Symmetry codes: (i)  $-y, x-y, z$ ; (ii)  $-x+y, -x, z$ ; (iii)  $-y+1, x-y+1, z$ ; (iv)  $-x+y, -x+1, z$ ; (v)  $y, x, -z$ ; (vi)  $-y+1, x-y, z$ ; (vii)  $-x+y+1, -x+1, z$

Table S27.  $T-O-T$  ( $^\circ$ ) angles,  $T = \text{Al, B}$  in the  $\text{K}_2\text{Al}_2\text{B}_2\text{O}_7$  structure at different temperatures.

T / K	98	123	173	223	298	348	$\Delta(98-348 \text{ K})$
Al1–O1–B1	133.1(3)	133.6(3)	133.5(2)	133.9(2)	134.6(3)	134.3(3)	1.2
Al2–O2–B1	138.7(2)	138.6(3)	139.0(2)	139.3(2)	139.7(2)	140.6(2)	1.9
Al3–O3–B1	131.0(2)	131.4(2)	131.70(17)	132.05(18)	132.24(19)	132.8(2)	1.8
Al1–O4–Al1 <sup>i</sup>	180.0(5)	180.0(5)	180.0(5)	180.0(5)	180.0(5)	180.0(5)	0
Al2 <sup>ii</sup> –O5–Al3	180.0(5)	180.0(5)	180.0(5)	180.0(5)	180.0(5)	180.0(5)	0

Symmetry codes: (i)  $y, x, -z+1$  (ii)  $y, x, -z$ .

Table S28.  $O-O-O$  ( $^\circ$ ) angles in the  $\text{K}_2\text{Al}_2\text{B}_2\text{O}_7$  structure at different temperatures.

T / K	98	123	173	223	298	348	$\Delta(98-348 \text{ K})$
O2 <sup>iii</sup> –O2–O3	157.15(12)	156.97(12)	156.51(11)	156.10(11)	155.78(12)	155.18(12)	–2.0
O1 <sup>i</sup> –O1–O2	154.31(18)	154.08(18)	153.97(16)	153.64(16)	153.07(17)	153.02(18)	–1.3
O1–O3–O3 <sup>vi</sup>	152.18(12)	151.84(12)	151.83(11)	151.59(11)	151.41(12)	150.99(12)	–1.2
O2 <sup>v</sup> –O5–O3 <sup>vi</sup>	164.97(6)	164.83(6)	164.67(5)	164.45(5)	164.29(5)	163.98(6)	–1.0
O1–O4–O1 <sup>ix</sup>	163.01(10)	162.87(10)	162.88(9)	162.72(9)	162.38(10)	162.44(10)	–0.6
O2 <sup>v</sup> –O5–O3	112.49(8)	112.43(8)	112.48(7)	112.39(7)	112.36(7)	112.22(8)	–0.3
O1–O4–O1 <sup>i</sup>	60.18(6)	60.07(7)	60.07(6)	60.14(6)	60.18(6)	59.97(7)	–0.2
O3–O5–O3 <sup>vi</sup>	60.23(11)	60.29(11)	60.12(9)	60.11(9)	60.20(10)	60.12(11)	–0.1
O1–O3–O2	60.20(11)	60.36(11)	60.16(9)	60.13(9)	60.14(10)	60.10(11)	–0.1
O2–O1–O3	59.59(11)	59.42(11)	59.53(9)	59.61(10)	59.77(10)	59.54(11)	–0.1
O2 <sup>v</sup> –O5–O2 <sup>x</sup>	60.60(12)	60.56(12)	60.55(10)	60.58(10)	60.44(11)	60.58(12)	0.0
O1 <sup>i</sup> –O1–O1 <sup>ii</sup>	60.00(12)	60.00(12)	60.00(11)	60.00(10)	60.00(11)	60.00(12)	0.0
O2 <sup>iii</sup> –O2–O5 <sup>v</sup>	59.70(8)	59.72(8)	59.72(7)	59.71(7)	59.78(8)	59.71(8)	0.0
O3 <sup>vi</sup> –O3–O5	59.89(8)	59.85(8)	59.94(7)	59.95(7)	59.90(7)	59.94(8)	0.0
O1–O4–O1 <sup>viii</sup>	112.08(6)	112.15(6)	112.15(5)	112.03(5)	111.88(6)	112.13(6)	0.0
O3–O2–O5 <sup>v</sup>	133.76(12)	133.73(12)	133.76(10)	133.82(11)	133.68(11)	133.83(12)	0.1
O1 <sup>i</sup> –O1–O4	59.91(6)	59.96(6)	59.96(6)	59.93(6)	59.91(6)	60.02(6)	0.1
O1–O2–O3	60.21(11)	60.22(11)	60.31(10)	60.26(10)	60.09(11)	60.35(11)	0.1
O2–O1–O4	119.61(9)	119.63(9)	119.69(8)	119.90(8)	120.07(9)	120.02(10)	0.4
O1–O4–O1 <sup>x</sup>	131.48(10)	131.69(10)	131.69(8)	131.74(8)	131.98(9)	132.13(10)	0.7
O1–O3–O5	110.88(10)	111.06(10)	111.05(9)	111.20(9)	111.45(10)	111.58(11)	0.7
O2 <sup>v</sup> –O5–O3 <sup>vii</sup>	129.72(8)	129.82(8)	130.03(7)	130.19(7)	130.34(8)	130.55(9)	0.8
O2–O3–O5	95.68(9)	95.88(9)	96.01(8)	96.22(8)	96.48(9)	96.78(9)	1.1
O3–O1–O4	92.06(10)	92.34(10)	92.43(9)	92.73(9)	93.13(9)	93.35(10)	1.3
O1–O2–O5 <sup>v</sup>	98.21(10)	98.35(10)	98.61(9)	98.99(9)	99.32(9)	99.61(10)	1.4
O1 <sup>ii</sup> –O1–O2	144.71(17)	144.97(17)	145.10(15)	145.48(15)	146.10(16)	146.17(17)	1.5
O1 <sup>ii</sup> –O1–O3	85.25(14)	85.67(14)	85.69(12)	85.98(12)	86.44(13)	86.74(14)	1.5
O1 <sup>i</sup> –O1–O3	142.61(15)	143.05(15)	143.10(13)	143.43(13)	143.92(14)	144.25(15)	1.6
O1–O3–O3 <sup>vii</sup>	141.70(14)	142.16(14)	142.25(12)	142.62(12)	142.95(13)	143.51(14)	1.8
O1–O2–O2 <sup>iv</sup>	82.59(12)	82.77(12)	83.16(10)	83.62(10)	84.12(11)	84.46(12)	1.9
O2–O3–O3 <sup>vii</sup>	82.86(10)	83.16(10)	83.43(9)	83.83(9)	84.13(10)	84.73(11)	1.9
O2–O3–O3 <sup>vi</sup>	141.92(10)	142.23(11)	142.50(9)	142.89(9)	143.20(10)	143.79(11)	1.9
O1–O2–O2 <sup>iii</sup>	142.20(16)	142.38(16)	142.78(14)	143.26(14)	143.76(15)	144.12(16)	1.9
O2 <sup>iv</sup> –O2–O3	140.42(10)	140.63(10)	141.12(9)	141.56(9)	141.94(10)	142.56(11)	2.1

(i)  $-y, x-y, z$ ; (ii)  $-x+y, -x, z$ ; (iii)  $-y+1, x-y+1, z$ ; (iv)  $-x+y, -x+1, z$ ; (v)  $y, x, -z$ ; (vi)  $-y+1, x-y, z$ ; (vii)  $-x+y+1, -x+1, z$ ; (viii)  $y, x, -z+1$ ; (ix)  $x-y, -y, -z+1$ ; (x)  $-x, -x+y, -z+1$ ; (xi)  $x-y+1, -y+1, -z$ ; (xii)  $-x+1, -x+y, -z$



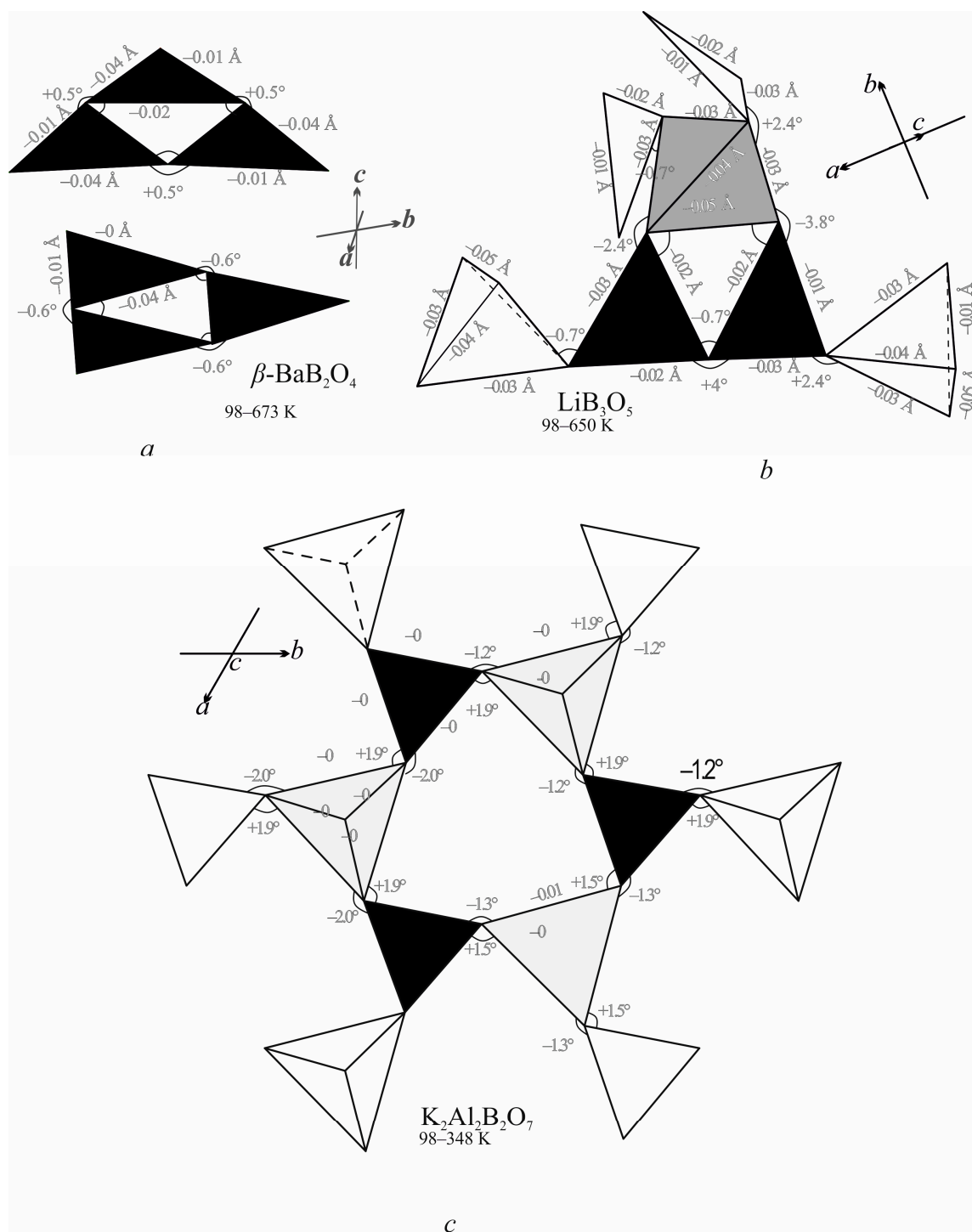


Figure S1. Changing of O–O distances and O–O–O in boron-oxygen groups in structures (a)  $\beta\text{-BaB}_2\text{O}_4$ , (b)  $\text{LiB}_3\text{O}_5$ , (c)  $\text{K}_2\text{Al}_2\text{B}_2\text{O}_7$ .