# 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. E*x*perimental details of $\beta$-$BaB_2O_4$ measurements

| Chemical formula | $BaB_2O_4$ | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $M_r$ | 223 | | | | | | | |
| Cr*y*stal s*y*stem, space group | Trigonal, *R*3*c* | | | | | | | |
| Temperature (K) | 98 | 123 | 173 | 223 | 298 | 323 | 293 | 693 |
| *a* (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) |
| *c* (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) |
| *V* (Å$^3$) | 1732.02 (14) | 1743.7 (4) | 1745.4 (4) | 1748.3 (4) | 1747.2 (4) | 1753.7 (4) | 1728.38(7) | 1771.7(5) |
| *Z* | 18 | | | | | | | |
| Radiation t*y*pe | Mo *K*α | | | | | | | |
| μ (mm$^{-1}$) | 10.18 | 10.11 | 10.1 | 10.08 | 10.09 | 10.05 | 10.20 | 9.95 |
| Cr*y*stal size (mm) | 0.10 ×0.12×0.20 | | | | | | 0.05 ×0.10×0.22 | 0.2×0.4×0.5 |
| Absorption correction | Based on cr*y*stal shape | | | | | | | |
| No. of measured, independent and observed [$I > 3\sigma(I)$] reflections | 5068, 1021, 1017 | 5100, 1033, 1027 | 5121, 1036, 1032 | 5084, 1040, 1032 | 5177, 1041, 1030 | 5166, 1043, 1028 | 30297, 3517, 3046 | –<br>914, 809 |
| $R_{int}$ | 0.090 | 0.079 | 0.078 | 0.079 | 0.082 | 0.082 | 0.078 | – |
| $(\sin\theta/\lambda)_{max}$ (Å$^{-1}$) | 0.685 | 0.686 | 0.686 | 0.686 | 0.685 | 0.686 | 1.034 | 1.087 |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S* | 0.034, 0.045, 4.02 | 0.025, 0.032, 2.84 | 0.029, 0.039, 3.49 | 0.024, 0.030, 2.54 | 0.024, 0.031, 2.66 | 0.029, 0.038, 3.28 | 0.031, 0.035, 1.17 | 0.037, 0.043, 1.26 |
| No. of reflections | 1021 | 1033 | 1036 | 1040 | 1041 | 1043 | 3517 | 914 |
| No. of parameters | 65 | | | | | | 90 | 65 |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 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$^2$) and site–occupanc*y* factors (SOFs) in the structure of $\beta$-$BaB_2O_4$ modifications at different temperatures.

| Atom | Occ. | *x* | *y* | *z* | 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 $\beta$-$BaB_2O_4$ at different temperatures.

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|
| | | | 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 (×$10^{-4}$)of the third and fourth order for barium atoms in the structure of $\beta$-$BaB_2O_4$ at 298 K obtained using Gram–CharLie model.

| $C_{111}$ | $C_{112}$ | $C_{113}$ | $C_{122}$ | $C_{123}$ | $C_{133}$ | $C_{222}$ | $C_{223}$ | $C_{233}$ | $C_{333}$ | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 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) | | | | | |
| $D_{1111}$ | $D_{1112}$ | $D_{1113}$ | $D_{1122}$ | $D_{1123}$ | $D_{1133}$ | $D_{1222}$ | $D_{1223}$ | $D_{1233}$ | $D_{1333}$ | $D_{2222}$ | $D_{2223}$ | $D_{2233}$ | $D_{2333}$ | $D_{3333}$ |
| 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 $\beta$-$BaB_2O_4$ structure at different temperatures.

| T / K | 98 | 123 | 173 | 223 | 298 | 323 | 693 | Δ(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 $^{i}$ | 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 $^{ii}$ | 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 $^{iii}$ | 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 $^{i}$ | 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 $^{i}$ | 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 $^{i}$ | 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 $^{ii}$ | 120.2(8) | 119.7(5) | 119.9(7) | 119.6(5) | 119.5(5) | 120.0(7) | 120.610(13) | 0.4 |
| O3 $^{i}$ –B1–O4 $^{ii}$ | 123.6(6) | 123.8(4) | 124.1(5) | 123.9(4) | 124.3(4) | 123.9(6) | 123.725(10) | 0.1 |
| O1 $^{iii}$ –B2–O1 $^{i}$ | 115.6(10) | 115.6(7) | 115.7(9) | 115.2(7) | 115.5(7) | 115.5(9) | 114.885(11) | –0.7 |
| O1 $^{iii}$ –B2–O2 $^{i}$ | 124.4(7) | 124.1(5) | 124.2(6) | 124.1(5) | 124.6(5) | 124.5(7) | 124.264(11) | –0.1 |
| O1 $^{i}$ –B2–O2 $^{i}$ | 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 $\beta$-$BaB_2O_4$ structure at different temperatures.

| T / K | 98 | 123 | 173 | 223 | 298 | 323 | 693 | Δ(98–693 K) |
|---|---|---|---|---|---|---|---|---|
| Ba1–O1 [i] | 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 [ii] | 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 [i] | 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 [iii] | 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 [ii] | 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 [i] | 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 [iv] | 2.632(6) | 2.638(4) | 2.642(5) | 2.646(4) | 2.643(4) | 2.648(6) | 2.6549(8) | 0.023 |
| O1 [i]–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 [i]–Ba1–O2 [ii] | 81.3(2) | 81.23(16) | 81.2(2) | 81.03(16) | 80.99(17) | 80.9(2) | 80.301(5) | –1.0 |
| O1 [i]–Ba1–O2 [i] | 50.32(16) | 50.30(11) | 50.27(14) | 50.31(11) | 50.12(12) | 50.14(15) | 50.188(9) | –0.1 |
| O1 [i]–Ba1–O3 [iii] | 128.27(16) | 128.19(11) | 128.17(14) | 128.00(11) | 127.96(11) | 128.00(15) | 126.903(10) | –1.4 |
| O1 [i]–Ba1–O4 [ii] | 79.4(2) | 79.35(15) | 79.38(19) | 79.31(15) | 79.35(16) | 79.4(2) | 79.112(12) | –0.3 |
| O1 [i]–Ba1–O4 [i] | 75.38(17) | 75.51(12) | 75.48(16) | 75.57(13) | 75.69(13) | 75.70(17) | 75.649(8) | 0.3 |
| O1 [i]–Ba1–O4 [iv] | 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 [ii] | 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 [i] | 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 [iii] | 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 [ii] | 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 [i] | 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 [iv] | 81.93(18) | 82.19(13) | 82.23(16) | 82.31(13) | 82.41(14) | 82.59(18) | 83.920(17) | 2.0 |
| O2 [ii]–Ba1–O2 [i] | 105.9(2) | 105.93(14) | 105.74(18) | 105.63(15) | 105.55(15) | 105.6(2) | 105.010(9) | –0.9 |
| O2 [ii]–Ba1–O3 [iii] | 72.3(2) | 72.33(14) | 72.35(18) | 72.36(15) | 72.29(15) | 72.3(2) | 72.515(9) | 0.2 |
| O2 [ii]–Ba1–O4 [ii] | 65.05(15) | 65.07(11) | 65.14(13) | 65.14(11) | 65.21(11) | 65.14(15) | 65.371(9) | 0.3 |
| O2 [ii]–Ba1–O4 [i] | 152.99(18) | 153.02(13) | 153.03(16) | 152.94(13) | 152.99(13) | 152.89(17) | 152.144(8) | –0.8 |
| O2 [ii]–Ba1–O4 [iv] | 68.43(16) | 68.32(11) | 68.19(14) | 68.13(11) | 68.04(12) | 68.04(15) | 67.685(15) | –0.7 |
| O2 [i]–Ba1–O3 [iii] | 178.09(16) | 178.08(11) | 177.93(14) | 177.80(11) | 177.59(12) | 177.71(15) | 176.816(4) | –1.3 |
| O2 [i]–Ba1–O4 [ii] | 129.5(2) | 129.41(14) | 129.41(18) | 129.39(15) | 129.22(15) | 129.3(2) | 129.038(12) | –0.5 |
| O2 [i]–Ba1–O4 [i] | 68.90(18) | 68.98(13) | 69.04(16) | 69.13(13) | 69.19(14) | 69.16(18) | 69.580(8) | 0.7 |
| O2 [i]–Ba1–O4 [iv] | 82.3(2) | 82.39(15) | 82.41(19) | 82.38(15) | 82.57(16) | 82.5(2) | 82.789(10) | 0.5 |
| O3 [iii]–Ba1–O4 [ii] | 49.3(2) | 49.26(14) | 49.22(18) | 49.13(15) | 49.09(15) | 49.1(2) | 48.269(12) | –1.0 |
| O3 [iii]–Ba1–O4 [i] | 112.35(19) | 112.17(13) | 112.26(17) | 112.24(13) | 112.22(14) | 112.14(18) | 111.613(7) | –0.7 |
| O3 [iii]–Ba1–O4 [iv] | 97.5(2) | 97.60(15) | 97.49(19) | 97.54(15) | 97.44(16) | 97.5(2) | 97.929(9) | 0.4 |
| O4 [ii]–Ba1–O4 [i] | 97.02(17) | 96.93(11) | 96.97(14) | 96.92(12) | 96.85(12) | 96.81(16) | 96.100(8) | –0.9 |
| O4 [ii]–Ba1–O4 [iv] | 129.03(19) | 128.98(13) | 128.87(17) | 128.81(13) | 128.76(14) | 128.72(18) | 128.439(7) | –0.6 |
| O4 [i]–Ba1–O4 [iv] | 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 β-$BaB_2O_4$ structure at different temperatures.

| | 98 | 123 | 173 | 223 | 298 | 323 | 693 | Δ(98–693 K) |
|---|---|---|---|---|---|---|---|---|
| B2[i]–O1–B2[ii] | 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 [i] | 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 $\beta$-$BaB_2O_4$ structure at different temperatures.

| T / K | 98 | 123 | 173 | 223 | 298 | 323 | 693 | Δ(98–693 K) |
|---|---|---|---|---|---|---|---|---|
| O1–O2–O1 [ii] | 59.9(3) | 59.9(2) | 59.8(3) | 59.7(2) | 59.7(2) | 59.8(3) | 58.957(11) | –0.9 |
| O3 [i]–O3–O4 [iii] | 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 [i] | 175.3(3) | 175.1(2) | 175.4(3) | 175.2(2) | 175.1(3) | 174.8(4) | 174.7351(19) | –0.6 |
| O3 [ii]–O3–O4 [iii] | 119.3(4) | 119.2(3) | 119.3(4) | 119.2(3) | 119.2(3) | 119.4(4) | 118.743(11) | –0.6 |
| O3 [v]–O4–O3 [vi] | 59.9(3) | 59.9(2) | 59.8(3) | 60.0(2) | 59.8(2) | 59.8(3) | 59.887(13) | 0.0 |
| O1 [i]–O1–O1 [ii] | 60.0(3) | 60.00(19) | 60.0(2) | 60.0(2) | 60.00(11) | 60.0(3) | 60.000(11) | 0.0 |
| O3 [i]–O3–O3 [ii] | 60.0(3) | 60.0(2) | 60.0(3) | 60.0(2) | 60.00(11) | 60.0(3) | 60.000(13) | 0.0 |
| O1 [ii]–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 [i]–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 [iii]–O3–O4 [iv] | 174.2(4) | 174.2(2) | 174.3(3) | 174.3(3) | 174.5(3) | 174.3(3) | 174.7211(15) | 0.5 |
| O3 [ii]–O3–O4 [iv] | 60.7(3) | 60.81(19) | 60.9(2) | 60.8(2) | 61.0(2) | 60.8(3) | 61.301(11) | 0.6 |
| O1 [ii]–O1–O2 [i] | 119.2(4) | 119.1(3) | 119.2(3) | 119.5(3) | 119.2(3) | 119.2(4) | 119.806(13) | 0.6 |
| O3 [i]–O3–O4 [iv] | 120.6(3) | 120.7(2) | 120.8(3) | 120.7(2) | 120.9(2) | 120.7(3) | 121.229(11) | 0.6 |
| O1 [i]–O1–O2 [i] | 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. E*x*perimental details of $\alpha$-$BaB_2O_4$ measurements.

| | | |
|---|---|---|
| Chemical formula | $BaB_2O_4$ | |
| $M_r$ | 223 | |
| Cr*y*stal s*y*stem, space group | Trigonal, *R*–3*c* | |
| Temperature (K) | 298 | 673 |
| *a*, *c* (Å) | 7.227 (6), 39.031 (2) | 7.242 (6), 39.250 (2) |
| *V* (Å$^3$) | 1765 (2) | 1783 (2) |
| *Z* | 18 | |
| Radiation t*y*pe | Mo *K*a | |
| m (mm$^{-1}$) | 29.96 | 29.67 |
| Cr*y*stal size (mm) | 0.11×0.14×0.21 | |
| Absorption correction | Based on cr*y*stal shape | |
| No. of independent and observed reflections | 1729,1558 | 760, 696 |
| $(\sin\theta/\lambda)_{max}$ (Å$^{-1}$) | 1.26 | 1.26 |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S* | 0.036, 0.041 | 0.037,0.032 |
| No. of parameters | 33 | |

Table S10. Atomic coordinates displacement parameters (Å$^2$) and site–occupanc*y* factors (SOFs) in the structure of $\alpha$-$BaB_2O_4$ modifications at different temperatures.

| Atom | Occ. | *x* | *y* | *z* | 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 $\alpha$-$BaB_2O_4$ at different temperatures.

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|
| | | | 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 | 0.01101 | 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 $\alpha$-$BaB_2O_4$ structure at different temperatures.

| | 293 | 673 | Δ(293–673 K) |
|---|---|---|---|
| B1–O1 | 1.42(2) | 1.45(2) | 0.030 |
| B1–O1$^{i}$ | 1.393(13) | 1.365(13) | –0.028 |
| B1–O2$^{ii}$ | 1.30(2) | 1.30(2) | 0.000 |
| O1–B1–O1$^{i}$ | 115.7(12) | 115.1(12) | –0.6 |
| O1–B1–O2$^{ii}$ | 120.9(8) | 120.1(8) | –0.8 |
| O1$^{i}$–B1–O2$^{ii}$ | 123.4(14) | 124.7(14) | 1.3 |

S*y*mmetr*y* 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 $\alpha$-$BaB_2O_4$ structure at different temperatures.

| | 293 | 673 | Δ(293–673 K) |
|---|---|---|---|
| Ba1–O1 | 3.080(14) | 3.107(14) | 0.027 |
| Ba1–O2 iii | 2.742(14) | 2.739(14) | –0.003 |
| Ba1–O2 vi | 2.83(3) | 2.86(3) | 0.03 |
| Ba2–O2 | 2.66(3) | 2/68(3) | 0.02 |
| O1–Ba1–O2 iv | 47.5(4) | 47.5(4) | 0 |
| O1–Ba1–O2 v | 66.9(3) | 66.9(3) | 0 |
| O1–Ba1–O2 viii | 67.1(8) | 67.5(8) | 0.4 |
| O2 vi –Ba1–O2 vii | 72.4(6) | 72.2(6) | –0.2 |
| O2 iii –Ba1–O2 vi | 76.8(7) | 76.8(7) | 0 |
| O2 vi –Ba2–O2 vii | 77.9(7) | 78.0(7) | 0.1 |
| O2 vi –Ba2–O2 i*x* | 87.0(8) | 86.9(8) | –0.1 |
| O2 iii –Ba1–O2 vii | 90.0(7) | 89.6(7) | –0.4 |
| O1–Ba1–O2 vii | 107.9(5) | 108.4(5) | 0.5 |
| O1–Ba1–O1 i | 111.7(5) | 111.3(5) | –0.4 |
| O2 iii –Ba1–O2 iv | 112.4(6) | 112.6(6) | 0.2 |
| O2 vi –Ba2–O2 *x*i | 134.9(5) | 135.0(5) | 0.1 |
| O2 vi –Ba2–O2 *x* | 140.0(5) | 139.8(5) | –0.2 |
| O1–Ba1–O2 iii | 145.0(10) | 144.8(10) | –0.2 |
| O2 iii –Ba1–O2 viii | 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;(*x*i) *x*,*x*–*y*,*z*–1/2

Table S14. O–O–O (°) angles in the $\alpha$-$BaB_2O_4$ structure at different temperatures.

| | 293 | 673 | Δ(293–673 K) |
|---|---|---|---|
| O1 i –O1–O1 ii | 60.0(5) | 60.0(5) | 0 |
| O1 i –O1–O2 iii | 119.6(5) | 120.1(5) | 0.5 |
| O1 i –O1–O2 iv | 60.0(5) | 59.5(5) | –0.5 |
| O1 ii –O1–O2 iii | 59.7(4) | 60.3(4) | 0.6 |
| O1 ii –O1–O2 iv | 119.9(5) | 119.4(5) | –0.5 |
| O2 iii –O1–O2 iv | 173(2) | 171(2) | –2 |
| O1 v –O2–O1 vi | 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 $LiB_3O_5$ measurements.

| Chemical formula | $LiB_3O_5$ | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $M_r$ | 119.4 | | | | | | | | |
| Crystal system, space group | Orthorhombic, *Pna*2$_1$ | | | | | | | | |
| Temperature (K) | 98 | 123 | 148 | 173 | 198 | 223 | 248 | 273 | 298 |
| *a* (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) |
| *b* (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) |
| *c* (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) |
| *V* (Å$^3$) | 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) |
| *Z* | 4 | | | | | | | | |
| Radiation type | Mo *K*α | | | | | | | | |
| μ (mm$^{-1}$) | 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 [$I > 3\sigma(I)$] 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 |
| $R_{int}$ | 0.044 | 0.032 | 0.046 | 0.041 | 0.039 | 0.049 | 0.065 | 0.076 | 0.064 |
| $(\sin\theta/\lambda)_{max}$ (Å$^{-1}$) | 0.688 | 0.687 | 0.688 | 0.693 | 0.686 | 0.685 | 0.688 | 0.686 | 0.686 |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.029, 0.029, 1.39 | 0.025, 0.025, 1.26 | 0.029, 0.030, 1.40 | 0.026, 0.027, 1.30 | 0.026, 0.025, 1.14 | 0.027, 0.027, 1.25 | 0.035, 0.035, 1.54 | 0.037, 0.040, 1.77 | 0.032, 0.034, 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$^{-3}$) | 0.20, –0.22 | 0.15, –0.17 | 0.20, –0.18 | 0.26, –0.24 | 0.17, –0.16 | 0.22, –0.23 | 0.21, –0.24 | 0.31, –0.30 | 0.19, –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$^2$) and site–occupancy factors (SOFs) in the structure of $LiB_3O_5$ at different temperatures.

| Atom | Occ. | *x* | *y* | *z* | *U* 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 $LiB_3O_5$ at different temperatures.

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|
| | | | 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 $LiB_3O_5$ 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 [i] | 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 [ii] | 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 [iii] | 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 [i] | 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 [i] | 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 [ii] | 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 [iii] | 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 [i] | 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 [i] –Li1–O4 [ii] | 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 [i] –Li1–O5 [iii] | 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) | 86.32) | –10.1 |
| O3 [i] –Li1–O5 [i] | 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 [ii] –Li1–O5 [iii] | 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 [ii] –Li1–O5 [i] | 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 [iii] –Li1–O5 [i] | 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 $LiB_3O_5$ 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 [i] | 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 [ii] | 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 [i] | 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 [iii] | 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 [i] –B2–O2 [ii] | 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 [i] –B2–O4 [i] | 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 [i] –B2–O5 [iii] | 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 [ii] –B2–O4 [i] | 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 [ii] –B2–O5 [iii] | 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 [i] –B2–O5 [iii] | 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 $LiB_3O_5$ structure at different temperatures.

| T / K | 98 | 123 | 148 | 173 | 198 | 223 | 248 | 273 | 298 | 500 | 650 | Δ(98 -650 K) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| B1–O1–B2 [i] | 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 [ii] | 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 [i] –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 [iii] –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 $LiB_3O_5$ structure at different temperatures.

| T / K | 98 | 123 | 148 | 173 | 198 | 223 | 248 | 273 | 298 | 500 | 650 | Δ(98 –650 K) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| O1 [v] –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 [i] –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 [v] –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 [ii] | 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 [v] | 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 v | 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 iii | 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 ii | 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 vi –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 ii | 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 vi –O5–O4 v | 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 v –O5–O2 vi | 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 i –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 i | 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 vi –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 i –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 iii –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 ii | 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 iv | 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 i –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 iii | 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 ii | 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 iv | 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 i –O1–O5 ii | 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 iii –O2–O5 iv | 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 v –O5–O4 v | 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 iii –O2–O5 iv | 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 i –O4–O5 ii | 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 iii | 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 iii –O2–O4 iii | 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 i | 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 ii | 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 |
| Crystal system, space group | Trigonal, *P*321 | | | | | |
| 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$^3$) | 535.14 (13) | 536.01 (13) | 541.64 (15) | 538.10 (13) | 541.56 (15) | 544.60 (15) |
| *Z* | 3 | | | | | |
| Radiation type | Mo *K*α | | | | | |
| μ (mm$^{-1}$) | 1.57 | 1.57 | 1.55 | 1.56 | 1.55 | 1.54 |
| Crystal size (mm) | 0.1×0.2×0.4 | | | | | |
| Data collection | | | | | | |
| Diffractometer | *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 |

| | | | | | | |
|---|---|---|---|---|---|---|
| $(\sin\theta/\lambda)_{max}$ (Å$^{-1}$) | 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, 1.52 | 0.023, 0.024, 1.34 | 0.022, 0.023, 1.31 | 0.021, 0.022, 1.22 | 0.023, 0.024, 1.27 | 0.025, 0.024, 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 Å$^{-3}$) | 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 (Å$^2$) and site–occupancy factors (SOFs) in the structure of $K_2Al_2B_2O_7$ at different temperatures.

| Atom | Occ. | *x* | *y* | *z* | *U* 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 | Δ(98–348 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 $^{i}$ | 2.680(3) | 2.684(3) | 2.693(2) | 2.689(2) | 2.700(3) | 2.701(3) | 0.021 |
| K1–O1 $^{iii}$ | 3.344(3) | 3.339(3) | 3.350(3) | 3.337(3) | 3.335(3) | 3.335(3) | –0.009 |
| K1–O2 $^{iv}$ | 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 $^{i}$ | 3.212(3) | 3.216(3) | 3.228(3) | 3.223(3) | 3.235(3) | 3.244(3) | 0.032 |
| K2–O2 $^{iv}$ | 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 $^{iv}$ | 3.252(2) | 3.251(2) | 3.259(2) | 3.246(2) | 3.250(2) | 3.251(3) | –0.001 |
| K2–O3 $^{ix}$ | 2.679(2) | 2.686(2) | 2.6979(19) | 2.6980(19) | 2.710(2) | 2.726(2) | 0.047 |
| K2–O3 $^{viii}$ | 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 $^{i}$–K1–O1 $^{ii}$ | 112.21(10) | 112.20(10) | 112.47(9) | 112.65(9) | 112.88(10) | 112.93(11) | 0.72 |
| O1 $^{i}$–K1–O1 $^{iii}$ | 79.63(7) | 79.80(7) | 80.04(7) | 80.23(7) | 80.49(7) | 80.64(8) | 1.01 |
| O1 $^{i}$–K1–O2 $^{iv}$ | 74.90(9) | 75.01(9) | 74.97(8) | 75.05(8) | 75.07(9) | 75.28(9) | 0.38 |
| O1 $^{i}$–K1–O2 $^{v}$ | 169.94(11) | 169.89(11) | 169.82(10) | 169.73(10) | 169.56(10) | 169.46(11) | –0.48 |
| O1 $^{i}$–K1–O3 | 74.16(6) | 74.26(6) | 74.23(5) | 74.36(5) | 74.53(6) | 74.68(6) | 0.52 |
| O1 $^{i}$–K1–O3 $^{iii}$ | 106.44(7) | 106.46(7) | 106.60(6) | 106.58(6) | 106.56(6) | 106.60(7) | 0.16 |
| O1 $^{i}$–K1–O5 | 128.78(8) | 128.70(8) | 128.73(7) | 128.81(7) | 128.79(8) | 128.80(8) | 0.02 |
| O1 $^{i}$–K1–O5 $^{vi}$ | 88.98(9) | 89.12(9) | 89.04(8) | 89.00(8) | 89.01(9) | 89.09(9) | 0.11 |
| O1 $^{ii}$–K1–O1 $^{iii}$ | 55.34(6) | 55.21(6) | 55.20(6) | 55.24(5) | 55.31(6) | 55.18(6) | –0.16 |
| O1 $^{iii}$–K1–O2 $^{iv}$ | 134.45(7) | 134.59(7) | 134.60(6) | 134.56(6) | 134.56(7) | 134.67(7) | 0.22 |
| O1 $^{iii}$–K1–O2 $^{v}$ | 99.86(6) | 99.80(6) | 99.81(6) | 99.90(6) | 99.82(6) | 99.97(7) | 0.11 |
| O1 $^{iii}$–K1–O3 | 138.34(9) | 138.53(9) | 138.72(7) | 138.95(7) | 139.32(8) | 139.51(9) | 1.17 |
| O1 $^{iii}$–K1–O3 $^{iii}$ | 42.70(9) | 42.72(9) | 42.71(8) | 42.68(8) | 42.58(9) | 42.72(9) | 0.02 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| O1 iii –K1–O5 | 142.91(7) | 142.90(7) | 142.78(6) | 142.70(7) | 142.70(7) | 142.62(7) | –0.29 |
| O1 iii –K1–O5 vi | 86.26(7) | 86.29(7) | 86.37(6) | 86.43(6) | 86.37(7) | 86.52(7) | 0.26 |
| O1–K1–O1 i | 55.34(8) | 55.21(8) | 55.20(7) | 55.24(7) | 55.31(7) | 55.18(8) | –0.16 |
| O1–K1–O1 ii | 79.63(8) | 79.80(8) | 80.04(7) | 80.23(7) | 80.49(7) | 80.64(8) | 1.01 |
| O1–K1–O1 iii | 95.67(8) | 95.83(8) | 96.03(7) | 96.29(7) | 96.75(8) | 96.79(8) | 1.12 |
| O1–K1–O2 iv | 99.86(8) | 99.80(8) | 99.81(7) | 99.90(7) | 99.82(7) | 99.97(8) | 0.11 |
| O1–K1–O2 v | 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 iii | 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 vi | 142.91(7) | 142.90(7) | 142.78(6) | 142.70(7) | 142.70(7) | 142.62(7) | –0.29 |
| O2 iv –K1–O2 v | 99.03(8) | 98.80(8) | 98.58(7) | 98.22(7) | 97.93(8) | 97.43(9) | –1.6 |
| O2 iv –K1–O3 | 67.91(8) | 67.93(8) | 67.96(7) | 68.15(7) | 68.23(8) | 68.35(8) | 0.44 |
| O2 iv –K1–O3 iii | 111.36(9) | 111.20(9) | 111.04(8) | 110.70(8) | 110.44(8) | 110.07(9) | –1.29 |
| O2 iv –K1–O5 | 80.97(7) | 80.77(7) | 80.79(6) | 80.77(6) | 80.61(7) | 80.46(7) | –0.51 |
| O2 iv –K1–O5 vi | 56.54(9) | 56.54(9) | 56.32(8) | 56.02(8) | 55.91(9) | 55.69(9) | –0.85 |
| O3–K1–O3 iii | 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 vi | 124.40(8) | 124.43(9) | 124.24(7) | 124.14(7) | 124.11(8) | 124.02(8) | –0.38 |
| O1 i –K2–O1 vii | 108.05(8) | 107.80(9) | 107.71(7) | 107.40(7) | 107.16(8) | 106.96(9) | –1.09 |
| O1 i –K2–O2 iv | 70.85(9) | 71.01(9) | 71.05(7) | 71.18(7) | 71.28(8) | 71.38(9) | 0.53 |
| O1 i –K2–O2 viii | 176.33(7) | 176.28(6) | 176.32(6) | 176.28(6) | 176.17(6) | 176.19(6) | –0.14 |
| O1 i –K2–O3 | 73.95(6) | 73.99(6) | 73.93(5) | 73.98(5) | 74.03(6) | 73.94(6) | –0.01 |
| O1 i –K2–O3 iv | 101.38(6) | 101.38(6) | 101.32(6) | 101.38(6) | 101.38(6) | 101.20(7) | –0.18 |
| O1 i –K2–O3 ix | 96.74(7) | 96.69(7) | 96.70(6) | 96.49(6) | 96.38(7) | 96.46(7) | –0.28 |
| O1 i –K2–O3 viii | 132.30(8) | 132.42(8) | 132.47(7) | 132.54(7) | 132.59(7) | 132.79(7) | 0.49 |
| O1 i –K2–O4 | 54.03(7) | 53.90(7) | 53.86(6) | 53.70(6) | 53.58(6) | 53.48(7) | –0.55 |
| O2 iv –K2–O2 viii | 110.47(10) | 110.41(10) | 110.39(8) | 110.45(8) | 110.50(9) | 110.48(10) | 0.01 |
| O2 iv –K2–O3 | 79.60(9) | 79.59(9) | 79.64(8) | 79.83(8) | 79.84(9) | 79.81(9) | 0.21 |
| O2 iv –K2–O3 iv | 45.57(7) | 45.49(7) | 45.50(6) | 45.55(6) | 45.53(7) | 45.41(7) | –0.16 |
| O2 iv –K2–O3 ix | 109.57(9) | 109.56(9) | 109.56(8) | 109.48(8) | 109.50(9) | 109.53(10) | –0.04 |
| O2 iv –K2–O3 viii | 81.67(9) | 81.76(9) | 81.81(8) | 81.89(8) | 82.04(8) | 82.25(9) | 0.58 |
| O2 iv –K2–O4 | 124.77(6) | 124.80(6) | 124.80(5) | 124.77(5) | 124.75(6) | 124.76(6) | –0.01 |
| O3 iv –K2–O3 viii | 84.41(7) | 84.55(7) | 84.76(6) | 84.94(6) | 85.20(7) | 85.58(7) | 1.17 |
| O3 iv –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 iv | 56.54(9) | 56.47(9) | 56.42(7) | 56.45(7) | 56.37(8) | 56.20(9) | –0.34 |
| O3–K2–O3 ix | 164.43(11) | 164.47(11) | 164.39(9) | 164.18(9) | 164.11(10) | 164.14(11) | –0.29 |
| O3–K2–O3 viii | 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 vi | 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 $K_2Al_2B_2O_7$ 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 v | 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 i | 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 v | 109.46(9) | 109.46(9) | 109.56(8) | 109.64(8) | 109.65(8) | 109.61(9) | 0.2 |
| O2 iii –Al2–O2 iv | 109.48(14) | 109.48(14) | 109.38(12) | 109.31(12) | 109.29(13) | 109.33(14) | –0.2 |
| O3–Al3–O3 vi | 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* (°) angles, *T* = Al, B in the $K_2Al_2B_2O_7$ structure at different temperatures.

| T / K | 98 | 123 | 173 | 223 | 298 | 348 | Δ(98–348 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$^{i}$ | 180.0(5) | 180.0(5) | 180.0(5) | 180.0(5) | 180.0(5) | 180.0(5) | 0 |
| Al2$^{ii}$–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 (°) angles in the $K_2Al_2B_2O_7$ structure at different temperatures.

| T / K | 98 | 123 | 173 | 223 | 298 | 348 | Δ(98–348 K) |
|---|---|---|---|---|---|---|---|
| O2$^{iii}$–O2–O3 | 157.15(12) | 156.97(12) | 156.51(11) | 156.10(11) | 155.78(12) | 155.18(12) | –2.0 |
| O1$^{i}$–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$^{vi}$ | 152.18(12) | 151.84(12) | 151.83(11) | 151.59(11) | 151.41(12) | 150.99(12) | –1.2 |
| O2$^{v}$–O5–O3$^{vi}$ | 164.97(6) | 164.83(6) | 164.67(5) | 164.45(5) | 164.29(5) | 163.98(6) | –1.0 |
| O1–O4–O1$^{i}$*x* | 163.01(10) | 162.87(10) | 162.88(9) | 162.72(9) | 162.38(10) | 162.44(10) | –0.6 |
| O2$^{v}$–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$^{i}$ | 60.18(6) | 60.07(7) | 60.07(6) | 60.14(6) | 60.18(6) | 59.97(7) | –0.2 |
| O3–O5–O3$^{vi}$ | 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$^{v}$–O5–O2*x*$^{i}$ | 60.60(12) | 60.56(12) | 60.55(10) | 60.58(10) | 60.44(11) | 60.58(12) | 0.0 |
| O1$^{i}$–O1–O1$^{ii}$ | 60.00(12) | 60.00(12) | 60.00(11) | 60.00(10) | 60.00(11) | 60.00(12) | 0.0 |
| O2$^{iii}$–O2–O5$^{v}$ | 59.70(8) | 59.72(8) | 59.72(7) | 59.71(7) | 59.78(8) | 59.71(8) | 0.0 |
| O3$^{vi}$–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$^{viii}$ | 112.08(6) | 112.15(6) | 112.15(5) | 112.03(5) | 111.88(6) | 112.13(6) | 0.0 |
| O3–O2–O5$^{v}$ | 133.76(12) | 133.73(12) | 133.76(10) | 133.82(11) | 133.68(11) | 133.83(12) | 0.1 |
| O1$^{i}$–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*x* | 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$^{v}$–O5–O3$^{vii}$ | 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$^{v}$ | 98.21(10) | 98.35(10) | 98.61(9) | 98.99(9) | 99.32(9) | 99.61(10) | 1.4 |
| O1$^{ii}$–O1–O2 | 144.71(17) | 144.97(17) | 145.10(15) | 145.48(15) | 146.10(16) | 146.17(17) | 1.5 |
| O1$^{ii}$–O1–O3 | 85.25(14) | 85.67(14) | 85.69(12) | 85.98(12) | 86.44(13) | 86.74(14) | 1.5 |
| O1$^{i}$–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$^{vii}$ | 141.70(14) | 142.16(14) | 142.25(12) | 142.62(12) | 142.95(13) | 143.51(14) | 1.8 |
| O1–O2–O2$^{iv}$ | 82.59(12) | 82.77(12) | 83.16(10) | 83.62(10) | 84.12(11) | 84.46(12) | 1.9 |
| O2–O3–O3$^{vii}$ | 82.86(10) | 83.16(10) | 83.43(9) | 83.83(9) | 84.13(10) | 84.73(11) | 1.9 |
| O2–O3–O3$^{vi}$ | 141.92(10) | 142.23(11) | 142.50(9) | 142.89(9) | 143.20(10) | 143.79(11) | 1.9 |
| O1–O2–O2$^{iii}$ | 142.20(16) | 142.38(16) | 142.78(14) | 143.26(14) | 143.76(15) | 144.12(16) | 1.9 |
| O2$^{iv}$–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;(*x*i) *x*–*y*+1,–*y*+1,–*z*;(*x*ii) –*x*+1,–*x*+*y*,–*z*

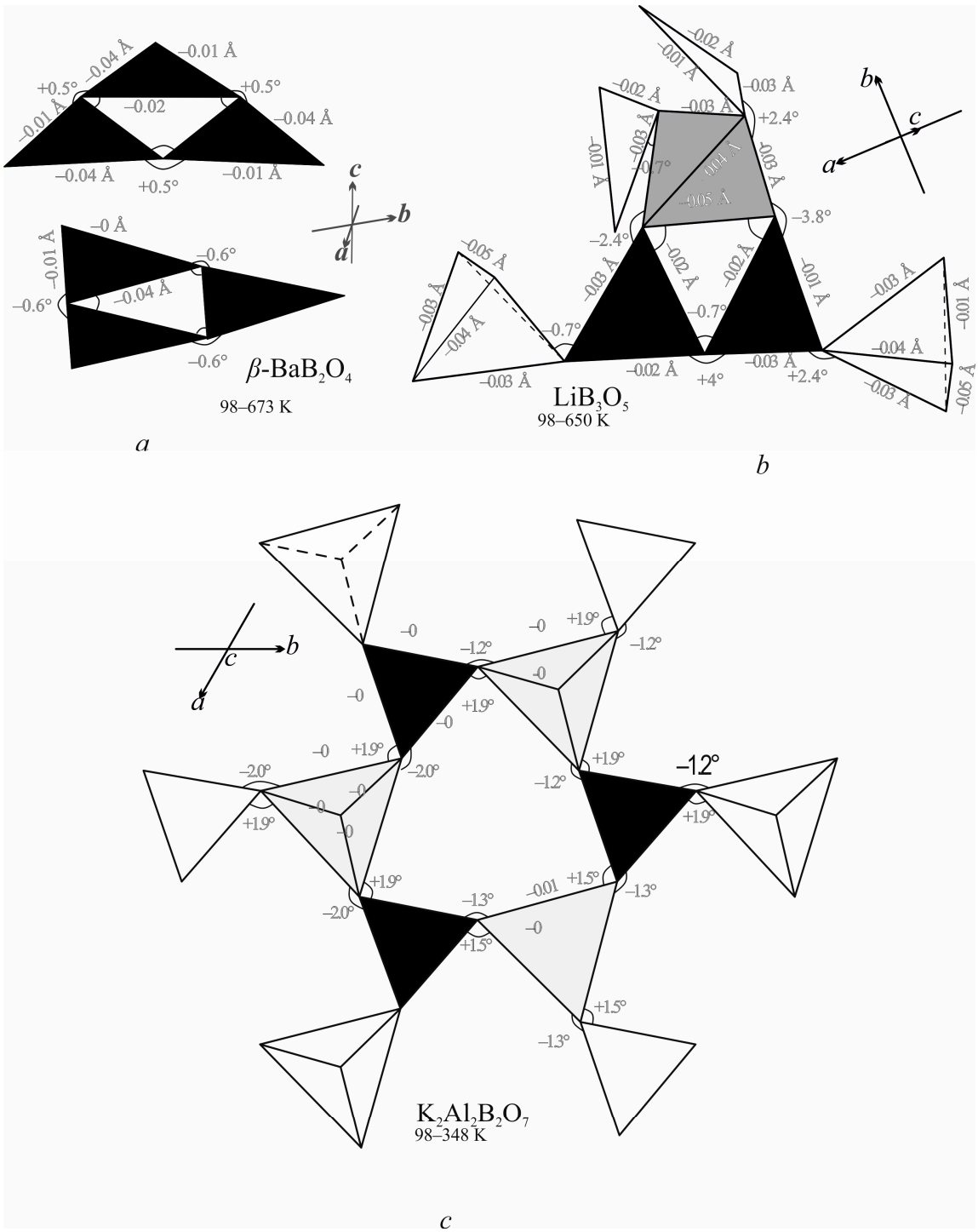


Figure S1. Changing of O–O distances and O–O–O in boron-oxygen groups in structures (a) β-$BaB_2O_4$, (b) $LiB_3O_5$, (c) $K_2Al_2B_2O_7$.