

Table S1. Temperature dependencies of the unit-cell parameters for Ca-borates and Sr₃B₁₄O₂₄ approximated by linear and quadratic polynomial functions $a_0 + a_1 \times 10^{-3} t + a_2 \times 10^{-6} t^2$

Parameter	a_0	a_1	a_2	a_0	a_1	a_2
Ca₃BO₆				CaB₂O₄		
$a(t)$, Å	8.646	0.07012	0.005422	6.213	0.1367	0.040
$b(t)$, Å	8.646	0.07012	0.005422	11.584	0.0689	-0.0046
$c(t)$, Å	11.871	0.3122	0.08619	4.275	-0.0017	0.020
$V(t)$, Å ³	768.527	32.55	7.17	307.684	8.473	3.377
α-CaB₄O₇				Sr₃B₁₄O₂₄		
$a(t)$, Å	12.267	0.0748	0.02525	6.642	0.0094	0.0400
$b(t)$, Å	9.898	0.0749	0.0106	11.604	0.1298	-0.0146
$c(t)$, Å	7.79885	0.0424	0.0170	21.906	0.3095	-0.0143
$\beta(t)$, °	91.264	0.0298	0.0707	93.313	-0.080	0.022
$V(t)$, Å ³	946.702	17.94	5.2	1685.62	45.09	7.5

Table S2 Thermal expansion coefficients for Ca-borates and Sr₃B₁₄O₂₄

	Temperature		
	25	200	600
$\alpha, \times 10^6 \text{ }^\circ\text{C}^{-1}$	Ca₃BO₆		
α_{11}	8.445(5)	8.609(3)	8.933(1)
α_{22}	8.445(5)	8.609(3)	8.933(1)
α_{33}	27.82(2)	30.85(1)	34.794(5)
α_V	45.71(2)	48.07(1)	52.660(5)
	CaB₂O₄		
α_{11}	22.31(4)	24.45(2)	29.25(2)
α_{22}	5.93(3)	5.78(2)	5.45(1)
α_{33}	0.16(1)	1.47(1)	5.207(8)
α_V	28.07(2)	31.71(2)	39.91(1)
	Sr₃B₁₄O₂₄		
α_{11}	1.711(31)	3.817(38)	8.602(69)
α_{22}	11.12(20)	10.66(11)	9.614(77)
α_{33}	14.18(26)	13.91(14)	13.32(11)
α_a	1.72(16)	3.828(97)	8.626(86)
α_b	11.12(34)	10.66(20)	9.61(18)
α_c	14.09(17)	13.831(99)	13.240(87)
α_V	27.01(49)	28.39(29)	31.53(25)
α_β	-0.85(14)	-0.762(84)	-0.571(80)
$\mu_{c,3} = (c^\wedge \alpha_{33})$	4.8	5.2	7.3
	α-CaB₄O₇		
α_{11}	8.469(7)	9.408(8)	11.545(9)
α_{22}	7.622(6)	7.988(7)	8.817(7)
α_{33}	3.156(3)	3.672(3)	4.834(4)
α_a	6.202(5)	6.914(3)	8.532(2)
α_b	7.622(8)	7.988(5)	8.817(3)
α_c	5.540(5)	6.297(3)	8.018(2)

α_V	19.25(2)	21.07(2)	25.20(2)
α_β	3.308(4)	3.577(3)	4.190(2)
$\mu_{c,3} = (c^\wedge a_{33})$	42.1	42.6	43.5