

SUPPLEMENTARY INFORMATION

Table S1 Three coordinated boron isotropic chemical shifts and quadrupole parameters extracted from DOR at three fields and independently from 3QMAS fitting. Boron site labels follow from the assignments detailed in Table 3 except for Na₂Cs₂B₁₀O₁₇ where the δ_{iso} , $\bar{\theta}$ linear relation is used.

Material	Site	Multifield DOR		3QMAS			
		δ_{iso} (ppm) ± 0.35	P_Q (MHz) ± 0.18	δ_{iso} (ppm) ± 0.30	C_Q (MHz) ± 0.10	η ± 0.10	P_Q (MHz) ± 0.10
CsB ₃ O ₅	B1	-	-	17.80	2.46	0.29	2.49
	B2	-	-	20.01	2.78	0.30	2.82
K ₂ B ₄ O ₇	B5	18.69	2.46	19.35	2.51	0.17	2.53
	B6	18.69	2.46	19.35	2.51	0.17	2.53
	B7	16.22	2.55	16.32	2.54	0.03	2.54
α -BaB ₄ O ₇ ³¹	B8	19.51	2.50	20.23	2.64	0.04	2.64
	B1	19.26	2.70	19.20	2.70	0.30	2.74
	B4	17.19	2.28	17.37	2.45	0.22	2.47
	B7	19.26	2.70	18.89	2.66	0.31	2.71
	B8	16.83	2.49	16.39	2.45	0.31	2.49
Na ₂ Cs ₂ B ₁₀ O ₁₇	B1			19.12	2.67	0.28	2.70
	B2			18.60	2.65	0.19	2.67
	B3			18.23	2.71	0.23	2.73

Table S2 Three coordinated boron isotropic chemical shifts and quadrupole parameters extracted from MAS at 14.1 T and used to calculate δ_{DOR} at 20 T for comparison with experimental values.

Crystal, boron site	14.1 T MAS fit			Calc. (20 T)	Measured	Difference
	δ_{iso} (ppm) ± 0.20	C_Q (MHz) ± 0.05	$\eta \pm 0.05$	δ_{DOR} (ppm) ± 0.22	δ_{DOR} (ppm) ± 0.20	(ppm) ± 0.4
α -CsB ₅ O ₈ ²⁴						
B2 (p)	19.10	2.613	0.22	16.77	16.80	-0.03
B3 (p)	16.09	2.546	0.24	13.87	13.69	0.18
B4 (p)	16.09	2.546	0.24	13.87	13.69	0.18
B5 (p)	19.10	2.613	0.22	16.77	16.80	-0.03
α -CsB ₅ O ₈ ²⁵						
B2 (p)	19.10	2.613	0.22	16.77	16.80	-0.03
B3 (p)	19.10	2.613	0.22	16.77	16.48	0.29
B4 (p)	16.09	2.546	0.24	13.87	13.69	0.18
B5 (p)	16.09	2.546	0.24	13.87	13.69	0.18
CsB ₃ O ₅ ²⁶						
B1 (t)	17.81	2.515	0.26	15.64	15.78	-0.14
B2 (t)	19.87	2.773	0.20	17.25	16.91	0.34
K ₂ B ₄ O ₇ ⁶³						
B5 (d)	18.75	2.52	0.12	16.61	16.68	-0.07
B6 (d)	18.75	2.52	0.12	16.61	16.68	-0.07
B7 (T ³)	16.11	2.553	0.06	13.91	14.00	-0.09
B8 (dt)	19.91	2.662	0.10	17.52	17.47	0.05
α -BaB ₄ O ₇ ³⁰						
B1 (dp)	19.23	2.774	0.11	16.64	16.84	-0.2
B4 (dp)	17.36	2.496	0.00	15.27	15.52	-0.25
B7 (dt)	19.23	2.774	0.11	16.64	16.84	-0.2
B8 (dp)	16.41	2.469	0.34	14.29	14.74	-0.45