Structural studies of a $Li_2O \cdot 4B_2O_3$ melt by high-temperature Raman spectroscopy and density functional theory

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Table S1 Convergence tests for the LiB_3O_5 melt total energy with respect to the *Γ*-centred *k*-point grids. The energy cutoff is fixed at 1300 eV.

k-point	Total energy (eV)
2×1×1	–4793.4938
2×2×1	–4793.5201
2×2×2	–4801.1595
2×2×3	–4800.8895
2×2×4	–4800.9013
2×3×3	–4800.8895
3×3×3	–4800.8894

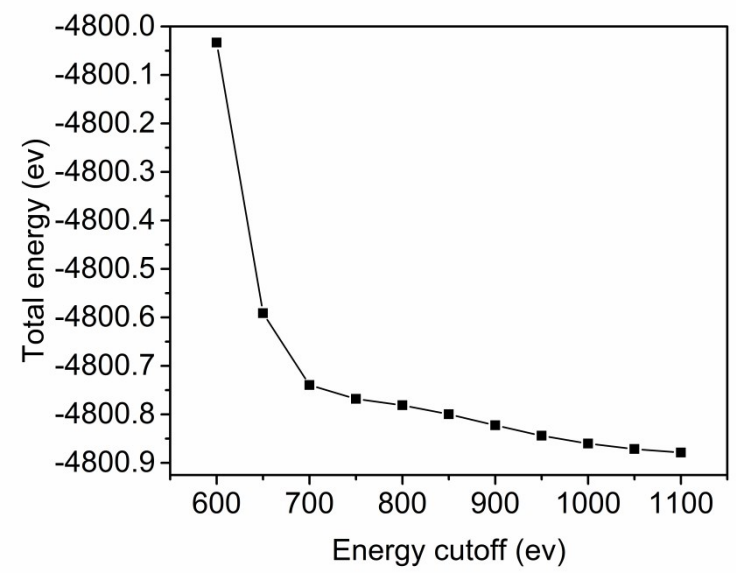
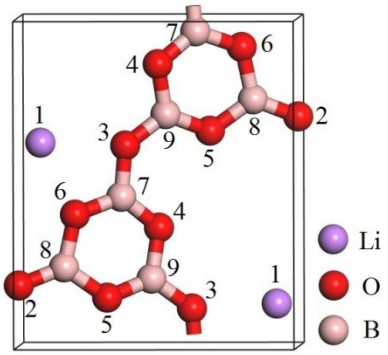


Fig. S1 Convergence tests for the LiB_3O_5 melt total energy with respect to the energy cutoffs. The *Γ*-centred *k*-point grid is fixed at 2 × 2 × 4.

Table S1 and Fig. S1 present the convergence test results for the LiB_3O_5 melt total energy with respect to the *Γ*-centred *k*-point grids and the energy cutoffs. According to the results, a *Γ*-centered *k*-point grid of 2 × 2 × 4 and an energy cutoff of 1000 eV are sufficient to give a well converged total energy.



Crystal system: Monoclinic

Space group: *P*21 (No. 4)

Unit cell parameters:

$a = 7.4498$ Å
$b = 8.7556$ Å
$c = 3.3101$ Å
$\alpha = 90.00°$
$\beta = 92.43°$
$\gamma = 90.00°$
$Z = 2$

Fig. S2 Optimized LiB_3O_5 melt structural model.

Table S2 Atomic coordinates for the optimized LiB_3O_5 melt structural model.

Atom	*x/a*	*y/b*	*z/c*
Li1	0.91310	0.12470	0.29520
O2	0.98750	0.69200	0.18660
O3	0.61530	0.11300	0.42260
O4	0.49980	0.36000	0.45530
O5	0.32250	0.15190	0.67980
O6	0.21010	0.40590	0.72310
B7	0.37000	0.45670	0.58240
B8	0.17120	0.24570	0.74450
B9	0.47500	0.20590	0.52310

Table S3 Selected geometric parameters for the optimized LiB_3O_5 melt structural model.

Bond length (Å)		Bond angle (degree)	
O2–B8	1.301	B7–O3–B9	130.82
O3–B7	1.373	B7–O4–B9	117.02
O3–B9	1.376	B8–O5–B9	122.74
O4–B7	1.365	B7–O6–B8	120.934
O4–B9	1.381	O4–B7–O6	122.71
O5–B8	1.418	O3–B7–O4	123.82
O5–B9	1.354	O3–B7–O6	113.47
O6–B7	1.371	O2–B8–O5	123.44
O6–B8	1.434	O2–B8–O6	123.28
		O5–B8–O6	113.28
		O3–B9–O5	122.98
		O4–B9–O5	121.56
		O3–B9–O4	115.45

Table S4 Calculated vibrational modes of the LiB_3O_5 melt and their frequencies.

No.	mode	ω/cm^{-1}	No.	mode	ω/cm^{-1}	No.	mode	ω/cm^{-1}
1	A^*	-0.04732	19	*B*	372.4875	37	*A*	773.0792
2	A^*	-0.03879	20	*B*	413.194	38	*B*	774.5616
3	B^*	-0.02727	21	*A*	428.5101	39	*A*	839.7464
4	*B*	38.79408	22	*A*	470.1411	40	*B*	902.6722
5	*B*	79.13959	23	*B*	481.4324	41	*A*	999.6381
6	*A*	79.95522	24	*A*	495.9622	42	*B*	1008.031
7	*B*	100.9505	25	*B*	496.3554	43	*A*	1080.905
8	*A*	110.1885	26	*A*	504.5112	44	*B*	1108.607
9	*B*	124.8035	27	*A*	525.5298	45	*B*	1245.343
10	*B*	143.8458	28	*B*	548.9694	46	*A*	1303.354
11	*A*	156.832	29	*A*	603.7891	47	*B*	1350.972
12	*A*	163.492	30	*B*	622.6508	48	*B*	1379.202
13	*B*	172.1861	31	*B*	643.8714	49	*A*	1391.875
14	*B*	183.6412	32	*A*	652.7105	50	*A*	1421.236
15	*A*	199.3748	33	*B*	655.1247	51	*B*	1426.053
16	*A*	235.9145	34	*A*	675.6798	52	*A*	1483.624
17	*B*	278.1262	35	*B*	678.7044	53	*B*	1538.339
18	*A*	325.9803	36	*A*	696.0214	54	*A*	1577.039

* Acoustic mode

The LiB_3O_5 melt unit cell belongs to the monoclinic *P*21 space group, containing 18 atoms. Therefore, the melt has 54 vibrational modes (27*A* + 27*B*). With exception of three acoustic modes (2*A* + *B*), the rest (25*A* + 26*B*) are optical modes and all Raman-active. All of the vibrational modes and their calculated frequencies are listed in Table S4.