Electronic Supplementary Material (ESI) for Journal of Materials Chemistry

Supporting Information for the manuscript

On the formation and structure of the first calcium borohydride borate, $Ca_3(BD_4)_3(BO_3)$

Phonon density of states

In order to understand the stability of the experimentally identified phase we have calculated phonon density of states for $Ca_3(BD_4)_3(BO_3)$ at the theoretical equilibrium volume (Fig. 1). For this phase no imaginary frequency was identified. This indicates that the experimentally identified structure is ground-state structures for the $Ca_3(BD_4)_3(BO_3)$ composition, or at least it is a dynamically stable compound.

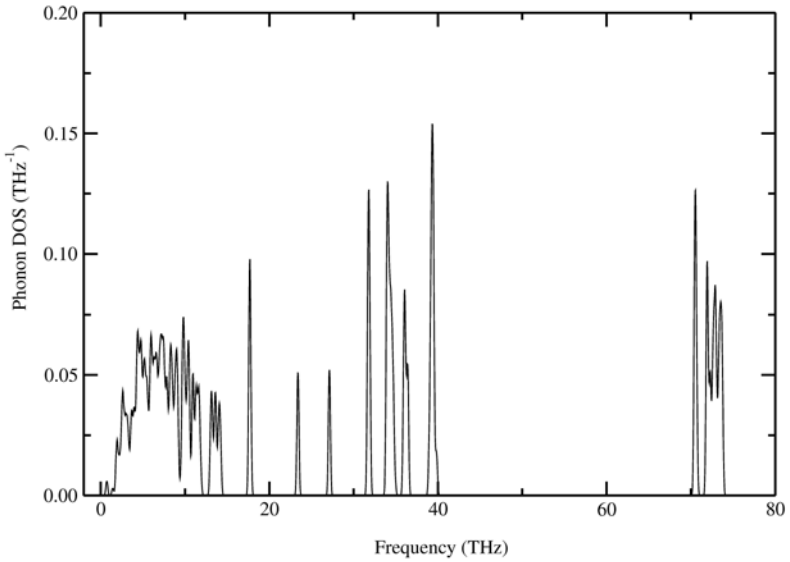

Fig. 1. Calculated total phonon density of states for the $Ca_3(BH_4)_3(BO_3)$ phase.

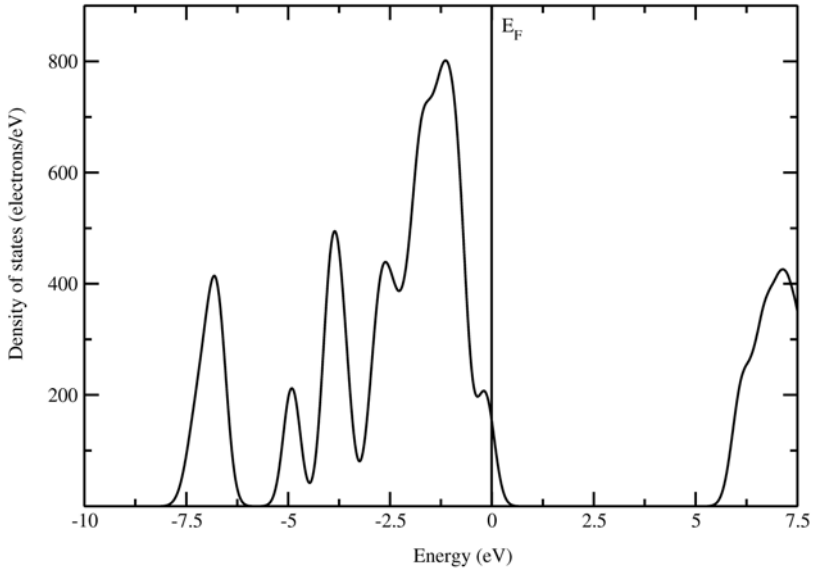

Fig. 2. Calculated total density of states for $Ca_3(BD_4)_3(BO_3)$ at the theoretical equilibrium volume. The Fermi level is set to zero energy and marked by the vertical line.

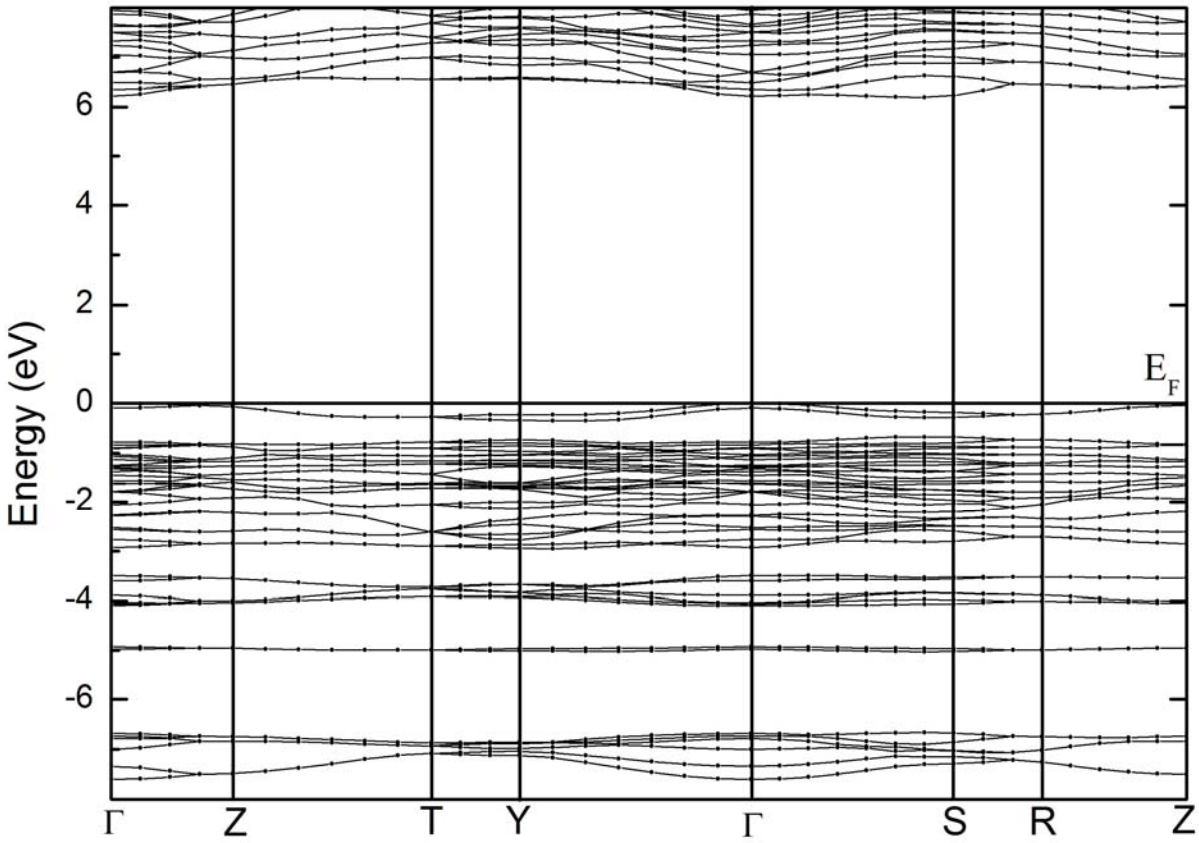

Fig. 3. Calculated band structure for $Ca_3(BD_4)_3(BO_3)$ at the theoretical equilibrium volume. The Fermi level is set at zero energy.

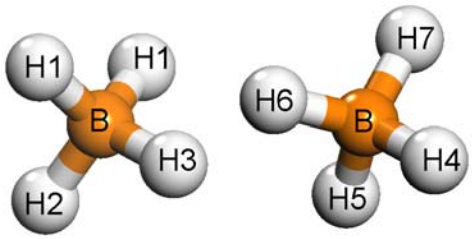

Fig. 4. The crystal structure fragment of the $Ca_3(BH_4/D_4)_3(BO_3)$ phase. Within the BH_4 units the different H/D sites are marked according to the positional parameters presented in Table 1, main article.

IR spectra simulation from theory

We try to identify the H and D positions in the $Ca_3(BD_4)_3(BO_3)$ phase. Hence, we have replaced the H atom by D in the H1 to H7 sites. The calculated frequencies for the IR active modes are given in Table 1. From the theoretical simulation we conclude that statistically H occupies D1 to D7 sites randomly. It does not occupy any single well-defined crystallographic sites. The experimentally obtained IR spectra show two B-H broad peaks (around 2297 and 2382 cm^{-1}). The net difference between these two peaks is only 80 cm^{-1}. From the theoretically simulated IR spectra for the different H occupancy (with respect to the sites D1-D7) the peak position varies within 80 cm^{-1}. The simulated IR spectra for one of the configurations are shown in Fig. 6.

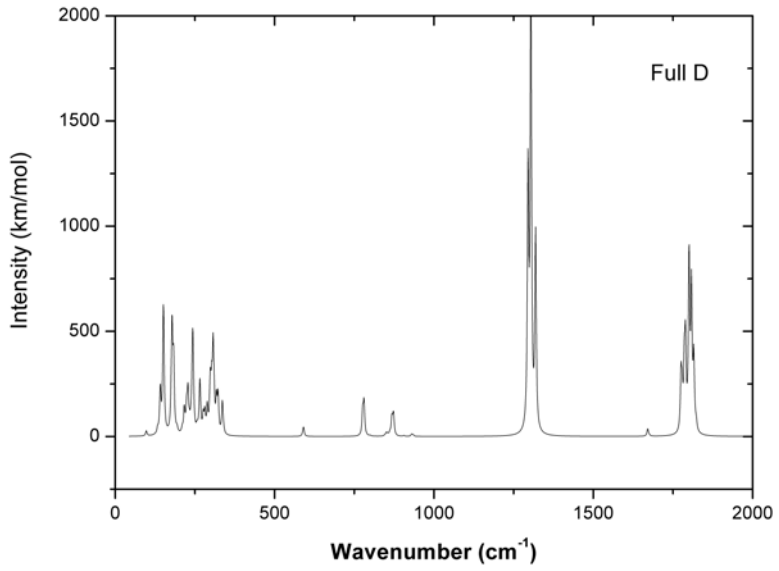

Fig. 5. Theoretically simulated IR spectra for the $Ca_3(BD_4)_3(BO_3)$ phase.

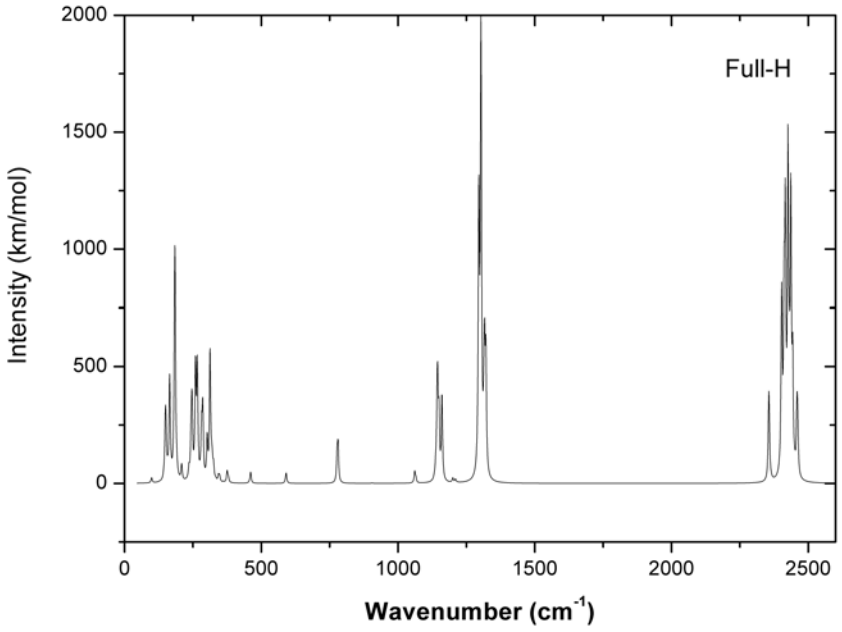

Fig. 6. Theoretically simulated IR spectra for the $Ca_3(BH_4)_3(BO_3)$ phase.

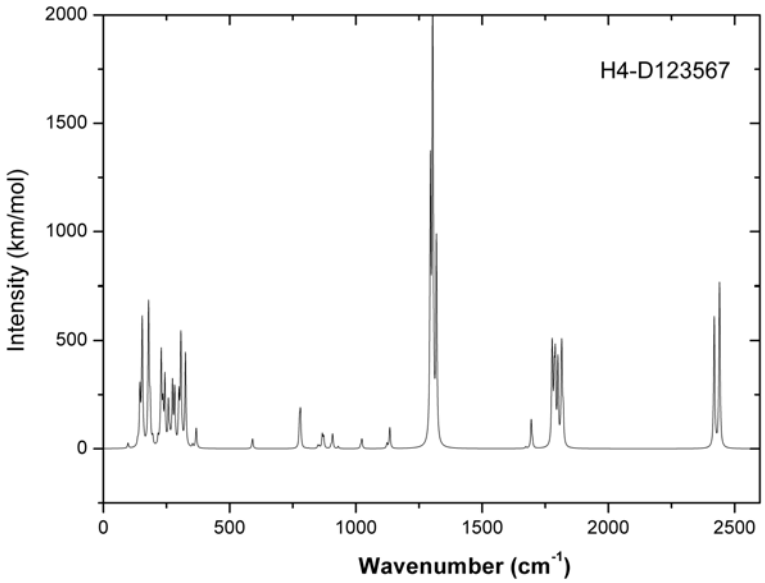

Fig. 7. Theoretically simulated IR spectra for the $Ca_3(BD_4)_3(BO_3)$ phase, where the D4 site is replaced by the H atom.

Table 1. Calculated frequency (in cm^{-1}) for the IR active modes, intensity (in km/mol), and the irreducible representation of the modes (irrep.) at the Γ point of the Brillouin zone for $Ca_3(BH_4)_3(BO_3)$, $Ca_3(BD_4)_3(BO_3)$, and $Ca_3(BHD_3)_3(BO_3)$ phases.

$Ca_3(BH_4)_3(BO_3)$			$Ca_3(BD_4)_3(BO_3)$			$Ca_3(BHD_3)_3(BO_3)$		
Frequency (cm^{-1})	IR intensity (km/mol)	Irrep.	Frequency (cm^{-1})	IR intensity (km/mol)	Irrep.	Frequency (cm^{-1})	IR intensity (km/mol)	Irrep.
98.97	21.808	B1	97.45	24.652	B1	97.58	23.758	B1
143.38	11.059	B1	132.88	23.259	B1	135.72	23.246	B1
144.22	2.867	A1	141.38	208.535	A1	144.33	27.633	A1
149.14	220.927	B1	143.54	2.885	B1	144.65	226.287	B1
151.45	153.246	B2	149.86	43.669	B2	149.95	42.885	B2
157.68	22.017	A1	151.28	578.992	A1	153.81	573.218	A1
168.18	31.760	B1	157.72	1.100	B1	158.89	5.862	B1
174.25	4.985	A1	176.01	87.841	A1	159.20	1.961	A1
183.28	510.251	B2	178.07	3.638	B2	178.09	203.475	B2
184.67	567.834	A1	178.35	460.229	A1	178.46	5.892	A1
189.99	1.611	B1	183.09	319.413	B1	179.31	473.759	B1
191.38	18.335	B2	191.29	1.643	B2	185.18	173.681	B2
208.71	66.982	B2	193.83	20.296	B2	195.33	36.325	B2
225.02	1.014	B1	210.25	22.701	B1	209.36	1.049	B1
230.90	1.230	A1	216.48	113.582	A1	216.60	39.614	A1
235.29	44.426	A1	221.17	16.834	A1	223.91	24.487	A1
243.27	165.725	B1	224.19	106.595	B1	227.49	22.568	B1
246.49	309.72	B2	228.04	185.865	B2	228.76	87.633	B2
252.57	3.613	B2	232.80	33.223	B2	229.34	325.272	B2
259.25	473.913	B1	237.01	36.996	B1	235.76	158.366	B1
265.65	362.276	A1	242.30	293.135	A1	243.40	310.003	A1
266.65	119.952	A1	244.23	271.935	A1	244.84	1.509	A1
281.21	202.646	B1	256.18	21.199	B1	257.44	198.594	B1
285.52	263.793	A1	258.51	11.763	A1	262.36	16.846	A1
286.92	49.007	B2	264.62	91.390	B2	263.17	26.187	B2
302.12	172.3013	A1	266.00	179.630	A1	267.73	12.577	A1
312.50	557.851	B2	275.99	79.610	B2	273.56	285.134	B2
318.20	47.315	A1	280.98	92.687	A1	281.62	113.430	A1
320.66	59.576	B1	288.66	118.355	B1	282.65	151.942	B1
325.31	56.864	B2	296.93	64.308	B2	299.27	219.772	B2
333.12	7.033	B1	298.53	183.252	B1	306.47	44.431	B1
343.44	26.997	B1	302.65	186.073	B1	306.80	408.238	B1
347.51	24.634	A1	307.16	375.802	A1	307.55	59.859	A1
361.78	3.187	B2	310.17	94.843	B2	313.16	18.665	B2
375.14	49.561	A1	317.52	145.516	A1	324.62	170.682	A1
379.48	19.911	B1	322.49	171.782	B1	324.99	262.586	B1
455.75	3.335	B2	336.01	102.071	B2	353.65	15.917	B2
460.82	43.079	A1	336.28	50.562	A1	367.60	90.378	A1
461.79	4.841	B1	339.89	16.308	B1	369.73	2.406	B1
588.38	7.012	B1	588.24	6.962	B1	588.27	7.055	B1
590.96	12.408	A1	590.77	29.730	A1	590.82	29.593	A1
591.08	29.314	B2	590.88	12.627	B2	590.88	12.684	B2
777.30	110.300	A1	776.43	111.821	A1	776.76	112.337	A1
780.65	148.968	B1	780.47	154.230	B1	780.49	153.975	B1
904.74	1.271	A1	801.08	1.245	A1	811.96	1.490	A1
1060.83	22.497	A1	846.46	3.829	A1	849.86	13.968	A1
1060.94	6.341	B2	851.06	15.059	B2	855.17	10.005	B2
1060.97	19.792	B1	855.35	6.273	B1	867.04	60.950	B1
1065.26	12.862	A1	861.71	13.630	A1	869.92	4.278	A1
1065.45	6.552	B1	866.89	11.306	B1	871.36	1.372	B1
1131.99	1.131	B2	868.09	69.868	B2	872.51	47.821	B2

1132.75	5.376	B1	871.59	39.642	B1	901.71	11.876	B1
1137.81	38.805	A1	873.49	75.849	A1	904.69	1.166	A1
1139.39	4.992	A1	904.96	2.243	A1	905.56	1.203	A1
1142.79	217.589	B2	906.32	1.586	B2	907.76	65.911	B2
1144.97	325.767	B1	929.77	9.119	B1	930.03	10.440	B1
1149.77	253.304	B2	931.34	1.614	B2	1018.64	12.174	B2
1160.43	364.538	A1	934.28	5.119	A1	1023.56	28.720	A1
1166.85	1.090	B1	934.80	2.384	B1	1023.61	14.875	B1
1200.48	18.661	B2	1295.16	1214.543	B2	1123.21	23.369	B2
1209.24	3.083	A1	1304.06	2188.409	A1	1134. 14	90.518	A1
1210.12	10.925	B1	1318.86	924.919	B1	1136.15	9.335	B1
1295.3	1151.894	A1	1670.36	19.313	A1	1295.23	1206.156	A1
1303.19	1876.971	B2	1670.89	13.487	B2	1304.19	2175.586	B2
1311.14	38.356	B2	1672.78	5.230	B2	1318.91	918.180	B2
1314.48	178.805	B2	1675.55	2.392	B2	1672.63	4.236	B2
1316.66	421.367	B1	1775.27	177.657	B1	1672.98	3.264	B1
1318.46	3.589	A1	1775.46	81.773	A1	1694.52	130.060	A1
1321.24	462.14	B1	1778.84	161.983	B1	1699.35	17.689	B1
2355.06	103.84	A1	1785.54	292.257	A1	1699.43	6.5007	A1
2355.96	186.674	B2	1789.26	389.512	B2	1776.33	158.398	B2
2357.27	135.348	B1	1798.77	28.003	B1	1777.05	203.817	B1
2365. 9	4.692	A1	1800.50	807.772	A1	1778.94	179.487	A1
2401.61	195.172	A1	1807.98	662.371	B1	1785.62	257.177	A1
2402.51	266.440	B1	1815.16	324.598	A1	1789.61	360.193	B1
2403.37	345.247	B2	1815.91	4.037	B1	1799.98	384.910	B2
2411.66	655.023	A1	1818.53	9.8262	B2	1813.77	177.706	A1
2416.04	1006.348	B1	1822.03	18.611	A1	1815.42	339.169	B1
2425.98	1330.444	B2	1823.89	21.432	B1	1820.34	87.802	B2
2431.04	207.708	B2				1821.89	46.446	B2
2436.25	1141.593	A1				1822.22	14.597	A1
2442.92	437.764	B1				2419.16	601.873	B1
2444.592	5.445	A1				2440.14	759.369	A1
2450. 82	20.326	B1				2446.91	1.2905	B1
2458. 05	179.484	B2						
2459. 77	145.763	A1						
2461. 02	125.783	B1						