

Electronic Supplementary Information

Title: Halide substitution in $\text{Ca}(\text{BH}_4)_2$

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Table S1. Computed unit cell parameters and volume of the four $\text{Ca}(\text{BH}_4)_{1-x}\text{Cl}_x$ and the four $\text{Ca}(\text{BH}_4)_{1-x}\text{Br}_x$ models with x ranging from 0 (pure tetragonal $P4_2$ $\text{Ca}(\text{BH}_4)_2$) to 1 (pure tetragonal $P4_2/mnm$ CaCl_2 or CaBr_2). Unit cell vectors are reported in Å, angles in degrees and volume in Å³.

$(1-x)\text{Ca}(\text{BH}_4)_2 + x\text{CaCl}_2$							
x	a	b	c	α	β	γ	Volume
0.00	6.643	6.643	4.405	90.0	90.0	90.0	194.4
0.25	6.608	6.541	4.348	90.0	90.0	90.0	188.0
0.50	6.443	6.556	4.304	90.0	90.0	89.6	181.8
0.75	6.337	6.478	4.223	90.9	90.7	90.5	173.3
1.00	6.404	6.404	4.266	90.0	90.0	90.0	175.0
$(1-x)\text{Ca}(\text{BH}_4)_2 + x\text{CaBr}_2$							
x	a	b	c	α	β	γ	Volume
0.00	6.643	6.643	4.405	90.0	90.0	90.0	194.4
0.25	6.727	6.559	4.394	90.0	90.0	92.8	193.7
0.50	6.831	6.453	4.340	90.5	88.4	91.6	191.1
0.75	6.548	6.759	4.329	89.8	89.8	88.5	191.5
1.00	6.793	6.793	4.415	90.0	90.0	90.0	203.7

Table S2. Computed unit cell parameters and volume of both orthorhombic and tetragonal CaCl_2 and CaBr_2 compared to the experimental values (references: C.J. Howard, B. Kennedy, Phys. Rev. B 70, 144102, 2004 for CaBr_2 and C.J. Howard, B. Kennedy and C. Curfs, Phys. Rev. B, 72, 214114, 2005 for CaCl_2).

CaCl_2							
$Pnnm$	a	b	c	α	β	γ	Volume
Computed	6.452	6.284	4.234	90.0	90.0	90.0	171.7
Experimental	6.438	6.288	4.178	90.0	90.0	90.0	169.1
$P4_2/mnm$	a	b	c	α	β	γ	Volume
Computed	6.404	6.404	4.266	90.0	90.0	90.0	175.0
Experimental	6.383	6.383	4.204	90.0	90.0	90.0	171.3
CaBr_2							
$Pnnm$	a	b	c	α	β	γ	Volume
Computed	6.941	6.473	4.371	90.0	90.0	90.0	196.4
Experimental	6.888	6.653	4.377	90.0	90.0	90.0	200.6
$P4_2/mnm$	a	b	c	α	β	γ	Volume
Computed	6.793	6.793	4.415	90.0	90.0	90.0	203.7
Experimental	6.811	6.811	4.418	90.0	90.0	90.0	204.9