Facile Solvent-free Synthesis of Alkali Metal Dodecaborate $M_2B_{12}H_{12}$ (M = Li, Na, K)

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Supporting Information

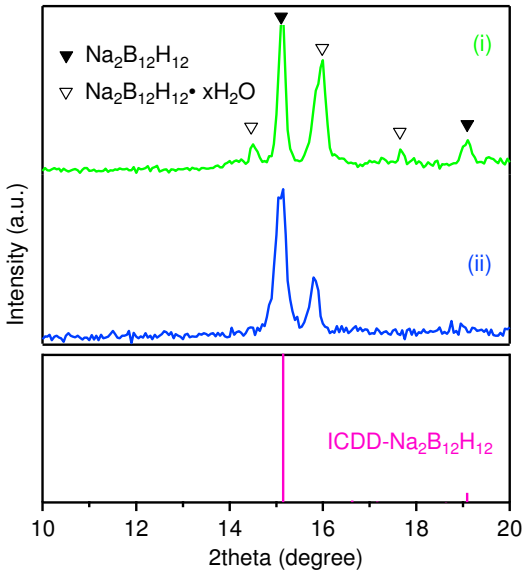

Figure S1. XRD patterns of synthesized $Na_2B_{12}H_{12}$ compared with ICDD. (i) 5h ball milled $2NaBH_4 + B_{10}H_{14}$ followed by heat treatment at 450 ℃ for 20 h (exposed in air for 1 min before measurement); (ii) 5h ball milled $2NaH + 1.2B_{10}H_{14}$ followed by heat treatment at 450 ℃ for 20 h.

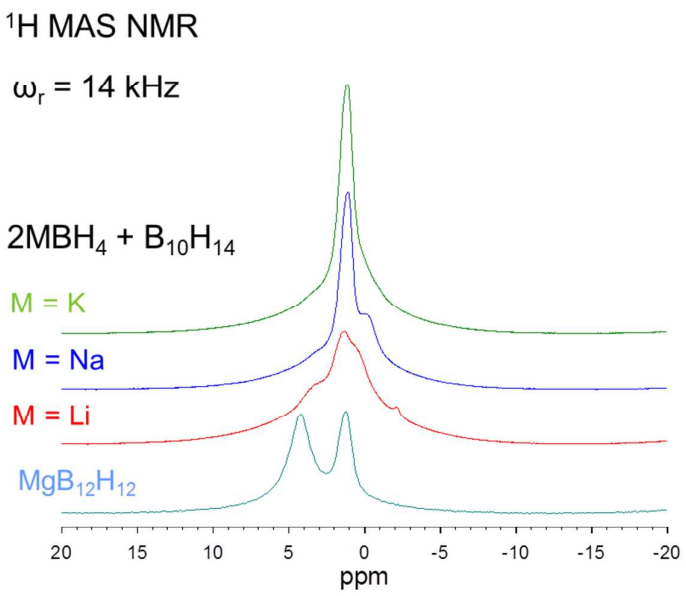

Figure S2. ^{1}H MAS NMR spectra of synthesized samples from $2MBH_4 + B_{10}H_{14}$ at different reaction conditions compared with $MgB_{12}H_{12}$ as reference ($2LiBH_4 + B_{10}H_{14}$: 5h ball milling, heat treatment at 200 ℃ for 15 h; $2NaBH_4 + B_{10}H_{14}$: 5h ball milling, heat treatment at 450 ℃ for 20 h; $2KBH_4 + B_{10}H_{14}$: 5h ball milling, heat treatment at 450 ℃ for 20 h). A peak at 4.8 ppm seen for $Mg_2B_{12}H_{12}$ is originated from crystalline water which would not be removed without decomposing the $B_{12}H_{12}$ anion.

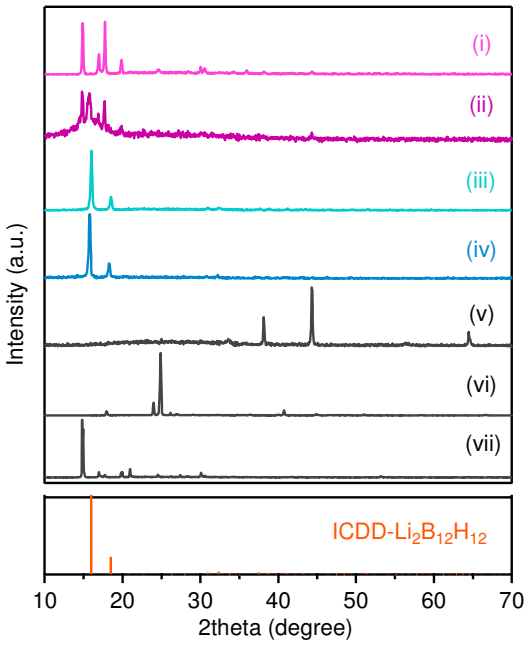

Figure S3. XRD patterns of synthesized $Li_2B_{12}H_{12}$ using different routes and conditions compared with ICDD. (i) and (ii) are 5h ball milled 2LiH + $1.2B_{10}H_{14}$ followed by heat treatment at 200 ℃ for 10 h and at 200 ℃ for 15 h; (iii) and (iv) are 5h ball milled $2LiBH_4$ + $B_{10}H_{14}$ followed by heat treatment at 200 ℃ for 10 h and at 200 ℃ for 15 h; (v), (vi) and (vii) are LiH, $LiBH_4$ and $B_{10}H_{14}$ as reference.