

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

Liqing He[†], Hai-Wen Li^{, ‡§}, Son-Jong Hwang[#], Etsuo Akiba^{†‡§}*

[†] Department of Mechanical Engineering, Faculty of Engineering, Kyushu University,

Fukuoka 819-0395, Japan

[‡] International Research Center for Hydrogen Energy, Kyushu University, Fukuoka

819-0395, Japan

[§] WPI International Institute for Carbon-Neutral Energy Research (WPI-I2CNER), Kyushu

University, Fukuoka 819-0395, Japan

[#] Division of Chemistry and Chemical Engineering, California Institute of Technology,

Pasadena, California 91125, USA

***Corresponding Author:** li.haiwen.305@m.kyushu-u.ac.jp.

Supporting Information

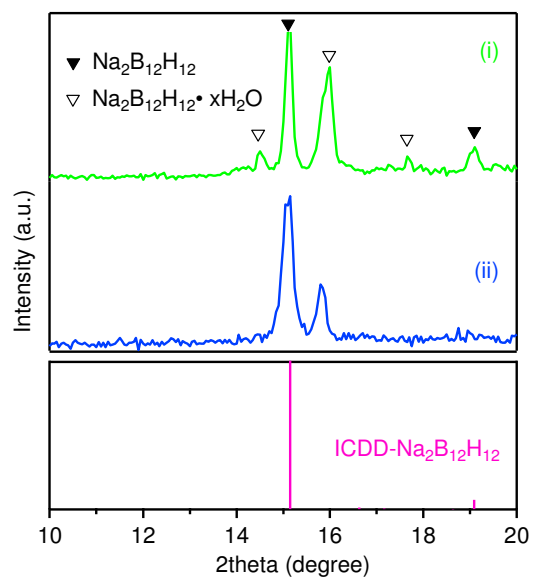


Figure S1. XRD patterns of synthesized $\text{Na}_2\text{B}_{12}\text{H}_{12}$ compared with ICDD. (i) 5h ball milled $2\text{NaBH}_4 + \text{B}_{10}\text{H}_{14}$ followed by heat treatment at $450\text{ }^\circ\text{C}$ for 20 h (exposed in air for 1 min before measurement); (ii) 5h ball milled $2\text{NaH} + 1.2\text{B}_{10}\text{H}_{14}$ followed by heat treatment at $450\text{ }^\circ\text{C}$ for 20 h.

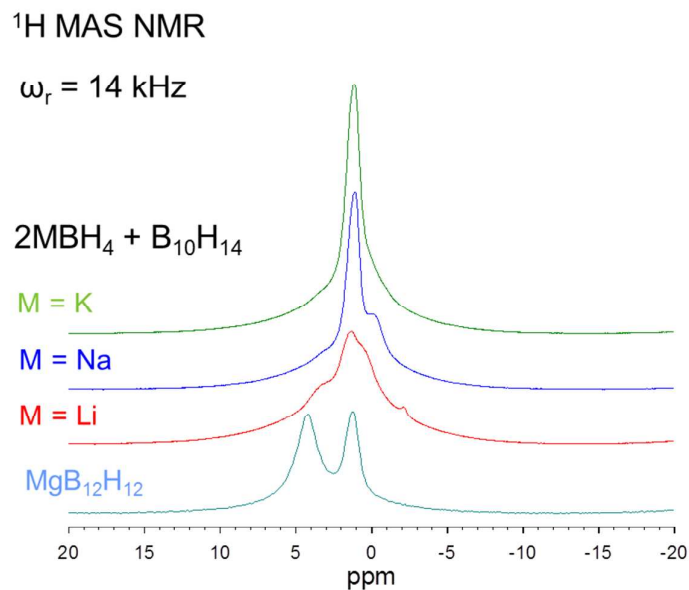


Figure S2. ^1H MAS NMR spectra of synthesized samples from $2\text{MBH}_4 + \text{B}_{10}\text{H}_{14}$ at different reaction conditions compared with $\text{MgB}_{12}\text{H}_{12}$ as reference ($2\text{LiBH}_4 + \text{B}_{10}\text{H}_{14}$: 5h ball milling, heat treatment at $200\text{ }^\circ\text{C}$ for 15 h; $2\text{NaBH}_4 + \text{B}_{10}\text{H}_{14}$: 5h ball milling, heat treatment at $450\text{ }^\circ\text{C}$ for 20 h; $2\text{KBH}_4 + \text{B}_{10}\text{H}_{14}$: 5h ball milling, heat treatment at $450\text{ }^\circ\text{C}$ for 20 h). A peak at 4.8 ppm seen for $\text{Mg}_2\text{B}_{12}\text{H}_{12}$ is originated from crystalline water which would not be removed without decomposing the $\text{B}_{12}\text{H}_{12}$ anion.

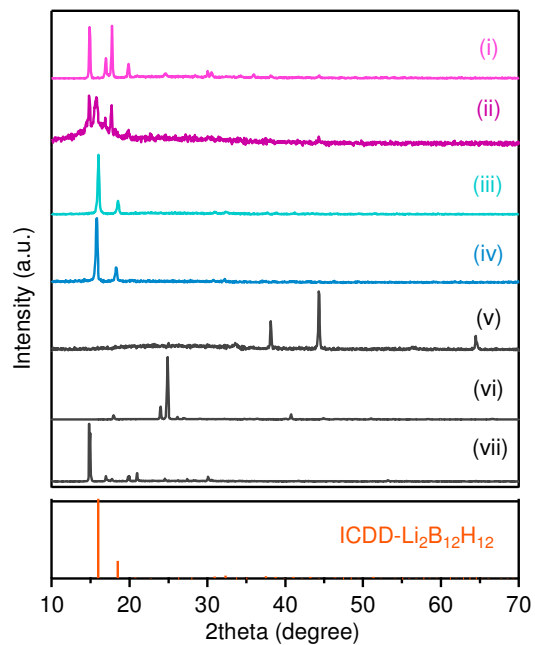


Figure S3. XRD patterns of synthesized $\text{Li}_2\text{B}_{12}\text{H}_{12}$ using different routes and conditions compared with ICDD. (i) and (ii) are 5h ball milled $2\text{LiH} + 1.2\text{B}_{10}\text{H}_{14}$ followed by heat treatment at $200\text{ }^\circ\text{C}$ for 10 h and at $200\text{ }^\circ\text{C}$ for 15 h; (iii) and (iv) are 5h ball milled $2\text{LiBH}_4 + \text{B}_{10}\text{H}_{14}$ followed by heat treatment at $200\text{ }^\circ\text{C}$ for 10 h and at $200\text{ }^\circ\text{C}$ for 15 h; (v), (vi) and (vii) are LiH , LiBH_4 and $\text{B}_{10}\text{H}_{14}$ as reference.