Synthesis of Unsolvated $M_xB_{12}H_{12}$(M=Na, K, Mg) by a Facile Autoclave Route

*J. Wang[a], H.W. Li[b], Y. Filinchuk[a] *, I. Golub[a] , T. Steenhaut[a]*

[a] Institute of Condensed Matter and Nanosciences, Université Catholique de Louvain, Place Louis Pasteur 1, 1348 Louvain-la-Neuve, Belgium
[b] Platform of Inter/Transdisciplinary Energy Research, Kyushu University, Fukuoka 819-0395, Japan

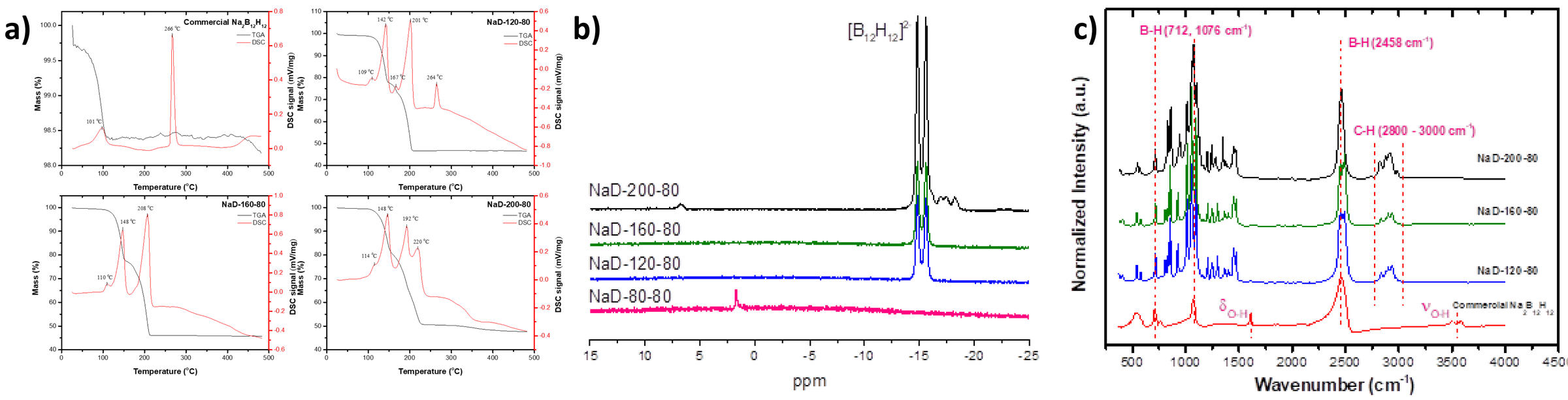
Contact email: yaroslav.filinchuk@uclouvain.be

Introduction

Metal dodecaborates ($M_xB_{12}H_{12}$), is a promising new class of solid-state electrolytes, that combine high conductivity with electrochemical and thermal stability. $M_xB_{12}H_{12}$ is generally synthesized using boranes and borohydrides followed by a careful purification process. In this study, we proposed a new and facile synthesis process of $M_xB_{12}H_{12}$ using borane complex and borohydrides with autoclave method. $M_xB_{12}H_{12}$ have been successfully synthesized by the reaction of MBH_4 with $DMS{\cdot}BH_3$, based on the equation: $M_xBH_4 + (CH_3)_2S{\cdot}BH_3 \rightarrow M_{2/x}B_{12}H_{12} + (CH_3)_2S + H_2$ (M = Na, K, Mg). Our first challenge focused on the synthesis of $Na_2B_{12}H_{12}$, and then applied the method to the synthesis of $MgB_{12}H_{12}$ and $K_2B_{12}H_{12}$.

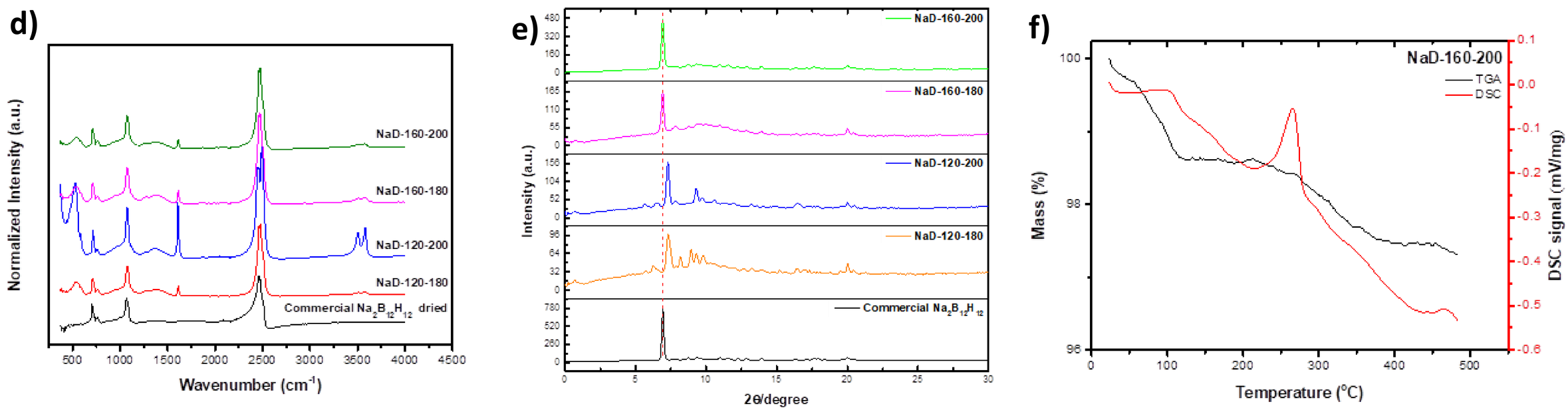
Results and Discussion

1st step: Effect of reaction temperature on the synthesis of $Na_2B_{12}H_{12}$



1. Characterization of as-synthesized NaD-X-80 samples. a) TGA/DSC, b) 11B NMR, c) FTIR

2st step: Effect of drying temperature on the synthesis of $Na_2B_{12}H_{12}$



2. Effect of drying temperature on as-prepared NaD-X-Y samples. d) FTIR spectrum, e) PXRD patterns, f) TGA/DSC patterns of NaD-160-200

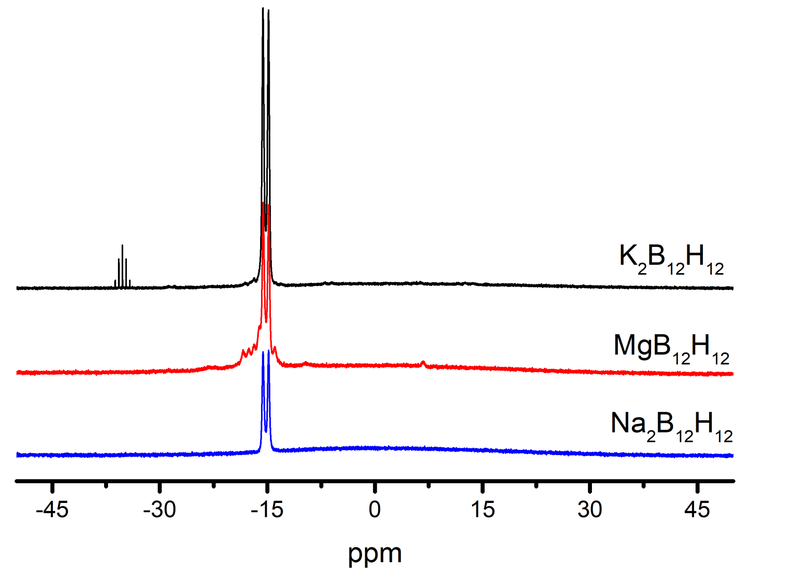
3st step: Synthesis of $M_xB_{12}H_{12}$

Table 1. ICP analysis of NaD-160-200

Materials	Fraction (wt %)		Na/B ratio	error
	Na	B		
NaD-160-200	22.11	61.40	0.3601	3.3%
Calculated Value	24.21	69.47	0.3485	

Proposed Equation: $MxBH_4 + (CH_3)_2{\cdot}BH_3 \rightarrow Na_{x/2}B_{12}H_{12} + (CH_3)_2S + H_2$

M-X-Y: M (MBH_4); **B** ($BH_3{\cdot}(CH_3)_2$); **X** (reaction temperature); **Y** (different drying temperature),



g) 11B NMR spectra of as-synthesized $M_xB_{12}H_{12}$

Conclusions & Perspectives:

1. A serious of alkali metal dodecaborates were successfully synthesized *via* reaction between metal borohydrides and borane complex.
2. Reaction temperature and drying temperature plays an important role on the final products.

Acknowledgements:

China Scholarship Council (CSC), FNRS, IMCN@UCLouvain, SNBL/ESRF

Reference:

[1] Chen, X. M., Ma, N., Liu, X. R., Wei, C., Cui, C. C., Cao, B. L., Guo, Y., Wang, L. S., Gu, Q., Chen, X. Facile Synthesis of Unsolvated Alkali Metal Octahydrotriborate Salts MB_3H_8 (M=K, Rb, and Cs), Mechanisms of Formation, and the Crystal Structure of KB_3H_8. *Angew. Chem. Int. Ed.* **2019**, *58,* 2720-2724.