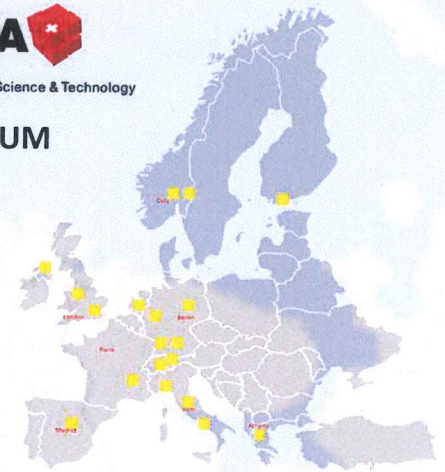


9th INTERNATIONAL SYMPOSIUM HYDROGEN & ENERGY

Integrating European Infrastructure to support and development of Hydrogen- and Fuel Cell Technologies towards European Strategy for Sustainable, Competitive and Secure Energy

www.H2FC.eu



SYNTHESIS AND CHARACTERISATION OF NEW AMIDOBORANES

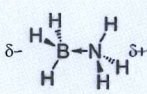
NIKOLA BILIŠKOV (1), IVAN HALASZ (1), ELSA CALLINI (2), ANDREAS BORGSCHULTE (2), ANDREAS ZÜTTEL (2)

(1) Ruđer Bošković Institute, Division of Materials Chemistry, 10000 Zagreb, Croatia

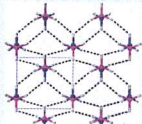
(2) EMPA, Materials and Technology, Dept. Hydrogen and Energy, 8600 Dübendorf, Switzerland

PROBLEM AND ASPECTS

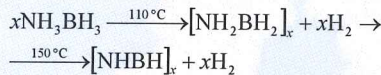
Ammonia borane (NH_3BH_3 , AB)



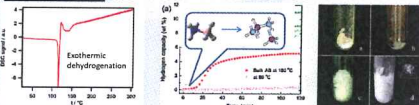
$M = 30,87 \text{ g mol}^{-1}$
 $w(\text{H}) = 19,6\%$
 $\rho(\text{H}) = 145 \text{ g dm}^{-3}$
 $t_1 = 110 \text{ }^\circ\text{C}$
 $t_2 = 150 \text{ }^\circ\text{C}$



Extensive dihydrogen bonding network



Drawbacks:

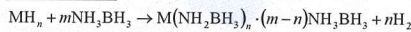


- Complex dehydrogenation mechanism
- Release of unwanted side-products

A combination of chemical modification (substitution of one protic hydrogen by electropositive metal) with destabilisation of dihydrogen bonding network was employed here to overcome these drawbacks.

EXPERIMENT OR MEASUREMENT EXECUTED

Preparation:



30 min milling in Ar

Characterisation:



Single-reflection ATR IR spectroscopy



Powder XRD



Variable-temperature Raman spectroscopy

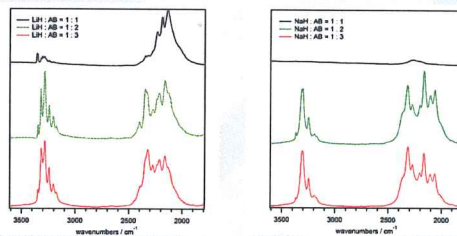


DSC

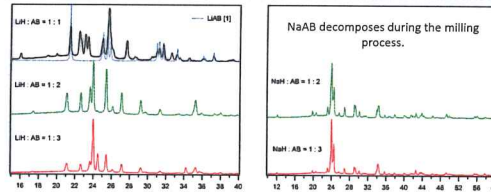
RESULTS AND CONCLUSION

MAB·MAB ($M = \text{Li, Na}; M = 0, 1, 2$)

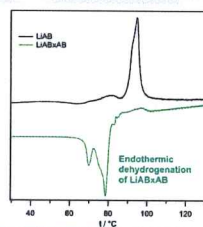
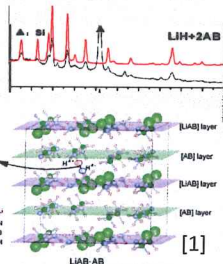
IR spectra



Powder XRD patterns

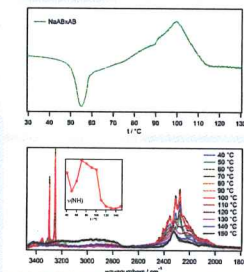
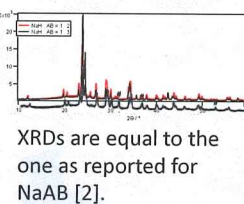


LiAB is present as a mixture of α and β phase [1]



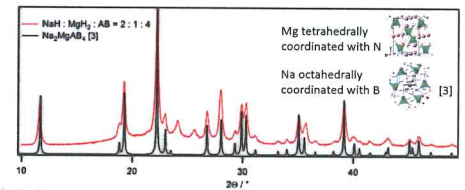
A considerable drop of dehydrogenation temperature for LiAB with respect to AB and LiAB.

All attempts to obtain NaAB by milling 1:1 mixture of NaH and AB were unsuccessful.

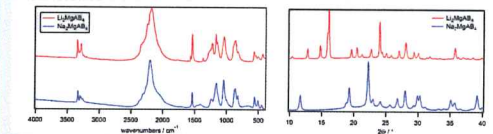


Decrease of both $\nu(\text{NH})$ and $\nu(\text{BH})$ intensity observed at $50 \text{ }^\circ\text{C}$, which is followed by a reorganisation. At $>110 \text{ }^\circ\text{C}$ a steep drop is evident.

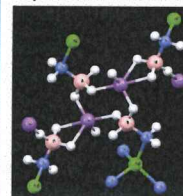
$\text{Li}_2\text{Mg}(\text{AB})_4$



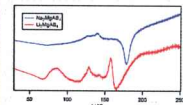
Successful preparation of $\text{Na}_2\text{Mg}(\text{AB})_4$ [3].



Very similar IR spectra, but different XRDs. Similar bonding in $\text{Na}_2\text{Mg}(\text{AB})_4$ and $\text{Li}_2\text{Mg}(\text{AB})_4$, but different packing in solid state, as confirmed by structure solved by Rietveld method.

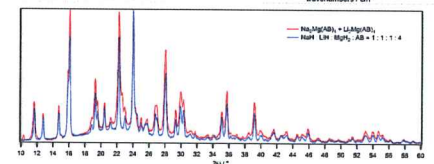
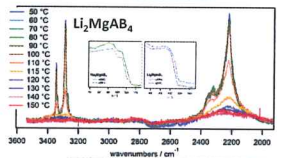


Structure of $\text{Li}_2\text{Mg}(\text{AB})_4$, as solved by Rietveld method: Mg tetrahedrally coordinated with N, Li coordinated with 5 B atoms.



Complexity of DSC indicates some solid-state phase transitions in $\text{Li}_2\text{Mg}(\text{AB})_4$.

Variable-temperature Raman spectra reveal synchronous decomposition of NH_3 and BH_3 groups.



Attempts to prepare trimetallic amidoborane $\text{LiNaMg}(\text{AB})_4$ as well as adducts of bimetallic MABs with AB, $\text{Li}_2\text{Mg}(\text{AB})_4 \cdot \text{AB}$ and $\text{Na}_2\text{Mg}(\text{AB})_4 \cdot \text{AB}$, were unsuccessful.

REFERENCES

- [1] Wu et al. *Inorg. Chem.* 49 (2010) 4319
- [2] Fijalkowski, Grochala, *J. Mater. Chem.* 19 (2009) 2043
- [3] Wu et al. *Chem. Commun.* 47 (2011) 4102

This project became indirectly funded through European Commission by occupying transnational access of H2FC European Infrastructure which is funded by FP7 Capacity Program, Grand Agreement no. FP7-284522