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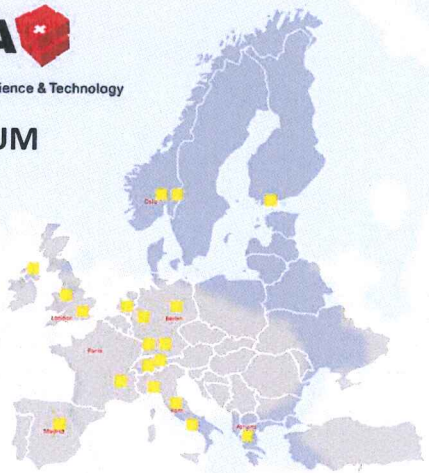

SYNTHESIS AND CHARACTERISATION OF NEW AMIDOBORANES

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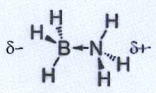
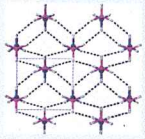
PROBLEM AND ASPECTS

Ammonia borane (NH_3BH_3, AB)



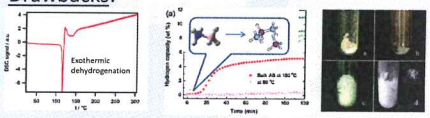
M = 30,87 g mol^{-1}
w(H) = 19,6%
ϕ(H) = 145 g dm^{-3}
t_1 = 110 °C
t_2 = 150 °C



Extensive dihydrogen bonding network

$$xNH_3BH_3 \xrightarrow{110\,^\circ C} [NH_2BH_2]_x + xH_2 \rightarrow$$
$$\xrightarrow{150\,^\circ C} [NHBH]_x + xH_2$$

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:

$$MH_n + mNH_3BH_3 \rightarrow M(NH_2BH_3)_n \cdot (m-n)NH_3BH_3 + nH_2$$

30 min milling in Ar

Characterisation:

Single-reflection ATR IR spectroscopy

Powder XRD

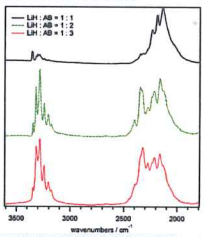
Variable-temperature Raman spectroscopy

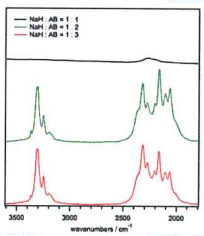
DSC

RESULTS AND CONCLUSION

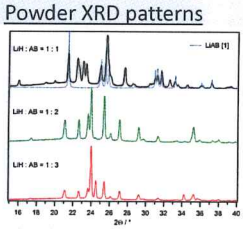
MAB·mAB (M = Li, Na; m = 0, 1, 2)

IR spectra

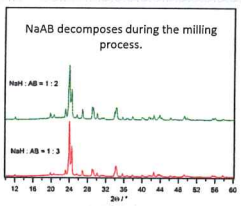




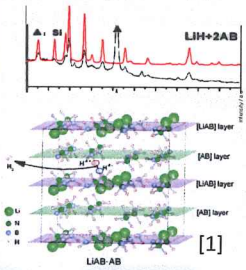
Powder XRD patterns

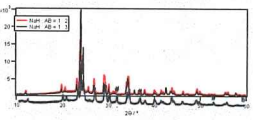


LiAB is present as a mixture of α and β phase [1]

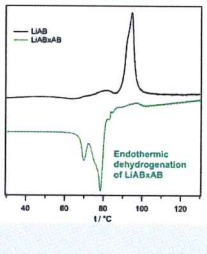


All attempts to obtain NaAB by milling 1:1 mixture of NaH and AB were unsuccessful.

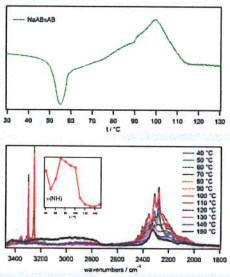




XRDs are equal to the one as reported for NaAB [2].

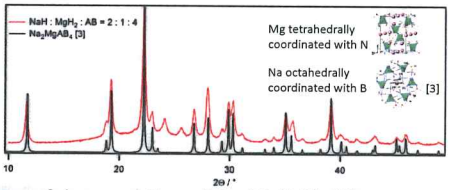


A considerable drop of dehydrogenation temperature for LiAB with respect to AB and LiAB.

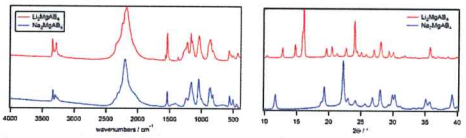


Decrease of both ν(NH) and ν(BH) intensity observed at 50 °C, which is followed by a reorganisation. At >110 °C a steep drop is evident.

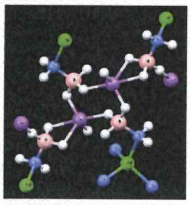
$Li_2Mg(AB)_4$



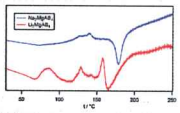
Successful preparation of $Na_2Mg(AB)_4$ [3].



Very similar IR spectra, but different XRDs. Similar bonding in $Na_2Mg(AB)_4$ and $Li_2Mg(AB)_4$, but different packing in solid state, as confirmed by structure solved by Rietveld method.

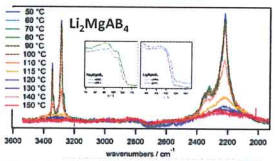


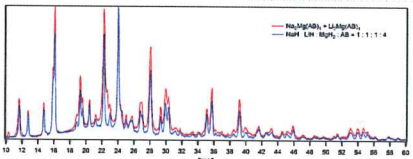
Structure of Li_2MgAB_4, as solved by Rietveld method: Mg tetrahedrally coordinated with N, Li coordinated with 5 B atoms.



Complexity of DSC indicates some solid-state phase transitions in Li_2MgAB_4.

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





Attempts to prepare trimetallic amidoborane $LiNaMg(AB)_4$ as well as aducts of bimetallic MABs with AB, $Li_2Mg(AB)_4$·AB and $Na_2Mg(AB)_4$·AB, were unsuccessful.

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[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

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