

[6] T. Bernert *et al.* (2016), *Acta Crystallogr. B.*, 72, 232–240.

[7] P. J. Schapiro (1962), PhD Thesis, Refcode CSD: DMABDI.

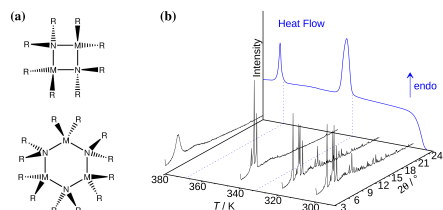


Figure 1. (a) Typical molecular structures of amino adducts of group 13 elements (M) with R = H or alkyl moieties. (b) *In-situ* diffractograms during heating of dimethylaminoalane together with DSC data.

Keywords: Solid-State Hydrogen Storage, Phase Transitions, Molecular Crystals, Aminoalanes, Aminoboranes

MS19-P4 Structural design principles for close packed Na and Li solid-electrolytes built from mixed anion borane lattices

Matteo Brighi¹, Pascal Schouwink¹, Yolanda Sadikin¹, Radovan Cerny¹

¹. Laboratory of Crystallography, DQMP, University of Geneva, 24 Quai Ernest-Ansermet, CH-1211 Genève

email: matteo.brighi@unige.ch

Energy storage solutions on a large scale have long been identified as a primary target within renewable energy research. While various complex hydrides, such as the salts built from the $[\text{BH}_4]^-$ anion, have shown high Li^+ ionic conductivity, the compound family of the metal boranes are more promising contenders when it comes to Na-superionics and all-solid battery concepts. Very recently, the complex anion landscape of complex hydrides has been extended to include the carborane (CB) $[\text{CB}_n\text{H}_{12}]^-$. When used to template close-packed ionic conductors, they show the highest reported Li^+ and Na^+ ionic conductivities of all reported complex hydrides¹ and are amongst the highest for Na solid electrolytes in general. Due to their quasi-spherical shape, this molecule easily forms the cubic close packed structure (ccp), an hard backbone to tailor vacancy concentration achieving high ionic mobility², which is boosted additionally by well-known “paddle wheel effect”³. We present different approaches to design in particular Na-conducting solid electrolytes with ever lower operating temperatures. On the one hand, it is conceptually straightforward to rebuild benchmark conductors from the literature. In this sense, the ionic conductor RbAg_4I_5 was taken as a template to reproduce its CB analogues, resulting in double cation phases containing alkali metals, and with an ideal composition of $\text{CsA}_4(\text{CB}_{11}\text{H}_{12})_5$ ($A = \text{Li}^+, \text{Na}^+$) in the specific case of the parent phase RbAg_4I_5 . The ionic mobility of the resulting new phases will be presented and related to the crystal structure. On the other hand, we show how the close packing of the anion lattice may be controlled by anion-mixing of CB $[\text{CB}_{11}\text{H}_{12}]^-$ and dodeca-boranes $[\text{B}_{12}\text{H}_{12}]^{2-}$, both their Na-endmembers known to have superionic *ht*-phases. Making use of the knowledge of preferred coordination polyhedra in higher boranes, this approach allows us to control the occupancy of tetrahedral (T) and octahedral (O) vacancies by modifying the carborane – dodeca-borane ratio, made possible due to the different charges of the polyanions. A control of site occupancies in packed lattices is known to be the key point to achieve high ionic conductivities at a suitable temperature and therefore highly promising approach to tailor metal boranes for battery application.

References: 1. Tang *et al* *Energy. Environ. Sci.*, 2015, 8, 3637 2. Wang *et al* *Nat. Mat.* 2015, 14, 1026 3. Jansen *Angew. Chem. Int. Ed.* 1991, 30, 1547

Keywords: ionic conductor, solid electrolyte, Li battery, Na battery, closo-boranes, carboranes