

**Experiment title:**

Mixed anion lithium and sodium closo-boranes/carba closoboranes and borohydrides/borates as ionic conductors

**Experiment number:**

01-02-1151

<b>Beamline:</b>	<b>Date of experiment:</b> from: 17.05.2017 to: 20.05.2017	<b>Date of report:</b> 13.09.2017
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**Report:***Synthesis*

The precursors  $\text{TiCl}_2$ ,  $\text{CrCl}_2$ ,  $\text{MnCl}_2$ ,  $\text{CoCl}_2$ ,  $\text{CuCl}_2$ ,  $\text{CuCl}$ ,  $\text{FeCl}_2$ ,  $\text{NiCl}_2$ ,  $\text{ZnCl}_2$ ,  $\text{MgCl}_2$  and  $\text{Na}_2\text{B}_{12}\text{H}_{12}$  (Katchem) were used as purchased. The samples were prepared by ball-milling the mixtures



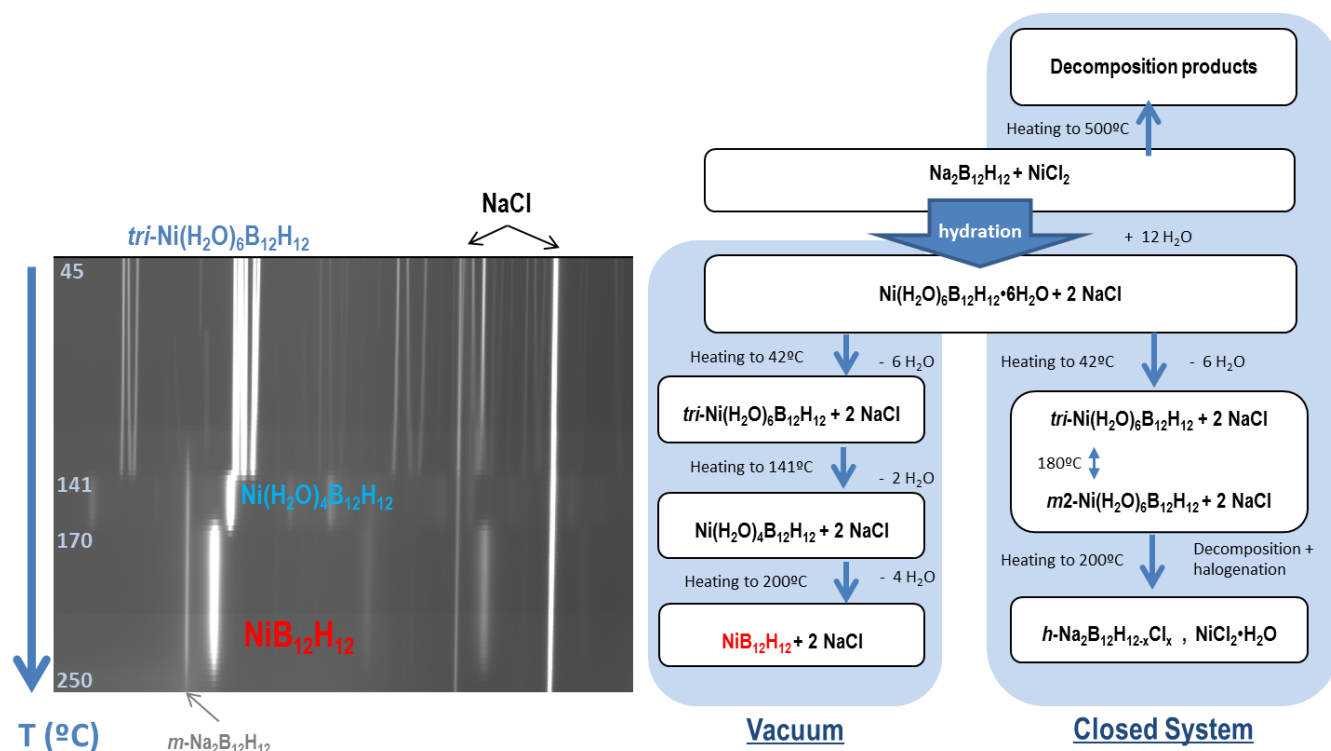
in a Fritsch Pulverisette 7 planetary mill, under Argon atmosphere. After the ball-milling, all samples (except the milled  $\text{NaB}_{12}\text{H}_{12} + \text{CuCl}$ ) were dissolved with 1 mL of water and then dried at 130 °C with a heating plate for 12 hours.

The data used for crystal structure and refinements were collected at the Swiss Norwegian Beamlines between 298 K and 673 K. SR-XPD were recorded on Dectris Pilatus M2 detector at a wavelength of 0.7225, 0.7280 and 0.8187 Å calibrated with NIST SRM640c Si standard. The 2D images were integrated and treated with the program Bubble. For all measurements, the samples were sealed into borosilicate capillaries of diameter 0.5mm (under Argon atmosphere), which were spun during data acquisition, and the temperature was controlled with a hot air blower calibrated with silver thermal dilatation. The dynamical vacuum was used to eliminate the solvent molecules in the capillaries during the measurement. Crystal structures were solved ab-initio using the software FOX and refined with the Rietveld method using TOPAS.

*Closo*-borane anion  $B_{12}H_{12}^{2-}$ , was modelled as rigid body with ideal icosahedral shape and with corresponding B-H and B-B distances.

$Ni^{2+}$

The thermally induced phase evolution in the samples depends on the gas pressure in the container. It is schematically drawn in the Fig. 1. Hydrated ball milled samples contain the hydrated phase  $Ni(H_2O)_6B_{12}H_{12} \cdot 6H_2O$  first reported in [1] with lower content of non-bonded water, and crystallizing in the cubic structure reported in [2]. Very rapidly by heating to 42 °C the non-bonded water molecules are removed, and novel structure of triclinic *tri*- $Ni(H_2O)_6B_{12}H_{12}$  is obtained. By further heating in a closed system first the polymorphic transition to novel monoclinic *m*<sub>2</sub>- $Ni(H_2O)_6B_{12}H_{12}$  is observed and then the decomposition to  $NiCl_2 \cdot H_2O$  and halogenated hexagonal *h*- $Na_2B_{12}H_{12-x}Cl_x$ . When heated under dynamic vacuum two bonded water molecules are removed before the polymorphic transformation and novel phase, *m*- $Ni(H_2O)_4B_{12}H_{12}$ , is obtained which by further heating releases remaining water molecules and forms anhydrous *m*- $NiB_{12}H_{12}$  stable on cooling to RT.



**Figure 1.** Left: Temperature dependent X-ray powder diffraction patterns (T-ramp) for water assisted ball-milled  $Na_2B_{12}H_{12} + NiCl_2$  mixture (heating rate 10 K/min under dynamic vacuum). Right: The reaction scheme for heating with dynamic vacuum and with closed system (capillary or aluminium crucible).

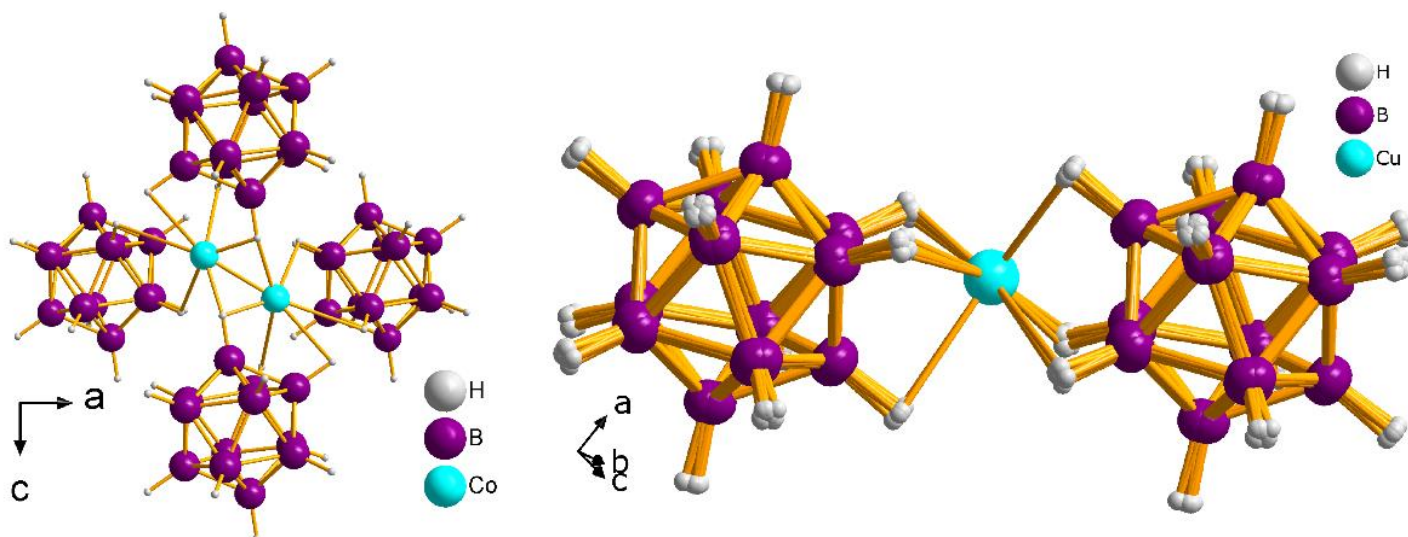
$Co^{2+}(Mn^{2+}, Fe^{2+}, Fe^{3+})$

Cobalt, manganese and iron containing samples prepared with water assisted ball-milling behave similarly. As the samples were annealed after ball-milling no phase containing six non-bonded water molecules was observed even if it was reported for cobalt [3]. The samples contain at RT already the phase with only six

bonded water molecules  $m_1\text{-M}(\text{H}_2\text{O})_6\text{B}_{12}\text{H}_{12}$   $\text{M}=\text{Co}, \text{Mn}, \text{Fe}$  described for Co in [3], structure type of  $\text{Cd}(\text{H}_2\text{O})_6\text{B}_{12}\text{H}_{12}$  [4]. On further heating in dynamic vacuum it releases 2 water molecules at 140 °C and the phase  $m\text{-M}(\text{H}_2\text{O})_4\text{B}_{12}\text{H}_{12}$   $\text{M}=\text{Co}, \text{Mn}, \text{Fe}$  is obtained, in analogy to Ni-system. On heating in closed system the all four six-water molecules complexes decompose into hydrated metal chlorides and monoclinic  $m\text{-Na}_2\text{B}_{12}\text{H}_{12}$ . In  $\text{Fe}^{3+}$  system the iron is reduced during synthesis to  $\text{Fe}^{2+}$  and hydrated iron chloride is present already in as prepared sample. Only anhydrous  $\text{CoB}_{12}\text{H}_{12}$  was obtained by further heating in dynamic vacuum and stays stable down to RT (Fig. 2), while manganese and iron sample shows presence of several phases from which only one was characterized in the iron sample as  $m\text{-Fe}(\text{H}_2\text{O})_2\text{B}_{12}\text{H}_{12}$  with novel structure type.

### $\text{Cu}^{2+}$ and $\text{Cu}^+$

In copper samples prepared by water assisted ball-milling no metal-water complexes form, but directly anhydrous cubic  $c\text{-Cu}_2\text{B}_{12}\text{H}_{12}$  is formed with copper in oxidation state (I) regardless the oxidation state in the starting copper chloride (Fig. 2).



**Figure 2.** Representation of Co and Cu *closo*-boranes:  $\text{Co}^{\text{II}}$  disordered on a tetrahedral site (left) and  $\text{Cu}^{\text{I}}$  bridging two *closo*-boranes (right).

- [1] Muetterties E.L., Balthis J.H., Chia Y.T., Knoth W.H., Miller H.C., *Inorg. Chem.*, **1964**, 3, 444-451.
- [2] V.Nguyen-Duc, *New Salt-Like Dodecahydro-Closo-Dodecaborates and Efforts for the Partial Hydroxylation of  $[\text{B}_{12}\text{H}_{12}]^{2-}$  Anions*, Thesis, University of Stuttgart, Stuttgart, 2009.
- [3] Tiritiris Io., *Untersuchungen zu Reaktivität, Aufbau und struktureller Dynamik von Salzartigen Closo-Dodekaboraten*, Thesis, University of Stuttgart, Stuttgart, 2004.
- [4] Tiritiris et al., *Z. Anorg. Allg. Chem.* **2005**, 631, 1593-1596.