ESRF	**Experiment title:** Metal borohydrides with spinel and garnet structure type: ionic conduction and hydrogen storage.	**Experiment number:** 01-02-1038
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Many different trimetallic borohydride systems containing two different alkali metal and rare-earth were checked in view of spinel or garnet types structure formation. A successful synthesis of the garnet borohydride $K_3Ce_2Li_3(BH_4)_{12}$ is reported in the ball-milled system:

$12\ LiBH_4 + 4\ BH_4 + 3\ CeCl_3$

with an ideal reaction as

$$9\ LiBH_4 + 3\ KBH_4 + 2\ CeCl_3 \rightarrow\ K_3Ce_2Li_3(BH_4)_{12} + 6\ LiCl$$

General formula for the garnet is $X_3Y_2Z_3O_{12}$ with three cation sites *X*, *Y* and *Z*:

	X_3	Y_2	Z_3	O_{12}
s.g. Ia-3*d*	24*c*	16*a*	24*d*	96*h*
	dist. cube	octa	tetra	
$Ca_3Al_2Si_3O_{12}$	Ca^{2+}	Al^{3+}	Si^{4+}	
$Y_3Al_5O_{12}$ (YAG-garnet)	Y^{3+}	Al^{3+}	Al^{3+}	
$K_3Ce_2Li_3(BH_4)_{12}$	**K^{1+}**	**Ce^{3+}**	**Li^{1+}**	**BH_4**

The garnet borohydride has been for the first time observed as a bimetallic $KCd(BH_4)_3$ [1]:

s.g. Ia-3	24*d*	8*a*,8*b*	24*d*	48*e*,48*e*
$KCd(BH_4)_3$	**K^{1+}**	**$K^{1+}Cd^{2+}$**	**Cd^{2+}**	**BH_4, BH_4**

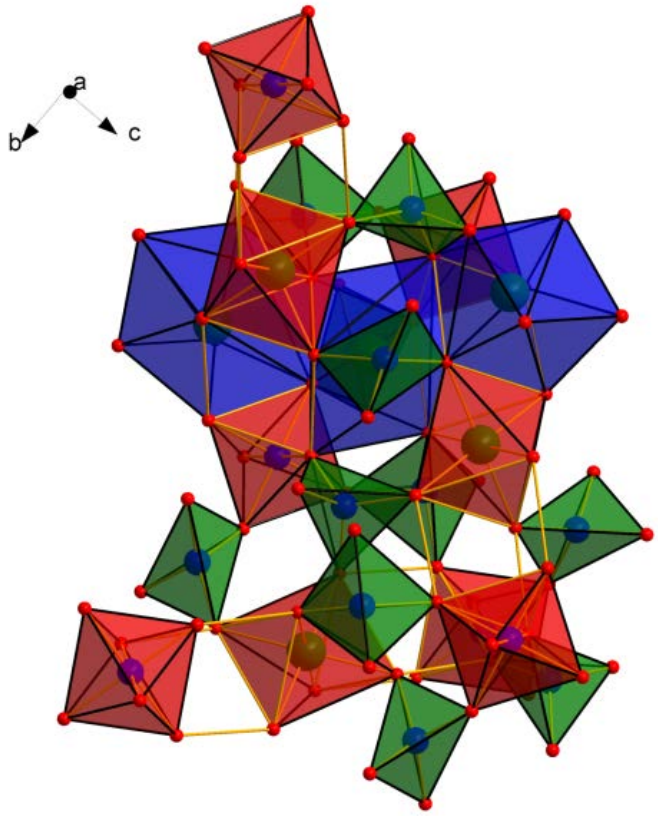

Figure 1: Typical view of a garnet-type structure with three cation sites: octahedral in red, tetrahedral in green and dodecahedral (twisted cube) in blue.

This first successful synthesis of a garnet borohydride is a starting point for preparation of borohydrides solid-state electrolytes. Disordered oxide garnets such as $La_3Ta_2Li_5O_{12}$, $(CaLa_2)Ta_2Li_6O_{12}$ or $La_3Zr_2Li_7O_{12}$ are ones of the best solid state electrolytes. We are currently preparing disordered garnet borohydrides by heterovalent substitution on the octahedral site which will create an additional disordered site for Li^+ as it is in garnet oxides.

[1] D. B. Ravnsbæk et al., *Angew. Chem. Int. Ed*. 2012, **51**, 3582.