Crystal chemistry of metal borohydrides

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An increasing number of novel single, double and triple cation homoleptic borohydrides have been structurally characterized in last few years. This allows us to make a thorough/profound crystal chemistry analysis of observed structures, to find the prototypes and draw conclusions about the bonding and building principles in this important category of hydrogen storage and battery materials.

It is interesting to note that the majority of novel metal borohydrides resemble structures of various metal oxides. This is not altogether surprising considering the fact that $[BH_4]^-$ and O^{2-} anions are isoelectronic. The similarity between borohydride and oxide structures shows that the homoleptic solid borohydrides are, just as oxides, ionocovalent structures with different degrees of electron transfer between the metal cation and the tetrahydroborate anion.

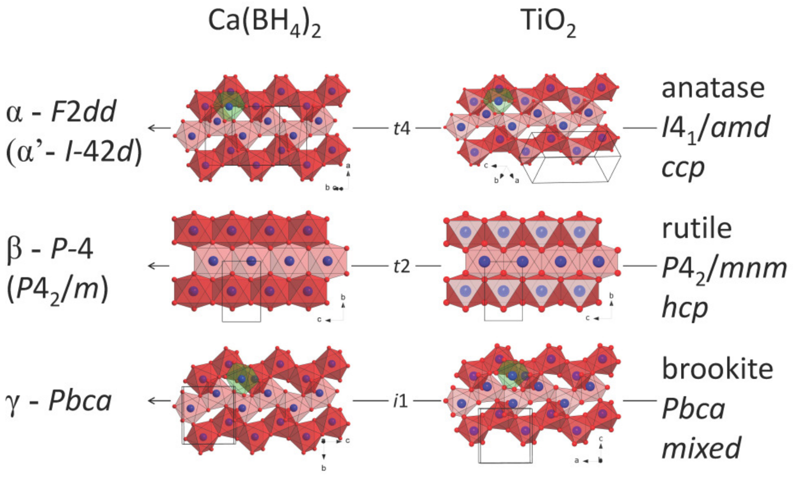

Figure 1: Structural relation between the polymorphs of $Ca(BH_4)_2$ and TiO_2. Different colours of the coordination polyhedra differentiate the brucite like layers of edge-sharing octahedra. The H atoms are omitted.

The crystal structures of homoleptic metal borohydrides have been analysed with respect to their structural prototypes found amongst metal oxides in the inorganic databases [1]. The coordination polyhedra around the cations and the borohydride anion are determined, and constitute the basis of the structural systematics underlying metal borohydride chemistry in various frameworks and variants of ionic packing, including complex anions and the packing of neutral molecules in the crystal. Underlying nets are determined by topology analysis. It is found that the Pauling rules for ionic crystals apply to all non-molecular borohydride crystal structures, and that the latter can often be derived by simple deformation of the close-packed anionic lattices *ccp* and *hcp*, by partially removing anions and filling tetrahedral or octahedral sites. The deviation from an ideal close packing is facilitated in metal borohydrides with respect to the oxide due to geometrical and electronic considerations of the BH_4 anion (tetrahedral shape, polarizability).

This contribution is expected to serve materials engineers as a roadmap to design new materials, synthetic chemists in their search for promising compounds to be prepared, and materials scientists in understanding the properties of novel materials.

[1] Cerny R. & Schouwink P. *Acta Cryst. B.* **2015**, 71, 619-640, dx.doi.org/10.1107/S2052520615018508.

Short abstract:

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