

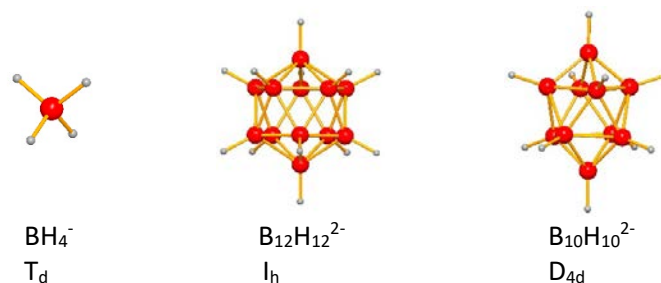
# Metal hydridoborates, novel materials for energy conversion and storage

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Metal hydridoborates are emerging class of materials for energy conversion and storage. The hydridoborates that form the compounds used in various applications are mostly based on borohydride  $\text{BH}_4^-$ , *closo*-dodecaborate  $\text{B}_{12}\text{H}_{12}^{2-}$ , *closo*-decaborate  $\text{B}_{10}\text{H}_{10}^{2-}$  anions, and their carbon-substituted derivatives (Figure 1). The non-crystallographic symmetry of both *closo*-clusters is at the origin of their orientation disorder in the *ht* phases of many hydridoborates and their classification as plastic (rotatory) crystals.



**Figure 1.** The three frequently used hydridoborate anions: borohydride (**left**), *closo*-dodecaborate (**middle**) and *closo*-decaborate (**right**) and their point group symmetries.

Hydrogen storage in solids was the initial interest in these fascinating compounds. Later on, the Lithium and Sodium hydridoborates have proven to be promising solid-state electrolytes [1]. Fast cationic motion generally occurs after a polymorphic transition towards higher-symmetry phases. However, such phase transition occurs usually above room temperature (*rt*), thus hampering practical applications. Lowering the temperature of phase transition has been made possible by chemical tuning, *i.e.*  $\text{BH}_4^-$  substitution by halides and mixing anionic hydridoborate clusters or by physical treatment implying formation of composites or nano-confined materials [2]. Recently, we have shown an effect of mechanical milling in stabilizing at *rt* the superionic conductive phase of a single-anion material,  $\text{NaCB}_{11}\text{H}_{12}$  [3]. The high-energy ball milling quenches the metastable, body-centred cubic (*bcc*) polymorph with a conductivity of  $4 \text{ mS cm}^{-1}$  at  $20^\circ\text{C}$ , without altering the electrochemical stability. Other applications have been studied and proposed for the hydridoborates:

Novel Gd-based mixed-metal borohydrides  $\text{A}_n\text{Gd}(\text{BH}_4)_{n+3}$  ( $\text{A} = \text{K}, \text{Cs}$ ) have been described in view of their magnetic cooling properties at cryogenic temperatures [4]. The isolated Gd-centres in five-fold coordination in  $\text{K}_2\text{Gd}(\text{BH}_4)_5$ , the first representative of a new structure type, lead to exceptionally high mass magnetic entropy change of  $54.6 \text{ J kg}^{-1} \text{ K}^{-1}$  at the maximum field change of 9 T.

Series of borohydride perovskites  $\text{AB}(\text{BH}_4)_3$  based on alkali metals and ammonium and on alkali and rare earths and lead have been studied with respect to their photophysical properties [5]. The lanthanide excited states, for example, those of  $\text{Eu}^{2+}$  or  $\text{Yb}^{2+}$ , are not quenched by B-H vibrations in a homoleptic  $\text{BH}_4^-$  environment, making the borohydride perovskites a new host family of phosphors.

A colossal barocaloric effect has been discovered in the isomers of carborane  $\text{C}_2\text{B}_{10}\text{H}_{12}$  [6]. The best performances are obtained in *para*-carborane with maximum entropy changes of about  $106.2 \text{ J kg}^{-1} \text{ K}^{-1}$  achieved under pressure changes below 30 MPa.

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