# 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 BH4−, *closo*-dodecaborate B12H122−, *closo*-decaborate B10H102− 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.

  

BH4- B12H122-  B10H102-

Td Ih  D4d

###### **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.* BH4− 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, NaCB11H12 [3]. The high-energy ball milling quenches the metastable, body-centred cubic (*bcc*) polymorph with a conductivity of 4 mS cm-1 at 20°C, without altering the electrochemical stability. Other applications have been studied and proposed for the hydridoborates:

Novel Gd-based mixed-metal borohydrides AnGd(BH4)n+3 (A = K, Cs) have been described in view of their magnetic cooling properties at cryogenic temperatures [4]. The isolated Gd-centres in five-fold coordination in K2Gd(BH4)5, the first representative of a new structure type, lead to exceptionally high mass magnetic entropy change of 54.6 J kg−1 K−1 at the maximum field change of 9 T.

Series of borohydride perovskites AB(BH4)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 Eu2+ or Yb2+, are not quenched by B-H vibrations in a homoleptic BH4− environment, making the borohydride perovskites a new host family of phosphors.

A colossal barocaloric effect has been discovered in the isomers of carborane C2B10H12 [6]. The best performances are obtained in *para*- carborane with maximum entropy changes of about 106.2 J kg−1 K−1 achieved under pressure changes below 30 MPa.

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