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Editorial

Boron-Based (Nano-)Materials: Fundamentals and Applications

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Abstract: The boron ($Z = 5$) element is unique. Boron-based (nano-)materials are equally unique. Accordingly, the present special issue is dedicated to crystalline boron-based (nano-)materials and gathers a series of nine review and research articles dealing with different boron-based compounds. Boranes, borohydrides, polyhedral boranes and carboranes, boronate anions/ligands, boron nitride (hexagonal structure), and elemental boron are considered. Importantly, large sections are dedicated to fundamentals, with a special focus on crystal structures. The application potentials are widely discussed on the basis of the materials' physical and chemical properties. It stands out that crystalline boron-based (nano-)materials have many technological opportunities in fields such as energy storage, gas sorption (depollution), medicine, and optical and electronic devices. The present special issue is further evidence of the wealth of boron science, especially in terms of crystalline (nano-)materials.

Keywords: benzoxaboronate; borane; borohydride; boron-based material; boron-treat steel; boron nitride; boronate; carborane; metallacarborane; polyborate

1. Introduction

Boron ($Z = 5$) is one of the lightest elements of the periodic table, coming just before carbon ($Z = 6$). It is also certainly the least well-known element with 2p valence shell. In comparison to the very popular carbon, it has not attracted as much attention (despite more than two centuries of use), but it has fascinated and exasperated generations of scientists. We, the contributors and editors of the present special issue, are proud to belong to the current generation, and we are equally enthralled but no longer exasperated.

Discovered in 1808, boron was isolated by Joseph-Louis Gay-Lussac (French chemist, 1778–1850) and Louis-Jacques Thénard (French chemist, 1777–1857), and independently by Sir Humphry Davy (English chemist, 1778–1829). The years that followed can be summarized by citing Grimes [1]. Boron “appeared normal—even boring—for a century following its isolation [. . .]. It behaved exactly as expected, forming trivalent compounds [. . .], and everyone [. . .] believed that its simplest hydride had to be BH_3 [. . .]. It took the great German chemist Alfred Stock [(1876–1946)] to uncover the truth about the boron hydrides [. . .]. Not until another half-century had passed did another towering scientist, William Nunn Lipscomb [(American chemist, 1919–2011)], finally crack the mystery of the three-center-bonded polyboranes”. Crystallinity of these polyboranes and the development of powerful characterization tools like X-ray diffraction within the 20th century, among other factors, have allowed the recent great advances in boron science.

Hosmane, in the preface of the book he edited, asks the question “*what is boron?*” and right after gives the answer “*the question itself may not seem very significant to many people*” [2]. Boron is indeed

little known. It may be confused with borax, which is the ore from which boron is extracted. This may appear to be unfair in comparison to the reputation of carbon, but obviously boron has shown to be versatile after two centuries of research and development. Let us again cite Hosmane [2]. “How many of us know that a regular intake of boron can lessen the chance of prostate cancer? How many of us know that boron plays a direct and critical role in combating cancer through a treatment called boron neutron capture therapy?” Medicine is clearly a highly important and crucial area of application. In fact, boron—especially boron-based compounds—have been widely used in many areas of application, including health (e.g., fungicides, detergents, soaps, antiseptics, and cosmetics), nutrition (e.g., additives, fertilizers), electronics, energy (e.g., nuclear energy, hydrogen storage, fuel cell), organic and inorganic chemistry, catalysis, metallurgy, enamels, and ceramics.

Accordingly, the present special issue focuses on fundamentals and applications of crystalline boron-based (nano-)materials, and aims at illustrating the recent great advances in boron science through several examples.

2. The Journal *Crystals*, an Already-Identified Forum for Boron-Based (Nano-)Materials

Boron scientists have not waited for the present special issue to report their cutting-edge research in this journal, *Crystals*. All of them are briefly cited hereafter, as they also illustrate the versatility of boron and the importance of crystalline boron-based (nano-)materials in several areas of application.

2.1. Attractive Physical Properties

Borophosphates are intermediate compounds made from the system $M_xO_y-B_2O_3-P_2O_5-(H_2O)$, where M is a transition metal like Fe. They are generally used as glasses, but borophosphates with open frameworks have been shown to be of interest as magnetic materials. This is the case, for example, for the new $KFe[BP_2O_8(OH)]$ reported by Wang and Mudring [3]. It shows a three-dimensional framework crystallizing in the monoclinic structure with a space group $P2_1/c$; it is formed by alternating $\{BO_3(OH)\}$ and $\{PO_4\}$ tetrahedrons.

Another class of compounds that show particular magnetic properties is constituted of substituted spirobiphenalenyl boron radicals (Figure 1). They are paramagnetic. Another of their physical properties interested Pag et al. [4]. These radicals are indeed attractive molecular conductors for optoelectronics, magneto-optics, and spintronics.

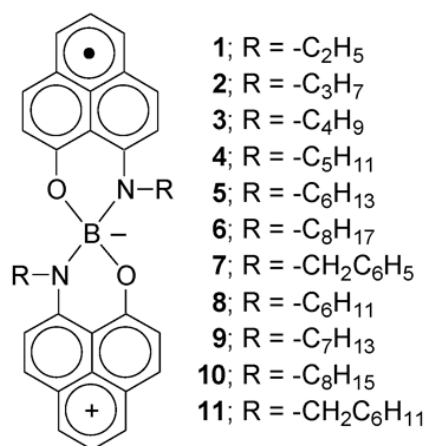


Figure 1. Molecular structure of substituted spirobiphenalenyl boron radicals. Adapted from reference [4]. Reproduced with permission from reference [4], published by MDPI, 2016.

Borates are mainly used as heat-resistant glass and insulator fiberglass, as detergent and soap, and as agricultural micronutrients. Other applications are also prospected as borates have interesting optical properties. Gallium borate $GaBO_3$ has notably been well studied with respect to luminescence

properties. This was reported by Wang et al. [5], who especially worked on the single crystal structure (trigonal calcite type, space group $R\bar{3}c$) and the band gap (3.62 eV) of GaBO_3 .

2.2. Attractive Chemical Properties

Boron hydrides (e.g., alkali borohydrides) are well-known as effective reducing agents. Sodium borohydride (NaBH_4) is certainly the most widely used in both organic and inorganic chemistry. Potassium borohydride (KBH_4) is an alternative. It was, for example, successfully used to reduce the oxide layer forming on the surface of the intermetallic material $\text{MnNi}_{3.6}\text{Co}_{0.85}\text{Al}_{0.3}\text{Mn}_{0.3}$ used as a fuel cell anode. This work was reported by Chen et al. [6].

Alkali borohydrides are also of interest in the field of energy, especially as solid-state chemical hydrogen storage materials. For this application, lithium borohydride (LiBH_4) is more suitable than the sodium and potassium counterparts, owing to the lightness of lithium ($M_w = 6.94 \text{ g/mol}$) and the highest gravimetric hydrogen density (18.5 wt % H). Destabilization of LiBH_4 has been widely investigated with the objective to decrease the dehydrogenation temperature, and Zavorotynska et al.'s contribution concerns the solid solution $\text{LiBH}_4\text{--LiCl}$ [7]. Liquid-state chemical hydrogen storage is also a possible application for alkali borohydrides, but NaBH_4 is better than the lithium and potassium counterparts in that case [8]. Other candidates for chemical hydrogen storage are boranes, the simplest candidate being ammonia borane (NH_3BH_3). Sagan et al. [9], for their part, considered derivatives with the following molecular structures: $\text{LiN}(\text{CH}_3)_2\text{BH}_3$ and $\text{KN}(\text{CH}_3)_2\text{BH}_3$.

The BH_3 entity is not stable enough to exist in an isolated form. It exists as a dimer, which is the diborane molecule B_2H_6 . Otherwise, it can be stabilized by complexation with a Lewis base like ammonia NH_3 or tetrahydrofuran $(\text{CH}_2)_4\text{O}$, leading to the formation of a Lewis adduct. Accordingly, BH_3 is of key importance in molecular (organic) chemistry, as it can be used as protecting group of a potential Lewis base. For example, one may cite the work reported by Mamat and Köckerling, who used BH_3 to protect a phosphane (Figure 2) [10]; another work belongs to Bourque et al. [11]. Both NaBH_4 and a complex of BH_3 were used for the synthesis of a maltolato compound; the former was used as reducing agent, and the latter as Lewis acid.

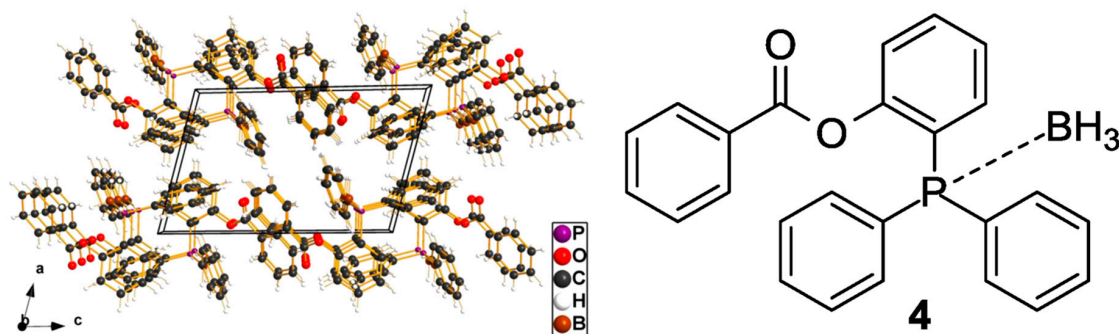


Figure 2. View of the packing of molecules in crystals of the phosphane borane adduct (denoted **4**) along the crystallographic b axis, and view of its molecular structure. Adapted from reference [10]. Reproduced with permission from reference [10], published by MDPI, 2016.

3. The Journal *Crystals*, a Key Forum for the Present Special Issue

The present special issue is constituted of nine review and research papers of high quality, reporting different boron-based (nano-)materials for different possible areas of application. They are briefly discussed hereafter.

3.1. Boranes and Borohydrides for Solid-State Hydrogen Storage

Owarzany et al. [12] present an overview on metal amidoboranes $\text{M}(\text{NH}_2\text{BH}_3)$ with $\text{M} = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}, \text{Mg}, \text{Ca}, \text{Sr}, \text{Y}, \text{Al},$ and Zn . Amidoboranes constitute a constantly growing family of NH_3BH_3

derivatives, especially investigated as solid-state chemical hydrogen storage materials. The authors propose the most exhaustive survey of the amidoborane reported so far. Their crystal structures are discussed first and in detail. Additional pieces of information are given based on nuclear magnetic resonance, infrared, and Raman spectra. The authors also scan the synthesis paths, while giving details about reactivity and selected properties, such as (among others) ionic conductivity, storage capacity, and interatomic distance. The conclusion of the article points out the issues that hinder the development and implementation of these chemical hydrogen storage materials.

We [13] have also contributed to the special issue with an article dealing with the in situ Synchrotron X-ray diffraction of boranes. Pristine ammonia borane (NH_3BH_3), hydrazine borane ($\text{N}_2\text{H}_4\text{BH}_3$), and two hydrazinidoborane derivatives ($\text{MN}_2\text{H}_3\text{BH}_3$; $\text{M} = \text{Li}, \text{Na}$), hydrazine bisborane ($\text{BH}_3\text{N}_2\text{H}_4\text{BH}_3$) and sodium triborane (NaB_3H_8) are analyzed. All are currently considered as potential chemical hydrogen storage materials. The boranes were investigated over a wide range of temperatures (80–300 K). Differences in crystal structures, the existence of phase transition, evolutions of unit cell parameters and volumes, and variation of coefficients of thermal expansion can be observed. The main results are presented and discussed.

Like Zavorotynska et al. [7] (cf. Section 2.2), Javadian et al. [14] investigated LiBH_4 . However, their approach is much different. They consider the destabilization of LiBH_4 via the combination of two approaches; that is, chemical doping with another hydride (sodium alanate, NaAlH_4) and nanoconfinement into a mesoporous carbon aerogel with high specific surface area ($689 \text{ m}^2/\text{g}$). The reciprocal is also true, because one may consider the destabilization of NaAlH_4 by the presence of LiBH_4 . In comparison to the pure and bulk parent materials, improved dehydrogenation and rehydrogenation properties are reported, making the authors positively conclude on the viability of the proposed approach.

3.2. Polyhedral Boranes and Carboranes

There are two review article contributions addressing boron-rich clusters, such as polyhedral boranes and carboranes.

The first is proposed by Planas et al. [15]. The review summarizes the synthetic routes, coordination chemistry, and properties of a series of carboranyl ligands containing N, O donors (e.g., *closo*-carbonylmethylalcohols with nitrogenated aromatic rings) as well as of metal (e.g., cobalt, iron, platinum, titanium) complexes of these N,O-type carborane ligands. The wealth of carborane chemistry is particularly remarked. It is of even more importance that N,O-type carborane ligand-based complexes show a variety of properties, such as those used in magnetic, chiroptical, nonlinear optical, catalytic, and biomedical applications. It is worth citing the last sentence of the authors' conclusion, as it is true for all of the articles of the present special issue: "New developments are appearing constantly and are limited only by our imagination".

The second review by Avdeeva et al. [16] is substantial, with 85 pages about silver and copper complexes with *closo*-polyhedral borane (10 or 12 boron atoms), carborane (1 carbon atom with 9 or 11 boron atoms) and metallacarborane (e.g., $[\text{3,3}'\text{-Co}(\text{1,2-C}_2\text{B}_9\text{H}_{11})_2]^-$) anions (Figure 3). Each of the complexes is reported in terms of synthesis and crystal structures. They demonstrate a wide variety of structural types, relating to both the metal coordination environment and coordination modes of boron hydride anions, which is discussed in detail by the authors. This review paper is of fundamental importance, with a major part dedicated to crystal structures and coordination chemistry.

3.3. Boronate Ligands and Derivatives

Sene et al.'s review [17] is about some of the key results on crystalline structures with boronate and benzoxaborolate ligands (anions) that can be used as building blocks (Figure 4). The authors emphasize the fact that such ligands "had up until recently hardly been looked into as possible building blocks for materials applications". With respect to these mentioned "materials applications", the authors have in mind coordination networks as well as metal organic networks (MOFs). The article is structured

around crystal structures involving simple boronates and benzoxaborolates, spectroscopic signatures in materials, and finally emerging applications like functional coordination polymers/networks with temperature-dependent luminescent properties or promising magnetic properties and benzoxaborole drugs (nanomedicine).

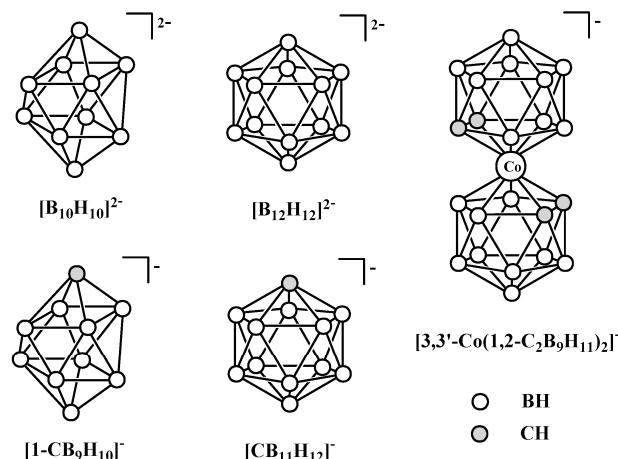


Figure 3. Anionic polyhedral boron hydrides discussed by Avdeeva et al. in reference [16]. Reproduced with permission from reference [16], published by MDPI, 2016.

3.4. Boron Nitride

Boron nitride is a non-oxide ceramic material of high interest. A first illustration of this is provided by Matarin and Rimola [18]. By using computational methods (B3LYP-D2* periodic simulations), they investigated the adsorption of molecules like water (H_2O), ammonia (NH_3), formic acid ($HCOOH$), benzene (C_6H_6), and methane (CH_4) onto boron nitride nanotubes showing defects derived from monovacancies of boron and nitrogen atoms. Distinction is made between the aforementioned polar (H_2O , NH_3 , $HCOOH$) and non-polar (C_6H_6 , CH_4) molecules. It is shown that nitrogen-rich boron nitride nanotubes are more reactive towards the adsorption of polar molecules (dictated by dative interactions), whereas the adsorption of non-polar molecules (physisorption governed by, e.g., π -stacking for C_6H_6) does not depend on the type of the nanotube. It is therefore concluded that adsorption onto boron nitride nanotubes may be modulated by the presence of surface defects.

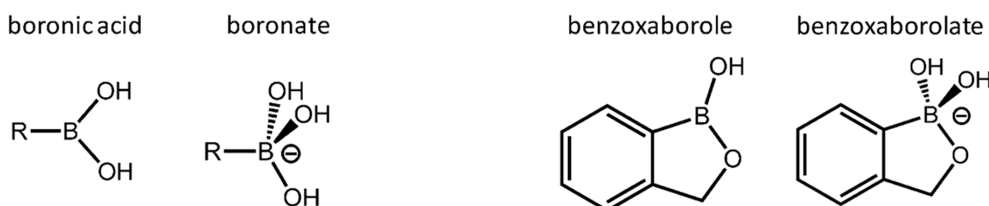


Figure 4. Representation of the structures of boronic acid/boronate (left); and benzoxaborole/benzoxaborolate (right). Only the tetrahedral-boron forms of boronate/benzoxaborolate anions are shown here. Adapted from reference [17]. Reproduced with permission from reference [17], published by MDPI, 2016.

Hexagonal boron nitride (h-BN; Figure 5) is principally used as lubricant in domains ranging from metallurgy to cosmetics. According to Yuan et al. [19], h-BN has other properties that may open new perspectives for engineering applications, for example, as a solid lubricant in aeronautics or as a perfect substrate to graphene for electronic devices. Such promising developments require tailored h-BN shapes displaying a high level of crystallization, ensuring its properties for the long term. This article aims at giving an overview of the strategies (rapid thermal annealing, Li_3N as crystallization promoter,

and spark plasma sintering) developed by the authors to prepare highly crystallized supported thick coatings and self-standing nanosheets. The advantages and limitations of the three strategies, as well as the main achievements, are reported and discussed. As a concluding remark, the authors optimistically expect the development of h-BN-based high performance devices in the future.

It is worth mentioning that boron nitride is the featured molecule of a special issue of a sister journal; that is, *Molecules* MDPI [20]. The issue title is “boron nitride: synthesis and application”, and is co-edited by one of the present co-editors, Philippe MIELE. This special issue is dedicated to the most recent development on the synthesis and applications of boron nitride, including synthesis of high-quality crystal, nanopowders, nanosheets, nanostructured and porous ceramic materials, high-performance composites, and optoelectronic and electronic devices.

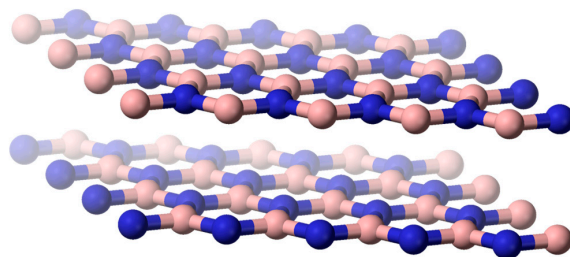


Figure 5. Representation of the structure of hexagonal boron nitride, the nitrogen atoms are represented in blue, and the boron atoms in pink.

3.5. Boron-Tread Steels

The last paper of the series falls in a different field. Through a research paper, Gao et al. [21] give an overview of the use of elemental boron as an effective alloying element employed to increase the hardenability of high strength low alloy steels. They particularly investigated the influence of boron on initial austenite grain size and hot deformation behavior of boron microalloyed steels. Among the various findings, the following one may be cited. Increasing the boron content of boron-tread steel increases the peak and critical strain of dynamic recrystallization, indicating that boron addition can delay the onset of dynamic recrystallization. We believe that the present work will give the reader a wider view of the application prospects of boron and related boron-based materials.

4. Conclusions

The present special issue gives an overview of the current works dedicated to crystalline boron-based (nano-)materials. Though the original review and research articles dedicate large sections to crystallinity and crystal structures, the authors also give details about various aspects, such as synthesis, spectroscopic signatures, physicochemical properties, and application prospects. With respect to this last aspect, advanced technologies, such as energy storage, gas sorption (energy and environment), biomedicine and nanomedicine, and optical and electronic devices are targeted. We cordially invite the reader curious about science, and especially boron science, to dip into each of the nine articles of the present special issue.

In conclusion, we would like to thank all of the authors who have contributed to this special issue. We again thank the main/correspondence authors who accepted our invitation several months ago. The present special issue is an important scientific contribution to the field of boron science, and we, the contributors, have all been actors of this successful publication. “*New developments are appearing constantly and are limited only by our imagination*” [15].

We wish all of the readers compelling reading.

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Conflicts of Interest: The authors declare no conflict of interest.

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