Recent Developments on Rare-Earth Hexaboride Nanowires

Zhen Wang and Wei Han

School of Microelectronics, Southern University of Science and Technology, Shenzhen 518055, China; wangz8@sustech.edu.cn
Department of Applied Physics, The Hong Kong Polytechnic University, Kowloon, Hong Kong 999077, China
* Correspondence: weihan@polyu.edu.hk

Abstract: With the rise of topological insulator samarium hexaboride (SmB₆), rare-earth hexaboride (RB₆) nanowires are the focus of the second wave of a research boom. Recent research has focused on new preparation methods, novel electronic properties, and extensive applications. Here, we review the recent developments in RB₆ nanowires in the past five years. Two main synthesis methods (chemical vapor deposition and high-pressure solid-state) of RB₆ nanowires are introduced and compared. Moreover, their electronic transport, magnetic properties, and superconducting properties are revealed. Furthermore, the applications of RB₆ nanowires are presented, including as field emitters, photodetectors, and in energy storage. Finally, we detail further research directions for RB₆ nanowires.

Keywords: rare-earth hexaboride; nanowire; field emission; chemical vapor deposition

1. Introduction

Rare-earth hexaborides (RB₆) have received substantial attention thanks to their high electrical conductivity, high melting points, and high chemical stability. Meanwhile, the strong correlation effect of 4f–5d electrons of rare-earth elements also brings some new-fangled physical properties of RB₆ [1–3]. For example, yttrium hexaboride (YB₆) is a superconductor with a Tc of 7.2 K, which is the second highest transition temperature among all borides [4]. Moreover, lanthanum hexaboride (LaB₆), possessing low work function of 2.7 eV, is a famous thermionic electron emission material with high current density and stability [5]. Cerium hexaboride (CeB₆) is an antiferromagnetic heavy-fermion metal, but recently, it was found to display low-energy ferromagnetic fluctuation [6]. Furthermore, as a ferromagnetic semimetal, europium hexaboride (EuB₆) recently exhibited a colossal magnetoresistance effect [7]. In recent years, the emergent topological insulator has increased interest in samarium hexaboride (SmB₆), which possesses both insulating bulk state and metallic surface state due to the inversion of the d and f bands. Experimental evidence proves that SmB₆ is the first strongly correlated 3D topological Kondo insulator [8].

Due to the small size effect and quantum confinement effect, one-dimensional (1D) nanomaterials have new properties compared with bulk crystals. With the rise of 1D nanomaterials, RB₆ experienced the first wave of a research boom from 2005 to 2015, and many RB₆ nanowires were prepared by chemical vapor deposition (CVD) [9–20]. These RB₆ nanowires achieved excellent field emission properties and mechanical properties [21–29]. From 2016, the second wave of research boom of RB₆ began as SmB₆ proved to be a topological insulator, and researchers began to explore the difference in topological properties between nanowires and bulk single crystals [8].

In this review, we summarize the recent developments in RB₆ nanowires. Two main synthesis methods of RB₆ nanowires are summarized. Furthermore, their electronic transport and magnetic properties are summarized. Finally, the applications of RB₆ nanowires are presented, including as field emitters, photodetectors, and in energy storage.
2. Growth of RB₆ Nanowires

The structural models of rare-earth hexaborides are shown in Figure 1a. RB₆ crystals are CsCl-type structures with a space group of Pm-3m. Among 17 rare-earth elements, only 13 can form hexaborides with boron, which are YB₆, LaB₆, CeB₆, PrB₆, NdB₆, SmB₆, EuB₆, GdB₆, TbB₆, DyB₆, HoB₆, ErB₆, and YbB₆. On the left side of Figure 1a, one B₆ octahedron is surrounded by eight R atoms, and RB₆ crystals generally have suitable conductivity. On the right side of Figure 1a, one R atom is encircled by eight B₆ octahedra, and B₆ octahedra are connected by covalent bonds, which give RB₆ high melting points, high hardness, and high chemical stability. From the study of electronic structure and bonding characteristics of LaB₆, lanthanum and adjacent boron atoms are not sufficiently bonded, indicating that lanthanum atoms can migrate efficiently [30]. During the thermal field emission, the lanthanum atoms can freely migrate in the boron frame to replace the lanthanum atoms evaporated on the surface, thus showing excellent field emission performance [31]. Rare-earth hexaborides share common properties, but the special electronic structure of each material determines their characteristic properties. For instance, YbB₆ was once proposed to be a topological insulator, but new evidence for the electronic structure suggests that its electronic states originate from the hybridization of the Yb d- and B p-orbits. This indicates that YbB₆ has a non-topological insulator electronic structure [32]. Although most of the RB₆ crystals are metals, SmB₆ can open the band gap at low temperature due to the hybridization of the 4f bands and 5d bands, and meanwhile, metallic surface states are topologically protected [33]. To study and utilize the properties of RB₆, high-quality crystals, especially low-dimensional nanowires, need to be prepared. Concerning materials preparation, only two methods are reported to obtain RB₆ nanowires, chemical vapor deposition (CVD) and high-pressure solid-state (HPSS), as depicted in Figure 1b. CVD is a tradition method to grow RB₆ nanowires using vapor–liquid–solid (VLS) or vapor–solid (VS) mechanisms at a high temperature. HPSS using autoclave is a new method to grow RB₆ nanowires at a low temperature.

![Figure 1](image.jpg)

**Figure 1.** (a) The ball-and-stick structural models of rare-earth hexaborides. (b) Sketch map of two growth methods of RB₆ nanowires.

### 2.1. CVD Growth

In the past 5 years, a series of RB₆ nanowires were prepared by the CVD method, namely, LaB₆, CeB₆, NdB₆, SmB₆, and ternary LaₓPr₁₋ₓB₆ nanowires, as shown in Figure 2. Different methods use different source materials and substrates, as summarized below.

\[
RCl₃ + B + B₂O₃ + H₂ \rightarrow RB₆ \quad (R = La, Sm)
\]  \(\text{(1)}\)
is deleterious to humans. The field emission properties of flexible CeB\textsubscript{6} nanowire arrays et al. used a CVD route to grow SmB\textsubscript{6} nanowires on Au-coated Si substrates [39].

The LaB\textsubscript{6} nanowires exhibit excellent field emission properties and stability, both at room temperature and at high temperatures [34]. Compared with bulk single crystals, the transport properties prove that SmB\textsubscript{6} nanowires have less residual resistance due to their large surface area [38].

Figure 2. SEM images of (a) CVD-grown LaB\textsubscript{6} nanowires [34] (Copyright 2017, The Royal Society of Chemistry), (b) CeB\textsubscript{6} nanowires [35] (Copyright 2017, Elsevier Science B.V.), (c) NdB\textsubscript{6} nanowires [36] (Copyright 2016, The Royal Society of Chemistry), (d) La\textsubscript{x}Pr\textsubscript{1−x}B\textsubscript{6} nanowires [37] (Copyright 2016, Elsevier Science B.V.).

From 2017 to 2019, Gan et al. used a Ni-catalyzed low-pressure CVD method to prepare high-quality LaB\textsubscript{6} and SmB\textsubscript{6} nanowires with a length of tens of microns, as depicted in Figure 2a [34,38]. The source materials of this method are LaCl\textsubscript{3} (SmCl\textsubscript{3}), H\textsubscript{2}, B, and B\textsubscript{2}O\textsubscript{3}, and they are non-toxic. Halides are common rare-earth sources, easy to decompose and reactive. The innovation of this method lies in the use of B and B\textsubscript{2}O\textsubscript{3} as the boron source, because boron powder alone is extremely difficult to change to a gaseous state and has low reactivity. At a high temperature of 1000 °C, the mixture of B and B\textsubscript{2}O\textsubscript{3} can produce active B\textsubscript{2}O\textsubscript{2} vapor, and then B\textsubscript{2}O\textsubscript{2} reacts with LaCl\textsubscript{3} (SmCl\textsubscript{3}) and H\textsubscript{2} to grow LaB\textsubscript{6} and SmB\textsubscript{6} nanowires on Ni-coated Si substrates. The LaB\textsubscript{6} nanowires exhibit excellent field emission properties and stability, both at room temperature and at high temperatures [34]. Compared with bulk single crystals, the transport properties prove that SmB\textsubscript{6} nanowires have less residual resistance due to their large surface area [38].

\[
\text{CeCl}_3 \cdot 7\text{H}_2\text{O} + \text{B}_2\text{H}_6 \rightarrow \text{CeB}_6
\]

(2)

In another method, Fu et al. applied a low-pressure CVD route to grow CeB\textsubscript{6} nanowires on Au-coated flexible carbon cloths using CeCl\textsubscript{3}·7H\textsubscript{2}O and B\textsubscript{2}H\textsubscript{6} as source materials, as depicted in Figure 2b [35]. In this method, the CeCl\textsubscript{3}·7H\textsubscript{2}O is safe, but the B\textsubscript{2}H\textsubscript{6} gas is deleterious to humans. The field emission properties of flexible CeB\textsubscript{6} nanowire arrays are outstanding, showing a low turn-on field and a high field emission enhancement factor. Meanwhile, the field current density can remain stable under bending conditions.

\[
\text{SmCl}_3 + \text{BCl}_3 + \text{H}_2 \rightarrow \text{SmB}_6
\]

(3)

Besides B\textsubscript{2}H\textsubscript{6} gas, BCl\textsubscript{3} gas is also a common source of gaseous boron. In 2016, Zhou et al. used a CVD route to grow SmB\textsubscript{6} nanowires on Au-coated Si substrates [39]. The electron transport testing on four-probe single-nanowire devices showed that the SmB\textsubscript{6}
nanowire has a saturated resistance under 10 K due to the presence of both insulating state in bulk and conductive state on the surface.

\[ R + BCl_3 + H_2 \rightarrow RB_6 \ (R = Nd, La, Pr_{1-x}) \]  

(4)

In addition to the catalytic growth using metal particles (Au, Ni), there is also self-catalytic growth using rare-earth metals themselves as catalysts. In 2016, Han et al. reported the self-catalytic growth of NdB₆ and ternary LaₓPr₁₋ₓB₆ nanowires by an ordinary-pressure CVD method, as shown in Figure 2c,d [36,37]. Besides the NdB₆ nanowires, they also acquired NdB₆ nanowires and nanotubes. The growth of ternary LaₓPr₁₋ₓB₆ nanowires reveals that this self-catalytic method is suitable for doping and preparation of RB₆ alloys.

2.2. HPSS Growth

Along with the CVD route, the solid-state method is also a route to prepare RB₆ crystals, including the high-pressure solid-state method [40–47], solution combustion method [48,49], and molten salt method [50,51]. However, because the diffusion rate of atoms in solid-state materials is extremely slow, it is difficult to obtain the nanowire morphology. At the same time, the low reactivity of solid source materials is also a problem restricting the development of 1D RB₆ nanomaterials. To solve such problems, from 2016, Zhao group utilized a rare-earth metal, self-catalytic, high-pressure solid-state method (HPSS) route to prepare various RB₆ nanowires, as shown in Figure 3a–f [52–57]. It is noteworthy that, until now, this is the only report on the synthesis of YbB₆ nanowires [56]. The general chemical reaction of the HPSS method is given below.

\[ R + 6 H_3BO_3 + 10 Mg + I_2 \rightarrow RB_6 + 9 MgO + MgI_2 + 9 H_2O \]

Figure 3. (a) TEM image of CeB₆ nanowires grown by HPSS method [52] (Copyright 2020, Elsevier Science B.V.). (b) SEM images of HPSS-grown SmB₆ nanowires [53] (Copyright 2016, The Royal Society of Chemistry). (c) EuB₆ nanowires [54] (Copyright 2021, Wiley-VCH GmbH). (d) GdB₆ nanowires [55] (Copyright 2017, Elsevier Science B.V.). (e) YbB₆ nanowires [56] (Copyright 2018, Elsevier Science B.V.). (f) YB₆ nanowires [57] (Copyright 2021, Elsevier Science B.V.).

In this equation, Mg is used for the reduction of H₃BO₃, and I₂ acts as the catalyst to boost the reaction of R and B atoms. From the literature, the Gibbs free energy (Δ_G)
and heat function ($\Delta_r H$) of this equation are about $-1900$ kJ mol$^{-1}$ and $-2000$ kJ mol$^{-1}$, respectively, demonstrating that the reaction is spontaneous and exothermic. Moreover, the high pressure in the autoclave is generated by iodine (higher than 45 atm), which is also a key to obtaining RB$_6$ nanowires. Due to high exothermic and high pressure, the trigger temperature of this HPSS method (200–260 $^\circ$C) is generally much lower than that of the CVD method (950–1100 $^\circ$C). From the ex situ time-dependent morphology study (5 min, 30 min, 360 min), we speculate that the growth of nanowires has three steps: (i) diffusion and reaction of R and B atoms; (ii) nucleation of RB$_6$ crystals; (iii) growth of RB$_6$ nanowires [53]. This HPSS route is a general method for the synthesis of rare-earth hexaborides, which we believe can be extended to the synthesis of other metal boride nanowires.

3. Properties and Applications of RB$_6$ Nanowires
3.1. Electronic Transportation

As an emerging topological insulator, many experiments and theoretical studies have been conducted on bulk SmB$_6$ single crystals [8]. From 2016, researchers began to investigate the novel electronic transport and magneto-transport properties of SmB$_6$ nanowires [37,38,53,58–62]. In 2017, Kong et al. reported the spin-polarized surface state transport of single SmB$_6$ nanowires (Figure 4a–c) [58]. Under 5 K, the resistance appears saturated and flat, indicating that the surface states control the transport behavior. The appearance of topological surface states is caused by the reversal of $d$ and $f$ electrons. The fitting of a temperature-dependent resistance curve reveals that SmB$_6$ nanowire has a bulk gap ~3.2 meV, which is opened by the hybridization of the 4$f$ bands and 5$d$ bands in SmB$_6$ nanowires. As shown in Figure 4c, the magnetoresistance (MR) of SmB$_6$ nanowires is negative and the MR shows no sign of saturation at high magnetic field up to 14 T. The negative MR indicates that this transport behavior is spin-dependent. Furthermore, the nonlocal tests reveal that the surface state transport of SmB$_6$ nanowires is spin-polarized. In another interesting work, Zhou et al. reported the positive planar Hall effect (PHE) of SmB$_6$ nanowires (Figure 4d–f) [59]. They found that as the temperature decreases, the amplitude increases sharply, but saturates at 5 K. This positive PHE is due to the surface states of SmB$_6$. In other studies, the researchers found the anomalous magnetoresistance and the hysteresis of magnetoresistance in SmB$_6$ nanowires [60–62].

In the RB$_6$ family, like SmB$_6$, YbB$_6$ is proposed to be a mixed-valent (Yb$^{2+}$/Yb$^{3+}$) topological insulator and demonstrates new quantum phenomena [63–65]. In 2018, Han et al. reported the semiconductor–insulator transition behavior in a YbB$_6$ nanowire (Figure 5) [55]. As shown in Figure 5b, as the temperature decreases from 300 to 2 K, the resistivity of the YbB$_6$ nanowire device undergoes a dramatic 49-fold increase ($\rho_{2K}/\rho_{300K} = 49$). They propose that the semiconductor–insulator transition is due to a small band gap opening at a low temperature induced by the slightly boron-rich or boron-deficient segments in YbB$_6$ nanowires. Furthermore, the magnetoresistance (MR) of the YbB$_6$ nanowire was tested with perpendicular magnetic field B = 0–7 T at various temperatures. As displayed in Figure 5c, the MR shows no sign of saturation at high magnetic field up to 14 T and has a linear dependence with $B^2$ at 2 K and 10 K, which follows Kohler’s law. Because a semiconductor–insulator transition occurred at 2 K for YbB$_6$ nanowires, the hole-dominant transport is credible at 2 K and the transport at 10 K is electron-dominant.

Of all the metal borides, YB$_6$ bulk crystals have the second highest superconducting transition temperature of 7.2 K after MgB$_2$. More superconducting properties have been studied in bulk YB$_6$ single crystals, but the superconducting properties of YB$_6$ nanowires have not been reported. Recently, Wang et al. reported the synthesis of 1D YB$_6$ nanowires by a high-pressure solid-state method and studied their magnetic properties (Figure 6). The temperature-dependent magnetization under zero-field cooling and field cooling revealed that the YB$_6$ nanowires have a superconducting transition with $T_c = 7.8$ K. Meanwhile, they found that the YB$_6$ nanowires exhibited a peak effect in the superconducting state
observed from the magnetic hysteresis loops obtained at 2 K and 10 K, indicating that YB$_6$ nanowires pertain to a type-II superconductor.

Figure 4. (a) SEM image of a SmB$_6$ nanowire device, the scalebar is 2 µm. (b) Temperature-dependent resistance of the SmB$_6$ nanowire. (c) Magnetoresistance curves under a parallel magnetic field at various temperatures [58]. Copyright 2017, American Physical Society. (d) Planar Hall resistivity with various angles at 1.6 K. (e) PHE amplitude and resistivity. Inset is the definition of tilting angle $\theta$. (f) Planar Hall resistivity with various angles at 80 K [59]. Copyright 2019, American Physical Society.

Figure 5. (a) SEM image of the YbB$_6$ nanowire device. (b) Resistivity as a function of temperature from 2 to 300 K. (c) Magnetoresistance (MR) as a function of $B^2$ at various temperatures [55]. Copyright 2018, Elsevier Science B.V.
LaB$_6$ bulk single crystals have been applied in commercial scanning electron microscopy and transmission electron microscopy. For RB$_6$ nanowires, the most attractive application is also the field emitter of an electron gun of an electron microscope (Figure 7) [66–68]. Published in Nature Nanotechnology, Zhang et al. reported the first application of a single LaB$_6$ nanowire to scanning electron microscopy, revealing excellent performance [66]. Their LaB$_6$ nanowire electron source shows low work function, is chemically inert, and has high monochromaticity. When assembled into a field-emission gun of SEM, it demonstrates ultra-low emission decay, and its current density gain is three orders of magnitude higher than traditional W tips. By this LaB$_6$ nanowire-based SEM, they obtained low-noise and high-resolution images, better than W-tip-based SEM. Recently, published in Nature Nanotechnology in 2021, Zhang et al. reported the installation of a single LaB$_6$ nanowire into an aberration-corrected transmission electron microscope [67]. The LaB$_6$ NW-based TEM achieved atomic resolution and probe-forming modes at 60 kV energy. Compared with the state-of-the-art W (310) electron source, the nanostructured electron source provides higher temporal coherence at a spatial frequency of 105 pm, showing a higher contrast transfer amplitude of 84% and a spectral energy resolution of 35%. The first demonstration of the LaB$_6$ nanowire electron source in SEM and TEM reveals that the RB$_6$ nanowires have notable application prospects and commercial value both in electron microscopy and other electron-emitting devices.

3.2. Optoelectronic Properties

Most of the RB$_6$ crystals are metals with zero band gap, and thus, they are not suitable for semiconductor devices, such as field effect transistors and photodetectors. However, as a topological Kondo insulator, SmB$_6$ shows a small gap (3 meV), evidenced by electrical transport measurements, and may have potential in fabricating devices. Recently,
Zhou et al. [69] first reported the self-powered SmB₆ nanowire photodetectors with broad-band wavelengths covering from 488 nm to 10.6 µm (Figure 8). They claimed that the photocurrent stemmed from the interface of SmB₆ nanowire and Au electrodes owing to the built-in potential, proved by the spatially resolved photocurrent mapping. The current on/off ratio, responsibility, and specific detectivity are 100, 1.99 mA/W, and 2.5 × 10⁷ Jones, respectively. The demonstration of a SmB₆ nanowire photodetector reveals its application potential in mid-infrared photodetectors.

Figure 8. (a) Current–time measurement of SmB₆ nanowire photodetector under illuminating of 10.6 µm light source. (b) Current–time curves of SmB₆ nanowire photodetector under illuminating with different light wavelengths [69]. Copyright 2018, AIP Publishing.

3.3. Electrochemical Performances

RB₆ crystals show excellent metal-like conductivity (>10⁵ S m⁻¹) and they are suitable for active electrochemical electrode materials for energy storage. Recently, Wang et al. [52] reported the application of CeB₆ nanowires as lithium-ion battery anode materials, and they obtained a capacity of ~225 mA h g⁻¹ after 60 cycles (Figure 9a). The kinetic analysis shows that the Li⁺ storage mechanism mainly comes from the surface capacitive behavior. Xue et al. [70] reported the application of CeB₆ nanowires on carbon fiber as electrode materials for supercapacitors (Figure 9b). The LaB₆ electrode materials showed a high areal capacitance of 17.34 mF cm⁻² and revealed suitable cycling stability after 10,000 cycles. The successful application of RB₆ nanowires in batteries and capacitors demonstrates their potential in the field of electrochemical energy storage.

Figure 9. (a) The charge–discharge curves of CeB₆ nanowire electrodes for lithium-ion battery anodes [52]. (Copyright 2020, Elsevier Science B.V.) (b) CV curves of CFC and LaB₆-CFC electrode for supercapacitors [70]. (Copyright 2018, Elsevier Science B.V.)

4. Conclusions and Outlook

In conclusion, we review in this paper the recent developments in RB₆ nanowires in the past five years. Two main synthesis methods (CVD and HPSS) of RB₆ nanowires are
outlined and compared. Moreover, their electronic transport, magnetic properties, and superconducting properties are summarized. Finally, the applications of RB_6 nanowires are revealed, including as field electron emitters, photodetectors, and in energy storage.

With the rise of two-dimensional (2D) materials, RB_6 nanowires should absorb some of the advantages of 2D material, such as atomically thin and large area lateral size. If RB_6 nanowires become thinner and wider, also called RB_6 nanobelts, they may reveal novel properties (Figure 10). In a recent study, Lee et al. reported the perfect Andreev reflection in a topological superconducting state based on SmB_6/YB_6 heterostructures [71]. We believe the heterostructures based on combinations of RB_6 nanowires or films may find new physical phenomena and represent future trends. In terms of the synthesis methods, CVD, solid-state, MBE, and PLD methods are all applicable, and only few improvements are needed. For instance, when using the CVD method to grow RB_6 nanobelts, mica substrates may be the best. Furthermore, adding some salts can improve the growth efficiency [72]. Meanwhile, 2D rare-earth materials have shown novel properties and applications, and thus, new discoveries and properties will also arise regarding the atomically thin 2D RB_6 nanobelts.

Figure 10. Outlook on the future growth, properties, and applications of RB_6 nanostructures.

**Author Contributions:** Writing—original draft preparation, Z.W., W.H.; writing—review and editing, Z.W., W.H.; supervision, W.H.; funding acquisition, W.H. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was funded by National Natural Science Foundation Committee of China (grant number 22105162).

**Acknowledgments:** The authors thank the grant from National Natural Science Foundation Committee of China (grant number 22105162).

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

**References**

1. Ji, X.H.; Zhang, Q.Y.; Xu, J.Q.; Zhao, Y.M. Rare-earth hexaborides nanostructures: Recent advances in materials, characterization and investigations of physical properties. *Prog. Solid State Chem.* 2011, 39, 51–69. [CrossRef]

2. Carenco, S.; Portehault, D.; Boissiere, C.; Mezailles, N.; Sanchez, C. Nanoscaled metal borides and phosphides: Recent developments and perspectives. *Chem. Rev.* 2013, 113, 7981–8065. [CrossRef] [PubMed]

3. Gan, H.; Zhang, T.; Guo, Z.; Lin, H.; Li, Z.; Chen, H.; Chen, J.; Liu, F. The growth methods and field emission studies of low-dimensional boron-based nanostructures. *Appl. Sci.* 2019, 9, 1019. [CrossRef]

4. Kunii, S.; Kasuya, T.; Kadowaki, K.; Date, M.; Woods, S.B. Electron tunneling into superconducting YB_6. *Solid State Commun.* 1984, 52, 659–661. [CrossRef]

5. Zhang, H.; Tang, J.; Zhang, Q.; Zhao, G.; Yang, G.; Zhang, J.; Zhou, O.; Qin, L.-C. Field emission of electrons from single LaB_6 nanowire. *Adv. Mater.* 2006, 18, 87–91. [CrossRef]

6. Jang, H.; Friemel, G.; Ollivier, J.; Dukhnenko, A.V.; Shitsevalova, N.Y.; Filipov, V.B.; Keimer, B.; Inosov, D.S. Intense low-energy ferromagnetic fluctuations in the antiferromagnetic heavy-fermion metal CeB_6. *Nat. Mater.* 2014, 13, 682–687. [CrossRef]

7. Pohlit, M.; Rößler, S.; Ohno, Y.; Ohno, H.; Von Molnar, S.; Fisk, Z.; Müller, J.; Wirth, S. Evidence for ferromagnetic clusters in the colossal-magnetoresistance material EuB_6. *Phys. Rev. Lett.* 2018, 120, 257201. [CrossRef] [PubMed]

8. Li, L.; Sun, K.; Kurdak, C.; Allen, J.W. Emergent mystery in the Kondo insulator samarium hexaboride. *Nat. Rev. Phys.* 2020, 2, 463–479. [CrossRef]

9. Zhang, H.; Zhang, Q.; Tang, J.; Qin, L.C. Single-crystalline LaB_6 nanowires. *J. Am. Chem. Soc.* 2005, 127, 2862–2863. [CrossRef]
10. Zhang, H.; Zhang, Q.; Tang, J.; Qin, L.C. Single-crystalline CeB₆ nanowires. *J. Am. Chem. Soc.* 2005, 127, 8002–8003. [CrossRef]

11. Zhang, H.; Zhang, Q.; Zhao, G.; Tang, J.; Zhou, O.; Qin, L.C. Single-crystalline GaB₆ nanowire field emitters. *J. Am. Chem. Soc.* 2005, 127, 13120–13121. [CrossRef]

12. Xu, J.; Zhao, Y.; Zou, C. Self-catalyst growth of LaB₆ nanowires and nanotubes. *Chem. Phys. Lett.* 2006, 423, 138–142. [CrossRef]

13. Zou, C.Y.; Zhang, L.C. Synthesis of single-crystalline CeB₆ nanowires. *J. Phys. D Appl. Phys.* 2006, 39, 112–116. [CrossRef]

14. Ding, Q.; Zhao, Y.; Xu, J.; Zou, C. Large-scale synthesis of neodymium hexaboride nanowires by self-catalyst. *Solid State Commun.* 2007, 141, 53–56. [CrossRef]

15. Xu, J.; Chen, X.; Zhao, Y.; Zou, C.; Ding, Q.; Jian, J. Self-catalyst growth of EuB₆ nanowires and nanotubes. *J. Cryst. Growth* 2007, 303, 466–471. [CrossRef]

16. Xu, J.; Hou, G.; Mori, T.; Li, H.; Wang, Y.; Chang, Y.; Luo, Y.; Yu, B.; Ma, Y.; Zhai, T. Excellent field-emission performances of single-crystalline LaB₆ nanostructures: Nanobelts, nanorods and their nanotubes. *Adv. Funct. Mater.* 2007, 17, 115621. [CrossRef]

17. Brewer, J.R.; Deo, N.; Wang, Y.M.; Cheung, C.L. Lanthanum hexaboride nanoobelisks. *Chem. Mater.* 2007, 19, 6379–6381. [CrossRef]

18. Wang, G.; Brewer, J.R.; Chan, J.Y.; Diercks, D.R.; Cheung, C.L. Morphological evolution of neodymium boride nanostructure growth by chemical vapor deposition. *J. Phys. Chem. C* 2009, 113, 10446–10451. [CrossRef]

19. Brewer, J.R.; Jacobberger, R.M.; Diercks, D.R.; Cheung, C.L. Rare earth hexaboride nanowires: General synthetic design and analysis using atom probe tomography. *Chem. Mater.* 2011, 23, 2606–2610. [CrossRef]

20. Chi, M.; Zhao, Y.; Fan, Q.; Han, W. The synthesis of PrB₆ nanowires and nanotubes by the self-catalyzed method. *Ceram. Int.* 2014, 40, 8921–8924. [CrossRef]

21. Zhang, H.; Tang, J.; Yuan, J.; Ma, J.; Shinya, N.; Nakajima, K.; Murakami, H.; Ohsako, T.; Qin, L.-C. Nanostructured LaB₆ field emitter with lowest apical work function. *Nano Lett.* 2010, 10, 3539–3544. [CrossRef] [PubMed]

22. Xu, J.; Chen, X.; Zhao, Y.; Zou, C.; Ding, Q. Single-crystalline PrB₆ nanowires and their field-emission properties. *Nanotechnology* 2007, 18, 115621. [CrossRef]

23. Xu, J.; Zhao, Y.M.; Zhang, Q.Y. Enhanced electron field emission from single-crystalline LaB₆ nanowires with ambient temperature. *J. Appl. Phys.* 2008, 104, 124306. [CrossRef]

24. Xu, J.Q.; Zhao, Y.M.; Ji, X.H.; Zhang, Q.; Lau, S.P. Growth of single-crystalline SmB₆ nanowires and their temperature-dependent electron field emission. *J. Phys. D Appl. Phys.* 2009, 42, 135403. [CrossRef]

25. Zhang, Q.Y.; Xu, J.Q.; Zhao, Y.M.; Ji, X.H.; Lau, S.P. Fabrication of large-scale single-crystalline PrB₆ nanorods and their temperature-dependent electron field emission. *Adv. Funct. Mater.* 2009, 19, 742–747. [CrossRef]

26. Xu, J.; Hou, G.; Li, H.; Zhai, T.; Dong, B.; Yan, H.; Wang, Y.; Yu, B.; Bando, Y.; Golberg, D. Fabrication of vertically aligned single-crystalline lanthanum hexaboride nanowire arrays and investigation of their field emission. *NPG Asia Mater.* 2013, 5, e53. [CrossRef]

27. Xu, J.; Hou, G.; Mori, T.; Li, H.; Wang, Y.; Chang, Y.; Luo, Y.; Yu, B.; Ma, Y.; Zhai, T. Excellent field emission performances of neodymium hexaboride (NdB₆) nanoneedles with ultra-low work functions. *Adv. Funct. Mater.* 2013, 23, 5038–5048. [CrossRef]

28. Li, Q.; Zhang, H.; Chen, J.; Zhao, Y.; Han, W.; Fan, Q.; Liang, Z.; Liu, X.; Kuang, Q. Single-crystalline La₆Nd₁₋ₓB₆ nanowires: Synthesis, characterization and field emission performance. *J. Mater. Chem. C* 2015, 3, 7476–7482. [CrossRef]

29. Zhang, H.; Tang, J.; Zhang, L.; An, B.; Qin, L.C. Atomic force microscopy measurement of the Young’s modulus and hardness of single LaB₆ nanowires. *Appl. Phys. Lett.* 2008, 92, 173121. [CrossRef]

30. Hossain, F.M.; Riley, D.P.; Murch, G.E. Ab initio calculations of the electronic structure and bonding characteristics of LaB₆. *Phys. Rev. B* 2005, 72, 235101. [CrossRef]

31. Liu, H.; Zhang, X.; Ning, S.; Xiao, Y.; Zhang, J. The electronic structure and work functions of single crystal LaB₆ typical crystal surfaces. *Vacuum* 2017, 143, 245–250. [CrossRef]

32. Neupane, M.; Xu, S.Y.; Alidoust, N.; Bian, G.; Kim, D.J.; Liu, C.; Belopolski, I.; Chang, T.-R.; Jeng, H.-T.; Durakiewicz, T.; et al. Non-Kondo-like electronic structure in the correlated rare-earth hexaboride YbB₆. *Phys. Rev. Lett.* 2015, 114, 016403. [CrossRef] [PubMed]

33. Dzero, M.; Xia, J.; Galitski, V.; Coleman, P. Topological kondo insulators. *Annu. Rev. Condens. Matter Phys.* 2016, 7, 249–280. [CrossRef]

34. Gan, H.B.; Peng, L.X.; Yang, X.; Tian, Y.; Xu, N.S.; Chen, J.; Liu, F.; Deng, S.Z. A moderate synthesis route of 5.6 mA-current LaB₆ nanowire film with recoverable emission performance towards cold cathode electron source applications. *RSC Adv.* 2017, 7, 24848–24855. [CrossRef]

35. Fu, C.; Xu, J.; Chang, Y.; Wang, Y.; Yang, Y.; Bu, H.; Guo, P.; Xu, J.; Sun, H.; Luo, Y.; et al. Flexible three-dimensional CeB₆ nanowire arrays and excellent field emission emitters. *J. Alloys Compd.* 2017, 729, 997–1003. [CrossRef]

36. Han, W.; Zhao, Y.; Fan, Q.; Li, Q. Preparation and growth mechanism of one-dimensional NdB₆ nanostructures: Nanobelts, nanoaws, and nanotubes. *RSC Adv.* 2016, 6, 41891–41896. [CrossRef]

37. Han, W.; Zhang, H.; Chen, J.; Zhao, Y.; Fan, Q.; Li, Q.; Liu, X.; Lin, X. Single-crystalline LaₓPr₁₋ₓB₆ nanoaws: Synthesis, characterization and growth mechanism. *Ceram. Int.* 2016, 42, 6236–6243. [CrossRef]

38. Gan, H.; Ye, B.; Zhang, T.; Xu, N.; He, H.; Deng, S.; Liu, F. A controllable solid-source CVD route to prepare topological Kondo insulator SmB₆ nanobelts and nanowire arrays with high activation energy. *Cyst. Growth Des.* 2019, 19, 845–853. [CrossRef]
39. Zhang, H.; Peng, Y.H.; Yin, Y.L.; Zhou, W.C.; Zhou, F.; Liu, C.; Liu, G.T.; Sun, L.F.; Tang, D.S. Large-scale synthesis and electrical transport properties of single-crystalline SmB$_6$ nanowires. J. Phys. D Appl. Phys. 2016, 49, 265302. [CrossRef]

40. Selvan, R.K.; Genish, I.; Perelshtein, I.; Calderon Moreno, J.M.; Gedanken, A. Single step, low-temperature synthesis of submicron-sized rare earth hexaborides. J. Phys. Chem. C 2008, 112, 1795–1802. [CrossRef]

41. Zhang, M.; Yuan, L.; Wang, X.; Fan, H.; Wang, X.; Wu, X.; Wang, H.; Qian, Y. A low-temperature route for the synthesis of nanocrystalline LaB$_6$. J. Solid State Chem. 2008, 181, 294–297. [CrossRef]

42. Zhang, M.; Wang, X.; Zhang, X.; Wang, P.; Xiong, S.; Shi, L.; Qian, Y. Direct low-temperature synthesis of RB$_6$ (R = Ce, Pr, Nd) nanocubes and nanoparticles. J. Solid State Chem. 2009, 182, 3098–3104. [CrossRef]

43. Zhang, M.; Jia, Y.; Xu, G.; Wang, P.; Wang, X.; Xiong, S.; Wang, H.; Qian, Y. Mg-assisted autoclave synthesis of RB$_6$ (R = Sm, Eu, Gd, and Tb) submicron cubes and SmB$_6$ submicron rods. Eur. J. Inorg. Chem. 2010, 8, 1289–1294. [CrossRef]

44. Pol, VG.; Pol, S.V.; Gedanken, A. Dry autoclaying for the nanofabrication of sulfides, selenides, borides, phosphides, nitrides, carbides, and oxides. Adv. Mater. 2011, 23, 1179–1190. [CrossRef]

45. Wang, L.; Xu, L.; Ju, Z.; Qian, Y. A versatile route for the convenient synthesis of rare-earth and alkaline-earth hexaborides at mild temperatures. CrystEngComm 2010, 12, 3923–3928. [CrossRef]

46. Chen, B.; Yang, L.; Heng, H.; Chen, J.; Zhang, L.; Xu, L.; Qian, Y.; Yang, J. Additive-assisted synthesis of boride, carbide, and nitride micro/nanocrystals. J. Solid State Chem. 2012, 194, 219–224. [CrossRef]

47. Zhou, L.; Yang, L.; Shao, L.; Chen, B.; Meng, F.; Qian, Y.; Xu, L. General fabrication of boride, carbide, and nitride nanocrystals via a metal-hydrolysis-assisted process. Inorg. Chem. 2017, 56, 2440–2447. [CrossRef] [PubMed]

48. Kanakala, R.; Rojas-George, G.; Graeve, O.A. Unique preparation of hexaboride nanocubes: A first example of boride formation by combustion synthesis. J. Am. Ceram. Soc. 2010, 93, 3136–3141. [CrossRef]

49. Kanakala, R.; Escudero, R.; Rojas-George, G.; Ramisette, M.; Graeve, O.A. Mechanisms of combustion synthesis and magnetic response of high-surface-area hexaboride compounds. ACS Appl. Mater. Inter. 2011, 3, 1093–1100. [CrossRef]

50. Portehault, D.; Devi, S.; Beaunier, P.; Gervais, C.; Giordano, C.; Sanchez, C.; Antonietti, M. A general solution route toward metal boride nanocrystals. Angew. Chem. Int. Ed. 2011, 50, 3262–3265. [CrossRef]

51. Liu, X.; Gong, Y. Molten salt synthesis of samarium borides with controllable stoichiometry and morphology. J. Alloys Compd. 2021, 867, 159174. [CrossRef]

52. Wang, Z.; Han, W.; Kuang, Q.; Fan, Q.; Zhao, Y. Low-temperature synthesis of CeB$_6$ nanowires and nanoparticles as feasible lithium-ion anode materials. Adv. Powder Tech. 2020, 194, 595–603. [CrossRef]

53. Han, W.; Qiu, Y.; Zhao, Y.; Zhang, L.; Chen, J.; Sun, S.; Lan, L.; Fan, Q.; Li, Q. Low-temperature synthesis and electronic transport of topological insulator SmB$_6$ nanowires. CrystEngComm 2016, 18, 7934–7939. [CrossRef]

54. Wang, Z.; Han, W.; Fan, Q.; Zhao, Y. High-pressure growth and magnetic and electrical properties of EuB$_6$ nanowires. Phys. Status Solidi (RRL) Rapid Res. Lett. 2021, 15, 2100249. [CrossRef]

55. Han, W.; Wang, Z.; Li, Q.; Liu, H.; Fan, Q.; Dong, Y.; Kuang, Q.; Zhao, Y. Autoclave growth, magnetic, and optical properties of GdB$_6$ nanowires. J. Solid State Chem. 2017, 256, 53–59. [CrossRef]

56. Han, W.; Wang, Z.; Li, Q.; Lian, X.; Liu, X.; Fan, Q.; Zhao, Y. Semiconductor-insulator transition in a YbB$_6$ nanowire with boron vacancy. J. Solid State Chem. 2018, 262, 244–250. [CrossRef]

57. Wang, Z.; Han, W.; Zhang, J.; Fan, Q.H.; Zhao, Y.M. Superconducing YB$_6$ nanowires. Ceram. Int. 2021, 47, 23788–23793. [CrossRef]

58. Kong, L.J.; Zhou, Y.; Liu, S.; Lin, Z.; Zhang, L.; Lin, F.; Tang, D.S.; Wu, H.C.; Li, J.F.; Lu, H.Z.; et al. Spin-polarized surface phase transport in a topological Kondo insulator SmB$_6$ nanowire. Phys. Rev. B 2017, 95, 235410. [CrossRef]

59. Zhou, L.; Ye, B.C.; Gan, H.B.; Tang, J.Y.; Chen, P.B.; Du, Z.Z.; Tian, Y.; Deng, S.Z.; Guo, G.P.; Lu, H.Z.; et al. Surface-induced positive planar Hall effect in topological Kondo insulator SmB$_6$ microribbons. Phys. Rev. B 2019, 99, 155424. [CrossRef]

60. He, X.S.; Gan, H.B.; Du, Z.Z.; Ye, B.C.; Zhou, L.; Tian, Y.; Deng, S.Z.; Guo, G.P.; Lu, H.Z.; Liu, F.; et al. Magnetoresistance anomaly in topological Kondo insulator SmB$_6$ nanowires with strong surface magnetism. Adv. Sci. 2018, 5, 1700753. [CrossRef]

61. Kong, L.J.; Zhou, Y.; Song, H.D.; Yu, D.P.; Liao, Z.M. Magnetoresistance hysteresis in topological Kondo insulator SmB$_6$ nanowire. Chin. Phys. B 2019, 28, 107501. [CrossRef]

62. Gan, H.; Ye, B.; Zhou, L.; Zhang, T.; Tian, Y.; Deng, S.; He, H.; Liu, F. Controllable synthesis of Gd-doped SmB$_6$ nanobelts for modulating their surface transport behaviors. Mater. Today Nano 2020, 12, 100097. [CrossRef]

63. Kang, C.J.; Denlinger, J.D.; Allen, J.W.; Min, C.H.; Reinert, F.; Kang, B.Y. Electronic structure of YbB$_6$: Is it a topological insulator or not? Phys. Rev. Lett. 2016, 116, 116401. [CrossRef] [PubMed]

64. Zhou, Y.; Kim, D.J.; Rasa, P.F.S.; Wu, Q.; Guo, J.; Zhang, S.; Wang, Z.; Kang, D.; Zhang, C.; Yi, W.; et al. Pressure-induced quantum phase transitions in a YbB$_6$ single crystal. Phys. Rev. B 2015, 92, 241118. [CrossRef]

65. Munarri, J.; Robinson, P.J.; Alexandrova, A.N. Towards a single chemical model for understanding lanthanide hexaborides. Angew. Chem. 2020, 132, 22873–22878. [CrossRef]

66. Zhang, H.; Tang, J.; Yuan, J.S.; Yamauchi, Y.; Suzuki, T.T.; Shinya, N.; Nakajima, K.; Qin, L.C. An ultrabright and monochromatic electron point source made of a LaB$_6$ nanowire. Nat. Nanotech. 2016, 11, 273. [CrossRef]

67. Zhang, H.; Jimbo, Y.; Nivata, A.; Ikeda, A.; Yasuhara, A.; Ovidiu, C.; Kimoto, K.; Kasaya, T.; Miyazaki, H.T.; Tsuji, N.; et al. High-endurance micro-engineered LaB$_6$ nanowire electron source for high-resolution electron microscopy. Nat. Nanotechnol. 2021, 1–6. [CrossRef]
68. Tang, S.; Tang, J.; Wu, Y.M.; Chen, Y.-H.; Uzuhashi, J.; Ohkubo, T.; Qin, L.-C. Stable field-emission from a CeB₆ nanoneedle point electron source. *Nanoscale* **2021**, *13*, 17156–17161. [CrossRef] [PubMed]

69. Zhou, Y.; Lai, J.W.; Kong, L.J.; Ma, J.C.; Lin, Z.L.; Lin, F.; Zhu, R.; Xu, J.; Huang, S.M.; Tang, D.S.; et al. Single crystalline SmB₆ nanowires for self-powered, broadband photodetectors covering mid-infrared. *Appl. Phys. Lett.* **2018**, *112*, 162106. [CrossRef]

70. Xue, Q.; Tian, Y.; Deng, S.Z.; Huang, Y.; Zhu, M.S.; Pei, Z.X.; Li, H.F.; Liu, F.; Zhi, C.Y. LaB₆ nanowires for supercapacitors. *Mater. Today Energy* **2018**, *10*, 28–33. [CrossRef]

71. Lee, S.; Stanev, V.; Zhang, X.; Stasak, D.; Flowers, J.; Higgins, J.S.; Dai, S.; Blum, T.; Pan, X.; Yakoveno, V.M.; et al. Perfect Andreev reflection due to the Klein paradox in a topological superconducting state. *Nature* **2019**, *570*, 344–348. [CrossRef] [PubMed]

72. Li, S. Salt-assisted chemical vapor deposition of two-dimensional transition metal dichalcogenides. *iScience* **2021**, *24*, 103229. [CrossRef] [PubMed]