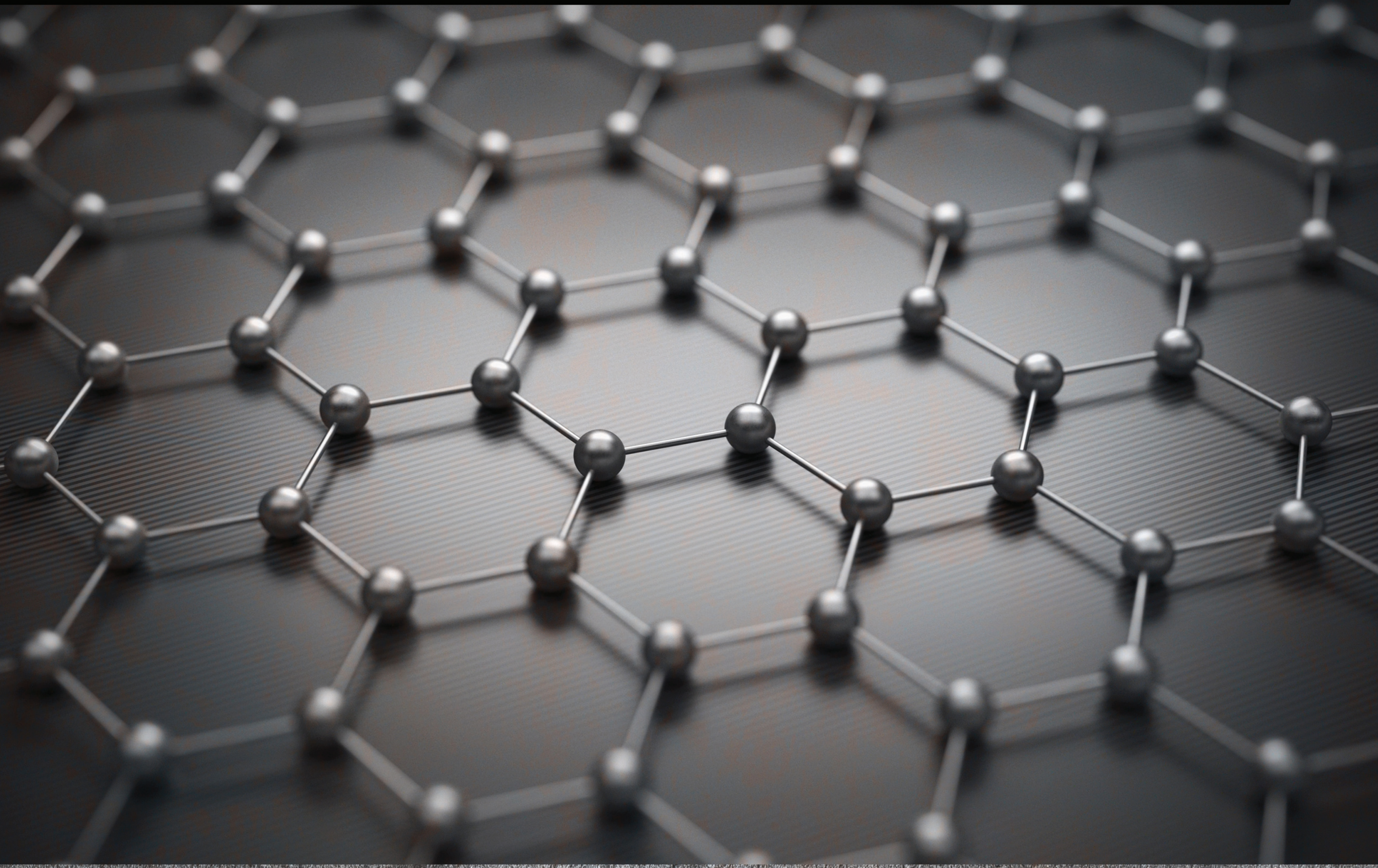
RARE-EARTH METAL HEXABORIDES:

SYNTHESIS, PROPERTIES, AND APPLICATIONS



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Rare-Earth Metal Hexaborides: Synthesis, Properties, and Applications

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CONTENTS

PREFACE

Rare-earth hexaborides have attracted continuous attention for more than half a century, both from the point of view of fundamental material sciences and for practical applications in various fields of engineering. These materials indicate a wealth of unusual electronic, mechanical, optical, and magnetic properties that have been closely investigated in recent decades using advanced spectroscopies and state-of-the-art physical characterization methods.

This book consists of a comprehensive collection of reviews offering a cutting-edge summary of the investigations based on rare-earth hexaborides from various viewpoints. The book includes chapters on the growth and characterization of different structure types of rare-earth hexaborides, and their theoretical and experimental descriptions, production methods, unusual properties, and improvements by alloying and compositing.

The book will appeal to anyone interested in material science, physics, and chemistry, especially researchers and postgraduate students who focus on production methods, structure types, and applications of rare-earth hexaboride compounds.

CONSENT FOR PUBLICATION

Not applicable.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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CHAPTER 1

The Rare-Earth Elements

Abstract: In this section, the elemental forms of rare-earth elements are iron gray to silvery lustrous metals that are typically soft, malleable, ductile, and usually reactive, especially at elevated temperatures or when finely divided. rare-earth elements are examined in terms of physical and chemical properties. This makes them essential components of diverse defense, energy, industrial, military technology, and low-carbon technologies. Furthermore, REEs are rapidly being used in magnet applications. For example, magnets produced by Neodymium-iron, the strongest known type of magnet, are used widely. Thus, their application areas vary from the electronic to glass industry. Also, information about the sources of rare-earth elements is given in this part.

Keywords: Light rare-earth elements, Heavy rare-earth elements.

1.1. INTRODUCTION

Rare-earth elements (REEs) consist of a group of 15 elements between Lanthanum and Lutetium. Based on their atomic mass, they are generally classified as light and heavy REEs (light rare-earth elements: Lanthanum (La), Cerium (Ce), Praseodymium (Pr), Neodymium (Nd), promethium (Pr), and Samarium (Sm), and heavy rare-earth elements: Europium (Eu), Gadolinium (Gd), Terbium (Tb), Dysprosium (Dy), Holmium (Ho), Erbium (Er), Thulium (Tm), Ytterbium (Yb) and Lutetium (Lu)). REEs are a group of chemically similar elements with atomic numbers from 57 to 71. Yttrium and Scandanium are 39 and 21 atomic numbers, respectively. They have also been recently regarded as REEs since they share chemical and physical similarities and have affinities with the Lanthanides [1 - 13]. The members of REEs are given in Fig. (**1.1**).

The principal economic sources of REEs are the minerals: bastnasite, monazite, loparite, and the lateritic ion-adsorption clays. rare-earth is a relatively abundant group of 17 elements composed of scandium, yttrium, and lanthanides. The elements range in crustal abundance from cerium, the most abundant element of the 78 common elements in the Earth's crust at 60 parts per million, to thulium and lutetium, the least abundant rare-earth elements at about 0.5 parts per million.

Mikail Aslan and Cengiz Bozada

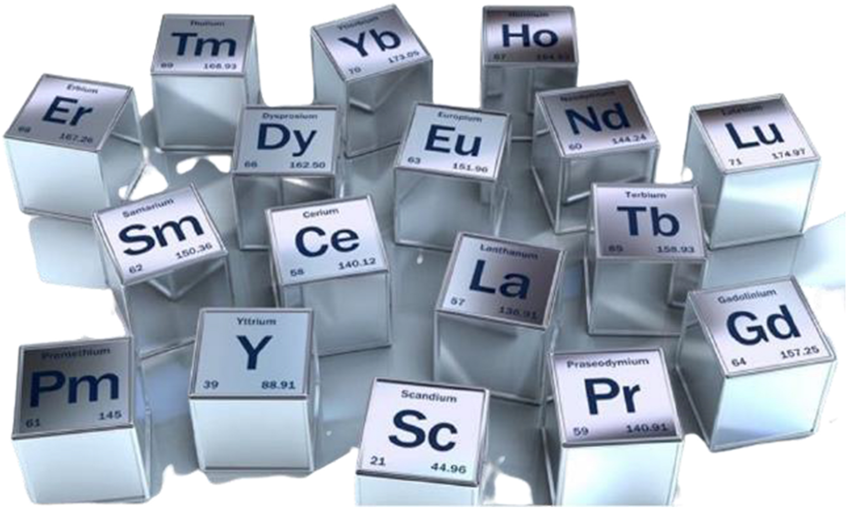


Fig. (1.1). The lists of rare-earth elements.

The elemental forms of REEs are iron gray to silvery lustrous metals that are typically soft, malleable, ductile, and usually reactive, especially at elevated temperatures or when finely divided.

The REEs have unusual physical and chemical properties, making them essential components of diverse defense, energy, industrial, military, and low-carbon technologies. The REE raw materials are widely consumed in the glass industry for glass polishing and as additives providing color and special optical properties to the glass. Lanthanum and cerium-based catalysts are preferred in petroleum refining and automotive catalytic converters, respectively. REEs are rapidly being used in magnet applications. For example, magnets produced by Neodymium-iron, the strongest known type of magnet, are used widely. Nickel-metal hydride batteries use anodes made of lanthanum-based alloys.

In this part, we have focused on the properties and the application areas of REEs, which will be discussed in detail in the following subchapters.

1.2. LIGHT RARE-EARTH ELEMENTS

1.2.1. Scandium (Sc)

Scandium (Sc) is in the IIIB group and is the lightest element of transition metals. Scandium is a white-silver metal. The atomic number of scandium is 21, and its atomic weight is 44.95 g/mol. It is a very hard-to-obtain, expensive, but precious element. Scandium which is between (REEs) and transition metals, increases the hardness of the material considerably, although it is added to the materials at a very small ratio. The properties of Sc are summarized in Table **1.1**.

Table 1.1. The properties of Scandium (Sc) [14].

Atomic weight	44.9559 g/mol
Pauling electronegativity scale	unknown
Intensity	3.0 g/cm^3 at 20 °C
Liquefaction point	1541 °C
Simmer point	2836 °C
Intermolecular forces	0.161 nm
Ionic radii	0.083 nm (+3)
Nuclide	7
Main energy level	[Ar] 3d^1 4s^2
First ionization energy	640.5 kJ/mol
Second ionization energy	1233 kJ/mol

It is used as a hardness-enhancing material in the body parts of bicycles, baseballs, and golf vehicles (Fig. **1.2**). It is also used in aviation, which includes warplanes. Recently, this element has been used as an important light source in high-quality lamps [13]. Generally,

- Scandium element is used in the production of powerful light bulbs used in night lighting and also has a daylight effect,

- Scandium-aluminium alloys are used in aircraft body production in terms of the lightness of warplanes and better maneuverability (Fig. **1.2**).

- Scandium-aluminum is used for the production of bicycle bodies due to its strong and lightweight,

- Gadolinium-scandium-gallium-garnet crystals are used in the production of defense materials and devices,

- Yttrium-scandium-gallium garnet laser is used for root canal treatments in dentistry,

- Scandium-aluminium is used in weapons production because it is light and resistant [15].

CHAPTER 2

The Rare-Earth Hexaborides

Abstract: Rare-earth hexaborides (REB_6) are composed of rare-earth elements and octahedral 3D boron units. In Chapter 1, rare-earth elements were examined in detail; in this part, the REB_6 will be explained. Hence, rare-earth hexaborides (REB_6) consisting of rare-earth elements and octahedral bor units are a group of ceramic materials that have a simple cubic structure with Pm3m symmetry. Their low electronic work function, low electrical resistance, and thermal expansion coefficient (in some temperature ranges), as well as high hardness and stiffness, high chemical and thermal stability, and melting points, provide a wide range of industrial uses from metallurgy to electronics.

Keywords: Nanomaterials, advanced ceramics, low work function.

2.1. INTRODUCTION

Due to the different properties of boron and its derivatives, Scientist and engineers have focused on its usage in industrial areas [1]. Turkey has 72.2% of the world's boron reserves; this is followed by Russia with 8.5% and the United States with 6.8% [2]. Boron, which has 5 atomic numbers, exhibits a semi-metallic characteristic [3]. They can be combined with almost all elements in the periodic table for the formation of the boride complex [4]. A system is required to classify a large group of boron compounds since boron can form compounds with most of the elements in the periodic table. Kiessling classified boride compounds into four main groups [1, 2].

I. Borates consist of isolated boron atoms such as M_4B and M_2B. When the percentage of boron in the compound increases, the formation of isolated pairs increases.
II. Borides consist of boron chains such as MB, and M_3B_4.
III. 3 borides of 2D boron atomic networks such as MB_2, and M_2B_5.
IV. Borides consist of 3D boron frames such as MB_4, MB_6, and MB_{12}.

The structural classification of Kiessling is shown in Table **2.1**. There are also other classification methods for borides, such as the content of boron in the comp-

Mikail Aslan and Cengiz Bozada

ound and the location of the metallic section in the periodic table [1]. The classification of binary metal borides can also be done by referring to the main metal group of the periodic table [3, 4].

Table 2.1. The classification of borides done by Kiesling [2].

Kiessling Group	Atomic Ratio	Examples
Isolated B atoms	M_4B, M_3B, M_2B	Mn_4B, Be_2B, Ni_3B
Pairs of B atoms	M_3B	V_3B_2
Single Chains	MB	FeB, NiB
Branched Chains	$M_{11}B_9$	$Ru_{11}B_9$
Doubled Chains	M_3B_4	Ta_3B_4, Cr_3B_4
Layer Networks	MB_2	TiB_2,MgB_2,YB_2,ReB_2
3D Frameworks	MB_4, MB_6, MB_{12}	CaB_6, ZrB_{12}, YB_{12}

This group of REB_6 has a wide range of industrial uses from metallurgy to electronics because of their low electronic work function, low electrical resistance, and thermal expansion coefficient (in some temperature ranges), as well as high hardness and stiffness, high chemical and thermal stability and melting points. These properties are due to the octahedron units providing strong covalent bondings. These bonds allow the REB_6 to exhibit superior properties [2].

The applications and developments of REB_6 nanostructures attract a lot of attention. Examining the mechanical properties of REB_6 structures is extremely important in widening their applications. Nonlinear effects are known to be important in nanostructural materials. The nonlinearity elastic properties are very important in defining nonlinearity influences in mechanical behavior. Therefore, nonlinear influences must work in the flexibility of REB_6 [3].

REB_6 are used in various materials, such as warplanes, bicycles, oil refineries, fiber optic cables, high-resolution cameras, telescopes, night vision binoculars, qualified camera lenses, fiber optic cables, artificial gemstones, lasers, magnets, electric vehicle engines, headphones, enamel colorings, computer chips, sunglasses, and tomography equipment.

In this part, we have focused on the chemical and physical properties and application areas of each REB_6 structure.

2.2. RARE-EARTH HEXABORIDES

2.2.1. Lanthanum Hexaboride (LaB_6)

Lanthanum hexaboride (LaB_6) is a vacuum-stable resistant advanced ceramic substance with a melting point of 2210 °C, unsolvable in H_2O and HCI acid. The stoichiometric samples are intensely purple-violet, whereas those rich in boron ($\geq LaB_{6.07}$) are blue [5]. The main usage areas of LaB_6 are; as a coated material in cathodes, as an optical MEMS-based sensor in the NIR range, in radar systems, in electronic and infrared applications, and environmental protection, as refining and synthetic organic chemicals. Due to the low evaporation rate concerning high-temperature electron emission and low work function [6], its application is wide. LaB_6 cathodes are used as devices and techniques such as X-ray tubes, electron lithography, electron microscopes, electron beam source, free-electron lasers, and microwave tubes (Fig. **2.1**.).

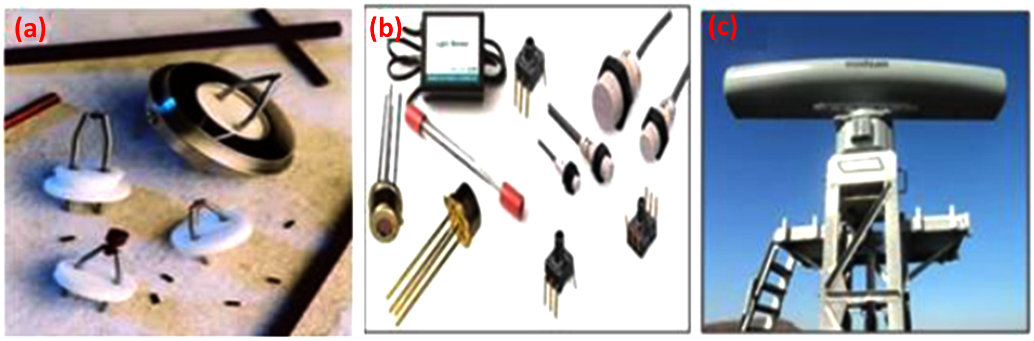


Fig. (2.1). Uses of LaB_6 **a)** LaB_6 cathode **b)** Optical MEMS-based sensor **c)** Radar system.

2.2.2. Cerium Hexaboride (CeB_6)

Among the rare-earth hexaboride family, cerium hexaboride (CeB_6) as an electron resource is appropriate to be used as thermionic electron emitters because it has a lower operating function, a lower operating temperature, and a higher electrical resistance. Recently, some investigators have focused on the field emission properties of one-dimensional nanoelectronic CeB_6, as well as nanomachine applications. It also has resistance to cathode poisoning. For this reason, it can be used in free-electron lasers, electron lithography, microwave tubes, X-ray tubes, electron beam welding, and electron microscopes [7]. Some of the applications are given in Fig. (**2.2**).

CHAPTER 3

The Structures of Rare-Earth Hexaborides

Abstract: The structures of rare-earth hexaborides can be nanoparticles, nanowires, nanotubes, nanorods, nano-obelisks, nanocubes, nanocrystals and nanocons. These types of structures indicate superior properties, such as excellent mechanical, electronic, and optical properties. For these reasons, they are used in thermionic materials, electrical coating for resistors, sensors, and high-energy optical systems. Furthermore, their low work functions make them special for the design of optical devices, such as a cathode substance for cold (field) emission

Keywords: Low work function, thermionic materials, nanostructures.

3.1. INTRODUCTION

Nano-sized materials are divided into different classes, such as nanoparticles, nanowires, nanotubes, nanorods, nano-obelisks, nanocubes, nanocrystals, and nanocons. The main step for new developments in nanotechnology includes the design, functional use, and production of nanostructured materials and tools in the production of nanoparticles. Nanosized materials always have exceptional mechanical, electronic, or optical properties. The optical features of nanomaterials are very significant to investigate because of their presence of surface plasmon resonance character and nanoscale dimension [1]. REB_6 nanostructures, both in the shape of nanorods, nanocubes, nanowires, nanoparticles, nanotubes, nano-obelisk, nanoblets, nanoawls, amorphous, nanocrystals, and nanocones, have drawn significant notice because of their extensive diversity of possible implementations in thermionic materials, electrical coating for resistors, sensors and high energy optical system. REB_6 nanostructures are considered the best thermionic electron source for field emissions applications due to their high melting point, high chemical resistance, high conductivity, low volatility at high temperatures, and low work functions. REB_6 are accepted as productive cathodes for improved vacuum electronic tools [2]. Having a low work function is a very important criterion in terms of being designed as a cathode substance for cold (field) emissions that offer more than a hundred times brightness. Hence, REB_6 is the most excellent thermionic electron resource [3].

Mikail Aslan and Cengiz Bozada

Many methods, such as spark plasma sintering (SPS), chemical vapor deposition (CVD), and mechanochemical, floating zone methods, have been used to produce REB_6 nanostructures. SPS is an important technique for REB_6 nanostructures at low temperatures. The SPS technique is one of the suitable methods to produce nanostructured intense REB_6 with superb properties [4]. One of the methods used to develop REB_6 nanostructures is chemical vapor deposition. REB_6 nanostructures are potentially used as point electron emitters for applications including cold emission, Edison effect (thermionic emission), and thermal field-induced electron emission for TEM, SEM, smooth panel screens, and other electronic tools that need high-performance electrons [5].

One of the methods used to produce high-purity REB_6 nanostructures is the mechanochemical method. The mechanochemical method is an important method for REB_6 nanostructures to show very good properties [6]. One of the methods used for REB_6 nanostructures to have excellent applications possibilities as thermionic cathode substances is the floating zone method. Moreover, this method usually provides a contamination phase that directly reduces emission and crystal quality characteristics [7]. The different structure types of REB_6 are listed in Table **3.1**.

In this part, we have focused on different types of REB_6 structures, such as nanowires, nanotubes, nanorods and nanocubes. Furthermore, recent developments and new trends have been discussed.

3.2. NANOSTRUCTURES

3.2.1. Nanowires

Nanowires are nanostructures in a cylindrical form quite similar to carbon nanotubes. Generally, nanowires have a thickness or diameter of tens of nanometers. There are several types of nanowire insulators (SiO_2, TiO_2), semiconductors (Si, Ge, InP, GaN), metallic (Ni, Pt, Au, Fe), and carbon nanotubes. In the production of nanowires, many common laboratory techniques, such as extraction, chemical deposition, vapor transport (deposition), and vapor-liquid-solid magnification, are used [8]. Nanowires have very important applications in optoelectronics (light-interacting electronic devices), electronics, tips for bio-molecular nano-sensors, nano-electromechanical devices, advanced composites, nano-scale quantitative instruments for metallic interconnections, and as field emitters [9]. Zou *et al.* synthesized CeB_6 nanowires by the self-catalyst method. Their results indicate that CeB_6 nanowires have a diameter of approximately 20-100 nm, and the longness recumbents to a few micrometers [10]. Fig. (**3.1**) illustrates the images of the CeB_6 dendritic crystal. The diameters are approximately 30 nm, and the trunk has a longness of approximately 4 mm. It is also observed that the diameter of the branches is about 30 nm.

Table 3.1. The structures of the given materials.

Material	Structure	Fabrication Method	References
CeB_6	Nanowires	Self-catalyzed CVD	[10]
NdB_6	Nanowires	Self-catalyzed CVD	[11]
LaB_6	Nanowires	Self-catalyzed CVD	[12]
GdB_6	Nanowires	Self-catalyzed CVD	[13]
SmB_6	Nanowires	Self-catalyzed CVD	[14]
EuB_6	Nanowires	Self-catalyzed CVD	[15]
LaB_6	Nanotubes	Self-catalyzed CVD	[12]
EuB_6	Nanotubes	Self-catalyzed CVD	[15]
LaB_6	Nanorods	Aluminum flux method	[18]
LaB_6	Nanocubes	Molten salt technique	[20]
LaB_6	Nanocubes	Solid-state technique	[21]
CeB_6	Nanocubes	Electrochemical synthesis	[22]
LaB_6	Nano-obelisk	Metal-catalyzed CVD	[24]
NdB_6	Nano-obelisk	Metal-catalyzed CVD	[25]
NdB_6	Nanoparticle	Mechano-chemical alloying	[28]
SmB_6	Nanoparticle	Solid-state technique	[29]
NdB_6	Nanoparticle	Melt spinning technology	[30]
PrB_6	Nanoparticle	Metal-catalyzed CVD	[2]
SmB_6	Nanobelts	Metal-catalyzed CVD	[32]
SmB_6	Nanobelts	Metal-catalyzed CVD	[33]
$La_xPr_{1-x}B_6$	Nanoawls	Simple flux-controlled technique	[34]
EuB_6	Amorphous	Liquid plasma technique	[36]
LaB_6	Amorphous	Solid-state technique	[37]
SmB_6	Nanocrystals	Mechanochemical synthesis	[29]
PrB_6	Nanocrystals	Solid-state technique	[40]
SmB_6	Nanocrystals	Metal-catalyzed CVD	[41 - 43]

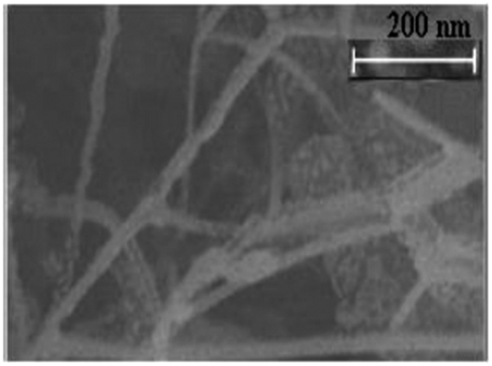


Fig. (3.1). SEM picture of a CeB_6 dendritic crystal Adopted from [10] (Copyright © 2006 Published by Elsevier B.V.).

CHAPTER 4

The Rare-Earth Hexaborides Production Methods

Abstract: To produce rare-earth hexaborides, some methods exist: direct solid phase, carbothermal reduction, borothermal reduction, self-propagating synthesis, aluminum flux method, spark plasma sintering, and mechanochemical synthesis, floating zone method, and chemical vapor deposition. In this section, the drawbacks and advantages of these production methods will be discussed.

Keywords: Production methods, raw materials, advanced materials.

4.1. INTRODUCTION

To prepare pure REB_6 powders, various methods, such as direct solid phase, carbothermal reduction, borothermal reduction, self-propagating synthesis (SHS), aluminum flux method, spark plasma sintering (SPS), mechanochemical synthesis, floating zone method (FZM), and chemical vapor deposition (CVD), were used [1 - 4]. The single-phased REB_6 is studied by the direct solid-phase technique of $NaBH_4$ with CeO_2 and Eu_2O_3. This technique indicates the benefits of inexpensive and controlled grain dimensions. Moreover, this method is considered significant for the development of new RE nanomaterials with a wide variety of probable applications. The microstructure of raw materials needs to be examined because the particle size of raw materials in solid-state reactions affects the particle size of final products [5]. Currently, the carbothermal reduction technique is broadly improved because of its simple equipment and inexpensive. In addition, powders made with those techniques have a few defects like poorer sintering properties, lower naivety, and larger particle size [6]. In other studies, the average particle dimension of REB_6 produced by SHS by reduction technique shows that the grain size prepared by conventional technique is less than 500 nm which is finer. The SHS method is capable of producing materials with ultrafine microstructures, but grain growth occurs during the combustion reaction method because of high synthesis temperatures and improved mass transfer. It is likely to check the grain development by varying the parameters. In recent years, SHS has attracted attention because of its proven advantages, such as high product purity, low energy expenditure, and simple operation. Therefore, SHS method can be a

Mikail Aslan and Cengiz Bozada

good choice for producing REB_6 powders [7]. The aluminum flux method is also very important. This method has a significant function in the production of REB_6. But the fabrication productivity is small, and it is tough to abstain from the existence of Al contaminations [8]. SPS is a valuable technique for quick sintering, which can enhance the intensity and mechanical features. In addition, SPS is an important technique for the rapid intensification of ceramic nanopowders at low temperatures. The SPS method showed a proper technique to fabricate nanostructured REB_6 with superior properties [9]. Mechanochemical synthesis enables quick preparation for amorphous materials; oxide dispersion strengthened alloys, non-equilibrium alloys, advanced materials, nanocomposites, solid solution alloys, ceramics, and intermetallics, which are difficult or not possible to be acquired by traditional fabrication methods. Mechanochemical production is important in many characteristics, such as the type of milling atmosphere, milling time, milling rate, milling container, milling speed, milling environment, and ball-to-powder weight ratio (BPR) process control agent size, and dispersion of milling media. Mechanochemical synthesis is associated with fracturing, repeated welding, and the contact points between powder particles, providing favorable conditions for the presence of crops [10]. FZM is well suitable for preparing big refractory crystals. The development of big crystals of substances is possible with the floating zone technique. It is possible to examine the work function and the crystal electronic structure of REB_6 *via* FZM [11]. CVD method successfully produces REB_6 with well-defined morphology. REB_6 produced by the CVD is potentially used as dot electron emitters for field-based emission applications. The TEM, SEM, and heat field-based emission of electrons for smooth panel displays, like another electronic tools requires high-performance electron sources [12 - 15]. The self-propagating high-temperature synthesis method uses less energy for the fabrication of materials. Physical vapor deposition method (PVD) is corrosion resistant and high temperature resistant. SPS has many advantages, such as high sintering speed, high repeatability, and safety. The mechanochemical method is notable for its higher yields and shorter reaction times. The fabrication methods are summarized in Table **4.1** [16 - 33].

In this part, we have focused on the main methods that produce REB_6 structures. Basic information, recent trends, and new developments have been discussed.

4.2. PRODUCTION METHODS

4.2.1. Carbotermic Reduction Method

Carbotermic reduction is the phenomenon of reduction of metal-oxides to carbon and carbon intermediates. It is possible to examine the reactions in two groups direct reduction and indirect (indirect) reduction. Direct reduction events are reactions that occur as a result of the reduction of metal-oxides directly with carbon, while indirect reduction is the reaction that occurs as a result of the reduction of metal-oxides with carbon monoxide (CO), which is caused by the gasification of carbon (C). Raw and mechanically activated powder mixtures are carried out by the carbothermic reduction process in high-temperature furnaces according to the following stoichiometric ratios.

$M_2O_3 + 3B_4C \rightarrow 2MB_6 + 3CO$ (M =La,Ca, Ce, Sm, Er and Eu)

Table 4.1. The fabrication methods of the given materials.

Material	Fabrication Method	References
LaB_6	Carbotermic reduction method	[3]
PrB_6	Float zone method	[5]
CeB_6	Float zone method	[6]
CeB_6	Float zone method	[7]
LaB_6	Electrochemical Synthesis	[9]
CeB_6	Electrochemical Synthesis	[10]
LaB_6	Solid-State Reaction	[12]
PrB_6	Borothermal (Carbothermal)	[15]
CeB_6	Low-Temperature Synthesis	[19]
GdB_6	Low-Temperature Synthesis	[20]
LaB_6	Self-Propagating High Temperature	[22]
CeB_6	Self-Propagating High Temperature	[23]
LaB_6	Physical vapor deposition	[25]
LaB_6	Spark Plasma Sintering	[27]
LaB_6	Spark Plasma Sintering	[28]
CeB_6	Spark Plasma Sintering	[29]
CeB_6	Spark Plasma Sintering	[30]
LaB_6	Mechanochemical Synthesis	[32]
LaB_6	Mechanochemical Synthesis	[33]

Low-cost boron-carbide powders can be advantageously produced with low-temperature carbothermic reaction processes [1]. Detailed characterization studies of the obtained powders are carried out using XRD, SEM / EDS, TEM, and DSC tools. The carbothermal reduction production method has some disadvantages. Due to kinetic limitations such as limited contact area between reactants and irregular carbon distribution, the reaction may take place at higher temperatures. However, due to these limitations and high temperatures, grain growth, irregular grain shape, and unreacted carbon may be observed as a result of this process. It is a form of production with high energy consumption since it takes time to process [2]. Yu *et al.* synthesized LaB_6 nanoparticles using the carbothermic reduction method. The high purity of the synthesized LaB_6 was shown, and no additional peaks were detected from the impurities. The XRD analysis of high-purity LaB_6 powders is given in Fig. **(4.1)** [3].

CHAPTER 5

The Rare-Earth Hexaboride-Based Alloys

Abstract: The rare-earth hexaboride can be both alloyed with alkaline earth hexaboride and rare-earth hexaborides. Both alloying types have different types of advantages. For example, large-size triple $La_xCe_{1-x}B_6$ single crystals produced by the floating zone method showed excellent field emission and thermionic emission characteristics. Thus, these types of alloys indicate superior performance (electronic, magnetic, excellent field emission, thermionic emission properties) when compared to their pure counterparts.

Keywords: Alkaline earth materials, optical performance, the density of state.

5.1. INTRODUCTION

The alloys are formed by mixing two or more elements [1]. Alloying elements are added to REB_6 to induce ductility, hardness, toughness, or other desired properties. Most alloys can be work-hardened by creating defects in their crystal structure. These defects are created during plastic deformation by hammering, bending, and extruding. The properties of many alloys can also be changed by heat treatment. Some of the metals can be softened by annealing, which recrystallizes the alloy and repairs the defects [2]. Alloying REB_6 with other metals improves the properties of REB_6. For example, the alloying reduces the total kinetic energy of the electrons of REB_6 and leads to the absorption valleys altering to a longer wavelength direction and the red-shift in the absorption valley [3]. The density of states (DOS) of a system defines the proportion of states that will be occupied by the system at each energy. Fermi energy is the difference in energy between the highest and lowest occupied single-particle states in a quantum system that is usually composed of fermions that don't interact at absolute zero temperature in quantum mechanics. The alloying of REB_6 can adjust DOS and the position of the Fermi energy level. In addition, the work function of REB_6 can be considerably reduced, providing better emission performance than REB_6. They also can considerably improve their thermionic emission property [4]. The optical properties of alloyed REB_6 draw attention. Plasmon energy is proportional to the square root of the free electron density in a metal. The plasma frequency is the frequency at which electrons in the plasma naturally oscillate

Mikail Aslan and Cengiz Bozada

relative to ions and has values between 2 and 20 MHz—excited as a collective oscillation of all valence electrons also in semiconductors and insulators. Among its optical properties, plasmon energy and plasma frequency behavior stand out. Alloying of REB_6 leads to a reduction of the plasmon energy and plasma frequency of REB_6. REB_6 has higher Fermi energy than alloyed REB_6 [5].

In this part, we have focused on the two types of REB_6-based alloy structures. The chemical and physical properties of these alloys have been discussed.

5.2. THE ALLOYED ALKALINE-EARTH METAL HEXABORIDES MB_6 (M=CA, SR, BA) WITH RARE-EARTH HEXABORIDES

The electrical and mechanical properties of both alkaline and rare-earth hexaborides are important. Alkaline earth metal hexaboride (MB_6), CsCl type simple cubic CaB_6, SrB_6, and BaB_6 have common properties with Rare-Earth hexaborides due to their high hardness, high melting points, good chemical stability, low thermal expansion coefficient, and low density. The mechanical properties of these hexaborides are very significant because of their use as structural ceramics [6].

Lanthanum hexaboride (LaB_6) is characterized by its high melting point, high electrical conductivity, and low operating function [7, 8], making it one of the best thermionic materials for high electron-density cathodes. LaB_6 nanoparticles are used as solar radiation heat protection material for automotive and architectural windows due to their high optical absorption coefficient in the near-infrared region and high permeability in the visible region [9]. In another study, Takeda *et al.* prepared LaB_6 nanoparticles by a ball milling method to obtain ultra-fine nanoparticles [10]. Lihong Bao *et al.* conducted a synthesis of $La_{1-x}Ba_xB_6$, a cubic-shaped triple nanocrystalline, by simple step solid-state reaction, and the effects of Ba-doping on the optical and magnetic properties were investigated. Interestingly, Ba doping caused the wavelength of the absorption valley and the absorption peak of LaB_6 to shift to red. In addition, Ba doping causes the fermentation of nanocrystalline LaB_6 at room temperature. According to the first principle calculation results, the doped Ba reduces the total kinetic energy of electrons of LaB_6, so the absorption valleys move towards a higher wavelength [11]. CeB_6 shows excellent optical absorption properties [12]. Xiaoping Qi *et al.*, nanocrystalline Ca-doped CeB_6 powders were synthesized under a vacuum condition with $NaBH_4$ in a solid-state reaction of CaO and CeO_2. The optical absorption properties and grain morphology of nanocrystalline CeB_6 and Ca doping effects on phase composition were investigated by Xiaoping Qi. Grain size and morphology are very sensitive to the reaction temperature. As a result of optical absorption, the absorption valley of the nanocrystalline CeB_6

shows a redshift from 619 nm to 685 nm with increasing Ca doping; this means adjustable optical absorption of nanocrystalline Ca doped CeB_6. In addition, a first principle calculation was used to reveal the origin of adjustable optical properties. Ca doping was found to reduce the total kinetic energy of the CeB_6 electrons and cause the absorption valleys to shift to the longer wavelength direction [13]. Fig. (**5.1a**) shows the XRD models of the nanocrystalline $Ce_{0.8}Ca_{0.2}B_6$ prepared at a reaction temperature of 900-1200ºC. Fig. (**5.1b**) shows the XRD patterns of nanocrystalline $Ce_{1-x}Ca_xB_6$ with various Ca doping contents x = 0, 0.2, 0.4, 0.6 and 0.8 prepared at 1200 ° C for 2 hours.

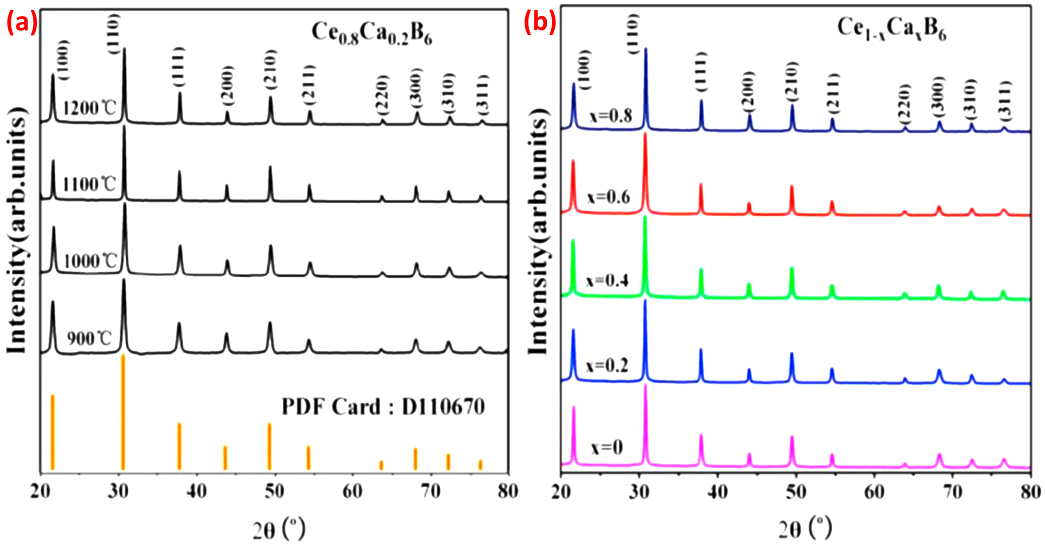


Fig. (5.1). (a) XRD patterns of nanocrystalline $Ce_{0.8}Ca_{0.2}B_6$ prepared at different temperatures for 2 hours; **(b)** XRD patterns of nanocrystalline $Ce_{1-x}Ca_xB_6$ prepared at 1200 ° C for 2 hours. Adopted from [13] (Copyright © 2017 Elsevier B.V.).

The origin of ferromagnetism in light electron-doped $Ca_{1-x}La_xB_6$ is a major problem in physics because there are no partially filled d or f orbitals required for magnetism [14]. In another study, EuB_6 has been extensively studied for its magnetic and transport properties for ferromagnetic transmission [15]. The ferromagnetism of EuB_6 was confirmed by neutron scattering measurements, and it was found that the magnetic moment stable Eu^2 moment was due to localized 4 f electrons [16]. In another study, Jong-Soo Rhyme *et al.* studied the temperature and field-dependent magnetic properties of the $Eu_{1-x}Ca_xB_6$ compounds. It was found that a ferromagnetic transition temperature up to Tc = 5.5 K is suppressed, and also, small Ca doping in $Eu_{0.87}Ca_{0.13}B_6$ caused the suppression of a ferromagnetic transition temperature from Tc = 12 K for EuB_6 to Tc = 5.5 K for $Eu_{0.87}Ca_{0.13}B_6$ [17]. Also, M. Batkova *et al.* conducted a study on the effect on the

CHAPTER 6

The Rare-Earth Hexaboride Based Composites

Abstract: Rare-Earth metal hexaborides (REB_6) can be composited with some kind of ceramics, such as SiC, MgO, Carbon Nanotube, and Alumina. These types of composites can show excellent mechanical, optical, and thermionic properties. For example, SiC ceramics have high condensation behavior, high corrosion resistance, high thermal shock resistance, and high hardness properties; MgO ceramics have high fire resistance, high thermal conductivity, and low electrical conductivity properties; Carbon nanotubes have high optical and mechanical properties and Al_2O_3 ceramics have high abrasion and corrosion resistance and low density. The sizes of these materials are also significant as nano, and micro-sized ceramic materials have different properties when forming a composite with REB_6 or any materials.

Keywords: Mechanical properties, High friction resistance, High thermal shock resistance, Microstructure.

6.1. INTRODUCTION

Due to their high melting points, excellent strength, and creep resistance, REB_6-based composites can be used as a good structural material at high temperatures (>1200°C) [1, 2]. REB_6 structures are composited with some kind of ceramics, such as $X^{IV}B_2$ (X^{IV}-Ti, Zr, Rf, and Hf), SiC, MgO, Carbon Nanotube, Alumina, *etc.* They indicate important properties, such as strong hardness and friction resistance at high temperatures, making them attractive as structural materials. For example, $X^{IV}B_2$ (X^{IV} - Ti, Zr, Rf, and Hf) ceramics have high hardness, bending strength, and stress hardening at high temperatures; SiC ceramics have high condensation behavior, high corrosion resistance, high thermal shock resistance, high hardness properties; MgO ceramics have high fire resistance, high thermal conductivity, and low electrical conductivity properties; CNT materials have high optical and mechanical properties and Al_2O_3 ceramics have high abrasion and corrosion resistance and low density. The sizes of these materials are also important since nano and micro-sized ceramic materials show different properties when forming a composite with REB_6 or any materials.

Mikail Aslan and Cengiz Bozada

There are many available methods for the production of composites consisting of REB_6 (see Chapter 4). For example, LaB_6-ZrB_2 composites are produced by vacuum hot press sintering technique and prepared by floating zone method based on melting of the crucible free zone of powders. LaB_6-TiB_2 composites are produced by the floating zone method. The method is based on crucible-free zone melting, and the products are obtained by dissolving them in argon flow in the electric arc. CeB_6-$TiSi_2$ composites are produced by sintering with reactive spark plasma (SPS). LaB_6-MgO composites are produced by the screen printing technique and magnetron spraying method. LaB_6-CNT and CeB_6-CNT composites are synthesized by physical (PVD) and chemical vapor deposition (CVD). LaB_6-Al_2O_3 composites are produced with high-energy ball grinding, annealing, and leaching processes. After synthesizing these composites, hardness, surface morphology, optical, discharge properties, fracture strength, condensation behavior, microstructure, and mechanical properties of REB_6 composites can be analyzed by TEM, XRD, SEM, Raman, and XPS.

In this part, we have focused on phase stability, microstructure, mechanical performance, and absorption properties of composites consisting of nano and micro ceramic materials with REB_6.

6.2. REB_6-XIVB_2 COMPOSITES

REB_6-$X^{IV}B_2$ (X^{IV}=Ti, Zr, Hf, or V) composites have low work functions, high thermionic current and electron emission density, mechanical properties, and enhanced thermal-shock resistance [3]. Due to these properties, REB_6-$X^{IV}B_2$ composites are one of the best candidates for electrode application in space propulsion [4]. $X^{IV}B_2$ has a higher melting point and Young's modulus than REB_6 single crystal [5]. REB_6-$X^{IV}B_2$ has a large improvement in current density compared to single-crystal REB_6. Furthermore, REB_6-$X^{IV}B_2$ composites exhibit improved thermal cycling reliability as compared with REB_6 [6].

Due to its high melting point, REB_6-$X^{IV}B_2$ can also be used as a good structural material at high temperatures. Existing oxide-oriented solidified composites have attracted much attention in this field because they exhibit excellent strength and frictional resistance at high temperatures (> 1200°C), making them attractive as structural materials [7, 8]. However, in this class of materials, the fracture strength is low since the interfaces between the two phases typically adopt low-energy bonding orientation relationships during the directional solidification process, which supports strong bonding and prevents the sticking of the interfaces [9]. Directly crystallized composites of REB_6-$X^{IV}B_2$ (X^{IV}-Ti, Zr, Rf, and Hf) are the most investigated ceramic materials [10 - 12].

6.2.1. LaB_6-ZrB_2 Composites

Zirconium diborides (ZrB_2) are grey, have a very high melting temperature (3245°C), and their crystal structures are hexagonal. ZrB_2, carbon, zirconium, and boron oxide can be produced by reacting in the electric arc furnace. Furthermore, ZrB_2 has oxidation resistance, high hardness, and thermal shock resistance. ZrB_2 ceramics are used as molten metal containers, diffusion barriers in semiconductors, and ignite absorbers in nuclear reactor cores [13].

Lanthanum hexaborides(LaB_6) have low work functions. LaB_6-ZrB_2 composites have a current density of 4-5 times higher than that of pure LaB_6. The resistance of LaB_6-ZrB_2 composites to thermal shock and poisoning is higher than that of pure LaB_6 [14]. Paderno *et al.* reported that the boron-boron (B-B) distance in LaB_6 can be modified by adding ZrB_2. They suggested that if the B-B distance in the hexaboride was close to the distance in the diboride, the semi-compliant interface could be formed between the LaB_6-ZrB_2 composite [11]. In a different study, Chen *et al.* prepared LaB_6-ZrB_2 composites from LaB_6 and ZrB_2 powders, then pressed and melted them with an electric arc to form rod samples. They performed directional solidification in a vacuum heated at 2900 ° C with the electron beam and floating zone melting furnace [12]. In a separate study, Wang *et al.* characterized the microstructures of LaB_6-ZrB_2 composites with transmission electron microscopes (TEM, 100CXII or HRTEM, TECNAI F-30, Philips, Holland) equipped with energy-separated X-ray spectrometry (EDS). LaB_6-ZrB_2 composites were able to magnify along one direction to show well-oriented ZrB_2 fiber and well-dispersed LaB_6 matrix after directional solidification [15]. In a different study, Min *et al.* produced polycrystalline LaB_6-ZrB_2 composites with different ZrB_2 content by vacuum hot press sintering technique 330.0MPa and 3.70 $MPa \cdot m^{1/2}$ according to the results obtained, the hardness and flexural strength of LaB_6-ZrB_2 polycrystalline increased with increasing ZrB_2 content; however, fracture toughness first reaches a peak corresponding to a content of ZrB_2 of 21% by weight. In the microstructure observation, a concentration was detected due to the addition of ZrB_2. Fig. (**6.1**) shows the detailed morphology of transgranular fracture in the LaB_6 matrix and intergranular in the ZrB_2 field [16]. In a similar study, Bogomol *et al.* prepared a directed LaB_6-ZrB_2 by floating zone method based on melting of the crucible free zone of compressed powders. ZrB_2 and LaB_6 powders were used as the first materials. The flexural strength of the composite was evaluated in the temperature range of 25-1600 °C and reached 950 MPa at 1600 °C. The fracture strength, SEM, and TEM hardening mechanisms were investigated under different conditions. They predicted that the strength of LaB_6-ZrB_2 at 25-1200 °C was mainly associated with crack deflection, bridge hardening mechanisms, increased plasticity of the ZrB_2

CONCLUSION

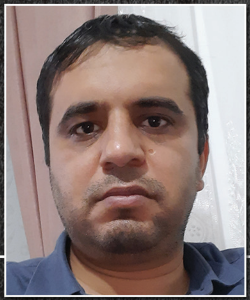
Rapid progress in several significant branches of modern industry will be directly affected by the development of new or improved technological instruments and machines, and thus, from this perspective, one of particular attention should be dedicated to the manufacture and extensive application of materials with tailor/superior properties, referring to increase in the life and operational reliability of instruments and machines. Certain metal-like compounds, specifically, hexaborides of rare-earth metals, have been seen as suitable for this purpose. With the aid of some of these materials, modern scientific and engineering problems can be handled, and advances in new technological instruments and machines can be moved to the next levels since rare-earth hexaborides are promising materials due to their unique characteristics, such as high melting point, hardness, chemical stability, low work function, low volatility at high temperatures, superconductivity, magnetic properties, efficiency, thermionic emission, and narrowband semiconductivity.

Metal hexaborides, including rare-earth element metals, are a class of simple cubic structured refractory materials with symmetry. This group of metal hexaborides has low electronic work function, low electrical resistance, and thermal expansion coefficient (at some temperature ranges), combined with high hardness and stiffness, high chemical and thermal stability, and melting points. Due to these properties, they can be used in a wide range of industrial applications, ranging from metallurgical to the electronics industry. High-resolution optical systems, welding technology, detectors, and metallic coatings based on high voltage and temperature, thermionic materials, electron microscopes, X-ray tubes, and nuclear materials are some of these areas. Furthermore, the use of metal hexaborides as a component of composite materials in the aerospace industry has gradually increased. To understand and improve the chemical and physical properties of the material, it is necessary to use the correct methods with high-purity production, and then the electronic properties of these structures should be investigated. Many production techniques have been applied in the preparation of rare-earth hexaborides. Traditionally, rare-earth borides are synthesized by high-temperature reaction processes, such as the direct solid-phase reaction of the corresponding elements/compounds, the carbothermal reaction of the rare-earth oxides, and B or boron carbide (B_4C). As a result, after the successful production of these materials, very fine powders with a high purity level can be produced homogeneously. After a successful production, microstructural, electronic, optical, mechanical, and thermal analyses should be examined. After these results, one of the doping, alloying, and compositing processes will be done to improve the properties of the materials. Before synthesizing rare-earth metal hexaborides, which materials and at what rate should be doped, alloyed, and composited should be reviewed.

This book presents an overview of synthesizes, properties, and application areas of rare-earth metal hexaborides to guide researchers and engineers in pursuing these interesting and unique materials. Also, this study focuses on recent developments and trends regarding the synthesis, characterization, and applications of these materials.

SUBJECT INDEX

> *A delightful guide, full of important information for those of us who want to investigate rare-earth hexaborides in detail.*
>
> ***Dr. Hasan Eskalen***
> *Sutcu Imam University*
> *Turkey*



MIKAIL ASLAN

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