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INVESTIGATION OF STRUCTURE, MORPHOLOGICAL AND OPTICAL PROPERTIES OF h-BN CERAMIC MATERIALS

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My love to my precious family.

ABSTRACT

INVESTIGATION OF STRUCTURE, MORPHOLOGICAL AND OPTICAL PROPERTIES OF h-BN CERAMIC MATERIALS

Boron is a important element and is not found alone in nature, it is present in compounds with other elements. Boron has a wide range of uses in modern technology, from the defence industry to the pharmaceutical industry, from cleaning agents to the nuclear industry.

In the future, this important and indispensable position of boron will continue to increase. In this study, the world and in Turkey's boron extremely important for many industrial structural, electrical, and provide information on the specifications. In addition, the production and construction properties of hexagonal boron nitride produced from boron will be explained.

Key words: Boron, hexagonal boron nitride, boron properties, boron nitride product, ceramic materials.

ÖZ

h-BN SERAMİK MALZEMELERİN YAPISI, MORFOLOJİK VE OPTİK ÖZELLİKLERİNİN İNCELENMESİ

Bor önemli bir elementtir ve tek başına doğada bulunmaz, başka elementler içeren bileşiklerde bulunur. Bor, savunma endüstrisinden ilaç endüstrisine, temizlik maddelerinden nükleer endüstriye kadar modern teknolojide geniş bir kullanım alanına sahiptir. Borun bu önemli ve vazgeçilmez konumu gelecekte de artarak devam edecektir.

Bu çalışmada borun, dünya ve Türkiye için son derece önemli olan endüstriyel yapısı, elektriksel ve teknik özellikleri hakkında bilgi vermektedir. Ayrıca bu çalışmada bor oksidin karbon ve nitrojen ile reaksiyonu sonucunda hekzagonal bor nitrür oluşumu araştırılmıştır.

Anahtar kelimeler: Bor, hekzagonal bor nitrür, borun özellikleri, bor nitrür üretimi, seramik malzemeler.

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ABBREVIATIONS

3D : There-dimensional

h-BN : Hexagonal Boron Nitride

PM : Powder Metallurgy

SFF : Solid Free-Form

CAD : Computer-Aided Design

MRI : Magnetic Resonance Imaging

UV : Ultraviolet

PC : Polycarbonate

2D : Two-Dimensional

CNC : Computer Numerical Control

SEM : Scanning Electron Microscopy

PLA : Poly(lactic acid)

PEG : Poly(ethylene glycol)

PVA : Poly(vinyl alcohol)

μm : Mikrometer

nm : Nanometer

SEM : Scanning Electron Microscope

XRD : X-ray Diffraction

FTIR : Fourier Transform Infrared Spectroscopy

PVD : Physical Vapor Deposition

GPa : Gigapaskal

MPa : Megapaskal

Å : Angström

eV : Elektron volt

kV : Kilovolt

mA : Milliampere

Maks. : Maximum

Min. : Minimum

ε_r: Relative Permeability or Dielectric Constant

X : Magnification Ratio in SEM Images

BN : Bor Nitrür

Cm : Centimeter

Mm : Millimeter

UAV : Unmanned Aerial Vehicle

IFF : Friend or Foe Identification

ICSD : Inorganic Crystal Structure Database

CHAPTER 1

INTRODUCTION

In general, borates are called natural minerals containing boron and borates have been used by humans for thousands of years. Boron; In addition to being a substance that spreads from cleaning materials to space technology and used in a wide range, it has become an important consumption product of many developed countries, especially USA, EU and Japan, as it has a wide spectrum of usage.

In parallel with the development of technology, boron chemicals will increase the position of being components that high technology needs. The increasing use of boron in industrial areas requiring high technology increases the use and value of boron as a raw material. 63 % of the world's boron ore reserves in Turkey and 16.4 % in the USA [1]. In this distribution; Turkey, in terms of reserves and ore quality is a very important part. the world's largest boron reserves is of great importance in terms of presence in Turkey.

Today, boron compounds such as boron oxide, phyuoborates, sodium borohydride, borates, meta borates, boron, boron nitride, boron carbide, boric acid esters, alkyl / aryl borones also occur. With the diversity of boron-based chemicals, studies are conducted to obtain semiconductor, protective, disinfecting, corrosion resistant materials.

In this study, the production and optimization conditions of hexagonal boron nitride, which has a very high added value and comes after diamond in hardness, are determined by using the raw materials of our country, and the syntheses obtained are used in defense industry and other technology fields and to support the formation of surplus products. There are serious reasons that make the study necessary. Especially in terms of raw materials, our country has 63 % of the world's boron reserves. Many boron compounds produced from boron ores and chemicals have very high added value, and boron-based ceramics have a great strategic importance among high-tech ceramics.

For example, materials such as hexagonal boron nitride are an example of boron-based products, which are high-tech materials with technical applications especially in the defense and technology industry.

These compounds are used in most of today's high-tech materials and are sold well above their cost values. By diversifying the use of boron, whose raw material source is mostly in our country, it can be evaluated both as a surplus product and as a technical application product in the fields of defense and technology.

In addition, hexagonal boron nitride, which is aimed to be synthesized, has physical and chemical properties that can create various added value and offer solutions to many sectors. Porous structure, low elasticity modulus, high thermal conductivity, electrical insulation, chemical stability and lubrication have formed the basis for this study.

With the results to be obtained, it is thought that hexagonal boron nitride will take place in an effective production system especially in the field of defense and technology industry.

It can be predicted that it can be used as an active material in applications such as high-frequency radar materials, signal cutters, microwave antenna circuit elements, missile tracking systems and microwave, where technical developments continue rapidly.

There are also studies in the field of 5G technology, which is one of the most important technological developments of recent days. The 5th generation mobile telecommunications service is a new generation of wireless transmission and radar technology.

It can also be called restructuring the technological infrastructure in cellular networks used by satellite, antenna, radar and mobile phones with new rules. In addition, it is a new technology system that provides approximately 10 times the data transmission speed of the fourth generation technology.

With the advancing technology era, modern telecommunication systems such as 5G technology and systems radio links, radars and mobile devices require antennas that

can operate in different complex environments. This is especially true for high-end devices such as smartphones, tablets and wireless sensor networks.

In particular, in addition to the usual voice and other services of standard previous systems, 5G generation devices, ultra-broadband Internet connection, IP telephony, mobile web access and other interesting multimedia applications, radar and jammer systems exist.

In such a framework, the design of an appropriate radiation system can play a key role in the design of next-generation telecommunications systems.

The antennas of these devices should be compact, light, inexpensive and should be able to maintain their performance at high levels in any environment. In such a framework, it is necessary to use compact and multifunctional antennas characterized by adaptive properties to significantly improve the performance of a telecommunications and defense industry system.

In addition, such antennas and technological systems can be used in various fields of civilian applications as well as military applications. Radars with these features can be very useful for airport surveillance and security, ground radar and unmanned aerial vehicle (UAV) tracking and tracking. In military applications, the use of smart antennas can be very useful for missile detection and tracking, anti-aircraft defense artillery and friend or foe identification (IFF) systems.

It is foreseen that the hexagonal boron nitrides to be obtained can create a management with added value in this technological system and create a field of use with the characterization and R&D to be obtained. For this reason, it is targeted with its optical, structural and morphological features and its suitability for resignation in radar, signal cutter, 5G technology, absorb material and defense fields.

1.1. What is Boron?

Boron elements as the 51st common element in the earth's crust and borosilicates have a concentration value of approximately 3 ppm. Its chemical symbol is “B” and it is the only non-metal element of the IIIA group in the periodic table.

Boron is not free in nature, it is always dependent on oxygen. The boron element has an atomic number of 5, atomic weight of 10.81, specific gravity of 2.30 - 2.46, and a melting point of approximately 2300 °C. The color of the boron element in the form of an amorphous powder is dark-brown. However, the color of the very crisp and hard monoclinic crystalline form is yellowish-brown. Boron element is the hardest element after diamond [2].

Boron is an element with the highest similarity to carbon and silicon elements in the IIIA group in the periodic table and with a high affinity for oxygen. Boron element; It has two balanced isotopes in nature, which are indicated by B^{10} and B^{11} at the rate of 19.10 - 20.31 % and 79.69 - 80.90 %, respectively [3]. The Figure 1.1 shows the boron element periodic table symbol.

According to the nature of the proportions of boron isotopes varies, B^{10} of the known ore deposits "amount, US-California, in the low, is high in Turkey.



Figure 1.1 A boron Element Periodic Table Symbol [69].

Various properties of the boron element with the compounds made with various metal and nonmetal elements allow many kinds of boron compounds to be used in the industry.

Important boron compounds include borax (tincal, boron compounds of sodium origin), colemanite (boron compounds of calcium origin), ulexite (boron compounds of sodium calcium), kernite, probertite, szyabelite, datolite, sasolite, turingan, borax decahydrate, borax pentahydrate, anhydrous borax, boric acid, sodium per borate, anhydrous boric acid, hydroboracite [4].

The value of boron mines is generally measured with B_2O_3 (boroxide), and those with a high content of B_2O_3 are considered more valuable. Boron acts as non-metal compounds in its compounds, but unlike pure boron is an electrical conductor like carbon. Crystalline boron is diamond-like in appearance and optical properties and is almost as hard as diamond.

1.2. History of Boron

History of elemental boron; It was obtained in 1808 by French Chemist Gay Lussac and British Chemist Sir Humphry Davy at the same time. These scientists have succeeded in obtaining a dark colored and flammable boron element, whose purity is not more than 50 % .

In 1895, Henri Moissari reduced boric acid and magnesium. It was able to obtain approximately 86 % purity and high amount of elemental boron. Moissan Process is still the basis for commercially obtaining low purity amorphous boron element [5].

In 1909, Weintraub decomposed the BCÇ compound in an electric arc furnace to obtain a 99 % purity boron element. After this date, new methods have been developed for obtaining high purity boron element [6].

Natural minerals containing boron are generally called borates and borates have been used by humans for thousands of years. The word “baurach”, which means borax in Arabic, is found in manuscripts dating back to 2000 years in ancient Iran and Arabia. The natural state of borax decahydrate chemical compound, tinkal, derives from "tinacana", which means borax in Sanskrit.

It is known that borates were used as melters for gold casting in Chinese ceramics dating back to BC 300 and before Babylonian Civilization. Marco Polo brought borax from Tibet to Europe at the end of the 13th century and it was started to be used as borax, soldering and glazing materials [7].

It is known that the city of Venice served as the main port in boron trade throughout the entire medieval period. The borates in Turkey, although it is known since the 13th century until recently has been used in very small amounts. In 1772, the mineral "sasolite", a natural boric acid, was discovered in the hot springs in the Tuscany region of Italy.

In 1836, borates were found in Chile and Argentina, and these deposits became the largest sources of boron in the world until the late 19th century. In 1864, the boron deposits of the U.S. in California and Nevada States were discovered [8]. A timeline for the development of boron can be found in Figure 1.2.

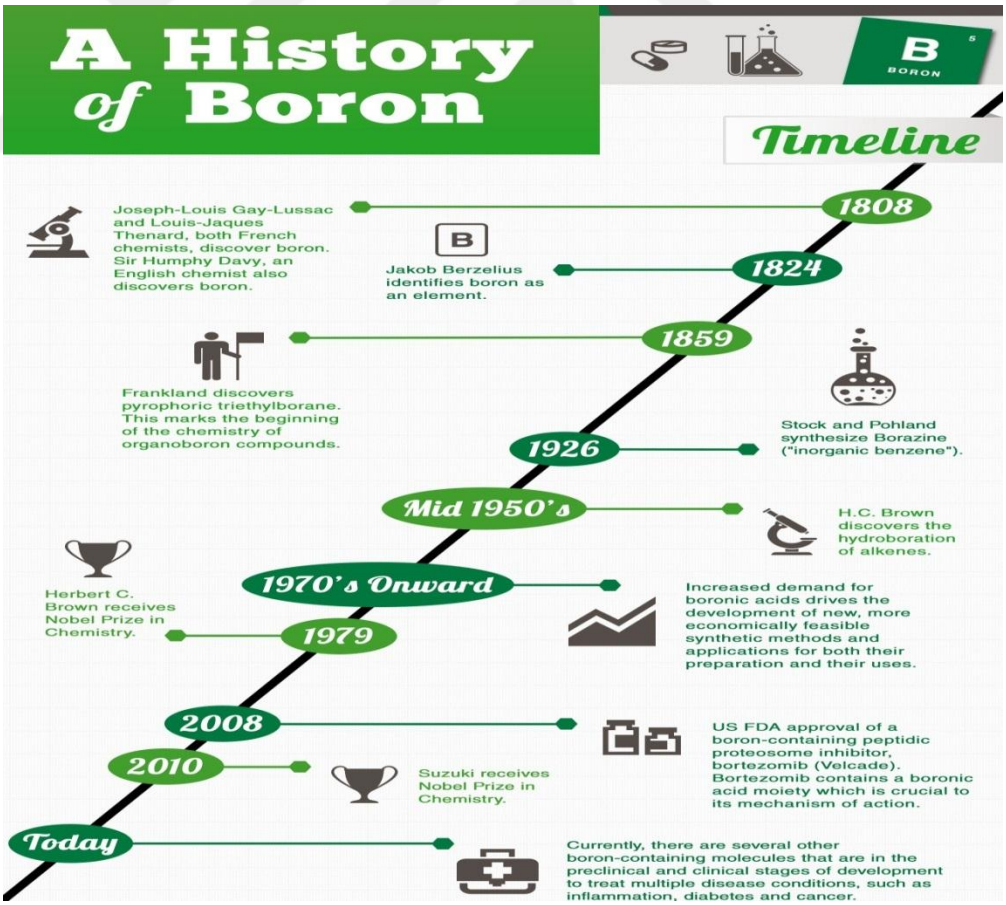


Figure 1.2 Timeline of the Boron [70].

1.3. Important Boron Minerals and Their Forms in Nature

Due to its high chemical interest in oxygen, the boron element is not found free in the earth's crust. Boron minerals; It contains minerals containing different amounts of boron oxide (B_2O_3) and it is known that more than 230 minerals in nature contain boron elements [9]. These minerals can be divided into three according to their origin and geological environment;

1. Scam minerals (mainly silicates and iron oxides) due to intrusive rocks.

2. Magnesium oxides due to marine sediments.

3. Hydrated sodium and calcium borates due to continental sediments and volcanic activities.

The minerals in the 1st and 2nd groups form the basis of Russian production and an important part of China (as datolite and asharite). The 3rd group includes minerals located in the main borax, kernite, colemanite and is ulexit, production in the world mainly in Turkey, some South American countries and is maintained by the US [10].

Table 1.1 Main Boron Minerals and Properties [71].

Mineral	**Chemical Composition**	**Boron %**
Boracite	$Mg_6B_{14}O_{26}CI_2$	19.30
Colemanite	$C_2B_6O_{11}.5H_2O$	15.78
Datolite	$CaBSİO_4.OH$	6.76
Hydroboracite	$CaMgB_6O_{11}.H_2O$	15.69
Kernite	$Na_2B_4O_7.4H_2O$	14.90
Priceite	$Ca_4B_{10}O_{19}.7H_2O$	15.48
Proberite	$NaCaB_5O_9.5H_2O$	15.39
Sassolite	H_3BO_3	17.48
Szaibelyite	$MgBO_2.OH$	12.85
Tincal(borax)	$Na_2B_4O_7.10H_2O$	11.34
Tincalconite	$Na_2B_4O_7.5H_2O$	15.16
Ulexite	$NaCaB_5O_9.8H_2O$	13.34

As shown in Table 1.1 main boron minerals and properties. Then, One of the common boron minerals is Tourmaline, which is a kind of aluminoborosilicate mineral and can contain up to 10 % boron in its structure.

However, tinkal, kernite, colemanite and ulexite, which are alkaline and alkaline earth boron minerals, are used in the industry. Turkey is the most limited commercial mineral deposits and the United States is also included.

1.3.1. Boraks Mineral

It is a much more important mineral for the boron industry than others. Its most prominent feature is its easy dissolution in water. Its solubility and dissolution rate increases with water temperature.

Although it is generally colorless and transparent, it can also carry pink or yellowish gray colors compared to other components. Its hardness is 2 - 2.5, and its cleavage is rarely good, brittle and concoidal diffraction. Its monoclinal and crystal structure is short prism.

Its specific weight is 1.72 and it is found in the mineral deposits with clays, ülexite and tinkalkonite. Borax mineral is mainly found in Boron-CA-USA, Kırka-Turkey and Tincalayu-Argentina [11]. The Figure 1.3 show that after the product packaged pure borax.



Figure 1.3 Packaged Pure Borax.

1.3.2. Colemanite Mineral

Colemanite mineral is monoclinal. It is located in many beds in bright crystals and in hollows. It has typical colors such as white-gray and greenish-gray.

Its hardness is 4 - 4.5 and its specific weight is 2.52. Colemanite is a calcium-containing borate primarily preferred by the sodium-free fiberglass industry [12].



Figure 1.4 Natural Colemanite Mineral.

It has a very low solubility in water and is very easy in acid It is dissolved. When heated above 400 °C, it is crunched and roasted in powder form (decrepitation).

Some chemical plants in Europe, because it is cheap, from Turkey. The Figure 1.4 show that after the product natural colemanite mineral.

It is found as large, shiny, transparent crystals in ore cavities within clays. Pure Colemanite dissolves slowly in water and rapidly in HCl. They produce boric acid from colemanite they take. Turkey is a most important source of high grade colemanite.

1.3.3. Ulexite Mineral

Ulexite is the most common boron mineral found in Playa-type lakes or near close-quaternary marshes. Such ulexites are available in the form of soft, high-moisture and fibrous crystals.

This type of ulexite is found in South America and China. With Boron produced in Turkey and in Death Valley (USA), located on the Neogene-aged ulexite harder, was intense and good bedding.

Due to its slightly transparent appearance that plays white, ulexite is also called "cotton rose". Its hardness is 2.5 and its specific weight is 1.96. It is easily soluble in cold water, hot water and acid [13].



Figure 1.5 Natural Ulexite Mineral.

The Figure 1.5 show that after the product naturel ulexite mineral. It plays an important role in heat and sound insulation, in the production of boric acid and borax in the glass, ceramic and fertilizer industry.

1.3.4. Kernite Mineral

Kernite, which is the metamorphic phase of the borax, is deposited in a small amount in Kırka and Tincalayu, but in Boron at the rate of 1/3 of the total reserve. Kernite contains more B_20_3 than borax.

However, due to its structural features, it causes blockages in the process and dissolves more slowly in water. Kernite is found in monoclinal crystal structure, colorless, transparent and longitudinal needle-shaped cluster crystals. Its hardness is 2.5 - 3 and its specific weight is 1.91 [14]. The Figure 1.6 show that after the product naturel kernite mineral.



Figure 1.6 Natural Kernite Mineral.

1.3.5. Tinkal Mineral

Although tinkal is colorless and transparent, it can be found in pink, yellowish, gray colors due to various impurities in its composition.Its hardness is 2 - 2.5 Mohs and its specific weight is 1.7 gr / cm^3. The B_2O_3 content of the tinkal ore extracted from the open pit ranges from 12 to 29 % [15].

Tinkal degrades quickly and turns into tinkalkonite by losing its water. It is present with tinkalkonite and ulexite with clay added. Turkey is in the Eskişehir-Kırka bed. The Figure 1.7 show that tinkal mineral for processing and industry.



Figure 1.7 Tinkal Mineral for Processing and Industry.

Tinkal, which makes the glass more resistant to physical impacts, is also actively used in the agricultural sector.It contributes to the world agricultural economy either alone or as a source of boron in compound fertilizers.

1.3.6. Ascharite Mineral

Ascharite forms an important part of Russian and Chinese boron deposits. Ascharite is a magnesium borate, it is slightly soluble in water like colemanite.

Its use is not satisfactory due to its magnesium content, but it is more common in Eastern European countries and Russia. Important it does not have an international trade in size. The Figure 1.8 show that the naturel form ascharite mineral.



Figure 1.8 Naturel Form Ascharite Mineral.

In Russia, using a significant amount of skarn borosilicates, mainly datolite and small amounts of danburite, ludvigit and tourmaline are produced. In order to make these minerals suitable for use in industry, enrichment and acid dissolution are needed to separate them from harmful compounds.

1.4. Boron Properties

1.4.1. Chemical Properties of Boron

When the chemical properties of boron are examined, boron takes the 5th place in the periodic table. The metal-nonmetal mixture with an atomic weight of 10.81 g / mol is a semiconductor element. It melts at 2090 °C and begins to boil at 2550 °C.

It appears in nature in a white and close to white color. Boron compounds have been used since ancient times. Today, its usage areas are developing rapidly. It has application areas especially in more than 400 industrial fields and it is known to have 230 kinds of boron minerals.

Boron is the element with the highest similarity to silicon and carbon elements. It is the hardest element after diamond with a hardness value of 9.35 Mohs [16]. The Table 1.2 show that hardness values of boron and some compounds.

Table 1.2 Hardness Values of Boron and Some Compounds [16].

Materials	Mohs Hardness
Boron	9, 30
Boron Carbide	9, 32
Boron Nitride	9, 34
Diamond	10, 00

Boron element is not found in nature in free form. Artificial boron is obtained in two ways as crystal and amorphous. The crystal boron is glossy black color with a density of 2.33 g / cm, is fragile and hard, and the amorphous boron is black or brown powder with a density of 2.34 g / cm³. Crystal boron has tetragonal and hexagonal crystal lattice structure. It reacts with hydrogen at 840 ºC, oxygen with 700 ºC water and over 100 ºC [17].

Table 1.3 Crystal Shapes and Parameters of Boron [72].

Crystal Shape	Lattice Parameter (A^0) a=b	Lattice Parameter (A^0) c
Tetragonal	8,13	8,57
Hegzogonal	9,54	11,98

The Table 1.3 show that crystal shapes and parameters of boron. The boron element consists of 19.57 % B^{10} and 80.43 % B^{11} isotopes. Boron has a large neutron absorption cross section. This value is 40.10 bar for B^{10} isotope and 0.75 bar for B^{11} isotope. The B_{10} isotope is of great importance due to the control of nuclear reactors and protection from nuclear radiation [18].

The electrical conductivity of the boron is quite low at room temperature. But it increases rapidly as it is heated. This is not just a feature of metals. It is a non-metal due to the very low metallic properties of the boron. When molten boron is cooled, it becomes a very hard and fragile structure. It has a green flame color.

Elemental boron transmits portions of infrared light. At room temperature, it is a weak electric conductor, but at high temperatures it has a good conductor property. Boron can form stable covalently bonded molecular networks.

Boron filaments have high strength but are light. The energy band range of the elemental boron is 1.50 to 1.56 eV, which is higher than silicon or germanium [19]. Although elemental boron is not considered a poison, assimilation of boron compounds has an cumulative toxic effect.

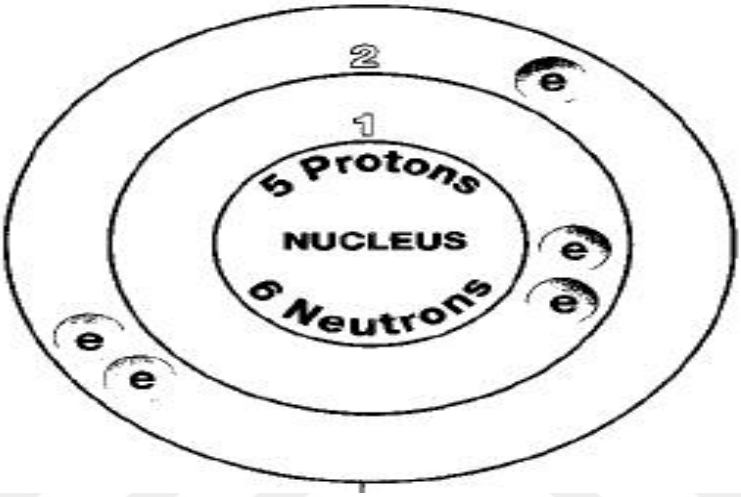


Figure 1.9 Atomic Structure of Elemental Boron [73].

Since the boron element has an empty p orbital, it is electron-poor. For this reason, it generally acts as lewis acid, in other words, it easily connects with electron-rich compounds and eliminates the need for electrons.

These compounds are Lewis acids in that they readily form adducts with electron-pair donors, which are called Lewis bases. The Figure 1.9 show that atomic structure of elemental boron.

In addition, since boron has the lowest electronegativity among non-metallic elements, it usually loses its electrons in reactions, in other words it is oxidized. Basic ores of boron; borates such as kernite, borax, colemanite and ulexite. The boron element is at the head of the 3rd group of the periodic system.

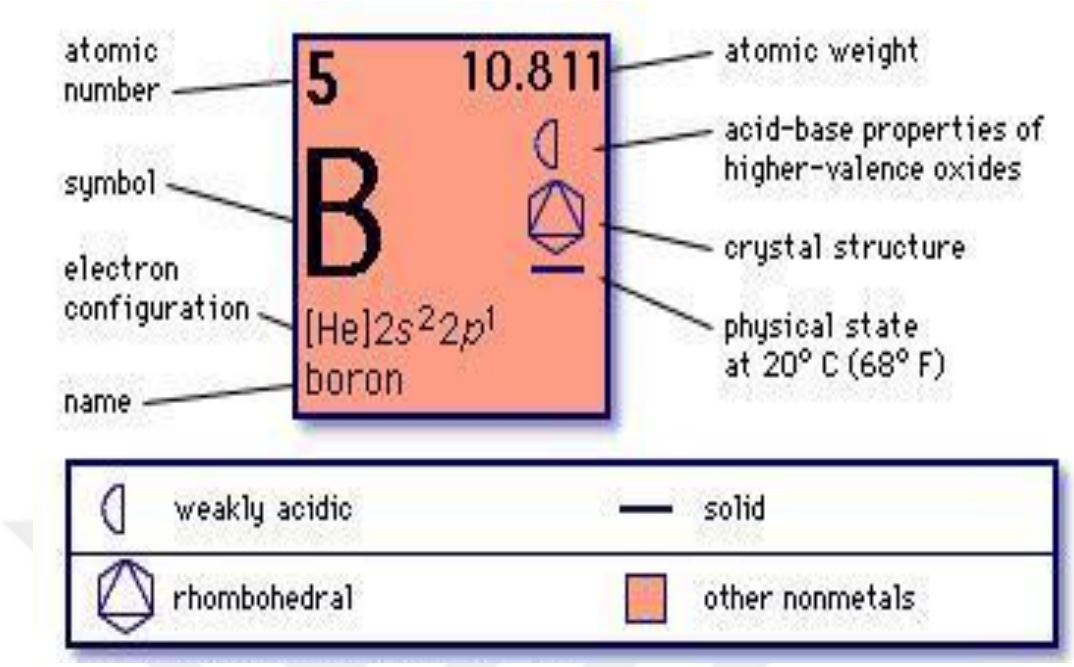


Figure 1.10 Boron Properties in the Periodic Table [74].

Of the group IIIA elements, only boron is nonmetal. Other elements in this group; aluminum, gallium, indium and thallium. Boron is a much smaller atom than other elements in the group.The show that the Figure 1.10 boron properties in the periodic table.

This causes certain differences between nonmetal boron and other metal group members. The atomic radius of Ga, In and Tl does not increase with the increasing atomic number of these elements in the periodic classification.

The relatively small size of these elements causes them to contain relatively high ionization potential, which does not decrease as expected even when descending from the group.

1.4.2. Physical Properties of Boron

Solid form boron is very hard and brittle. Boron is a semiconductor and its conductivity increases with increasing temperature. Semiconductivity can be explained as follows.At room temperature, electrons are tightly attached to the central nucleus and they are difficult to release [20].

As the temperature increases, they become free and act in the crystal. Although the resistance increases due to the increase of the vibration of the crystal lattice as the temperature rises, the conductivity of the substance increases as the number of electrons released increases. Physical properties of boron element is given briefly in the show that the Table 1.4

Table 1.4 Physical Properties of Boron Element [75].



Boron is available in various allotropic forms, one is amorphous and six is crystalline polymorph. Alpha and beta rhombohedral forms are the most studied crystalline polymorphs.

The alpha rombohedral structure is disrupted above 1200 ^{o}C and beta rombohedral form occurs at 1500 ^{o}C. The amorphous form turns into beta rombohedra above about 1000 ^{o}C and when it is heated and recrystallized above any pure boron melting point, it turns into a beta rombohedral form [21].

Although there have been many studies on polymorphic transformations of elementary boron, not all boron phases are still defined. The Figure 1.11 show that representation of some polymorphic transformations of boron (a) β-rombohedral boron (b) α-rombohedral boron (c) α-tetragonal boron is shown.

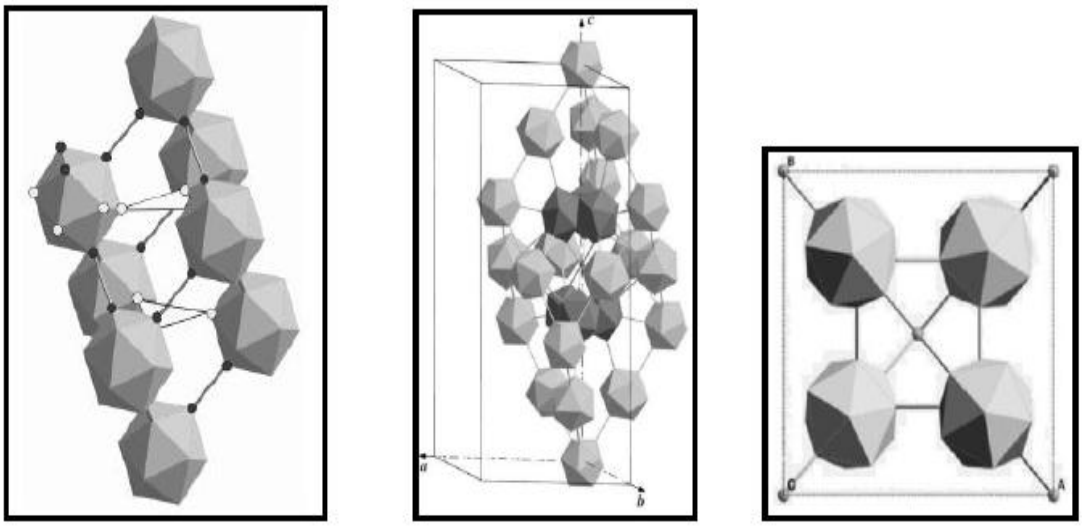


Figure 1.11 Representation of some polymorphic transformations of boron (a) β-rombohedral boron (b) α-rombohedral boron (c) α-tetragonal boron [76].

Different properties of the compounds made with various metal or nonmetal elements allow boron compounds to be used in many industries. Boron acts as non-metal compounds in its compounds, but unlike pure boron is an electrical conductor like carbon.

Crystalline boron is diamond-like in appearance and optical properties and is almost as hard as diamond. Besides being the second hardest element, boron finds use in many places thanks to its semiconductor feature, high melting temperature, high strength, high chemical resistance and excellent nuclear properties.

1.5. Boron Reserves

Boron is an element commonly found on earth, rocks and water. Although the boron content of the soil is 10-20 ppm on average, it is found in high concentrations in the western regions of the USA and the region extending from the Mediterranean to Kazakhstan. It is in the range of 0,5 - 9,6 ppm in sea water and 0,01 - 1,5 ppm in fresh water.

Although there are important differences between the information about published boron reserves. Considering the information provided by the American Mining Institute and ETI Mining Company, it is estimated that the total world visible reserves contain 1,140 million tons of ore containing 489 million tons of B_20_3.

When possible and possible reserves are added to these values, the total reserve; 3,199 million tons of ore containing 1,303 million tons of B_20_3. Approximately 72.8 % of these reserves in Turkey, Russia 7.6 %, U.S.A., 6.1 %. In other words, 4/5 of the world reserves are collected in these three countries [22].

In addition to having the majority of world reserves, our country has a natural superiority in terms of mineral diversity and ore grade. There is not much information in the literature about Independent State Communities and boron deposits estimated to be in China. The total reserve in South America is estimated to be 100 million tons of B_20_3 ore. The Figure 1.12 show that reserve ratio of boron between countries. Important in the world boron beds in Turkey, Russia and the United States are being collected in the commercial world boron reserves in the four regions.



Figure 1.12 Reserve Ratio of Boron between Countries [77].

1.5.1. Important Boron Deposits in the World

These; Located in the south of the US State of California "Mojave Desert", located "And Aqueduct in South America", Turkey is also located in the "South-Central Asian Orogenic Belt" East and Russia [23].

A high concentration of boron deposits in economic size, coupled with the compounds of the tube rather Turkey and US dry oxygen exists in the regions with high volcanic and hydrothermal activity. The Figure 1.13 show that boron deposits with significant potential in the world.



Figure 1.13 Boron Deposits with Significant Potential in the World.

1.5.1.1. Boron CA (Kramer) Boron Deposit

It is operated by Rio Tinto company with open pit operation method. Tinkal and kernite ore are produced. These ores are processed in the refining plants in the vicinity and boric acid and other boron derivatives are produced.

The first studies in the Boron region started with the discovery of colemanite mineral in 1913. In 1925, rich tincal and kernite formations were detected in the region. Ore has been mined and processed since 1927.

Later, in 1957 new refining facilities were established. The Boron deposit was formed in a Miocene lake, fed by thermal currents [24].

Tinkal deposits are deposited on the kernite ore in the depths and are surrounded by the formation of an ulexite colemanite. There are alluviums up to 15 m in thickness on the surface.

Under the alluviums there are 60-70 m thick sandstones and beneath this, about 35 m thick well layers. There are unevenly distributed ulexite-colemanite formations in these layers.

Tinkal and kernite are located in the middle of the borate layers, alternating with clay layers. Their thickness is around 80 m. All of the layers are on a basalt mass. Ore production in Boron is done through an open pit 2 km long, 1 km wide and 200 m deep.

The thickness of the cover layer varies between 60 - 150 m. Steps are loosened by drilling-blasting method and excavation is done by excavator. After the ore extracted is broken under 20 mm in the quarry, it is transported under the stockpile by conveyor. There are boron derivatives and boric acid plants in the region.

1.5.1.2. Death Valley/Billie Mine Boron Deposit

The deposit, which is operated by the underground mine operation method, contains colemanite, ulexite and propertite. It is near Nevada in the north of California. The reserve area has decreased to 80 - 90 m below sea level with active deposition in progress.

In the Death Valley Region, colemanite and ulexite, which are the main boron ores, are alternated with mudstone, limestone and conglomerates in lenses with a thickness of 70 m. There is also probertite formation in the bed.

The ulexite is deposited around the probertite formation, and colemanite surrounds these two mineralizations. Ulexite and probertite are primary minerals. The colemanite was formed secondary to the dissolution of sodium.

1.5.1.3. Searles Lake Deposit

It is operated by the firm Searles Valley Minerals through solution mining**.** These boron deposits are east of the Mojave Desert. The surface of the lake, usually covered with dry mud, covers an area of 100 km^2.

The Owens River feeding the lake carries about 800 tons of B_20_3 per year. 40 % of the bed is composed of saturated salts in varying proportions depending on the layers and in the spaces between the crystallized salts.The so-called upper and lower salt layers are permeable separates a non-mud layer. These salt layers have different B_20_3 content.

1.5.1.4. Asian Boron Deposits

Boron reserves in Asian countries generally consist of magnesium borat and limited regions, of tincal and borosilicate. The ores are generally of low grade and have technological difficulties in refined product production. Ascharite ore is mainly found in China and Kazakhstan. The natural boron deposits in China are large, more than 90 % of the deposits have low grade. Most of China's boron deposits are located in Liaoning and Jilin regions.

Boron deposits are concentrated in the region between the Caspian Sea and the Ural River. The beds were formed along a broken zone in the Permian salt dome, covering an area of 250 km^2, covered by the 2nd and 3rd time rocks by overlapping.

Borate formations are generally composed of magnesium borates and filled the cracks. The structure of İnder Lake is similar to Searles Lake. The surface of the lake is covered with a dry salt layer, and underneath it has a hollow salt mass of 36 m thickness.

The spaces between the crystals are filled with potassium chloride, bromide and boron-rich waters [25]. The Figure 1.14 show that Inder Lake in Kazakhstan includes boron reserve.



Figure 1.14 Inder Lake in Kazakhstan Includes Boron Reserve.

In addition, it has boron deposits in many places although it has a low reserve amount in different regions of the world. Argentine boron deposits are generally concentrated in the Tincalayu region. Boron ore is in Pliocene sediments, 30 m thick, 100 m in diameter, in the form of a very fine crystalline lens. The borax is seated on a massive halite mass and is partially bedded on sediments containing thin ulexite, inionite, kurnakovite layers.

Chile has boron deposits containing ulexite. Production in Chile, which offered large amounts of ulexite to the world boron market before the 1950s, is now done in a very small amount. In the most important bed, "Salar de Ascotan, ulexite is just below the surface and formed in irregular masses. Although the layers reach a thickness of 1 m in some places, the average thickness is 30 cm.

It is located in "Laguna de Salinas", a large basin in the east of the Arequipa Region, in Peru. As a result of the evaporation of lake waters every year, a layer of halides and sulfates is formed on the surface. The ulexite ore is below this layer and 1 cm from 10 cm. It spreads as an irregular mass in the form of lenses of varying thickness up to meters.

1.5.2. Important Boron Deposits in the Turkey

Boron deposits known in Turkey, especially in Kırka / Eskisehir, Bigadiç / Balıkesir, Kestelek / Bursa and Emet / Kütahya. The most abundant in terms of boron ore reserves in Turkey tinkal and colemanite. Kırka colemanite beds tinkal important deposits in Turkey are around the Emet and Bigadiç.

In addition, there is a small amount of ulexite reserves in Bigadiç and ulexite is sometimes obtained as a by-product in Kestelek. The Table 5. given reserve amounts in Turkey.

Table 1.5 The Amount of the Reserve Area in Turkey [78].

Region	Ore Type	Total (Ton)
Emet	Colemanite-Ulexit-Probertite	1.811.072.520
Kırka	Tinkal	824.720.950
Bigadiç	Colemanite-Ulexit	628.350.480
Kestelek	Colemanite	5.254.920

1.5.2.1. Eskişehir- Kırka Boron Deposit

It is located 60 km southwest of Eskişehir province. In the basin, exolations containing boric acid, sodium and magnesium, volcanic mud and ashes coming from the fault cracks formed at the end of Miocene, were deposited by mixing with the Neogene lake waters. While borax crystallizes in deep cuts, ulexite primary in shallow cuts It was deposited as.

Kırka - Sarıkaya formation, which has the biggest share among the world's tinkal reserves, constitutes approximately 20 % of the world reserves. Also constitute 25 % of the boron reserves in Turkey.

There is a limestone layer beneath the alluviums and basalt, and a clay-mam series 60 m thick beneath this layer. This series is followed by the borate series. Borates consist mainly of tinkal ore. In addition, there are minerals such as colemanite, kernite, ulexite, and aqueous magnesium borates such as indigne and inderborite.

However, these minerals are 10 - 15 % of the borates in the bed. The thickness of the borate layer varies between 2 - 130 m, and the average thickness is 70 - 80 m. Under the borate layer, there is a clay-mam series containing a small amount of thin borate layers. The thickness of this series is 40 m. The lower limestone series, 80 m thick, is followed by this layer [26].

1.5.2.2. Kütahya – Emet Boron Deposit

Boron deposits are located 60 km west of Kütahya province. Mineralization colemanite is predominant and there is arsenic in the bed up to 1 %. It appears as redness in colemanite due to arsenic, orpiment and realgar minerals [27].

Production is carried out in two different areas in the region. While underground operations are carried out on two quarries in the Espey region, the open pit method is applied in the Hisarcık region.

There are two types of mineralization in the Hisarcık ore deposit. Espey Hisarcik-formation, which accounts for approximately 40 % of the world reserves, while the reserves in Turkey constitute 55 %.

Boric acid; It plays an active role in eye, ear, skin treatment, pesticide and insecticide production, fiberglass, LCD screen, Prexy glass production and in the production of fire resistant clothing.

1.5.2.3. Balıkesir-Bigadiç Boron Deposit

Boron deposits are located 40 km south of Balıkesir province. The reserves in the region, like other Western Anatolian borate deposits, were formed within the Neogene lake sediments.

There is a weak tincal formation in the middle of the borate zone surrounded by limestone layers from the top and bottom. The circumference of this tinkal is surrounded by colemanite. Borates are located in clays in layers of 1 - 3 m. It is preferred in the market due to its low arsenic content.

It increased the production of ground products from 520,000 tons in 2016 to 570,000 tons in 2017 [28]. The Figure 1.15 show that Turkey's boron reserves pitches.



Figure 1.15 Turkey's Boron Reserves Pitches.

1.6. Boron Production Technology

1.6.1. Mineral Processing and Enrichment Methods

The ore preparation and enrichment method applied for each boron minerals may vary depending on the general trend and demand in the market for the boron product to be produced. Ore preparation methods applied to boron ores generally; It covers crushing, grinding, screening and classification processes and shows similarities to the methods applied for other industrial raw materials.

For example; While jaw crushers are used for coarse crushing processes, hammer and shock crushers are preferred for fine crushing processes. As the botanical boron ores are generally high grade, they can be easily enriched only through crushing, screening and classification processes.

The oldest and most important ore enrichment method applied for boron ores is triage method. In the triage method; After the tufted boron ores are broken under 100 mm length, they are sieved in a 25 mm sieve and passed through a (-100 +25) mm grain class belt [29].

The color, specific gravity, etc. between the useful boron mineral, which is distinguished by the workers around the belt. Enrichment process is realized by making use of such features. Triage process for high B_20_3 content and coarse-grained boron ore currently it is implemented in many facilities in Turkey.

The ore (-100 +25) mm is enriched with triage. The most common method used for (-25) mm ore is abrasion washing and classification by size. These processes are generally effective for the medium-sized grain class, but as the grains become thinner, the desired values cannot be achieved in the yield and tenor values. Since boron minerals are usually found in the ore deposits with clays, selective mining cannot be applied in these deposits with complex layers.

Despite the fact that the boron ores are easily removed from the large-sized flank stones, the ore can be separated from the clays by the friction by mechanical dispersion as the grain size becomes thinner, due to the more adherence of the clays on the boron minerals. Devices such as transfer drum, spiral classifier, propeller etching cells and hydrocyclone are used for separation.

Although boron minerals generally have a specific gravity similar to that of limestone, if the mineral deposit has lighter or heavier minerals than beneficial boron minerals, heavy enrichment based on the specific gravity difference can also be applied to these ores.

Gravity processes using devices such as jig and heavy media drums can generally be efficient in large grain classes. It is not possible to evaluate boron ores of very fine grain size with classical ore preparation and enrichment methods. The material with very fine grain size and high content of B_20_3 is described as “waste” in triage, abrasive washing and classification processes.

1.6.2. Metallurgical and Chemical Enrichment Methods

Boron ores need to be converted to refined boron compounds in some industries, and this requires metallurgical and chemical treatment. These methods are; Usually includes processes such as calcination and roasting, which are pre-metallurgical processes, or dissolution, solid-liquid separation, crystallization, evaporation, solvent extraction and melting, which are hydrometallurgical processes.

In order to obtain boric acid from colemanite ore, "decrepitation" or "calcination" process is applied, which is cracked and bursting during heating of colemanite. More efficient results can be obtained by dissolving concentrated colemanite after decrepitation instead of directly dissolving with sulfuric acid.

For the decrepitation process of colemanite, temperatures of 450 - 500 °C are generally used, and the material, which dissolves the crystal water in this way and becomes powdered, is sieved in a certain grain size and calcined product is obtained [30].

Refined borax from tinkal ores; For deca and pentahydrate production, tinkal is easily dissolved in hot water. Concentrated tincal is first dissolved in hot water at about 90 - 100 °C, then controlled cooling is done by crystallizer, and borax deca or pentahydrate is optionally obtained.

1.7. Boron Usage Areas

The importance and usage areas of boron compounds, which are very common in industry and have various usage areas, are increasing day by day. Commercially, borones are generally defined and sold according to the content of B_20_3 they contain.

Among the others, the most traded boron products are “borax pentahydrate” and “boric acid”. Usage areas vary by region. For example, in the United States, the most important use of boron products is insulation fibers, followed by textile fibers, borosilicate glass production, detergent and ceramic industry.

The detergent industry in Europe continues to be the most important area of use, while in Japan textile fibers take the first place.

1.7.1. Glass and Glass Fiber Industry

Today, 40 % of the boron produced is consumed in the glass and fiberglass industry. The main boron properties used in the glass industry are given below [31].

• It decreases the melting point of the raw material.

• It decreases the viscosity of the molten medium.

• It decreases the thermal expansion coefficient of the glass.

• My dear makes the refractive index larger.

• It increases the transparency and brightness of the glass.

The Figure 1.16 show that production conditions of boron in glass and fiber glass industry.



Figure 1.16 Boron in Glass and Fiber Glass Industry [85].

Boron is one of the basic raw materials of glass fiber (fiberglass), which is used for different purposes in a wide variety of fields from all kinds of insulation to the information sector. When boron is added to glass fiber, in addition to the above mentioned features;

• It decreases the crystallization tendency.

• Durability and moisture resistance of fibers increases.

Fiberglass types covered with various metals; Other boron derivatives are also used in the electronics industry, as they are used in the production of microchips, fiber optic cables, semiconductor elements and many similar electronic parts.

1.7.2. Metallurgy Industry

Properties utilized in metallurgy,

• It decreases the melting temperature.

• Increases the fluidity of the slag.

• It hardens the steel.

• It reduces the wear of kiln bricks.

It provides savings in the energy consumed by lowering the melting temperature of iron-steel raw materials. Due to the high hardness of the boron derivatives themselves or their alloys with steel, they are abraded and used in cutting tools.

In addition to rare metals, boron is also included in the magnets, which have revolutionized the use of magnetic separators and create continuous high magnetic field intensity. Boron is also used in the formation of electrolytes used in the coating industry and in soldering processes.

1.7.3. Cleaning and Whitening Industry

Approximately 20 % of the world boron consumption is for the production of cleaning products such as soap and detergents. The main boron properties utilized in this industry are,

• It is a powerful whitener.

• It dissolves the stains.

• Balances the pH, softens the water and breaks down the oils.

• Balances active oxygen.

• It is anti-bacterial.

The Figure 1.17 show that boron based cleaning product produced by Eti Mining.



Figure 1.17 Boron is Cleaning Product Produced by Eti Mining [79].

Thanks to these features, it wears the fabric very little; does not fade their colors. It gives effective results even at low temperatures. It decreases the washing time of the laundry. It reduces water consumption. It reduces the wear and dullness of the steel in the machines. Sodium perborate 20 - 25 % of the detergents creates.

1.7.4. Nuclear Industry

Boron isotopes help control nuclear reactions. Because the neutron absorption cross section of B^{10} and B^{11} isotopes high. In some types of power reactors, boric acid is added to the cooling water to prevent excessive reactivity. Control rods used in nuclear reactors are made of steel and aluminum alloy containing 2 % boron. The Figure 18. show that boron doped control rods used in nuclear reactors.



Figure 1.18 Boron Doped Control Rods Used in Nuclear Reactors.

In addition, in the Chemobil nuclear power plant disaster on April 26, 1986, in order to prevent new explosions, military helicopters dumped 5,000 tons of boron-containing mixtures on the main molten mass and the reactor was covered with boron cement [32].

The most important material used as a neutron absorber is boric acid as a coolant water additive in B^{10} or PWRs as $^{10}B_4C$ in control rods. The Figure 1.19 show that neutron cross section of boron, top curve is for B^{10} and bottom curve for B^{11}. Other important neutron absorbers that continue to be used heavily in nuclear reactors are as follows; xenon, cadmium, hafnium, gadolinium, cobalt, samarium, titanium, dysprosium, erbium, europium, molybdenum and ytterbium.

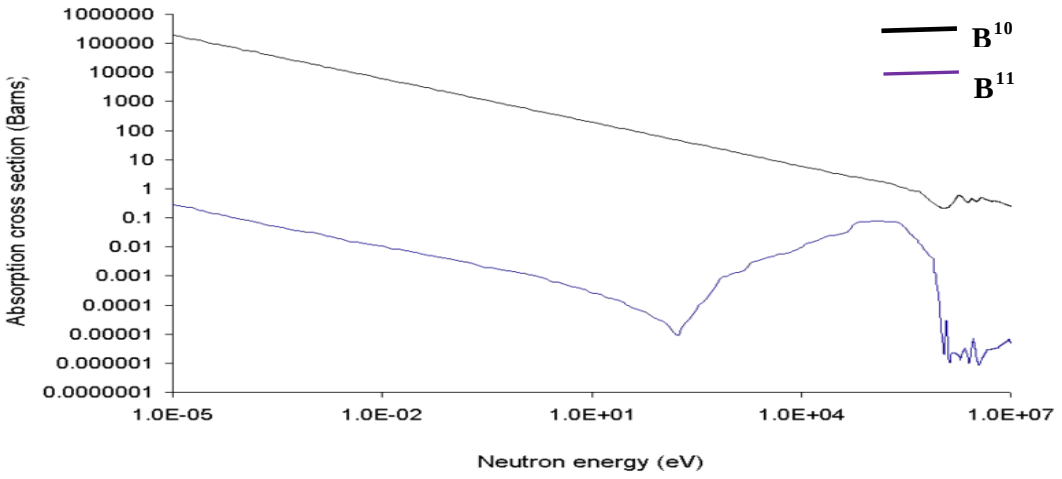


Figure 1.19 Neutron Cross Section of B^{10} and B^{11} [80].

1.7.5. Ceramic Industry

It is a widely used additive material for glaze in this industry. When boron is used for glazing ceramic materials, it provides the easy melting of silica and its rapid spreading on the ceramic surface. If the amount of silica is decreased in the mixture used for glaze, the amount of boron is increased; glaze gets a harder, more durable and shiny appearance.

In addition, boron is used in the enamel industry to increase the brightness, hardness and durability of enamels. This sector constitutes one of the areas where most of Turkey's boron consume.

1.7.6. Semiconductors

Boron is a substance with an important additive structure for semiconductors such as silicon, germanium and silicon carbide. Therefore, it is important in the semiconductor industry.

Due to the lack of an electron from the nucleus central atom, it had p-type conductivity. As a method of transforming pipes into semiconductors, it is generally provided by atomic diffusion at high temperatures. In this method, solid boron oxide, liquid boron tribromide or gaseous boron trifluoride are used.

In recent years, it has been provided by ion implantation on the basis of boron tribromide structure, especially as a boron source. There is a need for boron-based semiconductor chemicals in many ways.

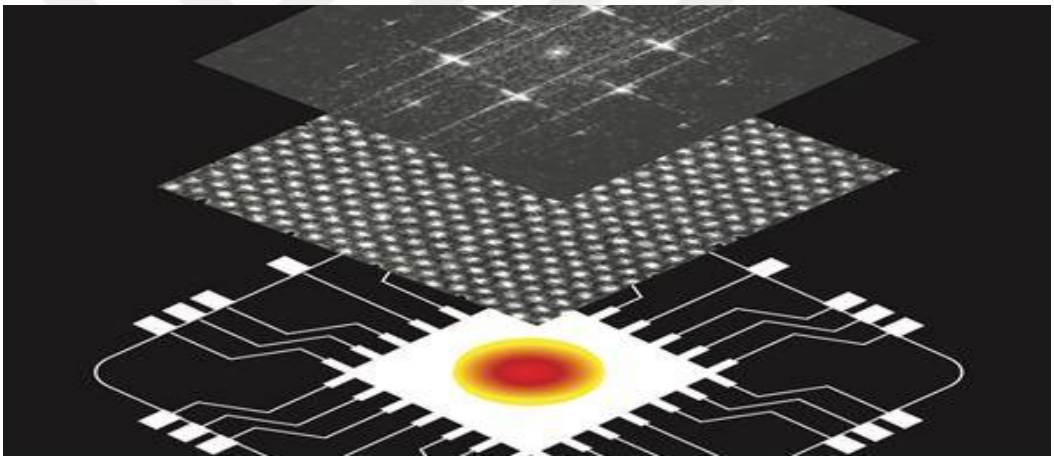


Figure 1.20 Semiconductor Boron Arsenide is Used in the Electronics Field [81].

For example, boron trichloride gas is a very important chemical in the semiconductor industry. In terms of this chemical function, it is not used for doping, but is used for plasma etching of metals and their oxides. In steam accumulation reactors, triethylborane is used especially as a boron source. The Figure 1.20 show that semiconductor boron arsenide is preferred to be used to keep the new generation electronic and optoelectronic devices cooler.

In addition, plasma deposition of boron-sourced silicon nitride-boron nitride films and synthesis of diamond film with boron are among the ways that boron is used in the semiconductor field.

CHAPTER 2

BORON NITRIDE

High-tech ceramics and especially non-oxide materials are widely used today in many commercial applications where long-lasting use, advanced performance, unique features and cost-effective use are required.

Many carbide, nitride and boride materials offer a variety of structural and electronic properties thanks to their high wear resistance, oxidation resistance at high temperatures, high hardness, high toughness, resistance to molten metals and glasses, high thermal conductivity, high electrical insulation, or combinations of these. they are used in applications.

Structural applications of these materials include armor technologies, parts that require wear resistance, corrosion resistant crucibles, igniters and machine parts that require high temperature resistance, and the like. Electronic applications are as semiconductors or in the form of backing material. In addition, they can find use in mining, metallurgy, paper industry, chemical industry, all kinds of machining, food processing, aerospace industry and medical devices.

Hexagonal boron nitride (h-BN), the lightest of ceramic materials, is often referred to as white graphite due to its physical and chemical similarity to graphite.

Thanks to its refractoriness at high temperatures, non-stick property, chemical inertness, high thermal conductivity, excellent thermal shock resistance, electrical insulation, machinability and lubricity, h-BN has a wide range of uses in chemistry, metallurgy, high temperature technology, electrotechnics and electronics.

Hegzagonal boron nitride can be used in powder form, hot pressed condensed form, as an additive to composite materials, in pyrolytic form and in spray form as coating suspension.

It is used as a powder and bulk product in a wide area due to its refractoriness at high temperatures, non-adherence, chemical inertness, high thermal conductivity, excellent thermal shock resistance, electrical insulation, workability and lubricity.

Boron nitride, which is a compound of boron and nitrogen atoms, is an important boron product that has unique characteristics and provides advantages in the areas where it is used.

Boron Nitride is a compound formed by boron and nitrogen elements, with a chemical formula BN, produced by chemical methods. Boron nitride is a synthetic material with superior properties such as high thermal shock resistance, thermal conductivity, electrical insulation, chemical stability and lubricity.

Boron nitride is an III-V group compound with wide optical energy band range due to its physical properties and chemical stability [33]. Boron nitride, an artificial material with unique properties, is increasingly used in many sectors. Today, boron nitride can be produced by different methods and has different usage areas.

2.1. What is Boron Nitride?

Boron nitride (BN) is a chemical compound that does not exist in nature, is produced synthetically, and contains equal proportions of boron and nitrogen atoms.

Its empirical formula is BN and it is white in solid form. Boron and nitrogen forming boron nitride are adjacent to the element carbon in the periodic table [34]. As a result, boron nitride is isoelectronic with the elemental form of carbon and isomorphism between the two materials.

There are three types of polymorph of boron nitride. Hexagonal boron nitride (h-BN) resembles graphite, cubic boron nitride (c-BN) to diamond, and wurtzite boron nitride (w-BN) to the polymorph of carbon resembling a hollow sphere as its crystal structure [35].

With the synthesis of h-BN, it was once made by Balmain in 1842, but the material was commercialized a hundred years later. Although the structural similarity of graphite and hexagonal boron nitride was known at that time, in 1957 Wentorf

succeeded in synthesizing cubic boron nitride with a structure similar to diamond under high temperature and pressure conditions [36].

Cubic boron nitride, the second hard material after diamond, has been used since 1969. Wurtzite boron nitride, on the other hand, is not stable under normal conditions, and it is a very hard form of boron nitride obtained at room temperature under 13 GPa pressure or by dynamic shock methods [37].

2.2. Crystal Structures of Boron Nitride

Boron and nitrogen are in groups III-A and V-A respectively in the periodic table and are neighbors to carbon and the boron nitride ball they form is isoelectronic with carbon-carbon bonds.

Thanks to the isoelectronic similarity in question, boron nitride has similar properties to carbon as well as its polymorphs and crystallographic phase transformations. Boron nitride has three types of widely known crystal structures.

2.2.1. h-BN (Hegzagonal Boron Nitride)

It has a layered hexagonal structure, very similar to graphite, hence it is called white graphite. It has a soft structure, its theoretical density is 2.27 g / cm^3. The Figure 2.1 shows the crystal structures of h-BN and graphite.

The lattice parameters of h-BN and graphite are very close to each other. Side lengths a and c are available for h-BN and graphite.

The interlayer distance is 3.33 Å for h-BN and 3.34 Å for graphite. In hexagonal boron nitride, hexagons are arranged along the c axis such that B and N atoms overlap each other (..AAAA ..).

It has very strong planar bonds and weak interplanar bonds, so it shows anisotropy, its thermal and electrical conductions differ in a and c directions [38].

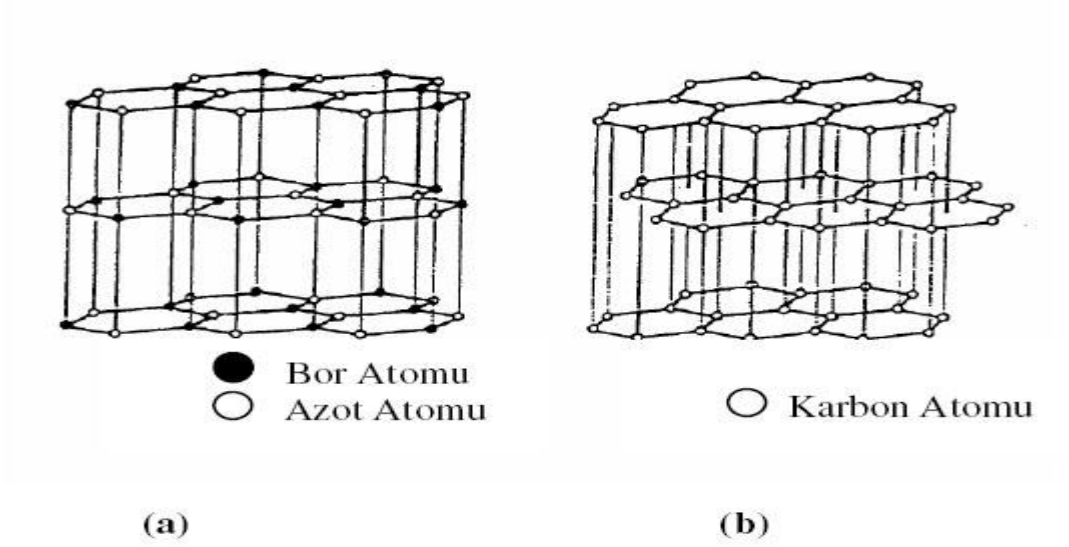


Figure 21 (a) Hexagonal Boron Nitride Structure (b) Graphite Structure [82].

The morphology of h-BN powders reflected in the scanning electron microscope is shown in the Figure 2.2.

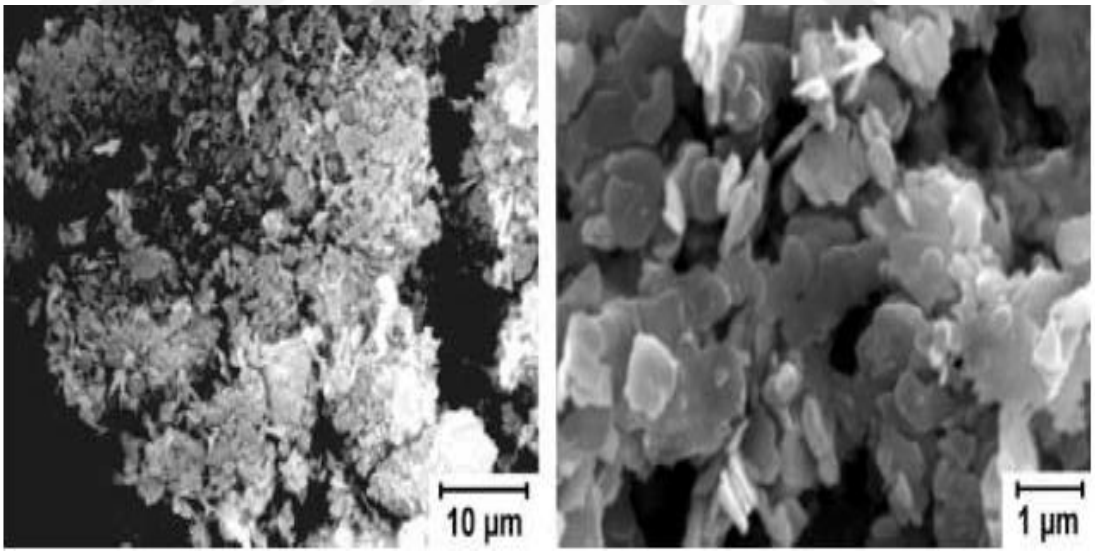


Figure 22 Morphology of h-BN Powders [37].

2.2.2. c-BN (Cubic boron nitride)

Cubic obtainable under high temperature and pressure. It is in zinc blend form. Its theoretical density is 3.48 g / cm^3. The Figure 2.3 shows the crystal structure of c-BN.

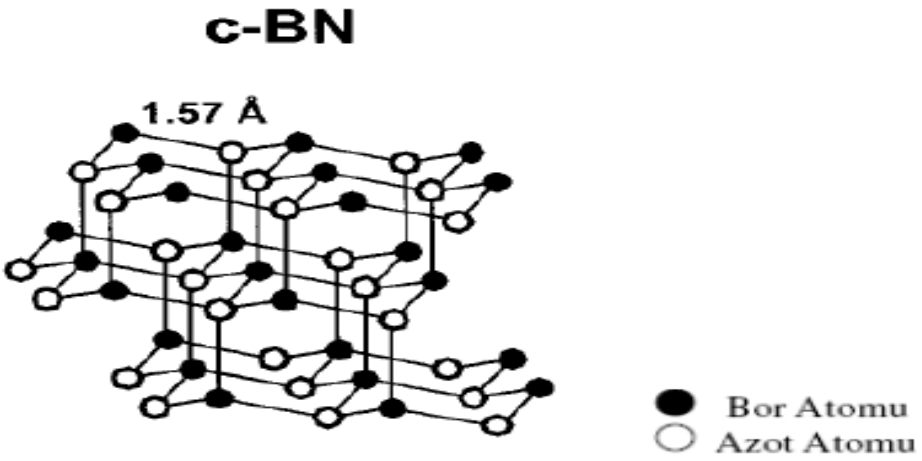


Figure 23 Cubic Boron Nitride Crystal Structure [40].

The crystal structure of cubic boron nitride is very similar to diamond. As in the diamond crystal, the boron and nitrogen atoms are coordinated in a tetrahedral fashion. In cubic boron nitride, the rings are arranged along the c axis such that the boron and nitrogen atoms overlap each other (… ABCABC…). Each boron atom is surrounded by four nitrogen atoms, there is sp^3 hybridization [39].

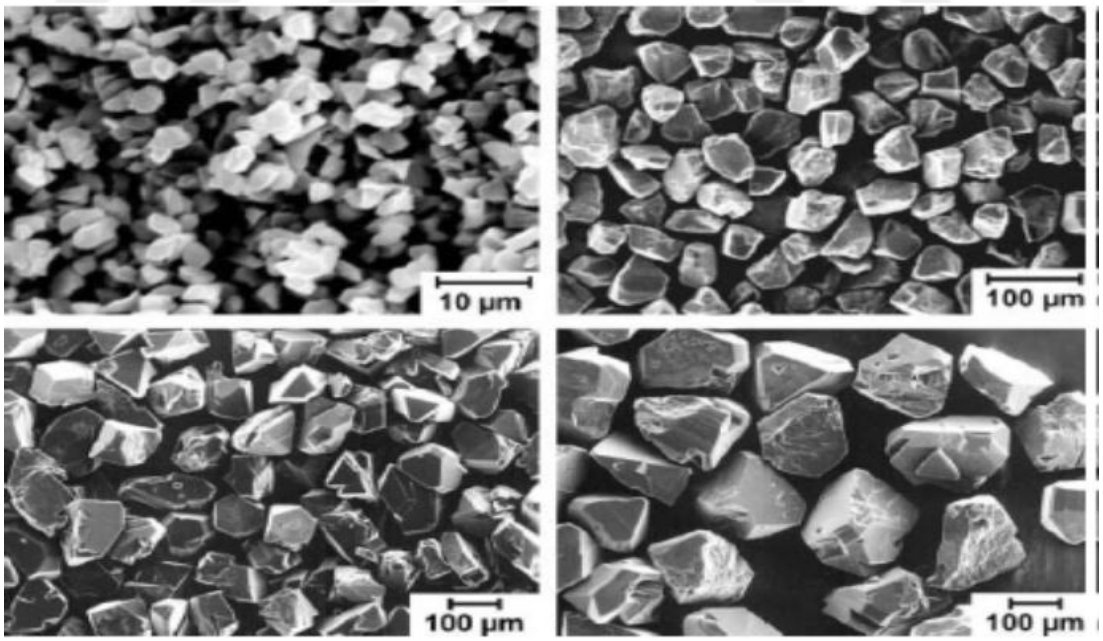


Figure 24 Morphology of c-BN in Different Grain Sizes [37].

The high thermal conductivity property is provided by phonons, not by the presence of electrons as in metals. The Figure 2.4 shows the c-BN particles that can be enlarged with the high temperature method.

2.2.3. w-BN (Wurtzite Boron Nitride)

It is the name given to the high density wurtzitic form. Its theoretical density is 3.48 g / cm^3. In wurtzit boron nitride, the rings are arranged along the c axis so that the boron and nitrogen atoms overlap each other (… ABABAB…) [40]. The crystal structure is seen in Figure 2.5.



Figure 25 Crystal Structure of Wurtzite Boron Nitride [37].

2.3. Properties of Hexagonal BN

The underlying properties of h-BN are highly dependent on manufacturing techniques due to differences in crystallinity, particle size distribution and purity.

The three most important properties of h-BN are electrical insulation, thermal conductivity and solid lubricity. It is also white, soft and inert. The specific resistance of boron nitride is greater than 1012 ohms at room temperature and drops to 1900 ohms at 2000 °C, which is better than most refractory oxides [41].

Similar to other covalently bonded nitrides, electrons are strongly and covalently bonded to the nucleus. This situation is not present for the metallic bond which is the cause of the high electrical resistance.

High thermal conductivity is another important property of h-BN. However, it decreases as the temperature increases. The thermal expansion of h-BN is low and increases with increasing temperature.

These thermal properties are the most important factor in the widespread use of this material in the manufacture of high temperature crucibles. Hexagonal boron nitride has a high solid lubricity due to strong covalent bonds between atoms on hexagonal layers, different from the weak van der waals bonds between these layers.

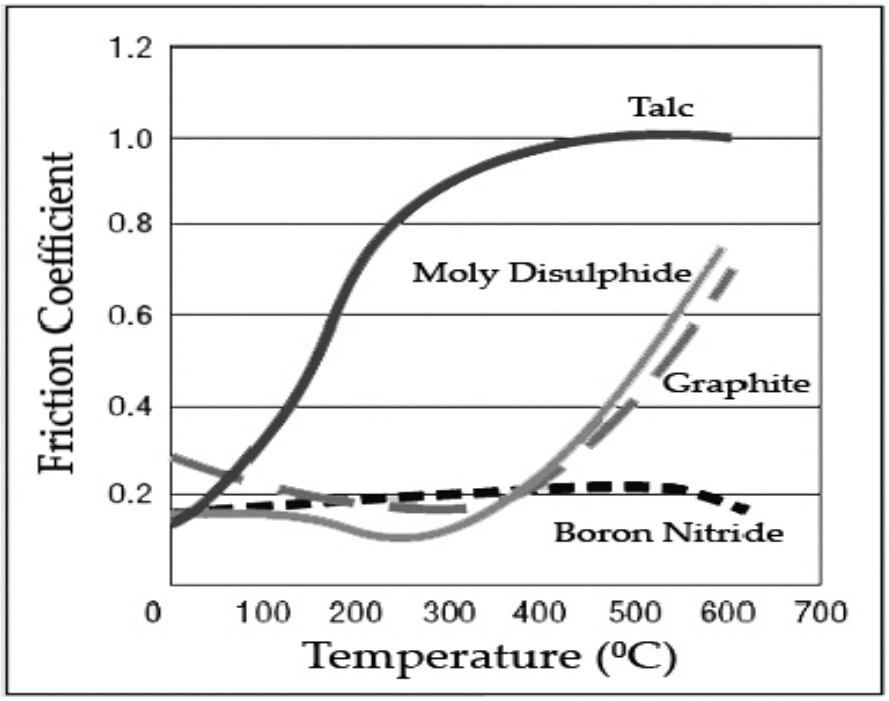


Figure 26 Crystal Friction Coefficient Variation of Some Important Lubricants Temperature [42].

Excellent lubrication performance is the result of the hexagonal layers sliding easily over each other. The low friction coefficient of h-BN does not increase at the high temperatures indicated in Figure 2.6 In this case, it is the most important factor in using this material in metalworking processes that require high temperature lubrication and cleaning.

Some important properties of h-BN compared to graphite are given in Table 2.1 Thermal expansion coefficient and thermal conductivity values are given for the direction perpendicular to C-axis.

Table 2.1 Some Properties of h-BN, Graphite [43].

Properties	**h- BN**	**Graphite**
Density (g / cm^3)	2.27	2.1-2.2
Melting Point ($^{\circ}C$)	3000	3700
Thermal expansion coefficient (1 / C*10^6)	0.7	32
Thermal Conductivity at RT (W / m.K)	121	138
Dielectric Constant	4.2	-

Hexagonal boron nitride powders are usually sintered by pressure-assisted sintering methods, which are hot pressing or hot isostatic pressing. During sintering, some B_2O_3 is used as a binder.

Unlike other non-oxide ceramics, h-BN does not form any solution during sintering. Also, these sintered materials can be easily processed to produce complex shapes due to the weak van der waals bonds between hexagonal layers.

2.4. Applications of Hexagonal BN

Thanks to its unique properties, h-BN has a wide range of uses in the fields of chemistry, metallurgy, high temperature technology, electrotechnics and electronics. Hexagonal boron nitride can be used in powder form, hot pressed condensed form, as an additive to composite materials, in pyrolytic form, and in spray form as coating suspension.

It is used as a powder and bulk product in a wide area due to its refractoriness at high temperatures, non-adherence, chemical inertness, high thermal conductivity, excellent thermal shock resistance, electrical insulation, workability and lubricity.

The use of h-BN as a starting material in the production of c-BN, which is the second hard material after diamond, is another important area of use. As a commercial application of h-BN powders, hexagonal boron nitride, which has a lubricating nature in powder form, is also often referred to as white graphite.

In addition to its electrical insulation feature, it is resistant to oxidation, has an operating temperature of up to 3000 °C and is highly resistant to corrosive effects [44].

As an additive, Hexagonal boron nitride is a slippery material in powder form, providing this material with a wide range of application areas where lubricity is required.

It is mainly used in high temperature applications as it does not lose its slipperiness at high temperatures. It is added to water, oil and water oil mixtures to increase lubrication. It is also added to solid lubricants such as plastics, rubbers and resins.

It is added to ceramics and alloys to reduce friction and wear, with the result that boron nitride is a suitable additive to the oil used in the slip of bearing steel. It was determined that the friction coefficient increased slightly, but when even small amounts of h-BN such as 1 % by weight were added, the abrasion of this material was extremely reduced.

Many ceramic and intermetallic composite boron nitride are added to improve performance characteristics. Composite SiC / BN, TiB_2 / BN, Si_3N_4 / BN, AlN / BN, ZrO_2 / BN and Al_2O_3 / BN make up only a part of them [45].

Additionally, the addition of h-BN to intermetallic composites provides excellent improvement in the properties of these materials. This makes composites thermally stable and chemically inert in vacuum and abrasive metal vapors. It also improves the machinability of these materials and allows the accommodation of conductivity and resistivity properties.

It has been determined that adding BN to some metal oxides (BeO, Al_2O_3) used in aviation applications increases the thermal shock resistance of the material. It was concluded that BN scale inclusions provide a high density in ceramic matrices that blocks crack propagation. Accordingly, these materials could be used in applications where thermal shock resistance is required [46].



Figure 27 Various Products of h-BN [83].

Another important application area of h-BN is the electronics industry due to its high thermal conductivity and good electrical insulation. It is used as substrate for semiconductors, windows for microwave apparatuses, and insulating layers for MISFET semiconductors. The Figure 2.7 show that various products of h-BN.

Since hexagonal boron nitride properties depend on the production technique, purity, particle size distribution and structure, the applications are also dependent on these parameters as expected.

For example, high purity is required for electronic applications and the cosmetics industry, while small grain size is a key feature for hot pressed or hot isostatically pressed shapes. In addition to application areas explained above, there is a growing market for h-BN usage as listed below:

- Radar windows and antennas,
- Heat absorbing material in aviation,
- Plasma rings,
- Insulator gap in tungsten resistant heaters,
- Anti- corrosive layers and oxidation- resistant coatings with pyrolytic films,
- Heat chamber in transistors,
- Substrates.

2.5. Production Methods of Hexagonal BN

Hegzagonal boron nitride is not found in nature in a neutral state. It was first produced in 1842 by reacting molten boric acid and potassium cyanide, but commercial production was not possible until the 1950s. Many methods have been used to produce boron nitride in the range of 900 - 1500 °C by reacting boron oxides and boric acid with ammonia or urea [47].

Other methods are nitriding by carbothermic reduction of boron oxide. Although there are many synthetic production methods using different starting materials; Three main methods are preferred for industrial applications:

• Nitriding,

• Carbothermic reduction of boron oxide,

• Pyrolytic production of boron nitride.

A ternary B-N-O diagram is used to graphically express the reactions of boron nitride. The system consists of five elements (H, B, C, N, O), a four-dimensional diagram is needed for this.

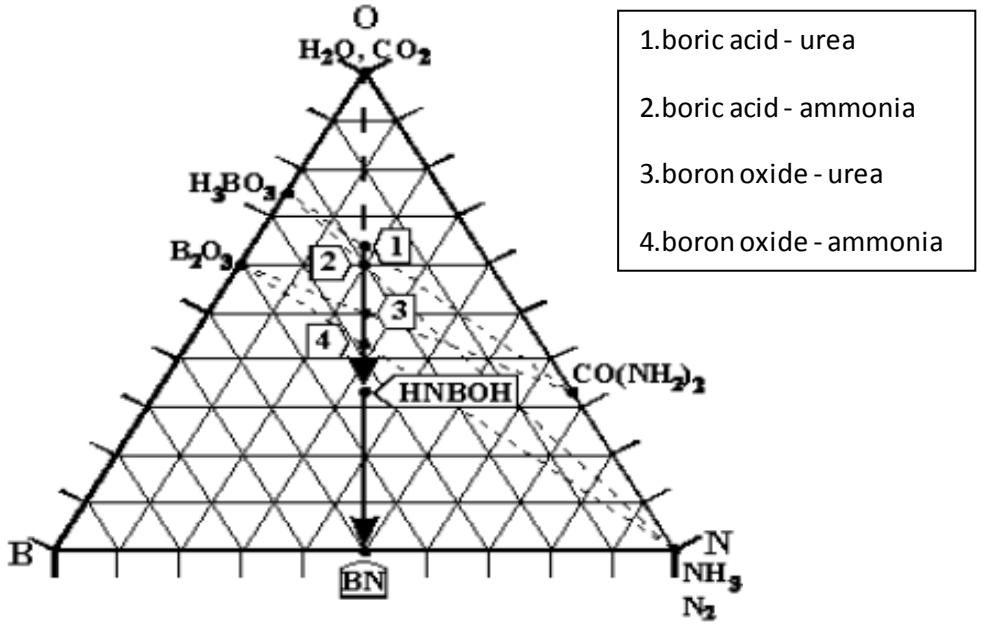


Figure 28 Ternary B-N-O Phase diagram [48].

In this way, the system has been reduced to three elements, as imaging can be difficult. The Figure 2.8 is shown, with the formation of boron nitride represented by numbers, with four subgroups.

2.5.1. Nitriding Method

It is carried out by the reaction of anhydrous boric acid and ammonia under inert gas.

$B_2O_3 + 2NH_3 \longrightarrow 2BN + H_2O$ (T = 900 °C)

The higher temperatures required for nitrogen atomization are essential for direct synthesis. It shows weak crystallization in the product obtained from the pure system due to oxygen deficiency.

The particle size of the boron nitride produced does not exceed the particle size of the elemental boron in the raw material. In this method, heat treatment is required under nitrogen gas at 1500 °C for the purification and stabilization of the products.

The chemical reaction of boric acid or borax with urea and melamine, which are organic nitrogen carriers, $B_2O_3 + CO(NH_2)_2 \longrightarrow 2BN + CO_2 + 2H_2O$ (T = 1000 °C) is shown.

In the presence of anhydrous boric acid, nitriding of calcium hexaboride under nitrogen atmosphere is indicated as $3CaB_6 + B_2O_3 + 10N_2 \longrightarrow 20BN + 3CaO$ (T = 1500 °C).

The Figure 2.9 with the product obtained from the aforementioned methods are soft and mostly white powders.

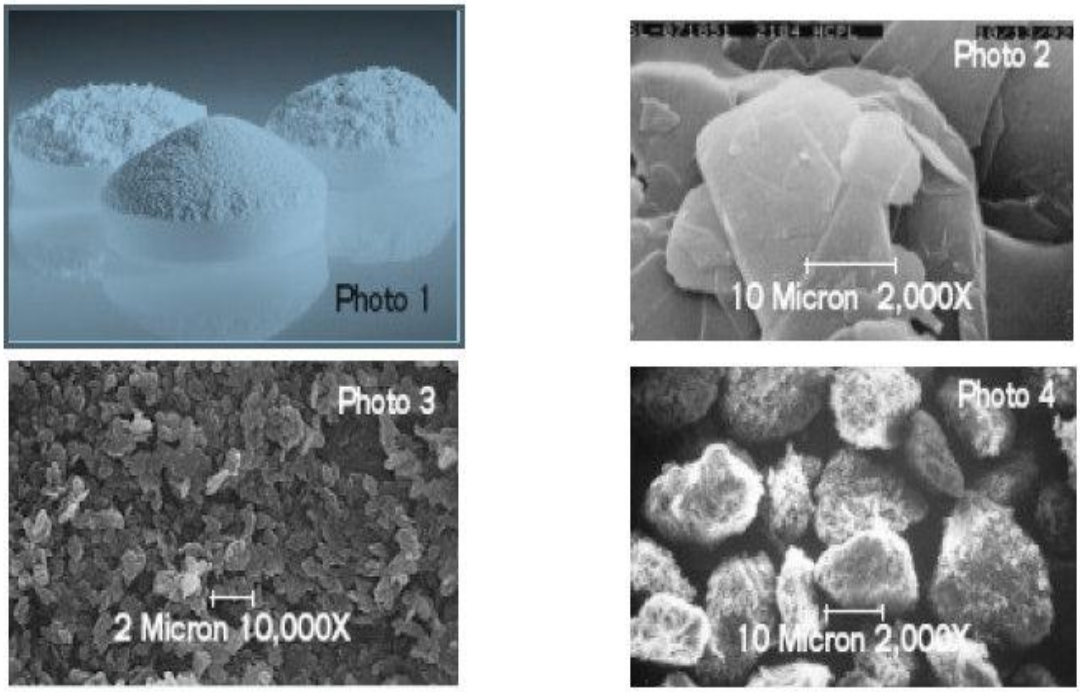


Figure 29 SEM Images of h-BN Powders [49].

1-SEM images of h-BN powders in three different particle sizes, 2-3-4 h-BN powders produced at different temperatures.

2.5.2. Carbothermic Method

In this method, anhydrous boric acid is reacted with carbon and nitrogen. First, anhydrous boric acid is reduced by carbon. In the next step, boron reacts with nitrogen to form h-BN.

I. $B_2O_3(s) \longrightarrow B_2O_3(l)$ (T = 1500 °C)

$B_2O_3 + 3C(s) + N_2(g) \longrightarrow 2BN(s) + 3\,CO(g)$

II. $B_2O_3 + 7C(s) + N_2(g) \longrightarrow 2B_4C(s) + 6CO(g)$

$B_4C + B_2O_3(g) + 7\,N_2(g) \longrightarrow 14BN(s) + 3CO(g)$

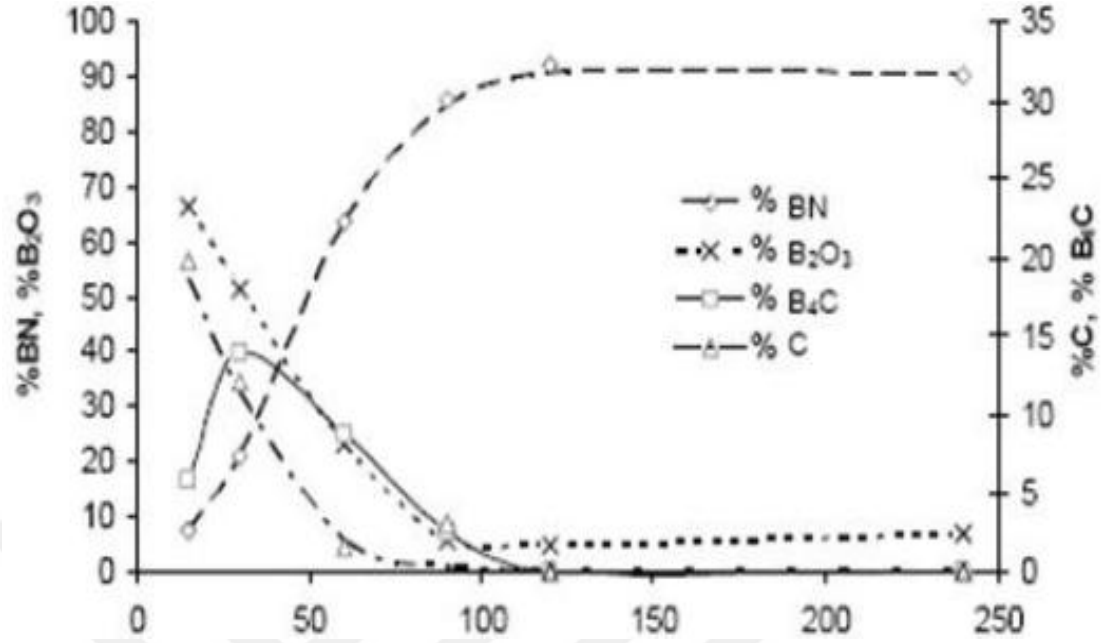
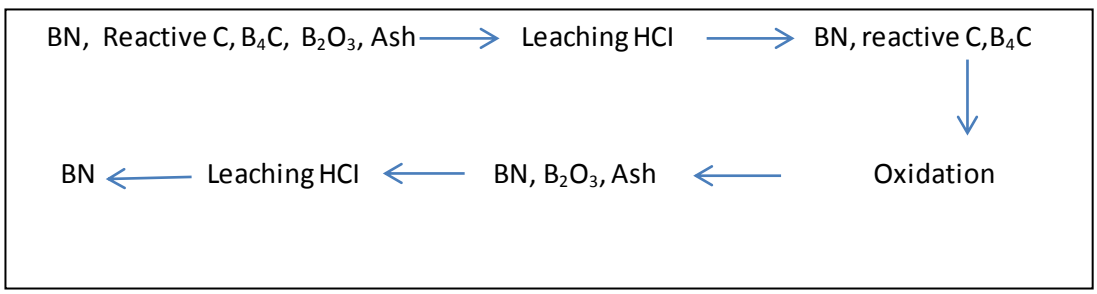


Figure 30 Change of Product and Semis Masses Over Time [34].

The Figure 2.10 is shown, change of product and semis masses over time. As seen in the reaction, the amount of the reaction product B_2O_3 and carbon decreases over time and the carbon is completely consumed within two hours at 1500 °C.

The mass of BN increases up to two hours and then remains constant. In this method, the amount of unreacted carbon shows a significant decrease above 1300 °C. In addition, the amount of B_4C formed in the reaction steps increases from 1200 °C to 1400 °C, it starts to decrease at 1500 °C above 1400 °C.

Table 2.2 Production of h-BN by Carbothermic Reduction of Anhydrous Boric Acid.



The Table 2.2 show that the production of h-BN by carbothermic reduction of anhydrous boric acid.

2.5.3. Pyrolytic Boron Nitride Production

This method involves the chemical vapor process, which is the result of some reactions of h-BN with graphite substrates. The basic raw materials are high purity gases such as boron hydride, nitrogen ammonia and hydrocarbon. The reaction product BN vapor is collected on the graphite substrate and the material is scraped off the substrate.

$BCl_3 + NH_3 \longrightarrow BH + 3HCl \quad (T = 2000\ °C)$

$BF_3 + NH_3 \longrightarrow BN + 3HF$

The Figure 2.11 is shown, change of product and semis masses according to temperature. This production technique makes it possible to obtain pyrolytic boron nitride with a high degree of crystal orientation with hexagonal layer lattice always parallel to the substrate surface. The high degree of crystal orientation provides anisotropy in 1000: 1 scale as in pyrolytic boron nitrile single crystals.The importance of this feature becomes evident when p-BN is used as a crucible or ladle.[50]

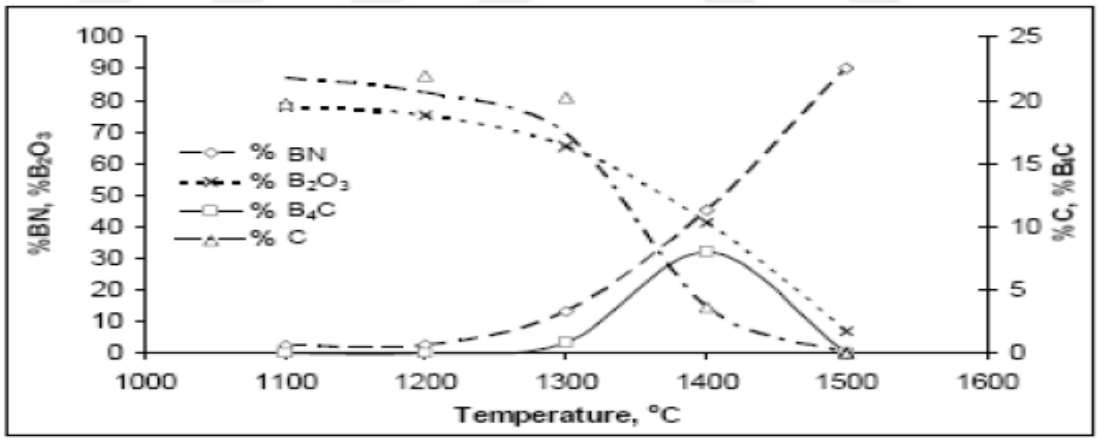


Figure 31 Change of Product and Semis Masses According to Temperature [34].

The thermal conductivity value is around 40 times higher on the outer wall of the crucible than the inner part. Although the pyrolytic boron nitride production method provides uneven and dense coatings with a purity of up to 99 %, its high cost and limited coating thickness are the disadvantages of the method. Its high orientation feature and consequently high anisotropy are shown among the important advantages of p-BN.

CHAPTER 3

LITERATURE REVIEW AND EXPERIMENTAL SET-UP

3.1. Literature Review

Studies about boron mine and boron-mixed structures are available today, and detailed analyzes have been made on the solutions they offer for different applications thanks to the superior properties of the mentioned structures. Hexagonal boron nitride is one of such structures. Hexagonal boron nitride is a structure with various production methods. However, the most common production technique in the industrial sense is the carbothermic production method. In one of these studies Pikalov's [51] work, it was assumed that separate reduction and nitriding processes occur for h-BN formation. At first, boron carbide formation occurred as the reduction products of boric oxide and carbon by the reaction.

$2B_2O_3 + 7C = B_4C + 6CO$

Then, the reaction of boron carbide and boric oxide in nitrogen environment takes place, h-BN formation occurs. In nitrogen, it has been established that the interaction of boron oxide and carbide occurs throughout the gas phase.

$3B_4C + B_2O_3 + 7N_2 = 14BN + 3CO$

In another study related to the production of boron nitride by the carbothermic method, Bartnitskaya et al [52]. Concluded that boron nitride is formed by the following general reaction with carbon particles that may be affected by nitrogen and the areas where boron suboxide will be in contact.

$B_2O_3 + 3C + N_2 = 2BN + 3CO$, It has been predicted that boron carbide may occur in areas where nitrogen feeding is blocked, according to reaction.

$2B_2O_3 + 7C = B_4C + 6CO$

According to the reaction, boron carbide formation in the first step of the reaction was explained by the inability of nitrogen to affect the boric oxide solution.

The presence of boron carbide and oxide, nitrogen in the environment leads to more reactions and more boron nitride to be produced.

In another study, Bartnitskaya et al [53]. Investigated the h-BN yield and the catalytic effect of some lithium-containing compounds such as Li_2CO_3 and LiOH in three-dimensional crystallographic sequencing.

In experiments carried out for 3 hours at 1500 °C in a nitrogen-dense environment, it was determined that when Li_2CO_3 was added to the initial boric acid-carbon mixture at a rate of 12 %, the amount of h-BN was approximately twice as compared to the experiments without Li_2CO_3.

It was found that the crystal structure of the produced h-BN was also improved by the addition of Li_2CO_3. In order to determine the effect of Li_2CO_3, a catalyst-solvent experiment has been proposed in which Li_2CO_3 will react with B_2O_3 and cause the melting of lithium borate. In the ongoing stages, h-BN is formed and crystallization occurs throughout the formed solution. The abundance and low cost of $CaCO_3$ in the environment make it preferred as a suitable catalyst for carbothermic production of h-BN.

Yoon and Jha [54] studied the B-N-C-O system in their studies. They revealed that BO is the gaseous species containing boron in the carbothermic formation of boron nitride.

In the studies conducted by Aydoğdu and Sevinç [55], it was determined that the equilibrium vapor pressure of BO was much lower than B_2O_3 at 1500 °C and it was observed that the reacting species was B_2O_3 in gaseous state.

In the next step, the formation of h-BN occurred as a result of exposing the pellets prepared from B_2O_3 activated C mixtures to N_2 gas at temperatures varying between 1100 °C and 1500 °C for 15 minutes to 4 hours.

Unreacted B_2O_3 will be finished in 2 hours at 1500 °C and B_4C, in addition to the formation of unreacted C and BN, in order to be found in the reaction products of the experiments in which the production of h-BN does not result.

From the results of the experiments for reaction steps by creating different geometric stages, they determined that liquid B_2O_3 and solid carbon do not need to be in interaction in the formation of BN from B_2O_3, C and N_2. However, they completed the general reaction;

$B_2O_3 + 3C + N_2 = 2BN + 3CO$

The experiment continued with the evaporation of B_2O_3 (1) and the reaction of B_2O_3 (g) with C(s) and N_2(g) with C(k). With the thermodynamic analysis based on reaction;

$3B_4C + B_2O_3 + 7N_2 = 14BN + 3CO$

they revealed that BN(s) or B_4C(s) cannot continue in the system in equilibrium and that B_4C(s) in the system are unstable when there is a ratio of CO to N_2 P^3_{CO}/P^7_{N2}.

In the experimental stages where there is a continuous N_2 gas interaction, it is thought that the ratio of P^3_{CO}/P^7_{N2} should be lower than the critical rate at which B_4C is not expected to be in the system. It has been suggested that pellet B_4C forms in regions where N_2 pressure is very low due to insufficient penetration of nitrogen gas.

It has been determined that some h-BN states occur successively according to the general reaction;

$3B_4C + B_2O_3 + 7N_2 = 14BN + 3CO$

some of them according to the reactions;

$2B_2O_3 + 7C = B_4C + 6CO$ and $3B_4C + B_2O_3 + 7N_2 = 14BN + 3CO$

and the B_4C - B_2O_3 mixtures have found the reaction rate in the experiments carried out with the effect of N_2(g). In some studies, B_4C was presented as a necessary intermediate product according to Pikalov, while Aydoğdu and Sevinç's evaluations concluded that B_4C was not necessary for the carbothermic formation of BN.

Özkenter [56] conducted studies involving a mixture of B_2O_3 and active carbon by adding pellets formed from $CaCO_3$ and CaO to N_2 gas at 1500 °C in order to investigate the effects of $CaCO_3$ and CaO additives and the amount and structure of h-BN. It was formed by carbothermic reduction in these studies.

It has been concluded that the addition of CaO, similar to the addition of $CaCO_3$, also causes a catalytic effect on h-BN formation. However, it was determined that the samples with $CaCO_3$ content had higher h-BN content in the product.

The reason for this difference was explained by the fact that the formation of CO_2 gas during the calcination process of $CaCO_3$ results from the higher porosity of the pellets with $CaCO_3$ added to the pellets with CaO. Later it was seen that $CaCO_3$ and CaO added samples caused a larger h-BN particle size.

In the ionic mechanism stage, the pellets produced by Özkenter from carbon-free B_2O_3 and B_2O_3-CaO mixtures were exposed to $N_2(g)$ at 1500 °C. It was observed that nitrogen was not dissolved in the B_2O_3 solution.

However, in the presence of BN particles, nitrogen was dissolved in the calcium borate solution that formed BN in order to nucleate. For this reason, it has been determined that BN production is possible with the ionic system in calcium borate solutions, but there is a nucleation barrier in stages.

Based on the results of the study, it has been proved that h-BN can occur with two different and similar stages, in short, reaction;

$B_2O_3(l) + 3C(s) + N_2(g) = 2BN(s) + 3CO(g)$ and ionic dissolution of nitrogen in h-BN forming calcium borate solution.

Akyıldız [57] investigated the effect of Na_2CO_3 addition on h-BN formation of carbothermic in his studies. In the first experimental study, the effect of the amount of Na_2CO_3 additives was tried to be investigated according to the reaction results by exposing the pellets prepared with different concentrations of 5 % to 40 % Na_2CO_3 additives at 1500 °C to nitrogen gas for 30 minutes.

It was determined that Na_2CO_3 contribution increased the amount of h BN in the products. With these results, an optimum concentration point cannot be found and the maximum amount of h-BN can be achieved by mixing it with 40 % by weight Na_2CO_3.

Experiments with higher amounts of Na_2CO_3 were not carried out as it was predicted that they would not result in yield. In his studies, investigated the effect of time on the carbothermic formation of BN in Na_2CO_3 doped samples. It was seen that the amount of h-BN in the production aggregate increased up to 3 hours.

While the process was continuing, it was found that the amount of H-BN did not increase in longer periods. In the experiments, B_2O_3 and Na_2CO_3 borate were not detected in the products obtained as a result of the reaction for 2 hours or longer, and it was thought that the reaction time should end with 2 hours.

During the experiments, the experiments continued to be carried out using different temperatures in order to examine the effect of temperature on the reaction. It showed that increasing the amount of h-BN by 40 % by weight of Na_2CO_3 increased the temperature of the added sample.

However, it was determined that the effect of the temperature on the amount of h-BN from the sample formed by adding Na_2CO_3 was less than the sample added with $CaCO_3$.

For this reason, it was thought in the experiment that the inclusion of Na_2CO_3 in the initial B_2O_3 activated C mixtures could be an effective method for lower temperatures and shorter times.

In addition, it was determined that the inclusion of Na_2CO_3 in the B_2O_3 - C mixture increased the average particle size amount of the h-BN generated by obtaining SEM images. It was concluded that the Na_2CO_3 incorporated samples caused a larger h-BN particle size compared to the $CaCO_3$ added samples.

In the studies of Çamurlu [58], they preferred the production of boron carbide with the carbothermic method of h-BN, and they examined the results by affecting the samples prepared from B_2O_3 and activated carbon in certain proportions with argon and nitrogen gases.

The amount of boric oxide in the samples showed that it was 100 % more than the amount calculated by reaction; $B_2O_3(l) + 3C(s) + N_2(g) = 2BN(s) + 3CO(g)$. He concluded that the formation of h-BN occurred by two parallel reactions.

Where the nitrogen gas pressure amount starts to rise, this reaction occur under the effect of nitrogen gas, which is the reduction of carbon and boron oxide to BN. The reaction was observed to take up to 3 hours at 1500 °C.

In areas where nitrogen gas could not affect the pellets, boron carbide formed by reaction; $2B_2O_3 + 7C = B_4C + 6CO$ and reacted B_2O_3 and N_2 according to reaction;

$3B_4C + B_2O_3 + 7N_2 = 14BN + 3CO$, it occurred to BN.

The main purpose of Çamurlu's study was pelleting samples of boron oxide and activated carbon to produce boron carbide, and they worked under the influence of argon gas at 1500 °C.

The produced boron carbide and boron oxide were mixed into a mixture and subjected to nitrogen gas at 1500 °C over a period of 3 hours. It was found that boron carbide was not completely converted to hexagonal boron nitrile during this time.

With this result, it was observed that the formation of boron carbide, boron nitride according to reaction; $3B_4C + B_2O_3 + 7N_2 = 14BN + 3CO$ occurred at a lower rate than the direct carbothermic reduction to boron oxide BN compared to reaction;

$B_2O_3(l) + 3C(s) + N_2(g) = 2BN(s) + 3CO(g)$. It was later revealed that boron carbide was not an important intermediate in the carbothermic formation of hexagonal boron nitride.

It was concluded that the boron carbide formed in the reaction process delayed the reaction because it caused the h-BN formation reaction to continue at a lower speed. It was thought that the formation of boron carbide should be prevented to increase the production rate of hexagonal boron nitride and to minimize the amount of boric oxide loss due to evaporation.

In another study, Kahramansoy [59] the pellet samples formed from boron oxide, activated carbon and colemanite mixtures were investigated to produce hexagonal boron nitride from boric acid and colemanite mixtures by carbothermic method by interacting with nitrogen gas at 1500 °C.

Similar to the $CaCO_3$ addition, colemanite addition to boron oxide and carbon mixtures has also been found to allow the formation of higher amounts of hexagonal boron nitride in the final product.

As a result of the studies carried out with colemanite and $CaCO_3$ additions providing the same amount of CaO to the initial mixture amounts, it was observed that the products from the reaction formed hexagonal boron nitride in similar proportions.

In the experiments conducted with different amounts of colemanite-boron oxide and carbon mixtures, the addition of 5 % colemanite by weight, which gives the highest hexagonal boron nitride, was determined as the ideal mixture composition.

It was determined that increasing the test time increased the amount and grain size of h-BN formed in the products. The ideal amount of colemanite adduct resulted in a larger amount of hexagonal boron nitride with larger grains than the ideal amount of $CaCO_3$ adduct.

3.2. Experimental Set- Up

3.2.1. Raw Materials Used

Activated carbon and boron oxide were used as basic raw materials in the experiments. The activated carbon was supplied from Nanography Company and boron oxide from Eti Mining Company. The information provided by the companies about these products is shown in The Tables 3.1, 3.2 and 3.3.

Table 3.1 Data Received from the Manufacturer for Activated Carbon.

Purity	99.99 %
Particle Size	4 µm
Cas	1333-86-4
Density	1.79 g/cm³
Melting Point	3500 °C
Form	Powder
Applications	Colorants Enamels Fabrics Inks Paints Paints- Primers Pigments Plastics



Figure 32 Activated Carbon.

The Figure 3.1 show that packed activated carbon, The Figure 3.2 show that boron oxide.

Table 3.2 Boron Oxide Chemical Specification.

Component	**Content**
B_2O_3	98.00% min.
SO_4	500 ppm max.
Cl	10 ppm max.
Fe	15 ppm max.



Figure 33.2 Boron Oxide [84].

Table 3.3 Boron Oxide Physical Properties.

Specific Weight	1,84 g / cm^3
Bulk (bulk) density	0,629 g / cm^3
Molecular weight	69,62 g / mol
Melting point	450 ^oC
Boiling point	1860 ^oC
Heat capacity	18,6 J / g ^oC
Thermal conductivity	0,138 W / mK
Specific surface area	< 1 m^2 / g
Diffusion coefficient	1,1 x 10^{-5} cm^2 / s
Surface tension	68.32 mN / m (1.0 % by weight aqueous solution)
Color measurement test	96,43
Size	+ 0.315 mm
Content	75.00 % min.

3.2.2. Tools and Devices Used

Within the scope of the powder preparation part of the experimental studies, an agate mortar with a depth of 100 mm was used for grinding and mixing activated carbon and boron oxide powders. The Figure 3.3 show that black agate mortar.



Figure 3.3 Black Agate Mortar.

In order to react the pelleted samples with nitrogen gas and perform sintering process, a high density, silicon carbide resistant Protherm brand tube furnace with a maximum temperature of 1650 ^{o}C was used. The Figure 3.4 show that high density tube furnace.



Figure 3.4 High Density Tube Furnace.

In order to remove the extra active carbon residues that may remain on the sample surface with dry air, a quartz tube, cantal type and Protherm brand oven which can reach a maximum temperature of 1110 ^{o}C has been used. The Figure 3.5 show that quartz tube furnace.



Figure 3.5 Quartz Tube Furnace.

The moist powders obtained after vacuuming were dried in a Nuve brand FN 500 series oven. The Figure 3.6 show that Nuve brand FN 500 series oven.



Figure 34.6 Nuve Brand FN 500 Series Oven.

In order to separate the sample mixes after leaching, 47 mm glass microfiber filter paper from Isolab was used. The Figure 3.7 show that glass microfiber filter paper.



Figure 35.7 Glass Microfiber Filter Paper.

In order to separate the dust part of the sample mixes in the liquid after leaching, a Rocker brand vacuum pump with a maximum vacuum power of 110 Torr and a maximum viscosity of 58 l / min was used. The Figure 3.8 show that the Rocker 500 vacuum pump.



Figure 36.8 Rocker 500 Vacuum Pump.

MSE brand manual press machine was used in order to pellet the mixture samples obtained properly. Press machine can press up to 10 tons as a maximum amount. The Figure 3.9 show that manual press machine.



Figure 3.9 MSE Manual Press Machine.

Shimadzu brand AP series precision balance were used to determine the amount of mixtures, pellets and processed sample powders. It have a five decimal digit, The Figure 3.10 show that Shimadzu AP series precision balance.



Figure 370 Shimadzu AP Series Precision Balance.

For the heating and mixing of the obtained mixtures during the leaching process, a quad analogue table top Velp AM4 serial multi-heater magnetic stirrer with a maximum mixing speed of 1500 rpm and a heating range of maximum 370 degrees was used. The Figure 3.11 show that Velp AM4 serial multi-heater magnetic stirrer.



Figure 3.11 Velp AM4 Serial Multi-Heater Magnetic Stirrer.

Empyrean multipurpose XRD system produced by Malvern Panalytical company was used for characterization of powder and pelleted samples. Empyrean pixel and strip-based detectors can be installed. In addition, the system allows for all high resolution thin film applications. The Figure 3.12 show that Malvern Panalytical Empyrean XRD.



Figure 38.12 Malvern Panalytical Empyrean XRD.

Particle size analysis of the samples obtained was made with the Mastersizer 3000 laser diffraction particle size analyzer of Malvern Panalytical company, which has the ability to measure between 10 nm - 3.5 mm. Particle size distribution has been achieved with both dry and wet dispersion units. The Figure 3.13 show that Malvern Panalytical Mastersizer 3000.



Figure 3.13 Malvern Panalytical Mastersizer 3000.

In order to measure the optical and reflection analysis of the samples in pellet and powder form, the UV- 3600 Plus model UV device modes of Shimadzu company were analyzed. UV-3600 Plus uses PMT (photomultiplier tube) in the ultraviolet and visible area, InGaAs and cooled PbS detectors in the near infrared region. The Figure 3.14 show that Shimadzu UV-3600 Plus.



Figure 3.139 Shimadzu UV-3600 Plus.

Hitachi FlexSEM 1000 brand scanning electron microscope was used to determine the nanoscale surface morphology of the synthesized hexagonal boron nitride samples. 450 mm wide system minimizes the footprint. FlexSEM is designed with detachable units for flexible system layout. The Figure 3.15 seen Hitachi FlexSEM 1000 brand SEM.



Figure 3.15 Hitachi FlexSEM 1000 Brand SEM.

The spectrum analyzer is an electronic equipment used to measure the magnitude of a given input signal over the full frequency range of the device. Rohde and Schwarz branded vector network spectrum analyzer was used to measure the exact frequency ranges of h-BN samples in the range of 10 Mhz to 40 Ghz. The Figure 3.16 show that Rohde and Schwarz 10 Mhz to 40 Ghz spectrum analyzer

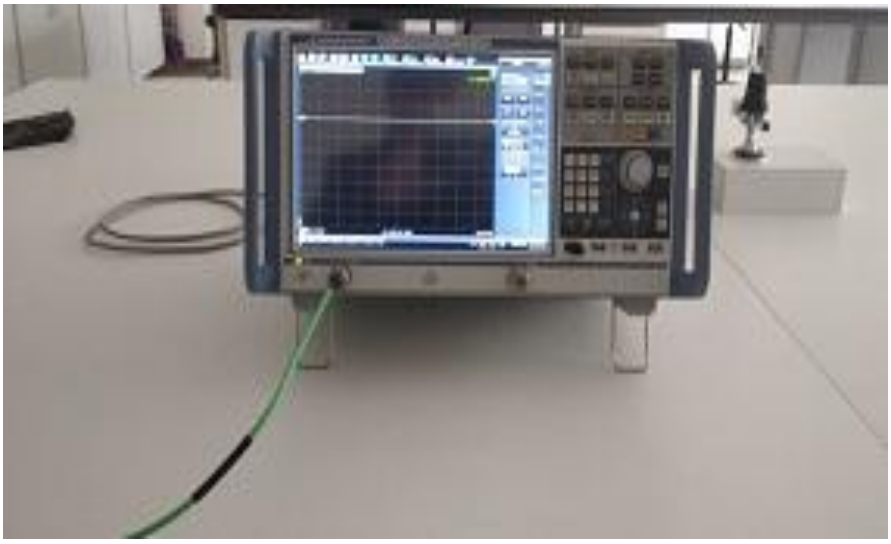


Figure 3.16 Rohde and Schwarz 10 Mhz to 40 Ghz Spectrum Analyzer.



Figure 3.17 Shimadzu IRAffinity-1S Fourier Transform Infrared Spectrophotometer.

For the chemical bond characterization of hexagonal boron nitride samples, Shimadzu IRAffinity-1S brand conversion infrared spectrophotometer was used.

IRAffinity-1S can reach the highest SN ratio thanks to its high energy ceramic light source, temperature-controlled, high-sensitivity detector, efficient optical element and optimization of the optical system with its electrical system. The Figure 3.17 seen the Shimadzu IRAffinity-1S fourier transform infrared spectrophotometer.

3.3. Conducting Experiments

Various experimental studies have been carried out to produce hexagonal boron nitride. In this study, it will be tried to obtain hexagonal boron nitride as a result of various processes by incorporating the mixtures to be prepared with boron oxide and activated carbon, which will be determined in different proportions, in interaction with nitrogen gas.

At first, the chemical equation was tried to be determined in terms of the reaction occurring. Aydogdu and Sevinc [60], determined it as the chemical equation; B_2O_3 + 3C + 2N(g) = 2BN + 3CO(g) for h-BN production in their work. The Figure 3.18 show that the reaction of the chemical process is seen in Equilibrium Amount (kmol) - Temperature (^{o} C).

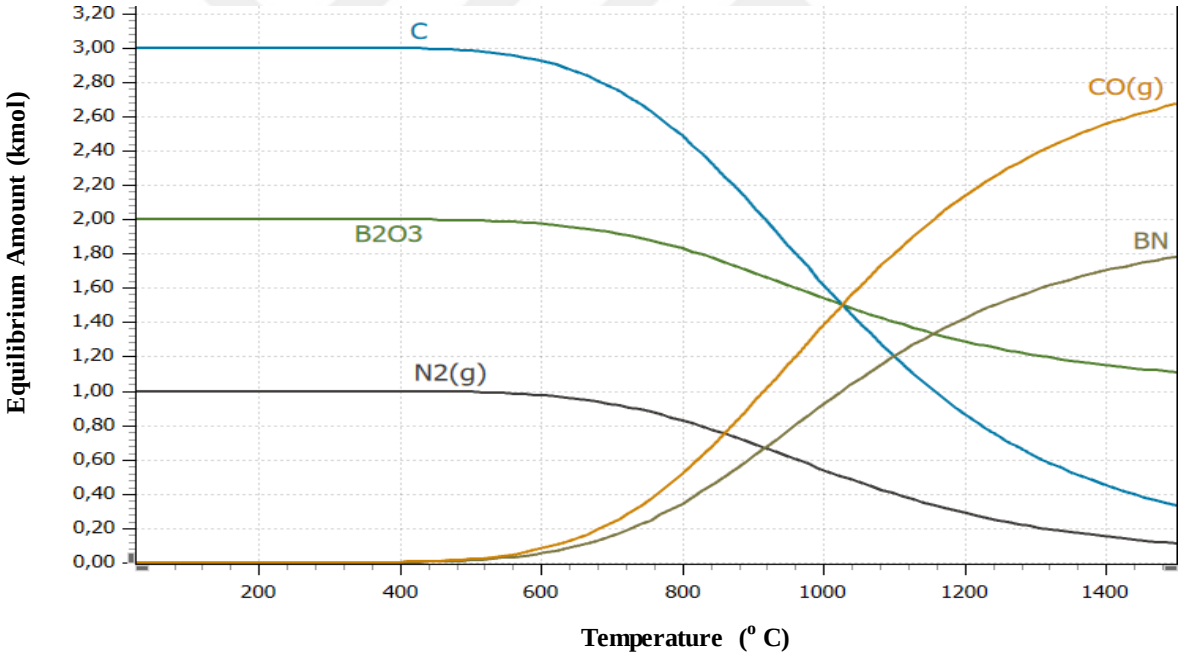


Figure 3.18 h-BN Production Equilibrium Amount (kmol) - Temperature (^{o}C).

In the same study, boron carbide can form as an intermediate type in the reaction process, and pure BN can be obtained after cleaning the reaction product from activated carbon ash and unreacted B_2O_3. B_4C can exist as an intermediate species in the reaction products of experiments in which the BN formation is not complete.

For this reason $2.5B_2O_3 + 8.5C + N(g) = BN + 7.5CO(g) + B_4C$ equation has been obtained in experimental studies. The Figure 3.19 as an intermediate species of B_4C reaction of the chemical process is seen in Equilibrium Amount (kmol) - Temperature (^oC) is observed.

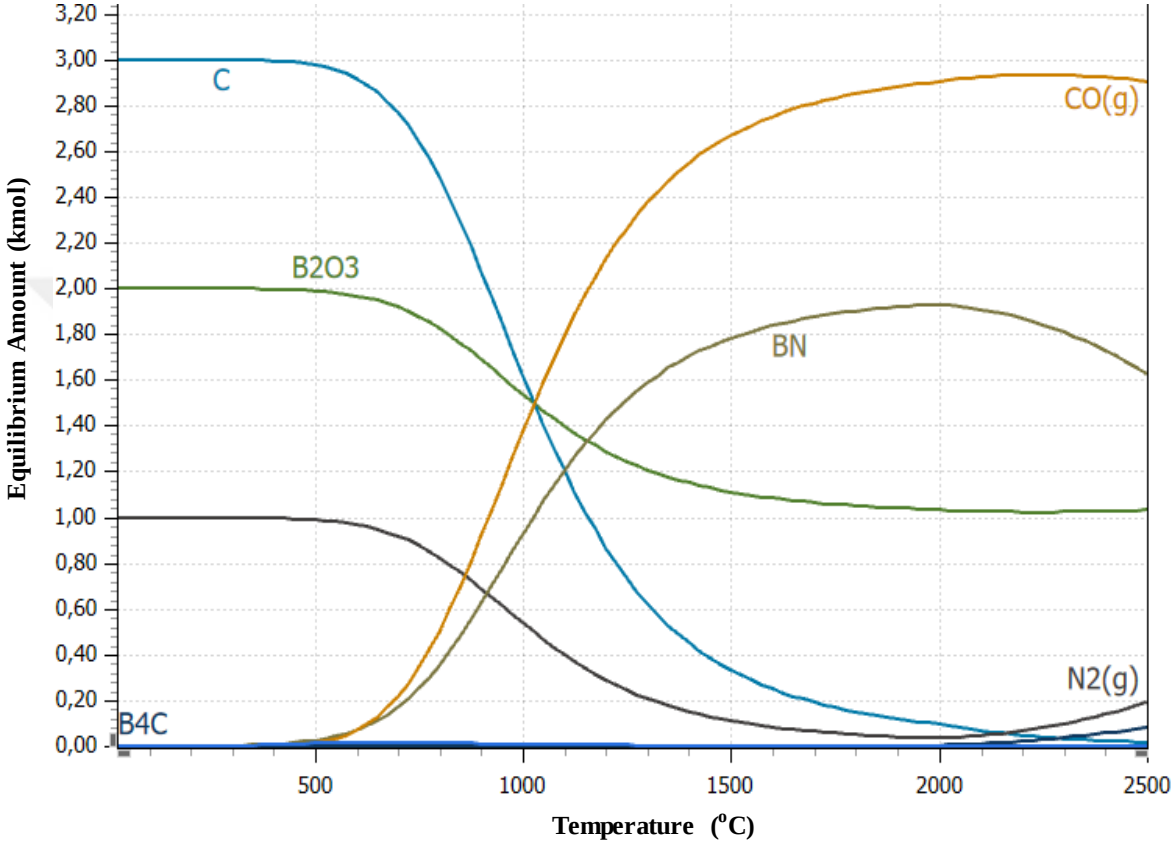


Figure 3.19 Equilibrium Amount (kmol) -Temperature (^oC) seen as an Intermediate Species of B_4C.

In order for the reaction to take place under standard conditions, there must be $\Delta G < 0$ Gibbs free energy during the h-BN formation process.

In the analyzes made according to the chemical equation of the exothermic reaction, it was predicted that the product could be formed in this way. The Figure 3.20 reaction is shown in Gibbs free energy ΔG (Kj) – Temperature (^oC).

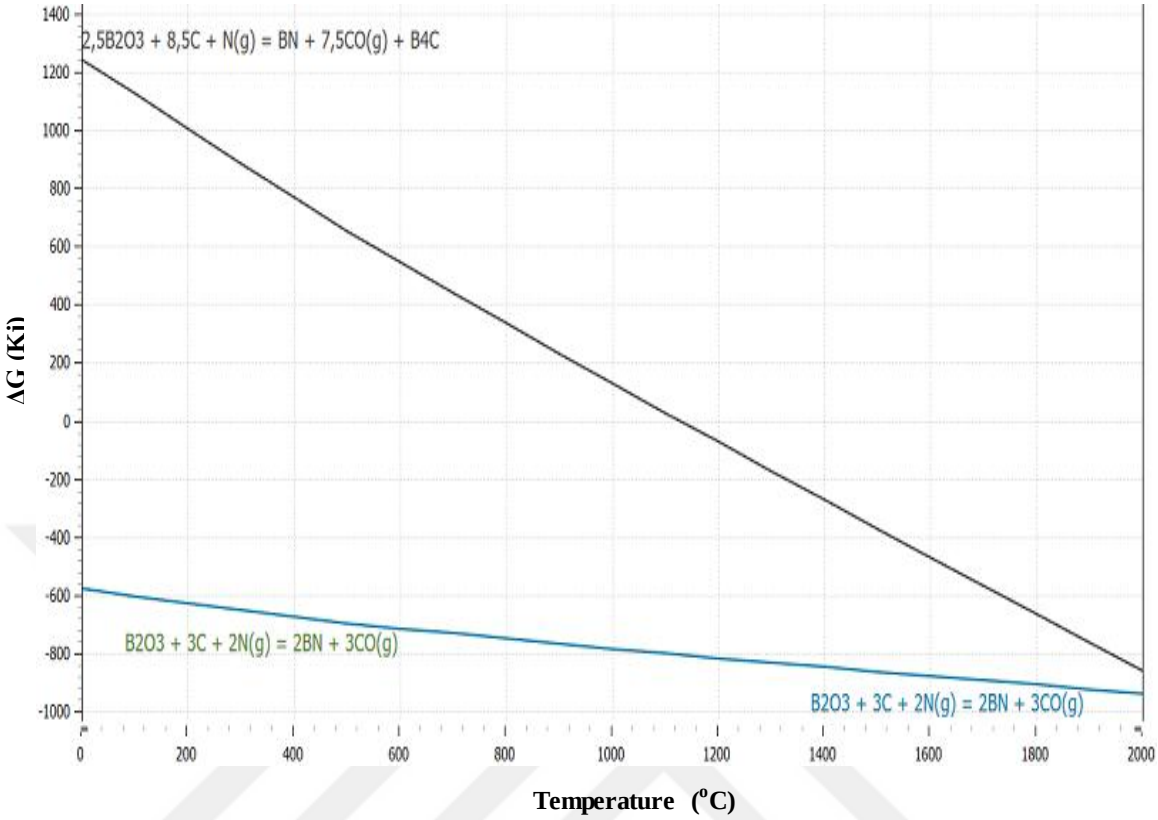


Figure 3.20 Gibbs Free Energy of the Reaction.

3.3.1. Preparation of Powders

Boron oxide powder obtained from Eti Mining and activated carbon powder supplied from Nanografi company started to prepare powder samples with a B_2O_3 ratio of 10 %, 25 %, 50 % and 75 % excess. Initially, the quantities of the samples according to the determined excess were calculated as follows.

$$B_2O_3(s) + 3C(s) + N_2(g) = 2BN(s) + 3CO(g)$$

1 mol 3 mol 2 mol

Y mol X mol 5 g

Bor oxide (B_2O_3) molar mass 69.62 g / mol, bor nitrür (BN) molar mass 24.81 g/mol and carbon (C) molar mass 12.01 g / mol are known. It was calculated that 1 mol boron nitride was 24.81 g while 5 g boron nitride was 0.2015 mol.

According to this result, 0.1007 mol of boron oxide and 0.3022 mol of carbon in the part of the reactants to form 0.2015 mol of boron nitride.(Y= 0.1007 mol B_2O_3, X= 0.3022 mol C)

69.62 g / mol B_2O_3 x 0.1007 mol B_2O_3 = 7.01 g B_2O_3 ,

12.01 g / mol C x 0.3022 mol C= 3.63 g C,

Amount of B_2O_3 + C = Amount of C + Amount of B_2O_3 (% 100 + % B_2O_3 Excess x 7.01 g B_2O_3).

The Table 3.4 show that the according to rate of bor oxcide excess powder rates and quantities for samples.

Table 3.4 Powder Rates and Quantities According to Samples.

Rate of B_2O_3 Excess	**Amount of B_2O_3 (g)**	**Amount of C (g)**	**Amount of B_2O_3 + C (g)**
% 10	7.71	3.63	11.34
% 25	8.76	3.63	12.39
% 50	10.52	3.63	14.15
% 75	12.27	3.63	15.90

The quantities of bor oxcide and activated carbon powders determined after analysis and calculations were started to be weighed using Shimadzu AP Series precision balance.

Later, B_2O_3 + C powder mixtures, which were taken into individual containers according to their ratios, were pounded in 40 minutes with a depth of 100 mm black agate mortar in order to homogenize better and to thin. The Figure 3.21 show that B_2O_3 + C powder mixture forged in mortar.



Figure 401 B_2O_3 + C Powder Mixture Forged in Mortar.

The mixtures obtained in the determined ratios after the process, using MSE brand manual press machine and powder mixture calculation method ;

$\pi.r^2 = 3.14 \times (5\ mm)^2 = 78.5\ mm^2$

$ton / mm^2 = 2 / 78.5 = 0.0254\ ton / mm$,

Convert 0.0254 ton / mm^2 to 253 MPa equal.

Compressed by applying a load of 253 MPa for 120 seconds, cylindrical pellet samples with a thickness of 0.5 mm and a diameter of 10 mm were obtained.

The Figure 3.22 show the after manual pressing process pelleted versions of B_2O_3 + C mixtures at the rates of a) 10 %, b) 25 %, c) 50 % and d) 75 %.

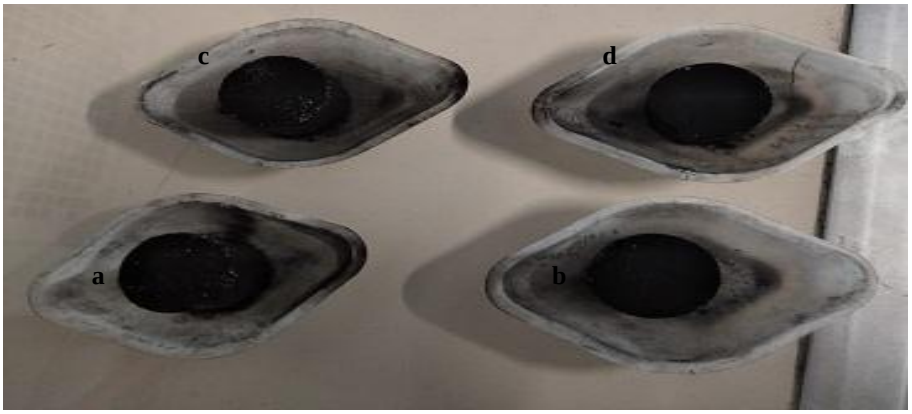


Figure 41.22 Pelleted Versions of B_2O_3 + C Mixtures at the Rates of a) 10 %, b) 25 %, c) 50 % and d) 75 %.

3.3.2. Oxidation Process

Pelleted samples from powder mixes were placed in a graphite crucible finely coated with boron nitride solution. The Figure 3.23 show the graphite crucible finely coated with boron nitride solution can be seen.



Figure 3.23 Graphite Crucible Finely Coated with Boron Nitride Solution.

The pelleted samples in the graphite crucible placed in the Proterm brand high density, silicon carbide resistant, horizontal tube furnace with 50 mm inner and 60 mm outer diameter and 1000 mm long tube, were increased to 1500 ^{o}C at 8 ^{o}C / min under nitrogen atmosphere. Samples were exposed to N_2(g) at 1500 ^{o}C for 120 minutes. Then the furnace is provided to cool down to 25 ^{o}C. The Figure 3.24 show that leaving the samples exposed to nitrogen to cool down to 25 ^{o}C in the furnace.



Figure 3.24 Leaving the Samples Exposed to Nitrogen to Cool Down to 25 ^{o}C in the Furnace.

Unreacted carbon ash was observed on the surface of the samples taken out in the graphite crucible after the furnace was cooled. The Figure 3.25 after the effect of nitrogen atmosphere, unreacted carbon ash can be seen on the surface of the samples that cool down.



Figure 3.25 Carbon ash Remaining Unreacted on Surface Parts of Samples.

In order to remove the carbon ashes seen on the surface from the samples, the samples obtained by Protherm brand, cantal type and quartz tube furnace were

increased to 850 ^{o}C with dry air at 10 ^{o}C / min. Unreacted carbon was burned with dry air at 850 ^{o}C for 120 minutes. The oven is left to cool.

The Figure 3.26 seen the quartz tube furnace for burning unreacted carbons with dry air. After cooling, samples were taken from the ladle and leaching preparations were made for cleaning.



Figure 3.26 Quartz Tube Furnace for Burning Unreacted Carbons with Dry Air.

3.3.3. Leaching Process

Pelleted samples are subjected to dry air and then pounded with pestle to be powdered before leaching. The Figure 3.27 show a) Dry Air Post Pellet Sample, b) Dry Air Powder Sample.



a **b**

Figure 3.27 Picture of a) Dry Air Post Pellet Sample, b) Dry Air Powder Sample.

Leaching was carried out in order to remove remaining carbon ash and unreacted structures in the samples. Therefore, a cleaning mixture of 100 ml of purified water, 100 ml of HCl (10 ml x 10 times) in total of 200 ml was formed in a 400 ml glass beaker previously prepared for leaching.

The Figure 3.28 seen the 100 ml distilled water and 100 ml HCl cleaning mixture prepared for the leaching process.



Figure 3.28. 100 ml Distilled Water and 100 ml HCl Cleaning Mixture Prepared for the Leaching Process.

The powdered samples were added into this mixture and the Velp AM4 serial multi-heater magnetic stirrer was left under stirring at 70 ^{o}C and 1000 rpm for 60 minutes. The Figure 3.29 is seen the samples in a multi-heater magnetic stirrer.



Figure 3.29 Samples in a Multi-Heater Magnetic Stirrer.

Vacuum filtration system was used to filter the mixtures obtained after this process. The Figure 3.30 a) is seen the Gooch vacuum filtration system and Rocker vacuum pump.



a **b**

Figure 3.30 Picture of a) Vacuum Filtration System and Pump, b) Filtering process with vacuum pump running.

Mechanism established with 400 ml Gooch flask, filter and clamp, with the help of Rocker 500 vacuum pump, Isolab 47 mm glass microfiber filter paper powder particles were separated from the mixture of HCl + pure water. The Figure 3.30 b) is filtering process is seen while the vacuum pump is running.

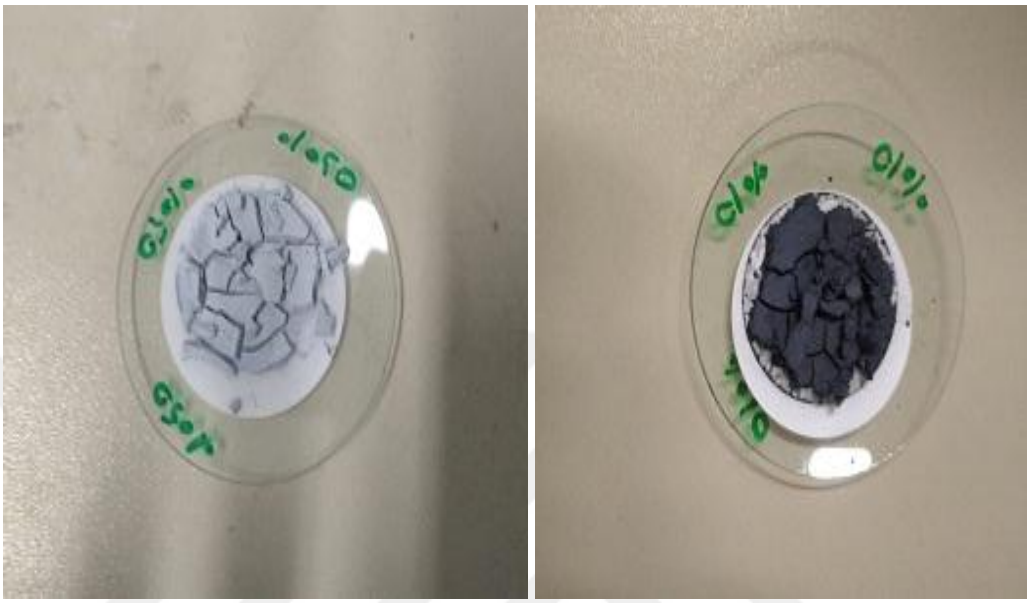


Figure 3.31 Powder Accumulated on the Filter Paper in Watch Glasses.

After separation during the leaching process, powder particles accumulated on the filter paper were placed on watch glasses with the help of tweezers. The Figure 3.31 show the powder accumulated on the filter paper in watch glasses.



Figure 42.32 Samples Taken From the Oven After Drying.

Then, the powder particles in the watch glasses were left to dry in the oven at 80 ^{o}C for 180 minutes in order to dry. The Figure 3.32 seen the samples that are about to be taken from the oven after drying.

After the powder particles obtained after the leaching process were dried in an oven, pellets were obtained by applying a load of 253 MPa to each sample in the MSE manual press machine to turn them into pellets. Pellets were prepared for sintering.

3.3.4. Sintering Process

The pelleted samples containing 10 %, 25 %, 50 % and 75 % B_2O_3 were placed in the high density furnace for sintering. At 8 ^{o}C / min, the temperature was raised up to 1500 ^{o}C.

The samples, which were exposed to nitrogen gas for 120 minutes at a temperature of 1500 ^{o}C, were allowed to cool in the furnace up to 25 ^{o}C. With the sintering process, the h-BN synthesis process has been completed.

The Figure 3.33 show that samples obtained after the sintering process for a) 10 %, b) 25 %, c) 50 % and d) 75 %.

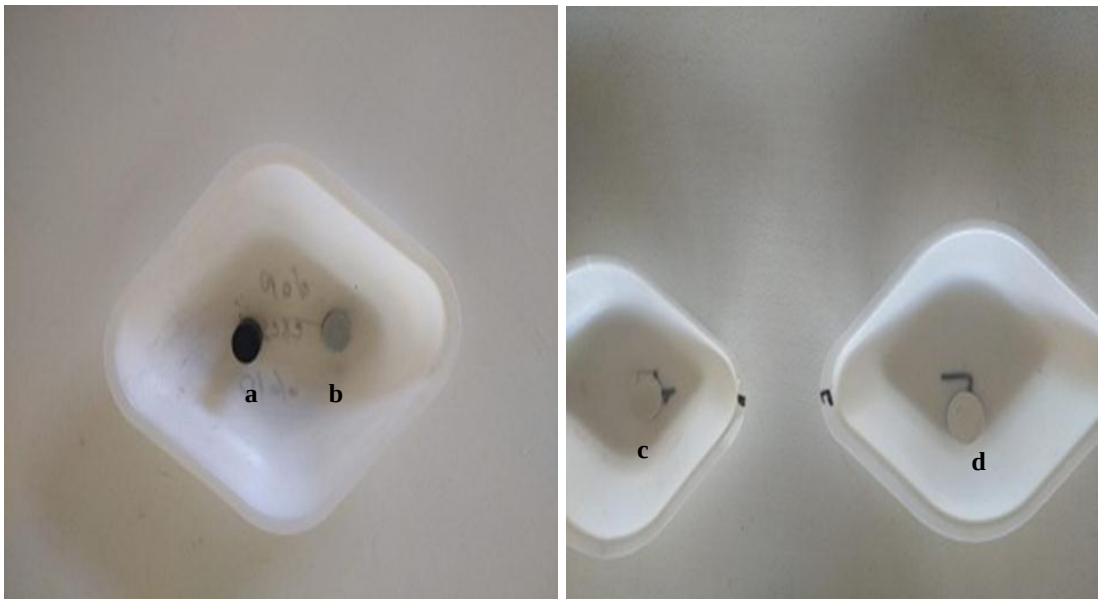


Figure 3.33 Samples Obtained After the Sintering Process for a) 10 %, b) 25 %, c) 50 % and d) 75 %.

CHAPTER 4

CHARACTERIZATION AND ANALYSIS PROCEDURES

Various characteristic properties of the samples with samples B_2O_3, obtained after the hexagonal boron nitride synthesis process were examined. Accordingly, XRD analysis, particle size analysis, optical characterization (UV), Four Transform IR (FTIR) spectroscopy, Scanning Electron Microscopy (SEM) and Vector Network Spectrum analyzes were performed.

4.1. XRD Analysis

X-ray diffraction analyzes of h-BN samples were obtained by using Malvern Panalytical Empyrean XRD in the process of synthesizing h-BN with samples boron oxide. With the help of X-ray diffraction patterns obtained from the prepared samples, information about the crystallization of the materials was obtained by looking at the peak intensities and half-peak widths. XRD analyzes of the samples were made after exposure to N_2(g), oxidation and leaching. The Figure 4.1 seen the XRD analysis results of 75 % sample.

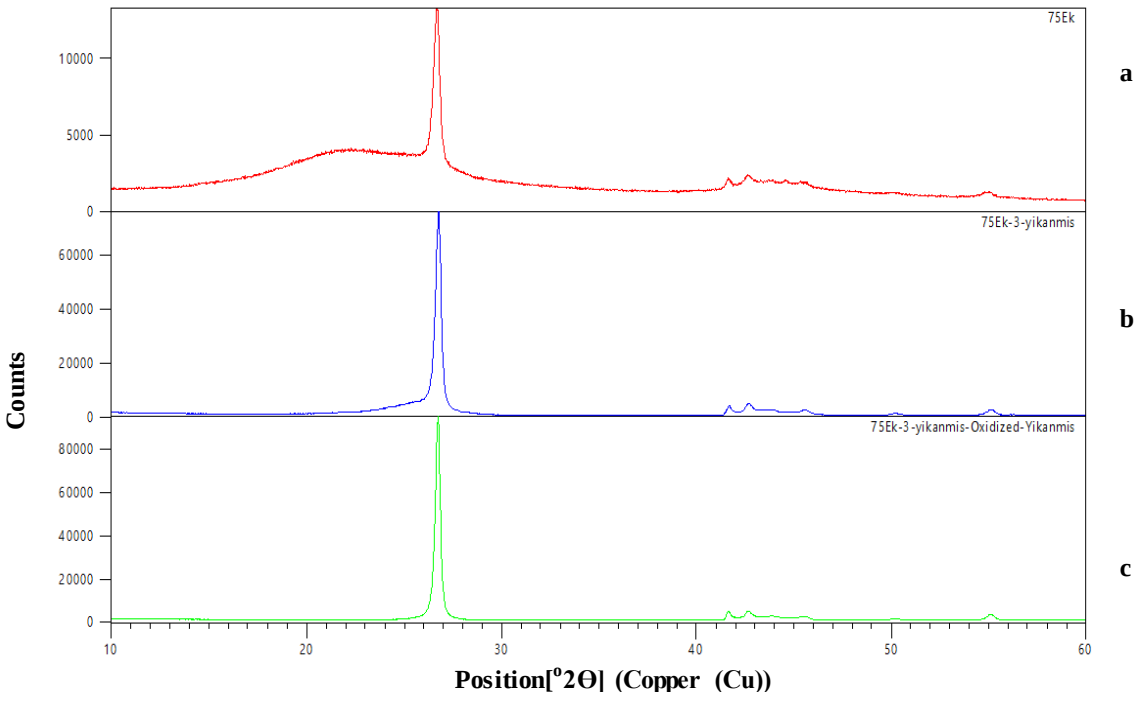


Figure 4.1 XRD analysis results of a) exposure to N_2, b) oxidation and c) leaching to 75 % sample.

In these processes, it has been tried to obtain the best structure h-BN. As a result of all the processes, the h-BN quality of the samples increased compared to the B_2O_3 ratio.

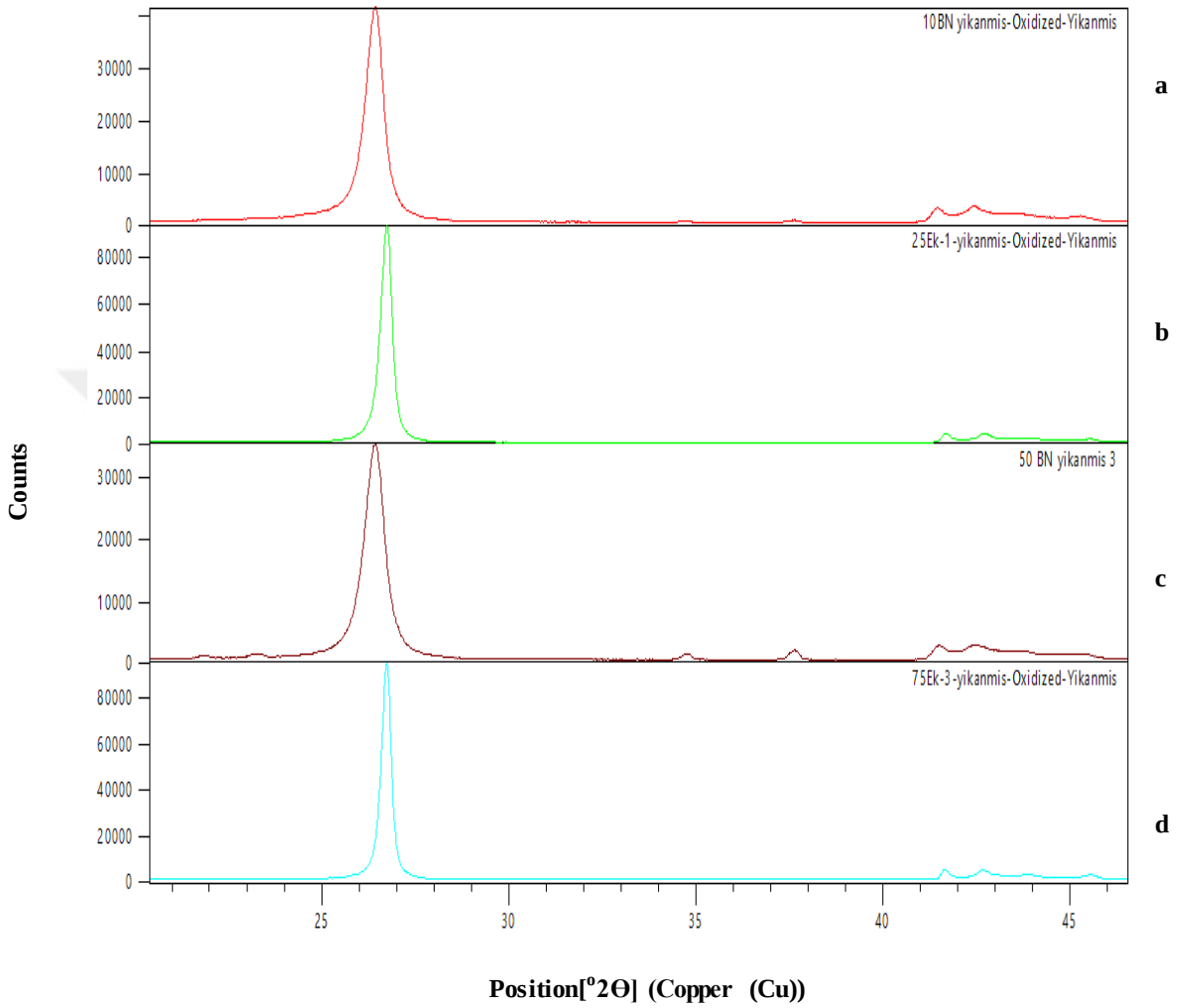


Figure 4.2 XRD analysis of a) 10 %, b) 25 %, c) 50 % and d) 75 % samples after synthesis.

The X-ray diffraction spectrum of the material with a good crystallization level has high intensity peaks and narrow half-peak widths on a substrate with minimum intensity. If the half peak widths are wide and the peak intensities are low, it can be said that the crystallization level is not good [61].

The Figure 4.2 show that the XRD analysis of a) 10 %, b) 25 %, c) 50 % and d) 75 % samples after synthesis. When the diffraction spectrum of the samples is examined,

it is seen that the nanostructured h-BN samples prepared are polycrystalline and there are differences between peak intensities and widths.

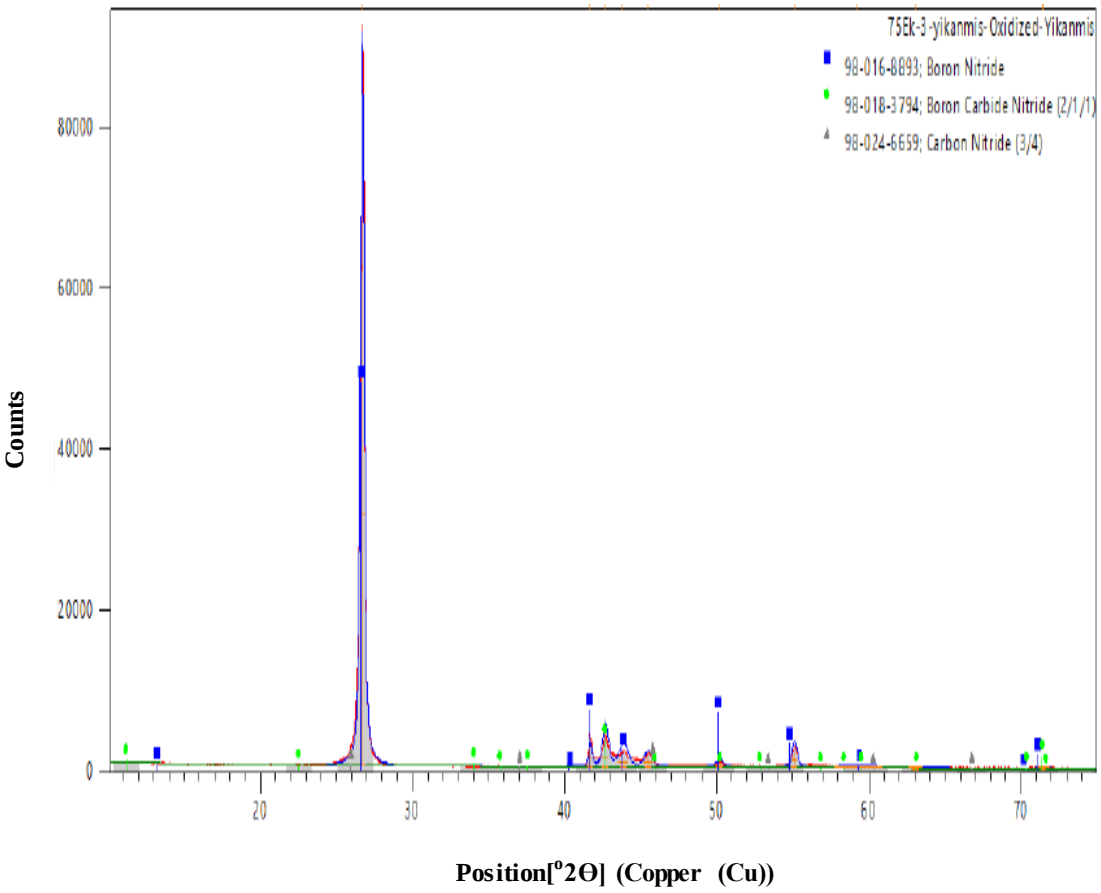


Figure 4.3 XRD Peak List Analysis of 75 % Sample after Synthesis.

The Figure 4.3 show that the XRD peak list analysis of 75 % sample after synthesis. Three types of peaks were observed in the synthesized sample, these are boron nitride, boron carbide nitride and carbon nitride. Supported by ICSD reference cards. Boron nitride was detected with reference code 98-016-8893 from the peaks obtained as a result of XRD [86].

Table 4.6 Boron Nitride Crystallographic Parameters with Reference Code 98-016-8893 [86].

Crystal System	Hexagonal
Space Group	P -6 m 2
Space Group Number	187
a (Å)	2.5040
b (Å)	2.5040
c (Å)	6.7020
Alpha (°)	90.0000
Beta (°)	90.0000
Gamma (°)	120.0000
Calculated Density (g/cm^3)	2.26
Volume of Cell (10^6 pm^3)	36.39
Compound Name	Boron Nitride
Chemical Formula	B_1N_1

Table 4.2 Boron Nitride Peak List.

No.	h	k	l	d [Å]	2θ [°]	I [%]
1	0	0	1	6.70200	13.200	0.0
2	0	0	2	3.35100	26.579	100.0
3	0	0	3	2.23400	40.340	0.0
4	0	1	0	2.16853	41.614	15.3
5	0	1	1	2.06321	43.845	5.0
6	0	1	2	1.82057	50.062	14.7
7	0	0	4	1.67550	54.741	6.8
8	0	1	3	1.55601	59.346	1.1
9	0	0	5	1.34040	70.154	0.0
10	0	1	4	1.32585	71.040	3.8
11	1	1	0	1.25200	75.941	5.9
12	1	1	1	1.23071	77.496	0.0
13	1	1	2	1.17282	82.112	9.2
14	0	1	5	1.14017	85.001	0.1
15	0	0	6	1.11700	87.199	1.3
16	1	1	3	1.09218	89.706	0.0

The Table 4.1 seen the boron nitride crystallographic parameters with reference code 98-016-8893 and the Table 4.2 show that the 2θ angles of the crystal properties of

this structure, the Miller indices of the planes and the values of the interplanetary distances are given.

The crystal atoms in the h-BN sample have preferential orientation in the (002), (010) and (012) planes. However, since the highest peak intensity belongs to the (002) plane, the preferential orientation of this plane is more dominant. The distance between the planes of the (002) plane at 2θ=26.579°, which has the highest peak intensity, was measured as d=0.3351 nm. In addition, the lattice constant of the hexagonal crystal lattice structure was calculated as a=b=2.504, c=6.702 nm.

Boron carbide nitride was detected with reference code 98-018-3794 from the peaks obtained as a result of XRD [87].

Table 7.3 Boron Carbide Nitride Crystallographic Parameters with Reference Code 98-018-3794 [87].

Crystal System	Orthorhombic
Space Group	P m m a
Space Group Number	51
a (Å)	2.5100
b (Å)	2.5100
c (Å)	7.8980
Alpha (°)	90.0000
Beta (°)	90.0000
Gamma (°)	90.0000
Calculated Density (g/cm^3)	3.18
Volume of Cell (10^6 pm^3)	49.76
Compound Name	Boron Carbide Nitride (2/1/1)
Chemical Formula	$C_1B_2N_1$

The Table 4.3 seen the boron carbide nitride crystallographic parameters with reference code 98-018-3794 and the Table 15. show that boron carbide nitride peak list result of 75 % sample.

Table 4.4 Boron Carbide Nitride Peak List.

No.	h	k	l	d [Å]	2θ [°]	I [%]
1	0	0	1	7.89800	11.194	8.4
2	0	0	2	3.94900	22.497	7.0
3	0	0	3	2.63267	34.026	15.8
4	0	1	0	2.51000	35.744	1.2
5	1	0	1	2.39211	37.570	7.4
6	0	1	2	2.11832	42.647	100.0
7	0	0	4	1.97450	45.924	0.0
8	1	0	3	1.81666	50.177	1.0
9	1	1	1	1.73165	52.825	1.9
10	1	1	2	1.61885	56.827	0.0
11	0	0	5	1.57960	58.373	0.0
12	1	0	4	1.55188	59.520	0.6
13	1	1	3	1.47165	63.125	0.6
14	0	1	5	1.33689	70.365	2.3
15	1	1	4	1.31996	71.405	48.2
16	0	0	6	1.31633	71.632	0.0
17	0	2	0	1.25500	75.727	10.9
18	0	2	1	1.23945	76.849	0.0
19	0	2	2	1.19605	80.187	0.2
20	1	1	5	1.17996	81.509	1.0
21	1	0	6	1.16575	82.718	7.2
22	2	0	3	1.13286	85.681	0.6
23	0	0	7	1.12829	86.113	0.2
24	2	1	0	1.12251	86.665	0.0
25	1	2	1	1.11134	87.756	0.4

Carbon nitride was detected with reference code 98-024-6659 from the peaks obtained as a result of XRD [88].

Table 4.5 Carbon Nitride Crystallographic Parameters with Reference Code 98-024-6659 [88].

Crystal System	Cubic
Space Group	P -4 3 m
Space Group Number	215
a (Å)	3.4300
b (Å)	3.4300
c (Å)	3.4300
Alpha (°)	90.0000
Beta (°)	90.0000
Gamma (°)	90.0000
Calculated Density (g/cm^3)	3.79
Volume of Cell (10^6 pm^3)	40.35
Compound Name	Carbon Nitride (3/4)
Chemical Formula	C_3N_4

Table 4.6 Carbon Nitride Peak List.

No.	h	k	l	d [Å]	2θ [°]	I [%]
1	0	0	1	3.43000	25.956	21.3
2	0	1	1	2.42538	37.036	9.6
3	1	1	1	1.98031	45.782	100.0
4	0	0	2	1.71500	53.379	5.2
5	0	1	2	1.53394	60.287	2.0
6	1	1	2	1.40029	66.748	1.9
7	0	2	2	1.21269	78.870	31.1
8	1	2	2	1.14333	84.711	1.1

The Table 4.5 show the carbon nitride crystallographic parameters with reference code 98-024-6659 and the Table 4.6 show that carbon nitride peak list result of 75 % sample.

It is seen that crystallization is good in peaks with large intensity and narrow width, and not good in peaks with small intensities and large widths. It can be seen that in the h-BNs synthesized due to the increase in the amount of boron oxide additives, the best crystallization is in 75 % of the sample due to the size of the peak intensity and the narrow width.

The peak intensity range 2Θ: 23 - 28° where crystallization is better than XRDs was observed. When the analyzes were examined, it was seen that although oxidation and leaching processes were performed in some peaks, B_4C was formed even if a little.

Along with the analysis process, using the X-ray diffraction result, the crystal size of the sample was calculated with the help of the equation known as the Debye-Scherrer equation.

$D = 0.9\lambda / \beta \cos \Theta$,

In this equation; D is the crystal size, β maximum intensity peak is half the peak width in radian, Θ is the Bragg angle and λ is the wavelength of the used beam. The Table 4.7 seen the crystal size calculation for h-BN samples.

Table 4.7 Crystal Size Calculation for h-BN Samples.

h-BN Excess (%)	Crystal Size (nm)
% 10	2.97
% 25	2.86
% 50	2.92
% 75	2.80

Crystal sizes of 10 %, 25 %, 50 % and 75 % h-BN excess samples obtained with the help of these values were calculated from the Debye-Scherrer formula.

4.2. Particle Size Analysis

After the leaching of the synthesized samples, the samples dried in the oven were processed in powder form for particle size analysis. In the Malvern Panalytical Mastersizer 3000 device, ultrasound was applied in a water environment for 60 seconds. Particle refractive index 1.800, particle absorption index 0.010, dispersant refractive index 1.330, laser obscuration 4.68 % were analyzed.

Due to laboratory conditions and technical equipment, particle size analysis could be applied to h-BN with 10 % B_2O_3 addition. The Figure 4.4 result of the analysis is seen. According to analysis, concentration 0.0012 %, uniformity 3.743, Dv (90) 13.432 µm, Dv (50) 1.044 µm, Dv (10) 0.043 µm were obtained.

It can be seen in the analysis that the hexagonal boron nitride particle size is less than 1.0 µm and the h-BN has an ideal particle structure, it can contain minimal B_4C and unreacted carbon particles in the analysis above 1.0 µm.

Crystal size was calculated as 2.97 nm by Debye-Scherrer formula calculation for 10 % B_2O_3 excess h-BN. Since the particle sizes analysis is performed as a micrometer, 10 % h-BN corresponds to the crystal size 0.297 µm. According to the result, it has an ideal hexagonal boron nitride crystal structure.

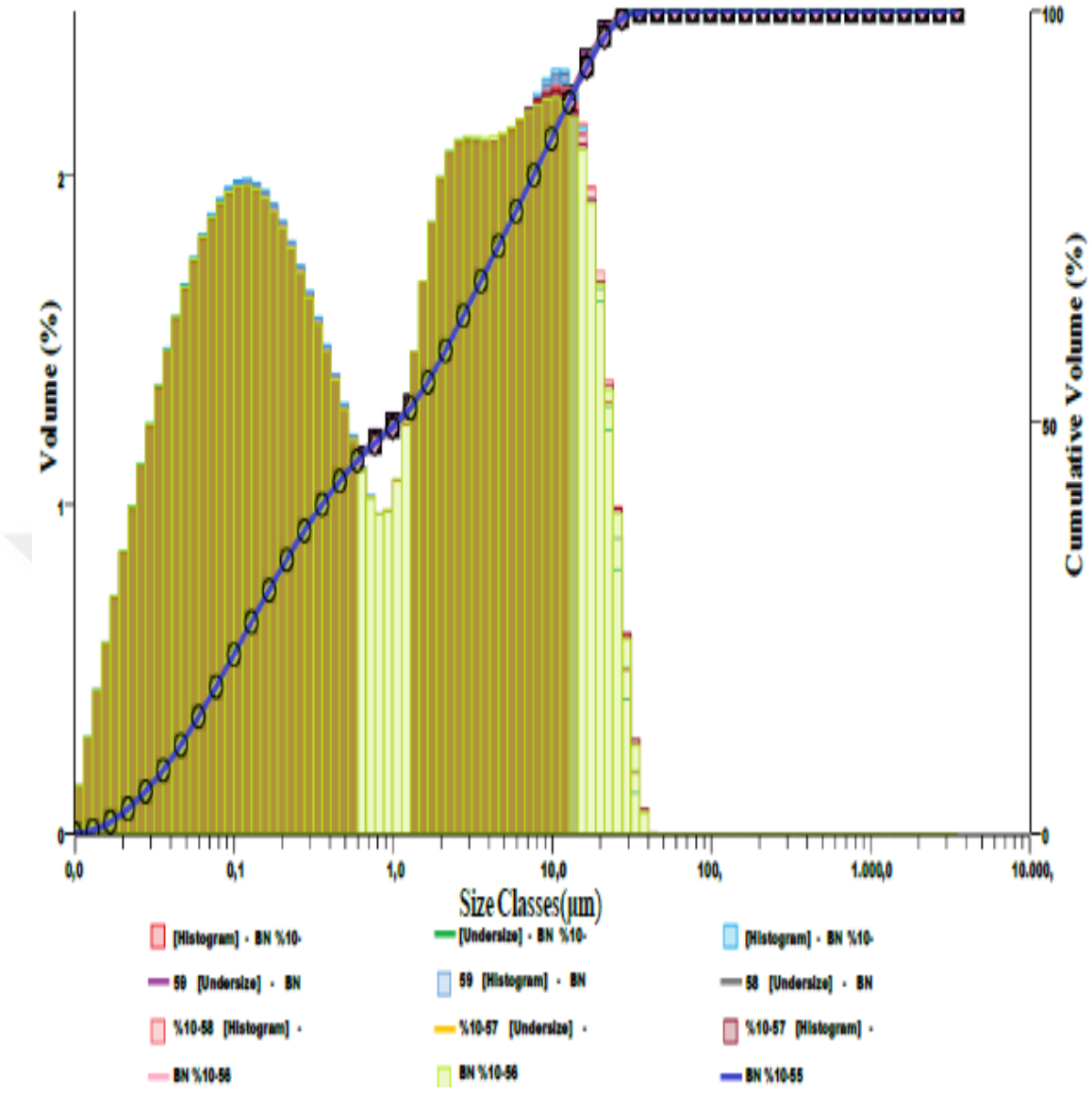
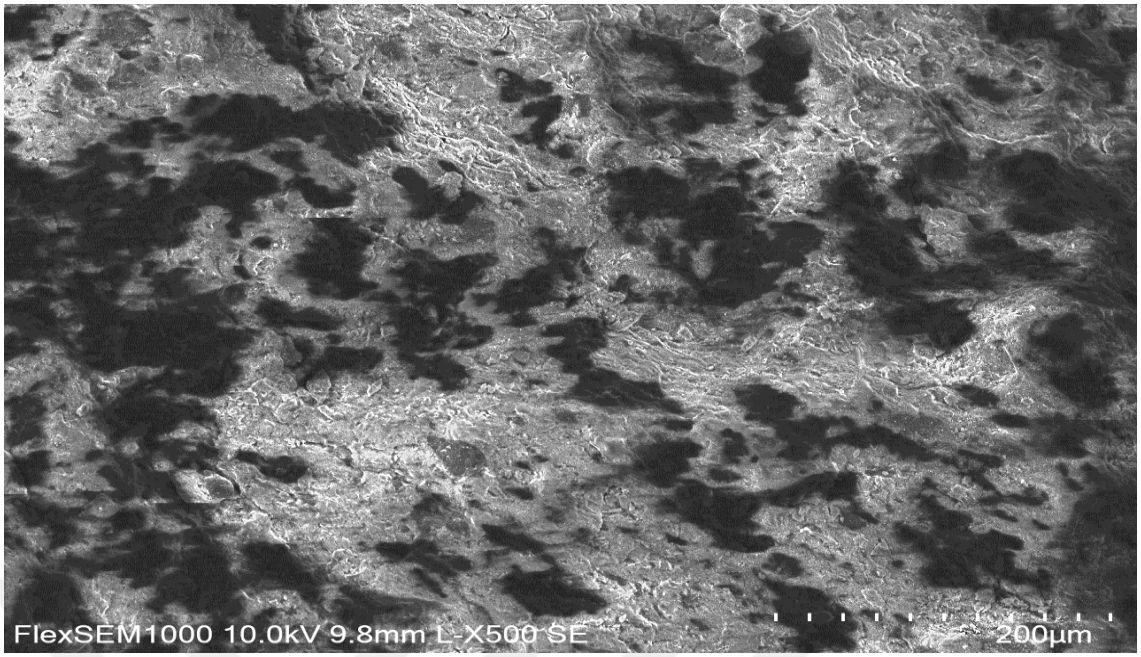


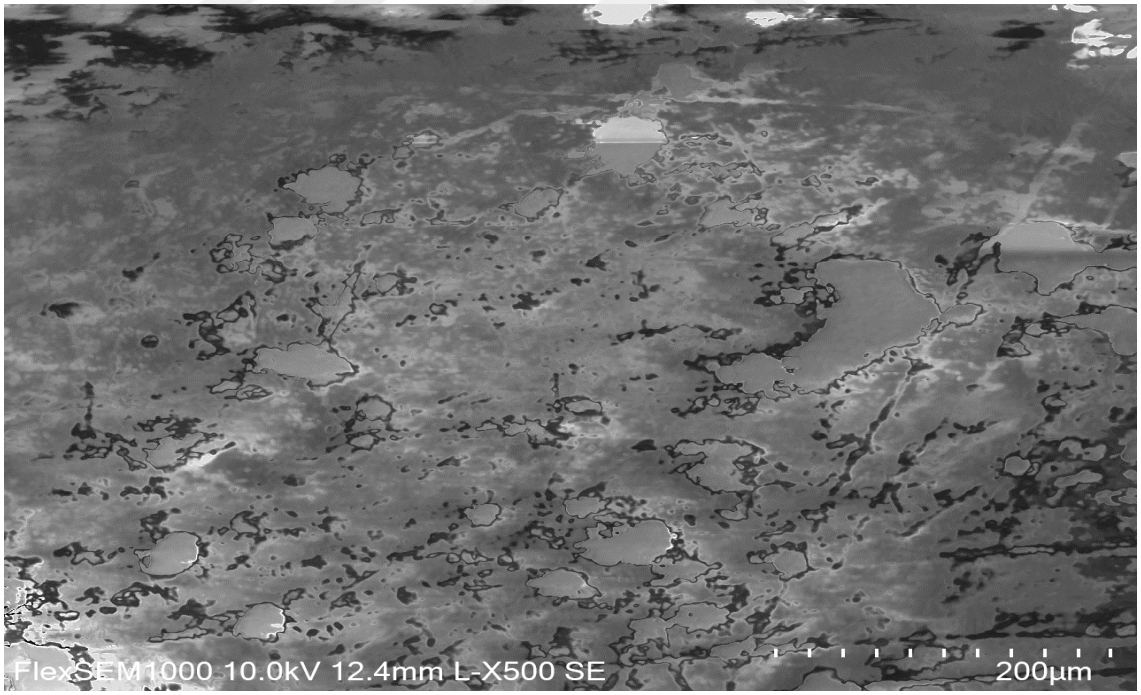
Figure 4.4 Particle Size Analysis of 10 % B_2O_3 excess h-BN.

4.3. Scanning Electron Microscopy (SEM) Analysis

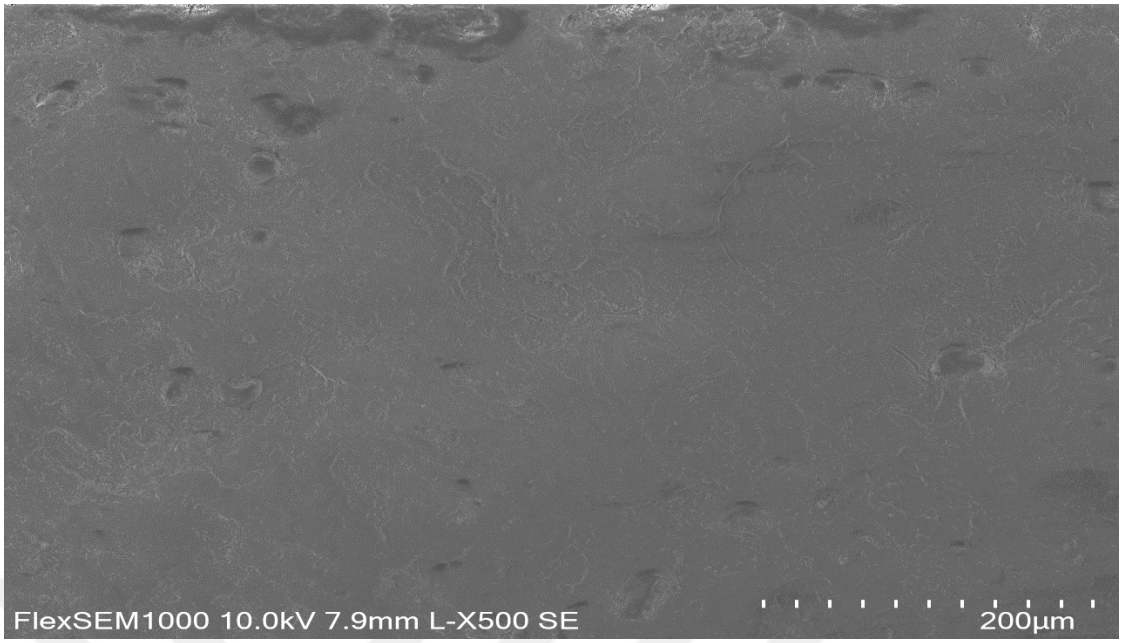
Hitachi FlexSEM 1000 brand scanning electron microscope was used to determine the nanoscale surface morphology of the prepared 10 %, 25 %, 50 % and 75 % B_2O_3 excess h-BN samples. SEM images were taken at 500X and 1000X magnifications for the h-BN samples produced.


FlexSEM1000 10.0kV 9.8mm L-X500 SE
200µm

a


FlexSEM1000 10.0kV 12.4mm L-X500 SE
200µm

b



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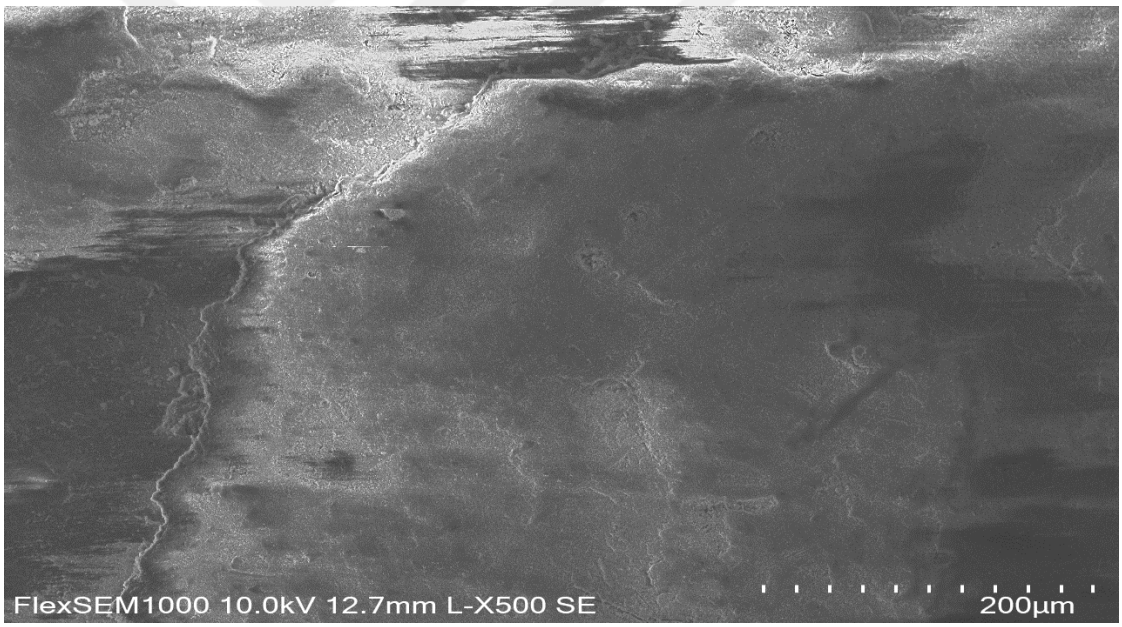
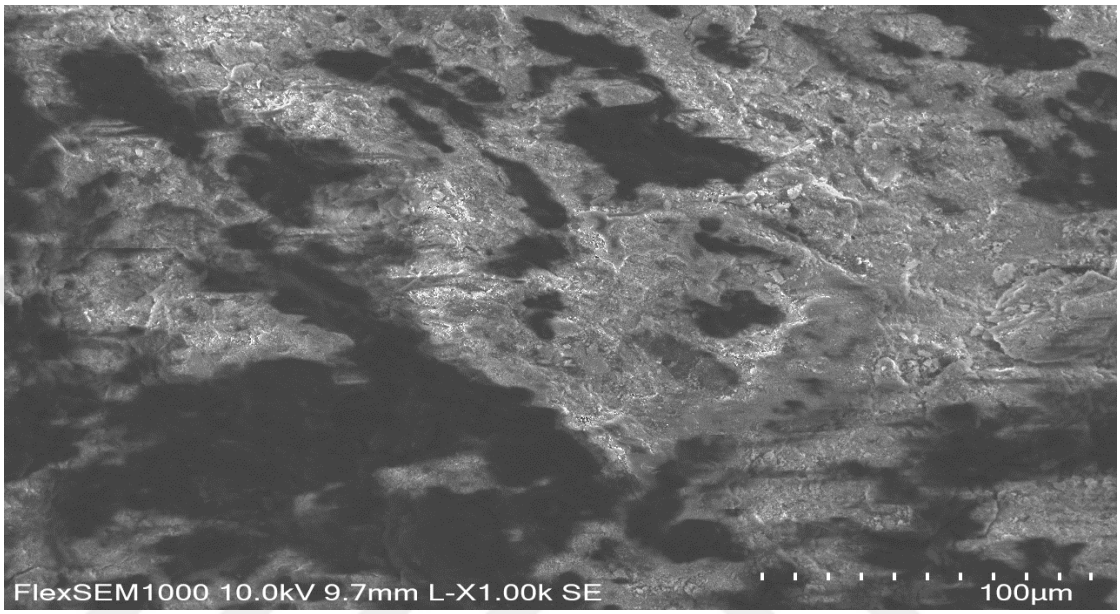


d

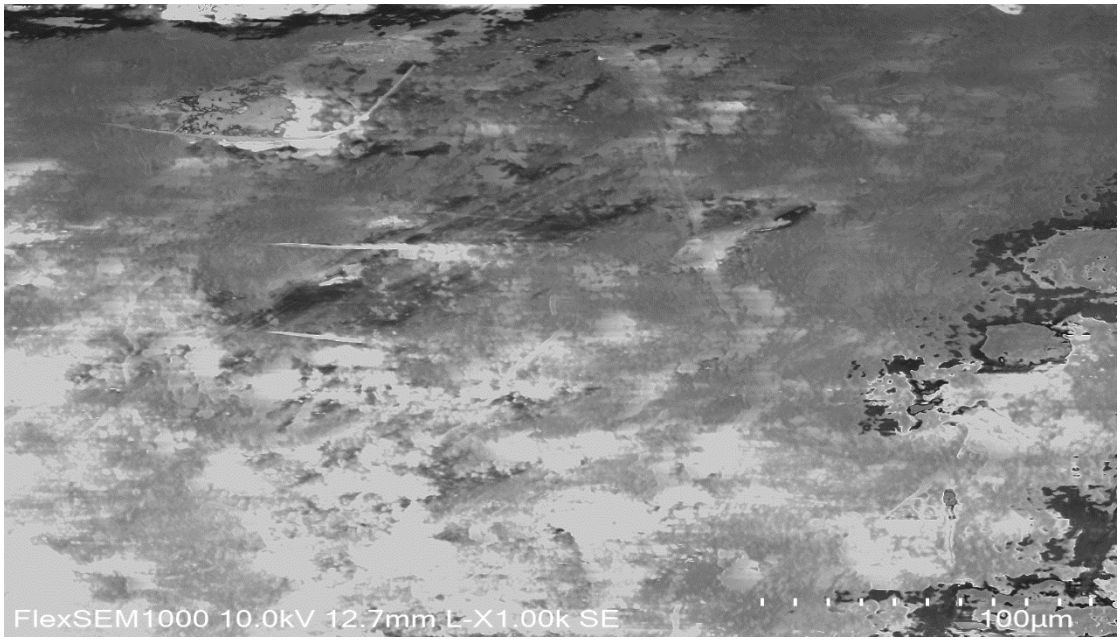
Figure 4.5 200 µm SEM images of a) 10 %, b) 25 %, c) 50 % and d) 75 % B_2O_3 excess h-BN samples.

The Figures 4.5 show nano-sized morphological SEM structures of h-BN samples imaged at 200 µm and 500X magnification. According to these images, it can be seen that hexagonal BNs increased more homogeneously in parallel with the increase in the ratio of B_2O_3. Although unreacted carbon is detected in a small amount in the sample morphology of 10 %, this situation disappears with the increase in rates.

The Figures 4.6 seen the images of nano-sized morphological SEMs of h-BN samples imaged at 100 µm and 1000X magnification. In these SEM pictures, a large number of hexagonal boron nitride has been analyzed with the increase in boron oxide ratio. These are in the form of overlapping coaxial homogeneously distributed hexagonal plates. There may be variations in size.



a



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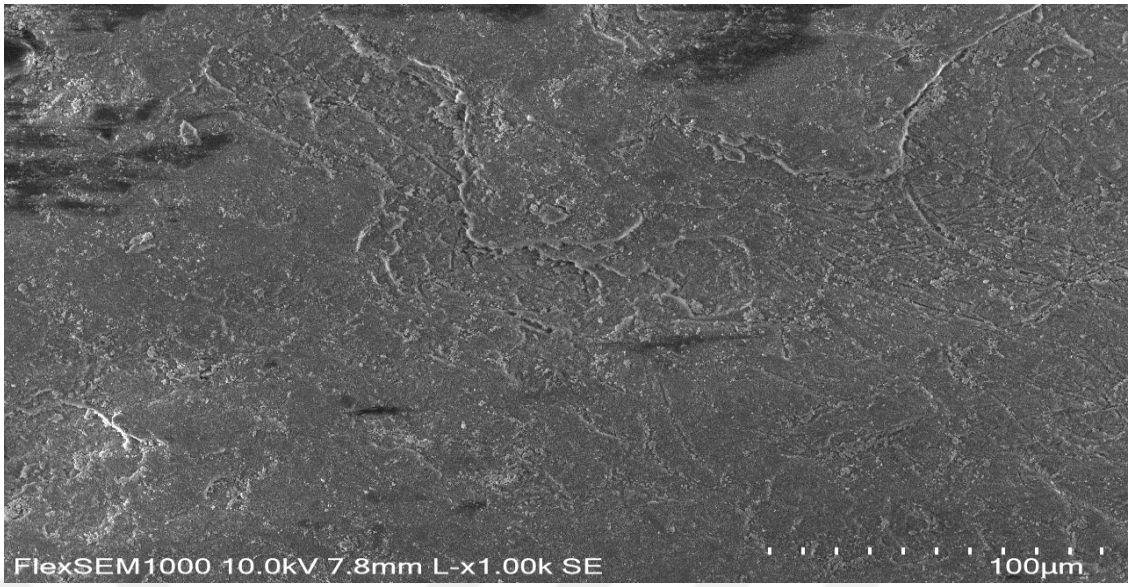

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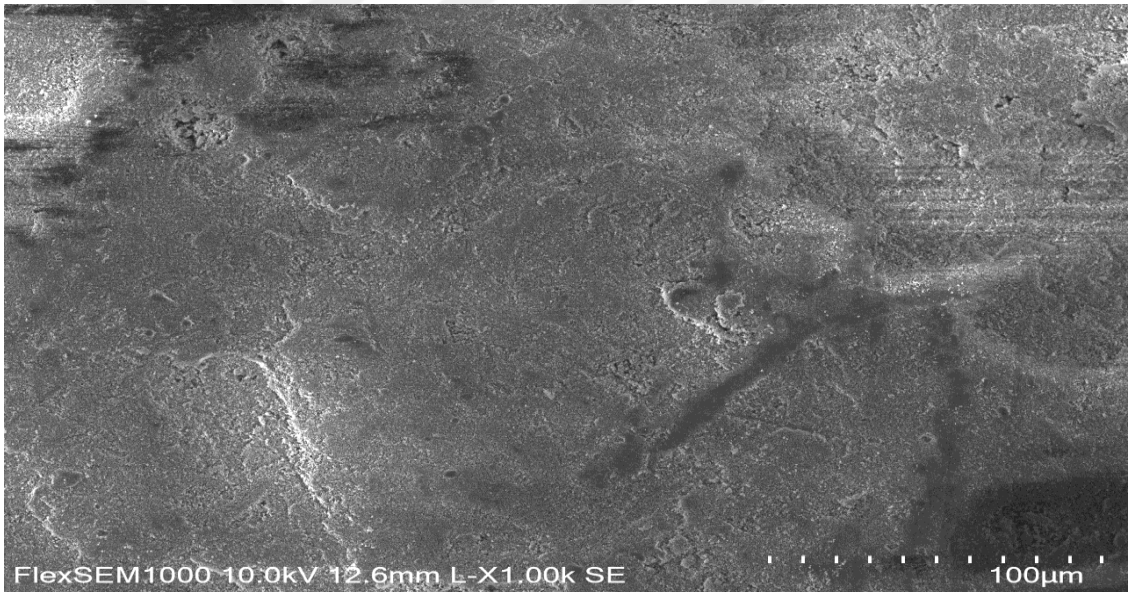


d

Figure 4.6 100 µm SEM images of a) 10 %, b) 25, c) 50 % and d) 75 % B_2O_3 excess h-BN samples.

It can be seen in high magnification SEM pictures that the plates are layered on each other and each BN layer formed consists of multiple BN nanoparticles. Although it appears that the h-BN samples produced are composed of large-sized hexagonal layers, it has been determined that the structures are in fact nano-sized and that the nanoscale grains come together to form large-sized grains. When evaluated jointly with XRD analyzes, SEM analyzes were compatible with h-BN production.

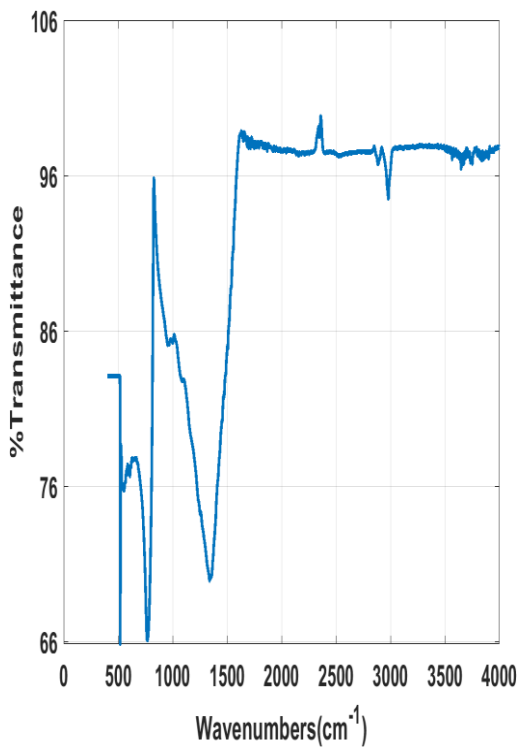
4.4. Fourier Transform IR (FTIR) Spectroscopy Analysis

FTIR analysis is of great importance in determining the chemical properties of the obtained h-BN powders and the controls during the reaction processes where the powders can be used. For this reason, FTIR spectroscopy was applied to investigate chemical bonding and chemical bond characterization between atoms in samples.

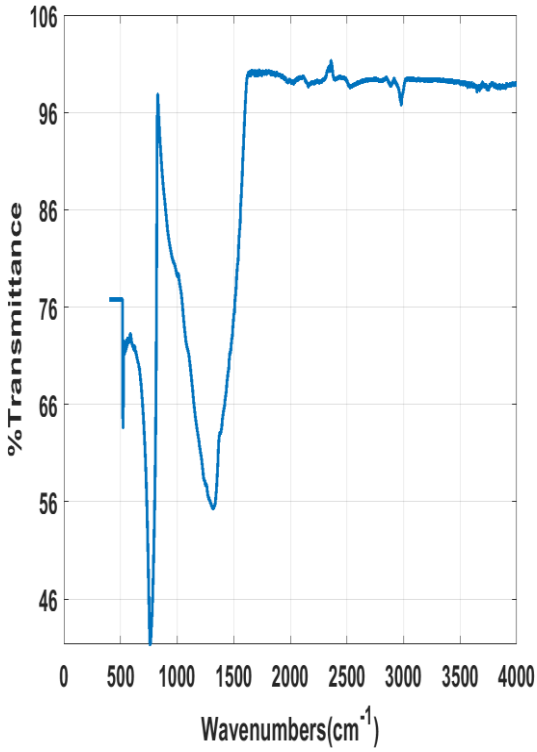
Shimadzu IRAffinity-1S fourier transform infrared spectrophotometer was used for chemical bond characterization of hexagonal boron nitride samples produced in excess of 10 %, 25 %, 50 % and 75 % B_2O_3.

FTIR analyzes were carried out between 500 and 4000 cm^{-1} wavelength range. The Figure 4.7 are show that FTIR spectrum analysis of h-BN samples.

The Table 4.8 as can be seen, two strong characteristic peaks of h-BN were detected in the FTIR spectrum of the samples. Of these, one peak is the out-of-plane B-N-B bending vibration of BN and the other peak is the in-plane B-N stress vibration of BN.The last peak shows the O-H stretch vibration caused by the moisture absorbed by the sample from the air.



a



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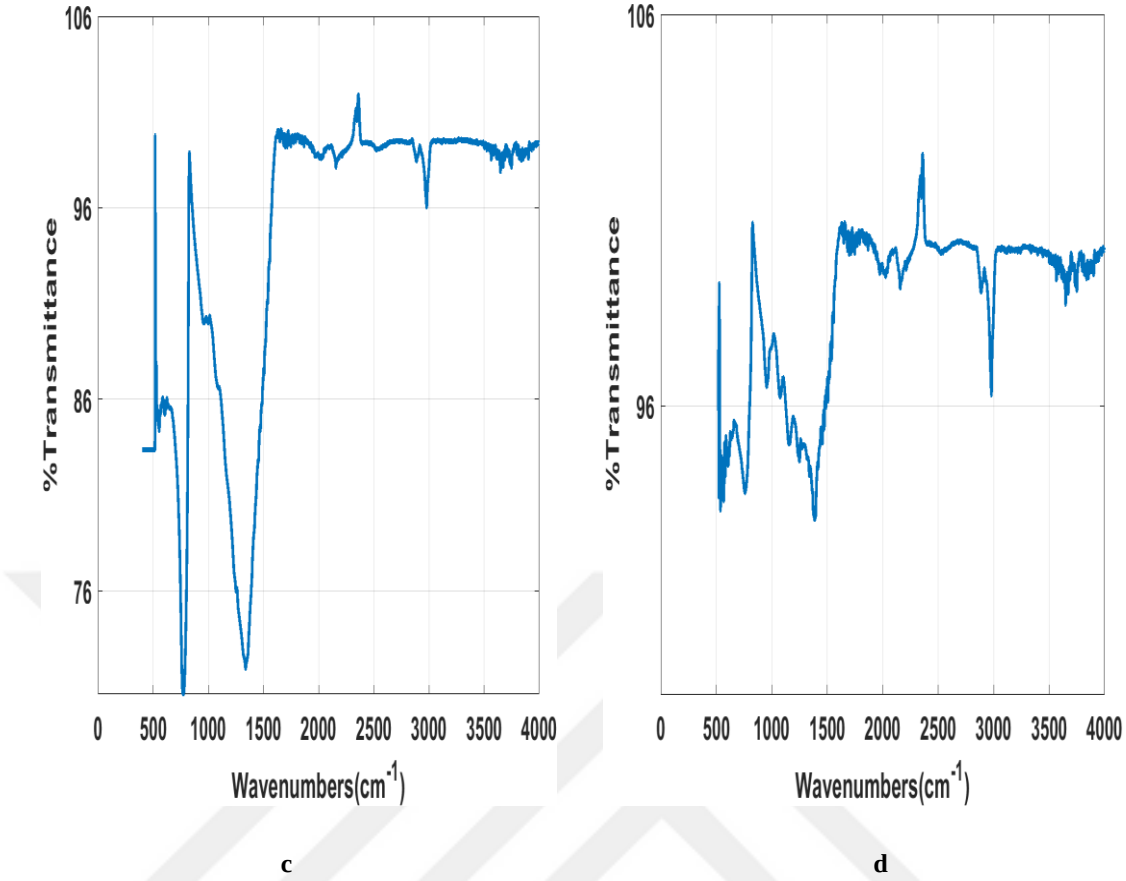


Figure 4.7 FTIR spectrum analysis of a) 10 %, b) 25 %, c) 50 % and d) 75 % B_2O_3 excess h-BN samples.

Table 4.8 Waves and Structures of FTIR Hills.

Wavenumbers (cm^{-1})	**10 %**	**25 %**	**50 %**	**75 %**	**Structure**
	706	740	760	780	B-N-B out-of-plane bending vibration, sp2 bond.[62]
	1380	1392	1398	1408	B-N in-plane stress vibration, sp2 bond.
	2990	2993	2995	2999	O-H tensile vibration.

As a result of FTIR analysis; It was determined that the h-BN peaks behave similar to the peaks obtained in the literature. Absorption peak values in the hexagonal boron nitride phase are observed at wavelengths of approximately 706 and 1408 cm [63].

As a result of the FTIR spectrums of the h-BN samples, it is seen that there are two strong characteristic peaks. Of these, the peak at 1380 cm^{-1} wave number for % 10 B_2O_3 excess sample is the in-plane B-N stretching vibration of BN, and the peak at 706 cm^{-1} is the out-of-plane B-N-B bending vibration of BN. The peak at approximately 2990 cm^{-1} shows the O-H stretching vibration caused by the moisture taken from the air by the sample.

For the sample in excess of 25 % B_2O_3, the peak seen at 1392 cm^{-1} wave number is the in-plane B-N stretching vibration of the BN, and the peak at 740 cm^{-1} is the out-of-plane B-N-B bending vibration. The peak at 2993 cm^{-1} refers to the O-H stretching vibration caused by the moisture taken from the air by the sample.

In the results obtained for the sample in excess of 50 % B_2O_3, the peak seen at 1398 cm^{-1} wave number corresponds to the in-plane B-N stretching vibration of the BN, the peak at 760 cm^{-1} corresponds to the out-of-plane B-N-B bending vibration, while the peak at 2995 cm^{-1} It reveals the O-H stretching vibration caused by the humidity of the sample from the air.

As a result of the analysis made for the sample in excess of 75 % B_2O_3, the peak at wave number of approximately 1408 cm^{-1} corresponds to the in-plane B-N stretching vibration of the BN, and the peak at 780 cm^{-1} corresponds to the out-of-plane B-N-B bending vibration, which is approximately 2999 cm^{-1} peak seen the result of O-H stretching vibration caused by the humidity taken from the air by the sample.

Each plane of boron and nitrogen atoms is bound together by weak Van der Waals forces. Atoms in each layer are held by strong covalent bonds. Peak analysis in FTIR demonstrates an effective bond strength between boron and nitrogen, since hexagonal boron nitride has smaller friction values attributed to weak Van der Waals forces in the interlayer. The covalent bond structure can be expressed in the samples obtained with the partial dipoleization.

FTIR spectrum results of the given h-BN sample are in agreement with XRD results and the results determined in the literature.

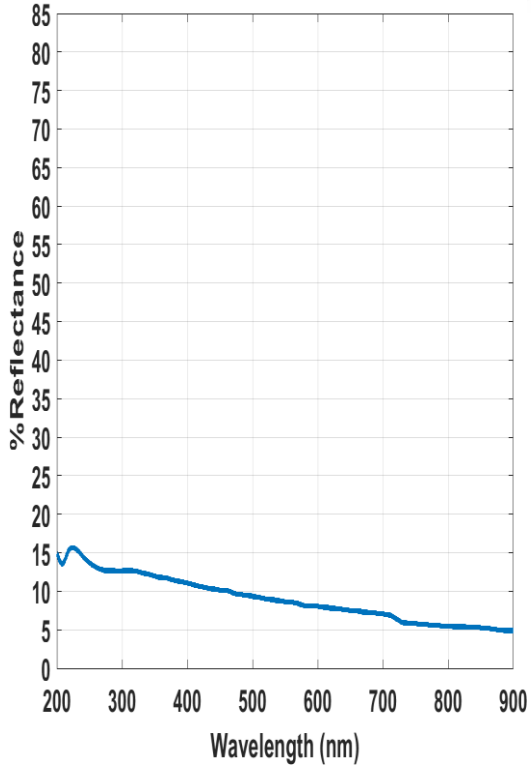
4.5. Optical Characterization (UV) Analysis

In order to examine the optical characterization of the obtained h-BN samples, Shimadzu UV-3600 Plus model spectrophotometer was used. In the characterization at room temperature, 10 %, 25 %, 50 %, 75 % B_2O_3 excess h-BN samples were applied through 200 - 900 nm wavelength.

First, h-BN samples were mixed with barium sulphate, which is used as the basic reflectance material, due to the linear spectral response character of ultraviolet wavelengths in optical applications such as color and light measurement.

Thanks to $BaSO_4$, it has the ability to activate integrated spheres, lamp housings, reflective plates and measuring eyes, which are the most important components of widely used light and color measurement devices.

Then, the optical characterization was completed by performing the total reflectance analysis of the samples, which were put into the integrating sphere (ISR) apparatus used for opaque (solid) samples and subjected to a wavelength of 200 - 900 nm.



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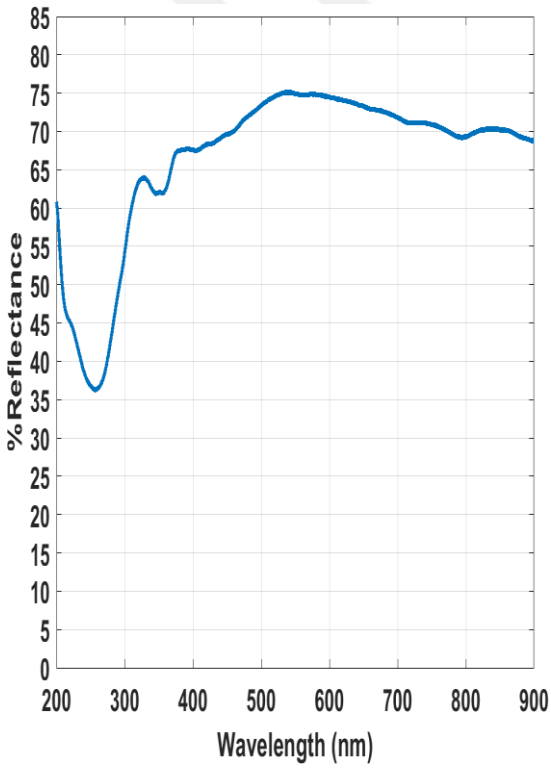

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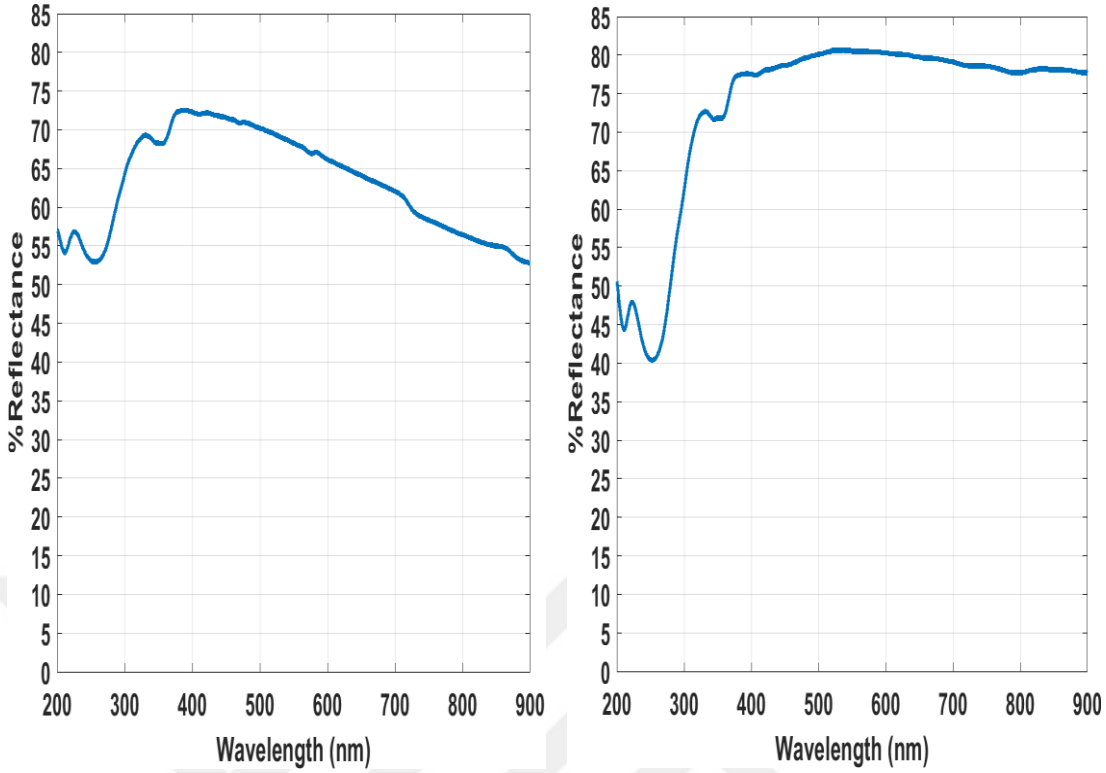


c **d**

Figure 4.8 Reflection spectrum analysis of a) 10 %, b) 25 %, c) 50 % and d) 75 % B_2O_3 excess h-BN samples.

The optical reflection spectra of the h-BN samples obtained at room temperature are shown in Figure 4.8.

As seen in a), the reflection curve of the sample shows that as the wavelength increases, the optical reflection decreases, and it increases as it shifts to short wavelengths.

In b), while the reflection curve increased in parallel with the increase in wavelength, the wavelengths increased between 250 and 550 nm, while a decrease in the reflection rate was observed above 550 nm.

As seen in c), the reflection curve of the sample increased between 250 and 390 of the wavelength, while the optical reflection ratio decreased with the increase of the wavelength regularly over 390 nm. In d), the reflection curve shows that the optical reflection increases as the wavelength increases and decreases as the wavelength increases.

These spectra occurring in the samples are thought to be due to the reduced interaction of the photons with electrons, atoms or crystal molecules and the reduced retroreflection due to the decreased energy of the photons [64].

4.6. Vector Network Spectrum Analysis

Rohde and Schwarz vector network spectrum analyzer was used to examine the relative permeability or dielectric constant characterization of the obtained h-BN samples. In the characterization performed at room temperature, spectrum analyzer was applied in 10 %, 25 %, 50 % and 75 % B_2O_3 excess h-BN samples in the frequency range of 10 Mhz to 40 Ghz.

The relative permeability or dielectric constant (ε_r) of the material is the permeability obtained as a result of a proportioning to the vacuum permeability. Permeability is a kind of material property that affects the Coulomb force between two point loads in the material structure.

Relative permeability is the factor by which the electric field between charges decreases relative to vacuum. Relative permittivity is also a measurement that tries to determine the dielectric properties of materials as a function of frequency. With this measurement, the dielectric properties of the materials can be examined in a wide frequency range such as 10^{-6} to 10^{12} Hz [65].

It is possible to find dielectric materials with a wide variety of compositions ranging from dielectric constants values in the literature. For this reason, it is divided into three different groups according to their dielectric constants [66].

The first group, materials with high dielectric coefficient is $\varepsilon_r \geq 50$. It is generally developed for microwave devices where miniaturization is at the forefront, such as mobile phones.

Materials with dielectric constants between ε_r =25 between 50 are considered as the second group. Such materials often contain materials that play a role in improving signal and noise ratios in satellite communications and mobile phone base stations.

The last group is materials with low dielectric constant $\varepsilon_r \leq 25$ values. Materials in this group are preferred as substrate material in microwave circuits as well as applications such as microwave antenna circuit elements operating at high frequency and missile tracking system [67]. Material groups with low relative permittivity generally have high bond strengths, in other words, covalent bond characteristics are high.

Therefore, due to the position of anions and cations in the crystal structure, the movement capability of electrical dipoles and the area to move is low, material with low polarization capability and low dielectric constant value is formed.

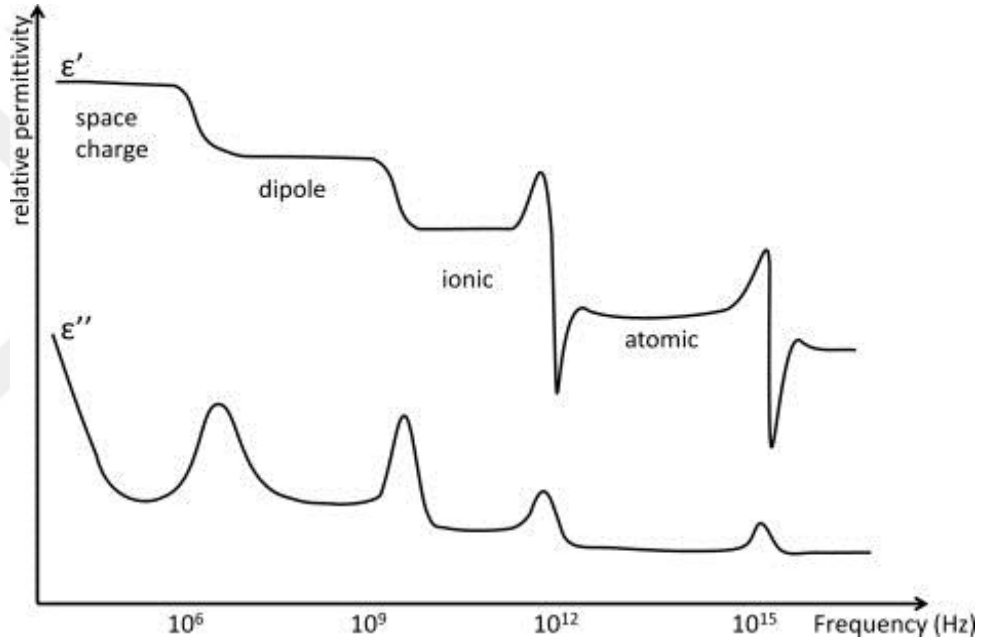
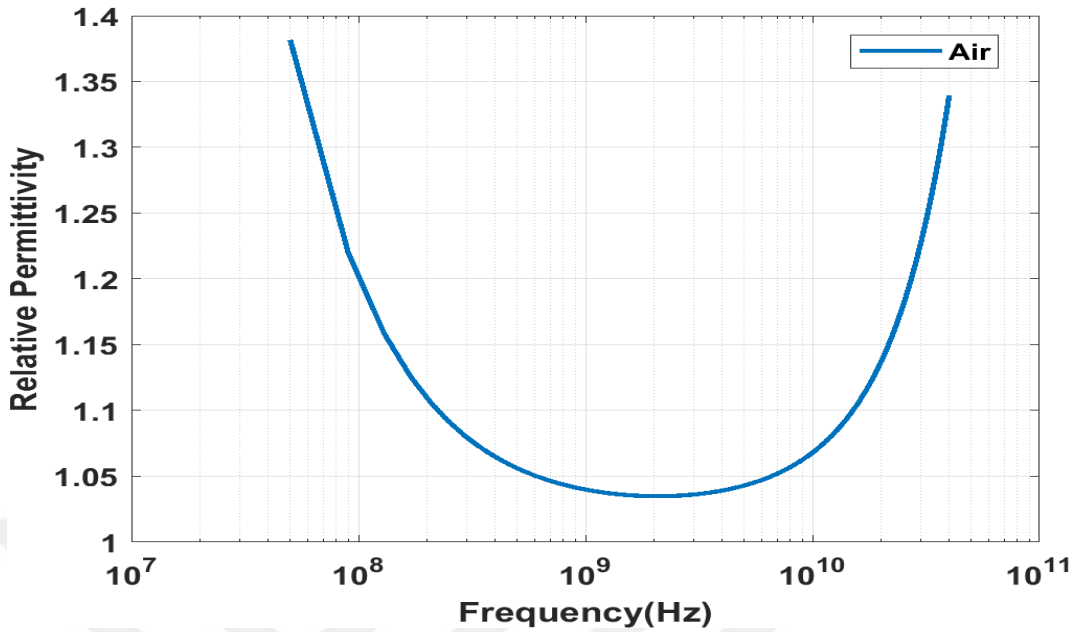


Figure 4.9 Relative Permittivity Active Bond Structures at Different Frequencies [68].

Some materials, electronic and atomic effects may not change significantly. But the microstructure of a material can have a huge impact on dipos, space charge, and ionic contributors. This situation can be seen in the Figure 4.9 in its clearest form.

They are the major contributors to the high relative permeability values reported for ferroelectric materials by shape. This means that the microstructure has a great influence on the relative permeability of such materials at different frequency values.

The Figure 4.10 a and b are given vector network spectrum analysis for air wide zone and narrow zone frequency measurement result samples.



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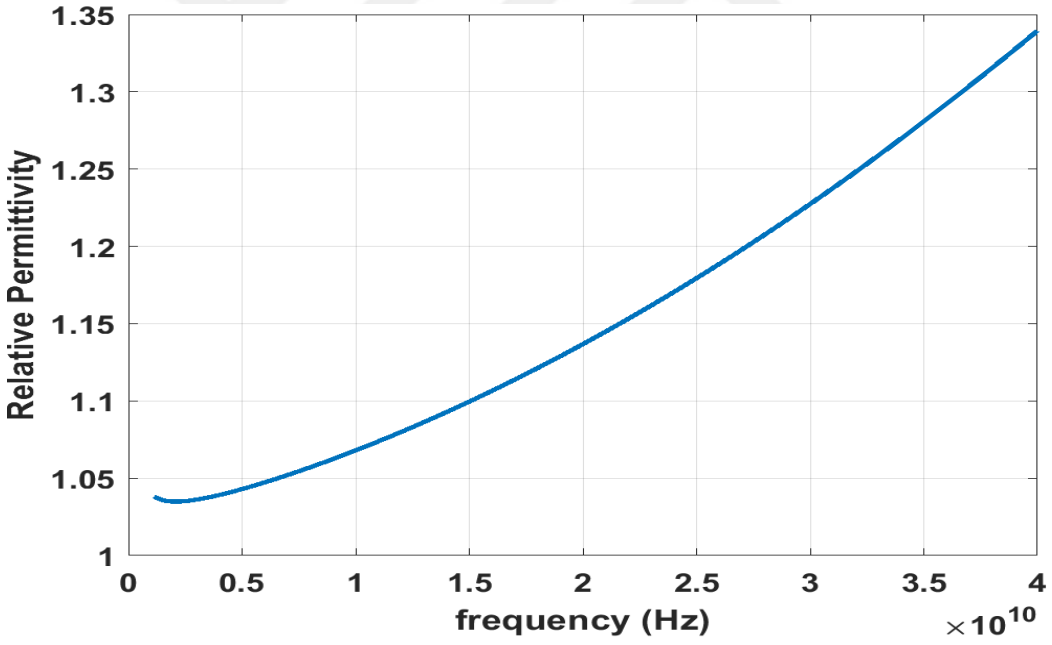
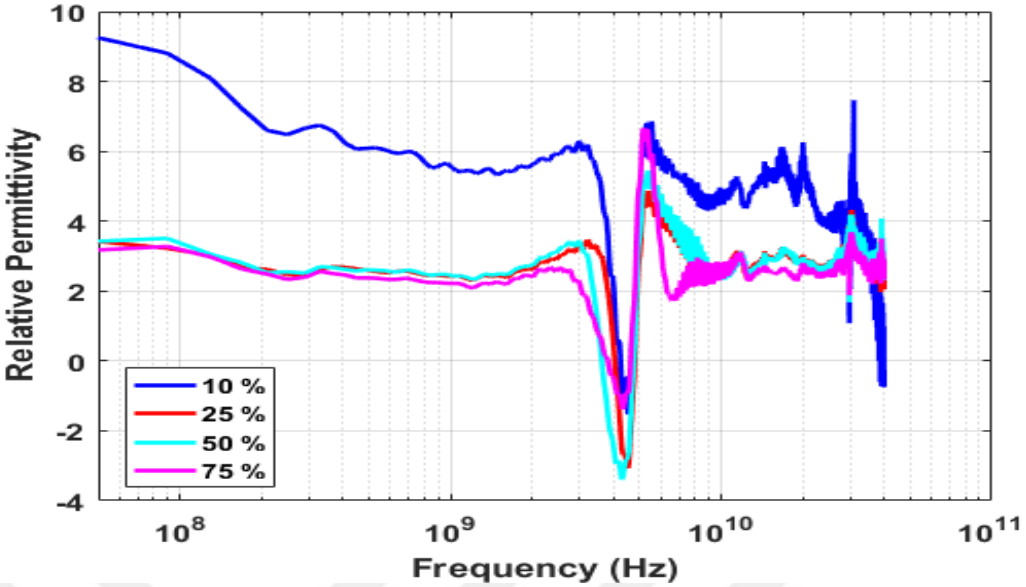


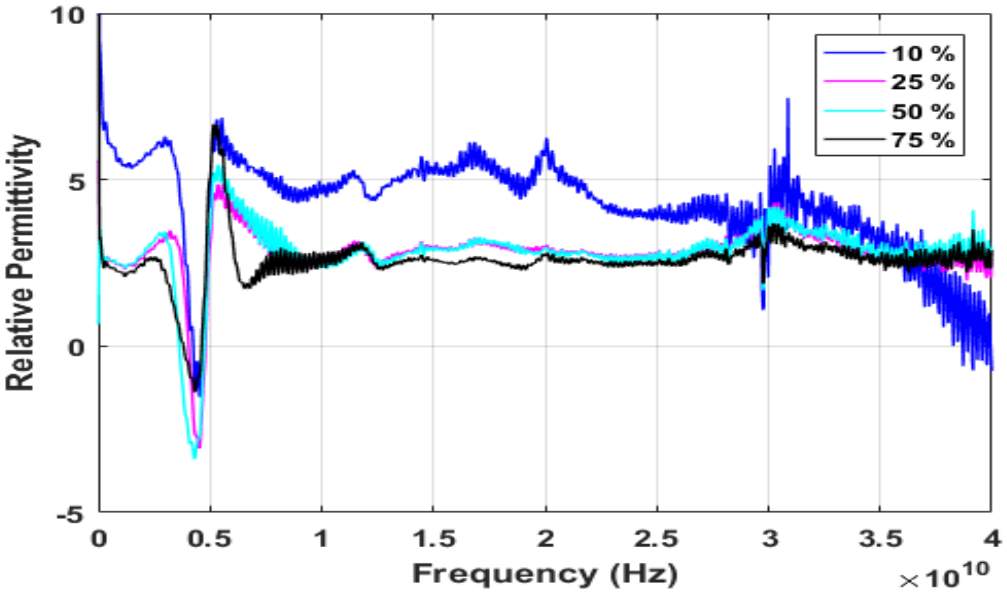
b

Figure 43.10 Vector network spectrum analysis for air a) wide zone and b) narrow zone frequency measurement.

Measurement results on samples prepared in 10 %, 25 %, 50 % and 75 % ratios. The Figure 4.11 a and b are given wide zone and narrow zone frequency measurement result 10 %, 25 %, 50 % and 75 % B_2O_3 excess h-BN samples.



a



b

Figure 4.11 Vector network spectrum analysis a) wide zone and b) narrow zone frequency measurement result 10%, 25%, 50% and 75% B_2O_3 excess h-BN samples.

Relative permittivity values in all samples obtained according to the measurement results in the frequency range of 10^8 Hz are in the value range $\varepsilon_r \leq 25$.

When the measurement results were examined, the relative permittivity value of the measurements obtained in the range of 10^8 and 10^{11} Hz frequencies continued to decrease.

When evaluated according to Figure 4.9, it was determined that the dipole structure between the particles between 10^9 and 10^{10} Hz started to turn into ionic state with the increase in frequency and this structure continued in the last measurement frequency of the analysis.

As seen in the $0.5x10^{10}$ Hz, it was revealed that all samples reached a good absorption. When the values obtained by this analysis are compared, all h-BN samples produced the maximum absorption at 5 GHz.

According to the literature, this situation reveals that the dielectric coefficients of all the samples obtained are low. According to literature, the reason that plays the most active role in this situation is the covalent bond system of the materials.

With this measurement obtained, these samples can be included as substrate material in microwave circuits as well as structures such as microwave antenna circuit elements and missile tracking systems operating.

In particular, in addition to the usual voice and other services of standard previous systems, 5G generation devices, ultra-broadband Internet connection, IP telephony, mobile web access and other interesting multimedia applications, radar and jammer systems exist at high frequency according to dielectric constant or relative permittivity values within the scope of the literature.

CHAPTER 5

CONCLUSION AND FUTURE PERSPECTIVE

Boron, which is the only non-metal element of the III A group of the periodic table, and boron-sourced minerals are important for various studies due to the advantages of their chemical and physical properties.

Boron is obtained by mineral processing, metallurgical and chemical enrichment production methods. With the developing technology, boron is used in ceramic, glass, nuclear, metallurgy and many fields.

Demand for boron products and chemicals in the world and their usage areas are increasing day by day. Accordingly, countries with significant boron reserves continue their activities and studies in technological secrecy and production in a way that will provide more economic returns.

Most of the world's boron reserves in Turkey with ongoing investments having boron and boron chemicals in the production and marketing of products aims to become a more important position.

Hexagonal boron nitride, which is a boron-based structure, is a III-V group compound with a wide range of optical energy bands with its various physical properties and chemical stability. Hexagonal boron nitride, which is an artificial material with many advantageous properties, is increasingly used in many areas. It can be produced by different methods such as boron nitride, nitriding, carbothermic reduction of boron oxide, pyrolytic production of boron nitride.

In this study, the carbothermic reduction of boron oxide method was used to synthesize h-BN. In this process, 10 %, 25 %, 50 % and 75 % excess B_2O_3 and activated carbon mixtures were formed. Preparation of powders, oven stduies, after leaching process, carbothermic formation of h-BN, B_2O_3 + C mixtures at 1500 ^oC under nitrogen atmosphere after 120 minutes of sintering, h-BN was obtained. Aydogdu and Sevinc [55] studies have made the carbothermic method advantageous as a production system. As a result of the synthesis, h-BN was obtained.

For the characterization analysis of the obtained h-BN samples, they have been characterized by using procedures such as XRD, SEM, FTIR, particle size analysis, optical characterization (UV) and vector network spectrum analyzes.

In the light of the data obtained, it has been observed that BN and boron nitride based products, whose usage is increasing day by day, can be produced by carbothermic method due to the combination of many properties.

It was observed that B_4C was present in reaction products in which the formation of h-BN was incomplete. It was observed that all of the C was consumed and the formed B_4C was converted to h-BN and the reaction was completed in 1500 ^oC and 120 minutes. It was understood that the B_4C formation decreased with the increase of the amount of B_2O_3 in the samples as a ratio. According to the literature, it was seen that all samples obtained as a result of the characterization processes had boron nitride purity, honeycomb and layered structures. The X-ray diffraction spectrum of the material, which has a good crystallization level in parallel with the increase rate of the B_2O_3 amount in the samples, with the data obtained as a result of the XRD analysis, has peaks with high intensity and narrow half peak widths on a ground with minimum intensity.

If the half peak widths are wide and the peak intensities are low, it has been determined that the crystallization level is not good, h-BN formation has occurred in all of the samples obtained, and it is seen that it is in harmony with the studies carried out by Aydın [61] within the scope of the literature.

In the particle analysis process, a positive result was obtained according to the literature, as a result of the treatment applied to the h-BN sample containing 10 % B_2O_3 execess, and a quality h-BN was obtained.

According to the analysis, It can be seen in the analysis that the hexagonal boron nitride particle size is less than 1.0 μm and the h-BN has an ideal particle structure, it can contain minimal B_4C and unreacted carbon particles in the analysis above 1.0 μm. The resulting density occurred below 1.0 μm.

As a result of the SEM process applied to the B_2O_3 excess h-BN samples obtained, it is clearly seen in the high magnification SEM pictures that the sample layers consist of multiple BN nano grains. Although it gives the impression that the produced h-BN samples are composed of large-sized hexagonal layers, it explains that the structure is actually nano-sized and nano-sized grains come together to form large-sized grains.

The obtained SEM images are in agreement with the XRD results, confirming the result that nano-sized h-BN has been produced. These results are in perfect agreement with the literature studies of Kimiyasu et al [89].

In the FTIR analysis study, separate peak graphs were obtained for each sample. Two strong characteristic peaks of h-BNs were detected in the FTIR spectrum. BN's in-plane B-N stretching vibration and BN's out-of-plane B-N-B bending vibration. In addition, the O-H stretching vibration caused by the humidity of the samples from the air was also detected.

With this analysis, dipolation effect and weak bonds and covalent bond effect as strong bond were observed between boron and nitrogen. FTIR spectrum results of 10 % , 25 % , 50 % and 75 % B_2O_3 excess h-BN are in agreement with XRD results and analyzes made with Aydın [63] literature studies.

Optical characterization (UV), the process was applied to each sample. In the spectrum results obtained, these spectra occurring in the samples are thought to be due to the reduced interaction of the photons with electrons, atoms or crystal molecules and the reduced retroreflection due to the decreased energy of the photos.

In the results obtained, variability was determined according to the ratio of B_2O_3 amount and Ram et al [64] showed agreement in the literature review.

Vector network spectrum analysis processes were applied to the h-BN samples produced from B_2O_3 excess. The dielectric obtained as a result of vector network spectrum analysis of all samples came out below the value constant $\varepsilon_r \leq 25$.

With the samples obtained as a result of all the characterization processes, it was concluded that the defense industry can be used as a substrate material in applications such as high-frequency radar material, signal interrupter, microwave antenna circuit elements, missile tracking systems and microwave circuits.

In addition to the usual voice and other services of standard previous systems, 5G generation devices, ultra-broadband Internet connection, IP telephony, mobile web access and other interesting multimedia applications, radar and jammer systems exist.

In addition, it was concluded that different relative permittivity values can be obtained in samples that can be made with different ratios in the range of 10 % to 25 % excess B_2O_3 in vector network spectrum analysis.

This study is evaluated in terms of our country, Turkey has rich reserves of the field in terms of boron minerals and raw materials and work, plenty of boron minerals and raw materials in Turkey, is important for a valuable boron products that h-BN production. With the development of defense industry and advanced technology ceramics in recent years, it is of great importance as it will pave the way to completely get rid of external dependency.

REFERENCES

[1] Güyagüler, T. Türkiye Bor Potansiyeli, 4 Endüstriyel Hammaddeler Sempozyumu, 18-İ910, Izmir, Türkiye, s. 18-27. 2001

[2] Smith, R. "Boric Oxide, Boric Acid, and Borates", Ullmann's Encyclopedia of Industrial Chemistry, Vol A4, pp 263-280. 1995

[3] Özkan, Ş. G. Çebi, H. Delice, S. Doğan, M. "Bor Minerallerinin Özellikleri ve Madenciliği", 2. Endüstriyel Hammaddeler Sempozyumu. 1997

[4] Kendall, T. "Borate Supply and Demand, More than a White Wash", Industrial Minerals, No 362, pp 51-69. 1997

[5] Berma Baudis, U. Fichte, R. "Boron and Boron Alloys", Ullmann's Encyclopedia of Industrial Chemistry, Vol A4, pp 281-293. 1995

[6] Baker, S. J. Ding, C. Z. Akama, T. Zhang, Y. K. Hernandez, V. Xia, Y. Therapeutic potential of boron-containing compounds, Future Med. Chem.,1, 1275-88. 2009

[7] Kistler, R. B. Helvacı, C. "Boron and Borates", Industrial Minerals and Rocks, 6 th Ed, Society of Mining, Metallurgy and Ex. Inc.. 1994

[8] Tolun, R. "Türkiye'de Bor Bileşikleri Üretim Teknolojilerinin Dünü, Bugünü ve Geleceği", Bor Bileşikleri Üretim Teknolojileri Araştırmaları Danışma Toplantısı, Gebze, 16 s. 1996

[9] https://www.boren.gov.tr/Sayfa/boron-minerals/102. Date of access - 02/05/2020

[10] Poslu, K. Aslan, İ. H. "Dünya Bor Mineralleri ve Bileşikleri Üretiminde Türkiye'nin Yeri, Endüstriyel Hammaddeler Sempozyumu, İzmir/Türkiye, s. 33-42. 1995

[11] Smith, R. "Boric Oxide, Boric Acid, and Borates", Ullmann's Encyclopedia of Industrial Chemistry, Vol A4, pp 263-280. 1995

[12] Sarıız, K. Nuhoğlu, İ. "Endüstriyel Hammadde Yatakları ve Madenciliği", Anadolu Üniversitesi, Yayın No 636, s. 58-86. 1992

[13] https://www.boren.gov.tr/Sayfa/boron-minerals Dateof access – 13/06/2020

[14] Lyday, P. "Boron-1990", Mineral Commodity Summaries, US Bureau of Mines, 9 p. 1991

[15] Ediz, N. Özdağ, H. "Bor Mineralleri ve Ekonomisi" D.P.Ü. FBE Dergisi, Sayı 2. 2001

[16] Angın, M. H. "Ferrobor fizibilite raporu", Eti Holding, Ankara, 3-26. 2003

[17] Duman, İ. "Bor", Bildiriler Kitabı, I.Uluslararası Bor Sem., 145-155. 2002

[18] Arkun, E. "Paslanmaz çelik saclarda şekillendirme karakteristikleri", Y.T.Ü Fen Bilimleri Enstitüsü, Istanbul, 155. 2006

[19] Holcombe, Jr. Smith, C. E. Lorc, D. D. Duerlesen, D. Carpenter, D. A. "Physical-Chemical Properties of beta-Rhombohedral B", 5 (5): 349–57. 1973

[20] Cowan, L. "Boron: A Better Energy Carrier than Hydrogen?", Canada. 2003

[21] Zarechnaya, E. Y. Dubrovinsky, L. Dubrovinskaia, N. Miyajima, N. Filinchuk, Y. Synthesis of an orthorhombic high pressure B phase, Science and Technology of Ad. 2008

[22] Önal, G. Burat., F. Boron mining and processing in Turkey, pp. 50-52. 2008

[23] Garrett, D. "Borates:Handbook of Deposits, Processing, Properties and Use". 1998

[24] Kendall, T. "Borate Supply and Demand, More than a White Wash", Industrial Minerals, No 362, pp 40-61. 1997

[25] Alexeev, V. P. Chernyshov, A. V. "Boron in the C.I.S., An Overview of Deposits", Industrial Minerals, No 359, pp 49-53. 1997

[26] İpekoğlu, Ü. Polat, M. "Bor Endüstrisine Genel Bakış", Madencilik Dergisi, Cilt XXVI, No 1, s. 5-16. 1987

[27] Sivrioğlu, İ. Bor mineralleri ve Bor Bileşikleri Üretiminde Etibank'in çalışmaları Planları, Tübitak MAM, Istanbul. 1996

[28] http://www.etimaden.gov.tr/bigadic. Date of access – 14/06/2020

[29] Üncü, R. Ü. Dünya Ham ve rafine Bor Pazarına Bir Bakış 4 Endüstriyel Hammaddeler Sem., İzmir,Türkiye, s 7-17. 2001

[30] Lyday, P. A. Boron Annual Report. Usgs, Minerals Information, Reston, Va, USA. 2006

[31] Ozpeker, Ö. Bor Yataklarının Değerlendirilmesi Türkiye Borat Yatakları, Workshop, İTÜ Maden Fakültesi, 163. 2001

[32] Bulutçu, N. "Türkiye'de Bor Bileşikleri Üretim Teknolojisinin Dünü, Bugünü ve Geleceği", Bor Bileşikleri Üretim Teknolojileri Araştırmaları Danışma Toplantısı, TÜBİTAK. 1996

[33] Şekerci, Y. Emrullahoğlu, F. Kalsiyum Hegzaboriir Üretimi Lisans Tezi, AfyonKocatepe Üniversitesi Mühendislik Fakültesi Seramik Mühendisliği Bölümü. 2002

[34] Ebin, B. h-BN, Hard Metal Compounds Lecture, İ.T.Ü. 2007

[35] Haubner, R. Wilhelm, M. Weissenbacher, R. Lux, B. BN – Properties, Synthesis and Applications, High Performance Non-Oxide Ceramics II.

[36] Wentorf, R. H. Jr. Cubic Form of Boron Nitride, J. Chem. Phys 26: 956. 1957

[37] Jansen, M. h-BN, High Performance Non-Oxide Ceramics II p.4-38. 2002

[38] Duclaux, L. Nysten, B. Issi, J. P. Moore, A. W. Structure-Low Temperature Thermal Conductivity of Pyrolitic BN, Physical Review B. 1992

[39] Bundy, F. P. Wentorf, R. H. Refined Phase Diagram of BN, Chem Phys. 1963

[40] Töre, I. h-BN Toz Sentezi ve Sinterleme Davranısları, Doktora Tezi, Anadolu Üniversitesi, Fen Bilimleri Enstitüsü, Eskisehir. 2006

[41] Kimura, Y. BN as a Lubricant Additive, Wear(232), p.199-206. 1999

[42] Lelonis, D. A. New Applications in BN Coatings, GE Company, number:81504. 2003

[43] Lelonis, D. A. Boron Nitride Powder a Review, M.P. Materials. 2007

[44] Lipp, A. Shwetz, K. A. Hunold, K. h-BN:Fabrication, Properties and Applications, Journal of European Ceramic Society, 5, 3-9. 1989

[45] Paine, R. T. Narula, C. K."Synthetic Routes to BN", Chem. Rev., 73-91. 1990

[46] Rossi, R. C. 'Thermal Shock Resistant Materials in Ceramics in Severe Environments", Plenum Press, 5, 123. 1970

[47] Ebin, B. h-BN, Hard Metal Compounds Lecture, İ.T.Ü. Istanbul. 2007

[48] Bundy, F. P. Wentorf R.H., Refined Phase Diagram of BN, Chem Phys 38: 1144-1149. 1963

[49] Jansen, M. h-BN, High Performance Non-Oxide Ceramics II, p.4-38. 2002

[50] Kaptay, G. Electrochemical Synthesis of Refractory, Borides from Molten Salts, Plasma and Ions. 1999

[51] Pikalov, S. N. Mechanism of Formation of Graphitelike Boron Nitride in the Carbothermal,Soviet Powder Metallurgy and Metal Ceramics 27, 404-406. 1988

[52] Bartnitskaya, T. S. Formation of BN Carbothermal Reduction. 1990-1994

[53] Bartnitskaya, T. S. Kurdyumov, A. V. Lyashenko, V. I. Ostrovskaya, N. F. Rogovaya, I. G. Catalytic Synthesis of Graphite-Like Boron Nitride, Powder Metallurgy and Metal Ceramics, 35, 296-300. 1996

[54] Yoon, S. J. Jha, A. Vapour-Phase Reduction and the Synthesis of B-Based Ceramic Phases, Journal of Materials Science, 30, 607- 614. 1995

[55] Aydoğdu, A. Sevinç, N. Carbothermic Formation of BN, Journal of the European Ceramic Society, 23, 3153-3161. 2003

[56] Özkenter, A. A. Effect Calcium Oxide Addition on Carbothermic Formation of h-BN, MSc Thesis, METU, Ankara. 2009

[57] Akyıldız, U. Effect of Sodium Carbonate Addition on Carbothermic Formation of h-BN, MSc Thesis, METU, Ankara. 2010

[58] Çamurlu, H. E. Sevinç, N. Topkaya, Y. Role of B4O in Carbothermic Formation of h-BN, Jounal of Materials Science, 41, 4921-4927. 2006

[59] Kahramansoy, E. Pro. Of h-BN by Carbothermic Reduction Of Colemanite-BO Mixtures, MSc Thesis, METU, Ankara. 2011

[60] Aydoğdu, A. Sevinç, N. Carbothermic Formation of BN, Journal of European Ceramic Society, 23, 3153-3161. 2003

[61] Aydin, C. Metal Oksit Katkılı Yarı İletken Malzemelerin Üretilmesi ve Karakterizasyonu,Fırat Üniversitesi Fen Bilimleri Enstitüsü Yüksek Lisans tezi, 29. 2010

[62] Mirkarimi, P. B. McCarty, K.. F. Meldin, D. L. Review of advances in c-BN film synt.,Mat. Sci. & Eng. R21, 47-100. 1997

[63] Aydın, H. The Production and Characterization of Nanostructured h-BN, Science and Eng. J of Fırat Univ. 30(2), 269-275. 2018

[64] Ram, S. S. Band gap effects of h-BN using oxygen plasma, Appl. Phys. Lett. 104, 163101 Surface Science, 350: 109-114. 2014

[65] Kremer, F. Broadband Dielectric Spectroscopy, Springer, Verlag. 2002

[66] Ohsato, H. Tsunooka, T. Sugiyama, T. Forsterite Ceramics for Milimeterwave Dielectrics, Journal of Electroceramics, 17, 445450. 2006

[67] Surendan, K. P. et al. (1-x) MgAl2O4xTiO2 Dielectrics for Microwave and Millimeter Wave Applications, Appl. Phys. Materials Science & Processing, 81, 823. 2005

[68] Dorey, R. Ceramic Thick Films for MEMS and Microdevices. 2012

[69] https://theodoregray.com/periodictable. Date of access – 24/05/2021

[70] http://www.andersondevelopment.com/blog. Date of access – 24/05/2021

[71] https://www.researchgate.net/publication. Date of access – 24/05/2021

[72] https://malzemebilimi.net/bor-nedir. Date of access – 24/05/2021

[73] http://www.chemistryexplained.com/elements. Date of access – 25/05/2021

[74] https://www.britannica.com/science/boron. Date of access – 25/05/2021

[75] https://www.askiitians.com/iit-jee-s-and-p . Date of access – 25/05/2021

[76] Werheit, H.et al. Sci. Technol. Adv. Mater., Vol. 11, no. 2, pp. 1-27. 2010

[77] https://www.etimaden.gov.tr/en/boron. Date of access – 25/05/2021

[78] https://www.enerjiportali.com/bor-nedir. Date of access – 25/05/2021

[79] https://www.etimaden.gov.tr/en. Date of access – 26/05/2021

[80] https://en.wikipedia.org/wiki/Boron. Date of access – 26/05/2021

[81] https://www.nanowerk.com/nanotechnology. Date of access – 26/05/2021

[82] Pease, R. S. Crystal Structure of Boron Nitride, Nature, 165, 722-72. 1950

[83] http://www.contenti.com/products/spin. Date of access – 26/05/2021

[84] https://www.albmaterials.com/high-purity. Date of access – 26/05/2021

[85] https://www.borax.com/applications. Date of access – 28/05/2021

[86] Bozkurt, C. Budak, E. Physica, B. Condensed Matter,4702 – 4705. 2010

[87] Zheng Wei, T. et al. Solid State Communications, 152, 71 – 75. 2012

[88] Wentzcovitch, R. M. Liu, A. Y. Physical Review, Condensed Matter, 10362 – 10365. 1994

[89] Kimiyasu, S.et al. Thermally conductive composite films of h-BN and polyimide with affinity enhanced, Journal of Mat. Che., 2749-2752. 2010