

**ABANT İZZET BAYSAL UNIVERSITY**  
**THE GRADUATE SCHOOL OF NATURAL AND APPLIED**  
**SCIENCES**  
**DEPARTMENT OF CHEMISTRY**



**SYNTHESIS OF HEXAGONAL BORON NITRIDE**  
**IN THE PRESENCE OF BORATES**

**MASTER OF SCIENCE**

**BİNNUR KANBUR**

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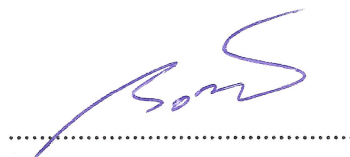
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**SYNTHESIS OF HEXAGONAL BORON NITRIDE IN THE PRESENCE OF THE BORATES** submitted by **Binnur KANBUR** in partial fulfillment of the requirements for the degree of Master of Science in **Department of Chemistry**, **Abant Izzet Baysal University** by,

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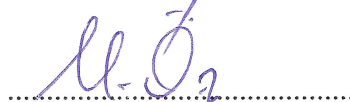
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July 24, 2015

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Director, Graduate School of Natural and Applied Sciences

To my family

## **DECLARATION**

I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

Binnur KANBUR

## **ABSTRACT**

### **SYNTHESIS OF HEXAGONAL BORON NITRIDE IN THE PRESENCE OF THE BORATES**

**MSC THESIS**

**BİNNUR KANBUR**

**ABANT İZZET BAYSAL UNIVERSITY GRADUATE SCHOOL OF  
NATURAL AND APPLIED SCIENCES**

**DEPARTMENT OF CHEMISTRY**

**(SUPERVISOR: PROF. DR. ÇETİN BOZKURT)**

**BOLU, JULY 2015**

Boron nitride (BN) is a synthetic product and not found in nature. Boron nitride is an extraordinary topic in the area of materials science. Due to the special bonding behaviors of boron and nitrogen the BN exists in many different structures.

In this study, hexagonal boron nitride (h-BN) was synthesized in the presence of borates by using modified O'Connor method. Using the Fourier Transform Infrared Spectroscopy (FTIR), X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) analysis, the structural properties were analyzed. The h-BN formation was observed by FTIR results. The interlayer distance was changed with using borates according to the XRD analysis and this is proved by TEM analysis.

Besides, the grain size and lattice parameters were calculated from XRD results. Results were very close to the values in the literature.

In the presence of lithium tetraborate, h-BN was formed as a nano rod at 1300°C.

#### **KEYWORDS:**

Hexagonal Boron Nitride, Interlaying Spacing, Synthesis, Characterization, Borates

# ÖZET

**BORAT VARLIĞINDA HEKZAGONAL BOR NİTRÜR SENTEZİ**  
**YÜKSEK LİSANS TEZİ**  
**BİNNUR KANBUR**  
**ABANT İZZET BAYSAL ÜNİVERSİTESİ FEN BİLİMLERİ ENSTİTÜSÜ**  
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**BOLU, TEMMUZ - 2015**

Bor nitrür doğada bulunmayan sentetik bir üründür. Bor nitrür malzeme bilimi alanında olağanüstü bir konudur. Bor ve azotun özel bağlanması nedeniyle bor nitrür birçok farklı yapılarda bulunmaktadır.

Bu çalışmada modifiye O'Connor metodu kullanılarak borat varlığında hekzagonal bor nitrür sentezi (h-BN) yapılmıştır. Fourier Dönüşüm Kızılötesi Spektroskopisi (FTIR), X-Işını Kırınım Ölçeri (XRD), Taramalı Elektron Mikroskobu (SEM) ve Geçirimli Elektron Mikroskobu (TEM) kullanılarak yapısal özellikleri analiz edilmiştir. FTIR sonuçlarından h-BN oluşumu gözlenmiştir. XRD sonuçlarına göre boratlarla birlikte tabakalar arası uzaklık değişmiştir ve bu TEM analizi ile kanıtlanmıştır.

Bunun yanında XRD sonuçlarından örgü parametreleri ve tanecik büyüklüğü hesaplanmıştır. Sonuçlar literatürdeki değerler çok yakındır.

1300°C'de lityum tetraborat varlığında h-BN nano çubuk şeklinde oluşmuştur.

## **ANAHTAR KELİMELELER:**

Hekzagonal Bor Nitrür, Tabakalar arası uzaklık, Sentez, Karakterizasyon, Boratlar

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## LIST OF ABBREVIATIONS AND SYMBOLS

<b>2<math>\theta</math></b>	: Bragg Angle Degree
<b>BN</b>	: Boron Nitride
<b>FTIR</b>	: Fourier Transform Infrared Spectroscopy
<b>h-BN</b>	: Hexagonal Boron Nitride
<b>SEM</b>	: Scanning Electron Microscopy
<b>TEM</b>	: Transmission Electron Microscope
<b>XRD</b>	: X-Ray Diffractometer
<b>c-BN</b>	: Cubic Boron Nitride
<b>r-BN</b>	: Rhombohedral Boron Nitride
<b>w-BN</b>	: Wurtzitic Boron Nitride
<b>EDX</b>	: Energy Dispersive X-Ray Spectroscopy
<b>ICDD</b>	: The International Centre for Diffraction Data

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# 1. INTRODUCTION

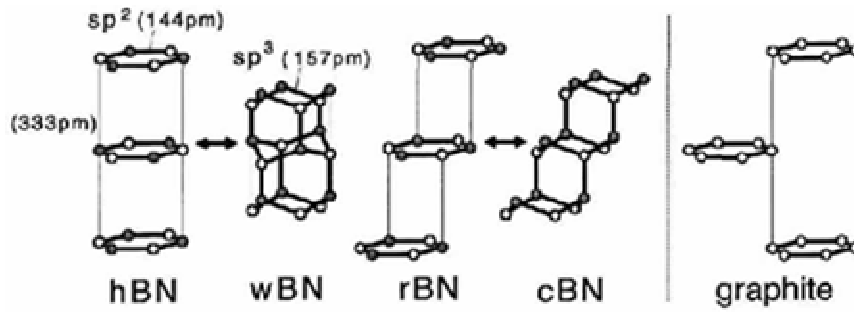
Boron nitride (BN) - in all its various structures - is a synthetic product and not found in nature. The first synthesis for h-BN was described in 1842 by Balmain, but h-BN became a commercial material about 100 years later (Balmain, 1842).

Boron and nitrogen are neighbors of carbon in the periodic table, and therefore BN phases are isoelectric to the corresponding carbon phases. The structure similarities between h-BN and graphite have been well known, and therefore in 1957 Wentorf successfully tried the high-temperature high-pressure synthesis of c-BN analogous to the diamond synthesis (Haubner et al, 2002).

The second hardest material - after diamond - was discovered, and since 1969 c-BN has been commercially available. Due to its excellent properties h-BN is mainly used as ceramic material, as lubricant and serves also as thin coatings for electronic devices. Utilization of cubic-BN are wear applications like machining tools and polishing powders (Haubner et al, 2002).

## 1.1 Boron Nitride

The compound boron nitride (BN) has no counterpart in nature on the earth (Balmain, 1842). After starting with the synthesis of a hexagonal layered compound in 1842, various types of BN have been synthesized (Balmain, 1842). Boron nitride is an extraordinary topic in the area of materials science. Due to the special bonding behaviors of boron and nitrogen the BN exists in many different structures. The well-defined crystallographic structures are hexagonal BN (h-BN), rhombohedral BN (r-BN), wurtzitic BN (w-BN), and cubic BN (c-BN). Additionally, other crystalline and amorphous structures exist (Haubner et al, 2002).



**Figure 1.** Structural relations among the four BN crystals

### 1.1.1 Hexagonal Boron Nitride(h-BN)

Hexagonal BN is mostly named h-BN, but also  $\alpha$ -BN or g-BN (graphitic-BN) are used. It crystallizes similar to graphite in a hexagonal sheet layered structure, and therefore it is often referred to as "white graphite" (Haubner et al, 2002).

The atomic planes are built by hexagonal rings formed by B and N atoms. The covalent bonds ( $\sigma$ -bonding,  $sp^2$ -hybridization) between the atoms forming the rings are very strong. Between the atomic planes the bonding forces are weak, being van der Waals bonding ( $\pi$ -bonding) (Haubner et al, 2002).

In addition, it has to be pointed out that the planes are stacked on top of one another, without any horizontal displacement (boron and nitrogen are alternating along the  $c$ -axis). Due to the higher electronegativity of nitrogen the  $\pi$ -electron is located at the nitrogen and therefore h-BN is an electrical insulator and its color is white (Haubner et al, 2002).

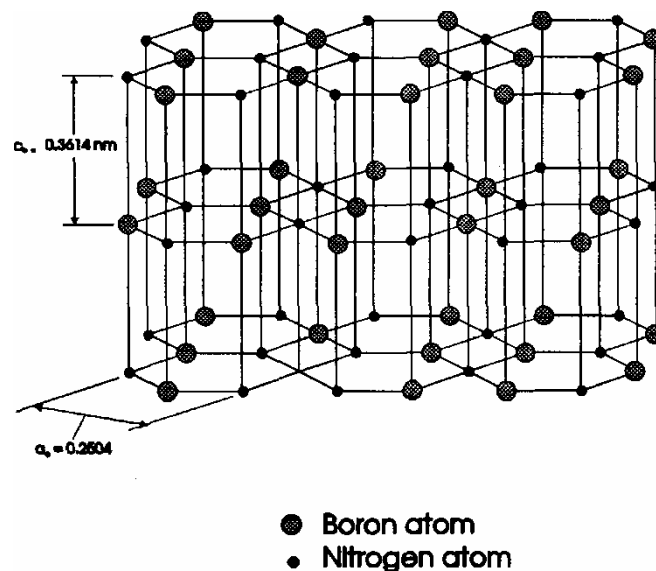
h-BN is a high-temperature solid lubricant, good thermal conductor, and good electric insulator. The specific gravity is low, it is stable in air up to 1000°C, under vacuum up to 1400°C, and in inert atmosphere it can be used up to 2800°C. Hence, the maximum application temperature is higher than that of  $Si_3N_4$ ,  $Al_2O_3$ , or SiC (Haubner et al, 2002).

BN shows higher thermal shock resistance than MgO, ZrO<sub>2</sub>, or CaO. BN is chemically inert and not wetted by many metallic (Al, Cu, Zn, Fe, steel, Ge) and non-metallic (Si, B, glass, cryolite, halides) melts (Haubner et al, 2002).

The hardness is similar to graphite and therefore BN materials, produced by hot-pressing, can be machined easily for low costs. Close tolerances for h-BN components can be reached using conventional shop tools. The thermal and mechanical properties show an anisotropic behavior parallel and perpendicular to the hot-press direction (Haubner et al, 2002).

### 1.1.2 Structure of Hexagonal Boron Nitride

Hexagonal boron nitride is composed of series of stacked parallel layer planes shown schematically in Figure 2. In this figure, the circles showing the position of the nitrogen and boron atoms do not represent the actual size of these atoms. In fact, each atom contacts its neighbors (Mishima and Era, 2000).



**Figure 2.** Schematic representation of the crystal structure of hexagonal boron nitride (h-BN)

The stacking of these layer planes occurs with the hexagon immediately above each other. The boron and nitrogen atoms alternate from one layer to the other; in other

words, each nitrogen atom has a boron atom directly above and below and vice versa. The stacking is thus different from graphite which has the same planar arrangement but offset planes so that only half the carbon atoms have neighbors directly above and directly below (Mishima and Era, 2000).

Within the layer plane, each nitrogen atom is bonded to three boron atoms (and vice versa) with a short bond length (0.1446 nm), forming a series of continuous hexagons in what can be considered as an essentially infinite two-dimensional array. The spacing between layer planes is relatively large (0.3615 nm) or more than twice the spacing between atoms within the layer plane. This means that h-BN should be able to accommodate intercalation elements or compounds. As a result of the large anisotropy in its crystal, h-BN has very anisotropic properties (Mishima and Era, 2000).

In contrast, the bond between the planes of h-BN is very weak and even weaker than that of graphite. It is readily broken and layers can be cleaved with a knife like an onion skin. However this bond is electronically different from that in graphite. In graphite, it stems from the hybridized fourth valence electron which is paired with another delocalized electron of the adjacent plane by a weak Van Der Waals bond ( $\pi$  bond). The high electrical conductivity of graphite is attributed to these delocalized electrons (Mishima and Era, 2000).

In h-BN, no free electrons are available since the corresponding  $p_z$  orbitals in the boron atom are vacant and those of the nitrogen atom are occupied by two electrons. Overlap to form  $\pi$  bonds is not possible. In addition, the relatively large difference in electronegativity between nitrogen (3.0) and boron (2.0) imparts greater localization of  $\pi$  electrons than in graphite. As a result, boron nitride is an electrical insulator (Mishima and Era, 2000).

### **1.1.3 Synthesis of Methods of Boron Nitride**

Balmain first synthesized BN in 1842 by reaction of molten boric acid with potassium cyanide (Balmain, 1842). More than 100 years later the commercial

production of BN was established. Although there are a lot of other general methods for producing BN, principally two reactions are used on the industrial scale (Haubner et al, 2002).

#### **1.1.3.1 Boric Acid with Carrier Substances**

Boric acid with ammonia reacts in the presence of carrier substances ( $\text{Ca}_3(\text{PO}_4)_2$ ,  $\text{CaCO}_3$ ,  $\text{CaO}$ ,  $\text{BN}$ ,  $\text{Zn}$ -borate). The carrier substances prevent the formation of a homogeneous melt of boric acid, which is not suitable because of its minimal surface: At reaction temperatures exceeding  $700^\circ\text{C}$  a thin film of molten boric acid covers each carrier substance particle. Because of the large surface a full reaction of the boric compound with ammonia is possible. After the reaction the carrier is leached with  $\text{HCl}$  and the remaining h-BN is washed with water. A second reaction at temperatures exceeding  $1500^\circ\text{C}$  with ammonia follows, resulting in h-BN powders with 97% purity. The h-BN crystallites are thin hexagonal platelets with a thickness of about  $0.1\text{-}0.5\ \mu\text{m}$  and a diameter up to  $5\ \mu\text{m}$  (Haubner et al, 2002).

#### **1.1.3.2 Boric Acid with Organic Nitrogen Compounds**

The second important way to produce h-BN is the reaction of boric acid or alkali-borates with organic nitrogen compounds (melamin, urea, dicyanamide, guanidine) in nitrogen atmosphere. These reactions are carried out at temperatures between  $1000^\circ\text{C}$  and  $2100^\circ\text{C}$  in  $\text{N}_2$  atmosphere. Before final thermal treatment, the product can be washed with methanol or diluted acids in order to remove all non-reacted products. For removing oxygen impurities a thermal treatment at  $1500^\circ\text{C}$  in inert  $\text{N}_2$  or  $\text{Ar}$  atmosphere is used. BN with turbostratic structure (t-BN) is obtained which is characterized by partial or complete absence of three-dimensional order in the stacking of its atomic planes (Haubner et al, 2002).

### 1.1.3.3 Various BN Synthesis Methods

- In carbothermal reactions BN is synthesized by reduction of boric acid or borates in nitrogen atmosphere at 1000-1500°C. One example is the reduction of boric acid or borates with carbon. The precursors are mixed intensively and after drying, the mixture is heated up to 1200-1500°C in nitrogen atmosphere, remaining at maximum temperature for 60-600 min. To enhance the yield of BN, catalysts ( $\text{CaCO}_3$ ,  $\text{MnO}_2$ ) are sometimes added to the mixture. However, too high carbon content of the mixture leads to the formation of boron carbide (Haubner et al, 2002).
- Reaction of amides, cyanides, cyanamides, and thiocyanates with boron compounds.  $\text{NaNH}_2$  forms boron nitride with boric acid or sodium borates at 300-500°C in ammonia atmosphere. At the end of the reaction the temperature is increased to 1000°C for the decomposition of the remaining nitrogenous compounds. After washing with water, the BN powder is stabilized by annealing at 1800°C in inert atmosphere. Cyanides ( $\text{NaCN}$ ,  $\text{KCN}$ ) react with boric acid at 800-1500°C by forming BN. As a byproduct, CO gas and C are produced. The reaction of cyanamides ( $\text{CaNCN}$ ) with boric acid is carried out at 1400-1750°C in a 93%  $\text{N}_2$  - 7%  $\text{H}_2$  atmosphere. After reaction the product is washed with diluted HCl. Carbon, which is produced as a by-product during the reaction, is burned in air at 1000°C (Haubner et al, 2002).
- Preparation of B-N containing precursors with subsequent decomposition is also a suitable method to produce BN. The adduct  $\text{BF}_3\text{-NH}_3$  is formed by reaction of  $\text{BF}_3$  with gaseous, liquid, or aqueous ammonia. From aqueous solutions the  $\text{BF}_3\text{-NH}_3$  adduct can be precipitated by adding NaOH. After drying the precipitate it is heated up to 800°C in inert atmosphere ( $\text{N}_2$ ,  $\text{H}_2$ , or  $\text{NH}_3$ ), and afterwards the BN is formed by pyrolytic reaction. After washing with hot water the h-BN is obtained (Haubner et al, 2002).
- Fine and ultra-fine BN is used for lubricants and toners and can be produced by combustion of boron powder at 5500°C in a nitrogen-plasma

(Haubner et al, 2002).

- Other ways for preparing BN are the reactions of calcium-boride ( $\text{CaB}_6$ ) with additions of boric acid in nitrogen atmosphere at temperatures exceeding  $1500^\circ\text{C}$ , or the synthesis from iron boride ( $\text{FeB}$ ) with ammonia at  $550^\circ\text{C}$  and subsequent annealing in ammonia at  $1000^\circ\text{C}$  (Haubner et al, 2002).
- Growing of h-BN crystals is possible in molten sodium at temperatures between  $700$  and  $800^\circ\text{C}$ . Starting materials are boron and  $\text{NaN}_3$  powders which are sealed in a stainless steel tube and heated up (Haubner et al, 2002).

#### **1.1.3.4 Gas Phase Deposition**

Using thermal CVD methods with  $\text{B}_2\text{H}_6\text{-NH}_3\text{-H}_2$  or  $\text{BCl}_3\text{-NH}_3\text{-H}_2$  gas mixtures, different BN-layers can be deposited; e.g., h-BN, t-BN, or a-BN. BN with higher boron contents can be deposited at enhanced deposition temperatures. To deposit crystalline h-BN from the gas phase, temperatures above  $1100^\circ\text{C}$  and a N/B ratio of 10:1 are necessary (Haubner et al, 2002).

In the last century a dramatic increase in the number of reports and patents describing the deposition of h-BN has taken place. Different methods for coating on a wide range of materials have been developed. The activation of the gas mixture can be achieved by various methods, e.g., plasma-assisted CVD as well as laser ablation techniques of BN bulk materials. The plasma is generated either by microwave discharge or by an RF (radio-frequency) discharge. The CVD process can also be conducted by laser driven reactions and pulsed laser deposition. A wide range of different gaseous precursors is used in all the CVD techniques. The gas mixture may consist of different boron and nitrogen sources like  $\text{B}_2\text{H}_6$ ,  $\text{BCl}_3$ ,  $\text{BBr}_3$ , and  $\text{NH}_3$ ,  $\text{N}_2$ , respectively (Haubner et al, 2002).

Most of the reports on h-BN deposition during the last years are in combination with the low-pressure nano-cBN deposition by PVD methods because a h-BN interlayer is formed before the c-BN is able to nucleate (Haubner et al, 2002).

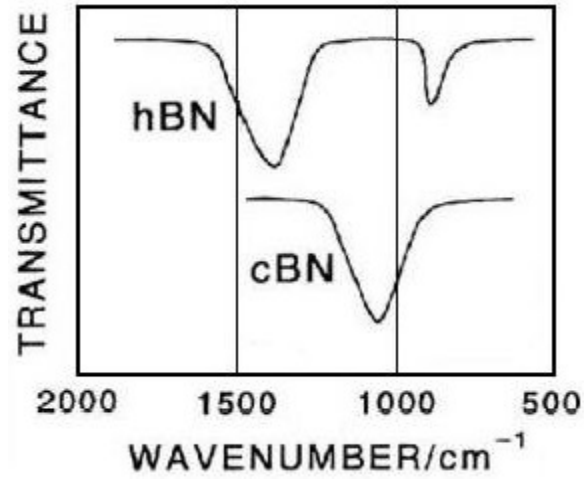
Layers of pure pyrolytic BN are generally produced by thermally induced CVD processes on graphite substrates. The reaction is performed using  $\text{BCl}_3$ ,  $\text{NH}_3$ , and  $\text{N}_2$  at low pressures (0.7-70 mbar) and temperatures in a range between  $1500^\circ\text{C}$  and  $1900^\circ\text{C}$ . For special applications, e.g., coating ceramic fibers for reinforcing purposes or nuclear fuel pellets, the temperature is kept below  $1100^\circ\text{C}$ . Vacuum evaporation of B-trichloro-borazine and decomposition on extremely hot surfaces (e.g., graphite or tungsten) gives pyrolytic BN layers (Haubner et al, 2002).

## 1.2 Characterization of Boron Nitride Products

Due to the complexity of BN-structures and atomic bonding situations, the characterization of BN-phases by spectroscopic methods (e.g., IR and Raman) is difficult. It is not possible to identify BN phases using only one analytical method. For example, the X-ray diffraction peaks of c-BN correspond to those of Cu, Ni, and many other cubic phases. Elemental composition must be known or measured to be sure that no other phases are present (Haubner et al, 2002).

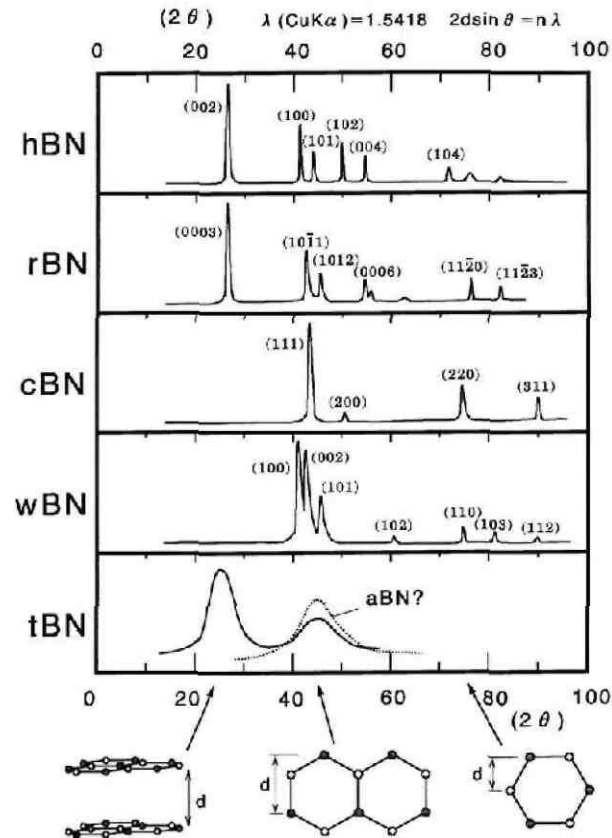
*Infrared spectroscopy (IR) or Fourier transform infrared spectroscopy (FTIR)* are often used to characterize BN products. If pure BN mixtures with BN ratio of 1:1 are analyzed, it will be easy to distinguish between h-BN and c-BN. However, if the chemical composition of the sample is unknown, many artifacts can occur and a clear statement is often not possible (Haubner et al, 2002).

The situation is more complex for h-BN, t-BN, and a-BN, because all of them show peaks between  $780$  and  $1370\text{ cm}^{-1}$ , which makes it impossible to distinguish among these phases (Haubner et al, 2002).



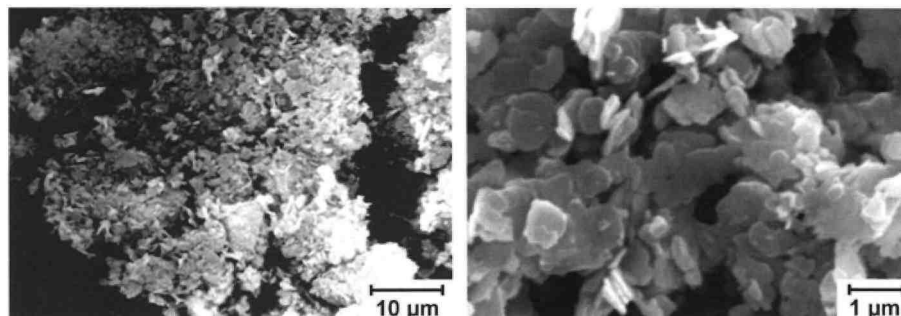
**Figure 3.** IR spectra of h-BN and cBN

*X-ray diffraction* is another possibility to distinguish between c-BN and h-BN. In that case again the elemental composition of the sample is important, because the diffractograms of many cubic substances can mimic the one of c-BN (e.g. Cu, Ni, etc.). The peak positions and their intensities are mainly influenced by grain size, stress in the layers and impurities (Haubner et al, 2002).



**Figure 4.** Schematic X-ray diffraction patterns of BN phases

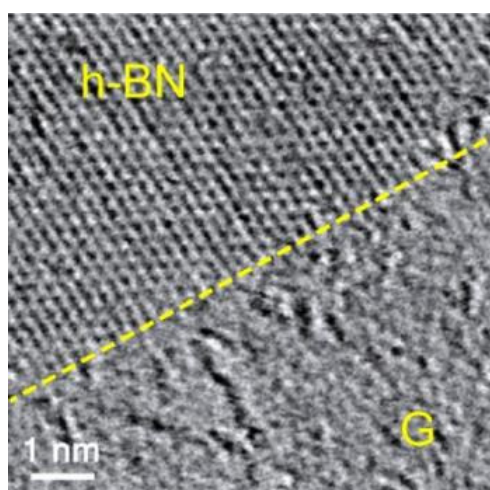
*The scanning electron microscope (SEM)* uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The signals that derive from electron-sample interactions reveal information about the sample including external morphology (texture), chemical composition, and crystalline structure and orientation of materials making up the sample (Pierson, 1996).



**Figure 5.** Pictures of h-BN powders

*Transmission electron microscopy (TEM)* is a microscopy technique whereby a beam of electrons is transmitted through an ultra thin specimen, interacting with the specimen as it passes through. An image is formed from the interaction of the electrons transmitted through the specimen; the image is magnified and focused onto an imaging device, such as a fluorescent screen, on a layer of photographic film, or to be detected by a sensor such as a CCD camera (Swapp, 2015).

TEMs are capable of imaging at a significantly higher resolution than light microscopes, owing to the small de Broglie wavelength of electrons. This enables the instrument's user to examine fine detail even as small as a single column of atoms, which is tens of thousands times smaller than the smallest resolvable object in a light microscope (Swapp, 2015).



**Figure 6.** TEM picture of h-BN

In the O'Connor method, the mixture of boron oxide ( $B_2O_3$ ) and urea ( $(NH_2)_2CO$ ) was heated under ammonia atmosphere at  $1600^\circ C$ . This method was chosen because of not requiring some expensive laboratory devices and poison gases.

## **2. AIM AND SCOPE OF THE STUDY**

h-BN is an important synthetic product because of its excellent properties as ceramic material, as lubricant and it serves also as thin coatings for electronic devices.

It can be said that the scope of this study is to be determine:

- synthesis of h-BN in the presence of the borates,
- reduction of temperature of synthesis with using borates as flux,
- the effect of borates on h-BN for increasing in grain size,
- the positive or negative action of cations,
- determination of morphology by using SEM and TEM analysis,
- difference in the interlayer distance
- and also determination of how is the crystallinity effected by using borate additives.

### **3. EXPERIMENTAL PART**

#### **3.1 Materials**

Boron oxide (Fluka, 97%), Urea (Fluka, 99%), Hydrochloric acid (Merck, 37%), Sodium tetraborate, Lithium tetraborate (Sigma-Aldrich, %99), Lithium metaborate (Sigma-Aldrich, %99.995), Calcium metaborate (Sigma-Aldrich, %39-44), Sodium perborate (Fluka, 97%), Ammonium baborate (Sigma-Aldrich, %98.9), Ammonium pentaborate (Sigma-Aldrich, %99).

#### **3.2 Synthesis h-BN samples**

The modified O'Connor method was used to synthesize h-BN compounds (O'Connor, 1962). The mixture of 1 g of boron oxide was mixed with 2 g of urea pulverized in ball-mill grinder. After that, different types of borates which are shown in Table 1 were added on to this mixture and ground in mortar. Then it was pre-heated at 200°C for 2 hours in furnace and precursor was obtained. Finally, the obtained precursor was re-pulverized in mortar and heated in tube furnace under ammonia atmosphere (120 mL/min) at different temperatures (for each precursor 1150, 1300 and 1450°C) for 2 hours.

The product was boiled in 10% HCl solution then leached in ethanol and dried in an oven at 100°C.

Borates	% Amounts	Temperature (°C)
Sodium tetraborate (Na <sub>2</sub> BO <sub>4</sub> )	1%	1450
	2%	
	7%	
	14%	
	20%	
	30%	
	40%	
Lithium tetraborate (Li <sub>2</sub> BO <sub>4</sub> )	1%	1450
	2%	
	7%	
	14%	
	20%	
	30%	
	40%	
Sodium perborate (NaBO <sub>3</sub> )	40%	1450
Calcium metaborate (CaB <sub>2</sub> O <sub>4</sub> )	40%	
Lithium metaborate (LiBO <sub>2</sub> )	40%	
Ammonium baborate ((NH <sub>4</sub> ) <sub>2</sub> B <sub>4</sub> O <sub>7</sub> )	40%	
Ammonium pentaborate ((NH <sub>4</sub> )B <sub>5</sub> O <sub>8</sub> )	40%	
Lithium tetraborate (Li <sub>2</sub> BO <sub>4</sub> )	40%	
	40%	1150
	40%	1300

**Table 1.** Amounts and types of borates used in synthesis

### 3.3 Preparation of h-BN Samples

#### 3.3.1 Ball-Mill Grinder

A mixture of boron oxide, urea and borates were ground in a ball mill rotated on a roll mixer (Pascall Engineering, 1600-VS-A roll mixer) at medium speed for 4 hours to obtain homogenous mixture. The resultant powder was sieved and 149 μm mixture particles were collected (Budak, 2009).



**Figure 7.** Pascall Engineering, 1600-VS-A roll mixer) and alumina jar

### 3.3.2 Camera Furnace

The precursor preparation was performed with Proterm PLF 140/5 (average heating speed: 10°C/min) camera furnace at 200°C under open atmosphere for 2 hours (Budak, 2009).



**Figure 8.** Proterm PLF 140/5

### 3.3.3 Tube Furnace

Final heating process was done with Proterm PTF 15/75/450 tube furnace (average heating speed: 16°C/min) at different temperatures (1150°C, 1300°C, and 1450°C) under ammonia atmosphere (ammonia flowrate adjusted as 120mL/min. by using flowmeter) for 2 hours (Budak, 2009).



**Figure 9.** Proterm PTF 15/75/450

### **3.4 Characterization of h-BN Samples**

#### **3.4.1 FT-IR Spectroscopy**

FTIR spectra of h-BN samples in KBr pellets were recorded on a Shimadzu FTIR-8400s Spectrometer in the range of  $400 - 4000 \text{ cm}^{-1}$ . To compare IR spectra of the samples all KBr pellets which composed of 0.0005 g of sample and 0.0195 g of KBr, were prepared in the same weight.



**Figure 10.** Shimadzu FTIR-8400s Spectrometer

### 3.4.2 XRD Measurement

XRD characterization of h-BN samples was done with Rigaku Multiflex diffractometer using  $\text{CuK}\alpha$  radiation. (40 kV / 30 mA, Goniometer: MultiFlex+ goniometer (with a shutter), Div Slit:  $\frac{1}{2}$  deg., Sct Slit:  $\frac{1}{2}$  deg., Rec Slit: 0.15 mm, Scan Speed: 3 deg / min., Attachment: Standard sample holder) (Budak, 2009).



**Figure 11.** Rigaku Multiflex

### 3.4.3 SEM Analysis

SEM photographs were taken Jeol JSM 6390LV and the samples used for SEM were coated with carbon (Budak, 2009).



**Figure 12.** Jeol JSM 6390LV

### **3.5 Sample Calculations**

#### **3.5.1 Calculation of Lattice Parameters**

Lattice parameters of the samples were calculated by using following equation for hexagonal systems.

$$\frac{1}{d^2} = \frac{4}{3} \times \left[ \frac{h^2 + hk + k^2}{a^2} \right] + \frac{1}{c^2}$$

d : Interlayer spacing

h, k, l : Related Miller indices

a, c : Lattice parameters

Calculation of “a” parameter of h-BN:

For 110 peak of h-BN d is 1.2521 Å

$$\frac{1}{(2.2521)^2} = \frac{4}{3} \times \frac{1^2 + 1 \times 1 + 1}{a^2} \times \frac{0^2}{c^2}$$

Calculation of “c” parameter of h-BN:

For 002 peak of h-BN d is 3.3280 Å

$$\frac{1}{(3.3280)^2} = \frac{4}{3} \times \frac{0^2 + 0 \times 0 + 0^2}{a^2} + \frac{2^2}{c^2}$$

### 3.5.2 Calculation of Grain Size

Scherrer equation relates the peak breadth of a specific phase of a material to the mean crystallite size of that material.

$$L = \frac{K\lambda}{\beta \cos\theta}$$

$\beta$  is difference of the width of the peak at half maximum intensity of a specific phase

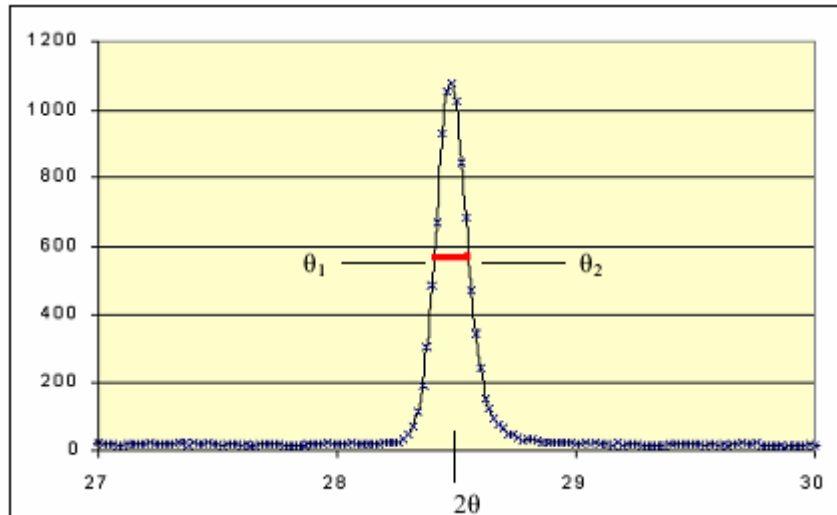
(hkl) in radians of reference material and sample.

$K$  is a constant that varies with the method of taking the breadth (0.9)

$\lambda$  is the wavelength of incident X-Rays (CuK $\alpha$ =1.504 Å).

$2\theta$  is the center angle of the peak of sample

$L$  is the crystallite size



$\theta_{\text{Ref.}(26.64^\circ)}$  and  $\theta_{\text{Ref.}(26.97^\circ)}$  are angles of the width of the peak at half maximum intensity in radians of reference material.  $\theta_{\text{samp } 1.(26.64^\circ)}$  and  $\theta_{\text{samp } 2.(26.97^\circ)}$  are angles of the width of the peak at half maximum intensity in radians of sample and  $2\theta$  is  $26.54^\circ$  for sample.

$$\beta = \sqrt{\left(\left(26.97 - 26.64\right) \times \frac{\pi}{180}\right)^2 - \left(\left(26.88 - 25.94\right) \times \frac{\pi}{180}\right)^2}$$

$$\beta = 0.02$$

$$L = \frac{\kappa\lambda}{\beta \cos\theta} = \frac{0.9 \times 1.504}{0.02 \times \left(\cos 13.27 \times \frac{\pi}{180}\right)}$$

$$L = 92.4 \text{ \AA}$$

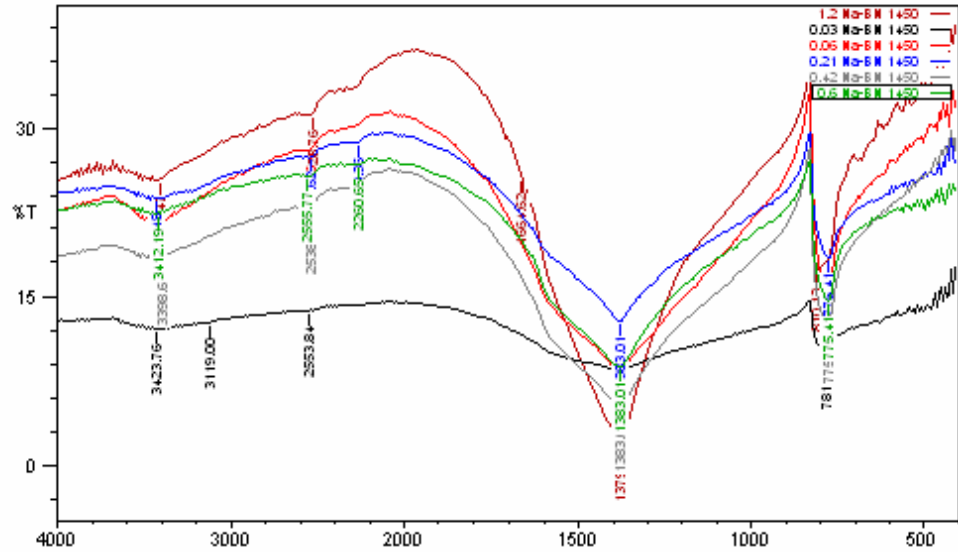
$$L = 9.24 \text{ nm}$$

## **4. RESULTS AND DISCUSSIONS**

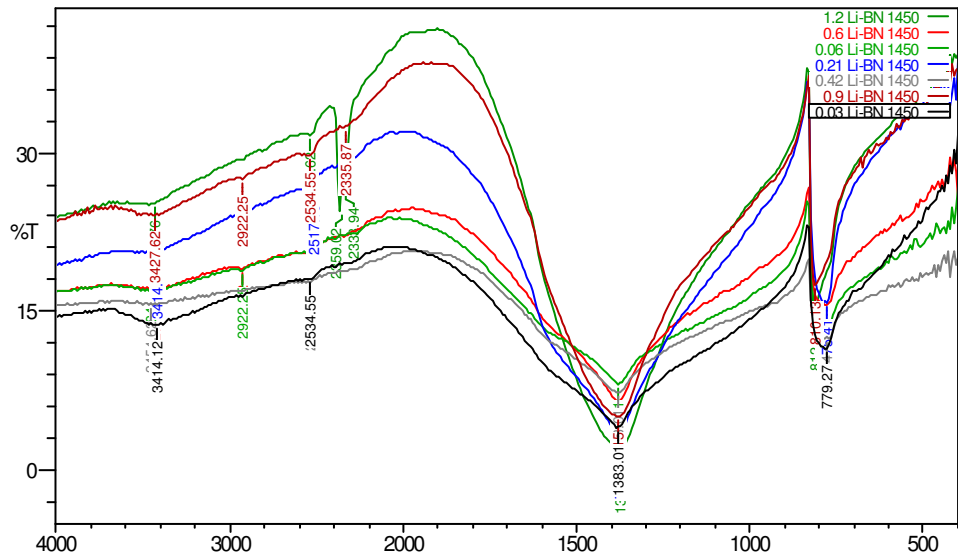
### **4.1 Characterization of h-BN Samples**

#### **4.1.1 FTIR Spectroscopy of h-BN Samples**

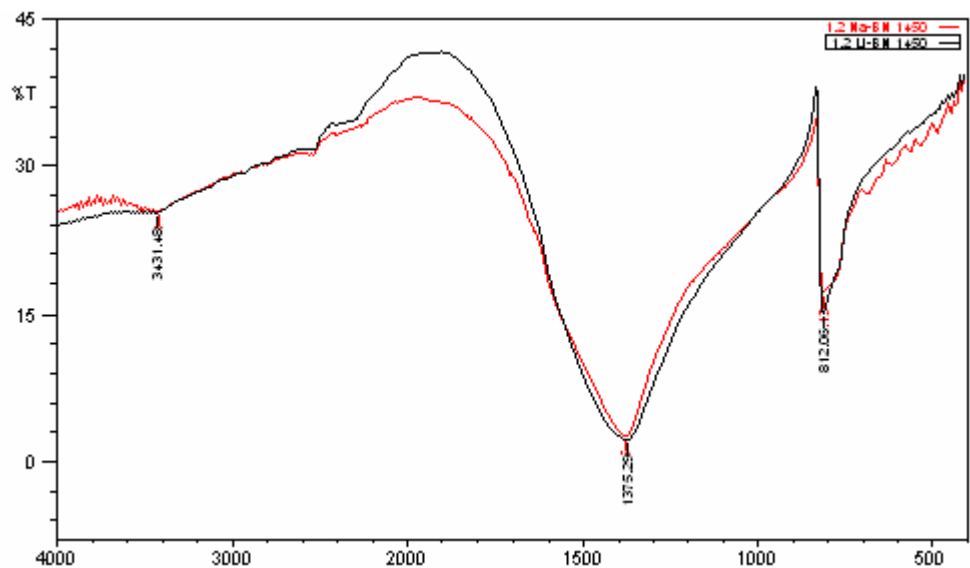
The FTIR measurement was performed to examine the types of chemical bonds of the obtained h-BN samples and there are several studies in the literature characterizing the formation and structure of h-BN by IR spectroscopy. Two strong characteristic bands locate at  $\sim 1390\text{ cm}^{-1}$  and  $\sim 780\text{ cm}^{-1}$  which were attributed to in-plane vibrations and out-of-plane bending vibrations of h-BN, respectively (Budak,1999; Hubacek et al, 1994; Chen et al, 2004). The broad absorption band near  $3200\text{ cm}^{-1}$ ,  $3400\text{ cm}^{-1}$  and a shoulder peak near  $\sim 1050\text{ cm}^{-1}$  can be ascribed to the N-H, -BO-H and B-O stretching vibrations of the terminal -OH, -NH and -B-OH groups that always appears when the boric acid or boron oxide and urea systems were applied. It can be easily understood that as the temperature increases, the intensity of the N-H, -BO-H and B-O stretching decreases or disappears. The intensity of these peaks decrease with increasing the temperature according to the Figure 16. In the IR spectrum of h-BN samples synthesized in the presence of borates, all characteristic bands are observed.



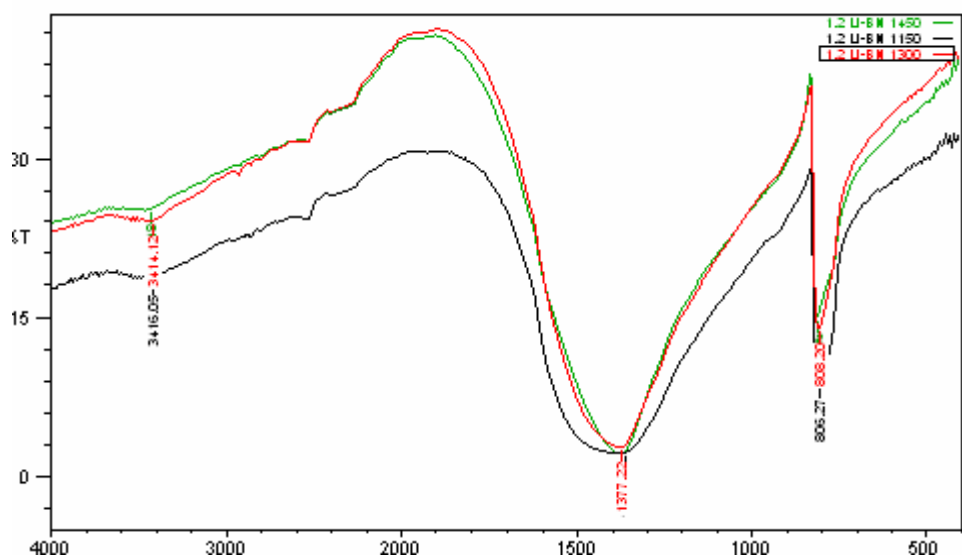
**Figure 13.** IR spectrum of h-BN synthesized with 0.03 g, 0.06 g, 0.21 g, 0.42 g, 0.6 g, 1.2 g sodium tetraborate at 1450°C



**Figure 14.** IR spectrum of h-BN synthesized with 0.03 g, 0.06 g, 0.21 g, 0.42 g, 0.6 g, 0.9 g and 1.2 g lithium tetraborate at 1450°C



**Figure 15.** IR spectrum of h-BN synthesized with 1.2 g sodium tetraborate and 1.2 g lithium tetraborate 1450°C

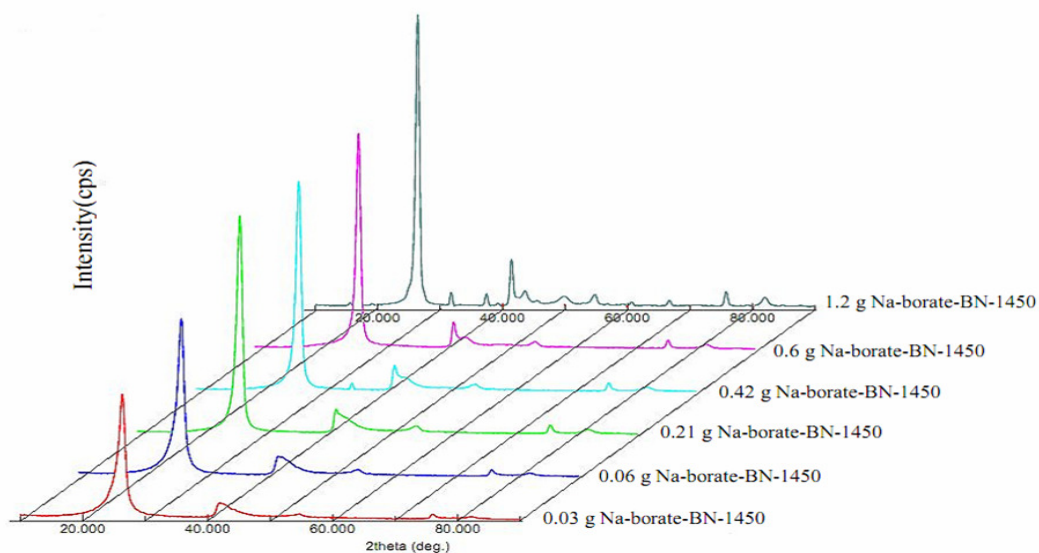


**Figure 16.** IR spectrum of h-BN synthesized with 1.2 g lithium tetraborate at 1150°C, 1300°C and 1450°C



### 4.1.2 XRD Pattern of h-BN Samples

The composition and crystallinity of BN samples were examined by XRD and the results were compared with standard h-BN (ICDD card no: 34 - 421). In all diffractograms, the main peaks of h-BN (002, 10, 004, 110, and 112) are observed.



**Figure 19.** XRD spectrum of h-BN synthesized with 0.03 g, 0.06 g, 0.21 g, 0.42 g, 0.6 g, 1.2 g sodium tetraborate at 1450°C

The use of small amounts of borates cause the structure is turbostratic or nanocrystalline. Crystallinity increases with increasing the amounts of the borates. In X-Ray Diffractogram, 100 and 101 peaks are clearly separated and 102 peak is appeared with increasing the crystallinity.

The lattice parameters of BN samples calculated from the XRD patterns are well consistent with the literature values (ICDD card no: 34 – 421,  $a = 2.5044 \text{ \AA}$ ,  $c = 6.6562 \text{ \AA}$ ,  $d = 3.3281 \text{ \AA}$ ). Calculated lattice parameters of h-BN in the presence of sodium tetraborate are given in Table 2.

**Table 2.** Lattice parameters of h-BN synthesized with 0.03 g, 0.06 g, 0.21 g, 0.42 g 0.6 g and 1.2 g sodium tetraborate

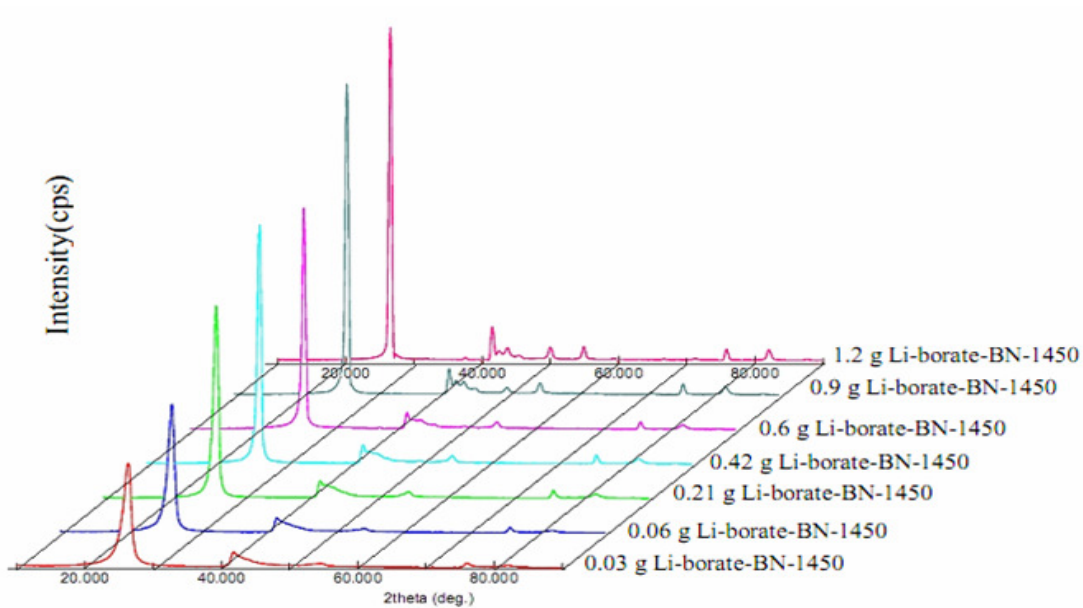
Used borates for preparing h-BN samples	Lattice Parameters		
	a(Å)	c(Å)	d(Å)
0.03 g Sodium tetraborate	2.502	6.756	3.378
0.06 g Sodium tetraborate	2.500	6.750	3.375
0.21 g Sodium tetraborate	2.502	6.760	3.380
0.42 g Sodium tetraborate	2.504	6.754	3.377
0.6 g Sodium tetraborate	2.502	6.716	3.358
1.2 g Sodium tetraborate	2.504	6.708	3.354

The broadening nature of the XRD peaks indicates that the particle size of the samples is within nanometer scale. By using the Scherrer equation the grain sizes of h-BN are calculated.

**Table 3.** Grain size of h-BN synthesized with of 0.03 g, 0.06 g, 0.21 g, 0.42 g 0.6 g and 1.2 g sodium tetraborate

Used borates for preparing h-BN samples	Grain size (nm)
0.03 g Sodium tetraborate	5.922
0.06 g Sodium tetraborate	6.415
0.21 g Sodium tetraborate	8.000
0.42 g Sodium tetraborate	8.733
0.6 g Sodium tetraborate	10.837
1.2 g Sodium tetraborate	11.811

According to calculation of grain sizes in the Table 3, when the amount of the sodium tetraborate increases, the grain size increases.



**Figure 20.** XRD spectrum of h-BN synthesized with 0.03 g, 0.06 g, 0.21 g, 0.42 g, 0.6 g, 1.2 g lithium tetraborate at 1450°C

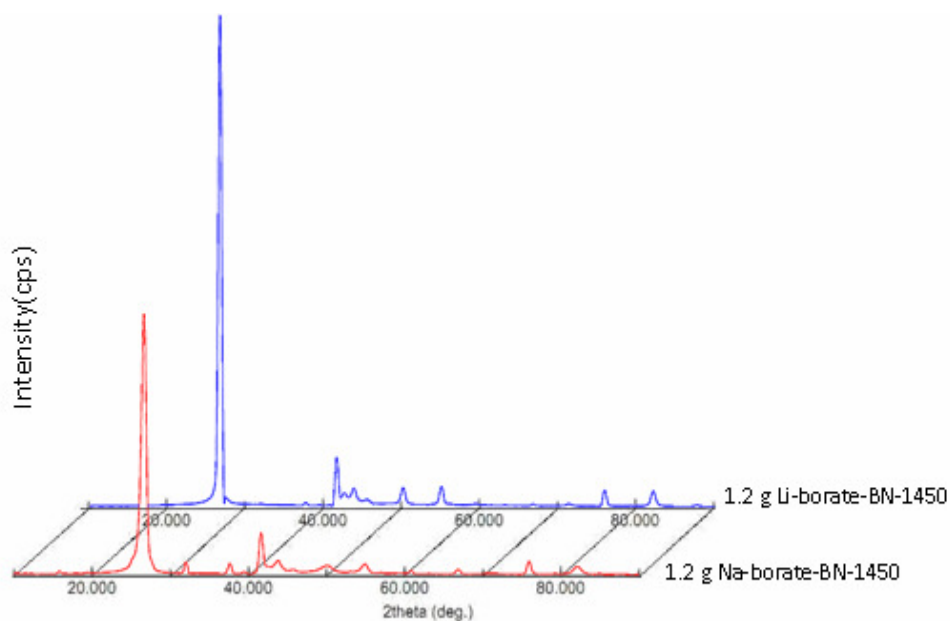
**Table 4.** Lattice parameters of h-BN synthesized with 0.03 g, 0.06 g, 0.21 g, 0.42 g, 0.6 g, 0.9 g and 1.2 g lithium tetraborate

Used borates for preparing h-BN samples	Lattice Parameters		
	a(Å)	c(Å)	d(Å)
0.03 g Lithium tetraborate	2.500	6.764	3.382
0.06 g Lithium tetraborate	2.502	6.748	3.374
0.21 g Lithium tetraborate	2.502	6.714	3.357
0.42 g Lithium tetraborate	2.504	6.718	3.359
0.6 g Lithium tetraborate	2.502	6.682	3.341
0.9 g Lithium tetraborate	2.506	6.696	3.348
1.2 g Lithium tetraborate	2.506	6.694	3.347

**Table 5.** Grain size of h-BN synthesized with 0.03 g, 0.06 g, 0.21 g, 0.42 g 0.6 g 0.9 g and 1.2 g lithium tetraborate

Used borates for preparing h-BN samples	Grain size (nm)
0.03 g Lithium tetraborate	5.816
0.06 g Lithium tetraborate	7.483
0.21 g Lithium tetraborate	10.497
0.42 g Lithium tetraborate	15.928
0.6 g Lithium tetraborate	21.144
0.9 g Lithium tetraborate	24.554
1.2 g Lithium tetraborate	42.757

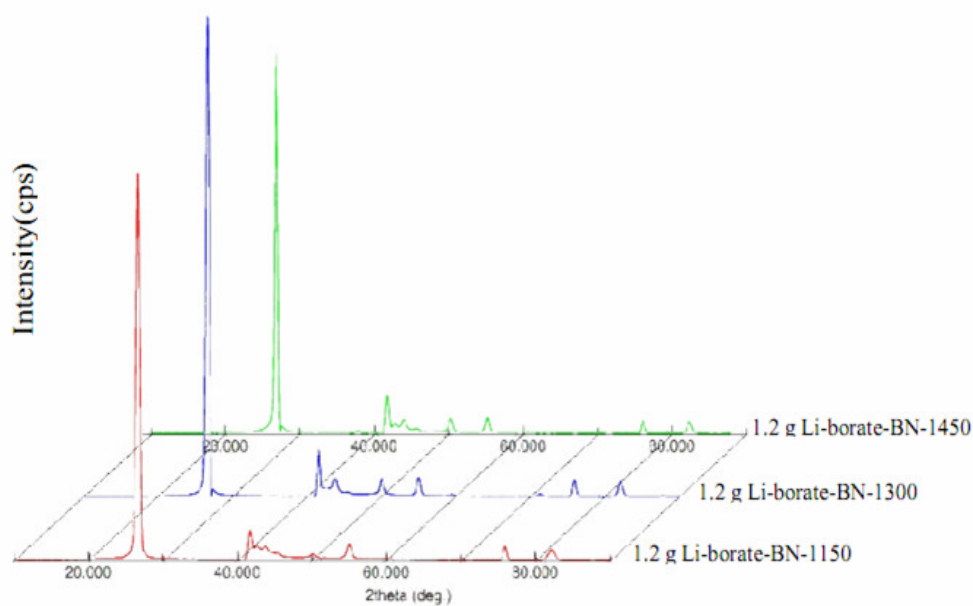
**Figure 21.** XRD spectrum of h-BN synthesized with 1.2 g sodium tetraborate and 1.2 g lithium tetraborate at 1450°C



**Table 6.** Grain size of h-BN synthesized with 1.2 g sodium tetraborate and 1.2 g lithium tetraborate at 1450°C

Used Borates of preparing h-BN	Grain size(nm)
1.2 g sodium tetraborate	11.811
1.2 lithium tetraborate	42.757

The lattice parameters in h-BN synthesized with sodium tetraborate and lithium tetraborate came very close to the original value. But in comparison the grain size, samples with lithium tetraborate has the greater than the samples with sodium tetraborate. This is explained that the lithium is smaller and active than the sodium. The intensity of 002 peak of the samples with lithium tetraborate demonstrates that the higher crystallization than the sodium tetraborate. Also, in each group the calculated the distance between layers is greater than the original value.



**Figure 22.** XRD spectrum of h-BN synthesized with 1.2 g lithium tetraborate at 1150°C, 1300°C and 1450°C

**Table 7.** Lattice parameters of h-BN synthesized with 1.2 g lithium tetraborate at 1150°C, 1300°C and 1450°C

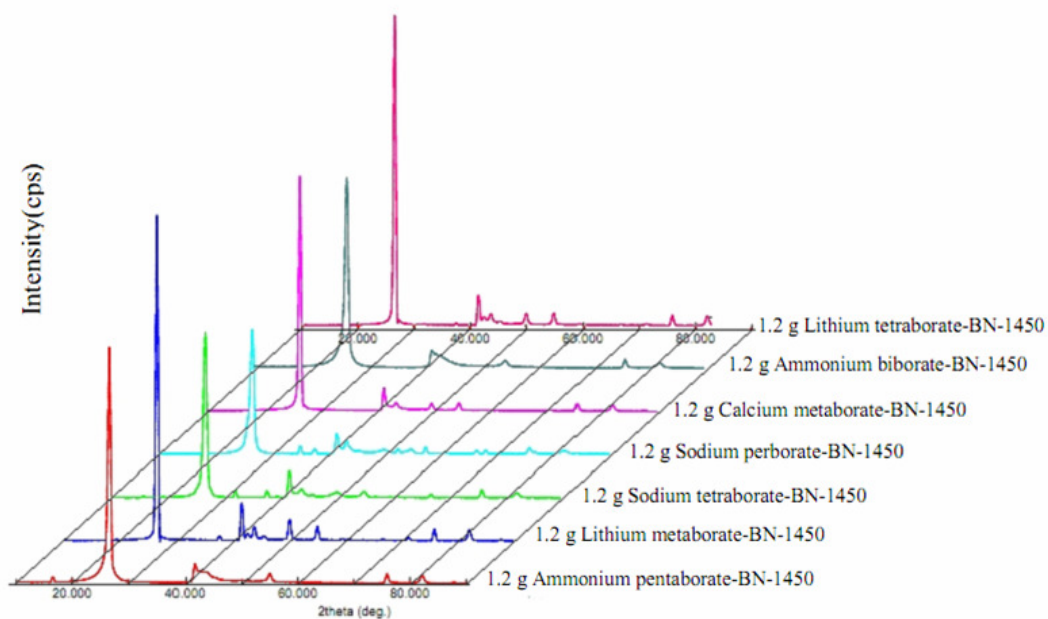
Temperature (°C)	1.2 g Lithium tetraborate		
	Lattice Parameters		
	a(Å)	c(Å)	d(Å)
1150	2.506	6.700	3.350
1300	2.506	6.682	3.341
1450	2.506	6.694	3.347

**Table 8.** Grain size of h-BN synthesized with 1.2 g lithium tetraborate at 1150°C, 1300°C and 1450°C

Temperature (°C)	1.2 g Lithium tetraborate
	Grain size (nm)
1150	22.733
1300	34.989
1450	42.757

At 1150°C, nanocrystalline h-BN is formed but at 1300°C h-BN is formed with high crystallinity. The splitting of the 100 and 101 peaks and the peak of 102 are observed at 1300°C in the XRD. So, this temperature is suitable for synthesis of crystalline h-BN. But also, grain size increases with rising the temperature. This represents the importance of the temperature.

Because of not splitting peaks and low intensity in XRD, other borates did not use in the lower temperature experiments.



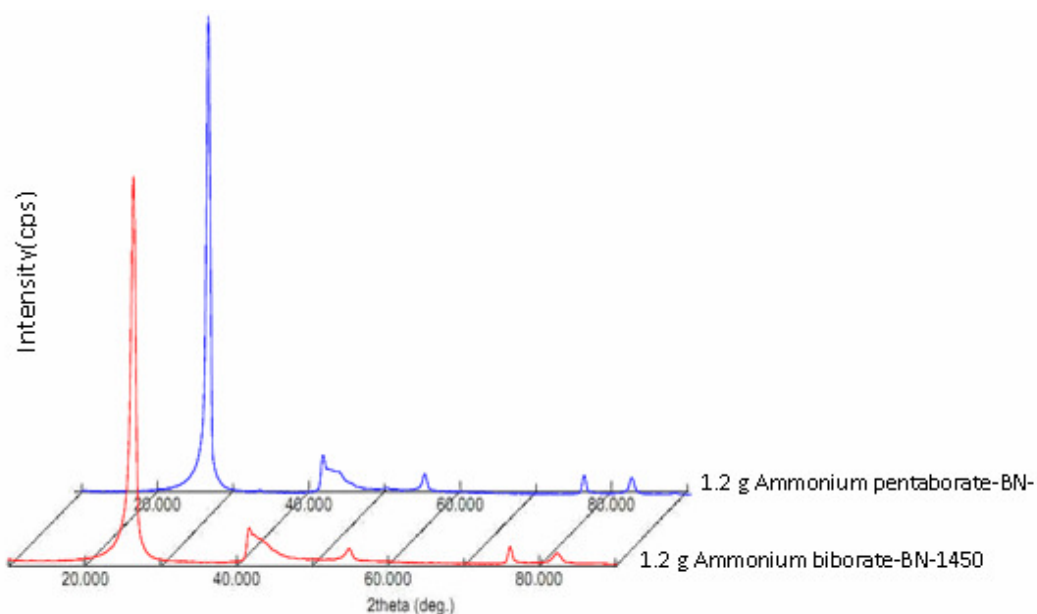
**Figure 23.** XRD spectrum of h-BN synthesized with 1.2 g Ammonium pentaborate, 1.2 g Lithium metaborate, 1.2 g Sodium tetraborate, 1.2 g Sodium perborate, 1.2 g Calcium metaborate, 1.2 g Ammonium baborate and 1.2 g Lithium tetraborate at 1450°C

**Table 9.** Lattice parameters of h-BN synthesized with 1.2 g sodium tetraborate, 1.2 g calcium metaborate, 1.2 g lithium metaborate, 1.2 g sodium perborate at 1450°C

Used borates for preparing h-BN samples	Lattice Parameters		
	a(Å)	c(Å)	d(Å)
1.2 g Sodium tetraborate	2.504	6.708	3.354
1.2 g Calcium metaborate	2.506	6.698	3.349
1.2 g Lithium metaborate	2.504	6.676	3.338
1.2 g Sodium perborate	2.504	6.694	3.347

**Table 10.** Grain size of h-BN synthesized with 1.2 g sodium tetraborate, 1.2 g calcium metaborate, 1.2 g lithium metaborate, 1.2 g sodium perborate, 1.2 g ammonium baborate, 1.2 g ammonium pentaborate and 1.2 g lithium tetraborate at 1450°C

Used borates for preparing h-BN	Grain size (nm)
1.2 g Sodium tetraborate	11.811
1.2 g Sodium perborate	13.621
1.2 g Ammonium baborate	14.170
1.2 g Ammonium pentaborate	20.735
1.2 g Calcium metaborate	31.523
1.2 g Lithium metaborate	32.109
1.2 g Lithium tetraborate	42.757



**Figure 24.** XRD spectrum of h-BN synthesized with 1.2 g Ammonium pentaborate and 1.2 g Ammonium baborate at 1450°C

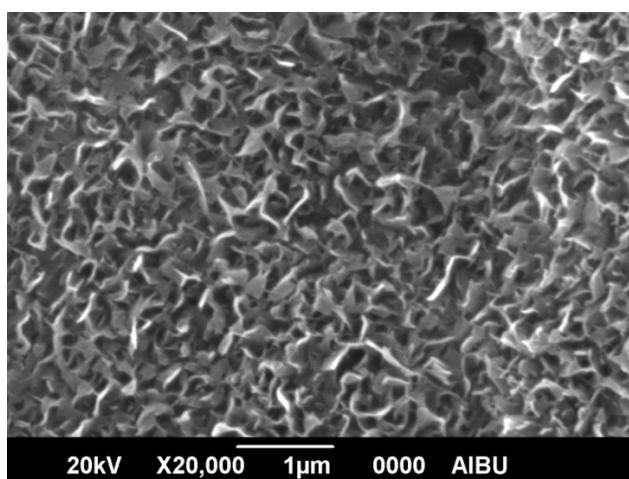
**Table 11.** Lattice parameters of h-BN synthesized with 1.2 g ammonium baborate and 1.2 g ammonium pentaborate at 1450°C

Used borates for preparing h-BN samples	Lattice Parameters		
	a(Å)	c(Å)	d(Å)
1.2 g Amonium baborate	2.504	6.708	3.354
1.2 g Amonium pentaborate	2.506	6.698	3.349

Ammonia is very important for this reaction because ammonia acts as a nitrogen source and reducing agent and also borates acts as a flux agent. If ammonium pentaborate are used in the synthesis instead of ammonium diborate, the grain size increases because of the greater amount of the borates in the structure. And also, in XRD spectrum 100 and 101 peaks are separated as a shoulder peak.

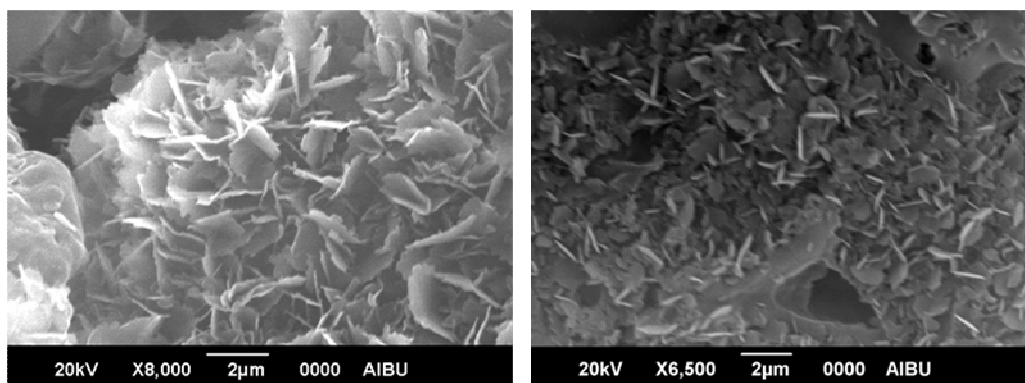
According to the Hubacek (Hubacek and Ueki, 1996; Hubacek et al, 1997), the positive role of the metal cations was observed on the crystallinity, grain size and interlaying spacing of h-BN at low temperature (1150°C). On the other hand, ammonium borates were used as a cation but the ammonium didn't show the same effect on the crystallinity, grain size and interlaying spacing of h-BN.

#### 4.1.3 SEM Analysis of h-BN Samples



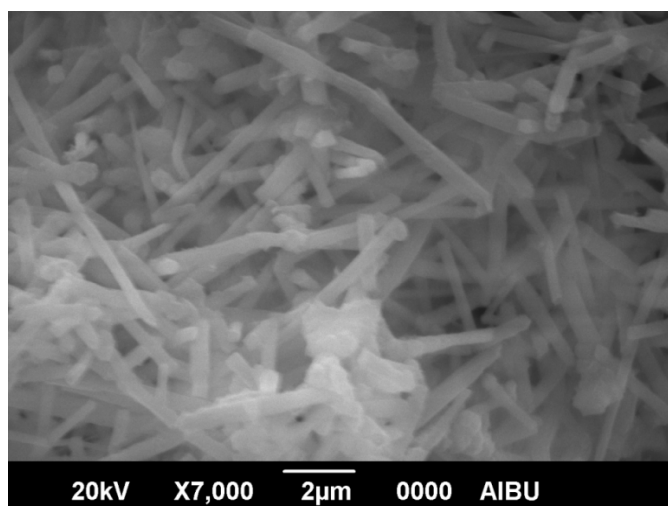
**Figure 25.** SEM image of h-BN synthesized in the presence of sodium tetraborate at 1450°C

At 1450°C, SEM image of h-BN synthesized in the presence of sodium tetraborate that indicates that grains are vertically aligned.



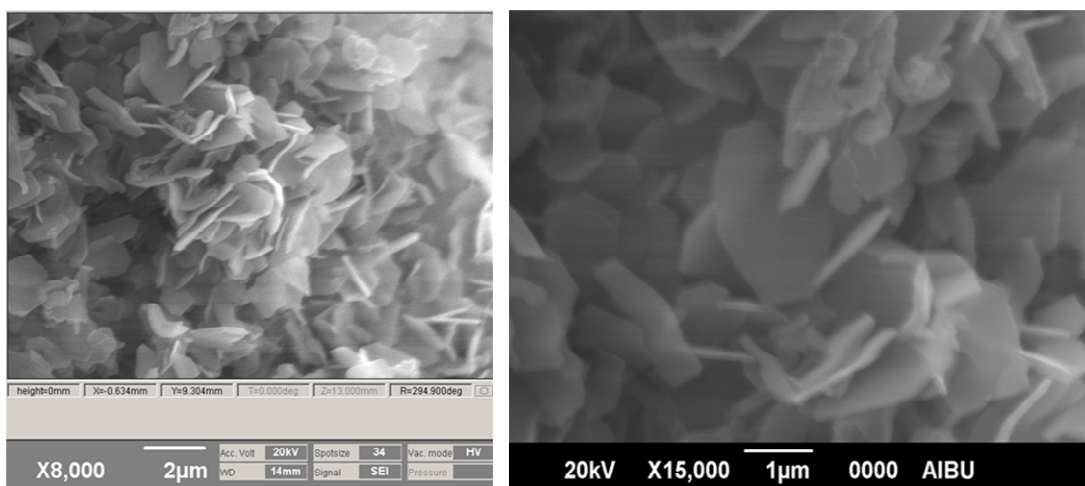
**Figure 26.** SEM image of h-BN synthesized in the presence of lithium tetraborate at 1150°C

At 1150°C, SEM images of h-BN synthesized in the presence of lithium tetraborate is observed that consisting of homogenous discs.

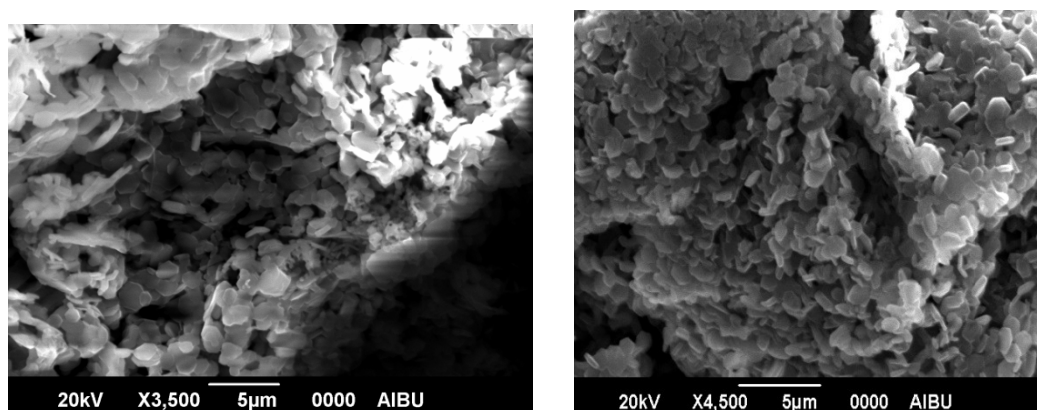


**Figure 27.** SEM image of h-BN synthesized in the presence of lithium tetraborate at 1300°C

In the SEM analysis of h-BN at 1300°C, nano rod formation is observed.



**Figure 28.** SEM image of h-BN synthesized in the presence of lithium tetraborate at 1450°C

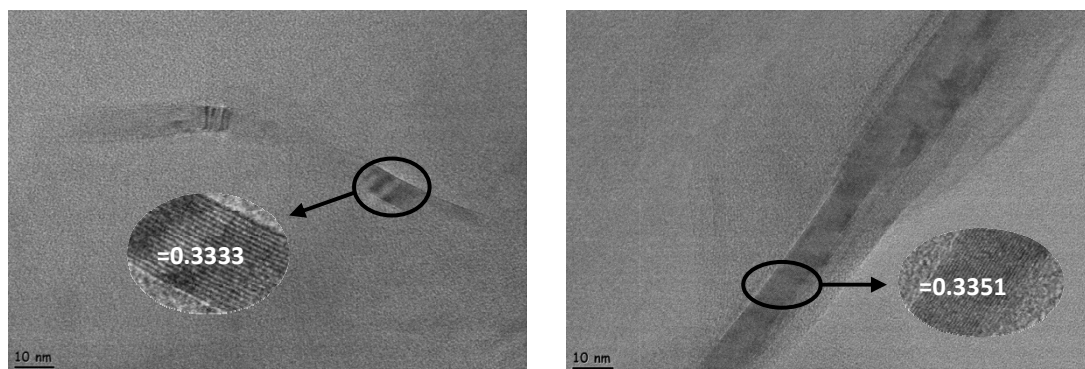


**Figure 29.** SEM image of h-BN synthesized in the presence of lithium metaborate at 1450°C

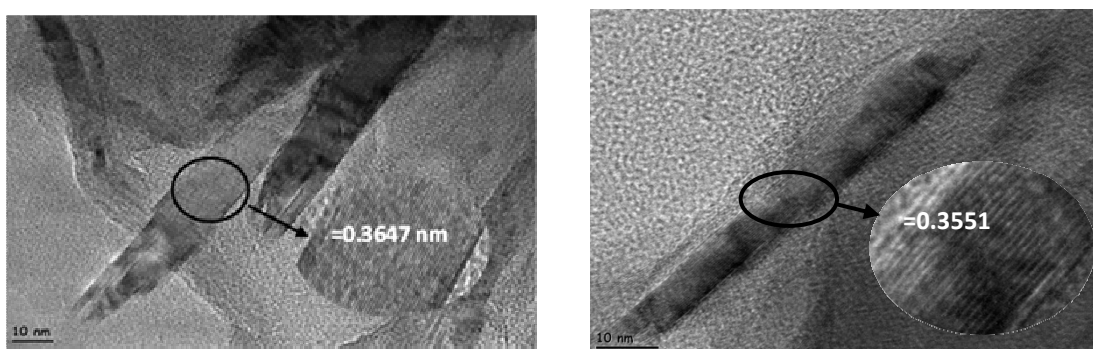
At 1450°C, homogenous disc-shaped plates are appeared in the synthesis of h-BN in the presence of lithium tetraborate.

And also, homogenous disc-shaped plates are observed in the synthesis of h-BN in the presence of lithium metaborate at 1450°C.

#### 4.1.4 TEM Analysis of h-BN Analysis



**Figure 30.** TEM image of h-BN synthesized in the presence of lithium tetraborate at 1450°C



**Figure 31.** TEM image of h-BN synthesized in the presence of lithium tetraborate at 1450°C

Because of the deficiency of SEM images for interlayer distances, h-BN synthesized in the presence of lithium tetraborate was analyzed by TEM techniques as shown Figure 30 and 31. According to the TEM analysis, interlayer distance was calculated as 0,3471 nm, averagely. This distance is greater than the original value of h-BN.

## 5. CONCLUSION and RECOMMENDATIONS

In this study, h-BN is synthesized in the presence of borates with modified O'Connor method at different temperatures.

The FTIR results were supported that the h-BN formation with in-plane and out-of-plane vibrations.

From XRD analysis, lattice parameters and grain sizes were calculated and they were very close to the original value in literature. According to the calculated results, if the types of borates are compared, lithium borates (especially lithium tetraborate) gave the better results in grain sizes and lattice parameters.

Furthermore, when the grain size increases directly proportional with the temperature rising, so the importance of the temperature was proved in this type of reactions. According to the XRD analysis, the best intensity in the presence of lithium tetraborate was observed at 1300°C. And also, h-BN was formed as a nano rod.

In this study, borates acts as a flux agent and lithium borates gave the best results because of the more little than the other metal borates. In the h-BN synthesized with lithium tetraborate, the interlayer distance was greater than the original value. Due to this, some metal may be intercalated but this is examine by EDX. Besides, other properties of h-BN synthesized with lithium tetraborate will be investigated.

## REFERENCES

- Anonymous-From Wikipedia, The Free Encyclopedia, Transmission Electron Microscopy, [http://en.wikipedia.org/wiki/Transmission\\_electron\\_microscopy](http://en.wikipedia.org/wiki/Transmission_electron_microscopy), 29 May 2015.
- Balmain W H (1842) "Bemerkungen über die Bildung von Verbindungen des Bors und Siliciums mit Stickstoff und gewissen Metallen", *J Prakt Chem.*, 27: 422- 430.
- Budak E (1999), The Synthesis and Modification of Hexagonal Boron Nitride, MSc Thesis, Abant Izzet Baysal University Graduate School of Natural and Applied Sciences, Bolu.
- Budak E and Bozkurt Ç (2004) "The Effect of Transition Metals on The Structure of h-BN Intercalation Compounds", *J. Solid State Chem.*, 177: 1768-1770.
- Budak E (2009), Comparison of The Effect of Representative Metal and Transition Metal Salts on The Formation of Hexagonal Boron Nitride, PhD Thesis, Abant Izzet Baysal University Graduate School of Natural and Applied Sciences, Bolu.
- Chen L, Huang M, Luo T, Gu Y, Shi L, Yang Z, and Qian Y (2004) "A Low-Temperature Route to Nanocrystalline Boron Nitride Whiskers and Flakes", *Mater Lett.*, 58 (27- 28): 3634-3636.
- Chen L, Gu Y, Li Z, Qian Y, Yang Z, and Ma J (2005) "Low- Temperature Synthesis and Benzene-Thermal Growth of Nanocrystalline Boron Nitride", *J Cryst Growth*, 273: 646- 650.
- Haubner R, Wilhelm M, Weissenbacher R, and Lux B (2002) *Boron Nitrides- Properties, Synthesis and Applications High Performance Non- Oxide Ceramics II*", Springer Berlin / Heidelberg.
- Hubacek M, Sato T, and Ishii T (1994) "A Coexistence of Boron Nitride and Boric Oxide", *J Solid State Chem.*, 109: 384– 390.
- Hubacek M and Ueki M (1996) "Orientation and Grain Growth in Copper- Activated Hot-Pressed Hexagonal Boron Nitride", *J Am Ceram Soc.*, 79 (1): 283-285.
- Hubacek M, Sato T, and Ueki M (1997) "Copper - Boron Nitride Interaction in Hot-Pressed Ceramics", *J. Mater. Res.*, 12 (1): 113-118.
- Kumashiro Y (2000) *Electric Refractory Materials*, Marcel Dekker Incorporated, New York.

Mishima O and Era K (2000) Science and Technology of Boron Nitride In: Kumashiro, Y. (ed.): Electric Refractory Materials. 498., Mercel Dekker Incorporated, New York, USA.

O'Connor (1962) "Synthesis of Boron Nitride", J Am Chem Soc., 84: 1753- 1754.

Pierson H O (1996) Handbook of Refractory Carbides and Nitrides, Covalent Nitrides: Composition and Structure, 213- 214, Noyes Publications, New Jersey, USA.

Swapp S (2015) University of Wyoming Scanning Electron Microscopy (SEM), [http://serc.carleton.edu/research\\_education/geochemsheets/techniques/SEM.html](http://serc.carleton.edu/research_education/geochemsheets/techniques/SEM.html), 29 May 2015.

Yu J, Qin L, Hao Y, Kuang S, Bai X, Chong Y, Zhang W and Wang E (2010) "Vertically Aligned Boron Nitride Nanosheets: Chemical Vapor Synthesis, Ultraviolet Light Emission, and Superhydrophobicity", ACS Nano, 414-422.

Yücel N (2005), Effect of Metal Carbonyls on The Formation of Hexagonal Boron Nitride, MSc Thesis, Abant Izzet Baysal University Graduate School of Natural and Applied Sciences, Bolu.

Zhu M, Wang J, Holloway B, Outlaw R, Zhao X, Hou K, Shutthanandan V, Manos D (2007) "A Mechanism for Carbon Nanosheet Formation", Elsevier, Carbon 45: 2229–2234.

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