BOLU ABANT IZZET BAYSAL UNIVERSITY
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
DEPARTMENT OF CHEMISTRY

LOW TEMPERATURE BORON CARBIDE SYNTHESIS

DEGREE OF MASTER OF SCIENCE IN THE DEPARTMENT OF CHEMISTRY

SERDAR HİZARCİ

BOLU, JANUARY 2019

APPROVAL OF THE THESIS

LOW TEMPERATURE BORON CARBIDE SYNTHESIS submitted by SERDAR HİZARCİ in partial fulfillment of the requirements for the degree of **Master of Science** in **Department of Chemistry, The Graduate School of Natural and Applied Sciences of BOLU ABANT IZZET BAYSAL UNIVERSITY in 18/01/2019** by

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To my family

I would like to thank my mother, my father, my brother and all my friends, for

supporting me all the time.

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.

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ABSTRACT

LOW TEMPERATURE BORON CARBIDE SYNTHESIS

MSC THESIS
SERDAR HİZARCİ
BOLU ABANT IZZET BAYSAL UNIVERSITY GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
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(SUPERVISOR: ASSIST.PROF.DR. ERHAN BUDAK)

BOLU, JANUARY 2019

Boron carbide (B_4C), the third hardest material in the World, was synthesized by carbothermic reduction reaction. Advanced ceramic B_4C synthesis was performed by recyclable of agricultural wastes. Three different methods were applied in this study and the synthesis reactions were carried out under air, nitrogen, and argon gas atmosphere. In the first method, different amount of unprocessed nut shells and boron oxide mixture were heated at between 1000-1250 °C. In the second method, nut shells were carbonized by leaching in sulfuric for one week. Different amount of carbonized shells and boric acid were mixed and heated at between 1300-1450 °C. Finally, in the third method, activated charcoal was obtained from shells. B_4C was synthesized by mixture of activated carbon and boric acid with different ratios at between 1400-1450 °C. After synthesis process, the obtained products were purified by classical hydrochloric acid treatment. The obtained B_4C products were characterized by FTIR, XRD, and SEM analysis.

KEYWORDS: Solid state, Carbothermic reduction, Advanced ceramic, Characterization, Agricaltural waste.

ÖZET

DÜŞÜK SICAKLIKTA BOR KARBÜR SENTEZİ
YÜKSEK LİSANS TEZİ
SERDAR HİZARCİ
BOLU ABANT İZZET BAYSAL ÜNİVERSİTESİ
FEN BİLİMLERİ ENSTİTÜSÜ
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(TEZ DANIŞMANI: DR. ÖĞR.ÜYESİ ERHAN BUDAK)

BOLU, OCAK - 2019

Dünyanın en sert üçüncü malzemesi olan bor karbür (B_4C), karbotermik indirgeme reaksiyonu kullanılarak sentezlenmiştir. İleri seramik mazlemesi olan B_4C sentezi, tarımsal atıkların tekrardan kullanılması ile denenmiştir. Bu çalışmada üç farklı method uygulanmıştır ve sentezlere hava, azot, ve argon gazı atmosferlerinde çalışılmıştır. Birinci metotta B_4C, farklı miktarlardaki işlem görmemiş kabuklar ve bor oksit karıştırılarak 1000-1250 °C arasında ısıtılarak sentezlenmiştir. İkinci metotta; kabuklar sülfirik asit içerisinde bir hafta bekletilerek karbonizasyon sağlanmıştır. Karbonize kabuklar ve borik asit farklı oranlarda karıştırılıp 1300-1450 °C arasında ısıtılarak B_4C sentezlenmiştir. Son olarak üçüncü metotta, kabuklardan aktif karbon edilmiştir. Aktif karbon tekrar borik asit ile farklı oranlarda karıştırılarak 1400-1450 °C sıcaklıklar arasında sentezlenmiştir. Elde edilen örnekler klasik hidroklorik asit ile saflaştırılnıştır. Elde edilen bor karbür ürünleri FTIR, XRD ve SEM analizleri kullanılarak karakterize edilmiştir.

ANAHTAR KELİMELER: Katı hal, Karbotermik indirgenme, İleri seramik, Karakterizasyon, Tarımsal atık.

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LIST OF ABBREVIATIONS AND SYMBOLS

rB_4C : rhombohedral boron carbide

h.s : hazelnut shells

w.s : walnut shells

a.c : activated charcoal

BN : boron nitride

hBN : hexagonal boron nitride

FTIR : Fourier Transform Infrared

XRD : X-Ray Diffractometer

SEM : Scanning Electron Microscopy

atm : atmosphere

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1. INTRODUCTION

1.1 Knowledge and History of Boron

“Boron” name comes from Buraq / Baurach in Arabic and Burah in Persian. It was obtained by heating the boron oxide with potassium by Gay-Lussac and Jacques Thenard and Sir Humphry Davy in 1808. Boron is the first and the lightest member of group III and it is a typical metalloid with semiconductor property. The basic state electonic configuration is $1s^2 2s^2 2p^1$. It is commonly found in the earth, rocks, and waters. ^{8}B, ^{10}B, ^{11}B, ^{12}B, and ^{13}B are typical isotopes of boron. The most stable isotopes are ^{10}B and ^{11}B with the natural abundance approx. 19% and 79%, respectively. Also, ^{10}B isotope exhibits high neutron capture property, so it can be used in nuclear materials and nuclear power plants. In addition, it was claimed that living things evolved in the presence of boron.

Boron compounds, especially borax, have been used for more than thousand years by ancient Greek, ancient Egypt, and Babylon for melting valuable jewels, for cleaning, curing illness and mummifying. It is known that boron salts were the first used in Tibet four thousand years ago. While Babylonians used boron salts for melting valuable jewelry, Egyptians used in the mummifying and ancient Greeks and Romans used for the cleaning of the arena. In 875, the Arabs has been made drugs from boron salts for the first time. The modern boron industry began in the 13th century by Marco Polo from Tibet to Europe.

1.2 Boron Developments

Important boron dates in the World and Turkey:

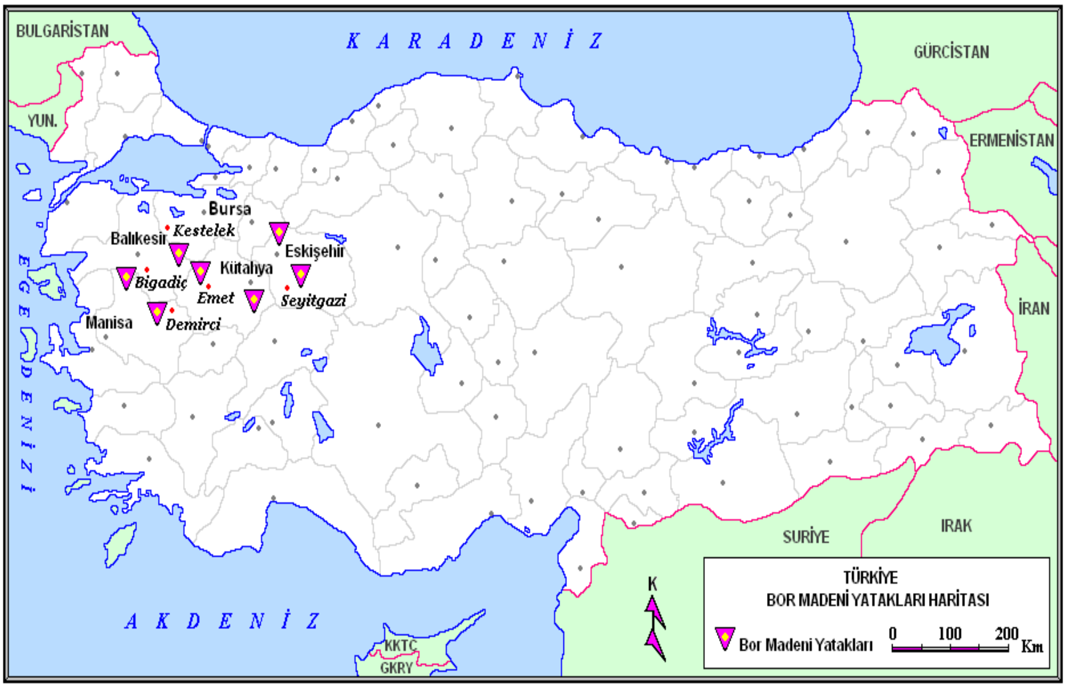
- In 1830, First boric acid production in Italy.
- In 1852, The first commercial boron mine business in Chile.
- In 1861, The First Ottoman Mining Law.

- In 1864, First commercial boron production in California.
- In 1865, in Aziziye / Susurluk (Balıkesir, Turkey), the right of operate of calcium borate (pandermite) was given to Compaigne Industrielle Desmazures, and thus the first boron mining in Anatolia.
- In 1872, The first ulexite ore was found in Nevada and California and production started.
- In 1881, The discovery of Borax reserves in Death Valley.
- In 1887, Sultançayır (Balıkesir, Turkey) reserves commissioning by the company of Charles Hanson & Co.
- In 1913, The presence of Kramer boron deposits (USA).
- In 1935, in Turkey, the establishment of Eti Bank and Mineral Exploration institutions for the purpose of mining exploration and to do their operating activities.
- In 1954, Sultançayır Mine was closed.
- In 1958, production of the first ore from Etibank Emet (Kütahya, Turkey) deposits
- In 1959, Turkey's first ore export.
- In 1960, the Kırka (Eskişehir, Turkey) Sodium Borate deposits were determined by Türk Boraks Madencilik A.Ş. and Turkish partners.
- In 1968, with the decision of the Council of Ministers, all mineral exploration and operation rights of Turkish Boraks Mining Inc. were transferred to Etibank.
- In 1975, the commissioning of Bandırma (Balıkesir, Turkey) Sodium Perborate Plant.
- In 1978, with the law no. 2172, all mining and operating rights of Boron reserves were granted to Etibank.
- In 2003, the establishment of the National Boron Research Institute (BOREN).

1.3 Boron and Turkey

The diversity of the underground, the use of these riches and the variety of products they produce by using these riches, enables the development of societies. Therefore, it is extremely important for our country to take maximum advantage of the boron mines which are of great importance. Sometimes countries are potentially advantageous because of their natural wealth. From this point of boron minerals it has a great importance as much as Turkey's geographical location and so is also a strategic mineral. The most important boron producers in the world; Eti Maden (Turkey) and Rio Tinto (USA). These two institutions meet 70% of world boron production.

Today Turkey has the largest boron ore reserve in the World, Figure 1. Its is located in Eskişehir-Kütahya-Balıkesir regions,Turkey (**Figure 1.1**). Approximately 953.000 tons bor reserve presence in our country (National Boron Research Institute (BOREN)). However, the production of "specialty boron chemicals" which is very important for industrial applications is very low. USA and NATO declared that the boron and its compouns are strategically important material in 1961.



Kaynak: MTA

R. SAYGILI 2010

Figure 1.1. Boron reserves in Turkey

1.4 Boron and Its compounds Usage Area

Glass Industry: Boron Silicate Glass, Isolated Glass Fiber, Textile Glass Fibers, Optical Fibers, Glass Ceramics, Bottles and Other Flat Glasses,

Ceramic Industry: Glaze Porcelain Paints and Enamel etc.

Nuclear Industry: Reactor Control Bars, Security Purpose in Nuclear Accidents and Nuclear Waste Storage,

In Space and Aviation Industry: Resistant to Friction-Wear and Heat Materials, Rocket Fuels

Military and Armored Vehicles: Armor Plates etc.

Electronics - Electrical and Computer Industry: Micro chips, CD-Drives, Computer Networks; Heat and Abrasion Durable Fiber Optic Cables, Semiconductors, Vacuum Tubes, Dielectric Materials, Electric Capacitors, Delayed Fuses, etc.

Communication Tools: Mobile Phones, Televisions, etc.

Construction Area (Cement Sector): For Strengthening and Isolation purposes

Metallurgy: Stainless and Alloy Steel, Anti-Friction against Wear Resistant Materials, Metallurgical Flux, Refractories, Briquette Materials, Soldering, Casting Materials as Additives, Cutters and so on.

Energy Sector: Solar Energy Storage and Solar Cells as preservatives etc.

Automobile Industry: Air Cushions, Hydraulics, Plastic Parts, In antifreeze to provide heat and insulation in oils and metal parts etc.

Textile Industry: Heat Resistant Fabrics, Fire Retardant and Preventive Cellulosic Materials, Insulation Materials, Textile Dyes Leather Colorants, Artificial Silk Polishing Materials, etc.

Pharmaceutical and Cosmetic Industry: Disinfectants, Antiseptics, Dental Putties, etc.

1.5 Boron Carbide

Boron carbide which is one of the specialty boron compounds, is a kind of non-oxide advanced ceramic and it is called black diamond with the formula of B_4C (Thevenot, 1990; Lipp, 1966). It is highly refractory material with excellent properties that are extreme hardness (Vicker / Mohs scale: 29,1 GPa), chemical inertness, high melting point (2450 °C), low weight, outstanding electro-conductivity (9.2 mho), low density (2,52 g /cm^3), high neutron absorption cross-section (3850 barn), and high temperature thermoelectric properties. It is also used as producing containers for keeping acids and high corrosive chemicals. Black diamond is the third hardest material after diamond and cubic boron nitride (Zhang, 1999; Subramanian, 2008; Goulden, 1958; Haighton, 1958; Goldstein, 2001; Hampson, 1969; Scott, 1964; Bauccio, 1994; Murthy, 1985; Jung, 2004; Matkovich, 1977). This combination of properties makes boron carbide a strong applicant for many high-tech applications and in different industry (Amberger, 1981; Lee, 1998). The combination of low specific weight, high hardness, and impact resistance makes it a suitable material as body and vehicle armor (Chen, 2006; Lee, 2004). Its high-temperature stability, it considered as a good candidate material for high-temperature thermoelectric converter, semiconductor, and thermocouples functioning at the temperature as high as 2200 °C (Fathi, 2012). Also, its outstanding hardness makes it suitable abrasive powder for lapping, polishing, and water jet cutting of metals and ceramic materials (Khanra, 2007). Its usage as sintered finding wide applications in sand blasting nozzles, ceramic bearing, and wire drawing dies. Black diamond uses as a rocket propellant due to its capacity to generate an intense amount of heat when combined with oxygen (Andrew, 1970; Bose, 1986; Bilsby, 1990). Moreover, it's also p-type semiconductor as a potential candidate material for electronic devices.

The other important usage is treatment of cancer by neutron capture therapy (Mortensen, 2006; Sasaki, 2005; Lee, 1992).

1.6 Boron Carbide History

At the end of the nineteenth century black diamond was produced and identified, and it is remained a laboratory curiosity for many years. First synthesis was made by Henri Moissan in 1899. The composition and structure were determined as a trial in 1934. Until the end of World War II, it was not that the primer large applications were improved in nuclear industry. In 1994, synthesis was predicted to reach $40 million (Jayakumar, 2012).

1.7 Crystal Structure of Boron Carbide

The bond between B-C and B-B atoms gives actual knowledge for understanding, describing and characteristic property of boron carbide. The main structure is 12-atoms icosahedra placed at the vertices of rhombohedral lattice of trigonal symmetry (**Figure 1.2**).

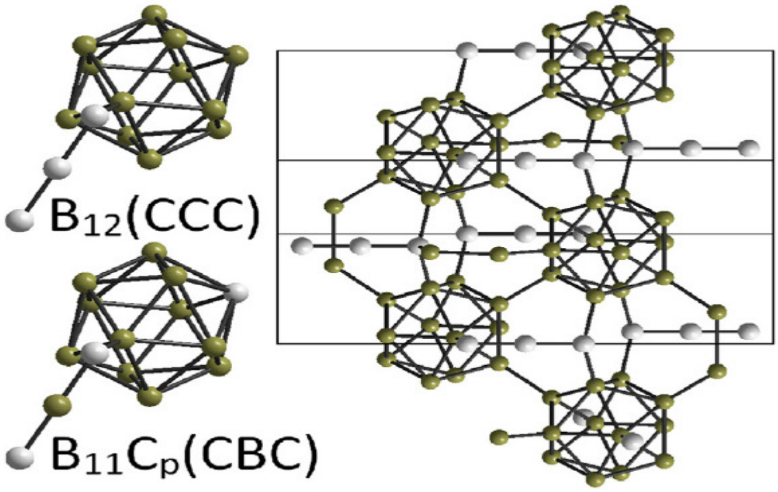


Figure 1.2. Some consequences of boron and carbon atoms.

The 3-atom linear chains that link the icosahedra along the (111) rhombohedral axis to form crystal structure, as 3D shown in **Figure 1.3** (Suri, 2012).

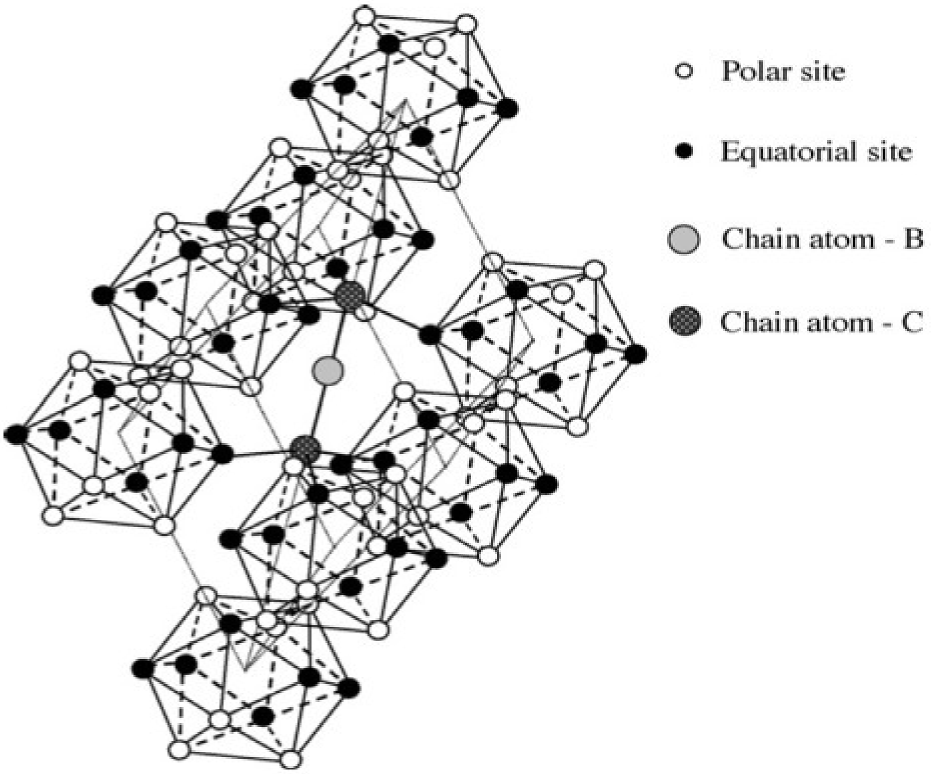


Figure 1.3. 3D Crystal structure of boron carbide with rhombohedral unit cell

Commonly icosahedra consist of 1 carbon atom and 11 boron atoms. In $B_{11}C$ structure, C atom placed in a polar site and in a few percent $B_{10}C_2$ structure or B_{12} structure, two carbon atoms placed in two antipolar sites. The presence of elemental boron lets to form caged structures of variety sizes in boron carbide; two pentagonal pyramids which bonded together describe the icosahedra in boron carbide (Jemmis, 1999). C-B-C is presence in the longest diagonal of the rhombohedral unit cell. Each the end atoms of the chain are bonded covalently (**Figure 1.4**).

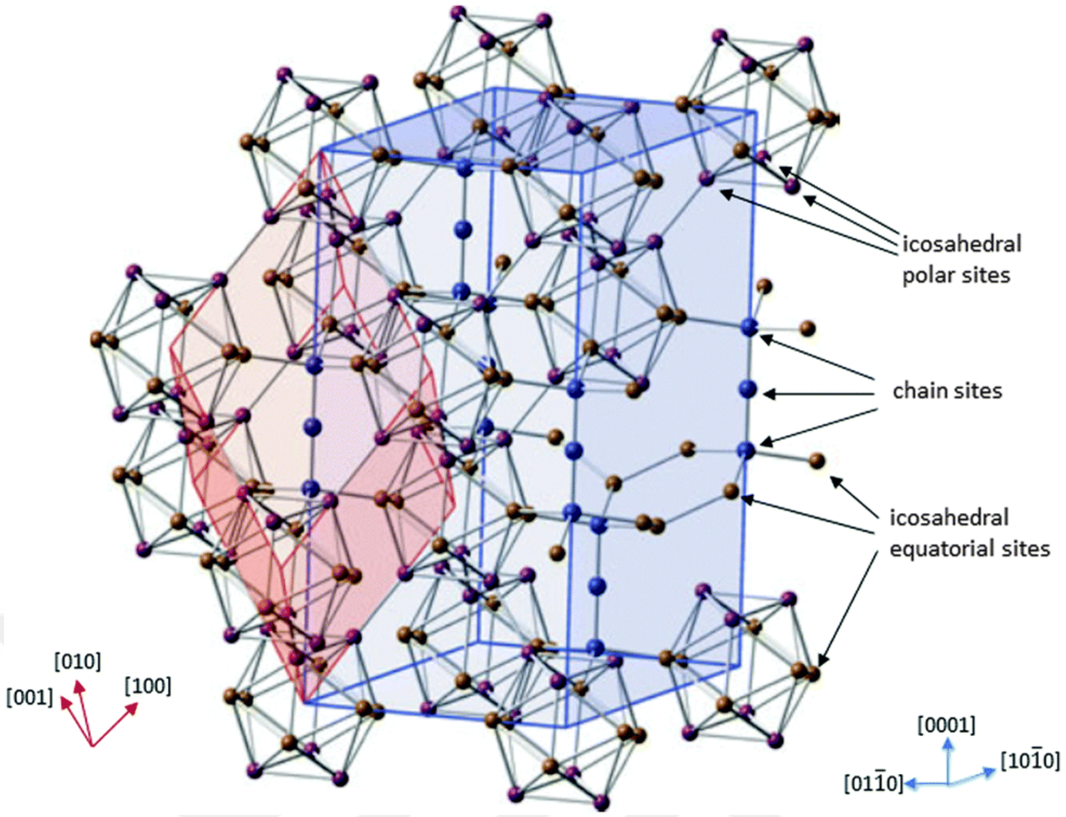


Figure 1.4. Correlation of boron carbide with hexagonal(blue) and rhombohedral (red) unit cells.

C-B-C, C-B-B, and B-B-B are prescribed types of three-atom chain. Variation of distribution of these chains depends on carbon concentration. Structure of B_4C, consist $B_{11}C$ and the chain is C-B-C when the carbon ratio is 20%. For carbon rich composition (20%), the structure is stable but at 13.33% C composition B_{12} / C-B-C structure was found as most stable (Mauri, 2001).

Depending on carbon content: density, electrical and thermal conductivity, hardness, heat capacity, charge carrier property, etc. of boron carbide changes.

1.8 Boron Carbide Synthesis Methods

Boron carbide is produced by carbothermic reaction by Moissan in 1899. In the carbothermic reaction, the mixture of boric acid or boron oxide, and carbon powder is heated under inert atmosphere. Advantages of this method is economic and availability of raw materials, so it is suitable for commercial production. General reaction is summarized as:

$$4\ H_3BO_3 + 7\ C \rightarrow B_4C + 6\ CO + 6\ H_2O$$

Reaction steps are dehydration of boric acid to boron oxide, reduction of boron oxide to elemental boron by CO_2, reaction of carbon and elemental boron to obtain B_4C respectively (Goller, 1996). On the other hand, there are few production methods such as magnesiothermic reduction reaction, synthesis from elements (but high cost of elemental boron), vapor phase synthesis, synthesis from polymer precursors, liquid phase reaction, ion beam synthesis, and vapor liquid solid growth (Suri, 2012).

According to A. Alizadeh, boric acid, activated carbon or petroleum coke were heated up with different ratios at 1400-1550 °C under Argon gas medium. The carbothermic reduction reaction was an economic process, so the carbothermic process was chosen and they were obtained boron carbide powder in different temperature and holding time. Boron carbide powder was not performed when the heating temperature was as low as 1400 ^{o}C (Alizadeh, 2004).

In a typical polymer precursor study was made by S. Mondal, polyvinyl alcohol and boric acid were used to obtain boron carbide. Polymer precursor materials are preferable and convenient for laboratory conditions because of alternative to high temperature reaction methods at the present time. Firstly, white floppy and rubbery material was obtained as a precursor. Pyrolysis of precursor was done and then boron carbide was obtained during the pyrolysis (Mondal, 2005).

Potassium carbonate and ferric chloride as a supporting material were examined for the catalyst effect on the formation of boron carbide. The removal of residual free carbon has been analyzed. The reaction was common carbothermic reduction reaction. Boron carbide was formed at 1625 °C (Krishnarao, 2010).

In different precursor study, hexagonal boron nitride (hBN) and carbon black were used as the precursor. Improvement of polymer precursor has significant interest for the producing of ceramic materials at lower temperatures. The specimen was milled in ethanol for twenty-four hours and then dried at 75 °C. Dried specimen fired at 1900 °C for 5 hr. Boron carbide were found as 100 nm powder (Zeng, 2010).

Boric oxide and sucrose were used in order to formation of gel precursor by Trinadha Raja Pilladi from India, besides, the reaction was done at 1773 K for 3 hours under Argon gas atmosphere. The main reaction of this study shown as;

$$24\ B_2O_3 + 7\ C_{12}H_{22}O_{11} \rightarrow 12\ B_4C + 72\ CO + 77\ H_2O \quad (1)$$

$$2\ B_2O_3 + 7\ C \rightarrow B_4C + 6\ CO \quad (2)$$

The reaction was taken place in molybdenum resistance furnace at 1773 K (Pilladi, 2013).

Besides, morphology of boron carbide was investigated with carbothermic reduction reaction. Ceramic powders have been preferred with various morphology like fiber, nanowire, whisker, prisms, rods which are reinforcements for ceramic composites. B_4C was synthesized with typical carbothermic reaction in order to observe the effects of heat treatment. Specimens in different ratios were heated by using boron oxide and carbon black at 1450 °C, 1550 °C, and 1650 °C, respectively. (Kobayashi, 2013)

One of the carbothermic study was done by Paviter Singh to produce boron carbide. Boric acid, acetone, and magnesium were used as reactants. Acetone and magnesium were used as the carbon source and the reducing agent, respectively. Hexagonal boron carbide was obtained according to ICDD card no.75-0424 (Singh, 2014).

Celalettin Ergun obtained B_4C by using boric acid, sugar, and sulfuric acid as starting materials. They had adjusted starting materials so that the B to C ratio was equal 1. Firstly, dehydration of sugar was taken place, moreover, C was obtained as the carbon source. Finally formed black material, had heated up at different temperature periods from 400 °C to 1600 °C (Ergun, 2015).

Furthermore, self-propagating high temperature (SHS) method was suitable for the magnesiothermic reduction reaction despite has disadvantage which products contaminated with $MgBr_2$, and Mg. In the other study, Nano-powder black diamond was made by SHS method. Boron oxide, Mg, and CH_2H_3Cl were used as reactants. Specimens were heated at 1700 °C (Wang, 2016).

Boron carbide was synthesized with using boric acid and lactose by Yasser M.Z. Ahmed. This reaction was typical polymer precursor process. In this study specimens were roasted at 280 °C. After this process, roasted specimens were calcined at 700 °C for 2 hr. Black diamond was obtained at 1500 °C for 3 hours under industrial Argon gas. Stoichiometric ratio was 1:1.75. They found that boron carbide according to their FTIR, XRD, and Raman spectra (Ahmed, 2017).

2. AIM AND SCOPE OF THE STUDY

Boron is an important ore for our country and future. Turkey has the largest boron reserves in the World (National Boron Research Institute (BOREN)) (**Figure 2.1**). When people especially scientist combines their knowledges with technology, we can create our own brand and become foremost country in the World. According to Globe Newswire report, the global boron carbide market is estimated to be valued at US$ 113.7 Mn in terms of value and 8,394 Tons in terms of volume by 2017 end. The global boron carbide market is expected to expand at a CAGR of 4.4% over the forecast period (2017–2027) to reach a value of US$ 174.5 Mn by 2027 end. One of the valuable boron products is, of course, boron carbide. It is known as the third hardest material and will make a great contribution to our industry (Valley Cottage, New York, Sept. 26, 2017). The aim of the current study is reducing formation temperature and production cost of boron carbide. In addition, recycling of nuts shell, to evaluate the natural agricultural waste, and to regulate the environmental pollution.

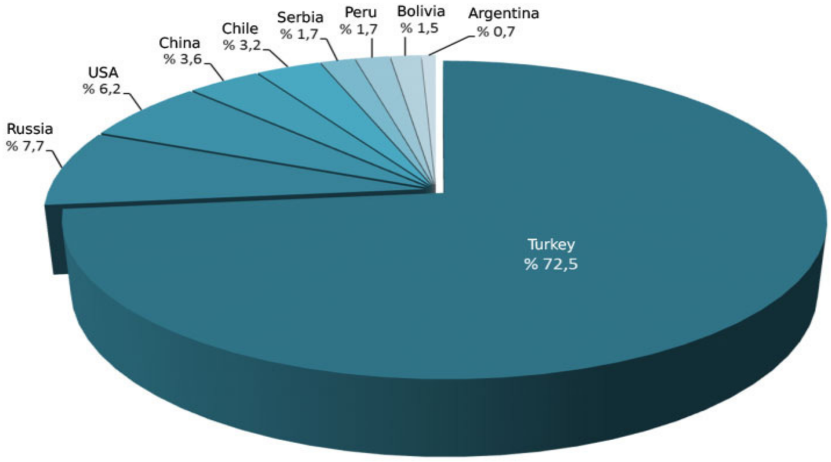


Figure 2.1. World Boron Mine Reserves

3. MATERIALS AND METHODS

3.1 MATERIALS

Boric acid was bought by Fluka AG and used without any puricification. Boron oxide was bought by Alfa Aesar and used without any purificaiton.

Nutshells were gathered from region of Bolu, Turkey. They used with some reaction.

Hydrochloric acid (37%) and sulfuric acid (95-97%) were purchased by Merck. Lithium oxide, strontium nitrate, sodium chloride and potassium carbonate were bought by Sigma Aldrich. These chemicals were used without any purification.

3.2 METHODS

This study was performed in three stages according to nutshells processes. Hazelnut shells (h.s) and walnut shells (w.s) used as a carbon source in this study:

1. Unprocessed Nutshells (Procedure I)
2. H_2SO_4 Treatment (Procedure II)
3. Activated Carbon Production (Procedure III)

Procedure I: In this method, different amounts shells and boric acid (H_3BO_3) / boron oxide (B_2O_3), boron nitride (BN), and lithium tetraborate ($Li_2B_4O_7$) were mixed and heated. All processes shown in **Table 3.1**.

Table 3.1. Unprocessed Nutshells Processes

Heating	Heat (℃)	Source of C (g)	Source of B (g)	Atmosphere	Additives (g)
Rapid and Slow	1000	1.5 h.s	1.5 B_2O_3	N_2(g)	X
Rapid and Slow	1000	1.5 w.s	1.5 B_2O_3	N_2(g)	X
Rapid and Slow	1000	0.75 a.c	0.80 B_2O_3	Air	X
Rapid and Slow	1000	2 w.s	1 B_2O_3	Air	X
Rapid and Slow	1000	3 w.s	1.5 B_2O_3	N_2(g)	X
Rapid and Slow	1000	2 h.s	1 B_2O_3	N_2(g)	Precursor
Rapid and Slow	1000	2 h.s	1 B_2O_3	N_2(g)	Precursor[1]
Rapid and Slow	1000	2 h.s	1 B_2O_3	N_2(g)	0.6 K_2CO_3
Rapid and Slow	1000	2 w.s	1 B_2O_3	N_2(g)	0.6 K_2CO_3
Rapid and Slow	1250	2 h.s	1 B_2O_3	N_2(g)	0.6 K_2CO_3
Rapid and Slow	1000	3 a.c	1 B_2O_3	N_2(g)	X
Rapid and Slow	1000	3 a.c	1 B_2O_3	N_2(g)	0.5 K_2CO_3
Rapid and Slow	1000	2 a.c	1 BN	Air	X
Rapid and Slow	1350	0.5 a.c	1.5 B_2O_3	N_2(g)	0.5 K_2CO_3
Rapid and Slow	1350	0.5 a.c	1.5 B_2O_3	N_2(g)	X
Rapid and Slow	1000	1 a.c	1 $Li_2B_4O_7$	N_2(g)	in toluene
Rapid and Slow	1000	0.5 a.c	1 $Li_2B_4O_7$	N_2(g)	in toluene
Rapid and Slow	1200	2 a.c	1 B_2O_3	N_2(g)	in toluene
Rapid and Slow	1200	3 a.c	1 B_2O_3	N_2(g)	in toluene
Rapid and Slow	1400	0.5 a.c	1.75 H_3BO_3	N_2(g)	X
Rapid and Slow	1400	0.5 a.c	1.65 H_3BO_3	N_2(g)	X
Rapid and Slow	1400	1.75 a.c	0.5 H_3BO_3	N_2(g)	X
Rapid and Slow	1400	1.65 a.c	0.5 H_3BO_3	N_2(g)	X

(h.s: hazelnut shell, w.s: walnut shell, a.c: activated.charcoal)

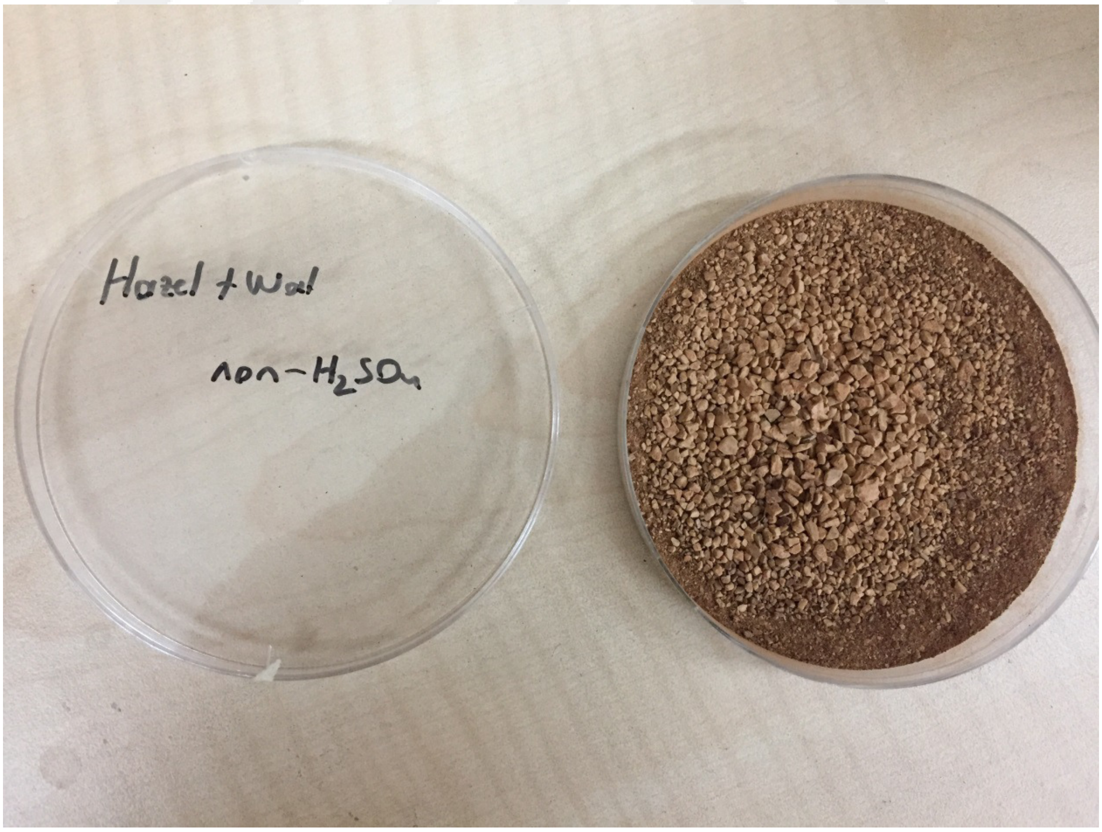


Figure 3.1. Unprocessed Nutshells

Procedure II: The shells were kept in concentrated sulfuric acid for about 1 week. Black and slime-shaped shells were obtained and filtered with the help of glass wool (**Figure 3.2**)**.** There was presence of sulfates and they were eliminated with the help of hot pure water. 5% strontium nitrate solution was used to control the absence of sulfates. After filtered process the product was dried (**Figure 3.3**). The charcoal product was obtained according to the IR results (Ergun, 2015) (**Figure 3.4 and 3.5**). All processes show in **Table 3.2.**

Table 3.2. H_2SO_4 Treatment Processes

Heating	Heat (℃)	Source of C (g)	Source of B (g)	Atmosphere	Additives (g)
Rapid and Slow	1450	1.5 h.s	1.5 H_3BO_3	N_2(g)	shells in H_2SO_4
Rapid and Slow	1450	1.5 w.s	1.5 H_3BO_3	N_2(g)	shells in H_2SO_4
Rapid and Slow	1450	3.5 h.s	1.5 H_3BO_3	N_2(g)	0.075 NaCl
Rapid and Slow	1450	3.5 w.s	1.5 H_3BO_3	N_2(g)	X
Rapid and Slow	1450	3.5 a.c	1.5 H_3BO_3	N_2(g)	X
Rapid and Slow	1450	3.5 h.s	1 H_3BO_3	N_2(g)	H_2SO_4 + H_2O_2
Rapid and Slow	1450	3.5 h.s	1.5 H_3BO_3	N_2(g)	H_2SO_4 + H_2O_2
Rapid and Slow	1450	3.5 h.s	1 H_3BO_3	N_2(g)	only H_2SO_4
Rapid and Slow	1450	3.5 h.s	1.5 H_3BO_3	N_2(g	only H_2SO_4
Rapid and Slow	1350	1.5 w.s	1.5 H_3BO_3	N_2(g)	only H_2SO_4
Rapid and Slow	1450	1.5 h.s	1.5 H_3BO_3	N_2(g)	only H_2SO_4
Rapid and Slow	1450	2 h.s	1.5 H_3BO_3	N_2(g)	only H_2SO_4
Rapid and Slow	1350	3.5 h.s	1.5 H_3BO_3	N_2(g)	only H_2SO_4
Rapid and Slow	1350	4.5 h.s	1.5 H_3BO_3	Ar(g)	only H_2SO_4
Rapid and Slow	1450	0.28 h.s	1 H_3BO_3	Ar(g)	0.1 NaCl
Rapid and Slow	1450	0.28 h.s	1 H_3BO_3	Ar(g)	X
Rapid and Slow	1350	1 h.s	1 H_3BO_3	Ar(g)	Li_2O & press
Rapid and Slow	1300	0.5 h.s	1 H_3BO_3	Ar(g)	Li_2O & press
Rapid and Slow	1300	0.75 h.s	1 H_3BO_3	Ar(g)	X
Rapid and Slow	1450	1 h.s	1 H_3BO_3	Ar(g)	X
Rapid and Slow	1450	0.5 a.c	1 H_3BO_3	Ar(g)	X
Rapid and Slow	1450	1 h.s	1 H_3BO_3	Ar(g)	Fe powder
Rapid and Slow	1450	1 h.s	1 H_3BO_3	Ar(g)	Fe powder
Rapid and Slow	1400	1 h.s	3.5 H_3BO_3	Ar(g)	Iranian
Rapid and Slow	1400	1 a.c	3.3 H_3BO_3	Ar(g)	Iranian
Rapid and Slow	1400	1.5 h.s	1.5 H_3BO_3	Ar(g)	Iranian
Rapid and Slow	1400	1.5 a.c	1 H_3BO_3	Ar(g)	Iranian
Rapid and Slow	1400	4.5 h.s	1 H_3BO_3	Ar(g)	Iranian
Rapid and Slow	1450	1 a.c	1 H_3BO_3	Ar(g)	Iranian
Rapid and Slow	1400	1 a.c	1 H_3BO_3	Ar(g)	Li_2O & press
Rapid and Slow	1400	1 h.s	1 H_3BO_3	Ar(g)	Li_2O & press
Rapid and Slow	1400	0.5 h.s	1 H_3BO_3	Ar(g)	only press

(h.s: hazelnut shell, w.s: walnut shell, a.c: activated.charcoal)

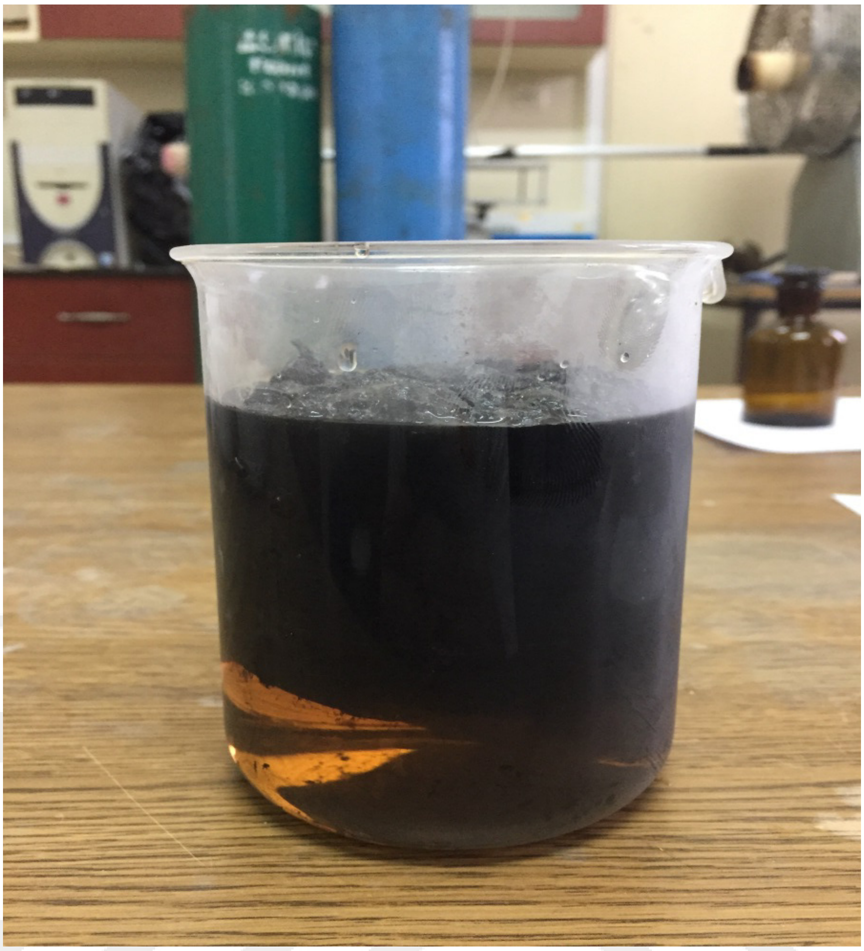


Figure 3.2. Black and slime-shaped nutshells 1

Figure 3.3. Black and slime-shaped nutshells 2

Figure 3.4. Filtered and dried carbonized nutshells 1

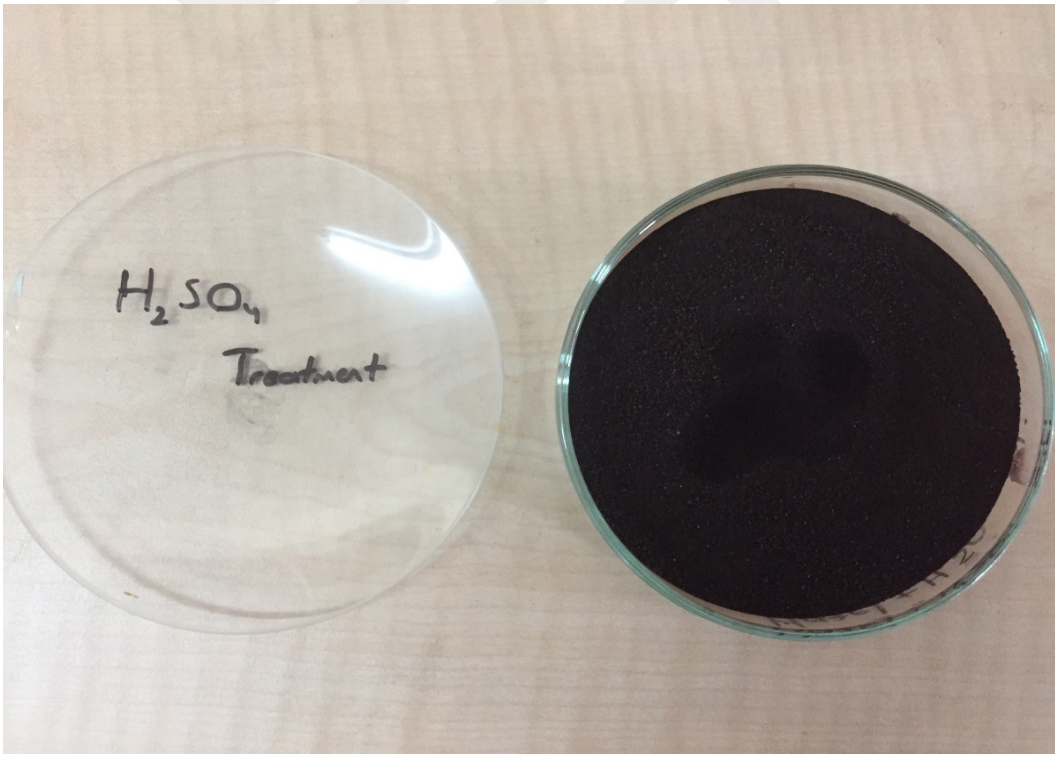


Figure 3.5. H_2SO_4 treatment process nutshells

Procedure III: The activated carbon was prepared according to A.Aygün (Aygün, 2003) (**Figure 3.6 and 3.7**). Then different amounts activated carbon and boric acid were mixed and heated. All processes show in **Table 3.3.**

Table 3.3. Activated Carbon Production Processes

Heating	Heat (℃)	Source of C (g)	Source of B (g)	Atmosphere	Additives (g)
Rapid and Slow	1400	1 h.s	1 H_3BO_3	N_2(g)	Shells in $ZnCl_2$
Rapid and Slow	1400	1 h.s	1 H_3BO_3	N_2(g)	0.0163 Li_2O
Rapid and Slow	1400	0.5 h.s	1 H_3BO_3	N_2(g)	0.0152 LiCl
Rapid and Slow	1400	0.25 h.s	1 H_3BO_3	Ar(g)	0.0101 Li_2O
Rapid and Slow	1400	0.5 h.s	1 H_3BO_3	Ar(g)	0.0170 Li_2O
Rapid and Slow	1400	0.5 h.s	2 H_3BO_3	Ar(g)	0.0237 Li_2O
Rapid and Slow	1400	0.5 h.s	2 H_3BO_3	Ar(g)	0.0204 Li_2O

Figure 3.6. Activated carbon process nutshells

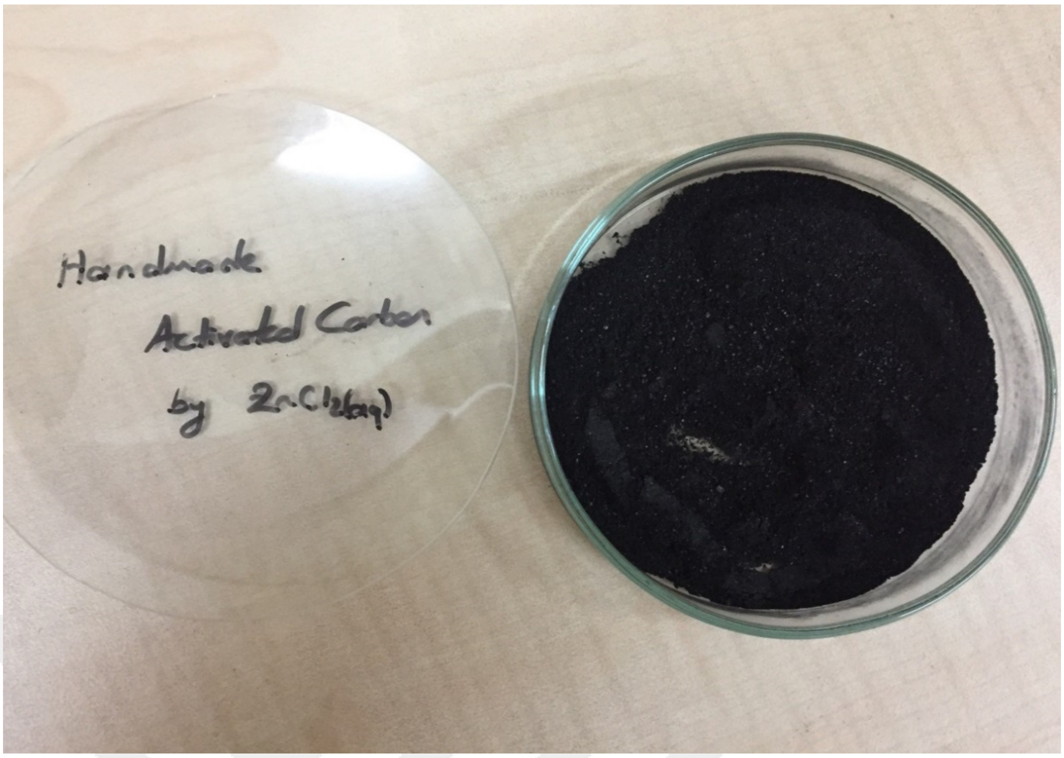


Figure 3.7. Activated carbon

All heating and cooling processes were carried out in a controlled manner in the atmosphere of inert gas (25 ml min^{-1} flow rate). After maing heating process, raw products were purified by leaching 6M HCl solutions.

3.3 INSTRUMENTS

3.3.1 Mortar and Pestle

The all samples were prepared and homogenized in mortar and pestle for 15 minutes.

Figure 3.8. Mortars and Pestles

3.3.2 Laboratory Hydraulic Press

The last part of procedure II samples and all procedure III samples were pressed with Shimadzu SSP-10A the laboratory hydraulic press.

Figure 3.9. Shimadzu SSP-10A Hydraulic Press

3.3.3 Camera Furnace

All rapid processes were heated in Protherm PLF 140/5 camera furnace. Also, precursor and precursor^{1} processes were heated in this furnace at 200^{o}C and 800^{o}C, respectively.

Figure 3.10. Protherm PLF 140/5

3.3.4 Tube Furnace

The all slow processes were heated in Protherm PTF 15/75/450 tube furnace under $N_{2(g)}$ or $Ar_{(g)}$ atmospheres.

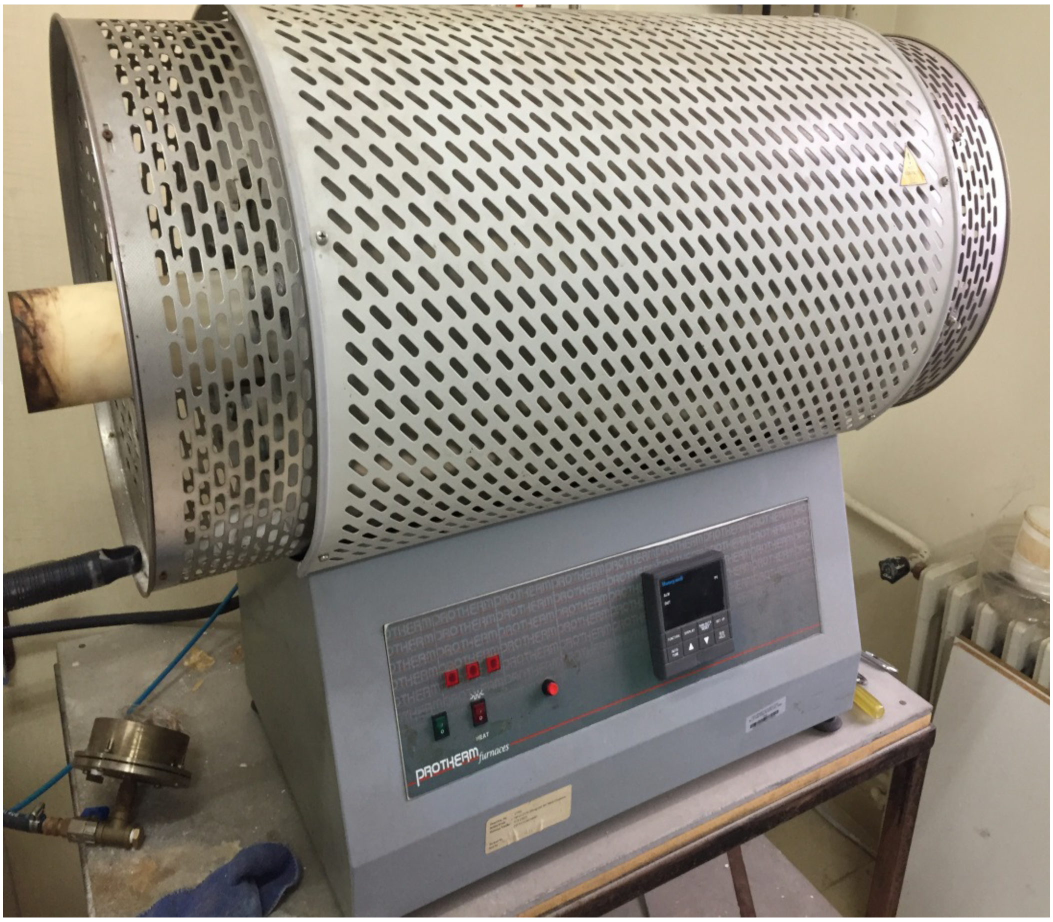


Figure 3.11. Protherm PTF 15/75/450

3.4 CHARACTERIZATION OF B_4C SAMPLES

3.4.1 FTIR Spectroscopy

Infared data of products were analyzed with the Perkin Elmer Spectrum Two IR Spectrometer which has ATR diamond accessory.

Figure 3.12. Perkin Elmer Spectrum Two IR Spectrometer

3.4.2 XRD Analysis

XRD diffractogram of rB_4C samples were analyzed with Rigaku Multiflex diffractometer using CuK_α radiation (40 kV / 30 mA, Goniometer: MultiFlex+ goniometer (with a shutter), Div Slit: ½ deg., Sct Slit: ½ deg., Rec Slit: 0.15 mm, Scan Speed: 5 deg/min., Attachment: Standard sample holder).

Figure 3.13. Rigaku Multiflex Diffractometer

3.4.3 SEM Analysis

Scanning Electron Microscope was applied for morphological examination at Research and Application Center for Scientific and Technological Researches, Düzce University (DÜBİT) by FEI Quanta FEG 250. The samples were coated with gold for 220 seconds at 4mA by using Coxem KIC-1A ION-COATER.

Figure 3.14. FEI Scanning Electron Microscope

4. RESULT AND DISCUSSION

4.1 Characterization of Nutshells by FTIR

Hazelnut and walnut shells are composed of cellulose, hemicelluloses, lignin, ash, tannins, and proteins (Sayın, 2015). In the FTIR spectrum the peak at 1550 cm^{-1} was assigned to stretching vibrations in the aromatic ring of lignin and the bands around 1550 cm^{-1} - 1700 cm^{-1} of conjugated C = O stretching, and C=C stretching of lignin while the sharp peak at 1050 cm^{-1} was labeled as the C-O-C ring skeletal vibration of halo cellulose. In addition, the peaks at 3300 cm^{-1} and 3400 cm^{-1} belong to end group of lignin O-H and N-H stretching (**Figure 4.1**). These signals were evidence for the ligno-cellulosic structures (Fan, 2012).

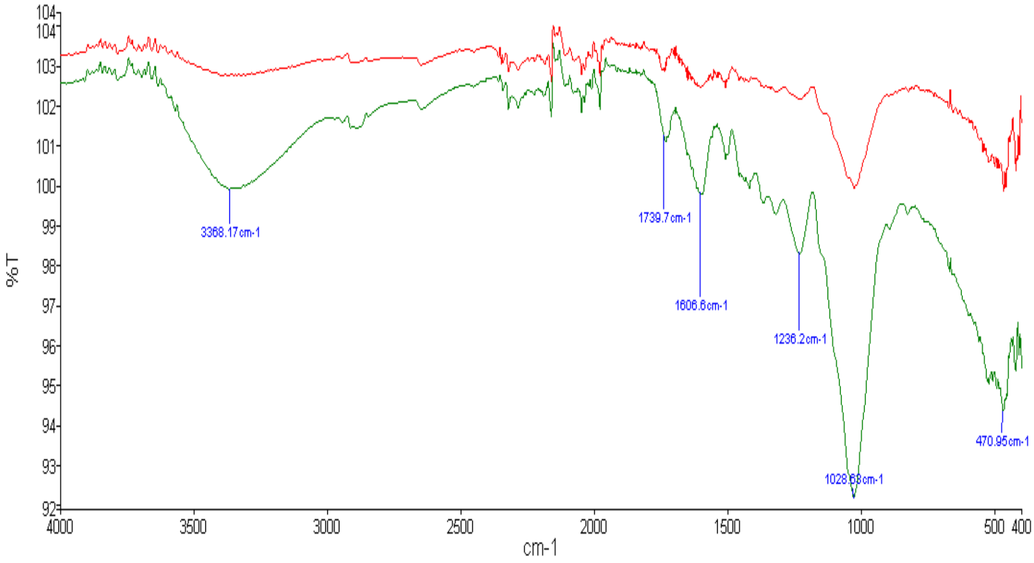


Figure 4.1. FTIR spectra of unprocessed hazelnut shell (red line), and walnut shell (green line)

After sulfuric acid treatment (the acid treatment is a kind of dehydration) of shells, the end group of lignocellulosic structures and C-O-C ring skeletal vibration are disappeared in the FTIR spectrum. However, aromatic ring of lignin was still observed (although intensity of peak decrease).

According to results it could be accepted that halo cellulose was almost transformed to graphitic carbon structure (**Figure 4.1**).

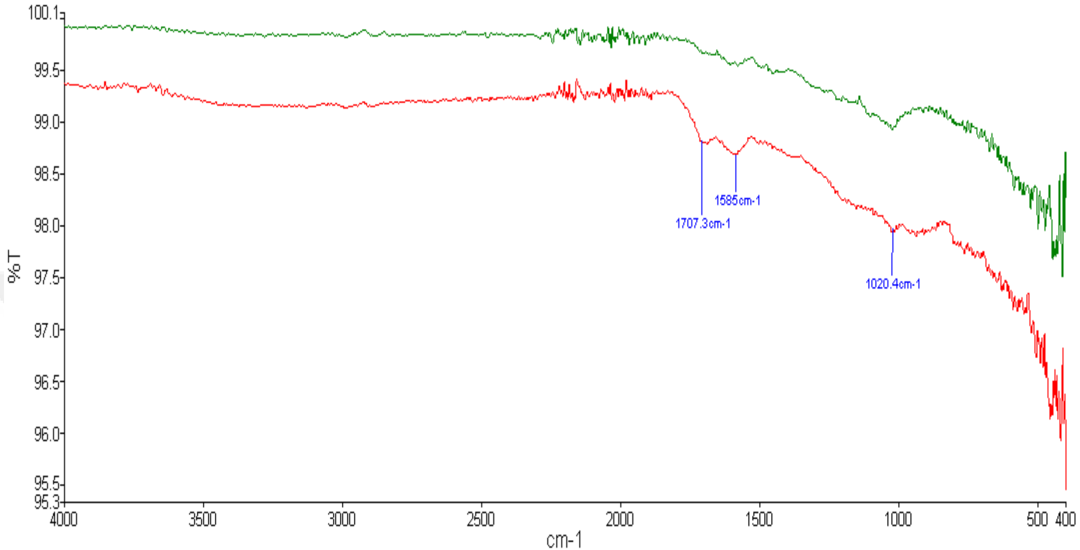


Figure 4.1. FTIR spectra of H_2SO_4 treatment of hazelnut shell (red line), and walnut shell (green line)

In the third procedure, activated carbon was synthesized using shells and they are compared with commercially obtained activated carbon (**Figure 4.2**). Hazelnut shells contain different percentage of chemical components such as 51.4% carbon, 5.95% hydrogen, 0.49% ash, and 7.7% moisture (Aygün, 2003) or 50.8% carbon, 44.4% lignin, 5.2% hydrogen, 26.9% cellulose, 28.7% hemicellulose, 8.7% moisture, 1.3% ash (Sayın, 2015).

Lignin is a polyphenolic, insoluble plant polymer, macro molecule. Generally, it contains phenolic compounds such as tar, 2,6-dimethoxy phenol, guaiacol and phenol. In addition, carbon dioxide, methane, and ethane are content of gas compounds. Lignin decomposes at the range of 280-500°C (Sayın, 2015). For this reason, shells were burned at 750 and 800°C in our study and activated carbon was obtained.

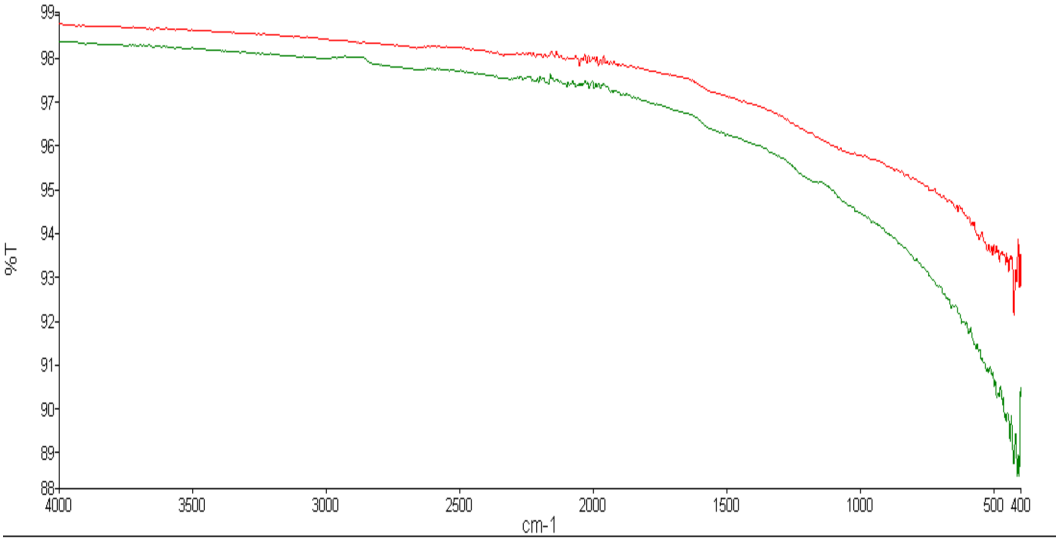


Figure 4.2. FTIR spectra of obtained activated carbon (red line), and Commercial activated charcoal (green line).

4.2 Characterization of Nutshells by XRD

XRD results indicated that the strong and weak diffraction peaks at 2θ=25° and 2θ= 45°, respectively (**Figure 4.3**). These peaks were the existence of graphite crystallite in nut shells and commercial active carbon (ICDD Card No: 48-1206) (Xie, 2014).

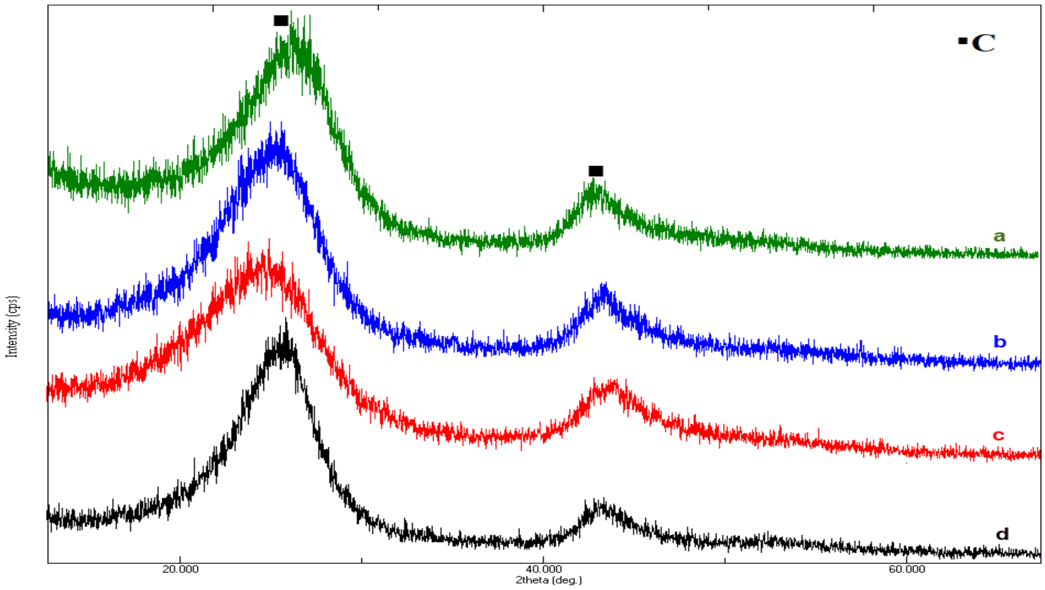


Figure 4.3. XRD pattern of synthesized activated charcoal (a–d). Hazelnut activated charcoal (a), Walnut activated charcoal (b), H_2SO_4 treated walnut shell (c), and H_2SO_4 treated hazelnut shell (d).

The diffraction peaks of hazelnut activated carbon are sharper than those activated carbon, indicating that crystallite size of nut shells active carbon is smaller. This result can be proven by the data of **Table 4.1**.

Table 4.1: Crystalline parameters of activated carbons.

Samples	a /Å	c / Å	d_{002} (nm)	d_{001} (nm)	Grain Size (nm)
Hazelnut activated charcoal	2.41	6.90	3.49	2.08	1.45
Walnut activated charcoal	2.41	6.90	3.45	2.09	1.22
H_2SO_4 treated hazelnut shell	2.40	7.10	3.55	2.08	1.11
H_2SO_4 treated walnut shell	2.41	7.10	3.55	2.08	0.99

4.3 Characterization of B_4C by FTIR

The FTIR measurements were performed to examine the types of chemical bonds of the obtained B_4C. In literature, there are several studies on B_4C characterization by FTIR (Mondal, 2005; Ergun, 2015). In the FTIR spectra the peak at 1200 cm^{-1} is labeled as B-C while the peak at 1400 cm^{-1} was assigned to B-O stretching. According to these explanations, procedure I results were given below.

2 g hazelnut shell and 1 g boron oxide were mixed and heated at 1000 °C under N_2 atmosphere (Sample I) and 3 g walnut shell and 1.5 g boron oxide were mixed in the same conditions (Sample II). But the formation of B_4C could not be observed at this temperature (**Figure 4.4**).

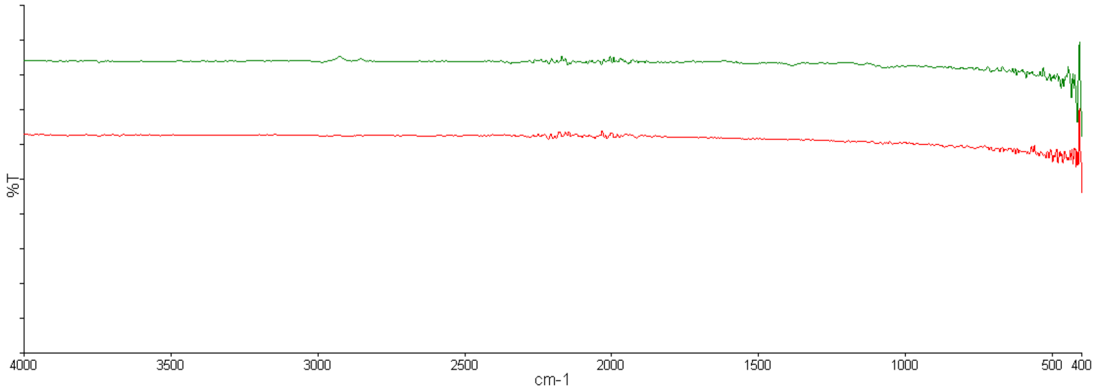


Figure 4.4. FTIR spectrum of Sample I (red line), and Sample II (green line).

Figure 4.5 indicated that the FTIR spectra of B_4C synthesised at 1200 °C with additives (Procedure I). It is known that alkaline halides decrease the amount of un-reacted raw materials and increase product during the reaction (Alizadeh, 2003). To do this, different mixtures were prepared containing 3.5 g hazelnut shells, 1 g boric acid, (sample I), 3.5 g walnut shells, 1 g boric acid, and 0.075 g NaCl (sample II), 3.5 g activated carbon, 1 g boric acid, and 0.075 g NaCl (sample III). Usage of NaCl caused to disappearing of end group O-H band but the B-C band at 1190 cm^{-1} was not detected. B-O stretching was detected at 1376 cm^{-1}. It could be said that NaCl had no effect on formation of B_4C when using procedure I.

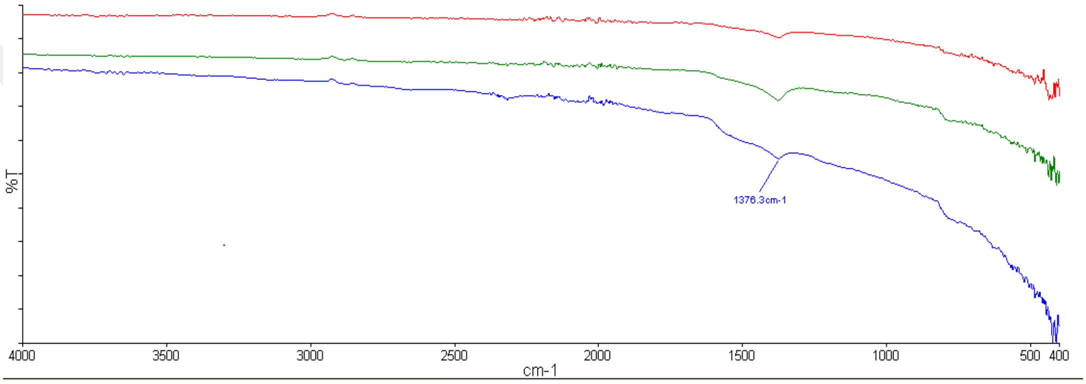


Figure 4.5. FTIR spectra of Sample I (red line) , II (green line), and III (blue line)

In procedure II, shells were traeted with sulfuric acid for carbonization of nutshells. The reaction mixtures were composed of boric acid or boron oxide, carbonizated nutshell, and different additives like Li_2O, K_2CO_3, and NaCl, and also mixture were pressed at 10 tones for 15 minutes. The additives like Li_2O, K_2CO_3, and NaCl were used as fluxing agent to reduce reaction temperature and to remove the amount of un-reacted raw materials and increase product during the reaction. These results were better than that of procedure I.

Accorging to Alizadeh and his friend's process (Alizadeh, 2003), the mixture containing 0.5 g carbonizated hazelnut shells and 1 g boric acid with and without 0.0152 g LiCl were mixed and pressed at 10 tones for 15 minutes. Then mixtures were heated at 1400 °C under argon atmosphere (heating rate 100 °C/min), (sample IV - V). Usage of LiCl gave better result than NaCl usage (procedure I). It increased the intensity of both B-C and B-O bands. In the FTIR spectra of sample IV and V

(**Figure 4.6**), two specific B_4C peaks were observed at 1200 and 1400 cm^{-1}. Also, the peak 3400 cm^{-1} was labeled as O-H.

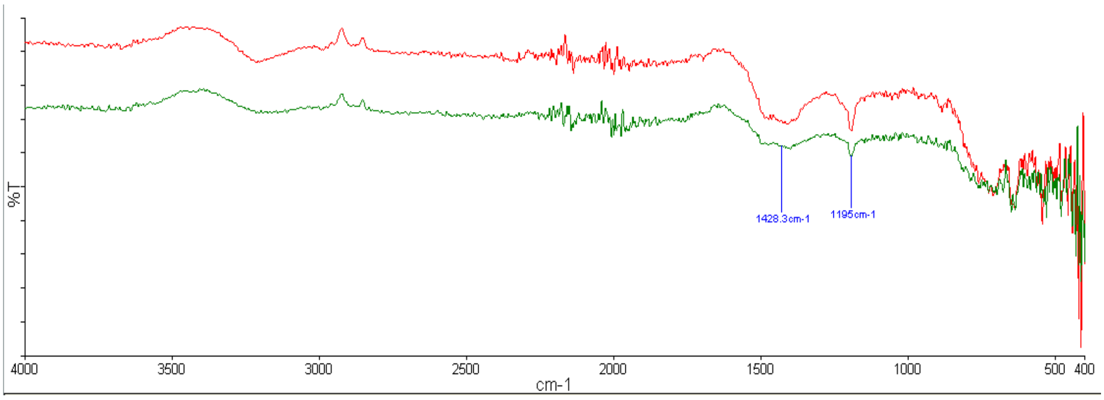


Figure 4.6. FTIR spectra of Sample IV-with LiCl (red line), and Sample V-without LiCl (green line).

In procedure III, hazelnut shells were converted to activated charcoal. The mixture was prepared by mixing of 0.25 g hazelnut shell activated charcoal, and 1.5 g boric acid (sample VI) and sample VII contained 0.25 g hazelnut shell activated charcoal, 1.5 g boric acid, and 0.01 g Li_2O.

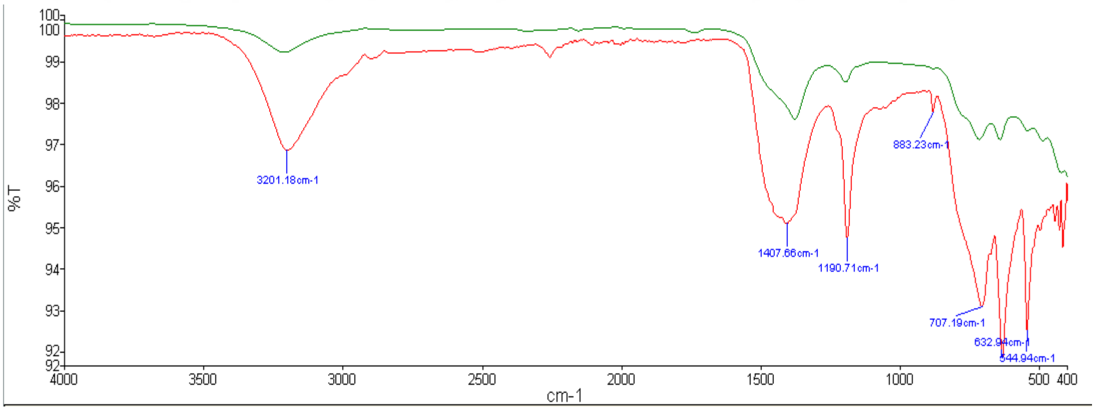


Figure 4.7. FTIR spectra of Sample VI (green line), and Sample VII (red line).

Figure 4.7 illustrated the FTIR spectra of sample VI and VII. Two typical B_4C peaks were observed at 1200 and 1400 cm^{-1} which belong to B-C and B-O stretching, respectively. When FTIR spectra of sample VI and VII were compared, it was clearly seen that peaks became sharper in the sample VII which contain Li_2O, and the peak at 883 cm^{-1} was detected as Li_2O. However, the peaks at 3200 cm^{-1} and between 500 and 700 cm^{-1} were labeled as N-H and C-O-C ring skeletal vibration, respectively. It was possibly caused by unremoved nitrogen and carbon which formed during the decomposition of hazelnut shell. Furthermore, see Appendix B.

4.4 Characterization of B_4C by XRD

X-Ray diffraction was applied for determination of B_4C crystallinity. In our study boron carbide signals were detected at 1400 °C by carbothermic reduction reaction like previously studies (Mondal, 2004; Pilladi, 2013; Ergun, 2015). However, the products prepared according to procedure I shown no significant data (**Figure 4.8**). It was probably caused by both low temperature and containing impurity in nutshells. Diffractogram was commented according to ICDD Cards no: 48-1206, 6-0297).

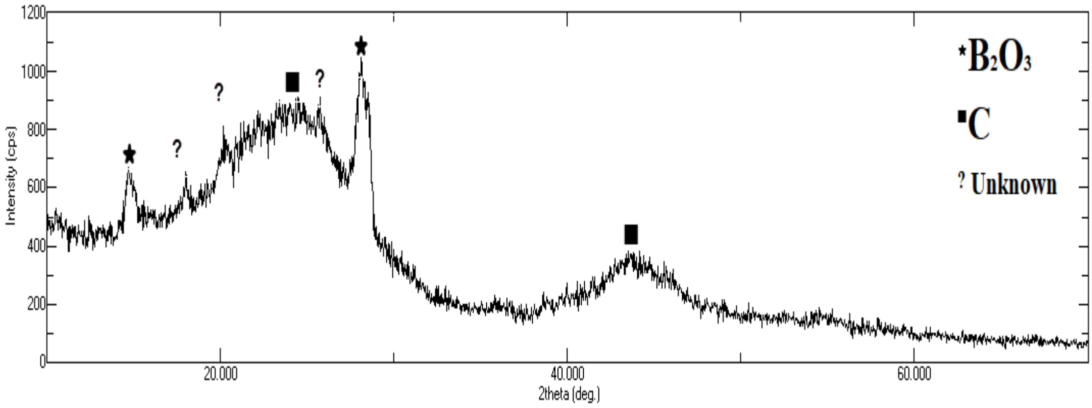


Figure 4.8. Typical XRD pattern of B_4C samples obtained by Procedure I.

In the XRD, the peaks at 2θ = 37.8° (021) and 2θ = 34.9° (104) were observed the first time at 1300 °C for hazelnut carbonized shell containing sample by Procedure II (**Figure 4.9**) (ICDD Cards No: 48-1206, 6-0297, 35-0798).

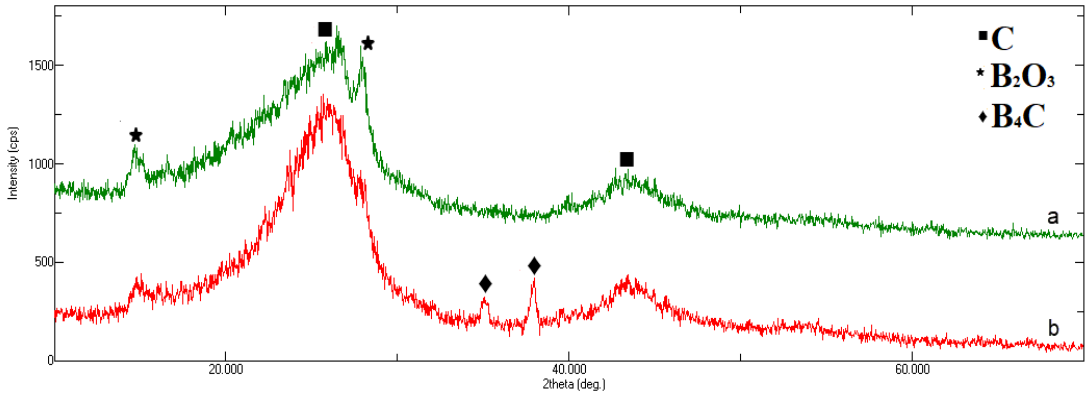


Figure 4.9. Typical XRD pattern of B_4C samples obtained by Procedure II at 1300°C.
a: H_2SO_4 treated walnut shell + boric acid mixture.
b: H_2SO_4 treated hazelnut shell + boric acid mixture.

However, there was no B_4C formation in walnut carbonized shell containing sample. It was probably caused by structure and hardness of the walnut shell (H_2SO_4 treatment time). Moreover, the presence of the peak at 2θ = 15° and 2θ = 28° (boron oxide), and 2θ = 28° (graphite) indicated that the samples contained impurities.

After observing of boron carbide XRD diffraction peaks, the synthesis temperature was increased to 1400 °C. There was an improvement in XRD peaks both hazelnut carbonized shell and walnut carbonized shell sample (**Figure 4.10**). In addition, the peak at 2θ =˜ 15° (boron oxide), and 2θ = ˜ 26° (graphite) indicated that the samples contained impurities, still (ICDD Cards No: 48-1206, 6-0297, 35-0798).

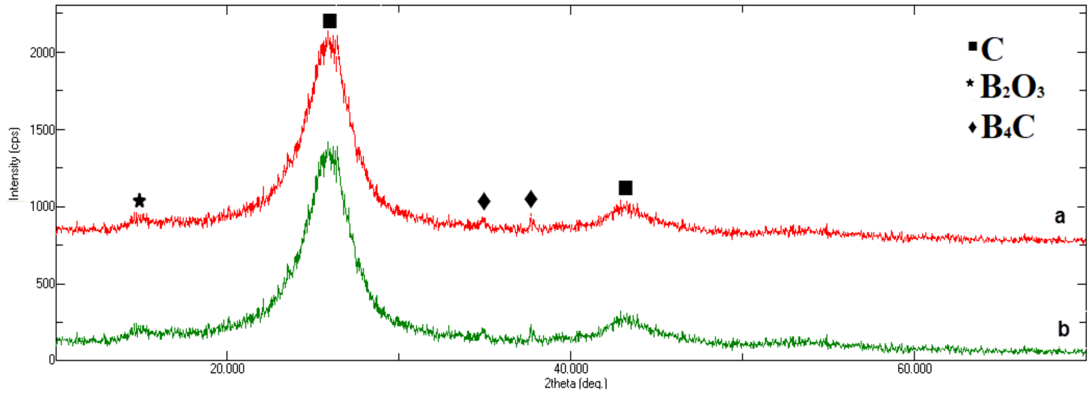


Figure 4.10. XRD pattern of B_4C samples obtained by Procedure II at 1400°C.
a: H_2SO_4 treated hazelnut shell + boric acid mixture.
b: H_2SO_4 treated walnut shell + boric acid mixture.

To remove these impurities, the samples were reheated at 800 °C. Although, amorphous carbon peak (002) intensity decreased extremely, the B_4C peaks were determined with small intensity and B_2O_3 was converted to unidentified different mixture of $B_xO_yH_z$ (**Figure 4.11**) (ICDD Cards No: 35-0798, 22-1109, 76-0746).

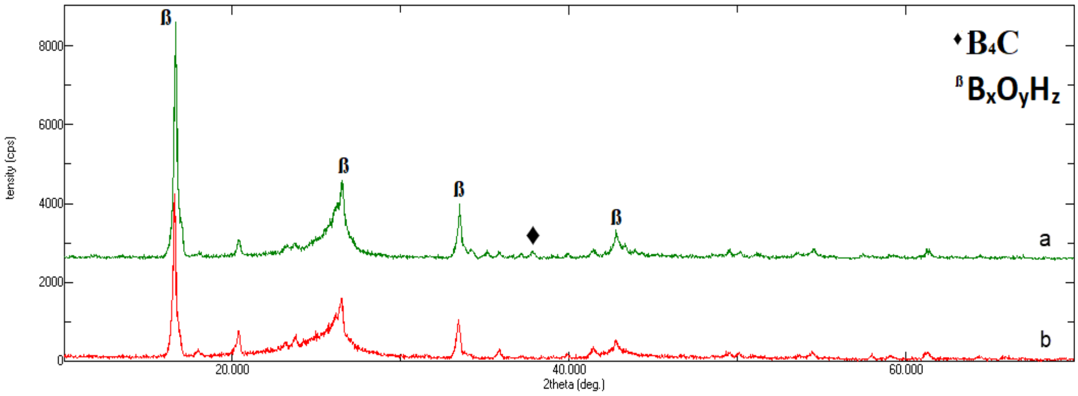


Figure 4.11. XRD pattern of reheated B_4C samples obtained by Procedure II.
a: H_2SO_4 treated hazelnut shell + boric acid mixture at 800°C.
b: H_2SO_4 treated walnut shell + boric acid mixture at 800°C.

Although the structure of both hazelnut shell and walnut shell are similar, the lignin and hemicellulose amount in walnut shell is higher than hazelnut shell. In addition, walnut shell carbonization percent is lower than hazelnut shell carbonization with the same process, so this situation affected our result. As a result, hazelnut shell was preferred the procedure III in all cases. Hazelnut shells were converted to activated charcoal according to Aygün and it was used for B_4C synthesis as a carbon source. Different amount of boric acid and hazelnut activated charcoal were mixed and heated at 1400°C. **Figure 4.12** indicated that the main peaks of boron carbide at $2\theta \cong 32°$, 35°, and 37.8° observed in the XRD analysis, and $B_{13}C_2$ peak at $2\theta \cong 34°$ was detected. Also, amorphous carbon and boron oxide diffraction peaks were labeled (ICDD Cards No: 48-1206, 6-0297, 35-0798).

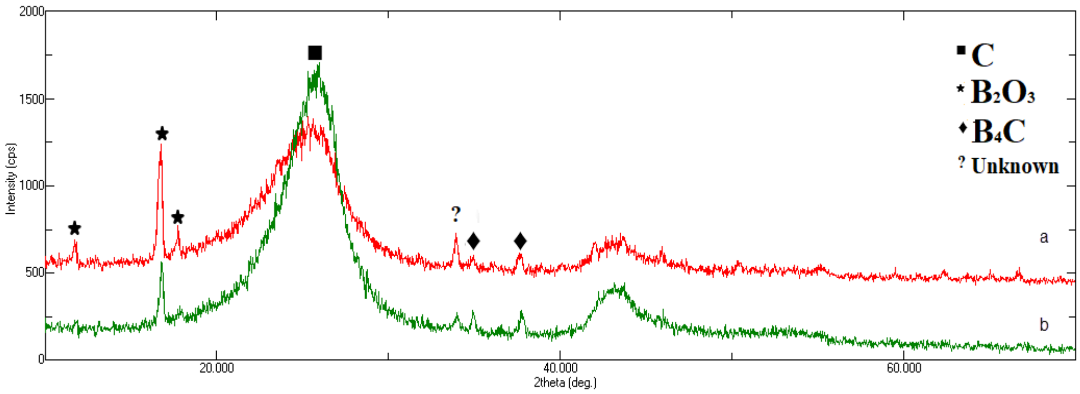


Figure 4.12. XRD pattern of B_4C samples obtained by Procedure III.
a: 0.25 g Hazelnut activated carbon + 1.0g boric acid mixture.
b: 0.50 g Hazelnut activated carbon + 1.0 boric acid mixture.

According to studies in the literature (Pilladi, 2013; Ergun, 2015), the boron oxide and amorphous carbon impurities can only remove ǀ 1600 °C. Because of lack of instrument, this current study was able to be performed max. 1400 °C. However, it is known that alkaline salts decrease the amount of un-reacted raw materials and increase product during the reaction (Alizadeh, 2003). To do this, different amount of alkaline salts like Li_2O, K_2CO_3, and NaCl were added to reaction mixtures. During studies the best result was obtained by Li_2O addition (**Figure 4.13**). The XRD result was compared to ICDD card no. 35-0798 and characteristic XRD peaks of B_4C, e.g., (003), (110), (104), (021), (211), (214), and (125) were labeled hexagonal boron carbide (ICDD Cards No: 48-1206, 6-0297,73-1640, 35-0798, 26-0233).

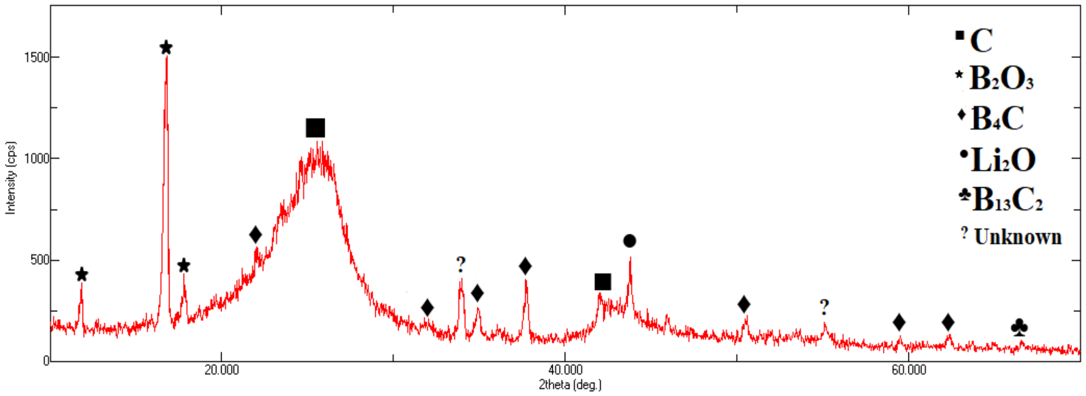


Figure 4.13. XRD pattern of B_4C samples obtained by Procedure III.
0.01 g Li_2O + 0.25 g Hazelnut activated carbon + 1 g Boric acid.

Furthermore, see Appendix C.

4.5 Characterization of B_4C by SEM

SEM analysis were applied for morphological examines. In general, B_4C images were monitored with impurities as expected according to XRD results. B_4C samples were obseved like porous material, rods, layered sturucture, and aggromalated structure. These different morphology could be caused by different synthesis methods (**Figure 4.14**).

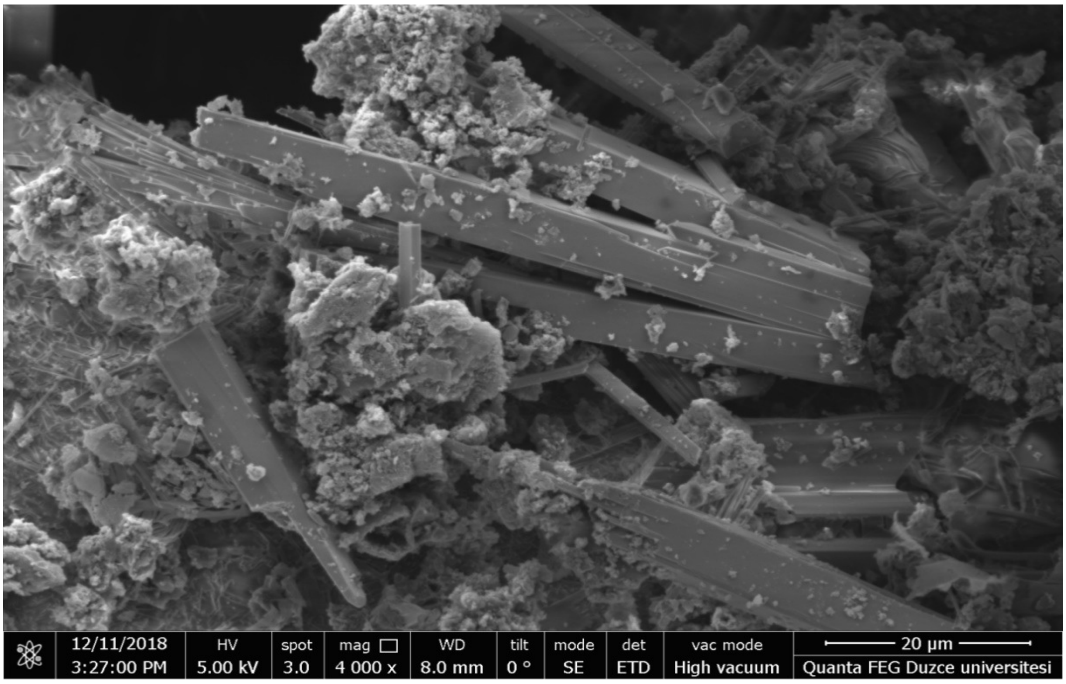


Figure 4.14. SEM image of rod shape boron carbide

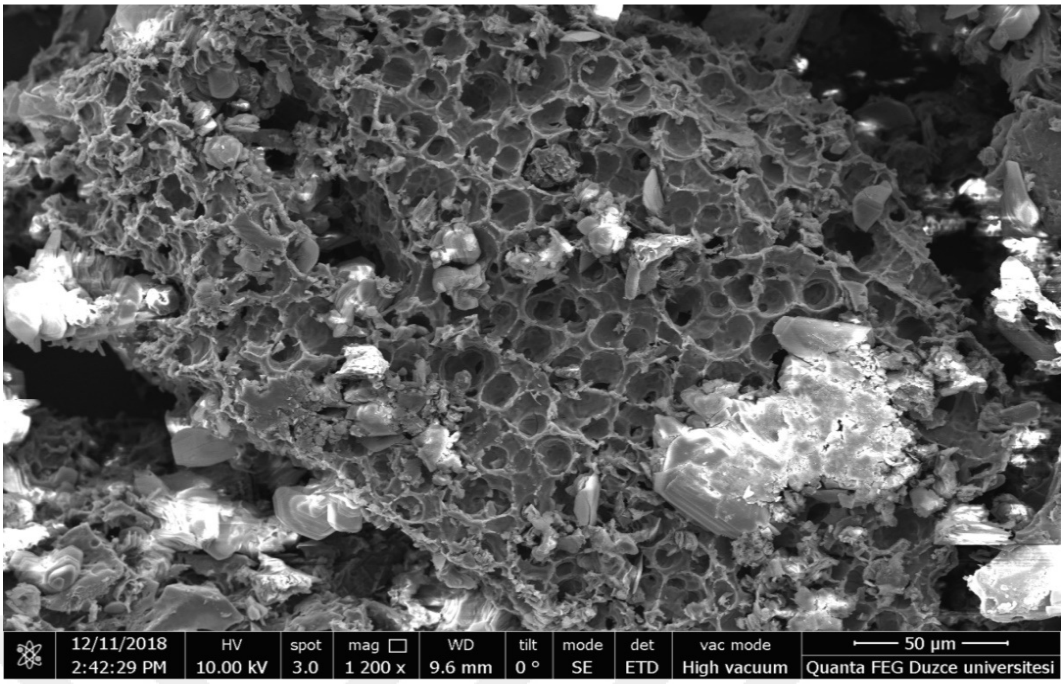


Figure 4.15. SEM image of boron carbide study as porous material

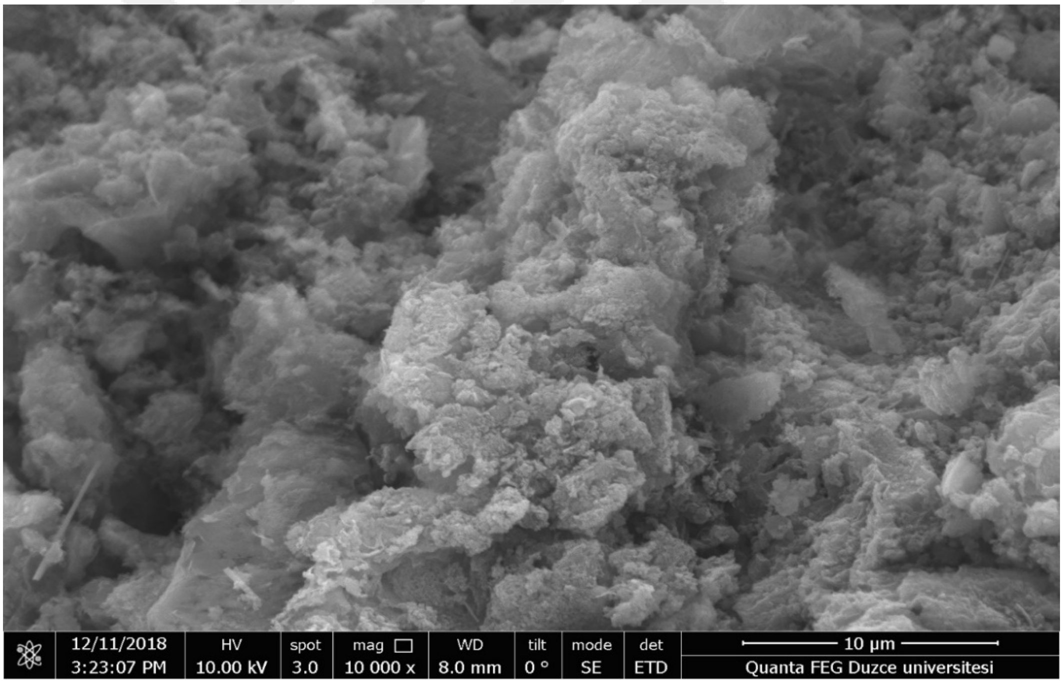


Figure 4.16. SEM image of aggromalated boron carbide

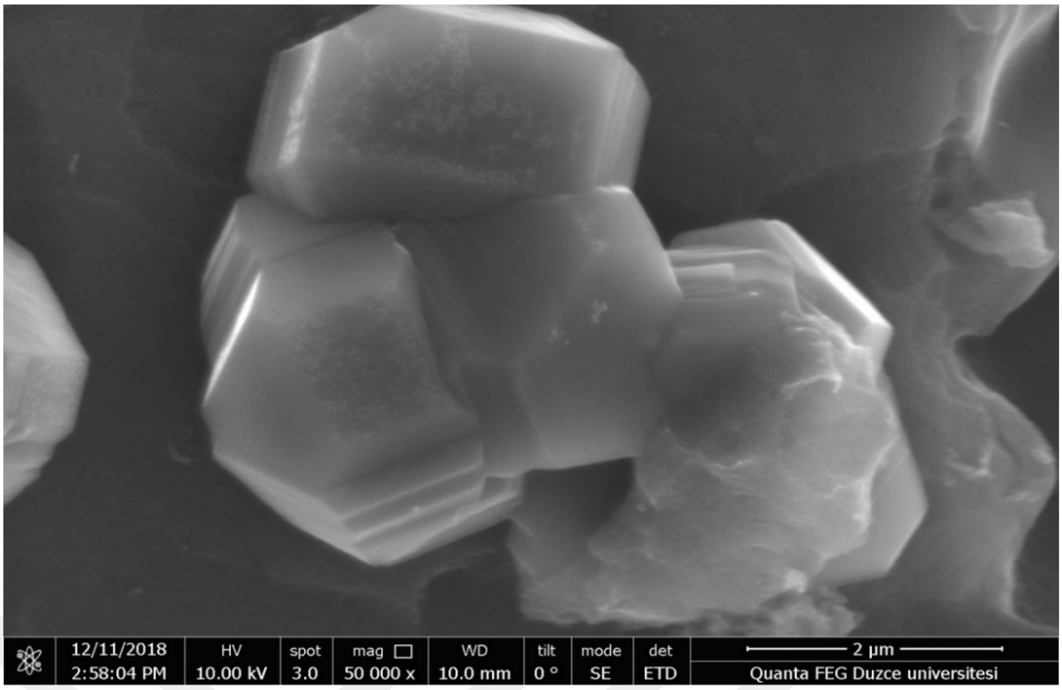


Figure 4.17. SEM image of icosahedral boron carbide

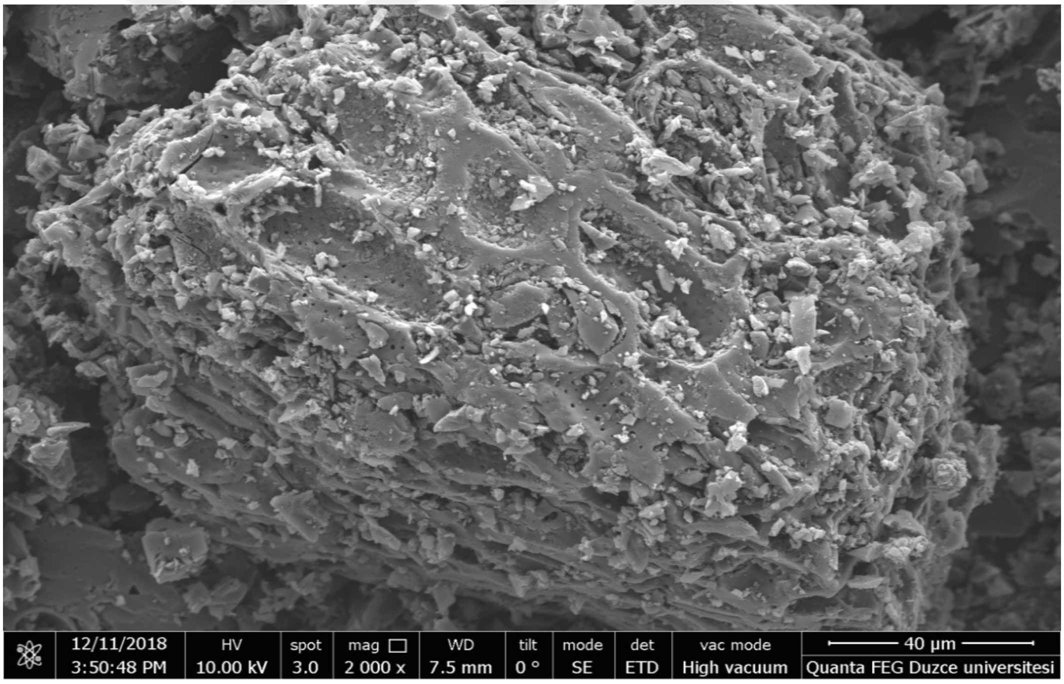


Figure 4.18. SEM image of layered structure

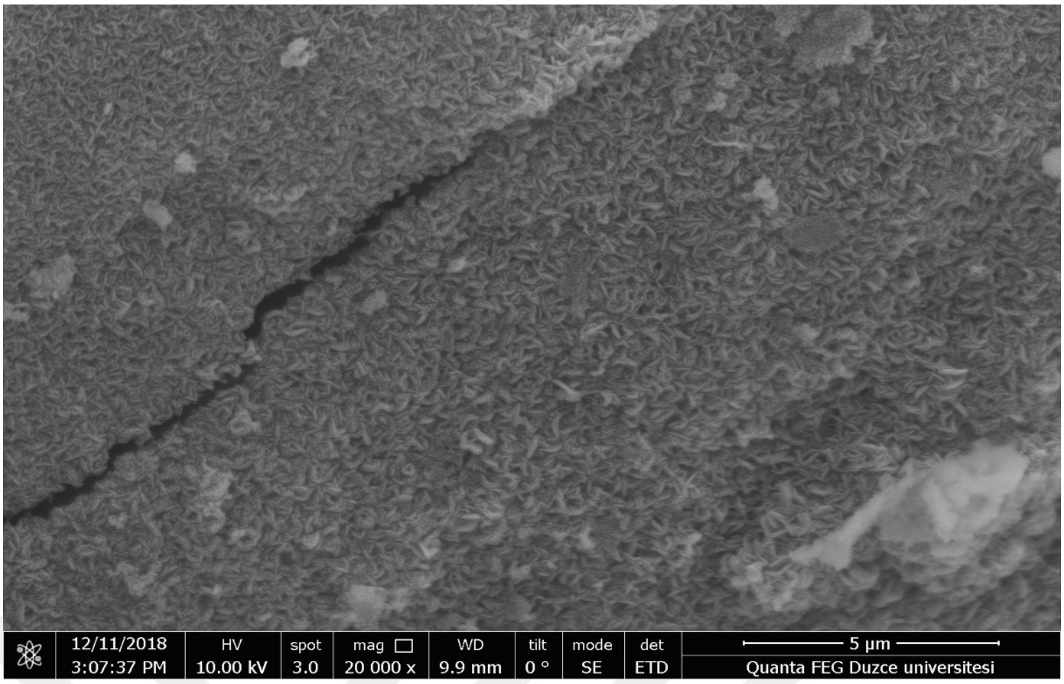


Figure 4.19. SEM image of wormy boron carbide

In addition, empirical formula for boron carbide were found theoretically from EDX analysis. It was found that the samples have different stoichiometric ratios like B_2C_{23}, BC_7, BC_4, and $B_{13}C_2$, etc. Furthermore, see Appendix D.

5. CONCLUSIONS AND RECOMMENDATIONS

In summary, boron carbide was synthesized by different methods using natural products. Carbothermic reduction reaction was preferred and used in this study because of low cost and more preferable in laboratory conditions. In addition, recycle of agricultural wastes which contain natural compounds and chemical components were reused. Characterization of boron carbide samples were performed by FTIR, XRD, and SEM instruments.

In current study, three different procedures were used. In the first procedure, nut shells were used directly. But it could not be obtained any reasonable results. Because the structure of nut shells was composed of cellulose, hemicellulose, lignin, ash, tannins, and proteins and decomposition products of these substances with high temperature gave some unwanted reactions and side products. As a result, the desired material was not achieved.

One of the simplest process for carbonization is sulfuric acid treatment. Nut shells were leached in sulfuric acid for one week. According to analyze results, it could be accepted as all shells were converted to graphitic amorphous carbon after purification process and they were used in experiment as carbon source in procedure II. However, unremoved or non-converted part of the shells affected the reaction pathway. Although boron carbide was synthesized by procedure II, the amount of impurities caused decreasing the crystallinity of boron carbide. To overcome this problem, metal salts were used as supporting material for decreasing formation temperature of boron carbide and removing of unreacted substances. This method provided better results but there were still impurities in the composition of materials despite reaction temperature was 1400 °C proven by FTIR and XRD.

In the third procedure, activated charcoal was produced using nut shells, so carbon content was increased. Different amount of boric acid and activated charcoal mixtures was tested and boron carbide formation was observed in all cases at 1400°C. The optimum reaction mixture ratio for boron carbide was found 0.25 g activated charcoal, and 1 g H_3BO_3. Also, inert atmosphere was changed; argon gas was used instead of nitrogen gas, so more sensible result was found. Metal salts were used as supporting material for this procedure to increase crystallinity of the boron carbide, too. Li_2O, K_2CO_3, and NaCl were used as additives and thorough these materials Li_2O gave the best result and new ideal mixture was found as 0.25 g activated charcoal, and 1 g H_3BO_3 and 0.01 g Li_2O. However, amorph carbon and boron oxide could not be removed. According to literature, for removal of these impurities is possible at ≥1600 °C when natural products or polymers were used as carbon source. Due to lack of instrumentation, we could not try this procedure at high temperature.

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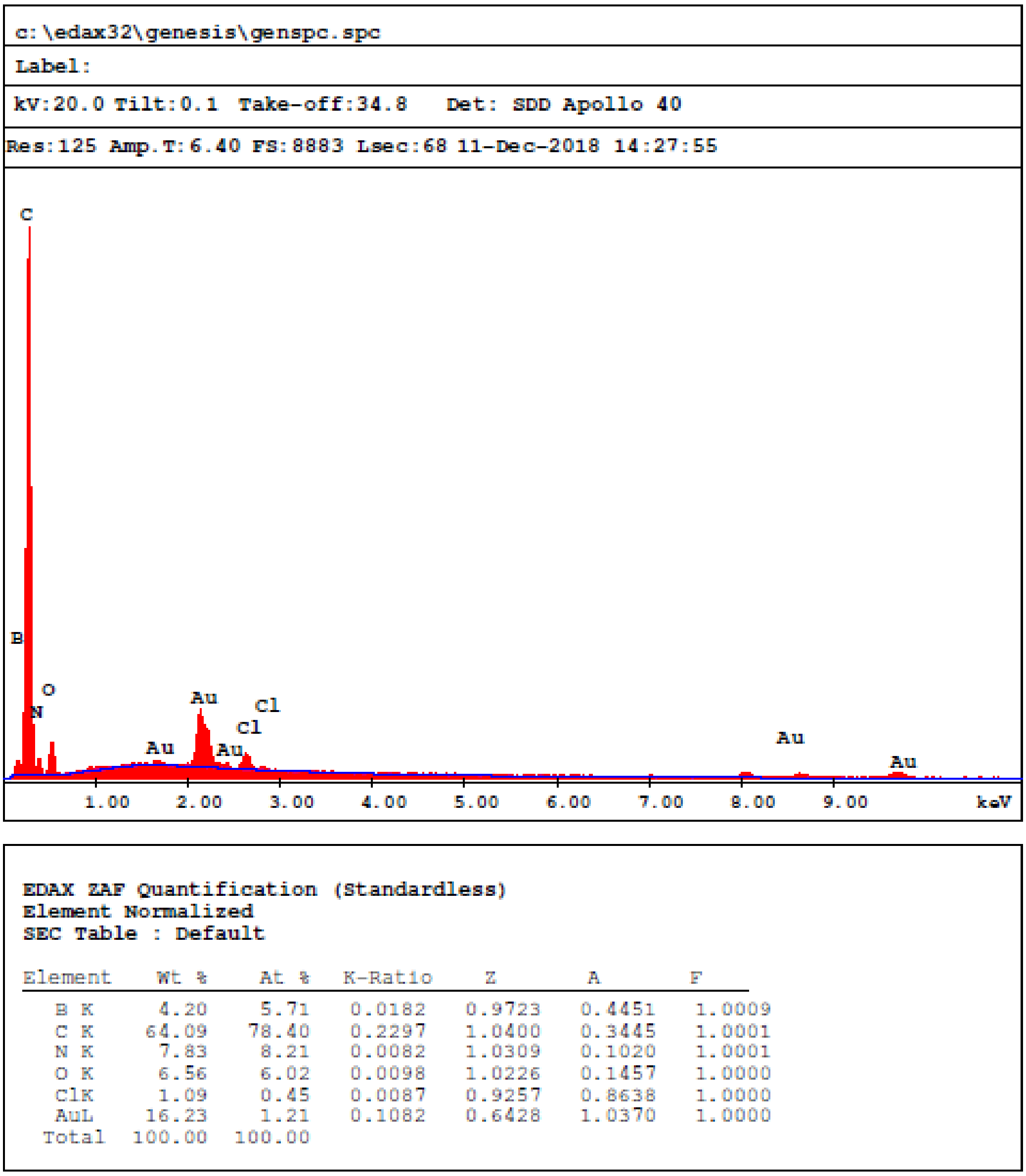
7. APPENDIX

7.1 Appendix A EDX Data of Samples



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c:\edax32\genesis\genspc.spc
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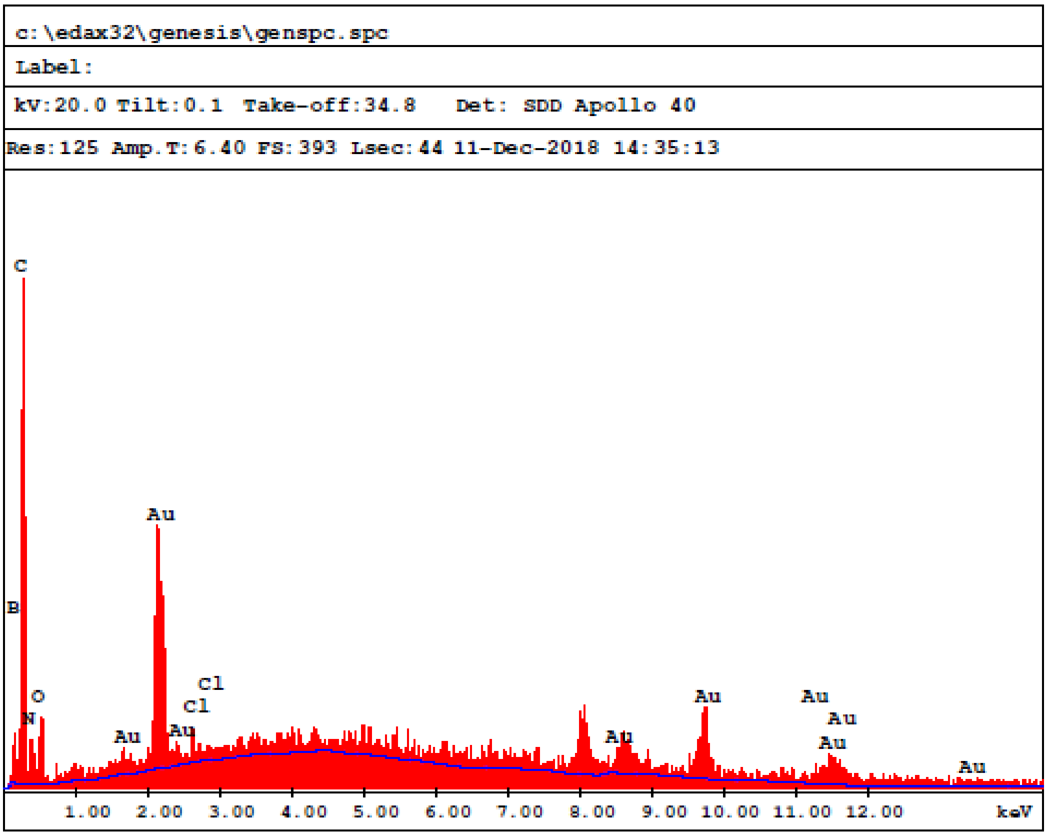
kV:20.0 Tilt:0.1  Take-off:34.8    Det: SDD Apollo 40
Res:125 Amp.T:6.40 FS:8883 Lsec:68 11-Dec-2018 14:27:55
```

```
EDAX ZAF Quantification (Standardless)
Element Normalized
SEC Table : Default

Element    Wt %     At %   K-Ratio      Z        A        F
   B K     4.20     5.71   0.0182   0.9723   0.4451   1.0009
   C K    64.09    78.40   0.2297   1.0400   0.3445   1.0001
   N K     7.83     8.21   0.0082   1.0309   0.1020   1.0001
   O K     6.56     6.02   0.0098   1.0226   0.1457   1.0000
   ClK     1.09     0.45   0.0087   0.9257   0.8638   1.0000
   AuL    16.23     1.21   0.1082   0.6428   1.0370   1.0000
  Total  100.00   100.00
```

Figure 7.1. EDAX data of 1.5 g h.s + 1.5 g at 1450 °C



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Res:125 Amp.T:6.40 FS:393 Lsec:44 11-Dec-2018 14:35:13
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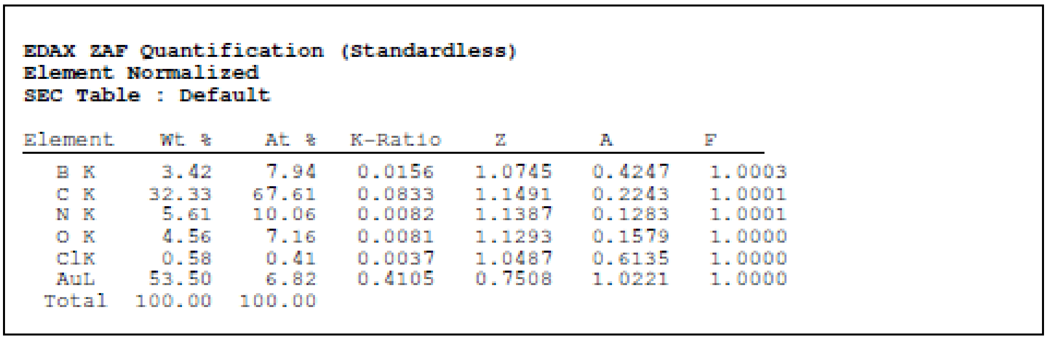
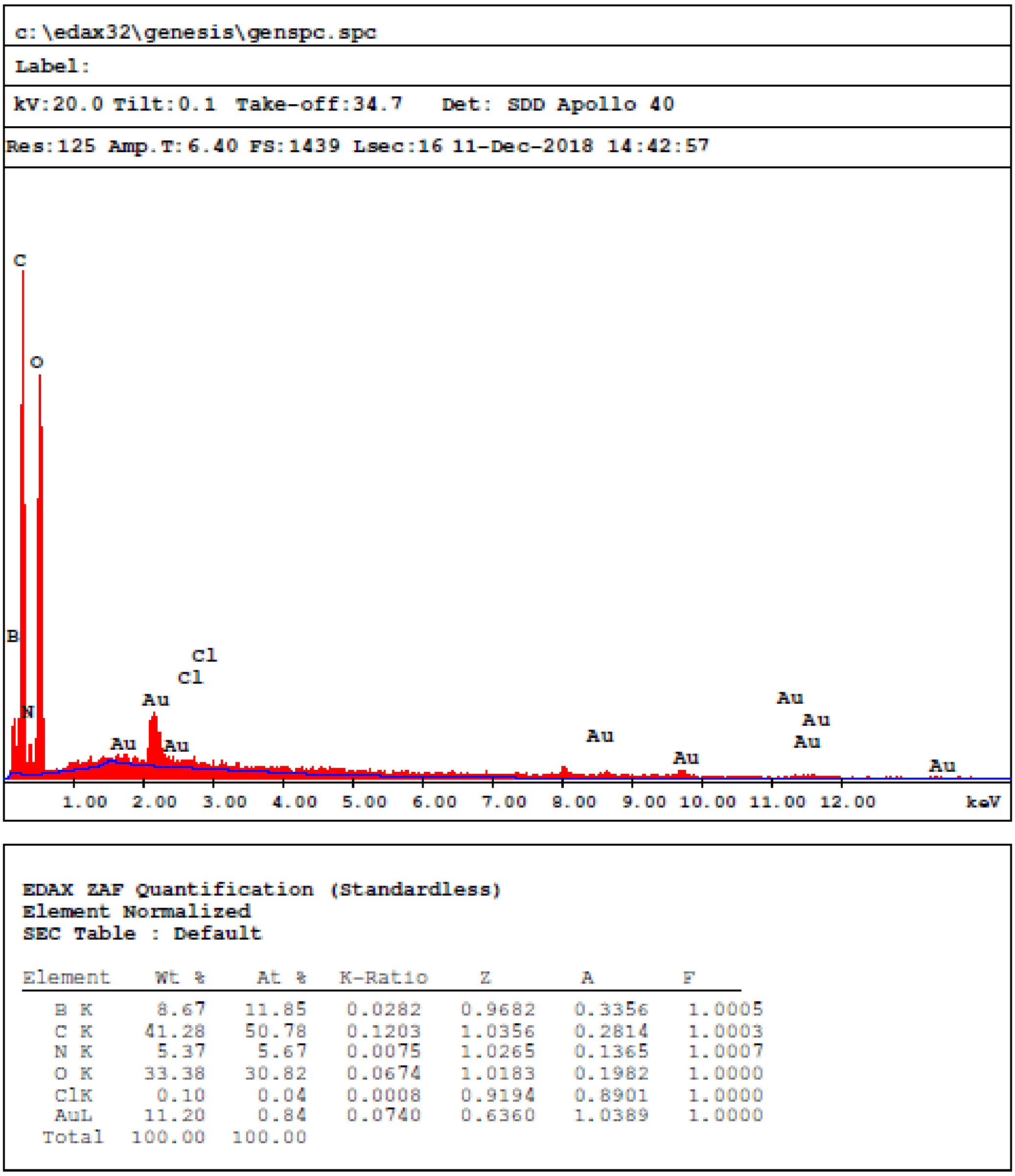


```
EDAX ZAF Quantification (Standardless)
Element Normalized
SEC Table : Default

Element    Wt %     At %   K-Ratio     Z        A        F
  B K      3.42     7.94   0.0156   1.0745   0.4247   1.0003
  C K     32.33    67.61   0.0833   1.1491   0.2243   1.0001
  N K      5.61    10.06   0.0082   1.1387   0.1283   1.0001
  O K      4.56     7.16   0.0081   1.1293   0.1579   1.0000
  ClK      0.58     0.41   0.0037   1.0487   0.6135   1.0000
  AuL     53.50     6.82   0.4105   0.7508   1.0221   1.0000
 Total   100.00   100.00
```

Figure 7.2. EDAX data of 3.5 g w.s + 1.5 g b.a at 1450°C

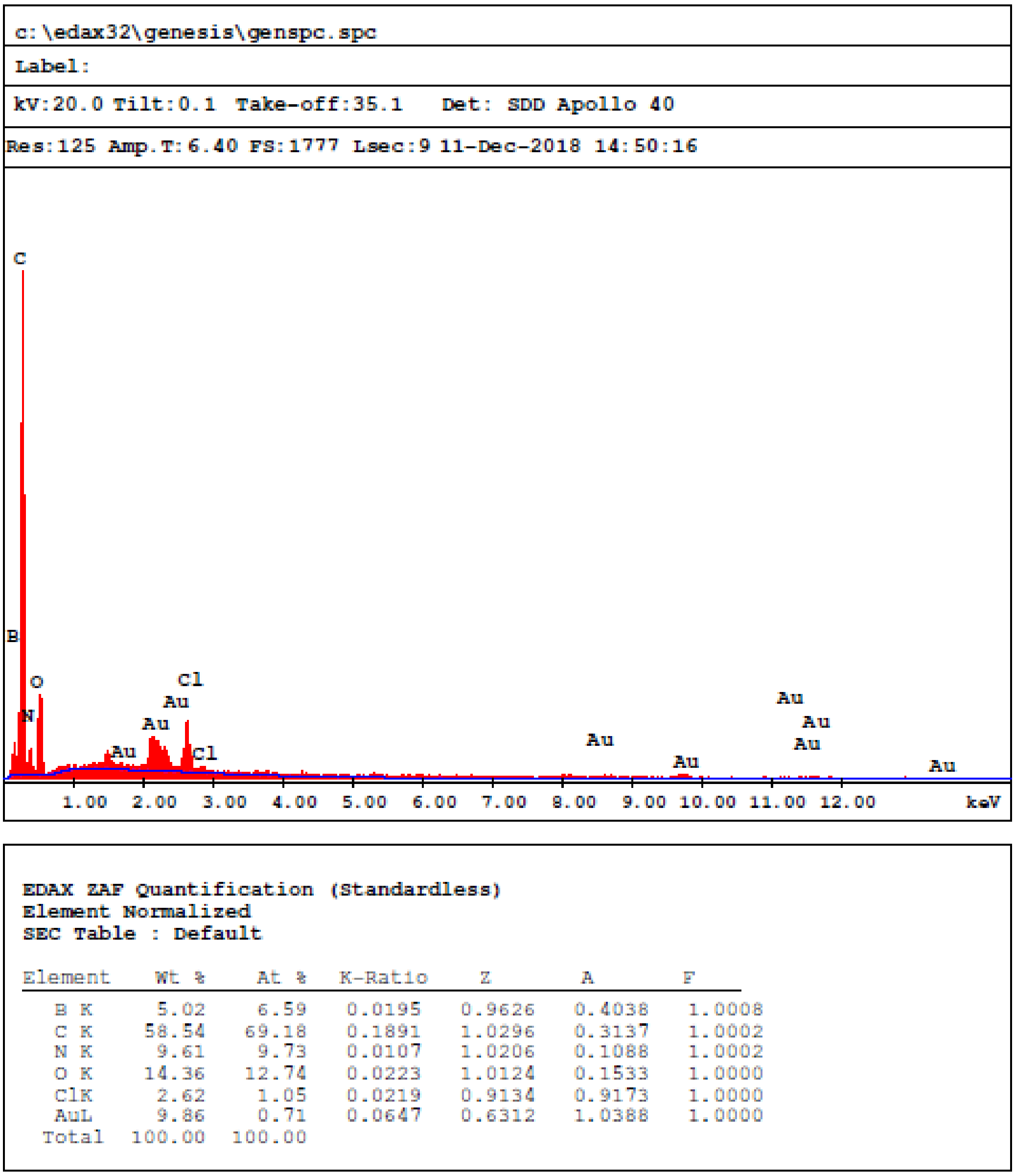


```
c:\edax32\genesis\genspc.spc
Label:
kV:20.0 Tilt:0.1  Take-off:34.7    Det: SDD Apollo 40
Res:125 Amp.T:6.40 FS:1439 Lsec:16 11-Dec-2018 14:42:57
```

```
EDAX ZAF Quantification (Standardless)
Element Normalized
SEC Table : Default

Element    Wt %     At %   K-Ratio     Z         A         F
   B K     8.67    11.85   0.0282   0.9682    0.3356    1.0005
   C K    41.28    50.78   0.1203   1.0356    0.2814    1.0003
   N K     5.37     5.67   0.0075   1.0265    0.1365    1.0007
   O K    33.38    30.82   0.0674   1.0183    0.1982    1.0000
   ClK     0.10     0.04   0.0008   0.9194    0.8901    1.0000
   AuL    11.20     0.84   0.0740   0.6360    1.0389    1.0000
  Total  100.00   100.00
```

Figure 7.3. EDAX data of 3.4 g h.s +1.5 b.a at 1450°C



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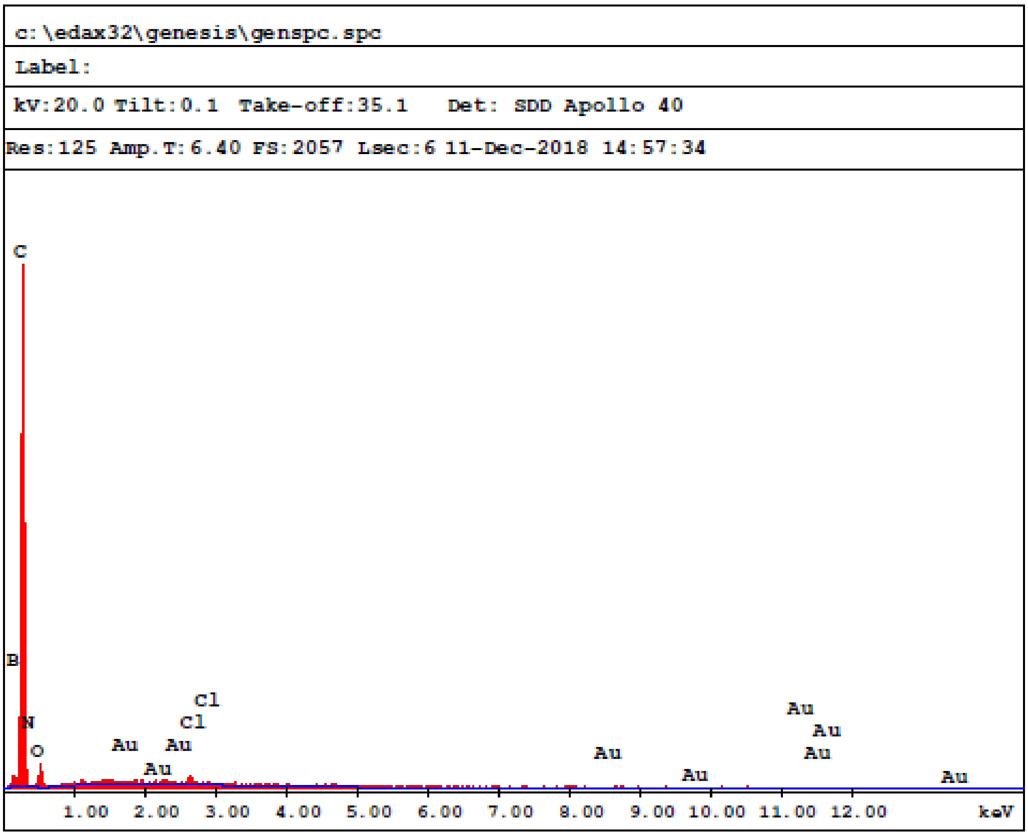
```

```
EDAX ZAF Quantification (Standardless)
Element Normalized
SEC Table : Default

Element    Wt %     At %   K-Ratio      Z         A         F
   B K     5.02     6.59    0.0195   0.9626    0.4038    1.0008
   C K    58.54    69.18    0.1891   1.0296    0.3137    1.0002
   N K     9.61     9.73    0.0107   1.0206    0.1088    1.0002
   O K    14.36    12.74    0.0223   1.0124    0.1533    1.0000
   ClK     2.62     1.05    0.0219   0.9134    0.9173    1.0000
   AuL     9.86     0.71    0.0647   0.6312    1.0388    1.0000
 Total   100.00   100.00
```

Figure 7.4. EDAX data of 1.5 g w.s +1.5 g b.a at 1450°C



```
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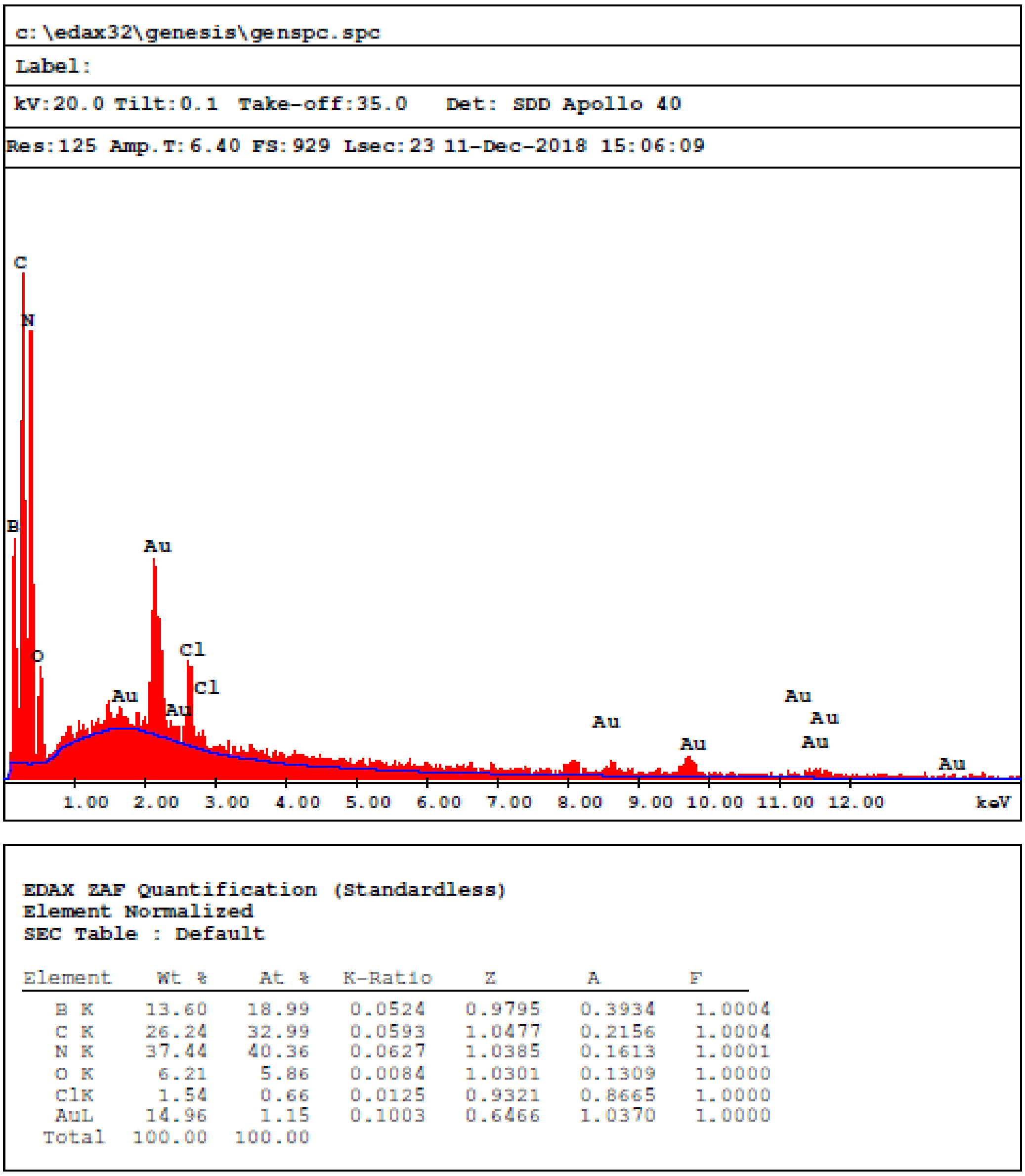
Res:125 Amp.T:6.40 FS:2057 Lsec:6 11-Dec-2018 14:57:34
```

```
EDAX ZAF Quantification (Standardless)
Element Normalized
SEC Table : Default

Element    Wt %      At %   K-Ratio     Z        A        F
  B K      6.02      6.91   0.0273   0.9434   0.4790   1.0014
  C K     84.28     87.06   0.3729   1.0092   0.4384   1.0000
  N K      0.00      0.00   0.0000   1.0004   0.0854   1.0001
  O K      7.34      5.70   0.0107   0.9924   0.1468   1.0000
  ClK      0.65      0.23   0.0058   0.8906   1.0175   1.0000
  AuL      1.71      0.11   0.0109   0.6115   1.0426   1.0000
 Total   100.00    100.00
```

Figure 7.5. EDAX data of 4.5 g h.s + 1.5 g b.a at 1450°C



```
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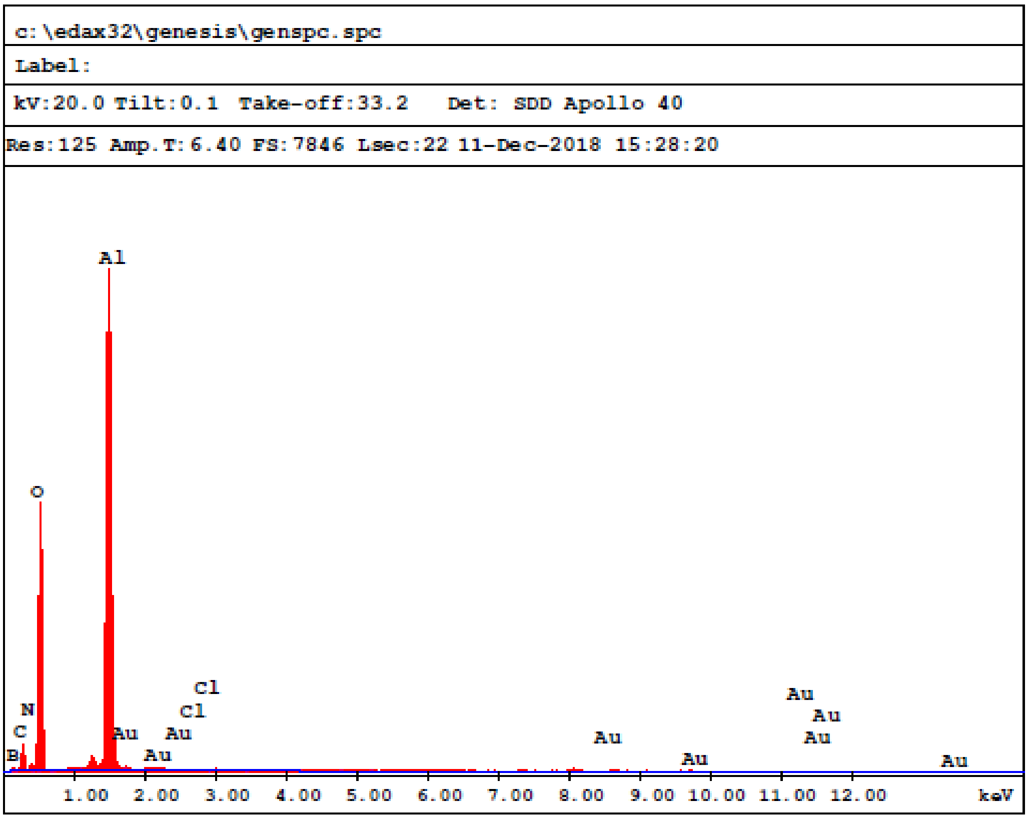
Res:125 Amp.T:6.40 FS:929 Lsec:23 11-Dec-2018 15:06:09
```

```
EDAX ZAF Quantification (Standardless)
Element Normalized
SEC Table : Default

Element      Wt %      At %    K-Ratio      Z          A          F
   B K      13.60     18.99    0.0524    0.9795     0.3934     1.0004
   C K      26.24     32.99    0.0593    1.0477     0.2156     1.0004
   N K      37.44     40.36    0.0627    1.0385     0.1613     1.0001
   O K       6.21      5.86    0.0084    1.0301     0.1309     1.0000
   ClK       1.54      0.66    0.0125    0.9321     0.8665     1.0000
   AuL      14.96      1.15    0.1003    0.6466     1.0370     1.0000
  Total    100.00    100.00
```

Figure 7.6. EDAX data of 2 g h.s + 1.5 g b.a at 1450°C



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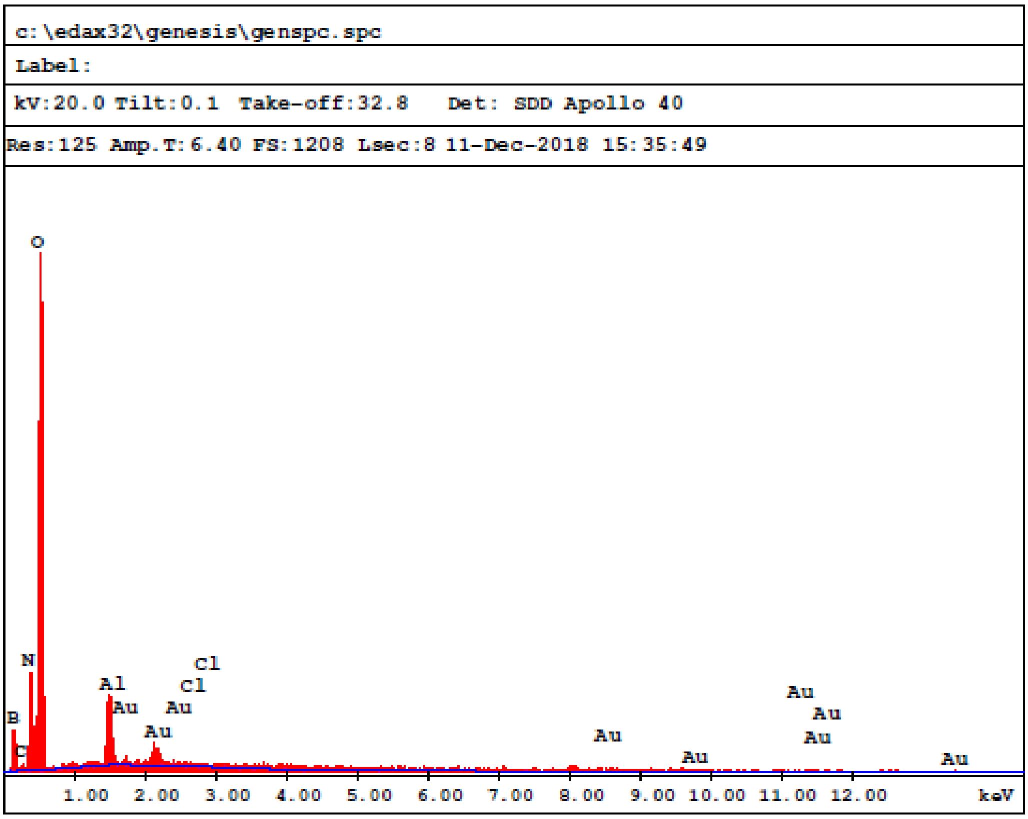
```

```
EDAX ZAF Quantification (Standardless)
Element Normalized
SEC Table : Default

Element    Wt %     At %   K-Ratio      Z        A        F
   B K     2.45     4.20   0.0023   0.9816   0.0934   1.0002
   C K    10.72    16.53   0.0173   1.0499   0.1537   1.0005
   N K     2.02     2.67   0.0041   1.0407   0.1939   1.0015
   O K    43.00    49.76   0.1346   1.0323   0.3031   1.0005
   AlK    38.66    26.52   0.2711   0.9615   0.7292   1.0000
   ClK     0.06     0.03   0.0004   0.9311   0.7839   1.0000
   AuL     3.08     0.29   0.0205   0.6414   1.0402   1.0000
  Total  100.00   100.00
```

Figure 7.7. EDAX data of h.s + b.a + NaCl / 0.28:1:0.1 under $Ar_{(g)}$ atm.



```
c:\edax32\genesis\genspc.spc
Label:
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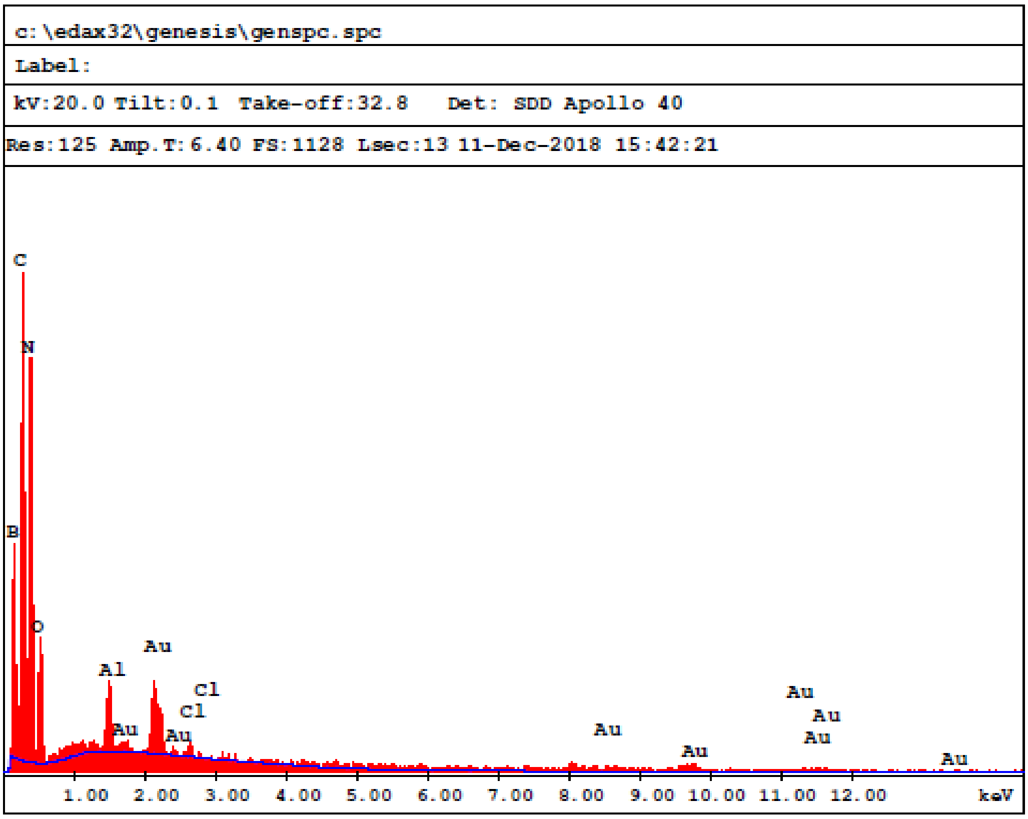
Res:125 Amp.T:6.40 FS:1208 Lsec:8 11-Dec-2018 15:35:49
```

```
EDAX ZAF Quantification (Standardless)
Element Normalized
SEC Table : Default

Element    Wt %     At %   K-Ratio      Z        A        F
    B K    17.89    24.95   0.0383   0.9676   0.2213   1.0003
    C K     1.43     1.80   0.0026   1.0350   0.1766   1.0008
    N K    15.50    16.68   0.0471   1.0259   0.2956   1.0018
    O K    57.42    54.11   0.1611   1.0177   0.2756   1.0000
    AlK     3.73     2.08   0.0228   0.9481   0.6443   1.0000
    ClK     0.17     0.07   0.0015   0.9158   0.9190   1.0000
    AuL     3.85     0.30   0.0253   0.6303   1.0433   1.0000
  Total   100.00   100.00
```

Figure 7.8. EDAX data of hazelnut shell + boric acid / 1.5:1.5 under N_2 atm.



```
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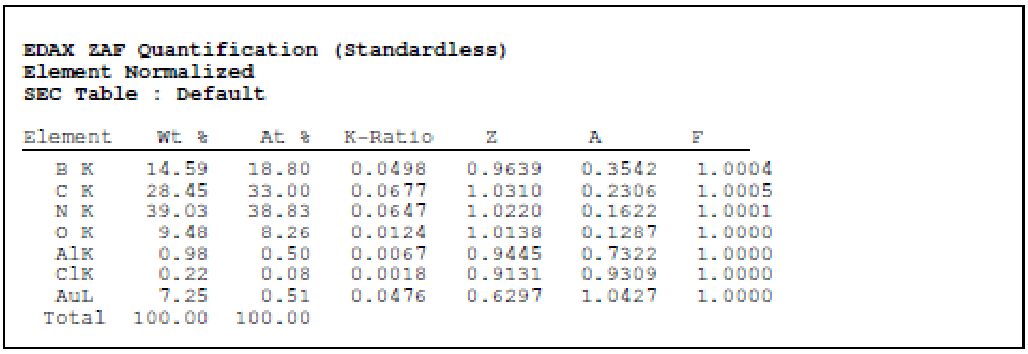
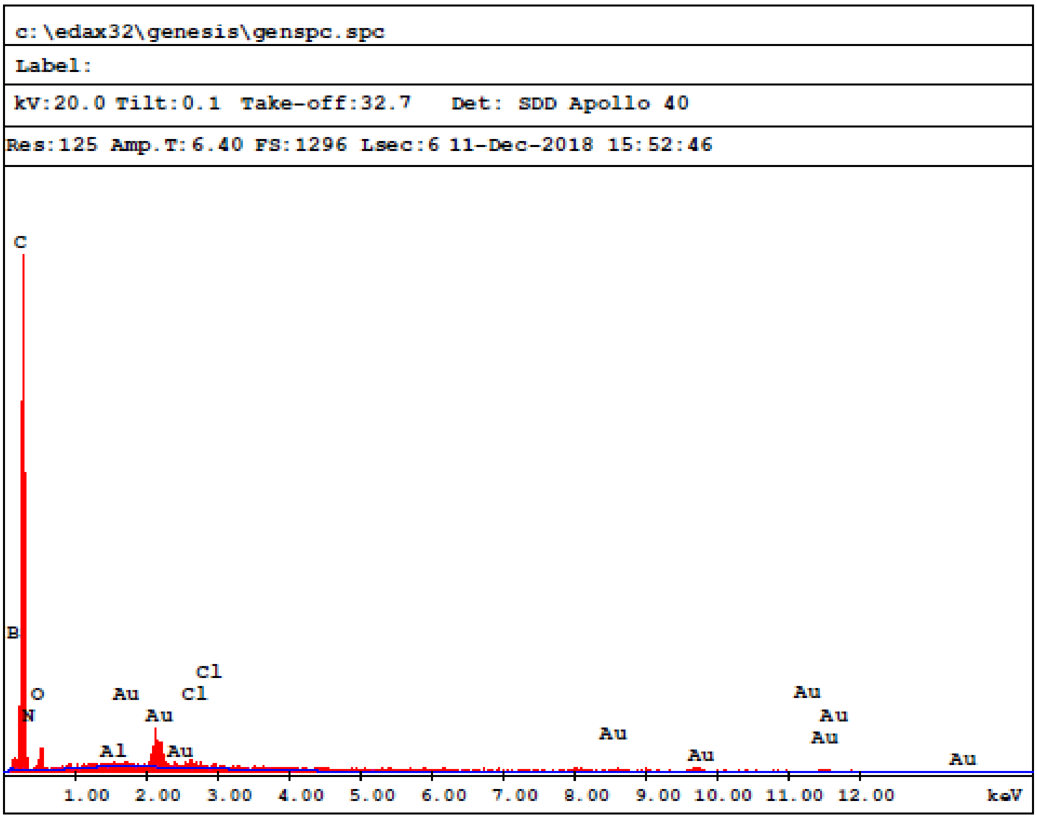
Res:125 Amp.T:6.40 FS:1128 Lsec:13 11-Dec-2018 15:42:21
```



```
EDAX ZAF Quantification (Standardless)
Element Normalized
SEC Table : Default

Element    Wt %     At %   K-Ratio      Z        A        F
  B K     14.59    18.80   0.0498   0.9639   0.3542   1.0004
  C K     28.45    33.00   0.0677   1.0310   0.2306   1.0005
  N K     39.03    38.83   0.0647   1.0220   0.1622   1.0001
  O K      9.48     8.26   0.0124   1.0138   0.1287   1.0000
  AlK      0.98     0.50   0.0067   0.9445   0.7322   1.0000
  ClK      0.22     0.08   0.0018   0.9131   0.9309   1.0000
  AuL      7.25     0.51   0.0476   0.6297   1.0427   1.0000
 Total   100.00   100.00
```

Figure 7.9. EDAX data of walnut shell + boric acid / 1.5:1.5 under N_2 atm.



```
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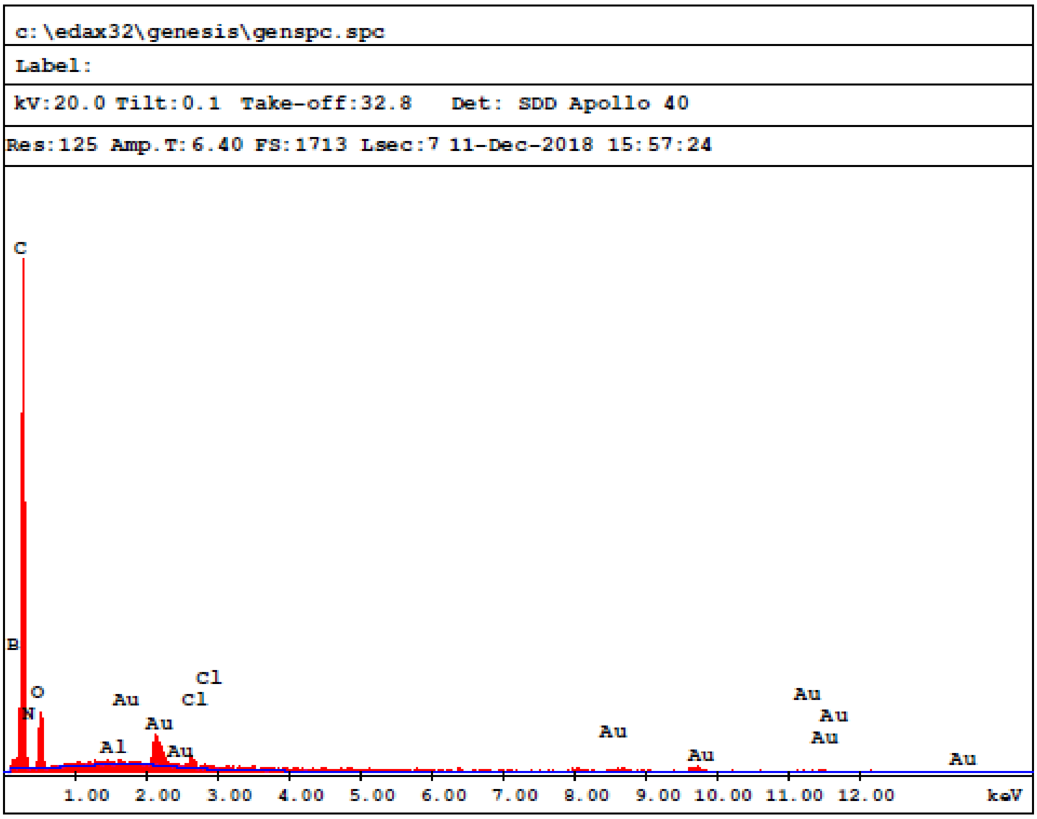
Res:125 Amp.T:6.40 FS:1296 Lsec:6 11-Dec-2018 15:52:46
```

```
EDAX ZAF Quantification (Standardless)
Element Normalized
SEC Table : Default

Element    Wt %     At %   K-Ratio      Z        A        F
   B K     4.87     6.25   0.0222   0.9647   0.4726   1.0011
   C K    76.19    88.07   0.2938   1.0318   0.3737   1.0000
   N K     0.00     0.00   0.0000   1.0228   0.0888   1.0001
   O K     5.19     4.50   0.0076   1.0146   0.1447   1.0000
   AlK     0.13     0.07   0.0009   0.9451   0.7637   1.0001
   ClK     0.48     0.19   0.0039   0.9165   0.8910   1.0000
   AuL    13.15     0.93   0.0869   0.6348   1.0406   1.0000
 Total   100.00   100.00
```

Figure 7.10. EDAX data of 0.5 g h.s +1 g b.ox + 0.0170 g Li_2O at 1400°C pressed

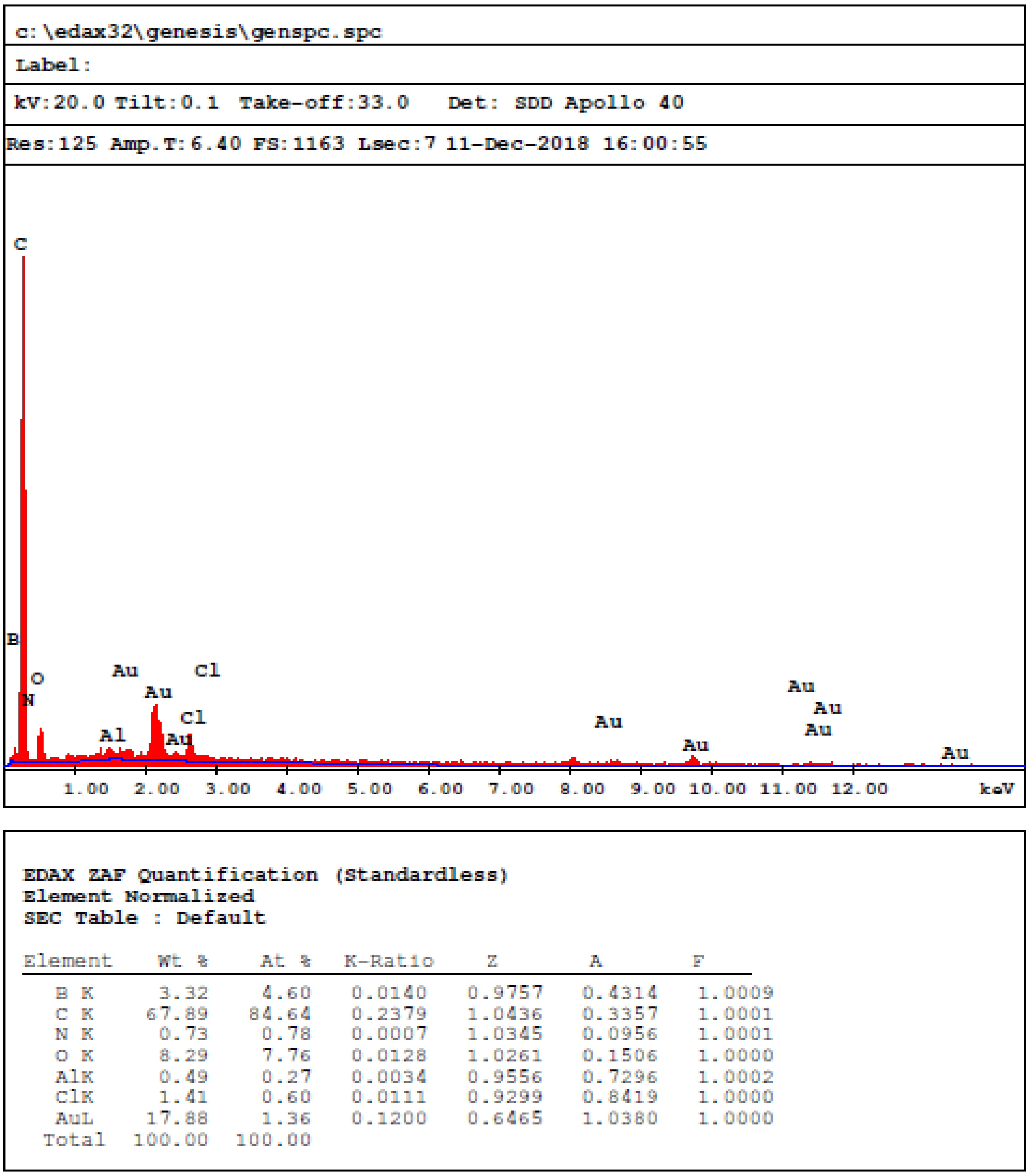


```
c:\edax32\genesis\genspc.spc
Label:
kV:20.0 Tilt:0.1  Take-off:32.8    Det: SDD Apollo 40
Res:125 Amp.T:6.40 FS:1713 Lsec:7 11-Dec-2018 15:57:24
```

```
EDAX ZAF Quantification (Standardless)
Element Normalized
SEC Table : Default

Element     Wt %      At %   K-Ratio      Z        A        F
    B K     4.93      6.34    0.0203   0.9618   0.4267   1.0010
    C K    70.05     81.05    0.2604   1.0288   0.3613   1.0001
    N K     0.00      0.00    0.0000   1.0198   0.0950   1.0002
    O K    13.22     11.48    0.0208   1.0116   0.1559   1.0000
    AlK     0.09      0.04    0.0006   0.9424   0.7493   1.0001
    ClK     0.80      0.31    0.0066   0.9128   0.9071   1.0000
    AuL    10.91      0.77    0.0717   0.6312   1.0412   1.0000
  Total   100.00    100.00
```

Figure 7.11. EDAX data of 1 g h.s + 1g b.a with pressed at 1400°C



```
c:\edax32\genesis\genspc.spc
Label:
kV:20.0 Tilt:0.1  Take-off:33.0    Det: SDD Apollo 40
Res:125 Amp.T:6.40 FS:1163 Lsec:7 11-Dec-2018 16:00:55
```

```
EDAX ZAF Quantification (Standardless)
Element Normalized
SEC Table : Default

Element    Wt %     At %   K-Ratio      Z        A        F
   B K     3.32     4.60   0.0140   0.9757   0.4314   1.0009
   C K    67.89    84.64   0.2379   1.0436   0.3357   1.0001
   N K     0.73     0.78   0.0007   1.0345   0.0956   1.0001
   O K     8.29     7.76   0.0128   1.0261   0.1506   1.0000
   AlK     0.49     0.27   0.0034   0.9556   0.7296   1.0002
   ClK     1.41     0.60   0.0111   0.9299   0.8419   1.0000
   AuL    17.88     1.36   0.1200   0.6465   1.0380   1.0000
  Total  100.00   100.00
```

Figure 7.12. EDAX data of 0.25 g h.s, 1 g b.a, 0.001 g Li_2O at 1400°C ext pure

7.2 Appendix B FTIR Spectra of Samples

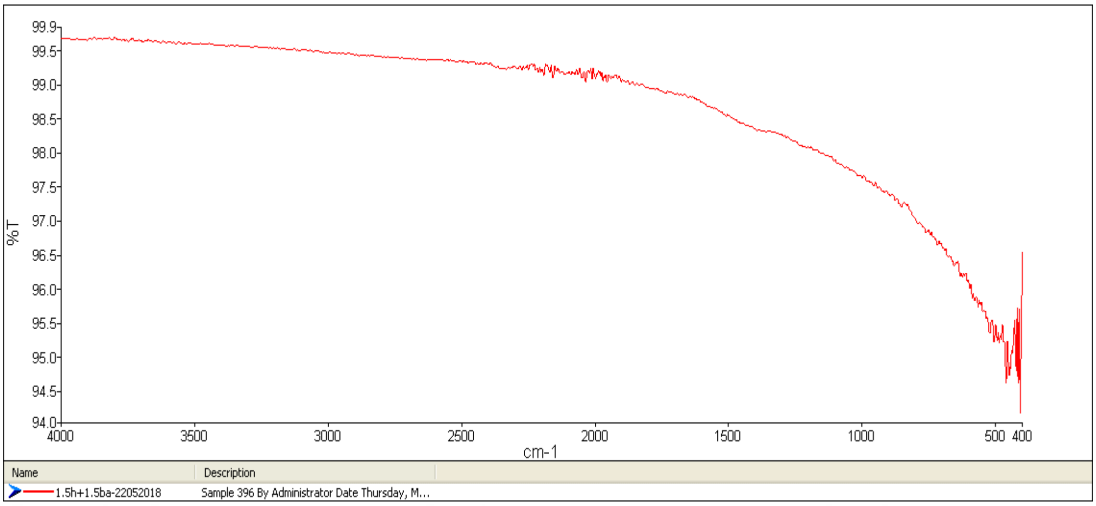


Figure 7.13. 1.5 g h.s + 1.5 g sample b.ox by procedure I

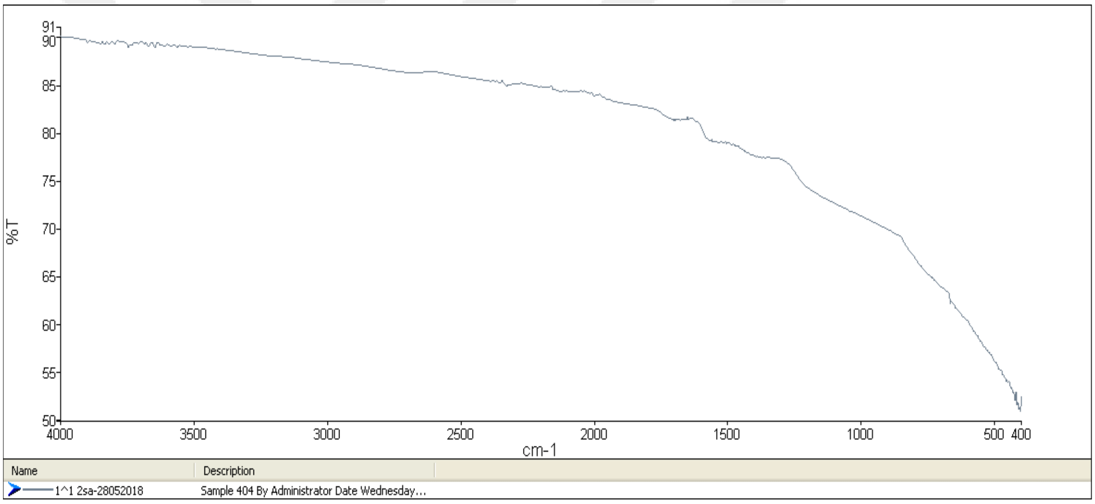


Figure 7.14. 1 g w.s + 1 g b.ox sample by procedure I

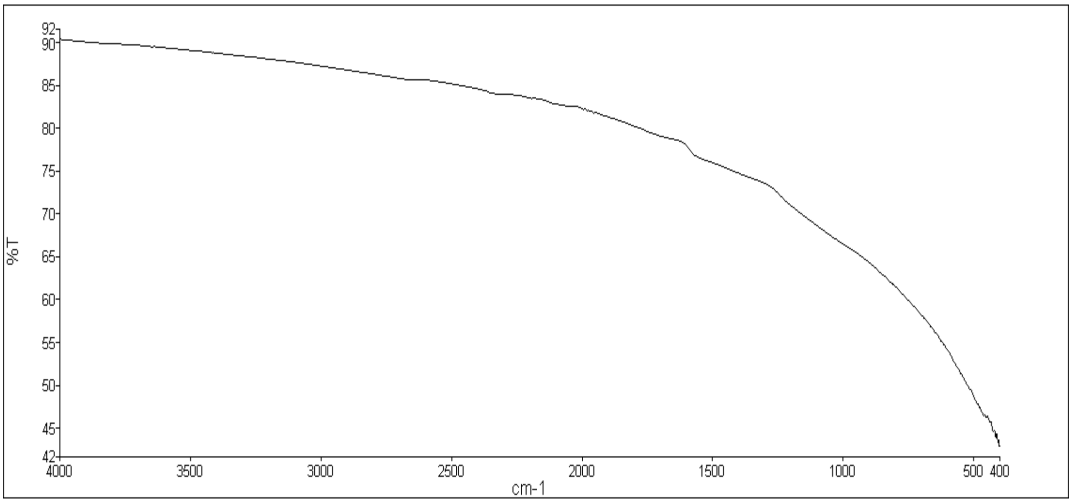


Figure 7.15. 0.75 g ac + 0.80 g b.ox sample by procedure I

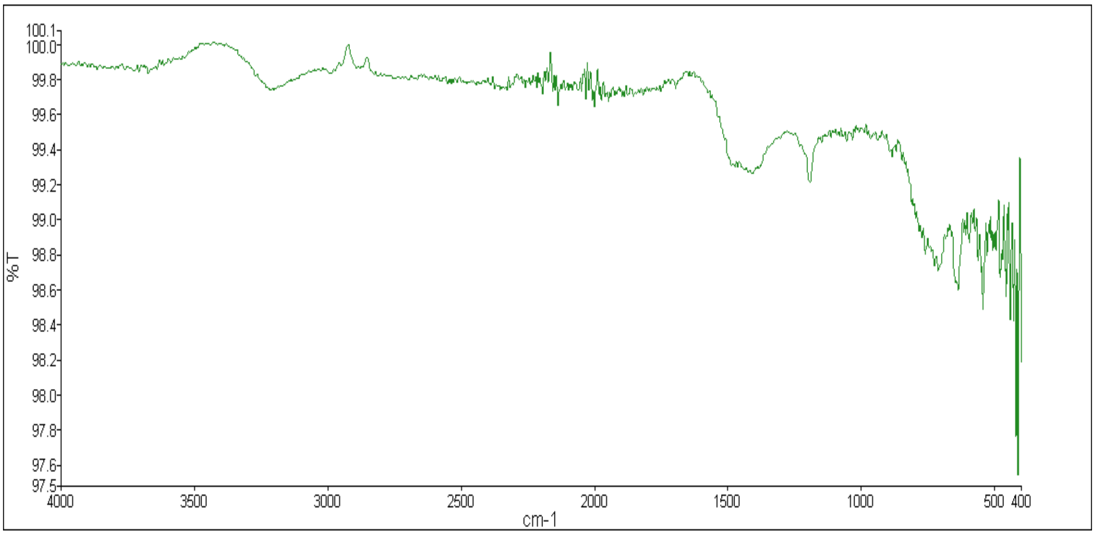


Figure 7.16. 1.5 g h.s + 1.5 g b.a at 800°C (reheated) by procedure II

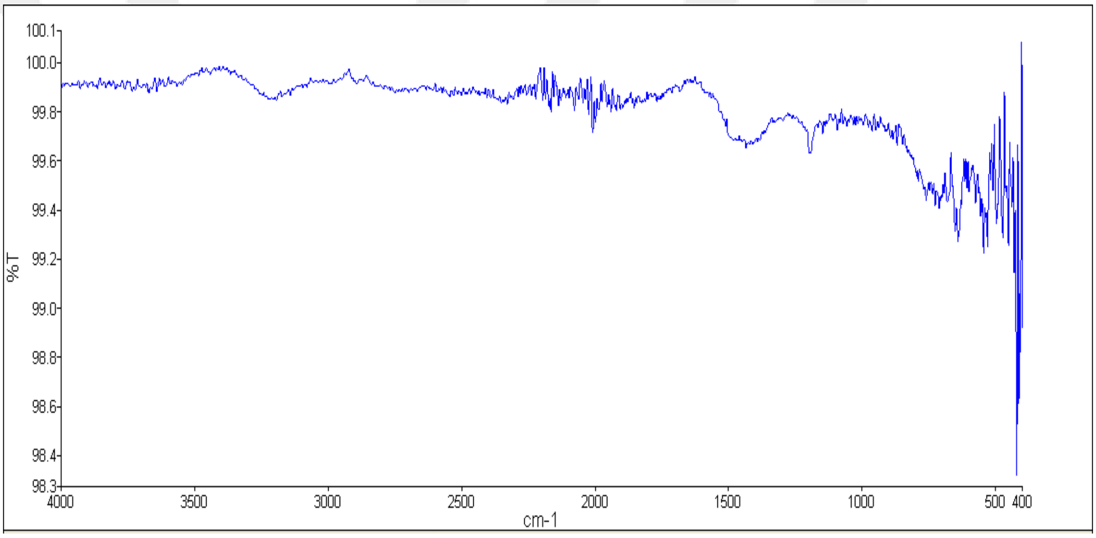


Figure 7.17. 4.5 g h.s + 1 g b.a at 800°C (reheated) by procedure II

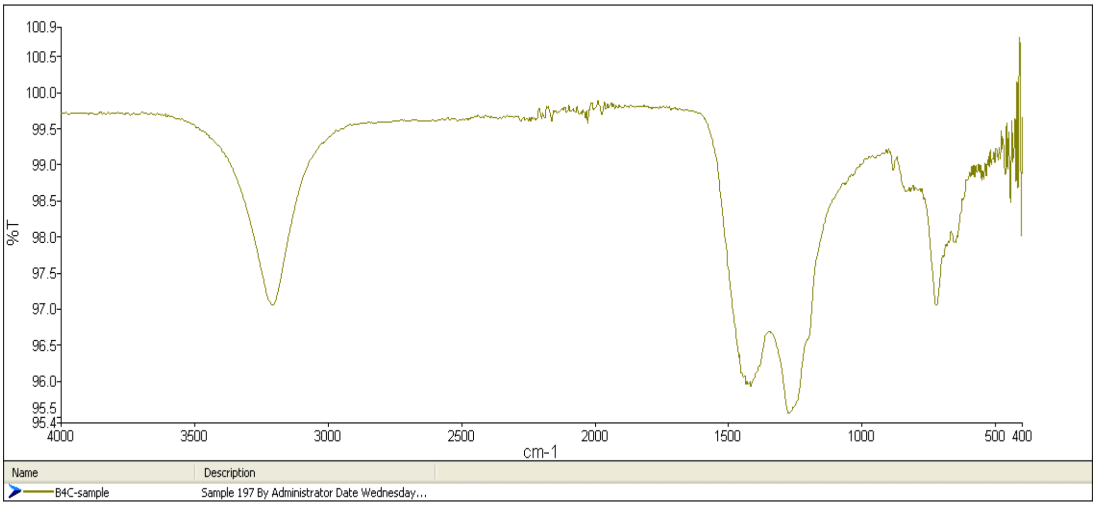


Figure 7.18. 1 g h.s + 4.5 g b.a sample by procedure II

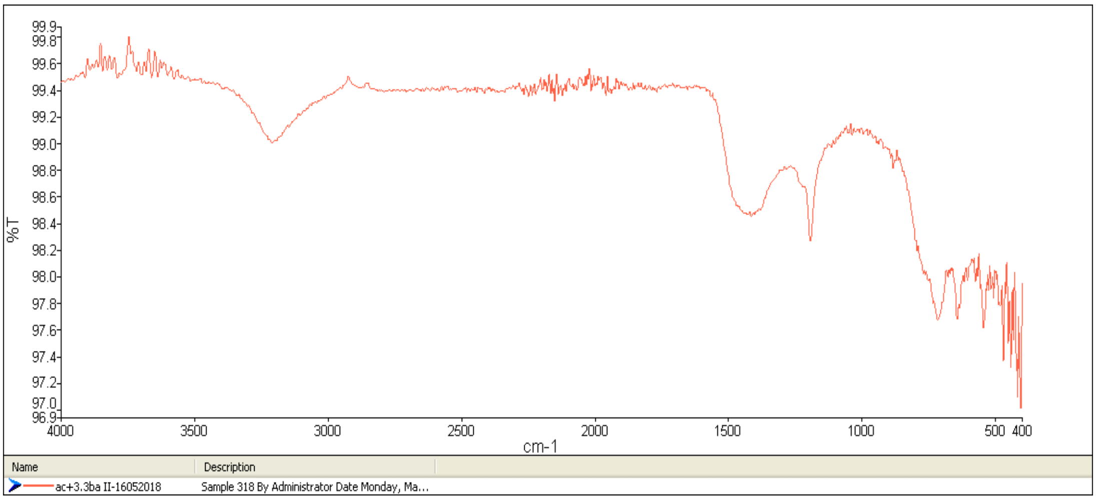


Figure 7.19. 1 g a.c + 3.3 g b.a sample by procedure III

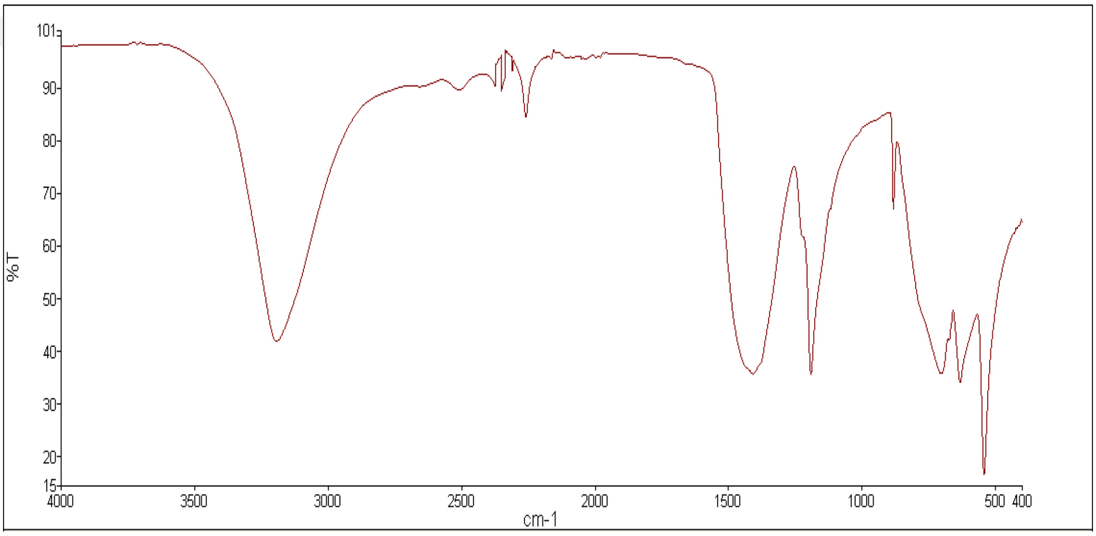


Figure 7.20. 1g h.s + 3.2 g b.a sample by procedure III

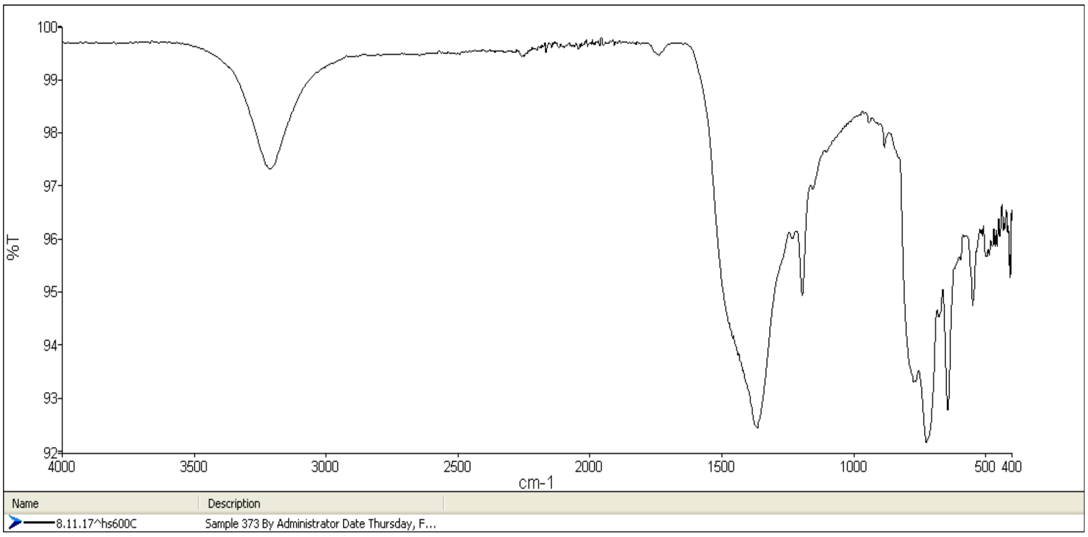


Figure 7.21. H.s sample at 600°C with 2 hr by procedure III (reheated)

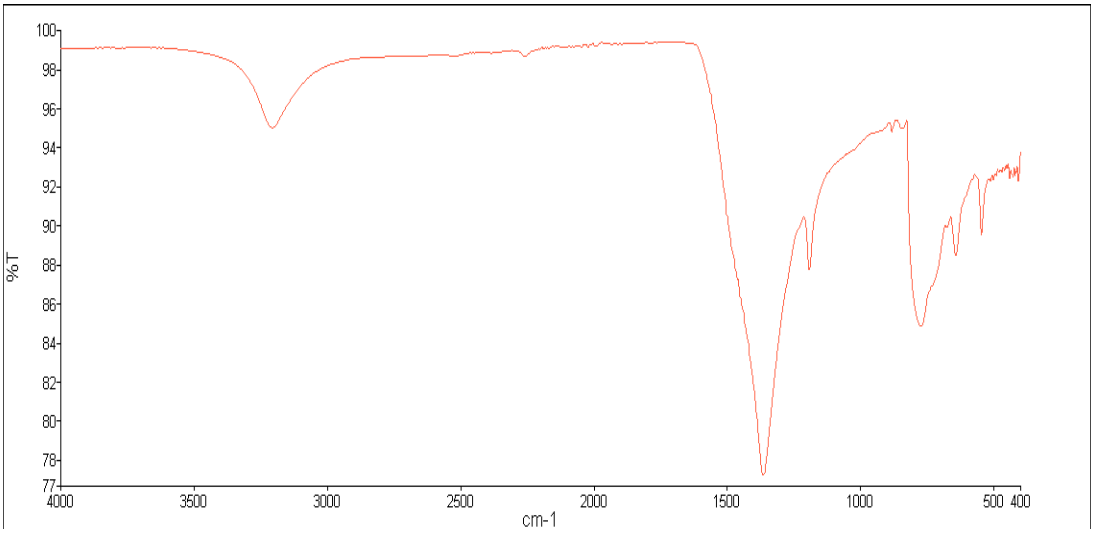


Figure 7.22. H.s sample at 600 °C with 4 hr by procedure III (reheated)

7.3 Appendix C XRD Diffractograms of Samples

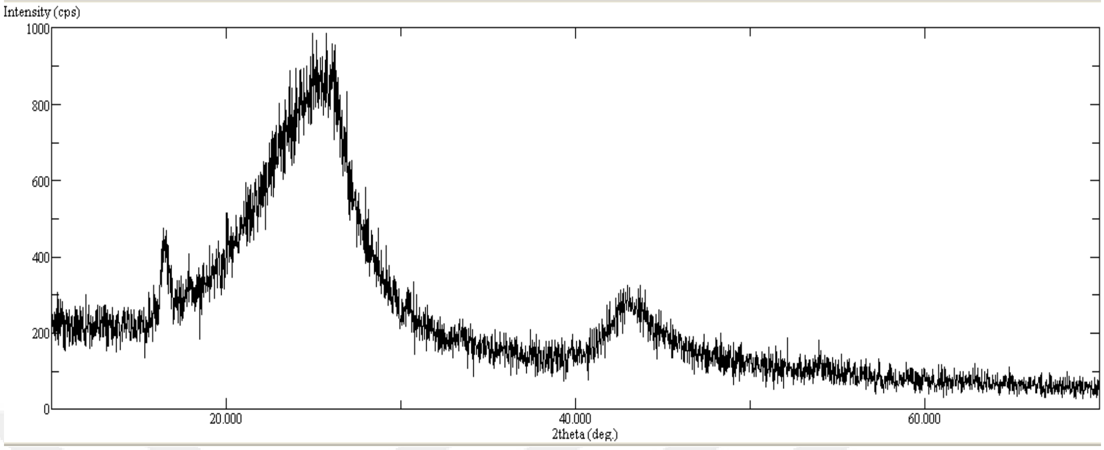


Figure 7.23. 1.5 g h.s + 1.5 g sample b.ox by procedure I (XRD)

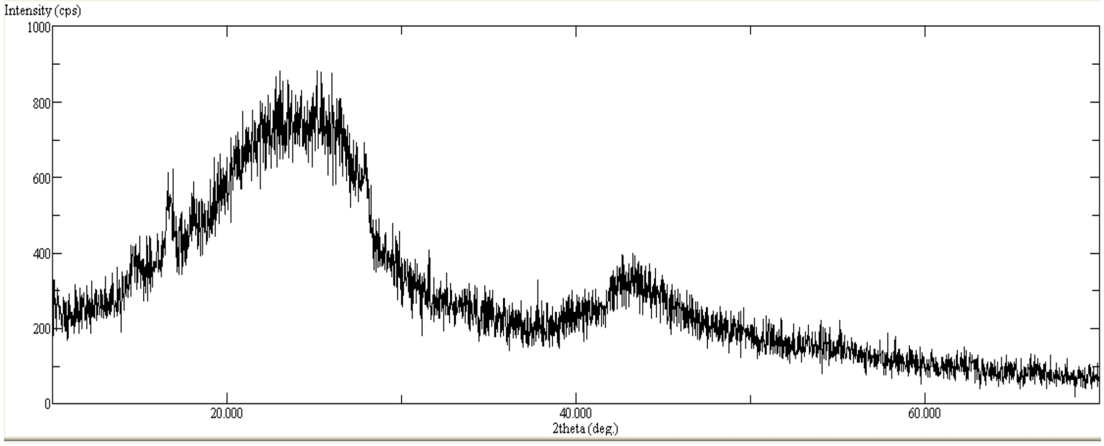


Figure 7.24. 1 g w.s + 1 g b.ox sample by procedure II (XRD)

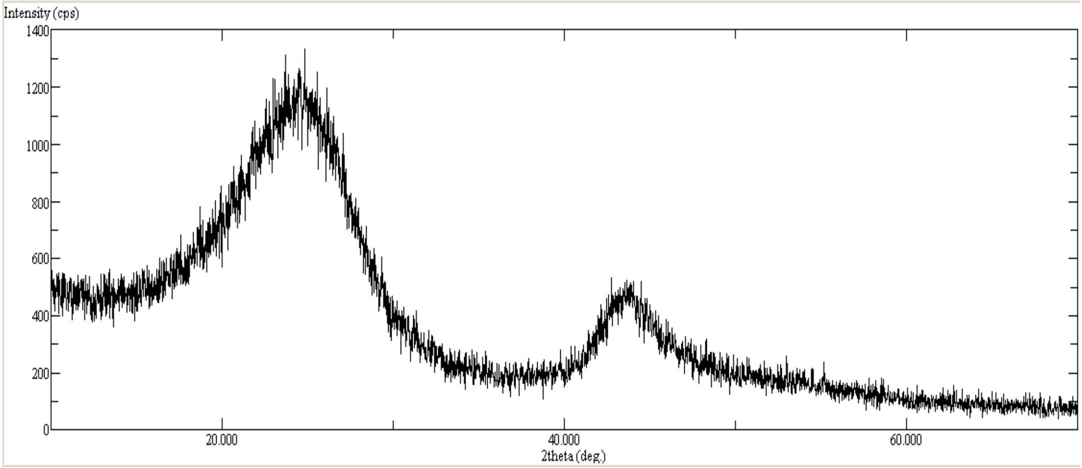


Figure 7.25. 0.75 g ac + 0.80 g b.ox sample by procedure I (XRD)

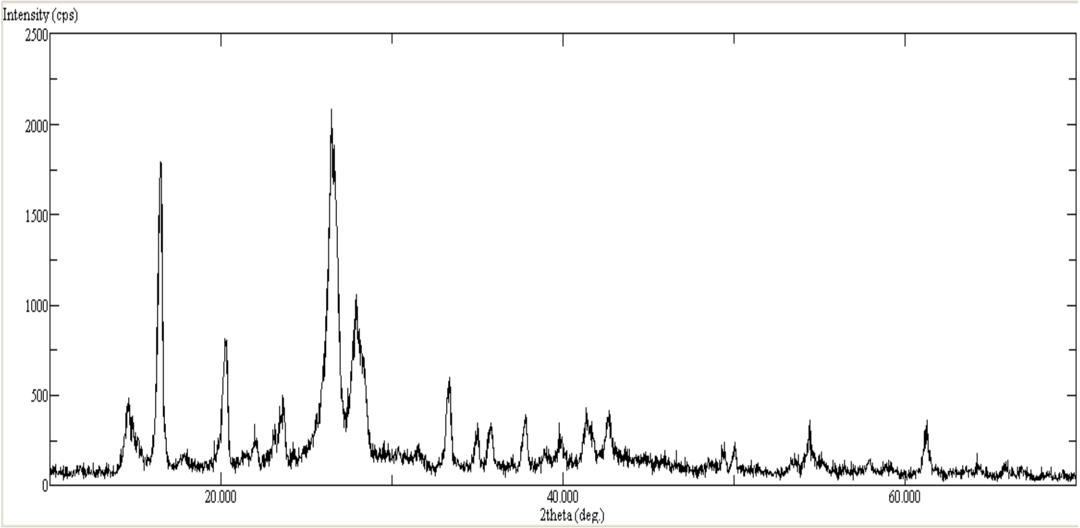


Figure 7.26. 4.5 g h.s + 1 g b.a sample at 1350 °C by procedure II (XRD)

7.4 Appendix D SEM Images of Samples

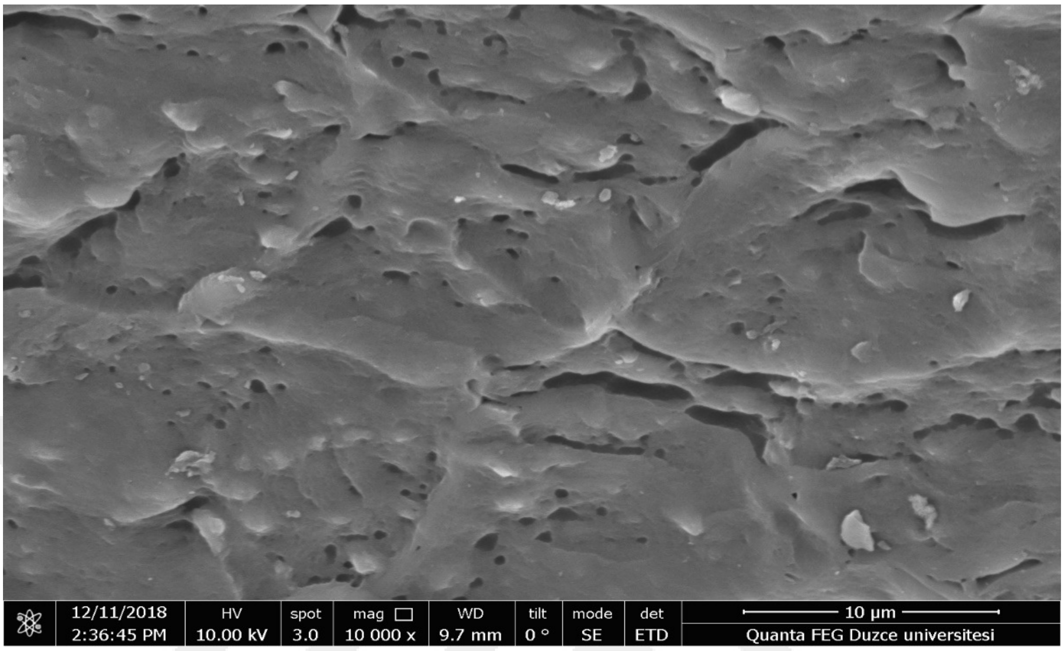


Figure 7.27. 0.75 g ac + 0.80 g b.ox sample by procedure I (SEM)

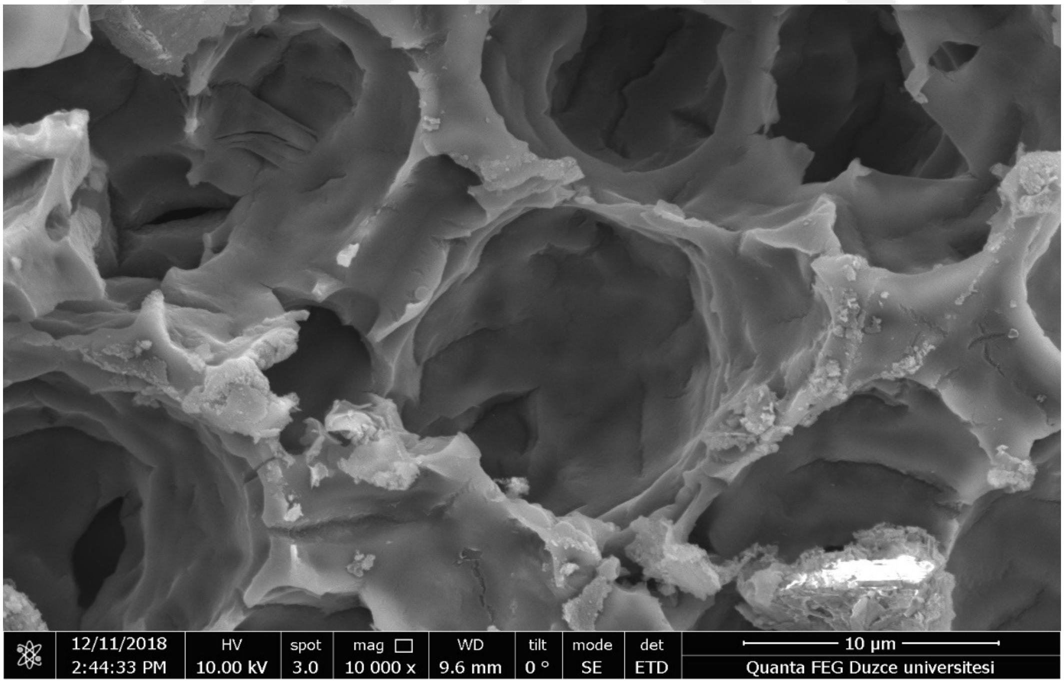


Figure 7.28. 1.5 g h.s + 1.5 g sample b.ox by procedure I (SEM)

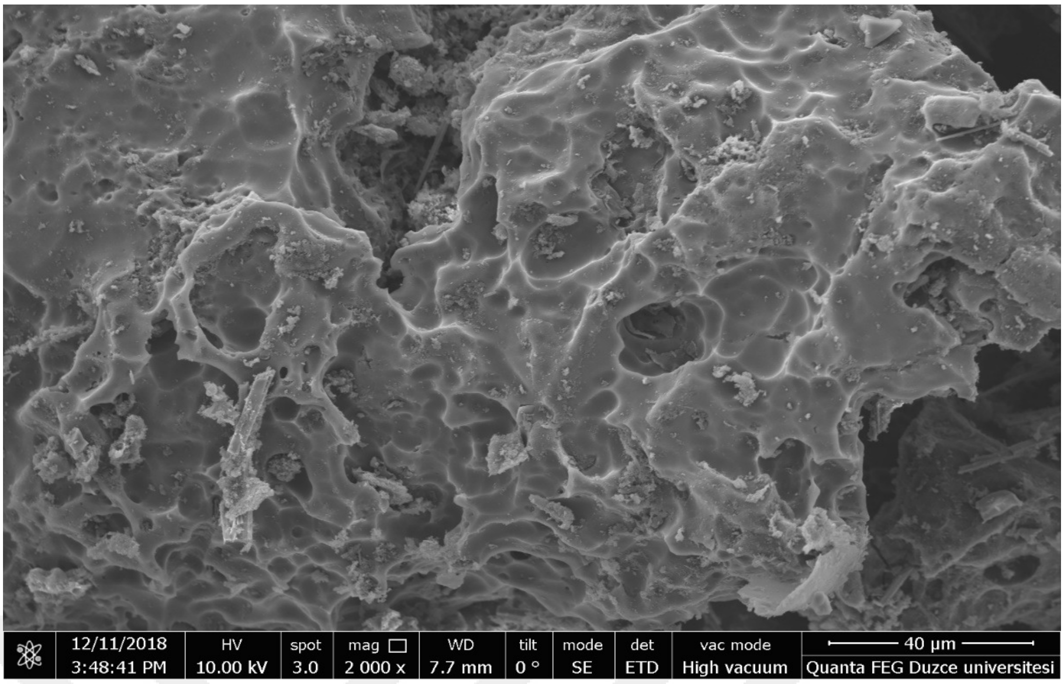


Figure 7.29. 1 g w.s + 1 g b.ox sample by procedure II (SEM)

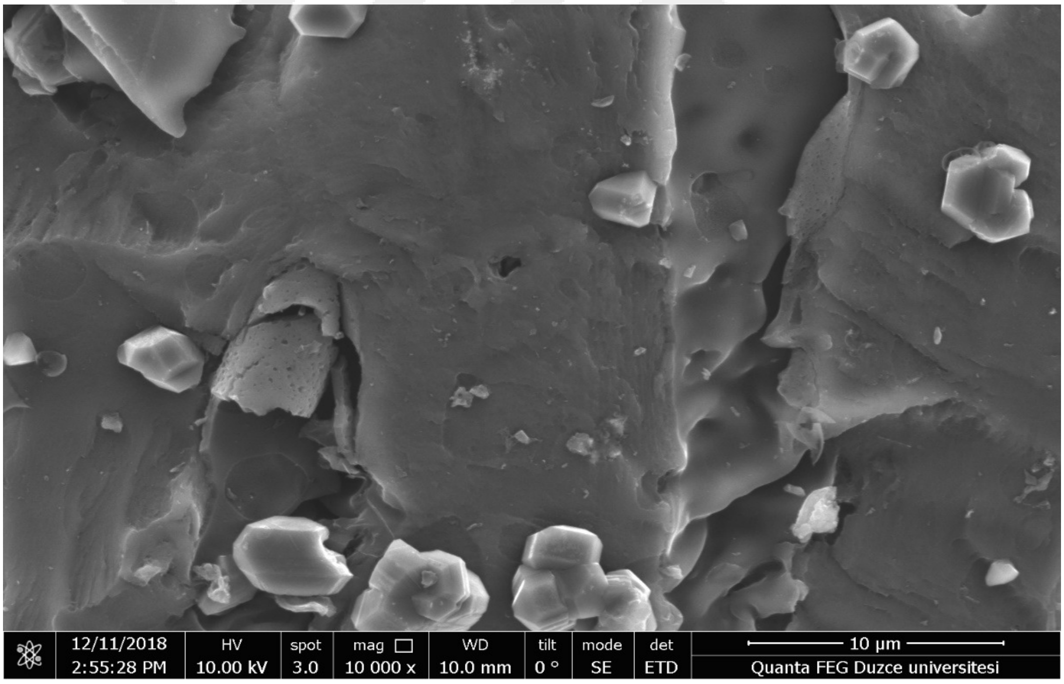


Figure 7.30. 4.5 g h.s + 1 g b.a sample at 1350 °C by procedure II (SEM)

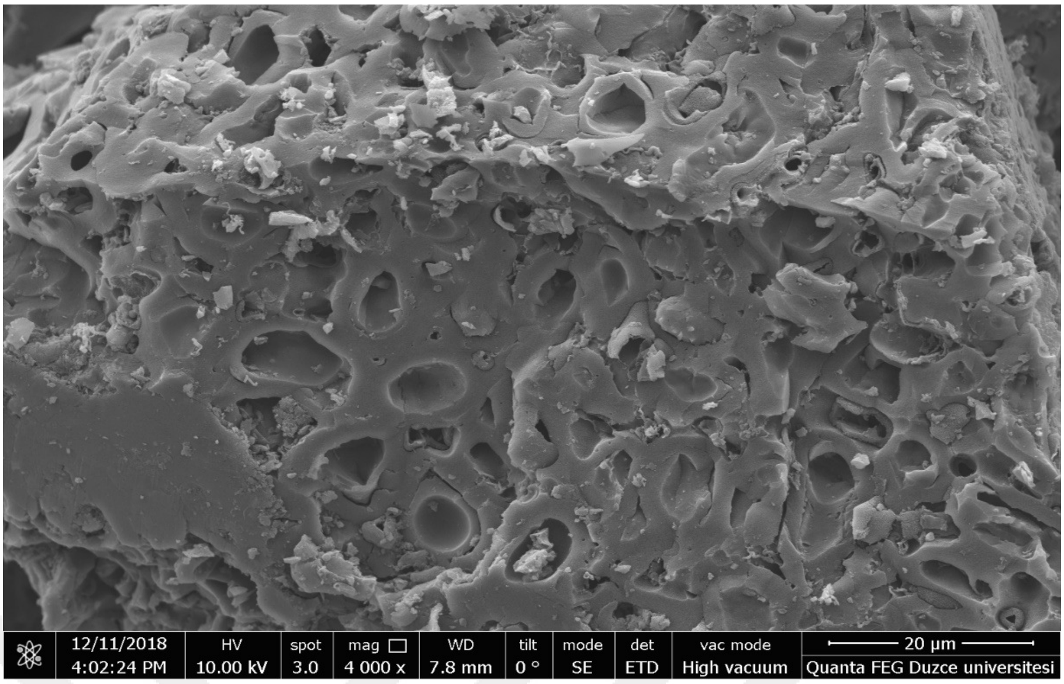


Figure 7.31. 1 g h.s + 4.5 g b.a sample by procedure II (SEM)

8. CURRICULUM VITAE

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