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

THE EFFECT OF REPRESENTATIVE METAL HALIDES ON SYNTHESIS OF HEXAGONAL BORON NITRIDE

MASTER OF SCIENCE

GÖKHAN UZUN

BOLU, JULY 2017

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APPROVAL OF THE THESIS

THE EFFECT OF REPRESENTATIVE METAL HALIDES ON SYNTHESIS OF HEXAGONAL BORON NITRIDE submitted by **GÖKHAN UZUN** 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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July 11, 2017

Prof. Dr. Duran KARAKAS ....

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.

GÖKHAN UZUN

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ABSTRACT

THE EFFECT OF REPRESENTATIVE METAL HALIDES ON SYNTHESIS OF HEXAGONAL BORON NITRIDE
MSC THESIS
GÖKHAN UZUN
ABANT IZZET BAYSAL UNIVERSITY GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
DEPARTMENT OF CHEMISTRY
(SUPERVISOR: ASSIST. PROF. ERHAN BUDAK)

BOLU, JULY 2017

Hexagonal boron nitride is a high temperature solid lubricant with having good electric insulator, inert material, and thermal conductor properties. The specific gravity is low, it is stable in air up to 1000°C. The temperature resistance of BN can be compared to MgO, ZrO_2 or CaO but BN shows higher resistance to thermal shock than others. The first synthesis of hexagonal boron nitride came true in 1842 by Balmain, but hBN began to work late as 100 years later in commercial area. In 1957 Wentorf successfully synthesized cBN that is the hardest material after diamond. Afterthat General Electric in USA De Beers in South Africa Sumitomo and Shawa Denko in Japan and some companies in Russia have been in progress to production of it since 1969. Hexagonal boron nitride, like graphite, Hexagonal boron nitride (hBN) has the identical layer structure and characteristic as graphite, and be called “white graphite”, has special bonding behaviors that can exist in many different structures. We can say for hexagonal boron nitride has also high refractoriness, lubricity, low thermal expansion, high thermal conductivity, electrical isolation, chemically inertness and easy workability. In this study, hexagonal boron nitride was synthesized with the modified O’Connor method in presence of different alkaline metal halides. X-ray diffraction (XRD) Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) is used to determine structural properties of synthesized specimens. XRD was the main device to determine properties of the samples. Main peaks of Hexagonal Boron Nitride were observed in XRD analysis, also lattice parameters were calculated by it. FTIR results was the first election for us and all of the samples gave main spectra results lastly SEM analysis confirmed nano scale of synthesized products.

KEYWORDS: Hexagonal boron nitride, O’Connor method, Alkaline metal halides

ÖZET

TEMSİLCİ METAL HALOJENÜRLERİN HEKZAGONAL BOR NİTRÜR SENTEZİNDEKİ ETKİSİ
YÜKSEK LİSANS TEZİ
GÖKHAN UZUN
ABANT İZZET BAYSAL ÜNİVERSİTESİ FEN BİLİMLERİ ENSTİTÜSÜ
KİMYA ANABİLİM DALI
(TEZ DANIŞMANI:YRD.DOÇ.DR. ERHAN BUDAK)

BOLU, TEMMUZ - 2017

Hekzagonal bor nitrür yüksek sıcaklık katı yağlayıcı, iyi elektrik yalıtkan, iyi ısı iletken ve kimyasal olarak inert olan ilgi çekici bir maddedir. Özgül ağırlığı düşük ve atmosferde 1000ºC dereceye kadar sağlamlığını koruyan bir materyaldir. Isı dayanımı konusunda MgO, ZrO_2, ve CaO gibi dayanıklı bileşiklerle kıyaslanabilir olsada ısıl şoka karşı direnci bakımından diğerlerinden daha dayanıklıdır. Bor nitrürün sentezi ilk olarak 1842 yılında Balmain tarafından gerçekleştirildi, fakat ticari alana 100 yıl kadar geç atıldı.1957 yılında Wentorf elmastan sonraki en sert madde olan kübik bor nitrürü başarılı bir şekilde sentezledi. Bundan sonra ABD'den General elektirik Güney Afrika'dan De Beers Japonya'dan Sumimoto ve Shawa Denko ve Rusyadan bazı şirketler 1969 yılından beri üretimine devam etmektedirler. Grafite benzeyen Hekzagonal Bor Nitrür, hekzagonal bor nitrür grafit ile aynı düzlemsel yapıya ve özelliklere sahiptir ki hatta 'beyaz grafit' olarak da adlandırılır, kendine has bağlanma davranışları sayesinde çok farklı yapılarda bulunabilir. Ayrıca Hekzagonal Bor Nitrür için şunu da söyleyebiliriz yüksek sıcaklığa dayanım, yağlama (kayganlaştırma), düşük ısıl genleşme, yüksek ısı iletimi elektirik yalıtkanlığı, kimyasal olarak tepkimelere girme eğiliminin düşük olması ve üzerinde çalışmanın kolay olması gibi özelliklere sahiptir. Bu çalışmada Hekzagonal Boron Nitrür modifiye edilmiş O'Connor methodu kullanılarak farklı alkali metal halogenür eşliğinde sentezlenmiştir. Örneklerin yapısal özelliklerinin belirlenmesinde X-Ray Diffraction (XRD) Fourier Transform Infrared spectroscopy (FTIR) ve Scanning Electron Microscopy (SEM) cihazları kullanılmıştır. Örneklerin özelliklerinin belirlenmesi için kullanılan ana cihazımız XRD idi. Hekzagonal Bor Nitrürün ana pikleri onunla görüldü ayrıca bağ parametreleri bununla hesaplandı. İlk süzgecimiz ise FTIR idi ve tüm örnekler aşağı yukarı aynı ana spectra sonuçlarını verdi. Son olarak SEM cihazı sonuçları sayesinde sentezlenen örneklerimizi yakından inceleme şansı elde edebildik.

ANAHTAR KELİMELER: Hekzagonal bor nitrür, O'Connor metodu, Alkali metal halojenürler

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LIST OF ABBREVIATIONS ANDSYMBOLS

2Θ	: Bragg angle degree
BN	: Boron Nitride
cBN	: Cubic Boron Nitride
EDX	: Energy Dispersive X-Ray Spectroscopy
hBN	: Hexagonal Boron Nitride
ICDD	: The International Centre for Diffraction Data
rBN	: Rhombohedral Boron Nitride
SEM	: Scanning Electron Microscopy
tBN	: Turbostratic Boron Nitride
wBN	: Wurtzitic Boron Nitride
XRD	: X – Ray Diffractometer
ND	: Not determined

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1. INTRODUCTION

Boron nitride (BN) was synthesized with the mixture of boric acid and potassium cyanide by Balmain in 1842. BN, white-colored powder, has excellent properties such as physical and chemical stability, electrical insulator, lubricant, high temperature resistivity and thermal conductivity. Due to its excellent properties BN is valuable for industrial applications such as electronic, automobile, ceramic industry and space applications etc. These properties make BN industrially important compound. Furthermore, BN is an unusual structure in the area of materials science. Because of the special bonding behaviors of boron and nitrogen, BN exists in many different phases. Also, it is important subject for Turkey because Anatolia has the largest boron mine in the world (Figure 1).

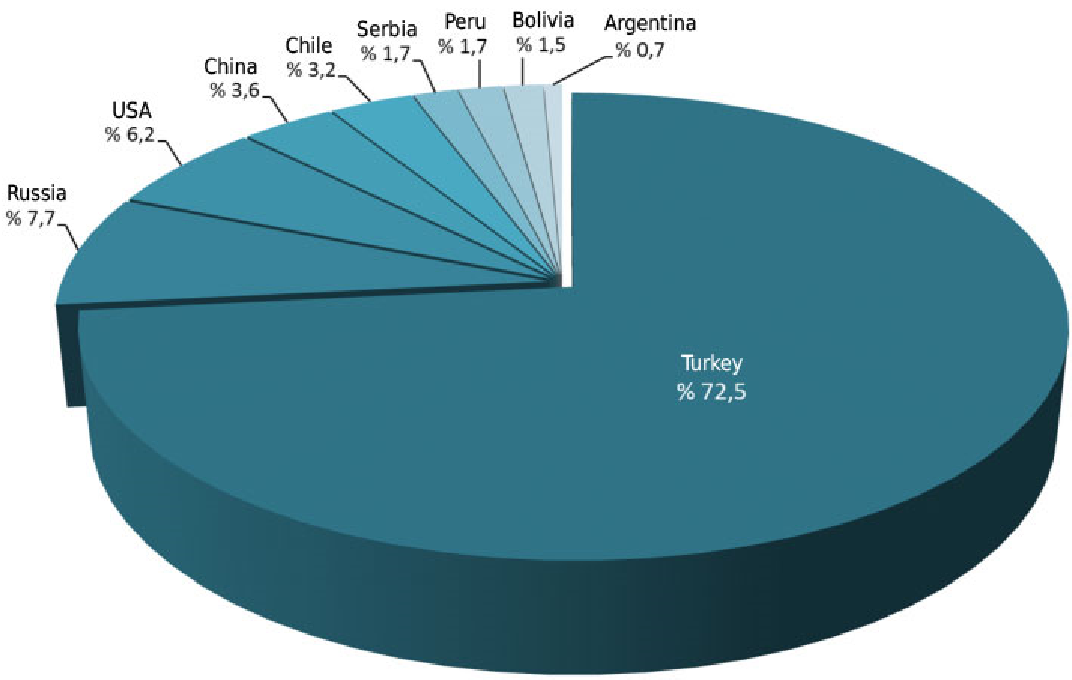


Figure 1. Distribution of Boron Reserves Around the Globe (2012) (Annual Report, Eti-Maden,2012)

2. BORON NITRIDE PHASES

In periodic table carbon is placed between boron and nitrogen, so BN phases are isoelectric to corresponding carbon phases e.g. hBN and graphite structure and properties are very similar to each other (except conductivity and color) for that reason hBN is called also “white graphite”. Moreover, due to special bonding behaviors of boron and nitrogen, BN exists in many different phases (figure 2).

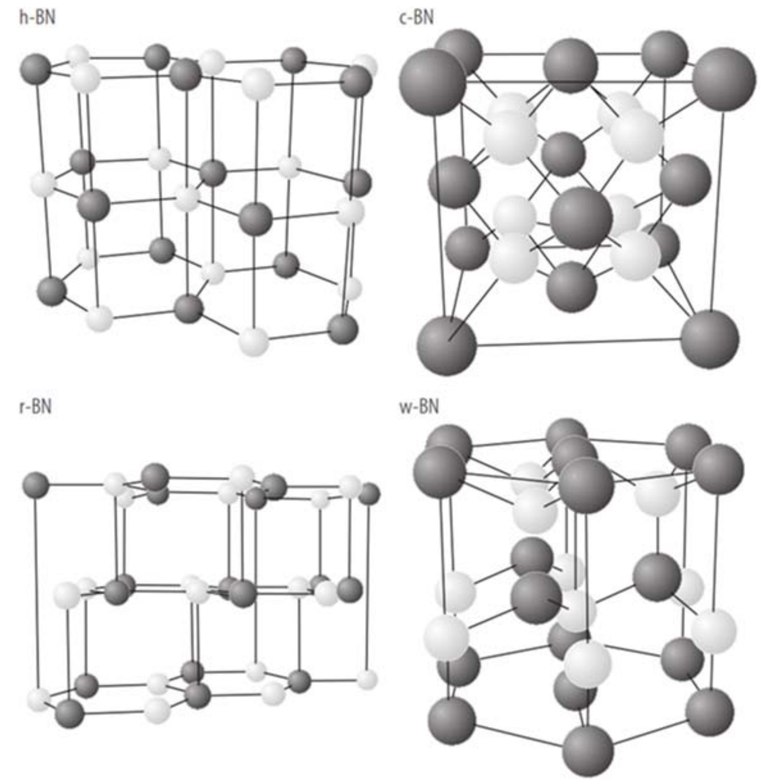


Figure 2. BN phases.

The well-defined crystallographic structures are hexagonal BN (hBN), rhombohedral BN (rBN), wurtzitic BN (wBN), and cubic BN (cBN). Additionally, other crystalline and amorphous structures exist. According to hybridization BN can be classified in two groups (Table 1).

Table 1. Types of Boron Nitride.

Boron Nitride	
sp^2 – BN	**sp^3 – BN**
hBN	cBN
rBN	wBN
tBN (amorphous)	aBN (amorphous)

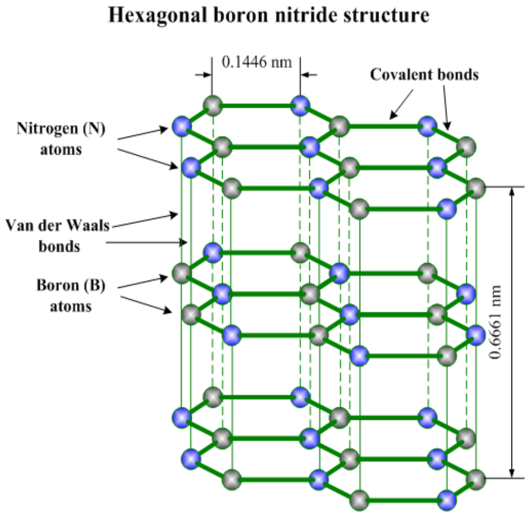
hBN has excellent properties so it is well-known type of BN. Also, cubic boron nitride (cBN) is the second familiar compound and the hardest material after diamond. Also, it is isoelectronic with diamond and used in turning machine instead of diamond.

rBN structure is similar to the hBN phase but the atomic layers sequence is ABCABC. It was reported that rBN is formed during conversion of cBN into hBN (*Sachdev H, Haubner R, Noth H, Lux B (1997) Diamond Related Mater 6: 286-292*).

wBN is a new superabrasive material that is manufactured by detonation. It is the next step in the boron nitride generation which includes a well-known superabrasive - cubic boron nitride. This new material has a polycrystalline structure that provides superior cutting properties and, moreover, sharpens itself during cutting. Polycrystalline structure means plenty of crystals are bonded chemically together that work at the same time.

In the structure of hexagonal boron nitride (hBN), each boron atom has a nitrogen atom directly above and below, and nitrogen has a boron atom directly above and below, too. It has a hexagonal structure with the series of stacked parallel layer planes. In this parallel layers, one boron atom has three bond with nitrogen, nitrogen vice versa (figure 3).

hBN has the same properties and layer structure with graphite and be called 'white graphite' the crystal cell parameters of them as shown at below.



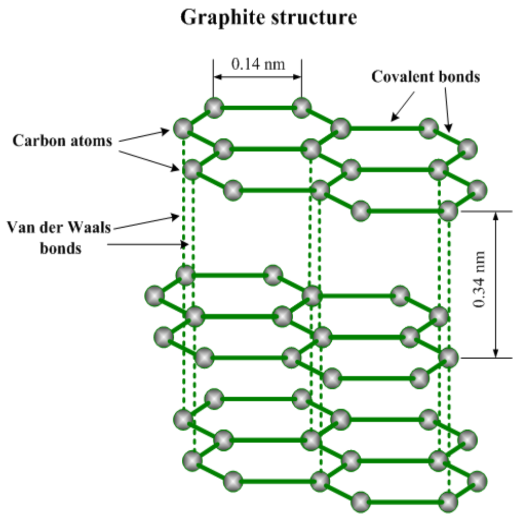


Figure 3. The structure of hBN **Figure 4**. The structure of graphite

They are isoelectronic both carbon and boron nitride rings have six electron and the interlayer interaction is van der Waals forces. Although the structure of hBN is so similar with graphite but graphite distinguishes from hBN in forming intercalation compounds. There are so many different types of graphite intercalation compounds. However there has been no hBN intercalation compound synthesized or reported yet. While graphite has been intercalating over the years, history of hBN has filled by many unsuccessful attempts until now. For example, in 1989, Doll et al. (G.L. Doll, J.S. Speck (1989) et al., J. Appl. Phys. 66 (6) 2554.) found that charge transfer from K to hBN is very small, implying no intercalation compound formed. (B.-Q. Dai and G.-L. Zhang (2002) Materials Chemistry and Physics, 78, 304–307)

2.1 Synthesis of Boron Nitride

After the first synthesize of BN by Balmain, there have been many routes (figure 5) found to produce boron nitride from direct synthesis of boron with nitrogen to get fine BN powder, another word boron nitride became popular subject for researches.

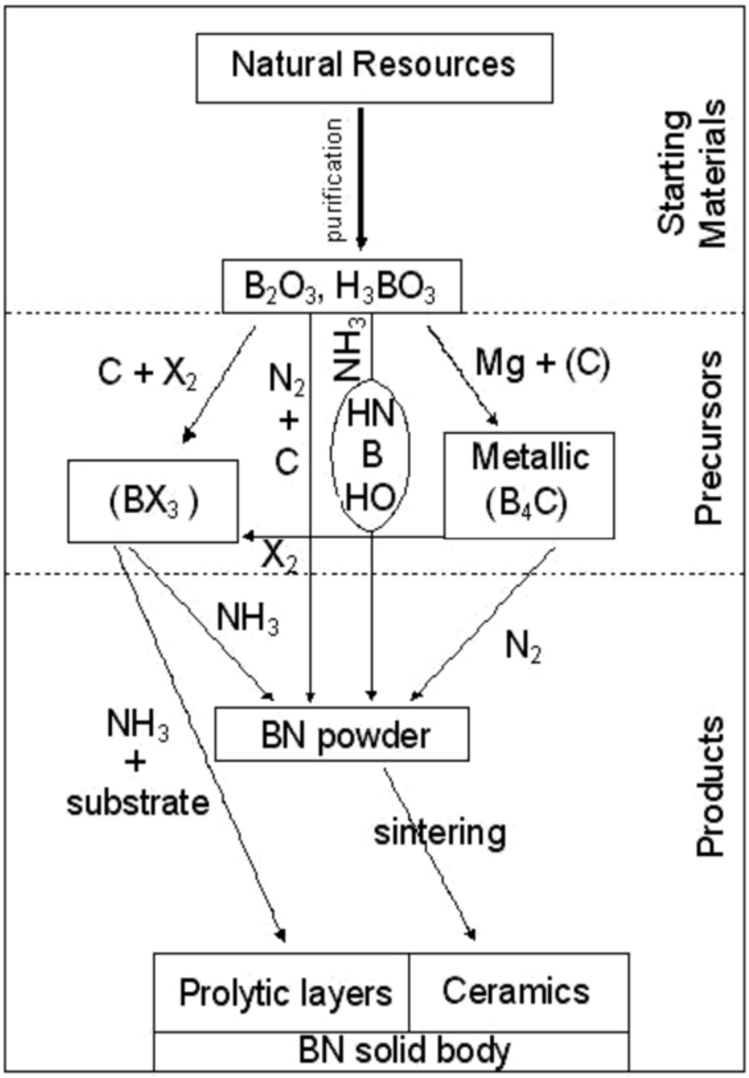


Figure 5. The routes of synthesis of BN

Although there are a lot of methods to produce hBN, principally two reactions are used on the industrial scale [Haubner R, Wilhelm M, Weissenbacher R, Lux B. Boron Nitrides — Properties, Synthesis and Applications. In: Jansen M, editor. High Performance Non-Oxide Ceramics II: Springer]:

I. The reaction of boric acid and ammonia in the presence of carrier substances ($Ca_3(PO_4)_2$, CaO, etc.) at 1500°C and above

II. Heating of boric acid and nitrogen containing organic compounds such as melamine, urea, and dicyanamide etc., up to 2100°C under nitrogen atmosphere.

Both methods are classical high temperature solid state synthesis and high temperature is necessary for the inorganic solids because of their low diffusion coefficient.

2.1.1 Boric Acid with Carrier Substances

In this procedure carrier substances ($Ca_3(PO_4)_2$, $CaCO_3$, CaO, BN, Zn-borate) is used as the presence for Boric acid with ammonia when they reacting with each other. The formation of a homogeneous melt of boric acid is prevented by the using of carrier substances. Homogeneous melt of boric acid is not suitable because of its minimal surface. Each carrier substance particle is covered by a thin film of molten boric acid at reaction temperatures exceeding 700°C. The large surface provides a full reaction of the boric acid with ammonia the carrier is leached away with HCl and residuary hBN is washed with water. When temperature exceeding 1500°C a second reaction occurs with ammonia follows resulting in hBN powders with 97% purity. The thin hexagonal platelets with a thickness of about 0,1-0,5 µm and a diameter up to 5 µm are formed as named hBN crystallites (Haubner et al, 2002).

2.1.2 Boric Acid with Organic Nitrogen Compounds

Reaction of boric acid or alkali borates with organic nitrogen compounds (melamin, urea, dicyanamide) in nitrogen atmosphere is the second important way to produce hexagonal boron nitride. Methanol or diluted acids can be used as cleaning agents to remove all non-reacted products before final thermal treatment and inert nitrogen and argon atmosphere is used for removing oxygen impurities with thermal treatment at 1500°C. Turbostratic boron nitride (tBN) 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).

2.1.3 Various BN Synthesis Methods

Reduction of boric acid of borates with carbon in nitrogen atmosphere is a way to produce BN; this type of reactions is named carbothermal reactions. In this way the temperature must be at 1000-1500°C.

At first the precursor is prepared, precursor is a substance having an unknown structure from which another substance or component is created. Then it is mixed intensively and after drying. The precursor is heated up to 1200-1500°C in following nitrogen atmosphere. The mixture remains at the maximum temperature for 60-600 min. Sometimes catalysts, like $CaCO_3$, can be used to the mixture in order to enhance the yield of boron nitride. Though using catalyst too high carbon content of the mixture leads to the formation of boron carbide (Haubner et al, 2002).

Boron nitride which is used for lubricants and toners are the ultrafine samples of boron nitride and they can be produced by combustion of boron powder at 1500°C in a nitrogen plasma (Haubner et al, 2002).

Another way for preparing boron nitride is utilization of calcium boride (CaB_6). In this way calcium boride reacts with additions of boric acid in nitrogen atmosphere at temperature exceeding 1500°C. The last example of production of boron nitride is usage of iron boride (FeB) as catalyst. Iron boride reacts with ammonia at 550°C subsequent annealing occurs in ammonia at 1000°C (Haubner et al, 2002).

The easiest and obvious method to obtain powder hBN is the O'Connor method boron oxide (B_2O_3) and urea $(NH_2)_2CO$ is mixed as weight 1:2. After that the mixture is heated under ammonia atmosphere at 1600°C. There is no poison gases like boron trichloride not requiring some expensive laboratory devices and doing modifications at preparation of precursor step. This is the biggest advantage of the O'Connor method ; cheap, safe and simple. (O'Connor, T. E.1962)

Boron oxide is the source of boron and the ammonia is the source of nitrogen in this method. So we can make this equation as shown;

$$\mathbf{B_2O_3 + 2NH_3 \rightarrow 2BN + 3H_2O}$$

The O'Connor method was performed in three steps. At first an ammonia molecule has to approach the surface of boric acid. New bonds are created due to the redistribution of electron densities in the system as the consequence of the redistribution (figure 6). The second step is trimerization in this step monomer is stabilized.

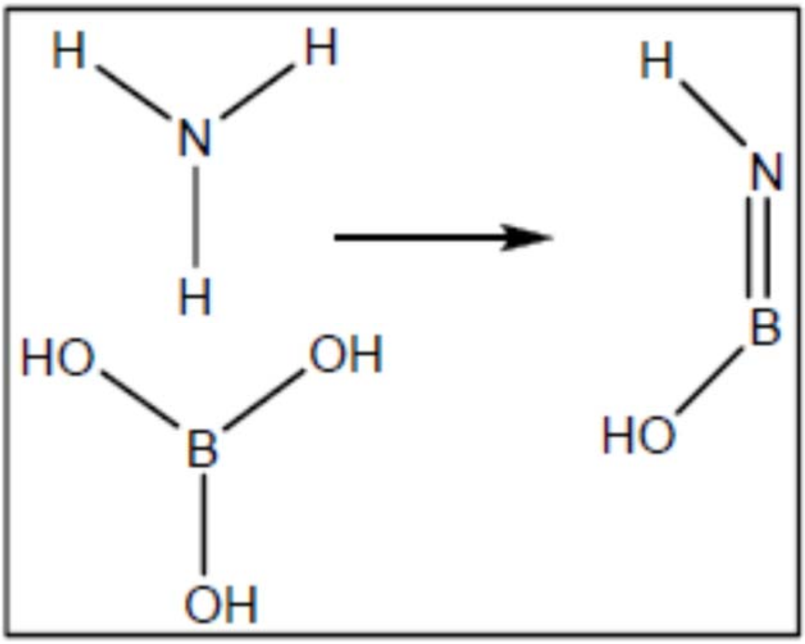


Figure 6. Redistribution of HO-B-N-H

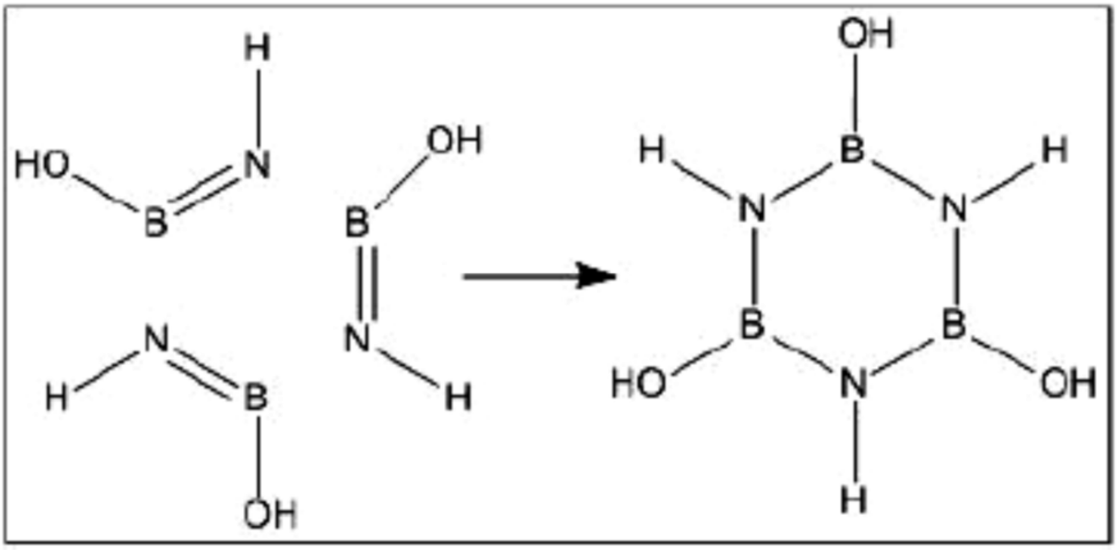
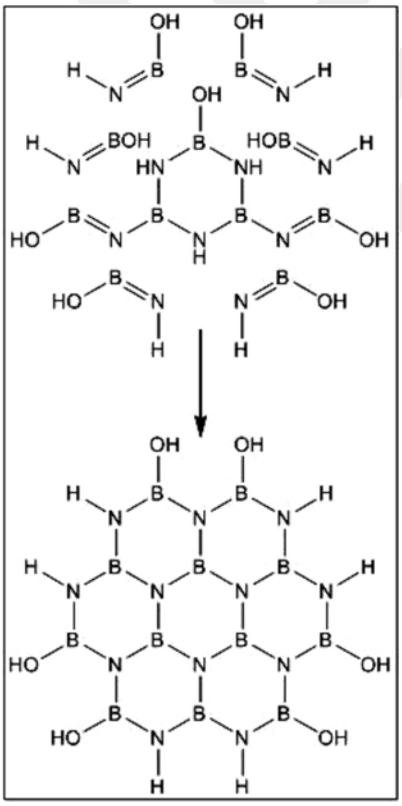


Figure 7. Trimerization of the monomer



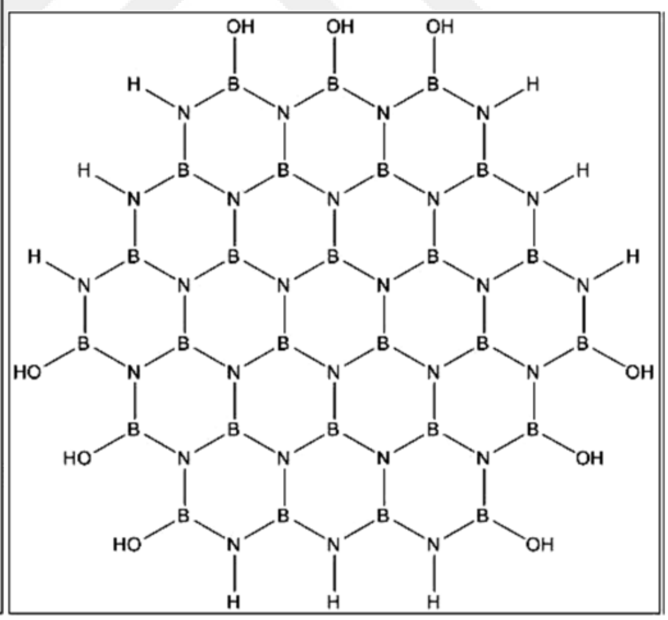


Figure 8. Macromolecules of BN **Figure 9.** Crystalline BN

In the last step a macromolecule is growing as shown in figure 8. This growing can continue till the size of it reaches that which can be found in tBN powders. The size is approximately equals 10 nm an expressed as crystalline width. A hexagonal macromolecule in this size corresponds to HO-$B_{27}N_{27}$-H formula (Hubacek, M. and, Sato, T.1995).

Particular monolayers which stacking each above other constitute real crystals of BN. This stacking layers are holding together with dipole dipole interaction. This interaction. This interaction is a chemical unit of hBN. The size of macromolecule can be different for all BN crystalline and that causes different width of the BN crystalline (Figure 9).

Hexagonal boron nitride macromolecules has hydrogen and oxygen atoms. They are constitutional elements terminating the two dimensional hBN macromolecules as shown in the previous figures. When ratio of circumference to area increases content of these elements decreases. So larger BN crystals have higher purity. This relationship means the principle of the purification process where BN is first crystallized in nitrogen gas and oxygen converted to boron oxide are washed out.

3. AIM AND SCOPE OF THE STUDY

hBN is an industrially important material. Some of the application area and properties of hBN is given in table:

Table 2. Some usage areas for BN

Usage area	The Desired Feature					
	Refractory	Thermal conductivity	Electronic isolation	Chemical inertness	Lubrication	Processing
Lubricant in high temperature	√			√	√	
Mold and mold release	√			√	√	
Active filler for petroleum products	√	√	√	√	√	
Transmission agent of high pressure	√			√	√	
the slots of the heater wires	√		√	√		
Melting crucibles of glasses and metals	√	√		√		√
Brake pads	√			√	√	√
High temperature furnaces	√	√	√	√		√
Magnetic - hydrodynamic devices	√		√	√		√
Dielectric for radar and antenna systems			√			
Isolator for high and low frequency devices	√		√			√
Neutron grabber in nuclear reactors	√	√		√		√
Ceramic production	√	√		√	√	√

hBN is remarkable subject for material science. Annual world consumption of hBN is about 1000 tons. This amount makes a value of 55 million USD (ETİ

Holding A.Ş, Bor Nitrür Raporu -2003). Under this circumstance the aim of this study:

- examine the effect of metal halides on the synthesis of hBN

- reduce the formation temperature of hBN

- increase the yield of hBN

- improve crystallinity of hBN

- investigate the morphology of hBN samples in nanoscale

- increase the grain size of hBN

- lower the cost of hBN production.

4. MATERIALS AND METHODS

4.1 Chemicals

Boron oxide (Fluka, 97%), Urea (Fluka, 99%), calcium bromide (Aldrich), calcium chloride (Aldrich), calcium fluoride (Aldrich), calcium iodide (Alfa Aesar), potassium bromide (Aldrich), potassium chloride (Merck), potassium fluoride (Abcr), potassium iodide (Aldrich), lithium bromide (Aldrich), lithium chloride (Abcr), lithium fluoride (Merck), lithium iodide (Alfa Aesar), magnesium bromide (Alfa Aesar), magnesium chloride (Aldrich), magnesium fluoride (Aldrich), magnesium iodide (Aldrich), sodium bromide (Alfa Aesar), sodium chloride (Alfa Aesar), sodium fluoride (Merck), sodium iodide (Alfa Aesar), ethanol (Merck, 99.5%) and hydrochloric acid (Merck, 37%) were commercially obtained and used without any purification.

4.2 Synthesis of hBN Samples

Synthesis of hBN compounds were carried out with modified O'Connor method. The mixture of 1g boron oxide 2g of urea and 0.6g of metal halides (NaCl, NaI, NaF, NaBr, KCl, KI, KF, KBr, $MgCl_2$, MgI_2, MgF_2, $MgBr_2$, $CaCl_2$, CaI_2, CaF_2, $CaBr_2$, LiCl, LiI, LiF and LiBr) were mixed and powdered with a mortar and a pestle. Followed by the mixture was preheated at 200°C for 2 hours in furnace to obtain precursor. Then the precursor re-powdered in mortar and heated in tube furnace under ammonia atmosphere (with a flow rate of 120 mL/min) at 1450°C for 3 hours.

Finally, the product was boiled in 10% HCl solution then filtrated in hot water (500 mL) and ethanol respectively and dried in oven at 100°C then bottled.

4.3 Preparation of hBN samples

4.3.1 Agate Mortar and Pestle

The mixture of boron oxide, urea and additive oxide were powdered and homogenized in agate mortar and pestle for 20 minutes.

Figure 10. Agate mortar and pestle.

4.3.2 Camera Furnace

The pulverized mixture located in a beaker was heated to obtain precursor in Protherm PLF 140/5 camera furnace at 200°C for 2 hours.

Figure 11. Protherm PLF 140/5

4.3.3 Tube Furnace

The main heating was done with Protherm PTF 15/75/450 tube furnace (average heating rate: 7°C/min) at 1450°C under ammonia atmosphere (flow rate 120 mL/min) for 3 hours.

Figure 12. Protherm PTF 15/75/450

4.4 Characterization of hBN Samples

4.4.1 FTIR Spectroscopy

FTIR spectrum analysis of hBN samples were recorded with Perkin Elmer Spectrum Two IR Spectrometer in a range between wavelengths of 400-4000 cm^{-1}.

Figure 13. Perkin Elmer Spectrum Two IR Spectrometer

4.4.2 XRD Measurement

XRD diffractogram of hBN samples were done 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 14. Rigaku Multiflex diffractometer

4.4.3 SEM Analysis

SEM images were obtained by Jeol JSM 6390LV. Before SEM analysis, the samples were coated with gold for 220 seconds at 4mA by using Coxem KIC-1A ION-COATER.

Figure 15. Jeol JSM 6390LV

Figure 16. Coxem KIC-1A IONCOATER

4.5 Sample Calculations

4.5.1 Calculation of Lattice Parameters

Lattice parameters of the samples were calculated by using Equation 1 for hexagonal systems.

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

d : Interlayer spacing

h, k, l : Related Miller indices

a, c : Lattice parameter

Calculation of “a” parameter of hBN:

For 110 peak of hBN 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 hBN:

For 002 peak of hBN d is 3.3280 Å

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

4.5.2 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.

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

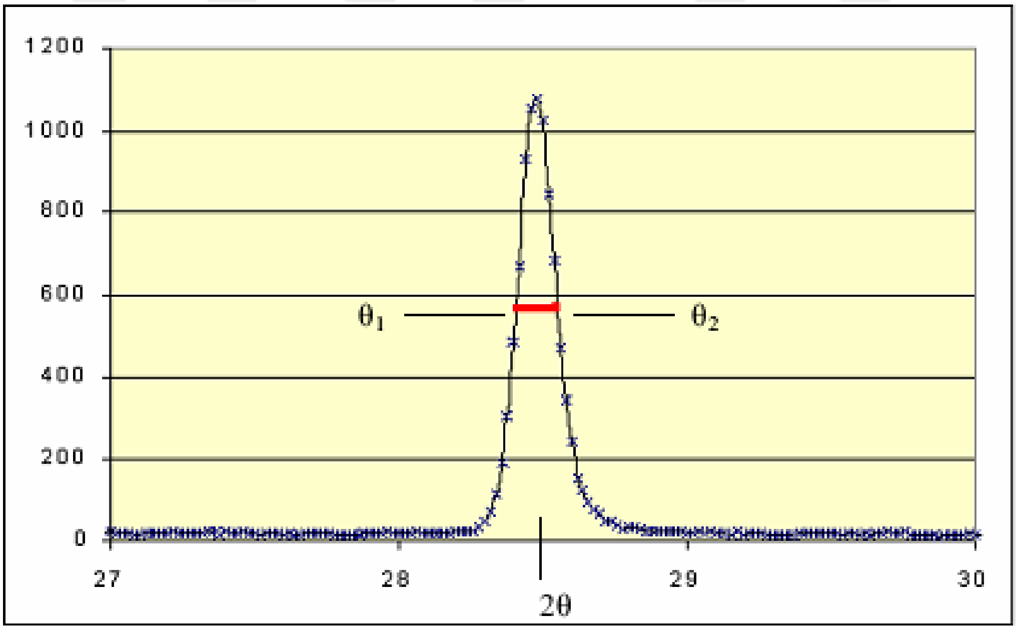
β is difference of the width of the peak athalf maximum intensity of a specific phase (hkl) in radians of reference material and sample.

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

λ is the wavelength of incident X-Rays (CuKα=1.504 Å).

2θis the center angle of the peak of sample

D is the crystallite size



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

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

$$\beta = 0.02$$

$$D = \frac{K\lambda}{\beta cos\theta} = \frac{0.9 \times 1.504}{0.02 \times (cos13.27 \times \frac{\pi}{180})}$$

D=92.4Å

D=9.24 nm

4.5.3 Calculation of graphitization index

The degree of crystallization of the hBN phase was appraised in terms of the "graphitization index" (G.I.) as three-dimensional order is the ratio of (102) into the (100) and (101) directions (Balint and Petrescu, 2009; Thomas et al, 1962), as;

$$\boldsymbol{G.I} = \frac{\boldsymbol{Area(100) + Area(101)}}{\boldsymbol{Area\ (102)}}$$

5. RESULTS & DISCUSSION

5.1 Characterization of hBN Samples

The modified O'Connor method was used to synthesize boron nitride for because it is the simplest method to form hBN with using easily purchasable chemicals and devices besides without using expensive laboratory devices (Budak, 1999).

5.1.1 FTIR Spectroscopy of hBN Samples

The FTIR measurement was performed to examine the types of chemical bonds of the obtained hBN samples (Figure A1.1. - A.1.20) and there are several studies in the literature characterizing the formation and structure of hBN by IR spectroscopy. Two strong characteristic bands locate at ~1390 cm^{-1} and ~780 cm^{-1} which were attributed to in-plane vibrations and out-of-plane bending vibrations of hBN, respectively (Budak,1999; Hubacek et al, 1994; Chen et al, 2004). In some FTIR spectrum of hBN absorption band near 3200 cm^{-1}, 3400 cm^{-1} and a shoulder peak near ~1050 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.

According to FTIR spectrum, there is no metal intercalation in to hBN. Hubacek and co-workers claimed that metal intercalation caused to disappear or weaken the out-of-plane B-N vibration (780 cm^{-1}) (Hubacek, M. and, Sato, T.1995). In all FTIR spectrum of hBN the out-of-plane B-N vibration can be easily observed.

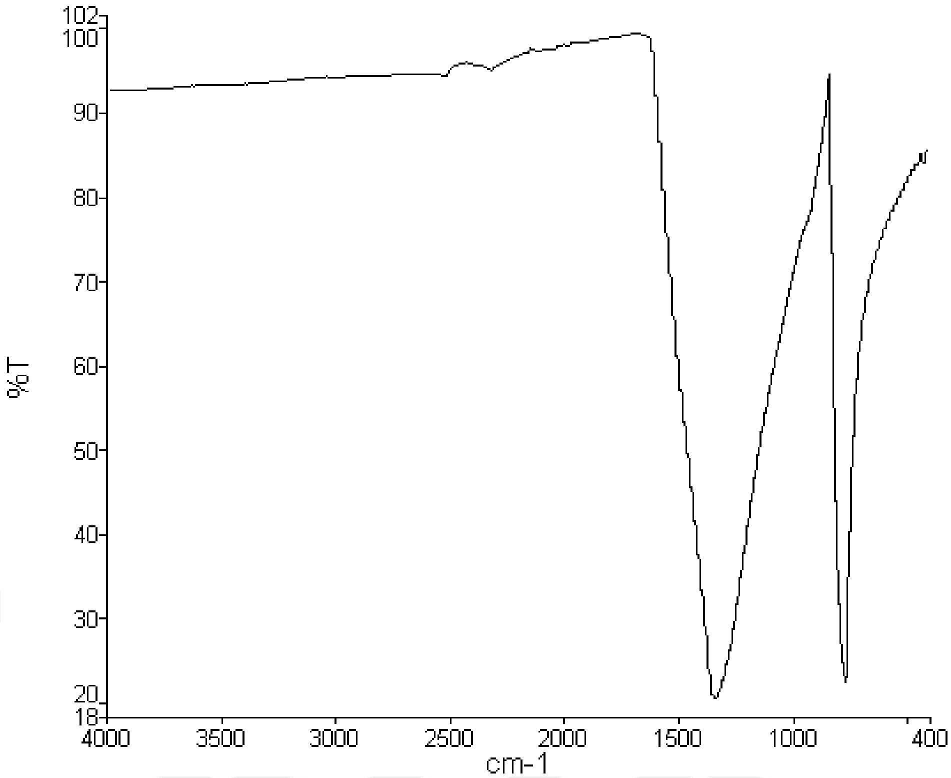


Figure 17. FTIR measurement of BN in the presence of $CaBr_2$

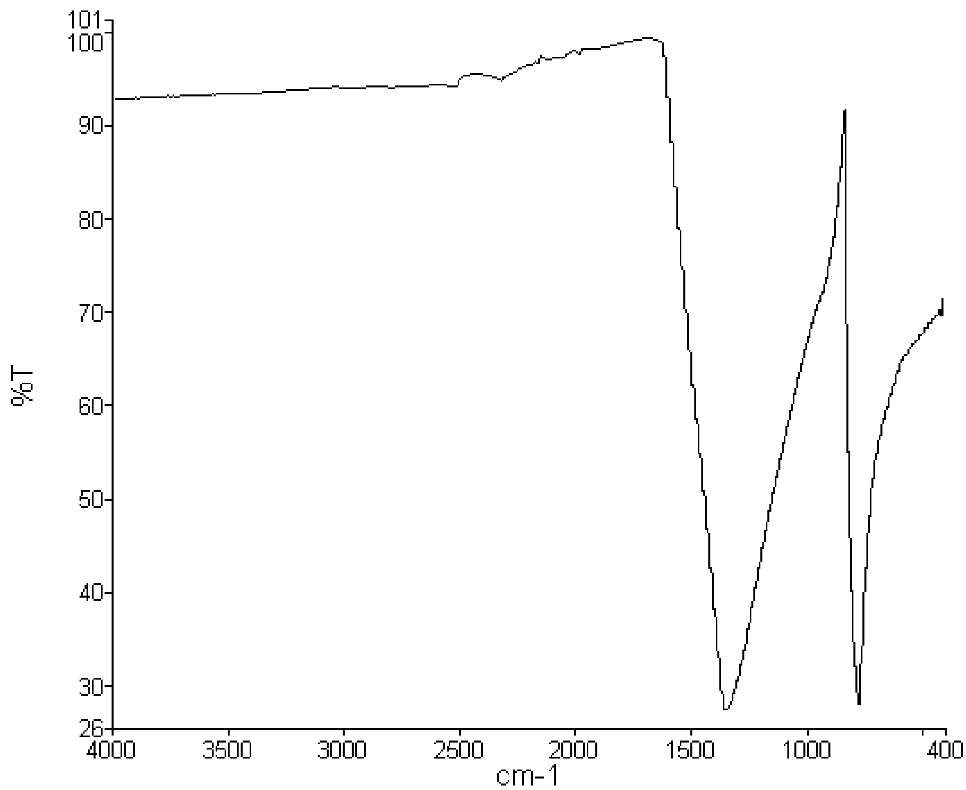


Figure 18. FTIR measurement of BN in the presence of LiCl

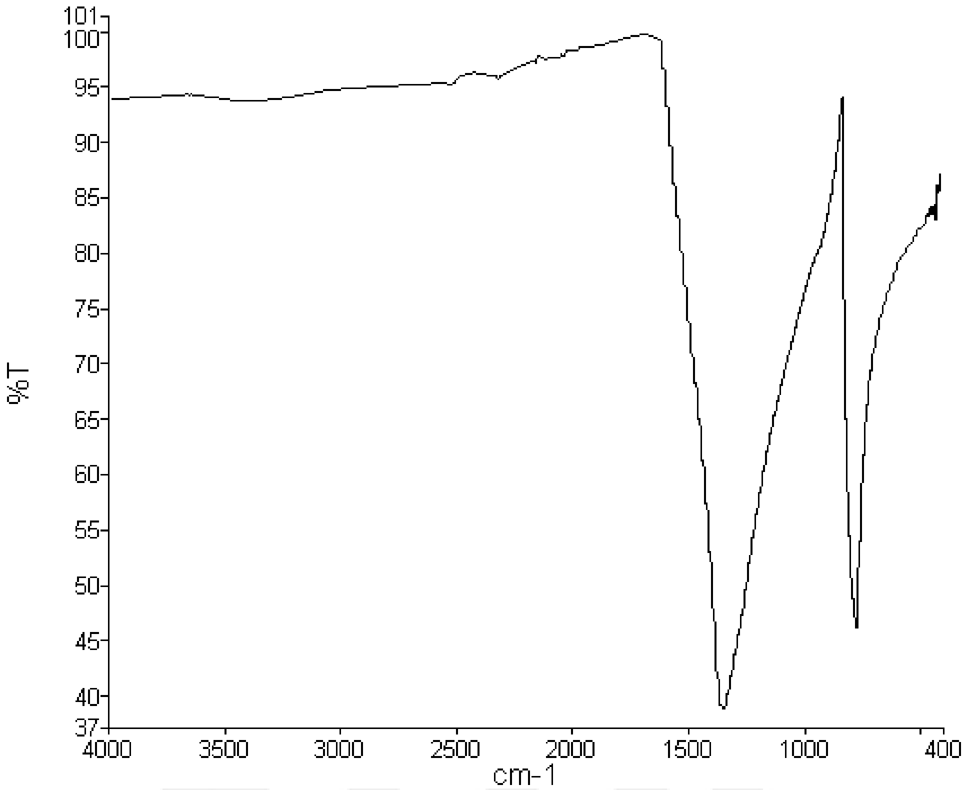


Figure 19. FTIR measurement of BN in the presence of LiI

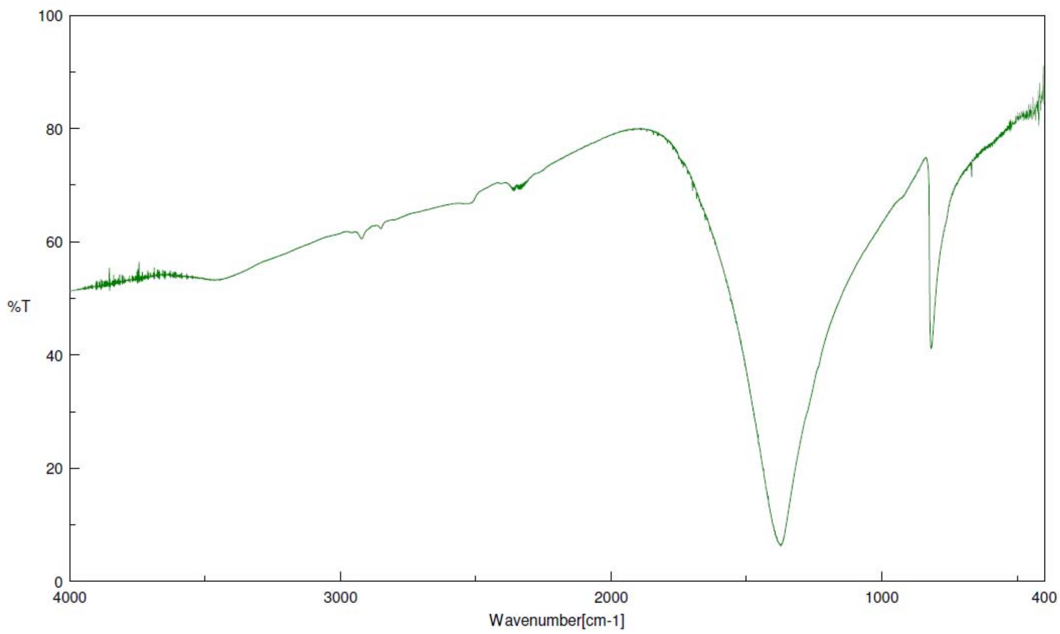


Figure 20. FTIR spectrum of pure hBN

5.1.2 XRD Pattern of hBN Samples

The composition and crystallinity of BN samples were examined by XRD (Figure B.1.1 – B.1.20) and the results were compared with standard hBN (ICDD card no: 34 - 421). In all diffractograms, the main peaks of hBN (002, 10X, 102, 004, 110, and 112) are observed.

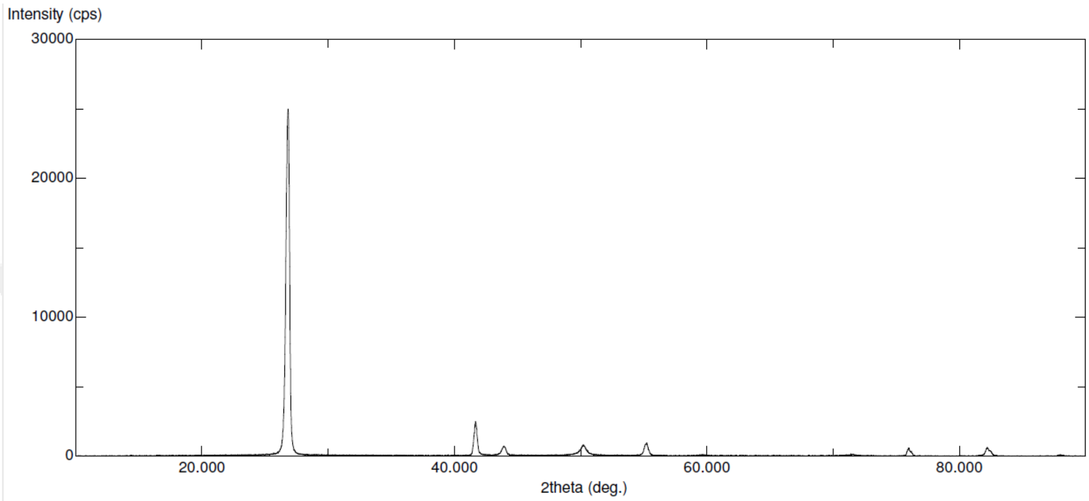


Figure 21. XRD pattern of pure hBN

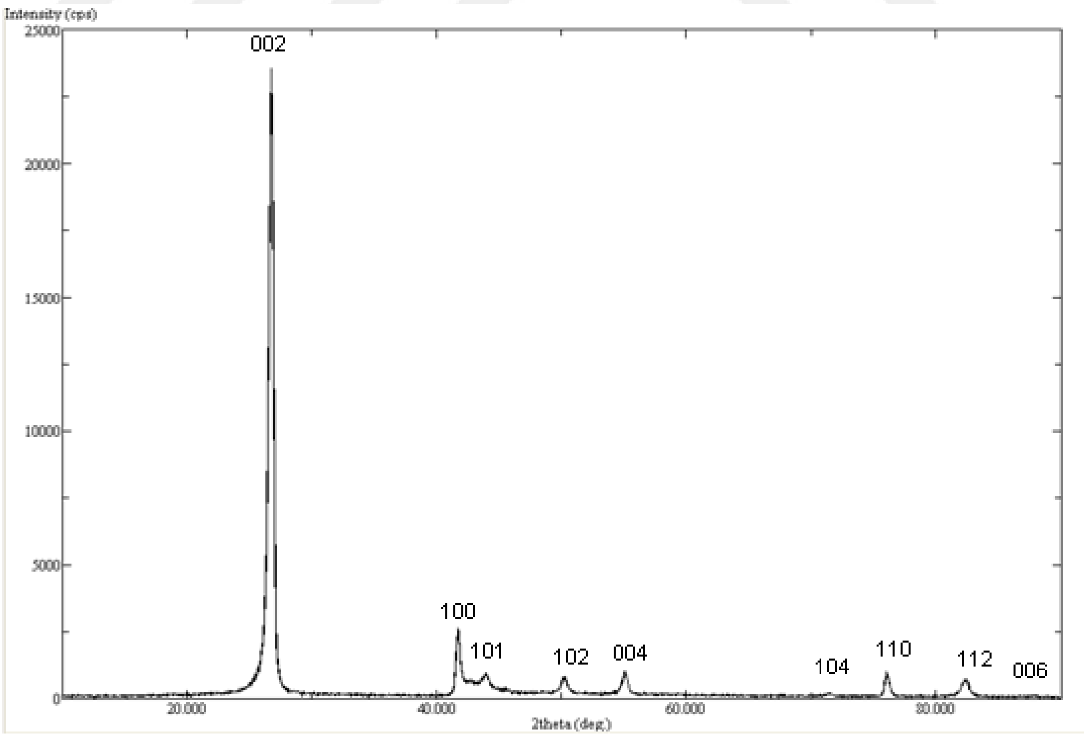


Figure 22. XRD measurement of BN in the presence of $CaBr_2$

The most significant evidence for formation of hBN is the presence of (002) peak which must be sharp and narrow and the separation of (10X) peaks (10 peaks indicates that 100 and 101 peaks that must be separated in BN, if not it is called 10 or 10X peaks) according to J. Thomas, N.E. Weston and T.E. O'Connor (1962). These conditions were provided in all XRD diffractograms of hBN. In addition, appearance of (004) and (102) peaks indicated increasing three-dimensional ordering i.e. high crystallinity. Moreover, the degree of crystallization of hBN phase was appraised in terms of the "graphitization index" (G.I.). For G.I., the best value is 1.60 and this means the structure is completely graphitized. If G.I. of hBN degree is ≥ 50, hBN is called as turbostratic (amorphous) boron nitride. The calculated G.I. values listed in table 3 illustrated that the most of hBN samples were accepted high crystalline structure.

The formation of a homogeneous melt of boron oxide which caused to minimal surface area is prevented by the using of carrier substances (Haubner, R., Wilhelm, M., Weissenbacher, R., and Lux, B. 2002). Metal halides used as carrier substance for heterogeneous melt in the mixture. Although Li- and Ca- halides gave the best result, the other halides provided average results. In our previous work (BOREN project 2013.Ç0375), it was found that the alkalinity of the dopant materials directly affected the formation and crystallinity of hBN and in that study Li_2O- containing mixture provided the best result.

Furthermore, lattice parameters were calculated from the XRD diffractograms (table 3). The results are very close to the reported value for hBN (a= 2.504Å, c= 6.656Å, and d= 3.328Å).

According to studies of P. Dibandjo, L. Bois, F. Chassagneux, P. Miele (2007) in J. Eur. Ceram. Soc. 27:313 and Y.J. Choi (1993) in J. Am. Ceram. Soc. 76:2525 some samples obtained might be accepted as amorphous because of inseparable 100 and 101 (10X) XRD peaks of hBN. However, other studies [L.Y. Chen, Y.L. Gu, Z.F. Li, Y.T. Qian, Z.H. Yang, J.H. Ma (2005) J. Cryst. Growth 273:646 and L. Shi, Y. Gu, L. Chen, Y. Qitan, Z. Yang, J. Ma (2004) J. Solid State Chem. 177:721 and L. Shi, Y. Gu, L. Chen, Z. Yang, J. Ma, Y. Qitan (2004) Mater. Lett. 58:3301.] have already pinpointed that ''10X'' peaks indicated hBN nanocrystal formation. Also, the broadening nature of the XRD peaks indicated that the particle sizes of the samples were within the nanometer scale when using the Debye–Scherrer equation. Results of the calculation illustrated in table 3. Hence it is known that usage of both ammonia and metals permits lowering of the formation temperature of hBN while the metal halides behave as catalysts while ammonia acts as the nitriding agent for metals and alloys at low temperature.

Table 3. Interlayer distance of hBN samples, calculated lattice parameters and calculated graphitization index and calculated average grain size of hBN in presence of metal halides.

Used halides	**a**	**c**	**d**	**Grain size**	**Graphitization index**
LiF	2.500	6.652	3.326	31.724	2,40
LiCl	2.506	6.706	3.353	20.265	3,04
LiBr	2.504	6.696	3.348	20.768	2,86
LiI	2.502	6.672	3.336	16.968	2,71
NaF	2.506	6.722	3.371	19.563	3,44
NaCl	2.500	6.688	3.344	13.719	N.D.
NaBr	2.504	6.710	3.355	13.843	N.D.
NaI	2.504	6.674	3.337	25.565	3,01
KF	2.504	6.690	3.345	13.596	N.D.
KCl	2.506	6.742	3.371	8.993	N.D.
KBr	2.504	6.726	3.363	7.758	N.D.
KI	2.502	6.672	3.336	26.714	N.D.
MgF_2	2.500	6.642	3.321	43.801	2,48
$MgCl_2$	2.506	6.698	3.349	29.070	2,67
$MgBr_2$	2.504	6.722	3.361	13.123	N.D.
MgI_2	2.506	6.712	3.356	20.574	3,24
CaF_2	2.508	6.700	3.350	63.135	2,00
$CaCl_2$	2.502	6.668	3.334	32.481	2,63
$CaBr_2$	2.500	6.648	3.324	24.553	2,59
CaI_2	2.500	6.654	3.327	24.948	2,60

5.1.3 SEM image of some hBN Samples

SEM images of the samples are shown in Figure(C 1.1 – C.1.20). In general, interpretations of hBN SEM images were based on Shimomura and defined as disc-shape homogeneous plates [Shimomura J, Funahashi T, Koitabashi T. Electron-Microscopy of Hexagonal Boron-Nitride Powder. J Mater Sci. 1995;30:3193-9]. However, SEM images indicated that irregularly grained powder with fractures and particles were in jagged shape. The fractures on these samples were intergranular and nucleate at the hBN boundaries because of the low bonding strength of BN grains.

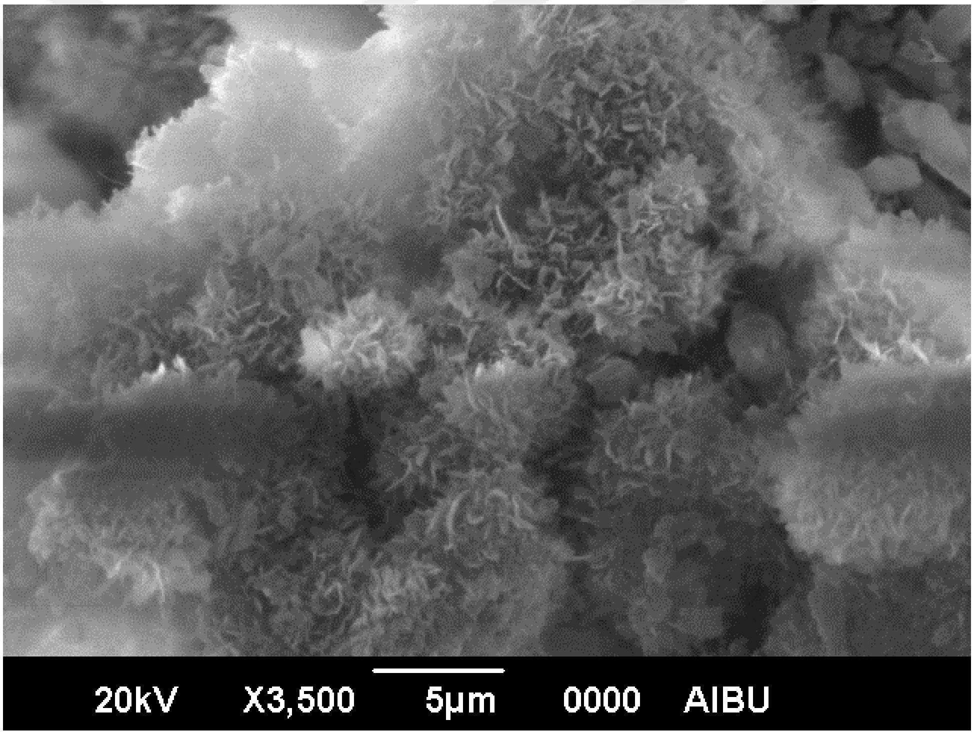


Figure 23. Sample SEM image of hBN in presence of KBr.

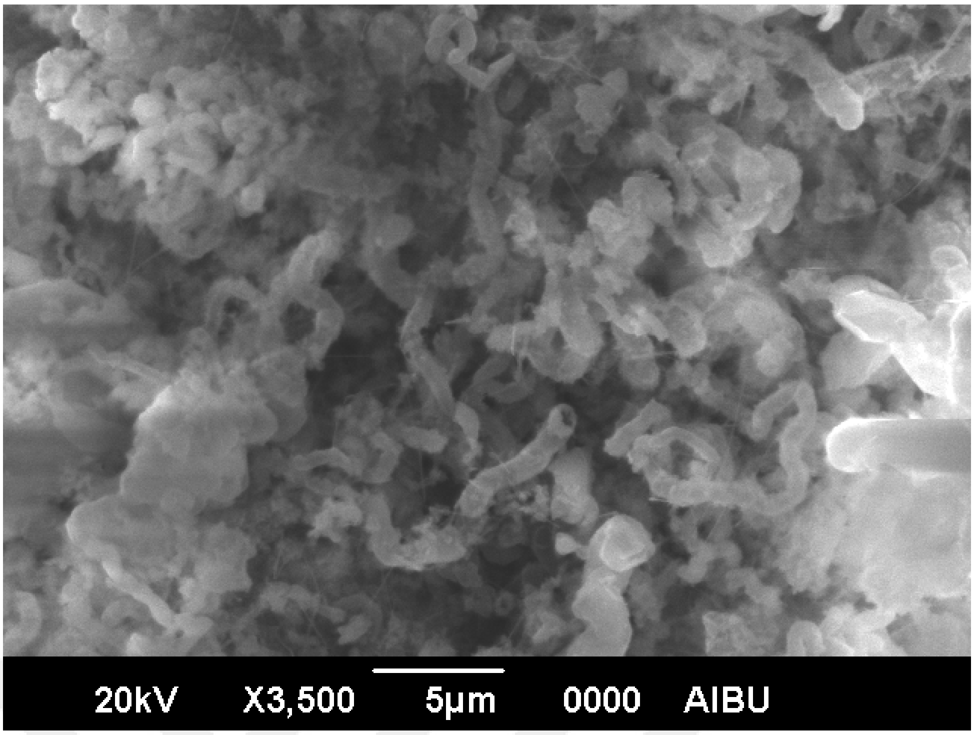


Figure 24. Sample SEM image of hBN in presence of CaI_2.

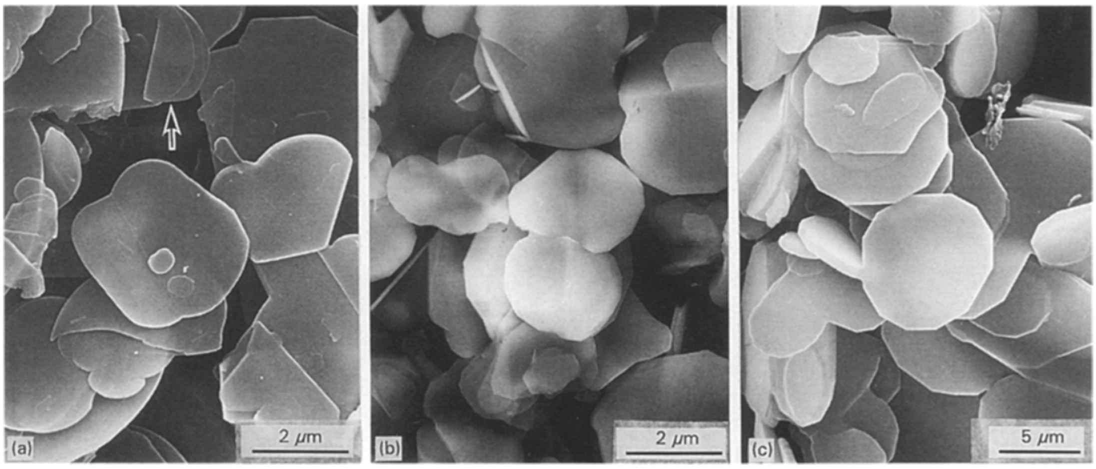


Figure 25. Sem images of hBN from Shimomura

6. CONCLUSION

Hexagonal Boron Nitride samples were successfully prepared by the modified O'Connor method at 1450°C under ammonia atmosphere and following conclusions can be stated:

1. The formation of hBN is confirmed by FTIR and XRD investigations.

2. XRD patterns of the samples are indexed as hBN and calculated lattice parameters are very close to reported values of hBN.

3. The broadening nature of the XRD peak (002) indicates that the particle size of the samples is within nanometer scale.

4. Among used halides, the most efficient halide types are found as CaF_2 and LiF.

5.The images of the nanoscale hBN samples indicated that irregularly grained powder with fractures and particles were in jagged shape.

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APPENDICES

7. APPENDICES

Appendix A. FTIR Spectra of hBN Samples

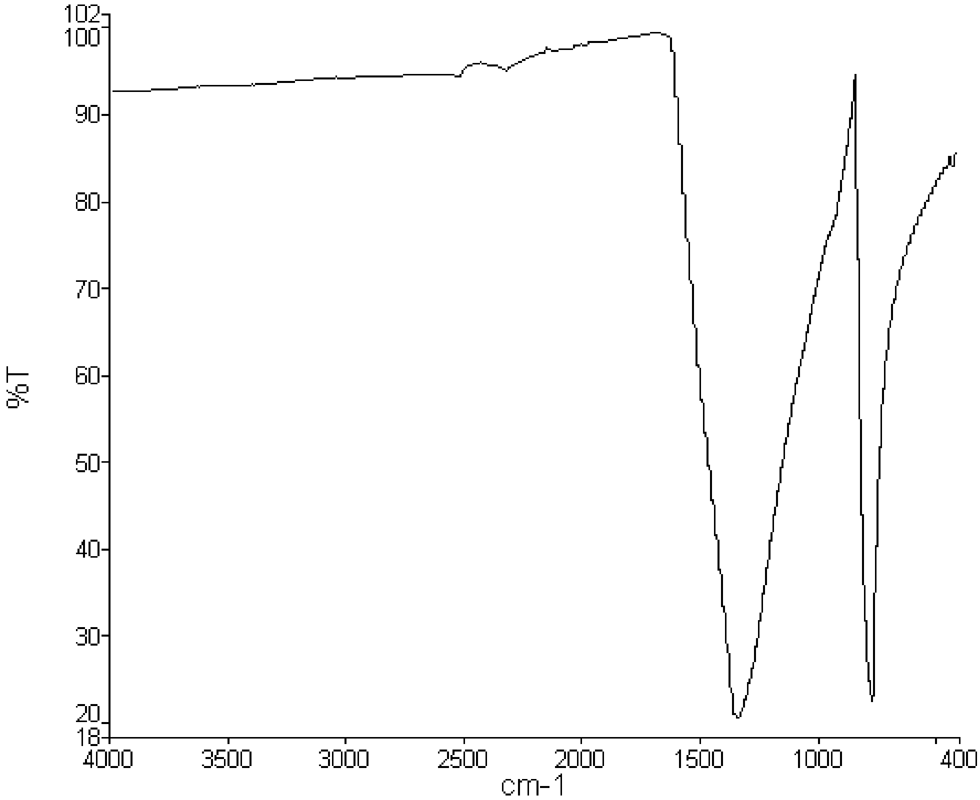


Figure A.1.1. FTIR spectrum of hBN in presence of $CaBr_2$.

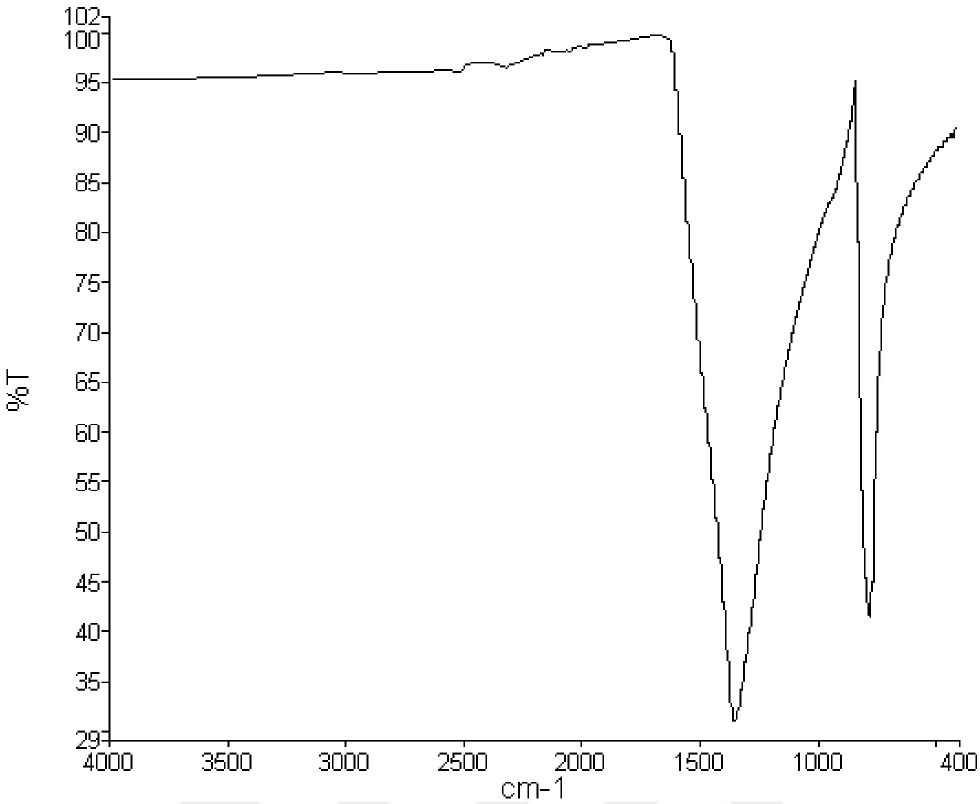


Figure A.1.2. FTIR spectrum of hBN in presence of $CaCl_2$.

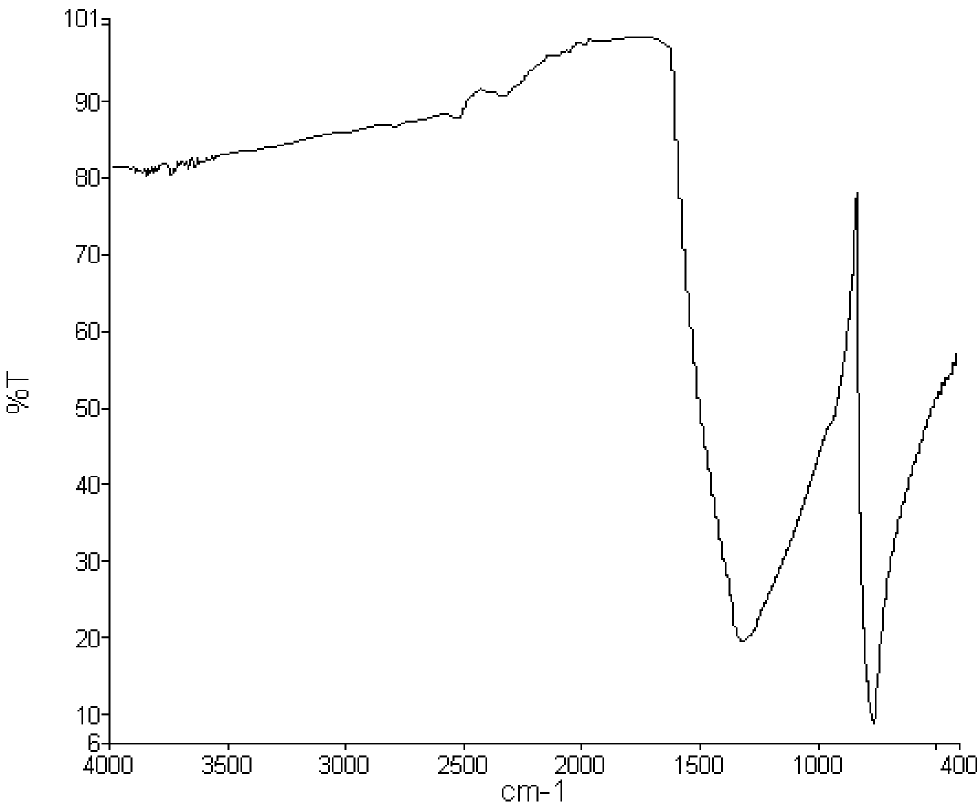


Figure A.1.3. FTIR spectrum of hBN in presence of CaF_2.

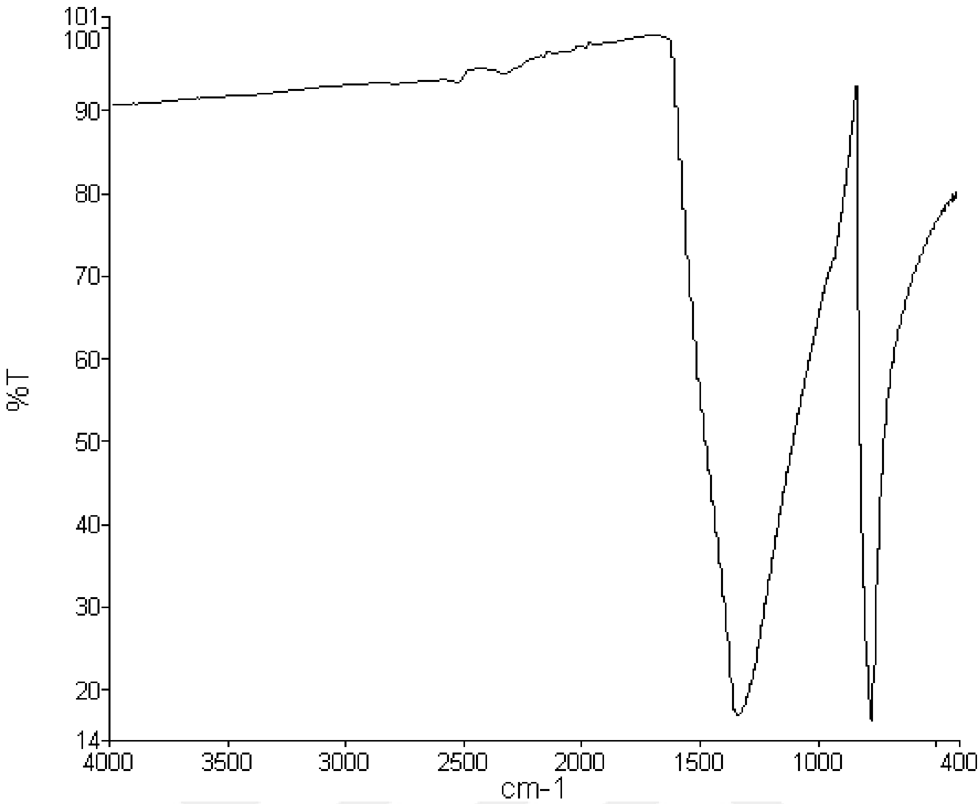


Figure A.1.4. FTIR spectrum of hBN in presence of CaI_2.

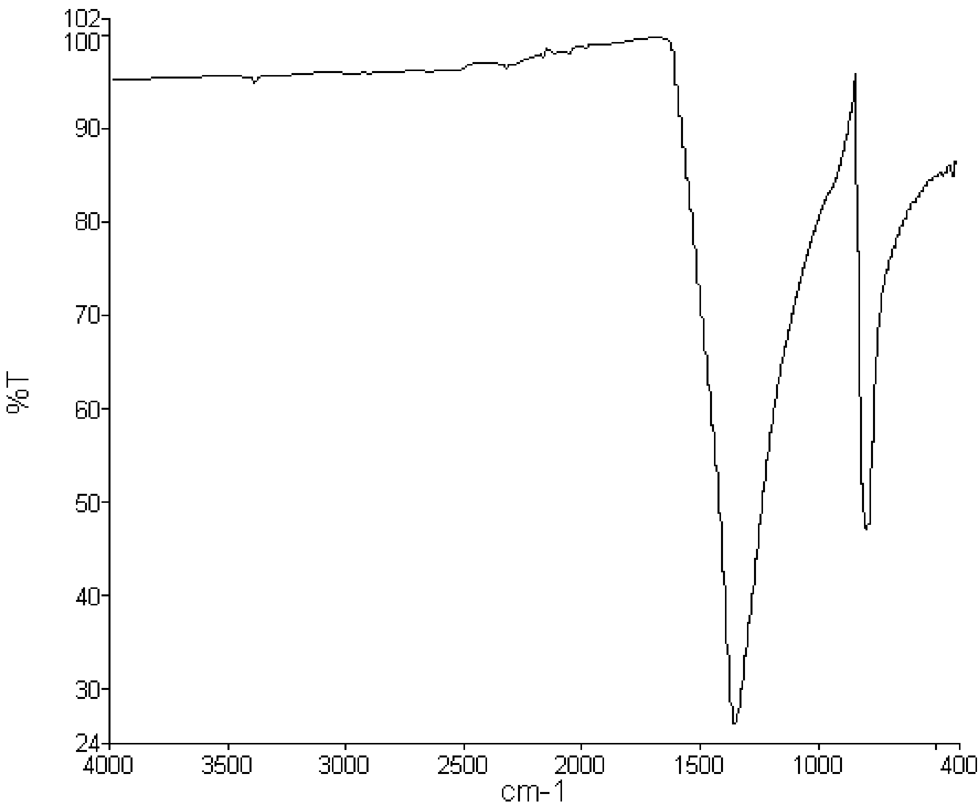


Figure A.1.5. FTIR spectrum of hBN in presence of KBr.

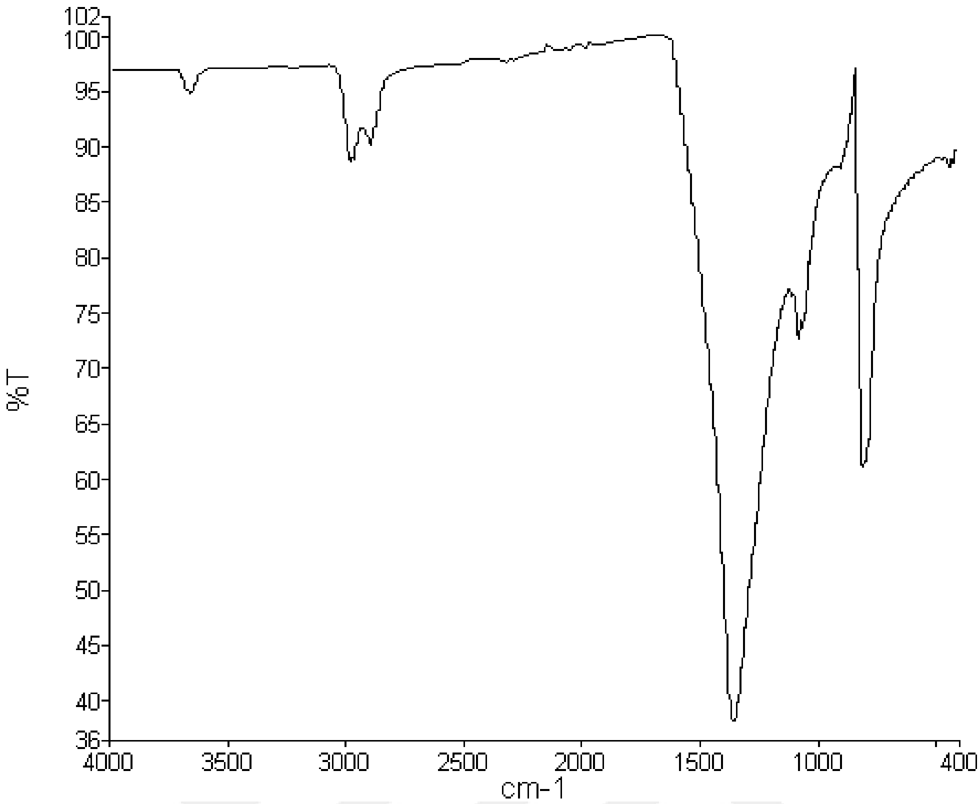


Figure A.1.6. FTIR spectrum of hBN in presence of KCl.

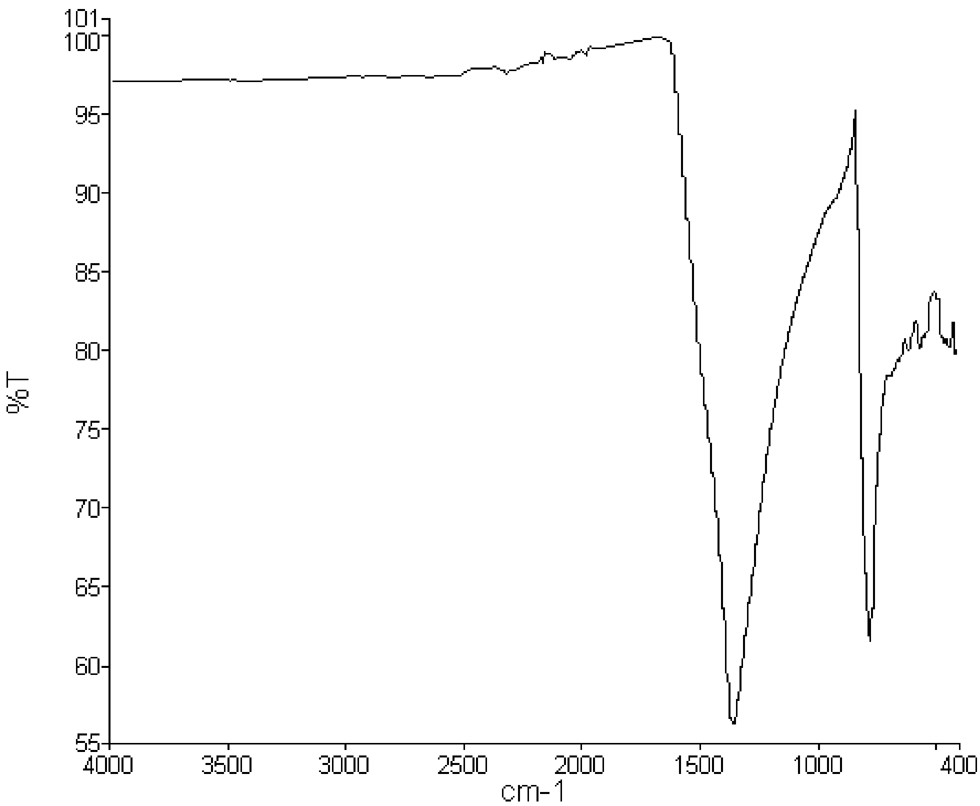


Figure A.1.7. FTIR spectrum of hBN in presence of KF.

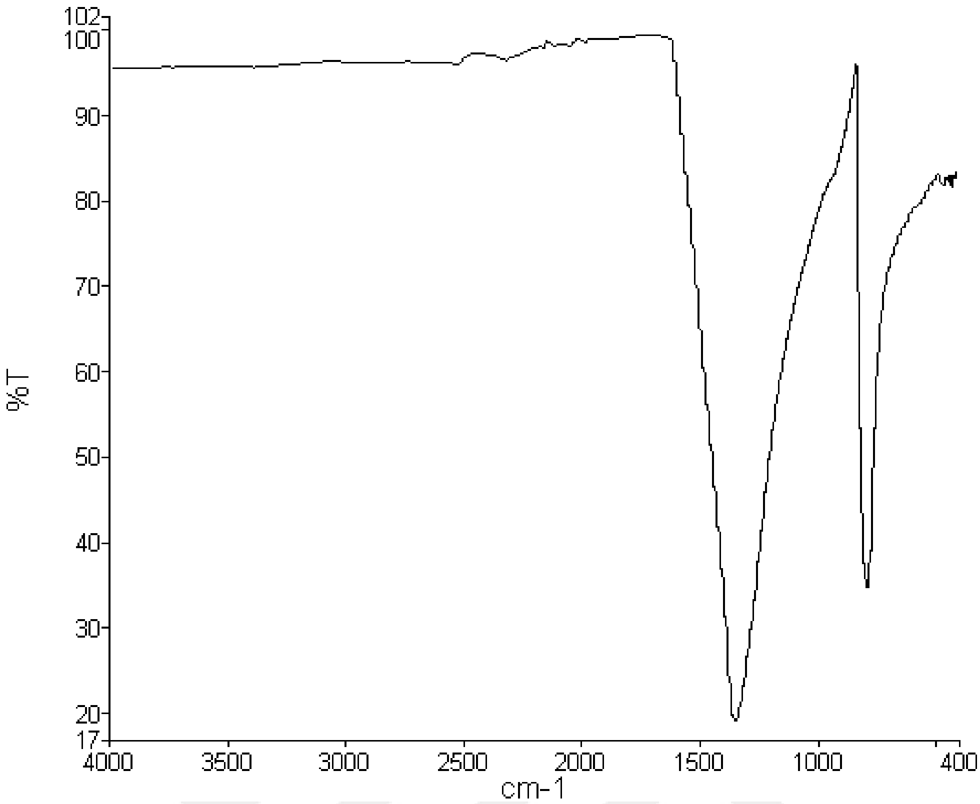


Figure A.1.8. FTIR spectrum of hBN in presence of KI.

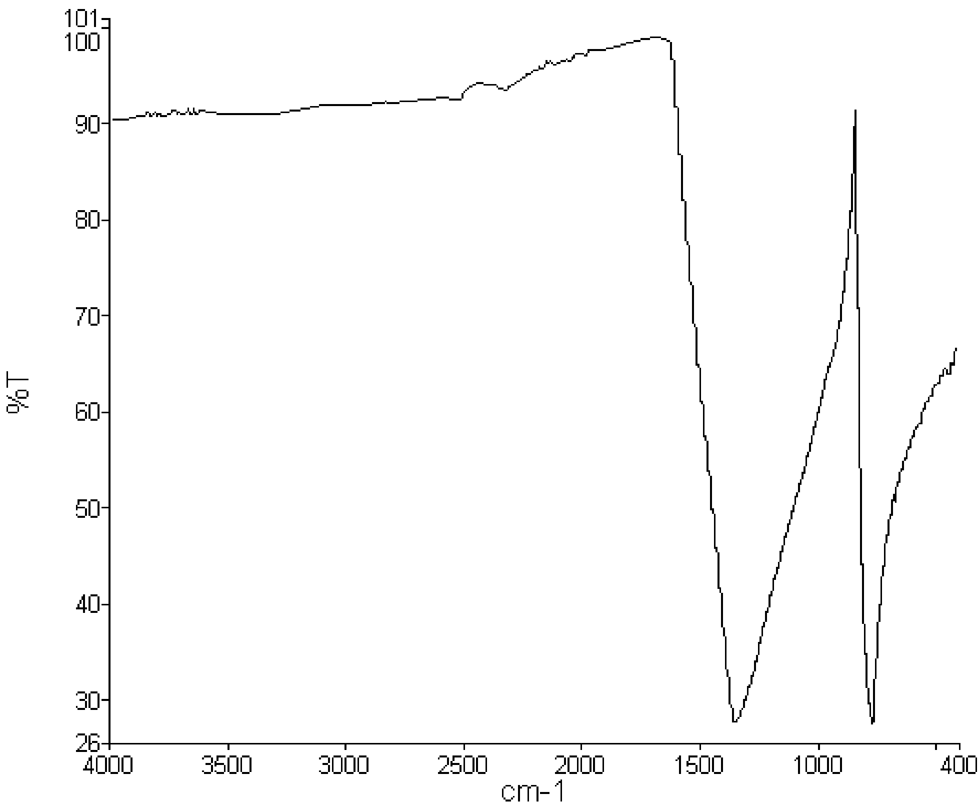


Figure A.1.9. FTIR spectrum of hBN in presence of LiBr.

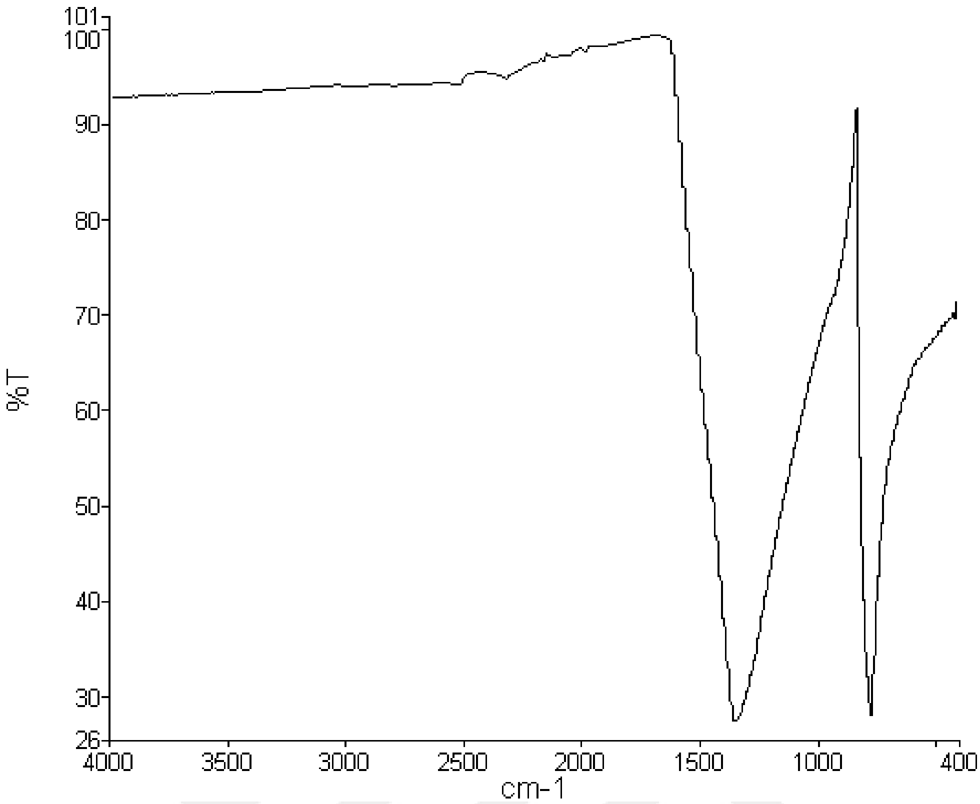


Figure A.1.10. FTIR spectrum of hBN in presence of LiCl.

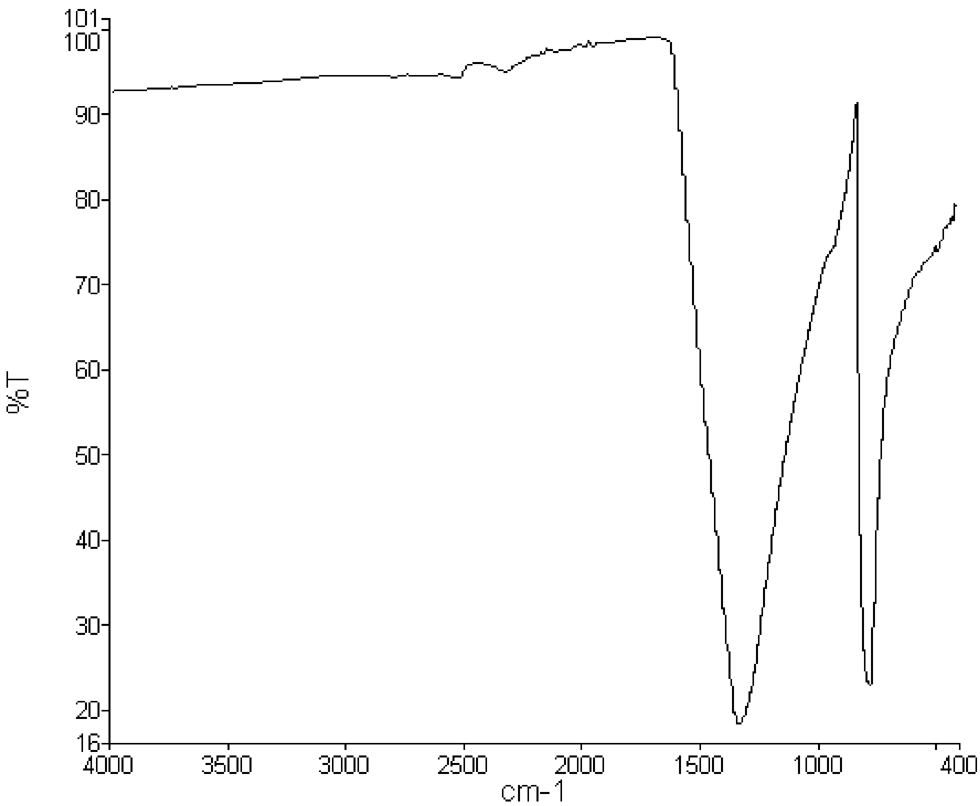


Figure A.1.11. FTIR spectrum of hBN in presence of LiF.

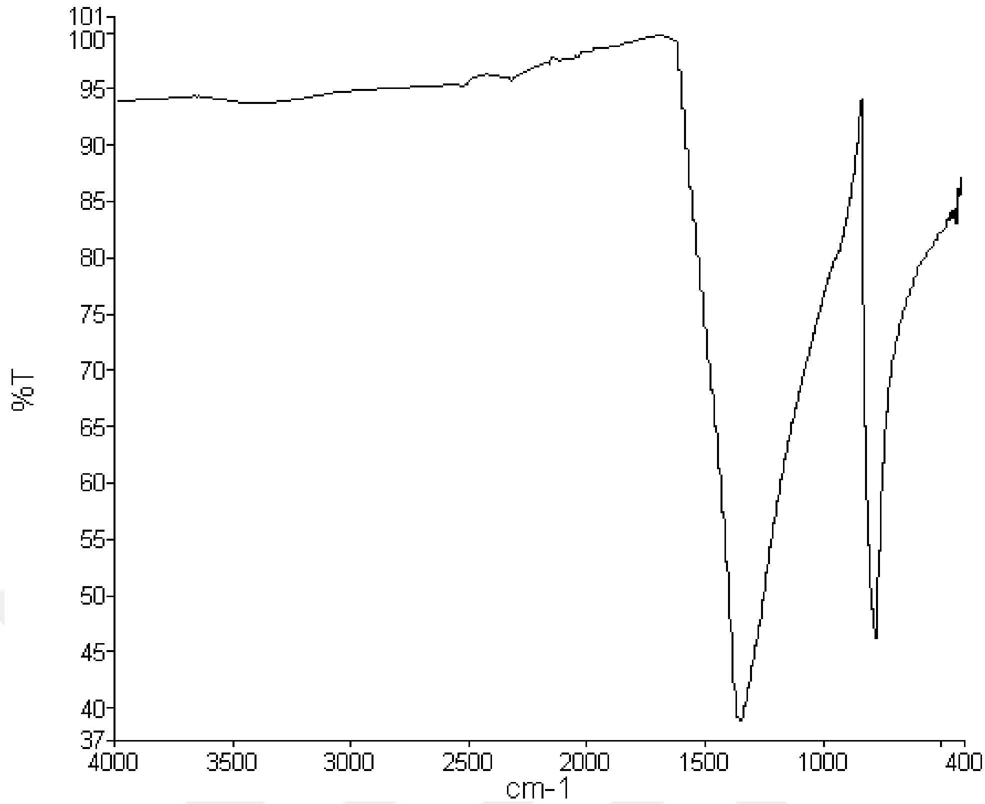


Figure A.1.12. FTIR spectrum of hBN in presence of LiI.

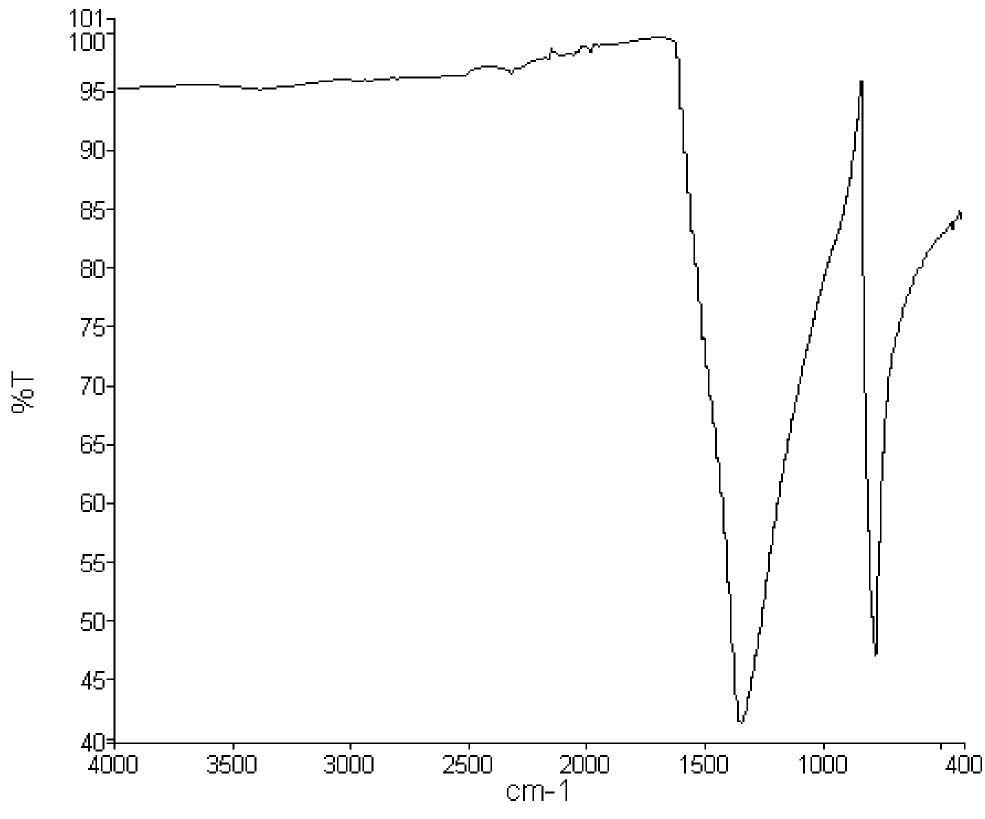


Figure A.1.13. FTIR spectrum of hBN in presence of $MgBr_2$.

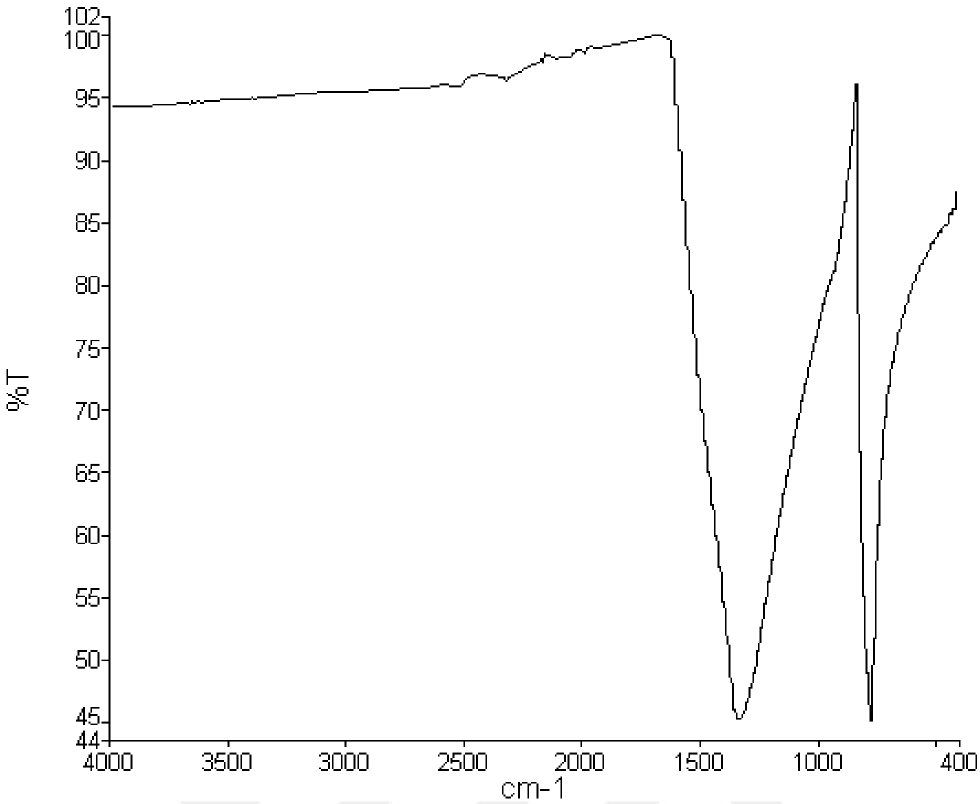


Figure A.1.14. FTIR spectrum of hBN in presence of $MgCl_2$.

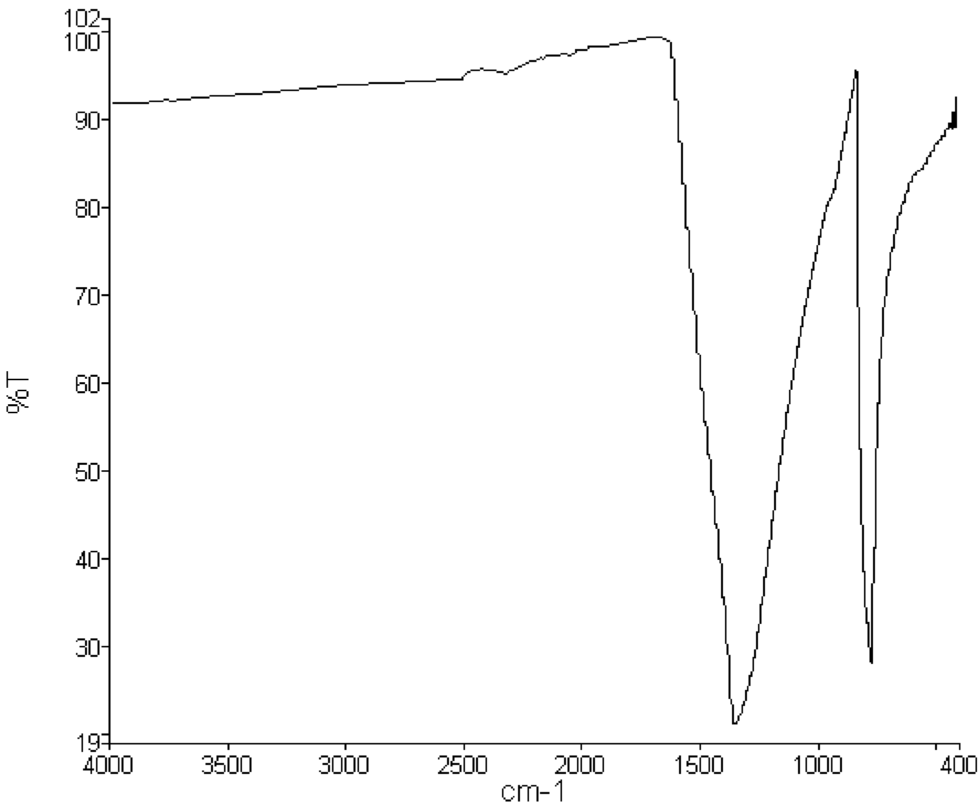


Figure A.1.15. FTIR spectrum of hBN in presence of MgF_2.

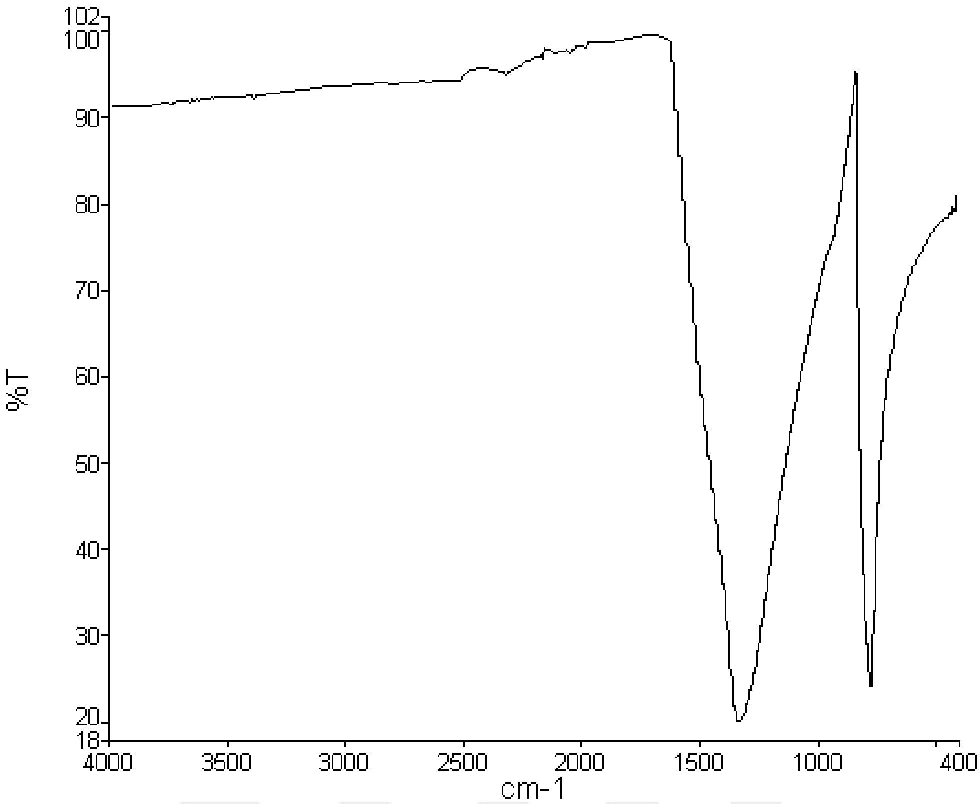


Figure A.1.16. FTIR spectrum of hBN in presence of MgI_2.

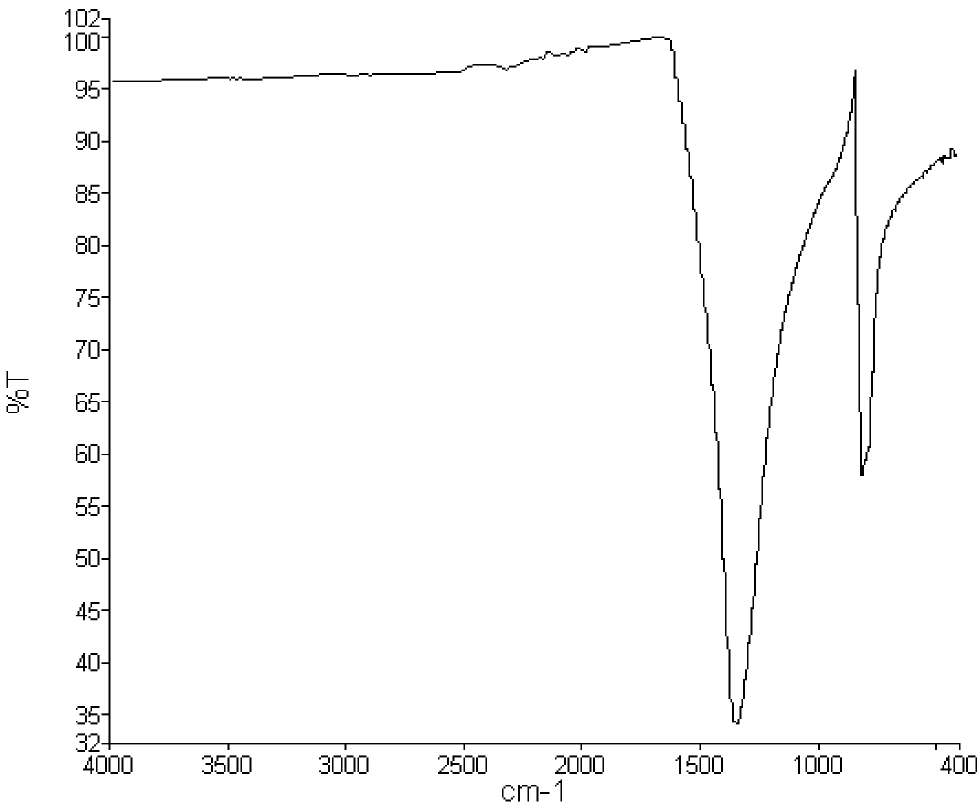


Figure A.1.17. FTIR spectrum of hBN in presence of NaBr.

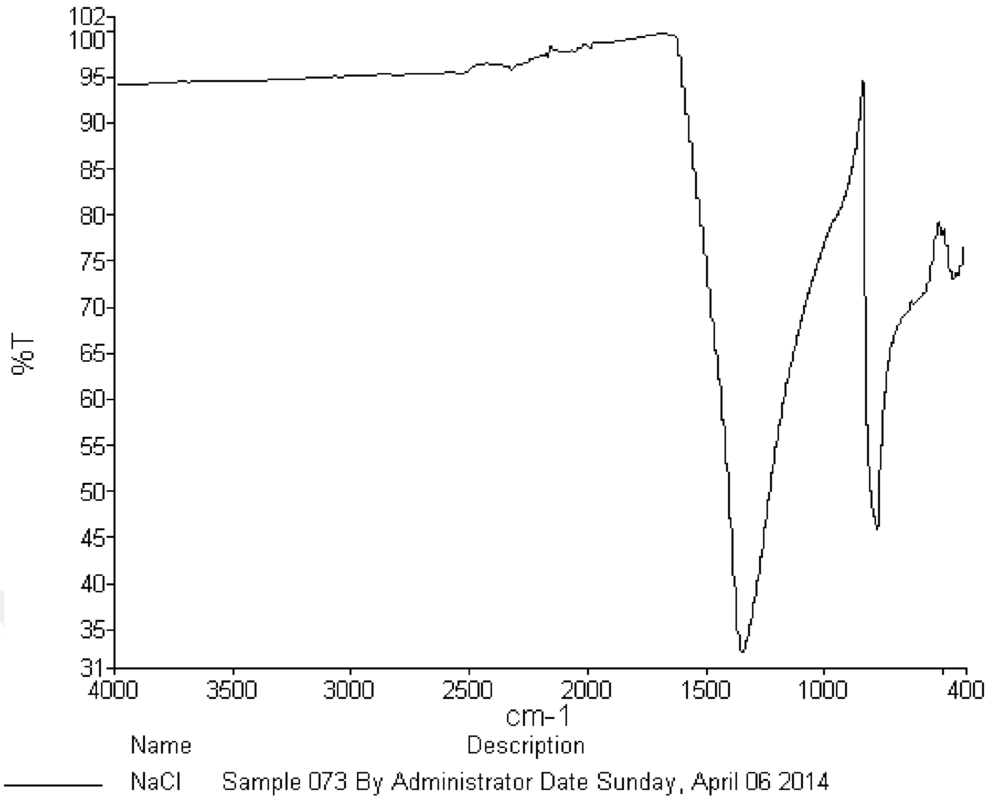


Figure A.1.18. FTIR spectrum of hBN in presence of NaCl.

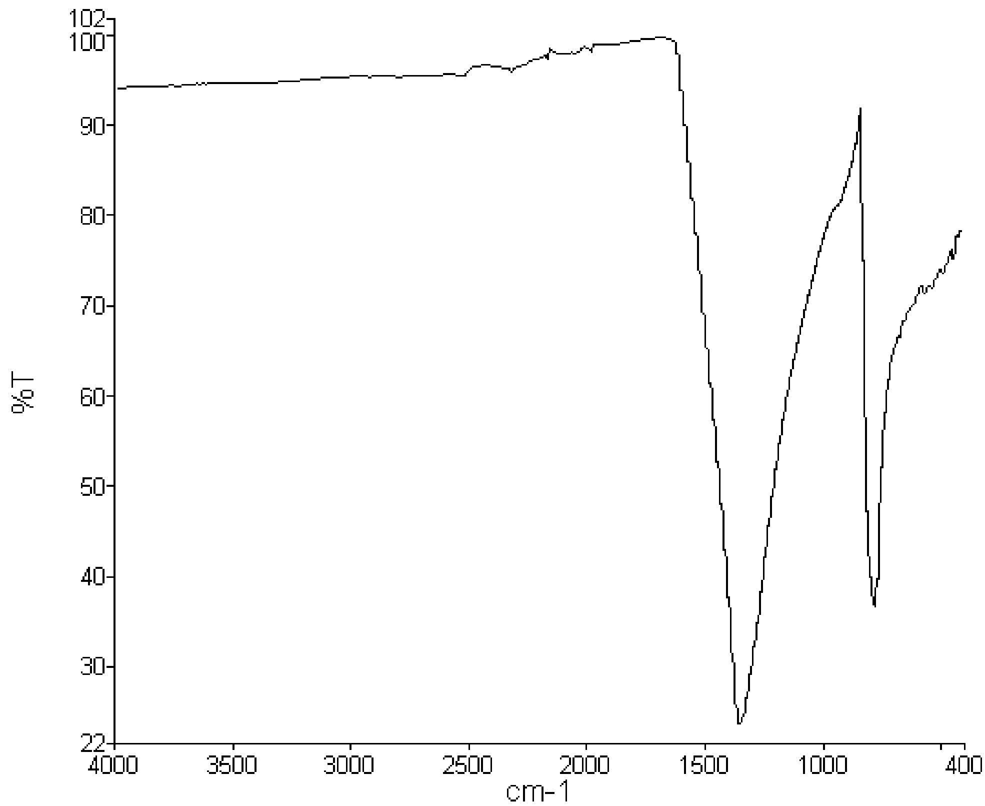


Figure A.1.19. FTIR spectrum of hBN in presence of NaF.

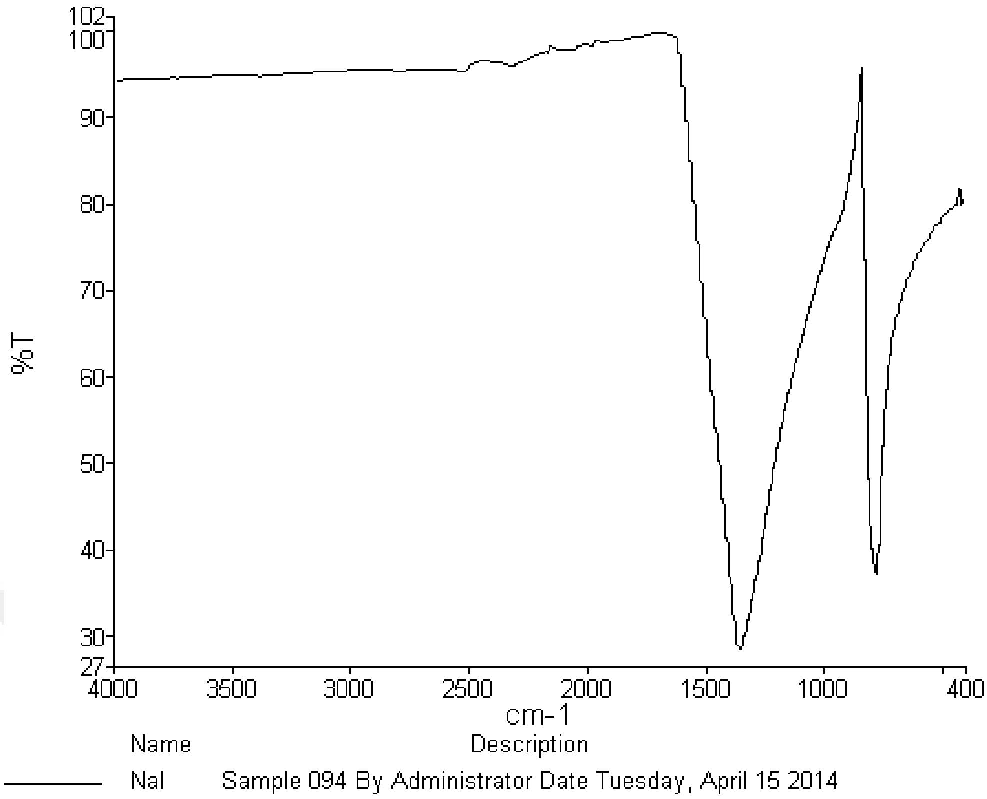


Figure A.1.20. FTIR spectrum of hBN in presence of NaI.

Appendix B. XRD pattern of hBN Samples

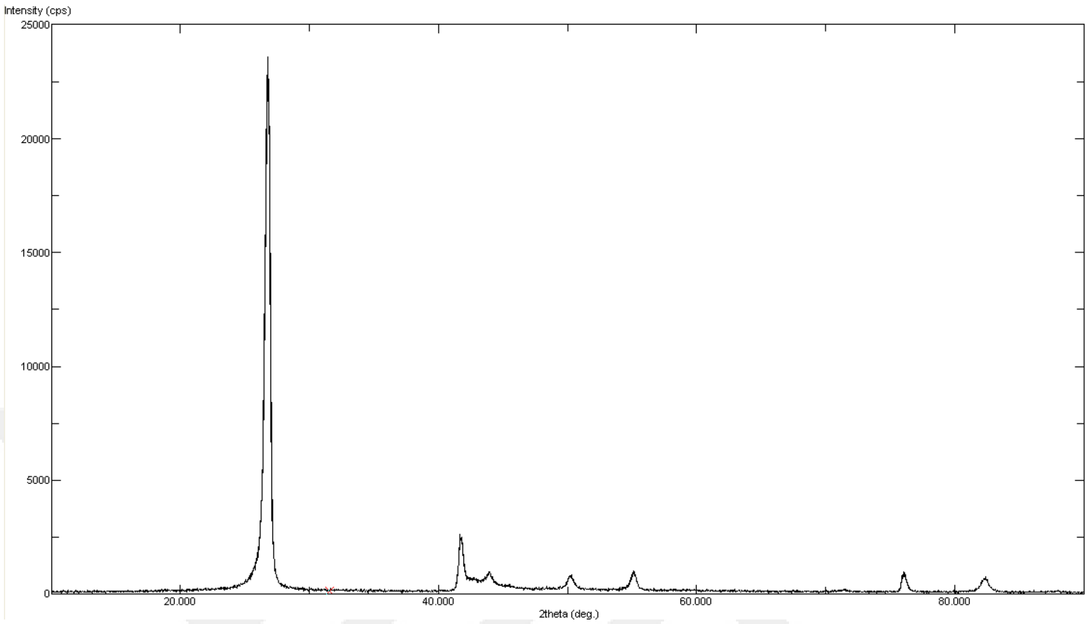
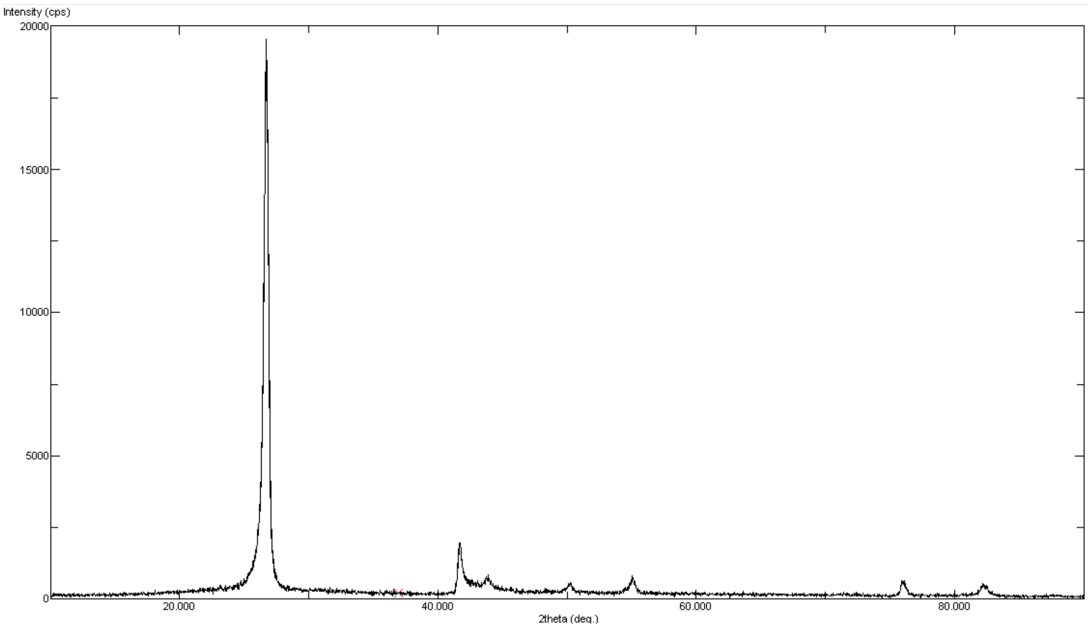


Figure B.1.1. XRD pattern of hBN in presence of $CaBr_2$.



. **Figure B.1.2.** XRD pattern of hBN in presence of $CaCl_2$.

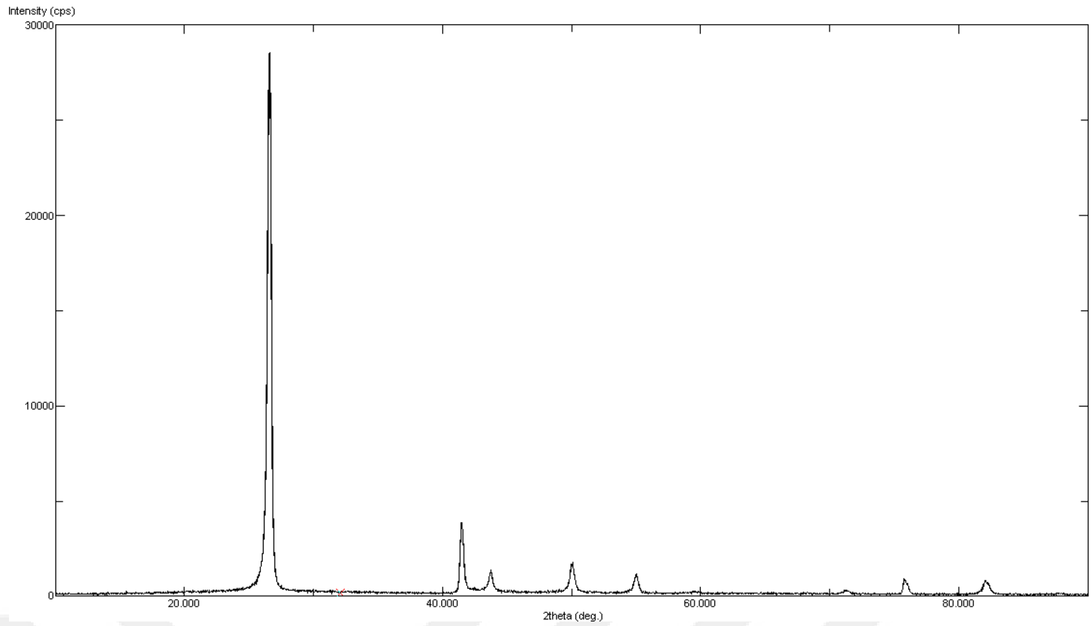


Figure B.1.3. XRD pattern of hBN in presence of CaF_2.

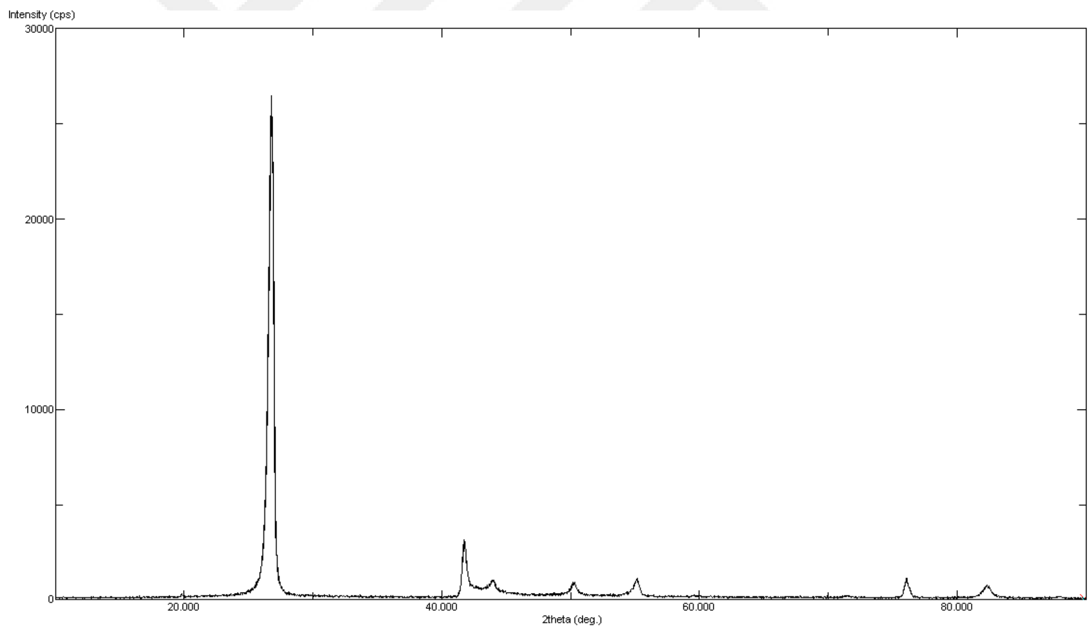


Figure B.1.4. XRD pattern of hBN in presence of CaI_2.

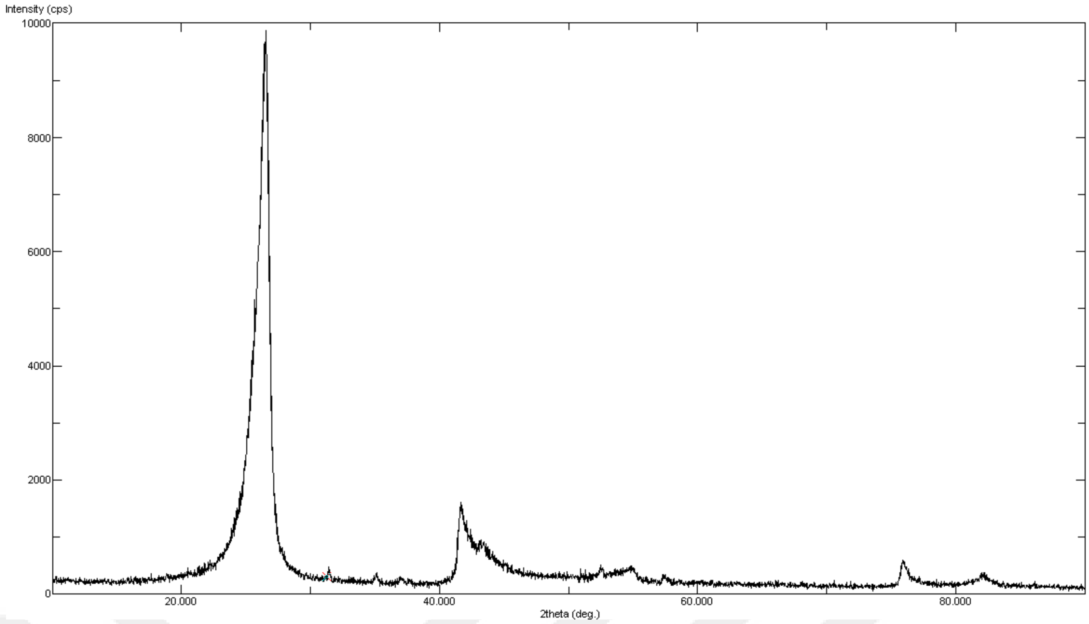


Figure B.1.5. XRD pattern of hBN in presence of KBr.

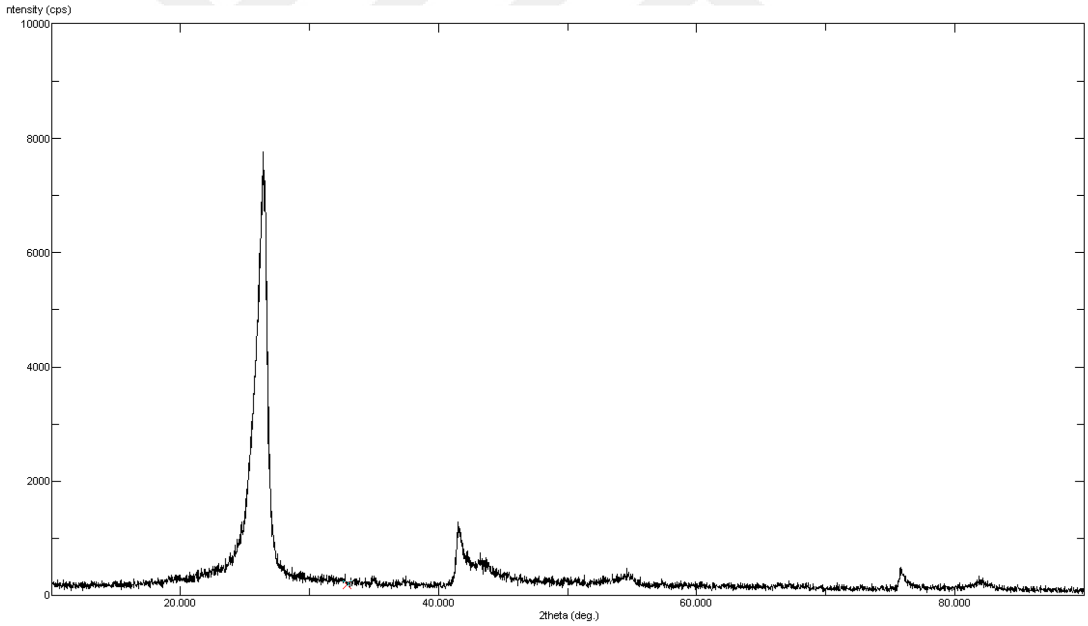


Figure B.1.6. XRD pattern of hBN in presence of KCl.

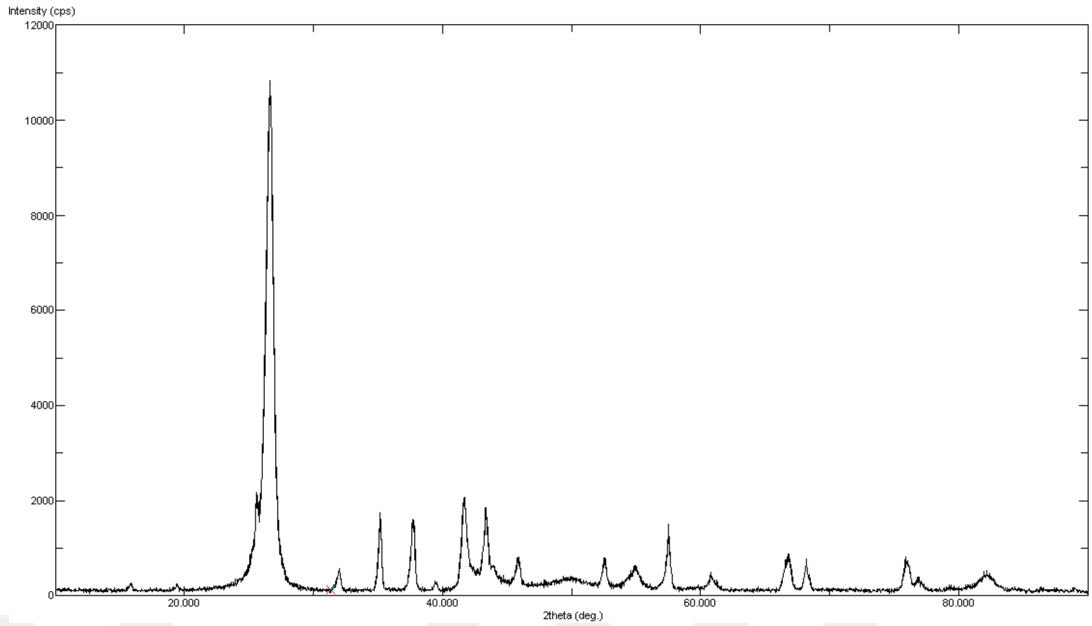


Figure B.1.7. XRD pattern of hBN in presence of KF.

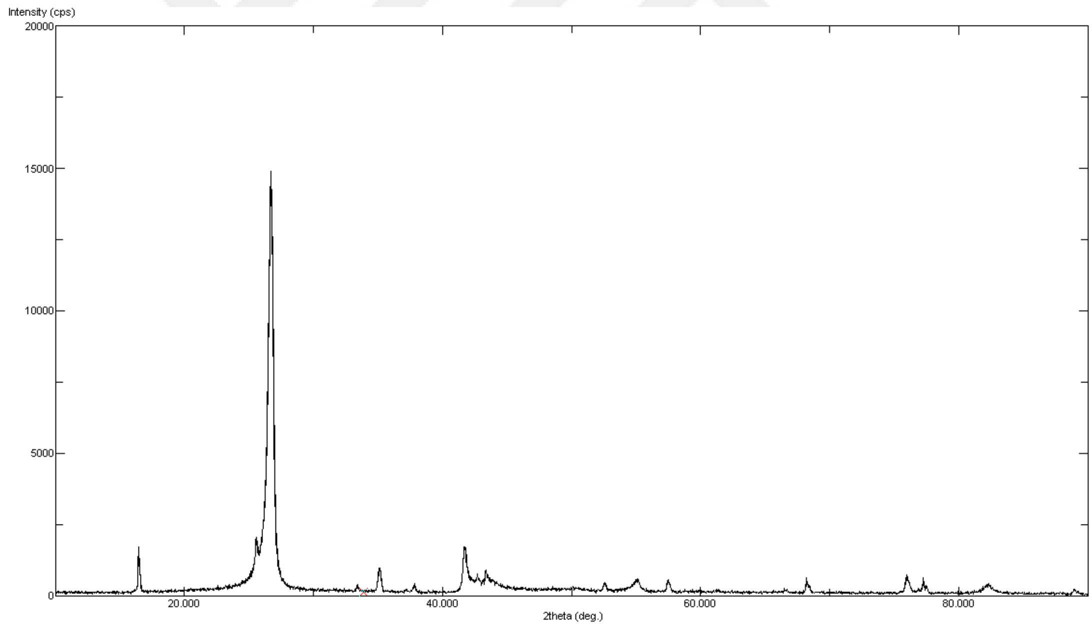


Figure B.1.8. XRD pattern of hBN in presence of KI.

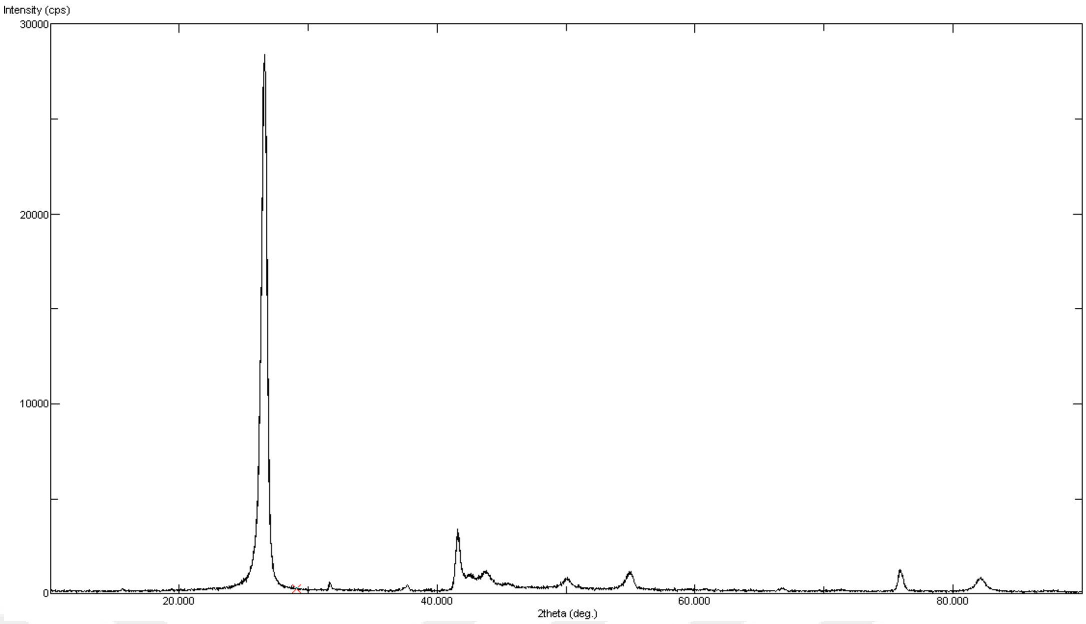


Figure B.1.9. XRD pattern of hBN in presence of LiBr.

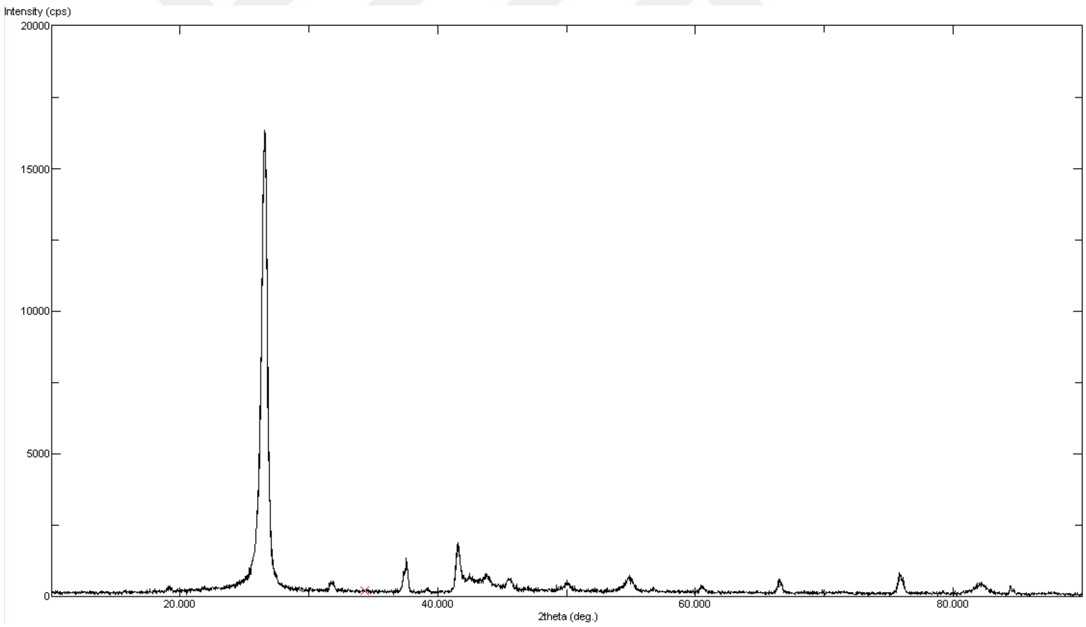


Figure B.1.10. XRD pattern of hBN in presence of LiCl.

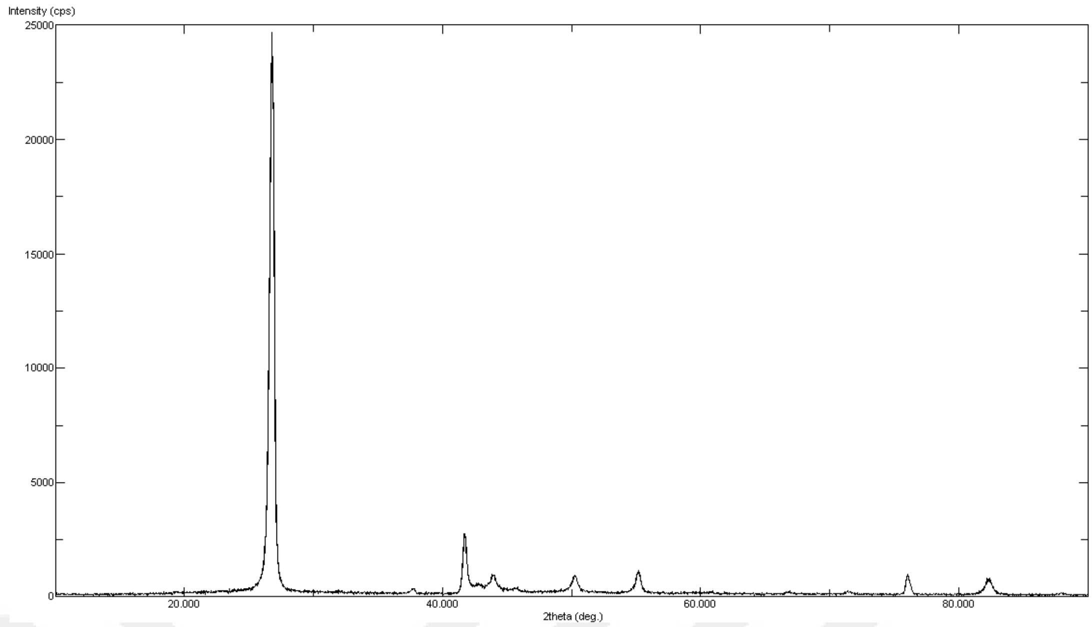


Figure B.1.11. XRD pattern of hBN in presence of LiF.

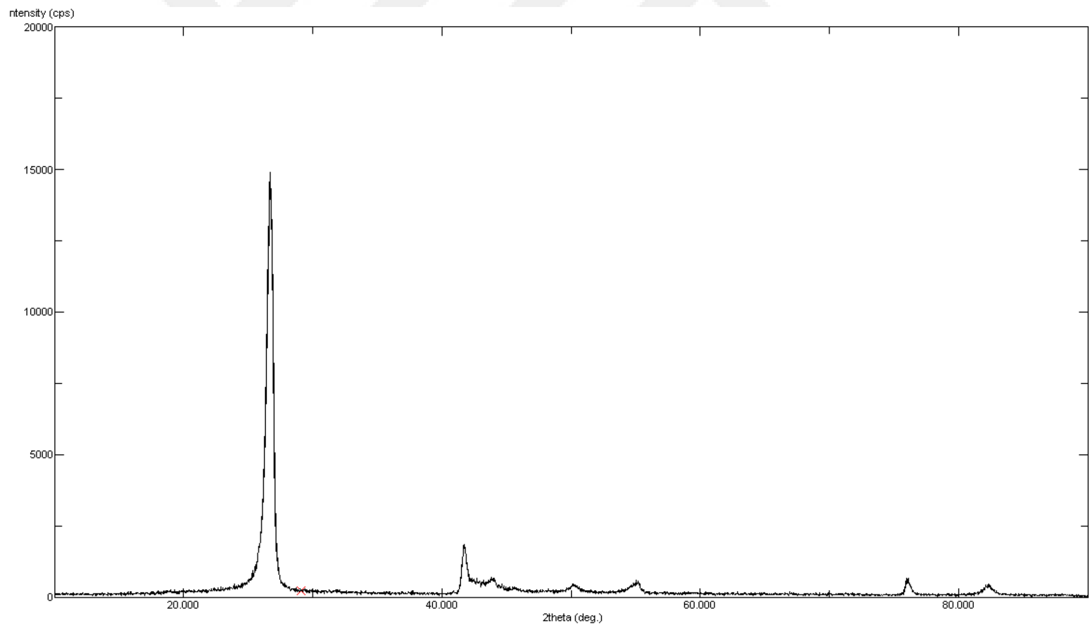


Figure B.1.12. XRD pattern of hBN in presence of LiI.

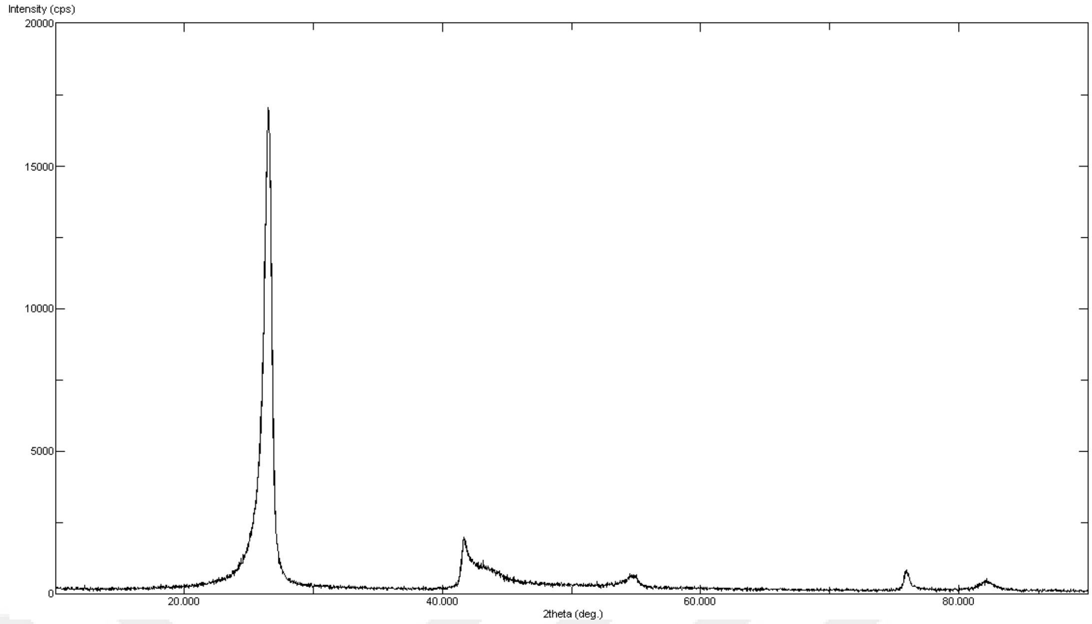


Figure B.1.13. XRD pattern of hBN in presence of $MgBr_2$.

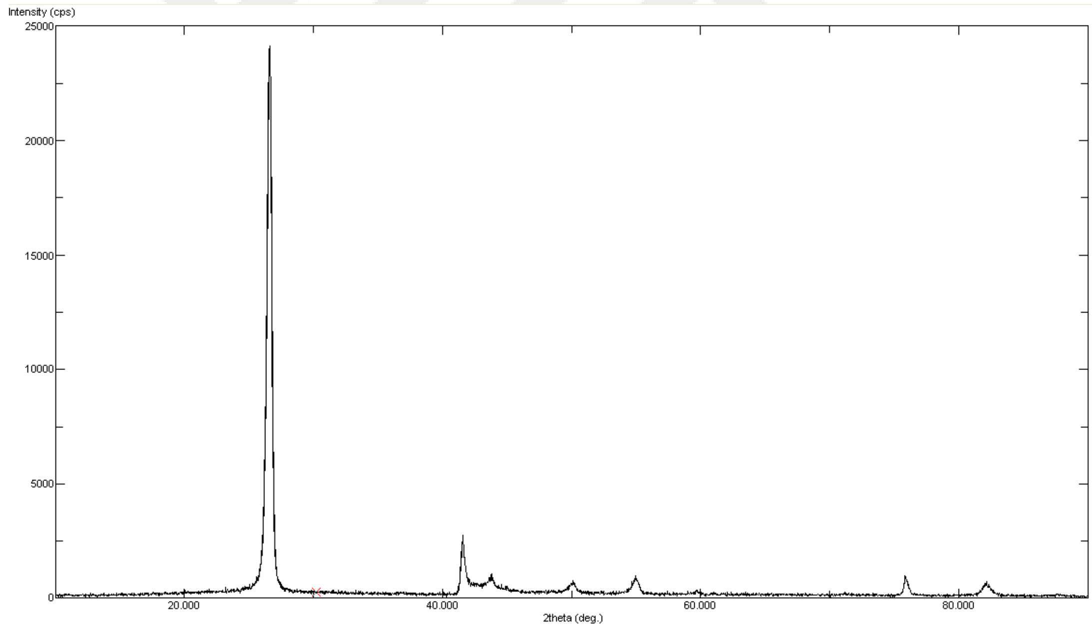


Figure B.1.14. XRD pattern of hBN in presence of $MgCl_2$.

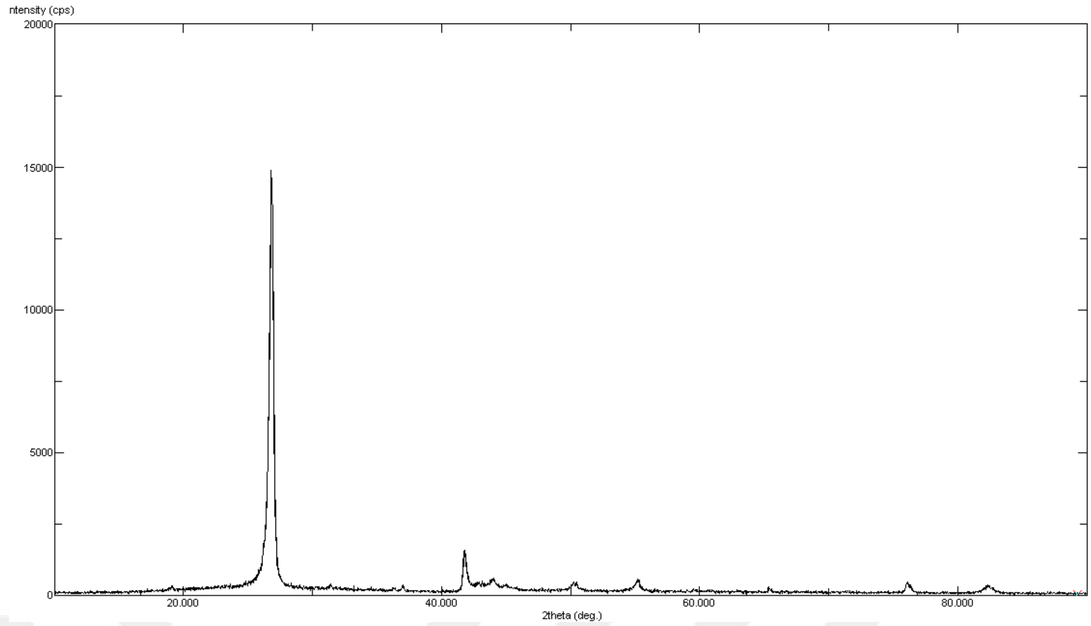


Figure B.1.15. XRD pattern of hBN in presence of MgF_2.

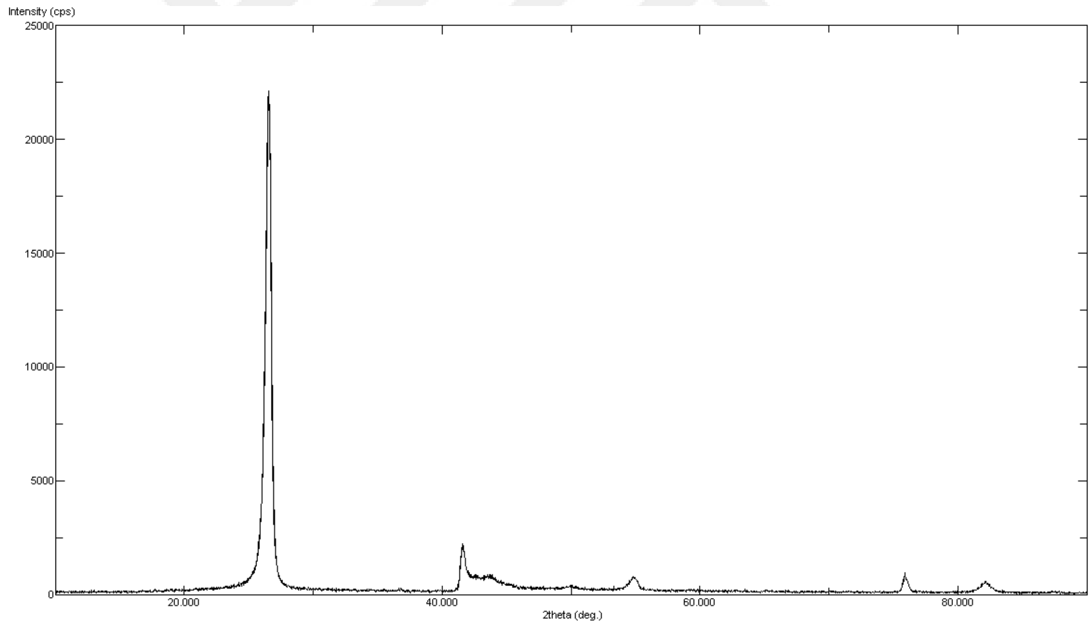


Figure B.1.16. XRD pattern of hBN in presence of MgI_2.

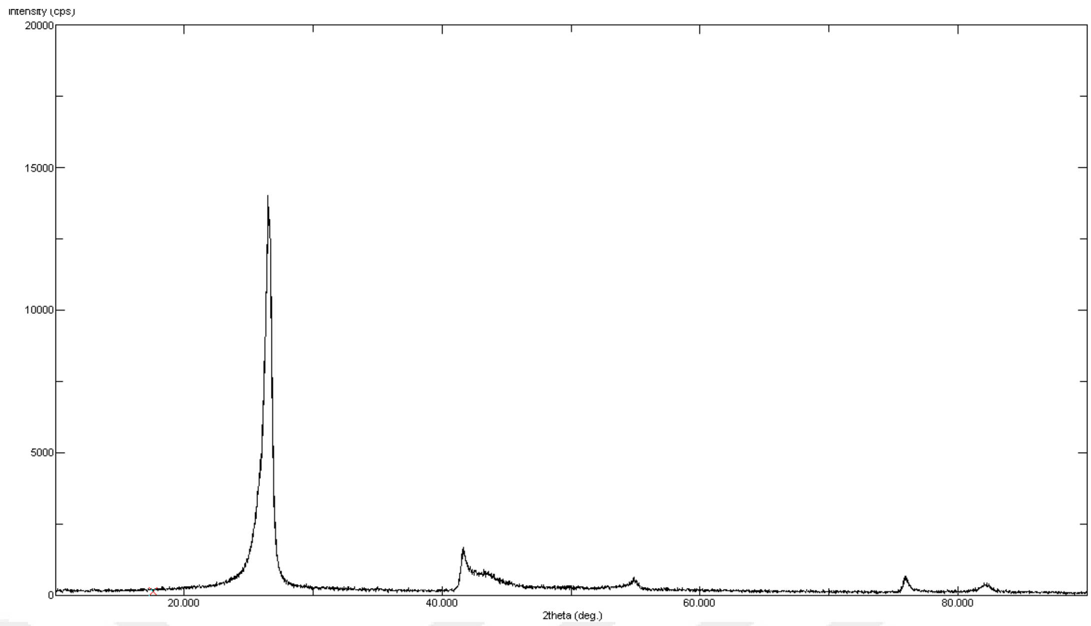


Figure B.1.17. XRD pattern of hBN in presence of NaBr.

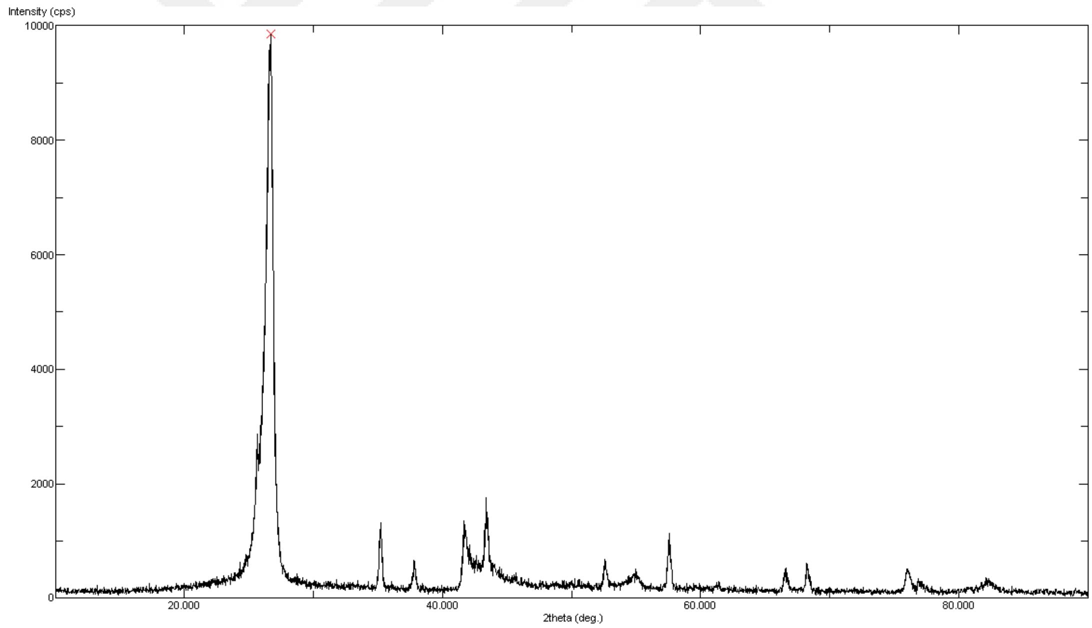


Figure B.1.18. XRD pattern of hBN in presence of NaCl.

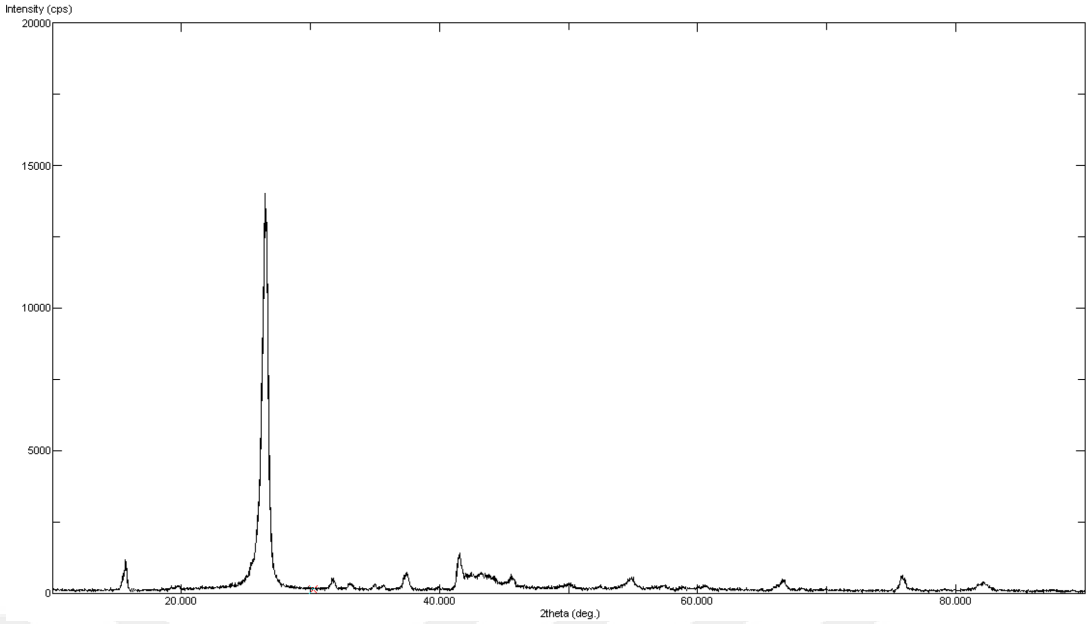


Figure B.1.19. XRD pattern of hBN in presence of NaF.

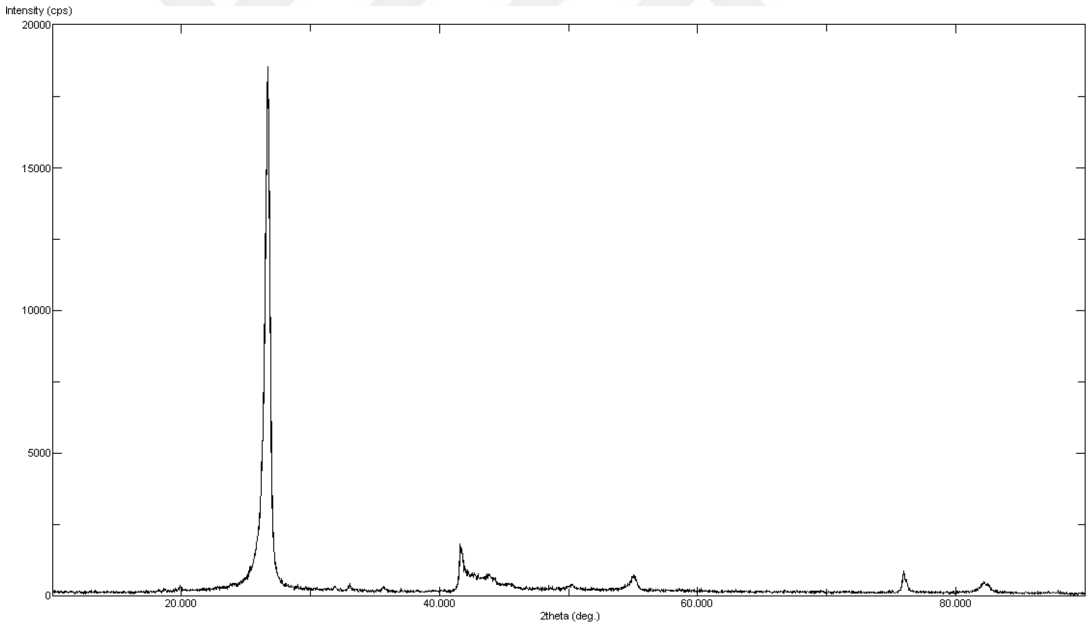


Figure B.1.20. XRD pattern of hBN in presence of NaI.

Appendix C. SEM images of hBN Samples

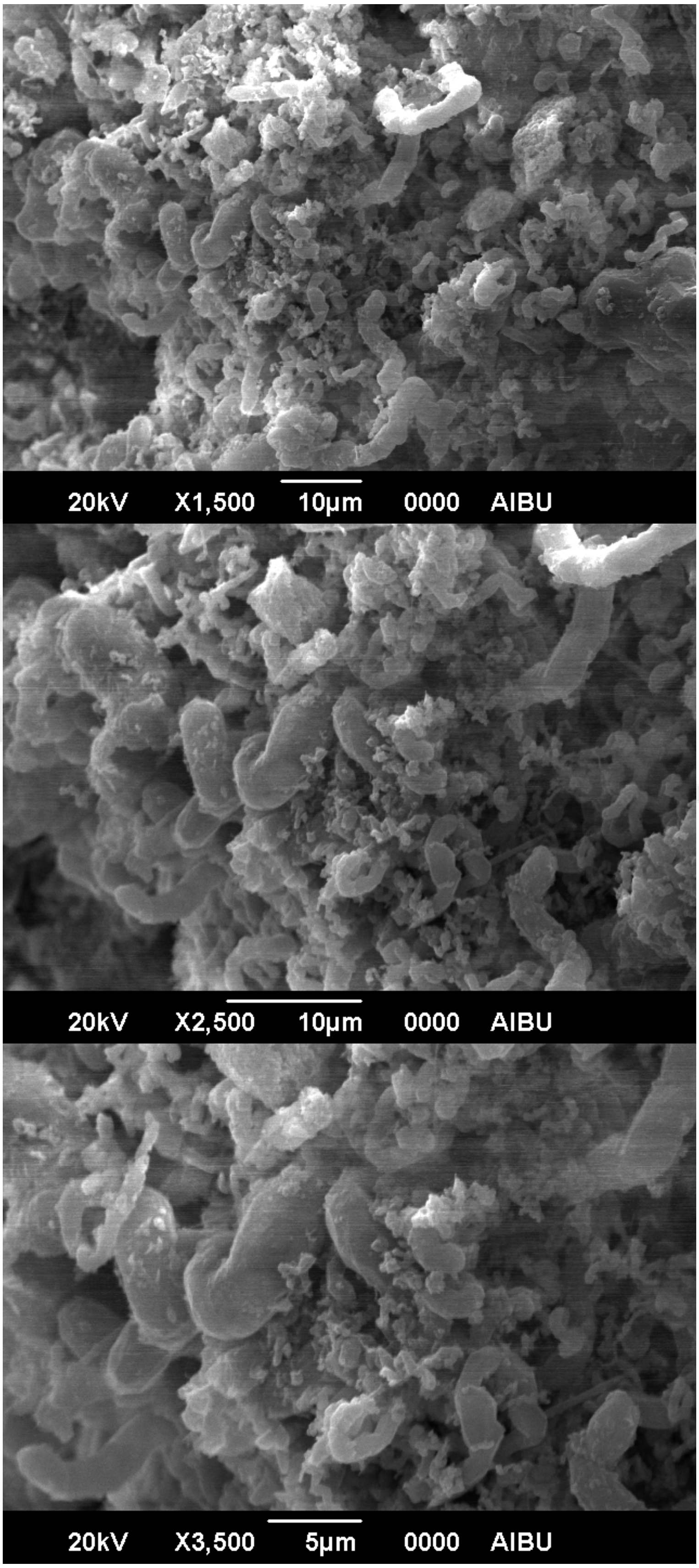


Figure C.1.1. SEM images of hBN in presence of $CaBr_2$.

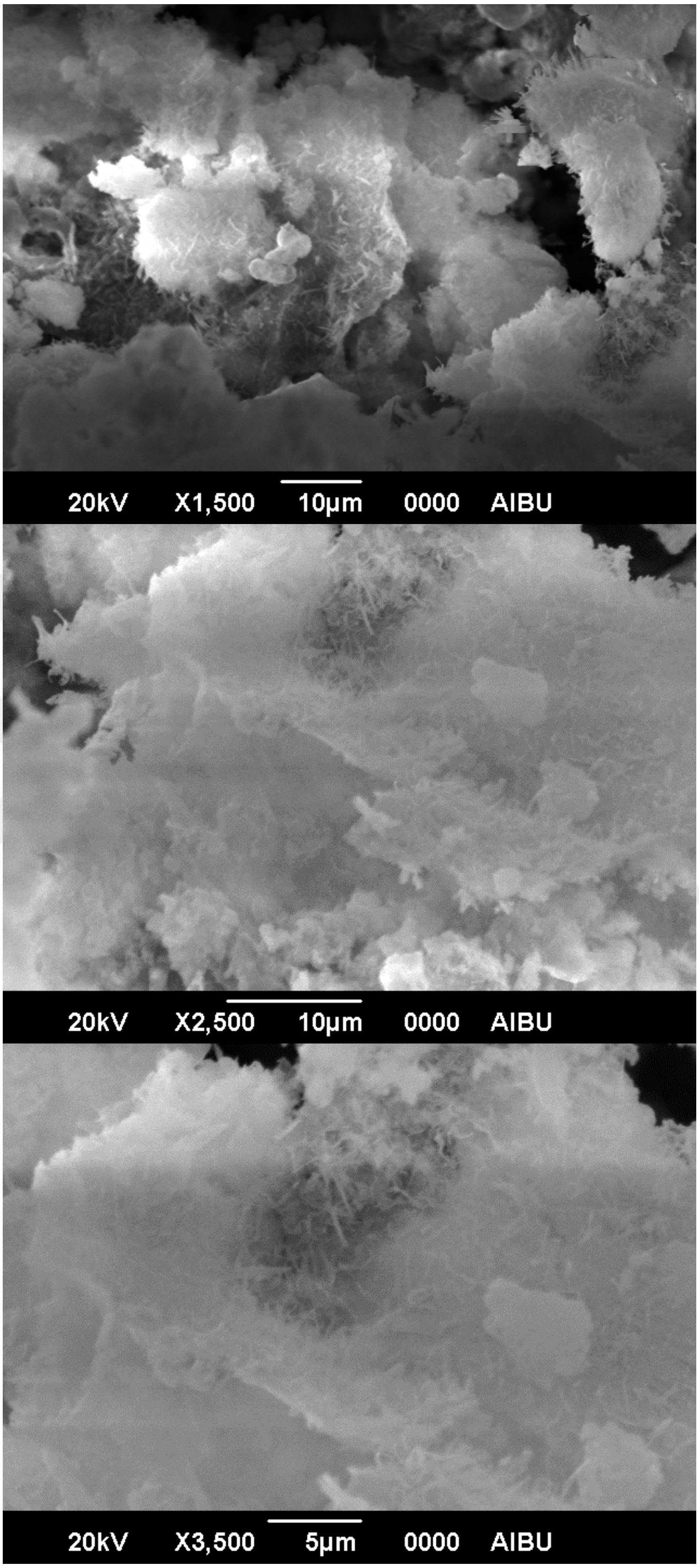


Figure C.1.2. SEM images of hBN in presence of $CaCl_2$.

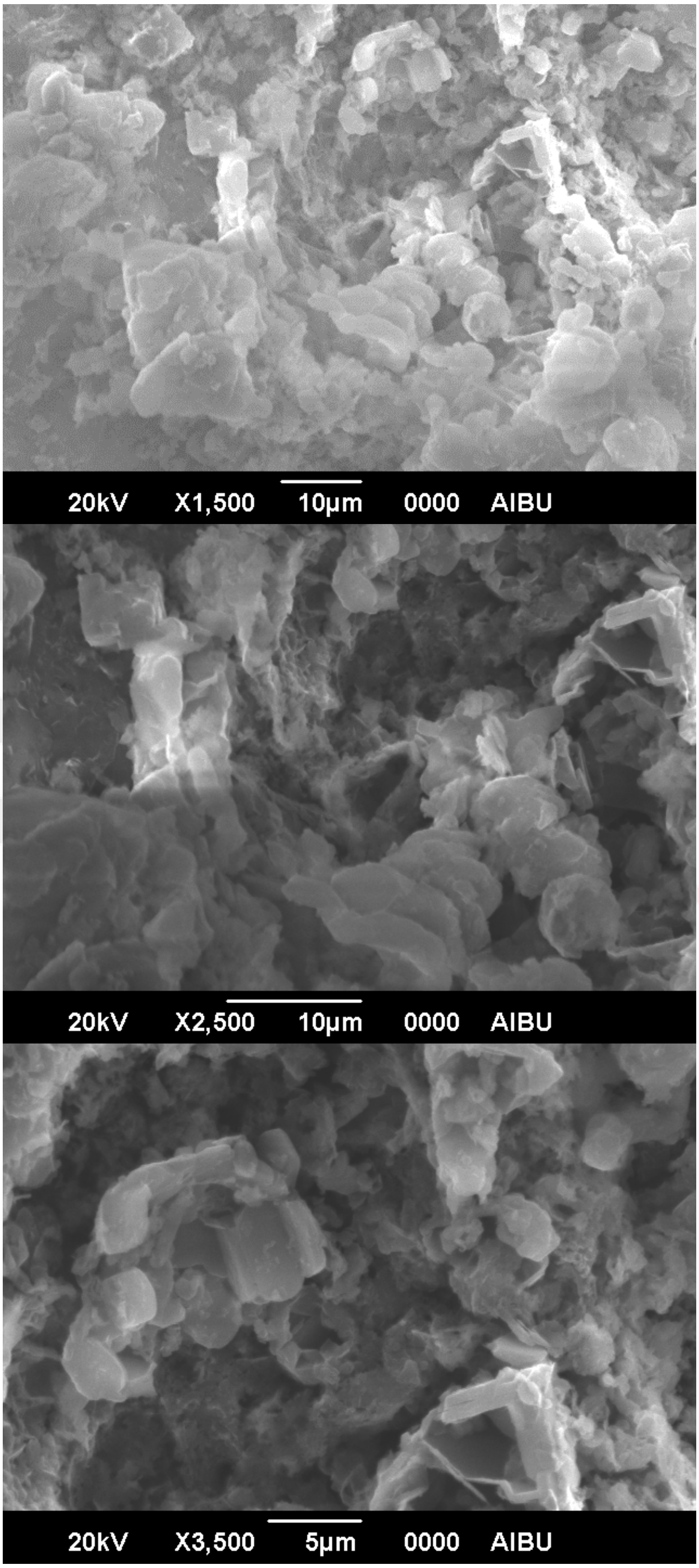


Figure C.1.3. SEM images of hBN in presence of CaF_2.

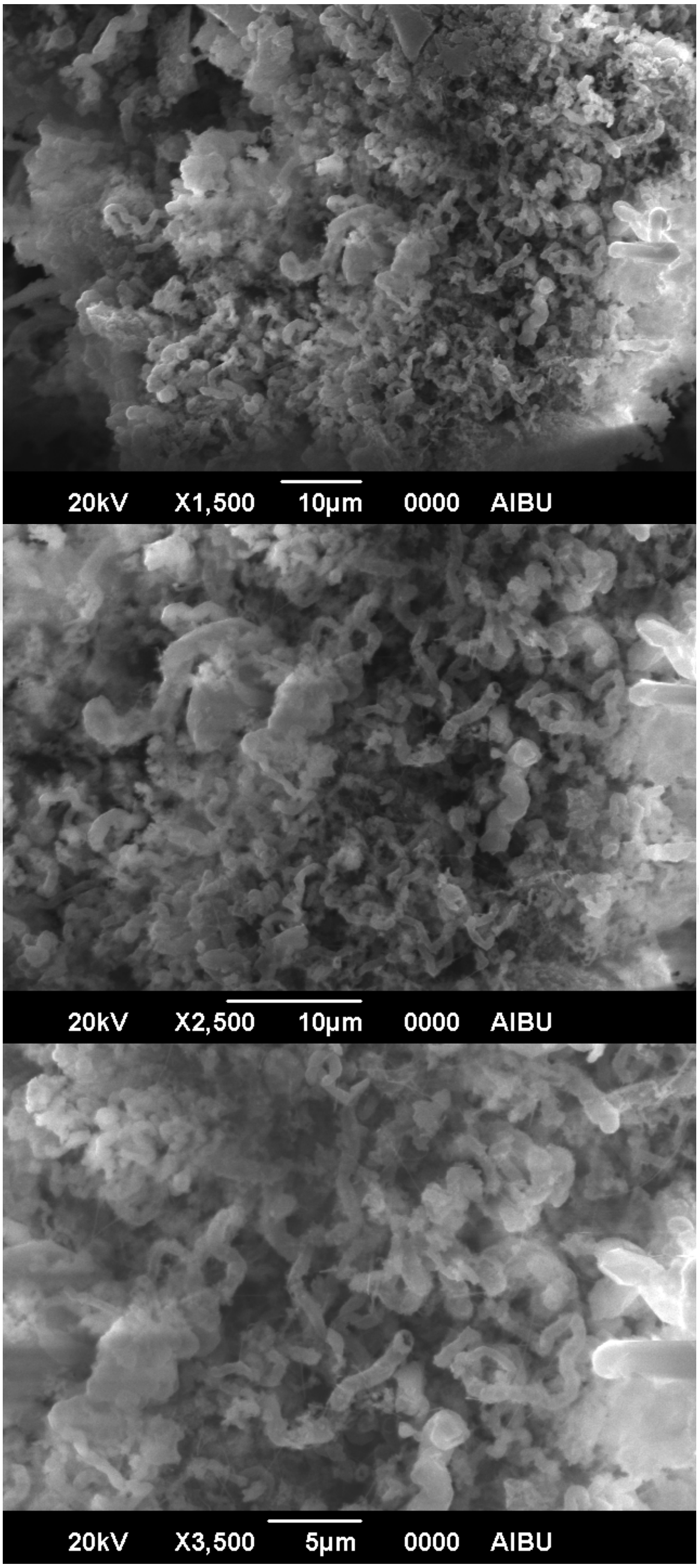


Figure C.1.4. SEM images of hBN in presence of CaI_2.

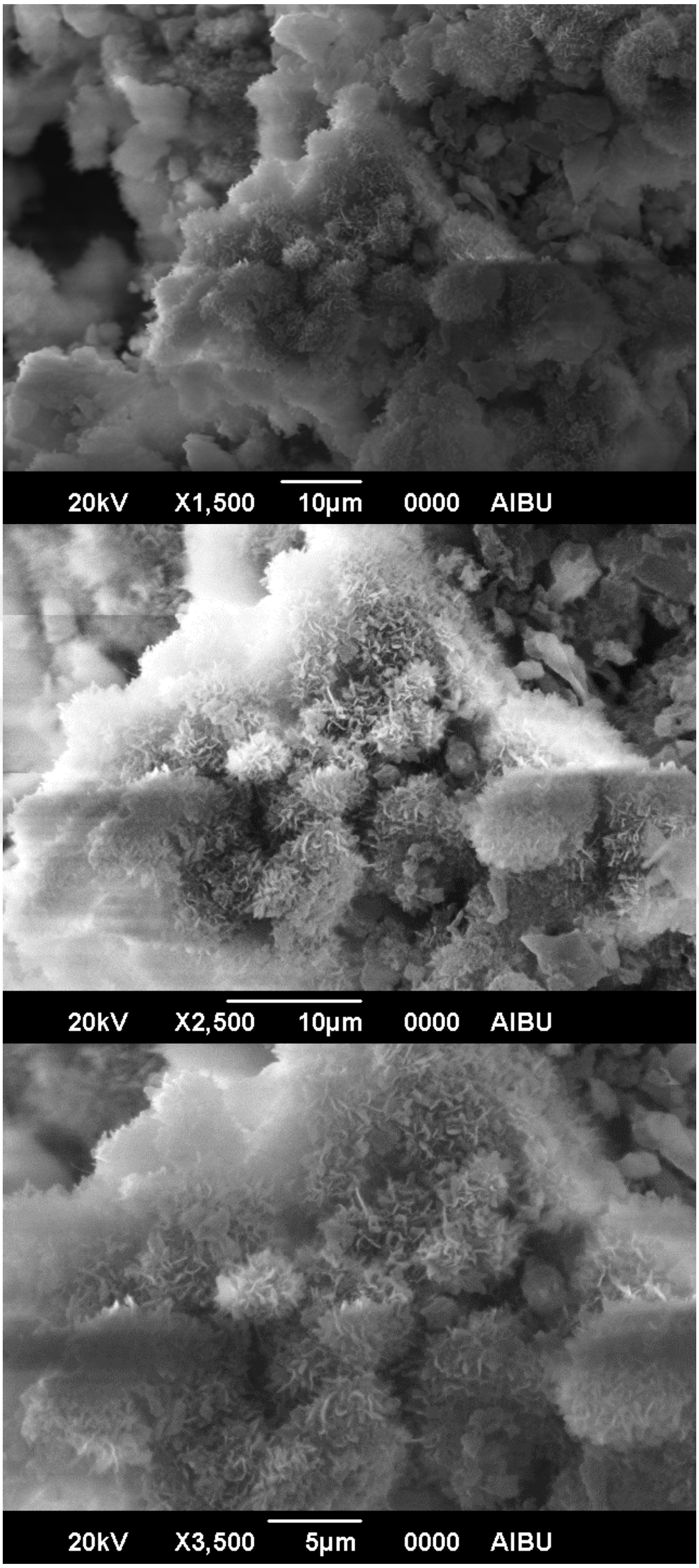


Figure C.1.5. SEM images of hBN in presence of KBr.

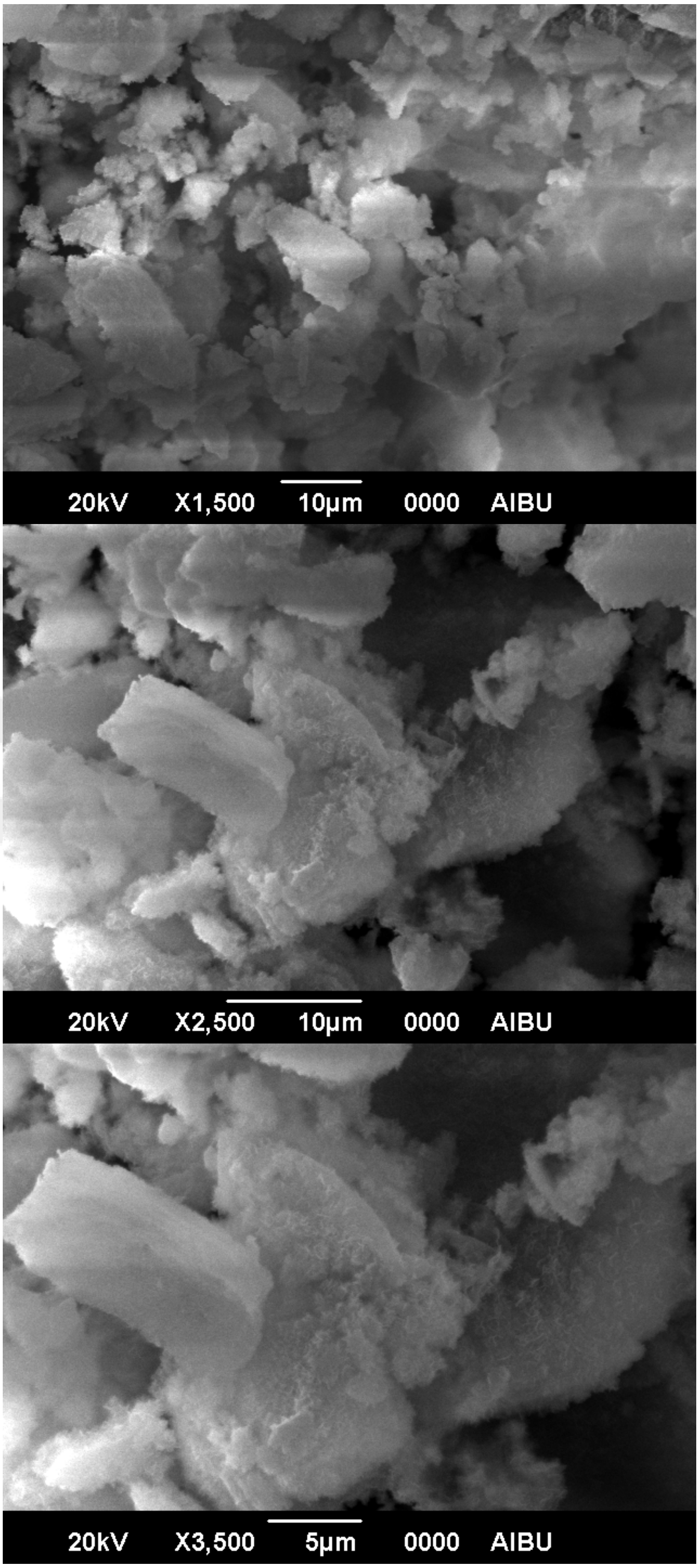


Figure C.1.6. SEM images of hBN in presence of KCl.

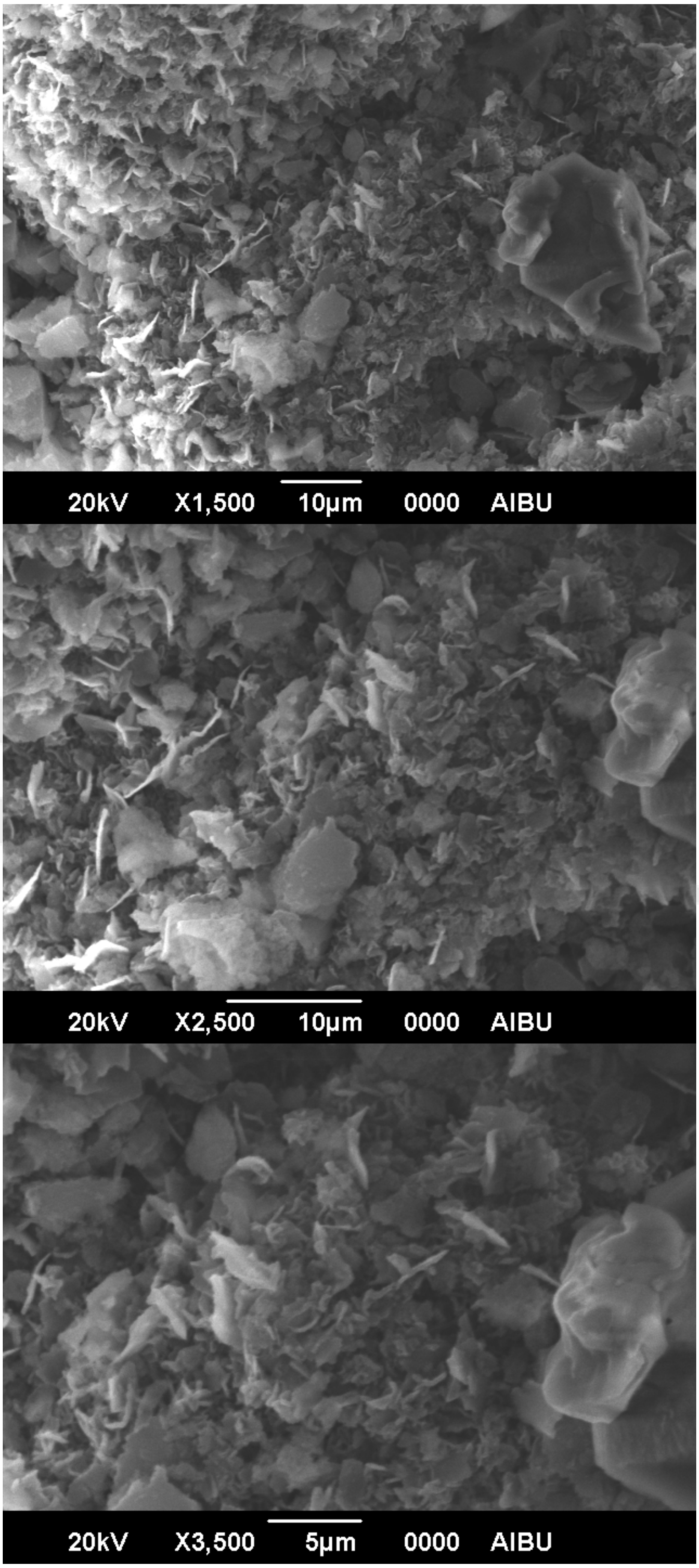


Figure C.1.7. SEM images of hBN in presence of KF.

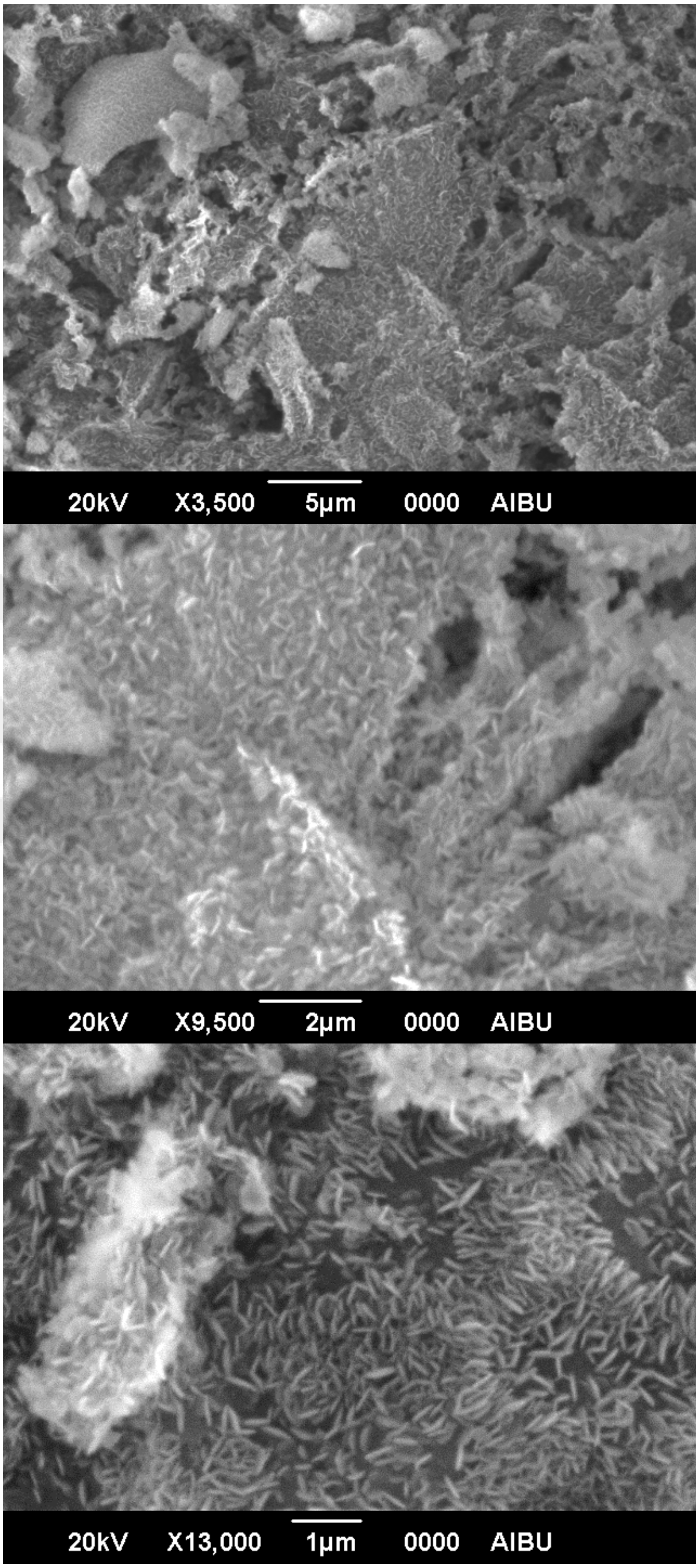


Figure C.1.8. SEM images of hBN in presence of KI.

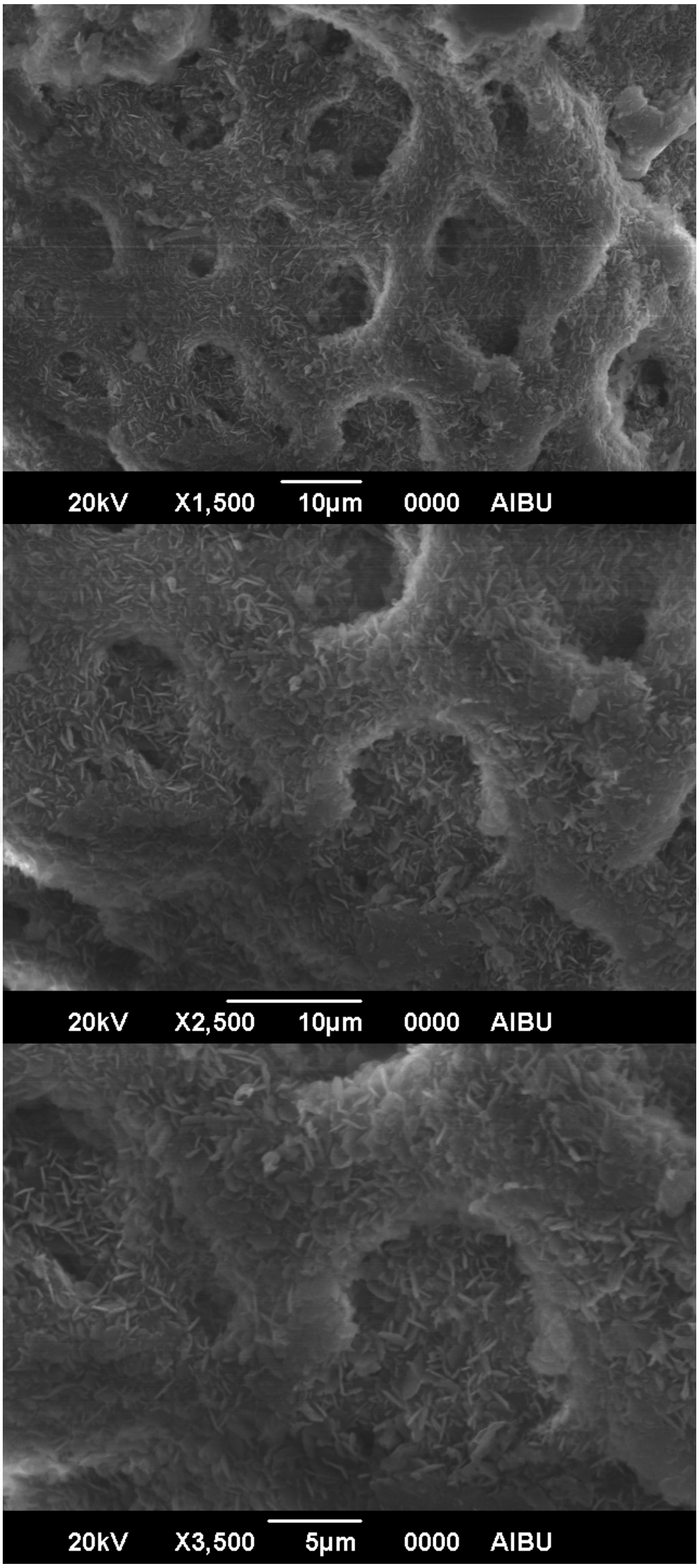


Figure C.1.9 SEM images of hBN in presence of LiBr.

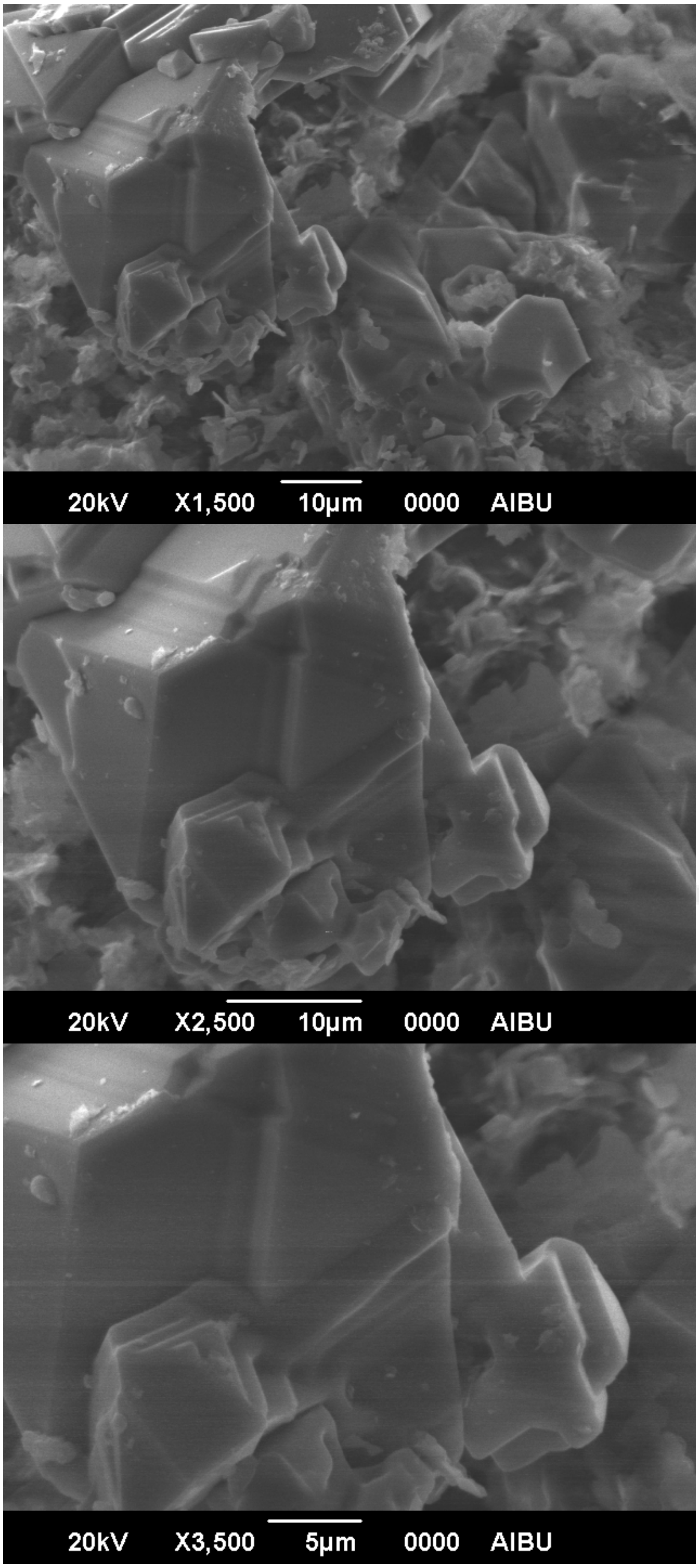


Figure C.1.10. SEM images of hBN in presence of LiCl.

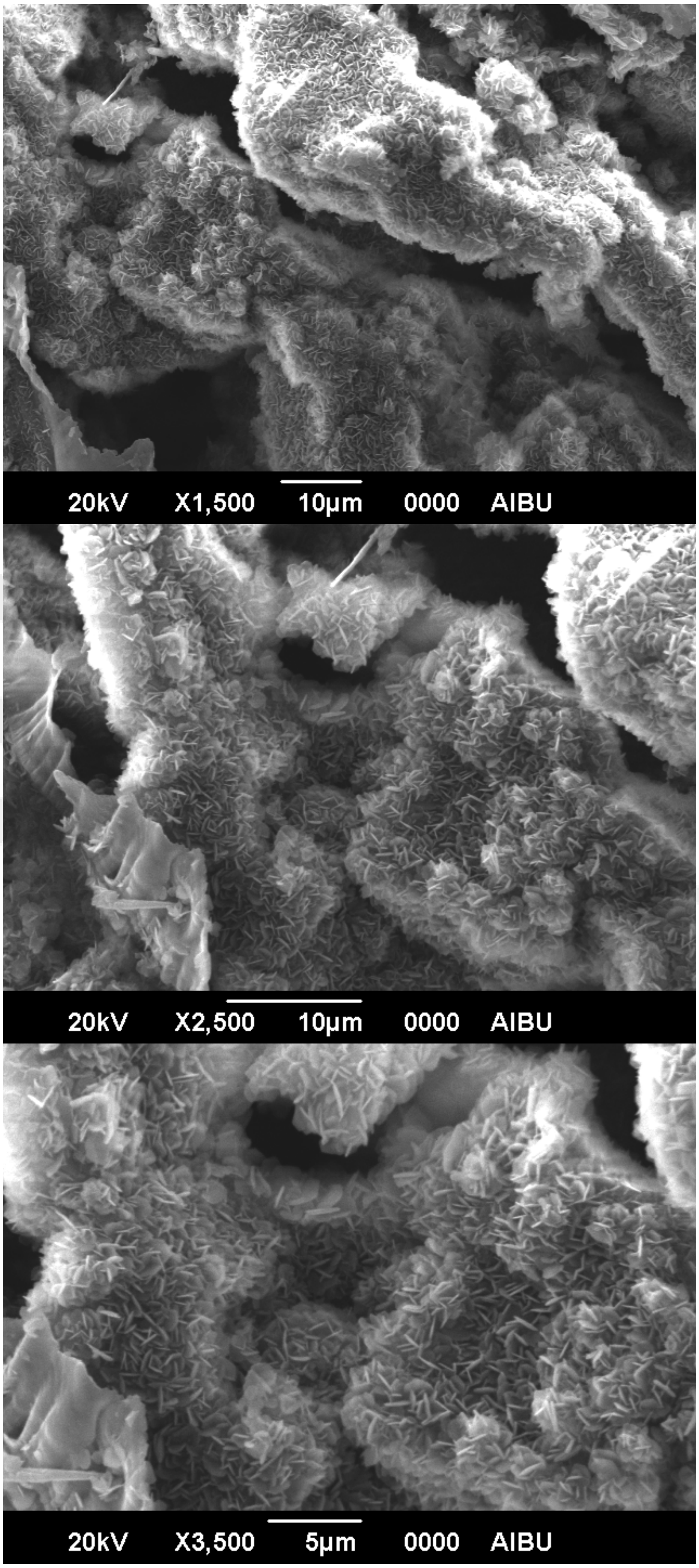


Figure C.1.11. SEM images of hBN in presence of LiF.

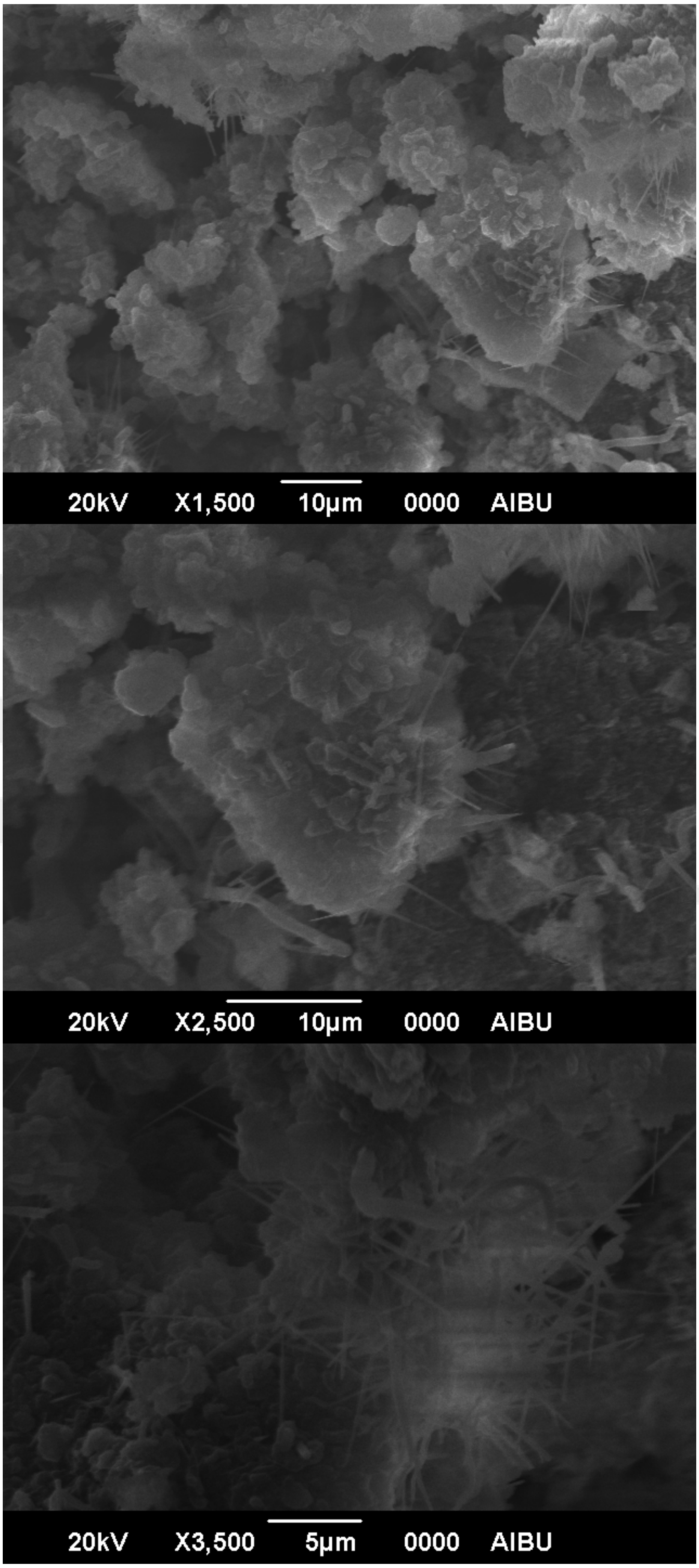


Figure C.1.12. SEM images of hBN in presence of LiI.

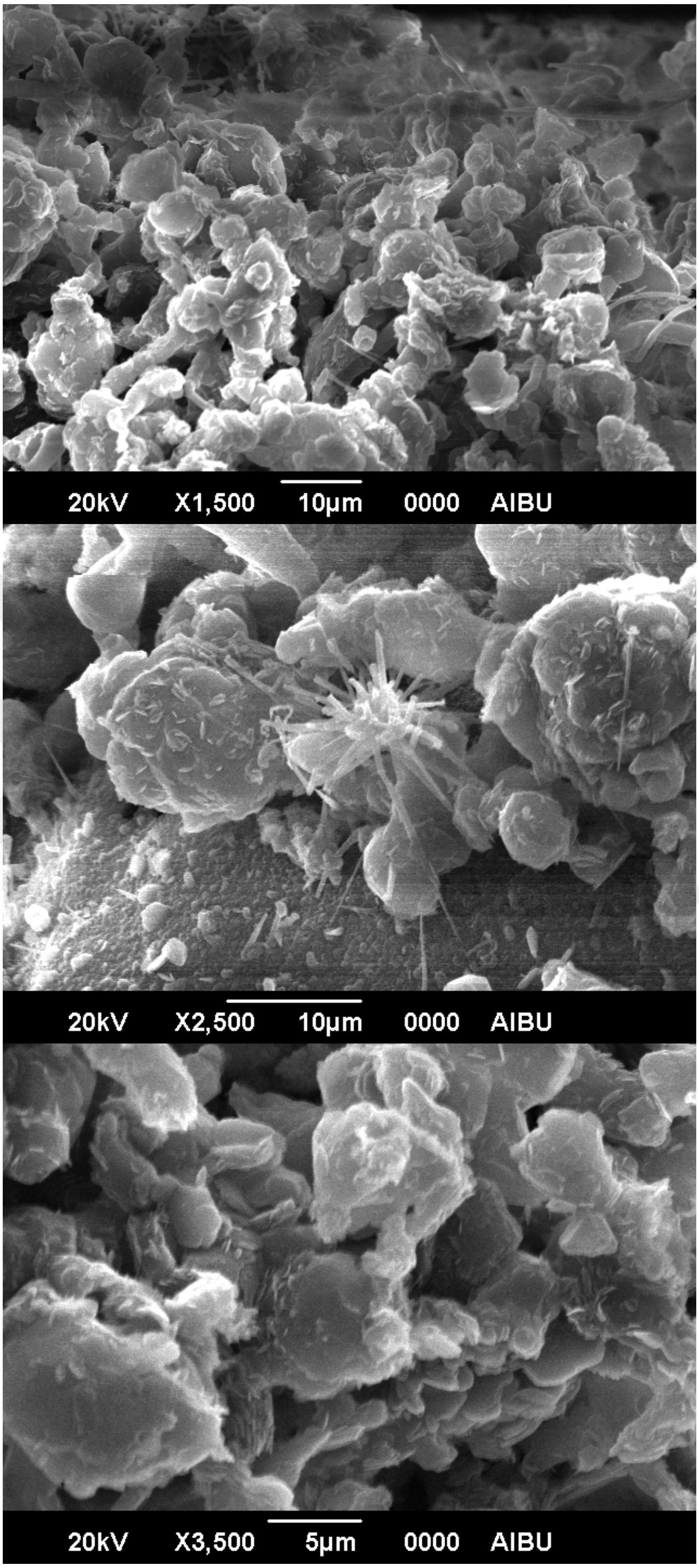


Figure C.1.13. SEM images of hBN in presence of LiI

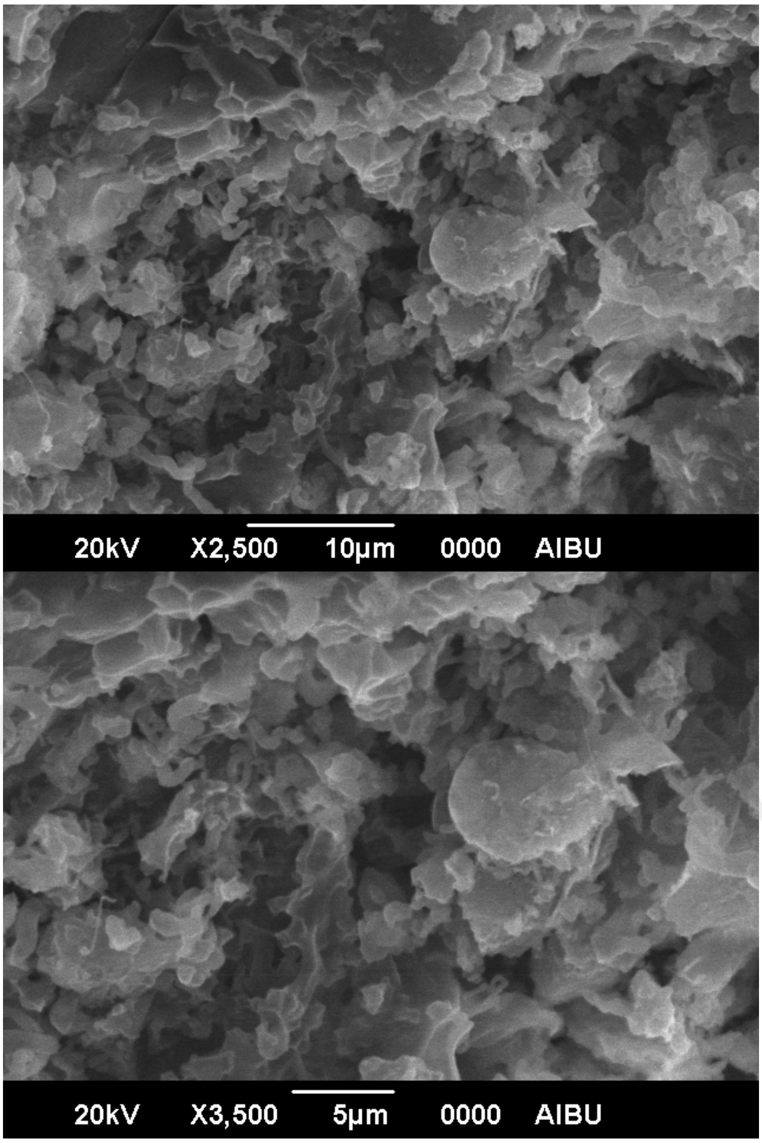


Figure C.1.14. SEM images of hBN in presence of $MgBr_2$.

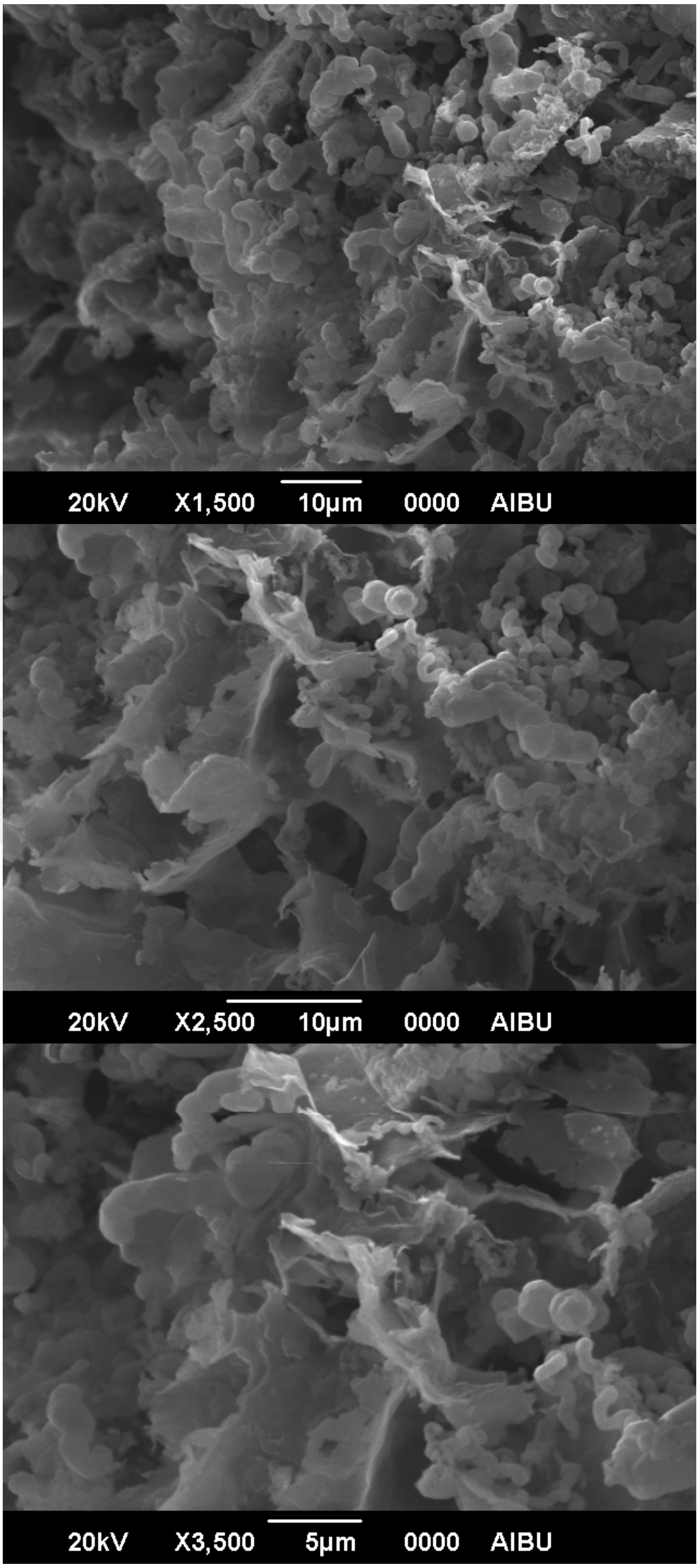


Figure C.1.15. SEM images of hBN in presence of MgCl.

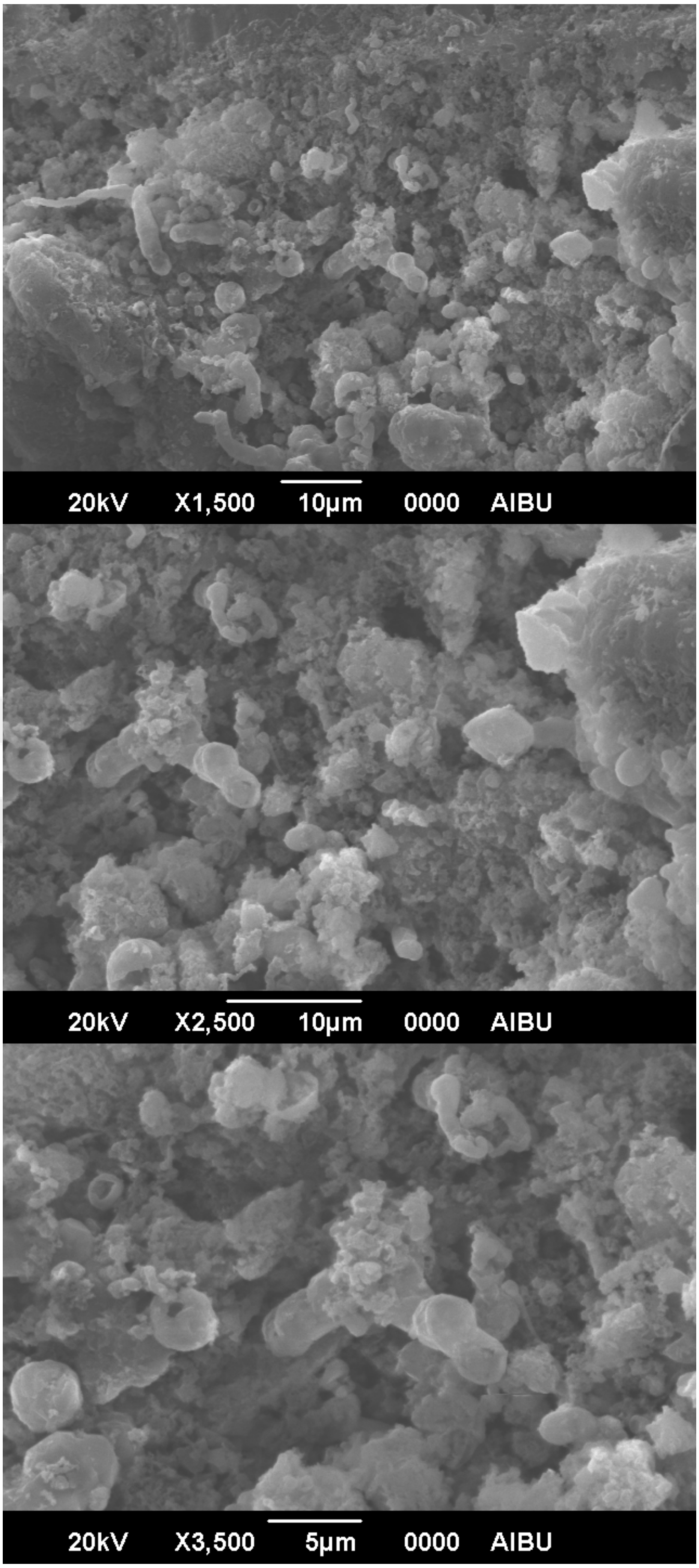


Figure C.1.16. SEM images of hBN in presence of MgF_2.

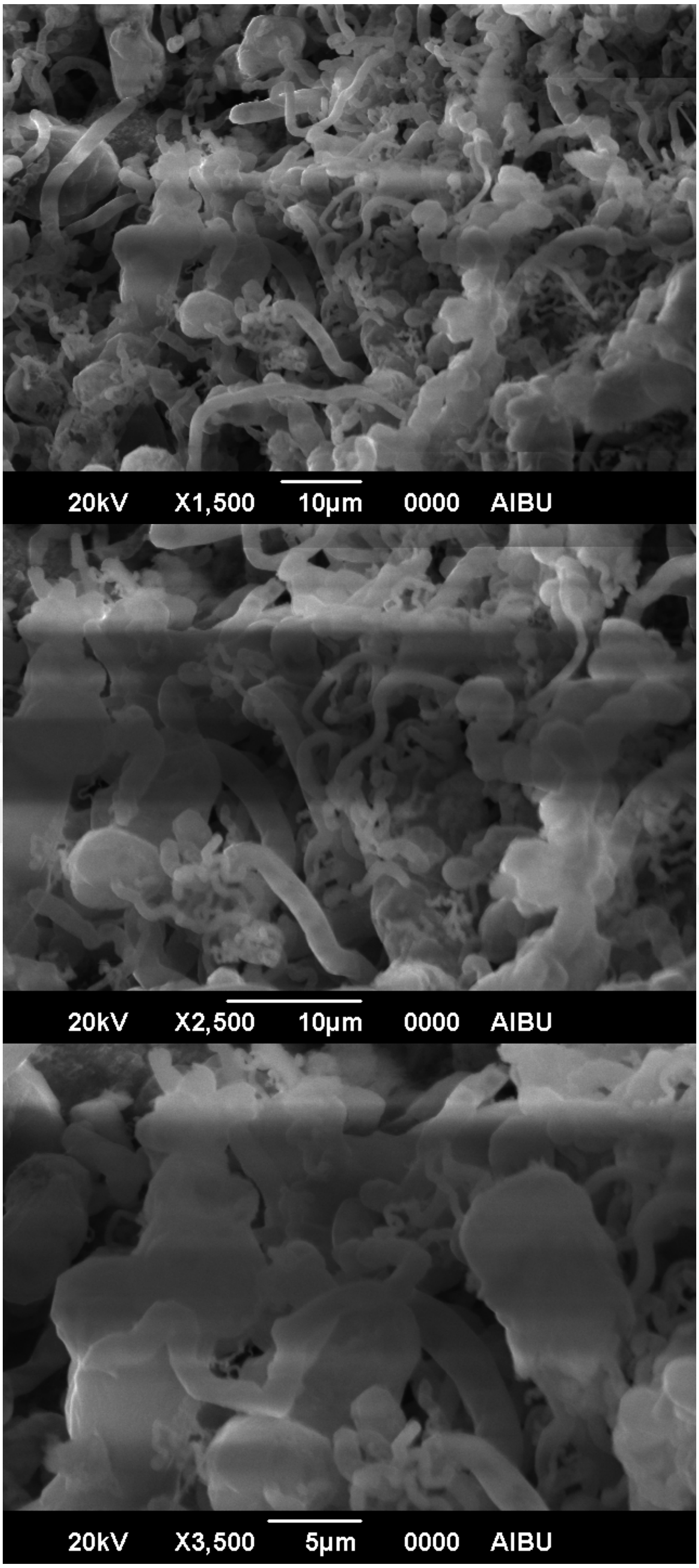


Figure C.1.17. SEM images of hBN in presence of MgI_2.

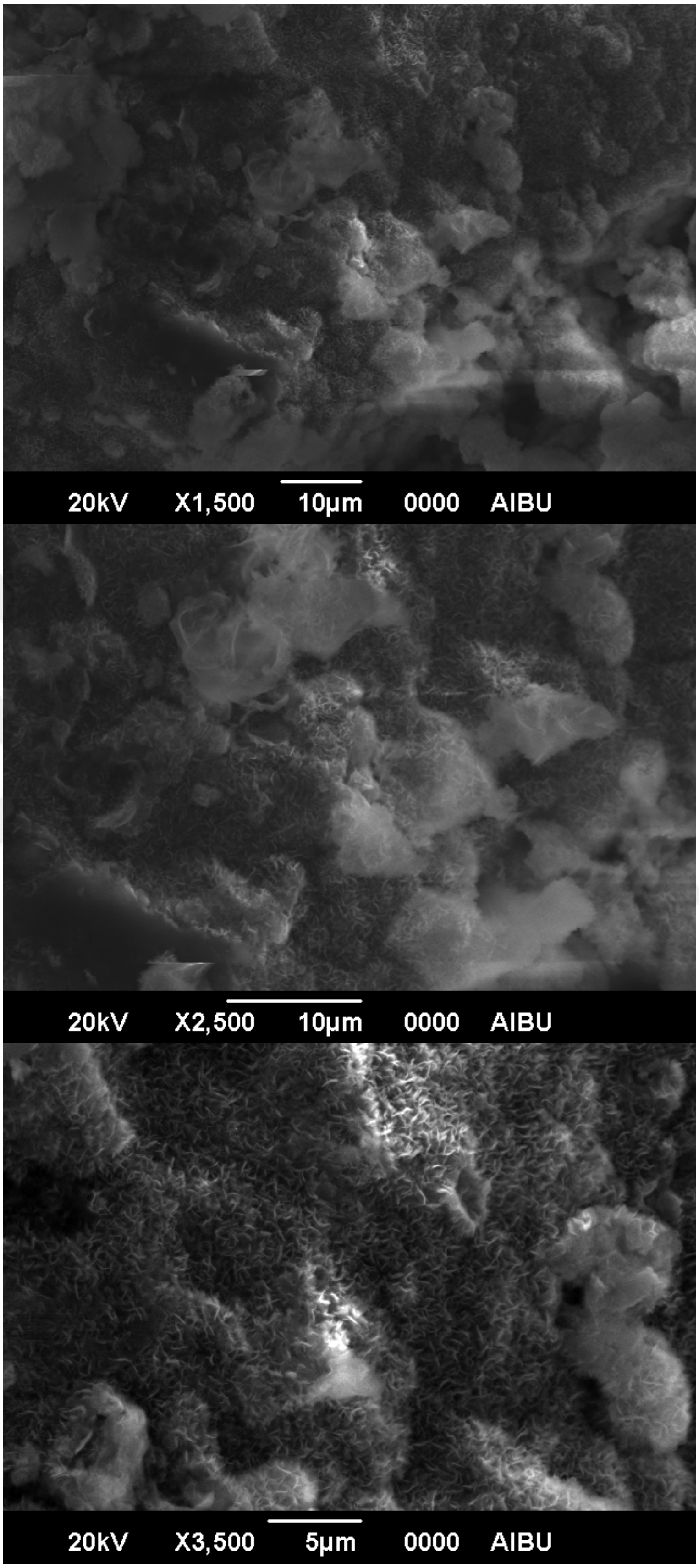


Figure C.1.18. SEM images of hBN in presence of NaBr.

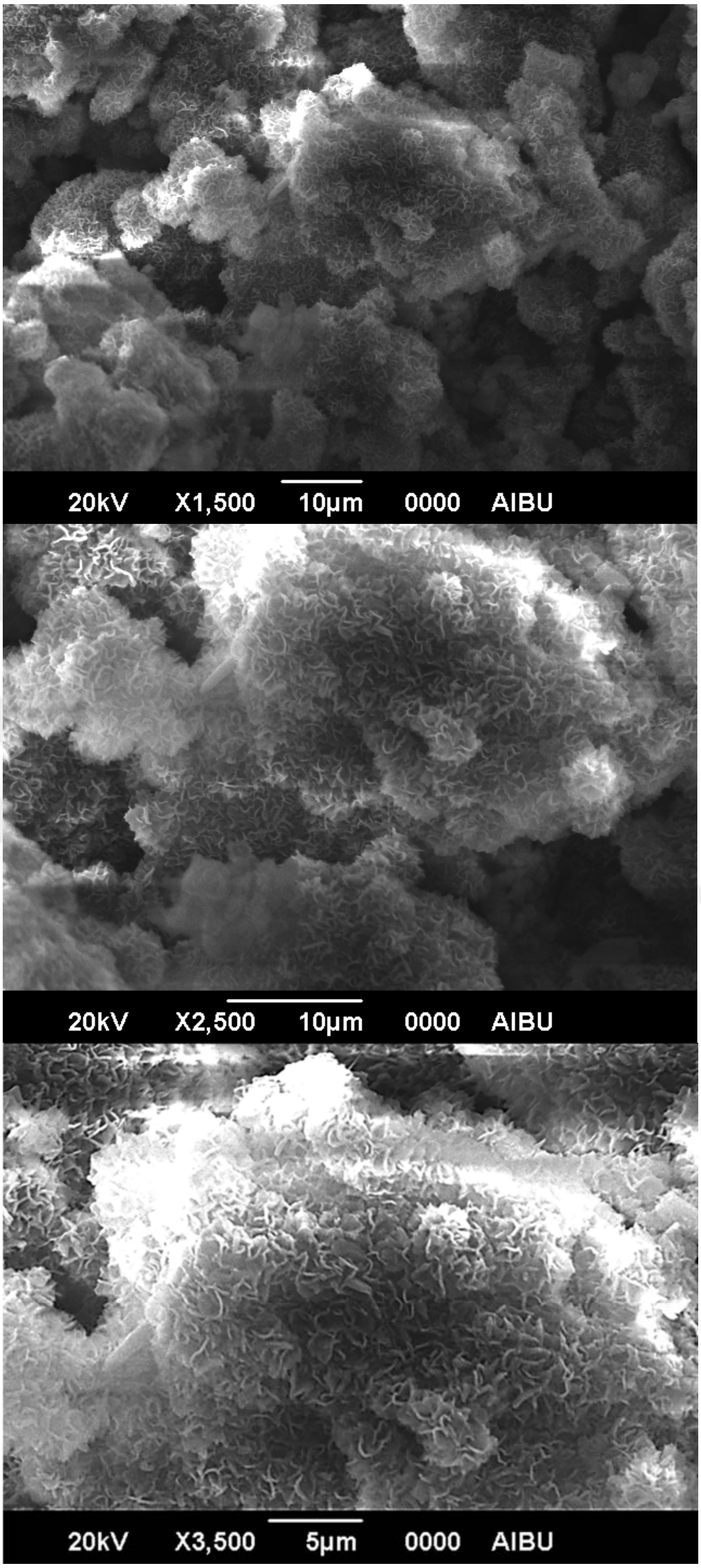


Figure C.1.19. SEM images of hBN in presence of NaCl.

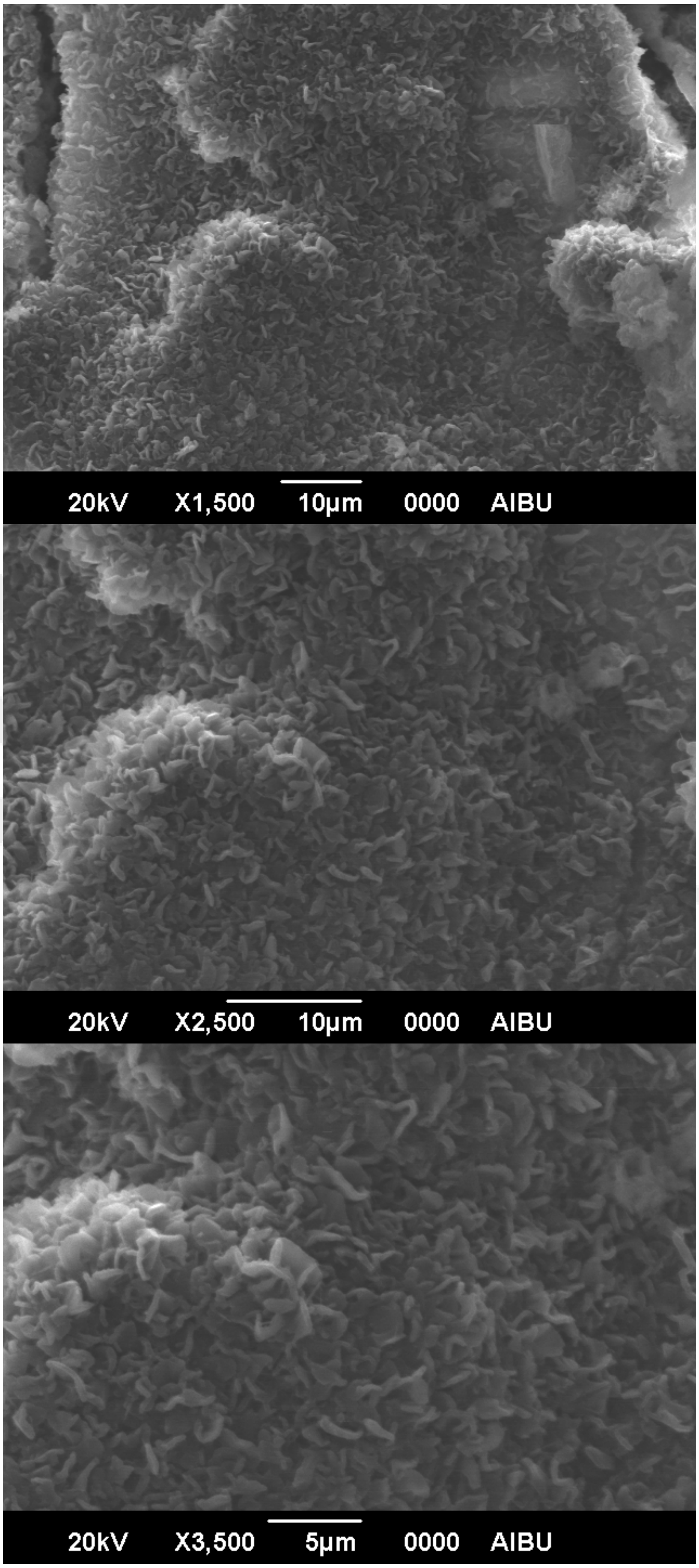


Figure C.1.20. SEM images of hBN in presence of NaF.

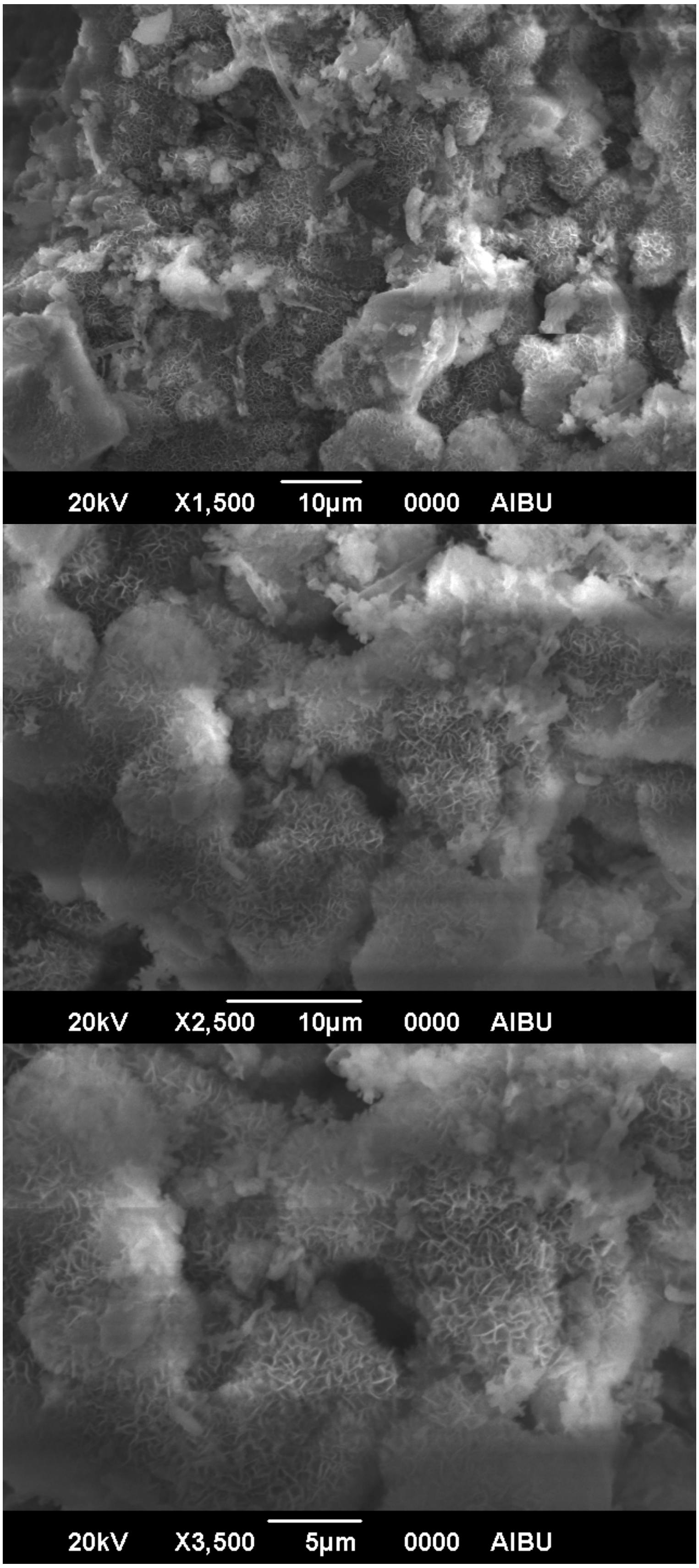


Figure C.1.21. SEM images of hBN in presence of NaI.

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