EFFECT OF METAL CARBONYLS

ON THE

FORMATION OF HEXAGONAL BORON NITRIDE

NİHAL YÜCEL

DECEMBER 2005

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by

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THESIS SUBMITTED TO

THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

OF

THE ABANT İZZET BAYSAL UNIVERSITY

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE

MASTER OF SCIENCES

IN

THE DEPARTMENT OF CHEMISTRY

DECEMBER 2005

Approval of the Graduate School of Natural and Applied Science.

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This is to certify that we have read this thesis and that in our opinion it is fully adequate, in scope and quality, as a thesis for the deqree of Master of Sciences.

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ABSTRACT

EFFECT OF METAL CARBONYLS

ON THE FORMATION OF HEXAGONAL BORON NITRIDE

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December 2005, 28 pages

In this study, by the modified O'Connor Method, hexagonal boron nitride (h-BN) was synthesized via intercalation of various metal carbonyls [$M(CO)_6$, M=Cr, Mo, W].

Using the FTIR, XRD & SEM techniques, the composites were analyzed and the formation of h-BN was proved. XRD analysis proved that the transition series elements are located between h-BN layers and changed the distance between layers. This chance could depends on first valance electrons of metals (d-π interaction). Interlayer spacing distances can be calculated from XRD analyses. According to SEM analysis results, the interlayer presence of metals causes an increase in the particle size.

In the presence of metal carbonyls, h-BN crystals can be produced at 1123°K (850°C) and the completion of reaction time is measured as 2 hours.

Keywords: Hexagonal boron nitride, metal carbonyls, interlayer spacing distance, d-π interaction

ÖZET

HEKZAGONAL BOR NİTRÜR OLUŞUMUNA

METAL KARBONİLLERİN ETKİSİ

Yücel, Nihal

Yüksek Lisans, Kimya Bölümü

Tez Danışmanı: Doç. Dr. Çetin BOZKURT

Aralık 2005, 28 sayfa

Bu çalışmada modifiye O'Connor Yöntemi ile çeşitli metal karboniller [$M(CO)_6$, M=Cr, Mo, W] kullanılarak hekzagonal bor nitrür sentezlenmiştir.

Fourier Transform Infrared Spectrofotometresi (FTIR) ve X-ışınları Difraksiyon analizleri ile h-BN kompozitlerinin oluştuğu kanıtlanmıştır. FTIR analizleri h-BN oluşumu ile uyum içindedir. Geçiş serisi elementlerinin h-BN tabakaları açısına yaklaştığı ve tabakalar arası uzaklığın değiştiği XRD analizleri ile ispatlanmıştır. Bu değişim metallerin değerlik electronları (d-π etkileşimi) ile bağlantılıdır. SEM analiz sonuçlarına göre, metal varlığı partikül boyutunun artmasına sebep olmaktadır.

Metal karbonil varlığında, h-BN kristal yapıda elde edilmesi 1123°K (850°C)'de gerçekleştiği ve tepkimenin 2 saatte tamamlandığı saptanmıştır.

Anahtar Kelimeler: Hekzagonal bor nitrür, metal karboniller, tabakalar arası uzaklık, d-π etkileşimi

ACKNOWLEDGEMENTS

I am in dept of gratitude to;

Assoc. Dr. Çetin Bozkurt who directed me by sharing his knowledge and help, who facilitated my study by answering all my questions sincerely and first of all who gave me the chance of studying with deepest thanks to;

Res.Assis. Erhan Budak who was near me with his endless help, support and patience during my study.

Assoc.Prof.Dr. Engin Özdaş and Res.Assis. Bora Kalkan for helping XRD analyses for this study.

My family who believes and support me patiently all the time and never left me alone.

My dearest friends Umut Ördekcioğlu and Esma Eda Sucu, who gave the power and motivation I needed during my study.

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1. INTRODUCTION

Boron Nitride, BN, is an inorganic, synthetic white solid material and is one of the oldest known boron-nitrogen compounds. The first synthesis was made in 1842 by W.H.Balmain using the action of molten boric acid on potassium cyanide [2]. Unfortunately, the new compound was unstable and it was not until the mid - 1950s and early 1960s that researchers were able to create more stable material in the form of powders and hot-pressed shapes.

BN is a non-oxide advanced ceramic material and has excellent physical and chemical properties as low density, high thermal stability and conductivity, high melting point, chemical stability, machinability and neutron capturing. These characteristics make BN valuable in many applications, especially in the area of technical ceramics. [1]

BN has many names and types: Hexagonal boron nitride (hBN), rhombohedral boron nitride (rBN), cubic boron nitride (cBN) or borazon, wurzit boron nitride (wBN), zinc blende (zBN), turbostratic boron nitride (tBN), pyrolytic boron nitride (pBN) – the mixture of hBN and tBN, amorphous boron nitride (aBN), and more. BN can be classified in two main groups: sp^2-hybridized BN and sp^3- hybridized BN (Table 1).

Boron Nitride

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

Table 1. Classification of BN.

The hBN and rBN have trigonal sp^2 bonding and their structures are similar each other, but not the same as, the graphite structure (Figure 1). Both hBN and rBN have flat sp^2-6-rings and the B–N distance is 144 pm. Although the B-N bonding in sp^2 system is stronger than the B-N bonding in sp^3 system (cBN and wBN), the distance between the layers of sp^2-6-rings is long (333 pm). This is caused by weak interaction between the layers. In addition, this weak interaction permits to change the structure to other forms under high pressure.

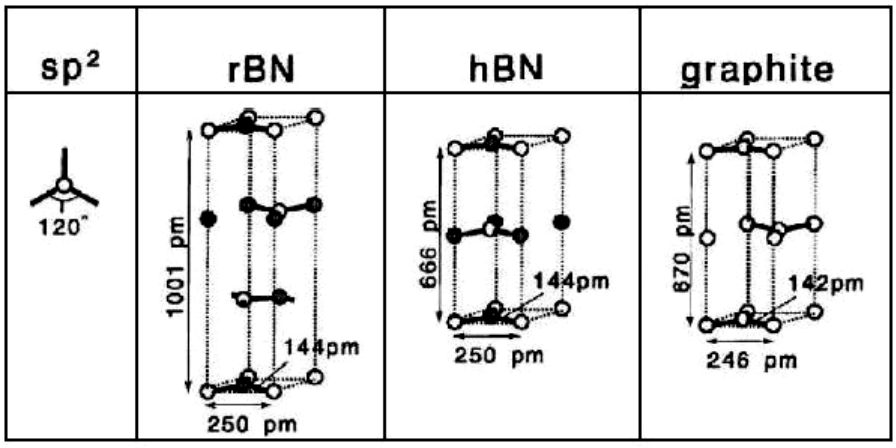


Fig.1 Structure of rBN, hBN and graphite.

Both cBN and wBN are packed in sp^3-*6*-ring (Figure 2) with a 157 pm layer distance and they can be prepared from the hexagonal. aBN, which has sp^3-layer structure, is the diamond like amorphous material.

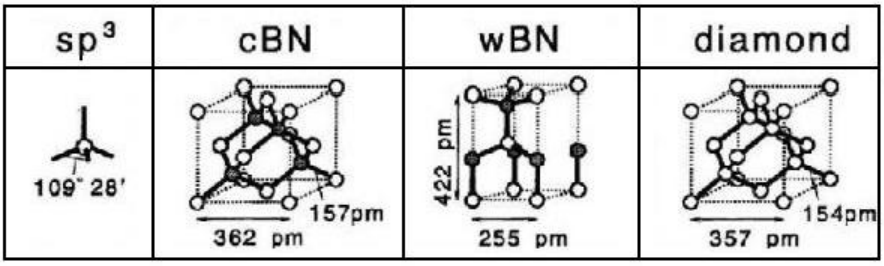


Fig.2 Structure of cBN, wBN and diamond.

The X-ray diffraction data of hBN, rBN, tBN, cBN, and wBN (Figure 3) gives information about the layer types and the distances.

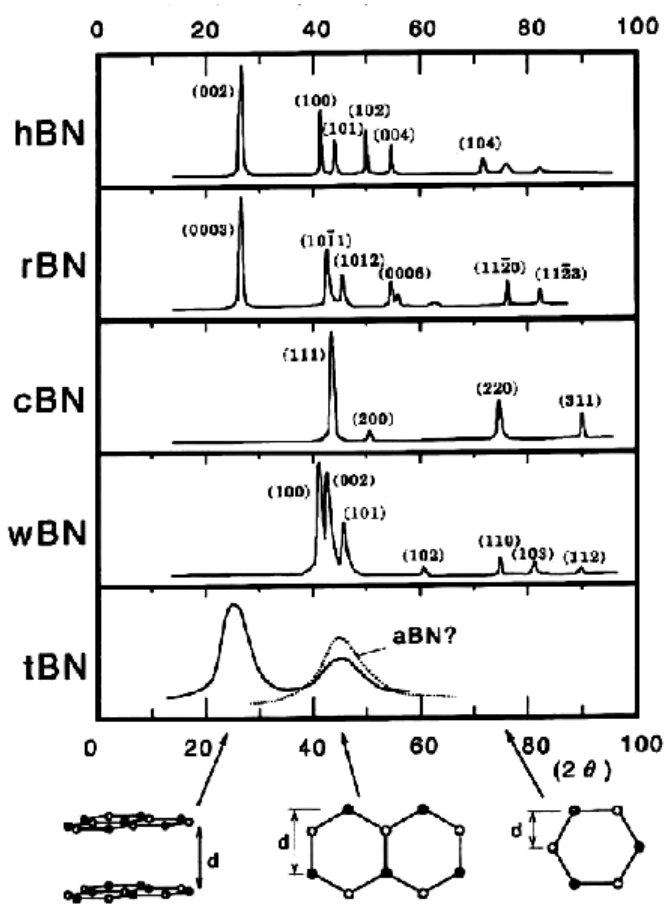


Fig. 3 The X-ray diffraction data of hBN, rBN, tBN, cBN, and wBN.

The spectral peaks around 2θ = 25° correspond to the distance (~333 pm) between the layers of the sp^2 networks. Some peaks around 2θ = 40-50° are due to the atoms in the sp^2 or sp^3-6-layer rings. tBN shows two broad diffraction peaks around 2θ = 25° and 40-50°. However, the species having sp^3 layers gives peak at 2θ = 40-50° with ~210 pm layer distance.

Because of the strong covalent bonding, cBN is expected to have high-frequency lattice vibration but the bonding in the flat sp^2 6-ring of hBN is stronger than in the cBN (Figure 4), as indicated by the higher frequency B-N vibrations exhibited by hBN u_{LO} = 1610 cm^{-1} –IR inactive- and u_{LO} = 1370 cm^{-1}-IR active- on the other hand, frequencies of B-N vibrations exhibited by cBN are u_{LO} = 1304 cm^{-1} –IR inactive- and u_{LO} = 1054 cm^{-1}-IR active.

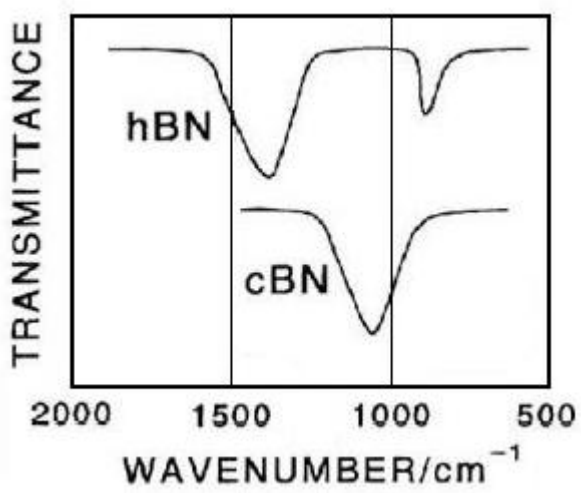


Figure 4. IR spectra of hBN and cBN.

tBN is a low temperature product. It is prepared at about 1000°C and often has a disordered structure. In accordance with disordered carbons which show only two X-Ray diffraction peaks (002) and (101), such a structure is called *turbostratic* [2]. The turbostratic structure can readily be converted to an ordered layer-lattice hexagonal form by treatment at high temperatures. The structural imperfectness, on the other hand, is an important technological requirement, as such powders possess good sinterability, when compared with crystalline material.

cBN is synthesized from hBN at high temperature and pressure. This process changes the structure from hexagonal to cubic-the same as that of diamond. Diamond is the only substance harder than cBN. One important fact about cubic boron nitride is that, unlike diamond, it does not react with ferrous alloys. There are several advantages that cBN has over competing materials. It is stable in air at temp. up to 1400 °C cBN is also chemically inert, exhibits extreme toughness and can be produced in a variety of uniform grain sizes.

w-BN, is a new super abrasive material that is manufactured by detonation. It is the next step in boron nitride generation. The material has a polycrystalline structure that provides superior cutting properties and will actually sharpen itself during cutting. The term “polycrystalling structure” means that plenty of crystals are bonded chemically together that work at the same time.

Experimental results show that transitions can be possible between the four crystalline boron nitride phases and the amorphous BN (Figure 5 and 6). For example, when hBN is compressed (10-15 GPa) at room temperature, it is converted to wBN. However, with the increasing temperature (~1350 °C) and at ~8 GPa pressure hBN transforms to cBN. When rBN is compressed at room temperature, its structure changes to an unknown form. Further compressing (approx. 20 GPa) this unknown structure transforms to cBN.

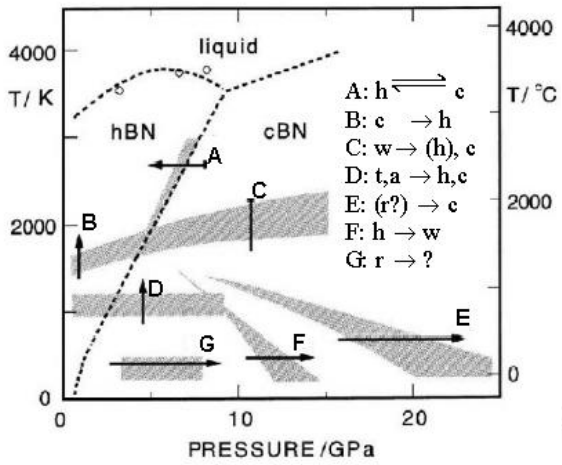


Fig. 5 The BN phase diagram.

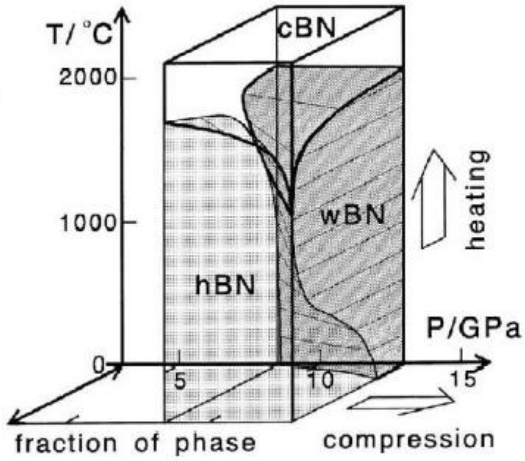


Fig. 6 Transition in BN during compression and heating.

1.1. Synthesis of Boron Nitride

Preparation of a binary compound of boron with nitrogen was first reported as early in 1842 [6]. Since then, there have been many routes found to synthesize boron nitride, from direct synthesis of boron with nitrogen to get fine BN powder to deposite on self consistent solid layers formed by pyrolyzing gaseous precursors typically consisting of boron halides and ammonia. Widespread, commercialized methods to prepare BN in the range of tons, however, are based on simultaneous reducing and nitriding of boric oxide, boric acid and its salts. The most obvious route to prepare boron nitride in mass quantity has been the carbo-reductive nitriding of boric oxide in nitrogen. The amount of carbon must be controlled very precisely to prevent contamination of boron nitride with unreacted carbon, and the product of the process must be washed from unreacted boron oxide.

To prepare boron nitride, three consequent processes have to be regarded:

1. Purification of the ore from alkaline metals and other impurities to get initial materials for boron nitride synthesis (typically boric acid and boron sesquioxide)
2. Conversion of the raw materials onto substances directly preceding formation of boron nitride (boron nitride precursors)
3. Completing the process by synthesizing BN powder or polycrystalline solids as ceramics.

There have been many synthetic methods described leading to boron nitride. But if they are compared, a common pattern fits to all of them, as shown in the Figure 7.

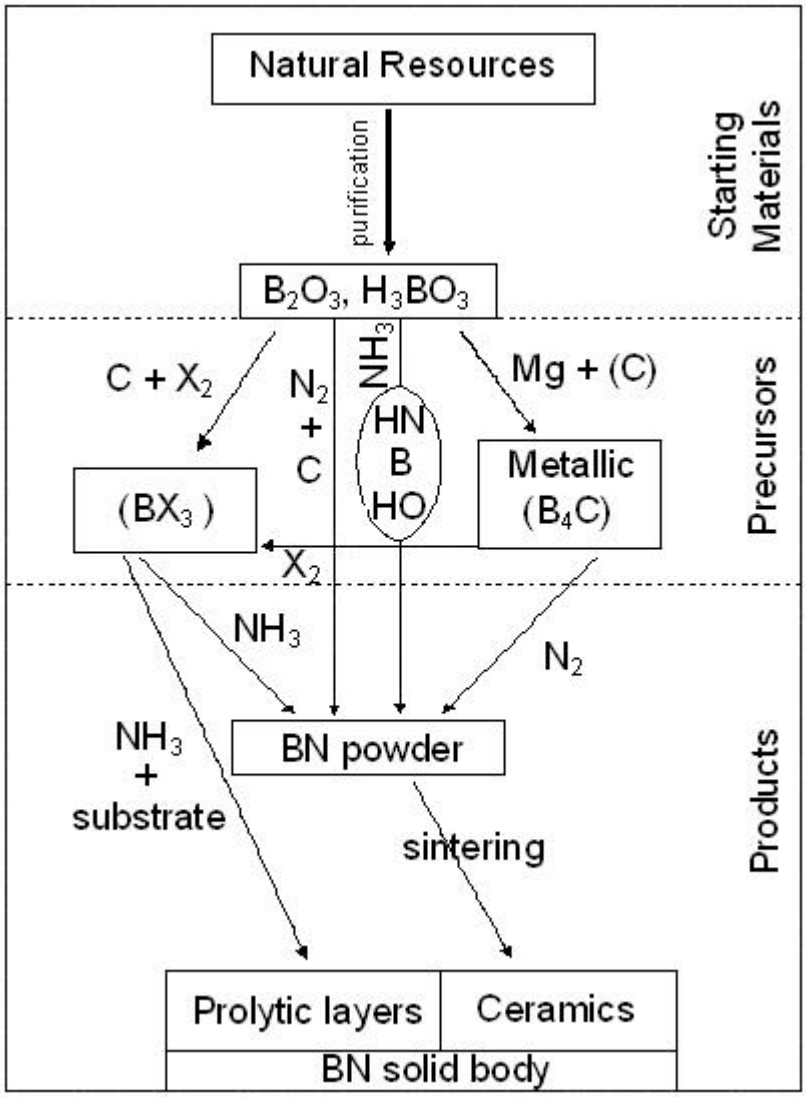


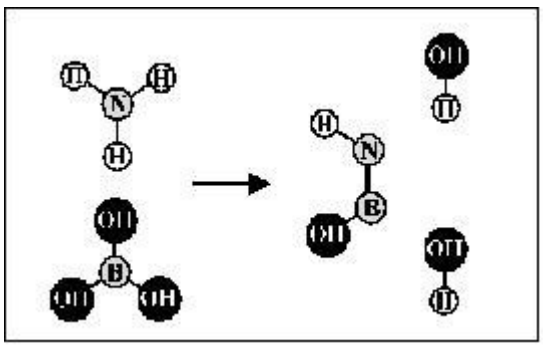
Fig. 7 The routes of synthesis of BN.

The O'Connor method is based on the mixture of one part by weight of boric acid was mixed with two parts of urea and heated under ammonia atmosphere at 1320 K. For all variants of description of hBN by reductive nitridation of oxidic boron compounds, boric oxide and ammonia can be considered as starting substances; these give boron nitride according to the overall equation:

$$B_2O_3 + 2NH_3 \longrightarrow BN + 3H_2O$$

So-called "amide method" will be used to model the formation of hexagonal boron nitride planar networks using the ammonia - boric acid system:

In the first step, an ammonia molecule has to approach the surface of a boric acid grain. Due to the redistribution of electron densities in the system, new bonds are created. HO-B-N-H monomer is formed and water is released as the consequence of the redistribution (Figure 8a). Afterwards, the monomer is stabilized by the trimerization (Figure 8b).



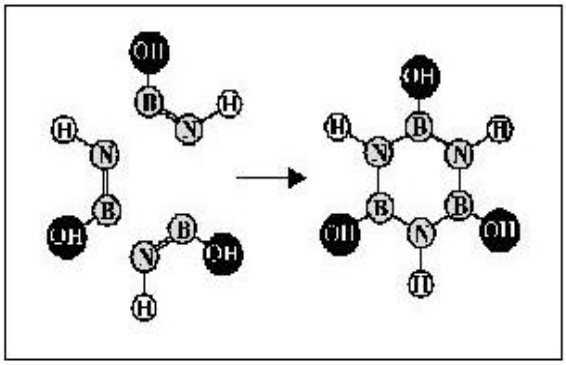


Fig. 8a Redistribution of HO-B-N-H monomer. **Fig. 8b Trimerization of the monomer.**

After the third step we can get a macromolecule as shown in the Figure 9 . The growth can continue till the size of the macromolecule reaches that which can be found in tBN powders. The size is mostly being expressed as the crystallite width, L_a, and approximately equals 10 nm. A hexagonal macromolecule with the formula HO-B27N27-H corresponds to this size.

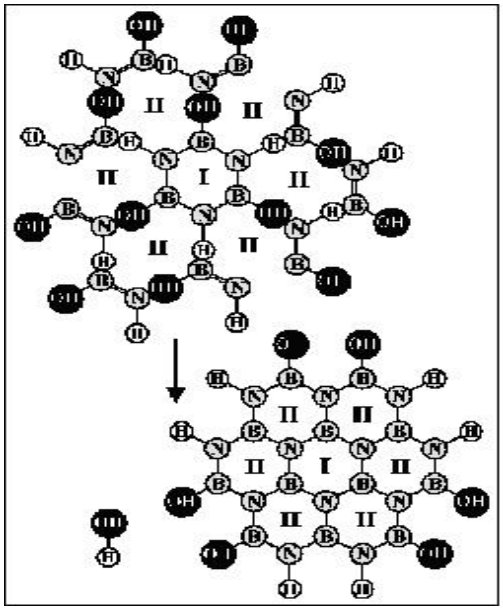


Fig. 9 Macromolecules of BN.

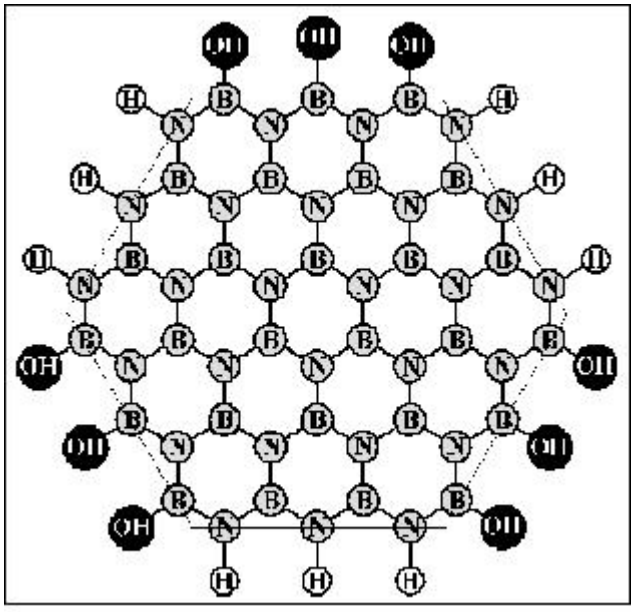


Fig. 10 Crystalline BN.

Real crystals of BN are constructed from particular monolayers by their stacking each above other. The dipole-dipole interaction mediating stacking the layers is a chemical of the second order; so that each and every monolayer (a macromolecule) is a chemical unit of hexagonal BN. The width of the BN crystallite is then identical to the size of a macromolecule (Figure 10).

As shown in the previous figures, oxygen and hydrogen must not be regarded as impurities, but they represent constitutional elements terminating the two-dimensional h-BN macromolecules. Since the contents of these elements are inversely proportional to the circumference-to-area ratio, it can be assumed that the larger are the BN crystals, the higher is the purity of BN. This relationship is actually the principle of the purification process, where BN is first crystallized by the thermal treatment in nitrogen gas, and oxygen impurities converted to boron oxide are washed out.

1.2. Intercalation of Boron Nitride with Metals

The effect of metal on crystallinity of boron nitride was studied by Hubacek and Sato [3]. Cu-hBN composites were obtained by two methods. The first one includes mechanical mixing and heating of hBN with copper powder. The second consists of the chemical treatment of mixtures of boric oxides, urea and copper nitrate. Both methods are considered to give the same product, which contains copper atoms between hBN layers. The copper containing powder turned to well crystallized ceramic, while the copper free specimen remains turbostratic and only a slight improvement of its crystallinity was noticeable. Moreover, in the copper containing sample formation of donor-acceptor complexes between copper electronic orbitals and π electrons of adjacent BN facets resembling metal-carbon interaction in ferrocenes, and coalescence of BN crystallites through copper –activated facets while releasing the copper atoms (Figure 11 and 12) .

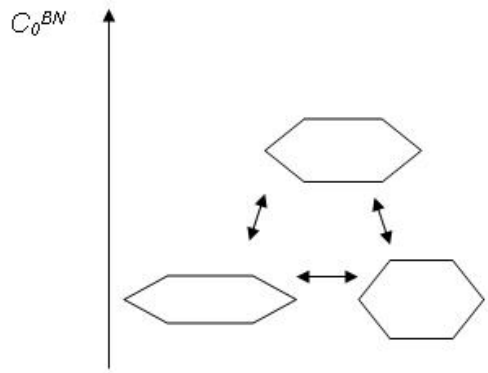


Figure 11. Irregular structure of Copper free BN

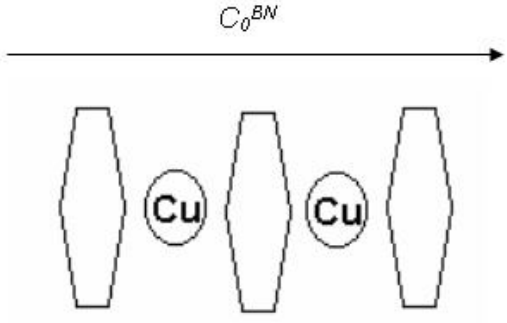


Figure 12. Formation of donor-acceptor complexes boron nitride-copper system

The effect of Cr, Mn, Fe, Co, Ni, Cu, Zn and Ag on crystallinity and interlaying spaces of hBN was studied by E. Budak [4]. By using different metals, interlaying spaces of h-BN was changed. This change depends on the interaction between d electrons of metal and π electrons of BN (d-π interaction) and atomic radius of metals.

The effect of cadmium on interlaying distance of h-BN was studied by G. Koç [17]. The effect of metal in different amounts was studied and by increasing the amount of metal, structure turns into crystal form, interlaying spaces between layers showed similar properties as with Ag as E. Budak obtained [16].

As it can be seen from these studies, when metal compounds were added in the synthesis of h-BN to the precursor mixture, it was possible to

obtain metal intercalated h-BN at relatively lower temperatures. On the other hand, metal carbonyls can be used as metal sources at to obtain that kind of metal intercalation compounds. The two different roles of the metal carbonyls would be observed: 1- The decomposition of metal carbonyls would give finest metal atoms by heating; therefore it is possible to obtain more uniform intercalation compounds, and 2- The evolved CO gas must be involved in the reduction reactions, similar to carboreductive formation of boron nitride [5].

1.3 Decomposition of Metal Carbonyls

$M(CO)_6$ [M= Cr, Mo, W], is decomposed to M-metal in two steps via thermally stable sub-carbonyl intermediate species, $M(CO)_3$. The order of increasing decomposition rate of $M(CO)_6$ is $Cr(CO)_6 < W(CO)_6 \leq Mo(CO)_6$. Accordingly, the decarbonylation of $M(CO)_6$ is controlled by the first M-CO bond scission [11].

$Mo(CO)_6$ decomposes at a temperature at 420 K. In decomposition, first CO loss occurs, with the other five CO being lost successively, each with dissociation energy equal or slightly less than that of the first eliminated CO [12]. $Cr(CO)_6$ decomposes by losing CO groups and forms very small metal agglomerates at 150°C [10]. $W(CO)_6$ decomposes to yield $W(CO)_x$ fragments and molecularly absorbed CO [13]. In this study, thermal decomposition of metal carbonyls ($Cr(CO)_6$, $W(CO)_6$, $Mo(CO)_6$) takes place in the precursor case at 473 K.

In the present study, the effect of metal carbonyls on the formation of hBN has been investigated.

2. EXPERIMENTAL

By using modified O'Connor method hBN was synthesized. After one part by weight of boron oxide and 2 parts of urea were mixed until obtaining a homogeneous mixture, metal carbonyl, $M(CO)_6$ (M= Mo, Cr, W) containing mixtures were prepared.

In order to form precursor, heating process was performed at 473K for two hours, then the precursor was pulverized in a grinder and annealed in a stream of NH_3 gas with the flow rate of 2 cm/s at 1323K, 1223K and 1123K for two hours in a tube furnace individually. Purifying the product was made by boiling in 5% HCl solution and the formed product was washed with ethanol. Drying process was done in an oven at 373K. The obtained powder was pressed by 10 tons at room temperature.

2.1. Chemicals:

Boron oxide and urea were purchased from Fluka AG and used without any purification. $Cr(CO)_6$, W(CO)6, $Mo(CO)_6$ and $Cr(NO_3)_3$ were purchased from Merck AG and used without any purification.

Hydrochloric acid were purchased from Riedel de Haen and used without any purification.

2.2. Instruments:

2.2.1. FTIR Measurements

The FT-IR characterization of h-BN was done with Jasco FT-IR 430 spectrophotometer. FT-IR spectra of samples were obtained from KBr pellets.

2.2.2. X-Ray Diffraction Measurements

X-Ray diffraction analyses were performed at Hacettepe University Physical Engineering Department. X-Ray Diffraction characterization of samples were done with a DMAX 2000/PC diffractometer using CuKα radiation at room temperature. Samples were pressed at 10 tons for 30 minutes prior to analysis.

2.2.3. SEM Analyses

SEM analyses were done with CAMECA SU-30 at Hacettepe University Geological Engineering Department.

3. RESULTS & DISCUSSION

The O'Connor method was chosen to synthesize boron nitride for because it was the simplest method to form BN and it worked successfully in the previous master studies [16,17].

There are several reports in the literature characterizing the formation and structure of h-BN by IR spectroscopy [6,7]. A typical IR spectrum of h-BN contains three main absorption peaks at ~3550, ~1430 and, ~800 cm^{-1} (figure x,x,x). The peaks at 1430 and 800 cm^{-1} refer to the in-plane and out-of-plane vibrations of h-BN while the 3550 cm^{-1} peak is assigned to the O–H stretching vibration of the terminal OH groups that always appears when the O'Connor synthetic procedure (figure 8, 9, 10) is applied [8].

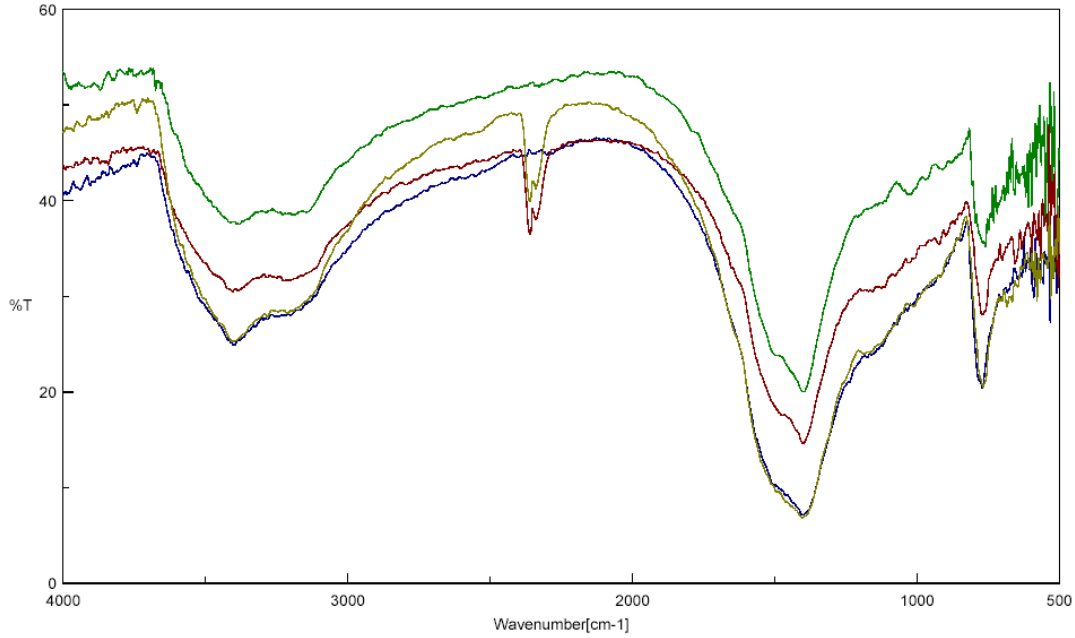


Figure13 . FTIR spectra of M-hBN composites at 1123K

— **$Cr(NO_3)_3$,** — **$Cr(CO)_6$,** —**Mo,** —**W**

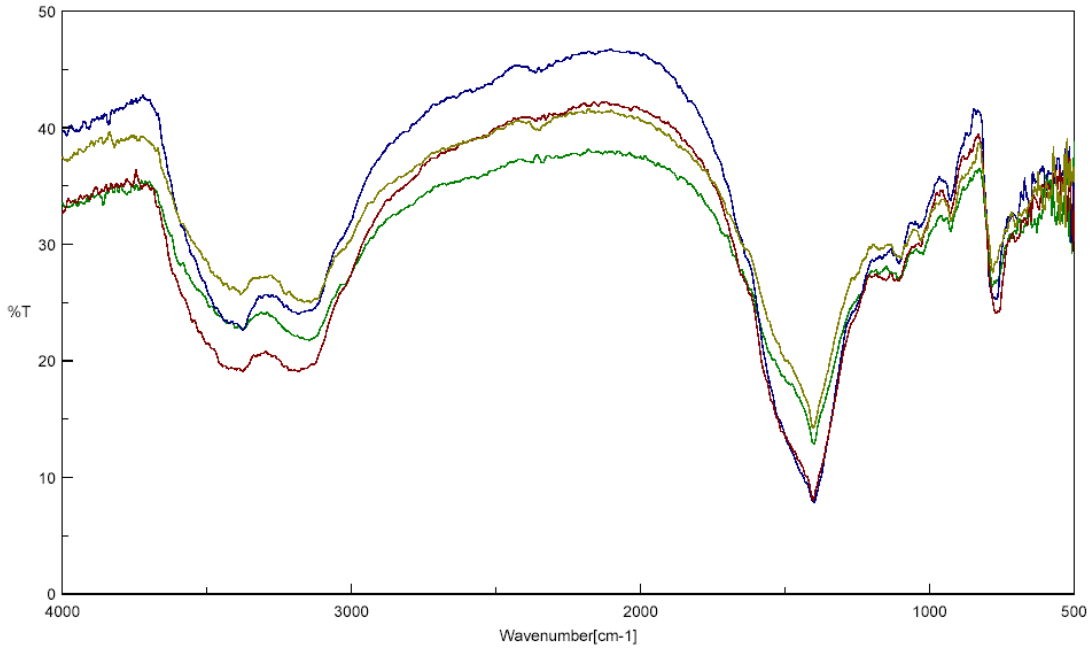


Figure14 . FTIR spectra of M-hBN composites at 1223K

— **$Cr(NO_3)_3$,** — **$Cr(CO)_6$,** —**Mo,** —**W**

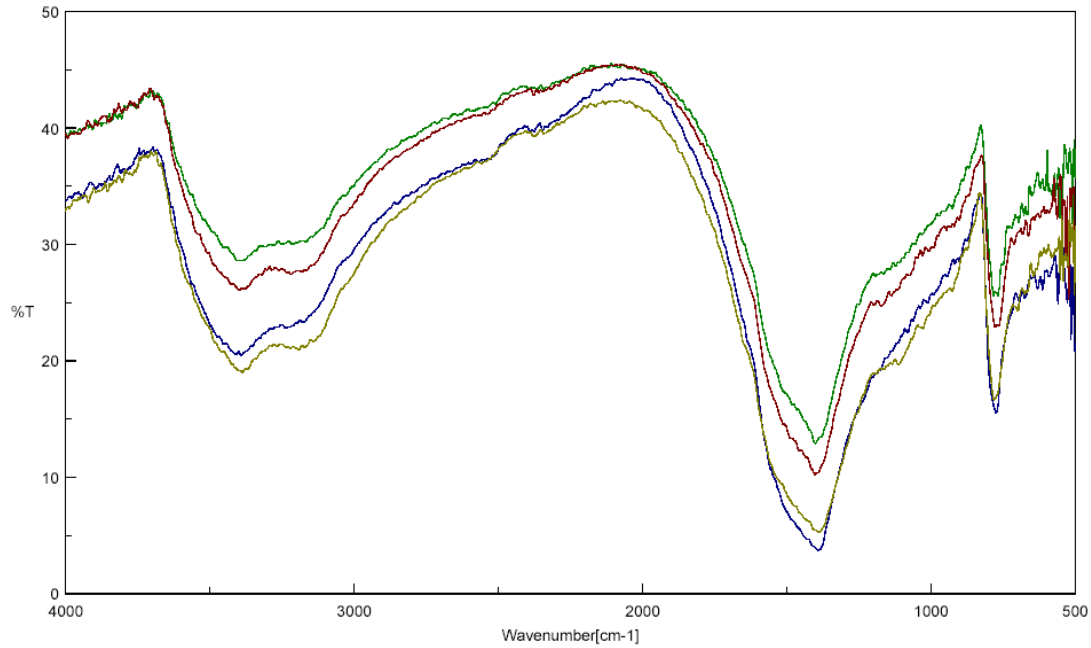


Figure15 . FTIR spectra of M-hBN composites at 1323K

— **$Cr(NO_3)_3$,** — **$Cr(CO)_6$,** —**Mo,** —**W**

In addition, in some cases, new bond formation, such as BC, CN can be seen from FTIR spectroscopy. This new bond formation makes B-N interlaying vibration peak broadened [9].

The structural analyses were done, and the interlayer spacing distances (d) were calculated from XRD. In X-Ray diffractograms the mean peaks of h-BN and in some cases B_4C peaks can be seen [15]. (Figure16).

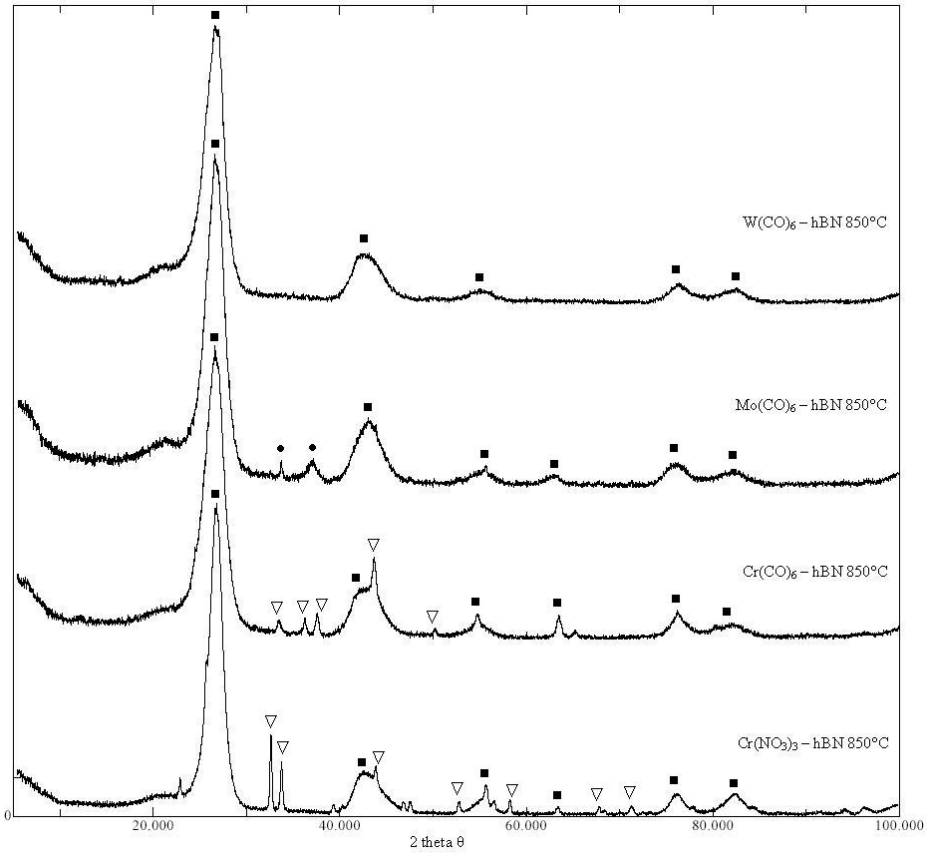


Figure16. XRD pattern of M-hBN at 1123K

■hBNpeaks,●B_4Cpeaks, ▽ Cr_2O_3 peaks

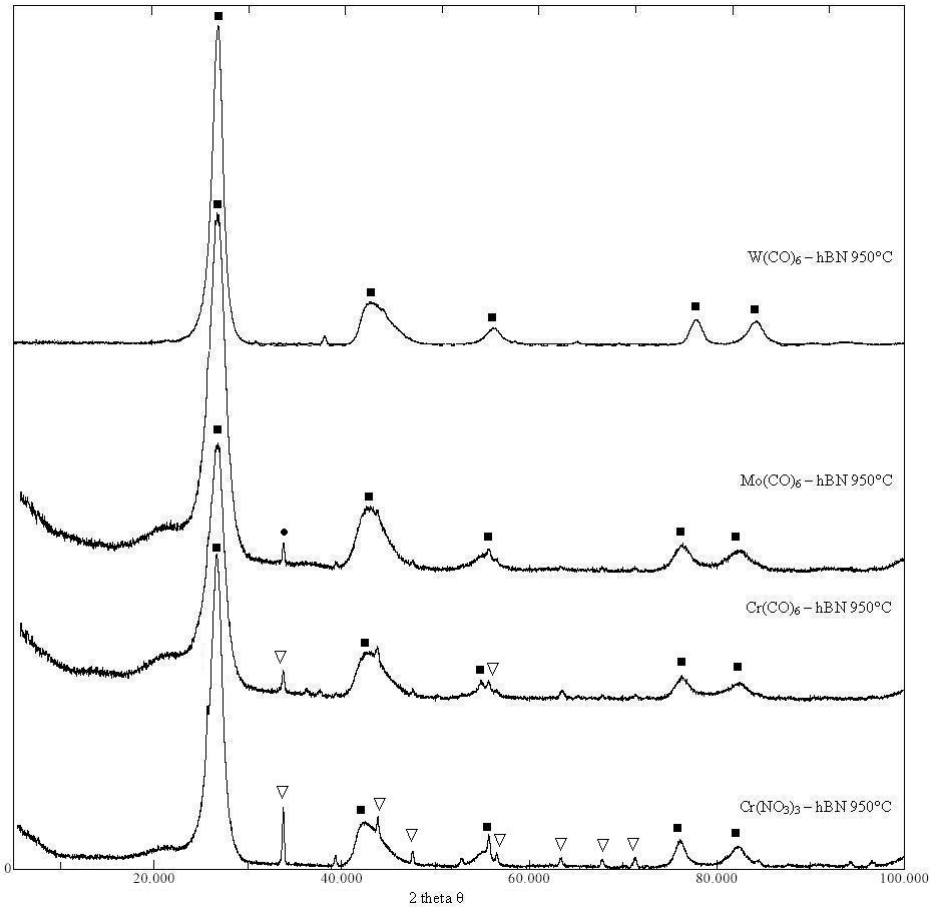


Figure17. XRD pattern of M-hBN at 1123K

■hBNpeaks,●B_4Cpeaks, ▽ Cr_2O_3 peaks

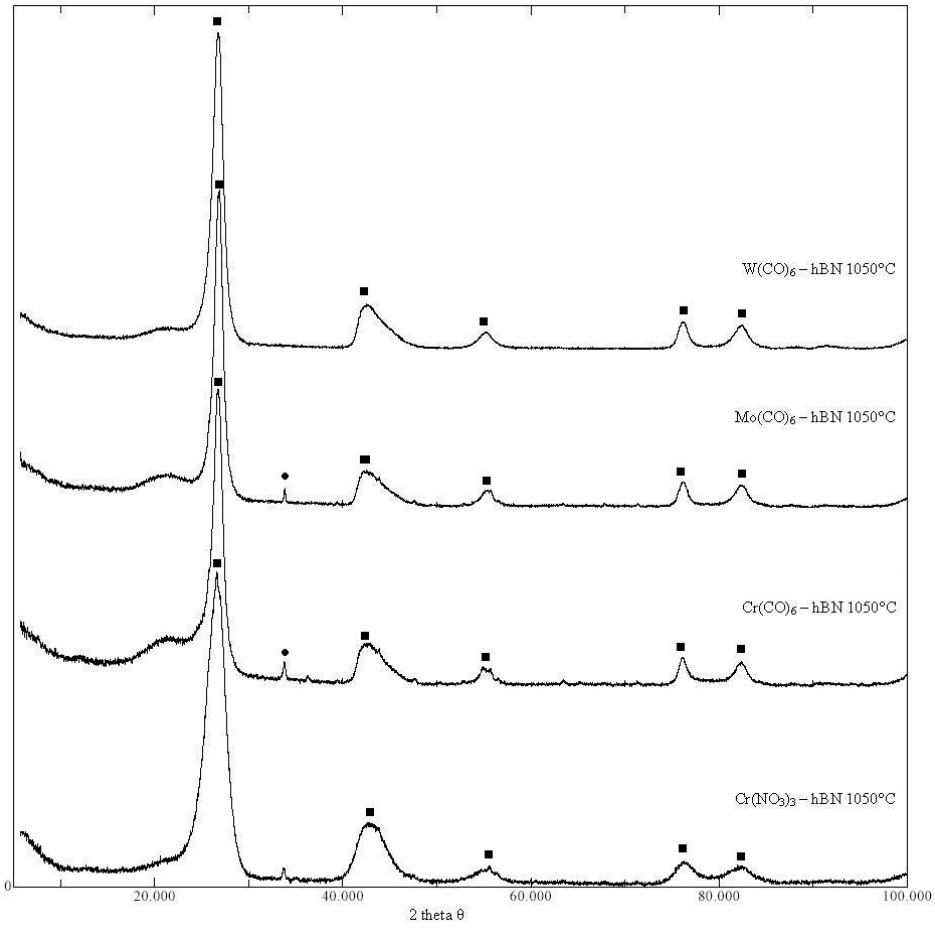


Figure18. XRD pattern of M-hBN at 1123K

■hBNpeaks, ●B_4Cpeaks, ▽ Cr_2O_3 peaks

Interlaying distances calculated from XRD based on different temperatures with different metal carbonyls are shown in table 2. Decreasing temperature on the formation of h-BN with metal carbonyls has no positive and negative effect on interlaying spacing.

M(CO)6	Temperature (C)	2Θ	d
Cr(CO)6	1323K	26,740	3,3320
	1223K	26,760	3,3287
	1123K	26,600	3,3484
Cr(NO3)3	1323K	26,780	3,3260
	1223K	26,640	3,3434
	1123K	26,780	3,3260
Mo(CO)6	1323K	26,620	3,3459
	1223K	26,720	3,3336
	1123K	26,580	3,3508
W(CO)6	1323K	26,760	3,3287
	1223K	26,880	3,3141
	1123K	26,920	3,3093

Table 2: Interlayer distance of metal carbonyls in different temperatures

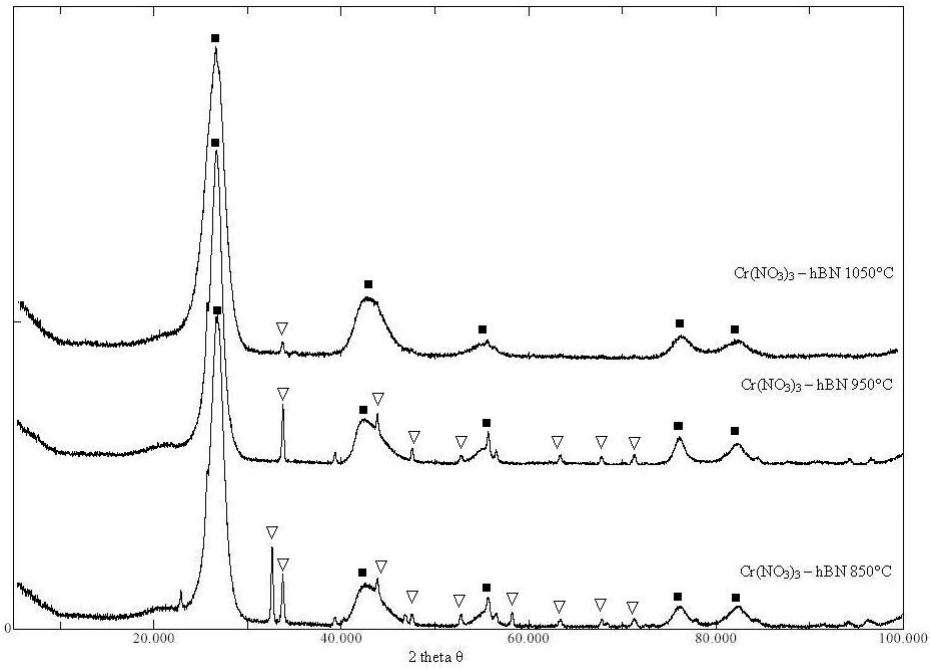


Figure19. XRD pattern of $CrNO_3$-hBN composites at different temperature
■ hBN peaks, ▽ Cr_2O_3 peaks

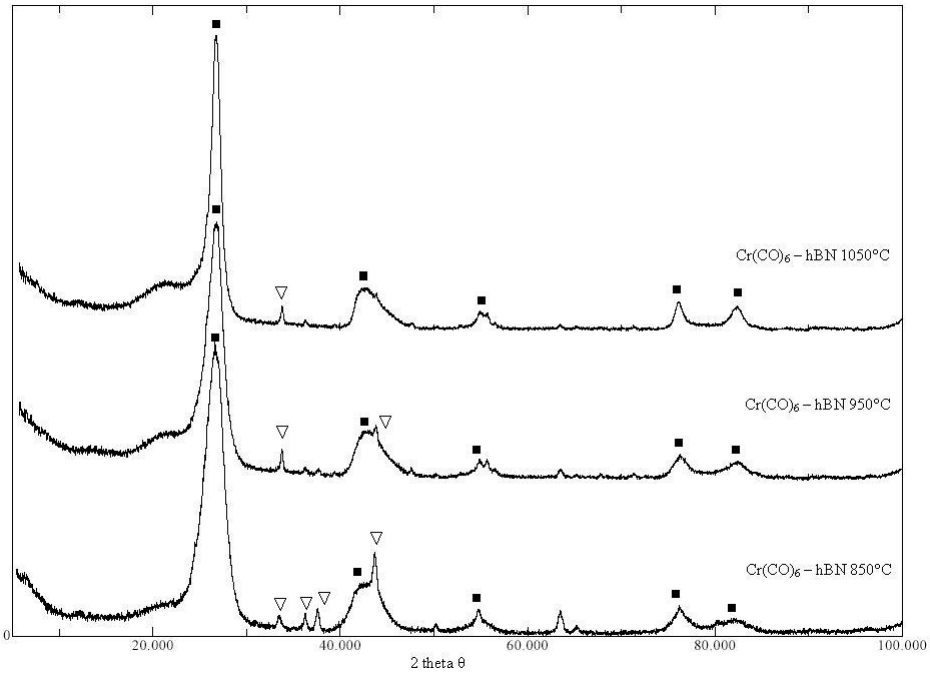


Figure20. XRD patterns of $Cr(CO)_6$-hBN composites at different temperature
■ hBN peaks, ▽ Cr_2O_3 peaks

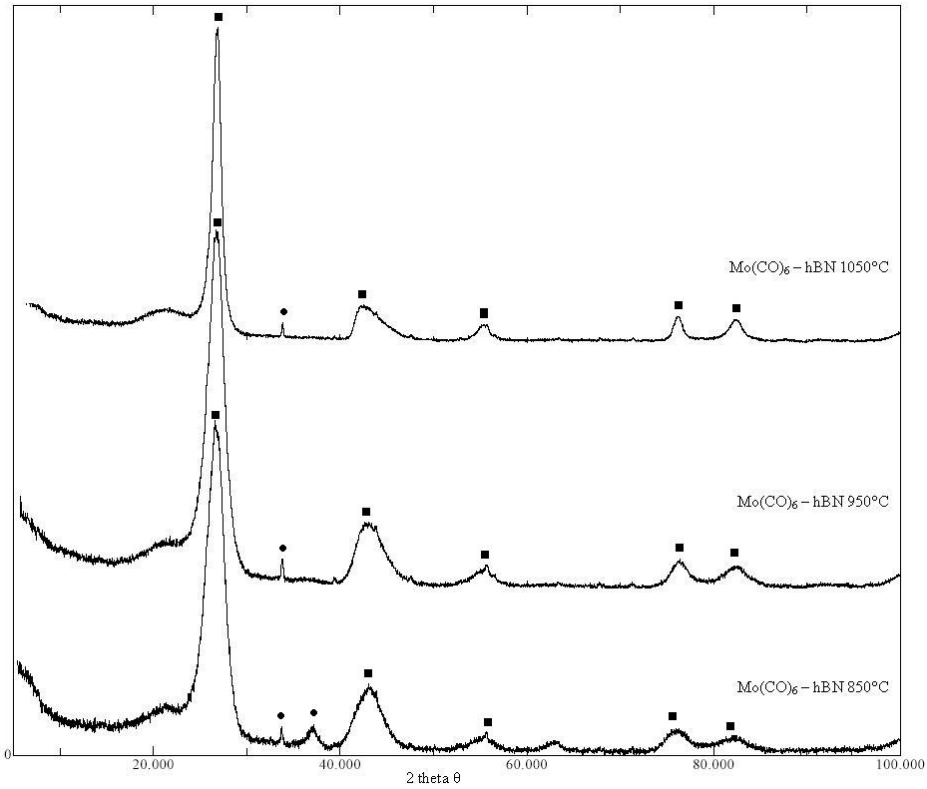


Figure21. XRD pattern of $Mo(CO)_6$-hBN composites at different temperature
■ hBN peaks, ●B_4Cpeaks

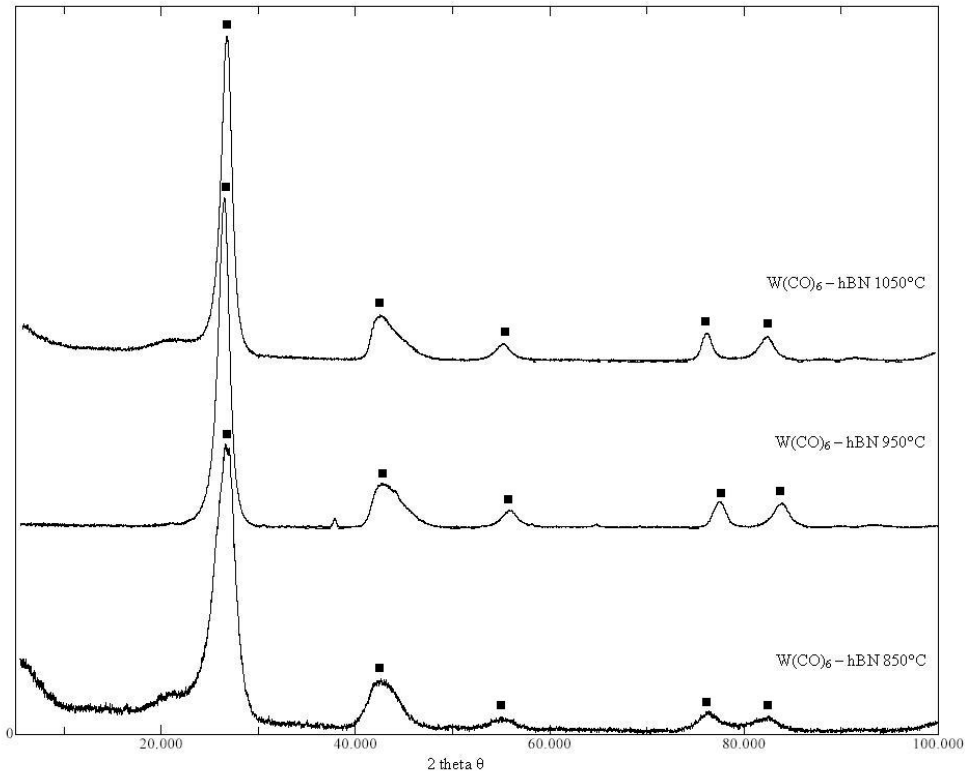


Figure22. XRD pattern of $W(CO)_6$-hBN composites at different temperature

■ hBN peaks

The interaction between d orbital of metal and π orbital of BN affects the interlaying spaces. Increasing valance electron in metal increases interaction with π orbital of BN and this causes decreasing interlaying spacing.

The previous studies [16,17] showed that metals with full or nearly full valance electrons increased crystallinity. Besides, they also showed increasing in the atomic diameter had not changed hexagonal structure. Interlaying distances calculated from XRD based on same temperatures with different metal carbonyls are shown in table 3. As in Ag and Cd intercalation [4,16,17], second row transition metal Mo intercalation also increased the distances between layers. It is seen that, interlaying spaces getting greater in the second row transition metal than first row transition metals. The

interlaying space is getting smaller for W atom. "*f*" orbital could effect the interlaying spaces in different way. This result is thought to be related with f orbital interaction.

1123K	**2Θ**	**d**
Mo(CO)6	26,580	3,3508
Cr(CO)6	26,600	3,3484
Cr(NO3)3	26,780	3,3260
W(CO)6	26,920	3,3093

1223K	**2Θ**	**d**
Cr(NO3)3	26,640	3,3434
Mo(CO)6	26,720	3,3336
Cr(CO)6	26,760	3,3287
W(CO)6	26,880	3,3141

1323K	**2Θ**	**d**
Mo(CO)6	26,620	3,3459
Cr(CO)6	26,740	3,3320
W(CO)6	26,760	3,3287
Cr(NO3)3	26,780	3,3260

Table 3: Interlayer distance of metal carbonyls in different temperatures

Boron nitride was not considered crystalline for practical purposes when the interlayer spacing is greater than 0.335 nm and the crystallites smaller than 50 nm [4]. In present study, SEM micrographs of the intercalated h-BN with metal carbonyls [M=Cr, Mo, W] are shown and the grain size values are respectively 4900, 4100 and 5180 nm. These samples are crystalline as can be clearly seen from their XRD patterns.

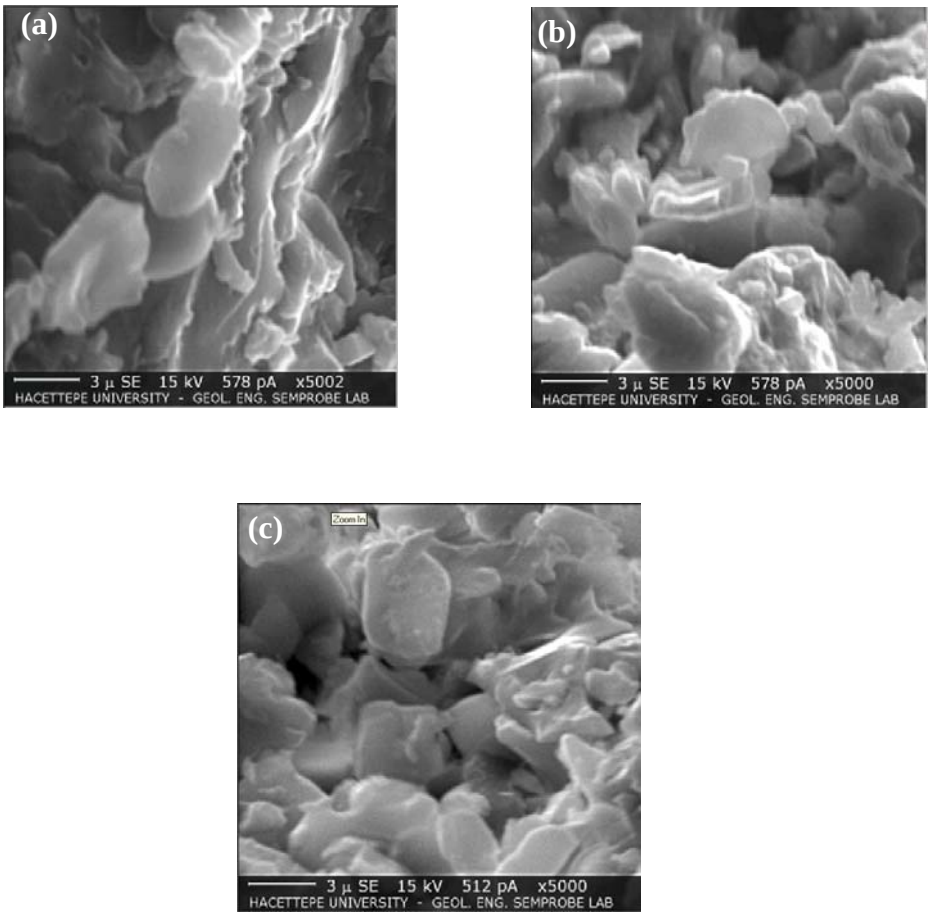


Figure 23: SEM images of (a)W-h-BN, (b) Cr-h-BN, (c) Mo-h-BN

Finally, metal carbonyls play an important role in the crystallization of h-BN by aiding the construction of hexagonal phases through electronic interactions. It is known that the hexagonal form of boron nitride can not be obtained below 1670K [14], when it is synthesized according to the O'Connor method. On the other hand, transition metal carbonyl [M=Cr, Mo, W] addition to the precursor mixtures decreases crystallization temperature to the 1123 K [4]. The metal containing h-BN composites are expected to possess interesting physical and chemical properties that are considered for future studies.

4. CONCLUSION

In present study, we examine the effect of metal carbonyls [M= Cr, Mo, W] on crystallization of h-BN. The crystallization degree and grain growth of hexagonal boron nitride can be improved by intercalation with various transition metal carbonyls at a relatively lower temperature (1123K).

The FTIR analyses indicate that the bond formation of in & out of plane B-N vibration stretching.

Interlaying distances were calculated from XRD analyses. In our calculation between layers, we found that molybdenum showed similar properties, which is found in the same period with Ag and Cd. Tungsten is used for the first time, the interlaying space is getting smaller however it is in the third row transition metal. This result is thought to be related with f orbital interaction. Particle size was examined with SEM analyses for samples synthesized at 1323K, and it indicated that grain size became greater than the original BN.

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