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Research Article

Effects of Metal Carbonyls on The Formation of Hexagonal Boron Nitride

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ABSTRACT

Hexagonal boron nitride (hBN) was synthesized by using O'Connor method with different metal carbonyls ($Mo(CO)_6$, $Cr(CO)_6$, and $W(CO)_6$) at 1373 K. FTIR, XRD, and SEM techniques were used for characterization of the samples. XRD results indicated an increase in interlayer spacing besides nano-scale products are formed, all that observed at 1373 K. The lattice parameters were computed and observed that the parameters were fairly approximate to the reported value for hBN and it has been found that grain size of the products is in nano scale according to Debye- Scherrer equation.

Keywords: *Hexagonal boron nitride, Nanocrystall, O'Connor method, Metal carbonyls.*

Metal Karbonillerin Hekzagonal Bor Nitrür Sentezi Üzerindeki Etkileri

ÖZET

Hekzagonal bor nitrür (hBN) numuneleri, 1373 K'de farklı metal karboniller, $M(CO)_6$, (M = Mo, Cr, W) ile modifiye edilmiş O'Connor yöntemi kullanılarak hazırlandı. Numuneler FTIR, XRD ve SEM teknikleri ile karakterize edildi. XRD sonuçları, katmanlar arası aralıkta bir artış olduğunu gösterdi ve 1373 K'de nano ölçekli ürünlerin oluşumu gözlendi. Hesaplanan kafes değerleri hBN için bildirilen değere çok yakındı ve Debye-Scherrer denklemine göre ürünlerin tane büyüklüğünün nano ölçekte olduğu bulundu.

Anahtar Kelimeler: *Hekzagonal bor nitrür, Nanokristaller, O'Connor metot, Metal karboniller*

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I. INTRODUCTION

Hexagonal boron nitride (hBN) is a typical layered substance with planar hexagonal networks which are stacked with van der Waals forces to form three-dimensional, graphite-like structure. Mainly, there are four different methods for preparing hBN, e.g. chemical vapor deposition (CVD) [1], polymer pyrolysis [2], carbothermic reduction [3] and high-temperature metallurgical synthesis [4].

In the present study, the modified O'Connor [5] method was chosen to synthesize hBN because of its simplicity. According to this method, it was confirmed that a positive effect of metals was observed on the formation of hBN at comparatively low temperatures in our work-group studies **[6,7]**. The current study deals with the formation of hBN in the presence of metal carbonyls according to modified O'Connor method. Two different roles of the metal carbonyls would be expected: Metal carbonyls may act as a source of metal atoms and CO release upon heating of the reaction mixture. Consequently, it would be possible to obtain uniformly crystalline products in the presence of metal atom. In addition, the released CO may involve in reduction reaction that is like carbo-reductive hBN synthesis [8].

II. EXPERIMENTAL

O'Connor method [5] was used for synthesis of hexagonal boron nitride. 2 g of B_2O_3, 4 g of $CO(NH_2)_2$ (urea), and 0.04 g of metal carbonyl ($Mo(CO)_6$, $Cr(CO)_6$, and $W(CO)_6$) were mixed for precursor preparation. It was pre-heated at 473 K for 2 hours, then it was pulverized in a grinder. After that, it was heated in a flow of ammonia gas (flow rate=120 mL/min) at 1323 K for 2 hours in a tube furnace. The raw product was leached in 3 M HCl solution, then washed with ethanol. Finally, hBN sample was dried in an oven at 373 K.

The types of chemical bonding were determined by Jasco 430 FTIR spectrophotometer using KBr pressed discs. The crystallinity of hBN was examined by the Rigaku DMAX 2000/PC diffractometer using CuK_α radiation. Morphological studies of hBN were obtained by Zeiss Evo 50.

III. RESULT AND DISCUSSION

Multiple studies are examined **[9–11]** in past for the construction of hBN by IR spectroscopy. The peaks at near ~1380 and ~780 cm^{-1} refer to the in-plane and out-of-plane vibrations of hBN [8-10, 12]. The broad absorption band near ~3200, and ~3400 cm^{-1} are assigned to the N–H, and O–H, stretching vibrations, respectively when the B_2O_3 (or H_3BO_3) and urea systems are used [13–14]. These groups were not suggested as contaminants [15], rather the contaminants are elements that the end group part of two-dimensional hBN macromolecules.

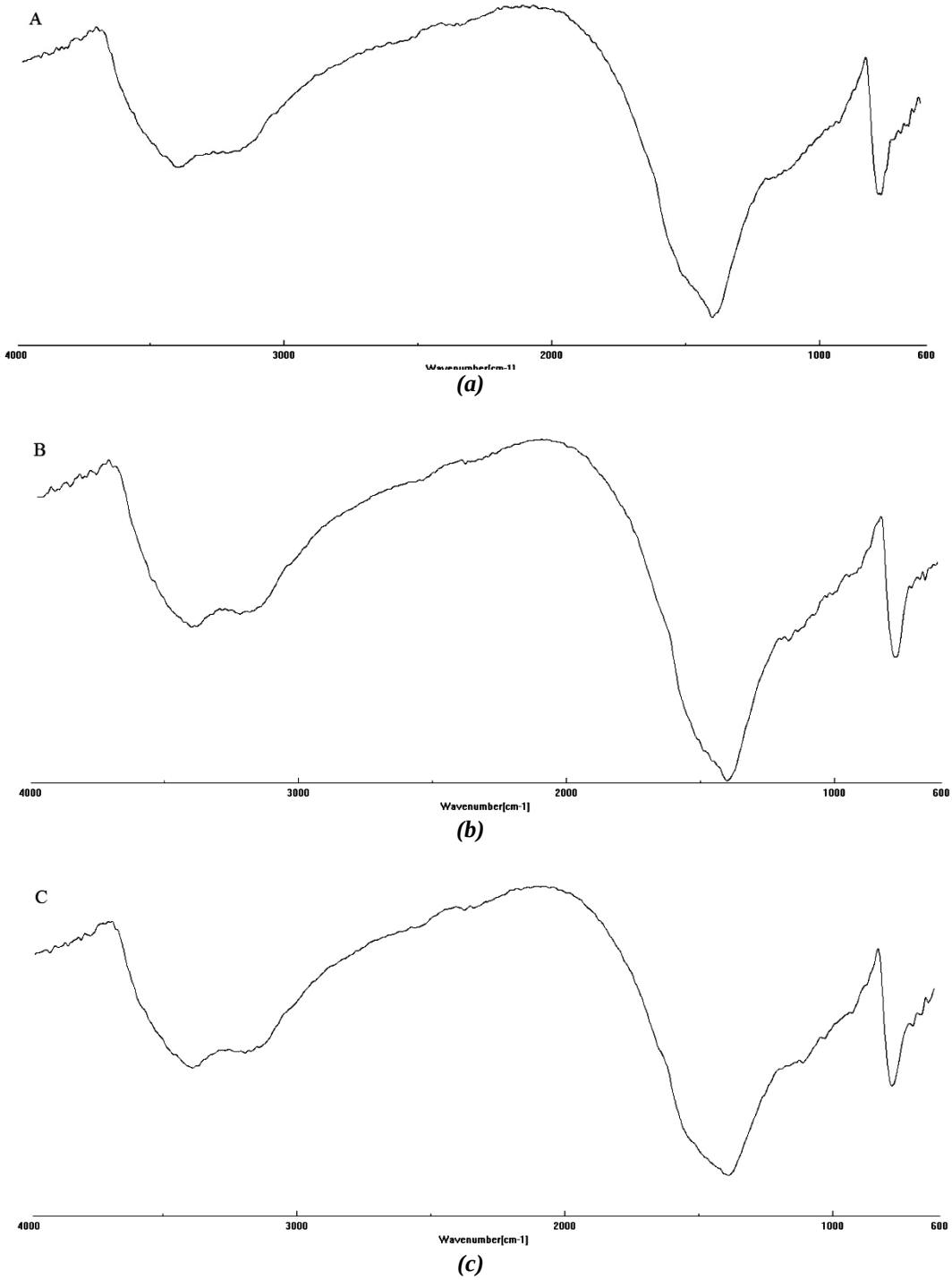


Figure 1. *FTIR spectrum of hBN samples. Sample prepared with a) $Cr(CO)_{6,}$ b) $Mo(CO)_{6,}$ and c) $W(CO)_{6.}$*

Figure 2 indicated the XRD pattern of hBN and its main peaks (002, 10X[1], 004, 110, and 112) was detected. According to studies **[16, 17]**, inseparable 100 and 101 (10X) was the indication of amorphous structure. However, current studies **[7, 11, 18, 19]** already identified that the unseparated ''10X'' peaks indicates formation of the nano-crystalline hBN. Moreover, reducing of the formation temperature of hBN is result from the utilization of ammonia and metal salt together; while the metal salts, as catalysts, ease to take place the reaction [15,19,20], ammonia act as the nitriding agent for metals and alloys at low temperature [9,21,22]. Also, the peak broadening showed that the grain sizes

[1] Unseparated 100 and 101 peaks of hBN.

of hBN in nano-size [18, 19]. The lattice constants were calculated from the patterns (Table 1), and the findings are approximate to the explained value for hBN (ICDD card no: 34- 0421).

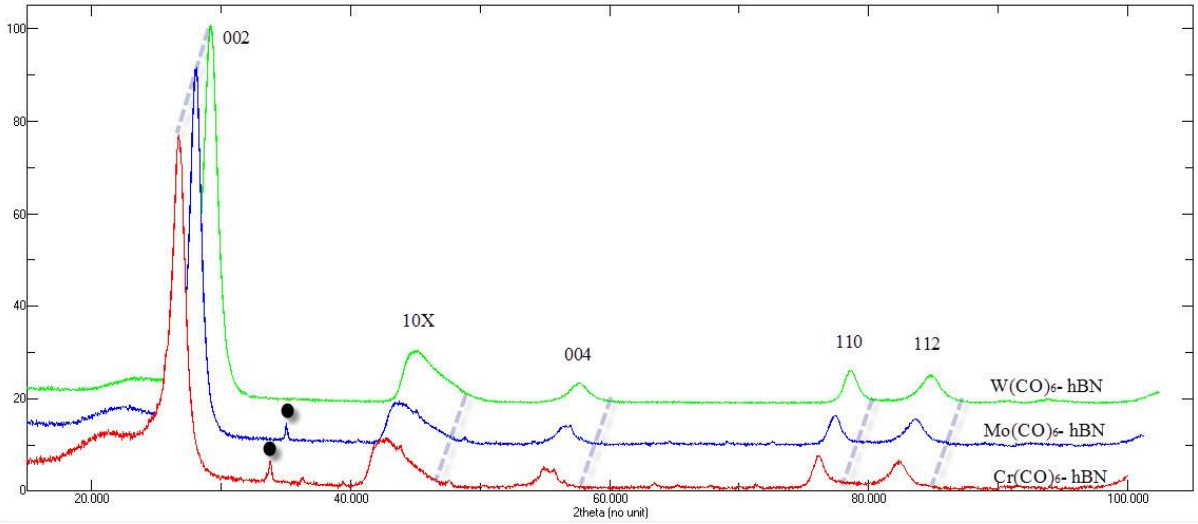


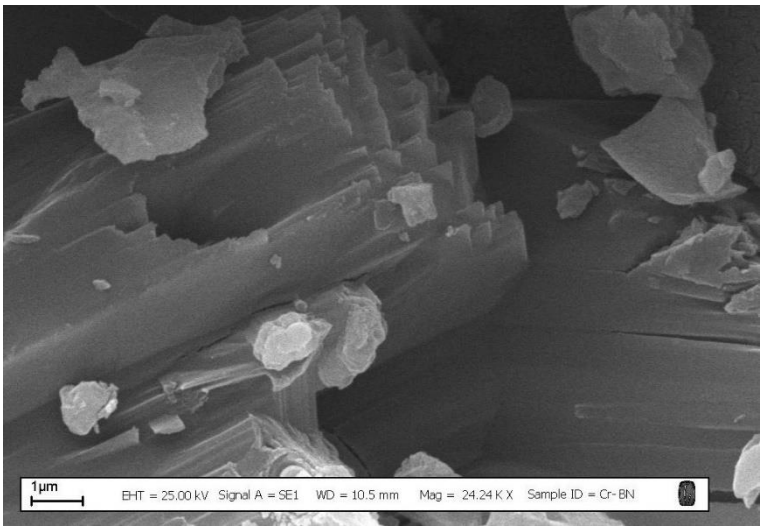
Figure 2. *XRD pattern of hBN samples, ●: unknown.*

The average particle size was calculated as 3.8 nm for Cr-hBN, as 7.85 nm for Mo-hBN, and as 6.25 nm for W-hBN by the Debye-Scherrer formula. In terms of these approaches our samples can be accepted as nano crystalline [7,11,15,18,19,23].

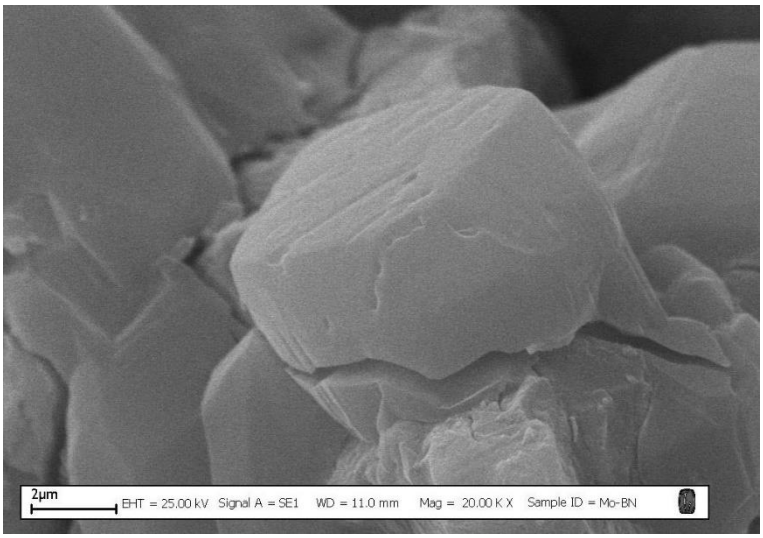
Table 1. *Calculated lattice constants of the samples.*

Sample prepared with $Cr(CO)_6$	**Sample prepared with $Mo(CO)_6$**	**Sample prepared with $W(CO)_6$**	**Original hBN**
a: 2.502 Å **c:** 6.664 Å **d_{002}:** 3.332 Å	**a:** 2.499 Å **c:** 6.692 Å **d_{002}:** 3.346 Å	**a:** 2.499 Å **c:** 6.657 Å **d_{002}:** 3.328 Å	**a:** 2.504 Å **c:** 6.656 Å **d_{002}:** 3.3281Å

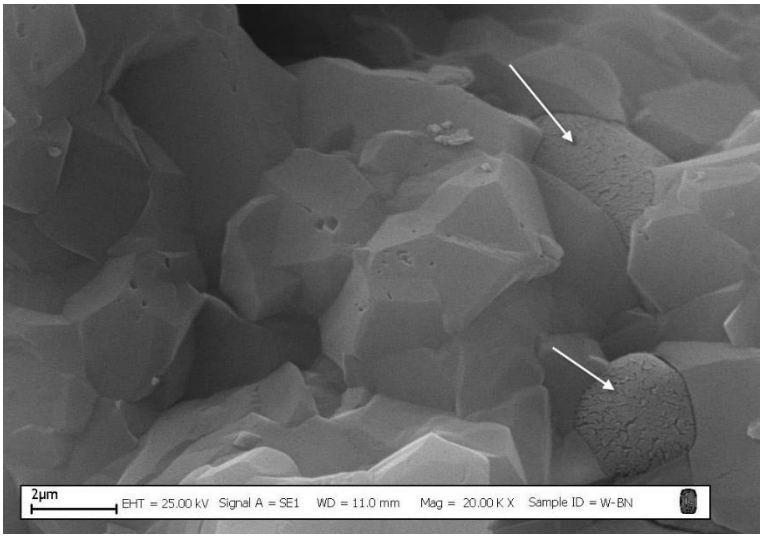
The morphology of hBN samples were investigated by SEM (Figure 3). SEM images shows regularly grained powder hBN particles with different shapes. In Figure 3 (a) rod-like particles and in Figure 3 (b) and 3 (c) pyramid-like structures were observed. According to Shuvaev [24] it was proposed that transition metal can located in pores and / or cracks of hBN, in Figure 3 (c) the matter on the boundary marked with arrow could be tungsten.



(a)



(b)



(c)

Figure. 3. *SEM images of hBN samples. Sample prepared with* ***(a)*** *$Cr(CO)_6$,* ***(b)*** *$Mo(CO)_6$, and* ***(c)*** *$W(CO)_6$.*

IV. CONCLUSION

In summary, nano-crystalline hBN was synthesized by O'Connor method with metal carbonyls, and it was found that the computed lattice parameters were fairly approximate to the stated valuence of hBN. Moreover, use of both metal carbonyls and NH_3 provided in nano-crystalline hBN formation at 1373 K. The prepared samples were in different shapes and tungsten could be placed on the grain boundaries of hBN.

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