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Incorporation of Cadmium into Hexagonal Boron Nitride by Solid State Reaction

Erhan Budak

Abstract

In this study, cadmium-hexagonal boron nitride (Cd-h-BN) was synthesized according to the O'Connor method with varying amounts of cadmium(II) nitrate. The structural characterizations were performed with FTIR, XRD, and SEM techniques while the cadmium contents in Cd-h-BN were determined by AAS. XRD results shown that an increase in interlayer distance of h-BN, and nano-scale products were observed at 1050°C. The lattice constants were calculated by Scherrer equation, and the results were very close to the original h-BN. Although different amounts of $Cd(NO_3)_2 \cdot 5H_2O$ were added in the starting mixtures, the cadmium contents of Cd-h-BN samples showed no significant difference, and few amounts of cadmium was intercalated to h-BN. In addition, increasing cadmium amount caused minor grain growth of h-BN samples.

Keywords: Hexagonal boron nitride; Metal intercalation; O'Connor Method; Nanocrystalline materials.

1. INTRODUCTION

Graphite-like hexagonal boron nitride (h-BN) is a typical layered substance which of planar hexagonal networks stacked with van der Waals forces to form three-dimensional structure. There are many techniques for h-BN synthesis, but the O'Connor method [1] was used to produce h-BN in the because of its easiness. According to this method in our previous study [2], it was claimed that a positive effect of transition metals was observed on the h-BN synthesis at relatively low temperatures. Moreover, an electronic interaction was occurred among the transition metal and h-BN layers (d–π interaction) which influenced the interlayer distance. In addition to the electronic effects, the size of transition metal also affected the interlayer distance, i.e., a second-row transition metal, silver had a larger size than all the other metals studied in the previous work [2] resulting in a greater interlayer distance.

In present work, cadmium was chosen as model element to investigate the effects of second row transition metals on the structure of metal intercalated h-BN. Thus, the cadmium contents of the h-BN were measured to examine relationship between grain size and metal amount.

2. EXPERIMENTAL

According to O'Connor method [1], h-BN sample was synthesized in the presence of cadmium salt. Boron oxide (4 g) was mixed with urea (2 g) and varying amount of cadmium (II) nitrate pentahydrate (0.08, 0.16, 0.32, and 0.64 g). In precursor formation step, the powder mixture was pre-heated at 200°C for 2 hours in furnace, and then the precursor was ground in a mortar. Main heating process was performed at 1050°C for 2 hours in a cylinder furnace under ammonia (flow rate 120 mL / min). The raw h-BN was leached in hot 10% HCl then washed with methanol, and

dried at 100°C. The solutions for AAS were prepared according to Tereshkova [3] from obtained gray-white powder.
Type of chemical bonds were detected by Shimadzu 8400 FTIR, and XRD examinations were performed by the Rigaku DMAX 2000/PC. h-BN surface was monitored by Zeiss Evo 50, and the amounts of cadmium were calculated by using Perkin Elmer Analyst 100 model AAS.

3. RESULTS AND DISCUSSION

There are some studies [4-6] in the literature for h-BN stretching vibrations by IR spectroscopy. Two distinguishing bands (**Fig. 1**) were detected at ~1380 and ~780 cm^{-1} and labeled as BN in-plane and out-of-plane vibrations respectively[4,6,7]. The broad absorption band near ~3200, and ~3400 cm^{-1} were identified as the –NH, and –OH, stretching vibrations, respectively when the boron oxide and urea systems were used [2,8–11].

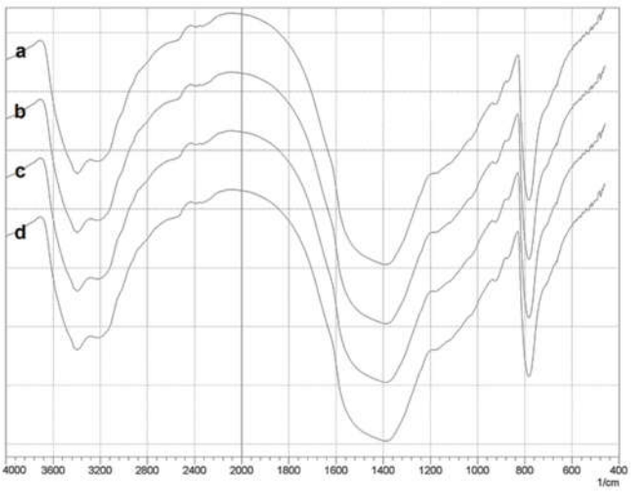

Fig. 1. FTIR spectrum of nano-crystalline h-BN compounds. The weight of $Cd(NO_3)_2$ amount in starting mixture a) 0.08 g, b) 0.16 g, c) 0.32 g, and d) 0.64 g.

The main peaks of h-BN (**Fig. 2**) (002, 10X, 004, 110, and 112) were observed (10X: Not separated 100 and 101 peaks of h-BN) in XRD patterns. Recent studies [6,12,13] have already pinpointed that the inseparable 100 and 101 peaks indicate formation of the nano-crystalline h-BN. Both NH_3 and metal salts lowers the synthesis temperature of h-BN; the metal salts pretend as catalytic agent [10,12,14] while NH_3 acts as the nitriding agent [4,15,16].
The enlargement in XRD peaks also illustrated that the grain sizes of h-BN were in nano-scale [12,13,17]. Average grain size of samples was found 5 nm using Scherrer equation. Also, the lattice parameters and interlayer distance were estimated and presented in **Table 1.**

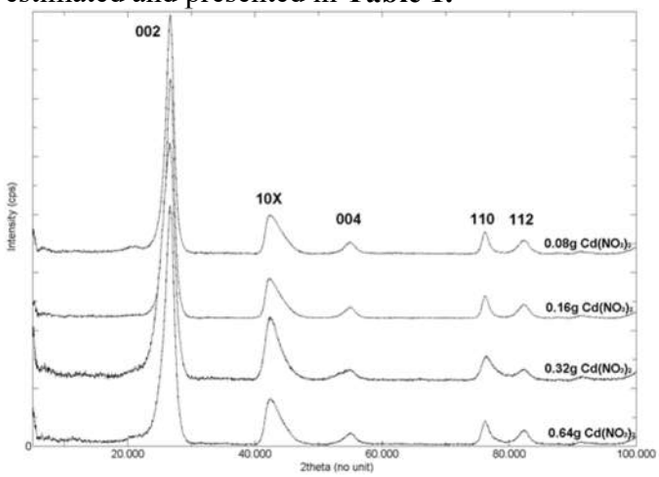

Fig. 2. XRD patterns of nano-crystalline h-BN samples.

Table 1. Computed lattice parameters of samples, and cadmium amount in the precursor and samples.

Cd in the precursor (%)	Lattice parameters		Cd in the Cd-h-BN (%, w/w)
0.49	a (Å)	2.496	0.0130
	c (Å)	6.686	
	d (Å)	3.343	
0.97	a (Å)	2.490	0.0134
	c (Å)	6.722	
	d (Å)	3.361	
1.94	a (Å)	2.496	0.0124
	c (Å)	6.678	
	d (Å)	3.339	
3.89	a (Å)	2.496	0.0130
	c (Å)	6.688	
	d (Å)	3.344	

In our previous study [2], we claimed that the interlayer spacing was affected by the size of the metal atoms and their electron configuration. In addition, it was found that silver containing sample had a greater interlayer spacing. In present study, interlayer distance of samples was also found larger than 3.3281 Å.

The morphological examination was performed by means of using SEM images (**Fig. 3 and 4**) indicated nearly homogenously grained h-BN particles with flaky and irregular shapes as reported before [18].

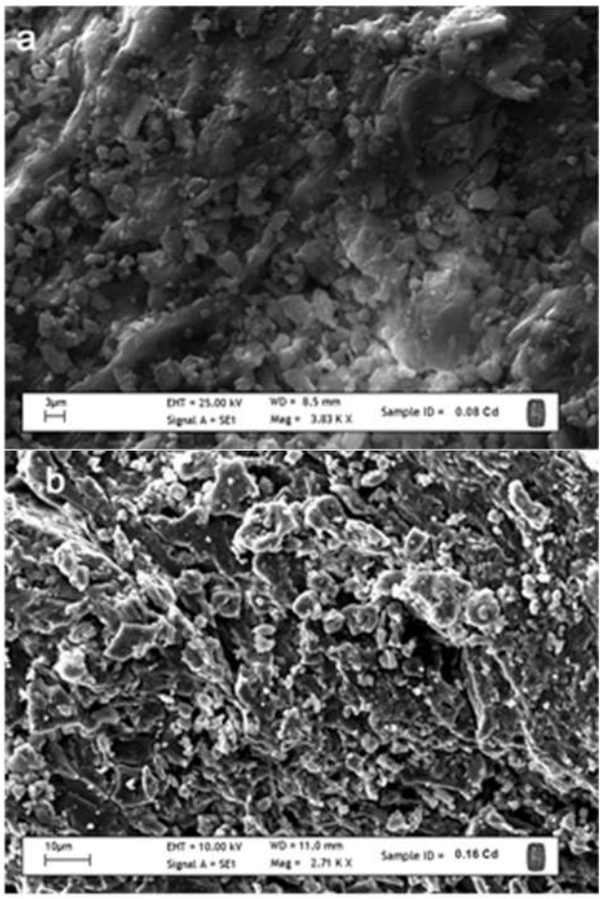

Fig. 3 SEM images of the samples. The sample was prepared with 0.08 g (a), and with 0.16 g (b) Cd (NO3)2.

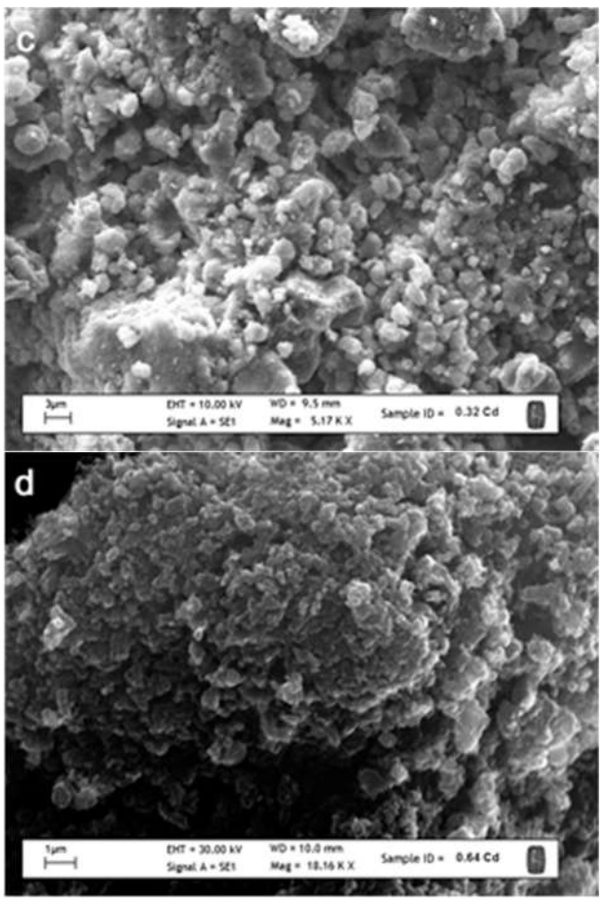

Fig.4 SEM images of the samples. The sample was prepared with 0.32 g (a), and with 0.64 g (b) Cd(NO3)2.

The cadmium amounts in the obtained samples were determined by AAS. Although different amounts of cadmium(II) nitrate pentahydrate were added in the starting mixtures, the cadmium contents of Cd-h-BN samples showed no significant difference (**Table 1**). Furthermore, using the values in **Table 1**, the ratio of B_3N_3 units to cadmium atoms was calculated as 5000:1 on molar basis. This ratio points out that few amounts of cadmium was intercalated to h-BN by modified O'Connor method. Shuvaev [19] proposed that transition metal can be located in pores and / or cracks of h-BN.

4. CONCLUSION

In summary, nano-sized h-BN were synthesized with varying amounts of cadmium (II) nitrate at 1050°C. It was found that the lattice parameters are very close to original h-BN. Traditional production of h-BN requires ≥1500°C in industrial scale. Reducing the temperature to 1000°C result with turbostratic (amorphous) structure. Usage of both ammonia and cadmium salt lower the formation temperature of h-BN. In addition, the electronic interaction among the transition metal and h-BN layers (d–π interaction) influenced the interlayer spacing of h-BN. In current study, according to AAS results, the cadmium contents of Cd-h-BN samples showed no significant difference, and the ratio of B_3N_3 units to cadmium atoms was calculated as 5000:1 on molar basis. This ratio indicates that few amounts of cadmium located in pores and / or cracks of h-BN.

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