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Synthesis of hexagonal boron nitride with the presence of representative metals

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Hexagonal boron nitride (h-BN) samples were prepared using the modified O'Connor method with KNO_3 and $Ca(NO_3)_2$ at different temperatures (1050, 1250, and 1450 °C). The samples were characterized by FTIR, XRD, and SEM techniques. Usage of representative metals exhibited a positive effect on the crystallization of h-BN and they caused the formation of nano-scale products at relatively low temperature. XRD results indicated that there was an increase in interlayer spacing due to the d–π interaction. The calculated lattice constants were very close to the reported value for h-BN.

1. Introduction

Experimental and theoretical research [1–9] on intercalation compounds of hexagonal boron nitride (h-BN) have received increasing attention due to their physical properties such as refractoriness and lubricance, thermal conductivity, electrical resistance, machinability, thermal shock resistance, and neutron capturing.

h-BN can be prepared by various methods such as chemical vapor deposition (CVD) [10], polymer pyrolysis [11], carbothermic reduction [12], and high-temperature metallurgical synthesis [13].

The modified O'Connor [14] method was chosen to synthesize h-BN in the present study due to its availability. Previously [7], the positive effect of metal salts on the formation of h-BN was observed. Also, it was claimed that there was an electronic interaction between the metal's outermost orbitals and the adjacent h-BN layers (d–π interaction) similar to the work of Hubacek et al. [2]. Here we report the effect of representative metals on the synthesis of h-BN.

2. Experimental

Boron nitride samples were prepared using the modified O'Connor method [5]. 2 g of boron oxide was mixed with 4 g of urea and 0.04 g of metal nitrates $[M(NO_3)_x]$ (M=K and Ca). The mixture was preheated to 200 °C for 2 h and then the obtained precursor was pulverized in a grinder. After that, the main heating process was performed in a stream of NH_3 gas (flow rate=120 mL/min) at different temperatures (1050, 1250, and 1450 °C) for 2 h in a tube furnace.

The obtained raw products were heated in 10% HCl solution, leached in 25 mL ethanol, and dried in an oven at 100 °C. The remaining gray-white powder was pressed by 100 bar at room temperature.

h-BN stretching vibrations were determined by a Jasco 430 FTIR spectrophotometer using KBr pressed discs. XRD patterns were obtained by a Rigaku DMAX 2000/PC diffractometer using CuK_α radiation. Micrographs were taken by Zeiss Evo 50. The samples used for SEM were coated with carbon.

3. Results and discussion

The FTIR measurements were performed to examine the types of chemical bonds of the obtained h-BN samples. There are several studies [15–17] in the literature characterizing the formation and structure of h-BN by IR spectroscopy. Two strong characteristic peaks (Fig. 1a and b) were observed at ~1380 and ~780 cm^{-1}, respectively. The observations of peaks at 1380 and 780 cm^{-1} were identified as BN in-plane and out-of-plane vibrations, respectively. These results are similar to those of earlier works [15,16,18]. When the boron oxide (or boric acid) and urea systems are used [19–22], the broad absorption band near 3200, 3400 cm^{-1}, and a shoulder peak at 1050 cm^{-1} are ascribed to the N–H, O–H, and B–O stretching vibrations, respectively. These groups should not be understood as impurities [21], rather they represent constitutional elements terminating the two-dimensional h-BN macromolecules. Since the contents of these elements are inversely proportional to

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the circumference-to-area ratio, it may be assumed that the larger the BN crystals, the higher the purity of BN. This relationship is actually the principle of the purification process where BN is first crystallized by the thermal treatment in ammonia gas, and the oxygen impurities converted to boron oxide are washed out. This can imply that the density of these stretching vibrations decreases as

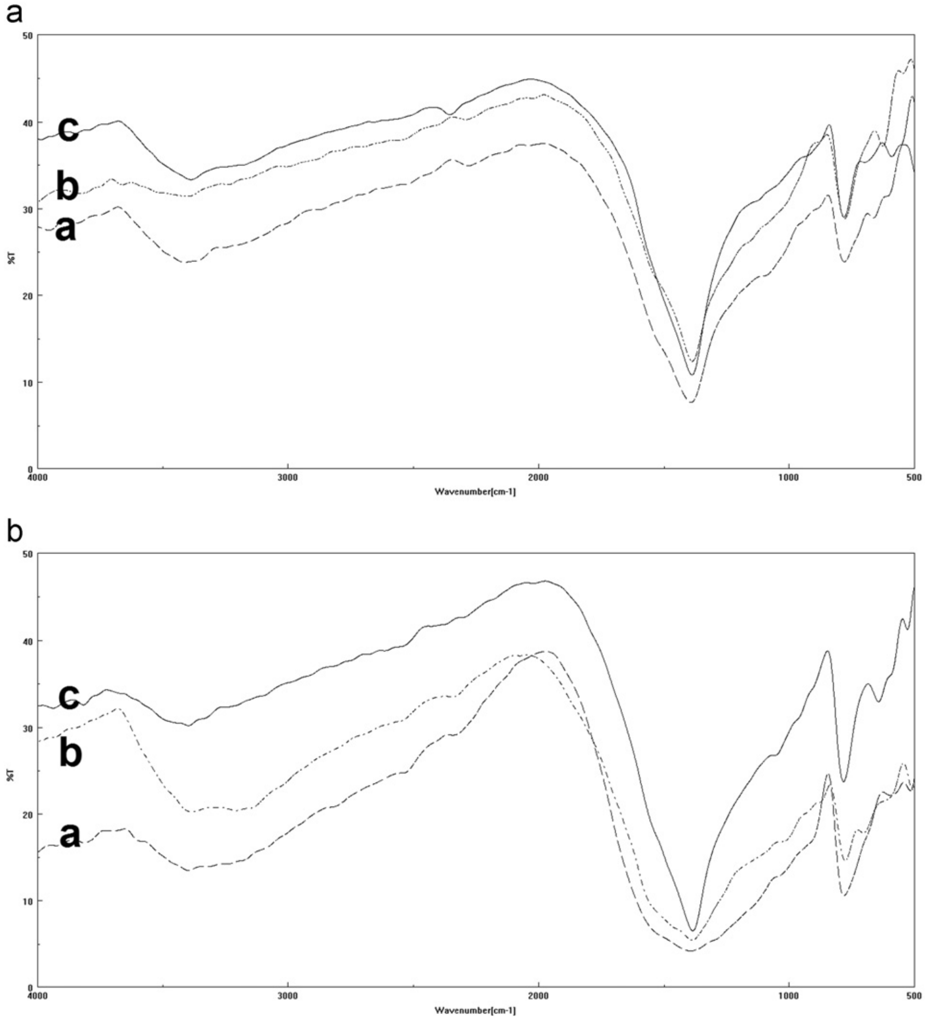

Fig. 1. FTIR spectrum of K-h-BN (a) and Ca-h-BN (b) at diffrent temperatures. The sample (a–c) was synthesized at 1050 °C (a), 1250 °C (b), and 1450 °C (c).

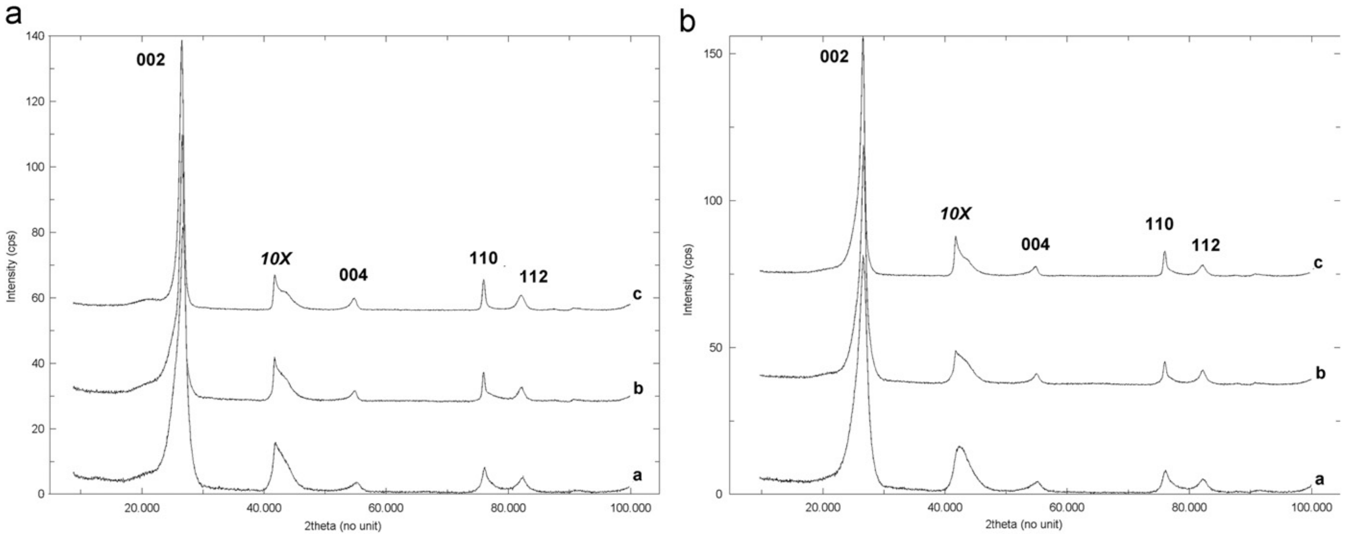

Fig. 2. XRD patterns of K-h-BN (a) and Ca-h-BN (b) at diffrent temperatures. The sample (a–c) was synthesized at 1050 °C (a), 1250 °C (b), and 1450 °C (c).

Table 1
Calculated grain size (nm)of the h-BN samples.

Samples	**Grain Size (nm)**		
	1050 °C	**1250 °C**	**1450 °C**
K-h-BN	4.72	10.58	11.08
Ca-h-BN	4.38	7.84	10.93

Table 2
Calculated lattice parameters of the h-BN samples.

Synthesis temperature (°C)	**Lattice parameters (Å)**	**K-h-BN**	**Ca-h-BN**
1050	a	2.498	2.500
	c	6.668	6.702
	d	3.334	3.343
1250	a	2.504	2.502
	c	6.702	6.686
	d	3.351	3.351
1450	a	2.504	2.502
	c	6.712	6.706
	d	3.356	3.353

the temperature increases. Also, the peak near 1050 cm^{-1} can be assigned as c-BN [23] but there is no evidence for the formation of c-BN in the XRD pattern.

The composition and crystallinity of the h-BN samples were examined by XRD and the results were compared with standard h-BN (ICCD card no: 34-421). In all diffractograms (Fig. 2a and b) the main peaks of h-BN (002, 10*X*[1] , 004, 110, and 112) were observed. According to previous studies [20,24], the products obtained might be accepted as amorphous because of inseparable 100 and 101 (10*X*) XRD peaks of h-BN. However, most recently some studies [17,25,26] have already pinpointed that "10*X*" peaks indicated h-BN nanocrystal formation. Hence it is known that usage of both ammonia and metals permits lowering of the formation temperature of h-BN; the metals behave as catalysts [21,26,27] while ammonia acts as the nitriding agent for metals and alloys at low temperature [15,28,29]. Moreover, internal stress decreases in the presence of metals because of reduction in content of the cubic boron nitride (c-BN) phase and increase in the h-BN phase [30]. Eventually, BN is formed easily when compared to c-BN at low temperatures, and h-BN can be the dominant phase in the samples [31].

The broadening nature of the XRD peaks indicated that the particle sizes of the samples were within the nanometer scale [11,25] when using the Debye–Scherrer equation. Results of the

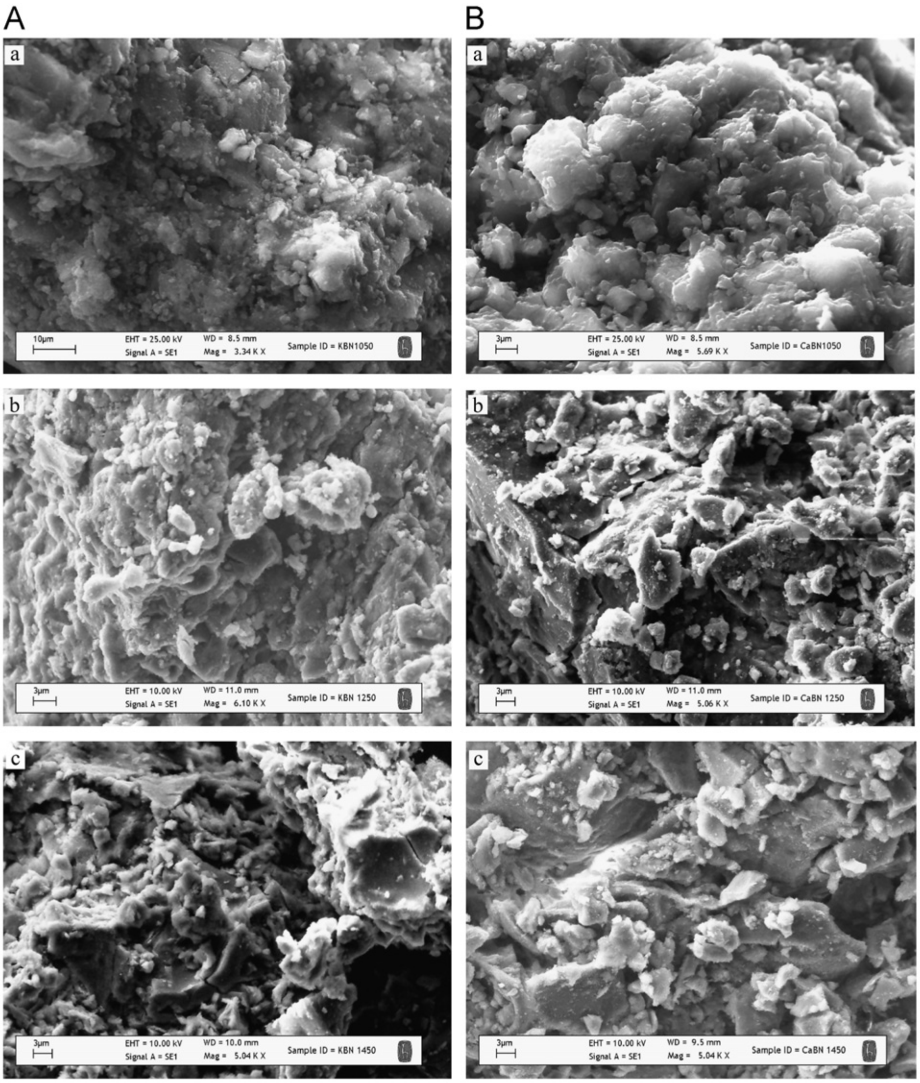

Fig. 3. SEM images of K-h-BN (column A) and Ca-h-BN (column B) at diffrent temperatures. The sample (a–c) was synthesized at 1050 °C (a), 1250 °C (b), and 1450 °C (c).

calculation illustrated that the grain size of the samples increases as temperature rises (Table 1).

The lattice constants and interlayer distance were calculated after refinement (Table 2). The results are very close to the reported value for h-BN (a=2.5044 Å, c=6.6562 Å, and d=3.3281 Å, ICCD card no: 34-421). In our previous study [7], we found that interlayer distance of h-BN increased with decrease in the d orbital electrons of used transition metal because of increasing d–π interaction. Similar to Sumiyoshi et al. [8] we observed interlayer distance of our products to be larger than 3.3281 Å and this might be due to empty d orbitals of potassium and calcium. As a result, more d–π interaction occurred between h-BN and the used metals.

SEM images (Fig. 3) indicated that irregularly grained powder with fractures and particles were in jagged shape. The fractures on these samples were intergranular and nucleate at the h-BN boundaries because of the low bonding strength of BN grains.

4. Conclusion

In summary, h-BN samples were prepared using representative metals at different temperatures. Usage of both metal nitrates and ammonia, which overcome internal stress, helped in nanocrystalline h-BN formation through the modified O'Connor method. The calculated lattice parameters for products are very close to the reported value of h-BN and the electronic interaction between h-BN and the metal affected the interlayer distance.

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[1] Not separated 100 and 101 peaks of hBN.