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# Effect of $Na_2CO_3$ on hexagonal boron nitride prepared from urea and boric acid

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**Abstract**

Formation of hexagonal boron nitride (hBN) from a precursor obtained by the reaction of urea and boric acid was studied in nitrogen, ammonia and argon atmospheres in 700–1200 °C temperature range. Effect of sodium carbonate ($Na_2CO_3$) addition on this process was investigated. Reaction products were subjected to X-ray diffraction, particle size distribution, gravimetric and Fourier transformed infrared spectroscopy analyses. Particle size and crystallite thickness of the formed hBN were seen to increase from about 60 nm and 5 nm at 700 °C to 230 nm and 19 nm at 1200 °C, respectively in $NH_3$ atmosphere with $Na_2CO_3$ addition. Highest conversion of boron in the precursor into hBN was achieved as 73.6% when $Na_2CO_3$ added precursor was reacted at 1200 °C in $NH_3$. hBN powder with high yield and relatively large particle size was obtained at low temperature such as 1200 °C with $Na_2CO_3$ addition. Role of $Na_2CO_3$ addition was suggested to be formation of a sodium borate melt from which hBN crystallized via the reaction of borate and nitrogen ions in the melt. Obtained hBN has the potential for utilization as a clean starting material for synthesis of *B* or N containing compounds.


*Keywords:* A. Grain growth; A. Powders: chemical preparation; D. Nitrides; D. Hexagonal boron nitride

## 1. Introduction

hBN is a multipurpose ceramic material, with exceptional properties and a wide area of application in industry. It is structurally similar to graphite and it resists oxidation to higher temperatures than graphite. It is used in powder form as a mold release agent in metal casting, as a high temperature lubricant or even in cosmetics. hBN can be shaped by hot-pressing and is used as molds or crucibles for liquid metal handling and as electrical insulator parts [1–3]. Consumption of hBN has increased in the last decades as a result of its unique properties and its utilization in composite materials [1–3]. hBN reduces the thermal expansion and friction coefficients, increases thermal conductivity and use temperatures of polymer matrix composites [3]. hBN has also been widely used in ceramic matrix composites to improve thermal shock resistance and machinability [4,5]. Due to increasing comsumption of hBN, cheaper and low temperature production methods are being searched for [1–3].

One of the common methods of h-BN production is the reaction of nitrogen bearing organic compounds (melamine, urea, dicyanamide) and boric acid under ammonia atmosphere [6–9]. Some catalysts are also added into this system in order to increase the yield and improve the crystal structure of the formed boron nitride. BN formed in low temperature methods, such as from boric acid and urea, is composed of hexagonal layers which are not in relative order with each other (low crystalline or turbostratic BN). Improvement in the crystal structure of hBN takes place by a decrease in the interplanar spacing value, *d*, to values closer to the theoretical value of 3.33 nm, and by increase in the crystal thickness, Lc which indicates the number of crystallographic layers in parallel orientation to each other in a hBN crystallite [6–9]. Addition of lithium carbonate on the formation of hBN from urea and boric acid was studied by Ostrovskaya et al. [10]. It was found that lithium carbonate was very effective in increasing the amount and improving the crystal structure of the formed hBN. It was suggested that hBN dissolves in a lithium borate melt and

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crystallizes from the melt, when lithium carbonate is used as a catalyst [10].

Carbothermic formation is another widely used method of hBN preparation. In this method, $B_2O_3$+C mixtures are reacted in $N_2$ atmosphere at temperatures higher than 1500 °C [11–14], thus the reaction temperatures are considerably higher than that applied in formation of hBN from urea and boric acid. Effect of alkaline earth oxides on carbothermic formation of hBN, was investigated by Çamurlu et al. [13,14]. Addition of $CaCO_3$ and other alkaline earth oxides was found to increase the amount of hBN formed. Addition of catalysts also caused a decrease in the $B_4C$ amount, which forms as a side product and slows down hBN formation during carbothermic process [11]. An ionic mechanism was proposed for formation of hBN from calcium borate melt, in addition to carbothermic formation of hBN. In ionic mechanism, hBN forms by the reaction of borate anions and dissolved nitrogen in the alkaline earth borate melt [13,14].

Role of copper on crystallization of hBN was investigated by Hubacek et al. [15]. It was reported that boron nitride in turbostratic crystal structure which contained Cu in atomically dispersed form showed an extensive increase in crystal structure ordering and in grain size when it was heated to 1950 °C in a hot press. Effect of copper on improving the crystal structure of hBN was proposed to be as a result of the interaction of the copper electronic orbitals with (0 0 2) planes of h-BN crystals. This interaction provided the growth of h-BN crystal by aligning and adjoining of the crystallites.

In the method of preparation from urea and boric acid, crystallinity of hBN is poor, particle size small and product yield is low. In order to improve these parameters $Na_2CO_3$ was utilized as a catalyst in this study. A precursor was prepared by the reaction of urea–boric acid mixtures then the precursor was kept in nitrogen, ammonia or argon atmospheres at 700–1200 °C with or without addition of sodium carbonate ($Na_2CO_3$). Effect of reaction atmospheres and $Na_2CO_3$ addition on the yield, crystal structure and particle size of hBN was investigated. Utilization of $Na_2CO_3$ and $NH_3$ together was found to have a pronounced contribution to the investigated parameters.

## 2. Experimental procedure

hBN was produced from urea and boric acid according to the method suggested by O'connor [9]. In this method, initially a precursor was produced by gradually heating urea–boric acid mixtures (1/1, n/n) up to 300 °C. During heating, the mixture liquefied and finally a foam-like white solid precursor was formed. After keeping it for 2 h at 300 °C, the product was collected and stored in a plastic jar. Formation of the precursor was suggested to take place by the reaction of boric acid and urea according to reaction (1) with the release of carbon dioxide and water [6]. About 23 g of precursor was formed from a total of 60 g of starting materials.

$$2H_3BO_3 + CO(NH_2)_2 = 2\,HNBOH + CO_2 + 3H_2O \quad (1)$$

The produced precursor was heated at 700–1200 °C under ammonia, nitrogen or argon atmospheres in order to form boron nitride. For this purpose, a horizontal tube furnace was utilized having inner and outer diameters of 5 and 6 cm, respectively. The furnace was equipped with electrical wire resistance and it had a maximum operating temperature of 1200 °C (Protherm). Before charging into the furnace, 10 wt.% $Na_2CO_3$ was added into the precursor and was mixed in a mortar and pestle in dry condition, for investigating its catalytic effect. The plain and $Na_2CO_3$ added precursors were placed into the preheated furnace in a crucible and kept for 2 h at the determined temperatures. XRD analyses were performed by a Rigaku Multiflex unit. Interplanar spacing and crystallite thickness of the formed hBN were calculated from the XRD data by Scherrer formula [9,16]. Particle size of the formed hBN was determined by a Malvern Zetasizer ZS particle size analyzer.

Products, obtained by reacting the plain or $Na_2CO_3$ added precursors, were leached in 1/1 (v/v) HCl/water solution for 1 h, in order to remove the unreacted precursor and sodium containing compounds from the formed hBN. Percent conversion of boron to hBN was calculated by means of dividing the amount of boron in the formed hBN by the amount of boron in the starting mixture.

## 3. Results and discussion

XRD pattern of the precursor is presented in Fig. 1a. It can be seen that the precursor had no definite XRD peak, indicating its amorphous structure.

### 3.1. Experiments performed in argon atmosphere

XRD patterns of the products obtained by reacting the plain precursor and $Na_2CO_3$ added precursor at 1200 °C for 2 h in argon atmosphere are presented in Fig. 1b and c, respectively. Argon atmosphere was selected since it is inert and it does not supply N into the system. It can be seen that peaks pertaining to crystalline hBN phase are present in the XRD patterns. As the reaction was conducted in argon

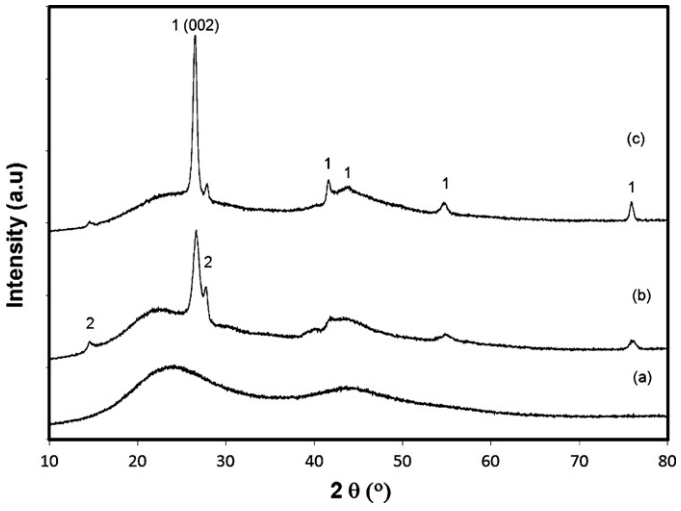


Fig. 1. XRD patterns of: (a) the precursor, and of the products after reacting, (b) the plain precursor, (c) 10 wt.% $Na_2CO_3$ added precursor in Ar atmosphere at 1200 °C for 2 h. (1) hBN, (2) $H_3BO_3$.

atmosphere and no gaseous N source was provided to the system, it can be inferred that N, which is present in the precursor reacts with *B* and therefore hBN formation occurs. In the study of Hubacek et al. [6] formation of BN from the precursor was proposed to take place by release of $B_2O_3$, $H_2$ and $N_2$, and release of $H_2O$ was omitted to keep the stoichiometric coefficients simple. Formation reaction of hBN from the precursor can be written as follows, by incorporating also the release of $H_2O$. $H_2O$ is released during heating of the precursor, as the hBN crystals grow and –H and –OH groups are liberated [6].

$$4H(NB)_xOH = (4x-2)BN + B_2O_3 + N_2 + H_2 + H_2O \quad (2)$$

Interplanar spacing values, *d* of the formed hBN were calculated according to Bragg's law [16]. *d* value of the formed hBN under Ar was calculated as 3.366 nm, as shown in Table 1. Theoretical value of *d* for fully crystalline hBN is 3.33 nm. As the 3-dimensional crystal structure ordering improves, *d* value decreases towards 3.33 nm [6,7,9]. Crystallite thickness, Lc of hBN formed under Ar from plain precursor was calculated as 12.27 nm. Lc is defined as the average thickness of a parallel layer group [9]. The calculated crystallite thickness of 12.27 nm for hBN formed from plain precursor in Ar is quite low, since it corresponds to the height of about 4 hBN unit cells.

Table 1
Parameters of the experiments and properties (% relative intensity, %RI, interplanar spacing, *d*, average crystallite thickness, Lc, percent conversion of boron in precursor to hBN) of formed hBN.

| *T* (°C) | Atm. | Additive | % RI (0 0 2) | *d* (nm) | Lc (nm) | Conv. of *B* (%) |
|---|---|---|---|---|---|---|
| 700 | $N_2$ | Plain | 15 | – | 4.04 | 2.20 |
| | | $Na_2CO_3$ | 13 | 3.414 | 9.25 | 5.18 |
| | $NH_3$ | Plain | 15 | – | 5.36 | 34.37 |
| | | $Na_2CO_3$ | 20 | 3.396 | 7.44 | 40.94 |
| 800 | $N_2$ | Plain | 17 | 3.368 | 5.21 | 10.22 |
| | | $Na_2CO_3$ | 20 | 3.373 | 9.79 | 24.68 |
| | $NH_3$ | Plain | 29 | 3.368 | 6.72 | 33.08 |
| | | $Na_2CO_3$ | 29 | 3.383 | 10.72 | 40.31 |
| 900 | $N_2$ | Plain | 22 | 3.360 | 7.97 | 21.26 |
| | | $Na_2CO_3$ | 27 | 3.361 | 11.06 | 25.81 |
| | $NH_3$ | Plain | 32 | 3.356 | 7.62 | 35.15 |
| | | $Na_2CO_3$ | 62 | 3.356 | 10.72 | 50.00 |
| 1000 | $N_2$ | Plain | 27 | 3.350 | 8.79 | 19.09 |
| | | $Na_2CO_3$ | 33 | 3.361 | 13.23 | 21.47 |
| | $NH_3$ | Plain | 32 | 3.363 | 9.01 | 34.14 |
| | | $Na_2CO_3$ | 64 | 3.356 | 14.36 | 55.86 |
| 1100 | $N_2$ | Plain | 27 | 3.351 | 10.72 | 20.63 |
| | | $Na_2CO_3$ | 45 | 3.350 | 15.70 | 23.67 |
| | $NH_3$ | Plain | 56 | 3.353 | 10.44 | 41.72 |
| | | $Na_2CO_3$ | 75 | 3.343 | 17.35 | 59.53 |
| 1200 | $N_2$ | Plain | 34 | 3.351 | 12.27 | 18.93 |
| | | $Na_2CO_3$ | 45 | 3.346 | 18.28 | 25.64 |
| | $NH_3$ | Plain | 91 | 3.351 | 12.72 | 59.16 |
| | | $Na_2CO_3$ | 100 | 3.343 | 19.39 | 73.60 |
| | Ar | Plain | 25 | 3.366 | 12.27 | 8.03 |
| | | $Na_2CO_3$ | 38 | 3.356 | 18.28 | 12.43 |

The large interplanar spacing value, low crystallite thickness (wide (0 0 2) peak at 26.5°) and unresolved (1 0 0) and (1 0 1) peaks at 41.5 and 43.8°, respectively [9], indicate the poor stacking efficiency of hexagonal crystal structure of the formed hBN by reaction of the precursor at 1200 °C under argon.

After reacting the precursor, boric acid peaks were seen to form in the XRD pattern given in Fig. 1b. Boric acid forms due to hydration of boron oxide, which is released during formation of hBN from the precursor as shown in reaction (2).

XRD pattern of 10 wt.% $Na_2CO_3$ added precursor is presented in Fig. 1c. Interplanar spacing, *d* was 3.356 nm and crystallite thickness was 18.28 nm when $Na_2CO_3$ added precursor was reacted under Ar atmosphere, as shown in Table 1. It can be inferred from the reduction in the interplanar spacing, and from the increase in crystallite thickness and relative intensity of the peaks pertaining to (0 0 2) planes that addition of $Na_2CO_3$ improves the crystal structure of the formed hBN, when compared to that of hBN obtained with plain precursor.

In Ar atmosphere at 1200 °C, conversion of boron from plain precursor was 8% and it was 12.4% when $Na_2CO_3$ was added to the precursor, as shown in Table 1. Mole of nitrogen atoms in the precursor was twice that of boron atoms, since urea and boric acid were used equimolar in preparation of the precursor. These results indicate that although formation of hBN can occur in Ar from boron and nitrogen that are present in the precursor, amount of formed hBN is quite low.

It was seen that when $Na_2CO_3$ is added to the precursor, amount and crystallite thickness of the formed hBN is larger, indicating the catalytic effect of $Na_2CO_3$. The mechanism is most probably similar to the one which operates when lithium carbonate [10] or calcium carbonate [13,14] was added. Crystallization of hBN from a lithium borate melt was proposed by Bartnitskaya et al. [10]. The mechanism was clarified by Çamurlu et al. In their study, formation of hBN was suggested to take place by the reaction of borate anions and dissolved nitrogen in the melt [13,14]. Nitrogen was suggested to dissolve in the borate melts in the form of $N^{3-}$ or $N^-$ cations [13].

When $Na_2CO_3$ is added to the precursor, it is expected to decompose into $Na_2O$ and $CO_2$ at 850 °C [17]. $Na_2O$ reacts with released $B_2O_3$ and forms a sodium borate melt. Formation of hBN takes place in the borate melt, which contains borate anions and dissolved nitrogen. The source of nitrogen is either urea, which was utilized for preparation of the precursor, or $N_2$ or $NH_3$ gas supplied to the system. It can be seen in the XRD patterns that when $Na_2CO_3$ is added, boric acid peaks diminish, indicating the occurrence of the reaction of $Na_2O$ with boric oxide. Due to the fast cooling of the products when they are taken out of the furnace at the end of the reaction, sodium borate is in amorphous structure, therefore it does not present any peaks in the XRD pattern.

### 3.2. Crystal structure and particle size of hBN

XRD patterns of the products of the experiments conducted in $N_2$ and $NH_3$ atmospheres at various temperatures in

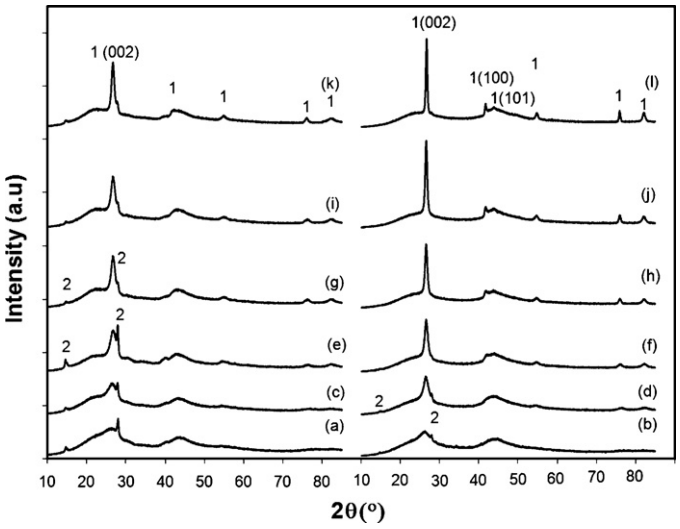


Fig. 2. XRD patterns of the products of the experiments conducted in $N_2$ with plain and $Na_2CO_3$ added precursors: (a) 700 °C – plain, (b) 700 °C – $Na_2CO_3$ added; (c) 800 °C – plain, (d) 800 °C – $Na_2CO_3$ added; (e) 900 °C – plain, (f) 900 °C – $Na_2CO_3$ added; (g) 1000 °C – plain, (h) 1000 °C – $Na_2CO_3$ added; (i) 1100 °C – plain, (j) 1100 °C – $Na_2CO_3$ added; (k) 1200 °C – plain, (l) 1200 °C – $Na_2CO_3$ added precursors. (1) hBN, (2) $H_3BO_3$.

700–1200 °C range are presented in Figs. 2 and 3, respectively. The hBN product having the highest intensity of (0 0 2) peak was assigned to the relative intensity value of 100%. (0 0 2) peak intensities of other products were calibrated relative to the highest peak. Calculated relative intensity values are presented in Table 1. It can be seen in Figs. 2 and 3 that the relative peak height increases and peak width decreases with increasing temperature. This indicates an improvement in stacking efficiency and mutual layer

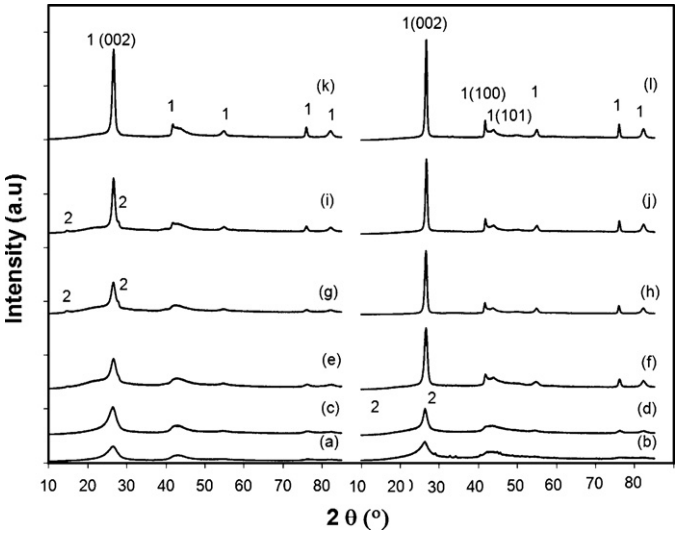


Fig. 3. XRD patterns of the products of the experiments conducted in $NH_3$ with plain and $Na_2CO_3$ added precursors: (a) 700 °C – plain, (b) 700 °C – $Na_2CO_3$ added; (c) 800 °C – plain, (d) 800 °C – $Na_2CO_3$ added, (e) 900 °C – plain, (f) 900 °C – $Na_2CO_3$ added, (g) 1000 °C – plain, (h) 1000 °C – $Na_2CO_3$ added, (i) 1100 °C – plain, (j) 1100° C – $Na_2CO_3$ added; (k) 1200 °C – plain, (l) 1200 °C – $Na_2CO_3$ added precursors. (1) hBN, (2) $H_3BO_3$.

orientation in crystal structure of formed hBN with increasing temperature [9,10].

Relative intensities of hBN are higher and the (0 0 2) peaks are narrower for all temperatures when $Na_2CO_3$ was added to the precursors for both atmospheres. In $N_2$ system, boric acid peaks are present in the products of plain precursor (Fig. 2, left column), on the other hand they diminish at temperatures higher than 800 °C when $Na_2CO_3$ is added (Fig. 2, right column). This result indicates that $Na_2CO_3$ reacts with boron oxide which is released during formation of hBN from the precursor. In $NH_3$ system, there is boron oxide at very low amount when plain precursor was reacted and there is no boric acid peak at all temperatures, when $Na_2CO_3$ was added to the precursor. This result can be taken as an indication that although $B_2O_3$ is released during formation of hBN (reaction (1)), it reacts with $NH_3$ to form the precursor according to reaction (3) [6].

$$H_3BO_3 + NH_3 = 2HNBOH + H_2O \quad (3)$$

High background in the XRD patterns of products obtained in $N_2$ atmosphere indicates that the precursor was not completely consumed (Fig. 2). On the other hand, clean background in the XRD patterns of the products obtained in $NH_3$ system given in Fig. 3 points out that the precursor was consumed at a higher amount during reaction. Therefore, amount of hBN in the products is expected to be higher when $NH_3$ gas was used, as compared to $N_2$ atmosphere.

Change in $d$ spacing values with temperature for all three atmospheres and for plain and $Na_2CO_3$ added systems are presented in Table 1. $d$ values of the products obtained in $N_2$ and $NH_3$ were seen to be not dependent on the atmosphere type used, or $Na_2CO_3$ content of the precursor. At 1200 °C all the samples obtained in $N_2$ or $NH_3$ had $d$ values of 3.345–3.350 nm. It can be inferred from these results that 1200 °C is not sufficient for obtaining the fully crystallized (or theoretical) $d$ value (3.33 nm) of hBN, even when $Na_2CO_3$ catalyst was used.

Width of the peaks pertaining to (0 0 2) plane at 26–26.5° are seen to be narrower when $Na_2CO_3$ was used for both atmospheres, indicating that the crystallite thickness of hBN is larger. Crystallite thickness values were calculated according to Scherrer formula [9,16], and they are presented in Table 1 and Fig. 4. Crystallite thickness of hBN prepared from plain precursor in $N_2$ atmosphere increases from 4 nm to 12 nm when reaction temperature is increased from 700 °C to 1200 °C; and from 9 nm to 18 nm when $Na_2CO_3$ was added to the precursor. In $NH_3$ atmosphere crystallite thickness of hBN prepared from plain precursor increases from 5 nm to 13 nm when reaction temperature is increased from 700 °C to 1200 °C; and from 7.5 nm to 19 nm when $Na_2CO_3$ was added to the precursor. Temperature appears to have an important effect on three dimensional ordering and increasing the crystallite thickness of the formed hBN. Additionally, these results reveal the significant influence of $Na_2CO_3$ on 3-dimensional ordering of hBN crystallites. $Na_2CO_3$ increases the crystal thickness of the formed hBN in both atmospheres. Role of $Na_2CO_3$ may be suggested to be bringing about the ionic mechanism, through

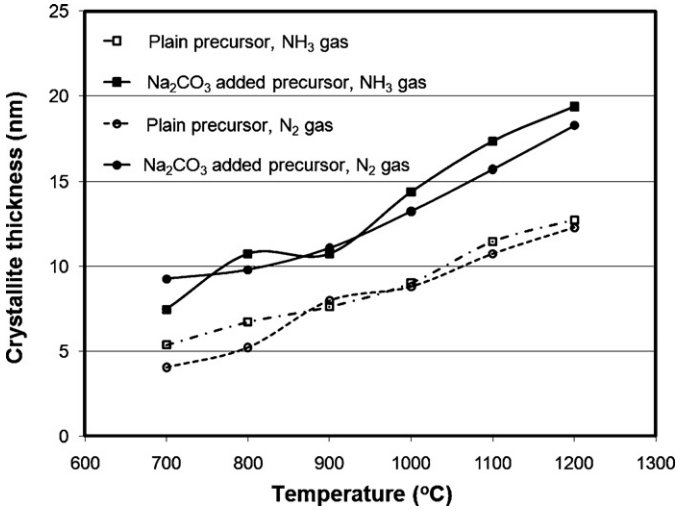


Fig. 4. Crystallite thickness values of hBN prepared in $N_2$ and $NH_3$ atmospheres as a function of temperature and $Na_2CO_3$ addition.

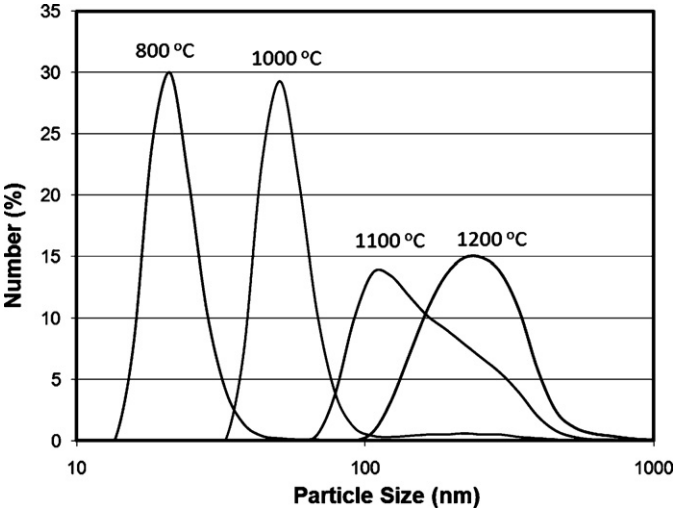


Fig. 6. Particle size distribution plots of hBN obtained in $NH_3$ atmosphere with $Na_2CO_3$ added precursors at 800–1200 °C.

which hBN crystallizes from a sodium borate melt that contains borate and nitrogen ions as described previously.

Particle size distribution of hBN powders obtained in $N_2$ or $NH_3$ atmospheres and from plain or $Na_2CO_3$ added precursors are presented in Fig. 5. Average particle sizes of hBN prepared without addition of $Na_2CO_3$ at 1200 °C in $N_2$ and $NH_3$ were 59 and 55 nm, respectively. When $Na_2CO_3$ was introduced into the precursor before reaction, formed hBN in $N_2$ and in $NH_3$ had average particle sizes of 160 and 230 nm, respectively. These results indicate quantitatively that $Na_2CO_3$ has an important effect on the particle size of hBN. Particle size distribution results are in parallel with results of crystallite thickness calculations. This is expected since hBN particles are composed of hBN crystallites. Without $Na_2CO_3$ addition, particle sizes of hBN formed in $N_2$ and $NH_3$ were similar to each other. However, when $Na_2CO_3$ was added, $NH_3$ appear to be more effective in growth of hBN particles than $N_2$. This may be due to a combined effect of $Na_2CO_3$ and $NH_3$.

Change in particle size distribution of hBN formed in $NH_3$ as a function of reaction temperature is presented in Fig. 6. It can be seen that average particle size of hBN increases from 25 nm at 800 °C to 230 nm at 1200 °C. Particle size distribution peak of hBN was seen to broaden as a result of $Na_2CO_3$ addition (Fig. 5) or increase in temperature (Fig. 6), along with the increase in the average particle size, indicating a wider particle size range.

### 3.3. hBN yield

Percent conversion of *B* into hBN values represent the ratio of *B* that was utilized in formation of hBN to that in the starting mixture (in $H_3BO_3$). Percent conversion of *B* values are presented in Fig. 7. They are higher when $NH_3$ was used, then when $N_2$ gas was used. This may be due to better nitridation property of $NH_3$. The influence of $NH_3$ may be two fold. First it

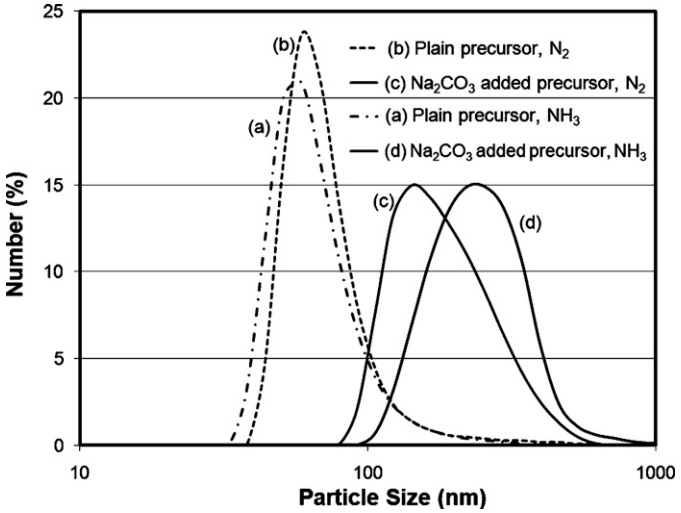


Fig. 5. Particle size distribution plots of hBN powders obtained at 1200 °C from plain and $Na_2CO_3$ added precursors in $N_2$ and $NH_3$ atmospheres.

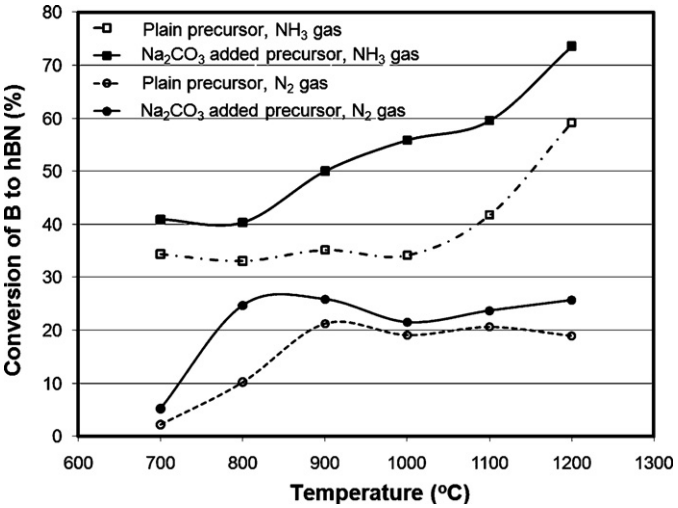


Fig. 7. Percent conversion of *B* in the starting mixture into hBN prepared in $N_2$ and $NH_3$ atmospheres as a function of temperature and $Na_2CO_3$ addition.

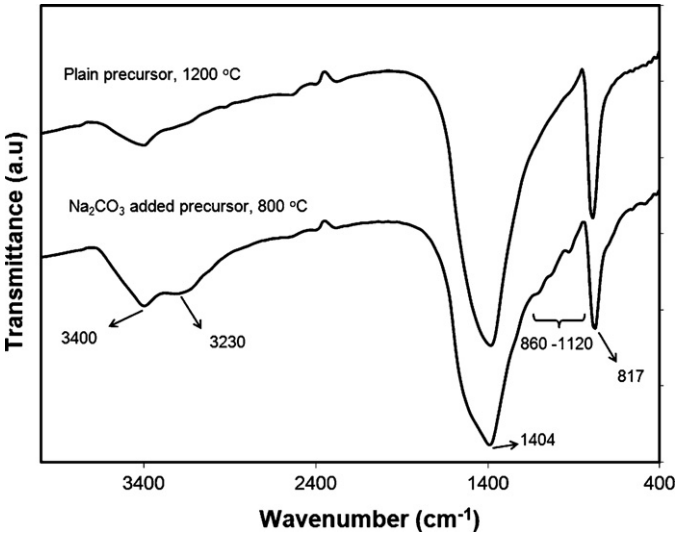


Fig. 8. FT-IR patterns of $Na_2CO_3$ added precursors reacted at 800 °C, and of plain precursor reacted at 1200 °C in $NH_3$ atmosphere.

can react with the boric acid released from the precursor, in order to convert it to the precursor according to reaction (3). Secondly, $NH_3$ thermally decomposes into hydrogen and nitrogen gas. Formed $H_2$ gas may also reduce boron oxide into elemental boron, which then can react with nitrogen to form hBN [18]. Percent conversion of *B* results are in accord with the relative peak heights of (0 0 2) peaks given in Table 1. In addition, the high background in the XRD patterns of the products obtained in $N_2$ indicates that the reaction was incomplete. Whereas, the clean background of the XRD patterns of the products obtained in $NH_3$ indicates that higher amount of precursor was converted into hBN. Percent conversion of *B* values presented in Fig. 7 are also in parallel with this observation.

In both $N_2$ and $NH_3$ systems, $Na_2CO_3$ added precursor yielded higher conversion of *B* into hBN than plain precursors. In $NH_3$ without $Na_2CO_3$, *B* conversion does not change with temperature up to 1000 °C, and *B* conversion increases afterwards. On the other hand, in the presence of $Na_2CO_3$ in $NH_3$, *B* conversion starts to increase after 800 °C. This suggests a combined or synergitic effect of $NH_3$ and $Na_2CO_3$. These results agree with the XRD patterns given in Figs. 2 and 3 and relative peak intensity values given in Table 1. When $Na_2CO_3$ was added to the precursor and reacted in $NH_3$ at 1200 °C, conversion of *B* was 74%. This is a quite high value for a relatively low synthesis temperature, such as 1200 °C.

FT-IR patterns of leached hBN powders obtained at 800 °C and 1200 °C are presented in Fig. 8. The peaks at 817 $cm^{-1}$ and 1404 $cm^{-1}$ belong to hBN. The origin of the small peaks between 860 and 1120 $cm^{-1}$ could not be identified [7]. The peak at 3230 $cm^{-1}$ in Fig. 8a belongs to boric acid, which is present in hBN obtained at 800 °C.

Hubacek et al. suggested a polymer-like structure for hBN crystals which consisted of hexagons containing *B* and N [6,7]. –H and –OH groups are suggested to be present on the periphery of the hBN crystals. As the hBN crystals grow by unification of the small hBN crystals, $H_2O$ is released [6,7]. Therefore the –OH vibration at 3400 $cm^{-1}$ in the FT-IR pattern of the sample obtained at 800 °C arises from the –OH groups around the hBN crystallites [6,7,19]. The intensity of vibration at 3400 $cm^{-1}$ was seen to decrease in the FT-IR analyses with increasing reaction temperature. In the FT-IR pattern of hBN which was obtained at 1200 °C in $NH_3$ atmosphere, the –OH peak at 3400 $cm^{-1}$ can be seen to have diminished but not completely removed (Fig. 8b). This result indicates that small amount of –OH exists in the obtained hBN powder at 1200 °C.

## 4. Conclusions

$Na_2CO_3$ addition was found to have a profound effect especially when $NH_3$ atmosphere was utilized on preparation of hBN from boric acid and urea. Average crystallite size, particle size and yield of hBN increased with addition of $Na_2CO_3$ into the precursor prepared from boric acid and urea. $Na_2CO_3$ was suggested to form a sodium borate melt from which hBN crystallized by the reaction of borate and nitrogen ions in the melt. Formation of hBN from the precursor in Ar and $N_2$ atmospheres was seen to be low, indicating that $NH_3$ is necessary for high yield of formed hBN. In the synthesis of *B* or N containing compounds, prepared hBN powder can be utilized as a clean starting material.

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