



The effect of strontium carbonate additive on the production of graphitic boron nitride using modified O'Connor method

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Abstract

In this study, it was investigated that whether the graphitic boron nitride was successfully synthesized by adding strontium carbonate (within the different amount of 20-40%) using O'Connor method which is the one of the solid-state methods or not. Fourier transform infrared spectroscopy FTIR, powder X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy (EDS) and scanning electron microscopy (SEM) methods were used to clarify the formation of boron nitride structure. Inter and intra-layer BN vibration movements of gBN were determined by FTIR method. Also, peaks belonging to the gBN formation were observed in the XRD analysis, and the distance between the layers was found to be close to both the theoretical values and data of commercially produced BN structure. The morphological examination was performed with SEM, and the planar properties of structure were determined. In addition, the EDS measurements supported that the crystal structure of powders include only nitrogen and boron atoms. In the light of these methods, it has been determined that the graphitic BN was able to synthesize at a lower temperature and in a more regular crystal structure compared to the O'Connor method with strontium carbonate additives.

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1. Introduction

Boron chemicals have been great importance in last two decades since the recent studies have intensified on these compounds that are produced from boron. At the same time, the boron compounds have a wide range of uses in many branches of industry, especially nuclear field, defense industry, jet and rocket fuel, soap, detergent, solder, photography, textile dyes, glass fiber and paper industry [1-3]. Boron nitride is a synthetic compound of boron and nitrogen atoms that are isoelectronic to the carbon analogue when they form a compound. Both are adjacent to the carbon atom in periodic table with atomic numbers 5 and 7, respectively. Boron nitride is an extraordinary synthetically produced chemical in the field of materials science due to its bonding behavior and can be found in many different crystal structures [4].

Boron nitride (in all its forms), which is naturally encountered in trace amounts, is a commercially valuable compound for industrial applications like other boron compounds because of its unique chemical and physical properties [4-6]. Moreover, the graphite-like BN is a technologically important compound due

to its properties such as high temperature stability, low dielectric constant, high thermal conductivity, high mechanical strength, hardness and chemical inertness [3]. It is synthesized by the solid-state reaction of boron compounds (boron oxide, boric acid, metal borates) and nitrogen compounds (urea, melamine, cyanamide etc.) at high temperatures (> 1600 °C) in nitrogen or ammonia gas atmosphere [7-8].

The layered-planar structure of BN is named as hexagonal crystalline morphology and is similar to graphite; for this reason, it is often referred to as "white graphite". In addition, the boron nitride has various crystal structures depending on the bond hybridization between boron and nitrogen atoms. Graphitic boron nitride (gBN), hexagonal boron nitride (hBN), turbostratic boron nitride (tBN), amorphous boron nitride (aBN) and rhombohedral boron nitride (rBN) are sp^2 hybridized while the cubic boron nitride (cBN) or borazone, and wurzite boron nitride (wBN) are sp^3 hybridized [4]. Besides, there are BN classifications according to the production methods such as ion-bombarded boron nitride (iBN), boron nitride (eBN), amber boron nitride (aBN), Showa Denko's cubic

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boron nitride (sBN), pyrolytic boron nitride (pBN) [4,5,9].

Various chemical additives, mostly metal salts, are used during the synthesis of graphitic BN, [10-12]. For example, the effects of metal carbonates on hBN layered structures are discussed in detail by Öz et al. [10-12]. In this scope, the metal carbonates were used to reduce the activation energy to increase the crystallinity, crystallite size and yield of hBN samples. It has been found that the critical properties of hBN synthesized by the applied methods were noted to increase significantly in the presence of metal carbonates [8-11]. In this study, synthesis of gBN was performed using the modified O'Connor method [7] by addition of strontium carbonate into the reaction mixture. The experimental findings showed that the positive effect of strontium carbonate addition on the crystal structure of gBN was determined at the relatively lower preparation temperature than that of O'Connor method.

2. Materials and Methods

Graphitic boron nitride was synthesized by using 1/2 ratio of boron oxide (Fluka, 97 %)-urea (Fluka, 99 %) mixture with the addition proportions (20, 30 and 40%) of SrCO₃ (Alfa Aesar, 99.9%) according to the O'Connor method. In the first stage, boron oxide, urea and SrCO₃ were mixed homogeneously and pre-heat treatment was applied at 200 ° C for 2 hours. In the second stage, the intermediate product obtained in the first step was annealed under ammonia (Linde Co. 99.9%) gas atmosphere at 1450 ° C for 3 hours. In the third stage, the room-temperature-cooled samples were purified by heating in 100 mL 1 M HCl (Merck, 37%) solution. In the last stage, the structure of products was examined using Fourier transform infrared spectroscopy (FTIR), powder X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy (EDS) and scanning electron microscopy (SEM) methods. KBr discs containing 2 % sample were prepared, and the vibration movements in the range of 400-4000 cm⁻¹ were determined with Shimadzu 8400S FTIR spectrometer. The powder gBN was investigated by XRD (a Rigaku Multiflex + XRD 2kW diffractometer with a CuK α target) in the range of 10° and 90° at 2 θ angles. Surface imaging analysis and EDS were performed with JEOL JST-6400 SEM after gold coating of the products.

3. Results and Discussion

The methods that used for the synthesis of boron nitride have great importance since the additives used as the dopant in mixture lead to discrete properties.

Constructive effect of metal carbonates on BN formation has significantly been deduced in literature when the metal carbonates are used as catalysts [8-11]. In these previous studies, the formation of layered structure and growth of graphitic boron nitride particles in the presence of metal carbonates were explained by the catalytic effect, however the catalyst-solvent effect was not discussed before. This effect has been determined in the previous studies to improve the synthesis positively depending on the increment of surface area and especially solvent-solute balance of additive [8-12]. It is anticipated that the successful results were obtained with the use of carbothermic methods [13, 14]. Therefore, in this study, the SrCO₃ compound which was not previously used as additive was preferred due to the positive contribution of metal carbonates on the synthesis of BN [10]. In this context, the SrCO₃ was added in different molar ratios (20, 30, and 40%) during the synthesis of BN to determine lowest concentration for the formation of highly crystalline boron nitride. The instrumental methods such as the FTIR, XRD and SEM were used to impress the formation of BN. Meanwhile, the first identification of samples has been investigated by the FTIR where the chemical bond vibrational modes of BN structure are apparently designated in this analysis method. The gBN with the form of sp² hybridized hexagons adjacent to each other is settled as lamellar or multilayer structure. Therefore, in the spectra two main peaks derived from the in-plane and out of plane interactions were observed at the wavenumbers of 1400 cm⁻¹ and 800 cm⁻¹, respectively [15]. Moreover, the synthesized samples have weak end-groups peaks derived from the N-H and B-OH vibrational modes at approximately 3500 cm⁻¹ accompanied to main vibrational modes of B-N (Figure 1). In addition, the crystalline morphology can be estimated from the FTIR spectra. Accordingly, Fig. 1 indicated the hexagonal (graphitic) form due to the range of the main peaks. In contrast to hexagonal form, the cubic morphology included the sharp peak in the wave number range of 1000-1100 cm⁻¹. In the spectra, the peak identified for cubic form did not exist while the observed peak values indicated the graphitic form as the conformation of gBN formation. The values are in accordance with the range given in the literature [16].

XRD crystallography is a method used to study the atomic and molecular structure of a crystal. Besides, the chemical bonds, irregularities in the crystal structure, distances between layers, lattice parameters and average positions of the atoms in the crystals can easily be determined by measuring the angles and amplitudes of diffracted beams.

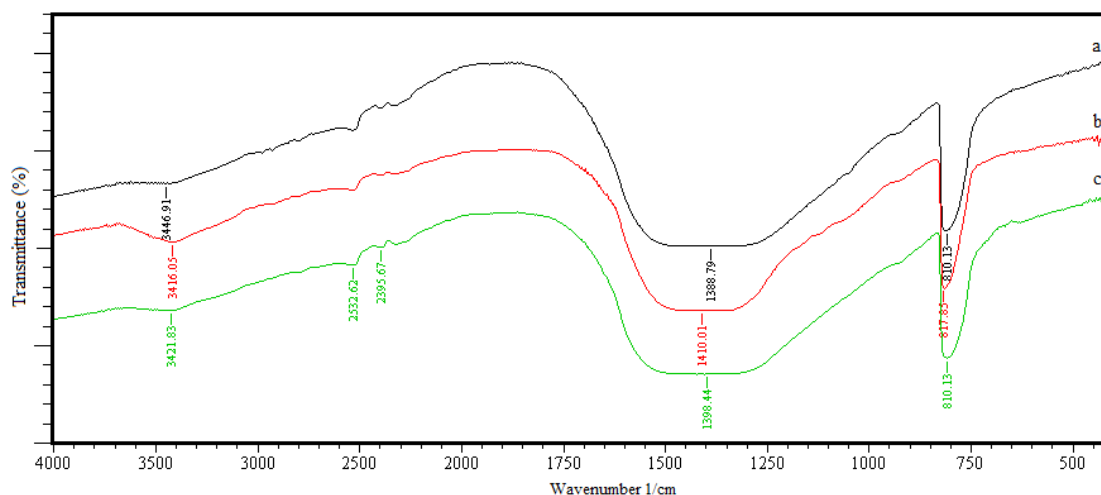


Figure 1. FTIR spectra of gBN obtained in presence of SrCO₃ additive: a) 40 %, b) 30 %, c) 20 %,

In this respect, the XRD analysis was performed to clarify the fundamental crystallographic properties such as the lattice parameters, inter-layer distance and crystal plane alignment of gBN samples. Meanwhile, the crystallite composition of products synthesized by adding SrCO₃ was examined and compared with the ICDD 34-421 card containing the main peaks of Miller indices of pure gBN [17]. The original XRD diffractogram of gBN structure includes the

characteristic planes: 002, 100, 101, 102, 004, 110 and 112 [18]. The presence of whole identified planes in the sample diffractograms was the evidence of gBN formation (Figure 2). As a result of the improvement of gBN crystal structure, the corresponding peak intensities were found to increase considerably when the dopant level of SrCO₃ concentration was chosen 20 % and more.

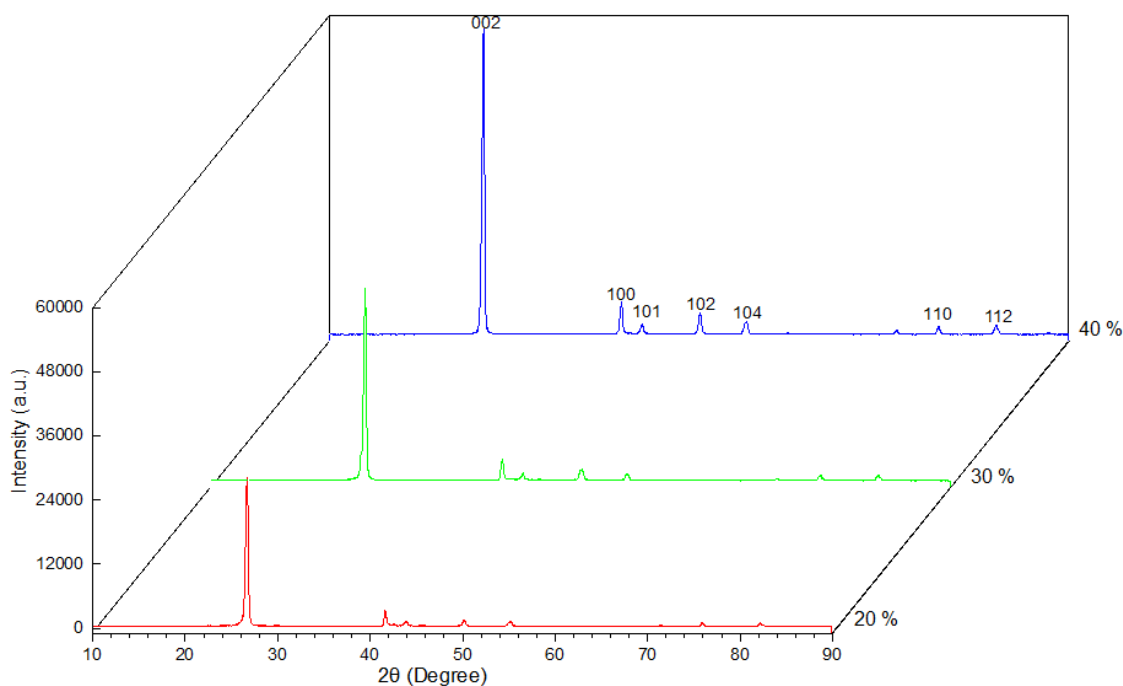


Figure 2. XRD diffractogram of gBN samples synthesized in presence of 20 %, 30 % and 40 % SrCO₃

In addition, the XRD experimental findings enable us to calculate the lattice cell parameters from the least squares method with the measured inter-layer distance "d" values and hkl planes for hexagonal unit cell

structure [10]. The lattice parameters for the hexagonal (graphitic) systems have "a" and "b" values that are equal to each other, and one can see the calculated lattice values of "a", "b", "c" and "d" in Table 1.

According to the table, the results of lattice parameter calculations were found to be close to the original literature values ($a = b = 0.2504$ nm, $c = 0.6656$ nm, $d = 0.3328$ nm) for all the gBN samples produced in presence of SrCO_3 (Table 1) [19]. The samples prepared by the SrCO_3 addition levels of 20 % and 40 % possessed closer values while the compound produced by 30 % had slightly higher than the literature values (Table 1). Consequently, the good agreements were obtained in terms of lattice parameters when 20 % or more strontium carbonate was used.

Table 1. Lattice parameters and average grain size values of gBN

		Amount of additive (%)		
		20	30	40
Lattice Parameters (nm)	a	0.2504	0.2506	0.2504
	c	0.6656	0.6676	0.6658
	d	0.3328	0.3338	0.3329
Average Grain Size (nm)		56,90	44,25	92,00

XRD measurements are also used to calculate crystallite and average grain size parameters by Debye-Scherrer equation (Eq. 1)

$$L = \frac{K \lambda}{\beta \cos \theta} \quad \text{Eq. (1)}$$

where K is the shape factor (which is 0.941), L is the average grain size, λ is the wavelength, B is the FWHM of the Bragg peak and θ is the Bragg angle [20]. It is determined that the grain sizes of gBN samples appreciated as accrual at the amount of SrCO_3 that the sample prepared by 40 % dopant level exhibits the highest average crystallite size among the samples. Moreover, 20 % addition level of SrCO_3 into the sample mixture also improved the grain size in contrast to undoped or plain mixtures.

The scanning electron microscopy (SEM) method was applied to clarify the surface morphology of SrCO_3 added gBN samples after the purification process [21]. SEM images include homogenous bulk gBN as shown in Fig. 3 and the structure consists of 1-3 μm particles formed from the coagulation of sub-particles. The average grain sizes of sub-particles calculated from the XRD diffractograms were found as approximately 100 nm where 10 to 30 small particles cause the greater particles by the agglomeration as well in SEM images. The SEM images include the hexagonal layered gBN with uniform nature while there is not any strontium carbonate traces in the views as well as EDS measurements (Fig. 4). Besides, one can deduce from

the EDS measurements that the samples comprised of only boron and nitrogen elements while the gold existence is mainly derived from the coating process.

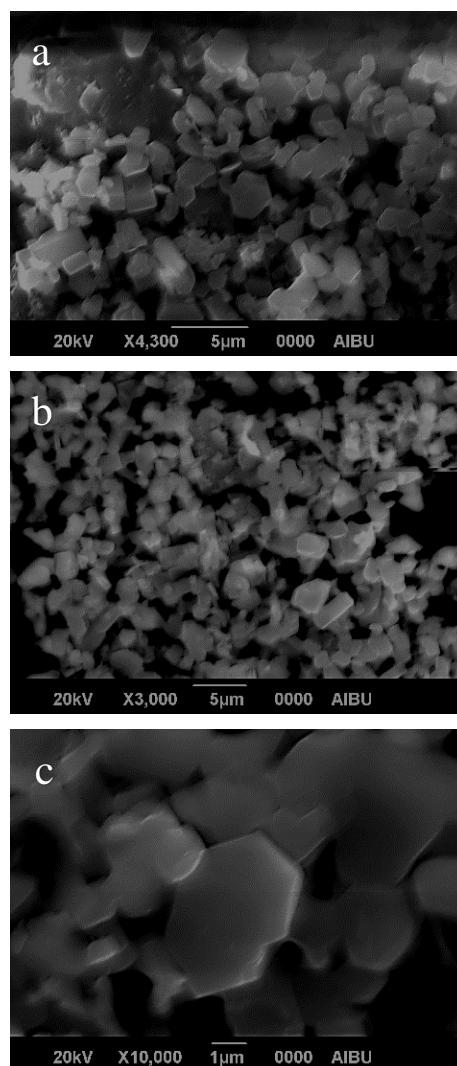


Figure 3. SEM images of the gBN synthesized in the presence of SrCO_3 with different magnifications a) 4300, b) 3000 and c) 10000 fold.

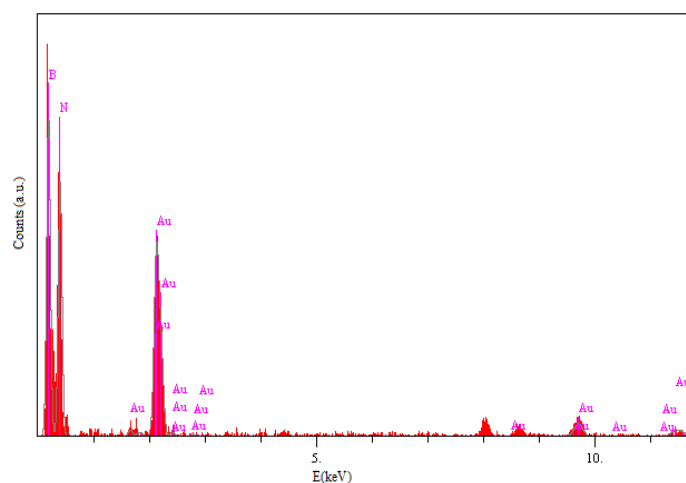


Figure 4. The EDS of the gBN synthesized in the presence of SrCO_3

3. Conclusion

In this study, it was aimed to determine both the effect of SrCO₃ additives on gBN formation and the lowest dopant amount for positively contribution to the ordered structure. In this context, the gBN samples were prepared by adding different concentration level of SrCO₃ (from 20% to 40% additive) at the temperature of 1450 °C by means of the O'Connor method. Powder samples have extensively been characterized by the stanrd characterization techniques such as the FTIR, XRD and SEM instrumental methods. According to all the experimental results obtained, it was determined that the favorable SrCO₃ contribution was in a range of about 20-40%.

According to FTIR studies, the presence of SrCO₃ content in the gBN crystal matrix caused an increase in the strength of the covalent bonds between boron and nitrogen atoms and a strong B-N lattice vibration in the flat plane. The absorbtion peaks at around 800 cm⁻¹ and 1400 cm⁻¹ in FTIR spectra verified the formation of the graphitic morphology. Besides, a wide peak was observed at around 3450 cm⁻¹ wavenumber assigned for the N-H and O-H groups at the end of chains as a signal for the lateral structure.

Experimental findings from the XRD patterns show that the presence of SrCO₃ powder activates the gBN formation to overcome the internal stress in the crystalline structure (meaning the reduction of residual stresses). The lattice parameters determined from the XRD results for all the materials have been calculated and compared to the literature findings. It was observed that all the comparision results were found to be in good aggrement with each other. The inter-layer distance of hBN samples synthesized in this study was oserved to be approximately 0.333 nm that was attributed to close to the theoretical value. Moreover, the SrCO₃ content improving the crystallinity of gBN converts the crystal structure to the highly graphitic nature. Thus, new crsytal structure exhibitied relatively lower temperatures as compared to the material synthesized by O'Connor method (at 1600 °C). At this point, the dopant level affected positively not only the lattice parameters but also the grain size related to the formation of graphitic BN. In this respect, the highest crystal size of aproximately 92 nm was obtained in case of 40 % SrCO₃ additive level.

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Conflicts of interest

The authors state that did not have conflict of interests.

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