Improving Formation Conditions and Properties of hBN Nanosheets Through BaF2-assisted Polymer Derived Ceramics (PDCs) Technique

Boitumelo J. Matsoso 1, Victor Vuillet-a-Ciles 1, Laurence Bois 1, Bérangère Toury 1 and Catherine Journet 1,*

1 Laboratoire des Multimatériaux et Interfaces, UMR CNRS 5615, Univ Lyon, Université Claude Bernard Lyon 1, F-69622 Villeurbanne Cedex-France; boijo.matsoso@gmail.com (B.J.M.); victor.vuillet-a-ciles@univ-lyon1.fr (V.V.C.); laurence.bois@univ-lyon1.fr (L.B.); berangere.toury@univ-lyon1.fr (B.T.)

* Correspondence: catherine.journet@univ-lyon1.fr; Tel.: +33-4724-335-64

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Abstract: Hexagonal boron nitride (hBN) is an attractive material for many applications such as in electronics as a complement to graphene, in anti-oxidation coatings, light emitters, etc. However, the synthesis of high-quality hBN at cost-effective conditions is still a great challenge. Thus, this work reports on the synthesis of large-area and crystalline hBN nanosheets via the modified polymer derived ceramics (PDCs) process. The addition of both the BaF2 and Li3N, as melting-point reduction and crystallization agents, respectively, led to the production of hBN powders with excellent physicochemical properties at relatively low temperatures and atmospheric pressure conditions. For instance, XRD, Raman, and XPS data revealed improved crystallinity and quality at a decreased formation temperature of 1200 °C upon the addition of 5 wt% of BaF2. Moreover, morphological determination illustrated the formation of multi-layered nanocrystalline and well-defined shaped hBN powders with crystal sizes of 2.74–8.41 ± 0.71 µm in diameter. Despite the compromised thermal stability, as shown by the ease of oxidation at high temperatures, this work paves way for the production of large-scale and high-quality hBN crystals at a relatively low temperature and atmospheric pressure conditions.

Keywords: hBN; PDCs; Li3N; borazine; BaF2; 2D material

1. Introduction

For over a decade, an enormous scientific research effort has been devoted to the synthesis, tuning, and investigating of various properties and applications of metallic, semiconducting, and insulating two-dimensional (2D) materials. This tremendous research interest in 2D materials is due to the successful isolation of graphene from highly-oriented pyrolytic graphite (HOPG) [1–3]. Amongst the most studied 2D materials, hexagonal boron nitride (hBN) continues to attract attention due to its unique physicochemical properties. Owing to the strong covalent sp2 bonds in the BN plane, hBN exhibits a large bandgap (~5.9 eV), high mechanical strength, good thermal conductivity, chemical inertness, and thermal stability. Moreover, the atomically smooth surface and close in-plane lattice mismatch to graphene (~1.8%) [4,5], renders hBN an important layered material complementary to graphene and other 2D materials [4,6–10]. As a result, this has led to a myriad of potential applications for hBN; ranging from encapsulation of graphene [4,11], tunneling barrier [12], deep ultraviolet light emitters [13], protective coatings and/or lubricants [14,15], hydrogen storage [16], all the way to dielectric substrates [5]. For instance, graphene-based transport devices integrated with an hBN dielectric layer have been found to exhibit enhanced mobility and excellent current on-off ratios, compared to those fabricated from graphene stacked on other substrates [5,17–21].
Furthermore, the absence of dangling bonds or trapped charges in hBN is of significant importance for enhancing the film performance especially when hBN is integrated with transition metal dichalcogenides such as MoS₂ [22–24]. Last but not least, the electrical insulating behavior of hBN enables it to serve as a platform for charge fluctuation, contact resistance, gate dielectric, a passivation layer, Coulomb drag, as well as the atomic tunneling layer in a variety of fundamental scientific and technological fields [12,15,23,25,26].

However, for hBN to reach its ultimate practical application in the optoelectronic and dielectric industry, synthesis of large-area high-quality single crystals of hBN, at cost effective conditions, is a very crucial issue. Consequently, numerous techniques have been developed and employed to produce hBN; these include processes such as mechanical exfoliation [5,27,28], sputtering [29,30], pulsed laser deposition (PLD) [31,32], atomic layer deposition (ALD) [33–35], and chemical vapor deposition (CVD) [36,37]. For instance, with graphene, mechanical exfoliation has been widely used to produce high-quality hBN nanosheets. On the contrary, mechanical exfoliation is strictly limited to the fabrication of small-scale devices as the process produces flakes of a limited size, inconsistent yields, and a variable number of hBN layers. Additionally, other techniques basically require extremely sophisticated equipment using high temperatures and pressures [13]. Therefore, in an attempt to circumvent these drawbacks, the use of the polymer derived ceramics (PDCs) [36–40] process coupled with the addition of a crystallization agent such as lithium nitride (Li₃N) has been reported to provide an alternative approach for preparing large-scale and high-quality single crystals of hBN nanosheets for further applications in next-generation electronics. During the PDCs method, a polymeric precursor is synthesized from its monomers, after which it is then converted into ceramic after shaping. Among the various precursors that have been used for the PDCs-synthesis of hBN nanosheets, polyborazylene (PBN) has shown to lead to the production of large-area highly crystallized hBN at temperatures as low as ~1400 ºC [36–40]. This is owing to its relatively high ceramic yield and high purity. Most importantly, the B/N ratio within PBN polymer is ideal to produce stoichiometric hBN, with the only contaminants being hydrogen atoms that are easily removed during the ceramization step. Despite the synthesis of large-area and well-crystallized hBN nanosheets via the conventional PDCs process, the search for further improvements so as to synthesize well-crystallized hBN nanosheets at relatively lower sintering temperatures, still remains a paramount necessity and occupies the activity of today’s scientific community. One such technology, which has been overlooked for almost a decade, is the use of halides in combination with lithium nitride (Li₃N) [41]. In this process, the Li₃N acts as a crystallization promoter to produce highly crystallized hBN, whereas the halides help to facilitate the melting of Li₃N, leading to the synthesis of hBN nanosheets at temperatures as low as ~800 ºC at a prolonged time of 22–56 h. As such, this work reports on the use of PDCs process coupled with Li₃N-additives in combination with the group II halides, in particular, barium fluoride (BaF₂), to produce large-area well-crystallized hBN nanosheets at low temperatures. The work provides a new platform for the large-scale synthesis of hBN nanosheets at cost-effective conditions without compromising the physicochemical properties of hBN nanosheets.

2. Materials and Methods

2.1. Procedure

The pure monomer of borazine was prepared from a reaction between ammonium sulfate ((NH₄)₂SO₄ ≥ 99%, Aldrich, Saint-Louis, MO, USA) and sodium borohydride (NaBH₄, 98% purity, Aldrich, Saint-Louis, MO, USA) in tetraethylene glycol dimethyl ether or tetraglyme (C₁₀H₂₂O₅, ≥ 99%, Alfa Aesar, Ward Hill, MASS, USA) solvent, as reported by Wideman et al [42]. After the purification of borazine via distillation, the polymeric precursor was obtained by through the poly-condensation of borazine at 55 ºC inside a pressure-sealed system under argon for 5 d; generating colorless polyborazylene (PBN) [15,39,43,44]. For the synthesis of boron nitrides nanosheets (BNNs); inside the glove-box and under argon atmosphere, lithium nitride (Li₃N, 99.4%, Alfa Aesar, Ward Hill, MASS, USA) at a 5 wt.% ratio, as a crystallization agent, and varying amounts (0–10 wt.%) of barium...
fluoride (BaF\textsubscript{2}, 99%, Alfa Aesar, Karlsruhe, Germany), as a melting-point reduction agent, were added to PBN, then the mixture was homogenized via stirring for 10 min. After which the suspension was heated to 200 °C in an alumina crucible and kept for 1 h to give a solid-state polymer [41]. Finally, the stabilized mixture was annealed for 1h at 1200 °C (1 °C/min) under inert nitrogen (N\textsubscript{2}, 98%, Air Liquide, Paris, France) atmosphere.

2.2. Methods

The morphology and electronic structure of the synthesized materials were ascertained using various characterization techniques. The crystal structure of the hBN nanosheets was confirmed using a powder X-ray diffractometer (Bruker, Billerica, MASS, USA) (PXRD) Bruker D8 Advanced, equipped with the Cu-K\textsubscript{α} radiation source and using the PMMA zero-background substrate. MEB Zeiss Merlin Compact scanning electron microscopy (SEM), at the accelerating voltage of 80 kV, was used to determine the morphology of the nanomaterials. Further morphological analyses were carried on the MET Phillips CM120 transmission electron microscope (TEM) (Philips, Amsterdam, the Netherlands) at 120 kV. The degree of crystallization of the hBN nanosheets was determined in the backscattering geometry using the HORIBA Jobin-Yvon Labram Evolution Raman spectrometer (Horiba, Kyoto, Japan) at 532 nm laser excitation wavelength. The functional groups and surface interactions of the BN nanosheets nanostructures were investigated using SAFAS Monaco SP2000-IR700 spectrometer in the range of 4000–600 cm\textsuperscript{-1}. The surface area, pore volumes, and diameters of the as-prepared samples were acquired from the BELsorpi mini, after degassing the samples for 4 h at 100 °C, thereafter, adsorption and desorption of ultra-pure N\textsubscript{2} gas was performed. Chemical composition and bonding configurations for the bulk hBN samples were determined by XPS using a PHI Quantera SXM spectrometer (Physical Electronics, Chanhassen, MN, USA). A monochromatized aluminum K\textsubscript{α} radiation was used with a 200 μm spot diameter and a take-off angle of 45°, before and after 2 μm sputtering with Ar\textsuperscript{+} ions. Charge compensation was provided by an in-lens electron flood gun and separate low energy argon ion source. Finally, thermogravimetric analyses were determined using the TGA/DSC2 form Mettler Toledo (Mettler Toledo, Columbus, Ohio, USA). An hBN sample of ~15 μL mass was placed into a 150 mg alumina crucible with pierced lid, after which the decomposition profile of the sample was established from 30–1400 °C, at a heating rate of 20 °C/min, under 50 μL mL\textsuperscript{-1} Ar.

3. Results and Discussion

Growth of large-area hBN nanosheets at low temperatures and atmospheric pressure conditions was successfully achieved through a BaF\textsubscript{2}-assisted PDCs technique. After synthesis, the structural, composition and electronic properties were investigated using XRD, XPS, Raman, and IR spectroscopies, whereas the morphological properties were determined using TEM and SEM microscopies.

3.1. Structural and Electronic Properties

3.1.1. Powder XRD Analysis

The composition and crystallinity of the BNNS samples synthesized with addition of various amounts of BaF\textsubscript{2} and annealed at 1200 °C were examined by the powder XRD (Figure 1a), after which their XRD patterns were compared with that of standard hBN (ICCD card #: 34–421). The results for all samples showed the characteristic fingerprint diffraction patterns for highly crystallized hexagonal boron nitride (hBN) (Figure 1a); evident by the pronounced (002) diffraction peak at 2θ ≈ 26.5–26.8°, as well as the less intense (004), (110) and (112) peaks centered at 2θ ≈ 55.4°, 2θ ≈ 76.2°, 2θ ≈ 81.7°, respectively. However, a much deeper investigation of the diffraction patterns revealed the formation of two phases of hexagonal (hBN) and rhombohedral (rBN) boron nitride (Figure 1b) for samples with low contents of BaF\textsubscript{2} (i.e. 0 and 2.5 wt%). On the other hand, upon increasing the BaF\textsubscript{2} content from 5–10 wt%, the XRD patterns indicated that the most favored principal phase is the hBN (Figure 1b), as the relative intensities of the (101) and (012) peaks for rBN are relatively diminished.
As such, the results showed the significance of the addition of BaF₂ to the PBN/Li₃N pre-ceramization mixture towards improving the crystallinity of the hBN phase. It can, therefore, be proposed that improved crystallinity of the hBN nanosheets is achieved through the facilitation of faster melting of Li₃N by BaF₂ [41], thereby leading to lower formation temperature as compared to our previous studies [38,40,43]. However, it is also noteworthy to mention that regardless of the improved crystallinity with increasing BaF₂ content (10 wt%), the presence of unmelted impurities from Li and Ba complexes is evident from the XRD patterns, thereby compromising the quality of the inherent as-synthesized BNNS samples. This was also observed with a further increase in BaF₂ content (20–30 wt%, not shown here). Thus, the addition of equally small amounts (5 wt%) of both Li₃N and BaF₂ led to the formation of crystalline hBN nanosheets at relatively low temperatures and atmospheric conditions.

![Figure 1. (a) and (b) XRD patterns for BNNS samples annealed at 1200 °C after the addition of 5 wt% Li₃N together with 0–10 wt% of BaF₂.](image)

A further indication of an improved crystallinity of the hBN phase within the BNNS samples was through the separation of the (100) and (101) peaks accompanied by the symmetrically sharpening of (002), as well as increasing intensities of (102), (110), and (112) peaks. Furthermore, the interlayer d₀₀₂-spacing values of ~3.34 Å for all samples were determined to be close to that of high-crystalline bulk value for the commercial hBN samples (Table 1), suggesting a good crystallization rate for each sample after the addition of BaF₂. The slightly lower interlayer distance for the 5 wt% BaF₂ sample (~3.331 Å) is indicative of the improved d-p interaction occurring between the p-orbital electrons in hBN and those in the d-orbital of barium [45], consequently resulting in a better-crystallized sample upon the introduction of BaF₂. Similar results were observed with the addition of higher BaF₂ contents, with the 20 wt% BaF₂ sample registering a d₀₀₂-spacing value of ~3.328 Å, whereas that of the 30 wt% BaF₂ sample was ~3.326 Å. Finally, the degree of crystallization of the hBN phase within the BNNS samples was evaluated in terms of the “graphitization index, GI” (Table 1), as indicated by Equation (1):
\[
GI = \left( \frac{(100)_{area} + (101)_{area}}{(102)_{area}} \right)
\]

Table 1. XRD parameters of hBN nanosheets in comparison to the commercial hBN.

| Amount of BaF₂ (wt%) | Graphitization Index (GI) | d_{002}-spacing (Å) | Position (2θ) |
|----------------------|--------------------------|---------------------|---------------|
| 0                    | -                        | 3.32                | 26.5          | -  | - |
| 2.5                  | -                        | 3.34                | 26.6          | -  | - |
| 5                    | 3.83                     | 3.33                | 26.7          | 41.57 | 43.83 |
| 10                   | 1.88                     | 3.34                | 26.8          | 41.56 | 43.81 |
| hBN \text{comm}      | 1.19                     | 3.33                | 26.7          | 41.60 | 43.83 |

The significance of the value for the G.I. is that the higher the value is the less the three-dimensional ordering is within the hBN and the reverse is true [46–50], therefore implying a lateral growth of the hBN crystallites. So, in the light of this information, Table 1 shows that BNNS samples synthesized with the addition of 5 wt.% BaF₂ can be considered to have a less three-dimensional ordering in the crystal structure, as evident by the G.I. value of 3.83. This has later been confirmed by TEM analyses which showed the formation of larger hBN nanosheets upon addition of 5 wt% BaF₂.

3.1.2. XPS Analysis

The XPS analysis was used as a surface-sensitive and standard technique for determining the overall elemental composition (at. %) and different bonding states within the as-synthesized samples. Figure S1a shows a typical surface XPS survey scan for the hBN samples and the spectra exhibited at least five peaks: two distinct peaks corresponding to B1s (190.9 eV) and N1s (397.8 eV), two weak peaks corresponding to O1s (532.1 eV) and Ba3d (780.1 eV), as well as another peak corresponding to advantageous C1s (284.2 eV). However, after sputtering a 2 µm surface from the samples with Ar⁺ ions, no carbon was found within the bulk of the samples: thus, indicating the removal of any adsorbed atmospheric carbon atoms. Therefore, by taking the integrated peak areas of the B1s, N1s, O1s, Li1s, and Ba3d from the XPS survey spectra, the overall elemental composition of the bulk samples was determined as a function of increasing BaF₂, as depicted in Table 2. It can be seen that both boron and nitrogen concentrations increased with addition of more BaF₂, thereby leading to B/N ratios of 1.62%, 1.64%, 1.57%, and 1.50% for the hBN nanosheets grown after addition of 0, 2.5, 5, and 10 wt% BaF₂, respectively (Table 2). The observed decrease in the B/N ratio corroborated XRD results by indicating that the addition of BaF₂ makes coalescence of bigger hBN domains more, thus compromising the quality of the resultant hBN nanosheets. On the other hand, the increasing lithium content between the addition of 0 and 2.5 wt% BaF₂ is suggestive of the formation of lithium complexes due to the presence of Ba as well as the formation of smaller hBN domains, as later confirmed by high-resolution XPS and TGA analysis. Improved growth of hBN domains through faster melting of these lithium complexes in the presence of Ba atoms was indicated by the decreasing Li1s content after the addition of 5 and 10 wt% BaF₂, which was also followed by further reduction of the oxygen content with increasing BaF₂ content.

Table 2. Atomic compositions of bulk samples of hBN nanosheets.

| Elements (at%) | B/N ratio |
|---------------|-----------|
| Amount of BaF₂ (wt%) | B | N | O | Li | Ba |
| 0             | 50.3 | 31.1 | 13.8 | 4.8 | _ | 1.62 |
| 2.5           | 52.3 | 31.9 | 9.9 | 5.3 | 0.5 | 1.64 |
| 5             | 56.9 | 36.3 | 5.8 | 1.0 | _ | 1.57 |
To determine the different bonding configurations of each constituent element (B, N, O, Li and Ba) in the bulk hBN samples as a function of BaF$_2$ content, their high-resolution XPS spectra were fitted with Lorentzian–Gaussian (GL30) peaks using the CasaXPS software. The B1s for all samples exhibited a broad spectral peak with a full width at half maximum (FWHM) was in the range of 1.8–2.7 eV (Figure 2a). This is wider than the reported FWHM value for B in high-quality hBN (0.92 eV) [51]. This signifies the presence of different bonding states for B atoms. Therefore, to determine the chemical environments of the B atoms in the nanosheets, the B1s spectral peaks were deconvoluted into three component peaks centered at 190.9–191.0, 192.0–192.1, and 193.2–193.4 eV, respectively. These corresponded to the contribution from sp$^2$-BN bonds in high-quality hBN, B–O bonds in B$_2$O$_2$, as well as Li$_2$B$_4$O$_7$ bonds, respectively [51–53]. The relatively high intensity for the sp$^2$-BN peak component is an indication that the boron atoms are expectedly and predominantly bonded to nitrogen atoms into a hexagonal lattice to form large domains of hBN. Furthermore, an increase in the relative concentration of the sp$^2$-BN up to addition of 5 wt.% BaF$_2$ could be suggestive of the presence of larger hBN domains, whilst a decrease in its concentration is an indication of a degradation of the hBN domains, but formation of smaller fragments of hBN that are prone to be terminated by oxygen atoms. The results thus corroborated XRD results, as the quality of the hBN nanosheets was observed to be compromised with the increasing addition of BaF$_2$. The formation of larger and better quality hBN domains was further ascertained by the position of the B–O bonds as a function of BaF$_2$ content. For instance, the positions of the B–O bonds were found to be red-shifted with increasing BaF$_2$ content up to the addition of 5 wt.% after which it continued to blue-shift with addition of more BaF$_2$. This, therefore, suggested the existence of different bonding states around/within the B–O domains. In particular, the B–O peak position in 0 wt.% BaF$_2$ hBN nanosheet sample (~193.2 eV) was closer to that of B–O bonds in B$_2$O$_2$ (~192.55 ± 0.05 eV) [52,54,55], an indication that boron atoms at the defective edges are surrounded by oxygen atoms to form regions of B$_2$O$_2$ domains. However, on increasing the BaF$_2$ content up to addition of 5 wt.%, the B–O peak position red-shifted to ~192.1 eV, an indication that there is substitution of the oxygen atoms in the B$_2$O$_2$ domains with boron and/or nitrogen atoms due to the formation of larger and better quality hBN domains, thereby leading to presence of less saturated B$_2$O$_2$ domains. Due to the degradation of the structure as a result of impurities from Ba and Li, the peak position of B–O bonds was observed to blue-shift to ~193.4 eV, signifying the formation of B$_2$O$_2$ domains at the defect regions of the hBN domains and/or the small fragments of uncoalesced PBN.

Confirmation of the bonding states obtained from the B1s was supported by the deconvolution of the XPS N1s spectra (Figure 2b). At least two component peaks centered at 397.9–398.0 eV and 398.9–399.5 eV were observed for all and these were ascribed to the formation of sp$^2$N–B and N–H$_2$ bonding configurations [36,51,53,56,57]. Lack of the component peak at higher binding energies (i.e. ~401 eV), corresponding to NO$_x$ bonding states, is indicative that all the nitrogen atoms within the samples have a high affinity of boron atoms to form hBN domains. Furthermore, the bonding states of the oxygen, lithium, and barium atoms was determined by peak fitting of the O1s, Li1s, and the Ba3d high-resolution XPS spectra, as shown in Figure S1. From Figure S1b, it can be seen that the O1s was fitted to at least two component peaks. The peaks centered at 531.8–532.4 eV and 529.5–530.1 eV can be ascribed to the contribution from O–B and O–Ba bonds, respectively [54,58]. Interestingly, the component peak at 529.5–530.1 eV could be attributed to the presence of metallic oxide bonds such as O–Li [59,60]; thus, highlighting the ambiguity of using the O1s to assign the bonding configurations of the as-synthesized samples. However, the relative concentrations of the component peaks indicate that most of the oxygen atoms are bonded to the metallic impurities. Moreover, the intensity of the O1s spectra for all samples is observed to decrease with increasing BaF$_2$ content, which is in good agreement with the survey spectra, thereby indicating the improved quality with BaF$_2$ content. The bonding states of oxygen atoms were confirmed by the deconvolution of the Ba3d spectra (Figure S1c), which depicted the presence of $\alpha$ (779.8–781.3 eV) and $\beta$ (795.1–798.8 eV) couplings of barium oxide [61,62]. Lack of component peaks corresponding to bonding states such as Ba–N [63] is suggestive that the Ba atoms remain bonded to oxygen atoms to form the stable oxide
form outside the hBN domains, thereby, having no impact on the overall structure of hBN nanosheets. Finally, the contribution from the residual lithium was indicated by the peak at ~55.7 eV on the Li1s spectra (Figure S1d), which can be attributed to the presence of Li2BO2 bonds [59,60]. The presence of these bonds can be ascribed to the role played by the crystallization agent (LiN) when it breaks down PBN, to form individual nucleates of B-N, that can aggregate and grow into hBN domains. The relatively large intensity of Li2BO2 peak at lower BaF2 content (0 & 2.5 wt.%) could suggest incomplete decomposition of PBN by LiN, whereas the decreasing intensity of peaks with increasing BaF2 content is indicative of the effect of BaF2 in dissolving the Li-complexes (i.e. Li2BO2, Li2BO4, or Li3BN2), thereby freeing and permitting boron and/or nitrogen atoms to contribute in the growth of hBN domains.

**Figure 2.** High-resolution XPS spectra showing a deconvoluted peak of (a) B1s, and (b) N1s for all hBN nanosheet samples after the addition of 0–10 wt% of BaF2.

### 3.1.3. Raman and FT-IR Analysis

Further structural and electronic properties of the as-synthesized BNNS materials were evaluated using Raman spectroscopy. Like graphene and despite the minor difference in the stacking sequence (i.e. AB4, graphene versus AA′hBN), Raman spectroscopy is also a powerful technique for determining the crystallinity and quality of hBN nanomaterials. As a result, Figures 3a display Raman spectra taken from ~10 different areas of the BNNS samples. The spectra showed the first-order active Raman vibrating mode of hBN (E2g) [27,64–67] centered at ~1365.4 ± 1.6 cm⁻¹. To determine the crystallinity of hBN materials, studies by Nemanich et al. have reported that there is a direct correlation between the finite-size effects within hBN with the inherent position and broadening of the Raman vibrational modes [67]. Their report indicated that the E2g vibrational mode blue-shifted and broadened with decreasing crystallites sizes. From Figure S2b, the full width at half maximum (FWHM) values for the samples was found to decrease with BaF2 content up to 5 wt%, from 17.01 cm⁻¹ for the 0 wt% BaF2 hBN sample to 11.07 cm⁻¹ for the 5 wt% BaF2 hBN sample (Figure S2b). The FWHM values thus signify the formation of larger crystallites and subsequently improvement in the crystallinity and quality of the 5 wt% BaF2 hBN sample. Further confirmation of improved crystallinity was observed through red-shift in the position of E2g vibrational mode from ~1366.9 ± 0.25 cm⁻¹ for the 0 wt% BaF2 sample to ~1365.3 ± 0.21 cm⁻¹ for the 5 wt% BaF2 sample, after which the peak position blue-shift up to ~1366.4 ± 0.08 cm⁻¹ upon increasing the BaF2 content to 10 wt.%. The proposed growth mechanism is illustrated in scheme 1. In summary, the Raman data demonstrated that it is possible to achieve high-quality and crystalline BNNS at atmospheric conditions and reasonably moderate temperatures, in comparison with those hBN nanosheets that have been prepared at high temperature and high pressure [13,38–40].
Figure 3. (a) Raman spectra, (b) FTIR spectra, and (c) TGA profiles for BNNS samples annealed at 1200 °C after the addition of 5 wt% Li3N and 0–10 wt% BaF2.

Fourier transform infrared (FT-IR) spectroscopy constitutes one of the most used techniques for the identification and characterization of phases in BN nanomaterials. This is due to the fact that the sp² and sp³ hybridization states of B-N bonds can be easily distinguished by the well-defined adsorption bands [68–70]. Therefore, to determine the influence of the addition of BaF2 on the surface functionalizations of the hBN samples, the FTIR measurements were performed at room temperature. As expected, by two IR active transverse optical (TO) phonon modes of sp² bonded B–N were observed (Figure 3b). The broad and asymmetrical E₁u adsorption band at ~1340–1360 cm⁻¹ corresponded to the in-plane boron-nitrogen-boron (B–N–B) stretching vibrational modes within one basal plane, whereas the sharp and symmetrical A₂u adsorption band, centered at ~740–760 cm⁻¹, can be ascribed to the out-of-plane B–N–B bending vibrational modes between two or more basal planes [68,70]. Further analysis of the FT-IR spectra of the modified hBN samples revealed a red-shift of the E₁u adsorption band, whilst the A₂u adsorption band was observed to blue-shift with increasing BaF2 content.

A slight red shift of the B–N–B stretching mode up to the addition of 5 wt% BaF2 relative to the 0 wt.% BaF2 sample (Figure S2c, blue line-circles) could be suggestive of the addition of strain in the crystal lattice due to the lateral growth of the crystal sizes within the basal plane. However, an introduction of impurities and incomplete and/or growth of individual small crystallites with increasing BaF2 content (10–30 wt.%), leads to a blue-shift in the A₂u vibrational mode due to removal strain. Similarly, a blue-shift was observed for the E₁u mode for 2.5 and 10 wt.% BaF2 hBN samples in comparison to the 5 wt.% BaF2 sample (Figure S2c, red line-squares). This can be attributed to the progressive loss of long-range order, in the form of the bond-angle and bond-length disorder, due to the formation of structural defects and distortion of the crystalline structures [71]. The results are in good agreement with the XRD data that indicated the presence of barium and lithium impurities upon the addition of more BaF2. On the contrary, a slight red-shift for the 5 wt.% BaF2 hBN sample further supported the formation of large-area hBN nanosheets, thus leading to the addition of strain in between the basal plane.
3.1.4. Thermal Stability Investigation

The thermogravimetric analysis (TGA) curves depicting the normalized percentage mass-change of the as-synthesized hBN samples as a function of temperature are illustrated in Figure 3c. The plots showed that the decomposition of the samples can be considered to occur in at least four steps. The samples are observed to be stable up to ~60 °C, after which subsequent decomposition begins at different on-set temperatures (region I), which can be ascribed to the varying crystallinity of the samples. In particular, the on-set temperature for the 0 wt% BaF$_2$ sample was determined to be ~74 °C; whilst those for modified samples were found to be ~67 °C, ~82 °C, and ~69 °C, for 2.5, 5, and 10 wt% BaF$_2$ hBN samples, respectively. The highest on-set temperature for the 5 wt% BaF$_2$ sample is in corroboration with XRD and Raman analyses which indicated improved crystallinity, thus indicating the difficulty of breaking the stable bonds at relatively low temperatures. On the other hand, the lowest onset decomposition temperature for 2.5 wt% BaF$_2$ sample can be attributed to the incomplete restructuring of the hBN lattice to form larger crystallites due to insufficient amount of BaF$_2$. Owing to the formation of these incomplete crystallites, the entire bond structure is weakened, thereby leading to faster degradation. In the case of 10 wt% BaF$_2$ sample, the earlier onset decomposition temperature can be ascribed to the disruption of the lattice of the hBN structure due to the fast melting of Li$_3$N in the presence of larger content of BaF$_2$ and formation of impurity complexes, as depicted by XRD analysis. Consequently, a weakened structure that is prone to easy loss of hydrogen atoms and faster decomposition is formed. Region II, with mass losses occurring at temperatures between 150–600 °C, is due to the decomposition of lower energy bonds, such as dehydrogenation of intercalated H$_2$ (~436 kJ/mol) between the hBN nanosheets as well as hydrogen atoms bonded to the edge-defects (i.e. B–H bonds at ~330 kJ/mol; N-H bond at 314 kJ/mol; O–H bond at ~428 kJ/mol; adsorbed H–OH bonds at ~498 kJ/mol) [72–74] within the hBN lattice. The decomposition of these low energy bonds is thus depicted by the presence of two peaks on the DTG curves (Figure S1d). Between 600–1200 °C (region III), an increase in mass of 0.22%, 0.35%, and 0.42% was observed for 2.5, 5, and 10 wt% BaF$_2$ hBN samples, respectively. On the contrary, further decrease in the decomposition profile of the 0 wt% BaF$_2$ hBN sample was recorded in this region, and corresponds to the removal of α-Li$_3$BN$_2$ and β-Li$_3$BN$_2$ complexes at ~860 °C and 920 °C, respectively [75,76], depicted by XPS. Thereafter, the final degradation of the 0 wt% BaF$_2$ hBN sample is observed beyond 1200 °C. Interestingly, the 0 wt% BaF$_2$ hBN sample does not decompose completely to 0 wt% (Figure S1d), however, only ~1.2 mg (8.52%) of the sample was decomposed (region IV). This can be attributed to the oxidation of BN by residual O$_2$ inside the TGA oven from the inert gas used (i.e. Ar, 99%, Alphagaz), leading to the subsequent formation of thin layer of thermally stable boron trioxide (B$_2$O$_3$, ~1850 °C$_{boiling}$, and ~1500 °C$_{sublimation}$) [77,78] on the surface of the nanosheets as well as evolution of a certain amount of nitrogen oxides (NO$_x$) [79], which ultimately prevents further decomposition. Upon addition of 2.5 wt% BaF$_2$, a mass increase of ~0.22% (~30.1 µg) in region III occurred within a temperature range of ~910–1220 °C, attributed to the removal of the α-Li$_3$BN$_2$ complexes as well as the formation of thermally stable B$_2$O$_3$ layer. However, with the addition of more BaF$_2$ from 5 to 10 wt%, the mass increase was recorded to be ~0.27% (~36.0 µg) and ~0.42% (~61.5 µg) in the temperature ranges of ~630–1330 °C and ~770–1310 °C, respectively. In both cases, the faster formation of the thermally stable B$_2$O$_3$ layer could suggest the lack of the Li$_3$BN$_2$ complexes as a result of the faster melting of Li$_3$N, which was facilitated by the addition of BaF$_2$, thereby corroborating the XRD data. The rate of oxidation for the BaF$_2$-samples can be ascribed to the purity, crystallinity and specific surface area (SSA) [80,81]. For instance, highly-crystalline BN with a small SSA, as in the case of the 5 wt% BaF$_2$ hBN nanoplatelets, provides less reactive sites for oxidation and thus a smaller weight gain, in comparison to moderately-crystalline BN with a small SSA (10 wt% BaF$_2$ hBN) and poorly-crystalline BN (2.5 wt% BaF$_2$ hBN). Beyond 1350 °C (region IV), the decomposition of the B$_2$O$_3$ layer by the residual boron atoms leads to the formation and removal of the gaseous dioxodiborane compounds (B$_2$O$_2$) [82–84], as based on Equation (2):
The differential scanning calorimetry (DSC) curve (Figure S3a) provided important information regarding the heat-flow arising by a series of physical or chemical procedures, such as decomposition, oxidation, as a function of temperature. An endothermic peak was observed for 0 and 5 wt.% BaF₂ hBN samples at ~151.1 °C and ~147.1 °C, respectively; whereas no thermal phenomena were observed for other samples (Figure S3i). This corresponded to the endothermic reactions associated with the dehydrogenation of the samples. Further endothermic reactions associated with the decomposition of all samples were depicted by the decrease in the heat flow in the temperature range of ~480–620 °C (Figure S3ii). Moreover, small exothermic peaks appeared in the temperature range of ~640–1400 °C (Figs. S3iii and S3iv), indicating the oxidation of the samples as shown by the increasing mass on TGA thermograms and hence confirming the transformation of BN to B₂O₃. All parameters related to the TGA/DSC measurements are presented in Table S2.

\[
\frac{3}{2}B_{(g)} + \frac{3}{2}B_2O_{3(\ell)} \rightarrow B_2O_{2(g)}
\] (2)

Scheme 1. Summary of growth mechanism for BNNS samples annealed at 1200 °C after the addition of 5 wt.% Li₃N and (a) 0-2.5 wt.%, (b) 5 wt.%, (c) 10 wt.% of BaF₂.

3.1.5. Surface Area Determination

Surface area and pore-size distribution of hBN are essential properties for its potential application in energy storage and conversion devices as well as in biotechnological applications. As such the specific surface area (SSA), pore-size distribution of the as-synthesized hBN samples were determined using the multi-point Brunauer–Emmet-Teller (BET) method through adsorption/desorption measurements of N₂ at 77K. From the N₂ adsorption/desorption isotherm curves (Figure 4a), the hBN synthesized with the addition of BaF₂ demonstrated a type II isotherm with increasing BaF₂ content; an indication of the formation of macroporous or non-porous materials [85]. Minor N₂ amounts were adsorbed under relatively lower relative pressures \((P/P_0 < 0.01)\) for all samples, with no hysteresis loop being observed under low pressure \((P/P_0 < 0.45)\); an indication of the absence of micropores and mesopores on the materials’ surface. Interestingly, the hysteresis loop
was observed to decrease between adsorption/desorption under higher pressures ($P/P_0 > 0.45$) with increasing BaF$_2$ content. Thus, the physical adsorption mechanism on the as-synthesized hBN samples can be described as follows: without BaF$_2$ content (i.e. 0 wt.%), the N$_2$ adsorption is a formation of an unrestricted multilayer after the completion of a monolayer, followed by delayed desorption of N$_2$. Thus, this accounts for the high specific surface area recorded for the 0 wt.% BaF$_2$ hBN sample (~8.7 m$^2$/g), which can then be attributed to the presence of a relatively small amount of macropores (Figure. 4b) and/or the external rough surface [80,86]. On the other hand, with the addition of BaF$_2$ content, the adsorption mechanism can be presumed to be following the adsorption and desorption of the monolayer of N$_2$ onto the material’s external rough surface of the basal planes due to the non-porous morphology of the samples. This is shown by the adsorption curve which does not reach a plateau at a relatively high pressure close to unity ($P/P_0 \sim 0.99$), but rather extends indefinitely. Therefore, based on the multi-point BET method, the specific surface areas for the samples were then determined from the BET plots extracted using points between $0.05 < P/P_0 < 0.30$ (Figure. S4) and these were found to be 8.7, 3.5, 3.6, and 2.9 m$^2$/g for samples prepared after addition of 0, 2.5, 5, and 10 wt% of BaF$_2$, respectively. Table S2 gives a summary of the textual properties of these samples.

![Figure 4.](image)

**Figure 4.** (a) N$_2$ adsorption/desorption isotherms and (b) pore-size distribution plots for the as-synthesized hBN samples annealed at 1200 °C after addition of 0–10 wt.% of BaF$_2$.

### 3.2. Morphological Analysis

The morphological properties of the hBN nanosheets obtained at 1200 °C after the addition of varying amounts of BaF$_2$ were investigated by scanning electron microscopy (SEM). Figure 5a displays the typical SEM micrographs of the as-synthesized 5 wt.% BaF$_2$ hBN nanosheets, whereas the micrographs of other samples, as well as the commercial sample of hBN (99.5%, Alfa Aesar), are represented in Figure S4. The dimensions of crystals of the hBN samples were then determined to be $2.74 \pm 0.67$, $8.41 \pm 0.71$, and $5.30 \pm 0.31$ µm for samples annealed after the addition of 2.5, 5, and 10 wt.% of BaF$_2$, respectively. On the contrary, it was difficult to determine the flake-size for the 0 wt.% BaF$_2$ hBN sample since the sample was an agglomerated mass of irregular shaped and jagged-edged plate-like crystals (Figure S5a). However, upon the introduction of BaF$_2$, the morphology of the crystals becomes more defined (Figures 5a and S5b,c); like that of the well-defined disc-shaped and homogenous nanoplatelets of the commercial hBN sample (Figure S5d). For instance, with the addition of 5 wt.% BaF$_2$, the hBN nanosheets display a much more well-defined, smooth-edged and homogenous plate-like morphology. This is expected as both Raman and XRD data suggested an improved crystallinity of the hBN nanosheets upon the addition of 5 wt% BaF$_2$. Although an increase in the BaF$_2$ content to 10 wt% (Figure S5c) also led to the formation of well-defined and plate-like nanosheets, the size of the nanosheets was compromised as evident by the breakage of the nanoplatelets. More degradation in the size of the nanoplatelets was also observed with samples synthesized with the addition of 20 and 30 wt% BaF$_2$. The formation of smaller hBN nanosheets with increasing BaF$_2$ content may be attributed to the abrupt melting of Li$_3$N due to the presence of more
cations form BaF$_2$, thus consequently leading to incomplete crystallization of $h$BN from PBN. Similar results were reported by various groups, whereby they showed that not only does the different usage of cations led to the formation of different morphologies of $h$BN nanosheets, but an increase in these cations resulted in compromised morphologies of such $h$BN nanostructures [87,88]. The final determination of the morphological properties of the $h$BNNS samples was performed using the transmission electron microscopy (TEM). Low magnification TEM micrographs (Figures 5b and Figure S6) illustrated that the samples are mainly composed of overlapping sheet-like structures, with crystal sizes of $0.89 \pm 0.01$, $2.88 \pm 0.74$, $3.32 \pm 0.25$, and $3.15 \pm 0.67$ µm, for samples annealed after addition of 0, 2.5, 5, and 10 wt.% of Ba F$_2$, respectively. Remarkably, the low-magnification TEM images further corroborated the SEM micrographs by depicting the formation of thinner and larger $h$BN nanosheets, with well-defined disc-shape, after the addition of 5 wt% of BaF$_2$.

**Figure 5.** (a) SEM and (b) TEM micrographs of as-synthesized BNNS materials annealed at 1200 °C after the addition of 5 wt.% BaF$_2$.

**4. Conclusions**

Hexagonal boron nitride ($h$BN) nanosheets exhibiting well-defined morphology and large crystal size were successfully synthesized at low temperatures (1200 °C) and atmospheric pressure through modification of the polymer-derived ceramics (PDCs) technique with varying amounts of barium fluoride (BaF$_2$). The XRD, Raman, and XPS data revealed the formation of highly-crystalline $h$BN nanosheets with the FWHM of 11.07 cm$^{-1}$ and a G.I. value of ca. 3.83 upon addition of 5 wt% BaF$_2$ to the pre-ceramization mixture of PBN and 5 wt% Li$_3$N. Morphological analysis revealed formation well-defined shape for the nanosheets with an average size ranging from 2.74 ± 0.67 µm to 8.41 ± 0.71 µm from SEM and 2.88 ± 0.74 µm to 3.32 ± 0.25 µm from TEM after chemical exfoliation. On the other hand, thermogravimetric analysis showed that the addition of BaF$_2$ led to the formation of less stable samples, as evidenced by the ease of oxidation at high temperatures. However, this work paves the way for the production of large-scale and good-quality $h$BN crystals at relatively low temperature and atmospheric pressure conditions.

**Supplementary Materials:** The following are available online at https://www.mdpi.com/2079-4991/10/3/443/s1, **Figure S1.** (a) Survey spectra of the sample before sputtering with Ar$^+$ ions, as well as high resolution of (b) O1s, (c) Ba3d, and (d) Li1s.; **Figure S2.** Relation of increasing addition of BaF$_2$ to (a) FWHM of (002) XRD peak (b) Raman peak FWHM, and (c) FTIR out- and in-plane vibrational modes. (d) DTG plot of the as-synthesized samples.; **Figure S3.** (a) DSC plots for the as-synthesized samples: (i)-(iv) Regions of exothermic and endothermic reaction during sample decomposition; **Figure S4.** Multi-point BET plots in the relative pressure range 0.05 < P/P$_0$ < 0.30 for the as-synthesized samples.; **Figure S5.** SEM micrographs of as-synthesized BNNS samples annealed at 1200 °C, after addition of 5 wt% Li$_3$N and (a) 0, (b) 2.5 and (c) 10 wt% BaF$_2$. (d) SEM micrograph of nanoplatelets of commercial $h$BN (99%, Alfa Aesar); **Figure S6.** Low magnification TEM images of BNNS samples annealed at 1200 °C, after addition of 5 wt%
Li3N and (a) 0, (b) 2.5 and (c) 10 wt% BaF2.; Table S1. TGA parameters for the as-synthesized hBN samples; Table S2. Textual parameters of the as-synthesized hBN samples

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Abbreviation:
PDCs—polymer derived ceramics
hBN—hexagonal boron nitride
wt%—weight percentage
Li3N—lithium nitride
BaF2—barium fluoride

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