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Preparation of Polyborazylene-Derived Bulk Boron Nitride with Tunable Properties by Warm-Pressing and Pressureless Pyrolysis

J. Li,[†] S. Bernard,*[,†] V. Salles,[†] C. Gervais,[‡] and P. Miele[†]

[†]*Laboratoire des Multimateriaux et Interfaces (UMR CNRS 5615), Université Lyon1, Université de Lyon, 43 bd du 11 Novembre 1918, 69622 Villeurbanne Cedex, and* [‡]*Laboratoire de Chimie de la Matière Condensée, UMR CNRS 7574, Université Pierre et Marie Curie, Collège de France, 11 place M. Berthelot, 75005 Paris, France.*

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The polymer-derived ceramics (PDCs) route has been combined with a warm-pressing process to synthesize for the first time boron nitride workpieces avoiding the conventional sintering process. A polyborazylene was synthesized with a controlled degree of cross-linking suitable to be warm-pressed into cylindrical green bodies which were pressureless pyrolyzed into disk-shaped boron nitride workpieces. On the basis of elemental analyses, differential scanning calorimetry (DSC), and thermomechanical analyses (TMA), the best polyborazylene candidates are those prepared by self-condensation of borazine ($B_3N_3H_6$) at 60 °C under static argon in an autoclave. They displayed a chemical formula of $[B_{3.0}N_{3.5}H_{4.5}]_n$, a glass transition in the temperature range 88−120 °C, a controlled dimensional change upon heating under load and a high ceramic yield. Such properties provided (i) adjusted viscoelastic properties and sufficient plasticity to be warm-pressed under 74 MPa at 60 °C into disk-shaped bodies with 13 mm in diameter in a stable operation and (ii) retention of the polymer shape during the further pyrolysis at 1450 °C in a nitrogen atmosphere. Disk-shaped $B_{3.0}N_{2.95}$ workpieces with a relative density of 86.3% were obtained. Solid-state ^{11}B NMR has been used to investigate the polyborazylene-to-BN conversion while XRD, SEM, and He-pycnometry have been performed on workpieces pyrolyzed between 1450 and 1800 °C. Densification occurred in this range to generate bulk boron nitride ($B_{3.0}N_{2.9}$) with a relative density as high as ~93%.

Introduction

In the development of materials that can be used at high temperatures, the interest for nitride ceramics grew during the past decades in relation to their thermostructural and chemical durabilities. In this category of materials, hexagonal-boron nitride (*h*-BN) is a specific binary compound that proposes similarities in its crystal structure with graphite. In *h*-BN, the in-plane atoms are bonded through localized sp^2 hybridization, whereas the out-of-plane layers are bonded by delocalized weak π orbital. This layered lattice structure of *h*-BN provides anisotropic properties. As general properties, it displays high-temperature stability, good lubricating properties, oxidation resistance, and good thermal conductivity, being an electrical insulator. In addition, it is nonreactive toward molten metals such as aluminum, iron, copper, and hot silicium, which reinforces its potential for high-temperature applications.[1]

The fabrication of hexagonal-boron nitride (*h*-BN but commonly expressed in the present paper as boron nitride or BN) is usually made by conventional powder technology requiring nitridation of boric oxide and use of additives during the further sintering process.[2−5] Beside the fact that the use of boric oxide inherently induces the presence of boron oxynitride phases BN_xO_y in the derived BN material,[6] the main disadvantage of the sintering process lies in the use of sintering additives which guarantee the densification of the material but tend to diffuse into the material. These drawbacks negatively influence the properties of the sintered material. As a consequence, it is required to develop alternative processing techniques that can avoid the use of oxygen-containing precursors and sintering additives to allow the production of pure bulk boron nitride with a compositional homogeneity. In a recent article, we reported the preparation of bulk boron nitride with a relative density of 96.3% through the combination of a spray-pyrolysis process from borazine followed by an additive-free sintering of derived ultrafine powders.[7] In the present study, we develop a second strategy from borazine based on the polymer-derived ceramics (PDCs) route in combination with a

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*Corresponding author. E-mail: Samuel.Bernard@univ-lyon1.fr. Tel: +33 472 433 612. Fax: +33 472 440 618.

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warm-pressing process that avoids the application of a sintering process while maintaining a high density.

The PDCs route is an attractive way for the production of advanced pure ceramic materials and offers significant advantages over traditional ceramic processing techniques.[8−11] The main motivation to implement the PDCs method lies in the special advantages that are offered by preceramic polymers in controlling ceramic compositions and structures, and in processing materials in particular shapes that are difficult, or even impossible to obtain by conventional routes. In details, the innovative idea behind this procedure is that the atomic structure of the final material is designed by the atomic composition and the structure of the preceramic polymers. The latter are organometallic/inorganic compounds containing the basal structure of the desired ceramics as well as peripherical organic components which can offer functionalities to some extent. Using the PDCs method, ceramics can be produced in the form of near dense materials without sintering process according to the strategy depicted in Figure 1a.

The successful fabrication of such materials requires first the optimization of the processing steps following the synthesis of a cross-linked and cross-linkable polymer, the polymer powder compaction, and the pyrolysis of the green parts into ceramics with a high ceramic yield upon pyrolysis.

Up to now, the preparation of polymer-derived boron nitride materials has concerned low-dimensional structures such as fibers,[12−16] coatings[17−20] and nanotubes,[21] as well as high-dimensional structures such as carbon fibers-reinforced BN composites (C_f/BN).[22] Most of the reports concerning the preparation of nonoxide ceramic workpieces from preceramic polymers are focused on highly cross-linked Si-containing polymers including polycarbosilane,[23,24] polycarbosilazanes[25−30] and boron-modified polysilazanes[31−33] to prepare dense and crack-free silicon carbide (SiC), silicocarbonitride (SiCN), and silicoboron carbonitride (SiBCN) materials, respectively.

Therefore, the intent of the present paper is to investigate for the first time the design and the processing of additive-free boron nitride from a polyborazylene based on the strategy shown in Figure 1a. The polyborazylene was synthesized from borazine with an adjusted cross-linking degree, and thereby was warm-pressed at different temperatures with controlled plastic and thermal properties and then pyrolyzed into bulk boron nitride specimens at various final temperatures following the strategy depicted in Figure 1b. In the present paper, we provide a detailed picture of the preparation process and report the full characterization of the polymer as well as the chemical composition, structure, and density of the final materials. The development of such materials may open new opportunities in exploring chemical and physical properties and can be useful for many areas of modern science and technology including thermal management and jewelry/watches (as solid lubricants) applications.

Experimental Section

Materials. Argon (>99.995%) was purified by passing through successive columns of phosphorus pentoxide, siccapent, and BTS catalysts. Schlenks were dried at 120 °C overnight before pumping under vacuum and filling them with argon for synthesis. Manipulation of the chemical products was made inside an argon-filled glovebox (Jacomex BS521; Dagneux, France) dried with phosphorus pentoxide. The borazine and derived polyborazylenes are unstable in air. Therefore, all manipulations were carried out under inert conditions.

Polymer Synthesis. The operating procedure to prepare borazine was reported in our previously published paper.[21] In a typical process, 22 mL (17.8 g) of the as-prepared borazine were introduced at 0 °C in a 75 mL autoclave (from Equilabo, France) with a temperature and pressure controller (Parr N 4836 Model) in an argon-filled glovebox using Teflon-lining to easily remove the polymer from the autoclave. Borazine was gradually heated to 60 °C (1 °C min^{-1}), and then kept at this temperature until stabilization of the internal pressure. The process created a final internal pressure of 121.1 bar after a dwelling time of ~240 h.

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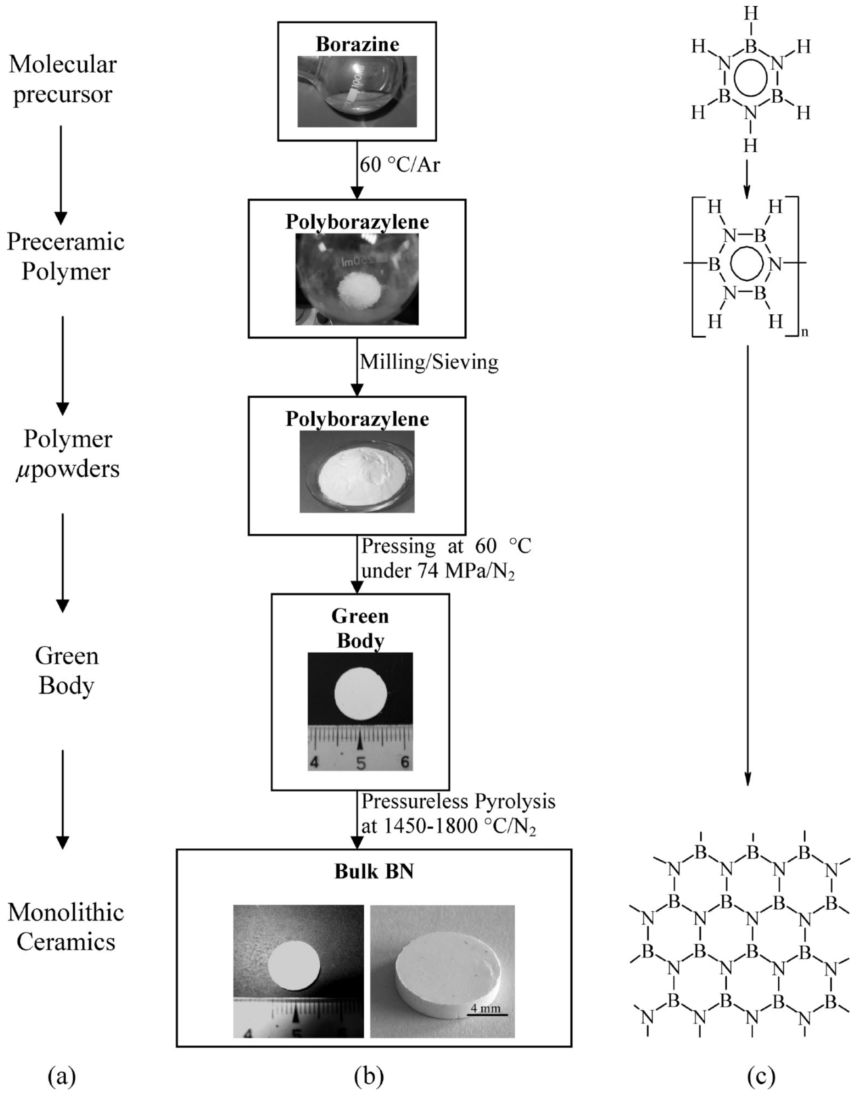

Figure 1. (a) Polymer-derived ceramics (PDCs) sequence to bulk ceramics. (b) Schematic illustration of the approach for preparing highly dense boron nitride: The first step corresponds to the milling and sieving of the polymer. The second step corresponds to the controlled warm-pressing of the powders into a green body, and the third step is the pressureless pyrolysis of the latter into a representative disk-shaped BN specimen. (c) Basic suggested structures involved in the synthesis procedure from borazine via polyborazylene to BN.

The condensation of borazine generated significant amounts of H_2 that were carefully removed from the autoclave after cooling to room temperature (RT). The autoclave was then introduced inside an argon-filled glovebox to recover ~15.2 g of a white powder.

Anal. Found (wt %): B, 37.46; N, 56.47; H, 5.26; O, 0.79 $[B_{3.0}N_{3.5}H_{4.5}O_{0.04}]_n$ ($[86.63]_n$). IR (KBr/cm^{-1}): ν(N−H) = 3445 m; ν(B−H) = 2509 m; ν(B−N) = 1435 s; δ(B−N−B) = 890 m; δ(BH) = 690 m. ^{11}B MAS NMR (128.28 MHz/ppm): δ = 31 (BN_2H), 27 (BN_3). TGA (N_2, 1000 °C, 90.9% ceramic yield): 25−70 °C, Δm = 0%; 70−280 °C, Δm = 4.5%; 290−750 °C, Δm = 3.5%; 750−1000 °C, Δm = 1.1%.

Warm-Pressing and Pyrolysis. The as-prepared polymer was milled then sieved into microparticles with size ≤80 µm. In the next step, polymer particles (~250 mg) were uniaxially warm-pressed with 74 to 133 MPa in a steel die (diameter 13 mm) with a heating mantle from RT to 110 °C using an automatic uniaxial press (Atlas Auto T8 model from Specac) setup in a nitrogen-filled glovebox (Table 1). The polymer powders were introduced in the steel die, heated to the set temperature, loaded at the temperature of warm-pressing and the temperature was held for 0.5 h. The samples were slowly deloaded during cooling down to RT within an 1 h. Typical dimensions of the cylindrical green bodies were 13 mm × 2.6 mm.

Table 1. Warm-Pressing Conditions

green bodies derived from 3	pressing temperature (°C)	pressure (Mpa)
3−1	RT	74
3−2	60	74
3−3	60	104
3−4	60	133
3−5	90	74
3−6	110	74

Green bodies were then placed in boron nitride boats, and then transferred into a silica tube inserted in a horizontal furnace which is connected to the glovebox to prevent oxygen contamination of the samples. The tube was pumped under vacuum and refilled with nitrogen (99.995%). Subsequently, the samples were subjected to a cycle of ramping of 0.5 °C min^{-1} to 1000 °C, dwelling there for 2 h, and then cooling down to RT at 1 °C min^{-1}. A constant flow (120 mL min^{-1}) of nitrogen was passed through the tube. Then, the pyrolyzed samples in boron nitride boats were introduced in a graphitic furnace (Gero Model HTK 8) and a boron nitride plate covered the workpieces placed in the BN boat avoiding possible carbon contamination from the furnace. The furnace was subsequently pumped then refilled with nitrogen to undergo a heating program through a cycle of ramping of 0.5 °C min^{-1} to 1450 °C, dwelling there for 2 h, and then cooling down to RT at 1 °C min^{-1}. A constant flow (200 mL min^{-1}) of nitrogen was passed through the furnace.

Anal. Found (wt %): B, 43.42; N, 55.01; O, 0.82; H, C < 0.30 ($B_{3.0}N_{2.95}O_{0.04}$). IR (KBr/cm^{-1}): ν(B−N) = 1385 s; δ(B−N−B) = 795 m.

In order to study the effect of the final pyrolysis temperature on the morphological, structural and textural properties of samples, bulk boron nitride were also prepared following the same procedure at 1600 and 1800 °C, dwelling there for 2 h, and then cooling down to RT.

Characterization. Thermal properties were studied by differential scanning calorimetry (DSC, Mettler Toledo DSC TA 8000) in an argon atmosphere between −50 and 150 °C at a heating rate of 10 °C min^{-1} in alumina crucibles. Thermomechanical analysis (TMA) of the uniaxially pressed polymer powders (Mold diameter 5 mm) has been investigated in a nitrogen atmosphere (Mettler Toledo TMA/SDTA 840) using a compressive load (0.8 N) upon heating to 400 °C. Thermogravimetric analysis (TGA) of the polymer-to-ceramic conversion was recorded on a Setaram TGA 92 16.18. Experiments were performed in a nitrogen atmosphere at 5 °C min^{-1} from RT to 1000 °C using silica crucibles (sample weight of ∼80 mg) at ambient atmospheric pressure. Experimental differential thermogravimetric (DTG) data were generated from TGA measurements. Bulk compositional evolution of the polymer was made in the Service Central de Microanalyse de Vernaison (Vernaison, France) for boron, carbon, and hydrogen and in SPCTS lab (Limoges, France) for nitrogen and oxygen elements. The methods included thermal decomposition of powders under oxygen to measure the hydrogen and carbon contents, under an inert atmosphere for the measurement of nitrogen and oxygen contents, and by ICP-MS (from Thermofisher) for boron content. ^{11}B MAS NMR spectra of pulverized polyborazylene intended for warm-pressing, and derived samples isolated at 300, 800, and 1800 °C were recorded at 9.4 T on a Bruker Avance400 wide-bore spectrometer operating at 128.28 MHz, using a Bruker 4 mm probe and a spinning frequency of the rotor of 12.5 kHz. Spectra were acquired using a spin−echo $\theta-\tau-2\theta$ pulse sequence with $\theta = 90°$ to overcome problems of probe signal. The τ delay (80 μs) was synchronized with the spinning frequency and recycle delay of 1s was used. Chemical shifts were referenced to $BF_3(OEt)_2$ ($\delta = 0$ ppm). Bulk materials were characterized using a Philipps PW 3040/60 X'Pert PRO X-ray diffraction system. Disk-shaped boron nitride was placed on XRD sample holders (PVC) for data collection. Cu Kα ($\lambda = 1.54$ Å) radiation with a Ni filter was used with a working voltage and current of 40 kV and 30 mA, respectively. Scans were continuous from 20 to 90° 2θ with a time per step of 0.85 s in increments of 0.017° 2θ. Peak positions were characterized by comparison with JCPDS files of the standard material (JCPDS card No 34−0421). Debye−Scherrer line broadening was used to calculate average crystallite sizes (out-of-plane size $\bar{L}_c$ and in-plane size of $\bar{L}_a$) from the XRD powder patterns. FTIR spectra of borazine and the derived polyborazylene were recorded from a Nicolet Magna 550 Fourier transform-infrared spectrometer by introducing the borazine between two KBr windows and by mixing 2 wt % polyborazylene with KBr powders followed by its compaction into a pellet. Infrared spectroscopy of the pulverized bulk BN samples was taken with a Nicolet 380 FT-IR spectrometer coupled with the Attenuated Total Reflectance (ATR) accessory. True densities of green bodies and bulk boron nitride were measured by Helium pycnometry (Micromeritics AccuPyc 1330). Comparison was made with the pulverized samples for the green bodies and with theoritical *h*-BN density (2.27 g.cm^{-3}) for bulk boron nitride samples. The microstructure of bulk boron nitride was characterized on polished surfaces (up to 9 μm with silicon carbide disk) by scanning electron microscopy (SEM) and optical microscopy with Hitachi S800 scanning electron microscopy and Olympus BX60 optical apparatus, respectively. For SEM observations, samples were mounted on stainless pads and, due to their insulating properties; they were sputtered with ∼10 Å of a Pd/Au mixture to prevent charging during observation.

Results and Discussion

Boron Nitride Workpieces Processing. As previously mentioned, boron nitride is known to exhibit poor sinterability most probably due to the low self-diffusion coefficients of boron atoms in the nitrides.[2−5,34] It is therefore required to use oxide sintering additives such as B_2O_3 and CaO to obtain boron nitride with a density approaching the density of pure boron nitride (∼90% of the theoretical density). However, it is not possible to obtain fully dense and pure boron nitride in such conditions. The application of sintering additives should be avoided whenever possible to reach the expected properties of *h*-BN. The objectives of the current study is to establish a detailed synthesis procedure and provide a comprehensive characterization of polyborazylenes with controlled degrees of cross-linking, and then explore their potential to be warm-pressed into disk-shaped specimens and produce dense and crack-free bulk boron nitride through a pressureless pyrolysis as schematically depicted in Figure 1b.

Synthesis of Polyborazylenes and Characterization. Keeping in mind that the ceramic retains a memory of its polymer origin, we have focused our work on the use of a polyborazylene as preceramic polymer. Such a polymer is synthesized with controlled cross-linking degrees by self-condensation of borazine at low temperature inside an autoclave (Figure 1c). A large number of studies have been focused on the thermopolymerization of borazine and the identification of polymerization mechanisms.[17,20,21,35−43] In the fifties and sixties, several authors

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Table 2. Properties of the Polyborazylenes That Have Been Prepared by Self-Condensation of Borazine in a 75 mL Autoclave under Argon

polyborazylene	M_{Borazine} (g)	$T_{\text{Synthesis}}$ (°C)	internal pressure (bar)	dwelling time (h)	$M_{\text{Polyborazylene}}$ (g)/physical State	empirical formulas[b]	weight loss (%)[c]
1[20]	14.6	45	5.6	~120	13/liquid	$[B_{3.0}N_{3.0}H_{4.8}]_n$	70
2[21]	16.2	50	30.1	~192	14.1/liquid	$[B_{3.0}N_{3.8}H_{4.0}]_n$	53.2
3	17.8	60	121.1	~240	15.2[a]/solid	$[B_{3.0}N_{3.5}H_{4.5}]_n$	9.1

[a] A low proportion of **3** could not be recovered from the autoclave. [b] Referenced to $B_{3.0}$; oxygen values < 2 wt%. [c] The weight loss was measured by TGA experiments performed in a nitrogen atmosphere up to 1000 °C (5 °C min^{-1}).

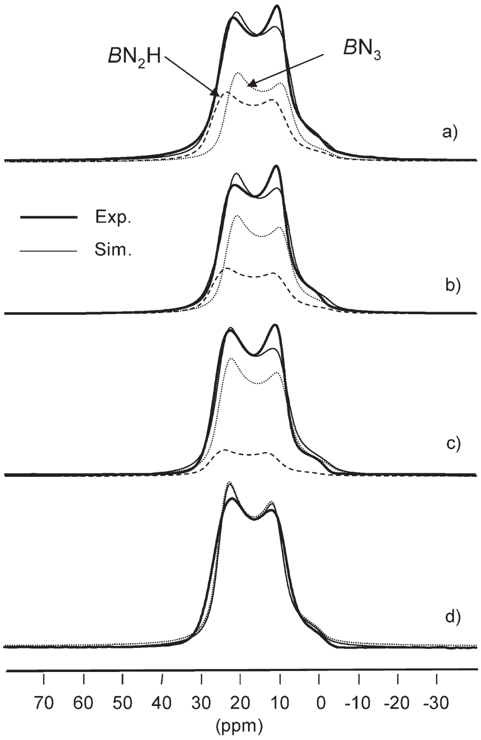

Figure 2. Solid-state ^{11}B MAS NMR experimental and simulated spectra of polyborazylene (a) **3** and **3**-derived samples pyrolyzed at (b) 300, (c) 800, and (d) 1800 °C.

studied the self-condensation of borazine forming biphenylic and naphtalenic-type structures given the ideal polyborazylene structure proposed in Figure 1c.[35-38] Sneddon et al. were the first to isolate a solid borazine-based polymer by heating the borazine under vacuum at 70 °C for approximately 48 h.[39-41] Elemental analyses of the polyborazylene suggested the formation of a branched-chain or partially cross-linked structure. The as-synthesized polyborazylene was purified in a second step before delivering boron nitride through pyrolysis under nitrogen to 1200 °C. Following a similar procedure, Kim and Economy developed a liquid polyborazylene without purification to infiltrate carbon fibers preforms and produce C_f/BN composites.[22] In 2001, Babonneau et al. reported the complete structural characterization of a solid polyborazylene by ^{15}N and ^{11}B solid-state NMR. Authors demonstrated the presence of two types of boron sites including *B*HN$_2$ and *B*N$_3$ and two types of nitrogen sites (*N*HB$_2$ and *N*B$_3$) as well as eight-members rings in addition to the expected six-members borazine rings.[43] More recently, we have focused on the design of polyborazylene-derived boron nitride shapes including coatings,[20] and nanotubes[21] by tuning the operating parameters of the polyborazylene synthesis. Table 2 reports some of the properties of the polyborazylenes that have been prepared at different temperatures by self-condensation of borazine in a 75 mL autoclave under static argon. It should be mentioned that the heating was stopped when internal pressure due to H_2 evolution did not increase anymore, and temperature was thus allowed to cool to RT.

NMR and FT-IR experiments confirmed that thermopolymerization proceeded through ring condensation forming naphthalene-like derivatives and hydrogen release (NH and BH absorption bands decrease in intensity and the sharp B−N absorption at 1454 cm^{-1} changes to a broad absorption band at 1435 cm^{-1}). The degree of cross-linking is controlled by the final polymerization temperature and the corresponding dwelling time.

Polyborazylenes **1** and **2** have been obtained by self-condensation of borazine at 45 and 50 °C, respectively. These compounds are liquid and they have been explored to prepare coatings[20] and nanotubes.[21] In contrast, heating of borazine at 60 °C (polyborazylene **3**, Table 2) results in a solid compound that is a prerequisite condition to generate workpieces. We have therefore focused on sample **3** to explore its potential as precursor of bulk BN.

The ^{11}B solid-state NMR spectrum of **3** (Figure 2a) shows a large signal in the region of tricoordinated boron atoms that was tentatively simulated with two sites at 27 ppm (C_Q = 2.7 MHz, η = 0.1) and 31 ppm (C_Q = 2.9 MHz, η = 0.1) assigned to *B*N$_3$ and *B*HN$_2$ environments, respectively, in good agreement with ref 43.

Weight losses and decomposition rates (Differential Thermogravimetric (DTG) data) of the polyborazylene **3** have been monitored during TG experiments in a nitrogen atmosphere up to 1000 °C (Figure 3).

As reported in Figure 3a, polymer **3** displays a low weight loss during polymer decomposition, suggesting that it can be directly warm-pressed into green body then converted into bulk samples with retention of the polymer shape by pyrolysis. In comparison, as-synthesized Si-containing polymers[23-33] need to be further cross-linked before warm-pressing to retain the polymer shape after pyrolysis.

In details, polyborazylene **3** undergoes a three-step weight loss with an initial weight loss occurring from 70 to 290 °C (4.5 wt %), a second one from 290 to 750 °C (3.5 wt %), and a third one from 750 to 1000 °C (1.1 wt %), which is the maximum temperature of the TG apparatus. The low weight loss of **3** is related to its highly cross-linked structure and its ability to further

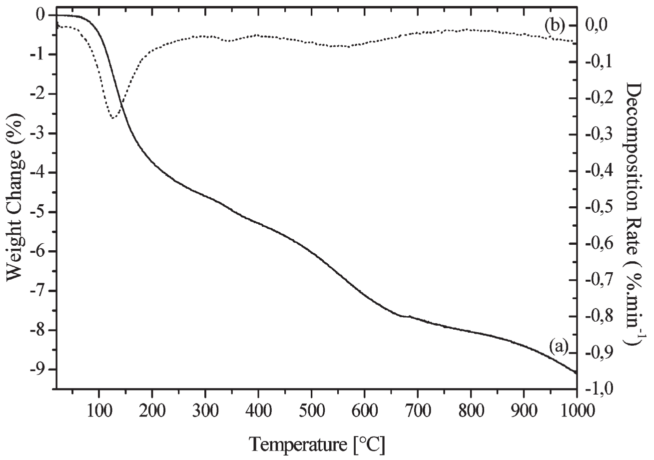

Figure 3. (a) TGA and (b) DTG curves for polyborazylene **3** in a nitrogen atmosphere. Heating rate: 5 °C/min.

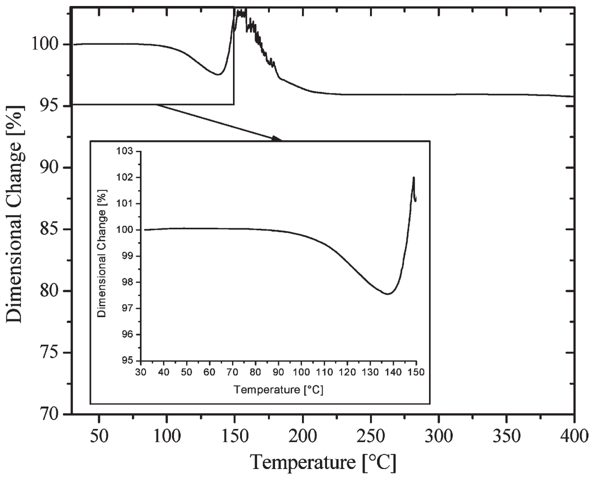

Figure 4. TMA curve for polyborazylene **3** in a nitrogen atmosphere. Heating rate: 5 °C/min.

cross-link by dehydrocoupling upon heating according to the presence of reactive B−H and N−H units. Both avoided depolymerization of **3** during the polymer-to-ceramic conversion. The polymer-to-ceramic conversion occurred with retention of the basic structure of the polymer as shown with the ^{11}B solid-state NMR spectra (Figure 2) of **3**-derived samples isolated at 300 (Figure 2b) and 800 °C (Figure 2c). Spectra showed an increase of the relative amount of $B\mathrm{N}_3$ environments compared to $B\mathrm{HN}_2$. However, it is clear that the polymer-to-ceramic conversion is not fully achieved at 1000 °C according to the fact that the polyborazylene-derived material produced at 1000 °C contains residual hydrogen. Residual hydrogen is removed during the further heat-treatment to 1200 °C.[39,41] The associated DTG curve (Figure 3b) confirmed data obtained from weight loss measurements, i.e., multistep weight loss, and it distinguished the starting of a fourth region at 900 °C.

It is important to emphasize that the overall weight loss measured at 1000 °C is closely related to the temperature at which polyborazylenes are synthesized. As illustrated in Table 2, the weight loss of polyborazylenes decreased from **1** to **3**, and thereby with the increase in their corresponding degree of cross-linking. Polyborazylenes synthesized at temperature higher than 60 °C based on the same procedure did not show fundamental changes in the ceramic yield. As an example, the latter is increased by only 1.7% for polyborazylene synthesized at 70 °C, which is not a fundamental improvement compared with polyborazylenes synthesized at 60 °C. Furthermore, reactivities of polyborazylenes decreased with the degree of cross-linking and those prepared at 70 °C showed reduced viscoelastic properties. Keeping in mind that both a high ceramic yield and polymer plasticity are prerequisite requirements for preparing polymer-derived workpieces, we definitely selected polyborazylenes prepared by self-condensation of borazine at 60 °C to deliver boron nitride workpieces.

We have investigated the capability of polyborazylene **3** to be plastically deformed during the further warm-pressing step. The as-synthesized polyborazylene was easily milled using an agate ball milling and then sieved through an 80 μm screen in an argon-filled glovebox to deliver fine-grained powders (see Figure 1b). Thermomechanical analysis (TMA) of the uniaxially pressed polymer powders (mold diameter 5 mm) has been investigated in a nitrogen atmosphere to study the plastic capability of polyborazylene **3** using a compressive load (0.8 N) upon heating to 400 °C. From the TMA curve (Figure 4), it is observed that the polyborazylene slightly shrinks in thickness starting from 60 °C and the low dimensional change (2.5%), reflecting the plastic deformation of the polymer, extends over 45 °C from 85 to 130 °C.

Above 130 °C, the polymer swells most probably because of the occurrence of the polymer decomposition, which is in good agreement with DTG and DSC data. The former highlighted the highest decomposition rate between 60 and 200 °C. The latter showed that polyborazylene **3** transforms into a softened compound through a glass transition that extended over ~30 °C going from 88 to 120 °C, whereas an exothermic peak due to the polymer decomposition was observed between 120 and 170 °C. These results prove that polyborazylene **3** contains a sufficient amount of peripheral single-bound borazine groups and displays a tailored cross-linking degree allowing it to be deformable upon heating through the application of uniaxial pressure for grain bonding and specimen consolidation. Such results showed that a maximum temperature of 130 °C is required to densify the polyborazylene **3**. However, warm-pressing tests showed that because of the higher pressure ($P \geq 74$ MPa) applied during the warm-pressing process in comparison with TMA ($P = 0.04$ MPa), the polyborazylenes **3** can already be compacted at lower temperatures. In accordance with the narrow temperature range over which warm-pressing occurs, we focused on the temperature range from RT to 110 °C for the warm-pressing step to precisely give the ideal temperature of warm-pressing at which sample **3** is consolidated.

Warm-Pressing Process. As previously mentioned, we investigated the uniaxial warm-pressing process of polyborazylene powders (~ 250 mg) in a steel die (diameter

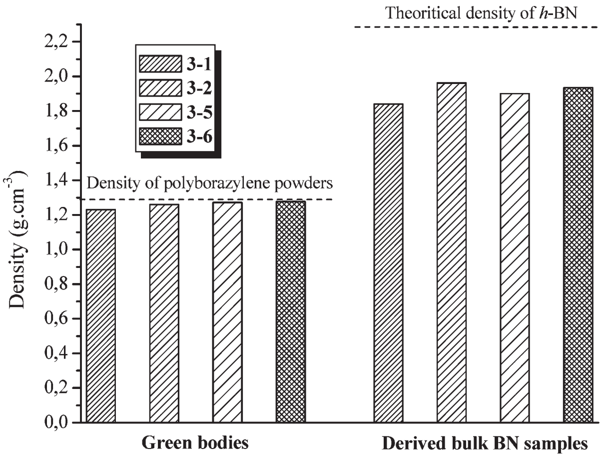

Figure 5. Changes in the density of samples **3−1**, **3−2**, **3−5**, and **3−6**: green bodies obtained with warm-pressing pressure of 74 MPa at RT (**3−1**), 60 °C (**3−2**); 90 °C (**3−5**) and 110 °C (**3−6**) (dwelling time of 0.5 h), and derived disk-shaped BN after pyrolysis at 1450 °C (dwelling time of 2 h) in a nitrogen atmosphere.

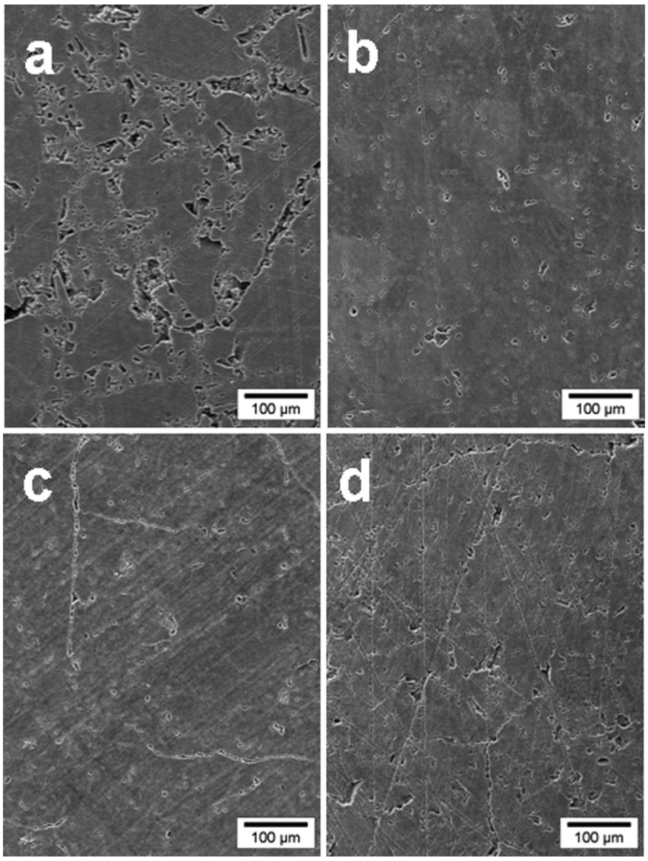

Figure 6. Scanning electron micrographs of the polished surface of representative disk-shaped boron nitride obtained by pyrolysis at 1450 °C (dwelling time of 2 h) in a nitrogen atmosphere: samples (a) **3−1**, (b) **3−2**; (c) **3−5**, and (d) **3−6**.

13 mm) under different conditions in terms of temperatures and pressures (Table 1). Figure 5 reports the variation of the bulk density of green bodies prepared at four temperatures under a pressure of 74 MPa (samples **3−1**, **3−2**, **3−5**, and **3−6**; see Table 1). The measured bulk density of the polyborazylene powders from helium pycnometry was 1.28 g cm^{-3}, which means that the compacted polyborazylene **3** reaches relative density from ~95% (sample **3−1**) to almost 100% (samples **3−5** and **3−6**). Especially, the sample **3−2** displays a relative density of ~99% (Figure 5).

These high density values are probably related to the plastic deformation capability of the polyborazylene **3**. The polymeric particles easily slide under pressure at RT to be arranged. However, the bulk density of the green body **3−1** obtained by pressing at RT is the lowest and the SEM image (Figure 6a) of the polished surface of the derived disk-shaped boron nitride specimen obtained after heat-treatment to 1450 °C in a nitrogen atmosphere shows that it contains a large proportion of pores with relatively large sizes.

According to the increase in density in the green bodies with warm-pressing, we suggest that the particles melt together upon heating at 60 °C (sample **3−2**) to form a relatively dense disk-shaped green specimen through an adequate cohesion of the particles. It is even probable that intra- and interparticular cross-linking reactions between pendant B−H and N−H groups of neighboring particles start at this temperature favoring the coalescence of particles, thereby increasing the bulk density of the green body. Such reactions probably occur faster at higher temperatures (90 °C (sample **3−5**) and 110 °C (sample **3−6**)) to slightly increase the bulk density values of corresponding green bodies. After a pyrolysis to 1450 °C with a dwelling time of 2 h, the relative density values are around 87% in the derived boron nitride samples, but SEM images showed that cracks and pores gradually appeared with the increase in the pressing temperature (Figure 6b−d). We therefore suggest that the occurrence of cross-linking reactions in samples **3−5** and **3−6** contributes to the highest interparticulate bonding of the particles during the warm-pressing at such temperatures delivering fully dense green bodies (see Figure 5). In contrast, this full densification probably prevents the diffusion of gaseous byproduct from the reaction sites to the surface of samples during the further pyrolysis involving foaming and appearance of pores and cracks. Within this context, we fixed the optimal temperature for warm-pressing at 60 °C. Concerning the pressure values, we observed that the green bodies obtained by warm-pressing under pressures of 104 MPa (**3−3**) and 133 MPa (**3−4**) were systematically damaged by the mechanical demolding. Delamination occurred after the warm-pressing process at 60 °C, especially when the thickness of the monoliths was higher than 3 mm, which is caused by the presence of interlaminar shear and normal stresses under impact loading. In contrast, the green body **3−2** (74 MPa) was reproducibily intact after mechanical demolding whatever the thickness. As a consequence, we concluded that the optimal pressure for warm-pressing at 60 °C was 74 MPa (sample **3−2**). In parallel, we anticipated the fact that the dwelling time at the pressing temperature affected the density of derived green bodies. In fact, we tested several dwelling time at 60 °C under 74 MPa going from 0.5 to 1.5 h, and density values did not change. We therefore deliberately fixed a dwelling time of 0.5 h.

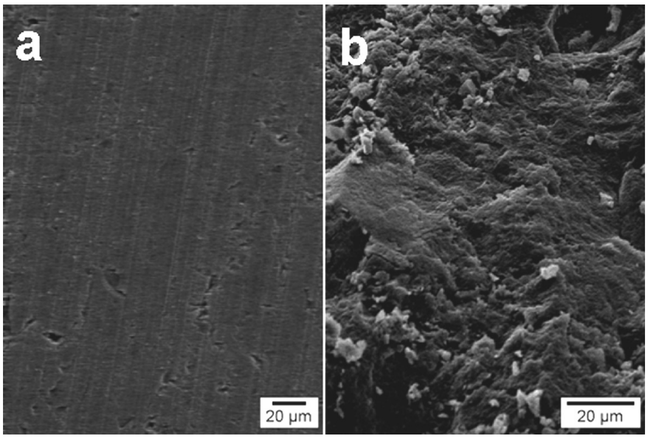

Figure 7. Scanning electron micrographs of the polished surface (a) and the fracture surface (b) of representative disk-shaped boron nitride (sample **3−2**) obtained at 1450 °C (dwelling time of 2 h) in a nitrogen atmosphere.

Pyrolysis Process. Green bodies obtained by warm-pressing at 60 °C under a pressure of 74 MPa for 0.5 h (sample **3−2** in Table 1) were pyrolyzed in a nitrogen atmosphere at 1450 °C into disk-shaped materials of an empirical formula $B_{3.0}N_{2.95}$. We referenced the found formula to $B_{3.0}$ and we deliberately omitted hydrogen and carbon (< 0.3 wt %) and oxygen (0.82 wt %) contents in accordance with their neglectable amount. Raman spectroscopy also confirmed the presence of *h*-BN and the absence of carbon (see Figure SI-1 in the Supporting Information); the latter could result from a contamination by the graphite furnace. Analyses were made on the pulverized samples of the material. On the basis of the composition found for the polymer, the compacted polyborazylene **3** transformed into a boron nitride material under nitrogen in 85.8% yield, which is lower than measurements made by TGA after pyrolysis at 1000 °C in a nitrogen atmosphere. This confirmed the fact that the weight loss is not fully achieved after TGA experiments (see Figure 3a). It is interesting to notice that warm-pressed samples shrank by 14.2% in thickness and by 13.5% in diameter with simultaneous change in density. Despite the loss in volume, the boron nitride bodies retained the cylindrical geometry of the green bodies. The resulting bulk boron nitride samples exhibit a surface with a low proportion of open pores with small sizes (Figure 7a) and an internal dense uniform monolithic texture (Figure 7b).

This confirmed the appropriate viscous behavior of the polyborazylene during warm-pressing and suggested that the most important operating factors including the properties of the starting polymer, the warm-pressing temperature, the pressure, and the residence time are controlled during processing. In particular, the incomplete densification after warm-pressing (relative density of ∼99%) seems important because it allows the volatilization of the gaseous byproduct during the pyrolysis step. This was already mentioned for the preparation of bulk Si-based ceramics.[27,33]

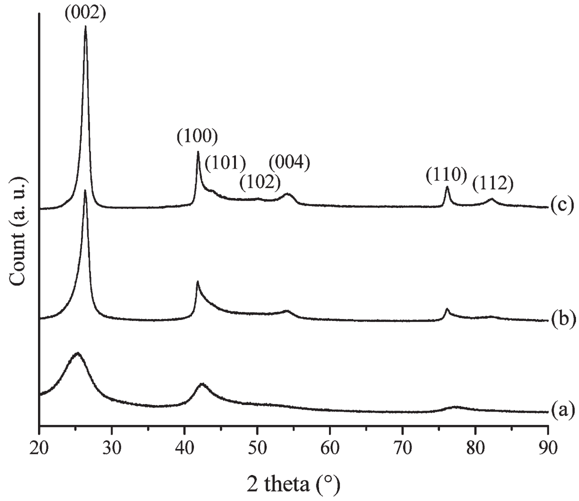

Figure 8. X-ray diffractograms of representative disk-shaped boron nitride (sample **3−2**) obtained at (a) 1450, (b) 1600, and (c) 1800 °C (dwelling time of 2 h for the final temperature) in a nitrogen atmosphere.

Furthermore, optical micrographs of the polished specimen pointed out that pull-out and/or cracking did not occur during polishing and that boron nitride disks displayed an excellent machinability.

Characterization of Bulk Boron Nitride Workpieces. $B_{3.0}N_{2.95}$ compacts prepared at 1450 °C have been characterized by X-ray diffraction (Figure 8a). To adjust the structure of bulk **3−2**-derived boron nitride samples, we prepared derived specimens at 1600 (Figure 8b) and 1800 °C (Figure 8c) for 2 h. This heat-treatment does not affect the chemical compositions of samples because the sample obtained at 1800 °C exhibited a chemical composition of $B_{3.0}N_{2.9}$.

In bulk samples prepared at 1450 °C (Figure 8a), the presence of the broad (002) peak ($2\theta = 25.35°$; fwhm = 3.5°) and diffuse (10)/(100) and (004) peaks which are shifted from the Bragg angles of BN is representative of a disordered structure. In particular, the asymmetric shape of the (002) peak and the absence of the (102) and (112) peaks suggests in a coherent way the presence of turbostratic boron nitride. It should be mentioned that two disordered BN phases, i.e., turbostratic-BN (*t*-BN) and amorphous-BN (*a*-BN), are usually found in addition to the hexagonal phase.[37,44−47] The turbostratic BN phase is characterized by a random stacking sequence of the (002) layers and a disorientation of these layers around the *c*-axis, whereas the amorphous BN phase represents a structure disordered at atomic level. XRD patterns of such phases are significantly distinct from that of *h*-BN.

For the sample treated at 1600 °C (Figure 8b), the (002) peak is more intense and sharper (fwhm = 1.14°), indicating that the crystallite size becomes larger in the *c*-axis direction. The peak position shifts toward 2θ values of BN (26.35 vs 26.76°, JCPDS card No 34−0421). This is

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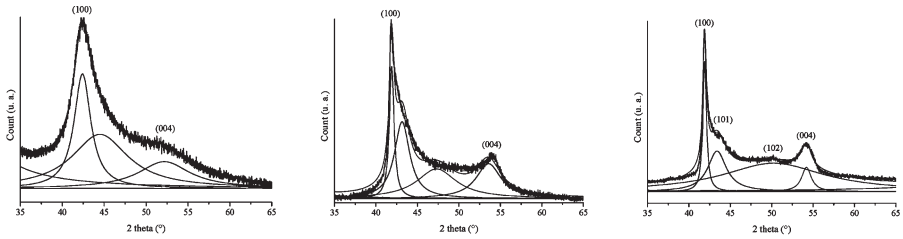

(a) (b) (c)

Figure 9. Deconvoluated (100)/(101) peaks for samples prepared at (a) 1450, (b) 1600, and (c) 1800 °C.

Table 3. Positions and FWHM of the (002) and Deconvoluated (100)/(101) Peaks and Calculated Out-of-Plane ($\bar{L}_c$) Size and In-Plane ($\bar{L}_a$) Size for Each Sample

samples **3**−**2**	(002) peak position (deg)/ width (deg)	(100) peak position (deg)/ width (deg) (deconvoluated)	$\bar{L}_c$ (nm)	$\bar{L}_a$ (nm)	d_{002} (nm)
as-prepared (1450 °C)	25.35/3.5	42.40/2.44	2.35	7.26	0.352
1600 °C	26.35/1.14	41.90/0.68	7.15	25.57	0.339
1800 °C	26.41/0.95	41.9/0.49	8.60	35.6	0.338

also the case for the more intense and sharper (100)/(101) peak (fwhm = 0.69°). In addition, the (004), (110) and (112) peaks appear. These observations point out the fact that the crystallization level is improved in samples annealed at 1600 °C. The increase of the heat-treatment temperature to 1800 °C (Figure 8c) allowed us to distinguish the (002), (100), (101), (102), (004), (110), and (112) peaks. The appearance of additional shoulders, i.e., (101) and even (102), results from an improvement in the structural ordering of bulk samples. According to the sharpening of the (002) and (100) peaks (fwhm = 0.95° (002) and 0.49° (100)), we can conclude that the crystallite size gradually increases in the *c*- and *a*-axis directions from 1450 to 1800 °C. The determination of the $\bar{L}_c$ size[47] is evident from the fwhm of the (002) peak. This is not the case for the measurement of the $\bar{L}_a$ size[47] from the (100) peak, especially for samples prepared at 1450 and 1600 °C. The (100) peak overlaps with the (101) peak which makes an accurate measurement of the $\bar{L}_a$ parameter difficult. Within this context, we deconvoluted the broad feature around 43° into single (100) and (101) peaks (and even the (102) peak for samples prepared at 1600 and 1800 °C) on the assumption that each peak originates mostly from a single component (Figure 9).

The improvement in the crystallization state is clear when focusing on the 2θ range 35−65 °C. The (004) peak is more and more defined with the increase of the temperature and it is even possible to identify a shoulder corresponding to the (102) peak of BN in the sample prepared at 1600 and 1800 °C that appears for three-dimensional ordering microstructure.

The obtained contributions to the (002) and deconvoluted (100) peaks are summarized in Table 3. In addition, Table 3 gives the calculated out-of-plane size $\bar{L}_c$ and in-plane size of $\bar{L}_a$ for each sample.

From the location of the (002) peaks in each sample, the interlayer distance between hexagonal sheets decreases from 0.352 nm for samples prepared at 1450 °C to 0.338 nm for samples prepared at 1800 °C (Table 3). Judging from the crystallite size in addition to the interlayer distances, the average number of boron nitride sheets increases from around 6 to 25. When samples are prepared at 1800 °C, the corresponding ^{11}B solid-state NMR spectrum (Figure 2d) is typical for trigonally coordinated boron nuclei surrounded by nitrogen atoms and can be simulated with a single signal characteristic of hexagonal boron nitride.[48] However, we should point out that the general crystallization level of the disk-shaped boron nitride samples produced from polyborazylene is lower than those proposed by sintered boron nitride specimens.[3,4,7] This could have effects on the density and some of the specific properties of *h*-BN. Within this context, we have followed the evolution of the bulk density with the temperature of preparation of bulk BN samples.

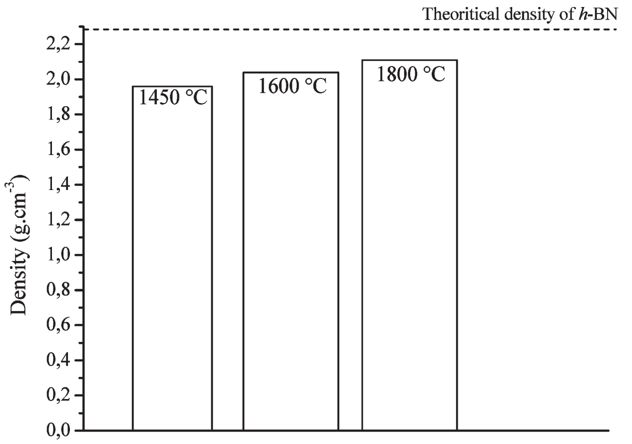

Figure 10. Changes in the density of representative disk-shaped boron nitride (sample **3**−**2**) obtained at 1450, 1600, and 1800 °C (dwelling time of 2 h for the final temperature) in a nitrogen atmosphere.

On the basis of the progress of the crystallinity of samples (See XRD) going from bulk $B_{3.0}N_{2.95}$ prepared at 1450 °C to those prepared at 1800 °C, the density has been anticipated to be increased with the temperature of annealing (Figure 10).

As expected, a gradual increase of the density from 1.96 ± 0.02 g cm^{-3} (bulk samples prepared at 1450 °C) to 2.11 ± 0.02 g cm^{-3} for those prepared at 1800 °C is observed. The helium density measured after heat-treatment

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to 1800 °C gives a value of ~93% of the theoretical density of *h*-BN. Measurements were performed on several parts of the sample presented in Figure 1b in order to examine the piece homogeneity and to be representative of the specimen. Keeping in mind that the warm-pressing of borazine-based polymers has not yet been investigated, there is a lack of evidence or discussion in the literature to support our contentment with regards to the relative density of bulk boron nitride derived from polyborazylene. We can compare our results with those obtained on sintered boron nitride. Poluboyarinov et al. produced sintered boron nitride with an apparent density ranging from 2.06 and 2.08 g cm^{-3}, but the material was not pure because of the use of sintering additive.[49] Hubacek et al. studied the effect of the addition of copper in hot-pressed boron nitride.[3,4] Sintering of copper-free BN powders (0.64 μm) at 1950 °C with 30 MPa of pressure led to relative density of around 90%, but no details on the purity of starting boron nitride powders have been supplied. In our recent article, we demonstrated the successful preparation of bulk boron nitride with a relative density of 96.3% through the spray-pyrolysis from borazine followed by an additive-free sintering step (1840 °C/1 h under 40 MPa) of derived ultrafine powders.[7] In the present paper, the use of a solid polyborazylene allowed reaching a very high density approaching the relative density of the bulk boron nitride we recently published,[7] but in the present article, we did not apply a sintering process.

Because the present orienting fabrication process is very promising, additional detailed investigations is ongoing. The main focus of this study is devoted to the chemical aspect and the design process based on PDCs route. The study of the properties, including mechanical properties (such as hardness, elastic strength, and fracture toughness), thermal properties, and electrical properties, is in progress to have a complete view of the potential applications of BN workpieces.

Conclusion

The warm-pressing of solid borazine-based polymers and the pressureless pyrolysis of derived green bodies have been combined for the first time to process bulk boron nitride. Using borazine as molecular precursor, we demonstrated that derived polyborazylenes with different degrees of cross-linking are recovered by adjusting the final synthesis temperature from 45 to 60 °C. Such modifications in the cross-linked structure involve changes in the chemical composition, ceramic yield and shaping capabilities. Ideal polyborazylenes for warm-pressing and pressureless pyrolysis are those synthesized at 60 °C. They display a chemical formula of $[B_{3.0}N_{3.5}H_{4.5}]_n$, a glass transition in the temperature range 88−120 °C, a controlled dimensional change and high ceramic yields. These features provide adjusted viscoelastic properties and sufficient plasticity to be (i) compacted in a stable warm-pressing operation at 60 °C under 74 MPa and (ii) pressureless pyrolyzed at 1450 °C to deliver disk-shaped bulk $B_{3.0}N_{2.95}$ compacts with a relative density of 86.3% under retention of the polymer shape upon pyrolysis. Densification in relation with the improvement of the crystallization state occurred in the temperature range 1450−1800 °C to generate boron nitride workpieces with a relative density of ~93%. This two-step process represents a novel method to generate bulk hexagonal-boron nitride materials with improved density and purity without sintering process. Research is now under way to investigate the mechanical, thermal, and electrical properties of BN workpieces that could provide further data to extend the application field of such PDCs.

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Supporting Information Available: Raman spectra of BN workpieces prepared at 1450 °C (dwelling time of 2 h) in a nitrogen atmosphere (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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