New Borate Precursors for Boron Nitride Powder Synthesis

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The thermal decomposition of guanidinium tetraborate, pentaborate, and nonaborate has been characterized under nitrogen and ammonia atmospheres, and conditions have been defined for bulk powder and aqueous aerosol transformations of these precursors to boron nitride (BN). The bulk pyrolyses under ammonia (600–1400 °C) produce micrometer- and sub-micrometer-sized platelet morphology particles with oxygen contents of 3–18 wt. %. Subsequent pyrolysis of these powders at 1600 °C under NH$_3$ reduces the oxygen contents to <1 wt. %. Pyrolysis of aqueous aerosols containing the guanidinium borates gives submicrometer spherical morphology BN particles. The chemistry and processing of guanidinium borates are compared with the behavior of alternative precursors.

Introduction

Hexagonal boron nitride (h-BN) is an industrially significant ceramic that enjoys wide use in a variety of refractory, electronic, and lubrication applications.[1–3] Standard commercial powders are obtained by multistep nitridation or carbothermal reduction of boric acid, boric oxide, or sodium borate, using one or more nitridation sources, including ammonia, urea, melamine, guanidine, and dicyanamide.[1,3,4–15] The chemical conversions are driven at high temperature (>1000 °C) and various "oxynitride" compositions,[16] BN$_x$-O$_y$C$_z$, are obtained as intermediates in the typical process stages. The oxynitride materials may have 10–40 wt. %

oxygen and 1–5% carbon depending upon the process utilized and the stage of the conversion. These materials are "finished" in secondary nitridation or carbothermal reduction stages in order to obtain the desired oxygen (4 to <0.1 wt. %) and carbon impurity concentrations. The resulting powders normally have a platelet-shaped primary particle morphology. Although the existing industrial manufacturing processes are mature, there continues to be interest in the development of alternative synthesis pathways for boron nitride particularly where process simplification might be realized or new material properties (e.g., particle morphologies) may be accessed. In the latter regard, aerosol[17,18] and chemical vapor deposition[19,20] approaches have recently been employed to prepare submicrometer spherical morphology BN powders that may be useful for the preparation of BN particle filled composites.[21] In the present study, bulk powder and aerosol syntheses of BN powders are described based upon guanidinium tetraborate and pentaborate as well as the recently reported guanidinium nonaborate.[22] The aerosol processing of these boron sources is compared against the previously reported precursor systems.

Experimental Section

Materials. Guanidinium tetraborate, pentaborate, and nonaborate samples were provided by U.S. Borax, Inc. Boric acid was purchased from Aldrich Chemical, Co., and ammonia was obtained from Air Products. Methanol was purchased from VWR.

Preparation of the Powders. Bulk pyrolyses of the guanidinium borates were performed in a horizontal single zone Thermolyne

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(1) Paine, R. T.; Narula, C. K. *Chem. Rev.* **1990**, *90*, 73.
(2) Narula, C. K. *Ceramic Precursor Technology and Its Applications*; Marcell Dekker: New York, 1995.
(3) Haubner, R.; Wilhelm, M.; Weissenbacher, R.; Lux, B. *Structure Bonding* **2002**, *102*, 2.
(4) O'Connor, T. E. *J. Am. Chem. Soc.* **1962**, *84*, 1753.
(5) Thomas, J., Jr.; Weston, N. E.; O'Connor, T. E. *J. Am. Chem. Soc.* **1962**, *84*, 4619.
(6) Economy, J.; Anderson, R. *Inorg. Chem.* **1966**, *5*, 989.
(7) Gontarz, Z.; Podsiadlo, S. *Pol. J. Chem.* **1984**, *58*, 3.
(8) Fister, D. *Ceram. Eng. Sci. Proc.* **1985**, *6*, 1305.
(9) Basu, R. K.; Mukerji, J. *Bull. Mater. Sci.* **1990**, *13*, 165.
(10) Hubáček, M.; Ueki, M.; Sato, T.; Brozek, V. *Thermochim. Acta* **1996**, *282/283*, 359.
(11) Yoon, S. J.; Jha, A. *J. Mater. Sci.* **1995**, *30*, 607.
(12) Yoon, S. J.; Jha, A. *J. Mater. Sci.* **1996**, *31*, 2265.
(13) Hubáček, M.; Sato, T.; Ishii, T. *J. Solid State Chem.* **1994**, *109*, 384.
(14) Gouin, X.; Grange, P.; Bois, L.; L'Haridon, P.; Laurent, Y. *J. Alloys Compds.* **1995**, *224*, 22.
(15) Hubáček, M.; Ueki, M. *J. Solid State Chem.* **1996**, *123*, 215.
(16) The use of the term "oxynitride" is not intended to suggest the existence of a bona fide quaternary compound, a solid solution of these elements, or a solid solution of BN and B$_2$O$_3$ or other boron oxide. Instead, the intermediate powders are believed to be mixtures of turbostratic BN, B$_2$O$_3$, or other boron oxide phase and an interfacial zone which has been studied and discussed by Hubáček and co-workers.[13]

(17) Lindquist, D. A.; Kodas, T. T.; Smith, D. M.; Xiu, X.; Hietala, S. L.; Paine, R. T. *J. Am. Ceram. Soc.* **1994**, *74*, 3126.
(18) Pruss, E. A.; Wood, G. L.; Kroenke, W. J.; Paine, R. T. *Chem. Mater.* **2000**, *12*, 19.
(19) Iltis, A.; Maguier, C. Eur. Patent 396,448, July 11, 1990.
(20) Tang, C.; Bando, Y.; Golberg, D. *Chem. Commun.* **2002**, 2826.
(21) Paine, R. T.; Pruss, E. A.; Wood, G. L.; Schwierkowski, C.; Hill, R. F.; Chappelle, C.; Kroenke, W. J. *ACS Symp. Ser.* **2001**, *804*, 27.
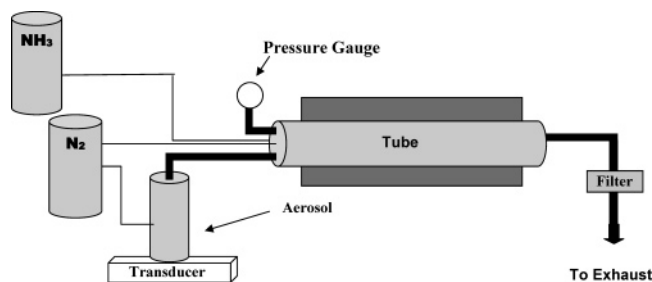(22) Schubert, D. M.; Visi, M. Z.; Knobler, C. B. *Inorg. Chem.* **2000**, *39*, 2250.

Figure 1. Schematic diagram of aerosol reactor.

tube furnace (Model 59300) fitted with an alumina tube (2 in. × 40 in.) having gastight end caps. The borate samples (∼5 g) were contained in boron nitride crucibles and the tube was continuously swept with NH_3 (0.5 L/min). The samples were placed in the furnace tube at 25 °C and the pyrolysis temperature maintained for 4 h (ramp rate 4 °C/ min). The aerosol syntheses were accomplished as described previously.[18] The apparatus is shown schematically in Figure 1. This includes a horizontal three-zone Lindberg tube furnace (Model 54779) fitted with a mullite tube (3.5 in. × 60 in.) having gastight end caps. Aqueous solutions of the guanidinium borates (2−2.3 wt/vol %) were placed in a glass tube (4.5 cm × 23 cm) closed at the bottom with a thin polyethylene bottle cap. The top of the tube was reduced in diameter (1.3 cm) and connected through a short section of Tygon tubing to the front end cap fitted on the horizontal mullite furnace tube. The aqueous aerosol mists containing dissolved borates were generated by placing the polyethylene capped tube end over an ultrasonic transducer operating at 1.7 kHz. The mists were swept with a controlled nitrogen gas stream (1.8 L/min) into the hot zone of the furnace. Ammonia gas was injected separately (2.0 L/min) into the hot zone via inlets passing through the front end cap. The exit end cap was connected to an impact filter from which the product powder was harvested.

Characterization of the Powders. The bulk pyrolysis and aerosol-generated powders were compositionally analyzed for oxygen (St. Gobain/Carborundum) and boron, nitrogen, hydrogen, and carbon (INEOS). In addition, the powders were examined by diffuse reflectance Fourier transform (DRIFT) IR (Mattson Galaxy 2020 FT IR with Specor 19900 Series DRIFT attachment), powder X-ray diffraction (XRD, Siemens D5000), and scanning electron microscopy (SEM, Hitachi S-800). Each precursor borate material also was characterized by thermal gravimetric analysis (TGA, Perkin-Elmer TGA7).

Results and Discussion

In a prior publication,[22] it was noted that guanidinium nonaborate, $[C(NH_2)_3]_3[B_9O_{12}(OH)_6]$ (**1**), has a 1:1 B/N mole ratio in its composition, and it was suggested that the molecule might serve as a simple precursor for the synthesis of boron nitride via the stoichiometric decomposition reaction shown in eq 1

$$[C(NH_2)_3]_3[B_9O_{12}(OH)_6] \rightarrow 9BN + 3CO_2 + 12H_2O \quad (1)$$
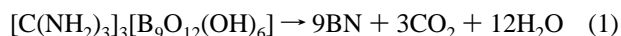
It was also reported that TGA mass spectrometry (MS) analysis showed that **1** begins to lose mass at about 220 °C and the gaseous product was identified as H_2O. Further heating resulted in formation of CO_2 as well as NH_3. The residual powder was compositionally analyzed and found to have a B/N mole ratio greater than 1. Further characterization of the residue was not attempted. Although, under the conditions utilized, the precursor did not display strict

adherence to the proposed stoichiometric decomposition shown in eq 1, the ease of the solid-state conversion remained intriguing.

In the present study, we have returned to examine in more detail the conversion of **1** to boron nitride, and we have also included comparison studies of the decomposition of guanidinium tetraborate, $[C(NH_2)_3]_2[B_4O_5(OH)_4]\cdot2H_2O$ (**2**),[23,24] and guanidinium pentaborate, $[C(NH_2)_3][B_5O_6(OH)_4]\cdot H_2O$ (**3**)[25] that have a molar excess and deficiency, respectively, of nitrogen relative to the ideal 1:1 ratio. The TGA of each compound was recorded under identical conditions using nitrogen or a nitrogen/ammonia gas mixture as the purge gas. The pyrolysis of **1**, idealized as shown in eq 1, would be expected to generate a weight loss from H_2O and CO_2 evolution of ∼60.9% (percent yield BN, 39.1%). The TGA trace recorded under nitrogen purge (50 mL/min) shows decomposition onset at ∼216 °C in agreement with the prior observation.[22] From 210−270 °C, there is an approximate 20% weight loss. This corresponds to about half of that expected for water loss alone (37.8% total water). A second more gradual loss (∼15%) occurs in the range 270−400 °C. A third regime, 400−815 °C results in an additional ∼13% weight loss. Finally, above 815 °C, another small loss (∼5%) occurs, resulting in a total mass loss of ∼53%. This indicates that the proposed stoichiometric nitridation/carbothermal reduction of the polyborate anion is not driven to completion by the guanidinium ion alone under these conditions. A comparable trace is obtained for **1** under an NH_3/N_2 (20 mL/min:30 mL/min) purge atmosphere although the final weight loss in this case is 47%. In addition, it is observed that constant weight is achieved already at 550 °C. For comparison, it is noted that guanidine hydrochloride begins to decompose under nitrogen at ∼260 °C. The TGA shows an approximate 75% weight loss in the range 50−390 °C and then ∼10% weight loss in the range 390−500 °C. The first loss is assumed to involve loss of NH_4Cl ($NH_3 + HCl$), although this was not independently confirmed.

The TGA for **2**, under nitrogen purge (50 mL/min), is similar to that of **1** except that the onset temperature is reduced to ∼130 °C and the total weight loss is 70%. This corresponds closely to the theoretical yield of BN (30.13%) based upon the boron content of the tetraborate. In the temperature range 130−350 °C, two thermal events are clearly resolved that account for ∼42% weight loss. It is interesting that the first event (∼130−200 °C) with a 20% loss is greater than would be assigned to simple dehydration from the waters of crystallization (10.4% theoretical). The TGA trace obtained for **2** under NH_3/N_2 (20 mL/min: 30 mL/min) is virtually identical. The TGA trace for **3** under nitrogen (50 mL/min) is somewhat different. The onset temperature is ∼80 °C, and a small loss (∼5%) occurs between 80 °C and 190 °C. This is less than the amount

(23) The first report of the synthesis of guanidinium tetraborate is found in: Rosenheim, A.; Lyser, F. *Z. Anorg. Allg. Chem.* **1923**, *119*, 1.
(24) An independent synthesis and crystal structure determination for guanidinium tetraborate is found in: Weakley, T. J. R. *Acta Crystallogr.* **1985**, *C41*, 377.
(25) The synthesis and X-ray crystal structure determination for guanidinium tetraborate will be reported separately: Schubert, D. M.; Visi, M. Z.; Knobler, C. B. To be submitted.

Boron Nitride Powder Synthesis

Chem. Mater., Vol. 17, No. 7, 2005 1857

Table 1. Elemental Analysis Data for 1*−3*

sample	T (°C)	time (h)	element (wt %)				
			B	N	C	H	O
1*	800	4	40.09	42.60	0.53	2.29	6.8
	1000	4	42.04	48.75	0.54	1.17	4.0
	1100	4	41.37	48.75	0.42	1.14	2.3
	1200	4	46.34	48.27	0.52	0.94	4.9
	1400	4	42.24	44.92	ND[a]	1.14	3.2
	1400	1					1.2
	1400	6					3.8
	1400	12					6.0
2*	1000	4	39.90	43.22	0.69	1.45	16.4
3*	1000	4	40.50	44.16	ND[a]	1.25	11.6

[a] ND = not detected, <0.2 wt %.

expected for dehydration of lattice water (11.5% theoretical). A second event takes place in the range 190−350 °C (∼23% loss), and a more gradual loss (∼10%) occurs between 350−710 °C followed by a small event at 710−750 °C. The total weight loss is ∼51%. The theoretical weight loss is 60.9% based on B or ∼76% based on N. The TGA trace obtained under NH_3/N_2 (20 mL/min NH_3:30 mL/min N_2) is comparable, although the total weight loss is slightly greater (56%), and the separate event at 710 °C was not observed.

On the basis of the results of the TGA, bulk pyrolyses of the three borates **1−3** were undertaken at 1000 °C for 4 h under a slow purge of NH_3 (0.5 L/min). Samples (5 g) were employed, and the borate powders were spread out in an open geometry boron nitride crucible. Following pyrolysis, the samples were collected and weighed, and portions were subjected to elemental (B, N, O, C, H), IR, XRD, and SEM analyses. Typical analytical data are summarized in Table 1.[26] The mass losses from the bulk pyrolyses generally correspond with expectations based upon the TGA runs performed under NH_3/N_2 purge conditions. In the case of **1**, the bulk pyrolysis mass loss, (**1** → **1***), is 59.5%. This is much closer to the mass loss expected from the ideal conversion process, (eq 1) 60.9%, than the values measured in the TGA: ∼53% under N_2; 47% under NH_3/N_2. However, elemental analysis of **1***[26] indicates that the product is nitrogen deficient, with a B:N ratio = 1.12, consistent with the prior observations made with nitrogen gas as the pyrolysis atmosphere.[22] In addition, the oxygen content, [O] = 4.0%, suggests the presence of a small amount of unconverted borate material in the **1*** product. For **2**, the observed bulk pyrolysis mass loss (**2** → **2***), is 70.2%, which is identical to that observed in the TGA experiments under NH_3/N_2 purge, ∼70%. Despite this, **2*** contains a significant amount of residual oxygen, [O] = 16.4%, and the B/N ratio is 1.20. For **3**, the observed bulk pyrolysis mass loss (**3** → **3***) is 73.4%, which is much greater than the value found in the TGA experiments under NH_3/N_2 purge, ∼56%. However, this is comparable with the predicted loss for the conversion of **3** based upon the nitrogen available in the starting material, ∼76%. The residual oxygen is [O] = 11.6%, and the B/N ratio for **3*** is 1.19.
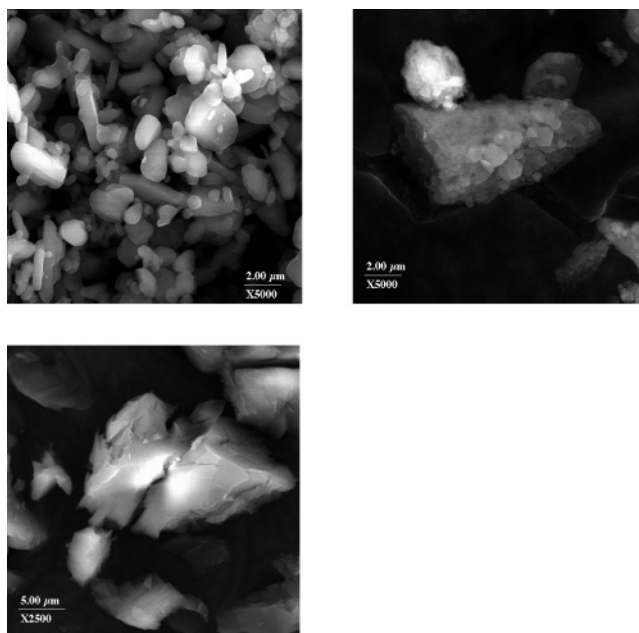
Figure 2. SEM micrographs of bulk pyrolysis boron nitride samples **1*−3*** (5000× magnification, space bar 2.0 μm): upper left, **1***; upper right, **2***; bottom left, **3***.

The DRIFT IR spectra for **1*−3*** are essentially identical to the spectrum of an authentic sample of turbostratic BN[1], although the bandwidth of the B−N stretching vibration (∼1370 cm^{-1}) is slightly narrower for **1*** compared to **2*** and **3***. This would result from the reduced presence of B−O stretching vibrations that appear in the same region. The XRD scans for **1*−3*** are all consistent with the formation of turbostratic BN. Typical SEM micrographs of **1*−3*** are presented in Figure 2, and they show noticeable differences in primary particle characteristics. All samples of **1*** examined showed well-defined, small, blocky platelet shaped particles with little agglomeration. The samples of **2*** and **3*** contained larger and highly agglomerated irregular shaped particles. The measured density of samples of **1***, 2.25 g cm^{-3}, is comparable with the theoretical density of h-BN, 2.27 g cm^{-3}.[27]

Given the pyrolysis characteristics displayed by **1** at 1000 °C, the bulk powder conversion was also examined at 800, 1100, 1200, and 1400 °C for 4 h under an ammonia purge (0.5 L/min). The elemental analysis data are presented in Table 1. The key observation is that the percent weight loss is approximately constant with increasing temperature in the range 800−1400 °C: 800 °C, 57.9%; 1000 °C, 59.2%; 1100 °C, 59.5%; 1200 °C, 57.2%; 1400 °C, 62.9%. In the same order, the percent oxygen decreases with increasing process temperature up to ∼1100 °C, and at 1200 °C the amount of oxygen in the product slightly increases again: 800 °C, [O] = 6.8%; 1000 °C, [O] = 4.0%; 1100 °C, [O] = 2.3%; 1200 °C, [O] = 4.9%; 1400 °C, [O] = 3.2%. The increase in the percent oxygen value at 1200 °C and above is similar to the observation made with the aerosol synthesis of BN from the H_3BO_3/NH_3 reaction wherein we proposed that the water present from the aqueous aerosol process (NH_3/N_2 pyrolysis atmosphere), at temperatures above ∼1200 °C, competitively

(26) It should be noted that the sum of the weight percentages typically do not add up to 100%. Nitrogen and oxygen analyses show the larger duplicate analysis variations and oxygen, at the 10−20% level, has the greatest sample to sample variation.

(27) Pease, R. S. *Acta Crystallogr.* **1952**, *5*, 356.

back reacts with BN, reforming boron oxide species.[18] In the bulk powder pyrolysis of **1**, the water would originate from the decomposition reaction and perhaps, due to the long pyrolysis time, from trace water impurity in the NH_3 purge gas. Powder XRD and SEM analyses of each sample indicate that the powders have closely comparable crystallinity and morphology to the 1000 °C powder described above.

The time evolution of the bulk pyrolyses of **1** at 1400 °C was also examined, and product powders **1*** were obtained after 1, 4, 8, and 12 h heating. The oxygen contents of these powders are summarized in Table 1. It is apparent that the conversion of **1** is complete even after only a 1-h heating period. Furthermore, the amount of oxygen increases with exposure time from 1.2 (1 h) to 6.0% (12 h). This is consistent with the purge gas containing a very small amount of water that reacts at 1400 °C with the BN powder formed.

The results from the bulk pyrolysis of **1−3**, both in the absence and the presence of added ammonia, indicate that the guanidinium borates do not give pure boron nitride under the conditions utilized. Nonetheless, the conversions are sufficiently advanced that **1−3** may be considered to be very useful precursor compounds for the aerosol preparation of BN powders. Initially, 2.0−2.3 wt/vol % solutions of **1−3** were prepared in distilled water, and an aerosol mist of each was generated by ultrasonic agitation. The borate/water aerosol droplets suspended in nitrogen were swept in a nitrogen gas stream (1.8 L/min) into the heated (1000 °C) tube furnace. Ammonia was simultaneously injected into the tube furnace (2.0 L/min), and the resulting boron nitride aerosol powders, **1ᵃ*−3ᵃ***, were collected on an impact filter at the exit end of the pyrolysis tube. In typical powder production runs (2−4 h), 60−80 mL of the borate solutions were used and powder formation rates were 0.1−0.2 g/h. For comparison, H_3BO_3/water solutions (5 wt/vol %) were employed to form aqueous boric acid aerosols and nitridation with NH_3 at 1000 °C under identical flow conditions gave **4ᵃ***. The production rate in this case was ∼0.3 g/h.

Since bulk pyrolysis of each precursor under NH_3 at 1000 °C was shown to produce BN_xO_y powders, only the oxygen contents of the aerosol-produced powders were obtained as an indicator of the degree of conversion of precursor to BN. As expected from our prior work,[18] samples of **4ᵃ*** display high oxygen contents: [O] = 44.4%. The guanidinium borates, on the other hand, display significantly lower oxygen contents: [O] = **1ᵃ***, 25.3%; **2ᵃ***, 28.8%; **3ᵃ***, 28.8%. These values, at the same time, are significantly higher than the [O] values recorded for the bulk pyrolysis powder products **1*−3***. This most likely reflects the short residence time (∼30 s) for the aerosol particles in the horizontal tube reactor hot zone compared to the 1−12-h bulk pyrolysis times.

DRIFT IR spectra for **1ᵃ*−3ᵃ*** closely resemble the spectra obtained from the bulk pyrolysis samples, **1*−3***. The spectrum for **4ᵃ*** differs slightly as indicated by a more prominent shoulder at ∼700 cm^{-1} that is tentatively assigned to B−O−B bending/torsion modes. This absorption would be expected to be more intense in **4ᵃ*** due to the higher concentration of oxygen in the sample. The powder XRD scans for **1ᵃ*−3ᵃ*** show a broad 002 reflection and a single, broad reflection for the unresolved (100) (101) doublet.
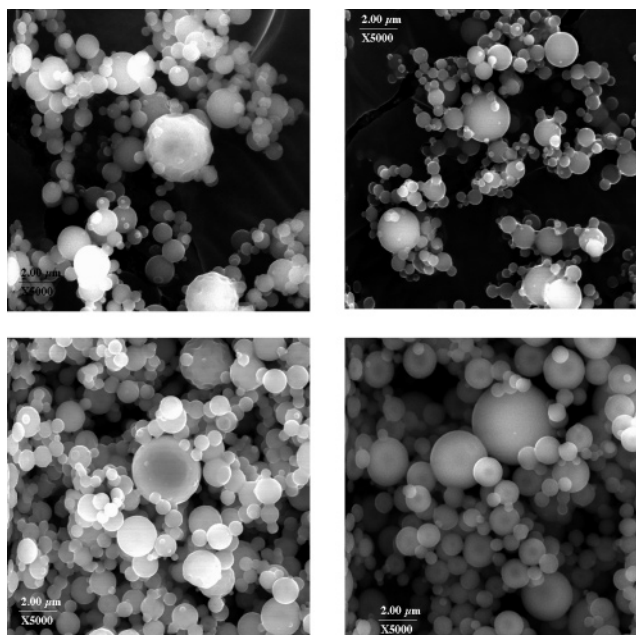

Figure 3. SEM micrographs of aerosol pyrolysis boron nitride samples **1ᵃ*−4ᵃ*** (5000× magnification; space bar 2.0 μm): upper left, **1ᵃ***; upper right, **2ᵃ***; bottom left **3ᵃ***; bottom right, **4ᵃ***.

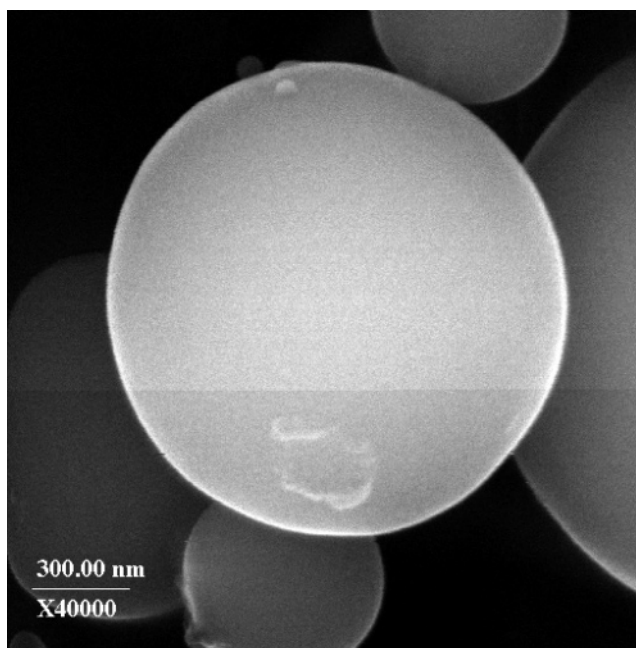**Figure 4.** SEM micrographs of **1ᵃ*** (40 000× magnification; space bar 300 nm).

Typical SEM micrographs for **1ᵃ*−4ᵃ*** are shown in Figures 3 and 4. In each case, the particles generally display a smooth, spherical primary particle morphology, and the majority of particles have a diameter < 1 μm. For **1ᵃ*−3ᵃ***, there are a few particles formed with diameters > 2 μm. The primary particles show a small amount of agglomeration, and the largest particles show surface cratering. This effect could be avoided by adopting a modified aerosol generation/injection arrangement. It should be noted that the boric acid based aerosol tends to produce samples, **4ᵃ***, that have little or no agglomeration or suface cratering.

Since the aerosol residence time in the reactor tube is short, the pyrolysis of **1** was also examined at 1200 and 1400 °C

to determine if higher process temperatures would result in lower oxygen contents. The powders **1ᵃ*** obtained at 1200 °C show a small decrease in oxygen, [O] = 23.5%, but those obtained at 1400 °C have increased oxygen content, [O] = 36.7%. A similar trend is observed for boric acid aerosols **4ᵃ***: 1200 °C, [O] = 38.0%; 1400 °C, [O] = 47.5%. As mentioned earlier, such increases in [O] above 1200 °C probably result from competitive back reaction of water with the BN formed from nitridation of the BO_x aerosol particles.

In other work from our group,[28−30] we noted that aerosols formed from neat organoborates $(RO)_3B$, organoborates in methanol, and H_3BO_3 in methanol produced BN particles with reduced concentrations of oxygen compared to particles formed from aqueous solutions of H_3BO_3. It was assumed that this is a consequence of carbothermal reductive assistance of the boron oxide nitridation. In the present study, methanol solutions of **1** (2 wt/vol %) were also used to generate aerosol droplets that were nitrided under N_2/NH_3 (1.8/2.0 L/min). The resulting powders had the following oxygen contents: 1000 °C, [O] = 19.4%; 1100 °C, [O] = 18.7%; 1200 °C, [O] = 18.7%; 1400 °C, [O] = 26.6%. As anticipated, these oxygen contents are smaller than those recorded using aqueous solutions of **1** and the highest oxygen content appears at 1400 °C where H_2O formed in the nitridation process is likely back reacting with the boron nitride.

To test the reactivity of **1ᵃ*** particles formed at 1000 °C, samples were further calcined (4 h, 1600 °C) under NH_3. The oxygen content drops to 2.68%. The B, N, and H weight percents are 39.75, 49.59, and 0.97%, respectively (B/N = 1.04), and C was undetected. The DRIFT IR spectrum shows narrowing of both of the absorption bands due to BN. The XRD for the powder is unchanged, and this indicates that the material is still turbostratic. A typical SEM for calcined material is shown in Figure 5.
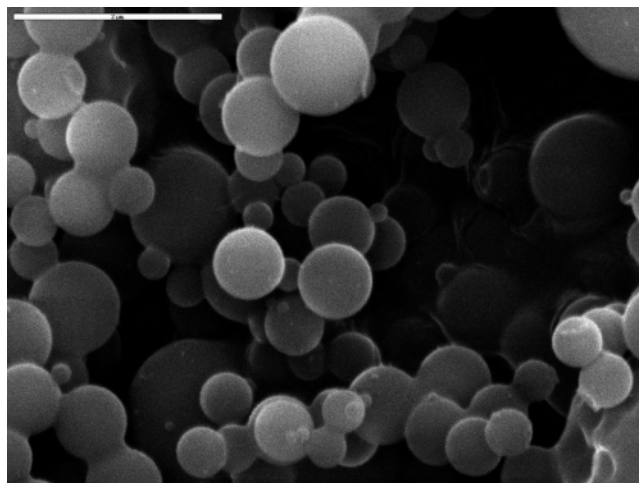
(28) Wood, G. L.; Janik, J. F.; Dreissig, D.; Paine, R. T. Manuscript in preparation.
(29) Dreissig, D. Ph.D. Thesis, University of New Mexico, 2002.
(30) Paine, R. T.; Kroenke, W. J.; Pruss, E. A.; Wood, G. L.; Janik, J. F. U.S. Patent 6,824,753B2, November 30, 2004.

Figure 5. SEM micrograph for **1ᵃ*** following calcination at 1600 °C (20 000× magnification, space bar 2 μm).

The results described clearly indicate that the guanidinium borates serve as good precursors for the aerosol preparation of spherical morphology BN particles. The rate of aerosol powder production is greater than that achieved with aqueous H_3BO_3 solutions[18] but significantly lower than that achieved with organoborates.[29,30] The oxygen impurity levels for the guanidinium borates also are significantly lower than those found with boric acid containing aerosols but higher than those found for organoborate aerosols. Additional modifications of the guanidinium borate systems to achieve higher production rates may be available and further work on these precursors is in progress.

Supporting Information Available: TGA of guanidium borates, DRIFT IR for pyrolysis and aerosol samples, and XRD for bulk pyrolysis samples. This material is available via the Internet at http://pubs.acs.org.

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