

# Synthesis of BN Using BPO<sub>4</sub> as the Boron Source

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*The reaction of BPO<sub>4</sub> with different amounts of NaCN to yield BN and sodium phosphates was studied, mainly as a function of temperature and of the ratio NaCN/BPO<sub>4</sub>. Gravimetric data, together with analytical results, allowed us to postulate and confirm that the yield of reaction products is dependent on the initial ratio NaCN/BPO<sub>4</sub>. An additional reaction between NaCN, BPO<sub>4</sub>, and Na<sub>3</sub>PO<sub>4</sub> yielding BN was also studied.*

HEXAGONAL BN is used in many applications which require a container material stable at high temperatures or a high-resistance electrical insulator. Because of the significant industrial interest in BN, a very large number of reactions have been reported for its synthesis.<sup>1</sup> Some of the early (1842) preparative methods for BN were based on reactions of oxygen-containing boron compounds with cyanides.<sup>2</sup> These reactions used the strong reducing conditions created by the cyanides and their ability to provide nitrogen to the medium. The boron compounds used more frequently were B<sub>2</sub>O<sub>3</sub>, H<sub>3</sub>BO<sub>3</sub>, and Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>, which were reacted directly with NaCN or with a mixture containing a sodium acceptor such as SiO<sub>2</sub>, e.g.



This process and other similar ones were patented in 1958.<sup>3</sup>

Our continuing interest in the use of BPO<sub>4</sub> as a reagent for synthesizing inorganic compounds<sup>4</sup> led us to study its reaction with NaCN for preparing BN; the results are reported here.

## EXPERIMENTAL PROCEDURE

### Reactions

The experiments consisted of heating intimately ground mixtures of NaCN and BPO<sub>4</sub> under flowing Ar or N<sub>2</sub> in crucibles sufficiently tall to prevent losses of material by foaming. The crucibles, made of various materials, were located in a nickel container (2.5-cm ID) topped by a bronze fitting\* which had 0.6-mm-OD copper connections for gas inlet and outlet. The reagents used were granular NaCN,<sup>†</sup> BPO<sub>4</sub>,<sup>‡</sup> ignited in air

at 1000°C before use, and Na<sub>3</sub>PO<sub>4</sub>.<sup>§</sup> Initially crucibles of high fired alumina were used; however, because of their corrosion by the reagents resulting in Al-contaminated products they were replaced by crucibles made of BN<sup>¶</sup> or of graphite. The mixtures of reagents were dried at 120°C in the crucibles before firing at desired temperatures between 700° and 1020°C. After the reaction was effected at high temperature, the weight losses were recorded and portions of the reaction products were subjected to analysis. A fraction of the products was washed with hot (≈80°C) water to remove soluble compounds, then with acetone followed by drying the residues at 120°C.

### Analyses

The analyses consisted of examination by X-ray diffraction (XRD) and energy-dispersive X-rays (EDX) for the solids, and Raman spectroscopy for solids and aliquots of aqueous extracts. The latter allowed for identifying the dissolved sodium phosphate species. This was done by comparison of the obtained spectra with the spectra of various phosphates in aqueous solution recorded by Steger and Herzog.<sup>5</sup>

Raman spectra were obtained with a spectrograph\*\* equipped with a photon counting system and a signal averager.\*\* The spectra were excited with the 514.5- or 488.0-nm line of an argon-ion laser or the 647.1-nm line of a krypton laser. Samples were placed in glass sample cells or melting point tubes and the Raman spectra observed at 90° to the exciting light. Fluorescent spectra were obtained by illuminating the samples with either the 457.9-nm argon-ion laser line or with an unfiltered short-wavelength mercury lamp and recording the resulting spectra with the Raman spectrometer.

## RESULTS AND DISCUSSION

### Effect of Temperature and of Time

Mixtures with different molar ratios NaCN/BPO<sub>4</sub> heated to 700° to 900°C for

≈17 h yielded products which had colors ranging from dark gray to black; it was assumed that this was caused by the presence of free carbon and no further analyses were performed. When the mixtures were heated to 1000°C for ≈17 h, the color of the products was dependent on the ratio NaCN/BPO<sub>4</sub>, black for values between 2 and 4 and light colors for values smaller than 2. Graphitized carbon was found to be present by Raman spectroscopy in those black products obtained at 1000°C. When gray-black preparations (NaCN/BPO<sub>4</sub>=1 to 1.5) made at temperatures below 1000°C were subsequently heated to ≈1000°C, they lost significant weight and changed color to light tan or white; in these cases XRD of the products showed the presence of hexagonal BN and sodium phosphates.

The temperature of ≈1020°C was chosen as our working temperature and we studied the effect of the length of the thermal treatment on the percent weight loss on heating. This temperature was reached using heating rates averaging between 9 and 11°C/min. It was found that after 20 h at 1020°C the weight remained essentially constant. Bright metallic-looking crystals were deposited on the copper inlet line located near the top of the furnace when mixtures with ratios NaCN/BPO<sub>4</sub>≥2 contained in BN or Al<sub>2</sub>O<sub>3</sub> crucibles or with ratios of ≈1.5 contained in a graphite crucible were heated to ≈1000°C. These crystals, identified as Cu<sub>3</sub>P by XRD and EDX, indicated that some of the phosphorus present as phosphate was reduced to its elemental state and volatilized from the system. Since it is known that molten sodium phosphates of varied compositions are partially reduced to elemental phosphorus by carbon at temperatures above 400°C,<sup>6</sup> and because crystalline phosphates were obtained as reaction products at 1000°C (see below), we have speculated that sodium polyphosphates must have formed at 400° to 700°C during the reaction of NaCN with BPO<sub>4</sub>.

### Effect of the Molar Ratio NaCN/BPO<sub>4</sub> on the Reaction

Based on the above, the experimental conditions of 1020°C for ≈17 h or more were adopted to study the effect of NaCN/BPO<sub>4</sub> on the identity of the light-colored products. On examination by Raman spectroscopy, neither the intense Raman peak of hexagonal BN at 1365 cm<sup>-1</sup> nor peaks corresponding to sodium phosphates were observable because all the samples were highly fluorescent when activated with 457.9-, 514.5-, or 647.1-nm laser light.

Hexagonal BN powders have been reported to give photoluminescence, especially samples containing traces of carbon.<sup>7-9</sup> Figure 1 shows a fluorescent spectrum of one of our samples obtained by illuminating it with an unfiltered short-wavelength mercury lamp. The peaks shown resemble closely those reported.<sup>8,9</sup> Our data do not show peaks below 400 nm due to the glass optics of the spectrometer

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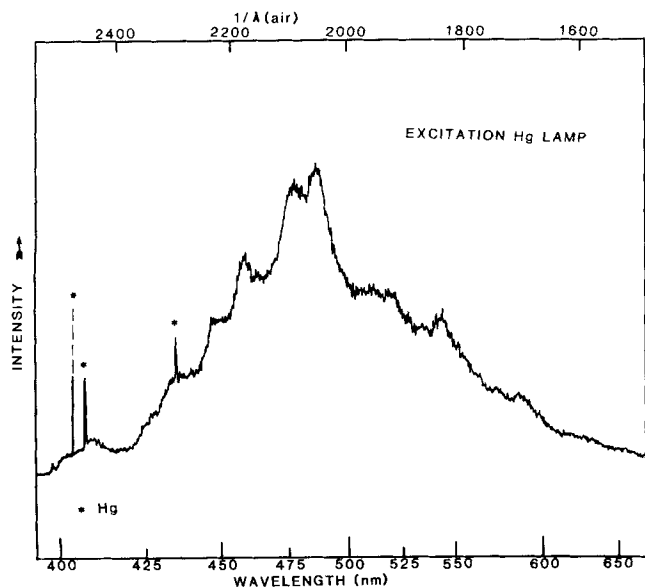


Fig. 1. Fluorescent spectrum for BN obtained by excitation with light from mercury lamp.

used. Excitation with the 457.9-nm line of the argon laser produced (Fig. 2) a very similar spectrum with slightly different weighing of the peaks produced. From these results we concluded that our BN preparations contained traces of carbon which accounted for their strong fluorescence.

The presence of hexagonal BN in all the preparations, before and after water extraction, was confirmed by XRD. In most preparations and depending on the initial ratio  $\text{NaCN}/\text{BPO}_4$ ,  $\text{Na}_3\text{PO}_4$ , and  $\text{Na}_4\text{P}_2\text{O}_7$  were found by XRD in addition to BN, in solids before water extraction and only  $\text{Na}_4\text{P}_2\text{O}_7$  after water extraction, in which case the presence of Na and P was confirmed by EDX. Raman spectra of aqueous extracts revealed the presence of  $\text{Na}_3\text{PO}_4$  and  $\text{Na}_2\text{HPO}_4$  and only occasionally  $\text{Na}_4\text{P}_2\text{O}_7$ . It was found that the residual  $\text{Na}_4\text{P}_2\text{O}_7$  could be removed from the once-water-extracted solids by regrinding them and subjecting them to a second water extraction. Since both  $\text{Na}_3\text{PO}_4$  and  $\text{Na}_4\text{P}_2\text{O}_7$  are sufficiently soluble in water and should have been removed simultaneously, we were led to speculate that  $\text{Na}_4\text{P}_2\text{O}_7$  formed first and was coated by BN, while  $\text{Na}_3\text{PO}_4$  formed later with the fraction of  $\text{BPO}_4$  that had not been consumed. Analysis by XRD

of the products of reactions with  $\text{NaCN}/\text{BPO}_4 \approx 1$  (Eq. (2)) did not show the presence of any crystalline sodium phosphate. The addition of a divalent cation ( $\text{Fe}^{2+}$ ) to the water extracts resulting from these products yielded precipitates, which was an indication of the presence of hydrolyzable alkaline phosphates. Graham's salt (glassy  $\text{NaPO}_3$ ) is the only metaphosphate which is readily soluble in water, as opposed to the crystallizable salts of Kurrol ( $\text{NaPO}_3\text{-IV}$ ) and Maddrell ( $\text{NaPO}_3\text{-II}$ ).<sup>10</sup> Since we were able to extract easily with water all the sodium and the phosphate (which for  $\text{NaCN}/\text{BPO}_4=1$  was a glass) and because the stoichiometry  $\text{NaPO}_3$  gave satisfactory agreement between calculated and observed weight losses, we concluded that Graham's salt was one of the products of reaction for ratios  $\text{NaCN}/\text{BPO}_4=1$  to 1.455 as shown below in Eq. (2a).

for  $1 \leq x < 1.455$

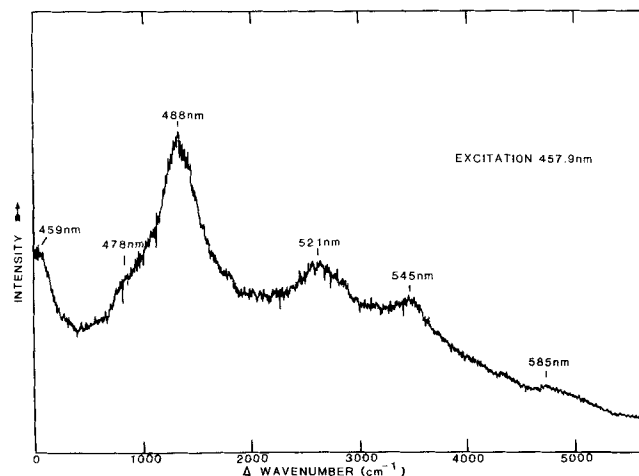
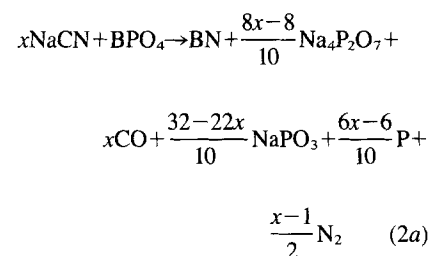


Fig. 2. Fluorescent spectrum for BN obtained by excitation with 457.9-nm light from argon-ion laser.

Table I. Comparison of Calculated and Experimental Values

NaCN/BPO <sub>4</sub> (mol)	Wt loss on heating (%)		Wt loss by water extraction (%)	
	Expected	Found	Expected	Found
1.00 (Eq. (2a))	18.1	20.5	80.4	82.2
1.24 (Eq. (2a))	25.5	26.0	80.0	79.4
1.50 (Eq. (2b))	32.5	31.7	79.5	79.6
1.78 (Eq. (2c))	35.8	35.5	78.5	78.8
1.93 (Eq. (2c))	32.0	38.6	77.4	83.6
1.05; y = 0.98 (Eq. (3))	11.7*	11.6	91.3	91.4
1.28; y = 1 (Eq. (3))	16.6*	18.0	91.4	89.6

\*Calculation included water content of  $\text{Na}_3\text{PO}_4$

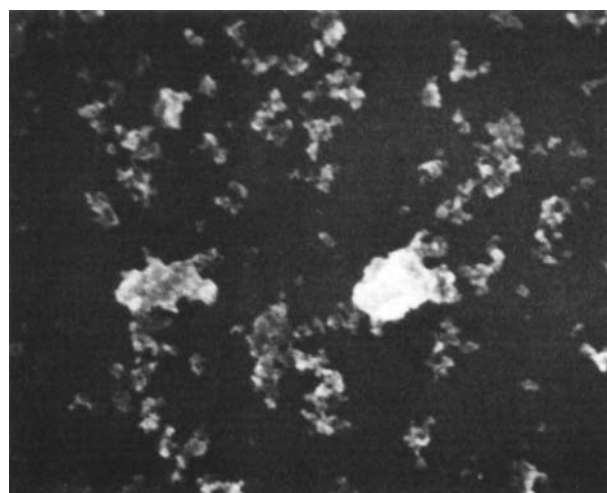
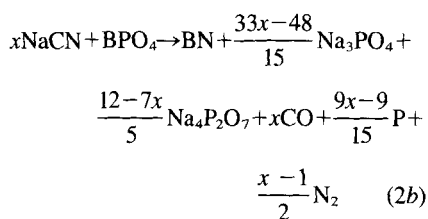
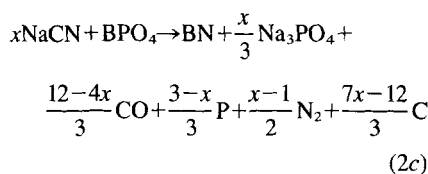


Fig. 3. Scanning electron micrograph of BN prepared by reaction of Eq. (2a) with  $\text{NaCN}/\text{BPO}_4=1.24$  and washed with hot water ( $\times 5000$ ).

for  $1.455 < x < 1.714$



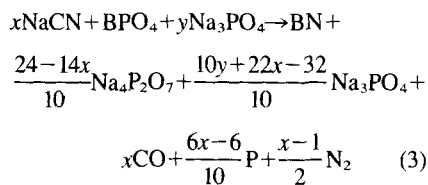
for  $1.714 \leq x \leq 2$



These equations have been balanced assuming that all the sodium will be converted to a phosphate (meta-, ortho-, pyro-) or their mixtures, and that, in addition to BN, the volatile reaction products will be at their lowest state of oxidation. As is reflected by Eqs. (2a) to (2c) the composition of the phosphates depends on the ratio NaCN/BPO<sub>4</sub>. A comparison of selected values of weight losses (on heating and by water extraction) calculated by means of Eqs. (2a) to (2c) with their corresponding observed values is shown in Table I. As can be seen the agreement between calculated and observed values is very satisfactory, especially if one takes into consideration the hygroscopicity of NaCN.

#### Alternative Reaction

The following alternative reaction was also analyzed:



When  $x=y=1$ , the only volatile species formed is CO. Reaction (3) was tested at several temperatures up to the preferred value of  $\approx 1000^\circ\text{C}$ . The information and analytical results obtained, part of which is shown in Table I, verified that Eq. (3) described correctly the formation of BN.

SEM examination of the hexagonal BN powders synthesized according to Eqs. (2a), (2c), and (3) revealed that the powder consisted of irregularly shaped particles of  $1 \mu\text{m}$  or less on their longest axis; a representative SEM microphotograph is shown in Fig. 3.

#### CONCLUSIONS

The stoichiometries of the reactions of BPO<sub>4</sub> with various amounts of NaCN have been postulated. BN is always a product of the reaction while the composition and abundance of the solid sodium phosphates (NaPO<sub>3</sub>, Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub>, and Na<sub>3</sub>PO<sub>4</sub>) formed vary in a systematic manner with the ratio NaCN/BPO<sub>4</sub>. The latter allows for predicting whether significant quantities of carbon will be present as a byproduct. An alternative reaction involving BPO<sub>4</sub>, NaCN, and Na<sub>3</sub>PO<sub>4</sub> was found which also can be used for producing BN. When Eqs. (2a) and (3) are used with, respectively,  $x=1$  and  $x=y=1$ , they present the additional advantage that no elemental phosphorus is vol-

atilized from the system. All the reactions studied can be used either as a method for producing BN or as a means of disposing of NaCN while converting it into a marketable product. The inherent high fluorescence of the BN powders obtained by means of the reactions studied may be applied to tribology studies in which the presence of minute amounts of fluorescent BN can be ascertained by means of an exciting light.

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#### REFERENCES

- (a) Gmelin Handbuch der Anorganischen Chemie, System No. 13, 8th ed. Springer-Verlag, Berlin, 1926; (b) Supplement, Vol. 1, 1954; (c) Part 1, 1974; (d) 1st Supplement, Vol. 2, 1980.
- Gmelin Handbuch der Anorganischen Chemie, System No. 13, 8th ed.; p. 106. Springer-Verlag, Berlin, 1926.
- Gmelin Handbuch der Anorganischen Chemie, System No. 13, 8th ed., Part 1; p. 3. Springer-Verlag, Berlin, 1974.
- C. E. Bamberger, "Preparation of Metal Phosphates by Metathesis Reaction with BPO<sub>4</sub>," *J. Am. Ceram. Soc.*, **65** [7] C-107-C-108 (1982).
- E. Steger and K. Herzog, "Infrared and Raman Spectra of Phosphate Solutions" (in Ger.), *Z. Anorg. Allg. Chem.*, **331**, 169 (1964).
- J. R. VanWazer, p. 780 in Phosphorus and Its Compounds, Vol. 1. Interscience, New York, 1958.
- A. Katzir, J. T. Suss, A. Zunger, and A. Halperin, "Point Defects in Hexagonal Boron Nitride. I. EPR, Thermoluminescence and Thermally-Stimulated-Current Measurements," *Phys. Rev. B*, **11** [6] 2370 (1975).
- D. N. Bose and H. K. Henisch, "Thermoluminescence in Boron Nitride Powders," *J. Am. Ceram. Soc.*, **53** [5] 281 (1970).
- S. Larach and R. E. Shrader, "Multiband Luminescence in Boron Nitride," *Phys. Rev.*, **104** [1] 68 (1956).
- J. R. Van Wazer, p. 665 in Phosphorus and Its Compounds, Vol. 1. Interscience, New York, 1958. □