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Contribution from the Plastics Department and the Industrial and Biochemicals Department, Experimental Station, E. I. du Pont de Nemours and Co., Inc., Wilmington, Delaware]

Turbostratic[1] Boron Nitride, Thermal Transformation to Ordered-layer-lattice Boron Nitride

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X-Ray diffraction studies are reported which show that boron nitride synthesized at 500–950° from a fused urea–boric acid intermediate and ammonia has a turbostratic structure which is formally analogous to that of turbostratic carbon. The turbostratic structure can be thermally transformed into an ordered-layer-lattice form (hexagonal) by a process which appears formally analogous to the carbon graphitization process. The boron nitride transformation is promoted at temperatures below 1800° by the presence of boron oxide impurities. The features of the transformation are deduced from changes readily observed in the diffraction patterns. An X-ray method is described for comparing the relative degree of three-dimensional ordering induced in the boron nitride during graphitization.

Introduction

Two well-defined solid phases of boron nitride, an ordered-layer-lattice form with hexagonal symmetry[3,4] and a cubic form,[5] which are structurally analogous to graphite and diamond, respectively, have been described. In addition, less well-defined structures have been mentioned.[6,7]

Recently, O'Connor[8] reported a new synthesis of boron nitride from the controlled reaction of a fused urea–boric acid intermediate and ammonia. In this paper we report the results of X-ray diffraction studies on the boron nitride resulting from this synthesis and also on the substance after it has been subjected to various thermal treatments. It is our purpose to show that further structural analogies exist between boron nitride and carbon. The unexpected role of boron oxide impurities in promoting structural changes in boron nitride is of interest.

Experimental

Materials.—Boron nitride of substantial purity was prepared from urea–boric acid and ammonia at 500–950° in accordance with the method cited.[8]

Anal. Calcd. for BN: B, 43.5; N, 56.5. Found: B, 43.9; N, 54.2.

Final traces of oxide impurity were removed in one lot of boron nitride by treating it with ammonia at a temperature slightly in excess of 1100°, and in another lot by heating it in a stream of nitrogen to 1650° where the oxide impurity volatilizes.

Anal. B, 44.2; N, 56.0.

To permit the study of the role of the impurity, B_2O_3, in promoting structural changes at elevated temperatures in the boron nitride, as synthesized, controlled quantities of B_2O_3 were blended with portions of the latter lots of boron nitride. Cylindrical carbon capsules with screw-in end caps were used as reactors for containing tightly packed charges of boron nitride, or mixtures predominantly of boron nitride, during the various thermal treatments.

Apparatus and Methods.—All X-ray diffraction investigations were made with polycrystalline samples. A Philips camera having a diameter of 114.6 mm. was used for powder photographs. Diffractometer scans were made either with a Norelco instrument with pulse height analysis, or with a General Electric XRD-5 unit without pulse height discrimination. Proportional counters (argon filled) were employed in counter work. Copper radiation, produced at 45 kv. and 18 ma, was used with a sufficiently thick nickel filter (0.0007″ to 0.0014″) to effectively remove the CuK_β component.

Measurements of crystallite size and "graphitization index" were made from diffractometer scans. With a scanning speed of 1°/minute, a chart speed of 76 cm./hour, and 1° (divergence) slits, recorded reflections could be planimetered to satisfactory reproducibility.

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(1) Unordered layer structure after J. Biscoe and B. E. Warren, *J. Appl. Phys.*, **13**, 364 (1942).

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(3) R. S. Pease, *Acta Cryst.*, **5**, 356 (1952).

(4) C. Coulson and R. Taylor, *Proc. Phys. Soc.*, **A65**, 815 (1952).

(5) R. H. Wentorf, *J. Chem. Phys.*, **26**, 956 (1957); U. S. Patent 2,947,617 (Aug. 2, 1960).

(6) H. J. Milledge, *Nature*, **184**, 715 (1959).

(7) I. L. Zagyansky and G. V. Samsonov, *J. Appl. Chem. U.S.S.R.*, **25**, 629 (1952).

(8) T. E. O'Connor, *J. Am. Chem. Soc.*, **84**, 1753 (1962).

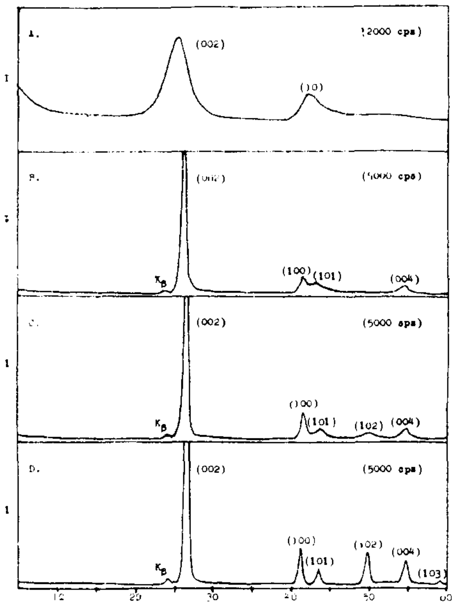


Fig. 1.—Diffraction patterns of boron nitride illustrating the transformation of turbostratic BN to the ordered-layer-lattice BN: (A) turbostratic; (B), (C) partial three-dimensional ordering; (D) "complete" three-dimensional ordering.

Samples were mounted in conventional sample holders for the diffractometer studies. Since bonds between layers in the ordered-layer-lattice boron nitride are easily ruptured, special care was taken to minimize preferred orientation effects during sample mounting. Samples were not ground but were run as received. Only slight pressure was needed to make the soft aggregates, in the majority of samples, conform to the sample holders.

Results and Discussion

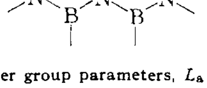
Turbostratic Boron Nitride.—Figure 1A illustrates a typical diffraction pattern of the boron nitride synthesized from urea–boric acid and ammonia. There are two diffuse diffraction maxima corresponding to (002) and (10) within the abbreviated range of 2θ illustrated. Typical diffraction data are summarized in Table I.

Table I

Turbostratic BN: X-Ray Diffraction Data

Reflection	2θ	d (Å.)	B (°2θ)	L (Å.)[9]
(002)	25.0	3.56	5.8	$L_c = 14$
(10)	42.4	2.13	3.8	$L_a = 46$

The synthesized boron nitride has a turbostratic structure, hereinafter designated BN_t, formally analogous to the structure of turbostratic carbon blacks in that layers of the form



are stacked roughly parallel to each other but show random rotation and translation about the layer normal.

Diffraction by a random-layer lattice has been investigated in detail by Warren[10] and Wilson.[11] The assignment of a turbostratic, or random-layer lattice, structure to BN_t rests primarily on (a) the relative integrated intensities of the diffraction peaks and their similarity to the relative integrated intensities of the (00*l*) and (*hk*0) reflections of ordered-layer-lattice boron nitride, hereinafter called "graphitic" boron nitride by analogy with graphite and designated BN_g, (b) the near coincidence of the Bragg angles of the diffracted beams with the Bragg angles of (00*l*) and (*hk*0) reflections of BN_g, (c) the fact that the diffraction pattern can be indexed on the basis of a hexagonal unit cell, but the general (*hkl*) reflections are missing, (d) the asymmetric shape of the (*hk*) reflections which show a pronounced tailing effect on the high Bragg angle side of the diffraction maxima while (00*l*) reflections show the expected nearly symmetrical profile, and (e) the fact that a graphitization transformation[12] analogous to that in carbon exists (*cf.* Fig. 1).

Here, the interlayer spacing is represented by $d(002)$. The d-value is larger than $d(002)$ for BN_g which is 3.330 Å.[3] L_c is the average stack height of a parallel layer group and L_a is the average layer diameter. It is seen that the average parallel layer group consists of four to five layers and is wafer-shaped since the layer extension represented by L_a is considerably greater than the stack height.

The peak positions of the two-dimensional (*hk*) reflections are a function of the average diameter (L_a), the peaks being displaced toward a larger Bragg angle from the corresponding (*hk*0) reflections in BN_g. The displacement increases with decreasing L_a values. The peak position of the (10) reflection relative to the (100) reflection of BN_g (d = 2.171 Å.)[3] thus can be ascribed to the relative sizes of the layer diameters of these materials. If L_a is calculated from this displacement according to the equation $\Delta(\sin\theta) = 0.16\ \lambda/L_a$ with $\Delta(\sin\theta) = (\sin\theta)_{hk} - (\sin\theta)_{hk0}$, a value of 40 Å. for L_a is obtained which is in close agreement with the value of 46 Å. calculated by the modified Scherrer equation.

To obtain further confirmation of the turbostratic nature of BN_t, calculation of the theoretical peak shape for a (10) reflection was carried out for comparison with the experimentally observed (10) profile. Warren[1,10] has shown that for the high angle tail of an (*hk*) reflection

$$P_{2\theta}' = \frac{KMF^2(1 + \cos 2\theta)}{4\sin\theta\,(\sin^2\theta - \sin^2\theta_0)^{1/2}} \qquad (1)$$

when θ is far enough removed from θ_0, the angular position of the diffraction maximum. Here K is a constant, M is the multiplicity factor, F is the structure factor for the (*hk*) reflection, (1 + cos

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(9) The parallel layer group parameters, L_a and L_c, were obtained by means of the well-known Scherrer equation, $L = k\lambda/\cos\theta\,(B^2 - B_1^2)^{1/2}$, where k = 0.9 (for L_c determination), or 1.84 (Warren modification for L_a determination), λ = 1.542 Å., B is the half-maximum breadth of the diffraction peak, and B_1 is the contribution to the half-maximum breadth by instrumental factors (determined using a silicon wafer having large crystallite size).

(10) B. E. Warren, *Phys. Rev.*, **59**, 693 (1941).

(11) A. J. C. Wilson, *Acta Cryst.*, **2**, 245 (1949).

(12) B. E. Warren, "X-Ray Study of Graphitization of Carbon Black," Proc. of the First and Second Conferences on Carbon, Univ. of Buffalo (1956). The term graphitization is applied to the boron nitride layer-ordering transformation in the present paper.

$2\theta)/2 \sin \theta$ represents the Lorentz-polarization factor, and $P_{2\theta}'$ is proportional to the observed intensity at 2θ. Near the peak position

$$P_{2\theta}' = \frac{KMF^2(1 + \cos^2 2\theta)}{2(\sin \theta)^{3/2}} \left(\frac{L_a}{\pi^{1/2}\lambda}\right)^{1/2} F(a) \quad (2)$$

where $a = 2\sqrt{\pi}\, L_a/\lambda\, (\sin \theta - \sin \theta_o)$.

In the calculation of a, the value of L_a = 40 Å. was used as determined from peak displacement. The function, $F(a)$, has been tabulated by Warren.[1,10] A comparison of theoretical and experimental curves for the (10) reflection is shown in Fig. 2. The experimental curve is scaled to the theoretical curve at the position of maximum intensity. It can be seen that the agreement is excellent over the regions of applicability of equations 1 and 2, and, hence, the (10) reflection has the profile expected from a turbostratic structure.

Transformation of Turbostratic BN to Ordered-Layer-Lattice BN.—Samples of BN_t of substantial purity (> 54 % N) which have been heated to about 2000° in open boron nitride ceramic containers in a stream of nitrogen show substantially unaltered diffraction characteristics. However, when samples of BN_t containing about 10 wt. % of boron oxide are heated in a N_2 or He stream under conditions where escape of volatile boron oxides is retarded (here enclosed in a carbon capsule), the $BN_t \rightarrow BN_g$ transformation commences at about 1450° and is complete at 1850°. Figure 1D illustrates a typical diffraction pattern for highly-ordered graphitic boron nitride. During the thermal transformation (graphitization) of BN_t to BN_g, in which temperature and B_2O_3 content influence the rate and extent of the transformation, the material passes through increasing degrees of three-dimensional ordering. Two of the intermediate stages are illustrated in Figures 1B and 1C. The term "mesographitic"[13] is used to describe the gamut of intermediate structural states between BN_t and BN_g.

The boron oxide required for the transformation below 2000° (in the absence of high pressure) may be in the form of residual oxide in the oxygenated intermediates of the urea-boric acid–ammonia synthesis of boron nitride (incomplete ammoniation) or as admixed B_2O_3. Very highly ordered BN_g[14] in the form of highly unctuous, crystalline platelets can be prepared by heating a mixture of pure BN_t (89%), B_2O_3 (9%), and preformed BN_g (2%) over the temperature range 1400–1850° in a closed carbon container where B_2O_3 volatilization is retarded. The process is improved after a few runs are made in the same container as an adherent layer of BN_g deposits on the inside wall of the carbon capsule. Apparently this reduces the initial porosity of the container and, thereby, decreases the volatilization rate of B_2O_3. A typical heating schedule comprises heating the capsule by 50° increments every 30 minutes over the temperature range followed by holding for 6 hours at 1850°; however, the time required for graphitization is markedly affected by the permeability of the capsule wall to boron oxide vapor and can be substantially reduced. In a properly prepared capsule, a quite substantial graphitization can be attained on heating to a maximum temperature of 1650°.

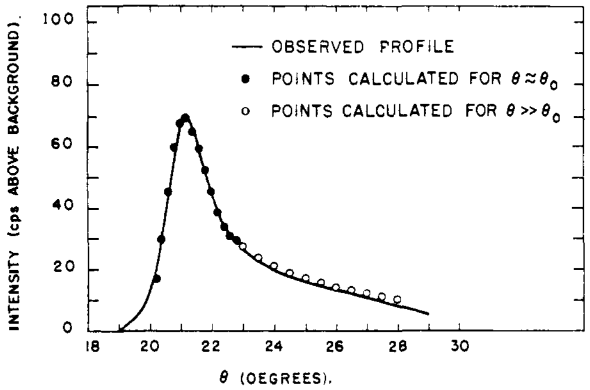

Fig. 2.—Comparison of the experimental and theoretical line profiles for the (10) reflection from turbostratic boron nitride.

Heating of pure BN_t with admixed BN_g "seed" alone in the capsule to temperatures of about 2000° gives a substantially unaltered product, except for the formation of boron carbide adjacent to the capsule wall. Heating of BN_t containing about 10 wt. % B_2O_3 in the capsule to about 1800°, in the absence of added BN_g "seed," gives a BN_g product, but it is inferior in the extent of three-dimensional ordering and in crystallite platelet size to the product obtained using both B_2O_3 and BN_g "seed" in the initial mixture.

During the graphitization process, the alignment of layers is denoted by the appearance in the diffraction pattern of the general (*hkl*) reflections and by the gradual replacement of the characteristic asymmetrical (*hk*) reflections of BN_t by the more symmetrical (*hk*0) reflection profiles of BN_g. In Table II are shown typical changes in c_0 (twice the interlayer spacing), the average layer diameter, and the average stack height as order increases from Sample A through Sample F.

TABLE II

STRUCTURE PARAMETER CHANGES IN BORON NITRIDE DURING "GRAPHITIZATION"

Sample	c, Å.	L_a, Å.	L_c, Å.	Order
A	7.11	..	...	Turbostratic
B	7.04	47	15	Turbostratic
C	6.92	103	Large	Mesographitic
D	6.77	..	...	Mesographitic
E	6.73	..	...	Mesographitic
F	6.66	500	Large	Graphitic

The decrease in c_0 with increasing degree of ordering is indicative of the improved interlocking of layers representative of the ordered BN_g structure. L_c data indicate a large initial growth in stack height relative to layer growth during the mesographitic stages.

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(13) In the strictest sense, of course, it may be argued that all boron nitride could be classified as mesographitic since there is no denial that some ordering, perhaps as rudimentary as that of layer pairs, exists in regions of BN_t, just as it is certain that some disorder exists in the most carefully prepared BN_g.

(14) For comparison with Pease's[3] structural data, the unit cell parameters of this material were determined at 25°, using CuKα radiation, photographic techniques, and well-known least squares treatment of powder data for diffraction lines with $\theta > 40°$. Values obtained were; $a_0 = 2.50435 \pm 0.00035$ Å., $c_0 = 6.6565 \pm 0.0028$ Å., which are in excellent agreement with Pease's values of, $a_0 = 2.50404 \pm 0.00005$ Å., $c_0 = 6.6590 \pm 0.0005$ Å., which have been corrected to 25° using temperature coefficients determined by him.

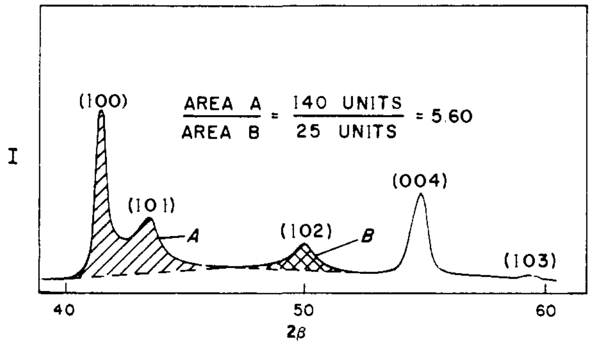

Fig. 3.—Illustration of the defined areas used in the determination of the graphitization index.

"Graphitization Index."—It was apparent during the study of variables influencing the transformation that a relatively simple method was needed for placing a given sample of BN in proper perspective with any other sample of BN as regards the degree of three-dimensional ordering present. This was true particularly for the more highly ordered samples where differences in appearance, texture, and density were not easily discernible but where differences in diffraction patterns were readily apparent. Such qualitative terms as "moderately mesographitic" or "highly mesographitic" were found inadequate. The "graphitization index," which simply is a ratio between the areas under selected recorded diffraction profiles, provides a relative number for comparison and should be useful for quick assessment of order in studies of other layer-lattice substances. The basis for the method is explained in the following paragraphs.

The most significant evidence marking the onset of three-dimensional ordering is the resolution of the broad (10) reflection into the (100) and (101) reflections, accompanied by the sharpening of the (002) reflection and the appearance of the (004) reflection (Fig. 1). As ordering proceeds, the (102) reflection appears and increases in intensity, while the resolution between the (100) and (101) reflections increases. In more highly ordered samples the (103) reflection appears. Other reflections become apparent with increasing order, of course, at angles (2θ) higher than the maximum (61°) illustrated. The transformation is defined as being "complete" when the resolution of the (100) and (101) reflections is complete at a counting rate of 2000 counts per second under the defined instrumental settings.

The graphitization index (*G.I.*) is defined by the expression

$$G.I. = \frac{\text{Area }[(100) + (101)]}{\text{Area }(102)}$$

(See Fig. 3 for areas involved.)

The (102) reflection was chosen for a part of this ratio since it is more sensitive to change as the degree of ordering changes than is the (103) or (004) reflections, and it is not influenced to nearly the same extent as the (001) reflection by preferred orientation effects induced during sample mounting.

It is immediately obvious that this method has utility only after the appearance of the (102) reflection. Appreciable ordering has occurred before the (102) reflection is measurable at the counting rates used. As it was pointed out earlier, however, it is in the more highly ordered samples where comparison by other means (*i.e.*, density) is most difficult and, thus, where the graphitization index is of most importance.

If preferred orientation effects are minimized, a *G.I.* value of 1.60 is obtained for completely graphitized BN_g and, as order decreases, these values increase to an upper range of 40–50, at which point the area of the (102) reflection becomes difficult to measure. Reproducibility, of course, becomes poorer as the *G.I.* value increases. Between *G.I.* values of 1.60 and about 5.00 the reproducibility is ±0.02, from 6.00 to 10.00, about ±0.05, from 11.0 to 20.0, about ±0.1, and from 25.0 to 40.0, about ±0.5 to ±1.0.

Serious preferred orientation effects can alter these values appreciably. Orientation is brought about during sample mounting by preferential layering of the crystallite platelets, and consequent (00*l*) planes, parallel to the diffracting surface of the material within the sample holder. These effects can be foretold readily by comparing the peak intensity of the (100) reflection with that of the (004) reflection. In the absence of orientation, the peak intensity of the (100) reflection to that of the (004) reflection should be in the ratio of 15:6 from Pease's[3] intensity data. Provided the intensity of the (004) reflection is less than that of the (100) reflection, the graphitization index is not seriously influenced. Severe orientation will give diffraction patterns in which the intensity of the (004) reflection is greater than three times that of the (100) reflection.

Conclusions.—The existence of a boron nitride having a turbostratic structure which is formally analogous to the turbostratic structure of carbon has been shown. Furthermore, the turbostratic structure of boron nitride can be thermally transformed into the well-known hexagonal structure, a process which appears to be analogous to the carbon graphitization process.

The exact mechanism of the $BN_t \rightarrow BN_g$ transformation is not clear at this time. It is a matter of a low-order, high-energy form achieving a high-order, low-energy form *via* layer realignment about the stacking direction accompanied by crystal growth. It is evident that the ordering process and crystal growth are promoted by the presence of a fluid B_2O_3 phase. Layer mobility apparently is increased. It does not seem unreasonable to consider that part of the mechanism may involve material transfer (by solubilization) from the preponderant high energy regions to the relatively few ordered regions (nuclei), a process which would be achieved more readily in the presence of the fluid B_2O_3 phase. This mechanism is given added impetus by the fact that an increase in the number of nuclei, by addition of BN_g "seed," further promotes the ordering process. Another consideration is that under the conditions used in this study, where B_2O_3 volatilization is retarded, a consequent increase in pressure also may influence the transformation.

Acknowledgment.—The authors are indebted to Mr. Harry B. West for supplying a large number of boron nitride samples having different thermal histories.