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Letter

On the influence of nitrogen pressure on the ordering of hexagonal boron nitride

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In the course of our experiments on high temperature synthesis of ternary boron nitrides through the nitration of elementary powder mixtures, amorphous boron (a-B) was used as a reference sample. Attention was drawn to the fact that both appearence and structural ordering of the reference varied markedly with changes of partial nitrogen pressure. This phenomenon gave rise to the present study.

Samples were prepared by 24 h heating of a-B powder (*ex diborane*, H.C. Starck, Goslar, Germany) at 2200 °C under a nitrogen/argon (AGA, Sundbyberg, Sweden; claimed purity 99.999%) atmosphere at various flow rates of the feed gases. The description of the furnace facilities used can be found elsewhere [1]. The structural investigation was performed with X-ray powder diffractometry and Raman spectroscopy using the same instruments and techniques as in Ref. [1].

The nitration of a-B in a pure nitrogen atmosphere results in the formation of a grey-coloured BN powder with a turbostratic graphite-like structure reported earlier [2]. The similarity of the in-plane lattice parameter value to that of an ordinary, commercially available BN (Elektroschmelzwerk Kempten GmbH, Kempten, Germany; claimed purity 98%; white powder) (Table 1) reveals the presence of quite perfectly ordered honeycomb layers in the sample obtained. At the same time the difference in the appearence of corresponding diffraction patterns (Figs. 1(a) and 1(c)) provides evidence, that these layers are of limited mean size

Table 1
Lattice parameters of various BN samples

Lattice parameter	BN sample		
	Partial pressure of N_2		Commercial
	100%	10%	
a, Å	2.5072(1) [2]	2.503(2)	2.5042(6)
c, Å	6.87(1)	6.678(5)	6.656(2)

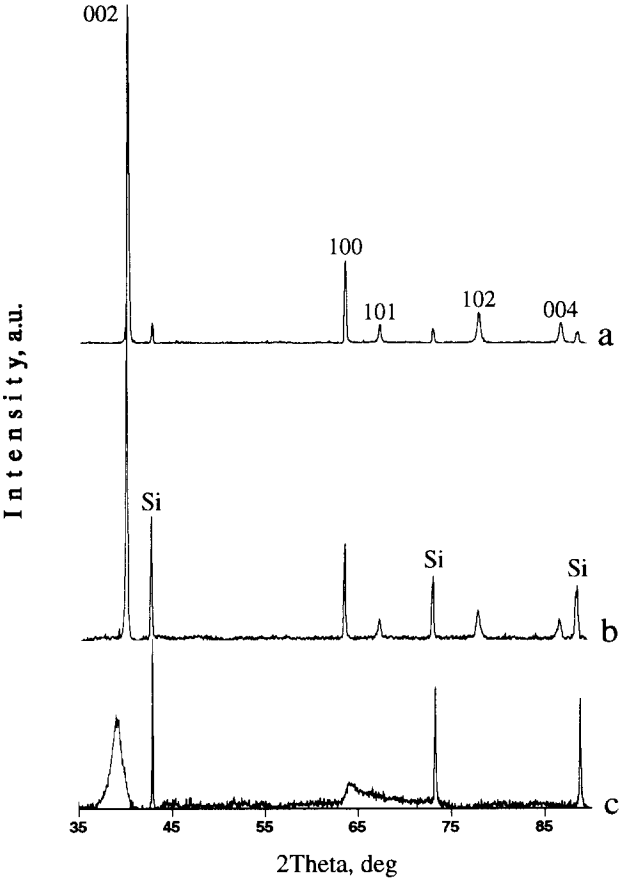

Fig. 1. Guinier-Hägg powder diffraction patterns ($CrK\alpha_1$) of BN samples: (a) commercially available; (b),(c) obtained by nitration of amorphous B at 2200 °C at 100% and 10% partial pressure of N_2 respectively.

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(146(2) Å [2]) and have no registry with respect to each other.

A gradual decrease of the partial nitrogen pressure in 10% steps from 100% to the 20% value leads to irregular changes of the in-plane crystallite size while preserving a turbostratic nature of the specimen structure. Simultaneously, the colour of the resulting powder changes progressively from grey to yellow. A change-over from 20% to 10% of the partial nitrogen pressure is accompanied by a drastic structural modification. The bright-yellow-coloured sample obtained exhibits well-defined three-dimensional ordering (Fig. 1(b)) comparable with that of the commercial BN. Raman spectroscopy data (Fig. 2) provide an additional indirect evidence of the perfect atomic arrangement. Analyses of carbon and nitrogen were carried out using conventional combustion methods. Carbon was determined with a LECO CS-444 apparatus and nitrogen with LECO TC-336 equipment. Results of the chemical analyses are presented in Table 2.

The general feature of compositions determined is the excess of boron with respect to the nitrogen found

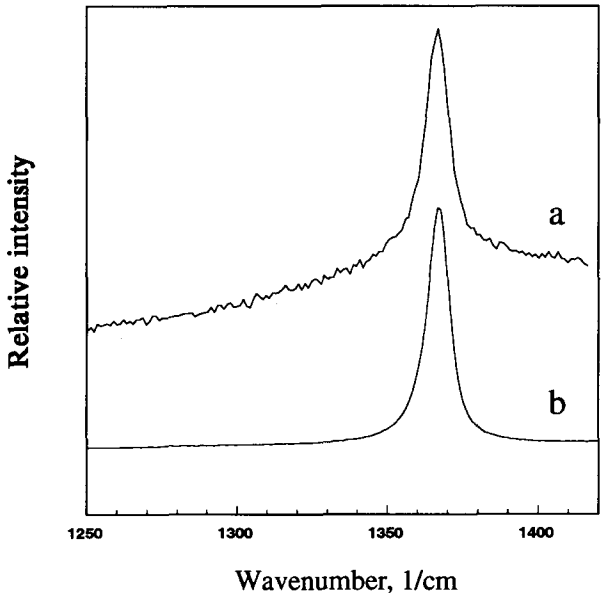

Fig. 2. Raman spectra of BN samples: (a) commercially available; (b) obtained by nitration of amorphous B at 2200 °C at 10% partial pressure of N_2.

Table 2
Sample composition according to chemical analysis

Sample	N, w.%	O, w.%	C, w.%	B, w.%[a]	Formula
100% N_2	40.7	0.26	0.35	58.7	$BN_{0.54}C_{0.005}$
10% N_2	53.1	0.33	0.64	45.9	$BN_{0.89}C_{0.01}$
Commercial	53.6	2.4	0.1	43.9	$BN_{0.94}$; $BN_{0.97}$[b]

[a]Determined as difference.
[b]Corrected on the assumption that all oxygen atoms are bound in B_2O_3 phase.

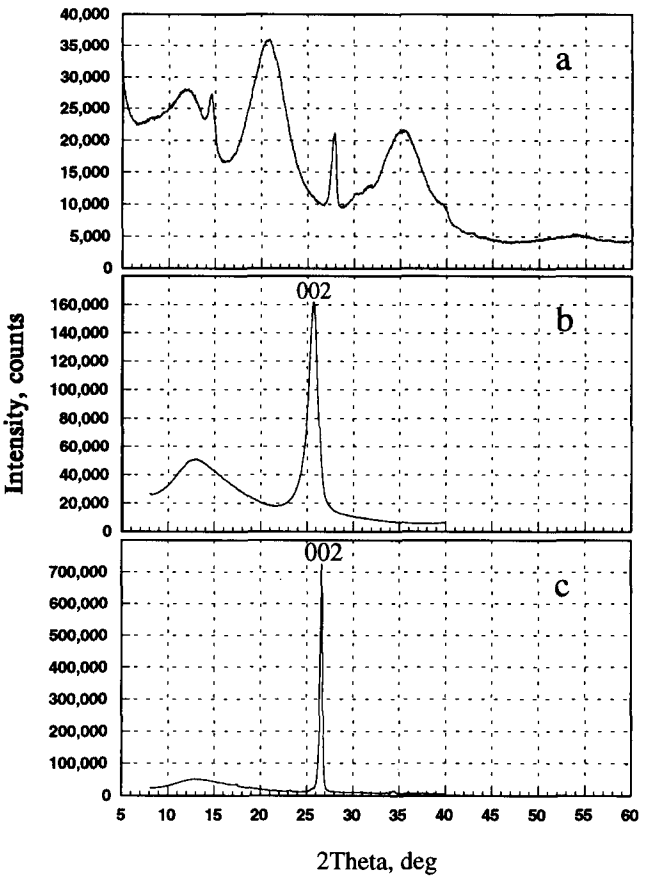

Fig. 3. Powder diffractometer patterns (CuK$\alpha_{1,2}$): (a) amorphous boron (narrow peaks at 14.6° and 28° are ascribed to a $B(OH)_3$ impurity); (b),(c) BN samples obtained by nitration of amorphous B at 2200 °C at 100% and 10% partial pressure of N_2 respectively.

in all specimens. Such an excess in the commercial BN may be attributed to the remainder B_2O_3, a lubricant added to BN powder to facilitate the compacting process. When corrected for the oxide content, the composition of the commercial nitride becomes near-stoichiometric (Table 2). In a similar way a remainder of unreacted a-B may explain the B:N ratio in the other specimens, especially if it is remembered that the *a* values do not support the presence of considerable amounts of vacancies in the layers. Fig. 3 shows diffraction patterns collected with an extended exposure time in the low Bragg-angle region. Both samples incorporate a noticeable amount of an amorphous phase and, according to the peak ratio, it is most likely that the one obtained at 100% of the nitrogen pressure (Fig. 3(b)) contains more a-B than that synthesized at 10% N_2 (Fig. 3(c)). An accurate quantitative estimation of the a-B phase content is hampered by a drastic modification of the amorphous phase during nitration (compare Fig. 3(a) with Figs. 3(b),(c)) and by the non-occurrence of a reliable procedure for calculation of a diffraction peak intensity from a turbostratic structure.

Acknowledgements

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References

[1] Yu.G. Andreev and T. Lundström, *J. Alloys Comp., 210* (1994) 311.

[2] Yu.G. Andreev and T. Lundström, *J. Appl. Crystallogr.*, in press.