Comments

Comments on the "Synthesis of Cubic Boron Nitride at Low-Temperature and Low-Pressure Conditions"

The following is a comment on a recent publication by D. L. Cui et al., published in *Chem. Mater.* **2002**, *13* (8), 2457−2459. In the presented XRD, IR, TEM, and XPS data there are significant criteria that are not consistent with the authors' interpretation of a low-pressure/low-temperature synthesis of cubic boron nitride.

1. Interpretation of XRD Pattern

In Figure 1, the authors claim the assignment of peaks in the XRD pattern as cBN, hBN, and oBN. According to the crystallographic data (JCPDS: cBN 25-1033, hBN 34-421, oBN 18-251) the reflections are as in Table 1.

The reported XRD patterns thus do not fit for cBN or hBN or oBN because the intensities or positions do not match at all. The deviations cannot be interpreted as a texture effect. Some important peaks are missing or display absolutely different intensities. The claimed assignment of oBN given by the authors also does not fit with the intensities or peak positions of the oBN phase obtained by shock wave compression. The authors refer in their paper to the orthorhombic BN phase with "$a = 0.86$ nm, $b = 0.774$ nm, $c = 6.35$ nm" (only a orthorhombic phase with $a = 8.6$ Å, $b = 7.74$ Å, $c = 6.35$ Å exists; see JCPDS card 18-251) and cite ref 13[1] in which the orthorhombic BN phase is correctly assigned with ICDD-JCPDS card 18-251 (literature reference no. 5[2] of ref 13[1]), displaying a peak at $2\theta = 14.09°$ of an intensity of 100%. This and other (*hkl*) reflections of the oBN phase are apparently missing in the presented XRD pattern in Figure 1, although the authors claim that the data can be indexed as oBN.

2. Interpretation of the Infrared Spectrum

Regarding the IR spectrum in Figure 3, the theoretical value for the cBN frequency is at 1056 cm^{-1}.[3] The authors also cite ref 14 in which the IR spectra and a frequency analysis are given for nanocrystalline cBN. The cBN mode ranges from 1050 to 1065 cm^{-1} (see also the literature (ref 14)[4]), which is not at all in accordance with the assignment of the authors. In the present paper, the authors claim a mode at 1134 cm^{-1} to be attributed to cBN. In the literature there are no reports for true cBN nanocrystals in this region.[3,4] The authors also do not explain their reasons for this assignment. (It would be a an unusual shift of approximately 80 cm^{-1}, which is not explainable for cBN!) According to the data in the literature[5,6] for hydrated boron oxide, boron−oxygen compounds, and others, more thorough IR studies of BN polymorphs,[3,4] the observed band is to be assigned as a B−OH bending mode. Those modes are reported[5,6] in the range approximately from 1100 to 1200 cm^{-1}, the B−O− stretching modes are in the range of 1450 cm^{-1} (in the paper a mode at 1409 cm^{-1} is assigned as "hBN"), and the B−OH twisting modes are in the range of 720 cm^{-1}. (In Figure 2 there are modes detected in all these regions.) In the IR spectra a strong OH−band is present at 3428 cm^{-1}, which has to be attributed to the presence of B−OH groups (hydroxy groups) correlating with the strong band at 1134 cm^{-1} wrongly assigned as cBN. The authors do not comment at all on their unusual shift and assignment.

Also the authors' assignment of hBN does not match because proper hBN or sp^2-type BN exhibits strong bands at ≈780 and ≈1370 cm^{-1}, as reported in the literature.[3,4] These data clearly indicate that an assignment of cBN or the postulation of the presence of cBN regarding IR data is very critical and doubtful and cannot be considered as proof for the existence of cBN, especially if traces of oxygen, water, or hydroxy groups are present.

3. TEM Analysis

Regarding the TEM data presented in Figure 2b, the authors state only that the "inner ring" of the electron diffraction pattern "agrees well" with a *d* value with one reflex of the XRD pattern and assume it to be cBN, but they do not present any data. This correlation is quite speculative, and in true samples of nanocrystalline cBN, also, the other diffraction rings are assignable, as reported in their ref 14[4] and the literature cited therein. Also, the authors cite in ref 11 JCPDS no. 25-1032 for cBN, which is actually yttrium boride.

4. Experimental Section

As known from the synthesis of boron nitride, samples obtained at ≈500 °C are either amorphous sp^2-type BN or mainly hBN with weak crystallinity, also displayed in the XRD patterns given in ref 6[7] by the authors. Thus, it is quite astonishing that the authors claim the presence of "crystalline" hBN, cBN, and oBN with an XRD pattern displayed in Figure 1, showing peaks of a crystalline sample with no matching peaks of the claimed phases. Furthermore, the experimental part is not correct at all because a mixture of benzene, BBr_3, and Li_3N will also lead to a reaction and decomposition

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† Tel.: +49 (0) 681 302-2465. Fax: +49 (0) 681 302 3995. E-mail: h.sachdev@mx.uni-saarland.de.

(1) Gasgnier, M.; Szwarc, H.; Ribez, A. *J. Mater. Sci.* **2000**, *35*, 3003.
(2) ICDD- JCPDS card No. 18-251.
(3) Doll, G. L. In *Properties of Group III Nitrides*; Edgar, J., Ed.; Inspec: London, 1994; pp 169 and 241.
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(5) Parsons, J. L.; Miolberg, M. E. *J. Am. Ceram. Soc.* **1960**, *43*, 326.
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(7) Rao, L.; Kaner, R. B. *Inorg. Chem.* **1994**, *33*, 3210.
(8) ICDD- JCPDS card no. 4-836.
(9) ICDD- JCPDS card no. 15-806.
(10) ICDD- JCPDS card no. 4-850.

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Table 1.

<table>
<tr><th>(*hkl*)</th><th>intensity (theor.)</th><th>position 2θ</th><th>assignment by the authors in Figure 1</th></tr>
<tr><td colspan="4">c-BN
25-1033</td></tr>
<tr><td>111</td><td>100%</td><td>43.29</td><td>assumed/assigned as c-BN (111) with intensity 100% (2θ position not given)</td></tr>
<tr><td>200</td><td>2%</td><td>50.43</td><td>assigned as c-BN (200), but observed intensity is ∼25%! (2θ position not given)</td></tr>
<tr><td>220</td><td>6%</td><td>74.09</td><td>assigned as c-BN (220), but observed intensity is ∼10%! (2θ position not given)</td></tr>
<tr><td colspan="4">true c-BN samples display (nearly) matching intensities with deviation <10%; texture effects cannot be responsible for such deviations; the assignment presented by the authors also does not match with c-BN card no. 35-1365!</td></tr>
<tr><td colspan="4">h-BN
34-421</td></tr>
<tr><td>002</td><td>100%</td><td>26.76</td><td>not present or with intensity far too small for h-BN (002)</td></tr>
<tr><td>100</td><td>15%</td><td>41.59</td><td>missing!</td></tr>
<tr><td>101</td><td>6%</td><td>43.87</td><td>peak assigned as (h-BN 101) displaying 100% intensity for all peaks assigned as h-BN</td></tr>
<tr><td>103</td><td><1%</td><td>59.53</td><td>intensity too high for h-BN (103) assignment</td></tr>
<tr><td>102</td><td>9%</td><td>50.15</td><td>wrong assignment at 2θ in Figure 1 at ∼63°!</td></tr>
<tr><td colspan="4">for this reason the assignment as h-BN is not correct!</td></tr>
<tr><td colspan="4">o-BN
18-251</td></tr>
<tr><td>001</td><td>100%</td><td>14.09</td><td>missing</td></tr>
<tr><td colspan="4">all other remaining reflections do not fit for o-BN, as claimed by the authors, if compared to ref 13[1] given in the publication</td></tr>
</table>

of benzene at 480 °C. (This procedure was reported by the authors.)

5. Summary and Conclusion

Because of these facts, the presented interpretation given by the authors is not consistent with their experimental data, a synthesis of nanocrystalline cBN cannot be claimed as a result of the significant mismatch of XRD and IR data, and the presented TEM data are not significant.

It is very important to consider the fact that some transition metals (e.g., copper,[8] cobalt,[9] and nickel[10]) do exhibit lattice constants as well as almost identical peak positions in XRD patterns similar to cubic boron nitride; only the intensities differ. Thus, TEM and XRD data will look similar! It is also not justified to interpret the TEM electron diffraction data of a “single diffraction ring” as proof for the presence of cBN because, as mentioned, many other compounds do have similar lattice spacing, leading to a diffraction pattern with one or some matching *d* values.

The presented XRD and TEM data display crystalline material, but neither cBN nor hBN because of unmatching or missing XRD peaks. A comparison of the XRD pattern in Figure 1 of the paper with JCPDS cards for Fe_2N 6-656, FeO 6-615, NiO 22-1159, Ni 4-850, Co 15-806, or LiBNO 37-823 shows that these phases and/or mixtures thereof may result in a peak pattern similar to that presented in Figure 1. The container material of the autoclave, which is described as stainless steel, contains also iron, nickel, and cobalt, and the presence of “nanoparticles” and of compounds containing these elements is possible, which are also “visible” in TEM studies.

Furthermore, the authors do not present a thorough chemical analysis and the XPS pattern in Figure 4 can also be obtained from a mixture of any compounds containing boron and nitrogen, neither the yield of the product is reported. The presented IR spectrum looks like a mixture of amorphous sp^2-type boron nitride and $B(OH)_3$ (boric acid), which is consistent with the authors’ notation of a boron excess of 10% in the XPS spectra! Although the title sounds very promising, the presented data and the interpretation given by the authors is not consistent given the mentioned facts and also is not consistent with their cited literature.

Hermann Sachdev†

Institut f. Anorg. Chemie Fakultät 8.11, P.O. Box
151150, D-66041 Saarbruecken, Germany

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