Diamonds from the Pressure Cooker—Science or Science Fiction?[**]

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Stichwörter:
chemical vapor deposition · correspondence · diamond synthesis · high-pressure chemistry · Raman spectroscopy · synthetic methods

Recently, a diamond synthesis was reported by Chen and co-workers under conditions of diamond being metastable,[1,2] and both publications deal with the synthesis of diamond by reduction of carbon dioxide or carbonates with sodium metal at about 460–500°C/800–860 atm, thus being quite comparable methods. Each of the papers is based on conclusions made from an interpretation of similar experimental data (one powder diffraction pattern (XRD spectrum), one Raman spectrum, and SEM pictures), all displaying only characteristics of the product. The authors do not present any experimental data regarding reaction intermediates in the publications or as supporting information, nor do they argue about similarities to already existing diamond-formation processes, although they claim to have characterized the intermediates.[2] In the case of the reduction of magnesium carbonate[2] the authors explain their results with the following reactions [Eq (1)–(3)]:

$$MgCO_3 \rightarrow MgO + CO_2 \qquad (1)$$

$$CO_2 + 4\,Na \rightarrow 2\,Na_2O + C \qquad (2)$$

$$Na_2O + CO_2 \rightarrow Na_2CO_3 \qquad (3)$$

In the experimental section, the authors argue that they have characterized the intermediates MgO and Na_2CO_3 besides graphite and diamond by XRD. In the case of the neat reduction of carbon dioxide[1] similar argumentations are made. No diamond formation was reported so far from alkali metal or alkaline earth metal carbides under the pressure/temperature conditions given by the authors in the concerned publications. It is known that the primary reaction of alkali metals (M) with carbon dioxide leads to oxalates by single electron transfer (SET) reactions [(Eq. (4), (5)]:[3]

$$M + CO_2 \rightarrow M^+\,CO_2^{*-} \qquad (4)$$

$$2\,M^+\,CO_2^{*-} \rightarrow M_2C_2O_4 \qquad (5)$$

The oxalates are prone to disproportionation at elevated temperatures and form the corresponding carbonates and carbon monoxide [Eq. (6)] (standard calibration of thermal gravimetric–differential thermal analysis (TG–DTA) devices by, for example, CaC_2O_4 decomposition):

$$M_2C_2O_4 \rightarrow M_2CO_3 + CO \qquad (6)$$

From a chemical point of view, a reduction of carbon dioxide or carbonates by sodium metal may form the corresponding oxalates, which finally decompose at higher temperatures to carbon monoxide. Carbon formation thus can occur by disproportionation of carbon monoxide to carbon and carbon dioxide [(Eq. (7)]. Therefore, it has to be considered whether a diamond formation from carbon monoxide is feasible.

$$2\,CO \rightarrow CO_2 + C_{(\text{graphite, diamond})} \qquad (7)$$

The diamond formation in the ternary C/H/O system under metastable conditions involving CO in the gas phase is well documented,[4] but not mentioned by Chen et al. In chemical vapor deposition (CVD) syntheses of diamond (performed at the pressure/temperature domain in which the diamond is metastable), usually the carbon–hydrogen system is used to deposit crystalline diamond. However, it is also possible to obtain well-grown diamond in the ternary C/H/O system. A diamond formation in a reductive system of carbon dioxide (e.g., sodium and carbon dioxide or sodium and carbonates), as presented by Chen et al.[1,2] in a pressure/temperature regime of diamond being metastable can not be excluded in principle and might be feasible, especially if traces of water are present. But it has to be considered whether the presented measurements and the spectroscopic data prove that the presented reactions have taken place and whether the experimental procedures are reproducible and consistent with the descriptions and interpretations.

The most critical points in these publications[1,2] will be discussed to evaluate the results claimed by the authors. In reference [1]

- no reference of the XRD interpretation of Figure 1 is given and no description of the XRD spectrometer is mentioned. The formation of graphite is based on the interpretation of a single diffraction peak in

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[**] Comments to the “Growth of Large Diamond Crystals by Reduction of Magnesium Carbonate with Metallic Sodium”

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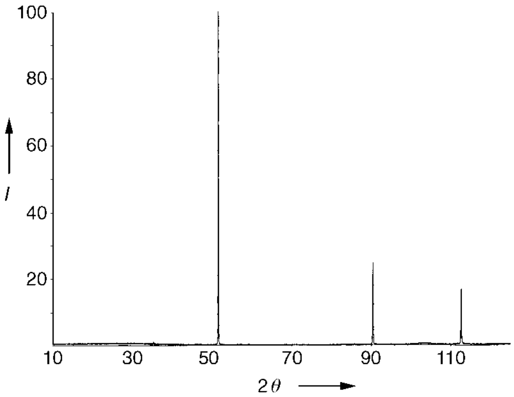

Figure 1. XRD spectrum of natural diamond grit displaying the 111, 220, and 311 reflections (measured with Co $_{K\alpha}$ radiation). I = relative intensity.[7]

the XRD spectrum of Figure 1, whereas no other diffraction peaks of graphite are present.

- the Raman spectrum displays additional features at about 1600 cm^{-1}, which are not discussed
- the crystal morphologies shown in Figure 3a, b and Figure 4 do not match (important note: similar magnification!): Figure 3 displays solid material that is not facetted and resembles dissolutive or broken material, whereas Figure 4 clearly shows an octahedral-shaped, facetted material of growth-type morphology. The morphological features of these "typical sample pictures" do not correspond with the described "diamond growth" and no explanation is given for this significant and obvious fact. Additionally, SEM pictures may display diamond but these cannot prove that diamond is present.
- supporting information is of no significance (a picture of an octahedral crystal).

With regard to reference [2] it is noted—besides the correspondence of the XRD pattern in Figure 1 with the spectrum shown in reference[1]—that:

- The XRD pattern in Figure 1 is referenced with a Joint Committee on Powder Diffraction Standards (JCPDS) file 75–0623, which actually is a calculated spectrum displaying explicitly only two calculated 2θ values (for the 111 and 220 reflections), whereas the calculated value for the 311 reflection is not mentioned. Thus it makes no sense to correlate this JCPDS card to the three diffraction peaks of the "obtained diamond spectrum" of Figure 1. Also, the legend of Figure 1 is in contradiction to the text and experimental section "XRD … of *as-prepared* diamond…" In this case, the reaction intermediates would also have to be present in the XRD spectrum, since it is referred to an "as-prepared" sample.

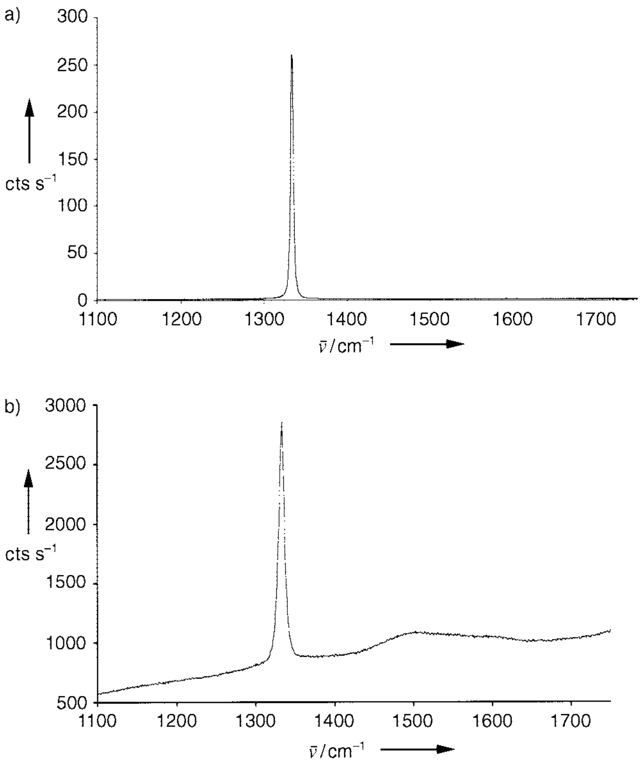

Figure 2. Raman spectra of diamond samples.[8] a) Raman spectrum of HPHT diamond (diamond peak at 1332 cm^{-1}). b) Raman spectrum of CVD diamond with traces of sp^2-type carbon (diamond peak at 1332 cm^{-1}, graphitic broad D- and G-modes centred at about 1350 and 1500–1600 cm^{-1}). Cts = counts.

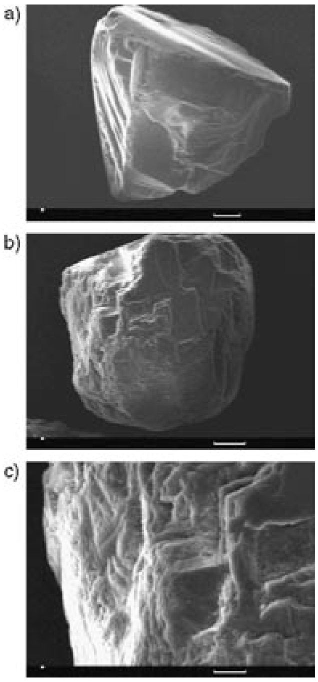

Figure 3. a)–c) SEM pictures displaying the morphology of natural diamond grit (broken, dissolutive) in the range of 200 μm. The bar in (a) and (b) is 30 μm long and 10 μm long in (c).

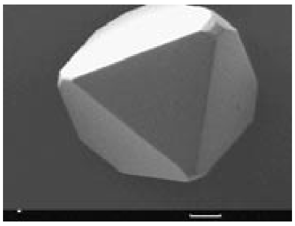

Figure 4. SEM picture displaying the morphology of a growth type HPHT diamond crystal. The bar is 30 μm long.

- The Raman spectrum in Figure 2 is from a diamond sample and exhibits a broad structure in the region of 2000 cm^{-1}. The authors do not mention this aspect or possible origin of this feature in the text.
- The SEM in Figure 3 displays a sample of solid material of broken or dissolutive nature. How does this crystal morphology correlate with diamond growth as claimed in the text?
- Regarding the experimental setup, from the presented data it is not evident how the pressure/temperature conditions were measured or maintained in the autoclave or recorded as described in the Experimental Section. No heating device or temperature-control unit is mentioned or depicted or referenced. The detailed experimental setup was never referenced or displayed properly in both publications. Furthermore, stainless steel will be severely corroded by the mentioned reaction parameters and may cause side reactions that initiate carbon formation.
- In their communication the authors themselves mention in the Experimental Section that their main identified products by XRD were "diamond, graphite, Na_2CO_3, and MgO". They state that they have detected Na_2CO_3 and MgO in the product mixture by XRD analysis and formulate the Equations (1)–(3). Neither in the publications nor in any supporting information were such XRD files or XRD spectra of any "as-prepared sample" presented.
- In the experimental section: perchloric acid ($HClO_4$) is mentioned as a reagent to dissolve graphite, but this procedure is also not cited and referenced. No concentration is mentioned. Reaction conditions, such as temperature or duration for the dissolution, are missing. A reaction of perchloric acid is strongly dependent on the concentration and finally may lead to a distinctive intercalation and oxidation product (graphite perchlorate), which itself has a crystalline nature (and might be detected by XRD), but graphite is not really being dissolved as described by the authors. No reaction parameters are given either.

In addition to these more specific points there are important general remarks with respect to both publications:[1,2] Neither publication gives detailed references for the experimental setup nor describes the autoclave, pressure and temperature measurements, which are the most critical parameters in these reactions, thus, the results can not be reproduced in a proper manner. Even if it is stated that the pressure is autogenic, how were the corresponding pressure/temperature values obtained and measured (e.g., 500 °C/860 atm in reference [2] 440 °C/800 atm in reference [1])? Furthermore, the materials used as described in the autoclave synthesis are highly corrosive at temperatures about 500–700 °C and thus can cause severe damage or corrosion to the described stainless-steel autoclave, which will lead to contamination of the reaction mixture, thus additional compounds may affect or catalyze the formation of carbon. In general, the experimental description is not sufficient to clarify or validate the claimed results. A total yield of carbonic material was not given for either reaction.

Are the presented analytical data (XRD, Raman, SEM) a sufficient proof of a new synthetic method as published by the authors? Broken natural or artificial high-pressure high-temperature (HPHT) diamond samples or CVD samples lead to similar XRD, Raman, and SEM data as presented by the authors in both articles,[1,2] especially if the crystal quality is quite good. Irrespective of how the XRD spectra in Figures 1 of both publications were obtained, the standard XRD spectra of natural, HPHT, or CVD diamond samples are rather similar and can not be distinguished by simple diffraction methods.

Such diamond samples exhibit almost identical XRD patterns under standard routine measurement conditions, especially if the diamond quality is good. The same argument is also valid for the Raman spectra[5,6] of Figure 2 of the concerned publications.

The presence of signals from sp^2-hybridized carbon atoms in the Raman spectrum may be due to surface reconstruction, additional carbonic matter on grain boundaries, or graphitic inclusions within the diamond crystal. In general, the Raman cross section of sp^2-hybridized carbon atoms is about 10^2 times higher than of sp^3-hybridized carbon atoms (depending on the excitation wavelength), therefore the presence of signals of sp^2-hybridized carbon atoms in the Raman spectra is no proof for the formation of crystalline graphite, which might be detected by XRD. The SEM pictures might be taken from any material, and no energy-dispersive X-ray (EDX) analyses are presented to proof the presence of carbon or any other element. Most of the SEM pictures display nonfacetted, dissolutive material although diamond growth is mentioned by the authors, the issue of the fragmented material is not discussed.

The spectra and pictures displayed in Figures 1–Figure 4 from diamond samples of different origin indicate that the conclusions drawn by Chen and coworkers[1,2] can not be solely based on their presented data, as there is no experimental support for the proposed reaction mechanism provided by the authors.

Even if it is assumed that the data presented by Chen and co-workers[1,2] are correct, they cannot be used as a unique and significant proof of the reported diamond synthesis as it is not possible to distinguish the presented analytical data (XRD, Raman spectrum, SEM micrograph) from other (crushed, broken) artificial or natural diamond samples of the same size and morphology.

When a new reaction pathway is claimed, the characterization and presentation of intermediates is necessary and mandatory in a communication, even if a full and thorough scientific interpretation cannot be given in the first instance. The mentioned reaction intermediates in the publications were not presented by the authors although the authors claimed several times to have identified them by XRD.[2]

The most critical parameters for diamond formation by any method are the pressure and temperature conditions. The experimental descriptions[1,2] do not allow a straightforward reproduction of the procedures, since there are no details of how the temperature/

pressure values were obtained. There are also other significant factors that may severely affect the reaction (e.g., moisture incorporated by weighing the solid carbon dioxide, influence of iron from the autoclave, etc.). From the way of handling the XRD and other data by the authors, together with the above raised aspects, there are severe doubts that both approaches of the diamond syntheses are based on the experiments as described by the authors,[1,2] even if they are not contradictory to the current models of diamond formation and might be feasible. At this stage the authors failed to prove their reported syntheses and their interpretation is not supported by the presented analytical data.

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[1] Z. Lou, Q. Chen, Y. Zhang, W. Wang, Y. Qian, *J. Am. Chem. Soc.* **2003**, *125*, 9302–9303.

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[3] A. F. Holleman, E. Wiberg, *Lehrbuch der Anorganischen Chemie* (Ed.: N. Wiberg),Walter de Gruyter, Berlin, **1996**, p. 100–105.

[4] P. K. Bachmann, D. Leers, H. Lydtin, *Diamond Relat. Mater.* **1991**, *1*, 1–12 and plenty of other reports in the same journal up to now.

[5] J. Wilks, E. Wilks, *Properties and Applications of Diamond*, Butterworth-Heinemann, Oxford, **1991**.

[6] J. E. Field, *The properties of natural and synthetic diamond*, Academic Press, London, **1992**.

[7] STOE STADI-P XRD diffractometer.

[8] S.A. T64000 Raman spectrometer [excitation wavelength: 514 and 488 nm (2 µm spot size, 8 mW power at sample), backscattering geometry].

[9] CamScan 44FE Field emission scanning electron microscope.