High-Pressure Polymerization

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Polymerization of Acetonitrile via a Hydrogen Transfer Reaction from CH_3 to CN under Extreme Conditions

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Abstract: *Acetonitrile (CH_3CN) is the simplest and one of the most stable nitriles. Reactions usually occur on the $C\equiv N$ triple bond, while the C–H bond is very inert and can only be activated by a very strong base or a metal catalyst. It is demonstrated that C–H bonds can be activated by the cyano group under high pressure, but at room temperature. The hydrogen atom transfers from the CH_3 to CN along the $CH\cdots N$ hydrogen bond, which produces an amino group and initiates polymerization to form a dimer, 1D chain, and 2D nanoribbon with mixed sp^2 and sp^3 bonded carbon. Finally, it transforms into a graphitic polymer by eliminating ammonia. This study shows that applying pressure can induce a distinctive reaction which is guided by the structure of the molecular crystal. It highlights the fact that very inert C–H can be activated by high pressure, even at room temperature and without a catalyst.*

Hydrogen bonding is the most important noncovalent interaction in biological systems, pharmaceutical applications, and material sciences.[1] It is a strong and directional intermolecular interaction, which plays a crucial role in the intermediates of chemical and enzymatic reactions. Pressure is proven to be a powerful tool for controlling the geometric properties of hydrogen bonding, which induces rich phenomena in supramolecular chemistry, including pressure-induced amorphization and phase transitions.[2] Furthermore, by compressing the intermolecular distance, hydrogen bonds can be strengthened[3] and hydrogen can transfer through the hydrogen bond accordingly. For example, in the classical hydrogen bonds, such as the $O-H\cdots O$ and $N-H\cdots N$ bond, proton hopping can be induced by high pressure, resulting in symmetric H-bonds in ice[4] and a solid ammonium amide phase in ammonia.[5] However, to our knowledge, for the weak $C-H\cdots A$ hydrogen bond (where A represents the hydrogen bond acceptor), there are very few reports showing that hydrogen can transfer from a carbon atom via hydrogen bonding under high pressure at room temperature.[6]

Acetonitrile (CH_3CN) and other nitriles are detected in the interstellar medium extensively and are believed to be a plausible source of the amino acids found in meteorites.[7] Previous studies show that in nitriles, including the cyanogens,[8] cyanoacetylene,[9] and tetracyanoethylene (TCNE),[10] the CN group undergoes a pressure-induced addition polymerization reaction, which is also supposed to be the main reaction site in acetonitrile.[11] Here we demonstrate that the inert CH bond can be activated under high pressure and the hydrogen migration from the carbon to the nitrogen atom is the crucial reaction that triggers polymerization. This reaction is guided by the topology of the crystal structure, which is governed by the weak $CH\cdots N$ bonds. To our knowledge, this is the first report of hydrogen hopping through weak $CH\cdots N$ hydrogen bonds. Our studies highlight the fact the high-pressure solid reaction, directed by the crystal structure, leads to a completely new reaction route.

Acetonitrile was compressed in a diamond anvil cell (DAC) up to 20 GPa. In agreement with the previous work,[11,13–15] the in situ Raman spectra indicate that acetoni-

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trile undergoes a minor phase transition at 5 GPa and turns into an amorphous state at about 19.5 GPa (Supporting Information, Figure S1). The fluorescence background was then irreversibly enhanced to cover all the features, which indicates the occurrence of a chemical reaction. In the IR spectra, $C{=}N$/$C{=}C$ groups were detected above about 23 GPa (Supporting Information, Figure S2). A broad peak of amino group in the range of 3000–3500 cm^{-1} was identified, and the characteristic Fermi resonance peaks of $-NH_2$ at 3201 cm^{-1} and 3337 cm^{-1} was detected when the sample was recovered to ambient pressure (Supporting Information, Figure S2). Above 32 GPa a yellowish polymer formed (Supporting Information, Figure S3). The presence of the $C{=}N$/$C{=}C$ and amino groups characterizes this polymer. The occurrence of amino groups reminds us that the cyano groups did not undergo simple addition polymerization, but a hydrogen transfer reaction instead.

To further understand the reaction process, the polymer was synthesized at milligram scale by the Paris–Edinburgh (PE) press at 25 GPa for structural characterization. Different from the yellow polymer obtained from the DAC, a black solid powder was obtained (Supporting Information, Figure S4c). Ammonia gas was released during decompression, which was confirmed by pH indicators and elemental analysis of the obtained solid material (Supporting Information, Figure S4a,b). It shows that the recovered material is enriched in carbon with a molar ratio of C, N, and H of 2:0.27:0.75 compared with the original acetonitrile (C/N/H = 2:1:3). The N and H loss ratio is 1:3.09(5), which is consistent with the release of ammonia (NH_3, N/H = 1:3).

The electron energy-loss spectroscopy (EELS), Raman, and neutron pair distribution function (PDF) results show this recovered material is a graphitic polymer (Supporting Information, Figures S5c, S6–S8). It exhibits a multilayered carbon onion structure and the distance between the curved layers is about 3.1 Å as determined by the aberration-corrected scanning transmission electron microscopy (STEM; Supporting Information, Figure S5a,b). The resistivity of this polymer is 90 Ohm m, similar to *trans*-rich polyacetylene film (100 Ohm m),[16] lower than that of silicon (10^3 Ohm m),[17] and higher than that of graphite (10^{-5} Ohm m).[18] This polymer has both sp^2 and sp^3 carbon, as identified in the ^{13}C solid-state nuclear magnetic resonance (ssNMR; Figure 1; Supporting Information, Figure S9). Besides the aromatic carbon connected in graphene-like networks, it also contains a $C{=}C(NR_2)_2$ group, as well as considerable carbon in sp^3 hybridization: methylene ($-CH_2-$) and/or methine carbon ($H-C-R_3$), and aminated carbon (NR_2-CR_3). The structure of this polymer can be described by the model shown in Figure 1. Typically, the cyano group is observed as a sharp peak at 117 ppm, and the methyl group between 0–20 ppm. What is striking is that neither was found in the ^{13}C NMR spectrum or in the ^1H magic-angle spinning (MAS) NMR spectrum (Supporting Information, Figure S10).[12] This further shows that the acetonitrile did not undergo a simple $C{\equiv}N$ addition polymerization and the methyl group participates in the hydrogen transfer reaction.

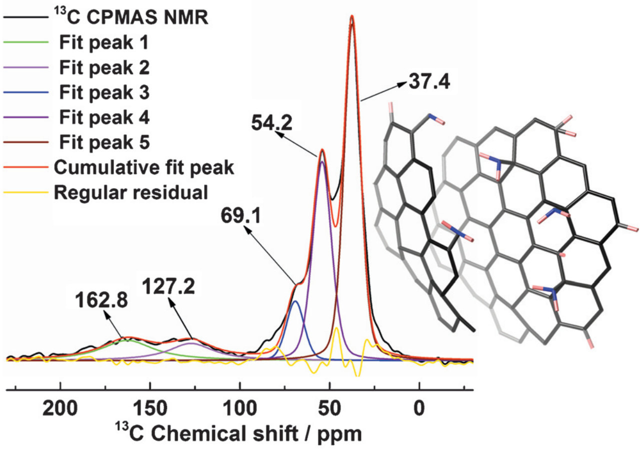

Figure 1. ^{13}C cross-polarization magic-angle-spinning solid-state NMR spectrum (^{13}C CPMAS ssNMR) of the graphitic polymer. In the sp^3 region, the carbon resonating at 37.4 ppm corresponds to methylene ($-CH_2-$) and/or methine carbon ($H-C-R_3$).[12] The peak at 54.2 ppm likely corresponds to aminated carbon (NR_2-CR_3).[12] The shoulder at 69.1 ppm is within the range of values of aliphatic amine carbon, while it may also be assigned as ene–diamine carbon, $-C{=}C(NR_2)_2$.[12] Such a possibility is also suggested by the presence of a high-frequency peak in the sp^2 region of the spectrum at 162.8 ppm, that could correspond to the aminated ene–carbon.[12] The other peak in the sp^2 region, at 127.2 ppm, is consistent with olefinic and/or aromatic carbon.[12]

To understand the reaction process in the acetonitrile crystal, we carried out in situ neutron powder diffraction and density functional theory (DFT) calculations. Both the diffraction and calculation results show acetonitrile maintains the orthorhombic structure with space group $Cmc2_1$ in the pressure range from 1.7 GPa to 20.6 GPa (Supporting Information, Figure S11). Every acetonitrile molecule is linked to six neighboring molecules by the $-C{\equiv}N\cdots H-CH_2-$ hydrogen bond, forming a diamond-type network (Figure 2a), with $C{\equiv}N$ as the hydrogen bond acceptor and CH_3 as the donor. The crystal is constructed by two interpenetrating networks, similar to that in ice-VII.[19]

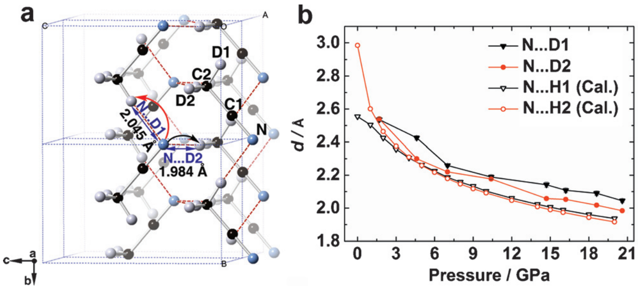

Figure 2. a) The crystal structure model of CD_3CN at 20.6 GPa; The possible hydrogen transfer routes (from $-CH_3$ to $-CN$) are indicated by the red and black arrows, which represent the direction of electron flow. b) Selected intermolecular atomic distances, $N\cdots D1$ and $N\cdots D2$ represent the corresponding intermolecular atomic distances obtained from the neutron diffraction data; $N\cdots H1$ (Cal.) and $N\cdots H2$ (Cal.) represent the distance obtained from our density functional theory (DFT) calculations.

The distances of N···D1 and N···D2 decrease quickly under compression, which are in good agreement with the results obtained from our DFT calculations (N···H1 and N···H2; Figure 2b). At 20.6 GPa, the D1···N and D2···N are 2.045(12) Å and 1.984(8) Å, respectively, which is shorter than the sum of the van der Waals radii of nitrogen and hydrogen (2.75 Å) by 25% and 28%. This suggests a high probability of hydrogen migration (Figure 2a). In qualitative comparison, the threshold distances of several hydrogen abstractions obtained from photochemical reactions are 2.26–2.58 Å for abstraction by oxygen and 2.66–2.89 Å by carbon. These are shorter than the corresponding sum of the van der Waals radii (2.72 Å for O···H and 2.90 Å for C···H) by 17% −5% for oxygen and less than 8% for carbon.[20] Furthermore, considering that the thermal vibrations[21] and the N−H bond length is around 1 Å, the H atom only needs to travel less than 1 Å to migrate. Thus, we can conclude that the hydrogen migrates from $-CH_3$ to −CN along the hydrogen bond. The possible reaction route is represented by the arrows in Figure 2a. This hydrogen transfer will produce active intermediates, such as $CH_2{=}C{=}NH$, which will initiate the polymerization reaction. Therefore, 1.98 Å (without a thermal vibration correction) can be referred as the critical distance of this hydrogen transfer reaction. Such critical distances may widely exist in other hydrogen abstraction reactions, which provide a crucial reference for the design and tailoring of the solid state reaction at a microscopic level.

We also performed metadynamic simulation on acetonitrile at 35 GPa based on DFT calculations to gain a better understanding of the reaction mechanism. As shown in Figure 3, in the molecular crystal (Figure 3a) the C−H bonds of the methyl group are activated and the hydrogen atom transfers to a cyano group, forming amino groups and dimer adducts (Figure 3b). Then, the reaction propagates to the rest of the molecules to polymerize into a 1D chain, which has alternating single and double bonds with sp^2-hybridizing carbon (Figure 3c). Finally, the 1D chain further polymerizes into a nanoribbon (Figure 3d). It has quite a low enthalpy, $-0.41\ \mathrm{eV\,atom^{-1}}$ to the initial state (acetonitrile molecule at 35 GPa), and is composed of sp^2 and sp^3 hybridizing carbon. The DFT calculation shows it is a semiconductor with a band gap of 2.0 eV, which absorbs blue and green light. That means the nanoribbon structure should be yellow and most likely corresponds to the product observed in the DAC (the yellowish polymer). Furthermore, according to Figure 3d, the methine carbon (−CH−), aminated carbon ($-C-NH_2$), enamine ($-C{=}C-NH_2$; the tautomer of the imine ($-CH-C{=}NH$) structure) and the amino groups ($-NH_2$) can be found in this structure, which fits our IR and NMR results perfectly.

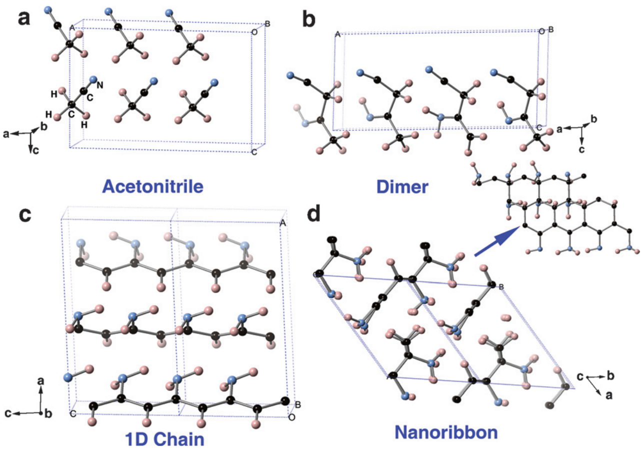

Figure 3. The possible reaction process of acetonitrile under high pressure indicated by metadynamic calculations at 35 GPa.

It is worth mentioning that the black graphitic polymer was produced when we use the PE press, which is different from the product obtained from the DAC, and indicates it contains a more conjugated structure. This is because cracks are easily produced in the gasket during decompression when using the PE press. The cracks are likely to provide a large pressure gradient and the space to release ammonia gas, which makes the sp^3 carbon convert to a more conjugated aromatic carbon. From the structure of the nanoribbon predicted above, we can also expect the elimination reaction between the amino group and neighboring hydrogen atom during decompression, which will lead to the formation of a graphene-like structure and ammonia.

So far, the whole reaction of acetonitrile under extreme conditions, including the structure of the reactant and product, as well as the process of polymerization and elimination, are well understood. It is described in Figure 4.

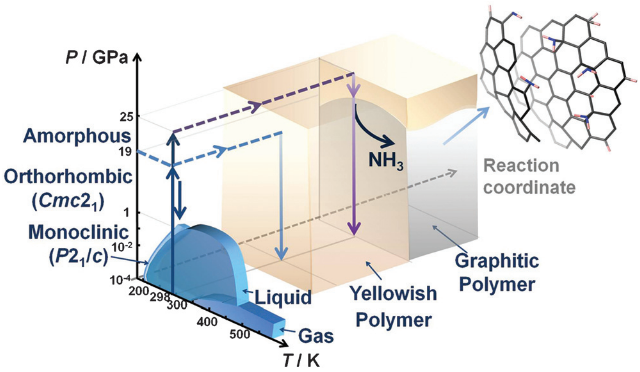

Figure 4. The acetonitrile reaction under high pressure at room temperature. The acetonitrile has an orthorhombic structure (space group *Cmc*2_1) from 1.7 GPa to 20.6 GPa obtained from in situ neutron diffraction. It forms an amorphous, yellowish polymer with $C{=}C/C{=}N$, $-NH_2$, $-C{=}C(NR_2)_2$, and sp^3 carbon($-CH_2-/H-C-R_3$ and NR_2-CR_3) as evidenced by the in situ Raman, IR spectra (in a DAC) and ssNMR (recovered graphitic polymer). After decompression, the sp^3 carbon converts into the aromatic carbon and ammonia gas is released.

Above 19 GPa, acetonitrile transforms to the yellowish polymer carrying the $C{=}C/C{=}N$, $-NH_2$, $-C{=}C(NR_2)_2$ groups and sp^3 carbon ($-CH_2-/H-C-R_3$ and NR_2-CR_3) through a hydrogen transfer reaction. This sp^3 carbon is metastable. When undergoing decompression, it converts into an aromatic carbon with sp^2 hybridization accompanied with the release of NH_3. The polymerization of the acetonitrile mentioned here is quite different from that in other nitriles like cyanogens,[8] cyanoacetylene,[9] and tetracyanoethylene (TCNE),[10] which are polymerized via the formation of a double bond between the neighboring cyano groups. This reaction process nicely demonstrates the relevance of the crystal structure to the solid-state reactivity. The reaction requiring minimum molecular displacement is more likely to occur. Under high pressure, the $-H_2C-H\cdots NC-$ hydrogen bonds facilitates the hydrogen transfer reaction. Furthermore, the release of small molecules is another peculiar feature in the high-pressure reaction of acetonitrile compared to other molecular crystals. By elimination and release of ammonia, unsaturated bonds are produced again. This would be another important reaction in the extreme conditions of the Universe, which is likely to generate complex aromatic molecules.

We also studied the temperature and time effect on the pressure-induced polymerization of acetonitrile. Indicated by the Raman spectra, the acetonitrile reacted at a much lower pressure, around 7.2 GPa when heated to 250 °C (Supporting Information, Figure S12 a). The IR spectrum of the recovered product is qualitatively similar to the one recovered from 32 GPa and at room temperature, which is also characterized by the amino and $C{=}C/C{=}N$ groups (Supporting Information, Figure S12 b). This indicates that high temperature can also promote the hydrogen migration and help to overcome the kinetic activation barriers under certain pressures. The time evolution IR spectra show that the conversion was increased when prolonging time. The increasing reaction rate upon further compression suggests the activation volume of this reaction is negative (Supporting Information, Figure S13).

In conclusion, the chemical reaction of acetonitrile shows peculiar features under high pressure that are quite different from those at ambient conditions. By applying the pressure at room temperature, instead of the polymerization of $C{\equiv}N$, the hydrogen atoms transfer from the carbon to nitrogen atom along the hydrogen bond to form a dimer, 1D chain, and 2D nanoribbon. This reaction correlates with the high-pressure crystal structure of the acetonitrile which is pre-organized by the $CH\cdots N$ hydrogen bond. This study nicely demonstrates that the solid-state reaction under high pressure is directed by the crystal structure and highlights the fact that even the weak $CH\cdots N$ hydrogen bonds can induce the hydrogen migration reaction under high pressure. The polymerization reaction, which is induced by the hydrogen migration in the heteronuclear hydrogen bonds, may be a prototype reaction happening in the crystal containing hydrogen bond network under high pressure.[6] Furthermore, our study also demonstrates that the methyl group, though very inert at ambient conditions, can be activated by the cyano group under high pressure and room temperature, without any catalyst or photonic excitation.

Experimental Section

High-purity acetonitrile (99.8%) and d_3-acetonitrile (99.8% D; Sigma Aldrich) were used in this work. For the Raman, IR, neutron diffraction study, and high-pressure synthesis, powder samples were prepared by loading and quickly sealing them under liquid N_2 temperature to avoid the possible formation of large grains or preferred orientation. A DAC with an anvil culet size of 400 μm in diameter was used for the in situ Raman and IR (type-IIA diamond anvil) measurements. Raman spectra were measured using a laboratory-made spectrometer, equipped with a Nd:YAG laser (operating at 532 nm) in a backscattering geometry. The in situ IR spectra were collected on a Bruker IFS 66v FTIR spectrometer and a custom IR microscope at beamline U2A of the National Synchrotron Light Source, Brookhaven National Laboratory. The recovered polymerized acetonitrile was synthesized by a VX3 PE Press at the Spallation Neutrons and Pressure Diffractometer (SNAP), Spallation Neutron Source (SNS), Oak Ridge National Laboratory (ORNL). The neutron powder diffraction data were collected at SNAP, SNS, ORNL. The details of the in situ Raman, in situ IR, in situ neutron measurements, high-pressure synthesis of the graphitic polymer, STEM, EELS, neutron PDF, ssNMR measurement, high temperature and high-pressure experiments, and metadynamic and DFT calculations are given in the Supporting Information.

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[1] a) L. Vilčiauskas, M. E. Tuckerman, G. Bester, S. J. Paddison, K.-D. Kreuer, *Nat. Chem.* **2012**, *4*, 461–466; b) D. Morozov, G. Groenhof, *Angew. Chem. Int. Ed.* **2016**, *55*, 576–578; *Angew. Chem.* **2016**, *128*, 586–588; c) L. Nisius, S. Grzesiek, *Nat. Chem.* **2012**, *4*, 711–717; d) G. R. Desiraju, *J. Am. Chem. Soc.* **2013**, *135*, 9952–9967.

[2] a) E. Patyk, J. Skumiel, M. Podsiadło, A. Katrusiak, *Angew. Chem. Int. Ed.* **2012**, *51*, 2146–2150; *Angew. Chem.* **2012**, *124*, 2188–2192; b) X. Tan, K. Wang, S. Li, H. Yuan, T. Yan, J. Liu, K. Yang, B. Liu, G. Zou, B. Zou, *J. Phys. Chem. B* **2012**, *116*, 14441–14450; c) A. K. Mishra, C. Murli, N. Garg, R. Chitra, S. M. Sharma, *J. Phys. Chem. B* **2010**, *114*, 17084–17091; d) J. Ridout, M. R. Probert, *Cryst. Growth Des.* **2013**, *13*, 1943–1948.

[3] K. F. Dziubek, D. Jęczmiński, A. Katrusiak, *J. Phys. Chem. Lett.* **2010**, *1*, 844–849.

[4] M. Guthrie, R. Boehler, C. A. Tulk, J. J. Molaison, A. M. dos Santos, K. Li, R. J. Hemley, *Proc. Natl. Acad. Sci. USA* **2013**, *110*, 10552–10556.

[5] C. J. Pickard, R. J. Needs, *Nat. Mater.* **2008**, *7*, 775–779.

[6] a) M. Citroni, R. Bini, M. Pagliai, G. Cardini, V. Schettino, *J. Phys. Chem. B* **2010**, *114*, 9420–9428; b) J. W. Brasch, *J. Phys.*

Chem. **1980**, *84*, 2084 – 2085; c) R. Engelke, D. Schiferl, C. B. Storm, W. L. Earl, *J. Phys. Chem.* **1988**, *92*, 6815 – 6819.

[7] a) An International Space Science Institute ISSI-Team: P. Ehrenfreund, W. Irvine, L. Becker, J. Blank, J. R. Brucato, L. Colangeli, S. Derenne, D. Despois, A. Dutrey, H. Fraaije, A. Lazcano, T. Owen, F. Robert, *Rep. Prog. Phys.* **2002**, *65*, 1427 – 1487; b) R. L. Hudson, M. H. Moore, *Icarus* **2004**, *172*, 466 – 478; c) H. Mita, N. Shirakura, H. Yokoyama, S. Nomoto, A. Shimoyama, *Adv. Space Res.* **2004**, *33*, 1282 – 1288; d) A. Belloche, R. T. Garrod, H. S. P. Müller, K. M. Menten, *Science* **2014**, *345*, 1584 – 1587.

[8] C.-S. Yoo, M. Nicol, *J. Phys. Chem.* **1986**, *90*, 6726 – 6731.

[9] K. Aoki, Y. Kakudate, M. Yoshida, S. Usuba, S. Fujiwara, *J. Chem. Phys.* **1989**, *91*, 778 – 782.

[10] H. Yamawaki, M. Sakashita, K. Aoki, *Phys. Rev. B* **1996**, *53*, 11403 – 11407.

[11] C. Ma, F. Huang, X. Wu, H. Cui, F. Li, H. Zhu, Q. Zhou, Q. Cui, *RSC Adv.* **2013**, *3*, 1509 – 1513.

[12] E. Pretsch, P. Bühlmann, M. Badertscher, *Structure determination of organic compounds*, 4th ed., Springer, New York, **2000**.

[13] A. Olejniczak, A. Katrusiak, *J. Phys. Chem. B* **2008**, *112*, 7183 – 7190.

[14] H. Yamawaki, K. Aoki, Y. Kakudate, M. Yoshida, S. Usubam, S. Fujiwara, *Chem. Phys. Lett.* **1990**, *169*, 77 – 80.

[15] K. M. Yenice, S. A. Lee, *J. Raman Spectrosc.* **1996**, *27*, 835 – 840.

[16] H. Shirakawa, *Rev. Mod. Phys.* **2001**, *73*, 713 – 718.

[17] G. Eranna, *Crystal growth and evaluation of silicon for VLSI and ULSI*, CRC Press, New York, **2015**, p. 27.

[18] B. Marinho, M. Ghislandi, E. Tkalya, C. E. Koning, G. de With, *Powder Technol.* **2012**, *221*, 351 – 358.

[19] B. Kamb, B. L. Davis, *Proc. Natl. Acad. Sci. USA* **1964**, *52*, 1433 – 1439.

[20] J. R. Scheffer, *Acc. Chem. Res.* **1980**, *13*, 283 – 290.

[21] L. Ciabini, M. Santoro, F. A. Gorelli, R. Bini, V. Schettino, S. Raugei, *Nat. Mater.* **2007**, *6*, 39 – 43.

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