

## Trigohexagonite

Michael J. Bucknum · Bin Wen ·  
Eduardo A. Castro

Received: 15 April 2010 / Accepted: 24 June 2010 / Published online: 7 July 2010  
© Springer Science+Business Media, LLC 2010

**Abstract** A novel 3-,4-connected network is reported in this communication that is a rare example of a three-dimensional (3D) network with a quaternary stoichiometry, in which 4 distinct sites of bonding occur in the unit of pattern of the material. The net lies in the hexagonal space group P-6m2 (#187) and there are 10 vertices (or atoms) in the unit cell, including 4 sites of approximately trigonal planar coordination and 6 sites of approximately tetrahedral coordination. All vertices (atoms) in the network sit on special positions in the P-6m2 space group, giving the network high sixfold symmetry axes parallel to the crystallographic *c*-axis. The structure has thus been named trigohexagonite in a loose analogy with its hexagonite crystalline homolog, sitting in the hexagonal space group P6/mmm (#191). The Wells point symbol for the trigohexagonite network is given by  $(7^3)(6^3 8^3)_3(6.7^2)_3(3.7^4.8)_3$  where this symbol indicates the quaternary stoichiometry of the network. The Wells point symbol also reveals that the only structural strain present in the network comes from the presence of the 3-gon, cyclopropane-like moieties in it, built on tetrahedral vertices. This structural motif of cyclopropane-like rings has precedent in organic chemistry and it adds character to the overall sixfold symmetry of the trigohexagonite pattern. Also, the overall network contains rare trimethylenemethane-like clusters of 4 trigonal planar vertices (atoms), bonded together, that constitute the 3-connected component of the network. Both  $c_{10}$  and  $B_{10}$  realizations are briefly described.

---

M. J. Bucknum · E. A. Castro (✉)  
INIFTA, Department of Chemistry, Universidad de La Plata, La Plata 1900, Buenos Aires, Argentina  
e-mail: eacast@gmail.com

B. Wen  
School of Materials Science and Engineering and State Key Laboratory of Materials Modification  
by Laser, Electron, and Ion Beams, Dalian University of Technology, 116023 Dalian,  
People's Republic of China

**Keywords** Trigo-hexagonite · Connected network · Quaternary stoichiometric

## 1 Introduction

Wells has outlined the basic characteristics of the mathematical-crystallographic problem of the systematic enumeration of the polyhedra, tessellations in 2-dimensions (2D), and crystallographic networks in 3-dimensions, in his important 1977 monograph on the subject [1]. In a later publication in 1984 [2] he reports on the systematic enumeration of about a hundred distinct and novel 3-,4-connected networks of semi-regular Catalan and irregular Wellsean topology, and 4-connected networks of semi-regular Archimedean topology. It should be mentioned, in this connection, that more recently, the group led by Delgado-Friedrichs has been applying mathematical algorithms towards the systematic derivation the 3-periodic networks of 3- and 4-connection [3–5]. This later group has enumerated 100s of such distinct networks thus far in their continuing project.

Building on the work of Wells in outlining the scope of the problem of the systematic enumeration of networks, Bucknum took the concept of the topology map in a Schläfli space (a space of  $n$  and  $p$ , the Schläfli symbols for networks) and extended it to include the 3D crystalline networks explicitly [6]. Bucknum showed in 2005 [7] how one could use the topological device that Wells had earlier invented to classify polyhedra, tessellations and networks [1,2], called the Wells point symbol, and translate this notation into an unambiguous and unique Schläfli symbol  $(n, p)$  for a structure, and thereby map that object in the Schläfli space described above. Such a topology map, in the approximation of the mapping out of the regular or Platonic structures, is indicated in Table 1 below.

## 2 Trigo-hexagonite structural-type

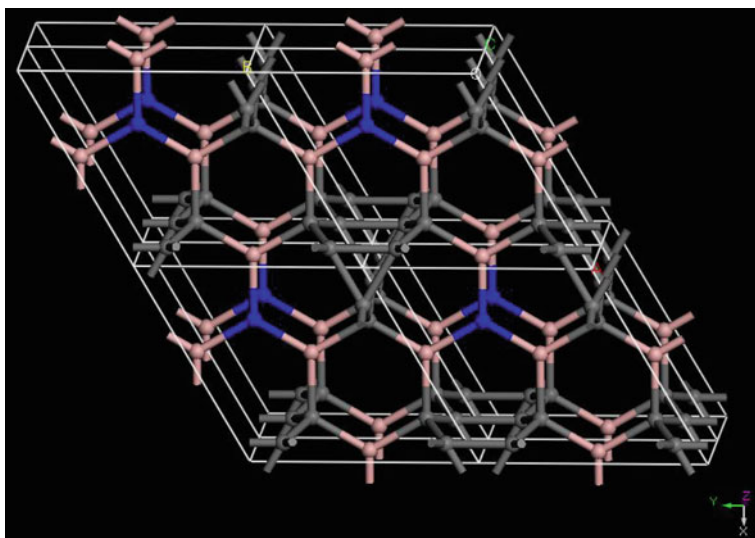
In this paper, the authors describe the enumeration of a network in the hexagonal symmetry class, lying in space group P-6m2 (#187), that possesses a rare quaternary stoichiometry of  $AB_3C_3D_3$ , as is readily revealed by consideration of its Wells point symbol, cited below. Table 2 lists the fractional hexagonal crystallographic coordinates

**Table 1** Topology map of Schläfli space for regular (Platonic) structures

n	p						
	3	4	5	6	7	8	...
3	↑	0	i	(3,6)	(3,7)	(3,8)	
4	c	(4,4)	(4,5)	(4,6)	(4,7)	(4,8)	
5	d	(5,4)	(5,5)	(5,6)	(5,7)	(5,8)	
6	(6,3)	(6,4)	(6,5)	(6,6)	(6,7)	(6,8)	
7	(7,3)	(7,4)	(7,5)	(7,6)	(7,7)	(7,8)	
8	(8,3)	(8,4)	(8,5)	(8,6)	(8,7)	(8,8)	
⋮							

**Table 2** Idealized set of fractional hexagonal crystallographic coordinates of trigohexagonite in the hexagonal space group P-6m2 (#187)

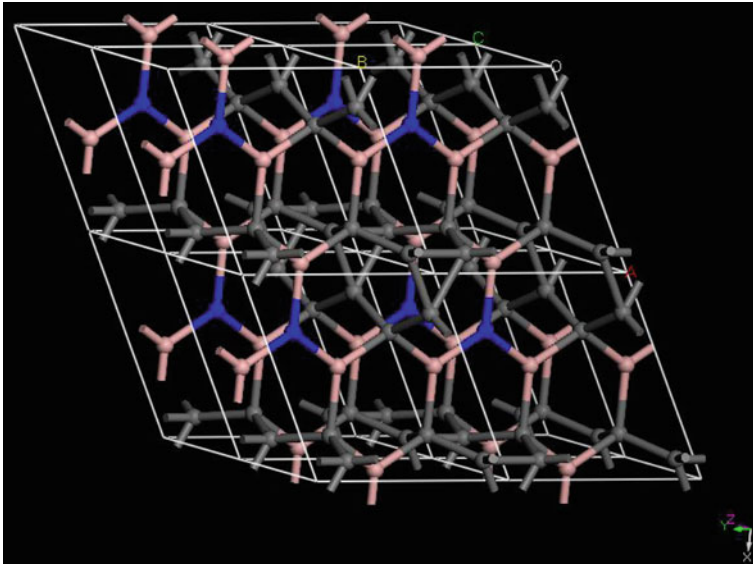
Atom #	x/a	y/b	z/c	a Å	c Å
1	1/2	1/2	1/2	5.200	2.718
2	0	1/2	1/2	5.200	2.718
3	1/2	0	1/2	5.200	2.718
4	5/6	1/6	1/2	5.200	2.718
5	5/6	2/3	1/2	5.200	2.718
6	1/3	1/6	1/2	5.200	2.718
7	0.90383	0.09617	0	5.200	2.718
8	0.90383	0.80767	0	5.200	2.718
9	0.19233	0.09617	0	5.200	2.718
10	1/3	2/3	1/2	5.200	2.718



**Fig. 1** View of the Wellsean trigohexagonite lattice in space group P-6m2 (#187), from a perspective along the **c**-axis: 3-connected vertices are blue and pink, 4-connected vertices are gray

of the 10 atoms within this so-called trigohexagonite unit cell, for a configuration of the hexagonal cell in which the lattice parameters are given as  $a = 5.200 \text{ \AA}$  and  $c = 2.718 \text{ \AA}$ . The cell is thus illustrated in Figs. 1 and 2, with the hexagonal structure shown, slightly tilted from plane projection, nearly along its crystallographic **c**-axis, in Fig. 1. Figure 2 shows a view of the hexagonal lattice nearly in the crystallographic **ab**-plane.

From the perspective of the structure shown in Fig. 1, along the **c**-axis, one can see that a thematic variation traced in the structure occurs in the form of the 3-ness of its substructures. The triangles seen perpendicular to the **c**-axis, represent locally  $D_{3h}$  symmetry, cyclopropane-like substructures of the lattice, arranged in a larger triad, about the principal crystallographic sixfold axis in the unit cell. Similarly, in the unit cell, there is the presence, arranged again in larger triads along the principal



**Fig. 2** View of Wellsean trigohexagonite lattice in space group  $P-6m2$  (#187), from the perspective of the  $ab$ -plane: 3-connected vertices are blue and pink, 4-connected vertices are gray

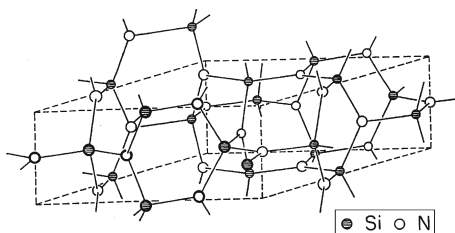
sixfold axis, of the locally  $D_{3h}$  symmetry, 1,3,5-trimethylene-cyclohexane-like, and trimethylene-methane-like, organic substructures of the lattice. These threefold symmetry substructures are thus seen to be stacked along the  $c$ -axis to generate the resulting three-dimensional (3D) network called trigohexagonite, as is evident from the view of the trigohexagonite structure in Fig. 1.

The overall trigohexagonite network, shown in Figs. 1 and 2, can thus be seen to have the relatively complex quaternary stoichiometry [2,7] reflected in the Wells point symbol given by  $(7^3)(6^3 8^3)_3(6.7^2)_3(3.7^4.8)_3$ . This Wellsean point symbol [2] can readily be translated into its corresponding Schläfli symbol of  $(n, p) = (6.75, 3.6)$  by the method already outlined by Bucknum et al. previously [7]. Finally, there is an alternative scheme for identifying the topology of arbitrary networks with a so-called vertex-symbol notation. This methodology is due to O’Keeffe [8] and will not be pursued further in this communication.

### 3 Survey of representative 3-,4-connected nets and trigohexagonite

One of the earliest 3-,4-connected nets to be described as such, was that of the phenacite structure-type, elucidated by Bragg et al. [9,10]. This was the structure of a silicate mineral ( $Be_2SiO_4$ ) which possessed a relatively complex, ternary stoichiometry. The structural-type was discovered from analysis of the parent beryllium-containing mineral structure of the formula  $Be_2SiO_4$ . It was an especially challenging structure determination as the unit cell was rhombohedral ( $R-3$ ), and there were 6 ( $Be_2SiO_4$ ) formula units within the unit cell.

**Fig. 3** A view of the crystallographic unit cell of the Wellsean phenacite network in space group R-3m (#166)



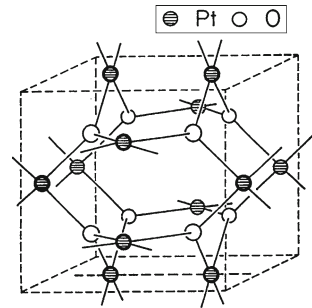
Bragg et al. identified the structural character of the net as follows, “It is difficult to give a clear figure of the structure, because the unit cell is large, and a pattern with rhombohedral symmetry is harder to depict than one based upon rectangular axes. The principles of the structure are very simple, however, and are readily traced in a model. It is formed of linked tetrahedra, with Si and Be at their centres. Each O of the independent  $\text{SiO}_4$  groups also forms part of two neighboring tetrahedra around Be atoms. Thus each Si is surrounded by 4 O atoms, and each Be by 4 O atoms, and each O is linked to 2 Be atoms and one Si atom at the corners of an equilateral triangle.” [9, 10] A general view of this phenacite lattice is taken from Wells [1], and shown in Fig. 3.

The complex ternary stoichiometry of phenacite is reflected in the Wells point symbol for this Wellsean network, as is given by Wells in his A.C.A. monograph on novel networks of 1984 [2] as,  $(8^3)_2(6^3)_6(6^3 8^3)_6$ . And this ternary Wells point symbol can therefore be translated into its corresponding Schläfli symbol [7] as  $(6^{4/5}, 3.4285\dots)$ .

We can thus see by comparison of the topological form indexes [11] of the respective structures, given by the definition  $l = n/p$ , that compared to the ideal (Platonic) unary, tetrahedral, 4-connected diamond network  $6^6$  or  $(6, 4)$ , in which  $l = n/p = 1.5$  [1, 11], the phenacite network is a slightly less compact ( $l = n/p = 1.9833\dots$ ) structure-type than diamond is, in its inherent topology. Taking this further, we see that in the quaternary stoichiometry, trigohexagonite network that it is, indeed, intermediate in compactness ( $l = n/p = 1.875$ ) between the most compact, diamond network, and the least compact phenacite network. It should be mentioned in this context, that perhaps the most open such structure that is possible, in terms of the topological form index  $l = n/p$  as a measure of “openness” [11], is the Wells constructed series of 3-connected topoisomers identified collectively as  $10^3$ , or by the translated Schläfli symbol  $(10, 3)$  [1], with a form index of  $3^{1/3}$ .

Bragg et al. later report [9, 10] that isostructural 3-,4-connected nets, in a binary  $\text{A}_3\text{B}_4$  stoichiometry, that is nonetheless patterned as the topologically ternary phenacite structure-type, might be possible for various combinations of Group 14 and 15 elements. From this insight, there were reported the synthesis of  $\text{Ge}_3\text{N}_4$  by Juza et al. [12, 13] in 1939–1940, and 17 years later the corresponding silicon-nitride binary compound,  $\text{Si}_3\text{N}_4$ , was produced by Hardie et al. [14] and Ruddlestone et al. [15], both with work reported in 1957. Therefore the germanium-nitride and silicon-nitride structures, referenced here, were seen to be entirely isostructural with the phenacite structure-type. In the currents of science today, is that elusive corresponding carbon-nitride,  $\beta - \text{c}_3\text{N}_4$ , suggested by Cohen et al. as a candidate for a superhard material

**Fig. 4** A view of the catalan unit cell of Waserite in space group Pm-3n (#223)



[16], carbon-nitride in the phenacite realization of Cohen et al. has, sadly, remained difficult to characterize in various, innumerable synthetic attempts carried out so far around the world [17].

The ternary phenacite structure was evidently the most complex network, in terms of the Wells point symbol, analyzed and published by Wells in his important works on 3-periodic networks of various valences [1,2]. It is therefore important to point out here in this communication, that the title material described here theoretically, called trigohexagonite, is perhaps the most complex material yet described, from purely a topological-stoichiometric point of view, as it possesses a quaternary stoichiometry reflected in the Wells point symbol  $(7^3)(6^3 8^3)_3(6.7^2)_3(3.7^4.8)_3$ .

In contrast to phenacite and trigohexagonite described above, a relatively simple topology for a 3-,4-connected net is that found in the so-called Waserite structure-type [18], which represents the anionic  $Pt_3O_4$  sublattice of certain alkali metal platinates of generic chemical formula  $MPT_3O_4$ . The Waserite structural-type is shown in Fig. 4.

It can be seen from Fig. 4 that all circuits in the Waserite structure-type are 8-gons, giving the lattice a classification as Catalan [7]. The Wells point symbol for this lattice is easy to write down as  $(8^4)_3(8^3)_4$  as one can readily trace from Fig. 4 [7].

Thus the Catalan nature, and the relatively simple binary stoichiometry, of this Waserite network distinguishes it from the otherwise complicated topologies of the phenacite and trigohexagonite networks described above. The relative orderings of the symmetry space groups of the lattices is also interesting as Waserite lies in the relatively high space group symmetry of Pm-3n (#223), while trigohexagonite is in space group #187 and phenacite is in space group #166. It is also true that Waserite can assume a configuration of its bonds such that all bond angles are ideal, with the square planar bond angles being  $90^\circ$ , and the trigonal planar angles of the 3-connected vertices being held at  $120^\circ$ . This further distinguishes this net as being closer to ideal, compared to the irregular networks of phenacite and trigohexagonite which cannot adopt ideal bond angles about all vertices in any configuration.

#### 4 B and C allotropes

Next, with the discussion bearing on a potential realization of the trigohexagonite lattice, we turn to some density functional theory optimizations of potential  $c_{10}$  and  $B_{10}$  trigohexagonite phases. The density functional theory (DFT) optimization

**Table 3** Set of fractional hexagonal crystallographic coordinates of trigohexagonite in the hexagonal space group P-6m2 in a C<sub>10</sub> realization

Atom #	x/a	y/b	z/c	a Å	c Å
1	0.4970	0.5029	1/2	5.316	2.562
2	0.0059	0.5029	1/2	5.316	2.562
3	0.4970	0.9940	1/2	5.316	2.562
4	0.8262	0.1738	1/2	5.316	2.562
5	0.8262	0.6525	1/2	5.316	2.562
6	0.3475	0.1738	1/2	5.316	2.562
7	0.9102	0.0898	0	5.316	2.562
8	0.9102	0.8205	0	5.316	2.562
9	0.1795	0.0898	0	5.316	2.562
10	1/3	2/3	1/2	5.316	2.562

**Table 4** Set of fractional hexagonal crystallographic coordinates of trigohexagonite in the hexagonal space group P-6m2 in a B<sub>10</sub> realization

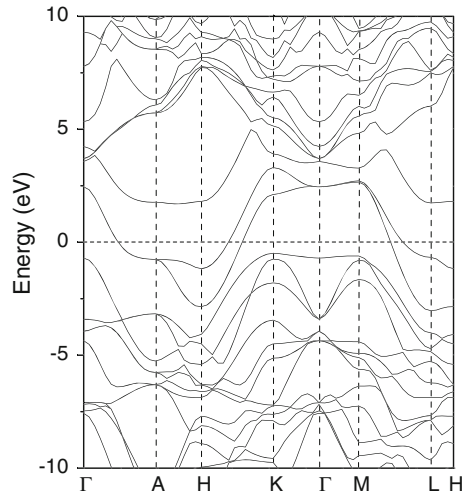
Atom #	x/a	y/b	z/c	a Å	c Å
1	0.4879	0.5120	1/2	5.818	2.965
2	0.0240	0.5120	1/2	5.818	2.965
3	0.4879	0.9759	1/2	5.818	2.965
4	0.7965	0.2035	1/2	5.818	2.965
5	0.7965	0.5929	1/2	5.818	2.965
6	0.4071	0.2035	1/2	5.818	2.965
7	0.8751	0.1249	0	5.818	2.965
8	0.8751	0.7501	0	5.818	2.965
9	0.2499	0.1249	0	5.818	2.965
10	1/3	2/3	1/2	5.818	2.965

calculations of the geometries of the C and B allotropes, together with a calculation of the electronic structure of each lattice, was carried out using the CASTEP method [19]. The details of this method are reported in [20–22].<sup>1</sup>

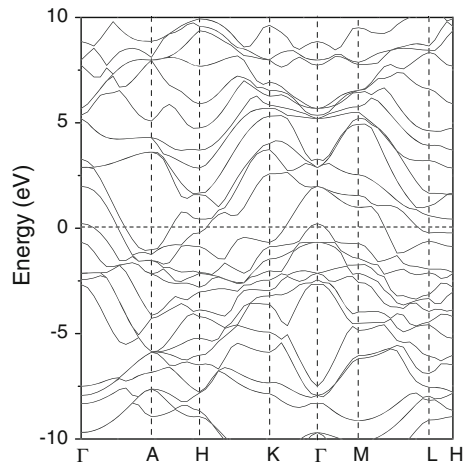
In Tables 3 and 4 are listed the optimized coordinates of the c<sub>10</sub> and B<sub>10</sub> lattices of trigohexagonite, note that the C (or B) atoms don't sit on ideal high symmetry positions, within the hexagonal space group, although the unit cell overall is still in the high symmetry space group of P-6m2 (#187). The lattice parameters of the C trigohexagonite lattice are given as **a** = 5.317 Å and **c** = 2.563 Å, with a corresponding density of 3.178 g/cm<sup>3</sup>. The c<sub>10</sub> realization is moderately dense, but not nearly so dense as cubic diamond is at 3.56 g/cm<sup>3</sup>. For the B<sub>10</sub> realization, the lattice parameters are **a** = 5.818 Å and **c** = 2.965 Å, with the density being given as 2.065 g/cm<sup>3</sup>, it is a

<sup>1</sup> In our calculations, lattice parameters of trigohexagonite were optimized by using density functional theory (DFT) and the plane-wave pseudopotential technique implemented in the CASTEP package [20]. The ion-electron interaction was modeled by ultrasoft pseudo potentials [21]. The generalized gradient approximation (GGA) with the PBE exchange-correlation functional [22] was used. The **k** point separation in the Brillouin zone of the reciprocal space was set to be 0.04 nm<sup>-1</sup>, that is, 5 × 5 × 10 **k** points mesh. A high cutoff energy of 800 eV was selected in this work.

**Fig. 5** CASTEP electronic band structure of  $C_{10}$  lattice



**Fig. 6** CASTEP electronic band structure of  $B_{10}$  lattice



more open trigohexagonite lattice with B than C, even given the lower atomic weight of B (10.811 g/mole) than C (12.011 g/mole).

Figures 5 and 6 report the CASTEP calculated electronic band structures of the C and B realizations, respectively. There are 40 bands in each band structure, the bands are generated by symmetry adapted mixing of the occupied  $s$ ,  $p_x$ ,  $p_y$  and  $p_z$  orbitals (through the reciprocal space of the lattice) of the C and B atoms making up the materials. There are thus 20 bonding ( $\sigma$  and  $\pi$ ) bands and 20 antibonding bands ( $\sigma^*$  and  $\pi^*$ ) in the electronic structure of each material, within a simplified Hückel approximation. The B realization is comprised of 30 valence shell electrons within the unit cell, and would be expected nominally to occupy the bottom 15 bands, in energy, in the band structure, while the C lattice with 40 valence shell electrons within the unit cell, would fill the bottom 20 bands in energy.



Both C and B trigohexagonite realizations are electrically conductive phases according to the CASTEP approximation of this complex lattice, as can be seen by the band crossings (much more numerous in the B than the C realizations) of the Fermi levels in the respective lattices. The Fermi level is indicated by the horizontal dashed line in each band diagram. It lies partially between the 20th ( $a\pi$  band) and the 21st ( $a\pi^*$  band) in the C realization, as would be expected for a metallic modification of C. Note also in this C lattice that the  $\pi^*$  bands (the 21st and 22nd bands in this case) dip down into the bonding manifold of the electronic structure to indirectly cross some of the  $\pi$  bands in the structure, at about symmetry points L and H in the Brillouin zone, and to create its metallic status. The B realization of trigohexagonite has a considerably more congested structure of bands about its Fermi level, in this case the Fermi energy is expected to be in the vicinity of the 15th band. There are many band crossings in the B structure and the lattice reflects its unique character from C in its very different and congested band profile.

## 5 Conclusions

In this communication, we have described a novel, crystallographic 3-dimensional (3D) network with an unprecedented quaternary stoichiometry, which we have called trigohexagonite. As revealed in the Wells point symbol for the novel network, given by the stoichiometric formula  $(7^3)(6^3 8^3)_3(6.7^2)_3(3.7^4.8)_3$ , there are indeed 4 distinct sites of bonding within the network and it is built upon an admixture of 4 distinct circuits of size 3, 6, 7 and 8. These 4 distinct circuit sizes are combined together with vertices in trigonal, 3-connection and tetrahedral 4-connection to generate the trigohexagonite lattice. It is not clear from the literature available to us, whether a quaternary network such as this one has ever been enumerated previously.

The relatively simple construction known as the Waserite network, corresponding to the anionic  $\text{Pt}_3\text{O}_4$  sublattice of the ionic conductor  $\text{Na}_x\text{Pt}_3\text{O}_4$ , provides an interesting counterpoint to the trigohexagonite structural-type. With the Wells point symbol for Waserite, given as  $(8^4)_3(8^3)_4$  we can see that this net is not only of a relatively simple binary stoichiometry ( $\text{A}_3\text{B}_4$ ), but that it is also a semi-regular Catalan network in which all circuits in the net are of 8-gon size. It is not clear at this juncture how the onset of topological complexity in a network like trigohexagonite correlates with the ability to realize such a network in an actual synthesis. Certainly, it would seem that Waserite, which was identified as early as 1951 [18], was synthesized because of the simplicity of its topology, combined with its high degree of symmetry (space group  $\text{Pm}\text{-}3\text{n}$ , #223). It therefore seems to be the case, that relatively simple topologies combined with high symmetries are desired characteristics in structures that Nature is able to readily adopt.

This preceding articulated realization, on symmetry and topology and their role in solid state synthesis, can be applied to the allotropes of C for example. The polytypes of diamond are of a Platonic topology given by  $6^6$  and the graphene grid is Platonic as well, with a Wells's point symbol of  $6^3$ . These archetypal, crystalline structures of C exist, as well, in high symmetry crystallographic space groups [9, 10]. It is also true that diamond, (in its cubic 3C polytype) and graphite, have been known since

antiquity. Yet a 3rd family of allotropes of C, the molecular and crystalline fullerenes [23], are collectively semi-regular, Archimedean polyhedra of icosohedral ( $I_h$ ), and lower degrees of symmetry, that were only discovered synthetically in 1985. The fullerenes collectively possess the Wells point symbol  $5^y6^x$ , where “y” is the number of 5-gons in the respective fullerene polyhedron, and “x” is the number of 6-gons in the respective fullerene polyhedron. Collectively, for this infinite family of fullerene polyhedra, the corresponding Schläfli symbol is thus given as  $(5^x/(x + y), 3)$  [24]. One can look to the future of C synthesis, and see that there have been various proposals for (1) Catalan graphite-diamond hybrid structures, collectively of orthorhombic symmetry, as envisioned by Balaban et al. [25], as well as (2) the original proposal of Karfunkel et al. [24,26], of Catalan allotropes of C having potentially high hexagonal symmetry (P6/mmm, #191). And (3) along these lines there are myriad other proposals<sup>2</sup> [27–31]] for C structures including alternative Archimedean, Catalan and Wellsean networks of various high and low symmetries.

## References

1. A.F. Wells, *Three Dimensional Nets and Polyhedra*, 1st edn. (Wiley & Sons, New York, 1977)
2. A.F. Wells, *Further Studies of Three-dimensional Nets*, American Crystallographic Association, *Monograph #8*, 1st edn. (ACA Press, 1979)
3. O. Delgado-Friedrichs et al., *Nature* **400**, 644 (1999)
4. O. Delgado-Friedrichs, M. O’Keeffe, *Acta Cryst.* **A59**, 351 (2003)
5. O. Delgado-Friedrichs et al., *Acta Cryst.* **A62**, 350 (2006)
6. M.J. Bucknum, *Carbon* **35**(1), 1 (1997)
7. M.J. Bucknum, E.A. Castro, *Comm. Math Comput. Chem.* **54**, 89 (2005)
8. M. O’Keeffe, B.G. Hyde, *Crystal Structures I: Patterns and Symmetry*, Mineralogical Society of America, 1st edn. (Mineralogical Society of America Press, Washington, 1996)
9. W.L. Bragg, W.H. Zachariasen, *Zeit. Fuer Kristoll.* **72**, 518 (1930)
10. W.L. Bragg, *Atomic Structure of Minerals*, Cornell University, 1st edn. (Cornell University Press, Ithaca, NY, 1937)
11. M.J. Bucknum, E.A. Castro, *J. Math. Chem.* **40**(4), 327 (2006)
12. R. Juza, H. Hahn, *Naturwissenschaften* **27**, 32 (1939)
13. R. Juza, H. Hahn, *Zeit. Anorg. Chem.* **244**, 125 (1944)
14. D. Hardie, K.H. Jack, *Nature* **180**, 332 (1957)
15. S.N. Ruddleston, P. Popper, *Acta Cryst.* **11**, 465 (1958)
16. A.Y. Liu, M.L. Cohen, *Science* **245**, 841 (1989)
17. T. Malkow, *Mater. Sci. Eng. A* **302**(2), 311 (2001)
18. J. Waser, E.D. McClanahan, *J. Chem. Phys.* **19**, 413 (1951)
19. M.C. Payne et al., *Rev. Mod. Phys.* **64**, 1045 (1992)
20. M.D. Segall, P.J.D. Lindan, M.J. Probert, C.J. Pickard, P.J. Hasnip, S.J. Clark, M.C. Payne, *J. Phys. Condens. Matter* **14**, 2717 (2002)
21. D.R. Hamann, M. Schluter, C. Chiang, *Phys. Rev. Lett.* **43**, 1494 (1979)
22. J.P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996)
23. H. Kroto, J.R. Heath, S.C. O’Brien, R.F. Curl, R.E. Smalley, *Nature* **318**, 162 (1985)
24. M.J. Bucknum, E.A. Castro, *J. Chem. Theory. Comput.* **2**(3), 775 (2006)

<sup>2</sup> In our calculations, lattice parameters of trigohexagonite were optimized by using density functional theory (DFT) and the plane-wave pseudopotential technique implemented in the CASTEP package [20]. The ion-electron interaction was modeled by ultrasoft pseudo potentials [21]. The generalized gradient approximation (GGA) with the PBE exchange-correlation functional [22] was used. The  $\mathbf{k}$  point separation in the Brillouin zone of the reciprocal space was set to be  $0.04 \text{ nm}^{-1}$ , that is,  $5 \times 5 \times 10$   $\mathbf{k}$  points mesh. A high cutoff energy of 800 eV was selected in this work.

25. A.T. Balaban, D.J. Klein, C.A. Folden, *Chem. Phys. Lett.* **217**, 266 (1994)
26. H.R. Karfunkel, T. Dressler, *J. Am. Chem. Soc.* **114**(7), 2285 (1992)
27. M.J. Bucknum, I. Stamatina, E.A. Castro, *Mol. Phys.* **103**(20), 2707 (2005)
28. M.C. Payne et al., *Rev. Mod. Phys.* **64**, 1045 (1992)
29. M.D. Segall, P.J.D. Lindan, M.J. Probert, C.J. Pickard, P.J. Hasnip, S.J. Clark, M.C. Payne, *J. Phys. Condens. Matter* **14**, 2717 (2002)
30. D.R. Hamann, M. Schluter, C. Chiang, *Phys. Rev. Lett.* **43**, 1494 (1979)
31. J.P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996)