

Получение, структура, свойства

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Towards the theory of hardness of materials

Recent studies have shown that hardness, a complex property, can be calculated using very simple approaches or even analytical formulae. These form the basis for evaluating controversial experimental results (as we illustrate for TiO₂-cotunnite) and enable a systematic search for novel hard materials, for instance, using global optimization algorithms (as we show on the example of SiO₂ polymorphs).

Key words: *evolutionary prediction of crystal structure, TiO₂-cotunnite, SiO₂ polymorphs, computational design of superhard materials.*

We all know that diamond is very hard, while graphite and talc are soft. Hardness, as a property of materials, determines many of their technological applications, but remains a poorly understood property. The aim of this Special Issue is to review some of the most important recent developments in the understanding of hardness.

Mohs's relative scale of hardness appeared in the XIX century and is still widely used by mineralogists; in this scale talc has hardness 1, and diamond has hardness 10. There are several absolute definitions of hardness—the most popular ones being the Knoop and Vickers tests of hardness, which involve indentation (rather than scratching, as in Mohs's hardness). The absolute hardness is measured in GPa, the same units as pressure or elastic moduli (bulk modulus, shear modulus). This hints that hardness may be correlated with the elastic properties — indeed, there is such a correlation, especially with the shear modulus. However, hardness is obviously a much more complex property than elasticity, as it involves also plastic deformation and brittle failure. For these reasons, a complete picture of hardness cannot be given only by the ideal crystal structure and its properties, but must include also defects (in particular, dislocations) and grain sizes. The latter is related to hardness through a particularly important phenomenon, known as the Hall-Petch effect — hardness increases as the particle size decreases (in reality, there is a maximum in the nanometer range). Thus, it is possible to significantly boost a material's hardness by creating nanoparticle aggregates and nanocomposites: while the hardness of diamond single crystals varies between 60 and 120 GPa depending on the direction [1], nanodiamond turns out to be much harder, with the isotropic hardness of up to 120—140 GPa [2]. Cubic BN has a

Vickers hardness of 40—60 GPa in bulk crystals, but its nanocomposites are almost as hard as diamond, with a Vickers hardness of 85 GPa [3]. Hardness of nanomaterials is discussed in reviews of Tse [4] and Gao [5] in this issue.

With the detailed understanding of the hardness still elusive, can one invent a practical recipe for predicting the hardness of a material on the basis of its crystal structure? This would mean ignoring dislocations and grain boundaries, which is fundamentally incorrect, but a number of practical recipes, invented recently, turn out to give reasonable results, certain predictive power, and great fundamental value. These include the ideal strength (which often attains values in surprisingly good agreement with experimental hardnesses, see [4] and analytical models [6—10], which hold a potential of revolutionizing the field of superhard materials. These are the focus of this Issue. Differing in mathematical and also somewhat in physical details, analytical models have much in common; the hardness is high when:

- (i) the average bond strength is high;
- (ii) the number of bonds per unit volume is high;
- (iii) the average number of valence electrons per atom is high;
- (iv) bonds are strongly directional (i.e. have a large covalent component — ionicity and metallicity decrease hardness).

The requirement of high bond strength indicates that compounds light elements, capable of forming extremely strong and short bonds, are particularly promising; some transition metals (e. g., W, Ta, Mo, Re) can also form very strong (although not quite as directional) bonds and have a high number of valence electrons and their compounds should also be carefully examined.

Diamond, a dense phase with strong and fully covalent bonds, satisfies all of the conditions (i)—(iv). Cubic BN, with partially ionic bonds, has a somewhat lower hardness. Graphite, though containing stronger bonds than in diamond, has a much lower number of atoms and bonds per unit volume, and must therefore be softer*. Cold compression of graphite [11] resulted in a peculiar superhard phase, the structure of which has been understood only recently [12] and has a much greater density and lower anisotropy than graphite.

The requirement of high bond density means that often superhard materials will have to be synthesized at high pressure—this is the case of diamond [13, 14], cubic BN [15], cubic BC₂N [16] and BCN [17], boron-enriched diamond with approximate composition BC₅ [18], and novel partially ionic phase of elemental boron, γ -B₂₈ [19, 20]. All the listed materials can be decompressed to ambient conditions as metastable phases, but this is hardly a limitation to their performance. Much more critical is the fact that to be practically useful, the material should be synthesizable at pressures not higher than ~ 10 GPa, because at higher pressures synthesis can be done only in tiny volumes (except in shock-wave synthesis, which may be a viable route for useful materials at ultrahigh pressures). High-pressure studies of materials are often tricky, and the field of high-pressure research is full of both exciting discoveries and misdiscoveries. For instance, it has been claimed [21] that TiO₂-cotunnite, quenched from high pressure, is the hardest known oxide with a Vickers hardness of 38 GPa. While it is hard to experimentally appraise such results obtained on tiny samples, theoretical models can help to distinguish facts from artifacts: within any of the models presented in this issue, the hardness of TiO₂-cotunnite varies in the range 7—20 GPa, our preferred and

* For materials like graphite, it is essential to take anisotropy into account; the hardness models presented in this Special Issue are isotropic (i.e. give a single overall value of hardness for the material), though an anisotropic extension has just appeared [10].

perhaps the most reliable result (based on the extended model [8]) being 15.9 GPa, i.e. this material is certainly about as soft as common quartz (whose Vickers hardness is 12 GPa) and softer than common corundum, Al_2O_3 (21 GPa), or stishovite, SiO_2 (33 GPa) [22], or B_6O (45 GPa) [23]. Such a relatively low hardness of TiO_2 -cotunnite is only natural, given its very large bond ionicity and high coordination number of Ti (ninefold), i.e. relatively weak and non-directional Ti—O bonds. Thus, ultrahard TiO_2 -cotunnite is a clear artifact.

Thanks to such models of hardness, it is now possible to systematically search for superhard materials. We performed a search for the hardest structure of SiO_2 at atmospheric pressure by combining the evolutionary global optimization algorithm USPEX (Universal Structure Predictor: Evolutionary Xtallography) [24—27] with an extended version of the hardness model [8]. To enable very fast exploratory calculations, we relaxed all trial structures using a simple interatomic potential based on the model of Sanders et al. [28] using the GULP (General Utility Lattice Program) code [29]. The hardness was evaluated on fully relaxed structures. Figure 1 shows how the computed hardness evolved during the simulation (shown here for the system with 24 atoms in the unit cell, though we also explored other system sizes), and it is clear how harder and harder structures are found as the run progresses. The four hardest structures found in all runs (Fig. 2) turned out to be (i—ii) two well-known phases stishovite (rutile-type structure) and seifertite (α - PbO_2 -type structure), (iii) a 3×3 kinked-chain structure, intermediate between stishovite and seifertite, and (iv) a cuprite-type phase (cuprite-type SiO_2 is hitherto unknown, but cuprite-type ice X is the densest known phase of ice [32] — and ice phases have strong structural similarities with tetrahedral silica polymorphs). We re-relaxed these structures with more accurate density-functional calculations using the generalized gradient approximation [33] and the VASP (Vienna ab initio simulation package) code [34], and the recomputed hardnesses were 28.9 GPa for stishovite (close to the experimental hardness of 33 GPa [22]), 29.6 GPa for seifertite, 29.3 GPa for the 3×3 -structure, and 29.5 GPa for SiO_2 -cuprite. All these theoretical hardnesses are underestimates, due to the known modest overestimation of bond lengths in the functional [33] and are extremely close to each other. In spite of the similarity of the computed hardnesses, it seems natural that seifertite, being the densest phase of silica known at 1 atm, is also the hardest one. Seifertite has a stability field on the phase diagram at high pressures (see [35] for discussion) and is quenchable to ambient conditions.

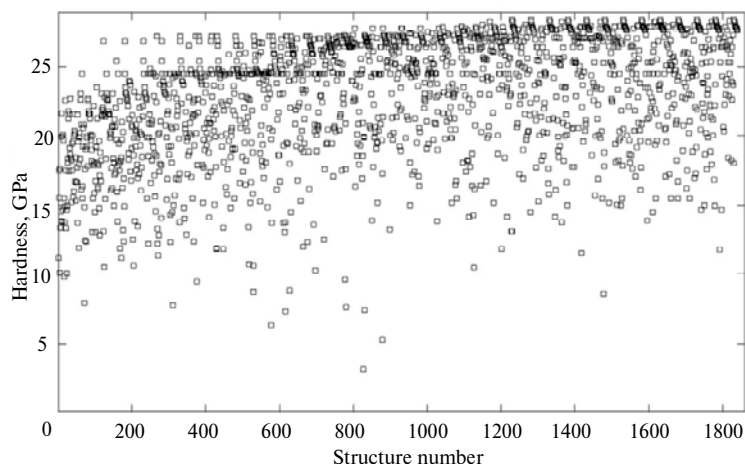


Fig. 1. Evolution of the theoretical hardness in an evolutionary global optimization run for SiO_2 with 24 atoms in the unit cell.

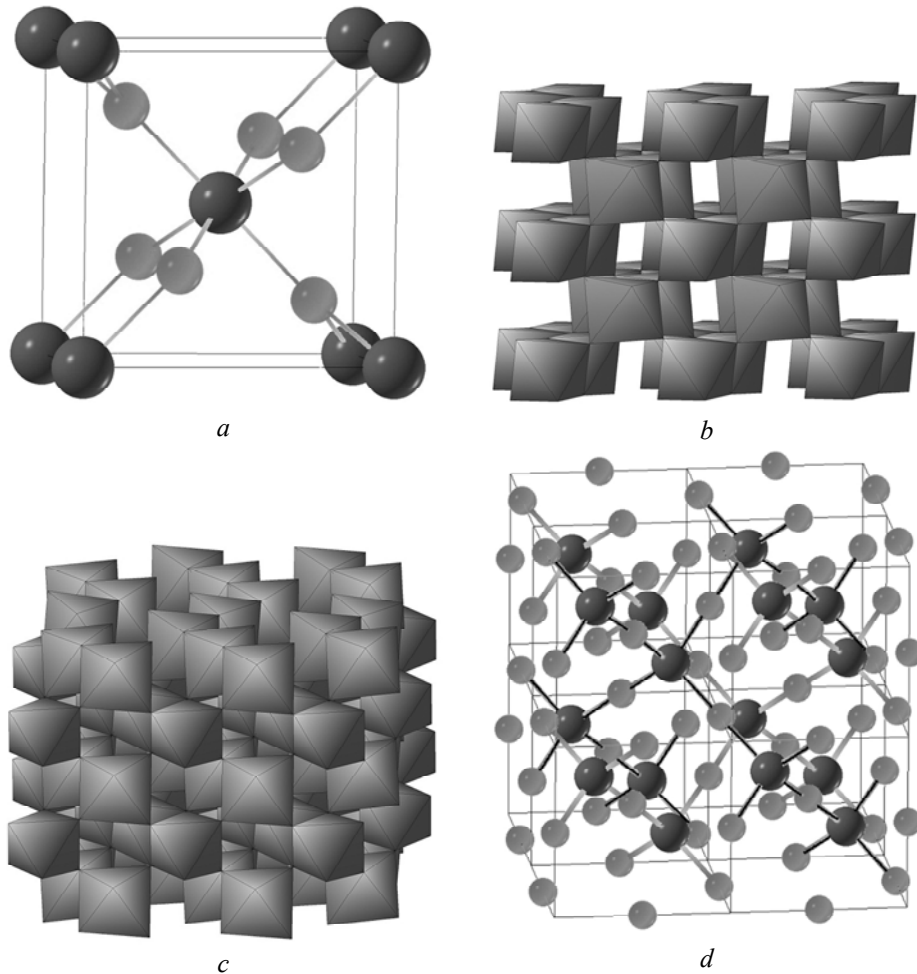


Fig. 2. Structures of stishovite (*a*), seifertite (*b*), 3×3 phase (*c*), and cuprite-type (*d*) modifications of SiO₂. Close-packed structures related to (*a*–*c*) were discussed in [30]. The cubic cuprite structure (space group *Pn3m*) has lattice parameter $a = 3.80 \text{ \AA}$ and the following atomic positions: Si (0.75, 0.75, 0.75) and O (0, 0.5, 0). The cuprite structure has two interpenetrating cristobalite-type (or diamond-like) structures (it is a “3D-catenane”, as P. M. Zorkii christened it by analogy with interlocked catenane molecules) —not surprisingly, this structure is almost twice (1.88 times) as dense as high cristobalite (it is also 1.45 times denser than quartz, and 1.14 times less dense than stishovite). Hypothetical cuprite-type BeF₂*SiO₂ was already suggested [31] to be a very hard material. Our DFT-computed bulk modulus of SiO₂-cuprite is 276 GPa, its pressure derivative $K_0' = 6.4$. This phase is 0.38 eV/atom less stable than quartz, and 0.2 eV/atom less stable than stishovite.

This simple test shows that systematic prediction and design of new ultrahard and superhard materials is now possible, and a central role in this new direction of research is played by the simple—yet powerful—models of hardness, which are the main topic of this Special Issue. Reviews by Gao and Gao [5], Tse [4], and Mukhanov et al. [36] discuss various theoretical models of hardness, while Li et al. [37] focus on the search for novel superhard crystal structures. Reviews of Mukhanov et al. [36] and Shirai [38] discuss in details a particularly important and interesting case of boron-rich solids, for which traditional models of hardness have difficulties due to the essential role of multicenter bonding (see also [39] for an exciting discussion). While many further developments are still needed in the

theory of hardness, the current state of this field, reviewed in this Special Issue, shows its great utility and promise.

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Недавні дослідження показали, що твердість, фізично складну властивість, можна розрахувати, використовуючи прості підходи і навіть аналітичні формули. Ці підходи дозволяють внести ясність в ситуації, коли експериментальні результати сумнівні (і це показано для випадку псевдотвердого TiO_2 зі структурою котунніта), і відкривають шлях до систематичного пошуку нових твердих матеріалів, зокрема, при використанні методів глобальної оптимізації (як це показано авторами на прикладі поліморфів SiO_2).

Ключові слова: еволюційний алгоритм передбачення кристалічних структур, TiO_2 котунніт, поліморфи SiO_2 , комп'ютерний дизайн надтвердих матеріалів.

Недавние исследования показали, что твердость, физически сложное свойство, можно рассчитать, используя простые подходы и даже аналитические формулы. Эти подходы позволяют внести ясность в ситуации, где экспериментальные результаты сомнительны (и это показано для случая псевдотвердого TiO_2 со структурой котунниита), и открывают путь к систематическому поиску новых твердых материалов, в частности, используя методы глобальной оптимизации (как это показано авторами на примере полиморфов SiO_2).

Ключевые слова: эволюционный алгоритм предсказания кристаллических структур, TiO_2 котуннит, полиморфы SiO_2 , компьютерный дизайн сверхтвердых материалов.

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