Functional Materials Design through the “Geo-inspired” Concept

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Abstract The “Geo-inspired” novel concept is proposed, based on using the crystal and bonding characteristics of existing minerals to devise novel man-made materials. It is also used to address grand challenges in designing next generation functional materials such as new ultra-hard materials and layered oxides. Extension is proposed for identifying exotic chemical systems, in order to further stress its generality.

Keywords Geo-inspired Materials, DFT, Hard Materials, Carbon Nitrides, Perovskite

1. Introduction

Biomimetism is widely found in nature. It can be understood by just watching how nature makes use of it. As an example, the orchid flower has a labellum (the lower petal) which mimics the insect shape to provide a sort of “landing platform” for the pollinator. Such an adaptation is clearly due to vital reproduction purposes.

From observing nature, man made several applications out of biomimetic hence opening a broad panel of applications in creative design, in architecture, etc. New materials were then found at the frontier between Biology and Materials Science. One application of the iridescence from the scales of butterfly wings is found in diffractive optics [1]. Also the widespread fast and easy fastening/hook facilities commonly known as VELCRO®1, is actually a mimic of the thistles and spikes that stick to one’s clothes upon walking through the woods.

In this context, we introduce the geo-inspired concept as an extension of the mimetic one to mineral matter, based on geological and structural characteristics and properties. The “geo-inspired” concept is then situated between Geosciences and Materials Science, applied by using crystal characteristics of existing minerals to devise novel functional compounds. Selective substitutions are guided by chemical intuition and theory within model initial structure. Replacing cations, anions or molecular assemblies is done while respecting certain rules such as those of isoelectronicity and bond energy rules underlying thermodynamics criteria. Ab initio calculations within what is admittedly called nowadays “Computational Materials Science”, are applied subsequently to the structural model to fully relax the composition into the ground state with computer codes built within the well established quantum theoretical framework of the density functional (DFT) (cf. [2] for a review on computational materials and details on the DFT). The calculations allow accessing accurate energies (ground state and optimized structures, enthalpies of formation, and energy derived properties such as elastic constants, bulk and shear modules, magnetic properties, etc.) from which the most stable systems are selected and proposed for synthesis.

2. Devising Novel Materials with Specific Properties

2.1. Within the BCN Triangle

Carbon is known in two main forms, two dimensional (2D) soft graphite and three dimensional (3D), ultra-hard diamond. Such an exceptional hardness is the result of strong covalent carbon-carbon bonds and their isotropic spatial distribution in sp3 hybridization of carbon s and p orbitals forming a tetrahedron while it is a planar sp2 hybridization of carbon such as in graphite. Industrial diamond was made available as early as the 1950s by General Electric company (Schenectady, USA) by use of high pressure –high temperature techniques [3]. Besides high cost a problem is raised by its application in tooling machines. This especially applies when industrial diamond is used in cutting steel, because of the chemical reactivity of carbon versus metals or alloys at high temperatures leading to the deterioration of both the steel and the tool. Due to the technological importance behind the possibility to discover novel classes of hard materials an enormous research effort has been

1 VELCRO is a patented trademark. Web site http://www.velcro.com
directed during the last decades towards the synthesis and characterization of promising carbon-based compounds such as carbon nitrides and boron carbon nitrides (Fig. 1). However, despite many attempts of synthesis and the indisputable progresses made in the field, amorphous samples with unclear crystallographic data have been often obtained in many research laboratories. In particular, several problems arise from the fact that most of the samples are of polymorphic nature, thus leading to a difficult and uncertain spectroscopic characterization. An extended understanding of the relations between composition and properties of electronic structure can be provided theoretically based on accurate energy and energy deriving quantities within density functional theory methodologies.

Boron nitride is an artificial imitation of carbon. From the electronic count standpoint, the electronic configurations of the neutral atoms: B ([He] 2s² 2p¹), N ([He] 2s 2 2p³) and C ([He] 2s²2p²), are such that “B + N = 2C”, i.e. summing up to 8 valence electrons on each side of the equality sign. Cubic boron nitride, c-BN is a good substitute for diamond with a hardness magnitude just below 10 which stands for the value assigned to diamond on the Moh scale of hardness [4]. This property is in part because, unlike diamond, BN does not dissolve into iron, nickel, and related alloys at high temperatures. Due to this electronic similarity, BN adopts similar atomic arrangements as in carbon: three-dimensional (3D) diamond with the cubic blende or the hexagonal wurtzite structure as well as two-dimensional (2D) graphite (h-BN). On the other side soft hexagonal boron nitride h-BN, a man-made material is used as lubricant replacing graphite.

The mechanical properties are derived from two characteristics pertaining to the strength of the bonding: this involves short interatomic distances on one hand and to the spatial arrangements of atoms at the microscopic scale: 3D sp³ hybridization of carbon in diamond and 2D sp² in graphite.

From all this, BN can be considered as geomimetic or “geo-inspired” of carbon, mirroring it at the different levels of crystal structures and properties. From the chemical nature of B, C and N which are light and small radii elements of the first period in the periodic table, a combination between C, B and N is very likely to lead to new materials with the condition that some rules are met. The isoelectronic with carbon is one of them. It is expressed as p Zv(B)+m Zv(C)+l Zv(N) = 4n, where p, m, l and n are integers and Zv(B), Zv(C) and Zv(N) are the electron counts of the atomic valence states (2s and 2p) for boron, carbon and nitrogen respectively. Note that by not obeying such a rule, extra electrons would be in unfavorable anti-bonding states -but still, compounds not obeying this rule can exist. This is why β-C₃N₄ ( vacancy) 3D hexagonal depicted in Fig. 2 the theoretically proposed ultra-hard material almost 30 years ago [5] is isoelectronic with BN (B₄N₄, 32 valence electrons). It is then clear why a vacancy has to be introduced at an empty fourth carbon site. Many new systems were identified as depicted in Fig. 1, all geo-inspired from 2D and 3D carbon, such as binary carbon nitrides, ex. CₓN₄ and C₁₁N₄ [6] and ternary BC₃N [7], this last material being considered as the solid solution (homogeneous mixture at x-ray level) between c-BN and diamond, all obeying the isoelectronic rule.
possibilities within the initial carbon lattice for three different species (B, C, N). Then beside the isoelectronic rule above, the so-called ‘bond counting rules’ [8] need to be obeyed. The underlying physics comes from the bond energies obtained from experimental standard formation enthalpies: They are the largest for B-N (4.00 eV) and C-C bonds (3.71 eV) and lowest for B-B (2.32 eV) and N-N (2.11 eV) bonds. This leads to favor a maximum number of C-C and B-N bonds; in particular it has been predicted that the most stable BC2N structures do not have B-B or N-N bonds and the number of C-C and B-N connections is made maximum while C-B (−1 eV) is not favored. That was validated for BC2N through DFT-based computations, proposed by us [7] as a new ultra-hard material with a bulk modulus B intermediate between diamond and c-BN as well as a negative magnitude of formation enthalpy (∆Hf=-208 kJ.mol.−1) which then favors its synthesis. From the elastic constants Cij one then calculates the isotropic shear modulus G which is a better indication for hardness than the bulk modulus B. For our proposed 3D BC2N, G is found in between the values of diamond and cubic boron nitride c-BN, i.e. G(c-BN) = 426 GPa < G(ζ-C2BN) = 482GPa < G(diamond) =559 GPa. Then it may be concluded that in B, N substituted diamond, a clear hardening of the system is found with respect to c-BN. We note that ultra-hard BC2N was synthesized by a French group almost simultaneously to our predictions [9]. More recently nanostructured BC2N was obtained by CVD [10].

The structure model for ultra-hard materials can be found outside of the Earth. Recently the carbon polymorphism in shocked meteorites [11] can be highlighted. It consists of a new ultra-hard rhombohedral carbon polymorph having a structure close to diamond but with a partial occupancy of some of the carbon sites. This could be an interesting structural model for the synthesis of materials.

3. Use of the Geo-inspired Concept for Solving a Problem in Materials Science

In recent decades nitrides have turned out to play a key role in technological applications of Materials Science as the III–V AlN, GaN, InN family for light emitting diodes (LED) and lasers [16], the investigation of silicon nitride (Si3N4) and ‘sialon’ (SiO3N2) as promising candidates for ultrathin high dielectric materials substituting SiO2 in the search for ever shrinking field effect transistor (FET) gate lengths [17], and ultra hard materials as C3N4 with a hardness close to that of diamond and better elastic properties [18].

In the framework of a TMR European network (Training and Mobility of Researchers: Synthesis, Structure, and Characterisation of New Carbon Based Hard Materials) regrouping research groups in Sweden, England, Hungary, Germany and France, we attempted to grow thin layers of nitrogen rich stoichiometries, close to C3N4. However all attempts failed to comply with the searched nitrogen rich stoichiometry because of the release of nitrogen upon injecting larger amounts of N2. The process of molecular nitrogen release from CNx deposited layers was to be investigated in details.

Several dinitrides are known as PtN2 and PdN2 cf. ref. [19] and therein cited works. Such binaries can only be prepared under high pressure conditions; probably for stabilizing N2 in the solid state. They crystallize in the pyrite FeS2 mineral which has a face centered cubic FCC network of Fe (Pt, Pd) with S2 (N2) dumbbells in the octahedral voids. Its use as a model for the study of the release of N2 by considering CN2 hypothetical system is also justified by the fact that C has a face centered cubic (FCC) substructure in TiC as well [20, 21]. Fig. 4 shows the structure with N-N dumbbells at the center of the lattice. After substitution, geometry optimization of the structure was carried out to find the minimum energy configuration, using DFT-based calculations and pseudo-potentials. The lattice constant at equilibrium a(CN2) = 3.98 Å, is found lower than a(SiC) = 4.35Å and a(TiC)= 4.46 Å, with a considerably enlarged N-N distance of 1.34 Å. The energy gain with respect to
atomic C and molecular N₂ leads to assume that CN₂ is at least thermodynamically metastable due to the fact that the strong N-N bond of N₂ does not have to be broken compared to the formation of other nitrogen poor CNₓ compounds. Fig. 5 shows the relaxed N-N distances versus lattice constants. \( d_{\text{N-N}} \) increases regularly with the cell constant within the elastic domain until a maximum value of 1.37 Å. At higher expansions (\( a > 4.3 \) Å) a rapid decrease of N-N distance is observed reaching double N≡N bond, then N≡N triple bond lengths of molecular N₂. This is the plastic, irreversible domain. The above introduced electron localization function (ELF) contours are shown in Fig. 6 illustrating the three major steps of lattice changes. Red, blue and green areas correspond to strong, no and free electron like localizations. The C-N-N-C bond chain is depicted, with N-N in the middle. From top to bottom, a progressive weakening of the C-N bonding is observed through the increase of C-C separation (\( d_{\text{C-C}} \)), concomitant with a strengthening of N-N bond, leading eventually to molecular N₂. For the molecular N₂, one can observe the lone electron pair on both sides of N-N bond (Fig. 6c). We also note that the departure of other volatile species such as C₂N₂ (cyanogen) was equally modeled with pyrite structure. This is however less likely because CN* radicals would need to be formed [22].

![Figure 4](image1.png)

**Figure 4.** “CN₂” nitride, geo-inspired from the pyrite structure FeS₂. The N₂ ‘dumbbell’ is depicted at the center.

![Figure 5](image2.png)

**Figure 5.** Variation of N-N distance at changing lattice spacing of geo-inspired “pyrite-CN₂”. Lines and dots connecting the calculated points are shown only as a guide of the eye, i.e. they do not result from a fit.

![Figure 6](image3.png)

**Figure 6.** Electron localization function ELF maps for C-N-N-C bonding (chair-like configuration) within CN₂. a) \( d_{\text{C-N}} = 1.67 \) Å; b) \( d_{\text{C-N}} = 1.84 \) Å; c) \( d_{\text{C-N}} = 2.3 \) Å. Blue, green and red contours point to no-, free electron-like and strong-localizations.

### 6- Post-Perovskite and Post-K₂nif₄: A Paradigm for Dense 2D Materials?

The Earth lower mantle is mainly composed of MgSiO₃ and CaSiO₃ with the perovskite structure and in the lowermost part of the mantle D″, below ~2700 km, a structural transformation from the perovskite structure (PV) to the post-perovskite (PPV) structure occurs [23]. Naturally occurring silicate perovskites cannot be studied in the laboratory because of their instability at the Earth’s surface. In 2004, using coupled DFT calculations and high pressure/high temperature experiments with a diamond anvil cell (DAC) apparatus, the structural transformation PV→PPV was shown to explain the unusual properties observed...
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in the Earth D” layer [24]; this so-called ‘post-perovskite’ structure being the same as that of the CaIrO$_3$ archetype structure stable at room pressure. Whereas the perovskite structure is characterized by corner sharing octahedra along the three dimensions as shown for orthorhombic CaRhO$_3$ in Fig. 7a, in post-perovskite there is a bi-dimensional 2D character of the octahedra which are edge sharing along the c axis as shown in Fig. 7b [25]. On another hand similar trend of edge sharing octahedra is observed in Ca$_2$IrO$_4$ archetype structure. This structure is adopted by some oxides as Na$_2$OsO$_4$. It is hexagonal with one dimensional files of edge sharing octahedra (Fig. 8a). In this context we have recently predicted this mechanism of lowering dimensionality for A$_2$BO$_4$ stoichiometry with pressure for K$_2$NiF$_4$–type structure (KNF) which can be visualized as 2D stacking of corner sharing BO$_3$ octahedra interlayered with rocksalt AO layers in a tetragonal structure (Fig. 8b). Calling Ca$_2$IrO$_4$ ‘PKNF’ for post-K$_2$NiF$_4$, DFT calculations of equations of states and energy criteria, allowed proposing the mechanism: 2D (KNF) $\rightarrow$ 1D (PKNF) with pressure [26]. In both transformations an enhancement of the B-O bond covalent character is expected as well as direct $t_{2g}-t_{2g}$ orbitals interactions of the transition element, thus leading to changes of the physical properties.

- In CaRhO$_3$ the DFT investigations of the magnetic properties show a metallic character and no magnetic polarization (nor long range magnetic order) in PV form while ferromagnetism occurs in PPV with a tendency to insulating behavior. This long range order is favored by direct $t_{2g}-t_{2g}$ interactions through edge sharing octahedra in PPV, stronger than super exchange indirect $t_{2g}-O_{p}-t_{2g}$ ones in PV [25]. On the basis of these physico-chemical factors the research of the PPV structure has been incentive of examining different families of materials besides the oxides, such as nitrides [27].

- In PKNF-Na$_2$OsO$_4$ osmium is ‘magnetically silent’ due to spin pairing ($S = 0$ for $d^9$ Os$^{III}$). On the contrary a semi-conducting behavior is observed (hypothetical) KNF with finite moment in half-metallic oxide ($S = 1$) [26].

7. Conclusions

In this work the original concept of “geo-inspired
materials” has been proposed and its application was illustrated for several classes of systems as well as for solving problems in materials science. The authors suggest that it should allow devising novel synthetic materials with specific properties to meet challenges encountered in Materials Science.

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