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

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.

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 biomimetism 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 biomimetic 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

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 *sp*³ hybridization of carbon *s* and *p* orbitals forming a tetrahedron while it is a planar *sp*² 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] $2s^2 2p^1$), N ([He] $2s^2 2p^3$) and C ([He] $2s^2 2p^2$), 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 *sp*³ hybridization of carbon in diamond and 2D *sp*² 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 $p Z_V(B) + m Z_V(C) + l Z_V(N) = 4n$, where p , m , l and n are integers and $Z_V(B)$, $Z_V(C)$ and $Z_V(N)$ 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. C₃N₄ and C₁₁N₄ [6] and

ternary BC₂N [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.

Figure 1. A sketch of the BCN ternary phase diagram with ultra-hard candidate compositions isoelectronic with carbon. Model CN₂ used to study nitrogen departure from CN_x layers is also positioned.

Figure 2. A sketch of the ultra-hard hexagonal β -C₃N₄ model with 14 atoms/unit cell (*P*3 space group). It consists of fourfold coordinated carbon and three fold coordinated nitrogen. It is a network of three-, four and six-fold rings of tetrahedra.

Figure 3. Rutile like SiNF with two adjacent cells along *c* tetragonal axis. Electron localization function (ELF) isosurfaces within SiN₃F₃ distorted octahedra. Note the skewing of the surface around N towards Si (unpublished).

Actually a complication arises for ternary systems such as BC₂N because of the large number of substitution

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 BC_2N 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 BC_2N 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 ($\Delta H_{f0}^0 = -208$ kJ.mol $^{-1}$) which then favors its synthesis. From the elastic constants C_{ij} one then calculates the isotropic shear modulus G which is a better indication for hardness than the bulk modulus B . For our proposed 3D BC_2N , G is found in between the values of diamond and cubic boron nitride c -BN, i.e. $G(c\text{-BN}) \sim 426$ GPa $< G(\zeta\text{-BC}_2\text{N}) = 482$ GPa $< G(\text{diamond}) \sim 559$ 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 BC_2N was synthesized by a French group almost simultaneously to our predictions [9]. More recently nanostructured BC_4N 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.

2.2. Nitride Fluorides

Within similar approach pertaining to the electrons counting rules, the geo-inspired concept shows a great flexibility for crystal systems modeling. For instance, the equivalence: $2\text{O} \equiv \text{N} + \text{F}$ can be underlined from the point of view of identical electron count, so that $M^{(\text{IV})}\text{O}_2$ is isoelectronic with $M^{(\text{IV})}\text{NF}$, where $M^{(\text{IV})}$ is a tetravalent element. Besides several known nitrides fluorides (cf. ref. [12] and therein cited works), new nitride fluorides can be devised such as SiNF [13] starting from anionic substitutions of oxygen within the different crystal varieties of SiO_2 , i.e. quartz (hexagonal) or stishovite (tetragonal, rutile). Regarding the latter, found as the most stable from energy calculations within DFT, the single cationic and anionic lattice types lead to use another rutile subgroup structure, the CoReO_4 -type allowing to account for both two cationic and two anionic sites. The energy results show that SiNF has favorable cohesive energy albeit with much less magnitude than SiO_2 . Furthermore, there is a bond length mismatch $d(\text{Si-N}) = 1.72$ Å $< d(\text{Si-F}) = 1.85$ Å explained from the fact

that Si-N bond is covalent-like while Si-F is ionic-like. This is illustrated by a direct space analysis of the charge density with the electron localization function (ELF) [14] isosurface plots shown in Fig. 3 within the distorted $\text{Si}_3\text{N}_3\text{F}_3$ octahedron. Covalent Si-N bond is exhibited by a skewed electron isosurface envelop around N towards Si whereas spherical and isolated isosurfaces can be observed around F illustrating an ionic behavior. Si, which is positively ionized in this compound, has no significant isosurface around it.

Such chemical properties can lead to original physical properties such as piezoelectric ones with dipole formation in metal-oxide-semiconductor devices based on SiO_2 [15]. Efforts to prepare SiNF and other hypothesized nitride fluorides in different ways are underway at our institute.

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 (Si_3N_4) and ‘sialon’ (SiO_xN_y) as promising candidates for ultrathin high dielectric materials substituting SiO_2 in the search for ever shrinking field effect transistor (FET) gate lengths [17], and ultra hard materials as C_3N_4 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 C_3N_4 . However all attempts failed to comply with the searched nitrogen rich stoichiometry because of the release of nitrogen upon injecting larger amounts of N_2 . The process of molecular nitrogen release from CN_x deposited layers was to be investigated in details.

Several dinitrides are known as PtN_2 and PdN_2 cf. ref. [19] and therein cited works. Such binaries can only be prepared under high pressure conditions; probably for stabilizing N_2 in the solid state. They crystallize in the pyrite FeS_2 mineral which has a face centered cubic FCC network of Fe (Pt, Pd) with S_2 (N_2) dumbbells in the octahedral voids. Its use as a model for the study of the release of N_2 by considering CN_2 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 $a(\text{CN}_2) = 3.98$ Å, is found lower than $a(\text{SiC}) = 4.35$ Å and $a(\text{TiC}) = 4.46$ Å, with a considerably enlarged N-N distance of 1.34 Å. The energy gain with respect to

atomic C and molecular N_2 leads to assume that CN_2 is at least thermodynamically metastable due to the fact that the strong N-N bond of N_2 does not have to be broken compared to the formation of other nitrogen poor CN_x compounds. Fig. 5 shows the relaxed N-N distances versus lattice constants. $d_{(N-N)}$ 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 $N \equiv N$ triple bond lengths of molecular N_2 . 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_{C-C}), concomitant with a strengthening of N-N bond, leading eventually to molecular N_2 . For the molecular N_2 , 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 C_2N_2 (cyanogen) was equally modeled with pyrite structure. This is however less likely because $CN^\bullet$ radicals would need to be formed [22].

Figure 4. “ CN_2 ” nitride, geo-inspired from the pyrite structure FeS_2 . The N_2 ‘dumbbell’ is depicted at the center.

Figure 5. Variation of N-N distance at changing lattice spacing of geo-inspired “pyrite- CN_2 ”. 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.

a)

b)

c)

Figure 6. Electron localization function ELF maps for C-N-N-C bonding (chair-like configuration) within CN_2 . a) $d_{C-N}=1.67$ Å; b) $d_{C-N}=1.84$ Å; c) $d_{C-N}=2.3$ Å. Blue, green and red contours point to no-, free electron-like and strong- localizations.

6- Post-Perovskite and Post- K_2nif_4 : A Paradigm for Dense 2D Materials?

The Earth lower mantle is mainly composed of $MgSiO_3$ and $CaSiO_3$ 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

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_2IrO_4 archetype structure. This structure is adopted by some oxides as Na_2OsO_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_2BO_4 stoichiometry with pressure for K_2NiF_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_2IrO_4 ‘PKNF’ for post- K_2NiF_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} d 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_2OsO_4 osmium is ‘magnetically silent’ due to spin pairing ($S = 0$ for $d^2 \text{Os}^{\text{VI}}$). On the contrary a semi-conducting behavior is observed (hypothetic) KNF with finite moment in half-metallic oxide ($S = 1$) [26].

Figure 7. CaRhO_3 : Arrangements of the RhO_6 octahedra in perovskite (a) and post-perovskite (b) structures.

Figure 8. A_2BO_4 : Arrangements of the BO_6 octahedra in Ca_2IrO_4 (post- K_2NiF_4) (a) and K_2NiF_4 -type (b) structures. A: grey spheres.

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.

REFERENCES

- [1] C. Lawrence, P. Vukusic, R. Sambles. *Appl. Opt.*, 41 (2002) 437.
- [2] S. F Matar. *Progress in Solid State Chemistry*, 31 (2003) 299.
- [3] Hazen, R. M. (1999). *The diamond makers*. Cambridge University Press. pp. 100–113. ISBN 0-521-65474-2.
- [4] F. P. Bundy and R. H. Wentorf, Jr., *J. Chem. Phys.* 38 (1963) 1144.
- [5] M. L. Cohen, *Phys. Rev. B*, 32 (1985) 7988.
- [6] A. Snis, S. F. Matar. *Phys. Rev. B*, 60 (1999) 10855
- [7] M. Mattesini, S.F. Matar, *Computational Materials Science*, 20 (2001) 107.
- [8] Y. Tateyama, T. Ogitsu, K. Kusakabe, S. Tsuneyuki, S. Itoh, *Phys. Rev. B* 55 (1997) 10161.
- [9] L. Solozhenko, D. Andrault, G. Fiquet, M. Mesour, D.C. Rubie, *Appl. Phys. Lett.*, 78 (2001) 1385.
- [10] Kalyan Raidongia, Dinesh Jagadeesan, Mousumi Upadhyay-Kahaly, U.V. Waghmare, Swapan. K. Pati, M. Eswaramoorthy, C. N. R. Rao, *J. Mater. Chem.*, 18 (2008) 83.
- [11] Tristan Ferroir, Leonid Dubrovinsky, Ahmed El Goresy, Alexandre Simionovici, Tomoki Nakamura, Philippe Gillet, *Earth and Planetary Science Letters*, 290 (2010) 150.
- [12] S.F. Matar, *J. Solid State Chem.*, 185 (2012) 25.
- [13] E. Betranhandy, G. Demazeau, S.F. Matar, *Computational Materials Science*, 34 (2005) 22.
- [14] A. D. Becke, K. E. Edgecombe, *Nature*, 371 (1994) 683.
- [15] Xiaolei Wang, Kai Han, Wenwu Wang, Shijie Chen, Xueli Ma, Dapeng Chen, Jing Zhang, Jun Du, Yuhua Xiong, *Anping Huang Appl. Phys. Lett.* 96 (2010) 152907.
- [16] O Ambacher, *J. Phys. D: Appl. Phys.* 31 (1998) 2653.
- [17] N. Konofaos, E.K. Evangelou, *Semicond. Sci. Technol.* 18 (2003) 56.
- [18] Fan Dong, Liwen Wu, Yanjuan Sun, Min Fu, Zhongbiao Wu, S. C. Lee, *J. Mater. Chem.*, 21 (2011), 15171 and D.M. Teter, R.J. Hemley, *Science*, 271 (1996) 53.
- [19] A. Houari, S.F. Matar, V. Eyert, *Phys. Rev. B* 82 (2010) 241201_R.
- [20] R. Wehrich, S.F Matar, E. Betranhandy, V. Eyert, *Solid State Sci.* 5 (2003) 701.
- [21] R. Wehrich, V. Eyert, S.F Matar, *Chem. Phys. Lett.*, 373 (2003) 636.
- [22] E. Betranhandy, S.F. Matar, *Diamond and Related Materials*, 15 (2006) 1609.
- [23] G. Fiquet, *Z. Krist.*, 216 (2001) 248.
- [24] A.R. Oganov, S. Ono, *Nature*, 430 (2004) 445.
- [25] S.F. Matar, G. Demazeau, A. Largeteau, *Solid State Sci.* 12 (2010) 373.
- [26] S.F. Matar, G. Demazeau, N. Ouaini, *Solid State Sci.* 13 (2011) 1396.
- [27] S.F. Matar, G. Demazeau, *Chem. Phys. Lett.* 498 (2010) 77.