A new theoretical superstoichiometric hard $TiN_x$ crystal

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Abstract

In this article we present the application of an ab initio methodology to design new hard materials with crystal behavior. In special, we applied this methodology in the search of new materials of the $TiN_x$ family. This search will find a set of structures super-stoichiometric $Ti_3N_4$ and properties of the candidate to greatest hardness are evaluated. Hardness model used in this work is described by Antonín Šimunek and Jiří Vackář [2006] [1].

Keywords: Hardness, Ab initio methods, Material design, Probabilistic ionic substitution, Evolutionary algorithms.

1 Introduction

Today, material and energy industry search innovative strategies based on computational methods and high performance computing, whose can explore nature in atomic lenght scale [2, 3]. Discover of new inorganics compounds is a critical factor in technology developments, however this searching process is commonly very slow and highly empirical [4].

The problem of crystal composition and structure prediction can be approximate as an optimization problem. An optimization algorithm is used...
to find structural parameters and atomic sites minimizing the total energy obtained by *ab initio* methods. This approximation requires high computational cost \[4–6\].

This optimization problem exhibits great difficulties due to the high dimensionality of coordinate space \((3N + 3\), where \(N\) is number of atoms in the system\), high roughness in the response surface of free energy, energy sensitivity to minor changes in interatomic distances, redundancy in the search spaces (because crystals are formed by unitary cells) and additional high computational cost of *ab initio* calculations \[4, 5\].

Due to the characteristics of the problem, it is suggested the use of evolutionary algorithms to sampling the search spaces \[5, 7\]. This model is explained in Artem R. Oganov and Colin W. Glass \[2006\] \[7\] and implemented in the code *USPEX* \[5\], in which random samples of crystals are building using symmetry criteria and are evaluated to find best total energies (or other properties), and then over the best candidates are applied evolutionary operators to enhance properties in next generations of crystals. However, not any random parameter with initial conditions of configuration file produce a first generation acceptable.

An alternative solution to this problem is using a data mining methodology which has less computational cost to produce new candidates to possible stable materials. Using an statistical model with a big database of inorganic compounds, chemical rules are extracted and are used with specific atomic species \[4\].

Geoffroy Hautier et al. \[2011\] developed a probabilistic model to quantify and predict new possible crystals based on the empirical model of ionic substitution of Goldschmidt (1926) \[4\]. This model obtain the probability of a given substitution could occur in the nature, using as the sample a big database of crystal structures. When this probability is greater than a certain threshold, we can accept the substitution as possible and obtain a new candidate material. Probabilistic ionic substitution is implemented in the online API and cloud service *Materials Project*\[4\] in *Structure Predictor*\[8\] module.

We combined both alternatives in one progressive methodology, in which data mining approach is used as a guest for composition and structural parameters in evolutionary algorithm, thus probability of failure in first generation of structure reduce. This article applied the methodology to the case of study of *TiN* \(_x\) family. The goal of this progressive methodology is not only predict new materials (data mining approach) also obtain properties
Table 1: Structure Predictor running with nitrogen and titanium atoms.

| Oxidation state | Number of candidates | Computing time (hh:mm) |
|-----------------|----------------------|------------------------|
| N:[-3], Ti:[2]  | 0                    | 0:51                   |
| N:[-3], Ti:[3]  | 6                    | 0:43                   |
| N:[-3], Ti:[4]  | 9                    | 1:00                   |
| N:[-3], Ti:[2, 3]| 0                    | 5:48                   |
| N:[-3], Ti:[3, 4]| 0                    | 3:06                   |
| N:[-3, 1], Ti:[2]| 0                    | 3:05                   |
| N:[-3, 1], Ti:[3]| 0                    | 14:18                  |
| N:[-3, 1], Ti:[2, 3, 4]| 0            | 1:14                   |
| N:[-3, 3, 5], Ti:[3, 4]| 0        | 1:00                   |

materials optimization with low computational cost.

2 Computational detail

Probabilistic ionic substitution is applied through the cloud service of Materials Project with the Structure Predictor module to nitrogen and titanium atoms. These selection of atoms correspond to an interest in possible new hard materials in the family of TiN$_x$ compounds.

Results of running this data mining procedure, are showed in table 1. We find two candidate compositions, 6 structures with relation 1:1 and 9 structures with composition Ti$_3$N$_4$. The last composition contain the following symmetry groups: Fd3m (Fig. 1a), I43d (Fig. 1b), P1 (Fig. 1c), P31c (Fig. 1d) and P63m (Fig. 1e).

Then, using these structure as guest in evolutionary algorithm, we find 94 stable structures in 9 generations. Here, we use Quantum Espresso[9] software to perform ab initio calculations. Pseudopotentials ultrasoft building by Vanderbilt method were used in ab initio calculations, type Perdew-Zunger (LDA) with exchange-correlation energy approximation.

The electronic energy threshold criteria was $10^{-6}$ Ry by unitary cell and the integration above Brillouin zone is performed in a Monkhorst-Pack grid of $36 \times 36 \times 54$. Gaussian occupation is setup to 0.136eV and system is in a low pressure condition. Band structure calculation is performed using 98 points over irreducible Brillouin contour.

Table 2 illustrate distribution of crystal structures obtained using the
Figure 1: \( Ti_3N_4 \) by probabilistic ionic substitutions.
Table 2: Crystal phases generated with USPEX evolutionary algorithm.

| Crystal system | Symmetry group | Number of structures |
|----------------|----------------|---------------------|
| Triclinic      | $P1$           | 52                  |
|                | $P\bar{1}$     | 4                   |
| Monoclinic     | $P2$           | 1                   |
|                | $P2_1$         | 2                   |
|                | $C2/c$         | 1                   |
| Orthorhombic   | $Pmn2_1$       | 2                   |
|                | $Cmc2_1$       | 1                   |
| Tetragonal     | $P4_22_12$     | 8                   |
|                | $P4nc$         | 8                   |
|                | $I4c2$         | 3                   |
|                | $P4/nmm$       | 1                   |
|                | $P4_2/mcm$     | 2                   |
|                | $P4_2/nmc$     | 4                   |
| Cubic          | $Im\bar{3}$    | 1                   |
|                | $Pm\bar{3}m$   | 3                   |
|                | $Im\bar{3}m$   | 1                   |

Evolutionary algorithm USPEX with optimization of hardness property.

Evolution of hardness property in generations and related with change in volume, is illustrated in figures 2. The evolution of hardness in figure 2a show a strong candidate to high hardness since first generation, which is an structure with symmetry group $P4_22_12$. Hardness relation with volume shows an inversed relation according to equation of Faming Gao et al. and Antonín Šimunek and Jiří Vackář [2006][1, 10, 11]. More compacts structures are more hardness.

This work use definition of intrinsic hardness by equations of Antonín
\[ e_i = \frac{Z_i}{R_i}, \]
\[ S_{ij} = \sqrt{e_i e_j d_{ij} n_{ij}}, \]
\[ f_e = 1 - \left[ k \left( \prod_{i=1}^{k} e_i \right)^{1/k} / \sum_{i=1}^{k} e_i \right]^2, \]
\[ H = \frac{C}{V n} \left[ \prod_{i,j=1}^{n} N_{ij} S_{ij} \right]^{1/n} \exp(-\sigma f_e), \]

where \( Z_i \) is the number of valence electrons of atom \( i \), \( R_i \) is the radii to integration of charge is neutral, \( n_{ij} \) is the number of bonds between atoms \( i \) and neighbour atoms \( j \) at distance \( d_{ij} \). Additional, \( N_{ij} \) is the number of binary systems with atoms \( i \) and \( j \) in the crystal, and \( k \) is the number of different atoms in the crystal. \( C \) and \( \sigma \) are experimental constants defined as typical values of 1550 and 4 for systems similars to diamond, silice (covalent behavior) and common salt (ionic bahavior).

3 Results

The phase \( Fd\bar{3}m Ti_3N_4 \) is also knowing as \( c-Ti_3N_4 \) or spinel phase. This phase is obtained by substitution of any other mineral with spinel phase, e.g. magnetite \( Fe_3O_4 \) and rescale lattice parameters (crystal coordinates are very similar). This spinel phase is a controversial theoretical phase predicted by Ching et al. [2000][12] and it is speculated as a transition phase in ammonolysis process of solution phase \( Ti(NMe_2)_4[13, 14]. \) \( Ab \ ini\io\) calculations by Ching et al., Edwin Kroke and Marcus Schwarz [2000, 2004] indicate a possible semiconductor with bandgap of 0.25eV and high hardness[12, 15]. \( c-Ti_3N_4 \) is the unique phase mentioned in literature with composition \( Ti_3N_4[12–16]. \)

We find using data mining 8 more structures candidates with the same stoichiometry, used as guest in evolutionary algorithm, in which 94 crystal structures are generated as stable structures.

The new theoretical hardness super-stoichiometric titanium nitride of phase \( P4_22_12 \) has total energy of -856.863483 Ry and Fermi energy of 6.4204
(a) Hardness evolution.

(b) Relation between hardness and volume in structures generated by USPEX.

Figure 2: Hardness behavior in structures generated in USPEX.
Table 3: Optimized parameters of $Ti_3N_4$ superhardness candidate. Position is in crystal coordinates.

| Celda          |            |
|----------------|------------|
| Crystal system | Cubic      |
| Symmetry group | $P4_22_1$ (94) |
| a (Å)          | 2.79339    |
| b (Å)          | 2.79339    |
| c (Å)          | 4.46395    |
| Asymmetrical unit |         |
| N              | 0.000000 0.193090 0.851679 |
| Ti             | 0.000000 0.000000 0.500000 |
| Ti             | 1.000000 0.500000 0.120679 |

Table 4: Partial charge and nominal valence over asymmetric unit.

| Atom         | Partial charge | Nominal valence |
|--------------|----------------|-----------------|
| Nitrogen     | 0.70425        | -2              |
| Titanium 1   | -0.86625       | +2              |
| Titanium 2   | -0.9906        | +3              |

eV, with total energy convergence of $2 \times 10^{-8}$ $Ry$ by unitary cell. Lattice parameters and atom sites are showing in table 3 and plot associated in figure 3.

Following we show the strength tensor in units of $kbar$

$$
\begin{pmatrix}
415.25 & 0 & 0 \\
0 & 415.24 & 0 \\
0 & 0 & 397.51
\end{pmatrix}
$$

In figure 4 band structure is illustrated, and we can see an overlapping around fermi energy of valence and conduction band, indicating a conductive behavior in this ceramic structure, a common characteristic with others titanium nitrides and carbon nitrides [17, 18].

In order to estimate hardness, we calculate also Lowdin population for the crystal, and the result is showing in sites of the asymmetrical unit in table 4.

Using values obtained in this work, with formulae of Antonín Šimunek and Jiří Vackář and literature data to titanium nitride (1:1), we can compare an
Figure 3: Optimized structure to superhardness.

Figure 4: Band structure of $Ti_3N_4$ candidate to superhardness.
adimensional value of hardness associated with titanium nitride (1:1) equal to 5.7082 and a value of 83.9252 for titanium nitride $Ti_3N_4 P4_2212$.

4 Conclusions

We find a new theoretical candidate super-stoichiometric titanium nitride $P4_2212$ to superhardness (and also electrical condutor) using a combined methodology of computational material design, searching guests by data mining approach and then optimized total energy and specific properties on the material with evolutionary algorithms.

Using the methodology we find more than one possible stable structures of $Ti_3N_4$, in which we can find also the unique precedence to this work, the c-$Ti_3N_4$. This observations agree with the work of Ching et al..

This methodology can be applied to diversity of properties, in a way to search specific material properties via *ab initio* calculatios. Application of great interest in material industry.

Acknowledgement

The authors thank to the Center of Scientific Computing APOLO of Universidad EAFIT and Juan David Pineda (systems engineer and system administrator of APOLO) for the contribution on computing resource.

Also, the authors thank (and posthumous memory) to Andriy Lyakhov, main developer of the USPEX code, who in cooperation we can port compatibility of USPEX code with octave instead of matlab.

Supporting Information Available

These results are part of the project ”Modelo computacional multiescala de nanoindentación para caracterización de nanomateriales” supported by the Administrative Department of Science, Technology, and Innovation of Colombia (COLCIENCIAS) and Universidad EAFIT on the 566 (Jóvenes investigadores e innovadores 2012) call.
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