MATCH
Communications in Mathematical and in Computer Chemistry

MATCH Commun. Math. Comput. Chem. **65** (2011) 153-162

ISSN 0340 - 6253

Omega Polynomial in TiO_2 Crystal Lattices

Mircea V. Diudea,[a*] and Aleksandar Ilić[b]

[a]Faculty of Chemistry and Chemical Engineering,
"Babes-Bolyai" University, 400028 Cluj, Romania
[b]Faculty of Sciences and Mathematics, University of Niš,
Višegradska 33, 18000 Niš, Serbia

(Received July 27, 2009)

Abstract

The topology of Inorganic Titanium oxide lattices called rutile and anatase is described in terms of Omega counting polynomial. Close formulas for calculating the polynomial and the Cluj-Ilmenau index derived from this polynomial are given.

1. Introduction

Various inorganic compounds including oxides, sulfides, selenides, borates, silicates, etc of many metals show very ordered structures at the nano-scale. Many of these compounds form nanotubes, similar to those of carbon: MX2, M=Mo, W, Ta, In, Zn, Ti, Cd, X=O, S, Se, Te, CB_x, BN, etc. In the last years, oxides and other above-mentioned inorganic substances found applications in the design of nanostructured functional materials as films, nanorods, porous systems, nanoclusters and nanocrystallites or as nanofibers, by filling the inner space of carbon nanotubes.[1-10]

Among numerous oxide nanostructures, the titanium nanotubular materials are of high interest due to their chemical inertness, endurance, strong oxidizing power, large surface area, high photocatalytic activity, non-toxicity and low production cost. TiO_2 nanotubes have found applications in photo-catalysis, in solar cells, as nanoscale materials for lithium-ion batteries or as gas-sensing materials.[4-11]

* This paper is dedicated to Dr. Peter John, Technical University Ilmenau, Germany, for his bright contribution to the development of Chemical Graph Theory.

The numerous studies on the use of titania in technological applications also required theoretical studies of stability and other properties of such structures.[12-15]

It is known that the morphology of TiO_2 nanotubes depends on the size and structure of the starting material. Well-crystallized nanotubes can be obtained by hydrothermal reaction of ultra-dispersed TiO_2 (rutile or anatase) with aqueous NaOH. These nanotubes preserve in some extend the structure of the starting material.

The present study is devoted to the study of rutile and anatase, as periodic crystal networks, by using a topological description in terms of the Omega counting polynomial.

2. Omega polynomial

Let $G(V,E)$ be a connected graph, with the vertex set $V(G)$ and edge set $E(G)$. Two edges $e = uv$ and $f = xy$ of G are called *codistant e co f* if they obey the following relation:[16,17]

$$d(v,x) = d(v,y) + 1 = d(u,x) + 1 = d(u,y) \qquad (1)$$

Relation *co* is reflexive, that is, *e co e* holds for any edge *e* of *G*; it is also symmetric, if *e co f* then *f co e*. In general, relation *co* is not transitive, an example showing this fact is the complete bipartite graph $K_{2,n}$. If "*co*" is also transitive, thus an equivalence relation, then G is called a *co-graph* and the set of edges $C(e) := \{f \in E(G);\ f\ co\ e\}$ is called an *orthogonal cut oc* of G, $E(G)$ being the union of disjoint orthogonal cuts: $E(G) = C_1 \cup C_2 \cup ... \cup C_k,\ C_i \cap C_j = \varnothing, i \neq j$. Klavžar[18] has shown that relation *co* is a theta Djoković-Winkler relation.[19,20]

Let $e = uv$ and $f = xy$ be two edges of G which are *opposite* or topologically parallel and denote this relation by *e op f*. A set of opposite edges, within the same face/ring, eventually forming a strip of adjacent faces/rings, is called an *opposite* edge *strip ops*, which is a quasi-ortogonal cut *qoc* (*i.e.*, the transitivity relation is not necessarily obeyed). Note that *co* relation is defined in the whole graph while *op* is defined only in a face/ring.

The *ops* relation has the properties: (i) any two subsequent edges of such a strip are in *op* relation; (ii) any three subsequent edges belong to adjacent (edge sharing)

faces/ rings; (iii) the inner dual of an *ops* is a path or a cycle, thus neither revisiting nor branching is allowed.

An *ops* starts/ends in either one even face/ring or in two odd faces/rings; in the first case, the *ops* is a cycle while in the second one it is a path. In case of open structures, the open (or infinite) faces are equivalent to the odd faces. There are cases in which the two odd faces/rings superimpose and *ops* is a *pseudo* cycle, because the *op* relation in the first/last odd face/ring is not obeyed.[16]

The length of *ops* is maximal irrespective of the starting edge. The choice is about the maximum size of face/ring, and the mode of face/ring counting, which will decide the length of the strip. In case of ring mode counting, the procedure will search for the detour of the inner duals of *ops*.

Let $m(G,s)$ be the number of *ops* strips of length s. The Omega polynomial is defined as[21]

$$\Omega(G,x)=\sum_s m(G,s)\cdot x^s \qquad (2)$$

The first derivative (in x=1) equals the number of edges in the graph

$$\Omega'(G,1)=\sum_s m(G,s)\cdot s = e = \left|E(G)\right| \qquad (3)$$

A topological index, called Cluj-Ilmenau,[22] $CI=CI(G)$, was defined on Omega polynomial

$$CI(G)=\left\{[\Omega'(G,1)]^2-[\Omega'(G,1)+\Omega''(G,1)]\right\} \qquad (4)$$

An example is given in Figure 1, which illustrates just the pattern of TiO_2 lattice.

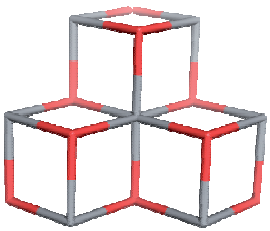

Figure 1. TiO_2 lattice; $\Omega(G,x)=3x^3+3x^5$; $\Omega'(G,1)=24=e(G)$; $CI(G)=474$

Data were calculated by an original program called Nano_Studio,[23] developed at the TOPO Group Cluj.

3. Rutile lattice

The rutile lattice is non-isotropic in the three directions of the Euclidean space (Figure 2), this anisotropy being reflected in their physical properties. Different views can also be seen in a "corner view" (Figure 2, d).

We took the repeat unit of the periodic structure as the cube of unity dimensions (x,y,z=1), superimposed (or not) to the crystallographic elementary cell.

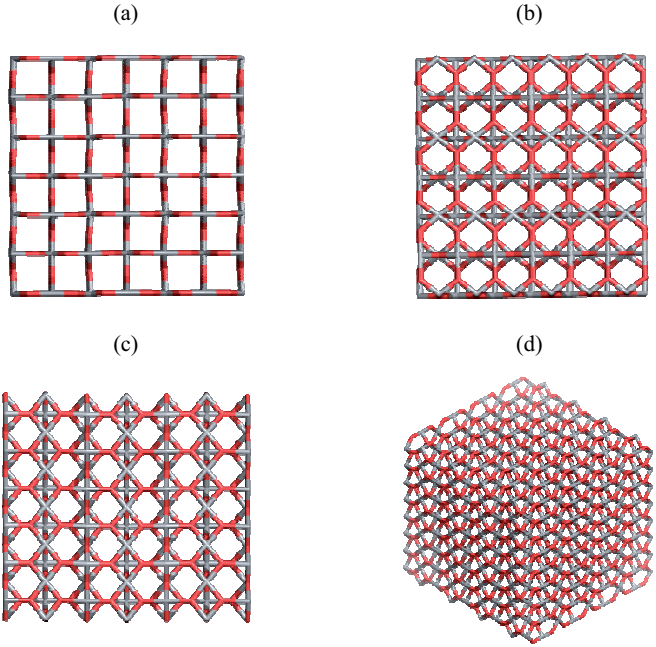

Figure 2. Rutile lattice *k*=3, *v*=864, cube face view (a,b,c), and *k*=4 , *v*=1912, corner view (d)

In calculating Omega polynomial, different results are obtained if the maximum ring R_{max} considered is varied. Thus, the form of polynomial was different for R_{max}[6] and [8], respectively. The general form of Omega polynomial in Rutile lattice is as below

$$\Omega(R_{(k,k,k)}, x, R_{\max}[6]) = a_1 X^{e_1} + a_2 X^{e_2} + X^{e_3} \quad (5)$$

$$\Omega(R_{(k,k,k)}, x, R_{\max}[8]) = X^{a_{1(6)}e_1} + X^{a_{2(6)}e_2} + X^{e_3} \quad (6)$$

i	a_i ; $R_{max}[6]$	e_i ; $R_{max}[6]$
1	$2k(2k+1)$	$2k$
2	$2k(2k+1)$	$2k+1$
3	1	$16k^2(2k+1) = 8k \cdot a_1$

From (5) and (6), the index CI can be derived as

$$\mathrm{CI}(R_{max}[6]) = 2k(2k+1)(-1+2k(2k+1)(-1+24k+80k^2)) \quad (7)$$

$$CI(R_{\max}[8]) = 16k^3(2k+1)^2(5+18k) \quad (8)$$

Some examples are given in Table 1.

Table 1. Omega polynomial in rutile: examples

	Rutile	Omega ($R_{max}[6]$/ $R_{max}[8]$)	v	CI
1	rutile_111	$6X^2+6X^3+X^{48}$	52	3702
		$X^{12}+X^{18}+X^{48}$		3312
2	rutile _222	$20X^4+20X^5+X^{320}$	292	146780
		$X^{80}+X^{100}+X^{320}$		131200
3	rutile _444	$72X^8+72X^9+X^{2304}$	1912	7127928
		$X^{576}+X^{648}+X^{2304}$		6386688
4	rutile _555	$110X^{10}+110X^{11}+X^{4400}$	3580	25639790
		$X^{1100}+X^{1210}+X^{4400}$		22990000
5	rutile _666	$156X^{12}+156X^{13}+X^{7488}$	6012	73567572
		$X^{1872}+X^{2028}+X^{7488}$		65999232
6	rutile _777	$210X^{14}+210X^{15}+X^{11760}$	9352	180236490
		$X^{2940}+X^{3150}+X^{11760}$		161758800

The number of atoms in a complete cube C(k, k, k) of the rutile net is calculated by the recursive formula:

$$v_k = \left(\frac{k}{k-1}\right)\left[2(k-7) + (k+1)\left(\frac{v_{k-1}}{k-1}\right)\right] \quad (9)$$

This linear inhomogeneous recurrent relation can be solved by the method of undetermined coefficients or mathematical induction,

$$v_k = 2k(12k^2 + 11k + 3) \quad (10)$$

Since the number of atoms increase quickly in the cubes of rutile, it is useful to have a composition rule of the polynomial for a given cube from non-complete cube fragments. The rule is based on "net-face identification" procedure, using the "net-face" (a) (Figure 2). The number of fragments used in composition scheme is denoted by *nf*. The composition rule, union of fragments and examples (Table 2) are given below.

$$\Omega(R_{(k,k,k),\bigcup},x)=a_1X^{\sum_f e_{1,f}}+a_1X^{\sum_f e_{2,f}-(nf-1)}+1X^{\sum_f e_{3f}} \quad (11)$$

$$\bigcup := [kk_a\_k(k-m_s)_b\_k(k-m_s)_c];\ \sum m_s = k$$

Table 2. Composition rule for Omega polynomial in rutile: examples.

	Fragment	Omega; R_{max}[6]	*nf*	*CI*
1	rutile_333	$42X^6+42X^7+X^{1008}$	1	1395282
2	rutile_333HALF	$42X^3+42X^4+X^{504}$	2	381738
3	rutile_33a_31b_31c	$42X^2+42X^3+X^{336}$	2	184674
	rutile_33a_32b_32c	$42X^4+42X^5+X^{672}$		649194
4	rutile_33a_31b_31c	$42X^2+42X^3+X^{336}$	3	184674
	rutile_33a_31b_31c	$42X^2+42X^3+X^{336}$		184674
	rutile_33a_31b_31c	$42X^2+42X^3+X^{336}$		184674

The formulas for Omega polynomial (relations 5 and 6) have been derived as follows.

Rutile R_{max}[8]:

$$\Omega(k)=X^{a_k}+X^{b_k}+X^{c_k}$$
$$a_k=4\cdot x_k$$
$$c_k=16\cdot x_k$$
$$x_1=3$$

Based on the composition rule for rutile cubes C(*k*, *k*, *k*), the following recurrent formula holds

$$x_{k+1}=\frac{(k+1)^3}{k^3}x_k-\frac{(k+1)^2}{k}.$$

After regrouping, we have

$$\frac{x_{k+1}}{(k+1)^3}=\frac{x_k}{k^3}-\frac{1}{k(k+1)}=\frac{x_k}{k^3}+\left(\frac{1}{k+1}-\frac{1}{k}\right)$$

Use telescoping series to solve the recurrent formula:

$$\frac{x_{k+1}}{(k+1)^3}=\frac{x_1}{1^3}+\left(\frac{1}{k+1}-\frac{1}{k}+\frac{1}{k}-\frac{1}{k-1}+\ldots+\frac{1}{2}-\frac{1}{1}\right)=3+\left(\frac{1}{k+1}-1\right)$$
$$x_k=k^2(2k+1)$$

In this way, the exponents a_k and c_k are computed. For the exponent b_k, notice the following

$$b_k = x_k \cdot \frac{2(2k+1)}{k} = 2k(2k+1)^2 .$$

Rutile R_{max}[6]:

$$\Omega(k) = d_k X^{2k} + d_k X^{2k+1} + X^{c_k}$$

For the coefficient d, there is the following recurrent formula

$$\frac{d_{k+1}}{(k+1)^2} = \frac{d_k}{k^2} - \frac{2}{k(k+1)}$$

Using the same method as above, it follows:

$$d_k = 2k(2k+1) .$$

4. Anatase lattice

The anatase lattice is also anisotropic, as can be seen from Figure 3. The Omega polynomial consists of three terms, as in case of rutile, but no variation with R_{max} was observed.

$$\Omega(An_{(k,k,k)}, x) = a_1 X^{e_1} + a_2 X^{e_2} + a_3 X^{e_3} \text{ ; } R_{max}[4] \qquad (12)$$

The index CI can be derived from (4) as

$$CI(R_{max}[6]) = 2k(4k+1)(-3+2k(-3+4k(25+108k+144k^2))) \qquad (13)$$

i	a_i	e_i
1	$4k(4k+1)$	1
2	$2k(4k(4k+1))$	2
3	$2k(4k+1)$	$4k+1$

Some examples are given in Table 3.

Table 3. Omega polynomial in anatase lattice: examples

	Anatase	Omega	v	CI
1	anat_111	$20X+40X^2+10X^5$	94	22070
2	anat_222	$72X+288X^2+36X^9$	547	940644
3	anat_333	$156X+936X^2+78X^{13}$	1648	9236682
4	anat_444	$272X+2176X^2+136X^{17}$	3685	48059816
5	anat_555	$420X+4200X^2+210X^{21}$	6946	174923070
6	anat_666	$600X+7200X^2+300X^{25}$	11719	506033100

The number of atoms in a complete cube C(k, k, k) of the anatase net is calculated by a similar procedure as in case of rutile. This leads to the close formula

$$v_k = 1 + 3k(3 + 12k + 16k^2) \qquad (14)$$

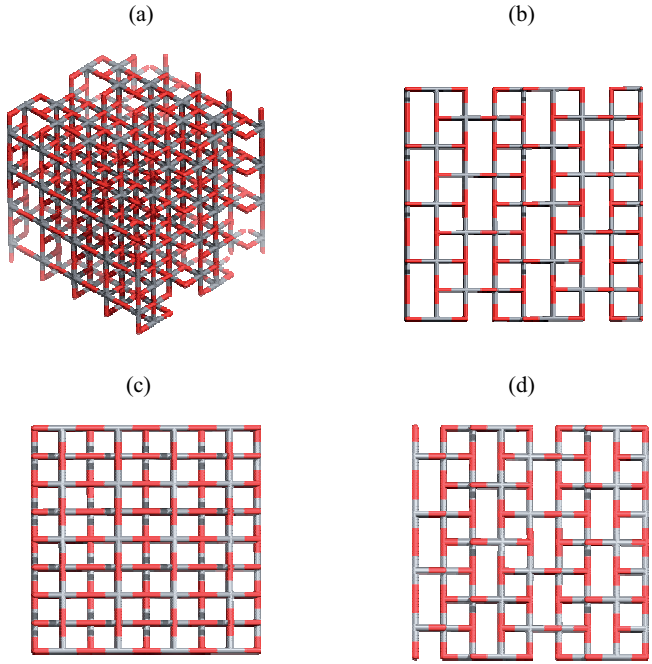

Figure 3. Anatase lattice k=2; v=547, (a) corner view and (b, c, d) cube face view.

5. Conclusions

The topology of Titanium oxide lattices, namely rutile and anatase can be described by sing the Omega counting polynomial. Close formulas for calculating the polynomial and the Cluj-Ilmenau index derived from this polynomial were given. A composition rule for the network or rutile was also found.

Acknowledgements: The second author (A. I.) is grateful to European Society of Mathematical Chemistry **ESMC**, for support in travelling and working at TOPO GROUP Cluj, Romania.

References

1. R. Tenne, *Chem. Eur. J*., **2002**, *8*, 5296.
2. C. N. R. Rao, M. Nath, *Dalton Trans.* **2003**, *1*, 1.
3. G. R. Patzke, F. Krumeich, R. Nesper, *Angew. Chem., Int. Ed.* **2002**, *41*, 2447.
4. H. Imai, M. Matsuta, K. Shimizu, H. Hirashima, N. Negishi, *Solid State Ionics*, **2002**, *151*, 183.
5. M. Adachi, Y. Murata, I. Okada, S. Yoshikawa, *J. Electrochem. Soc.* **2003**, *150*, G488.
6. Y. Zhou, L. Cao, F. Zhang, B. He, H. Li, *J. Electrochem. Soc.* **2003**, *150*, A1246.
7. O. K. Varghese, D. Gong, M. Paulose, K. G. Ong, C. A. Grimes, *Sens. Actuators B*, **2003**, *93*, 338.
8. O. K. Varghese, D. Gong, M. Paulose, K. G. Ong, E. C. Dickey, C. A. Grimes, *Adv. Mater.* **2003**, *15*, 624.
9. C. A. Grimes, K. G. Ong, O. K. Varghese, X. Yang, G. Mor, M. Paulose, E. C. Dickey, C. Ruan, M. V. Pishko, J. W. Kendig, A. J. Mason, *Sensors*, **2003**, *3*, 69.
10. G. K. Mor, M. A. Carvalho, O. K. Varghese, M. V. Pishko, C. A. Grimes, *J. Mater. Res*. **2004**, *19*, 628.
11. G. S. Zakharova, V. L. Volkov, V. V. Ivanovskaya, A. L. Ivanovskii, *Russ. Chem. Rev*. **2005**, *74*, 587.
12. Y. Q. Wang, G. Q. Hu, X. F. Duan, H. L. Sun, Q. K. Xue, *Chem. Phys. Lett.* **2002**, *365*, 427.
13. Y. Zhu, H. Li, Y. Koltypin, Y. R. Hacohen, A. Gedanken, *Chem. Commun.* **2003**, 2616.
14. V. V. Ivanovskaya, A. N. Enyashin, A. L. Ivanovskii, *Mendeleev Comm.* **2003**, *13*, 5.
15. A. E. Vizitiu, M. V. Diudea, *Studia Univ. Babes–Bolyai*, **2009**, *54*, 173.
16. M. V. Diudea, A. Ilić, *Carpath. J. Math.* **2009** (submitted).
17. A. R. Ashrafi, M. Jalali, M. Ghorbani, M. V. Diudea, *MATCH*, *Commun. Math. Comput. Chem.* **2008**, *60*, 905-916.

18. S. Klavžar, *MATCH Commun. Math. Comput. Chem.* **2008,** *59***,** 217.
19. D. Ž. Djoković, *J. Combin. Theory Ser. B*, **1973**, 14, 263.
20. P. M. Winkler, *Discrete Appl. Math*. **1984**, 8, 209.
21. M. V. Diudea, *Carpath. J. Math*. **2006,** *22*, 43.
22. P. E. John, A. E. Vizitiu, S. Cigher, M. V. Diudea, *MATCH Commun. Math. Comput. Chem.* **2007**, *57*, 479-484.
23. Cs. L. Nagy, M. V. Diudea, *Nano_Studio*, "Babes-Bolyai" Univ. **2009**.