Z. Kristallogr. Suppl. **26** (2007) 203-208

Predicted corner-sharing titanium silicates

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Keywords: crystal structure prediction, titanosilicates, inorganic compounds, Monte Carlo

Abstract. The prediction of mixed three-dimensional frameworks involving tetrahedra and octahedra sharing exclusively corners is undertaken by applying the Monte Carlo computer program GRINSP (Geometrically Restrained Inorganic Structure Prediction) to titanium silicates. More than 1000 models are selected and stored into the PCOD (Predicted Crystallography Open Database). A part of them is identified to real counterparts. The most porous hypothetical structures are presented. The final aim is to build a database of calculated powder diffraction patterns for identification by search-match procedures.

Introduction

As a consequence of the increase in computer power and due to the obvious interest in relying more on planning than on serendipity for chemical synthesis, times are coming for the systematic prediction of the crystal structures of inorganic compounds. A fabulous example consists in the more than 2.500.000 models gathered into the hypothetical zeolites database [1], which should facilitate the identification and structure determination of any new real zeolite by search-match against the calculated powder patterns. The recent publication of the GRINSP (Geometrically Restrained Inorganic Structure Prediction) computer program [2] for the building of N-connected 3D frameworks (N = 3, 4, 5, 6 and binary N/N' combinations) allows for the exploration of single or mixed frameworks of triangles, tetrahedra, square-based pyramids, triangle bipyramids, octahedra or trigonal prisms. Hypothetical GRINSP models built up from corner-sharing TiO_6 octahedra and SiO_4 tetrahedra are reported here. Mixed frameworks, minerals and synthetic compounds, are of great interest, particularly with respect to host-guest chemistry, ion-exchange, adsorption properties, and shape selective catalytic activity. The large class of titanium silicates is represented by more than about 70 minerals, mainly with mixed cation frameworks [3]. They display very exciting crystal chemistry and open an attractive outlook to synthesize them and their analogues. Many synthetic homologues of minerals have been reported as well as some new titanium silicates showing open frameworks or bidimensional structures [4,5]. Some compounds obtained by thermal decomposition of precursors (hydrates, etc) may not be well enough crystallized for a successful indexing of their powder pattern, so that the key for their structure determination is in the anticipation of their existence. The present predictions by GRINSP have led to the inclusion of more than 1000 structure-types into the PCOD [6].

Prediction conditions

The knowledge assumed in this study is limited to the M-O, O-O and M-M (M = Si^{4+}, Ti^{4+}) ideal first neighbour distances, and to the exclusive corner-sharing connection mode. GRINSP is a Monte-Carlo (MC) software, applying a pseudo-random number sequence to the heuristic solution of the structural problem. Once a space group (SG) is selected, a first Ti or Si atom (random choice) is placed in a box (with cell parameters relations in agreement with the SG) whose dimensions are selected themselves at random, at a Wyckoff position selected randomly. Then, a second (then a third, etc) Ti or Si atom is placed, if possible. It is checked if the model is not already fulfilling all requirements: one Ti atom should have six Ti or Si (and one Si should have four Ti or Si) first neighbours in the range of M-M distances defined by the user ± 0.4 Å. The fact that distances are given a large tolerance range allows many solutions to be captured which may not correspond to regular polyhedra at this stage. If after some trials, no satisfying model is found, a new first Ti or Si atom will be placed, and so on. For a given set of cell parameters, 300.000 MC events were performed, and at least 20.000 sets of random cell parameters were explored for each SG (230 days of calculation on a single processor running at 2.4 GHz). In this first step, atoms do not move (this is not a simulated annealing approach). The total number of (Ti/Si) atoms placed is not predetermined. For that first exploration, the cell parameters were not larger than 16 Å.

In a second step the O atoms were added at the midpoints of the Ti-Ti or Ti-Si or Si-Si first neighbours and it was verified by distance and cell improvements (by the MC method as well) that regular TiO_6 and SiO_4 polyhedra could really be built, i.e. that there was a deep local minima existing close to this previously selected rough arrangement of Ti/Si atoms. The cost function allowing to establish a minimum is based on the verification of the provided ideal distances Si-O (1.61Å), O-O (2.63 Å) and Si-Si (3.07 Å) for SiO_4 tetrahedra, and Ti-O (1.95 Å), O-O (2.76 Å) and Ti-Ti (3.80 Å) for TiO_6 octahedra. The total R factor is defined by the equation :

$$R = \sqrt{[(R_1+R_2+R_3)/(R_{01}+R_{02}+R_{03})]}, \qquad (1)$$

where R_n and R_{0n} for n = 1, 2, 3 are defined by the expressions :

$$R_n = \Sigma\,[w_n(d_{0n}-d_n)]^2, \qquad R_{0n} = \Sigma\,[w_n d_{0n}]^2, \qquad (2, 3)$$

where the d_{0n} values for n = 1 to 3 are the ideal first interatomic distances M-O (n = 1), O-O (n = 2) and M-M (n = 3), whereas the d_n values are the corresponding observed distances in the structural model for these atom pairs. The terms w_n are chosen in order to attribute more weight with respect to the M-O first distances. When Si-Ti neighbours occur, the ideal distance is estimated as being half the sum of the Si-Si and Ti-Ti distances. Models were retained if $R < 0.02$. Then, further optimizations could be performed by using bond valence rules, or energy minimization. However, in most cases the predicted cell parameters differ by less than 2% from the actual ones if the real compounds are built up from regular polyhedra, which was the case with dense SiO_2 polymorphs or zeolites previously studied by GRINSP [2] and AlF_3 phases [7]. During this second step, the atoms are moving, but no jump is allowed because such a jump would disregard the coordination sequence established at the first step. The change in cell parameters from the rough structure candidate to the final model may be quite considerable (up to 30%). During the optimization, the original space group may not be preserved, so that the final structure is always proposed in space group P1, presented in a CIF file. An ultimate choice of the real symmetry has to be done by using a program able to detect missing symmetries, like PLATON [8]. One given model can be identified in different space groups with slightly different or equal R values. The way GRINSP recognizes a structure-type is by comparing the coordination sequence (CS) [9] of any model with a list of previously established ones (as well as with the other CS already stored during the current run). That CS, originally developed for zeolites was extended to the N-connected frameworks inside of the GRINSP algorithm. Only one model was retained corresponding to one structure-type, selecting the model with best R value and higher symmetry. GRINSP is available via http://www.cristal.org/grinsp/. The software is free of charge for non-profit organizations and is delivered with the Fortran source code under the GNU Public Licence. Parallelization of the code is in progress.

Results

The more than 1000 hypothetical models which were produced exclude structures where edge- or face-sharing polyhedra would occur, and also the structures built up from TiO_5 polyhedra (a survey of the TiO_5/SiO_4 combinations is in progress). A vast majority (~70%) of the hypothetical models proposed by GRINSP corresponds to the general formula $[TiSi_nO_{(3+2n)}]^{2-}$. The most numerous models are those with n = 1, 2, 3, 4 and 6, with respectively 93, 179, 174, 205 and 158 models satisfying $R < 0.02$. These models are not electrically neutral. For existing, their framework will have to accommodate additional cations or charged molecules. Many known (~50) structures are recognized among the predicted models, some of them are listed in the next paragraph where it is demonstrated that the lack of consideration of an electrical neutrality has limited consequences on the cell parameters. The search by GRINSP is not exhaustive, a new campaign of calculations would allow many of the models to be found again but would also certainly reveal new ones. Moreover, enlarging the cell parameter limit to more than 16 Å would also allow for the building of many new models. The capacity of GRINSP was recently extended to models with a maximum of 192 cations instead of 64 at the time when these calculations were made.

Models corresponding to real structures

Identifying the hypothetical models which have a real counterpart is not an easy task. The technique applied here was to make a list of the known titanosilicates or similar materials from the ICSD database and to analyze them one by one, seeing first if they were built up exclusively from corner-sharing TiO_6 octahedra and SiO_4 tetrahedra, then calculating their CS and comparing to the full list of CS characterizing the hypothetical models. A selected list of frameworks having real titanosilicate counterparts is presented in Table 1. Some have low framework densities (FD : number of Si/Ti atoms in 1000Å^3) such as the nenadkevichite structure (FD = 16.4) or the umbite structure adopted by $K_2TiSi_3O_9{\cdot}H_2O$ (FD = 17.2) (figure 1). Considering that GRINSP estimates the cell parameters from the TiO_6/SiO_4 framework only, without any cation or water molecule (etc) inside of the cages or tunnels, the accuracy of the predictions appears not so bad, as defined by $|\delta| < 2\%$ (the average absolute value of the difference in percentage between the observed and predicted cell parameters), with an exception for titanite.

Table 1. Selection of five observed and predicted (italics, second line) $[TiSi_nO_{(3+2n)}]^{2-}$ frameworks. The PCOD column gives the entry number in the Predicted Crystallography Open Database [6].

Mineral/formula	n	SG/FD	a	b	c	α/β/γ	$\vert\delta\vert$ (%)	R(%)	Ref.	PCOD
Titanite	1	A2/a	7.050	8.681	6.539	113.90			[10]	
$CaTiSiO_5$		21.2	*7.365*	*8.284*	*6.853*	*115.85*	3.9	0.62		2200002
Nenadkevichite	2	Pbam	7.350	14.153	7.124	90.			[11]	
$NaTiSi_2O_7{\cdot}2H_2O$		16.4	*7.278*	*14.219*	*7.090*	*90.*	0.6	0.59		2200042
$K_2TiSi_3O_9{\cdot}H_2O$	3	$P2_12_12_1$	7.136	9.908	12.941	90.			[12]	
		17.2	*7.221*	*9.967*	*12.929*	*90.*	0.6	0.92		2200207
Penkvilskite 1M	4	$P2_1/c$	8.956	8.727	7.387	112.74			|13]	
$Na_2TiSi_4O_{11}{\cdot}2H_2O$		19.4	*8.890*	*8.426*	*7.469*	*112.78*	1.3	0.76		2200114
$K_2TiSi_6O_{15}$	6	$P2_1$	6.916	12.812	7.661	106.25			[14]	
		21.6	*6.906*	*12.914*	*7.604*	*107.35*	0.7	0.65		2200208

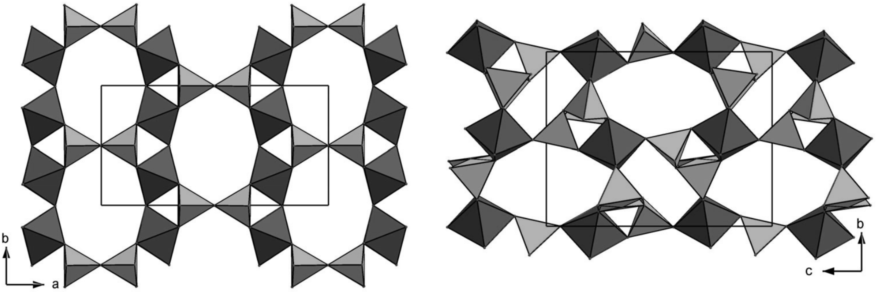

Figure 1. Predicted frameworks then identified as corresponding to the known structures nenadkevichite (left) and $K_2TiSi_3O_9{\cdot}H_2O$ (right, adopting the umbite mineral structure).

Models with the largest porosity

The models were classified according to their framework density, providing a list starting at FD = 10.6, corresponding to a porosity P = 70%, close to the smallest known FD values for zeolites. The determination of the pore volumes for the first 10 models in that list was made by using the options SOLV (using r(O) = 1.35 Å, a probe radius of 1.25 Å and a 0.12 Å grid step) of the PLATON computer program which was recently shown to be applicable to studies of microporous inorganic crystals [15]. The porosity P and the volume of pores V^P (according to the definitions in [15]) are presented in Table 2. All of these ten most porous hypothetical titanosilicates would behave as zeoates (pores have infinite extension in one direction – becoming a channel – $D^P = 1$, or in 2 or 3 directions – $D^P = 2$ or 3, then the pores form a "channel system"). Not surprisingly, models with the largest porosity have a Si/Ti ratio > 1. However, a $Si_2Ti_3O_{13}$ hypothetical compound is the fifth in the list, showing octahedra arranged into HTB (hexagonal tungsten bronze) planes interconnected by tetrahedra. Models denoted A to D, F, H and I in Table 2 have their three-dimensional channels ($D^P = 3$) kept with guest diameters > 3 Å whereas models E and J loose them. Model G has D^P=1, one of the two channels being reduced to isolated pores for larger guests.

Table 2. Pore volumes V^P (Å^3) are given for the pore dimensionalities D^P as derived by SOLV for the ten predicted titanosilicates with smallest framework densities, using a probe radius of 1.25 Å.

N°-formula	R(%)	FD	*P*(%)	SG	Vcell	$D^P = 3$	$D^P = 1$	Rings	PCOD
A-Si_6TiO_{15}	1.82	10.6	70.2	$P4_132$	2644	1855		9x9x9	3200086
B-Si_2TiO_7	1.33	12.0	61.7	Imma	998	616		10x8x8	3200867
C-Si_6TiO_{15}	1.82	13.0	61.8	Pn-3	2152	1305		12x12x12	3200081
D-Si_4TiO_{11}	1.75	13.0	59.6	$P4_2$/mcm	1535	915		12x10x10	3200026
E-$Si_2Ti_3O_{13}$	1.04	13.3	50.8	P-3	752	383		8x8x6	3200037
F-Si_4TiO_{11}	1.72	13.3	59.4	Cccm	1502	892		12x10x10	3200837
G-$Si_4Ti_3O_{17}$	1.94	14.2	47.3	$Pmc2_1$	983		358, 104	16+8	3200518
H-Si_6TiO_{15}	0.99	14.9	52.3	Pmma	937	490		10x8x6	2200205
I-Si_6TiO_{15}	0.97	14.9	52.3	P2/m	468	245		10x8x6	2200199
J-$Si_{12}TiO_{27}$	1.07	15.2	53.7	P-31c	1710	919		8+6x8x6	3200052

Some common building units are observed. (a) Isolated octahedra with 6 corners shared by 6 tetrahedra in two groups of 3 tetrahedra, either cyclo-three-connected (case of models A and C), or part of silicate chain with 2 connections (case of models D, F, H and I), or 3 groups of 2 tetrahedra (model J); (b) chains of trans-connected octahedra, the 4 remaining corners satisfied by tetrahedra (case of model B); (c) octahedra organized in HTB sheets interconnected by Si_2O_7 groups (case of model E); (d) cis-connected chains of either octahedra or trigonal prisms in model G presenting the largest pore aperture with 16-membered ring. Two models are depicted on figure 2.

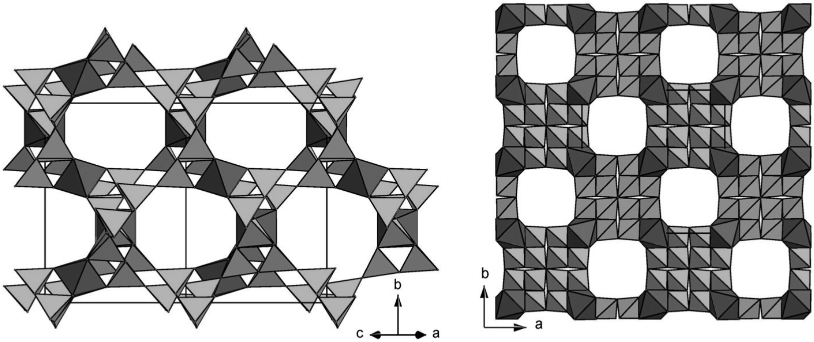

Figure 2. Predicted cubic frameworks with high porosity (P>60%). Models A (left) and C (right) in the Table 2 notation, both with $[Si_6TiO_{15}]^{2-}$ formulation.

Extension to isomorphous hypothetical compounds

Using GRINS, a satellite program inside of the GRINSP package, the feasibility of isomorphous compounds was tested. GRINS can read a multiple CIF issued from GRINSP and try a selected cationic/anionic replacement much faster (a few hours for one thousand models) than if a full prediction was undertaken. Series of zircono-, niobio-, vanadyl-, gallo-phosphates, as well as sulfates, were built starting from the titanium silicates and will be inserted into the PCOD, increasing soon the total number of entries to more than 10.000.

Concluding remarks

In spite of its limitations, GRINSP appears as an efficient generator of hypothetical crystal structures. Improvements would consist in the consideration of other linkage modes than only by corner-sharing (adding edge and face-sharing) and in the increase of the complexity to combinations of 3 different polyhedra, so as to be able to explore the large domain of the mixed octahedral-pentahedral-tetrahedral framework silicates, for instance. The usefulness of the PCOD will be maximal when powder patterns will be calculated and used by search-match tools for identification purposes. This cannot be done before to fill some frameworks by cations in order to attain electrical neutrality so as to calculate correct diffracted intensities. The target appears to be attainable with automatization (locating holes, filling them with appropriate ions, optimizing according to bond valence rules). Then, some badly-crystallized compounds, having non indexed powder patterns, may be finally identified. Identification will be equivalent to a structure determination, when crystal structure and properties prediction will attain total efficiency, in some expected future.

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