Inclusion of symmetry for the enhanced determination of crystalline structures from powder diffraction data using simulated annealing

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Significant improvements compared with the results obtained by other authors are achieved when space symmetry information obtainable from powder diffraction data is applied to the calculation of the TiO_2(anatase) and TiO_2-(rutile) structure; imposing symmetry conditions increases the number of times that the correct structure is generated in a set of runs and leads to more accuracy in the atomic positions.

Simulated annealing techniques have been shown to be very efficient for calculating crystal structures with only knowledge of the unit cell dimensions and content.[1,2] However, the computational demand of the method does not allow it to be applied to very complex structures. As the complexity of the structure increases, not only the computing time increases but also the number of times the system gets trapped in local minima. To avoid this problem it is necessary to impose more constraints to the system to force convergence to the global minimum. Concerning this subject, Deem and Newsam successfully made use of the known symmetry in their study of zeolites;[3] but these prediction methods, which are based on empirical relationships, seem to be more appropriate for specific families of materials, such as zeolites, whose topologic characteristics are well known.

In the present work we propose to optimise the method by using symmetry information, which is easily obtainable from a powder diffraction experiment, in such a way that it can be applied to a wide range of systems for which less restrictive assumptions can be made. To this purpose we chose TiO_2 (anatase), and TiO_2 (rutile) which have been already calculated by Freeman *et al.*[1]

Calculations of the lattice energy (which was initially used as the cost function) were performed using a code developed by us, which uses an Ewald summation for the coulombic term and a real space evaluation of the short range terms. Formal charges were used (Ti^{4+} and O^{2-}). Parameters for short range potentials are listed in Table 1. The minimisation was carried out using the Metropolis importance sampling algorithm.[4,5] We used a cooling algorithm defined by $T_{n+1} = \alpha T_n$, ($\alpha = 0.90$) with a starting temperature $T_0 = 1.0 \times 10^6$ K.

For anatase and when no symmetry restriction was imposed, over a total amount of 50 runs, we obtained the real structure only four times, in agreement with Freeman *et al.*[1] By imposing symmetry restrictions the number of independent variables in the cost function significantly decreases. The reason for this is that during simulation only the coordinates of a group of atoms are randomly generated, the rest are determined through space symmetry operations and consequently, those configurations with atomic coordinates which are not correlated by these symmetry operations are excluded from the configurational space.

Table 1 Short range potential model for TiO_2 (taken from ref. 6); $V(r) = A \exp(r/\rho) - Cr^{-6}$

A(Ti–O)/eV	754.2
ρ(Ti–O)/Å	0.3879
A(O–O)/eV	22764.3
ρ(O–O)/Å	0.1490
C(O–O)/eV Å^{-6}	27.88

From all the space symmetry operations present in each space group, only centring (A, B, C, I, F), screw axes of the type X_1 and glide planes can be used, the rest of space symmetry operations and all the point symmetry operations may produce the overlapping of one atom with its image generated by the symmetry operation (Deem and Newsam overcome this by using a merging term in the cost function[3]). All these particular space symmetry operations are, in principle, obtainable from the extinctions in the powder diffractogram.

We have calculated the structure of TiO_2(anatase) imposing I centring or 4_1 screw axis. By doing this, over a total of 50 runs we obtained the correct structure 30 times with the I centring and 37 with the 4_1 screw axis; which is a significant improvement compared with the results obtained with no symmetry imposition (4 out of 50). Moreover, the atomic positions are more accurate, (as compared with the experimental ones) (Table 2) obtaining thus a better starting structural model for Rietveld refinement. Fig. 1 compares the structures predicted by the calculations with and without symmetry restrictions. The former is indistinguishable from the experimental one within the accuracy of the plot.

Space symmetry operations sometimes might not be so easily obtained from the extinctions in a powder diffractogram because in structures with low symmetry the overlapping of reflections might not allow to do this unambiguously. Besides, for a primitive structure without screw axes and glide planes, all atoms contained in the unit cell must be considered in the calculations. For these reasons we also propose an additional term for the cost function, which takes into account the minimum symmetry of the crystal system independently of the Bravais lattice or space group.

This term is based on the fact that, for a given crystal structure, the structure factors [$F(hkl)$] of most sets of equivalent reflections which have the same d spacing and belong to different crystal planes must all be the same (the fact that the structure factors of a given set of reflections are all the same or not, depends on the point group; however, for each crystal system, it is always possible to find such a set of reflections).[7] For example, in the orthorhombic crystal system, the reflections 123, $\bar{1}23$, $1\bar{2}3$, $12\bar{3}$, $\bar{1}\bar{2}3$, $\bar{1}23$, $1\bar{2}\bar{3}$, $\bar{1}\bar{2}\bar{3}$ all must have the same $F(hkl)$ values. This will be true only if the distribution of atoms in the unit cell is consistent with the crystal system, otherwise different values will be obtained. In order to obtain the same weight for the different atoms within the cell we defined an $F'(hkl)$ value in which all the atomic scattering factors (f) are set equal to one. The proposed term is:

$$E_{\text{sym}} = \sum_{i_{\text{ref}}} \sum_{i_{\text{at}}} W_{i_{\text{ref}} i_{\text{at}}} \qquad (1)$$

where i_{ref} runs over each set of equivalent reflections and i_{at} runs

Table 2 Atomic coordinates: experimental and calculated by different means for TiO_2 (anatase) ($a = b = 3.785$, $c = 9.515$ Å). In the last two sets (centring and screw axis) the letters show atoms related by symmetry imposed to the system

	Experimental			Calculated without symmetry			Calculated with I centring			Calculated with screw axis 4_1		
	X/a	*Y/b*	*Z/c*	*X/a*	*Y/b*	*Z/c*	*X/a*	*Y/b*	*Z/c*	*X/a*	*Y/b*	*Z/c*
Ti(1)	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000 a	0.000	0.000	0.000 a
Ti(2)	0.500	0.500	0.500	0.336	0.336	0.500	0.500	0.500	0.500 a	0.500	0.500	0.500 a
Ti(3)	0.000	0.500	0.250	−0.165	0.501	0.250	0.000	0.500	0.250 b	0.000	0.500	0.250 a
Ti(4)	0.500	0.000	0.750	0.502	−0.163	0.750	0.500	0.000	0.750 b	0.500	0.000	0.750 a
O(1)	0.000	0.000	0.208	−0.133	−0.022	0.195	0.000	0.000	0.197 c	0.000	0.000	0.197 b
O(2)	0.000	0.000	0.792	−0.021	−0.132	0.805	0.000	0.000	0.803 d	0.000	0.000	0.803 c
O(3)	0.000	0.500	0.042	−0.032	0.479	0.055	0.000	0.500	0.053 e	0.000	0.500	0.053 c
O(4)	0.000	0.500	0.458	−0.142	0.367	0.445	0.000	0.500	0.447 f	0.000	0.500	0.447 b
O(5)	0.500	0.000	0.542	0.369	0.141	0.555	0.500	0.000	0.553 e	0.500	0.000	0.553 c
O(6)	0.500	0.000	0.958	0.479	−0.031	0.946	0.500	0.000	0.947 f	0.500	0.000	0.947 b
O(7)	0.500	0.500	0.708	0.470	0.358	0.696	0.500	0.500	0.697 c	0.500	0.500	0.697 b
O(8)	0.500	0.500	0.292	0.358	0.470	0.305	0.500	0.500	0.303 d	0.500	0.500	0.303 c

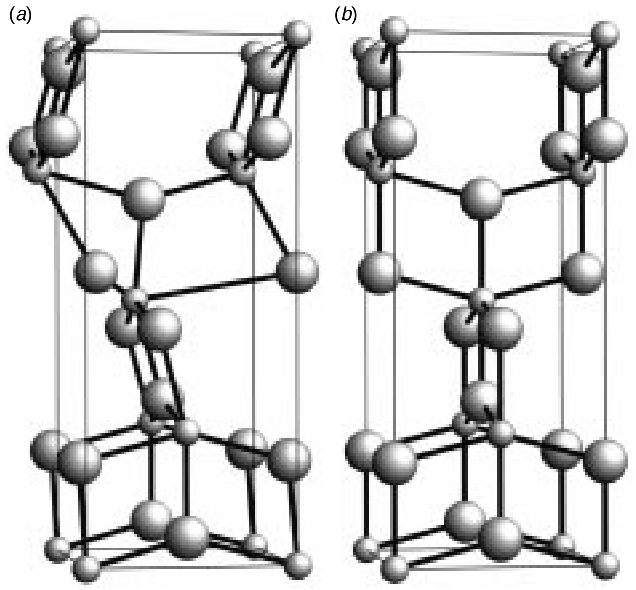

Fig. 1 Structures calculated without symmetry restrictions (*a*), and imposing I centring (*b*) for TiO_2 (anatase). Small spheres represent titanium atoms and large spheres, oxygen atoms.

over each kind of atom (in this case Ti^{4+} and O^{2-}). *W* is given by:

$$W = b\left(1 - \frac{1}{1 + a\sum_{j=1}^{K-1}\left|\left|F'_{j+1}\right| - \left|F'_j\right|\right|^n}\right) \tag{2}$$

where *b*, *a* and *n* are adjustable parameters and F'_j is the modified structure factor corresponding to the *j*th reflection of a group of *K* equivalent reflections (reflections which should have the same structure factor for all the point group within this crystal system) and *K* is the multiplicity factor used in the powder method.[7] Each F'_j is then given by:

$$F'_j = \sum_{m=1}^{N} \exp\left[i2\pi(h_j x_m + k_j y_m + l_j z_m)\right] \tag{3}$$

where *m* runs over the *N* atoms of a same kind and h_j, k_j, l_j are the Miller indexes of the *j*th reflection.

In eqn. (2) is observed that *W* tends to zero for distributions of atoms that are consistent with the crystal system symmetry and tends to *b* for distributions far from required symmetry.

For this particular case (tetragonal system) some of the $\{hhl\}$ and $\{h0l\}$ groups of equivalent reflections (which have a multiplicity of eight) were used[7] (use of the $\{hkl\}$ reflections, with a multiplicity of 16, would imply a previous assumption about the point group).

For anatase, a new set of calculations was run adding an E_{sym} term corresponding to the reflections {112}, {304} and {221} and imposing I centring. The values used were $a = 1.0 \times 10^{-3}$, $b = 20.0$ eV, $n = 3$. These values were those, which led to the best minimisation of all *W* values for a set of 50 runs.

Over a total of 50 runs we obtained the correct structure 36 times. Atomic positions thus obtained are the same as those obtained with I centring only (Table 2).

For rutile, over a total of 50 runs and with no imposition of symmetry we obtained the correct structure 44 times; and when we added this symmetry term to the cost function we obtained the correct structure in all of the 50 runs, with atomic coordinates being the same as those obtained by Freeman *et al.*[1]

The predictions of crystal structures by simulated annealing based only on energetic considerations is impracticable for very complex structures, because of the large amount of local minima, which causes that incorrect structures are obtained in a large number of runs. The imposition of symmetry restrictions may decrease this number of local minima and in consequence may increase the number of times that the correct structure is obtained. Although these symmetry restrictions are expected to be more effective when dealing with a more symmetric structure, their application is general and, as these results suggest, may extend the use of simulated annealing to more complex systems.

Footnote and References

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