PREDICTION OF THE CRYSTAL STRUCTURE OF BYNARY AND TERNARY INORGANIC COMPOUNDS USING SYMMETRY RESTRICTIONS AND POWDER DIFFRACTION DATA

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ABSTRACT

We undertake a set of studies using simulated annealing, concerning the prediction of the structures of compounds of the type $ATiO_3$ (A = Ca, Ba). A tremendous increase of the efficiency in obtaining the correct structure and in the accuracy of the atomic coordinates was obtained by the incorporation of space symmetry elements obtainable from powder diffraction.

In a second stage we also used a new stochastic optimization method, the "pivot method". Calculations performed for TiO_2 (anatase) and for $BaTiO_3$ with this method showed a dramatic increase in the number of times that the correct structure was obtained, compared to the classical simulated annealing algorithm.

INTRODUCTION

In the last decade, the prediction of the structure of inorganic solids from the only knowledge of its chemical composition and unit cell has become a great challenge[1-5]. The usual approach to this problem is to find the global minimum of a cost function that, in the case of inorganic solids, contains the potential energy of the system and some other additional constraints like the comparison of the calculated and experimental diffraction patterns[4]. We have previously shown that significant improvements can be achieved when space symmetry information obtainable from powder diffraction is used in the calculation of the structure of binary compounds[1] by means of simulated annealing.

In the first stage of the present work we undertake a set of studies using simulated annealing[6], concerning the prediction of the structures of compounds of the type $ATiO_3$ (A = Ca, Ba) Orthorhombic $CaTiO_3$ (S.G.= Pnma, a = 5.38, b = 5.44, c = 7.639 Å, Z = 4)[7] and hexagonal (S.G. = $P6_3/mmc$, a = 5.724 Å, c = 13.965 Å, Z = 6)[8] were used. For $CaTiO_3$, a remarkable increase of the efficiency in obtaining the correct structure and in the accuracy of the atomic coordinates was obtained by the incorporation of space symmetry elements[9]. For $BaTiO_3$, the incorporation of symmetry elements made the difference between solving and not solving the structure. The prediction of crystal structures by this "classical" simulated annealing, however, may not be very efficient for very large unit cells, because of the large amount of local minima[1]. In a second stage we also used a new stochastic optimization method, the "pivot method". This algorithm shows an excellent scaling with the cluster size for homogeneous and inhomogeneous Lennard-Jones clusters[10-12]. Calculations performed for TiO_2 (anatase) and $BaTiO_3$ with this method showed a dramatic increase in the efficiency in obtaining the correct structure.

POTENTIAL MODEL

These studies involve the calculation of the lattice energy, which was performed using an Ewald summation for the coulombic term and a real space evaluation of the short-range terms based in the Buckingham model, which states that this short-range term is given by: $V(r) = Ae^{r/\rho} - Cr^{-6}$. Formal charges were used (A^{2+}, Ti^{4+} and O^{2-}). Parameters of the short-range potential model were taken from refs 13 and 14.

GLOBAL OPTIMIZATION METHODS

Previous to the computer runs devoted to the prediction of the crystal structure, a set of preliminary studies can be made in order to analyze the behavior of the potentials[9]. As long as it is considered that the potentials behave well, we can assume that the configuration that yields the minimum value for the cost function corresponds to the arrangement of atoms in the real structure. The problem of solving the structure then reduces to that of finding the global minimum of this cost function.

In this work we used two different approaches to the problem of finding the global minimum of the cost function: the simulated annealing approach[6] and the pivot method approach[10, 11].

PIVOT METHOD

The pivot method begins with a given number of probes placed initially at random within the phase space. Each probe is the set of coordinates of all atoms inside the unit cell. In the current method, we start with $N = 2m$ initial probes of which m probes will act as the pivot probes, and the remaining m probes will be relocated. A local selection of the m pivot probes begins with a search at each probe for its nearest neighbor, based on the distance of the probes. Once we have paired the probes, the probe with the lower energy is defined as the pivot probe. The other one will be relocated around the pivot point according to a given probability distribution. We chose as distribution the generalized *q*-distribution based on the Tsallis entropy[15], which as been used with good results in simulated annealing[16] and pivot method[10-12]. The most relevant fact about this distribution is the introduction of the parameter *q*. Special cases that should be noted are the limit $q \to 1$ where the *q*-distribution goes to the gaussian distribution and $q = 2$ where the *q*-distribution is equal to the Cauchy-Lorentz distribution. We tested values of q in the range $1 \le q < 3$. For values of $q \ge 3$ the distribution becomes non-normalizable.

SIMULATED ANNEALING RESULTS

Results for BaTiO$_3$

We did not obtain the correct structure in any of the 40 runs. Comparison of the lowest energy of these 40 runs ($-143.033\ \text{eV}$) with the calculated energy of the crystallographic structure ($-143.178\ \text{eV}$) shows a small difference. In the structure with the lowest energy, which was obtained 3 out of 40 runs, a large portion of the unit cell resembles that of the real structure.

SYMMETRY ELEMENTS

Although the space group determination not always can be done without any ambiguity from powder diffraction, the presence of certain space symmetry elements such as screw axes or glide planes or centering (I, F, C, etc) can often be detected from an analysis of the systematic absences in a powder diffraction pattern. We have previously shown that the imposition of symmetry restrictions arising from the presence of one these symmetry elements can improve the efficiency of the global optimization procedure for binary compounds[1].

Results for $BaTiO_3$ with symmetry restrictions

A set of 40 runs was carried out imposing the glide plane *c* (S.G. $P6_3/mmc$). The correct structure was now obtained in 18 out of 40 runs compared with 0 out of 40 runs obtained with no symmetry restrictions. This specific case shows that the imposition of symmetry restrictions makes the difference between solving and not solving a compound with this complexity. Atomic coordinates are very accurate compared with those of the experimental one (not shown). Accuracy of atomic coordinates might be crucial for structure refinement by Rietveld analysis.

PIVOT METHOD RESULTS

Results for TiO_2 (anatase)

In our previous work we obtained the correct structure in 4 out of 50 annealing runs[1], with no symmetry imposition. A set of 50 runs with no symmetry imposition was carried using the pivot method. We obtained the correct structure 50 out of 50 runs, which shows a dramatic increase in the efficiency.

Results for $BaTiO_3$

For $BaTiO_3$, in a set of 60 runs with symmetry restrictions, the correct structure was obtained 31 times, which shows a large increase of the efficiency with respect to the annealing runs. Because of the complexity in analyzing whether the structures are correct or not, we develop a criterion that takes into account the deviation of the coordination environments of each of the cations from the real structure. We define *p* as the percentage deviation of the Ti-O and Ba-O bonding distances from their values in the real structure. Thus, taking as successful runs those that accomplish this criterion together with coordination numbers 6 and 12 for Ti and Ba respectively, we obtain for the pivot method for different *q* values the results shown in figure 1.

The structure obtained from the experimental one by means of a gradient relaxation is accepted for values of $p \geq 7\,\%$. When analyzing the structures obtained from the runs, we found that for values of $p < 7$ %, as expected, there is no accepted structure. There is a plateau in the graph for values of *p* around 20 %. Visual inspection of these structures showed that they were correct. This plateau shows that there are important differences between the correct structures and the incorrect ones obtained from the runs.

For greater values of *p,* the acceptance starts to grow because these values of *p* allow structures in which bond distances are much greater than the experimental ones. For even greater values of *p* the acceptance falls off to zero because the restriction in the coordination number of the cations can not be fulfilled any more.

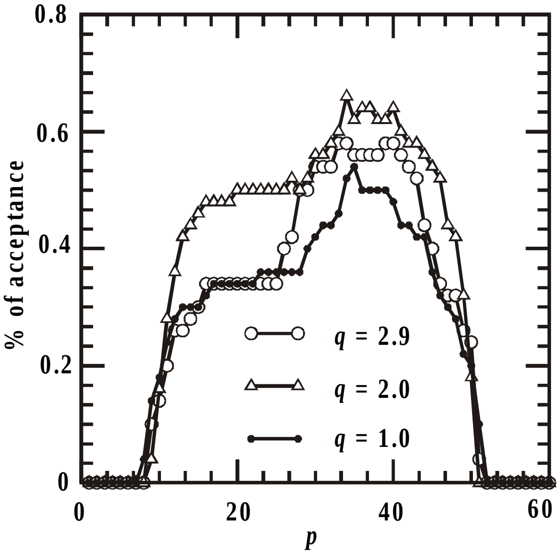

Fig. 1: Percentage of acceptance vs. parameter *p*.

CONCLUSIONS

We show that the interatomic potentials obtained from binary compounds are very good to predict the structures of ternary compounds using these global optimization methods with the only incorporation of the potential energy to the cost function.

For simulated annealing runs, a tremendous increase of the efficiency in obtaining the correct structure and in the accuracy of the atomic coordinates was obtained by the incorporation of spatial symmetry elements obtainable from powder diffraction. In the case of complex structures like, for example, hexagonal $BaTiO_3$, the incorporation of symmetry elements is crucial for the prediction of the correct structure. Even much better efficiencies were obtained when the global optimization method was the Pivot Method.

To the best of our knowledge, this is the first time a structure of the complexity of $BaTiO_3$ can be solved with the lone incorporation of the interatomic potentials in the cost function.

This methodology shows the real possibilities of these global optimization methods to predict unknown crystal structures of inorganic solids.

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