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# Structure prediction of titania phases: Implementation of Darwinian versus Lamarckian concepts in an Evolutionary Algorithm

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ABSTRACT

Darwinian and Lamarckian schemes within evolutionary algorithms have been implemented and optimised. We compare the performance of these two approaches applied to the problem of structure prediction of the titania polymorphs. A number of well-known phases have thus been reproduced as well as several plausible novel microporous and dense structures. Two different potential parameter sets, within the Born model description of a solid, were employed. Following the Lamarckian concept in a genetic or more generally in an evolutionary algorithm, all new candidate structures are immediately relaxed (analogous to the ageing process in nature); consequently, competition within any current population to procreate only occurs between mature candidate structures, which correspond to local minima on the energy landscape. In the Darwinian scheme, no local optimisation is performed, which should result in significant saving in CPU time per candidate structure considered. We show, however, that the Lamarckian scheme (which ultimately searches for the global minimum on a simplified landscape) is more successful and efficient at generating the target structures. Analysis of why the Lamarckian scheme produced a perfect success rate uncovered a weakness in the Darwinian approach when diversity of the population is allowed to reduce, and further methodological developments are suggested.



## 1. Introduction

Evolutionary algorithms have been developed and applied in many different fields, as demonstrated in the Genetic Algorithm Symposium in the 2007 EMRS autumn meeting, with applications ranging from optimising the process of bending steel plates for hulls of ships [1] and reduction of iron ore coal mixture in a packed bed reactor [2], to finding the most energetically favoured arrangement of water molecules [3] and the atomic structure of steps on stable crystal surfaces [4]. In the application to predicting organic crystal structures [5], drug companies are very interested in knowing what polymorphs an organic molecular solid can adopt as the different polymorphs may have different properties and, for example, a drug with the wrong polymorph that is administered as a pain killer could potentially be a source of a dangerous overdose. In another application, that of small sized nanoparticles [6–8], current experimental techniques cannot yield the information needed for a detailed understanding of (a) the structure, (b) their growth mechanisms, or (c) their specific properties. Computer simulations provide a complementary tool, in which key, low energy, configurations are found, and the relation between size of particle and their properties established. In particular, different structure prediction techniques have been employed to shed light on why certain sized clusters are more readily formed during their creation from either laser ablation or nucleation in water.

In this work we focus on the problem of crystal structure solution and prediction. In the case of bulk inorganic [9–11], organic [12,13], and inorganic–organic hybrid [14,15] materials that can only be synthesised in a powder form, only the unit cell dimensions, and possibly symmetry operations that the structure must obey, can be readily extracted and, importantly, an approximate structure must be deduced before the structure can be solved using powder refinement techniques [16–19]. We are interested in developing an efficient and reliable approach for predicting the low energy polymorphs of inorganic, crystalline materials. We assume that the dimensions of the unit cell and the ionic contents are known, from diffraction data, and by chemical analysis and knowledge of the preparation procedure for example. We have therefore developed a computational approach to predict the possible structures within a fixed, predefined cell unit and constituent ions [20]. In this article, we report two evolutionary approaches and compare their success

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in predicting several target structures. In line with previous authors [20–22], we choose, as our test system, to model the possible structures of titania. However, we do not restrict our study to the common phases, rutile [23], anatase [23] and brookite [24], but also include the metastable microporous structures, Hollandite [25] and Ramsdellite [26]. In Fig. 1, we show the structure of each of the target phases. During our search (when the cell parameters were also relaxed), other high-pressure phases of $TiO_2$ were found, including columbite, baddeleyite, fluorite and cotunnite, although some of these phases have not been synthesised in the laboratory.

We have developed our implementation of an evolutionary algorithm as a module within the General Utilities Lattice Program (GULP) [27]. Our method is based upon a multi-stage approach, whereby a genetic or evolutionary algorithm [28] is employed to find feasible approximate structural solutions that are then subsequently relaxed, using the main modules already available in GULP, so that the lattice energy, as defined using the Born model of a solid, is minimised. The code has been developed so that a range or variants of global optimisers are available; examples include, a genetic algorithm (GA) that uses genotype operators, a more general evolutionary algorithm (EA) that uses phenotype operators, and other Monte Carlo approaches, selectable via the input file. Using a Darwinian approach within the GA, the multistage scheme proved successful in the prediction of a previously unknown structure for lithium ruthenate, $Li_3RuO_4$ [29].

Simulated annealing, Monte Carlo approaches (SA-MC), have also been developed for predicting inorganic crystalline materials [30–32]. Likewise, in the field of predicting the most stable structures for small-sized inorganic nanoparticles, both GA and SA-MC, or SA-Molecular Dynamics, have been employed, but more importantly it is reported that hybrid methods, whereby each new candidate structure is immediately relaxed, have proved to be more reliable in locating the global minimum structures [33]; this approach is adopted by the so-called hybrid-GA and Monte Carlo basin hopping (MCBH) methods. The latter technique has been popularised by Wales, who has predicted the global minimum structures for Lennard–Jones clusters containing 1–110 particles [34]. In both cases, one can say (although perhaps less convincingly for MCBH) that Lamarckian concepts have been used. For a GA, Darwinian evolution is simulated whereby the genetic makeup of a candidate structure, the unknown ionic coordinates, does not change during its lifetime so, ignoring mutations created during procreation, offspring will resemble their parents, grandparents and so forth. For a hybrid-GA, Lamarckian evolution is simulated; the genetic makeup can change during the life of a candidate structure, when directly minimising the candidate's energy, and the modified genetic makeup is passed on to the next generation so offspring may not resemble their grandparents. The latter, therefore, combines global and local optimisation techniques during the global search. Below we present more details of our implementation to predicting the global minimum structures [35–37], albeit for bulk materials. The success of hybrid approaches is not confined to clusters; Turner et al. [38] showed that a hybrid-GA gave significant improvements in efficiency and reliability when used for organic crystal structure solution. In another recent application of crystal structure prediction to the problem of carbon polymorphism, Abraham and Probert [39] adapted a variable number approach of Chuang et al. [40] within their hybrid-GA so that, during the search, the number of carbon atoms within the candidate's supercell need not be constrained to a predefined value. Further hybrid methods include using MC, rather than a local optimiser during the mature phase of the GA [41] and the use of MCBH as steps within a set of MD runs, with temperature decreasing [36], both applied successfully to predicting low energy structures of carbon and titania clusters, respectively. Here we report and compare the performance, in predicting inorganic crystal structures, of an EA incorporating either Darwinian or Lamarckian concepts.

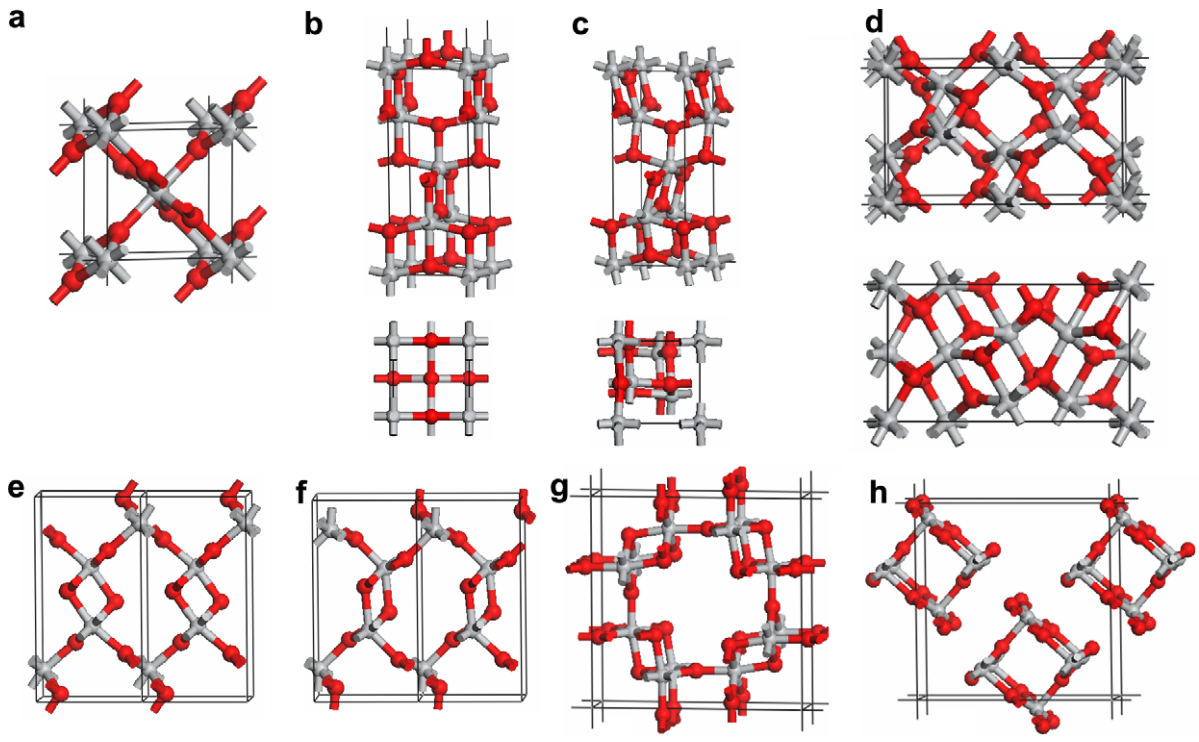


**Fig. 1.** The titania target phases, (a) rutile, (b) anatase (IP2), (c) distorted anatase (IP1), (d) brookite, (e) Ramsdellite (IP2), (f) distorted Ramsdellite (IP1), (g) Hollandite (IP2) and distorted Hollandite (IP1).