Using a novel parallel genetic hybrid algorithm to generate and determine new zeolite frameworks

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ABSTRACT

Zeolite structure determination and zeolite framework generation are not new problems but due to the increasing computer power, these problems came back and they are still a challenge despite the recent progress in terms of structural resolution from X-rays and electron diffraction. The infinite number of potential solutions and the computational cost of this problem make the use of metaheuristics significant for this problem. In this paper, we propose a new approach based on parallel genetic hybrid algorithm for zeolites using a modified modelization of the objective function to find hypothetical zeolite structures, close to the thermodynamic feasibility criterion. A population made of random atoms is initialized. At each generation, a crossover operator and a mutation heuristic are applied. Each individual of the population generates a potential zeolitic structure by applying the symmetry operators of a given crystallographic space group. This structure is evaluated with our objective function. From the unit cell parameters and the number of T atoms in the asymmetric unit, 6 possible zeolitic interesting structures have been found.

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1. Introduction

From the discovery of the first natural zeolite by the Swedish mineralogist Axel Fredrik Cronstedt (Cronstedt, 1756) to the most recent industrial applications, zeolites account for 250 years of history. Zeolites are crystalline microporous materials showing exceptional catalytic and sorption characteristics together and environmentally friendly. Their structures form micropores of molecular dimensions that contain exchangeable extra-framework cation. In the two centuries following this discovery, science of zeolites was limited only to natural zeolites discovered in large sedimentary basins. Note that it is almost impossible to have natural zeolites lots, homogeneous in composition and properties, considerably limiting their industrial use and reserving them for special

purposes directly related to people and their environment (insulating building materials, fish farming, livestock, etc.). It is only from the 1930s and Barrer pioneering work on the synthesis and adsorption properties of zeolites that the science of zeolites has really taken off (Barrer, 1982; Guisnet and Gilson, 2002). Over the years 1950s the first processes for the synthesis of zeolites A, X and Y are developed before their commercialization by Union Carbide in 1954 (Barrer, 1982). At that time, these molecular sieves were used for drying, as catalysts in isomerization and cracking processes and also for separation of linear and branched alkanes. One of the challenges of research in the field of zeolites is the discovery of new usable microporous materials of zeolite-type. They are used for applications in catalysis, separation and adsorption.

It is particularly interesting for the oil industry to have new wide-pore zeolite catalysts to promote diffusion phenomena and/or to make new reactions with molecules larger in size. Zeolites are composed mainly of silicon (Si) and aluminum (Al) atoms which represent two of the most abundant elements on earth. Experimentally speaking, the synthesis of a new zeolite framework designed computationally is still the biggest challenge. For a large majority

of cases, to synthesize a new zeolite, an organic structure directing agent (OSDA) is necessary. In terms of OSDA design, examples of the use of molecular modeling are rare, zeolite ZSM-18 being the most famous case (Schmitt and Kennedy, 1994). A more sophisticated method by Lewis et al. predicted an efficient OSDA that conducted to a molecular sieve having the chabazite topology in the aluminophosphate system (Lewis et al., 1997; Speybroeck et al., 2015). A similar methodology was developed by Pophale et al. (2013) and Schmidt et al. (2014). Both concepts are interesting but need further proofs in order to be considered as truly effective. Accordingly, the discovery of a novel zeolite is more or less serendipitous (Li et al., 2015) and it mostly remains a trial and error process. Nevertheless, a large effort has been devoted in the past decades to predict new zeolitic crystal structures. Started by the pioneering work of Wells (1954), the topology based approaches have been further applied by Smith (1977, 1978, 1979, 1988, 1989) and O'Keeffe (1991, 1995) who systematically enumerated the already existing and/or hypothetical zeolite structures. Analogical method of systematic enumeration, using tiling theory was successfully implemented by Foster et al. in order to identify thermodynamically feasible purely siliceous zeolites (Foster et al., 2004). The crystal structure modeling methods based on the topology principles are reviewed in detail by Woodley and Catlow (2008). Beyond the topology based methods, two major computational strategies have been successfully exploited in the zeolite structures prediction: the former one is simulated annealing (SA) (Pannetier et al., 1990) used in particular to the crystal structure resolution from experimentally available data. The second, more recent one is the genetic algorithm (GA) (Coley, 1998).

Genetic algorithms are useful to explore the search space and to find unexpected solution and have been successfully used to solve a problem from the computational chemistry, the so-called Lennard Jones (LJ) cluster problem (Bäck, 1996; Eshelman and Schaffer, 1993). For a given cluster of N atoms, the LJ cluster problem consists in finding the relative positions of atoms in the three dimensional Euclidean space at a minimum of the potential energy (Fan, 2002). Different works used also a genetic algorithm to solve the LJ cluster problem such as those published by Daven et al. (1996) and Barrón et al. (1999). This metaheuristic optimization method demonstrates a good ability to solve other chemical issues (Archibald et al., 2005). The 'Zeolites Structure Problem' (ZSP), so called by Falcioni and Deem (1999), is well within that concept. Beyond that, several complex inorganic solid structures have been successfully predicted through the GA combined to the force field based lattice energy minimization (Woodley et al., 1999). More recently, using GA, new feasible microporous framework structures have been generated based on exclusion zones approach (Woodley et al., 2004a,b). Baumes et al. have developed a methodology based on GA, after integration in the EASEA library (Collet et al., 2000) using a graphic processing unit (GPU) implementation (Baumes et al., 2011, 2013). Note that the last method was efficient to recover, for the most part, the complex interrupted framework of the meso-microporous silicogermanate ITQ-43 which was previously solved through advanced techniques of characterization (Jiang et al., 2011). Among the proposed set of frameworks, all had the difficulty of being interrupted. Speed up on GPU was the main objective of these initial works. It is worth mentioning here two independent specific computer programs that are related to ZSP, FOCUS (Grosse-Kunstleve et al., 1997, 1999) and Zefsa II (Deem and Newsam, 1989; Deem et al., 1992; Falcioni and Deem, 1999). They are real-space methods specific for zeolite structure solution from powder diffraction data. FOCUS combines automatic Fourier recycling with a zeolitic framework topology search and in the case of Zefsa II, the method of parallel tempering has been advantageously added to the biased Monte Carlo. Our contribution consists on creating a new objective function able to evaluate a viable zeolite

structure and a genetic algorithm hybridized with a heuristic to solve more efficiently the ZSP. Thus, our Parallel Genetic Hybrid Algorithm for Zeolites (P-GHAZ) pursues a double objective: first, to solve more effectively zeolite structures for which the structure elucidation, in the absence of large enough single crystals, needs techniques such as modern electron diffraction that are efficient but heavier and expensive to implement. The second objective consists in generation of thermodynamically stable hypothetical zeolite structures with original topologies.

2. Methods and materials

2.1. Zeolites structure problem

Zeolites are crystalline microporous aluminosilicates for which the pores diameter, according to the nomenclature of IUPAC (McCusker et al., 2001), is less than 20 Å. Their structure results from the assembly of TO_4 tetrahedra (T = Si and Al), each oxygen atom being common to two tetrahedrons (Fig. 1). Microporosity is ordered and regular, leading to channels and cages distributed periodically in space (Fig. 2). The pores size is of the order of those of conventional molecules and is at the origin of the term "molecular sieve".

In theory, there is an infinite number of possible zeolitic structures (Treacy et al., 1997, 2004; Delgado et al., 1999) but up to date only 232 zeolitic structures are today recognized by the Structure Commission of the International Zeolite Association (SC-IZA) (Baerlocher and McCusker, 1996). Among them, only 40 are natural. The pore system of a zeolite can be mono- (1D), bi- (2D) or three-dimensional (3D), and each system is designated by its topology. The openings of the channels are generally characterized by the number of T component elements (e.g., 10MR means 10 tetrahedrons rings, or 10-membered ring, as in the case of ZSM-5, a 3D pore system zeolite). After the discovery of a new topology, a three-letter code is assigned by the SC-IZA. This three-letter code is generally linked to the name of the material or the research team responsible for its discovery. For example, the **MFI** code was assigned to zeolite ZSM-5 (Zeolite Socony **M**obil-5 (**FI**ve)) (Argauer and Landolt, 1972)
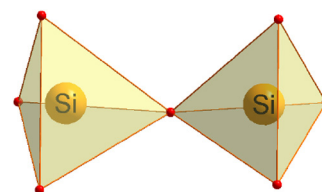

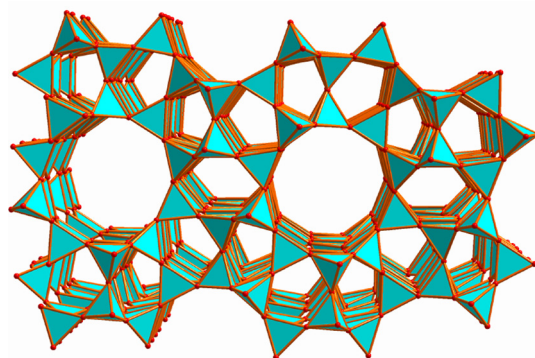**Fig. 1.** Two SiO_4 tetrahedrons linked via an oxygen bridge.

Fig. 2. Structure of zeolite ZSM-5 (Kokotailo et al., 1978) with its medium pores delimited by 10 tetrahedrons.
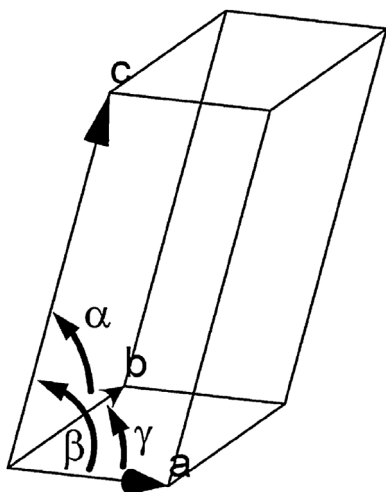
Fig. 3. The 6 parameters defining a unit cell, a, b and c are in Å, and α, β and γ in °.

and **UTL** for zeolite IM-12 (IFP Mulho**U**se-**T**we**L**ve) (Paillaud et al., 2004). Like any crystalline material, zeolites obey the laws of crystallography. Briefly, in any crystal structure, it is possible to define a repeating object by a simple translation along particular directions, thereby forming a crystal lattice. This object, which is the smallest unit of the crystal lattice is the unit cell (UC) (Fig. 3).

The complete unit cell is generated from the asymmetric unit (AU) after application of the symmetry operators of a given space group. So we can also classify structures by symmetry they possess, that is, the space group to which they belong. Due to the properties of the geometrical space, there exist only 230 space groups in crystallography. The space group is designated either by its number (from 1 to 230) or by symbols, which describe the symmetries of this group: it is a capital letter followed by a succession of numbers and letters (e.g. for ZSM-5, the space group is *Pnma*, #62). Fig. 4 shows a unit cell with the asymmetric unit before and after application of the symmetry operators, respectively.

Each atom position of the AU is defined by 3 atomic coordinates (x, y, z). To create potential zeolites by the P-GHAZ, the algorithm modifies the atom coordinates in the AU. Using the UC parameters, the system is created and evaluated. The UC is the smallest volume unit that contains all of the structural and symmetry information. Then, in order to form the bulk arrangement of atoms of the crystals, the unit cells stacked in the three-dimensional space.

The objective is to generate viable zeolite frameworks taking into account the constraints determined by the user input: number of T atoms per UC and UC dimensions, angles and space group. This strategy can be used to discover new hypothetical frameworks or, if appropriate, in order to determine the framework of an unknown synthesized materials. In the second case, the input parameters can be obtained from the experimental powder diffraction pattern, chemical analysis and material density measurement.

2.2. Parallel genetic hybrid algorithm for zeolites

The aim of our proposition is to find atoms positions to generate potential unknown zeolites structures. The evolutionary algorithms are naturally adapted to propose new structures (Jones et al., 1995). In this work, a parallel genetic hybrid algorithm is proposed. The approach uses the EASEA library which manages the parallelism of individuals on GPU. Our contribution is the proposition of an efficient genetic algorithm with a new objective function to get energetically stable zeolites structures. Our algorithm is designed to search complex structures that are difficult to find. Thanks to the

parallel design of our proposition, the P-GHAZ is able to retrieve stable structures in a short time. It allows the algorithm to be restarted several times to increase the chances of finding new structures. The main difficulty that the algorithm has to deal with is that all the structures generated must respect the symmetry of the space group provided at the beginning of each execution. This restriction makes the search more complex, but allows the algorithm to converge to a set of structures which are easy to minimize. Algorithm 1 presents the pseudo-code of the P-GHAZ algorithm.

Algorithm 1. The P-GHAZ pseudo-code.

```
1:   Input: UC parameters: the unit cell parameters; initAtoms: total
     number of initial atoms in the AU; N: the size of the population; step:
     the defined step to move the atom for mutation; ObjF: the objective
     function; currentFitness: the current fitness of the current individual;
2:   /* Initialization */
3:   for each individuals of the N population in parallel do
4:      for i = 1 to initAtoms do
5:         Set randomly the position x of atom(i) inside the UC parameters
           box;
6:         Set randomly the position y of atom(i) inside the UC parameters
           box;
7:         Set randomly the position z of atom(i) inside the UC parameters
           box;
8:      end for
9:   end for
10:  repeat
11:     /* Selection */
12:     for each individuals of the N population in parallel do
13:        Select randomly one parent from the population;
14:     end for
15:     /* Crossover */
16:     for each individuals of the N population in parallel do
17:        Crossover between the current individual and the parent selected;
18:     end for
19:     /* Mutation */
20:     Select randomly a percentage of mutant individuals;
21:     for each mutant individuals in parallel do
22:        Select randomly one mutant atom from the mutant individual;
23:        Move the mutant atom with the step value and evaluate the best
           movement;
24:     end for
25:     /* Evaluation */
26:     for each individuals of the N population in parallel do
27:        Evaluate currentFitness of the individual with ObjF;
28:     end for
29:  until stopping conditions are satisfied
```

2.2.1. Representation and selection

Our algorithm generates a random population. Each individual from this population represents the AU which means the initial atoms coordinates (x, y, z). For example, if the AU of a zeolite is composed of 4 atoms T, the individual is composed of 12 coordinates. The selection operator uses a tournament between the actual and a random individual. The P-GHAZ algorithm manages only atoms T positions. The oxygen atoms are added at the end of the algorithm at the center of two connected atoms T.

2.2.2. Crossover operators

In this work, we implemented two crossover strategies. The first strategy is the one-point crossover (OPX). It performs a crossover between the atoms of two parents at a random position.

Example of the OPX:

Crossover(parent1;parent2;position 3)

Parent1($\underline{x_{1.1}, y_{1.1}, z_{1.1}}; \underline{x_{1.2}, y_{1.2}, z_{1.2}}; \underline{x_{1.3}, y_{1.3}, z_{1.3}}; x_{1.4}, y_{1.4}, z_{1.4}$)

Parent2($x_{2.1}, y_{2.1}, z_{2.1}; x_{2.2}, y_{2.2}, z_{2.2}; x_{2.3}, y_{2.3}, z_{2.3}; \underline{x_{2.4}, y_{2.4}, z_{2.4}}$)

Child($x_{1.1}, y_{1.1}, z_{1.1}; x_{1.2}, y_{1.2}, z_{1.2}; x_{1.3}, y_{1.3}, z_{1.3}; x_{2.4}, y_{2.4}, z_{2.4}$)

The second strategy is the uniform crossover (UX). It performs a crossover between the atoms of two parents with a ratio of 50%. The crossover positions are randomly selected.
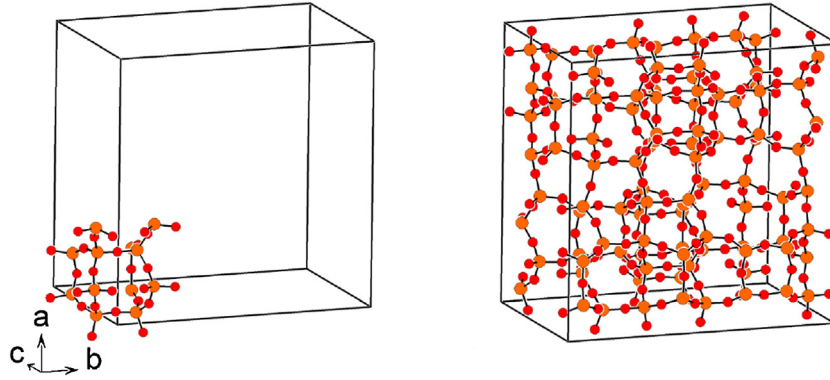
Fig. 4. A unit cell of zeolite ZSM-5 of topology **MFI** with the asymmetric unit before (left) and after application of the symmetry operators (right). Orange and red spheres are silicon and oxygen atoms, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

Example of the UX:

Crossover(parent1;parent2;select{0;1;1;0})

Parent1($\underline{x_{1.1}}, \underline{y_{1.1}}, \underline{z_{1.1}}; x_{1.2}, y_{1.2}, z_{1.2}; x_{1.3}, y_{1.3}, z_{1.3}; \underline{x_{1.4}}, \underline{y_{1.4}}, \underline{z_{1.4}}$)

Parent2($x_{2.1}, y_{2.1}, z_{2.1}; \underline{x_{2.2}}, \underline{y_{2.2}}, \underline{z_{2.2}}; \underline{x_{2.3}}, \underline{y_{2.3}}, \underline{z_{2.3}}; x_{2.4}, y_{2.4}, z_{2.4}$)

Child($x_{1.1}, y_{1.1}, z_{1.1}; x_{2.2}, y_{2.2}, z_{2.2}; x_{2.3}, y_{2.3}, z_{2.3}; x_{1.4}, y_{1.4}, z_{1.4}$)

2.2.3. Mutation operator

In our proposition, the mutation is a heuristic method which allows an atom selected randomly to be moved. The atomic position is here defined in fractional coordinates i.e., the edges of the unit cell are used as the basic vectors to describe the atomic position, the unit cell being a parallelepiped defined by the lengths of its edges a, b, c and angles between them α, β, and γ as shown in Fig. 3. The individuals are selected for the mutation with a defined probability. A random atom for each selected individual is moved with a selected step in the space. The atom is moved along the axes (x, y, z) and the algorithm keeps the best movement. Fig. 5 shows the mutation of one individual after the crossover.

Algorithm 2 presents the pseudo-code of the mutation heuristic.

Algorithm 2. The mutation pseudo-code.

1:   *Input*: **step**: the defined step to move the atom for mutation; **ObjF**: the objective function; **currentFitness**: the current fitness of the mutant individual; **bestFitness**: the best fitness among all the moves; **mutantAtom**: the selected atom for mutation; **mutantIndividual**: the selected individual for mutation;
2:   *bestFitness = currentFitness*;
3:   **for** coord = 1 to 3 /* x,y,z coordinates*/ **do**
4:       Add *step* to position *coord* of *mutantAtom*;
5:       Evaluate *currentFitness* of *mutantIndividual* with *ObjF*;
6:       **if** *currentFitness < bestFitness* **then**
7:           *bestFitness = currentFitness*;
8:           save the movement of *coord*;
9:       **end if**
10:      Remove 2 × *step* to position *coord* of *mutantAtom*;
11:      Evaluate *currentFitness* of *mutantIndividual* with *ObjF*;
12:      **if** *currentFitness < bestFitness* **then**
13:          *bestFitness = currentFitness*;
14:          save the movement of *coord*;
15:      **end if**
16: **end for**

2.2.4. Objective function

The objective function of our algorithm is the main difference compared to other published works. This function is designed to allow our algorithm to find unknown structures. It is possible thanks to an experimental setting of the objective function penalties (each penalty is associated with the non-compliance of a constraint among the ones defined by Eqs. (1)–(7)). This control of penalties enables the algorithm to avoid the generation of too many
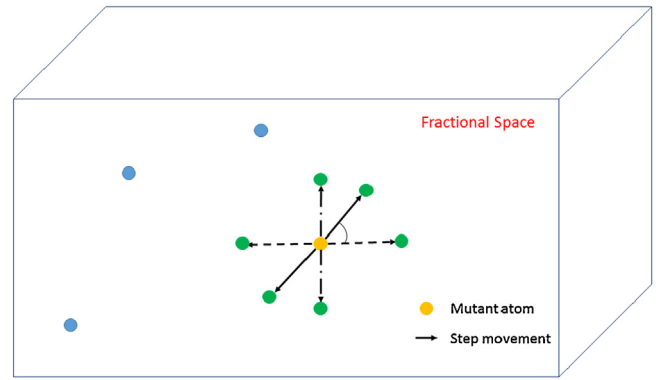

Fig. 5. Representation of a mutation of an individual.

candidates that are thermodynamically unfeasible and, at the same time, to allow a certain flexibility that leads to the determination of new and difficult structures. This method can find, not only the structures that are optimal under certain chemical compositions such as pure silica frameworks (which is the case of this paper), but also other structures that are possible with a higher degree of flexibility.

Before each evaluation, the UC of the individual is generated from the random initial atoms positions and the input parameters. This unit is evaluated using our objective function. This function is a set of penalizations or constraints that allow to evaluate the potential of the zeolite structure. The ZSP can be considered as a minimization problem, i.e. if all the constraints are satisfied then the structure gets the optimum value which is zero. The aim is to get a structure for which the objective function is equal to zero, this structure is then considered as a potential zeolite.

Our objective function is made of 6 penalizations. Each penalization is computed independently and added to the final evaluation. Eqs. (1)–(7) propose a formulation of the objective function.

$$Min \sum_{i=1}^{6} C_i \tag{1}$$

$$C_1 = Nb_{connectedstructure} - 1 \tag{2}$$

$$C_2 = \sum_{j=1}^{n} |NbLinks_j - 4| \tag{3}$$

$$C_3 = \sum_{j=1}^{n} P : \begin{cases} P = 1, & If \qquad XMR_j < MinXMR \\ P = 0, & Otherwise \end{cases} \tag{4}$$
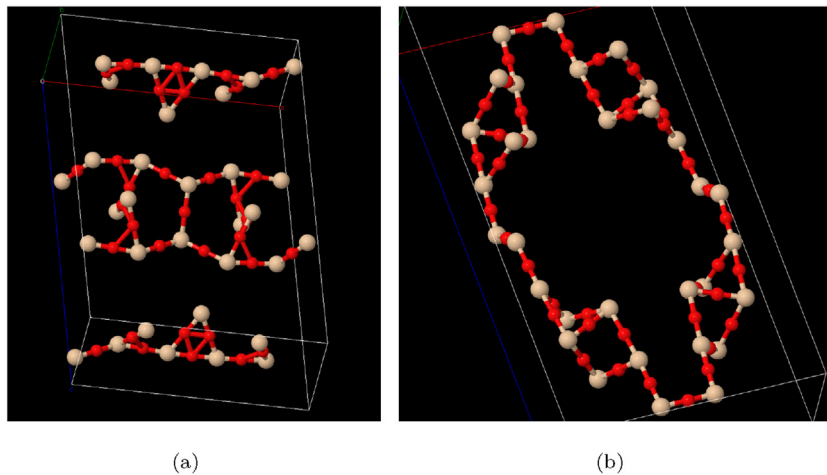
Fig. 6. Two examples of connectivities, (a) wrong connectivities, (b) correct connectivities.

$$C_4 = \sum_{j=1}^{n} P : \begin{cases} P = 1, & If \quad 3MR_j \quad exists \\ P = 0, & Otherwise \end{cases} \tag{5}$$

$$C_5 = \sum_{j=1}^{n} P : \begin{cases} P = 1, & If \quad DisA_j <= L1 \quad or \quad DisA_j >= L2 \\ P = 0, & Otherwise \end{cases} \tag{6}$$

$$C_6 = \overline{P} : \begin{cases} \overline{P} = \dfrac{TAn}{10}, & If \quad \overline{a} <= L3 \quad or \quad \overline{a} >= L4 \\ \overline{P} = 0, & Otherwise \end{cases} \tag{7}$$

Fig. 7. Examples of three different rings present in zeolites, (a) 4MR, (b) 6MR and (c) 12MR.

The first penalization (C_1) is on the connection between all the atoms of the UC. All the generated atoms need to be connected to each other through an atom O to create a viable zeolite. The $Nb_{connected\ structure}$ value (see Eq. (2)) is equal to 1 if the UC is composed of only one structure. Fig. 6 shows the correct connectivity with one connected structure and the wrong connectivity with two connected structures. Structure with correct connectivity will have a zero value in its penalization C_1.

The second penalization (C_2) is about the formation of tetrahedrons. Each atom T needs 4 links with the other atoms T to become stable. The algorithm controls all the n atoms T (number of atoms T in the UC) and computes the number of links for each atom (NbLinks in Eq. (3)). If it is not equal to 4, the structure is penalized.

The third penalization (C_3) is the creation of rings formed by X tetrahedrons or Xmembered rings (XMR). Zeolites are characterized by these XMR which are at the origin of the porosity and therefore to their ability to adsorb molecules. These XMR need to be large enough to become interesting (greater or equal than MinXMR of Eq. (4), where MinXMR is equal to 4 MR).

The fourth penalization (C_4) is the existence of 3MR. It consists on three successive tetrahedrons rings which is impossible to synthesize in pure silica or aluminosilicate systems. These 3MR are fund in silica based microporous materials that contain hetero elements such as beryllium, germanium or zinc (Baerlocher and McCusker, 1996). Each time a 3MR is detected, the structure is penalized. Fig. 7 shows several XMR most commonly encountered.

The fifth penalization (C_5) is about the distances between atoms. Two atoms T must be at the right distance (between L1 and L2, see Eq. (6), where L1 and L2 are respectively 2.4 Å and 3.6 Å), not too far to be connected to an O atom and not too close to prevent them from
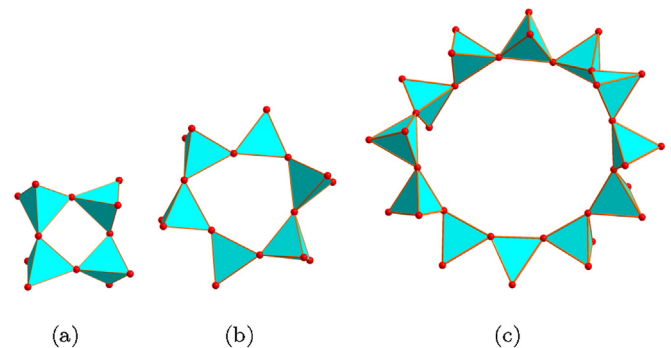
being attached. Typically, for pure silica zeolites, the Si–Si distance between two neighboring silicon atoms, is about 3.1 Å.

The final penalization (C_6) is about the $\widehat{TTT}$ angles between atoms T. The average of all the angles ($\overline{a}$ in Eq. (7)) is computed and if it is not inside a fixed range (L3 and L4, see Eq. (7), where L3 and L4 are respectively $60°$ and $180°$), the structure is penalized with $TAn/10$ where TAn is the total number of angles. It is divided by 10 to have a fair penalization between the six constraints.

Penalization 5 and 6 define the energy stability. Fig. 8 presents the formation of angles between the centre of two tetrahedrons for a zeolite structure. Normally, the β angles range from about 90 to 150°. Algorithm 3 presents the pseudo-code of the angles evaluation.
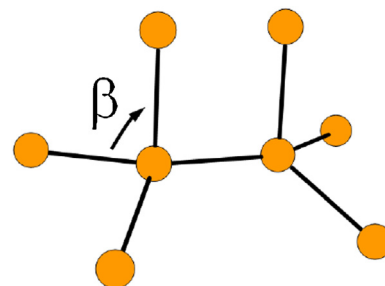

Fig. 8. The $\widehat{TTT}$ β angles between silicon atoms.

Table 1
parameters of *P-GHAZ*.

Parameters	Value
Population size	32,768
Number of generation	200
Mutation step	0.1
Mutation probability	0.02
L1	2.4
L2	3.6
L3	60
L4	180
MinXMR	4

Algorithm 3. The Angles evaluation

```
1:    Input: NbA: total number of atoms in the UC; TAn: the total number of
      angles; TSA: the total angle value; ā: Average size of all angles; C₆: the
      value of the penalization 6;
2:    TAn = 0; TSA = 0;
3:    for i = 1 to NbA-2 do
4:       for j = i+1 to NbA-1 do
5:          if atom(i) has a link with atom(j) then
6:             for k = j+1 to NbA do
7:                if atom(k) has a link with atom(j) then
8:                   TAn = TAn + 1;
9:                   TSA = TSA + value of Angle(i,j,k);
10:               end if
11:            end for
12:         end if
13:      end for
14:   end for
15:   ā = TSA / TAn;
16:   if ā is not in the fixed range then
17:      C₆ = TAn/10;
18:   end if
```

3. Results

3.1. Test conditions

A set of parameters is used in our test protocol. Our proposition uses 32,768 individuals that are parallelized with GPU. EASEA manages the parallelization of GPU where each individual is executed in a GPU thread. More information on GPU programming can be found in Kirk and Hwu (2010). Three stopping conditions are defined. The first one fixes the maximum number of generations to 200. The second one is triggered if an objective function value of zero is reached. In this case, the structure is a potential stable zeolite. The last condition is triggered if the best solution found is not improved during 100 successive generations (stagnation criterion). The mutation step value is set to 0.1 to move the selected atom. Only 2% of the population is selected in each generation to execute the mutation heuristic. Table 1 presents the parameters used on P-GHAZ.

3.2. Application to zeolites

The main idea of the test protocol is to use particular set of parameters of known zeolites. The first objective is to confirm that our P-GHAZ is able to recover the structure of known zeolites when initialized with a random positions set of the *T* atoms in the AU. If the target zeolites are found, it can confirm that our objective function is working well. However, with this approach, there are many possible structures for a given input parameters that can satisfy the objective function. The main goal of our work is to solve silica-based zeolitic structures only from a set of experimental parameters, i.e., unit cell parameters, chemical formula and space group that can be determined experimentally. Table 2 lists three target zeolitic topologies with the corresponding parameters. *SpGrpNb* is the space group number; *NbSymOp* is the multiplicity of

Table 2
Target zeolites.

Topologies	SpGrpNb	NbSymOp	NbAuAtoms	NbUcAtoms
ITE	63	16	4	64
RTH	12	8	4	32
ITW	12	8	3	24

Table 3
Zeolites benchmark execution.

Runs	ITE				RTH				ITW			
	OPX		UX		OPX		UX		OPX		UX	
	F	Ti	F	Ti	F	Ti	F	Ti	F	Ti	F	Ti
1	16	60.2	0	32.6	1	19.9	4	14.7	0	0.9	0	1.5
2	9	71.9	19	65.1	0	5.3	4	18.3	0	1	0	0.8
3	8	80.4	0	31.2	2	19.3	4	15.9	0	0.8	0	1.7
4	8	88.5	0	26.8	0	4.3	4	17.9	0	1.2	0	1.6
5	8	60.4	0	29.5	1	21.1	4	17.9	0	0.7	0	1.1
6	9	55.7	0	28.2	1	18.7	4	15	0	1	0	1.2
7	2	83.4	17	77.8	0	3.6	4	15.3	0	1.3	0	1.1
8	8	55.8	0	20.1	0	9.2	5	14.5	0	1	0	1.3
9	0	24.4	0	27.8	3	21.3	5	15.7	0	0.9	0	1.3
10	16	54.8	0	32.1	1	19.5	6	14.9	0	1.4	0	0.9
Average	8.4	63.5	3.6	37.1	0.9	14.2	4.4	16	0	1	0	1.3

the space group (number of general positions generated after application of the symmetry operations of the involved space group); *NbAuAtoms* is the number of initial *T* atoms inside the AU and the *NbUcAtoms* is the total number of the *T* atoms inside the UC (after application of the symmetry operations) to be evaluated.

3.3. Numerical validation of a zeolitic topology

The numerical validation is the capacity of the P-GHAZ to satisfy all the constraints. Two crossover operators are used in our work, the OPX and the UX. The complexity of the evaluation depends on the initial number of atoms and the number of symmetry operations. These two parameters define the *NbUcAtoms*. The greater this number is, the more the algorithm spends time on the evaluation.

The algorithm executes the crossover between the positions generated in the AU. Table 3 presents the fitness (F) and execution time (Ti) of the three zeolites benchmark using UX and OPX. A set of 10 runs are executed for each instance and the execution time is expressed in minutes.

Table 3 shows the results of the two crossover operators. OPX has the capacity to get the optimum value for the three zeolite benchmarks. UX cannot get optimum results on **RTH** benchmark. However, UX is more efficient with **ITE** benchmark. We can observe that the P-GHAZ can get the optimum value zero in many runs with these two crossover operators. The second step of the work is the validation of the obtained structures.

3.4. Validation of the zeolite structures

The structures with an optimal evaluation must be validated. For that, the best candidates are minimized in order to properly place the oxygen and silicon atoms in an acceptable configuration without taking into account of the electrostatic interactions from molecular modeling using the Universal force field (UFF) (Rappe et al., 1992) implemented in the Cerius^2 software (Cerius^2, 2000). Thus, three zeolites benchmark parameters were experimented. As a result, we validate six possible framework topologies. Three of them are already known and the three others being new. For the last three, a subsequent optimization is performed by using the non-polarizable Bushuev-Sastre (BS) force field able to reproduce with high accuracy the structure and particularly the

Table 4
Force field parameters.

Species	Partial charge (e)	$D_{0,ij}$ (eV)	$R_{0,ij}$ (Å)
Non-bonded potential parameters			
Si	2.1	0.79812×10^{-7}	3.7064
O	−1.05	0.67388×10^{-2}	3.5532
Interacting species	k_{ijk} (eV Å^{-2})		$\theta_{0,ijk}$ (°)
Intramolecular, three-body potential			
O–S–O	1.2614		109.47
Si–O–Si	1.4		142.0

energetic of the pure silica zeolites (Bushuev and Sastre, 2009). From the available, commonly used force fields for the zeolite structure geometry optimization, we have selected the BS one since it has been demonstrated that it reproduces, with the highest accuracy, the experimentally measured zeolite enthalpies (Bushuev and Sastre, 2010; Zwijnenburg et al., 2007). It is the only one force field for zeolite structures optimization, including as parameter the $\widehat{TOT}$ angle bending term, which might explain its superiority compared to others. In the BS force-field the non-bonded interactions include two contributions: the electrostatic one described via the Coulombic term and the van der Waals one taken into account through the Lennard-Jones potential (Eq. (8)).

$$E_{ij}^{vdw} = D_{0,ij} \left[\left(\frac{R_{0,ij}}{R_{ij}} \right)^{12} - 2 \left(\frac{R_{0,ij}}{R_{ij}} \right)^{6} \right] \tag{8}$$

The bonded interaction is expressed through a three-body angle bending term (Eq. (9)). All the applied force field parameters are summarized in Table 4. The cross parameters were calculated through the Lorentz–Berthelot combining rule.

$$E_{ijk}^{3body} = \frac{1}{2} k_{ijk}^{3b} (\theta_{ijk} - \theta_{0,ijk})^2 \tag{9}$$

The geometry optimization of the considered hypothetical zeolite structures within the purely siliceous form has been achieved using the General Utility Lattice Program (GULP) (Gale, 1997). All the considered hypothetical structures have been first transformed within the *P1* space group in order to avoid any symmetry constraint. The energy minimizations were carried under constant pressure allowing to fully relax both the atomic positions as well as the unit cell parameters, applying the pseudo Newton–Raphson minimizing algorithm with the BFGS Hessian matrix updating scheme. We have systematically verified that a true minimum on the hypersurface of potential energy has been reached through the final phonon calculation and subsequently checking the absence of soft modes.

3.4.1. Results from the **ITE** set of parameters

From the **ITE** topology parameters, the search found three viable zeolites. As represented in Fig. 9, the **ITE** topology itself was found. The second topology found is different from **ITE**, it corresponds to the **MER** topology which is normally described in the tetragonal space group *I4/mmm* (**SpGrpNb** is 139, **NbSymOp** is 32 and **NbAuAtoms** is 1). This result proves that our P-GHAZ is able to find several structures from one set of parameters such as the **ITE** parameters. Fig. 10 shows the **MER** zeolites found by P-GHAZ.

The third stable zeolite found by P-GHAZ is a new framework topology that is not listed on the web site of the SC-IZA (Baerlocher and McCusker, 1996) or in the Atlas of Prospective Zeolite Structures (Foster and Treacy, 2004). This fact confirms the potential of our proposition. Fig. 11 shows the new zeolite structure found by P-GHAZ from the **ITE** set of parameters. As illustrated in Fig. 12, this new topology possesses a three-dimensional pore system constituted of large 12MR and small 8MR pores. The structure of this new
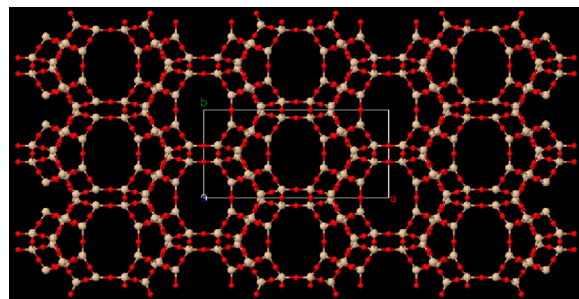

Fig. 9. The **ITE** topology recovered by P-GHAZ (before minimization (UFF) and optimization (BS)).
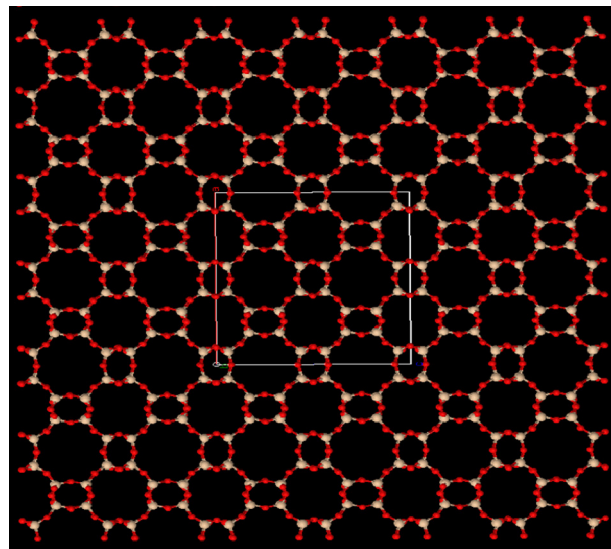

Fig. 10. The **MER** topology recovered by P-GHAZ (after minimization (UFF) and before optimization (BS)).
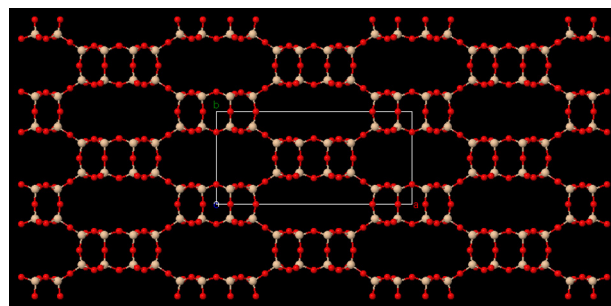

Fig. 11. The first new zeolite *HZM*#1 computed by P-GHAZ (after minimization (UFF) and before optimization (BS)).

topology can be described as a combination of composite building units or CBUs. Thus, as illustrated in Fig. 12, double-4MR and double-8MR (*d4r* and *d8r*) are stacked along the *c*-axis to form columns. The full structure is obtained by connecting these columns via oxygen bridges forming 4MR. We have named this new hypothetical structure *HZM*#1 for *Hypothetical Zeolite of Mulhouse*#1. Subsequently, the following new zeolitic topologies will be named incrementally.

3.4.2. Results from the **ITW** set of parameters

From the **ITW** set of parameters, P-GHAZ found 2 potentially viable zeolites. The **ITW** zeolite was not recovered but the algorithm proposes other close structures. Unfortunately these structures are
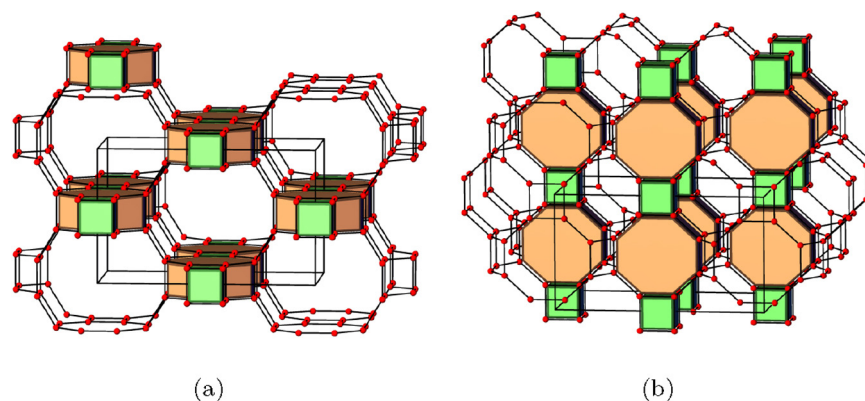
Fig. 12. Net and tiling (calculated with ToposPro (Blatov et al., 2014) and embedded with 3dt (Delgado-Friedrichs, 2003)) of the new topology *HZM*#1 found by P-GHAZ after minimization (UFF) and optimization (BS) (a) along [001] and (b) along [100]. The *d4r* and *d8r* are in green and brown, respectively. Oxygen atoms have been omitted for reasons of clarity. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)
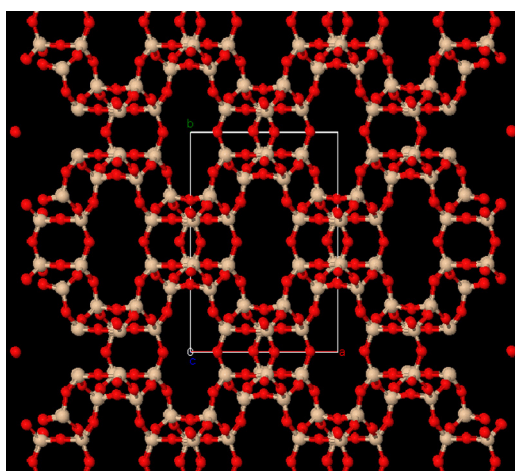

Fig. 13. Topology **CHA** computed by P-GHAZ in space group *C2/m* after minimization (UFF) and before optimization (BS).

Fig. 14. The second novel zeolite (*HZM*#2) computed by P-GHAZ after minimization (UFF) and before optimization (BS).

not viable even after minimization. An adjustment of the objective function could solve this problem but it would reduce the ability of the algorithm to discover unknown structures. However, unexpectedly, the topology **CHA**, a zeolite classified by the SC-IZA, was found. It is worthy to note that the true space group for this topology is $R\bar{3}m$ (**SpGrpNb** 166, **NbSymOp** 36 and **NbAuAtoms** 1). Fig. 13 shows the **CHA** zeolite found by P-GHAZ.

The second zeolite (*HZM*#2) found by P-GHAZ and with **ITW** set of parameters and not listed in any database is represented in Fig. 14. As illustrated in Fig. 15, this new topology possesses a three-dimensional pore system constituted of large 12MR and small 8MR pores which is related to the preceding case. Indeed, the structure may be described in the same way but with the absence of intercalated *d4r* CBUs in the columns of fused *d8r* units.

3.4.3. Results from the **RTH** set of parameters

From the **RTH** set of parameters, the **RTH** topology was not found but other unknown frameworks close to the **RTH** topology were generated although energetically not stable. However, a potential new zeolite structure (*HZM*#3) emerged from the calculations. In Fig. 16 is drawn the third new zeolite found by P-GHAZ from the **RTH** set of parameters before energy minimization. As illustrated in Fig. 17, *HZM*#3 possesses a two-dimensional pore system constituted of small 8MR pores lying along [001] and [101]. In this
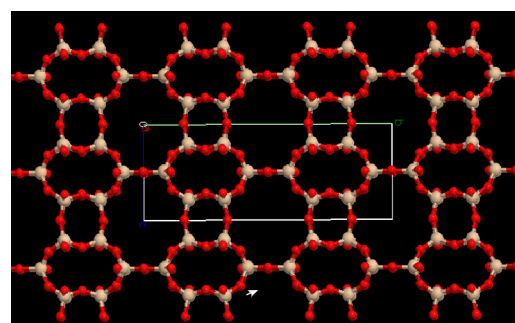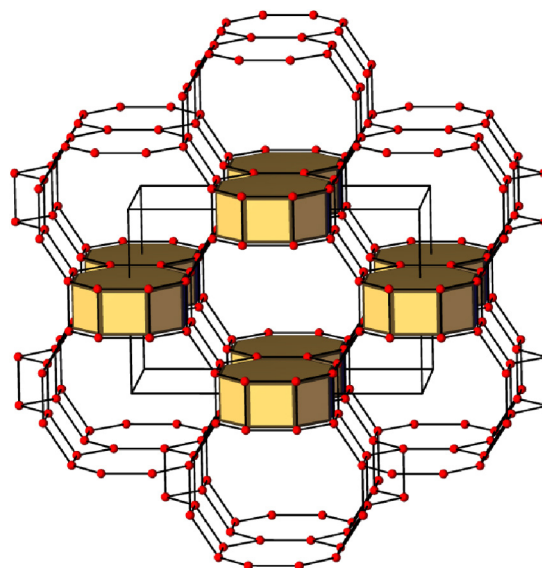

Fig. 15. Net and tiling of *HZM*#2 found by P-GHAZ after minimization (UFF) and optimization (BS). The CBUs *d4r* are absent between the *d8r* units in comparison with the first unknown topology described above. Oxygen atoms have been omitted for reasons of clarity.

topology, the connectivity between the Si tetrahedrons leads to the formation of a new CBU (Fig. 17a). It is formed by four 4MR and four 6MR, they are designed as $[4^4 6^4]$. Infinite chains of fused $[4^4 6^4]$ units lie along [001].
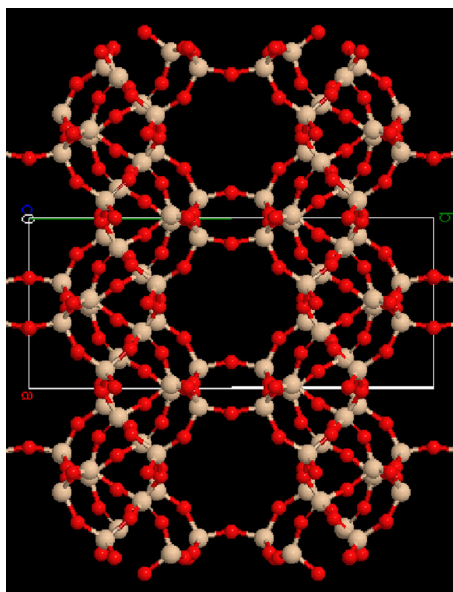
Fig. 16. Third new zeolite computed (*HZM*#3) by P-GHAZ from the **RTH** set of parameters after minimization (UFF) and before optimization (BS).

4. Discussion

We have established an order of relative stabilities of the three new topologies by respectively comparing the energies of the geometry optimized structures. The most stable structure is *HZM*#1, followed by *HZM*#2 and finally *HZM*#3. The relative stability difference is insignificant between the first and the second one ($\Delta E_{12} = 0.7$ kJ/mol/SiO$_2$), while it is meaningful between the most stable and the less stable structure ($\Delta E_{13} = 5.9$ kJ/mol/SiO$_2$, $\Delta E_{2-3} = 5.2$ kJ/mol/SiO$_2$). Furthermore, the question of thermodynamic feasibility of the investigated hypothetical pure silica zeolite structures has been addressed. It has been previously established that the pure silica zeolites are metastable phases with respect to the alpha quartz by the excess energy of 16 kJ/mol/SiO$_2$ (Bushuev and Sastre, 2010). Furthermore, the thermodynamic feasibility is well predicted by the excess energy density lower that 0.5 kJ/cm^3. In consequence, the excess energies with respect to the alpha quartz of the investigated zeolites as well as the excess energy densities have been evaluated. The calculated excess energies are of 23.4, 18.2 and 17.5 kJ/mol/SiO$_2$ respectively for *HZM*#3, *HZM*#2 and *HZM*#1. Additionally, the calculated excess energies densities are

of 0.66, 0.59 and 0.51 kJ/cm^3. Beyond, more recently Coudert suggested to include the elastic anisotropy ($\eta \leq 4$) as a third criterion of the purely siliceous zeolites feasibility (Coudert, 2013). The calculated values of anisotropy, accordingly to Coudert's definition are of 3.4, 3.3 and 2.3 for *HZM*#3, *HZM*#2 and *HZM*#1, respectively. Thus, on the one hand, any of the three investigated hypothetical zeolite structures does not fulfill the thermodynamic criterions of feasibility but *HZM*#1 is very close to them (the energy excess being about 1.5 kJ/mol/SiO$_2$ higher; the energy density excess about 0.01 kJ/cm^3 higher). On the other hand, the three hypothetical zeolites obey the mechanical feasibility criterion, since the calculated elastic anisotropy is lower than 4. Also, recently, post treatments on an existing zeolite allowed Masur et al. to synthesize two thermodynamically 'unfeasible' zeolites, IPC-9 and IPC-10 through a multi-step process named 'assembly disassembly organization reassembly' (ADOR) mechanism (Mazur et al., 2016).

The potential of metaheuristics to solve zeolites structure problem is clear. In this work, our proposition shows the capacity to find viable zeolites that could be synthesized and used in multiple applications.

Some properties of the zeolites structure, such as the distances and angles between atoms T, are known (approximately 3 Å for the distances and a wider range for the $\widehat{TTT}$ β angles, i.e. between about 60° and 180°). We use a relaxation to take into account these properties. Experimentation reveals that the more our penalization is aggressive, the less our genetic algorithm proposes new solutions. However, this relaxation can lead to many optimal solutions that actually correspond to structures with a high energy value, which means that the structures can not be synthesized. The obtained results confirm that our objective function is working correctly but further adjustments are probably needed.

The results presented in this study show the effectiveness and efficiency of the proposed algorithm. It has shown its capacity to discover new hypothetical zeolites structures, and further experimentation can probably lead to other interesting new zeolites. The viability of the structures is a priority in our work. The execution times come in a second place.

5. Conclusion and future works

In this work, we have presented and validated a parallel genetic hybrid algorithm called P-GHAZ to solve the Zeolites Structure Problem. P-GHAZ is based on a population of random AU and on crossover operator and mutation heuristic to get a viable zeolite structure. The crossover is performed between atoms positions of
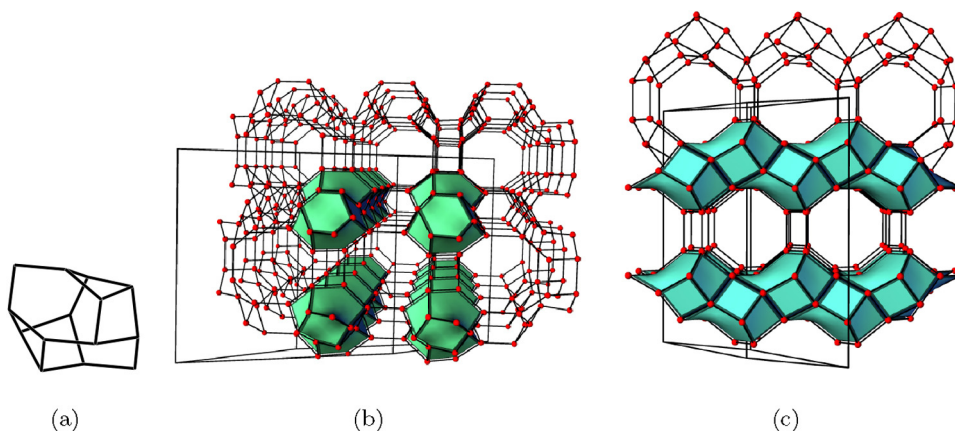

(a)   (b)   (c)

Fig. 17. (a) The new [4⁴6⁴] CBU observed in *HZM*#3 found by P-GHAZ and after minimization (UFF) and optimization (BS), (b) nets and tiling along [001] and (c) along [101]. The columns of [4⁴6⁴] CBUs are in blue azure. Oxygen atoms have been omitted for reasons of clarity. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

the AU and the mutation is a movement in the search space applied to several selected individuals.

Our approach demonstrates a good capacity to generate stable zeolitic frameworks. We evaluated our approach on 3 real zeolites benchmarks for which a code was assigned by the *SC-IZA*. Indeed, our approach is competitive and provides 6 stable structures of which 3 present unknown topologies. It shows a capacity to recover unexpected framework topologies such as **MER** from the **ITE** parameters and **CHA** from the **ITW** parameters. P-GHAZ shows the potential of metaheuristics to solve the ZSP.

In summary, two main contributions are proposed in this work. The first one is to propose a new modelization of the objective function and an efficient genetic algorithm able to provide stable zeolites. The second one is the discovery of novel zeolitic structures which could be synthesized by the zeolite chemists.

As future works, there are several possible ways to extend this work. One possibility is to experiment other parameters to get better results. Another possibility is to investigate another level of the parallel design with a distributed algorithm. We can also use other crossover operators to improve the results and to find other structures. Finally, there are many other metaheuristics which can be interesting to experiment for this problem.

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