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Synthesis and Monte Carlo Method for resolution structural of LTA zeolite crystal

Bouchra Ba mohamed, Khalid Yamni, Najib Tijani
Laboratoire de Chimie des Matériaux et Biotechnologie des Produits Naturels
Département de Chimie, Faculté des sciences, Université Moulay Ismail, Meknès, Maroc.

Abstract: *In this study, the Monte Carlo approach was successfully applied to solve the framework of LTA zeolite from X-Ray powder data. In this work the samples of LTA zeolite were synthesized from the two precursors of aluminate and silicate. The characterization was accomplished by using X-Ray diffraction powder. Then the obtained spectra were indexed to obtain the unit cell using DICVOL (1), ITO (2), and TREOR (3) programs. The research of the best space group is come up with CHECKGROUP (4) program. Afterward, the structure modeling of LTA zeolite was made in direct space by the Monte Carlo approach using rigid and soft restrictions, by means of FOX(5), EXPO(6) and ESPOIR(7) programs .*

Keywords: *Zeolite, DICVOL program, ITO program, TREOR program, CHECKGROUP program, FOX program , EXPO program, ESPOIR program .*

I. Introduction

Zeolites are crystalline porous solids and are one of the most important and valuable classes of materials in industry and society in general. They are used as catalysts, adsorbents, molecular sieves, and ion exchanges, other application connected with their structural architecture. Therefore elucidation of their crystal structure is vitally important in determining the potential of new zeolites.

Zeolites have structures composed of 4-coordinated tetrahedral atoms (for example silicon , aluminum, orgemanium) linked to one another by 2-coordinated oxygen atoms . The International Zeolite Association currently recognizes the existence of 176 unique zeolite topologies. In general, the resolution structural of crystal structures consists of three steps. In the first step the unit cell parameters are determined from the powder X-ray diffraction and possible space groups. The second and most crucial step is deriving an initial structural model that is chemically correct and consistent with experimental data this second step, is the most challenging referred to 'structure solution'. Last the structural model is completed and then refined.

In this paper, we report a Monte Carlo method for solving crystal structures of LTA zeolites "Figure" 1 outlines the strategy of Monte Carlo method as applied to structure determined from powder diffraction in which we determined the unit cell parameters and space group from powder diffraction, while the crucial step of structure solution is achieved by Monte Carlo method were shown to be able to solve complicated zeolite structure, into ZEFSA II(8) program has since been successfully used to solve the structure of at least a dozen newly synthesized zeolites. In the present study, we have used similar programs FOX and ESPOIR, EXPO to crystal structure determination for LTA zeolite from powder diffraction data. Furthermore the success of the method is based on the location of building blocks in the elementary cell by using random or systematic moves and/or modification of the blocks to minimized cost function (CF).

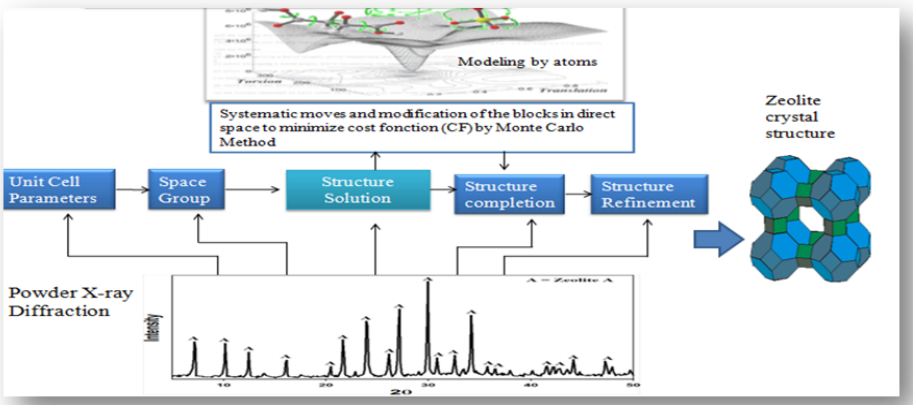

Fig 1: A typical flow chart of the structure determination for zeolite crystal structure by a Monte Carlo Method from X-ray diffraction in which the crucial step of structure solution is determined using global optimization method with Monte Carlo algorithm.

II. Experimental Section

Sample preparation:

The synthesis procedure indented into two stages:

-Preparation of germination and the growth gel.

-Mixture of the precursors previously prepared (global gel).

The germination gel is prepared by the following method in first we prepared solution of sodium, by adding distilled water and stirring at 250 rpm, in last step the aluminate solution is prepared by mixing the solution of sodium with 0.7517 g of sodium aluminate.

Then the silicate solution is prepared by mixing 1.536 g of sodium silicate, and the solution of sodium, and then stirring and heated on the hot water at 100 °c. After the solution of sodium silicate are added to the aluminate precursor. The obtained mixture is aging for 24 h at room temperature undustirring .

The growth gel is prepared by the following manner NaoH and aluminate of sodium are dissolved in distilled water. The solution of sodium .silicate areaddevery slowly on the aluminate precursorun vigorous stirring. The gel is made to nature for two hours .

Furthermore the Global Gel is prepared by mixing the gel growth and germination gel. The growth of frost is stirred magnetically and at the same time, the nucleation gel is added., the mixture is stirred for two hours at room temperature. The mixture is then transferred into an autoclave for aging / 24h at room temperature. After aging, the whole is placed in an oven at T = 100/24. The solid product was separated by vacuum filtration and washed with hot distilled water and dried at T = 100 ° C / overnight.

Powder X-ray diffraction:

Of prepared zeolite by X-Ray powder diffraction data were collected with diffractometer Shimadzu 6100.

Table 1.Experimental conditions:

Radiation	X-Ray
Spectrum	Monochromatic
Wavelength	Cu(k α) λ= 1.5418 A°
Collection duration	3s / step
Measuring conditions	0≤2Θ≤70 °
Maximum Resolution	(sin Θ / λ) = 0.6 A max °

The measured 2theta range (5-60°) was scanned in steps of 0.02 ° with. The apertum and the solver slits were set at 1.0 °.

Indexation:

The indexation was executed by means of FULLPROF (13) program, which is designed to launch the most collective indexing programs: TREOR, ITO, DICVOL. The solutions were obtained with DICVOL, and tool up the following cells: a= 24.55 (A°).

By examining the data with CHECKGROUP program the space groups were unambiguously found to be $Fm\bar{3}c$.

Structure solution:

The crystal structures of the LTA zeolite was accomplished using the Monte Carlo method with simulated annealing algorithm implemented in ESPOIR and EXPO programs and with parallel tempering algorithm implemented in FOX program. The success of the method depends on an appropriate modeling a non molecular structure from building blocks implies describing the structure from a number (N) of Degrees of Freedom (DOF): Rotation and translation of the molecule externals DOF and internal DOF like bond length, and bond angles, torsion angles .

The algorithm modeling six free parameters: the tree translations, and the tree Euler angles relating the cartersian frame tied to the model to the crystallographic axes, in this way, the step performs by Monte Carlo algorithm, the translation and rotation of the model inside the cell, then the free parameters in the model structural are varied randomly with the maximum amplitude of random moves followed an exponential decrease.

To improve the convergence of the global optimization, the correctness of the building block (its deformation, rigidity, bonding distances is known from literature or experience), must be examined carefully.

For the LTA zeolite using all the a priori information about chemical formula of compounds and the connectivity of the atoms, we tested the two possible parameterization for the structure: (i) using free independent atoms or (ii) using molecul fragment .

III. Results And Discussion

Powder XRD of synthesized material provided the following unit cell, a=24.55A° and the space group $Fm\bar{3}c$. Then for structure solution of the zeolite framework, the correct solution was found by FOX and EXPO programs using molecul fragment in a z-matrix description, create with one atom (Al) and one tetrahedron (SiO_4) (9 DOF), and with ESPOIR program the correct structure was made starting from eight free atoms (three Na and one Al and one Si and three O) (24 DOF).

By FOX we come to the following results:

Table 2. Atomic coordinates of LTA zeolite and their occupancy factor with symmetry and multiplicity by FOX program.

Atom	x	y	z	occ	site symmetry	Multiplicity and Wyckoff letter
Si	0	0.8150	0.5931	100%	m...	96 i
Al	0	0.9096	0.6872	100%	m...	96 i
O2	0	0.8541	0.6446	100%	m...	96 i
O1	0	0.7534	0.6137	100%	m...	96 i
O3	0.9462	0.8284	0.5586	100%	1	192j

The structure of LTA zeolite was solved after many trial configuration by FOX requiring 3 min on a 2 GHZ computer of calculation time , the structure solution contains five atoms in the asymmetric unit (Al, Si ,three oxygen's), the framework atoms , Aluminum , and Silicium, two atom oxygen on special position and one oxygen in general position .

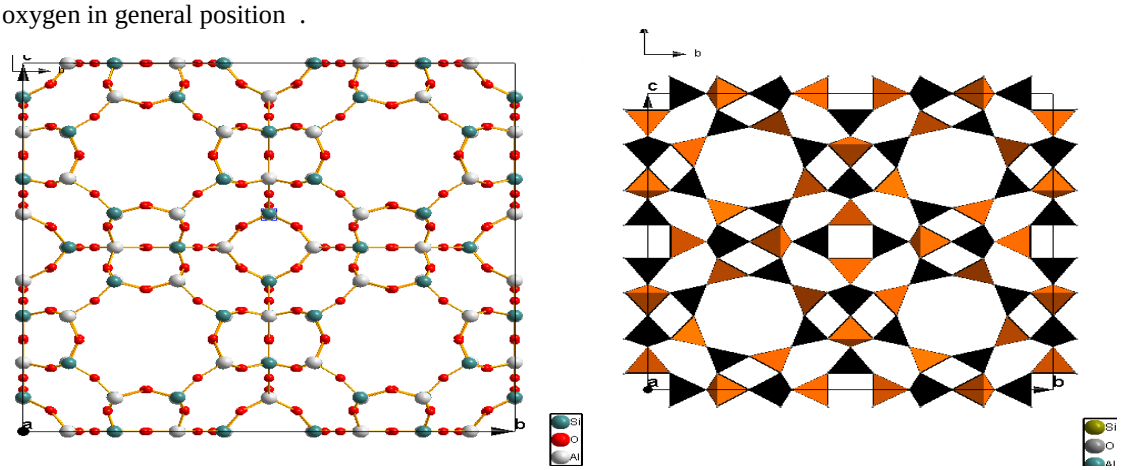

Fig 2. Representation of the crystal structure of LTA zeolite phase solved by FOX program, projection along (001) (view along c ascis) have been made by DIAMOND (9).

Table 3 outlines, the values of bond length calculation with FOX program and literature value of bond length for LTA zeolithe .

Table 3. Calculated values (A°) of bond obtained with program FOX, and Literature values (A°) (10)

Atom1	**Atom2**	**Bond cal**	**Bond Lit**
Si	O2	1.58	1.58
Si	O1	1.60	1.60
Si	O3	1.59	1.59
O1	Al	1.72	1.72
O2	Al	1.71	1.71
O3	Al	1.73	1.74

Table 4 shape, the values of bond angle calculation with FOX program and literature value of bond angle for LTA zeolithe .

Table 4. Calculated values of angle obtained with program FOX, and literature values

Atom1	**Atom2**	**Atom3**	**Angle cal**	**Angle Lit**
O2	Si	O1	108.73	108.82
O2	Si	O3	107.20	107.21
O1	Si	O3	111.31	111.25
Si	O1	Al	142.11	142.24
Si	O2	Al	164.74	164.71
Si	O3	Al	144.76	144.80
O1	Al	O2	108.12	108.14
O1	Al	O3	112.36	112.28
O2	Al	O3	105.96	106.01

By EXPO we come to the following results:

Table 5. Atomic coordinates of LTA zeolite and their occupancy factor with symmetry and multiplicity by EXPO program.

Atom	x	y	z	occ	site symmetry	Multiplicity and Wyckoff letter
Si	0.5000	0.8150	0.9069	100%	m...	96 i
Al	0.5903	0.8128	1.0000	100%	m...	96 i
O2	0.5000	0.8541	0.8554	100%	m...	96 i
O1	0.5000	0.7534	0.8863	100%	m...	96 i
O3	0.5537	0.8284	0.9414	100%	1	192j

The structure of LTA zeolite was solved by EXPO program after many trial configurations, requiring 1h 30 min on 2 GHZ computer of calculation time. The oxygen atoms positions were determined if their known tetrahedral coordination around the Si, and the Al position cannot be found reliably only if we restricted their coordination with silica tetrahedrom using ,T-O-T angle and T-O bond T(Si, Al). The Fig 2 represented crystal structure model of LTA zeolite obtained with EXPO program.

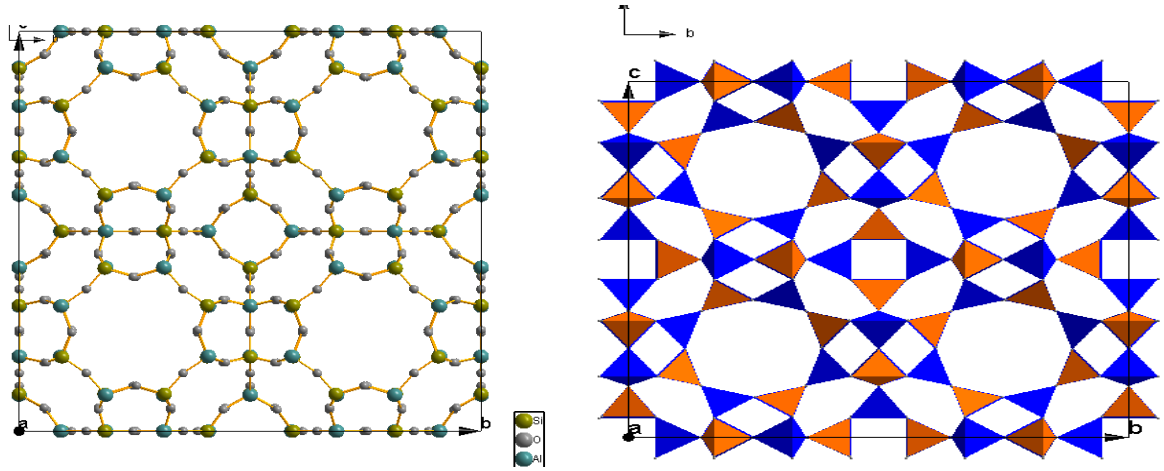

Fig 2. Represented the crystal structure model of the LTA zeolite obtained with EXPO program projection along (001) (view along c ascis) have been made by DIAMOND .

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Table 6 represented, the values of bond length calculation with EXPO program and literature value of bond length for LTA zeolithe .

Table 6 . Calculated values of bond obtained with program EXPO, and literature values

Atom1	**Atom2**	**Bond cal**	**Bond Lit**
Si	O2	1.58	1.58
Si	O1	1.60	1.60
Si	O3	1.59	1.59
O1	Al	1.72	1.72
O2	Al	1.71	1.71
O3	Al	1.73	1.74

The values of bond angle calculation with EXPO program and literature value of bond angle for LTA zeolithe are represented in table 7.

Table 7. .Calculated values of angle obtained with program EXPO, and literature values

Atom1	**Atom2**	**Atom3**	**Angle cal**	**Angle Lit**
O2	Si	O1	108.73	108.82
O2	Si	O3	107.20	107.21
O1	Si	O3	111.31	111.25
Si	O1	Al	142.24	142.24
Si	O2	Al	164.71	164.71
Si	O3	Al	144.80	144.80
O1	Al	O2	108.12	108.14
O1	Al	O3	112.35	112.28
O2	Al	O3	105.97	106.01

By ESPOIR we come to the following results:

Table 8. Atomic coordinates of LTA zeolite and their occupancy factor with symmetry and multiplicity by ESPOIR program.

Atom	x	y	z	occ	site symmetry	Multiplicity and Wyckoff letter
Si	0	0.9069	0.1850	100%	m...	96 i
Al	0	0.8129	0.0910	100%	m...	96 i
O1	0	0.7529	0.6130	100%	m...	96 i
O2	0	0.1439	0.1460	100%	m...	96 i
O3	0.9420	0.8280	0.0540	100%	1	192j

The optimization with ESPOIR program was made using 158 extracted intensities about 12 hour 57 min 17 s best solution was found with R_{WP} =0.148 .

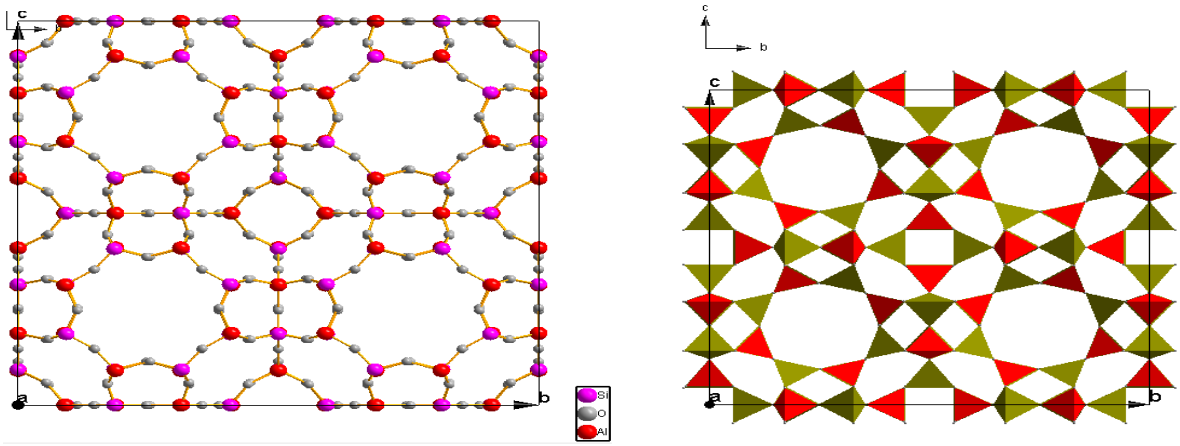

Fig 3. Represented the crystal structure model of the LTA zeolite obtained with ESPOIR program projection along (001) (view along c ascis) have been made by DIAMOND .

Table 9 represented, the values of bond length calculation with EXPOIR program and literature value of bond length for LTA zeolithe .

Table 9. Calculated values of bond obtained with program ESPOIR, and literature values

Atom1	**Atom2**	**Bond cal**	**Bond Lit**
Si	O2	1.57	1.58
Si	O1	1.59	1.60
Si	O3	1.61	1.59
O1	Al	1.70	1.72
O2	Al	1.71	1.71
O3	Al	1.72	1.74

Table 10 outlines, the values of bond angle calculation with ESPOIR program and literature value of bond angle for LTA zeolithe .

Table 10. Calculated values of angle obtained with program ESPOIR, and literature values.

Atom1	**Atom2**	**Atom3**	**Angle cal**	**Angle Lit**
O2	Si	O1	109.56	108.82
O2	Si	O3	107.66	107.21
O1	Si	O3	110.61	111.25
Si	O1	Al	143.70	142.24
Si	O2	Al	165.46	164.71
Si	O3	Al	146.03	144.80
O1	Al	O2	109.59	108.14
O1	Al	O3	111.62	112.28
O2	Al	O3	106.41	106.01

IV. Conclusion

In this study the LTA zeolite compound were synthesized and the characterization was achieved by using X-Ray diffraction powder. Then the powder XRD of LTA zeolite have been used for ab initio structure determination.. The structural model was accomplished by a ‘parallel tempering ‘ Monte Carlo algorithm

implemented in FOX, and by a ‘ simulated annealing ‘ Monte Carlo algorithm implemented in EXPO and ESPOIR programs, with the hand of the z-matrix representation .

This work shows that the framework structure can be afforded by means of powder diffraction with the programs ESPOIR, EXPO and FOX. The perspective is the completed structure with the non framework atoms using synthetic Fourier difference.

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