A THEORETICAL STUDY OF ZEOLITE ABW: ITS MECHANICAL AND AUXETIC PROPERTIES.

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Abstract: *Atomistic simulations are carried out for zeolite with ABW framework. The structure is modeled and force field simulations are preformed to investigate its elastic properties, bulk, shear modulus and auxeticity. Bulk moduli (Ks), Shear moduli (G), and Poissons ratios (v) were found to be K_S= 79.71725 GPa, G= 16.93265 GPa, v_{xy} = -0.2207, v_{xz}= -0.5730, v_{yx}= -0.71717, v_{yz}= 0.87013, v_{zx}= -0.33097 and v_{zy}= 1.54568 for ABW; the negative value of Poisson's ratios reflects an auxetic behavior of material. An evaluation of the directional young's moduli shows that the compressibility of ABW is not uniform along [100], [010] and [001] axes.*
All calculations were performed using GULP program.

Keywords*: elastic constant, auxetic, zeolite, GULP, simulation, energy minimization.*

1. INTRODUCTION

Zeolites have found various commercial uses in the catalysis, adsorption, and ion exchange industries. However, their mechanical properties of zeolites have not been well studied. As zeolites find more uses in other areas, the properties of strength and hardness are becoming critical parameters.

These periodic, microporous materials are generally composed of aluminosilicate tetrahedral frameworks that have channel and cage dimensions ranging between 0.2 and 2.0 nm with approximately 140 distinct framework types classified to date according to their unique, specific framework topologies [1]. In this paper, the low silica, $Si_4Al_4O_{16}$ zeolite with ABW topology is studied (Fig. 1). The framework of this zeolite consists of tetrahedral chains with topological symmetry P $na2_1$.

Recently, several studies attempt to predict elastic behavior of zeolites, such as those by

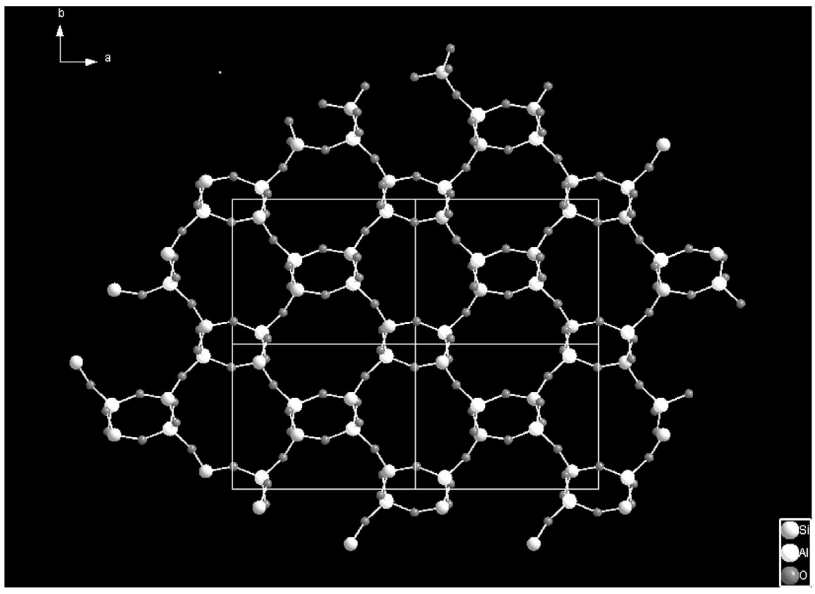

Fig. 1. Projection of zeolite with ABW topology along c axe.

Grima [2], Sanchez-valle [3] and Williams [4]; These studies have used simulation technique to investigate and predict the elastic constants and mechanical properties of zeolitic like materials such as natrolite, analcime and α-cristobalite. In order to verify the predicted elastic properties of zeolites, it is important to have access to experimental data concerning elasticity. Such data would also provide an important means of validation of the force fields used in performing simulations of the solid state. Of the numerous zeolites now known, there are only three zeolites for which single-crystal elastic constants have been measured experimentally, chlorosodalite, natrolite, and analcime. So, the only way to estimate the mechanical properties of zeolites is theoretically or by simulation.

Theoretical calculations predict that certain zeolites will have negative Poisson's ratios and be known as auxetic materials (Grima [5], Evans and Alderson [6]). In fact, the unusual framework topology of zeolite allows for "negative" thermal and mechanical behavior [3].

Force field models have been used to investigate the elastic and other structural properties of silica zeolite ABW. The auxetic behavior can be explained by the geometric features and the deformation mechanisms of the internal structure. Auxetic materials are resistant to indentation and fracture and have high shear stiffness.

In this paper, the elastic constant, Poisson's ratios, bulk and shear moduli are reported for the first time using the GULP program.

2. METHODS

2. 1. Simulation Principle

The structural and mechanical properties of ABW zeolite were simulated using GULP program [7]. This program offers the added advantage that it permits the inclusion of atom polarisability through the use of the core-shell model [2].

The potential model describing the effective forces acting between the atoms in the structure has the following components [8]:

1. A two-body short-range term which describes repulsions from the electron cloud overlap and attractions due to dispersion and covalence. In this study we describe cation-O and the O-O interactions using a Buckingham function: $U_{sr} = Aexp(-r/\rho) - C/r^6$, where the exponential term describes the repulsive energy and the r6 term the longer range attraction (Table 1).

2. A three-body short-range term which describes the angular dependent covalent forces. A simple approach is to include bond-bending terms about the tetrahedral cation of the type: $U_{thb} = 1/2K_{thb}(\theta - \theta_0)^2$. where K_{thb} is the harmonic three-body force constant, and θ and θ_0 are the observed and ideal tetrahedral O-T-O bond angles, respectively (Table 1).

3. A term to describe electronic polarizability is required if the dielectric and dynamic properties are to be modeled accurately. In this study the shell model was used, which provides a simple mechanical model of electronic polarizability. The core-shell self energy is given by $U_s = 1/2K_{sr}^2$ where K_s is the harmonic spring constant and r is

Table 1. Potential used in simulation.

General interatomic potentials					
Atom1	Atom2		A/eV	ρ/Å	C/eVÅ^6
Al1 c	O1 s	Buckingham	0.146E+04	0.299	0.00
Si1 c	O1 s	Buckingham	0.146E+04	0.321	0.00
O1 s	O1 s	Buckingham	0.228E+05	0.149	27.9
O1 c	O1 s	Spring (c-s)	74.9	0.00	0.00
General Three-body potentials					
Atom 1	Atom 2	Atom 3	K_{thb}/eV rad^{-2}	θ/°	
Al1 c Si1 c	O1 s O1 s	O1 s O1 s	2.097 2.097	109.470 109.470	

the core-shell separation (Table 1).

In this study, the libraries of the potentials used were those from Catlow 1992 library [9-17]. The minimum energy configurations were derived by minimizing the potential energy as a function of the atomic coordinates and unit cell parameters.

2. 2. Elastic Constant

The elastic constant tensor C_{ij}, is calculated analytically using standard procedures, which require the prior calculation of the second derivatives of the total lattice energy with respect to the six bulk strain components and with respect to the atomic coordinates [2, 4, 18]. The single crystalline mechanical properties were obtained by simulating the 6x6 stiffness matrix *C* of the minimized systems which can be calculated from the second derivative of the energy expression, *E*, since:

$$C_{ij} = \frac{1}{v}\frac{\partial^2 E}{\partial \varepsilon_i \partial \varepsilon_j}, \quad i,j = 1,2,\ldots,6 \qquad (1)$$

where *V* is the volume of the unit cell, ε_1, ε_2 and ε_3 are the strains in the X,Y and Z directions respectively, whilst ε_4 , ε_5 and ε_6 are the shear strains in the YZ, XZ and XY planes respectively. The on-axes Poisson's ratios were then calculated from the terms of the compliance matrix $S=C^{-1}$ since for example:

$$\nu_{yz} = -\frac{\varepsilon_z}{\varepsilon_y} = -\frac{S_{\varepsilon z}}{S_{zz}} \text{ and } \nu_{zy} = -\frac{\varepsilon_y}{\varepsilon_z} = -\frac{S_{z\varepsilon}}{S_{\varepsilon\varepsilon}} \qquad (2)$$

2. 3. Young's and Shear Mouli

Another special feature of auxetic materials is they have higher resistance to shear strain, caused by twisting or tearing forces [19]. Shear resistance is particularly important in structural components such as sheets or beams in buildings, cars and aircraft. This feature can be qualitatively explained by the relations among the shear (or rigidity) modulus G, the Young's modulus E, and bulk modulus K (the inverse of the compressibility) and Poisson's ratio (υ) [20, 21].

3. RESULTS AND DISCUSSION

$Si_4Al_4O_{16}$ with ABW topography belong to the orthorombic crystal family with a space group P $na2_1$ non centrosymmetric (Patterson group: P-m-m-m).

The simulated structural parameters of the ABW zeolite are compared with experimental data (Anderson and Ploug-Sorensen [22]), and the value of total lattice energy and volume are reported in table 2. Interatomic distances generated using the crystal data from experiment and modeling agree within ±0.02 Å, demonstrating that we are able to reproduce accurately the atomic-scale structure of ABW

Table 2. The experimental and simulated unit cell, atomic coordinates of ABW zeolite.

Structure	Experimental (Anderson and Ploug-Sorensen)	Simulated (this study)
a (Å)	10.313	10.311
b(Å)	8.194	8.196
c(Å)	4.993	4.995
Si1 x,y,z	0.354, 0.375, 0.249	0.354,0.375,0.249
Al1 x,y,z	0.159, 0.081, 0.250	0.159,0.081,0.250
O1 x,y,z	0.006, 0.158, 0.197	0.006,0.158,0.197
O2 x,y,z	0.273, 0.219, 0.139	0.273,0.219,0.139
O3 x,y,z	0.191, 0.039, 0.590	0.191,0.039,0.590
O4 x,y,z	0.180, -0.100, 0.068	0.180,0.899,0.068
Total lattice energy (eV)	-	-861.061
Volume ($Å^3$)	422.20	422.122

Table 3. Interatomic distances.

Atom1	Atom2	Distance (Å)
Si	O1	1.610
	O2	1.621
	O3	1.630
	O4	1.648
Al	O1	1.723
	O2	1.729
	O3	1.756
	O4	1.765

Table 4. Band angles (degrees).

Atom1	Atom2	Atom3	Angle (Atom2,Atom1,Atom3)
Si	O1	O2	107.911
	O1	O3	110.168
	O1	O4	112.874
	O2	O3	109.722
	O2	O4	107.987
	O3	O4	108.131
Al	O1	O2	109.489
	O1	O4	110.289
	O1	O3	112.903
	O2	O4	107.975
	O2	O3	107.892
	O4	O3	108.144
O1	Si	Al	143.322
O2	Si	Al	139.465
O3	Si	Al	124.865
O4	Si	Al	124.829

zeolite. Different value of inter atomic distance and angles is represented in table 3 and 4. It is important to note that the Si-O, Al-O distances and the associate intra-tetrahedral angles are close to those found in previous prediction studies [23].

The predicted elastic constant values of materials are represented in Table 5. These values reflect the dense packing of zeolite with ABW framework and the rigidity of the SiO_4 tetrahedral. In fact, C11>C22>C33 indicating that the *c* axis is most compressible and the *a* axis least compressible [24]. This material is elastically anistropic as indicated by its three different axial compressibilities. The negative value of C22, C33 and C23 reflect instability of the crystal structure.

Table 5. Calculated elastic constant for ABW Zeolite.

Elastic constant (GPa)	
C11	87.773
C22	-76.788
C33	-37.84
C44	16.868
C55	13.071
C66	21.503
C12	78.662
C13	63.417
C14	0.000
C15	0.000
C16	0.000
C23	-71.323
C24	0.000
C25	0.000
C26	0.000
C34	0.000
C35	0.000
C36	0.000
C45	0.000
C46	0.000
C56	0.000

The bulk moduli (Ks) presented on Table 6 is equal to 79.71725 GPa which reflects a high value compared to other zeolites (Natrolite, Ks=45.8 GPa; Analcime, Ks=59.86 GPa and Mordenite, Ks=57 GPa). This is probably due to the crystal structure instability or the constraints required to stabilize this symmetry during energy minimization [25].

The aggregated elastic properties of this material was evaluated using Voigt-Reuss-Hill averaging.

A study of Table 6 shows that ABW framework structure is generally characterized by relatively high bulk *Ks* and shear *G* moduli, reflecting that it is more unlikely undergo shear deformations than many other aluminosilicates (zeolites).

A striking observation is that the elasticity of

Table 6. Mechanical properties of ABW zeolite.

	Reuss	Voigt	Hill
Bulk Modulus (GPa) (Ks)	79.717	12.823	46.270
Shear Modulus (GPa) (G)	16.932	3.831	10.382

Table 7. Directional Poisson's ratios and Young moduli of ABW zeolite.

Orientation	Parameter	ABW Zeolite
(100) plane	ν_{yz}	0.870
	ν_{zy}	1.545
(010) plane	ν_{xz}	-0.057
	ν_{zx}	-0.330
(001) plane	ν_{xy}	-0.220
	ν_{yx}	-0.717
[100] direction	E_1(GPa)	165.165
[010] direction	E_2(GPa)	50.828
[001] direction	E_3(GPa)	28.610

the ABW zeolite (Table 7) is highly anisotropic: Young's modulus in the [0 0 1] direction (E_x) is larger than those in the [0 0 1] and [0 1 0] directions (E_z and E_y). The anisotropy of the elastic constants reflects the anisotropy of the atomic-scale structure. Thus, the structure is rather less dense in the *bc* plane and this explains the lower Young's moduli E_y and E_z compared to Ex, where the presence of relatively dense chains along *a*, containing rings linked by Si-O-Al bonds, would present less flexibility [23].

The Poisson's ratios calculated in the major crystallographic planes are listed in Table 7. These exhibit prominent anisotropy, with values ranging from -0.71 to ±1.54. The negatives values of Poissons ratios are respectively ν_{xy} = -0.220, ν_{xz}= -0.573, νyx= -0.717(1) and ν_{zx}= -0.330(9), reflecting an auxetic behavior of materials on (xy) and (xz) planes and non auxetic properties on the (yz) plane (ν_{yz}=0.87013 and ν_{zy}=1.54568).

4. CONCLUSION

This paper reports the prediction of the elastic constants of ABW zeolite. The complete Cij elastic moduli were determined using computer simulations. The result show that the material is highly anisotropic, with [*100*] direction the most rigid while the [*010*] and [*001*] directions are the softest. Predicted values of Poisson's ratios show that the zeolite with ABW topology is characterized by auxetic properties in two planes (*010*) and (*001*) and non auxetic in (*100*) plane. However, contrary to these recent theoretical calculations, no experimental evidence has been found for the predicted auxetic behavior of ABW zeolites.

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