Research Article

On the suitability of empirical models to simulate the mechanical properties of α-cristobalite

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Summary. *The silicate α-cristobalite exhibits the unusual property of becoming wider when stretched and thinner when compressed, i.e. it has a negative Poisson's ratio (auxetic). Here we show that the behaviour of this silicate can be modelled through empirical simulations and that a number of force-fields can reproduce the experimentally measured single crystalline negative Poisson's ratios.*

Keywords: *Cristobalite, negative Poisson's ratios, auxetic*

Introduction

Auxetic materials (Evans 1990, see Appendix 1), also know as 'anti-rubber' (Lakes 1987a) or 'self expanding' (Grima *et al.* 2000) exhibit the counterintuitive property of becoming wider when stretched and thinner when compressed, i.e., they have a negative Poisson's ratio. Auxeticity imparts many beneficial effects on the materials' macroscopic properties which make them more useful than their conventional counterparts in many practical applications. For example, auxetics exhibit an increased ability to resist indentation (Lakes and Elms 1993, Alderson 1999), have a natural ability to form dome-shaped surfaces (Evans 1991), and have an enhanced ability to absorb vibrations (Scarpa *et al.* 2005). These properties make products made from auxetic components superior to ones made from conventional materials (Alderson 1999).

It has long been known that negative Poisson's ratios are theoretically feasible: the theory of classical elasticity suggests that isotropic materials may exhibit Poisson's ratios within the range $-1 \le \nu \le +0.5$. However, it was generally assumed that there was little scope in studying this property as materials with negative Poisson's ratios were unlikely to be encountered in everyday life. However, in recent years, there has been a growing interest in materials exhibiting this unusual yet very useful property, especially following the report in 1987 that samples of auxetic foams had been produced from conventional ones through a simple compression/heating process (Lakes 1987b). Since then, several other auxetics have been predicted, discovered and/or manufactured including various naturally occurring auxetics such as cubic metals (Baughman *et al.* 1998), zeolites (Grima *et*

al. 2000a, Grima *et al.* 2000b) and silicates (Keskar and Chelikowsky 1992) (Yeganeh-Haeri *et al.* 1992) and man-made auxetics such as nanostructured polymers (Evans *et al.* 1991, Baughman and Galvao 1993, Grima and Evans 2000, Grima *et al.* 2005a, Grima *et al.* 2005b) liquid crystalline polymers (He *et al.* 1998, He *et al.* 2005) and microporous polymers (Caddock and Evans 1989, Alderson and Evans 1993), (Pickles *et al.* 1996) and foams (Lakes 1987b, Evans *et al.* 1994, Smith *et al.* 2000, Gaspar *et al.* 2005, Grima *et al.* 2005c). In all of these cases, the negative Poison's ratios can be explained in terms of models based on the geometry of the materials' nano/microstructure and the way this geometry changes as a result of uniaxially applied loads (the deformation mechanism).

This can be illustrated by considering a two-dimensional honeycomb structure deforming through hinging of the ribs forming the network. As illustrated in Figure 1, stretching of this traditional honeycomb will result in the cells getting longer in the loading direction and narrower along the transverse direction, i.e. they exhibit a positive Poisson's ratio (see Fig. 1a). Auxetic behaviour may be obtained by performing a simple modification in the honeycomb geometry to obtain a re-entrant structure. Stretching of this re-entrant honeycomb will result in opening-up of the cells which will now get longer in both the loading and transverse directions with the effect that the structure exhibits a negative Poisson's ratio (see Fig. 1b).

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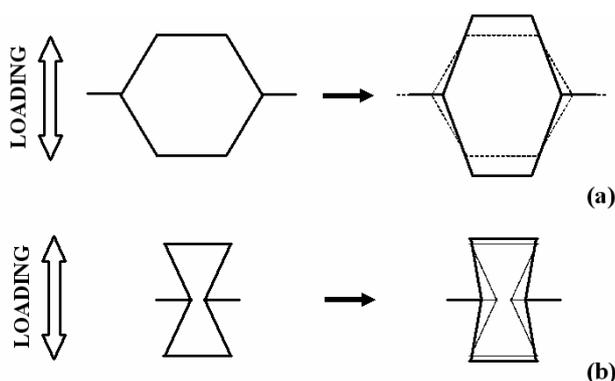
Figure 1: (a) conventional and (b) auxetic hexagonal honeycombs.

Negative Poisson's ratio in α-cristobalite

An auxetic material which has attracted considerable attention is the naturally occurring silicate α-cristobalite for which auxetic behaviour for loading in certain directions was independently discovered and reported more than ten years ago by Keskar and Chelikowsky (Keskar and Chelikowsky 1992) who studied this mineral using *ab initio* modelling techniques and by Yageneh–Haeri and co-workers (Yeganeh-Haeri *et al.* 1992) who measured the single crystalline mechanical properties of α-cristobalite experimentally using Brillonium spectroscopy.

The experimental work of Yageneh–Haeri *et al.* (Yeganeh-Haeri *et al.* 1992) suggests that in single crystalline α-cristobalite, negative Poisson's ratios can be measured in the family of planes passing through the [001] direction where the most negative Poisson's ratios are found for loading at approximately ±45° to [001] direction. Thus, for example, as illustrated in Fig. 2a, negative Poisson's ratios can be found in the (100) plane of α-cristobalite with the most negative Poisson's ratios being measured for loading in approximately the [011] and the [01$\bar{1}$] directions.

This silicate is particularly interesting because it illustrates how nature can produce a material where the extent of the single crystalline auxeticity is so pronounced that the isotropic polycrystalline aggregate Poisson's ratios are also predicted to be negative. This is very significant as chemists could be inspired by this material in their quest for synthesising new man-made materials which exhibit negative Poisson's ratios.

In this work we examine the suitability of various empirical models to reproduce the crystal structure and mechanical properties of α-cristobalite. In particular, we will attempt to reproduce the single crystalline negative Poisson's ratios of α-cristobalite as experimentally measured by Yageneh–Haeri *et al.*

Methods used

The structural and mechanical properties of α-cristobalite were simulated using two software packages, namely:

1. The Open Force-Field module, OFF, within the commercially available molecular modelling package *Cerius²* (Release 3.0 and 4.1) developed by Accelrys Inc., and,
2. The General Utility Lattice Program, GULP (Version 1.3.2), a molecular modelling program created by Prof. Julian D. Gale, formerly of the Royal Institution of Great Britain (now at Curtin University of Technology, Australia).

Within the OFF *Cerius²* package, one can find several force-fields which are parameterised for simulating SiO_2 systems. These include the **Universal** (Rappe *et al.* 1992); **Burchart** (de Vos Burchart 1992); **BKS** (van der Beest *et al.* 1990); **CVFF** (MSI 1997) and **COMPASS** (Sun *et al.* 1998) force-fields which were used in this study. These force-fields differ from each other in the formulation of their energy expression, were for example, in the case of the BKS force-field, the energy expression is composed solely from non-bonding Van der Waals (VDW) and Coulombic terms (i.e. the system is treated solely as an 'ionic' system) whilst in the case of the Burchart force-field, in addition to the VDW and Coulombic non-bond terms, one also encounters simple bonding terms, for example, a Morse term for 1-2 connected atoms (bond lengths) and the harmonic term for 1-3 connected atoms (a Urey-Bradley term to describe the bond-angles). The other *Cerius²* force-fields used, i.e. the Universal, CVFF and COMPASS force-fields have even more complex energy expressions, which, for example include torsion terms and/or cross-terms.

The GULP package offers the added advantage over the *Cerius²*-OFF that it permits the inclusion of atom polarisability through the use of the core-shell model. Various GULP compatible force-fields (or 'libraries of potentials') have been developed, some of which have been used in this study as they were reported to be suitable for modelling of zeolites and silicates. In GULP, a polarisable atom is represented by a positive core coupled with a negative mass-less shell where in a non-polar atom, the centre of the shell coincides with the centre of the core whilst in polar atoms, the shell is offset from the core with the result that one side of the 'atom' appears as 'positive' whilst another side appears as 'negative'. An energy expression constructed from a GULP library is generally made up from non-bond terms (Coulombic and VDW), simple bond terms (typically describing bond lengths and/or angles) and the implementation of the Core-Shell model.

In this particular study, the libraries of potential used were the **Catlow 1992** library (Sanders *et al.* 1984; Jackson & Catlow 1988; Schroder *et al.* 1992; Gale & Henson, 1994; Jentys & Catlow 1993; Lewis *et al.* 1995; den Ouden *et al.* 1990); the **Parker 1992** library (Sanders *et al.* 1984; Baram & Parker 1996); the **Sauer 1997** library (Sierka & Sauer 1997; Sauer *et al.* 1998), and the **Sastre 2003** library (Sastre & Gale 2003) and the **Glass** library (Blonski and Garofalini 1997) These libraries have all been parametrised for SiO_2 systems.

In the simulations, the unit cell of α-cristobalite was aligned relative to the global *XYZ*-coordinate system in such a way that the [100], [010] and [001] directions were aligned parallel to the *X*, *Y* and *Z*-axes respectively[†].

In *Cerius²*, for all simulations, the energy expressions were set up using the default force-field parameters and settings. (In the case of the Universal force-field, the charges used were calculated using the Charge Equilibration procedure developed by Rappé and Goddard (Rappe and Goddard 1991) since this force-field does not contain any information on the atomic charges.) Non-bond interactions were summed up using the Ewald method (Ewald 1921) and the energies of these systems were minimised to the default *Cerius²* high convergence criteria which include a condition that the RMS gradient must be less than 0.001 kcal mol⁻¹ Å⁻¹. No constraints on the shape and size of the unit cell were applied during the minimisations. For each force-field, the single crystalline mechanical properties were obtained by simulating the 6x6 stiffness matrix **C** of the minimised systems which can be calculated from the second derivative of the energy expression, *E*, since:

$$c_{ij} = \frac{1}{V} \frac{\partial^2 E}{\partial \varepsilon_i \partial \varepsilon_j} \qquad i,j = 1,2,...,6$$

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:

$$\nu_{yz} = -\frac{\varepsilon_z}{\varepsilon_y} = -\frac{s_{32}}{s_{22}} \quad \& \quad \nu_{zy} = -\frac{\varepsilon_y}{\varepsilon_z} = -\frac{s_{23}}{s_{33}}$$

The off-axes mechanical properties were then obtained using standard transformation of axes techniques (Nye 1957).

A similar procedure was carried out with GULP, where once again the default GULP settings for energy minimisation and calculation of the stiffness matrices was used. In particular, the Ewald summation was also used to sum up the non-bond interactions and minimisations were stopped after the GULP high convergence criteria were satisfied (i.e. 10⁻¹⁰ fractional units were imposed for function, gradient and parameter tolerances).

Results and Discussion

The stiffness matrices as simulated by the various *Cerius²*-OFF and GULP models are shown in Table 1 whilst a graphical comparison of the simulated and the experimental crystal structure and Poisson's ratios in the

(100) plane are shown in Figure 2. These are followed by a comparison of the simulated lattice parameters and various mechanical properties (see Table 2 and Figure 3).

Experimental
$$\begin{pmatrix} 59.4 & 3.8 & -4.4 & 0.0 & 0.0 & 0.0 \\ 3.8 & 59.4 & -4.4 & 0.0 & 0.0 & 0.0 \\ -4.4 & -4.4 & 42.4 & 0.0 & 0.0 & 0.0 \\ 0.0 & 0.0 & 0.0 & 67.2 & 0.0 & 0.0 \\ 0.0 & 0.0 & 0.0 & 0.0 & 67.2 & 0.0 \\ 0.0 & 0.0 & 0.0 & 0.0 & 0.0 & 25.7 \end{pmatrix}$$

Symmetry requirements
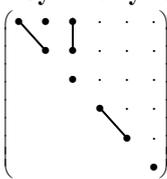
● Non-zero value
· Zero value

COMPASS
$$\begin{pmatrix} 96.0 & 11.7 & -4.3 & 0.0 & 0.0 & 0.0 \\ 11.7 & 95.9 & -4.3 & 0.0 & 0.0 & 0.0 \\ -4.3 & -4.3 & 49.9 & 0.0 & 0.0 & 0.0 \\ 0.0 & 0.0 & 0.0 & 54.8 & 0.0 & 0.0 \\ 0.0 & 0.0 & 0.0 & 0.0 & 54.8 & 0.0 \\ 0.0 & 0.0 & 0.0 & 0.0 & 0.0 & 35.1 \end{pmatrix}$$

CVFF
$$\begin{pmatrix} 146.7 & 14.9 & -12.0 & 0.0 & 0.0 & 0.0 \\ 14.9 & 146.7 & -12.0 & 0.0 & 0.0 & 0.0 \\ -12.0 & -12.0 & 68.2 & 0.0 & 0.0 & 0.0 \\ 0.0 & 0.0 & 0.0 & 79.5 & 0.0 & 0.0 \\ 0.0 & 0.0 & 0.0 & 0.0 & 79.5 & 0.0 \\ 0.0 & 0.0 & 0.0 & 0.0 & 0.0 & 52.2 \end{pmatrix}$$

Burchart
$$\begin{pmatrix} 104.0 & 21.1 & 1.3 & 0.0 & 0.0 & 0.0 \\ 21.1 & 104.0 & 1.3 & 0.0 & 0.0 & 0.0 \\ 1.3 & 1.3 & 45.6 & 0.0 & 0.0 & 0.0 \\ 0.0 & 0.0 & 0.0 & 59.5 & 0.0 & 0.0 \\ 0.0 & 0.0 & 0.0 & 0.0 & 59.6 & 0.0 \\ 0.0 & 0.0 & 0.0 & 0.0 & 0.0 & 31.4 \end{pmatrix}$$

BKS
$$\begin{pmatrix} 70.4 & 11.7 & 4.3 & 0.1 & -0.1 & -0.1 \\ 11.7 & 69.8 & 4.1 & 0.0 & 0.0 & 0.1 \\ 4.3 & 4.1 & 47.2 & -0.1 & -0.1 & 0.0 \\ 0.1 & 0.0 & -0.1 & 71.4 & 0.0 & 0.0 \\ -0.1 & 0.0 & -0.1 & 0.0 & 71.5 & 0.0 \\ -0.1 & 0.1 & 0.0 & 0.0 & 0.0 & 24.6 \end{pmatrix}$$

Universal
$$\begin{pmatrix} 298.42 & 40.44 & 26.70 & 0.0 & 0.0 & 0.0 \\ 40.44 & 298.42 & 26.70 & 0.0 & 0.0 & 0.0 \\ 26.70 & 26.70 & 169.50 & 0.0 & 0.0 & 0.0 \\ 0.0 & 0.0 & 0.0 & 118.65 & 0.0 & 0.0 \\ 0.0 & 0.0 & 0.0 & 0.0 & 118.65 & 0.0 \\ 0.0 & 0.0 & 0.0 & 0.0 & 0.0 & 89.03 \end{pmatrix}$$

Catlow 1992
$$\begin{pmatrix} 74.3 & 4.4 & 9.6 & 0.0 & 0.0 & 0.0 \\ 4.4 & 74.3 & 9.6 & 0.0 & 0.0 & 0.0 \\ 9.6 & 9.6 & 69.2 & 0.0 & 0.0 & 0.0 \\ 0.0 & 0.0 & 0.0 & 74.7 & 0.0 & 0.0 \\ 0.0 & 0.0 & 0.0 & 0.0 & 74.7 & 0.0 \\ 0.0 & 0.0 & 0.0 & 0.0 & 0.0 & 30.0 \end{pmatrix}$$

Parker 1992
$$\begin{pmatrix} 74.3 & 4.4 & 9.6 & 0.0 & 0.0 & 0.0 \\ 4.4 & 74.3 & 9.6 & 0.0 & 0.0 & 0.0 \\ 9.6 & 9.6 & 69.2 & 0.0 & 0.0 & 0.0 \\ 0.0 & 0.0 & 0.0 & 74.7 & 0.0 & 0.0 \\ 0.0 & 0.0 & 0.0 & 0.0 & 74.7 & 0.0 \\ 0.0 & 0.0 & 0.0 & 0.0 & 0.0 & 30.0 \end{pmatrix}$$

Sauer 1997
$$\begin{pmatrix} 77.83 & 4.09 & 23.21 & 0.0 & 0.0 & 0.0 \\ 4.09 & 77.83 & 23.21 & 0.0 & 0.0 & 0.0 \\ 23.21 & 23.21 & 70.62 & 0.0 & 0.0 & 0.0 \\ 0.0 & 0.0 & 0.0 & 68.40 & 0.0 & 0.0 \\ 0.0 & 0.0 & 0.0 & 0.0 & 68.40 & 0.0 \\ 0.0 & 0.0 & 0.0 & 0.0 & 0.0 & 21.45 \end{pmatrix}$$

Sastre 2003
$$\begin{pmatrix} 61.81 & 1.64 & 17.73 & 0.0 & 0.0 & 0.0 \\ 1.64 & 61.81 & 17.73 & 0.0 & 0.0 & 0.0 \\ 17.73 & 17.73 & 60.80 & 0.0 & 0.0 & 0.0 \\ 0.0 & 0.0 & 0.0 & 63.96 & 0.0 & 0.0 \\ 0.0 & 0.0 & 0.0 & 0.0 & 63.96 & 0.0 \\ 0.0 & 0.0 & 0.0 & 0.0 & 0.0 & 18.75 \end{pmatrix}$$

Glass
$$\begin{pmatrix} 240.82 & 23.71 & 68.28 & 0.0 & 0.0 & 0.0 \\ 23.71 & 240.82 & 68.28 & 0.0 & 0.0 & 0.0 \\ 68.28 & 68.28 & 165.77 & 0.0 & 0.0 & 0.0 \\ 0.0 & 0.0 & 0.0 & 113.42 & 0.0 & 0.0 \\ 0.0 & 0.0 & 0.0 & 0.0 & 113.42 & 0.0 \\ 0.0 & 0.0 & 0.0 & 0.0 & 0.0 & 52.05 \end{pmatrix}$$

Table 1: The stiffness matrices (**C**=[c_{ij}]) obtained for α-cristobalite using the various force-fields in this study, and the symmetry requirements for α-cristobalite (Nye 1957).

[†] Note that for non cuboidal unit cells, the software packages *Cerius²* and GULP orient the unit cells in a different manner. In a particular, in *Cerius²*, the cells are aligned in such a way that the [001] direction is aligned parallel to the Z-axis and the (100) plane is aligned parallel to the *YZ*-plane whilst in GULP, the [100] direction is aligned with the *X*-axis and the (001) plane is aligned parallel to the *XY*-plan. Since α-cristobalite has a cuboidal unit cells, this difference in alignment will not affect the way that the crystal is algned in the *XYZ*-global coordinate system.

(a) Experimental
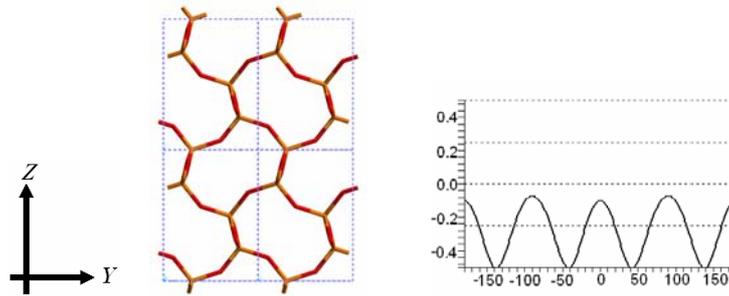
(b) Simulated with Cerius²-OFF

(b-i) COMPASS **(b-ii) CVFF** **(b-iii) Burchart** **(b-iv) BKS** **(b-v) Universal**

(c) Simulated with GULP

(c-1) Catlow 1992 **(c-ii) Parker 1992** **(c-iii) Sauer 1997** **(c-iv) Sastre 2003** **(c-v) Glass**
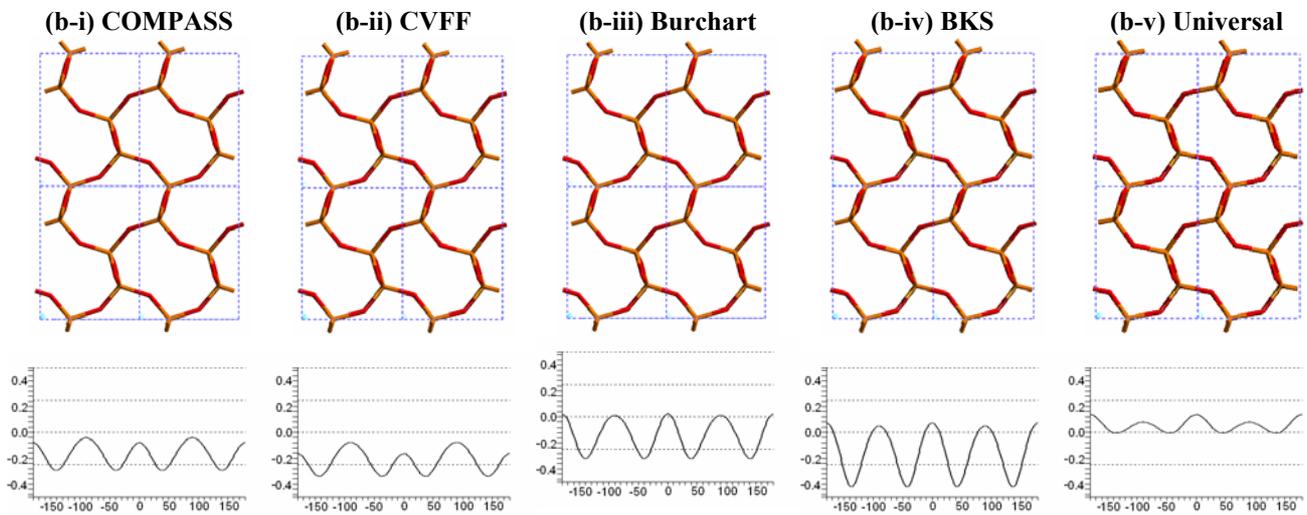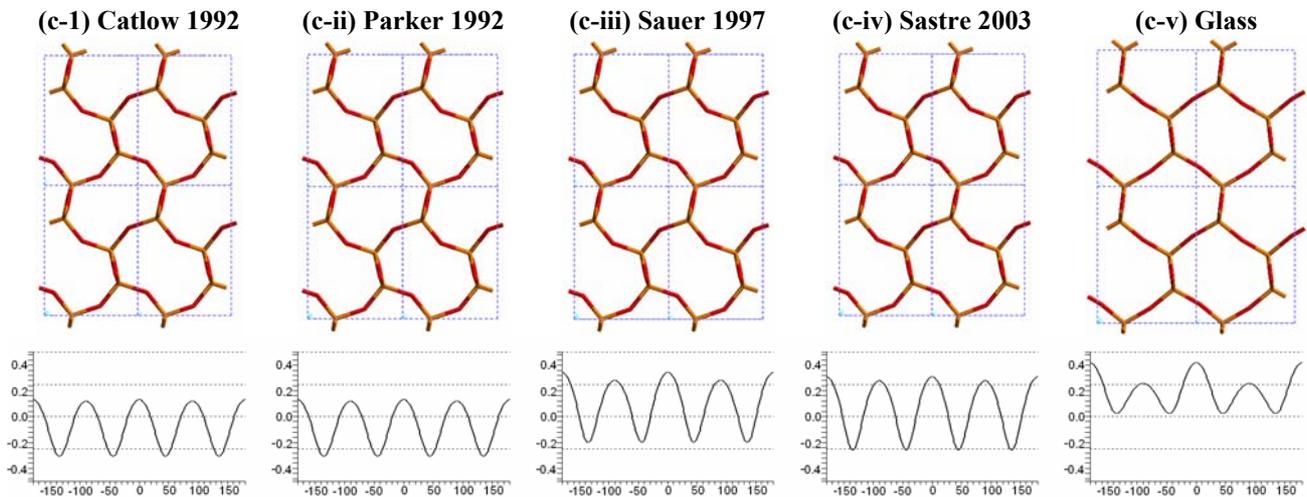
Figure 2: A graphical comparison of the simulated and experimentally determined crystal structure of α-cristobalite in the (100) plane and the Poisson's ratios in the (100) for loading in a direction in the same plane.

	Lattice Parameters			Single crystalline Poisson's ratios in the (100)-plane (YZ plane)				Single crystalline Young's moduli		Polycrystalline aggregate	
				on-axis		45° *off-axis*					
	a, b (Å)	*c* (Å)	α, β, γ (deg.)	ν_{yz}	ν_{zy}	ν_{yz} (45°)	ν_{zy} (45°)	E_x, E_y (GPa)	E_z (GPa)	ν_{max}	ν_{min}
Experimental	*4.978*	*6.948*	*90.000*	*-0.098*	*-0.070*	*-0.497*	*-0.497*	*58.75*	*41.79*	*-0.211*	*-0.115*
COMPASS	5.050	6.842	90.000	-0.077	-0.043	-0.280	-0.280	94.19	49.42	-0.080	-0.004
CVFF	4.965	6.619	90.000	-0.160	-0.074	-0.317	-0.317	143.49	66.43	-0.127	-0.026
Burchart	4.978	6.684	90.000	0.020	0.011	-0.305	-0.305	**	45.62	-0.039	0.072
BKS	4.889	6.528	90.000	0.073	0.050	-0.417	-0.417	*	46.86	-0.074	0.026
Universal	4.635	6.068	90.000	0.138	0.079	-0.007	-0.007	289.75	165.29	0.092	0.125
Catlow 1992	4.971	7.009	90.000	0.132	0.122	-0.303	-0.303	72.85	66.91	-0.034	0.025
Parker 1992	4.970	7.008	90.000	0.132	0.122	-0.303	-0.303	72.81	66.89	-0.035	0.025
Sauer 1997	4.979	7.095	90.000	0.345	0.283	-0.198	-0.198	70.02	57.46	0.071	0.148
Sastre 2003	5.001	7.138	90.000	0.310	0.279	-0.256	-0.256	56.42	50.89	0.026	0.120
Glass	5.289	7.432	90.000	0.420	0.258	0.024	0.024	212.61	130.52	0.176	0.210

Table 2: The lattice parameters, the on-axis and 45° off axes single crystalline Poisson's ratios, the Young's moduli and the Polycrystalline aggregate values. * In the case of the BKS force-field $E_x \neq E_y$ and the specific values are $E_x = 27.81$ GPa and $E_y = 60.89$ GPa. ** In the case of the Burchart library, the values were: $E_x = 99.94$ GPa and $E_y = 99.87$ GPa.

(a)

(b)

(c)
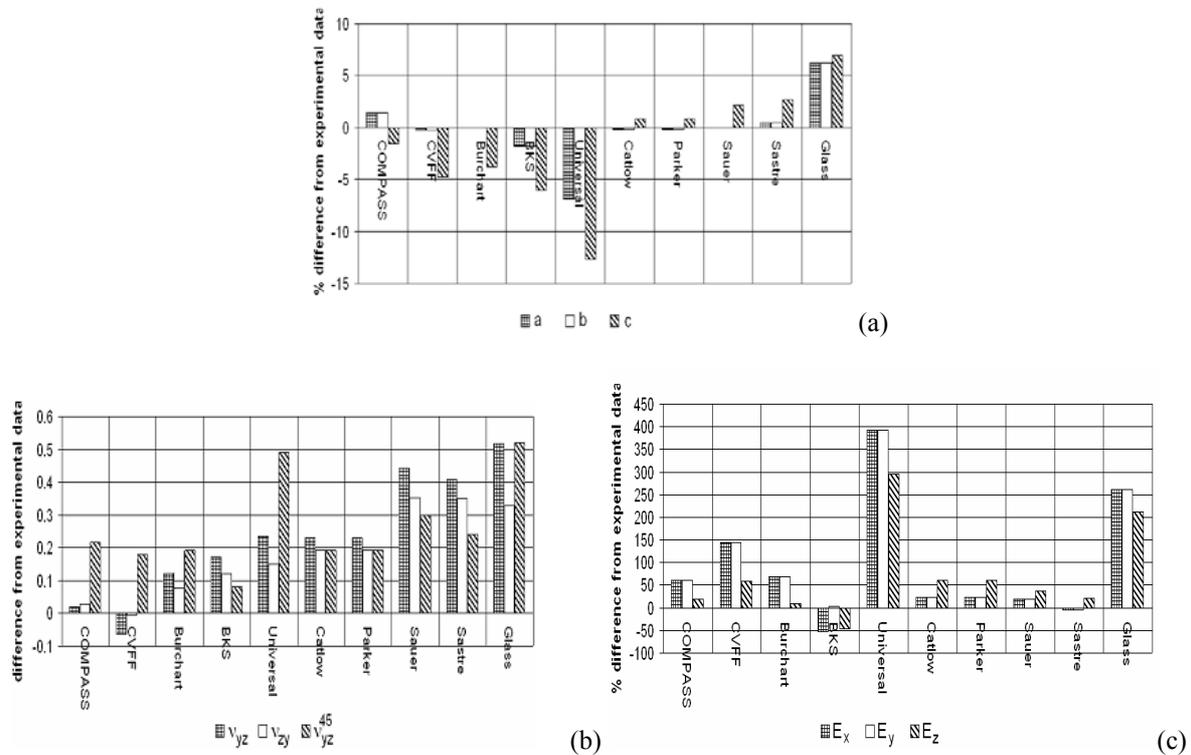
Figure 3: A graphical comparison of the differences (or % differences) between simulated and experimentally determined properties of various structural and mechanical properties of α-cristobalite. The upper and lower boundaries of the Poisson's ratios are also shown.

These results and comparisons show very clearly that the there is no single force-field or library that can reproduce <u>all</u> the experimental properties to a high degree of accuracy but there are a number of force-fields which can successfully reproduce all the general features of this silicate.

In particular, referring to Figure 2, we may see that all the models used (except for the Glass library) produce a structure of α-cristobalite which is very similar to one obtained experimentally from X-Ray data. Furthermore, referring to Table 2 and Figure 3a it may be deduced that with the exception of the Universal force-field and to a lesser extent the BKS force-field (*Cerius²* force-fields) and the Glass library (a GULP library), all models can successfully reproduce the lattice parameters of α-cristobalite within ±5%. In this respect, the models which best reproduce the structural parameters (i.e. the crystal structure and lattice parameters) are the Catlow and Parker libraries (GULP libraries).

A comparison of the stiffness matrices in Table 1 suggests that all force-fields predict a stiffness matrix for α-cristobalite which is of the form expected for a system with a tetragonal symmetry (α-cristobalite has a $P4_12_12$ symmetry). In fact, the only force-field where the matrix deviated slightly from the expected form was the BKS force-field and this may be due to the formulation of the BKS force-field, which, unlike the other force-fields used, contains only the non-bond terms, i.e., it does not take covalent character into consideration. However, it should be noted that the values of the terms in the stiffness matrices as simulated by the different models are very different from each other and different from the experimentally obtained matrix. This suggests that the different models do not predict the 'stiffness' of the material very accurately and precisely. Nevertheless, referring to Figure 2, it is very significant to note despite the differences in the actual values of the matrix terms, all the models correctly predict that the Poisson's ratios in the (100) plane of α-cristobalite are most auxetic for loading at approximately 45° to the major axes (i.e. approximately the [011] and $\left[0\overline{1}\overline{1}\right]$ directions).

Furthermore, referring to Figure 2, Table 2 and Figure 3, one may observe, that with the exception of the Glass model, all models predict that α-cristobalite exhibits auxetic behaviour to some extent or another since all models (with the exception of the Glass library) correctly predict that α-cristobalite is auxetic in the (100) plane for loading at approximately 45° to the major axes.

It can also be observed that the COMPASS and CVFF force-fields (*Cerius²* force-fields) are extremely suitable for modelling the Poisson's ratios of α-cristobalite, since:

– These force-fields correctly predict that α-cristobalite is auxetic for loading in any direction in the (100) plane;
– They correctly predict that the polycrystalline aggregate are expected to be negative;

– The CVFF force-field predicts polycrystalline aggregate values for the Poisson's ratios which are very similar to those predicted by experimental data whilst the COMPASS force-field predicts lattice parameters and Young's moduli which are very similar predicted by experimental data.

All this is very significant as it shows that it is possible to use empirical simulations to study the Poisson's ratios of single crystalline materials, including those which exhibit the unusual property of having a negative Poisson's ratio. In fact, the simulations suggest that in such cases, the simulations generally predict values of the Poisson's ratios which are close to those measured experimentally. Secondly, these simulations show that in such studies, it is very important to use more than one force-field to study such materials, and rather than discussing the 'exact' values of mechanical properties as smilulated by some particular force-field, it is more useful to discuss 'trends' were different force-fields provide similar results. For example, in this case, despite the fact that the different models gave different values for the elastic constants, they correctly and consistently predicted that α-cristobalite exhibits auxetic bahaviour, particularly in the (100) plane when loading at approximately 45° to the major axes.

Finally, the simulations suggest that in the case of α-cristobalite, it is not essential to include the effect of atom polarisability to be able to correctly describe the structural and mechanical properties. In fact, the simulations suggest that the best force-fields which can reproduce the auxetic behaviour of α-cristobalite are the CVFF and COMPASS force-field which unlike the GULP models, are unable to represent atom polarisability.

Conclusion

It has been showed that empirical simulations can successfully reproduce the structural and mechanical properties of α-cristobalite and that the quality of the simulated properties depenend primarily on the force-field used. In particular, it has been shown that the *Cerius²* force-fields CVFF and COMPASS are particularly suitable for simulating the properties of this silicate. All this is very significant as it suggests that empirical simulations can be successfully used to study α-cristobalite in more detail in an attempt to understand more clearly the way how nature can achieve the very usual property of a negative Poisson's ratio. It is hoped that through such studies, scientists and engineers will be one step closer to obtain materials and structures which expand when stretched by mimicing the behaviour of this naturally occurring auxetic.

Appendix 1*

The term 'auxetic' derives from the Greek word αυξετοσ *(auxetos)* meaning 'that may be increased', referring to the width and volume increase when stretched (Evans *et al.* 1991). In modern Greek, we also find the word αυξάνω *(auxano)* meaning 'to increase'. Since no equivalent word is available in the Maltese language to describe systems which experience a width increase when stretched, we propose that in Maltese, systems which expand when uniaxiually stretched will be termed 'awksetiku' (singular masculine), 'awksetika' (singular femine) or 'awksetiċi' (plural). Thus for example, the terms 'an auxetic material', 'an auxetic structure', 'auxetic materials' and 'auxetic structures' will translate to 'materjal awksetiku', 'struttura awksetika', 'materjali awksetiċi' and 'strutturi awksetiċi' respectively.

(*) The contribution of Professor Oliver Friggieri, Professor of Maltese, University of Malta is gratefully acknowledged.

Appendix 2

The isotropic polycrystalline values of the Poisson's ratios relate to an idealised scenario where the crystal domains in a sample of α-cristobalite are arranged in such a way that the resulting material is isotropic, in which case the maximum and minimum values of the polycrystalline Poisson's ratios may be calculated using:

$$\nu^{\max} = \frac{3K^{\text{Voigt}} - 2G^{\text{Reuss}}}{6K^{\text{Voigt}} + 2G^{\text{Reuss}}} \ \& \ \nu^{\min} = \frac{3K^{\text{Reuss}} - 2G^{\text{Voigt}}}{6K^{\text{Reuss}} + 2G^{\text{Voigt}}}$$

where K^{Voigt} and G^{Voigt} are the greatest possible bulk and shear polycrystalline moduli respectively as estimated using the Voigt method (Voigt 1928, Hill 1952), i.e.:

$$K_V = \frac{A + 2B}{3} \ \& \ G_V = \frac{A - B + 3C}{5}$$

where:

$$A = \frac{1}{3}\left(c_{11} + c_{22} + c_{33}\right), \ B = \frac{1}{3}\left(c_{23} + c_{31} + c_{12}\right)$$

$$C = \frac{1}{3}\left(c_{44} + c_{55} + c_{66}\right)$$

whilst K^{Reuss} and G^{Reuss} are the lowest possible polycrystalline bulk and shear moduli respectively as estimated using the Reuss method (Reuss & Angew 1929, Hill 1952), i.e.:

$$K_R = \frac{1}{3a + 6b} \ \& \ G_R = \frac{5}{4a - 4b + 3c}$$

where:

$$a = \frac{1}{3}\left(s_{11} + s_{22} + s_{33}\right), \ b = \frac{1}{3}\left(s_{23} + s_{31} + s_{12}\right)$$

$$c = \frac{1}{3}\left(s_{44} + s_{55} + s_{66}\right)$$

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