A Letters Journal Exploring the Frontiers of Physics

July 2008

EPL, **83** (2008) 26002
doi: 10.1209/0295-5075/83/26002

www.epljournal.org

Flexibility window controls pressure-induced phase transition in analcime

A. Sartbaeva[1(a)], G. D. Gatta[2] and S. A. Wells[3]

[1] *Inorganic Chemistry Laboratory, University of Oxford - South Parks Road, Oxford OX1 3QR, UK, EU*
[2] *Dipartimento Scienze della Terra, Università degli Studi di Milano - Via Botticelli 23, I-20133 Milano, Italy, EU*
[3] *Department of Physics and Centre for Scientific Computing, University of Warwick - Gibbet Hill Road, Coventry CV4 7AL, UK, EU*

received 9 May 2008; accepted in final form 5 June 2008
published online 8 July 2008

PACS 61.50.Ks – Crystallographic aspects of phase transformations; pressure effects
PACS 64.60.Ej – Studies/theory of phase transitions of specific substances
PACS 81.30.Hd – Constant-composition solid-solid phase transformations: polymorphic, massive, and order-disorder

Abstract – Analcime under pressure undergoes a phase transition at ∼1.0 GPa from a cubic ($Ia\bar{3}d$) form to a low-symmetry triclinic ($P\bar{1}$) form. We use geometric simulation to relate the pressure behavior of analcime to a recently discovered property of zeolite frameworks, the "flexibility window", defined as the range of densities over which the tetrahedral units in the framework can in principle be made geometrically ideal. Our results show that the range of stability of the cubic phase in analcime is defined by the flexibility window of the cubic framework. Analcime at low density can undergo tetragonal distortion while remaining within the flexibility window, consistent with experimental reports of non-cubic symmetries. On compression to higher densities, the capacity for tetragonal distortion is greatly reduced, accounting for the dramatic reduction in symmetry at the pressure-induced phase transition.

Introduction. – Zeolites are both naturally occurring aluminosilicate minerals and important synthetic materials [1]. They crystallize in a variety of low-density framework structures built from corner-sharing TO_4 tetrahedra (T representing the tetrahedrally coordinated cations in the framework) with micropores in the form of cages or channels. The interest surrounding zeolite structures derives from their widespread industrial applications [2,3], such as petroleum production, ion exchange, gas purification, radioactive waste disposal, and pollution control. These applications make use of the unique physiochemical properties of zeolites, including selective ionic exchange, catalysis and related molecular sieve properties.

In previous studies we have applied geometric simulation [4–10] to investigate the compression mechanisms of the zeolites edingtonite and levyne [4,5]. We have recently applied geometric simulation to define the "flexibility window" [10] as a property of zeolite frameworks. The flexibility window is a range of densities over which the corner-sharing TO_4 units making up the zeolite framework can in principle be made perfectly tetrahedral. This window is limited at high density by contacts between oxygen atoms on neighboring tetrahedral units, and at low density by extension of the TO bonds (though not, in general, by linear TOT angles). High-silica zeolites are found experimentally to exist at the low-density end of the window, indicating that zeolites are maximally extended structures [10].

Analcime (from the Greek *analkimos* —"weak") is a zeolite with formula $NaAlSi_2O_6 \cdot H_2O$ and ANA topology. It is commonly defined as a feldspathoid, although the Commission of the International Mineralogical Association includes analcime in the zeolite group [11]. In cubic analcime there is a statistical Si/Al distribution in the tetrahedral framework. Our recent experimental study on analcime [12] observed a pressure-induced phase transition at about 1 GPa from a cubic to a triclinic form. The pressure at which the transition occurs is relatively low, and the bulk modulus of the triclinic analcime is the lowest reported in the literature for natural open framework silicates. It is striking that the structure passes from a highly symmetric cubic form, space group

(a) E-mail: asel.sartbaeva@chem.ox.ac.uk

$Ia\bar{3}d$, to the low-symmetry space group $P\bar{1}$ without apparently passing through any intermediate-symmetry form (tetragonal, orthorhombic or monoclinic). For comparison, the cubic form under ambient conditions has cell parameter $a = 13.0765(8)$ Å, the cubic form at 0.91 GPa has $a = 13.6288(5)$ Å, and the triclinic form at about 1.08 GPa has parameters $a = 13.5707(7)$, $b = 13.5345(12)$, $c = 13.5277(12)$ Å, $\alpha = 89.688(4)^\circ$, $\beta = 89.215(4)^\circ$, $\gamma = 90.707(3)^\circ$ [12]. Cell volumes for the cubic form run from 2575.0(5) to 2531.5(6) Å^3, and the cell volume of the first triclinic form is 2484.2(3) Å^3.

Our work on the flexibility window [10] included a simulation of a pure-silica cubic ANA framework. This ANA framework displays one of the narrowest windows among zeolite frameworks, being capable of little compression ($V/V_0 = 0.97$) before oxygen atoms come into contact. In this paper we investigate the connection between the compression behaviour of analcime and the flexibility window of the ANA framework, using a combination of geometric simulation and previously obtained experimental data. Simulations of the framework using experimentally obtained cell parameters during compression allow us to determine whether the experimentally observed structures lie within the flexibility window or not. Simulations of hypothetical distortions (tetragonal, orthorhombic, monoclinic and trigonal) of the cubic structure allow us to quantify the theoretical limits of the window and explain why the phase transition occurs as it does.

Method. – Geometric simulation is a method for rapid, simplified simulation of the behaviour of flexible framework structures, in which the bonding constraints in a group of atoms (in this case, tetrahedral TO_4) are represented by a template or "ghost" of ideal geometric shape. The use of such simplified simulations is complementary to more detailed conventional simulations using interatomic potentials and is helpful in the interpretation of experimental results [8,9].

Our simulation methodology is as in our previous work [10,13]. The input to the simulation is a single unit cell of the ANA framework; interstitial atoms are omitted. The structure is represented in $P1$ symmetry, that is, with all atoms explicitly present and independently mobile, and periodic boundary conditions are enforced. The cell parameters are held constant during each simulation. The initial fractional coordinates of the atoms are taken from experimental data. The simulation proceeds by minimizing a penalty function representing a) the mismatch between atoms and the vertices of the ghost templates, and b) steric overlap of oxygen atoms. The positions of the atoms and the positions and orientations of the templates vary during the simulation, but the templates do not change shape. Minimization proceeds by a steepest-descent algorithm. A structure lies within the flexibility window if after this geometric relaxation the bond lengths vary by no more than 0.001 Å and bond angles by no more than 0.01 degrees from the tetrahedral ideal.

In zeolites a typical Si–O bond length is 1.61 Å and a typical Al–O bond length is 1.75 Å [1]. The analcime sample in the recent experimental study [12] had a composition of $(Na_{0.887}K_{0.001}Ca_{0.001})(Al_{0.905}Si_{2.102})O_6 \cdot 0.994H_2O$, with a Si : Al ratio of 2.3 : 1, and refinement of the unit cell in the cubic space group ($Ia\bar{3}d$) showed no evidence of Si/Al ordering. We therefore model analcime using tetrahedral ghosts with a weighted-average TO bond length of 1.65 Å. Oxygen atoms were assigned a radius of 1.35 Å [1]. Since all tetrahedra in our simulation are identical, we only study variations in the cell parameters of the structure and do not address the influence of Si/Al ordering on the development of tetragonal symmetry [14]. We will discuss the range of variations of the crystal cell in terms of cell parameters, a in Å, and in terms of framework density, measured in terms of number of tetrahedral units per 1000 Å^3, a conventional unit in zeolite studies.

The flexibility window is a geometric property of the tetrahedral zeolite framework. However, it also has a physical significance. Consider a division of the atomic interactions in the zeolite into most-local (bonding and steric contact) terms U_b, which favour ideal tetrahedral geometry for TO_4 units, and longer-range terms (for example dispersion and electrostatic interactions) U_l. Distortions of the TO_4 units arise from a trade-off between U_b and U_l terms. Geometric simulation is equivalent to the introduction of only the U_b terms. If the structure lies within the flexibility window, it can reach the global minimum for the energy of the U_b terms. The energy cost for small distortions of the TO_4 units, when we introduce the U_l terms, is then minimal and second-order. If, on the other hand, the structure is outside the flexibility window, it cannot reach the global minimum for the U_b terms, as the TO_4 units are intrinsically strained. Therefore, the energy cost for further distortions of the TO_4 units, when we introduce the U_l terms, is obviously higher and first-order.

The channel contents of zeolites are of unquestioned importance in determining the minerals' physico-chemical properties. However, it should now be clear that the nature of the interactions between the framework and the channel contents depends on whether the structure lies within its flexibility window or not. Geometric simulation can thus provide additional information that complements the results of empirical-potential or *ab-initio* simulations.

Results and discussion. –

Analysis of experimental results. Cell parameters for the unit cell of analcime were obtained at 6 points in the cubic phase between ambient pressure and 0.91 GPa, and at 5 points in the triclinic phase between 1.08 and 1.71 GPa [12]. To assess whether each point lies within or outside the flexibility window for analcime, we performed geometric simulations of the analcime framework using the cell parameters for each data point in turn. In each case the initial atomic coordinates were taken from the ambient-pressure refinement [12] and randomly perturbed by up to 0.01 Å at the start of the simulation.

For all data points for the cubic structure, the framework could be made ideal; all these points therefore lie within the flexibility window for cubic analcime. The cubic cell parameter a for these data points ranges from 13.7065(8) Å to 13.6288(5) Å, with densities ranging from 18.64 T/1000 Å^3 to 18.96 T/1000 Å^3, respectively. The first two points for the triclinic phase could also be made ideal (corresponding to pressures of 1.08 and 1.23 GPa, with densities 19.32 T/1000 Å^3 and 19.40 T/1000 Å^3); however, the remaining points could not be made ideal, indicating that at higher pressures the structure has been compressed beyond the limits of the flexibility window.

The fact that structures on both sides of the phase transition are perfectible indicates that the zeolite prefers to remain in a perfectible state as long as possible. This suggests that the phase transition is caused by the cubic structure approaching the high-density edge of its flexibility window, a possibility we now explore by testing the theoretical limits of the flexibility of the analcime framework.

Theoretical limits of flexibility. We can find the theoretical limits of the cubic flexibility window by simulating analcime with a cubic cell at a variety of cell volumes. From the ambient-pressure cubic polymorph, with cell parameter $a = 13.7065(8)$ Å, we can increase the cell parameter gradually, relaxing the structure at each new cell parameter, until we reach the maximally expanded, low-density edge of the window. This occurs at $a = 13.73$ Å. Similarly, from the last reported cubic high-pressure polymorph, with cell parameter $a = 13.6288(5)$ Å, we can gradually decrease the cell parameter, with relaxation, until we reach the high-density edge of the window (limited by contact between codimeric oxygen atoms [10], that is, the closest oxygen atoms on adjacent tetrahedra forming a dimer). This limit is reached at $a = 13.59$ Å.

This is illustrated in fig. 1. Point A is ambient-pressure cubic analcime. Point B is the high-density edge of the flexibility window for cubic analcime on compression; point C is the low-density edge on expansion. The dashed line between B and C is the extent of the flexibility window for cubic analcime. Point D is the highest-density experimental data point for cubic analcime. It is clear that the experimentally observed range of cell parameters for cubic analcime are bounded by the theoretical limits of the flexibility window, and that as expected the ambient-pressure structure lies slightly inside the low-density edge of the window.

In terms of framework density, the low-density edge of the window lies at 18.55 T/1000 Å^3, while the high-density edge lies at 19.12 T/1000 Å^3. The experimentally observed range of cubic framework densities run from 18.64 T/1000 Å^3 to 18.96 T/1000 Å^3. The framework density of the triclinic structure at 1.08 GPa is 19.32 T/1000 Å^3, well above the density achievable within the cubic window.

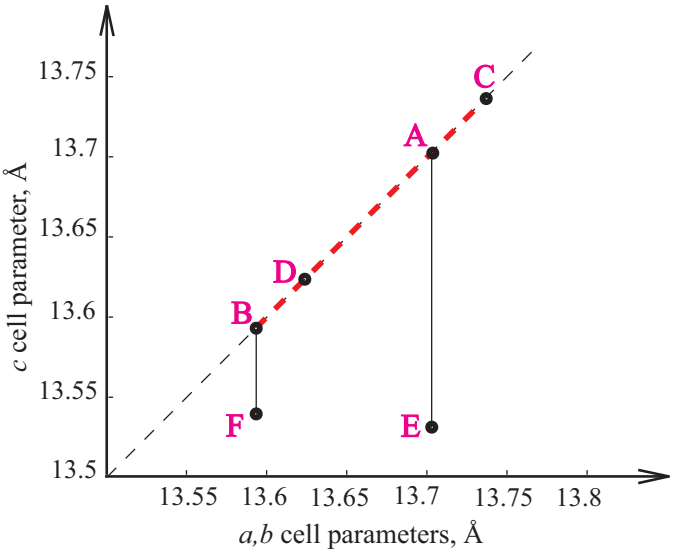

Fig. 1: (Colour on-line) Flexibility window for cubic/tetragonal analcime framework depending on cell parameters. Metrically cubic structures lie along the diagonal (thin dashed) line. Point "A" shows the structure at ambient conditions; "B" and "C" —high- and low-density edges of the flexibility window for the cubic cell; "D" —last experimental point on compression of the cubic analcime. The thick (red) dashed line from B to C is the flexibility window of cubic analcime. "E" and "F" points indicate high-density edges of the flexibility window for tetragonal distortions of analcime, where the c parameter only is compressed, starting from the ambient and most-compressed cubic points, respectively.

This implies that the phase transition occurs because further compression of the cubic cell would take the structure outside the flexibility window (creating intrinsic strain in the tetrahedral network), whereas in the triclinic form the structure can become denser while remaining within its flexibility window. This is a striking result; while it is characteristic of zeolites that the ambient-pressure form lies at the low-density edge of its flexibility window [10], this is the first case in which we can assign a significance to the high-density edge of a flexibility window.

We might suppose that the structure would remain in a more symmetric (tetragonal or orthorhombic) form if it could reach significantly greater densities while remaining within the flexibility window of the more symmetric form. To assess this, we can investigate the effect of transitions to intermediate-symmetry forms by varying one or more of the cell parameters independently. We have investigated the limits of the flexibility window as a function of such variations, starting first from the ambient-pressure cubic form, and second from the densest cubic form found while examining the limits of the cubic window.

From the ambient cubic form, with unit cell edge 13.7065(8) Å, we introduce a tetragonal distortion by varying only the c cell parameter. We can reduce this parameter considerably ($\Delta c = -0.2$ Å) before the framework

can no longer be made ideal, with a proportionate decrease in cell volume ($\Delta V/V = -0.015$). This is illustrated by the line A-E on fig. 1. An orthorhombic distortion can be introduced by varying a second cell parameter, but we find this does not permit a significantly greater variation in cell volume near the E-point. The cubic analcime framework's scope for metrically tetragonal and orthorhombic distortions at ambient pressure is consistent with previous reports of orthorhombic [14,15] and tetragonal [15] analcime, though these symmetry variation also involve some Al/Si ordering. Small degrees of variation are also possible for monoclinic and trigonal polymorphs, again with only small variations in cell volume.

From the high-density edge of the window for cubic analcime, however (with unit cell edge 13.59 Å), we can make only small reductions in any one cell edge ($\Delta c = -0.06$ Å) before the framework can no longer be made ideal. This is illustrated by the line B-F on fig. 1, and indicates that there is little scope to reduce the cell volume further by a tetragonal distortion while remaining within the window. Orthorhombic, monoclinic and trigonal distortions also do not allow for any significant reduction in cell volume while remaining within the window. On this basis, the transition to a triclinic cell is understandable, as it allows the structure to remain within its flexibility window, minimizing strain on the tetrahedral units, while reducing its volume considerably.

It is difficult to establish the theoretical limits of the triclinic flexibility window, as all six cell parameters are independently variable and there is no theoretical need for the flexibility window to have a particularly obvious shape. We do not find any relaxable triclinic structures along the phase-space line defined by linear interpolation between the first triclinic set of cell parameters and the last cubic set. We are currently investigating methods for efficiently searching for the flexibility windows of low-symmetry zeolite structures.

The flexibility window is, in principle, an entirely abstract property of a tetrahedral network; the atomic positions in refined crystal structures of zeolites always display some variation from perfectly tetrahedral geometry, to say nothing of thermal fluctuations. The window was originally defined for structures modeled as pure silica, whereas in the present case we have an Si : Al ratio of 2.3 : 1, and the compression limit of the window is defined by hard-sphere contact between oxygens, whereas in reality electrostatic and dispersion interactions have a longer range, and we have neglected channel content entirely. It is therefore very striking that we obtain such good agreement between the theoretical limits of the flexibility window for the cubic ANA framework and the experimental range of the cubic analcime structure using such a simple model. A detailed comparative study of the analcime-leucite-wairakite system, currently under way, will undoubtedly shed more light on the significance of the flexibility window in the zeolite compression behaviour.

Conclusions. – In conclusion, the experimentally observed range of cubic analcime under compression ($a = 13.7065(8)$ Å–$13.6288(5)$ Å, framework density 18.64 T/1000 Å^3–18.96 T/1000 Å^3) is bracketed by the theoretical range of the flexibility window for the cubic ANA framework ($a = 13.73$ Å–13.59 Å, framework density 18.55 T/1000 Å^3–19.12 T/1000 Å^3. The triclinic structure, observed at 1.08 GPa after a pressure-induced phase transition at about 1 GPa, initially lies within its flexibility window. On further compression, however, the structure passes out of the window and distortions of the tetrahedral framework are inevitable. Simulations of distortions of the cubic structure near the high-density edge of the window indicate that no significant increase in density could be achieved by tetragonal, orthorhombic or monoclinic distortions of the unit cell while remaining within the flexibility window. The abrupt change in symmetry at the phase transition can thus be accounted for on the basis of the structure attempting to remain within its flexibility window, requiring the transition to the triclinic $P\bar{1}$ space group. This is a remarkable demonstration of the significance of framework flexibility in zeolites.

* * *

We would like to acknowledge stimulating discussions with Prof. M. F. Thorpe and Prof. M. M. J. Treacy (ASU). AS thanks the Samuel and Violet Glasstone Fellowship for funding, and SAW thanks the Leverhulme trust. The authors are grateful to two anonymous reviewers for constructive and helpful comments.

REFERENCES

[1] Baerlocher Ch., Meier W. M. and Olson D. H., *Atlas of Zeolite Framework Types* (Elsevier, Amsterdam) 2001.
[2] Breck D. W., *Zeolite Molecular Sieves* (Krieger, Malabar, Fla.) 1984.
[3] Davis M. E., *Nature*, **417** (2002) 813.
[4] Gatta G. D. and Wells S. A., *Phys. Chem. Miner.*, **31** (2004) 465.
[5] Gatta G. D. and Wells S. A., *Phys. Chem. Miner.*, **33** (2006) 243.
[6] Wells S. A., Dove M. T. and Tucker M. G., *J. Phys.: Condens. Matter*, **14** (2002) 4567.
[7] Wells S. A., Dove M. T. and Tucker M. G., *J. Appl. Cryst.*, **37** (2004) 536.
[8] Sartbaeva A., Wells S. A. and Redfern S. A. T., *J. Phys.: Condens. Matter*, **16** (2004) 8173.
[9] Sartbaeva A., Wells S. A., Redfern S. A. T., Hinton R. W. and Reed S. J. B., *J. Phys.: Condens. Matter*, **17** (2005) 1099.
[10] Sartbaeva A., Wells S. A., Treacy M. M. J. and Thorpe M. F., *Nat. Mater.*, **5** (2006) 962.
[11] Coombs D. S., Alberti A., Armbruster T., Artioli G., Colella C., Galli E., Grice J. D., Liebau F.,

Mandarino J. A., Minato H., Nickel E. H., Passaglia E., Peacor D. R., Quartieri S., Rinaldi R., Ross M., Sheppard R. A., Tillmanns E. and Vezzalini G., *Canad. Mineral.*, **35** (1997) 1571.
[12] Gatta G. D., Nestola F. and Boffa Ballaran T., *Am. Mineral.*, **91** (2006) 568.
[13] Sartbaeva A., Wells S. A., Thorpe M. F., Bozin E. S. and Billinge S. J. L., *Phys. Rev. Lett.*, **97** (2006) 065501.
[14] Mazzi F. and Galli E., *Am. Mineral.*, **63** (1978) 448.
[15] Hazen R. M. and Finger L. W., *Phase Trans.*, **1** (1979) 1.