Supplementary Material (ESI) for Chemical Communications

Supplementary Information

ITQ-12: A new microporous silica polymorph and its potential for light hydrocarbon separations

Philip A. Barrett, Teresa Boix, Marta Puche, David H. Olson, Edgar Jordan, Hubert Koller, and Miguel A. Camblor

Structure Solution: X-ray diffraction data were recorded on a Philips PW1829 Xpert diffractometer in flat plate geometry. The program TREOR successfully indexed the majority of the reflections in monoclinic symmetry with unit cell having approximate dimensions a= 10.332, b=15.013, c=8.862 Å and β=105.337.[1] Other small peaks in the diffraction data indicated the presence of a small ZSM-22 impurity. Where possible these additional peaks were excluded from the subsequent structure solution and refinement. Systematic absences suggested the space group to be C2/m, C2 or Cm. The highest symmetry C2/m was selected and Le Bail extraction and Direct Methods were attempted using the program EXPO,[2] producing a full connectivity with three Si sites all tetrahedrally coordinated by oxygen. The presence of Si-O-Si angles of 180º suggested a symmetry lower than C2/m, which was subsequently corroborated by the presence of five distinct $Si(OSi)_4$ resonances in the ^{29}Si MAS NMR spectrum. Details on Rietveld refinement in space groups C2/m and Cm and energy minimization calculations, as well as crystallographic data are provided as supplementary information.

Rietveld Refinement: The model from Direct Methods in C2/m was refined using the program GSAS with a Pseudo-Voigt function to describe the peak shape and a 5 coefficient shifted Chebyshev algorithm to describe the background.[3] Data from 17 up to 85˚ 2θ were included in the refinement. Peaks below 17˚ 2θ were affected by both the ZSM-22 impurity as well as severe asymmetry. In the first cycles of refinement the scale factor, background, cell parameters and zero point were allowed to refine whilst the atomic positions were kept fixed. The profile parameters were then introduced into the refinement and finally the atomic positions and isotropic temperature factors. Constraints were applied to the Si-O bond lengths and the isotropic temperature factors for the oxygen atoms were refined so as to be equal. A calculation of the distances and angles revealed the structure to be reasonably well described by C2/m but an unrealistic Si-O-Si angle of 180˚ was present associated with one oxygen atom (O10 see Table 2) constrained on the inversion center. This suggested that the real symmetry of ITQ-12 might be lower than C2/m, which was subsequently confirmed by ^{29}Si MAS NMR spectroscopy (see article). This aspect is probed by energy minimization techniques and will be discussed later. In the final cycles of refinement the Si-O distance constraints were removed and the model refined to convergence. The final residuals were Rwp =14.99 and Rp=11.46 (See Tables 1-3 for full details and Figure 1).

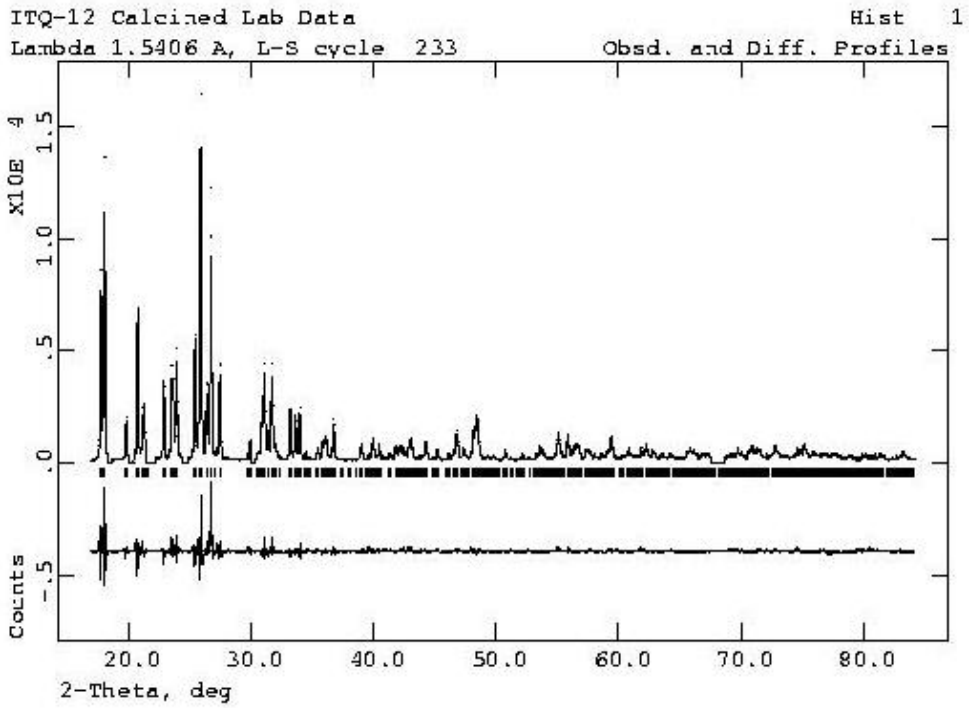


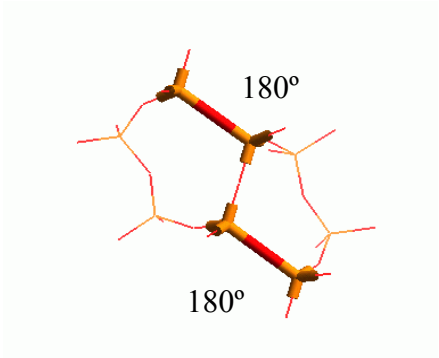
Figure 1.- Rietveld plot in space group C2/m for calcined pure silica ITQ-12 (with a small ZSM-22 impurity): experimental data (+), calculated (—) and diference (lower trace). Tick marks represent the positions of allowed reflections.

Energy Minimisation: The GULP program,[4] together with the interatomic potentials for silicates developed by Sanders et al.,[5] were used to probe the symmetry of calcined ITQ-12. The coordinates from the Rietveld refinement in space group C2/m were used as the starting point for the calculations. The structure was firstly relaxed using the RFO method (Rational Functional Optimization) under constant pressure conditions (the unit cell parameters are allowed to vary), with symmetry applied. This calculation confirmed the presence of 180˚ angles for oxygen O10 and that this was not an artifact of the structure refinement. The symmetry constraint was then removed and the structure minimized once more. A more conventional geometry resulted from this new calculation with the 180˚ angles relaxing to values more typical for silicate materials. The optimized atomic coordinates and cell parameters were input into the Cerius[6] program and a symmetry search was then performed. The result suggested the space group for this minimum energy structure to be close to Cm. The original atomic positions from the Rietveld refinement were transformed from C2/m to Cm and the structure was minimized again from this position applying symmetry constraints once more. The minimum energy structure resulting from this calculation possessed an acceptable distribution of distances and angles.

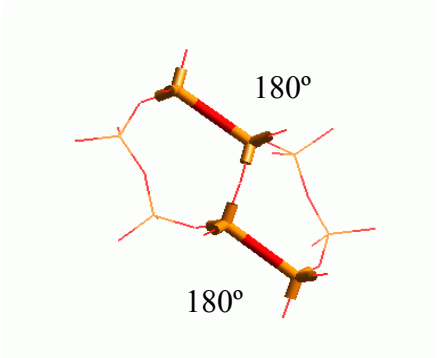
Figure 2 summarizes graphically the results of the minimization work. It shows the part of the ITQ-12 structure in space group C2/m affected by the 180 degree angles and the same fragment of the structure after minimization in C2/m, Cm and C2. Since the 180º angles are associated with the 2-fold axis, they remain in both C2/m and C2 minimized structures, while a more conventional geometry is obtained in Cm. In fact the calculated minima are the same for both C2/m and C2 while Cm is slightly lower in

energy (Table 4). However, the difference in energy is small, and this may be a consequence of the fact that the structure is pretty well described in C2/m, i.e. there are good Si-O distances throughout and the vast majority of the angles are close to typical values generally reported for other porous silicates. Finally, we note that in both C2/m and C2 there is one very negative phonon mode, which is indicative of a false minimum, while in Cm the calculated phonons are all aceptable.

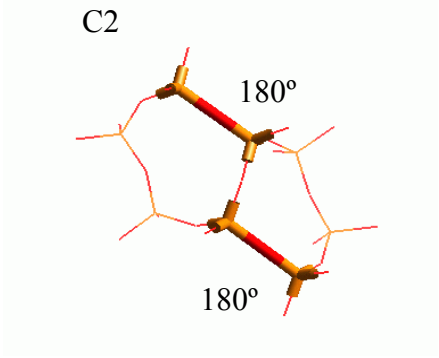
Model from XRD in C2/m



Model from EM in C2/m



Model from EM in C2



Model from EM in Cm

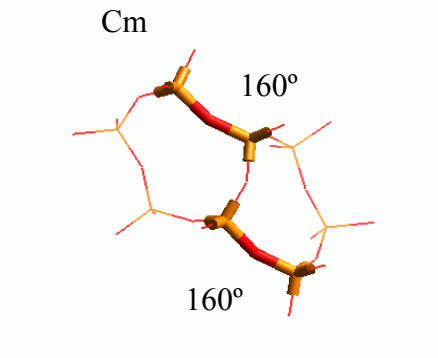


Figure 2.- a fragment of the ITQ-12 structure as derived by X-ray diffraction (XRD) in space group C2/m and results from energy minimization calculations (EM) in C2/m and sub groups Cm and C2.

Rietveld Refinement in Cm:

A model for the structure in space group Cm was generated from the experimental atomic coordinates derived in C2/m. The same profile type and background functions were used as before. Once again constraints were applied to the Si-O distances. The refinement in Cm proved to be more demanding and is possibly at the limits of what can be achieved with low resolution X-ray diffraction data. Nevertheless the model was brought to convergence and the details are given in tables 5-7. The Rietveld plot is shown in Figure 2. The R factors are improved in Cm (Rwp=14.39 and Rp=10.87) and perhaps more significantly the Si-O-Si angles are improved relative to C2/m. However, the O-Si-O angles, Si-O and even the Si-Si distances are slightly worse overall. This is most likely to be a consequence of the larger number of parameters and some correlation between them. Both energy minimization and Rietveld refinement do support a model in Cm symmetry, fully consistent with ^{29}Si MAS NMR results, but higher resolution data would be needed to derive the atomic coordinates with more precision.

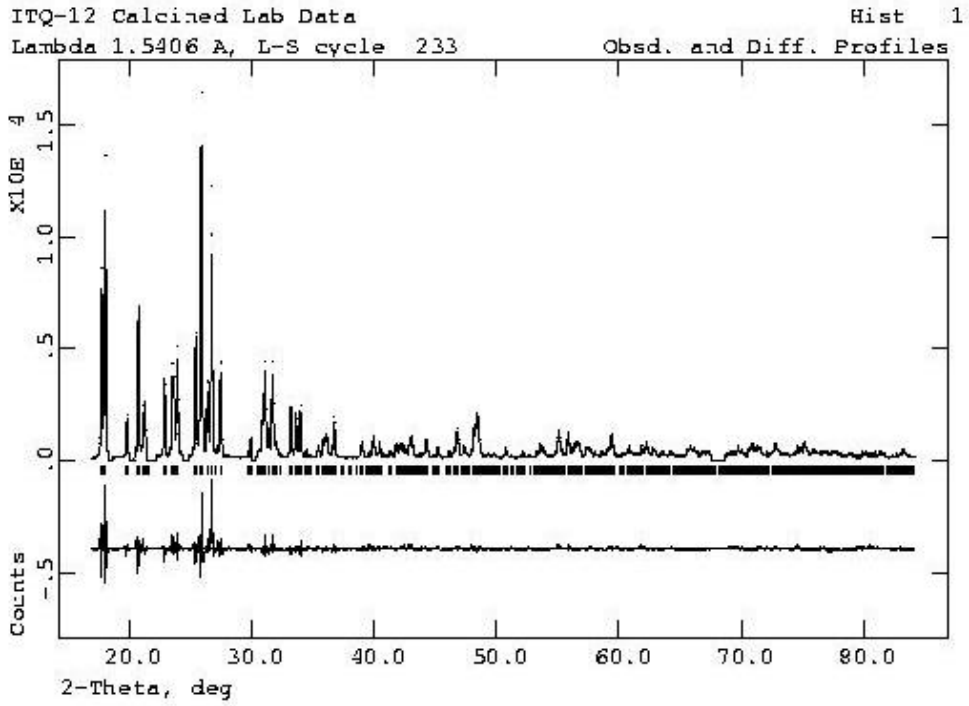


Figure 2.- Rietveld plot for calcined pure silica ITQ-12 (with a small ZSM-22 impurity): experimental data (+), calculated (—) and diference (lower trace). Tick marks represent the positions of allowed reflections.

Supplementary Material (ESI) for Chemical Communications

Crystallographic Data, Atomic Positions and Distances and Angles: Model 1 (C2/m)

Table 1. Crystallographic Data for Calcined ITQ-12: Model 1

Wavelength	Cu K_α
Temperature	298K
2θ Range	4-85 (Range used 17-85)
Step size	0.01 ˚2θ
Count Time	4-50 ˚2θ 1 s/p 50-85˚2θ 2 s/p
No. of Data Points	6713
No. of Reflections	1042
No. of non-structural parameters	17
No. of Structural parameters	30
No. of Constraints	1
Unit Cell Parameters	
a	10.33010(25)
b	15.00957(32)
c	8.85938(21)
β	105.3404(14)
Space Group	C12/m1 (No. 12)
Residuals	
R_{exp}	4.23
R_{wp}	14.99 (-Background 14.30)
R_p	11.46 (-Background 11.13)
R_b	7.88
χ^2	12.66

Table 2. Atomic Positions and Isotropic Temperature Factors for Calcined ITQ-12 with e.s.d's in parentheses: Model 1

Name	*x*	*y*	*z*	*Uiso*
Si(1)	0.6480(4)	0.24388(26)	0.1039(4)	0.97(14)
Si(2)	0.6961(4)	0.39836(27)	0.6658(5)	0.72(14)
Si(3)	0.5986(4)	0.39831(28)	0.3124(5)	1.55(15)
O(4)	0.5	0.2252(6)	0	0.99(12)
O(5)	0.8096(7)	0.3379(5)	0.7829(9)	0.99(12)
O(6)	0.6168(9)	0.5	0.2721(11)	0.99(12)
O(7)	0.6524(7)	0.3359(5)	0.1904(9)	0.99(12)
O(8)	0.4403(8)	0.3779(4)	0.2866(7)	0.99(12)
O(9)	0.6737(7)	0.3794(5)	0.4836(9)	0.99(12)
O(10)	0.75	0.25	0	0.99(12)
O(11)	0.7302(9)	0.5	0.7014(11)	0.99(12)

Table 3. Selected Distances and Angles for Calcined ITQ-12: Model 1

Atom Pair	*Distance (Å)*	*Angle*	*(º)*
Si(1)-O(4)	1.587(4)	O(4)-Si(1)-O(5)	107.2(5)
Si(1)-O(5)	1.573(7)	O(4)-Si(1)-O(7)	109.7(5)
Si(1)-O(7)	1.574(7)	O(4)-Si(1)-O(10)	111.2(2)
Si(1)-O(10)	1.575(4)	O(5)-Si(1)-O(7)	114.0(4)
		O(5)-Si(1)-O(10)	107.6(4)
		O(7)-Si(1)-O(10)	107.2(4)
Si(2)-O(5)	1.622(7)	O(5)-Si(2)-O(8)	105.1(4)
Si(2)-O(8)	1.604(6)	O(5)-Si(2)-O(9)	115.7(4)
Si(2)-O(9)	1.594(7)	O(5)-Si(2)-O(11)	109.1(5)
Si(2)-O(11)	1.579(4)	O(8)-Si(2)-O(9)	109.3(4)
		O(8)-Si(2)-O(11)	107.3(5)
		O(9)-Si(2)-O(11)	109.9(5)
Si(3)-O(6)	1.590(5)	O(6)-Si(3)-O(7)	108.7(4)
Si(3)-O(7)	1.635(7)	O(6)-Si(3)-O(8)	109.0(4)
Si(3)-O(8)	1.619(7)	O(6)-Si(3)-O(9)	109.9(5)
Si(3)-O(9)	1.536(7)	O(7)-Si(3)-O(8)	107.7(4)
		O(7)-Si(3)-O(9)	112.1(4)
		O(8)-Si(3)-O(9)	109.4(4)
		Si(1)-O(4)-Si(1)	159.7(8)
		Si(1)-O(5)-Si(2)	151.3(5)
		Si(3)-O(6)-Si(3)	147.4(8)
		Si(1)-O(7)-Si(3)	148.6(5)
		Si(2)-O(8)-Si(3)	148.3(5)
		Si(2)-O(9)-Si(3)	150.0(5)
		Si(1)-O(10)-Si(1)	180.0(0)
		Si(2)-O(11)-Si(2)	150.2(8)

Energy Minimization Results

Table 4.- Energy minimization results for pure silica ITQ-12

Space group	Lattice energy/eV	a /Å	b/Å	c/Å	Beta/º	Volume/Å^3
C2/m	-3085.19	10.3003	15.0000	8.8431	105.271	1318.05
C2	-3085.19	10.3003	15.0000	8.8431	105.271	1318.05
Cm	-3085.22	10.1725	15.0432	8.8345	105.172	1304.81

Supplementary Material (ESI) for Chemical Communications

Supplementary Material (ESI) for Chemical Communications

Crystallographic Data, Atomic Positions and Distances and Angles: Model 2 (Cm)

Table 5. Crystallographic Data for Calcined ITQ-12: Model 2

Wavelength	Cu Kα
Temperature	298K
2θ Range	4-85 (Range used 17-85)
Step size	0.01 ˚2θ
Count Time	4-50 ˚2θ 1 s/p 50-85˚2θ 2 s/p
No. of Data Points	6713
No. of Reflections	1042
No. of non-structural parameters	17
No. of Structural parameters	58
No. of Constraints	26
Unit Cell Parameters	
a	10.33039(24)
b	15.00977(31)
c	8.85956(21)
β	105.3395(14)
Space Group	C1m1 (No. 8)
Residuals	
R_{exp}	4.23
R_{wp}	14.39 (-Background 13.79)
R_p	10.87 (-Background 10.57)
R_b	6.47
χ^2	11.80

Table 6. Atomic Positions and Isotropic Temperature Factors for Calcined ITQ-12 with e.s.d's in parentheses: Model 2

Name	*x*	*y*	*z*	*Uiso*
Si(1)	0.6447(13)	0.2437(7)	0.1005(14)	1.24(9)
Si(2)	0.6917(11)	0.3969(7)	0.6737(11)	1.24(9)
Si(3)	0.6037(11)	0.3961(6)	0.3187(11)	1.24(9)
Si(4)	-0.6515(13)	0.2452(7)	-0.1058(14)	1.24(9)
Si(5)	-0.6987(11)	0.4013(7)	-0.6583(11)	1.24(9)
Si(6)	-0.5934(10)	0.4005(7)	-0.3033(11)	1.24(9)
O(7)	0.6324(15)	0.3400(10)	0.1733(16)	0.05(12)
O(8)	0.4454(13)	0.3795(13)	0.3095(17)	0.05(12)
O(9)	0.6814(19)	0.3856(13)	0.4934(13)	0.05(12)
O(10)	0.7537(19)	0.2696(10)	0.0061(26)	0.05(12)
O(11)	0.7198(23)	0.5	0.6713(21)	0.05(12)
O(12)	0.5008(17)	0.2267(6)	-0.0192(23)	0.05(12)
O(13)	0.8093(20)	0.3374(14)	0.7840(25)	0.05(12)
O(14)	0.6172(26)	0.5	0.2950(23)	0.05(12)
O(15)	-0.8080(20)	0.3384(13)	-0.7778(25)	0.05(12)
O(16)	-0.6130(25)	0.5	-0.2495(24)	0.05(12)
O(17)	-0.6700(15)	0.3330(10)	-0.2057(16)	0.05(12)
O(18)	-0.4336(13)	0.3783(13)	-0.2587(18)	0.05(12
O(19)	-0.6693(19)	0.3742(12)	-0.4777(14)	0.05(12)
O(20)	-0.7422(21)	0.5	-0.7358(21)	0.05(12)

Table 7.1 Si-O Distances and O-Si-O Angles for Calcined ITQ-12: Model 2

Atom Pair	*Distance (Å)*	*Angle*	*(°)*
Si(1)-O(7)	1.601(11)	O(7)-Si(1)-O(10)	97.6(11)
Si(1)-O(10)	1.617(12)	O(7)-Si(1)-O(12)	104.6(10)
Si(1)-O(12)	1.601(11)	O(7)-Si(1)-O(15)	117.3(15)
Si(1)-O(15)	1.626(12)	O(10)-Si(1)-O(12)	110.3(13)
		O(10)-Si(1)-O(15)	113.4(15)
		O(12)-Si(1)-O(15)	112.4(13)
Si(2)-O(9)	1.582(12)	O(9)-Si(2)-O(11)	93.2(10)
Si(2)-O(11)	1.575(10)	O(9)-Si(2)-O(13)	113.0(15)
Si(2)-O(13)	1.613(12)	O(9)-Si(2)-O(18)	121.2(12)
Si(2)-O(18)	1.588(11)	O(11)-Si(2)-O(13)	116.1(12)
		O(11)-Si(2)-O(18)	110.5(14)
		O(13)-Si(2)-O(18)	103.4(11)
Si(3)-O(7)	1.631(12)	O(7)-Si(3)-O(8)	105.7(10)
Si(3)-O(8)	1.635(12)	O(7)-Si(3)-O(9)	125.5(11)
Si(3)-O(9)	1.552(11)	O(7)-Si(3)-O(14)	111.3(11)
Si(3)-O(14)	1.584(9)	O(8)-Si(3)-O(9)	106.1(11)
		O(8)-Si(3)-O(14)	105.4(17)
		O(9)-Si(3)-O(14)	101.1(12)
Si(4)-O(10)	1.583(12)	O(10)-Si(4)-O(12)	111.9(13)
Si(4)-O(12)	1.582(12)	O(10)-Si(4)-O(13)	100.3(15)
Si(4)-O(13)	1.563(12)	O(10)-Si(4)-O(17)	117.9(11)
Si(4)-O(17)	1.571(12)	O(12)-Si(4)-O(13)	102.9(12)
		O(12)-Si(4)-O(17)	112.2(11)
		O(13)-Si(4)-O(17)	109.9(16)
Si(5)-O(8)	1.621(12)	O(8)-Si(5)-O(15)	106.3(12)
Si(5)-O(15)	1.630(12)	O(8)-Si(5)-O(19)	100.6(11)
Si(5)-O(19)	1.600(12)	O(8)-Si(5)-O(20)	105.7(12)
Si(5)-O(20)	1.644(10)	O(15)-Si(5)-O(19)	114.7(14)
		O(15)-Si(5)-O(20)	100.6(11)
		O(19)-Si(5)-O(20)	127.2(13)
Si(6)-O(16)	1.597(11)	O(16)-Si(6)-O(17)	107.4(11)
Si(6)-O(17)	1.662(12)	O(16)-Si(6)-O(18)	108.7(15)
Si(6)-O(18)	1.627(11)	O(16)-Si(6)-O(19)	117.0(12)
Si(6)-O(19)	1.587(12)	O(17)-Si(6)-O(18)	109.9(10)
		O(17)-Si(6)-O(19)	100.1(9)
		O(18)-Si(6)-O(19)	113.2(12)

Table 7.2 Si-O-Si Angles for Calcined ITQ-12: Model 2

Angle	*(°)*
Si(1)-O(7)-Si(3)	146.6(14)
Si(3)-O(8)-Si(5)	156.0(13)
Si(2)-O(9)-Si(3)	151.1(16)
Si(1)-O(10)-Si(3)	157.1(12)
Si(1)-O(11)-Si(3)	158.3(20)
Si(1)-O(12)-Si(3)	157.4(11)
Si(1)-O(13)-Si(3)	147.9(18)
Si(1)-O(14)-Si(3)	159.6(21)
Si(1)-O(15)-Si(3)	154.9(18)
Si(1)-O(16)-Si(3)	138.6(18)
Si(1)-O(17)-Si(3)	143.2(14)
Si(1)-O(18)-Si(3)	138.4(12)
Si(1)-O(19)-Si(3)	145.6(15)
Si(1)-O(20)-Si(3)	128.5(15)

[1] P.E. Werner, TREOR, Trial and Error Program for Indexing of Unknown Powder Patterns, University of Stockholm, Sweden, **1984**.
[2] A. Altomare, M. C. Burla, M. Camalli, B. Carrozzini, G. Cascarano, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni, G. Polidori, R. Rizzi, EXPO: a program for full powder pattern decomposition and crystal structure solution, *J. Appl. Cryst.* **1998,** *32*, 339-340.
[3] A. Larson, R. B. Von Dreele, GSAS Manual, Los Alamos Report 1986, LA-UR-86-748.
[4] J. D. Gale, *J. Chem. Soc. Faraday Trans.* **1997**, *93*, 629-637.
[5] M. Sanders, M. Leslie, C. R. A. Catlow, J. Chem. Soc. Chem. Commun. 1984, 1271 ± 1273.
[6]Cerius2, Molecular Simulations, 9685 Scranton Road, San Diego CA.