Computer modeling of apparently straight bond angles: the intriguing case of all-silica ferrierite.

SUPPORTING INFORMATION

Federica Trudu, Gloria Tabacchi, Ettore Fois

Contains: computational details, data tables, graphical representations

Computational details

The construction of the Si norm conserving pseudopotential (NCPP) was performed according to Troulliers and Martins, Ref. (Troullier and Martins 1991). For the 4 valence electrons of Si, we considered different non-spin-polarized valence configurations (see below). Non-linear core corrections were adopted. The parameters of the Si-NCPP were modified until we achieved a satisfactory agreement of bond lengths and angles with the corresponding results obtained with the ultrasoft pseudopotential (USPP)(Vanderbilt 1990) of Si available in the QE-distribution (Giannozzi et al. 2017) and utilized for the calculation of the cell parameters. The Si-O bond lengths and Si-O-Si angles of Si-FER *Immm* and Si-FER *Pmnn* from the optimized geometries at fixed cell parameters calculated with the two kinds of pseudopotentials and equal computational setups (Code, Brillouin-zone sampling, number of atoms, etc) are reported in Tables 1a- 4a. In such tables, the convergence of the results with the kinetic energy cutoff for the plane-wave expansion is also shown.

The NCPP parameters characterizing the NCPP are:

- The cutoff radii for each angular momentum channel. Specifically:
    - s-channel: 1.42 bohr
    - p-channel: 1.47 bohr
    - d-channel: 1.53 bohr
- The cutoff radius for the nonlinear core correction: 1.14

In the reported NCPPs, the absence of ghost states was carefully checked. The above-reported parameter values refer to the three best-performing PPs, providing the structural results reported in the Tables. These three NCPPs (NCPP1, NCPP2, and NCPP3, respectively) differ only in their electronic configuration (namely, 3s2 3p1 3d1; 3s1 3p3 3d0; 3s2 3p2 3d0). We selected the former one, named as NCPP1 (3s2 3p1 3d1), because it provided slightly better results, although there is little difference among the performances of the three NCPPs. Overall, such Si-NCPP1 gives a satisfactory comparison of the structural data against both QE calculations (performed with USPP) and experimental data. Moreover, it is sufficiently soft to be used for computationally demanding FPMD simulations, as the results appear to be well converged even at relatively low plane-wave cutoffs (25 Ry). On this basis, Si-NCPP1 has been used to perform the vibrational analysis as well as the first-principles molecular dynamics simulations discussed in this contribution.

All the calculations reported in the tables have been performed using the optimized cell parameters obtained with the QE code, 60 Ry and 360 Ry energy cutoff for wavefunction and density, respectively, a $1\times1\times2$ k-points grid for the Brillouin zone sampling, 108 atoms in the simulation cell ($Si_{36}O_{72}$), PBE functional + D2-dispersion correction, and the USPP for Si and O present in the standard QE distribution. Results obtained with this simulation setup, labeled QE 60/360 USPP, represented our reference values in testing home-built NCPPs.

The labels on top of the tables indicate the code (QE,CPMD), energy cutoff for wavefunction and density, and type of pseudopotentials adopted in the calculations. All calculations performed with QE comprise 108 atoms in the simulation cell. For all the calculations performed with the CPMD code (IBM Corp. 1990–2017 and MPI für Festkörperforschung Stuttgart 1997–2001 2017), the cell parameters were taken from the optimized cell calculated with QE and by doubling the *c* cell parameter. The CPMD simulation cell contains thus 216 atoms (stoichiometry: $Si_{72}O_{144}$).

Figures of the paper in color version

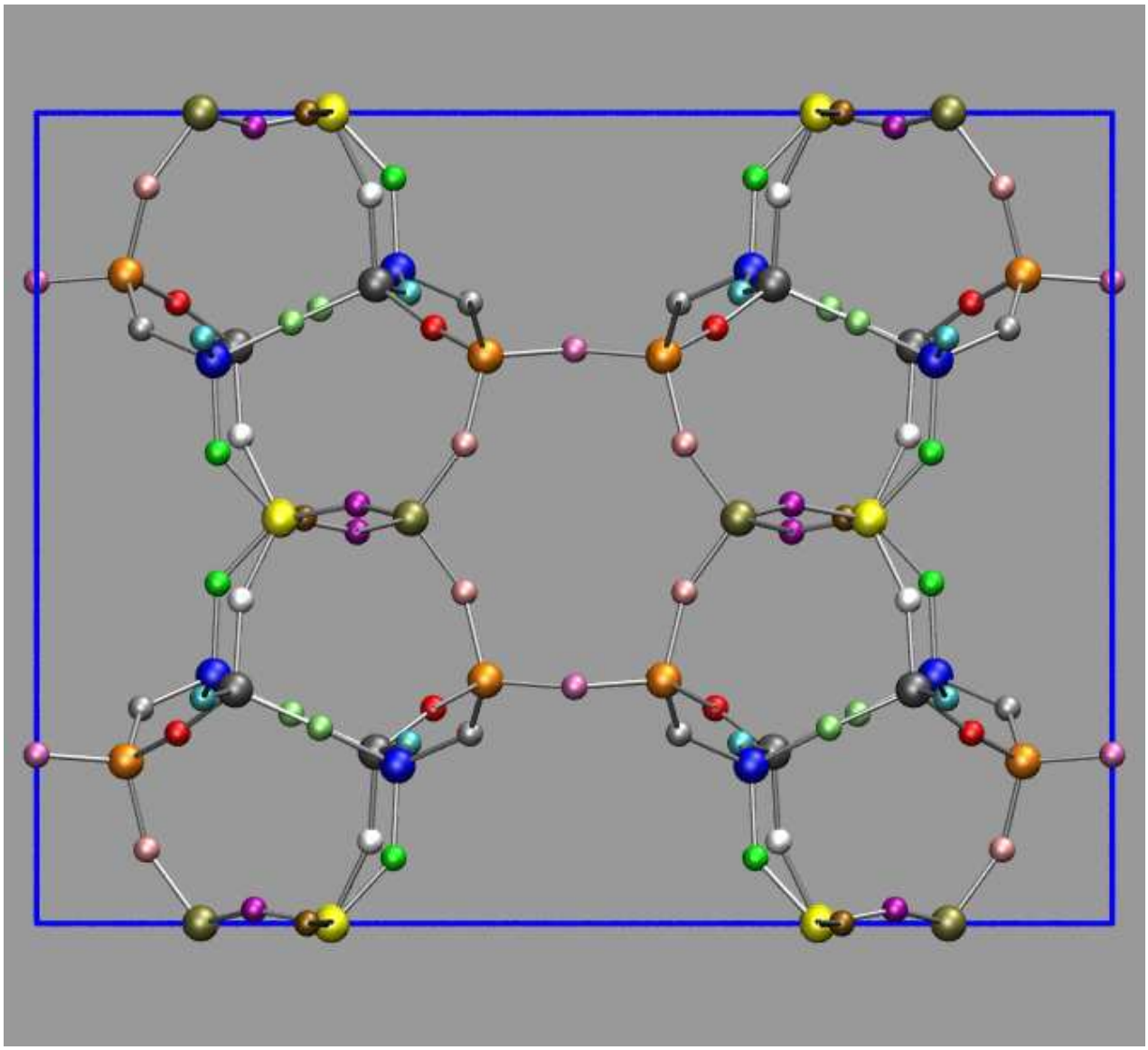

Figure 1: Optimized structure of *Pmnn* Si-FER. Solid blue line represents the simulation cell. The FER structure is projected in the *ab* plane. Atom labels are in color codes and correspond to the labels in the black-and-white Figure 1 of main text. Color codes: Si1=blue; Si2=dark grey; Si3=orange; Si4=yellow; Si5=bronze; O1=red; O2=silver; O3=green; O4=white; O5=pink; O6=cyan; O7=purple; O8=lime; O9=mauve; O10=brown.

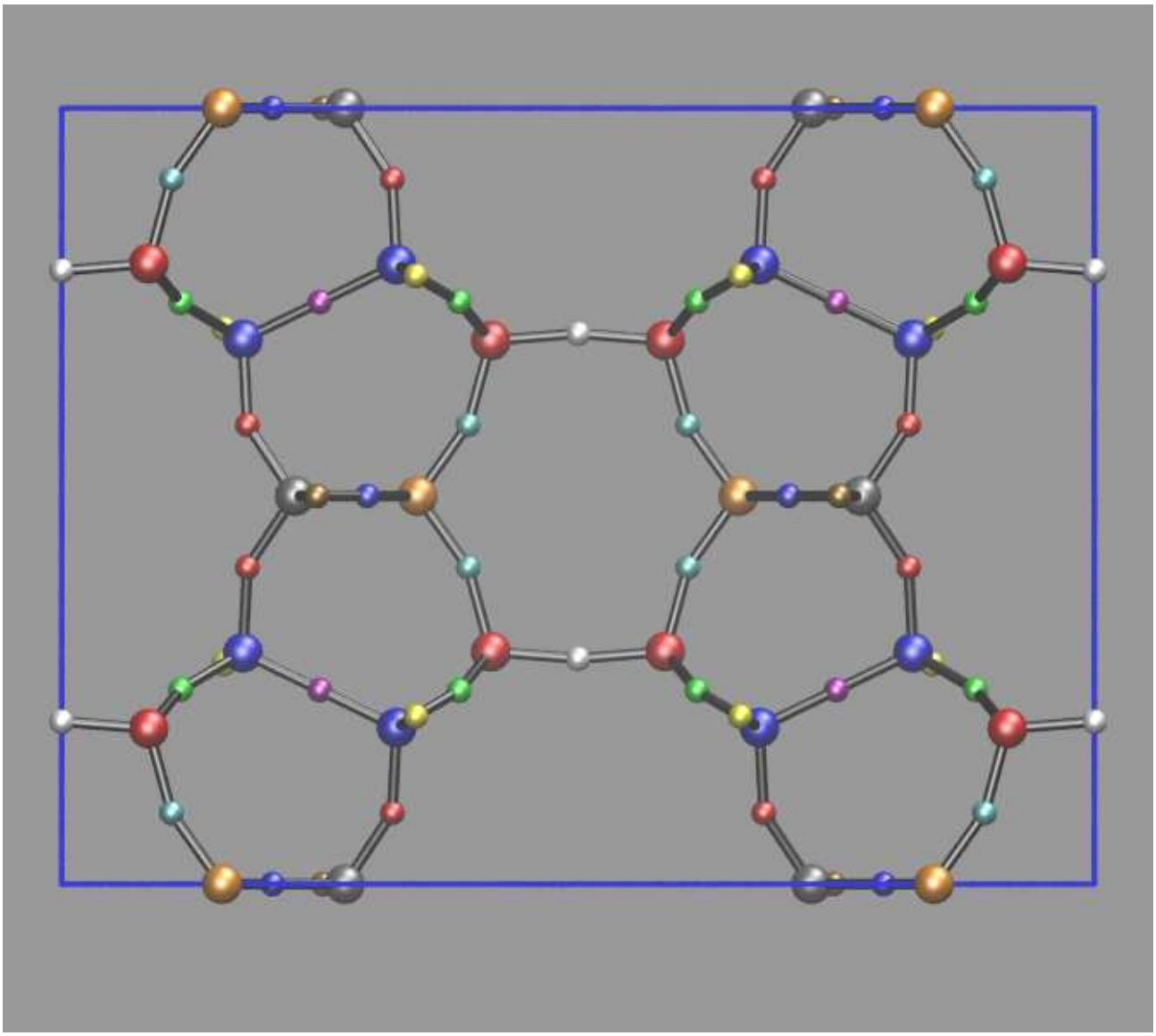

Figure 2: Optimized structure of *Immm* Si-FER. Solid blue line represents the simulation cell. The FER structure is projected in the *ab* plane. Atom labels are in color codes and correspond to the labels of the black-and-white Figure 2 in the main text. Color codes: Si1=blue (big sphere); Si2=red (big sphere); Si3=grey; Si4=orange; O1=red (big sphere); O2=green; O3=yellow; O4=purple; O5=cyan; O6=white; O7= blue (small sphere); O8=brown.

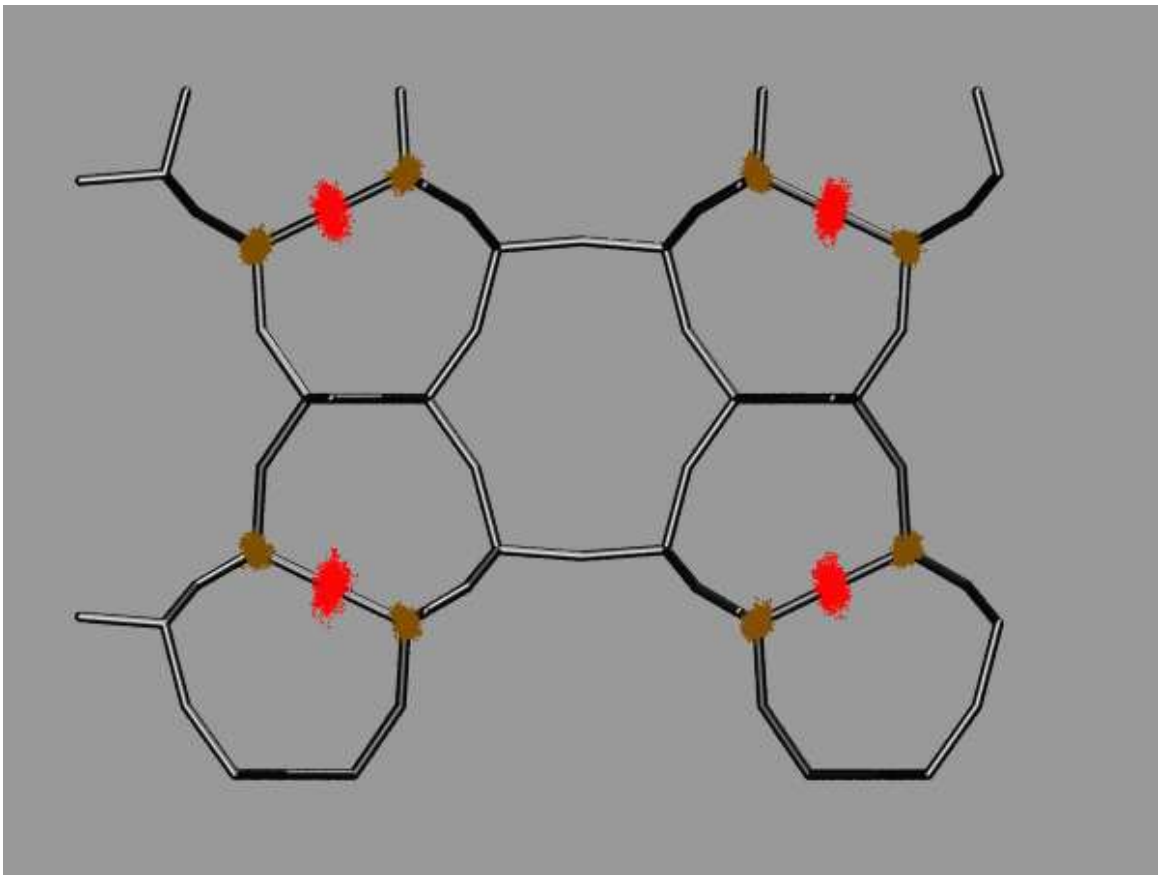

Figure 3: Instantaneous positions of the Si1, O4, Si1 centers sampled along the FPMD simulation at 60 fs time intervals (dots) superposed to the average structure of Si-FER *Immm* obtained from the time-average of the atomic positions (grey sticks). Color codes: O4 instantaneous positions = red dots; Si1 instantaneous positions = brown dots. The FER structure is projected in the *ab* plane.

TABLES OF STRUCTURAL DATA OBTAINED FROM THE CALCULATIONS

Table 1a. Test of different pseudopotentials: results for the Si-O bond leghts (Å) for **FER-*Immm* (QE)**

Bond	QE 60/360 USPP	QE 30/240 USPP	**QE 30/240 NCPP1[#]**	QE 30/240 NCPP2	QE 30/240 NCPP3
SI1-O1	1.616	1.617	**1.619**	1.619	1.619
SI1-O2	1.605	1.605	**1.607**	1.607	1.607
SI1-O3	1.611	1.611	**1.613**	1.613	1.613
SI1-O4	1.614	1.615	**1.616**	1.617	1.617
SI2-O2	1.614	1.614	**1.614**	1.615	1.615
SI2-O2	1.614	1.614	**1.614**	1.615	1.615
SI2-O5	1.612	1.612	**1.613**	1.613	1.613
SI2-O6	1.598	1.597	**1.598**	1.598	1.598
SI3-O1	1.614	1.615	**1.617**	1.617	1.617
SI3-O1	1.614	1.615	**1.617**	1.617	1.617
SI3-O7	1.613	1.614	**1.616**	1.616	1.617
SI3-O8	1.615	1.616	**1.618**	1.618	1.618
SI4-O5	1.605	1.605	**1.607**	1.607	1.607
SI4-O5	1.605	1.605	**1.607**	1.607	1.607
SI4-O7	1.617	1.618	**1.619**	1.619	1.619
SI4-O7	1.617	1.618	**1.619**	1.619	1.619

[#]Results from the NCPP1 pseudopotential adopted for vibrational analysis and FPMD simulations are in bold.

Table 1b. Test of different Si pseudopotentials:– Si-O bond leghts (Å) for **FER-*Immm*** (CPMD)

Bond	CPMD 60/360 NCPP1	**CPMD 30/240 NCPP1**	CPMD 30/240 NCPP2	CPMD 30/240 NCPP3	**CPMD 25/200 NCPP1[#]**
SI1-O1	1.619	1.619	1.619	1.619	**1.618**
SI1-O2	1.607	1.607	1.607	1.607	**1.607**
SI1-O3	1.613	1.613	1.613	1.613	**1.612**
SI1-O4	1.616	1.617	1.617	1.617	**1.616**
SI2-O2	1.614	1.615	1.615	1.615	**1.614**
SI2-O2	1.614	1.615	1.615	1.615	**1.614**
SI2-O5	1.612	1.613	1.613	1.613	**1.612**
SI2-O6	1.599	1.598	1.598	1.598	**1.598**
SI3-O1	1.616	1.617	1.617	1.618	**1.617**
SI3-O1	1.616	1.617	1.617	1.618	**1.617**
SI3-O7	1.616	1.616	1.616	1.616	**1.616**
SI3-O8	1.618	1.618	1.619	1.619	**1.618**
SI4-O5	1.607	1.608	1.608	1.608	**1.607**
SI4-O5	1.607	1.608	1.608	1.608	**1.607**
SI4-O7	1.619	1.619	1.619	1.619	**1.619**
SI4-O7	1.619	1.619	1.619	1.619	**1.619**

[#]Results obtained with the lowest cutoff values (then selected for FPMD simulations) are in bold.

Table 2a. Test of different Si pseudopotentials with QE – Si-O bond lenghts (Å) for **FER-*Pmnn*.**

Bond	QE 60/360 USPP	QE 30/240 USPP	**QE 30/240 NCPP1**[#]	QE 30/240 NCPP2	QE 30/240 NCPP3	CASTEP* USPP
SI1-O2	1.612	1.613	**1.618**	1.619	1.620	1.613
SI1-O3	1.619	1.619	**1.624**	1.624	1.625	1.619
SI1-O6	1.612	1.612	**1.618**	1.618	1.619	1.613
SI1-O8	1.622	1.623	**1.626**	1.627	1.628	1.620
SI2-O1	1.600	1.601	**1.606**	1.606	1.607	1.602
SI2-O4	1.615	1.615	**1.618**	1.618	1.619	1.614
SI2-O6	1.614	1.614	**1.619**	1.619	1.620	1.614
SI2-O8	1.617	1.617	**1.621**	1.621	1.622	1.616
SI3-O1	1.609	1.609	**1.613**	1.613	1.614	1.609
SI3-O2	1.621	1.622	**1.626**	1.626	1.627	1.621
SI3-O5	1.616	1.617	**1.621**	1.621	1.622	1.616
SI3-O9	1.606	1.607	**1.613**	1.613	1.614	1.608
SI4-O3	1.619	1.619	**1.624**	1.624	1.625	1.618
SI4-O4	1.610	1.611	**1.615**	1.615	1.616	1.611
SI4-O7	1.615	1.616	**1.620**	1.620	1.621	1.615
SI4-O10	1.613	1.613	**1.617**	1.617	1.618	1.613
SI5-O5	1.609	1.609	**1.615**	1.615	1.616	1.610
SI5-O5	1.609	1.609	**1.615**	1.615	1.616	1.610
SI5-O7	1.618	1.618	**1.622**	1.622	1.623	1.617
SI5-O7	1.618	1.618	**1.622**	1.622	1.623	1.617

*From ref. (Fischer et al. 2016): calculations with CASTEP (PBE-D2, On-the-fly USPP, 800 eV cutoff, 1×1×2 BZS, 108 atoms). [##]Results from the NCPP1 pseudopotential selected for vibrational analysis and FPMD simulations are in bold.

Table 2b. Test of different Si pseudopotentials – Si-O bond lenghts (Å) for **FER *Pmnn*** – CPMD.

Bond	CPMD 60/360 NCPP1	CPMD 30/240 NCPP1	CPMD 30/240 NCPP2	CPMD 30/240 NCPP3	**CPMD 25/200 NCPP1[#]**	**CASTEP USPP(*)**
SI1-O2	1.618	1.619	1.619	1.620	**1.618**	1.613
SI1-O3	1.623	1.624	1.623	1.624	**1.623**	1.619
SI1-O6	1.617	1.618	1.618	1.619	**1.617**	1.613
SI1-O8	1.625	1.627	1.626	1.627	**1.626**	1.620
SI2-O1	1.605	1.606	1.607	1.607	**1.606**	1.602
SI2-O4	1.617	1.619	1.618	1.619	**1.618**	1.614
SI2-O6	1.618	1.619	1.619	1.620	**1.618**	1.614
SI2-O8	1.620	1.621	1.621	1.622	**1.621**	1.616
SI3-O1	1.612	1.613	1.613	1.614	**1.613**	1.609
SI3-O2	1.625	1.626	1.626	1.627	**1.625**	1.621
SI3-O5	1.620	1.621	1.621	1.622	**1.621**	1.616
SI3-O9	1.612	1.613	1.614	1.615	**1.613**	1.608
SI4-O3	1.623	1.624	1.623	1.624	**1.623**	1.618
SI4-O4	1.614	1.615	1.615	1.616	**1.615**	1.611
SI4-O7	1.619	1.621	1.620	1.621	**1.620**	1.615
SI4-O10	1.616	1.617	1.617	1.618	**1.617**	1.613
SI5-O5	1.614	1.615	1.616	1.616	**1.615**	1.610
SI5-O5	1.614	1.615	1.616	1.616	**1.615**	1.610
SI5-O7	1.621	1.623	1.622	1.623	**1.622**	1.617
SI5-O7	1.621	1.623	1.622	1.623	**1.622**	1.617

(*): from Ref. (Fischer et al. 2016): calculations with CASTEP (PBE-D2, On-the-fly USPP, 800 eV cutoff, 1×1×2 BZS, 108 atoms). [#]Results obtained with the lowest cutoff values (then selected for FPMD simulations) are in bold.

Table 3a. Test of different pseudopotentials – Si-O-Si bond angles (°) for **FER-** ***Immm*** (QE)

Angle	QE 60/360 USPP	QE 30/240 USPP	QE 30/240 NCPP1[#]	QE 30/240 NCPP2	QE 30/240 NCPP3
SI1-O1-SI3	148.88	148.74	**148.30**	148.18	153.35
SI1-O2-SI2	154.02	153.86	**153.44**	153.35	148.60
SI1-O3-SI1	149.42	149.09	**148.69**	148.60	180.00
SI1-O4-SI1	180.00	180.00	**180.00**	180.00	157.79
SI2-O5-SI4	158.37	158.44	**157.84**	157.79	168.97
SI2-O6-SI2	169.38	169.73	**168.90**	168.97	157.86
SI3-O7-SI4	158.34	158.09	**157.95**	157.86	147.16
SI3-O8-SI3	148.22	148.30	**147.38**	147.16	147.42

[#]Results from the NCPP1 pseudopotential adopted for vibrational analysis and FPMD simulations are in bold.

Table 3b. Test of different pseudopotentials – Si-O-Si bond angles (°) for **FER-** ***Immm*** (CPMD)

Angle	CPMD 60/360 NCPP1	CPMD 30/240 NCPP1	CPMD 30/240 NCPP2	CPMD 30/240 NCPP3	CPMD 25/200 NCPP1[#]
SI1-O1-SI3	**148.36**	148.28	148.25	148.10	**148.40**
SI1-O2-SI2	**153.57**	153.42	153.39	153.28	**153.56**
SI1-O3-SI1	**148.49**	148.51	148.47	148.51	**148.52**
SI1-O4-SI1	**180.00**	180.00	180.00	180.00	**180.00**
SI2-O5-SI4	**157.77**	157.64	157.60	157.70	**157.78**
SI2-O6-SI2	**168.86**	168.64	168.58	168.92	**168.98**
SI3-O7-SI4	**157.93**	158.04	158.04	157.79	**157.90**
SI3-O8-SI3	**147.98**	147.38	147.34	147.11	**148.13**

[#]Results obtained with the lowest cutoff values adopted for vibrational analysis and FPMD simulations) are in bold.

Table 4a. Test of different pseudopotentials – Si-O-Si bond angles (°) for **FER- *Pmnn***- QE

Angle (°)	QE 60/360 USPP	QE 30/240 USPP	**QE 30/240 NCPP1[#]**	QE 30/240 NCPP2	QE 30/240 NCPP3
SI2-O1-SI3	166.40	166.37	**166.02**	166.02	166.01
SI1-O2-SI3	138.31	138.19	**137.14**	137.05	136.83
SI1-O3-SI4	139.85	139.72	**138.32**	138.25	138.08
SI2-O4-SI4	158.48	158.44	**159.72**	159.79	159.92
SI3-O5-SI5	149.63	149.56	**148.10**	148.00	147.75
SI1-O6-SI2	146.73	146.65	**145.99**	145.94	145.80
SI4-O7-SI5	151.89	151.85	**150.77**	150.67	150.49
SI1-O8-SI2	159.91	159.90	**158.42**	158.32	158.07
SI3-O9-SI3	149.58	149.35	**147.50**	147.35	146.97
SI4-O10-SI4	150.03	150.02	**150.40**	150.44	150.52

[#]Results from the NCPP1 pseudopotential adopted for vibrational analysis and FPMD simulations are in bold.

Table 4b. Test of different pseudopotentials – Si-O-Si bond angles (°) for **FER *Pmnn*** - CPMD

Angle (°)	CPMD 60/360 NCPP1	CPMD 30/240 NCPP1	CPMD 30/240 NCPP2	CPMD 30/240 NCPP3	**CPMD 25/200 NCPP1[#]**
SI2-O1-SI3	166.02	166.12	166.49	166.51	**166.66**
SI1-O2-SI3	137.34	136.92	136.60	136.35	**136.86**
SI1-O3-SI4	138.58	138.45	139.21	139.11	**139.08**
SI2-O4-SI4	159.45	159.54	158.56	158.64	**158.91**
SI3-O5-SI5	148.41	147.95	147.68	147.40	**148.26**
SI1-O6-SI2	146.04	145.73	145.84	145.73	**145.68**
SI4-O7-SI5	150.96	150.70	151.10	150.94	**150.97**
SI1-O8-SI2	158.58	158.19	158.72	158.46	**158.56**
SI3-O9-SI3	147.85	147.08	146.43	145.99	**146.93**
SI4-O10-SI4	150.31	150.69	149.85	149.88	**150.59**

[#]Results obtained with the lowest cutoff values adopted for vibrational analysis and FPMD simulations) are in bold.

Table 5. Si-O-Si angles (°) for FER-*Immm* calculated from the average atomic positions obtained by first principles molecular dynamics (first column) compared with the corresponding values in the FER-*Immm* minimum energy structure from geometry optimization (CPMD). Average temperature of FPMD: 438 ± 17 K.

Angle**(°)**	CPMD 25/200 Molecular Dynamics NCPP1	CPMD 60/360 Geometry Optimization NCPP1
SI1-O1-SI3	149.98	148.36
SI1-O2-SI2	154.78	153.57
SI1-O3-SI1	149.73	148.49
SI1-O4-SI1	180.00	180.00
SI2-O5-SI4	159.08	157.77
SI2-O6-SI2	170.65	168.86
SI3-O7-SI4	158.66	157.93
SI3-O8-SI3	148.91	147.98

Table 6. Average bond distances (Å) for FER-*Immm* from first principles molecular dynamics calculated from istantaneous atomic positions, r ± Δr (first column), and from average atomic positions (second column), compared with bond distances in the FER-*Immm* minimum energy structure from geometry optimization (CPMD). Average temperature of FPMD: 438 ± 17 K.

Bond distances (Å)	**CPMD 25/200 NCPP1 Molecular Dynamics from inst. positions** r ± Δr[a]	**CPMD 25/200 NCPP1 Molecular Dynamics from average positions**	CPMD 60/360 NCPP1 Geometry Optimization
SI1-O1	1.630 ± 0.036	1.611	1.619
SI1-O2	1.622 ± 0.036	1.606	1.607
SI1-O3	1.626 ± 0.036	1.610	1.613
SI1-O4	1.628 ± 0.036	1.607	1.616
SI2-O2	1.630 ± 0.037	1.613	1.614
SI2-O2	1.630 ± 0.037	1.613	1.614
SI2-O5	1.628 ± 0.036	1.610	1.612
SI2-O6	1.618 ± 0.036	1.597	1.599
SI3-O1	1.628 ± 0.037	1.610	1.616
SI3-O1	1.628 ± 0.037	1.610	1.616
SI3-O7	1.628 ± 0.036	1.609	1.616
SI3-O8	1.629 ± 0.037	1.611	1.618
SI4-O5	1.622 ± 0.036	1.603	1.607
SI4-O5	1.622 ± 0.036	1.603	1.607
SI4-O7	1.631 ± 0.036	1.607	1.619
SI4-O7	1.631 ± 0.036	1.607	1.619

[a]Δr indicates the average amplitude of thermal oscillations of the Si-O bond distances

Graphical representation of the four imaginary frequency modes found for Si-FER *Immm.*

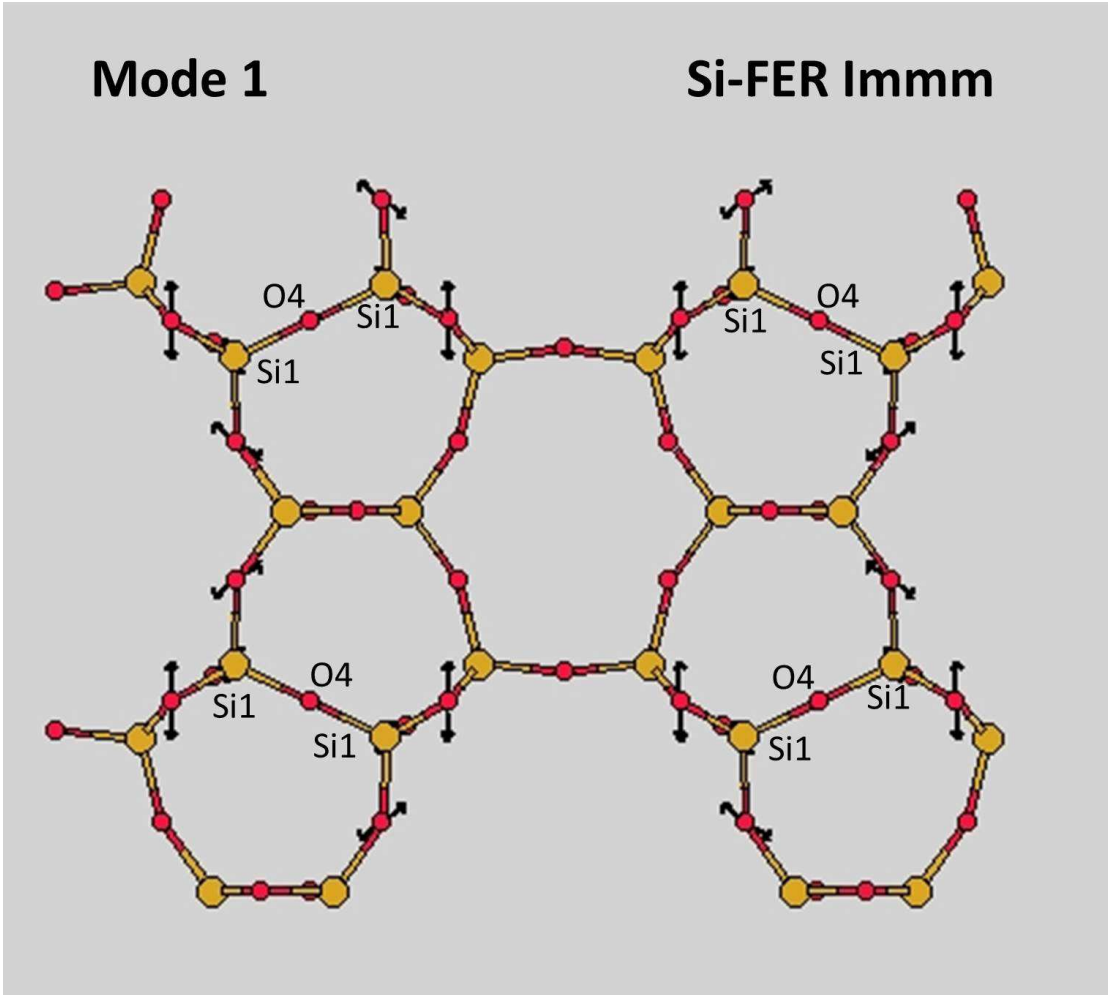

Figure 4. Graphical representation of Mode 1 projected in the *ab* plane. The arrows represent the eigenvector of the mode in terms of atomic displacements. This mode is not localized on the Si1-O4-Si1 angle, occurs in the *bc* plane and is mainly related to distortion of the 10-MR. Color codes: Si=yellow; O=red.

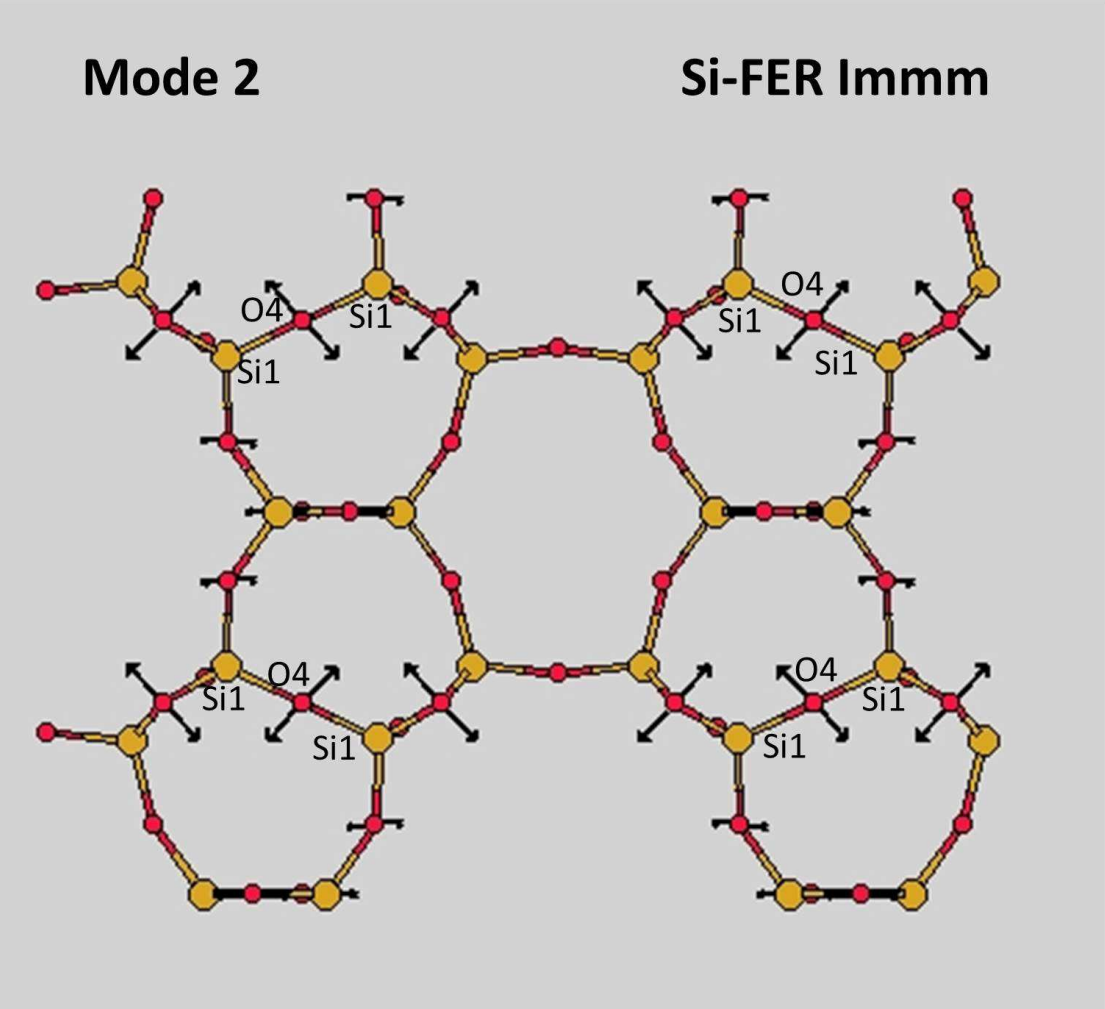

Figure 5. Graphical representation of Mode 2 projected in the *ab* plane. The arrows represent the eigenvector of the mode in terms of the associated atomic displacements. This mode is localized on the Si1-O4-Si1 angle, and takes place essentially in the *ab* plane. Color codes: Si=yellow; O=red.

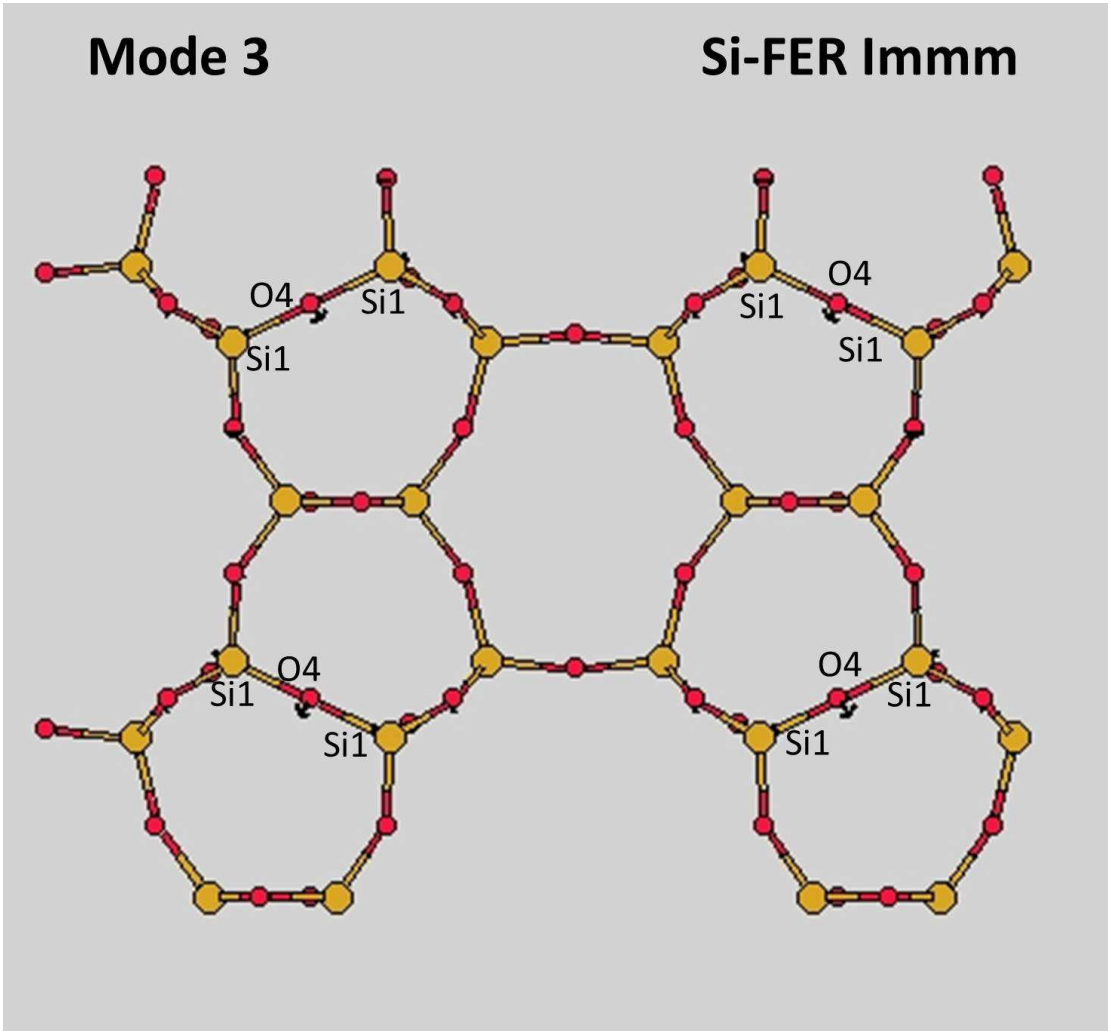

Figure 6. Graphical representation of Mode 3 projected in the *ab* plane. The arrows represent the eigenvector of the mode in terms of the associated atomic displacements. This mode is localized on the Si1-O4-Si1 angle, and takes place mostly in the *ac* plane. Color codes: Si=yellow; O=red.

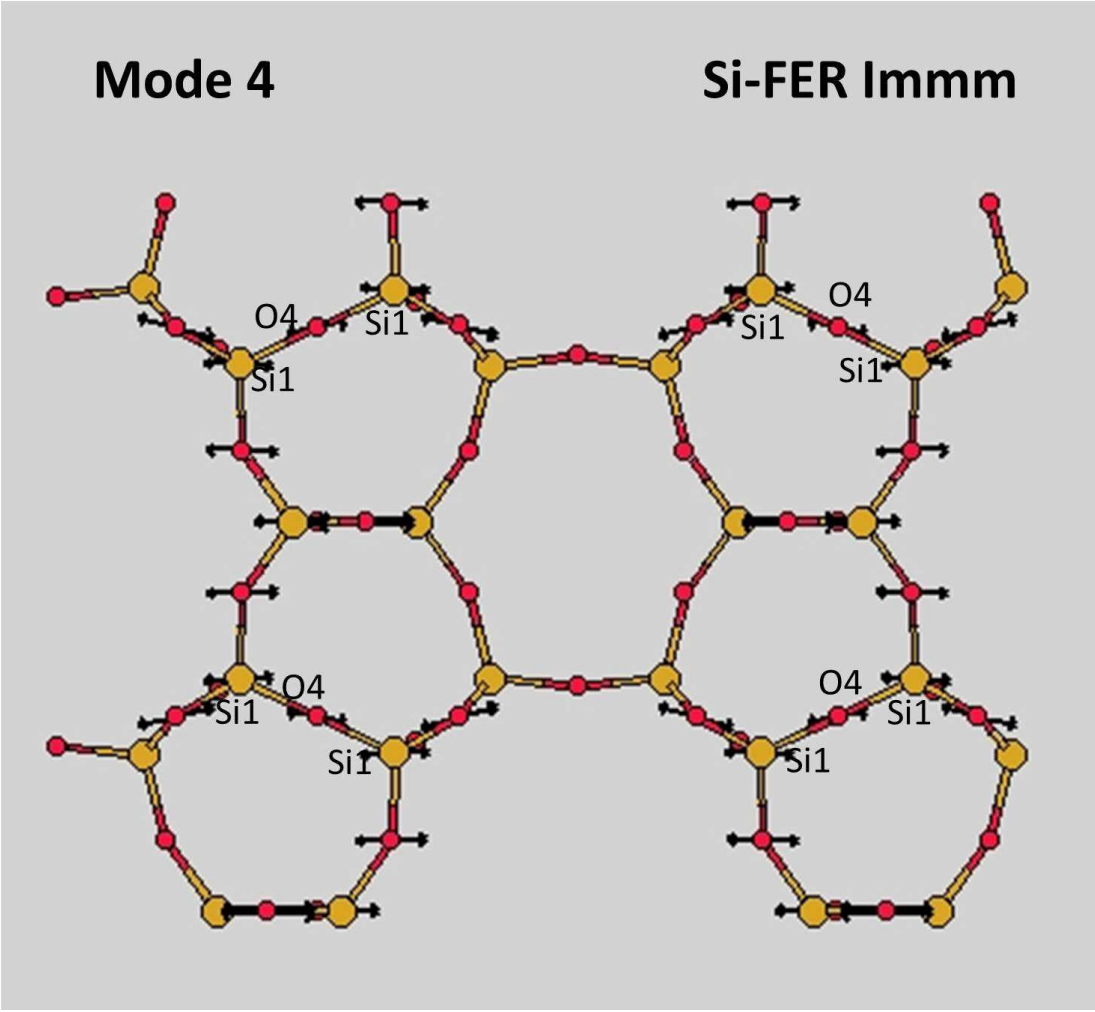

Figure 7. Graphical representation of Mode 4 projected in the *ab* plane. The arrows represent the eigenvector of the mode in terms of the associated atomic displacements. This mode is localized on the Si1-O4-Si1 angle, and takes place mostly in the *bc* plane. Color codes: Si=yellow; O=red.

REFERENCES:

Fischer, M., Evers, F.O., Formalik, F., and Olejniczak, A. (2016) Benchmarking DFT-GGA calculations for the structure optimisation of neutral-framework zeotypes. Theoretical Chemistry Accounts, 135, 257.

Giannozzi, P., Andreussi, O., Brumme, T., Bunau, O., Buongiorno Nardelli, M., Calandra, M., Car, R., Cavazzoni, C., Ceresoli, D., Cococcioni, M., and others (2017) Advanced capabilities for materials modelling with Quantum ESPRESSO. Journal of Physics: Condensed Matter, 29, 465901.

IBM Corp. 1990–2017, and MPI für Festkörperforschung Stuttgart 1997–2001 (2017) CPMD: Car Parrinello Molecular Dynamics.

Troullier, N., and Martins, J.L. (1991) Efficient pseudopotentials for plane-wave calculations. Physical Review B, 43, 1993–2006.

Vanderbilt, D. (1990) Soft self-consistent pseudopotentials in a generalized eigenvalue formalism. Physical Review B, 41, 7892–7895.