**Supplementary information - the structural properties of dense $\beta$-phases, and internal coordinates of silica MFI**

TABLE I: Lattice parameters, Si-O distances (Å), Si-O-Si angles and O-Si-O angles (degrees) for $\beta$-quartz, $\beta$-cristobalite and $\beta$-tridymite. The space group of $\beta$-quartz was constrained to $P\,6_2\,2\,2$, $\beta$-cristobalite was to $I\,\bar{4}\,2\,d$ and $\beta$-tridymite to $P\,63/m\,2/m\,2/c$. The star (*) denotes an average.

| | $a$ | $c$ | d(Si-O) | Θ(Si-O-Si) | Θ(O-Si-O) |
|---|---|---|---|---|---|
| **$\beta$-quartz** | | | | | |
| This work, LDA | 5.01 | 5.51 | 1.59 | 154.0 | 108.0-110.8 |
| This work, PW-91 | 5.08 | 5.58 | 1.61 | 154.3 | 108.3-110.4 |
| Experiment[1] | 4.9977 | 5.4601 | 1.59 | 153.1 | 107.0-111.3 |
| **$\beta$-cristobalite** | | | | | |
| This work, LDA | 5.00 | 7.29 | 1.60 | 151.3 | 109.0,110.5 |
| This work, PW-91 | 5.07 | 7.38 | 1.61 | 152.3 | 109.1,110.2 |
| Experiment[2] | 5.042 | 7.131 | | | |
| **$\beta$-tridymite** | | | | | |
| This work, LDA | 5.20 | 8.46 | 1.59 | 180 | 109.3,109.6 |
| Experiment[3] | 5.06 | 8.28 | | | |

TABLE II: The internal coordinates of the relaxed asymmetric unit of orthorhombic $P\ n\ m\ a$ silica MFI, calculated using DFT-LDA.

| | $x$ | $y$ | $z$ |
|---|---|---|---|
| Si | 0.07772 | 0.55667 | 0.15961 |
| Si | 0.19456 | 0.52937 | 0.30785 |
| Si | 0.22031 | 0.56045 | 0.52812 |
| Si | 0.37823 | 0.56418 | 0.52173 |
| Si | 0.43025 | 0.52786 | 0.31177 |
| Si | 0.31624 | 0.56033 | 0.17088 |
| Si | 0.07744 | 0.32798 | 0.17273 |
| Si | 0.19346 | 0.36939 | 0.31474 |
| Si | 0.22637 | 0.32823 | 0.53219 |
| Si | 0.37949 | 0.32691 | 0.52799 |
| Si | 0.42996 | 0.36963 | 0.31603 |
| Si | 0.31438 | 0.32677 | 0.17868 |
| O | 0.92380 | 0.75000 | 0.85308 |
| O | 0.68887 | 0.75000 | 0.85493 |
| O | 0.77912 | 0.75000 | 0.44580 |
| O | 0.61511 | 0.75000 | 0.43918 |
| O | 0.13246 | 0.55528 | 0.24527 |
| O | 0.18988 | 0.55845 | 0.41841 |
| O | 0.29938 | 0.55854 | 0.52259 |
| O | 0.40506 | 0.56500 | 0.41031 |
| O | 0.38844 | 0.55249 | 0.21785 |
| O | 0.26213 | 0.55433 | 0.25766 |
| O | 0.12844 | 0.34184 | 0.26123 |
| O | 0.19262 | 0.34515 | 0.42766 |
| O | 0.30313 | 0.35035 | 0.52959 |
| O | 0.40840 | 0.33452 | 0.41800 |
| O | 0.38532 | 0.34234 | 0.22661 |
| O | 0.25834 | 0.34094 | 0.26065 |
| O | 0.19449 | 0.44929 | 0.31010 |
| O | 0.42062 | 0.44884 | 0.32693 |
| O | 0.07938 | 0.62779 | 0.10409 |
| O | 0.09096 | 0.49867 | 0.07956 |
| O | 0.09955 | 0.36772 | 0.07482 |
| O | 0.31090 | 0.63217 | 0.11874 |
| O | 0.30476 | 0.50349 | 0.08888 |
| O | 0.30327 | 0.37247 | 0.08264 |
| O | 0.50638 | 0.54545 | 0.29175 |
| O | 0.50562 | 0.35242 | 0.29231 |

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