Prediction of ten-fold coordinated TiO$_2$ and SiO$_2$ structures at multimegabar pressures

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We predict by first-principles methods a phase transition in TiO$_2$ at 6.5 Mbar from the Fe$_2$P-type polymorph to a ten-coordinated structure with space group I4/mmm. This is the first report of the pressure-induced phase transition to the I4/mmm structure amongst all dioxide compounds. The I4/mmm structure was found to be up to 3.3% denser across all pressures investigated. Significant differences were found in the electronic properties of the two structures and the metallization of TiO$_2$ was calculated to occur concomitantly with the phase transition to I4/mmm. The implications of our findings were extended to SiO$_2$ and an analogous Fe$_2$P-type to I4/mmm transition was found to occur at 10 TPa. This is consistent with the lower-pressure phase transitions of TiO$_2$, which are well established models for the phase transitions in other AX$_2$ compounds, including SiO$_2$. As in TiO$_2$, the transition to I4/mmm corresponds to the metallization of SiO$_2$. This transformation is in the pressure range reached in the interiors of recently discovered extrasolar planets and calls for a reformulation of the equations of state used to model them.

Significance

The highest-pressure phase of TiO$_2$, SiO$_2$, and several other important oxides, was hitherto believed to be nine-coordinated Fe$_2$P-type. We searched for low-enthalpy phases of TiO$_2$ using density-functional-theory methods, finding that the most stable form of TiO$_2$ at pressures above 650 GPa is a ten-coordinated structure with space group I4/mmm. TiO$_2$ is the well-established high-pressure model for many AX$_2$ compounds, and our study shows that SiO$_2$ should also form in the I4/mmm structure above 10 TPa. The high-pressure I4/mmm polymorph of SiO$_2$ is likely to be a major constituent of giant rocky planets at multi-TPa pressures, and our results call for a reformulation of the equations of state used to model them.
are likely to possess symmetry [34]. Symmetry constraints prevent some structural relaxations, but searching with symmetry constraints is very useful because it often leads to the identification of low-enthalpy structures. In our searching we have employed numbers of formula units per cell of 1, 2, 3, 4, 6, 8, 12, and 16.

Results and Discussion

Static enthalpy differences ($\Delta H$) calculated relative to the high-pressure Fe$_2$P-type structure are plotted in Fig. 1 as a function of pressure. Figure 1 (a) illustrates the structural phase transitions up to the cotunnite-type structure. At ambient pressure, the enthalpy of rutile is calculated to be slightly higher than that of FeO$_2$-type, which is consistent with other theoretical investigations [2]. The calculated static enthalpies of the known high-pressure polymorphs: baddeleyite, orthorhombic (OI), and cotunnite are shown.

Figure 1 (b) portrays the post-cotunnite regime of the phase diagram. The cotunnite-Fe$_2$P-type transition is calculated to occur at 143 GPa, in good agreement with previous investigations [2]. The high-density Fe$_2$P-type structure has previously been thought to be the final high-pressure phase in several diocides [2, 8]. However, we found an even higher density structure with space group $I4/mmm$ that becomes more stable than FeO$_2$-type above about 530 or 647 GPa, using the LDA+U and PBEsol density functionals, respectively. We found the TiO$_2$ $I4/mmm$ structure using AIRSS, although this structure has also been predicted as a high pressure phase of TiS [41].

The crystal structures of the Fe$_2$P-type and $I4/mmm$ polymorphs are compared in Fig. 2. The hexagonal unit cell of Fe$_2$P-type (space group $P6_3/mmc$) contains three ninefold coordinated Ti polyhedra. Conversely the lower (tetragonal) symmetry unit cell of the $I4/mmm$ structure contains a single Ti atom that is tenfold coordinated, which is the new record for the coordination number in a dioxide. The Ti–O bond distances are 1.65–1.80 Å and 1.75–1.80 Å in Fe$_2$P-type and $I4/mmm$ structures at 645 GPa, respectively. This indicates that the higher densities achieved in $I4/mmm$ arise from the higher coordination and denser polyhedral packings. Volume compression curves show that the $I4/mmm$ unit cell volume is smaller than that of Fe$_2$P-type across all pressures studied, and that $I4/mmm$ is 3.3% more dense at the transition pressure. The greater density of $I4/mmm$ leads directly to greater stability than Fe$_2$P-type at sufficiently high pressures.

Charge densities of the Fe$_2$P-type and $I4/mmm$ structures of TiO$_2$ are illustrated in Fig. 3. In Fe$_2$P-type, the charge densities are observed to be mostly spherical and centred on the atoms. This is consistent with a Bader analysis of the electron density, which assigns net charges on the Ti and O atoms of +1.91 and −0.96e, respectively. This corresponds to an ionicity of $\sim$48%. In $I4/mmm$, the charge densities are seen to be deformed between neighbouring atoms and take the form of O lone pairs, which is in agreement with an electron localisation-function (ELF) analysis. The Bader charges are +1.67 and −0.84e on the Ti and O atoms, respectively, equating to a lower ionicity of $\sim$42%. This is interesting since structures with lower ionicities are less sensitive to the Coulomb interactions with neighbouring atoms. This means that the stabilising effect of tenfold coordination is less pronounced in $I4/mmm$ than Fe$_2$P-type which is in agreement with an electron localisation-function (ELF) analysis. Also, with the longer bond distances in $I4/mmm$, we expect the favourable energetics of the $I4/mmm$ structure to arise from the efficient packing of O lone pairs when the material is highly compressed.

Calculated band gaps of these phases are shown in Fig. 4 as a function of pressure. The band gaps are observed to correlate negatively with pressure. Tsujiya and coworkers [2] previously found the Fe$_2$P-type structure to have the smallest band gap of any known TiO$_2$ polymorph; they calculated a band gap of 0.66 eV at 160 GPa, which compares well with our value of 0.50 eV. Above 160 GPa, we find the band gap is further reduced until the $I4/mmm$ transition at 647 GPa, where TiO$_2$ becomes a metal (we calculate the $I4/mmm$ structure to be metallic at all pressures). Figure 5 depicts the band structures and densities of states of these phases. Both structures have dominant O 2$p$ and Ti 3$d$ components in the valence and conduction bands, respectively. The band gap narrowing in Fe$_2$P-type is seen to arise from a single Ti 3$d$ state in the conduction band, which appears to be preferentially stabilised by pressure near the Γ-point.

Low-pressure structures of silica (e.g., quartz, zeolites) adopt tetrahedral Si coordination, but at pressures between 10 and 250 GPa, sixfold coordination is preferred, e.g., the stishovite (a rutile-type silica), CaCl$_2$, α-PbO$_2$, and pyrite structures. The cotunnite transition (ninefold coordination) becomes stable at about 700 GPa and, at about the same pressure, Fe$_2$P-type silica becomes most stable. Recent theoretical investigations have shown that MgSiO$_3$ and CaSiO$_3$, which are major constituents of the Earth’s mantle, separate into I$_4$ and P$_2$ (C$_{4v}$-silicate) oxides at extrasolar planet core conditions [5, 8]. This highlights the importance of SiO$_2$ as a mantle mineral at very high pressures.

We performed calculations with the PBEsol functional for silica in the Fe$_2$P-type and $I4/mmm$ structures described above up to pressures of 17 TPa. PBEsol has been shown to outperform other functionals in silica [42] and we found the same when optimising quartz and cristobalite at ambient pressure. Static enthalpies are plotted in Fig. 6, revealing a high-pressure analogue to the phase diagram found for TiO$_2$. The Fe$_2$P-type to $I4/mmm$ transition was found to occur at 9.8 or 10.0 TPa using the PBEsol or LDA functional, respectively. This pressure corresponds to the core of an extrasolar planet with a mass 40 times that of Earth (40M$_{\oplus}$). The Si–O bond lengths at 10 TPa are 1.14–1.27 Å and 1.29 Å in the Fe$_2$P-type and $I4/mmm$ structures, respectively. The $I4/mmm$ silica is denser than Fe$_2$P-type across all pressures tested and is 1.4% denser at the transition pressure. This indicates a need to reformulate the equations of state used to model the deep mantles of terrestrial exoplanets and the cores of gas giants.

Silica is found to maintain much wider band gaps than isostructural TiO$_2$, even at terapascal pressures. The compression-induced band gap narrowing is seen to metallise the $I4/mmm$ structure by 1.4 TPa, while no metallization was observed in Fe$_2$P-type at the pressures tested. Hence, as well as altering the coordination environment and density, the $I4/mmm$ transition also brings about the metallization of silica.

Computational Details

The first-principles DFT calculations were performed using the CASTEP plane-wave basis set code [35] and ultrasoft pseudopotentials [36]. We tested several density functionals and found that the LDA + U functional [37] with $U = 5$ eV predicts the correct energy ordering of rutile < brookite < anatase at low pressures, but it fails to predict the experimentally verified transition to the cotunnite structure at high pressures. See Ref. [38] for further discussion of values of $U$ for TiO$_2$.  

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The PBEsol functional [39] correctly predicts the stability of cotunnite and other known high-pressure phases. The PBEsol functional is also essentially exact in the limit of a uniform electron gas and it provides an excellent description of the response of the electron gas to an applied potential. These properties, which are also shared by the LDA and PBE functionals [40], are particularly useful at high pressures, where the charge density becomes more uniform. Spin polarization is accounted for within LDA+U, though no magnetically-ordered phases were found in our low-enthalpy structures. Brillouin zone sampling grids of spacing $2\pi \times 0.07 \text{ Å}^{-1}$ and an energy cutoff of 340 eV were used for the searching. For the final results reported in this paper, we used a smaller k-point spacing of $2\pi \times 0.03 \text{ Å}^{-1}$ and energy cutoffs of 700 and 850 eV for TiO$_2$ and SiO$_2$, respectively. We relaxed about 6,000 structures obtained from AIRSS and a further 2,500 from the ICSD. Vibrational contributions to the TiO$_2$ enthalpies were considered within the quasi-harmonic approximation using PBEsol and resulted in no adjustments to the static transition pressure.

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Fig. 1. Relative static lattice enthalpies of TiO$_2$ structures, plotted with respect to the Fe$_2$P-type structure. (a) The pressure regime between 0 and 40 GPa, and (b) the high-pressure post-cotunnite regime. The inset focusses on the Fe$_2$P-type to $I4/mmm$ transition, which is predicted to occur at 636 and 647 GPa, using the LDA+U and PBEsol functionals, respectively.
Fig. 2. Crystal structures of a Fe$_2$P-type and b $I4/mmm$ TiO$_2$ at 645 GPa. The hexagonal unit cell of the Fe$_2$P-type structure (space group $P6_2m$) and tetragonal unit cell of $I4/mmm$ TiO$_2$ are depicted. The lattice parameters for the Fe$_2$P-type structure are $(a, b, c, \alpha, \beta, \gamma) = (4.4157, 4.4157, 2.3998, 90^\circ, 90^\circ, 120^\circ)$. The atomic coordinates are Ti$_1$ (1a) (1, 1, 0), Ti$_2$ (2d) (1/3, 2/3, 1/2), O$_1$ (3g) (0.26168, 1, 1/2), and O$_2$ (3f) (0.59427, 0, 0). The lattice parameters and atomic coordinates for the $I4/mmm$ structure are $(a, b, c, \alpha, \beta, \gamma) = (2.2060, 2.2060, 5.3699, 90^\circ, 90^\circ, 90^\circ)$. Ti (2b) (1/2, -1/2, 0), and O (4e) (1, -1, 0.16336).

Fig. 3. Charge densities of the two high-pressure polymorphs of TiO$_2$ at 645 GPa. (a) The (001) plane of the Fe$_2$P-type structure. (b) The (010) plane of the $I4/mmm$ structure.

Fig. 4. Calculated band gaps of Fe$_2$P-type and $I4/mmm$ TiO$_2$ structures as a function of pressure. A vertical red line represents the static PBEsol transition pressure, which is also the metallization pressure.
Fig. 5. Electronic band structures of Fe$_2$P-type and I$\bar{4}$/mmm TiO$_2$ at 645 GPa. The calculated Fermi energies ($E_F$) are indicated by horizontal black lines. Electronic densities of states, and their projections onto atomic orbitals, are also shown.

Fig. 6. Relative static lattice enthalpies of high-pressure silica structures, plotted with respect to the Fe$_2$P-type structure. The inset focuses on the Fe$_2$P-type to I$\bar{4}$/mmm transition, which is predicted to occur at 9.8 or 10.0 TPa using the PBEsol or LDA functional, respectively. This pressure corresponds to the core of an extrasolar planet with a mass 40 times that of Earth (40$M_E$).