Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary information

Ten-fold Coordinated Polymorph and Metallization of TiO_2 under High Pressure

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Index **page**

Computational details

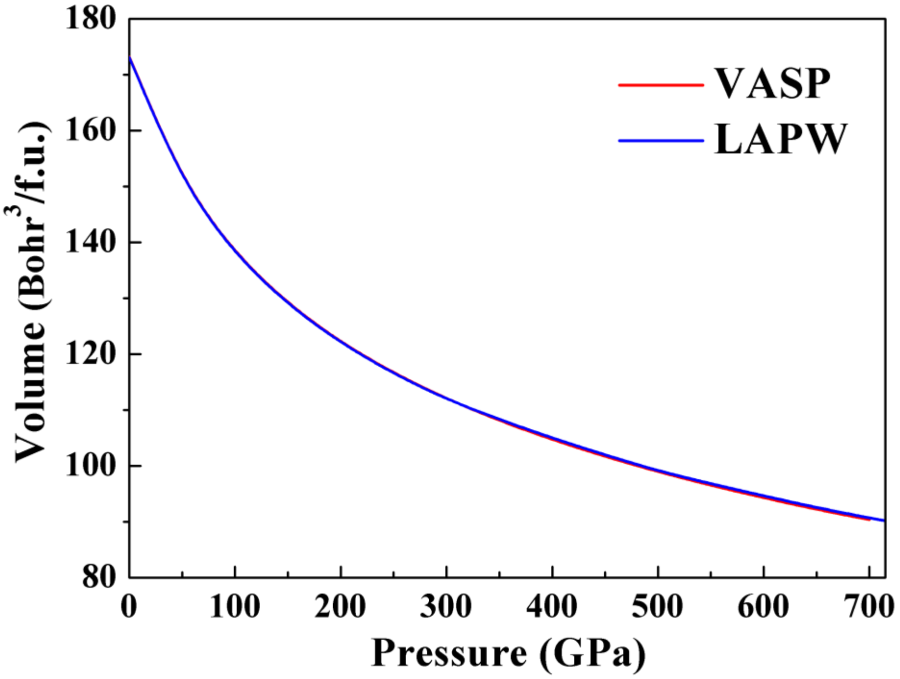
Our structural prediction approach is based on a global minimization of free energy surfaces merging *ab initio* total-energy calculations through CALYPSO (Crystal structure AnaLYsis by Particle Swarm Optimization) methodology as implemented in its same-name CALYPSO code.[1,2] The structures of TiO_2 were searched with simulation cell sizes of 1−4 formula units (f.u.) at 0~800 GPa, respectively. In the first step, random structures with certain symmetry are constructed in which the atomic coordinates are generated by the crystallographic symmetry operations. Local optimizations using VASP code,[3] were done with the conjugate gradients method and were stopped when the enthalpy changes became smaller than 1×10^{-5} eV per cell. After processing the first generation structures, 60% of them with lower enthalpies are selected to produce the next generation structures by PSO. 40% of the structures in the new generation are randomly generated. A structure fingerprinting technique of bond characterization matrix is applied to the generated structures, so that identical structures are strictly forbidden. These procedures significantly enhance the diversity of the structures, which is crucial for the efficiency of the global search of structures. For most of the cases, the structure searching simulation for each calculation was stopped after we generated 1000 ~ 1200 structures (e.g., about 20 ~ 30 generations).

To further analyze the structures with higher accuracy, we select a number of structures with lower enthalpies and perform structural optimization using density functional theory within the generalized gradient approximation[4] as implemented in the VASP code. The cut-off energy for the expansion of wavefunctions into plane waves is set to 1000 eV in all calculations, and the Monkhorst–Pack *k*-mesh with a maximum spacing of 0.03 $Å^{-1}$ was individually adjusted in reciprocal space with respect to the size of each computational cell. This usually gives total energy well converged within ~ 1 meV/atom. The electron-ion interaction was described by means of projector augmented wave with $3d^2 4s^2 3p^6 3s^2$ and $2s^2 2p^4$ electrons as valence for Ti and O atoms, respectively.

The electron-phonon coupling calculations are carried out by linear response density functional theory as implemented in the QUANTUM ESPRESSO package.[5]The norm-conserving pseudopotentials for Ti and O are adopted. The kinetic energy cutoffs of 80 Ry are chosen for all phases. And 24 x 24 x 8 *k* meshes and 6 x 6 x 2 q meshes in the Brillouin zone are used for TiO_2 in CaC_2-type.

In order to test the validity of the PAW potentials for Ti and O provided by the VASP PAW library, we calculated the equation of states (EOS) for TiO_2 in CaC_2-type structure. The calculations are performed by use of PAW method as implemented in VASP code as well as a full-potential linearized augmented plane wave (FP-LAPW) method as implemented in the ELK code.[6] Thus, our adopted pseudopotentials are feasible under high pressure.

Supplementary Figures



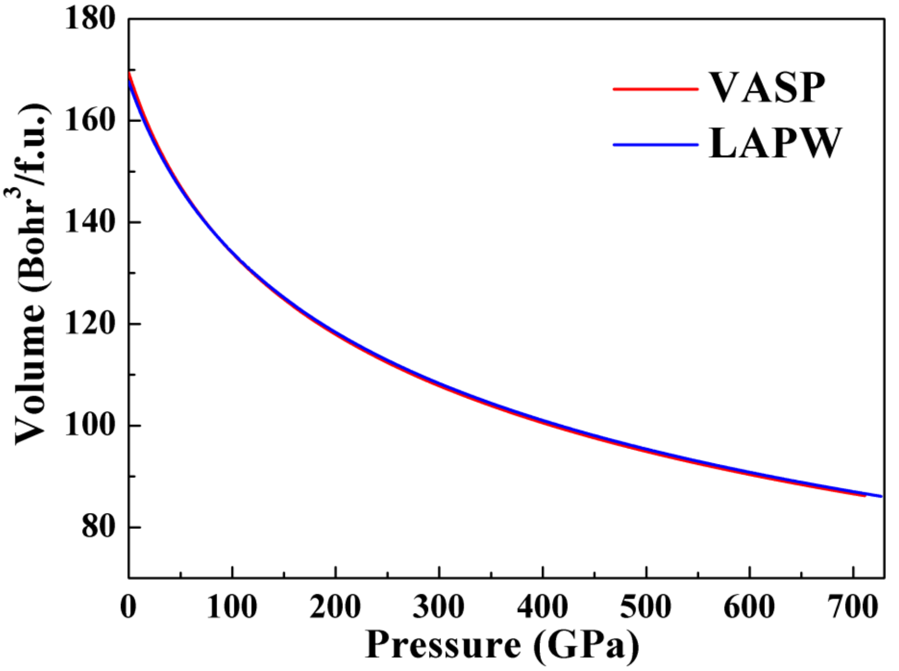


Figure S1. Comparing the Birch-Murnaghan equation of state by PAW potentials and ELK methods for Fe_2P-type structure (top) and CaC_2-type structure (bottom). These results indicate that the PAW potentials are applicable to TiO_2 under high pressure.

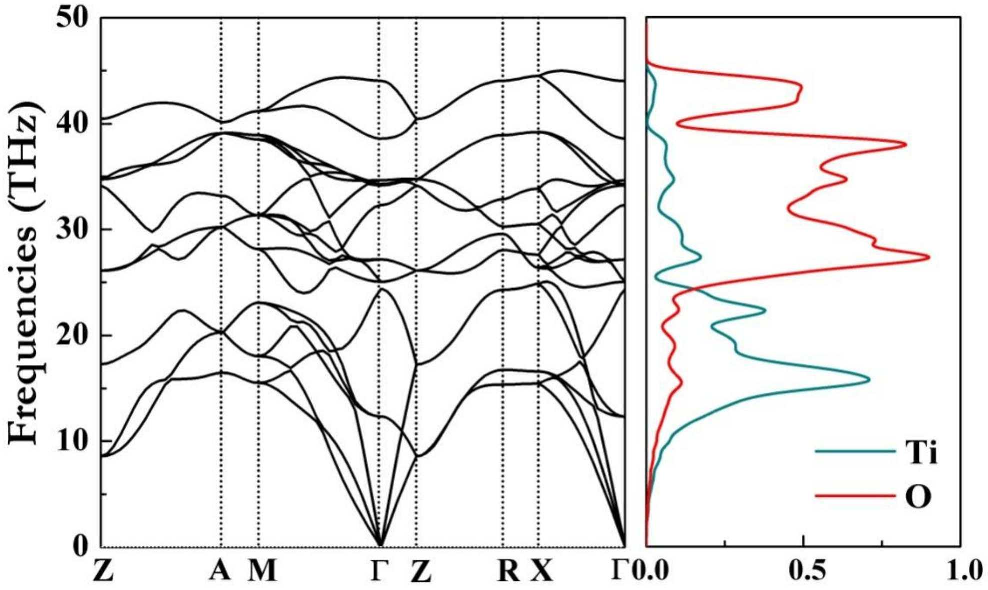
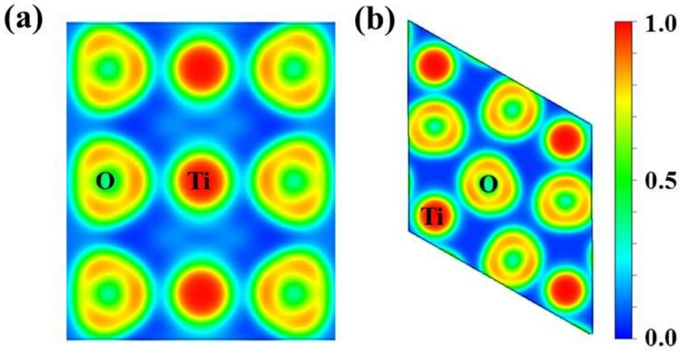
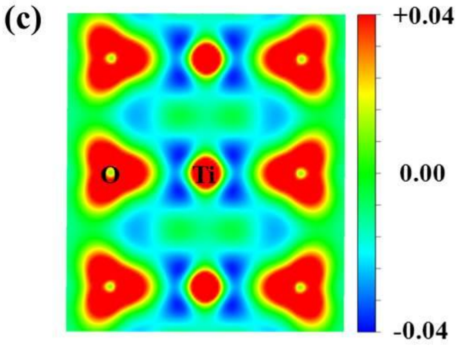


Figure S2. Calculated phonon dispersions (left panel) and projected phonon density of states (right panel) at 700 GPa. The motions of Ti atom dominate mainly the low frequency regimes, while O atoms contribute to the high frequency regimes,



CaC_2-type (010) Fe$_2$P-type (001)



CaC_2-type (010)

Figure S3 (a) and (b) Electron localization function (ELF) plots for CaC_2-type and Fe_2P-type structures at 700 GPa, respectively. (c) difference charge density plot of

CaC_2-type structure at 700 GPa. The difference charge density plot is further supported the charge transfer from Ti atoms to the O atoms.

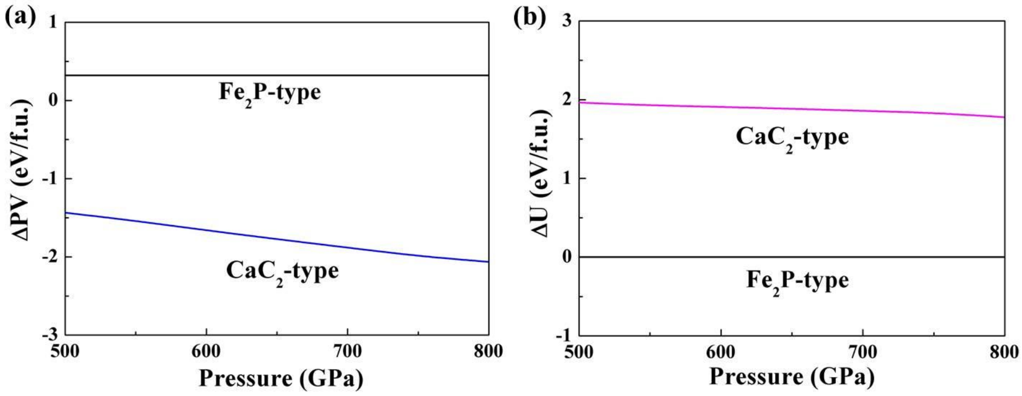


Figure S4 (color online) (a) and (b) PV curve and U curve for CaC_2-type and Fe_2P-type of TiO_2 structures, respectively.

Supplementary Tables

Table S1. Optumized cell parameters *a*, *b*, *c* (**Å**) and volume of Cotunnite and Fe_2P-type TiO_2 at the temperature T = 0 K and selected pressures.

Phase	**Ref.**	**Pressure (GPa)**	**Lattice constant(Å)**			**Volume(Å^3)**
			a	*b*	*c*	
Cotunnite *Pnma* (62)	This work(GGA)	100	4.923	2.856	5.795	40.76
	This work(GGA)	60	5.049	2.938	5.955	44.18
	Expt.[7]	61	5.163	2.989	5.966	46.03
	Other calc.[8]	60	5.028	2.933	5.896	44.28
Fe_2P-type *P*-62*m* (189)	This work(GGA)	160	4.91		2.750	19.12
	Expt.[9]	160	4.863		2.744	
	This work(GGA)	0	5.319		3.126	25.53
	Other calc.[10]	0	5.330		3.127	25.53

Table S2. Calculated structural parameters of the CaC_2-type, Fe_2P-type and Cotunnite TiO_2 at selected pressures.

Phase	**Pressure (GPa)**	**Lattice parameters (Å,)**	**Atomic coordinates (fractional)**			
CaC_2-type ***I4/mmm***	700	$a = b = 2.1985$	Ti(2b)	0.000	0.000	0.500
		$c = 5.3617$	O(4e)	0.000	0.000	0.837
		$\alpha = \beta = \gamma = 90.000$				
Fe_2P-type ***P*-62*m***	200	$a = b = 4.8061$	Ti(2d)	0.333	0.667	0.500
		$c = 2.6976$	Ti(1a)	0.000	0.000	0.000
		$\alpha = \beta = 90.000$	O(3g)	0.000	0.259	0.500
		$\gamma = 120.000$	O(3f)	0.406	0.406	0.000
Cotunnite ***Pnma***	100	$a = 4.9233$	Ti(4c)	-0.758	0.250	-0.625
		$b = 2.8563$	O(4c)	-0.643	0.250	-0.931
		$c = 5.7946$	O(4c)	-0.471	0.750	-0.665
		$\alpha = \beta = \gamma = 90.000$				

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