



Rapid communication

Novel high-pressure phase of ZrO<sub>2</sub>: An *ab initio* prediction

Murat Durandurdu

Department of Materials Science &amp; Nanotechnology Engineering, Abdullah Gül University, Kayseri, 38080, Turkey

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## ABSTRACT

The high-pressure behavior of the orthorhombic cotunnite type ZrO<sub>2</sub> is explored using an *ab initio* constant pressure technique. For the first time, a novel hexagonal phase (Ni<sub>2</sub>In type) within P6<sub>3</sub>/mmc symmetry is predicted through the simulation. The Ni<sub>2</sub>In type crystal is the densest high-pressure phase of ZrO<sub>2</sub> proposed so far and has not been observed in other metal dioxides at high pressure before. The phase transformation is accompanied by a small volume drop and likely to occur around 380 GPa in experiment.

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## 1. Introduction

ZrO<sub>2</sub> adopts a monoclinic baddeleyite structure at ambient conditions and shows a rich variety of crystalline phases at high pressure and temperature conditions. Two phases, a tetragonal (P4<sub>2</sub>/nmc) and a cubic (Fm3m), form at high temperatures. The high-pressure behavior of ZrO<sub>2</sub> is, however, not as clear as its high temperature behavior. Experiments and theoretical investigations have proposed various high pressure phases [1–14] including orthorhombic (Pbcm) [1,2], orthorhombic (Pbca) [3–5], orthorhombic (Pnma) [7,9], orthorhombic-II and orthorhombic-III [4], tetragonal (P4/m, P4<sub>2</sub>/n, P4/mmm, or P4/mbm) [10], tetragonal (MnF<sub>2</sub>) [9], hexagonal [11], orthorhombic (Pbcm) [12] and tetragonal (P4/nmm) [12] phases.

Among these high pressure phases of ZrO<sub>2</sub>, the orthorhombic crystal with space group Pnma, isostructural to the cotunnite (PbCl<sub>2</sub>) phase has attracted particular attention because it is quenchable to ambient conditions [5,8] and suggested as a promising candidate for superhard material. The prediction of new crystalline phases (post-cotunnite) is not only scientific interest but also technological interest because stable or metastable phases might serve as a potential candidate to engineer new materials with desirable properties [15,16]. To date several types of post-cotunnite structure have been proposed for AX<sub>2</sub> type compounds [17–23] but the preference of the cotunnite type ZrO<sub>2</sub> under pressure is still not well established yet. Recent experiment reported the detection of a quenchable Fe<sub>2</sub>P type phase in ZrO<sub>2</sub> [24]. The cotunnite-to-Fe<sub>2</sub>P type phase transformation took place at 175 GPa after heating the sample to 3000 K. This phase transformation was also supported by *ab initio* calculations [24].

In this work, we explore the high-pressure behavior of ZrO<sub>2</sub> using a well-test constant pressure *ab initio* technique. The cotunnite crystal is compressed up to the molecular dynamic (MD) pressure of 2.0 TPa and for the first time a hexagonal phase having P6<sub>3</sub>/mmc symmetry, different than the Fe<sub>2</sub>P type crystal, is predicted through simulation. Regrettably the hexagonal phase is found to be unquenchable.

## 2. Computational method

We used the *ab initio* program SIESTA [25] in the present work since it was successfully applied to investigate the monoclinic baddeleyite structured ZrO<sub>2</sub> under different stress conditions [12,26,27]. The generalized gradient approximation of PBE was adopted to estimate for the exchange-correlation energy [28]. Pseudopotentials were constructed using the Troullier-Martins scheme [29]. The DZP basis set (*s*, *p* and polarized *d* orbitals) was employed. The simulation supercell has 192 atoms with periodic boundary conditions. Γ-point was used for the Brillouin zone integration. The MD simulations were achieved by means of the isoenthalpic-isobaric ensemble (NPH). The Parrinello and Rahman technique [30] was used to control external pressure. Pressure was increased by an increment of 50 GPa. At each applied pressure, the structure was equilibrated with a period of 3000 femtosecond (fs). Each MD time step was 1.0 fs. The unit cell of the cotunnite and new high-pressure crystals was used to calculate the energy–volume relation. The Brillouin zone integration was carried out with 6 × 8 × 6, 8 × 8 × 8, 8 × 8 × 8 k-point mesh for cotunnite, Fe<sub>2</sub>P, and new high-pressure crystals via the Monkhorst and Pack method [31]. The Fermi–Dirac smearing scheme was employed to select the electronic occupations. To visualize the phases and transformation

E-mail address: [murat.durandurdu@agu.edu.tr](mailto:murat.durandurdu@agu.edu.tr)

mechanism, the VESTA program was used [32].

### 3. Results

The KPLOT program [33] is applied to identify symmetry modification at each applied pressure. The cotunnite phase resists up to 500–600 GPa at which point a novel hexagonal structure having the space group  $P6_3/mmc$  is predicted to form. No other phase transition is observed up to the MD simulation pressure of 2.0 TPa. Probably the energy barrier for transforming from the hexagonal phase to a denser phase is too high to see a pressure induced phase transformation in the simulation (see the limitation of the Parrinello–Rahman method below).

The atomic positions and lattice parameters of the hexagonal phase at zero pressure obtained by the fixed volume conjugate gradient relaxation technique are given in Table 1. The hexagonal state has a  $Ni_2In$  type structure (see Fig. 1) and is indeed a subgroup of the cotunnite crystal having an ideal hexagonal closed packed anion lattice [23]. The  $Ni_2In$  type phase is considered as one of possible post-cotunnite phases of some  $AX_2$  type compounds and it has been observed experimentally in some fluorides [17,23] but to our knowledge not in metal dioxides. Therefore its observation in  $ZrO_2$  is particularly important and might lead to new high-pressure research directions in metal dioxides.

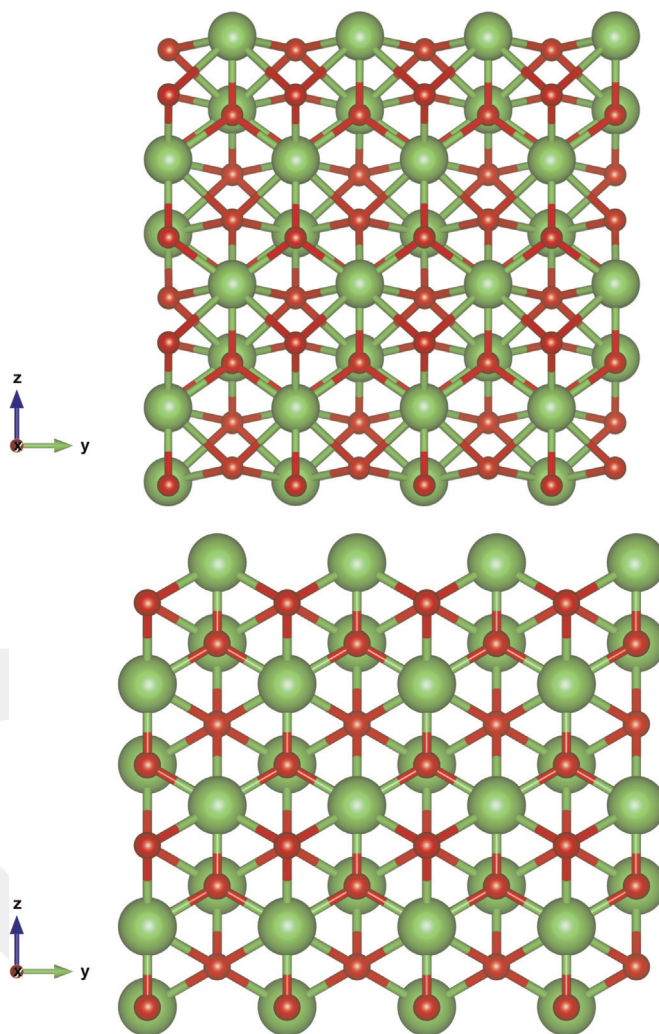
To address the thermodynamic nature of this phase change, we next inspect the variation of volume under pressure. As shown in Fig. 2, the volume decreases monotonically up to 500 GPa and then it shows a fast modification between 500 GPa and 600 GPa. Above 600 GPa, the volume reduces gradually again. Upon pressure release from 650 GPa, the volume increases smoothly and jumps suddenly to a larger value at 150 GPa. At this pressure, the  $Ni_2In$  type crystal transforms back to the cotunnite phase again. Consequently this phase change is a first order phase transformation with a small volume modification and regrettably it is reversible, similar to what has been observed in some fluorides [23].

A surprising observation is that the orthorhombic to  $Ni_2In$  type phase transformation does not involve any shear deformation as indicated by the simulation cell angles that remain null during the transformation. The transformation mechanism is indeed quite simple and due to a noticeable compression along the  $a$ -axis ( $x$ -direction) and an expansion along  $b$ -axis ( $y$ -direction) as seen in Fig. 3. The modification of the lattice parameters further suggests that the compression of the cotunnite crystal is quite anisotropic:  $b$ -axis is more compressible than the other axes until the phase transformation occurs. Owing to the phase change, Zr atoms form a new bond with the second nearest two O atoms in the cotunnite phase located around 3.34 Å at zero-pressure. A schematic representation of transformation mechanism and the formation of two new bonds are illustrated in Fig. 4. As can be understood from the figure, the phase change is mostly due to the drastic rearrangements of O-atoms. In the hexagonal crystal, each Zr atom is elevenfold coordinated while half of the O atoms are fivefold coordinated and the other half are sixfold coordinated. The Zr–O bonds are around 2.20 Å and 2.48 Å. Note that in the  $Fe_2P$  phase, O atoms have a different coordination environment was well. It is

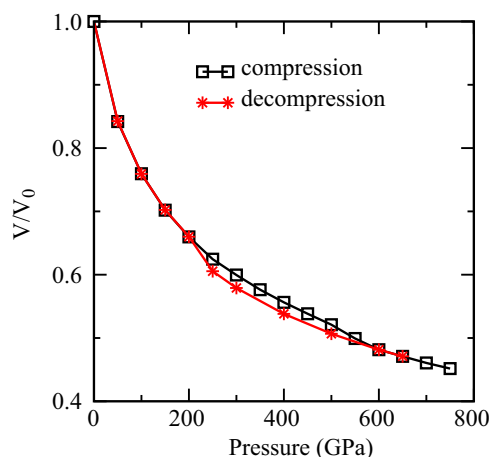
**Table 1**

The atomic fractional coordinates and the lattice parameters of the  $Ni_2In$  type hexagonal phase at zero pressure.

$a(\text{Å})$	$b(\text{Å})$	$c(\text{Å})$		$x$	$y$	$z$
3.82	3.82	4.62	Zr	0.3333	0.6666	0.75
			O	0.3333	0.6666	0.25
			O	0.0000	0.0000	0.00



**Fig. 1.** Cotunnite type phase (top panel) and  $Ni_2In$  type hexagonal phase (bottom panel) viewed along  $x$ -direction.



**Fig. 2.** Normalized pressure–volume curve. For clarity of volume changes, the  $P$ – $V$  data are plotted up to 800 GPa since no phase change observed up to 2.0 TPa in the simulation.

shown that such a feature affects the ionization potential and electron affinities of a material, which can be cooperative in explaining some physical phenomena [34].

A hexagonal structure was obtained in thermally quenched

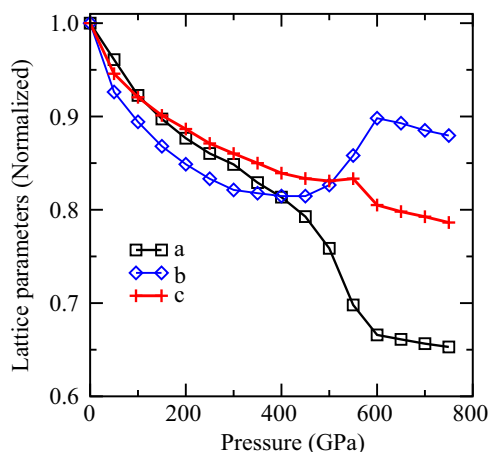


Fig. 3. Normalized lattice parameters as a function of pressure.

ZrO<sub>2</sub> powders in an experimental study before [11]. Yet the hexagonal crystal predicted in the present simulation differs in several ways from it. Namely, our hexagonal phase is elevenfold coordinated and denser than cotunnite (see below) while the experimental one is ninefold coordinated and less dense than cotunnite. Also upon pressure release, our hexagonal phase transforms back to its original structure whereas the experimental one reverts to a monoclinic state.

The Parrinello–Rahman technique appears to be very successful in reproducing experimentally observed high-pressure phases or predicting novel high-pressure phases of materials with *overestimated transition pressures*. The overstated critical pressures are attributed to the simulation conditions, for example, lack of surface effects, ideal structure, fast loading etc. The thermodynamic criterion of equal free Gibbs energies, on the other hand, commonly gives comparable transition pressures and parameters relative to experiments and hence the cotunnite-to-Ni<sub>2</sub>In type phase transformation is further considered from the thermodynamic theorem. For comparison purpose, the cotunnite-to-Fe<sub>2</sub>P type phase change is also investigated. The variation of energy at different volumes (constant volume calculations) is first investigated to calculate static enthalpy,  $H = E + PV$ , where  $E$ ,  $V$  and  $P$  is the energy, volume, and external pressure, respectively. The data presented in Fig. 5 are then fitted to the third-order Birch–Murnaghan equation of state to estimate pressure (using the relation  $P = -dE/dV$ ) and some equilibrium parameters. Finally the enthalpy as a function of pressure is computed. The enthalpy curve of these phases is illustrated in Fig. 6. The critical pressure for the cotunnite-to-Fe<sub>2</sub>P type and the cotunnite-to-Ni<sub>2</sub>In type phase transformations is estimated to be at around 134 GPa and 380 GPa, respectively, which are comparable with a plane wave calculation result of 143 GPa [22] and 389 GPa [35]. Consequently, the cotunnite-to-Ni<sub>2</sub>In type phase transition is anticipated to take place near 380 GPa in experiments as suggested by *ab initio* calculations and involve about 3.5% volume drop. Since temperature increases thermal fluctuations that commonly drive phase transformations, using thermal treatments, the critical pressure of the cotunnite-to-Ni<sub>2</sub>In type phase change might be reduced to lower values in experiments only if no other phase change is favorable at those specific high pressure–temperature ranges. The thermodynamic theorem also suggests a possible phase transition between the Fe<sub>2</sub>P and Ni<sub>2</sub>In type phases at near 370 GPa, which is again accord with the plane wave simulation value of about 350 GPa [35].

The equilibrium atomic volume of the Ni<sub>2</sub>In, Fe<sub>2</sub>P and cotunnite type phases is 29.21 Å<sup>3</sup>/ZrO<sub>2</sub>, 30.17 Å<sup>3</sup>/ZrO<sub>2</sub> and 30.88 Å<sup>3</sup>/ZrO<sub>2</sub>, respectively. The bulk modulus and its pressure derivative are calculated to be 238.7 GPa and 3.86 for the Ni<sub>2</sub>In type crystal, 248 GPa and 3.76 for the Fe<sub>2</sub>P type phase, and 211.3 GPa and 4.01

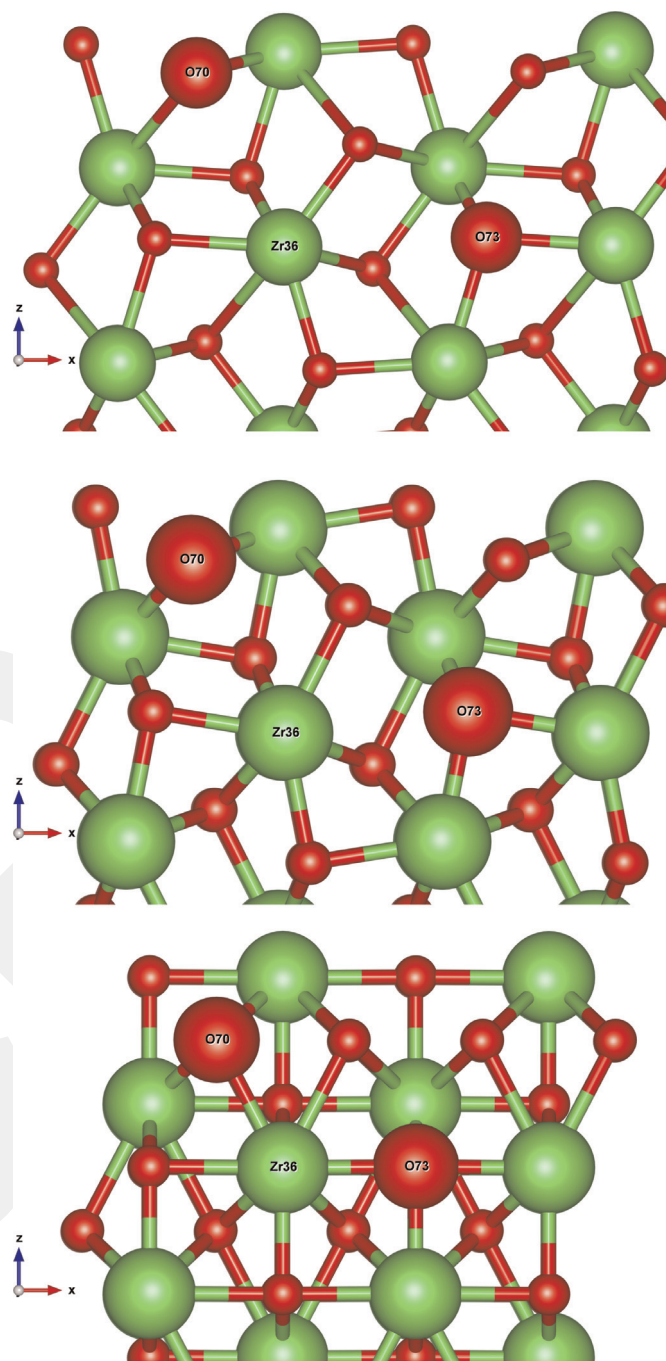


Fig. 4. Transformation mechanism viewed along  $y$ -direction ( $b$ -axis). Cotunnite type phase (top panel), an intermedated phase (middle panel) and Ni<sub>2</sub>In type hexagonal phase (bottom panel). In order to see the formation of new bonds, the size of two O-atoms is enlarged and Zr atom and enlarged O atoms are labeled.

for the cotunnite state. The Ni<sub>2</sub>In phase has a slightly larger bulk modulus than the cotunnite structure. Analogous behavior was reported in fluorides in which the modulus was predicted to be similar to or even less than that of cotunnite phase [23].

#### 4. Conclusions

In summary, we have investigated the high-pressure behavior of the cotunnite type ZrO<sub>2</sub> using a constant pressure *ab initio*

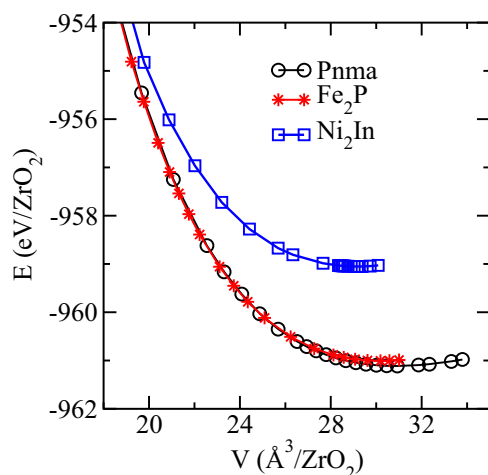


Fig. 5. The energy–volume values of the cotunnite and the  $\text{Ni}_2\text{In}$  type phases obtained from the simulation and fit.

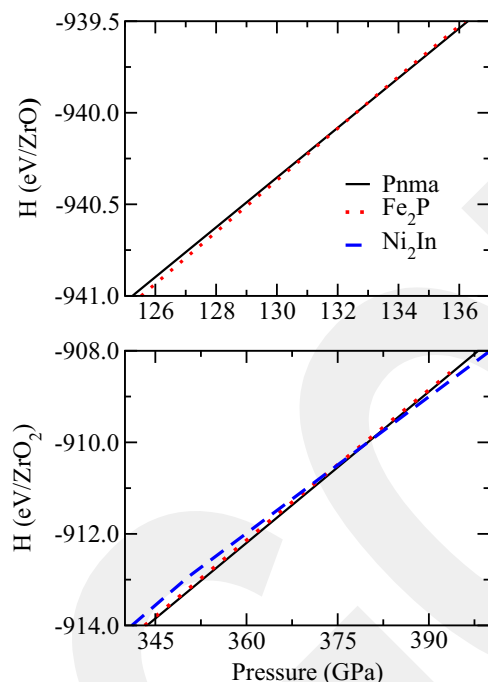


Fig. 6. The calculated enthalpy of the cotunnite and the  $\text{Ni}_2\text{In}$  type structures as a function of pressure.

technique. Among the proposed several post-cotunnite phases,  $\text{ZrO}_2$  adopts the  $\text{Ni}_2\text{In}$  type structure at high pressure. The preferred mechanism in  $\text{ZrO}_2$  appears to be different from the other metal dioxides such as  $\text{TiO}_2$  and  $\text{TeO}_2$  (Refs. [20–22]) but similar to that of some fluorides [17,23]. Additional studies on the other

dioxides via the same simulation technique are absolutely desirable to recognize the physical origin of their different tendency at high pressures.

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