Study of the crystal structure and mechanical properties of ZrTi$_2$ under pressure

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Abstract.

The pressure-induced modifications in the crystal structure and mechanical properties of ZrTi$_2$ have been systematically studied by using the first-principle methods. The calculation of the enthalpy of formation was carried out using an efficient evolutionary algorithm at different pressures, as implemented in the USPEX code. The results revealed that the $P6_{3}mm$ (space group #183) are stable at 0 GPa and it change rapidly to space group #164 close to 0 GPa and then at a pressure around 2 GPa to up around 60 GPa, the most stable phase is the crystal structure $P6_{3}m1$ with the space group #194. Finally, the space group #164 returns to its stability between 60 and 100 GPa.

The elastic constants obtained suggest that $\alpha$-ZrTi$_2$ (space group #194), $P-3m1$ (space group #164), and $P6_{3}mm$ (space group #183) are mechanically stable at 0 GPa, while the space group #194 and #164 are stable in the other pressures evaluated (25, 50, 75, and 100 GPa). Finally, the $\beta$-ZrTi$_2$ phase (space group #229) and $\omega$-ZrTi$_2$ (space group #191) showed a high enthalpy of formation with respect the other phases analyzed.

1. Introduction

Group IV transition metals and their alloys have attracted great scientific and technological interest, due to its strength-to-weight ratio, high rigidity-to-weight ratio, good biocompatibility, low neutron-capture, and excellent corrosion resistance [1,2]. Particularly, Ti-Zr alloys, as one combination of the elements of group IV, have potential uses in aerospace, medical, and nuclear industries [1–3].

The use of titanium (Ti) alloys is increasing due to their excellent mechanical strength, corrosion resistance, and good biocompatibility [4]. These properties are attributable mainly to the formation of a stable titanium oxide (TiO$_2$) layer on the surface [5]. However, the mechanical strength of commercially pure titanium is insufficient for its use as screw, pin, or artificial hip joints [5]. On the other hand, zirconium (Zr) is known to have chemical properties similar to those of titanium and it belong to the same group of this one in the periodic table [5]. It is remarkable that Zr compounds have no toxic effects on the human body [5,6]. For instance, Kobayashi et al. prepared a Ti-Zr binary alloy as a material for use in medical devices, such as hip joints and bone plates [6].

Titanium and zirconium at normal conditions are also stable in the hexagonal close-packed structure (HCP, $\alpha$ phase) and transform to the body-centered cubic (BCC, $\beta$ phase) above 1155
and 1136 K, respectively. The hexagonal $\omega$ phase becomes stable for both metals under pressures above to 2 GPa at room temperature [7]. Ti-Zr alloys form homogeneous solid solutions in solid state [1]. They are of considerable interest because those alloys have a tight $d$ band in the midst of a broad $sp$ band, which has a great impact on their electronic and superconducting properties. Electronic transfer between the free-electron $s$ band and the tight $d$ band is considered to be the driving force behind many structural transformations [1,8].

2. Computational method

Prediction of the most energetically favorable crystal structures of ZrTi$_2$ in the pressure range from 0, 25, 50, 75, and 100 GPa was carried out using the USPEX (Universal Structure Predictor: Evolutionary Xtallography) code and ab-initio total-energy calculations. USPEX code can predict stable chemical compositions and corresponding crystal structures, given just the names of the chemical elements [9–14]. This code can also be used for finding low-energy metastable phases, as well as stable structures of nanoparticles, surface reconstructions, molecular packings in organic crystals, and for searching for materials with desired physical (mechanical, electronic) properties [9,10,10–15]. The USPEX code is based on an efficient evolutionary algorithm developed by A.R. Oganov’s group. Currently, the effectiveness of this method has been strongly confirmed by recent successes in predicting high-pressure structures of various systems, ranging from fundamental elements to binary and ternary compounds [13,14,16]. On the other hand, the fixed-composition search for ZrTi$_2$ was performed using different cells containing one and two chemical formula units (f.u.). The crystal structures were produced randomly in the first generation. The subsequent generation was created from 50% of the lowest-enthalpy structures of the preceding generation (population size: 20–30 structures). New structures were created by heredity (50%), symmetric random (20%), permutation (10%), and lattice mutation (10%) operations in the next generations. The best structure of each generation was also carried over to the next generation. The calculation stops when the best structure does not change for more than 3-5 generations.

The total energy and electronic structure calculations were carried out by the VASP code (Vienna ab-initio simulation package) [17] using the density functional theory (DTF) [18] within the generalized gradient approximation (GGA) and the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional. Projector augmented wave (PAW) method was used to describe the core electrons and their effect on valence orbitals. The pseudopotentials of Ti and Zr elements were treated their respective orbitals $3p^{6}3d^{2}4s^{2}$ and $4s^{2}4p^{6}4d^{2}5s^{2}$ as valence electronic configurations. The cut-off energy for plane-wave was set to 500 eV. The $k$–point mesh with resolution of $2\pi^{*}0.06\text{Å}^{-1}$ in reciprocal space were used for all structures to ensure the sufficient convergence in total energy during optimization.

For USPEX, the maximum total numbers of atoms in the unit cell were limited to 6 (2 atoms of Zr and 4 atoms of Ti). According to the previous studies [1], three possible structures were chosen to study with USPEX: $\alpha$–ZrTi$_2$ with hcp structure ($P63/mmc$, space group #194), $\omega$–ZrTi$_2$ with hexagonal AlB$_2$ structure ($P6/mmm$, space group #191), and $\beta$–ZrTi$_2$ with bcc structure ($Im3m$, space group #229). Additionally, three structures obtained with same software were used to refine the search for stable structures: $P6mm$ (space group #183), $P4mcm$ (space group #127) and $P-3m1$ (space group #164). All of aforementioned structures were studied in fixed-composition with their respective space group.

The enthalpy of the formation of ZrTi$_2$ was calculated as

$$\Delta H_f (ZrTi_2) = E_{ZrTi_2} - \frac{1}{3}E_{Zr} - \frac{2}{3}E_{Ti}$$

where $E_{ZrTi_2}$, $E_{Zr}$, and $E_{Ti}$ are the total energies of ZrTi$_2$, zirconium and titanium, respectively. The implication of this definition is that if the $\Delta H_f$ is negative, the considered
compound is thermodynamically stable; while it is positive, the compound is thermodynamically unstable. After the structure search, the constant elastics of ZrTi$_2$ were calculated by performing finite distortions of the lattice and deriving the elastic constants from the strain-stress relationship. For these calculations, Based on these constants, the mechanical stability of the predicted phases was examined thought Born stability criteria. Finally, the structures of interest were graphed with the xcryden software [19].

3. Results and discussion
Pressure, as a fundamental physical variable, notably affects the chemical and physical properties of materials. After analyzing the six structures with the software USPEX and DTF method, the enthalpy of formation (per formula unit, f.u.) curves relative to ZrTi$_2$ compound as a function of the studied pressures at 0 K for the lowest-energy structures are shown in figure 1(a). It is clearly seen that ZrTi$_2$ compound is thermodynamically stable in the evaluated pressures. In the figure 1(a), the four structures with the lowest enthalpies showed that the calculated values of enthalpy of formation at 0 GPa are very close, as observed in the first point of the curves in figure 1. These values of enthalpy of formation for the space groups #183, #164, #191, and #194 were -1.009, -1.0078, -1.0066 and -0.9985 eV/atom*f.u., respectively. It is important to highlight that the calculations performed by the USPEX software, the phase $\beta$–ZrTi$_2$ (space group #229) presented a high enthalpy of formation with respect to the other selected space groups.

According to figure 1, the first structure more stable at 0 GPa is the space group #183, which changes to #164 close to 0 GPa and then at a pressure around 2 GPa to up around 60 GPa, the most stable phase is the crystal structure $P63/mmc$ with the space group #194. Above the latter mentioned pressure, the space group #164 returns to its stability until the maximum pressure studied (100 GPa). In order to analyze the pressure behavior of ZrTi$_2$ compound, figure 1(b) shows the relation of volume as a function of pressure according to the space groups #191, #164, and #194. The calculated volumes are slightly bigger than the theoretical and experimental data showed in the previous study of researchers as Yuan, X. L. et. al. [1].

![Figure 1](merged-image.png)

**Figure 1.** (a) Enthalpies of formation as a function of the pressure with respect to the $E_{Zr} + E_{Ti}$ (eq) and (b) volume as a function of pressure for ZrTi$_2$ compound.

Predicted four novel structures of ZrTi$_2$ compound with the lowest enthalpies at 0 GPa are presented in figure 2, and their structural parameters are presented in table 1. Figure 2(a) shows
the P-3m1 phase (space group #164), which displays four atoms of Ti located in the center of the structure and two in the corner with a separation of 2.7201Å for Ti-Ti and 3.111Å for Ti-Zr. The α-ZrTi2 phase (P63/mmc, #194) is shown in figure 1(b). The Zr atoms, presented a position of (1/3, 2/3, 1/2) and (2/3, 1/3, 1/2), are similar to the proposed by Yuan [1] and the structure showed a separation of 3.9958Å for Zr-Zr bond length and 3.0878Å for Zr-Ti. Figure 1(c) shows the ω-ZrTi2 phase (P6/mmm, #191), which presented a lowest enthalpy with 3 atoms per cell than the structure calculated with 6 atoms per cell at 0 GPa and 25 GPa. The separation of the two Ti atoms in the center of the structure #191 was 2.7113Å, while the Zr-Ti bond length was 3.1024Å. Finally, the P6mm phase (#183) of the hexagonal system is shown in the figure 1(d). This structure presented four Zr atoms in the center of crystal with a separation of 2.719Å for Ti-Ti bond length, 3.1105Å for Zr-Ti bond length, and 3.0196Å for Zr-Zr bond length.

Table 1. Structural information of four stable ZrTi2 structures at 0 GPa. Lattice constants are presented in Å

| Phase         | Space Group | a    | b    | c    | α   | β   | γ   | System    |
|---------------|-------------|------|------|------|-----|-----|-----|-----------|
| P-3m1         | #164        | 4.711| 4.711| 6.042| 90  | 90  | 60  | Trigonal  |
| P63/mmc       | #194        | 4.709| 4.709| 5.857| 90  | 90  | 120 | Hexagonal |
| P6/mmm        | #191        | 4.666| 5.605| 5.605| 65.04| 114.15| 114.28| Hexagonal |
| P6mm          | #183        | 4.710| 4.710| 6.039| 90  | 90  | 120 | Hexagonal |

3.1. Elastic properties

Elastic constants determine the mechanical properties of materials, such as Young’s modulus, bulk modulus and shear modulus. For hexagonal crystals found in this study (space group #183 and #194), the mechanical stability conditions of crystal can be written as [20]: $C_{44} > 0$, $C_{11} > |C_{12}|$, $(C_{11}+C_{12})C_{33} > 2C_{13}^2$. For the P-3m1 structure with space group #164 (trigonal crystal system), the rhombohedral (I) system was used to evaluated its stability according the Laue groups [20]. The four necessary and sufficient conditions for rhombohedral (I) system are: $C_{44} > 0$, $C_{11} > |C_{12}|$, $\frac{1}{2}(C_{11}+C_{12})C_{33} > C_{13}^2$, and $C_{14}^2 < \frac{1}{2}C_{44}(C_{11}-C_{12}) = C_{44}C_{66}$.

The independent components as a function of pressure are listed in table 2. All of structures satisfied the criteria of mechanical stability of Born, which means that these structures are mechanically stable and could be used in mechanical engineering applications.
Table 2. The calculated independent elastic constants $C_{ij}$ (GPa) as a function of pressure (P) for space group #164, #194 and #183.

| Phase       | P (GPa) | $C_{11}$ | $C_{22}$ | $C_{33}$ | $C_{14}$ | $C_{66}$ | $C_{12}$ | $C_{13}$ |
|-------------|---------|----------|----------|----------|----------|----------|----------|----------|
| $P-3m1$ (#164) | 0       | 162.6    | 162.6    | 196.8    | 50.5     | 39.2     | 84.1     | 58.6     |
|             | 25      | 200      | 200      | 281.7    | 45.2     | 55.5     | 88.8     | 81.4     |
|             | 50      | 341.1    | 343.4    | 388.3    | 37.9     | 93.3     | 151.8    | 104.3    |
|             | 75      | 200.8    | 202      | 212.2    | 50.7     | 52.4     | 96.8     | 89.6     |
|             | 100     | 360.9    | 349.8    | 310.1    | 57.7     | 94.1     | 162.8    | 155.9    |
| $P63/mmc$ (#194) | 0       | 185.7    | 185.7    | 229.7    | 42.4     | 54       | 77.7     | 50.1     |
|             | 25      | 273.6    | 273.6    | 324.4    | 44       | 76.4     | 120.8    | 83.2     |
|             | 50      | 351.6    | 351.6    | 408.4    | 38.9     | 93.6     | 164.4    | 102.9    |
|             | 75      | 420.1    | 420.1    | 460.1    | 26.9     | 104.9    | 210.2    | 124.5    |
|             | 100     | 497.2    | 497.2    | 510.3    | 4.4      | 115.3    | 266.5    | 139.8    |
| $P6mm$ (#183) | 0       | 161.7    | 161.7    | 197      | 50.5     | 39.2     | 83.3     | 58.5     |

3.2. Electronic properties
The total density of state (DOS) for ZrTi$_2$ compound (space groups: #164, #194, and #183) at different pressure is shown in figure 3. In general, the DOSs for different pressures show a similar qualitatively behavior, and the ZrTi$_2$ compound remains its metallic character with the increase in the pressure. The different phases of the ZrTi$_2$ compound (#164, #194, and #183) also show no significant alteration of its electronic structure. However, for the space group #164 at pressure of 75 GPa (as shown in figure 3(a)), the compound slightly increase its electronic transport properties and could be a better electrical conductor. This behavior is due to the fact that this phase shows a greater number of states available at the Fermi level (Vertical dashed line, figure 3(a)) compared with the other pressures evaluated in the same space group (#164).

Figure 3. Electronic density of states for the phases (a) $P-3m1$, space group #164 (b) $P63/mmc$, space group #194 (c) $P6mm$, space group #183 of ZrTi$_2$ compound. Vertical dashed line represents the Fermi level.

4. Conclusion
In summary, the theoretical study was performed for the possible phases of ZrTi$_2$ at pressure up to 100 GPa using USPEX code in combination with first-principles calculations. It has
been found that the $\alpha$–ZrTi$_2$ phase (space group #194), $P-3m1$ (space group #164) and $P6mm$ (space group #183) are mechanically stable at 0 GPa, while the space group #194 and #164 are stable in the other pressures evaluated (25, 50, 75, and 100 GPa). Finally, features above indicate that the phases of ZrTi$_2$ compounds under pressure up to 100 GPa possess the necessary stability for applications in aerospace and nuclear industries. In addition, the electronic structure calculations show that the ZrTi$_2$ compound preserves its metallic properties even at high pressures.

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