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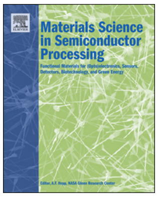

Structural, elastic, and mechanical properties of germanium dioxide from first-principles calculations

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ABSTRACT

The structural, elastic, and mechanical properties of the available experimental and theoretical phases of germanium dioxide (GeO_2) are investigated. Germanium dioxide (GeO_2) is an important material in science and technology due to its wide-ranging applications, and many researches have been proposed to investigate its crystalline polymorphs. Although many phases have been reported, the systematic analysis and comparison of various phases are still lacking. In our paper, the energy, structural, elastic, mechanical properties and mechanical stability of the available experimental and theoretical phases of GeO_2 are investigated from first-principles within the density-functional theory (DFT) plus the local density approximation. The order of increasing ground-state energy is as follows: $P4_2/mnm$, $Pnnm$, $P2_1/c$, $Pbcn$, $Pnma$, $P3_221$ ($P3_121$), $P4_12_12$, $C2/c$, $P6_3/mmc$, $Pa\overline{3}$, $P4/mcc$, $P6_222$, $C222_1$, $Pn\overline{3}m$ and $P\overline{6}2m$, indicating that tetragonal $P4_2/mnm$ phase and hexagonal Fe_2P-type $P\overline{6}2m$ phase have minimum and maximal ground-state energy, respectively. The structural parameters, elastic constants, bulk modulus, shear modulus, Young's modulus, Poisson's ratio, Lamé's constants as well as mechanical stability have been obtained and discussed, indicating that $P6_222$ and $P\overline{6}2m$ phases are unstable under zero pressure. These results may help to understand GeO_2 for future applications.

1. Introduction

Germanium oxide (GeO_2), a chemical analog of silicon dioxide (SiO_2), has been studied intensively due to its interesting and various phase transitions [1] as well as its many more applications such as optical-fiber materials [2,3], resistive random access memory [4], multifarious GeO_2-based glasses [5–8], microelectronic devices [9,10], piezoelectric materials [11,12]. The high temperature and high pressure phase transitions of GeO_2 have attracted a great deal of attention because of its scientific interest and technological significance (e.g., a pressure-driven amorphous-amorphous transformations (AATs) in GeO_2 for glass theory [13–15]).

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At ambient temperature and pressure, GeO_2 occurs in three stable phases: amorphous phase (a-GeO_2), α-quartz phase (α-GeO_2 or q-GeO_2) and rutile phase (r-GeO_2). For a-GeO_2 with a tetrahedral network based on corner-shared GeO_4 units at ambient pressure [15], the nature of pressure-induced AATs is a tremendous challenge and attracts more and more scientists to understand the glass behavior under pressure [13–23]. Itie et al. [24] observed a pressure-induced AAT from fourfold to sixfold coordination (from GeO_4 units to GeO_6 units) at 6.6–8.0 GPa and shown a first-order phase transition in a-GeO_2 due to the presence of sixfold coordinated Ge, which has been confirmed at 6–13 GPa by using a Raman spectroscopic study [25]. Later studies have presented a two-domain region composed of both GeO_4 and GeO_6 units at 4–7 GPa [26,27]. Between 6 and 10 GPa, a new metastable, intermediate structure with a constant average coordination of ~5 has been reported [28], and *in situ* inelastic x-ray-scattering measurements at the oxygen *K*-edge were consistent with the fivefold coordinated Ge in a-GeO_2 at 5–8 GPa [15]. A fully sixfold coordinated glass has been measured at 15 GPa [28], which was in agreement with the nearly complete transition of octahedral form at 13 GPa [20], but recent Paris-Edinburgh press coupled to EXAFS spectroscopy study shown that the structural change of a-GeO_2 is quite continuous and gradual, and the full octahedral sate is not reached at 13 GPa [14]. Under higher pressure range between 13 and 30 GPa, Baldini et al. [13] observed a mixture of fourfold and fivefold coordinated germanium-centered polyhedra. As the pressure was further increased to 160 GPa, the coordination numbers of Ge changed as follows: from 6 to 6.3 at 40–60 GPa, from 6.5 to 7.4 at 90–140 GPa, and finally to 7.6 at 160 GPa by using molecular dynamics simulations [16]. It can be seen that the mechanism of AATs remain confused. Furthermore, the challenges of pressure-driven crystalline-amorphous transformations (CATs) [29] and pressure-driven amorphous-crystalline transformations (ACTs) [1,16] are also interesting and wondering. For trigonal α-GeO_2 ($P3_121$, D_3^4, $Z=3$) with the Ge atoms in 3a position (u,0,1/3) and O atoms in the general 6c position (x,y,z) [11] (or the space group and local symmetry of α-GeO_2 are $P3_221$ and D_3^6, respectively [1,12]), its structure is characterized by a GeO_4 tetrahedral framework, where a Ge atom is surrounded by four O atoms [13]. For tetragonal r-GeO_2 ($P4_2/mnm$, D_{4h}^{14}, $Z=2$) with the Ge atoms in 2a position (0,0,0) and O atoms in 4f position (u,u,0), its structure consists of chains of GeO_6 octahedra and each pair shares opposite edges, where each Ge atom is surrounded by a distorted octahedron of six O atoms and each O atom is bonded to three Ge atoms arranged as corners of an equilateral triangle in a planar trigonal configuration [30].

The pressure-driven crystalline-crystalline transformations (CCTs) in GeO_2 are reported largely both experimentally [31–40] and theoretically [41,42] (some experiments of pressure-driven CCTs combine with high temperature), and many new phases have been addressed such as hexagonal Fe_2N-type (the disordered niccolite (d-NiAs-type), $P6_3/mmc$, D_{6h}^4, $Z=2$) [32,34], orthorhombic post-$CaCl_2$-type ($Pnnm$, D_{2h}^{12}, $Z=2$) [32,34,35,37–41], orthorhombic α-PbO_2-type ($Pbcn$, D_{2h}^{14}, $Z=4$) [32,37–39,41], cubic pyrite (modified-fluorite) FeS_2-type ($Pa\overline{3}$, T_h^6, $Z=4$) [32,38,41,42], monoclinic distorted rutile-type ($P2_1/c$, C_{2h}^5, $Z=6$) [33,34,40], orthorhombic cotunnite α-$PbCl_2$-type ($Pnma$, D_{2h}^{16}, $Z=4$) [42], hexagonal Fe_2P-type ($P\overline{6}2m$, D_{3h}^3, $Z=3$) [42]. Haines et al. [34] reported that α-GeO_2 undergone a transition to $P2_1/c$ phase above 6 GPa at room temperature, which is metastable up to at least 50 GPa at room temperature. However, upon heating it transforms to r-GeO_2 at pressure up to 22 GPa, then forms a mixture of $Pnnm$ and $P6_3/mmc$ phases at 43 GPa [34]. Prakapenka et al. [37] also found a transition from α-GeO_2 to $P2_1/c$ phase above 7 GPa, and it was observed to at least 52 GPa at room temperature. During laser heating to ~1600 K, it transforms to $Pnnm$ phase above 36.4 GPa and $Pbcn$ phase above 41 GPa [37]. The high pressure and high temperature structural transformations of GeO_2 have been shown [32]: (amorphous or α-quartz)⇒d-NiAs⇒rutile⇒$CaCl_2$⇒α-PbO_2⇒pyrite types, where the d-NiAs phase exists in a narrow temperature interval 1000–1300 K. Theoretically, Łodziana et al. [41] shown that the pressure-induced CCTs in GeO_2 are rutile⇒(~19 GPa)⇒$CaCl_2$⇒(36 GPa)⇒α-PbO_2⇒(65.5 GPa)⇒pyrite types by using a density functional theory approach. Recently, in the further multimegabar pressure region, two high-pressure phase transitions (FeS_2⇒(~300 GPa)⇒α-$PbCl_2$⇒(~600 GPa)⇒ Fe_2P-types) have been discovered by using first-principles calculations [42].

Besides above phases, there are other structures in GeO_2, which have been synthesized or calculated. Sharma shown that α-GeO_2 transformed to hexagonal β-quartz-type ($P6_222$, D_6^4, $Z=3$) at ~1050 K [43]. In 1971, Seifert et al. [44] discovered tetragonal α-cristobalite phase ($P4_12_12$, D_4^4, $Z=4$) with the Ge atoms in 4a position (0.328,0.328,0) and O atoms in 8b position (0.255,0.166,0.215), which has been calculated by using quantum mechanical ab initio study [45]. Lately, a novel low temperature tetragonal phase l-GeO_2 ($P4/mcc$, D_{4h}^2, $Z=20$) has been synthesized under hydrothermal conditions, where the alternate linking of D4R units and GeO_4 tetrahedra formed the 1D 12-member ring channels along the [001] direction [46]. Theoretically, monoclinic coesite ($C2/c$, C_{2h}^6, $Z=16$) [47] and cubic inverse Ag_2O ($Pn\overline{3}m$, O_h^4, $Z=2$) [48] structures have been investigated within the framework of density functional theory. The conventional unit cell of monoclinic coesite phase contains 16 GeO_2 molecules and the primitive cell includes 8 GeO_2 molecules. The inverse Ag_2O phase of SiO_2 has been reported [49], and this structure with two fourfold-coordinated Ge atoms occupying the 2*a* site and four bridging O atoms occupying the 4*b* site has been applied in GeO_2 [48]. The various GeO_2 phases [50,51] including the hypothetical phases are so much interesting, which are shown in Fig. 1.

Though its widespread use and technological importance induce the quite enhanced interests, its experimental studies face enormous challenges due to so many high-temperature/high-pressure phases that are not stable at ambient conditions. It is therefore difficult to measure physical properties such as elasticity at extreme conditions, which results in that many basically mechanical aspects of GeO_2 have not been fully elucidated. More theoretical works using the accurate density-functional theory (DFT) to describe the related physical properties are desirable. This is therefore the main purpose of this work. We describe results of a detailed study of the structural, elastic, and mechanical properties and mechanical stability of these phases; we believe this will provide useful insights for future experimental work.