

High-pressure Synthesis of α -PbO₂-type Phase of GeO₂

V. Prakapenka,¹ G. Shen,¹ L. Dubrovinsky,² M. Rivers,¹ S. Sutton¹

¹Consortium for Advanced Radiation Sources (CARS),
The University of Chicago, Chicago, IL, U.S.A.

²Bayerisches Geoinstitut, Universität Bayreuth, Bayreuth, Germany

Introduction

The high-pressure behavior of both the α -quartz-type and rutile-type phases of GeO₂ has been studied intensively for the last three decades because of its industrial applications and its analogy to geologically important silica at relatively moderate pressures [1]. However, there are inconsistencies in the results of high-pressure phase transformations of GeO₂ reported by different groups.

Recent *ab initio* calculations predict the following sequence of phase transformations of GeO₂: rutile \Rightarrow (19 GPa) CaCl₂ \Rightarrow (36 GPa) α -PbO₂ \Rightarrow (65.5 GPa) Pa-3 (pyrite) [2]. Such phase transitions were either observed or theoretically predicted for silica SiO₂ [3-5]. A second-order transition from the rutile-type to the CaCl₂-type phase of GeO₂ has been reported at 25-27 GPa and room temperature [6-8]. An orthorhombic high-pressure phase of GeO₂ was synthesized at pressure of \sim 50 GPa and 1300K by Ming and Manghnani [9]. However, according to Ming and Manghnani [9], the x-ray diffraction patterns of quenched samples are not the α -PbO₂ phase of GeO₂. Evidence of the coexistence of rutile-type and disordered Fe₂N-type structures of GeO₂ up to 32 GPa after heating of vitreous GeO₂ at \sim 1300K have also been reported [9, 10]. Compression of rutile-structured GeO₂ to \sim 36 GPa and subsequent laser annealing at \sim 1300K, as described by Haines et al. [7], also did not result in the transformation of CaCl₂-structured GeO₂ to the α -PbO₂-type phase. Laser heating above 43 GPa of both monoclinic structured (α -quartz type GeO₂ starting material) and CaCl₂-type structured phases (rutile or vitreous glass starting materials) resulted in a mixture of the CaCl₂-type and Fe₂N-type phases [11]. Ono et al. [8] observed only the CaCl₂-type post-rutile phase at pressures up to 45 GPa and temperatures up to 2300K. We can see that, despite extensive studies of GeO₂, high-pressure polymorphism of GeO₂ remains unclear. No evidence of the theoretically predicted α -PbO₂ phase has been reported. This report provides information on *in situ* x-ray studies of phase transformations of GeO₂ at high pressures and temperatures to α -PbO₂-type GeO₂ from the CaCl₂-structured phase. The detailed description of the results can be found in Refs. 12 and 13].

Methods and Materials

In our high-pressure experiments, α -quartz-type GeO₂ powder (Alfa, purity 99.9999%) was used. Various types of diamond anvil cells (membrane, symmetrical, and four-pin) were used for pressure generation up to \sim 60 GPa. The samples were loaded in the 100- to 150- μ m holes in stainless steel or rhenium gaskets pre-indented to a thickness of 30 to 40 μ m. Platinum powder of 1-3 wt% (Aldrich, purity 99.9%) was mixed with the GeO₂ in order to absorb the laser radiation and to measure pressures by using its equation of state [14]. Ruby luminescence was also used for pressure measurements at room temperature [15].

High-resolution angle-dispersive x-ray diffraction experiments were performed at GeoSoilEnviroCARS (GSECORS sector) at the APS by using an on-line image plate or a charge-coupled device (CCD) detector. The double-sided laser-heating technique with a laser spot of 20 to 40 μ m was used [16]. Details of the experiments are described elsewhere [17].

Results

The high-pressure orthorhombic phase of GeO₂ with CaCl₂-type structure (space group *Pnmm*, *Z* = 2) was synthesised from α -quartz-type GeO₂ powder pressurized to 36 GPa after laser heating for \sim 10 minutes at \sim 1600K. Upon further compression to 41 GPa and laser heating at \sim 1600K, the reflections from a new high-pressure phase appeared (Fig. 1). The relative intensities of the reflections corresponding to the CaCl₂-structured phase decreased with increasing pressure to 43 GPa. Above 44 GPa, the diffraction intensities from the new phase were greater than those from the CaCl₂-type phase, although co-existence of both phases was observed up to 60 GPa.

The new phase can be indexed as the α -PbO₂-type structure. To determine the stability field of the α -PbO₂-type phase, a reversal experiment was conducted, and the pressure was released from 44.5 to 41.3 GPa. After laser heating at \sim 1600K, the relative intensity of α -PbO₂ reflections decreased by a factor of \sim 15. In a separate experiment, heating of the monoclinic P2₁/c-type phase of GeO₂ at 39.5 GPa and \sim 1600K resulted in almost the same ratio of α -PbO₂-type to CaCl₂-type phases as the ratio for the decompressed and heated one at 41.3 GPa. Upon decompression at room temperature

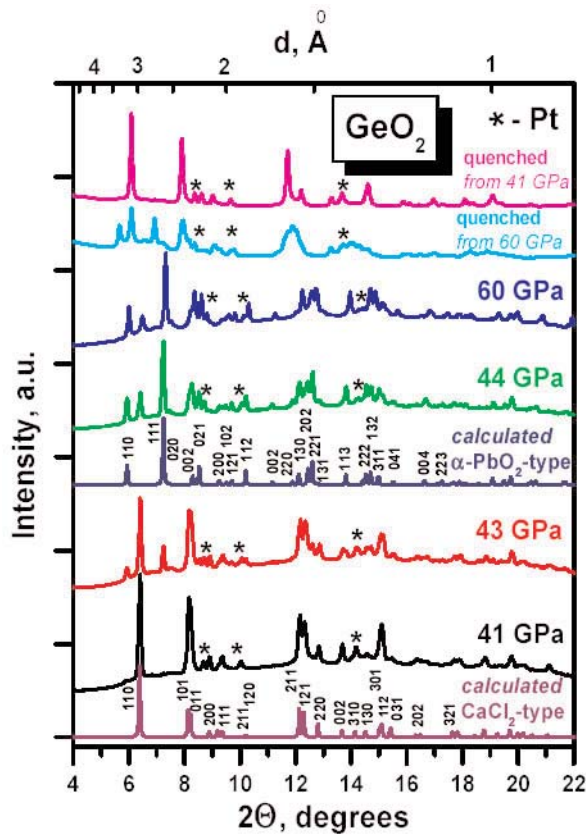


FIG. 1. High-pressure-induced transformation of CaCl_2 -type GeO_2 to $\alpha\text{-PbO}_2$ -type phase after heating for ~ 20 minutes at different temperatures. Two bottom lines are theoretically calculated based on CaCl_2 -type and $\alpha\text{-PbO}_2$ -type structures.

from 60 to 29 GPa, the proportion of CaCl_2 -type and $\alpha\text{-PbO}_2$ -type of GeO_2 was not changed, but transformation of the CaCl_2 -type to the rutile-type structure was observed at ~ 27 GPa. At ambient pressure, a mixture of rutile-type and $\alpha\text{-PbO}_2$ -type structures were detected in almost equal proportions, with molar volumes of $16.65 \pm 0.05 \text{ cm}^3/\text{mol}$ and $16.41 \pm 0.08 \text{ cm}^3/\text{mol}$, respectively.

Discussion

The crystal structure of the new phase of $\alpha\text{-PbO}_2$ ($Pbcn$ space group symmetry) can be described in terms of an hcp packing of oxygen with one-half of the available octahedral interstices occupied by germanium ions to form 2×2 zigzag chains of GeO_6 edge-sharing octahedra (Fig. 2). In the case of the CaCl_2 ($Pnmm$) or rutile ($P4_2/mnm$) structures, germanium ions are arranged in such a way as to generate straight chains of edge-sharing octahedra, which are corner-linked to form a 3-D network with hcp or distorted hcp arrays of oxygen, respectively (Fig. 3) [18]. The molar volume versus pressure data were fitted by using a third-order

Birch-Murnaghan equation of state with K' fixed to 4 [19]. The fit gave values of the bulk modulus for $\alpha\text{-PbO}_2$ and rutile-type phases of $256 \pm 0.2 \text{ GPa}$ and $247 \pm 0.3 \text{ GPa}$, respectively, in good agreement with the bulk modulus of $250 \pm 0.9 \text{ GPa}$ for the rutile-type phase of GeO_2 reported by Haines [7].

In contrast to the rutile/ CaCl_2 -type second-order phase transition (when tetragonal symmetry breaks due

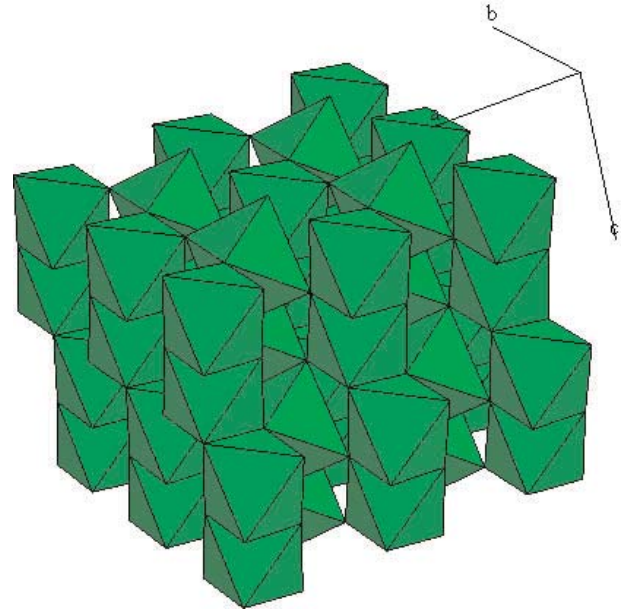


FIG. 2. Representation of the $\alpha\text{-PbO}_2$ -type structure in terms of edge-sharing octahedra.

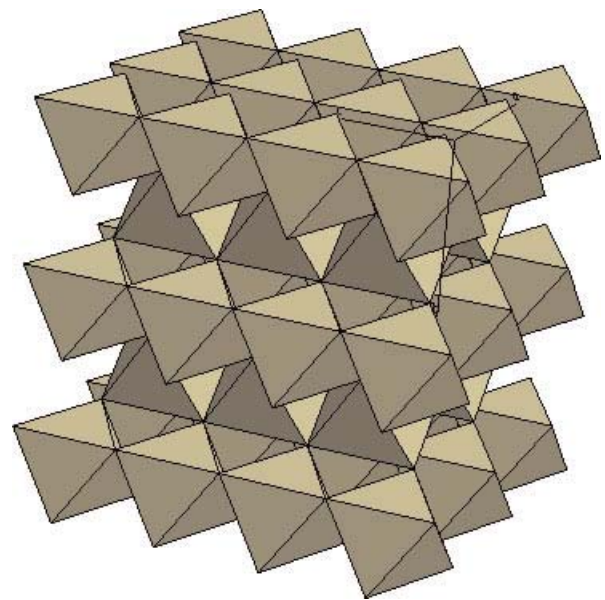


FIG. 3. Straight chains of edge-sharing octahedra with hcp (CaCl_2 -type) or distorted hcp (rutile) arrays of oxygen.

to distortions of O-Ge-O bond angles), when the Ge ions reside at their previous equilibrium positions, the $\text{CaCl}_2 \Rightarrow \alpha\text{-PbO}_2$ phase transformation is accompanied by a large displacement of the cations. The alignment of the octahedra along the *c* direction is lost, and the *c* lattice vector is almost doubled with respect to the CaCl_2 structure. The higher density of the $\alpha\text{-PbO}_2$ structure (compared to the *Pnmm*-type arrangement) allows greater oxygen-oxygen separation [5]. The finite volume difference (1.4% at 44.5 GPa, for example) indicates its first-order character. This kind of transformation does not occur readily at ambient temperature, and it requires significant activation energy to induce cation displacements or, as has been proposed for SnO_2 , it requires a rutile to $\alpha\text{-PbO}_2$ transition via a *P112₁/a* intermediate phase, which is formally identical to baddeleyite [20, 21]. Our observation of the increasing proportion of the $\alpha\text{-PbO}_2$ type phase with respect to the CaCl_2 structured phase, even at room temperature with increasing pressure, as well as our observation of the higher density of $\alpha\text{-PbO}_2$ modification of GeO_2 , lead us to conclude that the stable phase of GeO_2 in the pressure range of 44-60 GPa is in the $\alpha\text{-PbO}_2$ -type structure, which is in agreement with theoretical simulations [2]. The observation of the $\alpha\text{-PbO}_2$ phase for GeO_2 supports a possible common sequence of high-pressure-induced transformation of group IV element dioxides (SiO_2 , GeO_2 , SnO_2 , and PbO_2):rutile-type \Rightarrow CaCl_2 -type \Rightarrow $\alpha\text{-PbO}_2$ -type [12].

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