High-pressure Synthesis of $\alpha$-PbO$_2$-type Phase of GeO$_2$

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Introduction

The high-pressure behavior of both the $\alpha$-quartz-type and rutile-type phases of GeO$_2$ 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]. There are inconsistencies in the results of high-pressure phase transformations of GeO$_2$ reported by different groups.

Recent ab initio calculations predict the following sequence of phase transformations of GeO$_2$: rutile $\Rightarrow$ (19 GPa) CaCl$_2$ $\Rightarrow$ (36 GPa) $\alpha$-PbO$_2$ $\Rightarrow$ (65.5 GPa) Pa-3 (pyrite) [2]. Such phase transitions were either observed or theoretically predicted for silica SiO$_2$ [3-5]. A second-order transition from the rutile-type to the CaCl$_2$-type phase of GeO$_2$ has been reported at 25-27 GPa and room temperature [6-8]. An orthorhombic high-pressure phase of GeO$_2$ 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 $\alpha$-PbO$_2$ phase of GeO$_2$. Evidence of the coexistence of rutile-type and disordered Fe$_2$N-type structures of GeO$_2$ up to 32 GPa after heating of vitreous GeO$_2$ at $\sim$1300K have also been reported [9, 10]. Compression of rutile-structured GeO$_2$ to $\sim$36 GPa and subsequent laser annealing at $\sim$1300K, as described by Haines et al. [7], also did not result in the transformation of CaCl$_2$-structured GeO$_2$ to the $\alpha$-PbO$_2$-type phase. Laser heating above 43 GPa of both monoclinic structured ($\alpha$-quartz type GeO$_2$ starting material) and CaCl$_2$-type structured phases (rutile or vitreous glass starting materials) resulted in a mixture of the CaCl$_2$-type and Fe$_2$N-type phases [11]. Ono et al. [8] observed only the CaCl$_2$-type post-rutile phase at pressures up to 45 GPa and temperatures up to 2300K. We can see that, despite extensive studies of GeO$_2$, high-pressure polymorphism of GeO$_2$ remains unclear. No evidence of the theoretically predicted $\alpha$-PbO$_2$ phase has been reported. This report provides information on in situ x-ray studies of phase transformations of GeO$_2$ at high pressures and temperatures to $\alpha$-PbO$_2$-type GeO$_2$ from the CaCl$_2$-structured phase. The detailed description of the results can be found in Refs. 12 and 13.

Methods and Materials

In our high-pressure experiments, $\alpha$-quartz-type GeO$_2$ 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$60 GPa. The samples were loaded in the 100- to 150-$\mu$m holes in stainless steel or rhenium gaskets pre-indent ed to a thickness of 30 to 40 $\mu$m. Platinum powder of 1-3 wt% (Aldrich, purity 99.9%) was mixed with the GeO$_2$ 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 $\mu$m was used [16]. Details of the experiments are described elsewhere [17].

Results

The high-pressure orthorhombic phase of GeO$_2$ with CaCl$_2$-type structure (space group $Pnma$, $Z = 2$) was synthesised from $\alpha$-quartz-type GeO$_2$ 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$1600K, the reflections from a new high-pressure phase appeared (Fig. 1). The relative intensities of the reflections corresponding to the CaCl$_2$-structured phase decreased with increasing pressure to 43 GPa. Above 44 GPa, the diffraction intensities from the new phase were greater than those from the CaCl$_2$-type phase, although co-existence of both phases was observed up to 60 GPa.

The new phase can be indexed as the $\alpha$-PbO$_2$-type structure. To determine the stability field of the $\alpha$-PbO$_2$-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 $\alpha$-PbO$_2$ reflections decreased by a factor of $\sim$15. In a separate experiment, heating of the monoclinic P2$_1$/c-type phase of GeO$_2$ at 39.5 GPa and $\sim$1600K resulted in almost the same ratio of $\alpha$-PbO$_2$-type to CaCl$_2$-type phases as the ratio for the decompressed and heated one at 41.3 GPa. Upon decompression at room temperature...
from 60 to 29 GPa, the proportion of CaCl₂-type and α-PbO₂-type of GeO₂ was not changed, but transformation of the CaCl₂-type to the rutile-type structure was observed at ~27 GPa. At ambient pressure, a mixture of rutile-type and α-PbO₂-type structures were detected in almost equal proportions, with molar volumes of 16.65 ±0.05 cm³/mol and 16.41 ±0.08 cm³/mol, respectively.

**Discussion**

The crystal structure of the new phase of α-PbO₂ (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 GeO₆ edge-sharing octahedra (Fig. 2). In the case of the CaCl₂ (Pnnm) or rutile (P4₂/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 α-PbO₂ and rutile-type phases of 256 ±0.2 GPa and 247 ±0.3 GPa, respectively, in good agreement with the bulk modulus of 250 ±0.9 GPa for the rutile-type phase of GeO₂ reported by Haines [7].

In contrast to the rutile/CaCl₂-type second-order phase transition (when tetragonal symmetry breaks due...
to distortions of O-Ge-O bond angles), when the Ge ions reside at their previous equilibrium positions, the CaCl$_2$ $\Rightarrow$ $\alpha$-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 $\alpha$-PbO$_2$ structure (compared to the $Pnmn$-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 $\alpha$-PbO$_2$ transition via a $P112_1/a$ intermediate phase, which is formally identical to baddeleyite [20, 21]. Our observation of the increasing proportion of the $\alpha$-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 $\alpha$-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 $\alpha$-PbO$_2$-type structure, which is in agreement with theoretical simulations [2]. The observation of the $\alpha$-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 $\Rightarrow$ $\alpha$-PbO$_2$-type [12].

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**References**