

α -PbO₂-type high-pressure polymorph of GeO₂Vitali B. Prakapenka,¹ Leonid S. Dubrovinsky,² Guoyin Shen,¹ Mark L. Rivers,¹ Stephen R. Sutton,¹ V. Dmitriev,³ H.-P. Weber,³ and T. Le Bihan⁴¹*Consortium for Advanced Radiation Sources, University of Chicago, Chicago, Illinois 60637*²*Bayerisches Geoinstitut, Universität Bayreuth, D-95440 Bayreuth, Germany*³*SNBL, European Synchrotron Radiation Facility, Grenoble 38043, France*⁴*European Synchrotron Radiation Facility, Grenoble 38043, France*

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We have studied the high pressure polymorphism of GeO₂ at pressures up to 60 GPa and temperatures to ~1800 K in a laser-heated diamond anvil cell. We have synthesized an α -PbO₂-type (space group *Pbcn*) phase of GeO₂ and demonstrated that it is the stable post-CaCl₂-type (space group *Pnmm*) polymorph at pressures above 44 GPa. The α -PbO₂-structured GeO₂, with a bulk modulus of 256(5) GPa, is denser than CaCl₂ type by 1.6% at 60 GPa. Our study shows that group-IV element dioxides (SiO₂, GeO₂, SnO₂, and PbO₂) have a common sequence of high-pressure structural transformations: rutile-type \Rightarrow CaCl₂-type \Rightarrow α -PbO₂-type.

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The great interest in the polymorphism of GeO₂ comes from both the fundamental point of a possible common sequence of high pressure structural transformations of group-IV element dioxides (SiO₂, GeO₂, SnO₂, and PbO₂), and practical application as a material with unique optical properties. There are two well established polymorphs of GeO₂ at ambient pressure: α -quartz and rutile-type structures with fourfold- and sixfold-coordinated germanium ions, respectively. The rutile structure of GeO₂ is stable under ambient conditions and transforms to α -quartz at 1280 K.¹ The high pressure behavior of both the quartz and rutile phases of GeO₂ has been studied intensively for the last three decades because its structure is believed to display the high pressure properties of geologically important silica at relatively moderate pressures.² However, there are inconsistencies in the results of high pressure phase transformations of GeO₂ reported by different groups.

A phase transition of α -quartz-type GeO₂ above 6 GPa has been observed with various techniques: x-ray diffraction, extended x-ray absorption fine structure (EXAFS), and infrared and Raman spectroscopy.^{3–13} It has been established that transformation results in an increase of the Ge coordination number with pressure from 4 to 6. The amorphous structure of this high pressure phase of α -quartz-type GeO₂ above 6 GPa has been reported by several groups.^{3–7} Theoretical molecular dynamic studies indicate that under hydrostatic compression a pressure-induced amorphization of quartz-type GeO₂ originates from the mechanical instability of the quartz lattice.^{8,9} Meanwhile, a crystalline high pressure phase of α -quartz-type GeO₂ with an undetermined structure was observed by several investigators^{10,11} and later a monoclinic structure (space group *P2₁/c*, *Z*=6) of this phase was reported.^{12,13} The post α -quartz GeO₂ monoclinic-type phase was found to be metastable up to 50 GPa at room temperature.¹³

Recent *ab initio* calculations predict following sequence of phase transformations of GeO₂: rutile \Rightarrow (19 GPa) CaCl₂ \Rightarrow (36 GPa) α -PbO₂ \Rightarrow (65.5 GPa) *Pa*3 (pyrite).¹⁴ Such phase transitions were either observed, or theoretically pre-

dicted for silica SiO₂.^{15–17} The second order transition from rutile- to CaCl₂-type phases of GeO₂ has been reported at 25–27 GPa and room temperature.^{18–20} An orthorhombic high pressure phase of GeO₂ was synthesized at pressure ~50 GPa and 1300 K by Ming and Manghnani.²¹ However, according to Ming and Manghnani²¹ the x-ray diffraction patterns of quenched samples are not the α -PbO₂ phase of GeO₂. Evidence of coexisting rutile and disordered Fe₂N-type structures of GeO₂ up to 32 GPa after heating of vitreous GeO₂ at ~1300 K have also been reported.^{21,22} Compression of rutile-structured GeO₂ to ~36 GPa and subsequent laser annealing at ~1300 K, as described by Haines *et al.*,¹⁹ also does 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) or CaCl₂-type structured phases (rutile or vitreous glass starting materials) results a mixture of the CaCl₂ and Fe₂N-type phases.¹³ At pressures up to 45 GPa and temperatures up to 2300 K, Ono *et al.*²⁰ observed only the CaCl₂-type post-rutile phase. In summary, despite extensive studies of GeO₂, a high pressure polymorphism of GeO₂ remains unclear. No evidence of the theoretically predicted α -PbO₂ phase has been reported. In this paper we report *in situ* x-ray studies of phase transformations of GeO₂ at high pressures and temperatures, direct synthesis of α -PbO₂-type GeO₂ from the CaCl₂-structured phase, and structural refinement of GeO₂ polymorphs up to 60 GPa.

In our high pressure experiments α -quartz-type GeO₂ powder (Alfa, purity 99.9999%) was used. The cell constants (space group *P3₂21*, *Z*=3) were found to be *a* = 4.9862(8) Å and *c* = 5.6440(4) Å, in good agreement with literature data. Various types of diamond anvil cells (membrane, symmetrical, and four-pin) were used for pressure generation up to ~60 GPa. The samples were loaded in the 100–150- μ m holes in stainless steel or rhenium gaskets preindented to a thickness of 30–40 μ m. Platinum-black powder (1–3 wt. %) was mixed with the GeO₂ in order to absorb laser radiation for heating and to provide an internal pressure calibrant for high temperature experiments. The

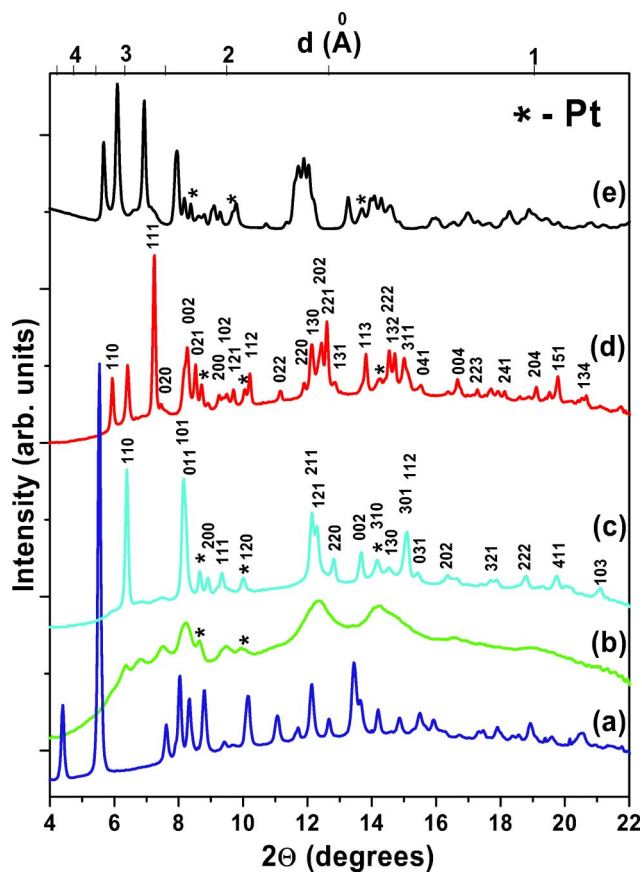


FIG. 1. (Color online) Integrated x-ray diffraction spectra of various GeO_2 phases collected at different pressure-temperature conditions: (a) starting material α -quartz-type at ambient conditions after loading in a DAC. (b) Monoclinic- $P2_1/c$ -type structure at 34 GPa at room temperature. (c) CaCl_2 -type structure at 36.4 GPa after laser heating at 1600 ± 100 K. (d) Mixture of α - PbO_2 -type (shown by indices) and CaCl_2 -type structures at 44.6 GPa after laser heating at 1600 ± 100 K. (e) Sample recovered from 60 GPa after laser heating at 1800 ± 100 K.

equations of state of Pt or Au, and/or ruby luminescence, were used for pressure measurements in ambient temperature experiments.²³

High resolution angle dispersive x-ray diffraction experiments were performed at the Advanced Photon Source (APS) at Argonne National Laboratory (GSECARS, sector 13, Chicago, Ill) and the European Synchrotron Radiation Facility (ESRF, ID30 and SNBL beamlines, Grenoble, France) using an on-line image plate or a CCD detector. Details of the experiments are described in our earlier publications.²⁴ At the APS the double-sided laser-heating technique, with a laser spot of 20–40 μm , was used.²⁵ The temperature was measured with a Kaiser holographic spectrometer coupled with a CCD. The laser heating at ESRF was carried out using a Nd-YAG (yttrium aluminum garnet) laser ($\lambda = 1064$ nm, 17 W).

Examples of diffraction spectra integrated with FIT2D software²⁶ are shown in Fig. 1. The high pressure induced phase transformation of an α -quartz-type structure of GeO_2 to a poorly crystalline monoclinic structure (space group $P2_1/c$)¹³ phase is detected above 7 GPa [Fig. 1(b)]. This

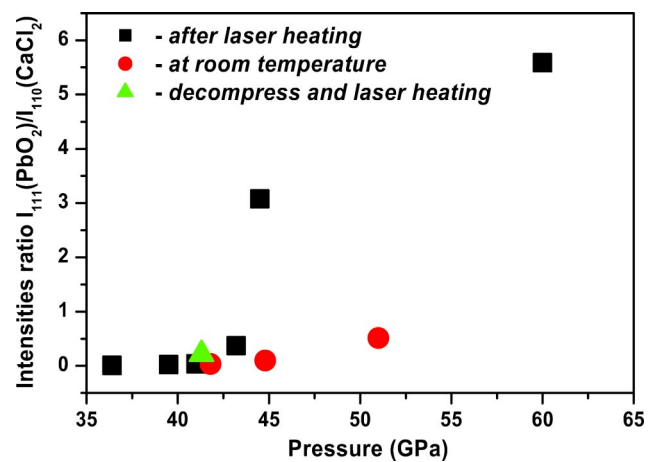


FIG. 2. (Color online) Ratio of relative intensities of the strongest reflections from α - PbO_2 - and CaCl_2 -type structures of GeO_2 vs pressure at room temperature (\bullet) and after laser heating (\blacksquare , \blacktriangle) at 1600 ± 100 K (at 60 GPa the temperature was 1800 ± 100 K).

crystalline phase was observed to at least 52 GPa. During laser heating, as the temperature was increased to 1600 ± 100 K, the gradual transformation of the monoclinic phase directly to the orthorhombic structure was observed at 36.4 GPa [Fig. 1(c)]. The high pressure phase has the CaCl_2 -type structure (space group $Pnmm$, $Z=2$). The lattice parameters at 36.4 GPa, for example, $a=4.2617(4)$ \AA , $b=4.1268(2)$ \AA , and $c=2.7817(4)$ \AA , and unit cell volume of $14.73(1)$ cm^3/mol is just slightly smaller than that reported for the same high pressure phase ($14.90(9)$ cm^3/mol at 36 GPa) (Ref. 19) obtained by pressurizing rutile-type GeO_2 at quasihydrostatic (methanol-ethanol-water pressure medium) conditions. Detailed results of high- P and $-T$ behaviors of monoclinic and orthorhombic phases will be published elsewhere.

On further compression to 41 GPa and laser heating at ~ 1600 K the reflections from a new high pressure phase started to grow. The relative intensities of the reflections corresponding to the CaCl_2 -structured phase decreased with increasing pressure (Fig. 2). Above 44 GPa [Fig. 1(d)] the diffraction intensities from the new phase are greater than those from the CaCl_2 -type phase (Fig. 2), although the coexistence of both phases was observed up to 60 GPa.

The structure of the new phase is an orthorhombic α - PbO_2 type (Fig. 3). The crystal structure of α - PbO_2 ($Pbcn$ space group symmetry) can be described in terms of a 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. 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 three-dimensional network with hcp or distorted hcp arrays of oxygen, respectively.²⁷ The molar volume of α - PbO_2 type is smaller than CaCl_2 type: at 44.5 GPa the difference is 1.4% [$14.36(1)$ and $14.56(5)$ cm^3/mol , respectively], and at 60 GPa it is 1.6% [$13.89(0)$ and $14.12(1)$ cm^3/mol , respectively]. The molar volume versus pressure data were fitted using a third-order Birch-Murnaghan equation of state with

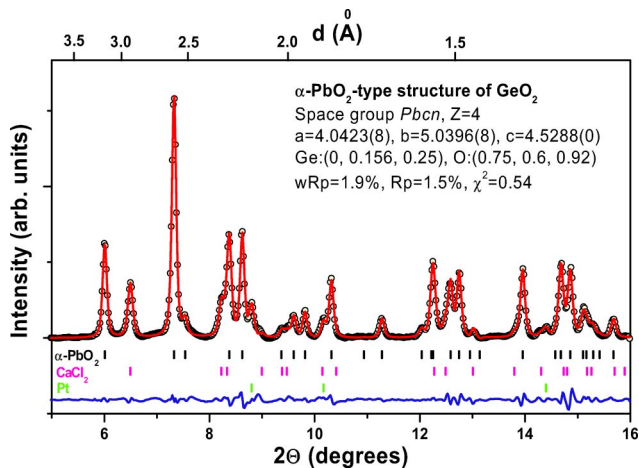


FIG. 3. (Color online) Rietveld full profile refinement of the α - PbO_2 -type phase of GeO_2 at 60 GPa after annealing at 1800 ± 100 K.

K' fixed to 4.²⁸ The fit gave values of the bulk modulus for α - PbO_2 and rutile-type phases of 256(5) and 247(3) GPa, respectively, in good agreement with bulk modulus of 250(9) GPa for the rutile-type phase of GeO_2 reported by Haines.¹⁹

To determine the relative phase stability of the α - PbO_2 -type structure, a reversal experiment was conducted, and the pressure was released from 44.5 to 41.3 GPa. After laser heating at ~ 1600 K the relative intensity of α - PbO_2 reflections decreased by a factor of ~ 15 (Fig. 2). In a separate experiment, heating of the monoclinic $P2_1/c$ -type phase of GeO_2 at 39.5 GPa and ~ 1600 K results in almost the same ratio of α - PbO_2 to CaCl_2 -type phases as for the decompressed and heated one at 41.3 GPa. Compression at room temperature of the sample heated at 41 GPa results in the growth of the α - PbO_2 -type phase (Fig. 2). Laser heating at 60 GPa initiated significant increase in the amount of the α - PbO_2 -structured GeO_2 (Fig. 2). On decompression at room temperature from 60 to 29 GPa the proportion of CaCl_2 - and α - PbO_2 -type GeO_2 was not changed, but transformation of a CaCl_2 - to a rutile-type structure was observed at ~ 27 GPa. At ambient pressure, a mixture of rutile-type and α - PbO_2 -type structures was detected in almost equal proportions [Fig. 1(e)] with molar volumes of 16.65(5) and 16.41(8) cm^3/mol , respectively.

Though a theoretical calculation¹⁴ predicts a single stable phase in a pressure range of 36–65 GPa, we have observed the coexistence of both CaCl_2 - and α - PbO_2 -type structured GeO_2 up to 60 GPa [Fig. 1(d)]. The nonhydrostatic conditions and temperature gradients in laser-heated diamond anvil cells (DACs) could be the one of reasons for incomplete transformation to α - PbO_2 -type GeO_2 , especially near the diamond surface, where the temperature can drop by a factor of 5.^{29,30} In contrast to the rutile- CaCl_2 -type second order phase transition, when tetragonal symmetry breaks due to distortions of O-Ge-O bond angles, but the Ge ions reside at their previous equilibrium positions, the $\text{CaCl}_2 \Rightarrow \alpha$ - PbO_2 phase transformation is accompanied by a large displacement of the cations. The alignment of the octahedra along the c

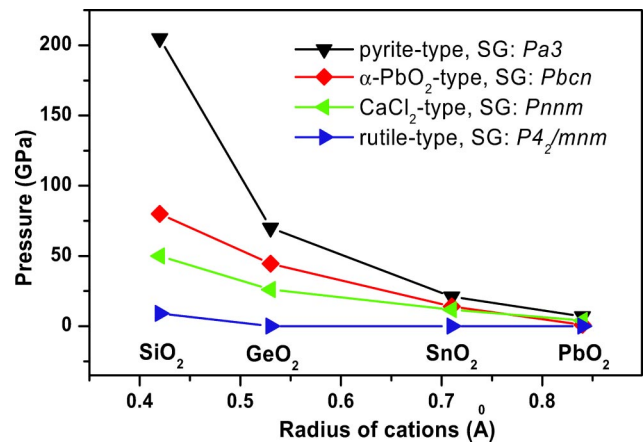


FIG. 4. (Color online) Phase pressure boundary vs metal ionic radius for the group-IV metal dioxides (the solid lines are guides to the eye). Data for pyrite-type structure of SiO_2 (Ref. 17) and GeO_2 (Ref. 14) are theoretically predicted. Experimental data are from Refs. 31 and 33–38, and this study.

direction is lost, and a c lattice vector is almost doubled with respect to the CaCl_2 structure. The higher density of the α - PbO_2 structure (compared to the $Pnmm$ -type arrangement) allows a greater oxygen-oxygen separation.¹⁷ 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 requires significant activation energy to induce cations displacements or as has been proposed for SnO_2 , with a rutile to α - PbO_2 transition via a $P112_1/a$ intermediate phase formally identical to baddeleyite.^{31,32} Our observation of the increasing proportion of the α - PbO_2 type phase with respect to the CaCl_2 structured phase, even at room temperature with increasing pressure, as well as the higher density of α - 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 the α - PbO_2 -type structure. Thus, theoretical simulations¹⁴ of the high pressure behavior of GeO_2 are in good agreement with our experimental results.

The observation of the α - PbO_2 phase for GeO_2 supports a possible common sequence of high pressure induced transformation of group-IV element dioxides. The α - PbO_2 -structured phases have been reported for the analogous metal dioxides: SiO_2 (between 40 and 80 GPa, depending on starting material and conditions of high- P and $-T$ treatment),^{33–35} SnO_2 (at ~ 12 GPa),^{31,36} and PbO_2 (at 1.3 GPa).³⁷ In the cases of SiO_2 , GeO_2 , and SnO_2 even with temperature treatment at high pressures^{33,36} a wide range of coexistence of orthorhombic CaCl_2 - and α - PbO_2 -type structures have been observed. Figure 4 illustrates the systematic high pressure behavior of group-IV dioxides that all adopt the rutile-type structure with a precise linear relationship between the ionic radii of the cation and the lattice constants a and c .³⁸

In summary, x-ray *in situ* studies show that on compression at room temperature α -quartz-type GeO_2 transforms to a poor crystalline phase with monoclinic structure (space

group $P2_1/c$) at 7 GPa, and this exists at least up to 52 GPa. A temperature induced transformation of the monoclinic phase to the CaCl_2 -type (space group $Pnmm$) at pressures up to 36.4 GPa was detected. We experimentally observed the first order phase transformation of the CaCl_2 -type structure of GeO_2 to the α - PbO_2 -type (space group $Pbcn$) starting at 41 GPa. A mixture of the CaCl_2 -type and the α - PbO_2 -type were found to exist up to 60 GPa, but the relative intensity of

the α - PbO_2 -type reflections significantly increased with increasing pressure and temperature. The α - PbO_2 -type structure of GeO_2 is quenchable and denser than the rutile-type by 1.4% [densities are 6.37(0) and 6.27(9) g/cm^3 , respectively] at ambient pressure. Our study shows that group IV element dioxides (SiO_2 , GeO_2 , SnO_2 , and PbO_2) have a common sequence of high-pressure structural transformations: rutile-type \Rightarrow CaCl_2 -type \Rightarrow α - PbO_2 -type.

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