High-pressure form of pyrite-type germanium dioxide

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Structural phase transitions of germanium dioxide (GeO_2) have been investigated at pressures up to 120 GPa, which was heated to a temperature above 2000 K, using a laser-heated diamond anvil cell technique. A phase transition between $CaCl_2$-type and α-PbO_2-type phases was observed at about 50 GPa. At pressures higher than 90 GPa, we also observed the occurrence of a new high-pressure phase of pyrite-type (modified-fluorite type) structure ($Pa\overline{3}$) that is denser than other known GeO_2 phases. Our results were consistent with the high-pressure transition sequence of tin dioxide (SnO_2) as analog of GeO_2. The new structure of the GeO_2 high-pressure phase may be that of high-pressure silica (SiO_2) phase predicted by the theoretical investigations.

I. INTRODUCTION

The great interest in the high-pressure phase transitions in silica SiO_2 comes from the possible geophysical repercussions. The high-pressure polymorphs of silica have been studied quite intensively. Theoretical calculations[1,2] have predicted that silica shows a high-pressure sequence of phase transitions: stishovite, $CaCl_2$-type, α-PbO_2-type, and pyrite type. In the case of high-pressure experiments, however, the transition pressure between the $CaCl_2$ and α-PbO_2-type in silica is still uncertain, with conflicting values reported in the literature.[3–6] Moreover, there is no experimental evidence of pyrite-type silica. In germanium dioxide, GeO_2, a similar series of phase transitions between rutile-type and $CaCl_2$-type phases was measured.[7–9] Interest can therefore be focused on investigations of this silica analogy.

In tin dioxide, SnO_2, considered as a silica analogy, a similar sequence of phase transitions (from rutile-type to $CaCl_2$-type, then α-PbO_2-type, and finally a pyrite-type or modified-fluorite type) were measured.[10,11] In the case of GeO_2, the Fe_2N-type structure was at first observed instead of the $CaCl_2$-type structure.[12] However, recent studies[7–9] reported that the $CaCl_2$-type structure had been identified. This seemed to be a result of the kinetics of the phase transitions. Materials tend to transform into denser phases under pressure. Under low-temperature conditions, however, they are often compressed metastably over their phase boundaries because of the small thermal energy of the atoms compared to the activation barrier for the transition. Silica, for example, is known to follow different transition paths under high pressure at room temperature, depending on the starting material.[5,13,14] There is an extensive literature on the low-pressure behavior of GeO_2, but information on the experimental observation of the higher-pressure phases is scarce. In particular, there is no confirmation that GeO_2 undergoes the same series of phase transitions under pressure as silica or SnO_2. In order to avoid formation of metastable phases, we used a laser-heated technique to release the stress in the sample and to enhance phase transitions. The pyrite-type (modified-fluorite-type) phase in SnO_2 was reported to be unquenchable, converting to the α-PbO_2-type phase upon release of pressure. Therefore, the method of *in situ* observation is necessary to identify the pyrite-type phase in GeO_2, using an intense x-ray source of synchrotron radiation.

II. EXPERIMENT

The high-pressure x-ray diffraction experiments were performed using a laser-heated diamond anvil cell high-pressure apparatus.[15] Synthetic powdered α-quartz-type GeO_2 was loaded into 50–100 μm diameter hole drilled into a rhenium gasket, which was pre-indented to a thickness of 40–70 μm. Platinum powder was mixed with the sample to absorb the laser radiation for heating, and to provide an internal pressure calibrant. The samples were heated with a multimode continuous wave Nd:YAG (yttrium aluminum garnet) laser employing a double-sided laser heating technique, which minimized any temperature gradients across the heated area.[16] The size of the heating spot was about 70–100 μm. The sample temperature was measured on one side of the sample using the spectroradiometric method. A pressure medium was not used in our experiments except for second run, because the diffraction of a pressure medium would interfere with that of the sample. Although accurate diffraction patterns of the sample could be acquired without a pressure medium, the temperature gradient across the sample was large. It was difficult to measure the axial temperature gradient because it varied with each experiment. However, other studies have calculated the temperature gradient in a laser heated diamond anvil cell.[17,18] According to these studies,
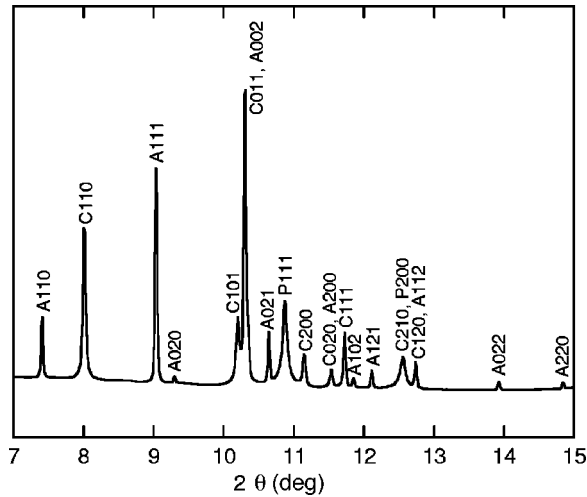
FIG. 1. X-ray diffraction pattern for GeO_2 phases obtained at 300 K and 41 GPa. Abbreviations of peaks are as follows: A, α-PbO_2-type GeO_2; C, $CaCl_2$-type GeO_2; P, platinum. Unit cell constants: $CaCl_2$-type, $a = 4.257(1)$ Å, $b = 4.114(2)$ Å, $c = 2.776(1)$ Å.; α-PbO_2-type, $a = 4.111(1)$ Å, $b = 5.099(1)$ Å, and $c = 4.583(1)$ Å.

FIG. 2. X-ray diffraction pattern for GeO_2 phases obtained at 300 K and 60 GPa using the pressure medium of sodium chloride. Abbreviations of peaks are as follows: A, α-PbO_2-type GeO_2; N, sodium chloride; P, platinum. Unit cell constants: α-PbO_2-type GeO_2: $a = 4.045(2)$ Å, $b = 5.033(2)$Å, and $c = 4.527(2)$ Å.

the estimated uncertainty of temperature in our experiments without the pressure medium would be higher than 500 K at high temperatures. The heated samples were probed by the angle-dispersive x-ray diffraction technique using the synchrotron beam line BL10XU at SPring-8, at the Japan Synchrotron Radiation Research Institute (JASRI) in Japan. A monochromatic incident x-ray beam at a wavelength of ~ 0.413 Å was used. The x-ray beams ware collimated to diameters of 20 and 40 μm. The angle-dispersive x-ray diffraction patterns were obtained on an imaging plate. The observed intensities on the imaging plates were integrated as a function of 2θ using the FIT2D code[19] in order to obtain conventional, one-dimensional diffraction profiles. The diffraction profile refinements with the program package GSAS (Ref. 20) were applied to the diffraction patterns to cell parameters and volumes for GeO_2 and Pt. The pressure was determined from the observed unit cell volume of platinum using the equation of state (EOS) for platinum given by Holmes *et al.*[21] The uncertainty in the pressure value was related to the experiment temperature, because of the use of the platinum EOS. There are discrepancies between various reference EOS values.[22,23] Moreover, a pressure gradient could have existed in the sample, even at high sample temperatures. Therefore, the maximum pressure error was greater than 5 GPa at the high temperatures used.

III. RESULTS

Two experimental runs were carried out, at pressures of 40 and 120 GPa. In each run, the sample was compressed to the desired pressure and then heated to synthesize the high-pressure phases of GeO_2. X-ray diffraction data were acquired at several temperatures at fixed press loads. The acquisition time was typically 3–5 min. Typical diffraction patterns are reproduced in Figs. 1 and 2 . In addition to the
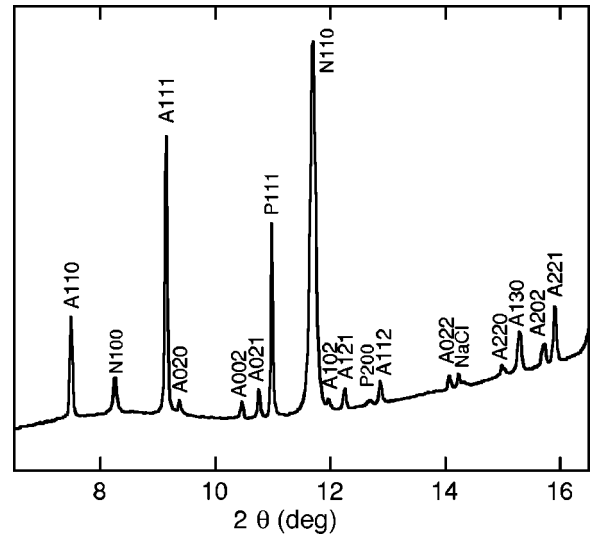
diffraction peaks of the GeO_2 phase and Pt, there are several intense diffraction peaks from the sodium chloride pressure medium (Fig. 2) and the rhenium gasket (Fig. 3). However, several diffraction lines, which are free from the interference, make it possible to identify the GeO_2 phase and calculate the unit cell dimensions. Pressure was determined from the unit cell volume of Pt using two diffraction lines (*111* and *200*).

In the first experiment the sample was compressed to 45 GPa and then heated at about 1400 K. After heating, the pressure decreased to 41 GPa due to stress relaxation in the sample chamber. The sample was found to have crystallized to a dense form of GeO_2 at the heated area (Fig. 1). X-ray diffraction showed a mixture of three phases: Pt, a $CaCl_2$-type phase (*Pnnm*), and an α-PbO_2-type phase (*Pbcn*). Two high-pressure phases of GeO_2 coexisted in the sample chamber. This is because the *P-T* condition of this run was close to the phase boundary between $CaCl_2$ and α-PbO_2-type phases and the laser heating produced a large temperature inhomogeneity in the sample. The highest temperature part is at the center of the sample. Away from the heated center, both in the axial and radial directions, the temperature decreases rapidly. Therefore, two GeO_2 phases were observed in this run. The diffraction pattern of the $CaCl_2$-type phase is very similar to that of the rutile-type phase (*P4$_2$/mnm*). In this experiment, however, some double peaks of *101-011* and *210-120* were clearly identified (Fig. 1). This strongly suggests that one of high-pressure phases was the $CaCl_2$-type phase. Recently, Lodziana *et al.*[24] studied the phase transition between $CaCl_2$ and α-PbO_2-type phases by means of accurate *ab initio* calculations. They reported that the transition occurred at a pressure of about 36 GPa at 0 K. This calculated boundary agrees quite well with our experimental results.

In the next experiment, we used the pressure medium of sodium chloride to reduce the stress and temperature inho-
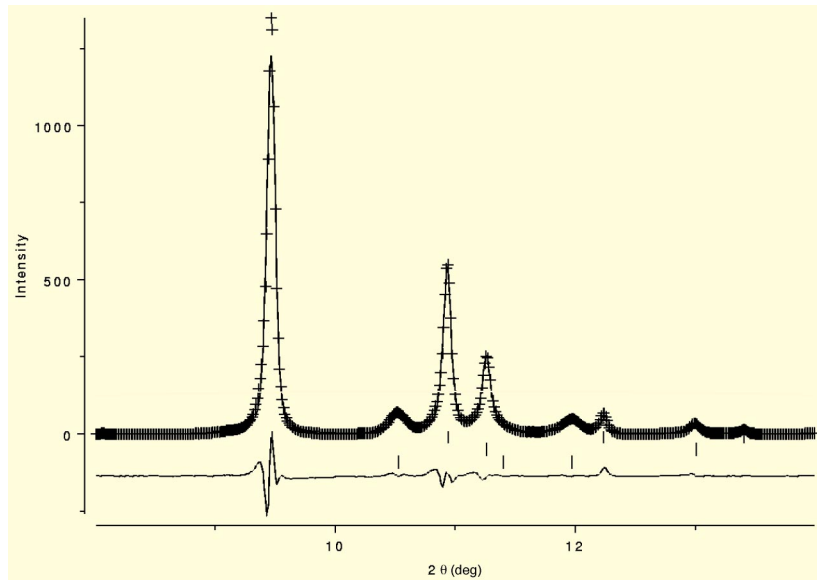
FIG. 3. Observed and calculated x-ray diffraction pattern for pyrite-type GeO_2 phases obtained at 108 GPa and 300 K. The short vertical bars mark the positions of the allowed Bragg reflections: upper, pyrite-type GeO_2; middle, platinum; lower, rhenium gasket. Structural data of pyrite-type GeO_2: $Pa\bar{3}$, $Z=4$, $a=4.333(1)$ Å; Ge^{4+}, $4a$, $(0,0,0)$;O^{2-}, $8c$, $(0.347,0.347,0.347)$.

mogeneity in the sample. The sample was compressed to 60 GPa and then heated at 2100 K. After heating, the pressure in the sample camber was 60 GPa. The sample was found to crystallize completely to the α-PbO_2-type phase (Fig. 2). Therefore, this indicates that the α-PbO_2-type structure is a stable high-pressure phase in GeO_2.

In the third experiment the sample was compressed to a load of about 100 GPa and then heated. The starting material transformed to a new high-pressure phase of the cubic structure when the temperature reached 1900 K. The presence of the *210* reflection of the cubic phase indicates that the structure of the phase is not the fluorite type suggested in the SnO_2 analogy,[25] but a pyrite-type structure belonging to space group $Pa\bar{3}$, as pointed out by Haines and Leger.[10] The cubic phase was observed to persist up to 2600 K (Fig. 3) and on cooling to 300 K at a constant press load (Table I). Previously calculated results[24] showed that the α-PbO_2-type phase transformed to the pyrite-type phase at about 65 GPa and 0 K. The occurrence of the pyrite-type phase in our experimental study is consistent with this calculation if this

phase boundary has a positive dP/dT slope. As shown in (Table II), the α-PbO_2-type phase has a molar volume 1% smaller than the $CaCl_2$-type phase at 41 GPa and 300 K. The pyrite-type phase at 107 GPa has a molar volume 12% smaller than the α-PbO_2-type phase at 60 GPa.

IV. DISCUSSION AND CONCLUSIONS

Previous studies reported the Fe_2N-type structure in GeO_2 at pressures higher than 25 GPa.[12,26,27] Therefore, the identification of high-pressure phase of GeO_2 seemed to be wrong. However, this Fe_2N-type structure ($P6_3/mmc$) is very similar to the α-PbO_2-type structure ($Pbcn$). Recently, Rechenbaach and Jacobs[28] reported that the $\zeta-Fe_2N$ structure came into the space group $Pbcn$ using the neutron and synchrotron powder diffraction methods. The observed structure in this study was the space group $Pbcn$, which was the same as α-PbO_2 and $\zeta-Fe_2N$ type structures. Therefore, this high-pressure phase of GeO_2 should be called the α-PbO_2-type structure. Ming and Manghnani[26] reported an unknown orthorhombic phase at pressures higher than 28 GPa. This orthorhombic phase seems to be the metastable because of the following reasons. First, the estimated heating temperatures in these studies were about 1300 K, which seemed to

TABLE I. Assignments of reflections and comparison between observed and calculated d values at 2600 K and 126 GPa. Calculated d-spacings are based on unit cell dimensions; pyrite-type phase, a=4.331(1) Å ; Pt, a=3.647(2) Å ; Re, a=2.600 Å and c=4.162 Å .

	Pyrite-type			Pt		Re	
d_{obs}Å	I	hkl	d_{cal}	hkl	d_{cal}	hkl	d_{cal}
2.5022	100	111	2.5007				
2.2520						100	2.2520
2.1672	40	200	2.1657				
2.1047				111	2.1060		
						002	2.0808
1.9806						101	1.9806
1.9375	5	210	1.9370				
1.8245				200	1.8239		
1.7696	<2	211	1.7683				

TABLE II. The P-V-T data of GeO_2 phases.

T(K)	P(GPa)	V(Å^3)
$CaCl_2$-type		
300	41.1 (1.5)	48.59 (3)
α-PbO_2-type		
300	41.1 (1.5)	96.07 (2)
300	60.0 (2.0)	92.16 (8)
Pyrite-type		
1900	85.8 (6.0)	83.77 (19)
2400	121.5 (6.0)	81.80 (13)
2600	125.7 (6.0)	81.24 (3)
300	107.8 (3.0)	81.48 (4)

be too low to enhance the phase transition. Second, the stress and large temperature inhomogeneity might exist in the sample because the orthorhombic phase always coexisted with the α-PbO$_2$-type (Fe$_2$N-type) phases. Therefore, we used the double-sided laser heating technique to minimize any temperature gradients across the heated area. Furthermore, the heated temperature in our second run was 2100 K, enough to synthesize the stable phase. As a result of the improvement of experimental techniques, the orthorhombic phase was not observed in this study.

In the case of SiO$_2$, the high-pressure transition may play an important role in the dynamics and the evolution of the Earth's mantle. Silica is thought to represent about 10% and 20% by volume of the subducted mid-oceanic ridge basalt in the Earth's upper and lower mantles, respectively.[29] The transition from the CaCl$_2$-type to the α-PbO$_2$-type silica phase is predicted to involve a volume discontinuity, which may destabilize the silicate perovskite as most abundant mineral in the lower mantle.[30] Therefore, the α-PbO$_2$-type silica phase is a candidate for one of constituent minerals in the lower mantle. The transition of silica from a rutile-type (stishovite) phase to a CaCl$_2$-type phase occurs in the vicinity of 50 GPa at room temperature, as reported from experimental studies.[3,6,13] The experimental reports of the high-pressure transition from CaCl$_2$-type to α-PbO$_2$-type SiO$_2$ are unclear. There is experimental evidence for such a transition,[3] but other data indicate the persistence of the CaCl$_2$ structure to at least 120 GPa.[4] Recently, a new silica phase with a α-PbO$_2$-like or baddeleyite like structure was reported in the Martian meteorite Shergotty.[31] Moreover, recent diamond anvil cell experiments indicated that different transition paths were obtained at room temperature depending on the starting material.[5,14] The reports of these experiments and those from a study of the meteorite have been controversial. The kinetic effect of the phase transition often causes the metastable phase to persist in its phase boundaries. The high-temperature heating method has a significant advantage if it is desired to synthesize the thermodynamically stable phase. In this study and previous work[9] using the high-temperature
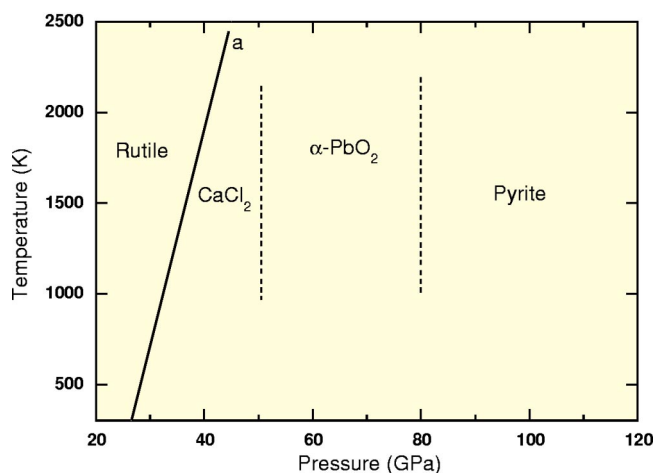

FIG. 4. Phase diagram of GeO$_2$. Solid line (a) is a phase boundary between the rutile and CaCl$_2$-type structures reported by Ono *et al.* (Ref. 9). Dashed lines indicate the estimated phase boundaries of GeO$_2$ in this study.

heated method, GeO$_2$ showed a sequence of phase transitions: rutile-type, CaCl$_2$-type, α-PbO$_2$-type, and pyrite-type (Fig. 4). This sequence is same as that of tin dioxide (SnO$_2$) reported by previous studies.[10,11] According to the analysis of the silica analogs, GeO$_2$ and SnO$_2$, the high-pressure transition sequence of silica — rutile-type, CaCl$_2$-type, α-PbO$_2$-type, and pyrite-type — seems to be reasonable. Further careful experiments, especially high temperature conditions, are needed to access these issues.

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