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# High pressure induced phase transformation of SiO<sub>2</sub> and GeO<sub>2</sub>: difference and similarity

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## Abstract

We report high pressure polymorphism of SiO<sub>2</sub> and GeO<sub>2</sub> at room and high temperatures. It was found that kinetics has a large effect on pressure induced phase transitions of SiO<sub>2</sub> and GeO<sub>2</sub>. The high pressure behavior of SiO<sub>2</sub> and GeO<sub>2</sub> polymorphs depends on the starting material and pressure–temperature history. Our studies show that SiO<sub>2</sub> and GeO<sub>2</sub> have a common sequence of high pressure, high temperature structural transformations when the same type of starting material (amorphous or  $\alpha$ -quartz) was used: (amorphous or  $\alpha$ -quartz)  $\Rightarrow$  d-NiAs  $\Rightarrow$  rutile  $\Rightarrow$  CaCl<sub>2</sub>  $\Rightarrow$   $\alpha$ -PbO<sub>2</sub>  $\Rightarrow$  pyrite (*Pa-3*) types. In the case of cristobalite as starting material, the  $\alpha$ -PbO<sub>2</sub>-type phase can be synthesized directly from the high pressure room temperature phase omitting rutile- or CaCl<sub>2</sub>-type structure. The crystallization of the d-NiAs phase in a narrow temperature interval 1000–1300 K can be used as an indicator of presence of a cation disordered network in both SiO<sub>2</sub> and GeO<sub>2</sub> materials at high pressure before heating.

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## 1. Introduction

Silica is a major component of the Earth's interior. At ambient pressure, SiO<sub>2</sub> has four major polymorphs: cristobalite (low temperature tetragonal, S.G.: P4<sub>1</sub>2<sub>1</sub>2 and high temperature cubic, S.G.: Fd-3m), tridymite (hexagonal, S.G.: P6<sub>3</sub>/mmc), quartz (low temperature ( $\alpha$ -quartz) trigonal, S.G.: P3<sub>2</sub>21 and high temperature ( $\beta$ -quartz) hexagonal, S.G.: P6<sub>2</sub>22) and glass (amorphous network). There are a number of theoretical and experimental reports concerning the behavior of various high pressure silica phases: keatite, coesite, stishovite, CaCl<sub>2</sub>-,  $\alpha$ -PbO<sub>2</sub>-, I2/a, baddeleyite, fluorite, and pyrite(*Pa-3*)-types. First-principles, total-energy calculations for specific structures are used to provide an explanation for a number of recent high pressure results for crystalline silica [1]. However, the experimental evidence of phase boundaries is still not clear, and some reported results were contradictory among different groups on phase transformations at high pressures. For example,

the phase boundary between stishovite and  $\alpha$ -PbO<sub>2</sub> type phase was observed at  $\sim$ 80 GPa and 2500 K [2] when cristobalite was used as a starting material. Meanwhile, no evidence was found for a further transformation of the CaCl<sub>2</sub>-type structure up to 128 GPa using stishovite as a starting material [3,4]. Above 121 GPa the pressure boundary for CaCl<sub>2</sub> and  $\alpha$ -PbO<sub>2</sub> phases was reported recently with positive slope when amorphous silica was used as a starting material [5]. Even for the 'well' studied stishovite to CaCl<sub>2</sub>-type SiO<sub>2</sub> transition, there is scatter in the reported phase boundary pressures, e.g.: 49–50 GPa [6,7], 54–55 GPa [3,8] and  $\sim$ 60 GPa [4]. It appears likely that high pressure phase transitions are dependent on the starting materials and pressure/temperature history.

The high pressure behavior of both the  $\alpha$ -quartz and rutile type phases of GeO<sub>2</sub> has been studied intensively at relatively moderate pressures for the last three decades because of the analogy to geologically important silica [9]. There are two well established polymorphs of GeO<sub>2</sub> at ambient conditions:  $\alpha$ -quartz-type structure and rutile-type structure with fourfold- and sixfold-coordinated germanium ions, respectively. However, there are inconsistencies in the results of high pressure phase transformations of GeO<sub>2</sub>

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reported by different groups. The amorphous structure of the high pressure phase of  $\alpha$ -quartz type  $\text{GeO}_2$  above 6 GPa has been reported by several groups [10–14]. Theoretical molecular dynamic studies indicate that under hydrostatic compression a pressure-induced amorphization of quartz-type  $\text{GeO}_2$  originates from the mechanical instability of the quartz lattice [15,16]. Meanwhile, a crystalline high pressure phase of  $\alpha$ -quartz-type  $\text{GeO}_2$  with undetermined structure was observed by several investigators [17,18] and later a monoclinic structure (space group  $P2_1/c$ ) was attributed to this phase [19–21]. Recently, the  $\alpha$ - $\text{PbO}_2$ -type phase (space group  $Pbcn$ ) of  $\text{GeO}_2$  has been synthesized in the diamond anvil cell (DAC) [21,22]. It was demonstrated that  $\alpha$ - $\text{PbO}_2$ -type is the stable post- $\text{CaCl}_2$ -type (space group  $Pnmm$ ) polymorph of  $\text{GeO}_2$  at pressures above 44 GPa and group-IV element dioxides ( $\text{SiO}_2$ ,  $\text{GeO}_2$ ,  $\text{SnO}_2$ , and  $\text{PbO}_2$ ) have a common sequence of high pressure structural transformations: rutile-type  $\Rightarrow$   $\text{CaCl}_2$ -type  $\Rightarrow$   $\alpha$ - $\text{PbO}_2$ -type [21].

In this paper we present new results of pressure induced phase transitions of  $\text{SiO}_2$  and  $\text{GeO}_2$  under various temperatures using different starting materials. The new data together with previous results for  $\text{SiO}_2$  and  $\text{GeO}_2$  are compared, and polymorph sequences are discussed.

## 2. Experimental details

A few crystalline types of phase were used as starting materials: the  $\alpha$ -quartz type of  $\text{SiO}_2$  and  $\text{GeO}_2$  (Alfa, purity 99.9999%), cristobalite [23] and tridymite [24]. To reduce the influence of starting material structure on high pressure behavior, the amorphous phase could be used. However, a typical silica glass still consists of corner-linked  $\text{SiO}_4$  tetrahedra with an average Si–O bond length of 1.61 Å. The wide Si–O–Si angle distribution with an average of  $144^\circ$  becomes sharper and closer to  $120^\circ$  under applied pressure, which is similar with the high pressure behavior of quartz. To synthesize the highly disordered silica network we used sol–gel technique [23]. In general, the sol–gel process involves the transition of a system from a liquid ‘sol’ (mostly colloidal) into a solid ‘gel’ phase. Hydrolysis of the metal alkoxide produces reactive monomers, which through polycondensation reactions promotes cross-linking, leading to a three-dimensional matrix. The silicon atoms are bonded to oxygen atoms in an irregular non-crystalline network, forming a gel. Thus, the sol–gel amorphous structure of very disordered silica network can be used as model material of free  $\text{SiO}_2$ , which might be produced in chemical reactions at the cold subducting slabs of the Earth. The sol was prepared from a mixture of tetraethoxysilane:water:ethanol:hydrochloric acid in mole ratio of 1:4:6:0.3 (the purity of all precursors was 99.999%). After drying at  $60^\circ\text{C}$  for 24h the xerogel was heated to  $650^\circ\text{C}$  for 4h in air to remove all organic solvents [23].

The high pressure was generated by a symmetric DAC. The samples were loaded in the 100–150  $\mu\text{m}$  holes in stainless steel or rhenium gaskets pre-indented to a thickness of 30–40  $\mu\text{m}$ . The Pt, Fe, TiC or B powder (1–3 at.%) was mixed with the  $\text{SiO}_2$  or  $\text{GeO}_2$  in order to enhance absorption of laser radiation for heating and to provide an internal pressure calibrant for high temperature experiments. The equations of state of Pt, Fe, Au, and/or ruby luminescence were used for pressure measurements [25,26].

High resolution, angle dispersive X-ray diffraction experiments were performed at the Advanced Photon Source (APS) at Argonne National Laboratory (GSECARS, sector 13, Chicago, USA) and the European Synchrotron Radiation Facility (ESRF, ID30 beamline, Grenoble, France) using on-line imaging plate or a CCD detector. Details of the experiments are described in our earlier publication [23]. At the APS the double-sided laser-heating technique with laser spot of 20–40  $\mu\text{m}$  was used [27]. The one-side laser heating at ESRF was carried out using an Nd-YAG laser ( $\lambda = 1064\text{ nm}$ , 17 W).

## 3. Results and discussion

### 3.1. $\text{SiO}_2$ polymorphism

High pressure induced phase transformation of the most abundant  $\alpha$ -quartz-type phase of  $\text{SiO}_2$  at ambient temperature without pressure medium is shown on Fig. 1. Above 16 GPa the quartz II high pressure phase was detected, in good agreement with previous observation under quasi-hydrostatic conditions [28]. Increasing pressure to 25 GPa results in new diffraction peaks corresponding to a polycrystalline structure in contrast to reported early pressure induced amorphization of  $\alpha$ -quartz at pressure above 25 GPa [29]. The low intensity and broad diffraction lines can be due to partial disordering of crystalline structure arising from uniaxial stress conditions in the DAC chamber. This poorly crystalline structure could be indexed based on the monoclinic cell with  $P2_1/c$  symmetry [28]. On decompression, the same diffraction patterns as those at high pressure (48 GPa) were preserved down to ambient pressure.

After laser heating above  $1000 \pm 100\text{ K}$  we have observed gradual transformation of the poorly crystalline monoclinic structure to tetragonal rutile-type (stishovite) structure at pressures up to 55 GPa (Fig. 2). Both monoclinic and rutile type structures can be described in terms of silicon filling the one-half of octahedral interstices formed by distorted hexagonal close packing sequences of oxygen anions. The cations build up the  $3 \times 2$  zigzag chains of  $\text{SiO}_6$  octahedra for monoclinic structure ( $P2_1/c$  symmetry) and straight chains of edge-sharing octahedra for rutile-type ( $P4_2/mnm$  symmetry).

Above 55 GPa we detected the temperature induced transformation of the monoclinic phase directly to

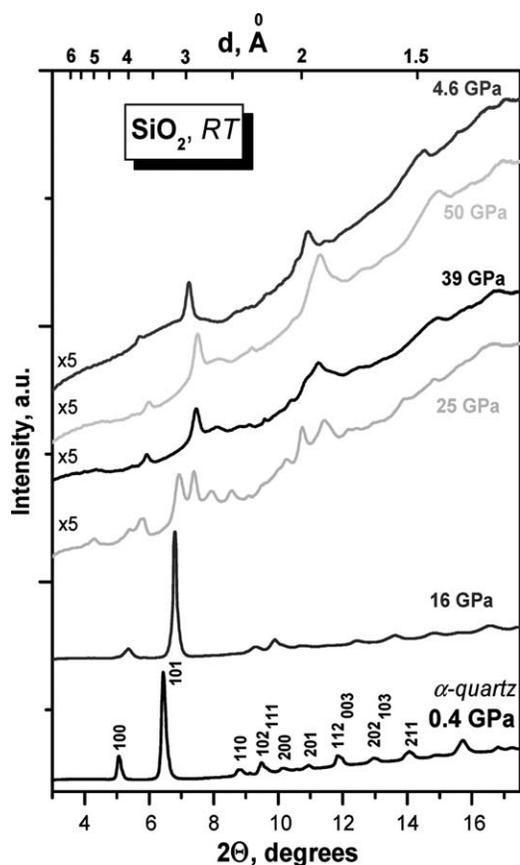


Fig. 1. X-ray diffraction spectra collected on compression of  $\alpha$ -quartz  $\text{SiO}_2$  at room temperature. The intensities of spectra collected above 25 GPa have been multiplied by 5 with respect to the lower pressure data.

the  $\text{CaCl}_2$ -type that has less distorted *hcp* arrangement of anions than that in rutile-type structure. The transition pressure of rutile- to  $\text{CaCl}_2$ -type phases of  $\text{SiO}_2$  has been early reported in the range of 50–60 GPa [3,4,6–8].

At room temperature, the high pressure studies on tridymite show crystalline–crystalline phase transition at pressures up to  $\sim 20$  GPa under non-hydrostatic conditions. But the structures of these phases are still undefined. At pressures between 21 and 47 GPa only a few very broad and low intensity diffuse scattering could be detected (Fig. 3). Temperature induced transformation of tridymite to rutile-type phase at a pressure range of 30–50 GPa was observed. The diffraction pattern at high pressure and room temperature with tridymite as starting material can be considered as a superposition of both high pressure phases with  $\alpha$ -quartz and amorphous as starting materials at 40–50 GPa (Fig. 3b–d). Thus, we could consider the similar high pressure–high temperature induced phase transformation for all these starting materials: amorphous,  $\alpha$ -quartz and tridymite at pressures above 21 GPa.

The high pressure phase transformation with cristobalite as starting material is different from those with  $\alpha$ -quartz or tridymite as starting materials at room and high temperatures (Fig. 3). At room temperature and non-hydrostatic conditions, the low temperature cristobalite undergoes

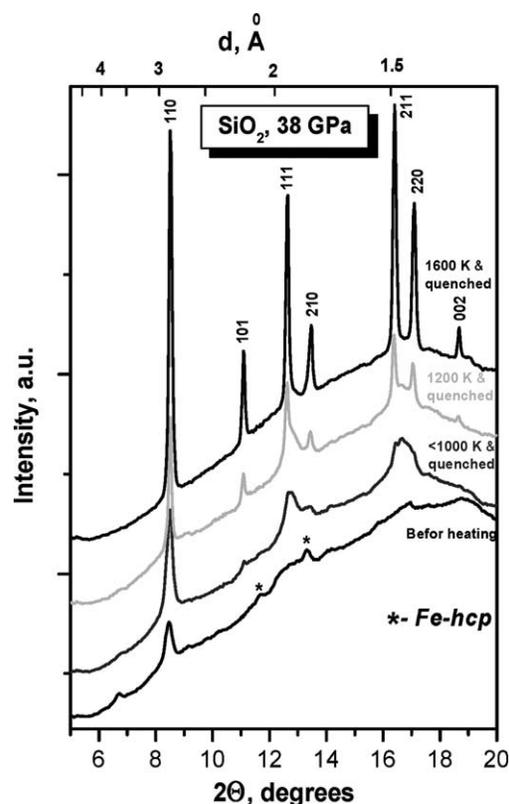


Fig. 2. Temperature induced transformation of the monoclinic high pressure phase of  $\text{SiO}_2$  at 38 GPa to the stishovite phase (temperature quenched samples after laser heating for  $\sim 10$  min using iron powder as a laser absorber mixed with  $\alpha$ -quartz  $\text{SiO}_2$  powder).

transformation to a three different crystalline phases: at 0.2–14 GPa—C-II (monoclinic B-face centered,  $P2_1$ -type), at 14–30 GPa—C-III (undefined) and above 35 GPa—C-IV (monoclinically distorted  $\alpha$ - $\text{PbO}_2$ -type,  $Pbcn$ ) [23]. The last high pressure phase existed at least up to 90 GPa at temperature range of 300–900 K and is quenchable to ambient conditions. With laser heating at temperatures above  $\sim 2000$  K and pressures above  $\sim 80$  GPa, this phase transforms to the  $\alpha$ - $\text{PbO}_2$ -type structure [2]. Such ‘low’ transition pressure for  $\alpha$ - $\text{PbO}_2$ -type was never observed for other silica polymorphs: glass,  $\alpha$ -quartz or tridymite as starting materials. The transition pressure of 121 GPa was reported with silica glass as starting material [5]. However, the  $\alpha$ - $\text{PbO}_2$ -type structure was not detected up to 128 GPa after laser heating using stishovite as starting material [4].

The above observations clearly show that the high pressure behavior of silica depends on the starting material in experiments. Ideally, to synthesize a stable high pressure–high temperature polymorph, we should melt material at high pressure first and then gradually reduce temperature to obtain a thermodynamically stable crystalline phase. However, such experiments are currently challenging. Therefore we have synthesized amorphous sol–gel silica with a very disordered network. At each pressure, we gradually heated the sample to induce crystallization. We believe that using amorphous silica we

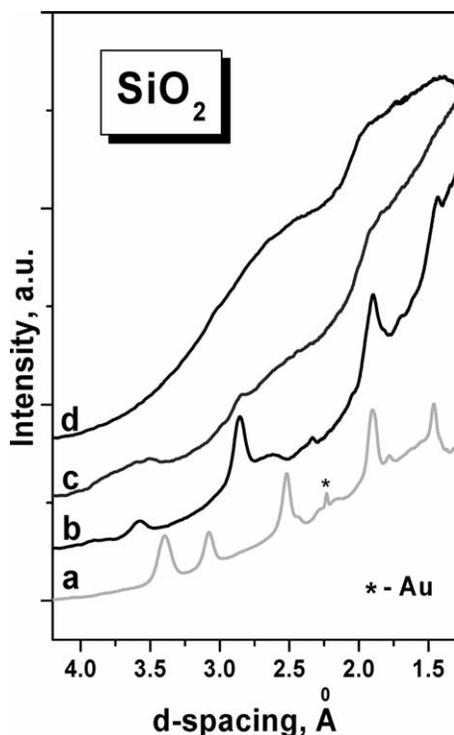


Fig. 3. X-ray diffraction spectra collected at room temperature for  $\text{SiO}_2$  after compression of different starting materials: (a) cristobalite (42 GPa), (b)  $\alpha$ -quartz (50 GPa), (c) tridymite (47 GPa), (d) sol-gel amorphous (50 GPa).

can minimize the effect of starting materials on the stability field of high pressure polymorphs. The laser heating above 1000 K effectively reduce differential stress in the pressure chamber of DAC under uniaxial loading even without pressure medium [30].

Fig. 4 shows the diffraction spectra of temperature quenched silica collected at 40 and 58 GPa after laser heating for  $\sim 10$  min at each temperature. The temperature induced gradual transformation of amorphous silica to a new crystalline structure (peak positions are 1.238, 1.456, 1.887, 2.146 Å) was observed in a temperature range of 1000–1300 K. Around 40 GPa and temperatures above  $1400 \pm 100$  K, the stishovite phase starts to grow and above  $1800 \pm 100$  K only stishovite was detected.

In the case of laser heating at 58 GPa the following phase transformation sequence as a function of temperature was observed: amorphous silica  $\rightarrow$  (1000–1300 K) new phase (peak positions: 1.233, 1.444, 1.874, 2.134 Å)  $\rightarrow$  (above 1400 K)  $\text{CaCl}_2$ -type structures. The X-ray diffraction spectra were collected in both conditions: in situ at high temperatures and pressures and at room temperature and high pressures on temperature quenched samples across heated area. Our X-ray beam ( $\sim 8 \mu\text{m}$  in diameter) was smaller than the laser heated spot ( $\sim 25 \mu\text{m}$  in diameter). On the boundary of the heated area we observed no other phases, only the relative intensity of diffraction peaks from the new crystalline phase is changed.

The structure of the new phase can be described as hexagonally close-packed oxygen with cations randomly filling one half of the octahedral sites that adopt the disordered niccolite (d-NiAs-type) structure with space group  $P6_3/mmc$  (#194). Rietveld full profile refinement of the d-NiAs-type phase at 53 GPa after annealing at  $1200 \pm 100$  K is shown on Fig. 5.

The d-NiAs-type structure as a possible metastable post-rutile phase of  $\text{SiO}_2$  and  $\text{GeO}_2$  was reported on the basis of static and shock-wave experiments on vitreous silica glass [20,31]. However, we have determined that the d-NiAs-type structure precedes rutile/ $\text{CaCl}_2$ -types and can be synthesized only from disordered materials in the narrow temperature range of 1000–1300 K and pressures above 30 GPa to at least 60 GPa (the maximum pressure in this study). Moreover, the stishovite and  $\text{CaCl}_2$ -type structures of silica are denser than the d-NiAs-type structure, although higher density for d-NiAs at high pressures was predicted [32]. In analogous experiments for silica mixed with Pt and compressed without pressure medium to 30 and 55 GPa after laser heating at  $1200 \pm 100$  K for  $\sim 10$  min, the unit cell molar volumes of d-NiAs were 13.22 and 12.45  $\text{cm}^3/\text{mol}$ , respectively, larger than stishovite by 1.3–2% (12.95 and 12.29  $\text{cm}^3/\text{mol}$ , respectively) synthesized by heating same samples at  $1800 \pm 100$  K for  $\sim 10$  min at those pressures. The similar unit cell volumes for stishovite compressed to 29.4 and 55.9 GPa (12.97 and 12.26  $\text{cm}^3/\text{mol}$ , respectively) were reported recently [4] (in both studies, the same equation of state for Pt was used [26]). The d-NiAs-type structure is meta-quenchable and gradually transforms to stishovite at ambient conditions with time (in  $\sim 20$ –60 h), which could explain why this phase appears to be absent in nature.

### 3.2. $\text{GeO}_2$ polymorphism

The high pressure behavior at room temperature of  $\alpha$ -quartz-type  $\text{GeO}_2$  phase is very similar to  $\alpha$ -quartz  $\text{SiO}_2$ . Above 7 GPa the  $\alpha$ -quartz-type  $\text{GeO}_2$  transforms to a poorly crystalline monoclinic structure that can be described by the same structure as for  $\text{SiO}_2$ —on the basis of  $P2_1/c$  space symmetry (Fig. 6). However, no intermediate phase, analogous to quartz-II for  $\text{SiO}_2$ , has been detected for  $\text{GeO}_2$  in our and other studies [33]. This monoclinic phase was observed to at least 52 GPa and remains stable on decompression to ambient pressure. There was no sign of amorphization and broad diffraction lines are mainly due to uniaxial stress in the DAC.

During laser heating, as temperature was increased from  $1200 \pm 100$  to  $1600 \pm 100$  K, the gradual transformation of the monoclinic phase directly to an orthorhombic structure was observed at 36 GPa (Fig. 7). The high pressure orthorhombic phase has the  $\text{CaCl}_2$ -type structure (space group  $Pnmm$ ,  $Z = 2$ ). The lattice parameters at 36 GPa, for example,  $a = 4.2617(4)$  Å,  $b = 4.1268(2)$  Å,  $c = 2.7817(4)$  Å, and unit cell volume of 14.73(1)  $\text{cm}^3/\text{mol}$

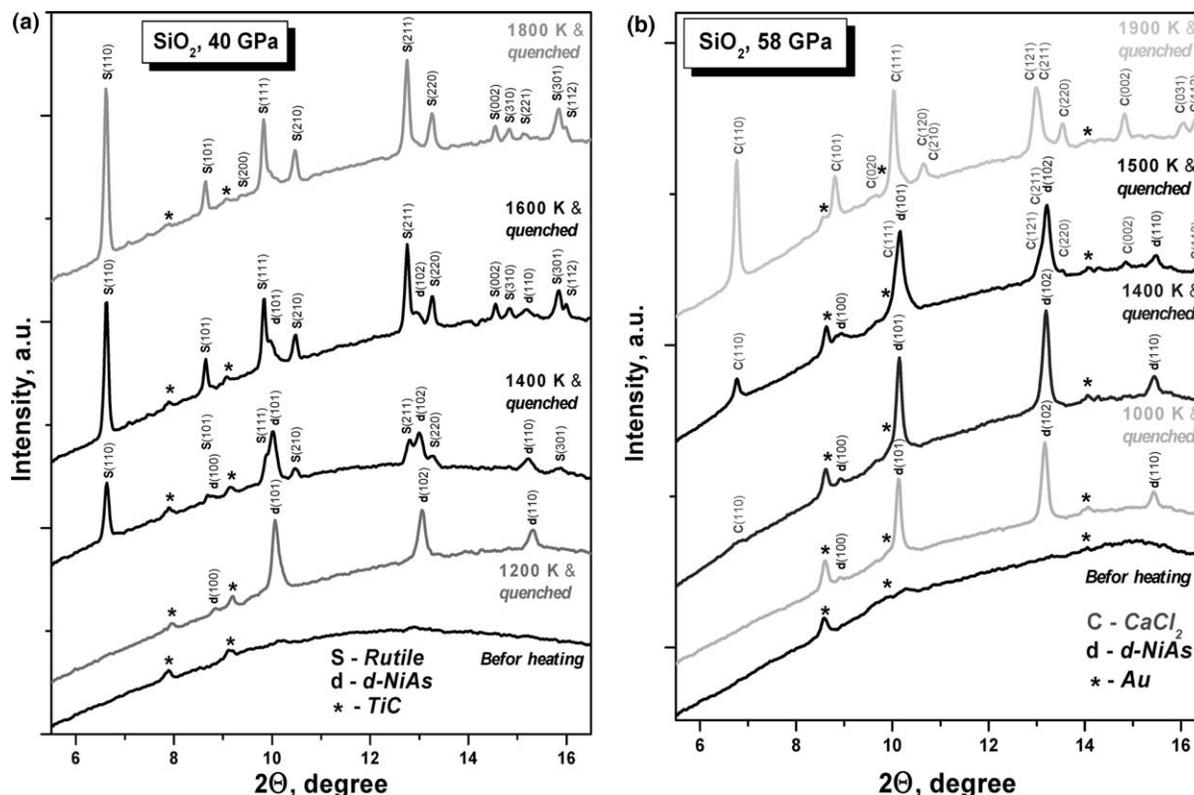


Fig. 4. Temperature induced phase transformation of sol–gel amorphous silica to rutile-type (a) and  $\text{CaCl}_2$ -type (b) structure through an intermediate d-NiAs phase (shown by indices). The weak X-ray scatters TiC (a) and boron (b) powder were used as laser absorbers. Diffraction spectra were collected on temperature quenched samples after laser heating for  $\sim 20$  min at each temperature step. Same phase transformation sequence was observed for other laser absorber materials: Pt and Fe.

is slightly smaller than that reported for the same high pressure phase ( $14.90(9) \text{ cm}^3/\text{mol}$  at 36 GPa) [33] obtained by pressurizing rutile-type  $\text{GeO}_2$  at quasi-hydrostatic (methanol–ethanol–water pressure medium) conditions.

On further compression to 41 GPa and laser heating at  $1600 \pm 100 \text{ K}$  (Fig. 8), the diffraction from the  $\alpha\text{-PbO}_2$ -type high pressure phase appeared. The relative intensities

of the diffraction peaks corresponding to the  $\text{CaCl}_2$ -type phase decreased with increasing pressure (Fig. 8). Above 44 GPa, the diffraction intensities from the  $\alpha\text{-PbO}_2$ -type phase are greater than those from the  $\text{CaCl}_2$ -type phase (Fig. 8), although coexistence of both phases was observed up to 60 GPa and on decompression to ambient pressure. The crystal structure of  $\alpha\text{-PbO}_2$  ( $Pbcn$  space group

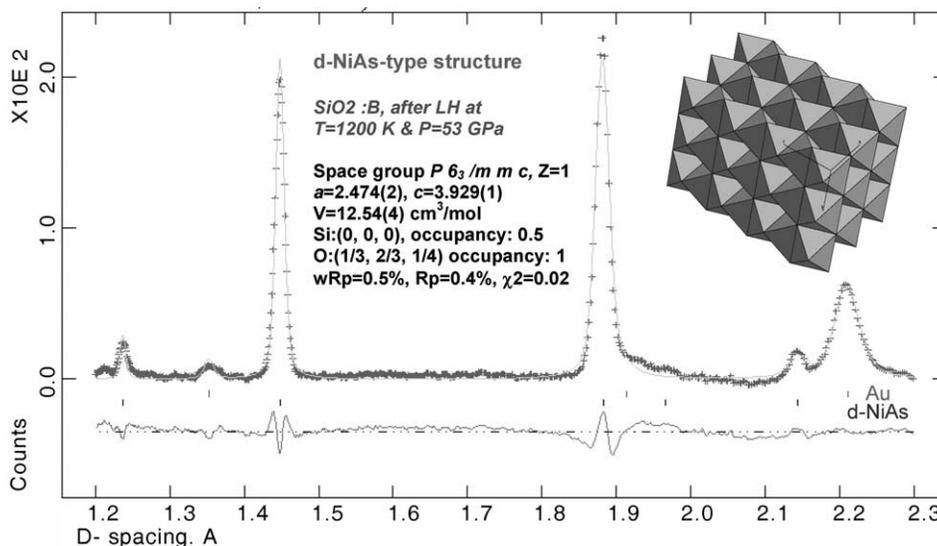


Fig. 5. Rietveld full profile refinement of the d-NiAs-type phase of  $\text{SiO}_2$  at 53 GPa after laser annealing at  $1200 \pm 100 \text{ K}$  for 20 min.

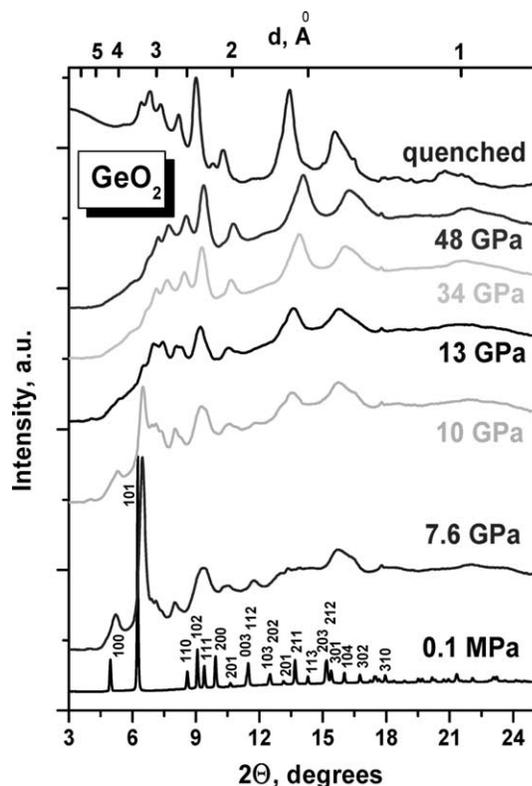


Fig. 6. X-ray diffraction spectra collected on compression of  $\alpha$ -quartz-type  $\text{GeO}_2$  at room temperature.

symmetry) can be described in terms of *hcp* packing of oxygen with one-half of the available octahedral interstices occupied by germanium ions to form  $2 \times 2$  zigzag chains of  $\text{GeO}_6$  edge-sharing octahedron [21]. On decompression the  $\text{CaCl}_2$ -type phase transforms to rutile-type phase at  $\sim 28$  GPa, while the  $\alpha$ - $\text{PbO}_2$ -type phase persists down to ambient pressure.

The unit cell volumes of the  $P2_1/c$ -type,  $\text{CaCl}_2$ -type and  $\alpha$ - $\text{PbO}_2$ -type phases are 14.84(5), 14.38(5) and 14.21(8)  $\text{cm}^3/\text{mol}$  at 48 GPa. For quenched samples at ambient condition, the volumes are 16.90(9), 16.65(3) and 16.41(9)  $\text{cm}^3/\text{mol}$ , respectively. Note that at ambient pressure the rutile-type phase should replace the  $\text{CaCl}_2$ -type.

### 3.3. Comparison

The high pressure behavior of different polymorphs of  $\text{SiO}_2$  and  $\text{GeO}_2$  are summarized on Fig. 9. The main structural difference for these two materials at ambient pressure and temperature is that  $\text{SiO}_2$  has four major polymorphs (cristobalite, tridymite,  $\alpha$ -quartz and glass) with four-coordinated Si, while  $\text{GeO}_2$  has two similar to  $\text{SiO}_2$  polymorphs ( $\alpha$ -quartz and glass) and one rutile-type phase with six-coordinated Ge.

Amorphous phases of both silica and germania at ambient pressure have four-coordinated cations that gradually transform to six-coordinated above 10 and 6 GPa, respectively. Temperature induced crystallization of

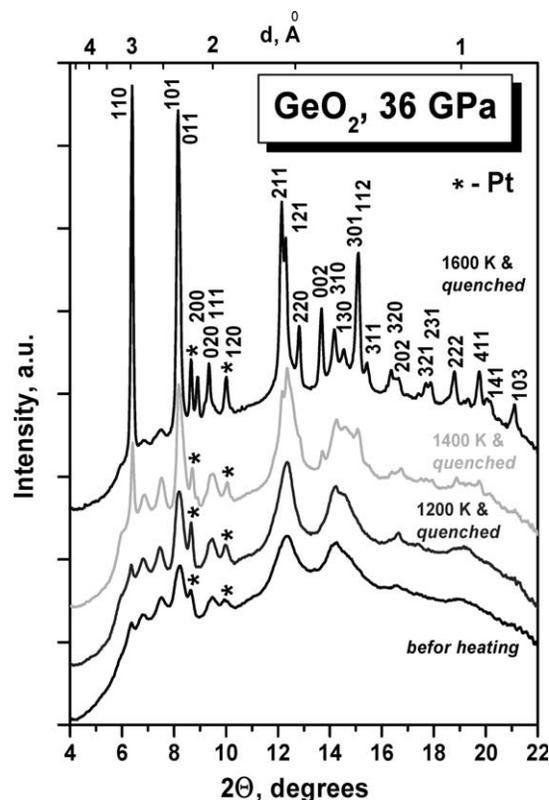


Fig. 7. Temperature induced transformation of the monoclinic high pressure phase of  $\text{GeO}_2$  at 36 GPa to the  $\text{CaCl}_2$ -type phase (temperature quenched samples after laser heating for  $\sim 10$  min using platinum as a laser absorber mixed with  $\alpha$ -quartz  $\text{GeO}_2$  powder).

the amorphous phase to the disordered NiAs-type structure was detected for  $\text{SiO}_2$  at pressures above  $\sim 30$  GPa to at least 60 GPa in a temperature interval of 1000–1300 K. The disordered NiAs-type structure as a possible metastable post stishovite phase was reported on the basis of static and shock-wave experiments on vitreous glass above 30 GPa for  $\text{SiO}_2$  and above 25 GPa for  $\text{GeO}_2$  [32] [20,31]. However, the high pressure–temperature stability range of the d-NiAs phase and its relation to the rutile phase remains undefined. In our studies, for the first time we have isolated the d-NiAs type phase that allowed us to define the lattice parameters using Rietveld full profile refinement at different pressures and temperatures.

The observed d-NiAs structure in laser-heated DACs could be synthesized only when amorphous starting materials were used. The presence of a small amount of d-NiAs phase together with other phases (rutile- or  $\text{CaCl}_2$ -types and untransformed material) in the case of  $\alpha$ -quartz as starting material has been observed in shockwave experiments [31] and DAC experiments after laser heating [20]. According to our data, the d-NiAs is a pre-rutile/ $\text{CaCl}_2$ -types phase and can be formed only by heating of disordered structures. We interpret the presence of the d-NiAs phase in experiments using  $\alpha$ -quartz as starting material as follows. During compression, the sample may partially transform to a disordered network, especially at room temperature and on



CaCl<sub>2</sub>-type phase at high pressure in a narrow temperature interval of 1000–1300 K, where energy is insufficient to overcome the kinetic barrier to order cations inside a hexagonal close packing oxygen network.

After increasing temperature above  $1400 \pm 100$  K, the d-NiAs type phase transforms for both materials SiO<sub>2</sub> and GeO<sub>2</sub> to rutile- or CaCl<sub>2</sub>-types depending on pressures—below/above  $\sim 55$  GPa for silica and  $\sim 27$  GPa for germania. Further pressurization results in phase transformation of CaCl<sub>2</sub>-type phase to  $\alpha$ -PbO<sub>2</sub>-type at high temperatures for both materials SiO<sub>2</sub> and GeO<sub>2</sub> but at different pressures (121 and 44 GPa, respectively). The experimentally observed cubic structure pyrite-type phase with *Pa-3* symmetry was reported only for GeO<sub>2</sub> at  $\sim 80$  GPa [22] consistent with the theoretically predicted value [34]. The pyrite-type (*Pa-3*) phase of SiO<sub>2</sub> is predicted above 205 GPa on the basis of local density approximation theory [1] but is yet to be observed experimentally.

The  $\alpha$ -quartz-SiO<sub>2</sub> (as a starting material) transforms to monoclinic *P2<sub>1</sub>/c* type structure at pressures above 22 GPa through intermediate crystalline phase quartz-II at room temperature. In the case of  $\alpha$ -quartz-type GeO<sub>2</sub>, the high pressure phase above 7 GPa can be also described with *P2<sub>1</sub>/c* type structure, however, no intermediate phase was observed at room temperature in contrast to the case of SiO<sub>2</sub>. With increasing temperature, the gradual transformation of *P2<sub>1</sub>/c* type structure to rutile- or CaCl<sub>2</sub>-types was detected for both materials: SiO<sub>2</sub> and GeO<sub>2</sub>. No sign of d-NiAs phase was observed in our experiment with this starting material. Further pressure–temperature induced transformations of SiO<sub>2</sub> and GeO<sub>2</sub> with  $\alpha$ -quartz-type structure as starting phase are the same as those when amorphous phase was used as starting material: rutile  $\Rightarrow$  CaCl<sub>2</sub>  $\Rightarrow$   $\alpha$ -PbO<sub>2</sub>  $\Rightarrow$  pyrite-type (*Pa-3*).

The high pressure–temperature behavior of a rutile type GeO<sub>2</sub> synthesized at ambient pressure is similar to that of a rutile phase synthesized from starting phase of  $\alpha$ -quartz-GeO<sub>2</sub> or amorphous-types at high pressure and temperature.

Diffraction patterns of poor crystalline tridymite high pressure phase at room temperature are very similar to those of the monoclinic structure of pressurized  $\alpha$ -quartz-type SiO<sub>2</sub> with some amorphous phase present. After heating, the high pressure disordered monoclinic-like phase (tridymite as starting material) transforms to rutile- or CaCl<sub>2</sub>-type structures depending on pressure. The behaviors of post rutile- or CaCl<sub>2</sub>-type are the same as those when  $\alpha$ -quartz or amorphous silica are used as starting materials.

At room temperature cristobalite undergoes three phase transitions: C-II, C-III and C-IV [23]. The C-IV phase persists to at least 90 GPa and temperatures to  $830 \pm 10$  K and can be described as monoclinically distorted  $\alpha$ -PbO<sub>2</sub>. After laser heating at pressure above  $\sim 80$  GPa, the C-IV phase transforms to the  $\alpha$ -PbO<sub>2</sub>-type structure. This pressure is much lower than that observed for other polymorphs of SiO<sub>2</sub> and predicted by theory. It is well known that existence of nucleation centers can significantly

change a path of crystal growth and it was experimentally observed for films deposited on structurally-different substrates. From this point of view the grains of monoclinically distorted  $\alpha$ -PbO<sub>2</sub>-type structure of C-IV phase can easily transform to the  $\alpha$ -PbO<sub>2</sub>-type by tilting of SiO<sub>6</sub> octahedra produced by *hcp* oxygen anions, while orthorhombic structure (CaCl<sub>2</sub>-type) require higher energy for this transformation that involves shifting of cations and significantly altering the unit cell [21].

A similar sequence of the phase transition for rutile-type phases SiO<sub>2</sub> and GeO<sub>2</sub> was observed for SnO<sub>2</sub> and PbO<sub>2</sub> but at significantly lower pressures [35,36]. The variety of low pressure phases of SiO<sub>2</sub> at room temperature and its high pressure phase transformations could be explained from a crystallographic point of view. All dioxide cations (Si, Ge, Sn and Pb) belong to the same group IV of the periodic table. Assuming anions and cations as quasi-elastic spheres, the diversity of high pressure phases with six-coordinated cations can be described by occupation of cations at different octahedral sites formed by *hcp* oxygen network [1]. The small radius of the Si cation ( $r_{\text{cat}} = 0.42$  Å) compared to the anion O ( $r_{\text{an}} = 1.32$  Å) allows Si to migrate within *hcp* oxygen network and occupy different octahedral sites forming varieties of phases with energetically competitive structures that do not exist for larger cations: Ge—0.53 Å, Sn—0.71 Å and Pb—0.84 Å. In general, the pressure induced phase transformation takes place at lower pressures for materials with larger interatomic distance and weaker bond energy for the same type structure. At ambient pressure the rutile-type of SiO<sub>2</sub> has stronger interatomic bond at higher ratio of  $r_{\text{an}}/r_{\text{cat}} = 3.07$  and shorter shared edge distance of O–O (2.29 Å), than those of other group IV element dioxides: GeO<sub>2</sub>—2.42 Å ( $r_{\text{an}}/r_{\text{cat}} = 2.49$ ), SnO<sub>2</sub>—2.61 Å ( $r_{\text{an}}/r_{\text{cat}} = 1.86$ ) and PbO<sub>2</sub>—2.7 Å ( $r_{\text{an}}/r_{\text{cat}} = 1.57$ ) [21,37]. Thus, the dense *hcp* oxygen network of SiO<sub>2</sub> with small Si atoms results in a variety of phases and phase transitions at relatively high pressures comparing to those of GeO<sub>2</sub>, SnO<sub>2</sub> and PbO<sub>2</sub>.

#### 4. Summary

In this study, we showed that the kinetics plays an important role in high pressure phase transformations of SiO<sub>2</sub> and GeO<sub>2</sub>, reflecting the strong dependence on starting material (especially at room temperature) and high pressure–temperature history. The temperature induced high pressure transitions of silica and germania polymorphs in general have similar sequences: (amorphous,  $\alpha$ -quartz)  $\Rightarrow$  d-NiAs  $\Rightarrow$  rutile  $\Rightarrow$  CaCl<sub>2</sub>  $\Rightarrow$   $\alpha$ -PbO<sub>2</sub>  $\Rightarrow$  pyrite-types (*Pa-3*). For the cristobalite polymorph of SiO<sub>2</sub>, that does not exist for GeO<sub>2</sub>, the transition sequence is different. The  $\alpha$ -PbO<sub>2</sub>-type phase can be synthesized using cristobalite as starting material directly from low temperature high pressure phase (monoclinically distorted  $\alpha$ -PbO<sub>2</sub>-type) omitting

the stishovite/CaCl<sub>2</sub>-type phase and at significantly lower pressures than for amorphous or  $\alpha$ -quartz starting materials.

This systematic study also led to the determination of a high pressure–temperature stability range for d-NiAs phase of SiO<sub>2</sub>. For the first time, we have isolated disordered nicolite-type structure that exists in a narrow temperature range of 1000–1300 K at pressures between 30 and 60 GPa and can be synthesized only by using amorphous phase as precursor. The structure of this temperature-intermediate phase can be described as hexagonally close-packed oxygen with cations randomly filling one-half of the octahedral sites (space group  $P6_3/mmc$ , for silica at 53 GPa the unit cell parameters:  $a = 2.474(2)$ ,  $c = 3.929(1)$ , Si(0,0,0), O(1/3,2/3,1/4)]. The temperature induced formation of the d-NiAs phase can be used as an indicator of presence of cation disordered network in both SiO<sub>2</sub> and GeO<sub>2</sub> materials at high pressure before heating.

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