



**Pressurization and heating of silica glass with a multi anvil press:  
Implications for structure, hardness and density of densified silica  
glass and coesite**

Niklas Ottersberg, Christian-Albrechts-Universität zu Kiel, Germany

September 2015

Supervisor

Dr. Norimasa Nishiyama

Eleonora Kulik

**Abstract**

During the summer school program at the DESY site in Hamburg a series of high pressure and temperature experiments was performed. Therefore silica glass was pressurized to a pressure of 8 GPa and heated to temperatures between 800 and 1600 °C. XRD measurements showed that under a temperature of 1200 °C densified silica glass were synthesized whereas higher temperatures formed crystalline coesite. This increasing portion of crystallinity leads to an increase of the density of the samples. Hardness measurements showed similar hardness around 8.5 GPa for both kinds of resulting material what was surprising and can't be explained so far.

## Table of Contents

1 Introduction .....	3
2. Experimental set up.....	3
2.1 Multi Anvil Press.....	3
2.2 Cell assembly .....	7
2.3 Temperature and pressure calibration .....	8
3 Experiments .....	9
4 XRD measurements .....	11
4.1 Theory .....	11
4.2 Results .....	11
5 Hardness measurments.....	14
5.1 Theory .....	14
5.2 Results .....	16
6 Density measurements.....	17
6.1 Theory .....	17
6.2 Results .....	18
7 Summary .....	19
8 References.....	20
9 Appendix .....	21
Figure 1: Schematic way of pressurize the sample in a multi anvil press .....	4
Figure 2: The eight insulated anvils [Gaida, 2014].....	5
Figure 3: Experimental set up of multi anvil press experiments [Gaida, 2014]. .....	6
Figure 4: Dimension of the parts for the experimental set up [Gaida, 2014] .....	8
Figure 5: Illustration of the installed sample during the experiment [Gaida, 2014] .....	8
Figure 6: Example of a pressure calibration for the 5000 tn press in Bayreuth [Frost et al, 2004].....	9
Figure 7: XRD measurements of the starting material and the densified glass samples.....	12
Figure 8: XRD measurements of the coesite.....	13
Figure 9: XRD measurements of kyanite glass and composite of stishovite and corundum .....	14
Figure 10: Knoop indenter and resulting imprint [Blau and Shives, 1985].....	15
Figure 11: Indentation imprints for a load of 500 g and picture of sample H173 .....	16
Figure 12: Results of the hardness measurements of the SiO <sub>2</sub> samples .....	17
Figure 13: Installation for the measurement of the mass $m_{\text{air}}$ and $m_{\text{liq}}$ [Gaida, 2014] .....	18
Figure 14: Results of the density measurements from 800 to 1600 °C .....	19

## **1 Introduction**

High pressure devices mostly are used by geoscientists and material scientists due to their unique possibility to simulate pressures up to 25 GPa and temperatures of 2500 °C and higher. Under these extreme conditions geoscientists are able to study processes like phase transformations which take place several hundred kilometer insight the earth. One example of this phase transformation is the reaction of olivine to ringwoodite and wadsleyite between 410 and 670 km.

High pressure devices attract the interest of material scientist due to the chance of synthesizing materials which are able to replace ceramics and metals because of their improved properties such as indentation hardness and fracture toughness (in the following hardness and toughness). These investigations are supported by for example the Japanese government (2007) and the European Union (2008). This support can be explained by the limitation of natural resources like rare earth elements which are mostly located in China and energetically unfavorable production [Gaida, 2014].

During the summer school program high pressure and temperature experiments with the starting materials  $\text{Si}_3\text{N}_4$ ,  $\text{Al}_2\text{SiO}_5$  (kyanite) and SK-1310 (pure  $\text{SiO}_2$ ) were performed. After synthesizing these materials XRD measurements were performed to solve the structure of the product. Furthermore the mechanical properties (toughness and hardness) and density were measured.

## **2. Experimental set up**

### **2.1 Multi Anvil Press**

For the experiments a 6/8 Kawai-type multi anvil press [Kawai and Endo, 1970] with a Walker module [Walker et al, 1990] were used at the DESY, Hamburg. The name 6/8 relates on the number of the components of the first and second stage which will be explained later. The pressure was generated by a hydraulic ram (oil) with a maximum load of 1000 tn (effective 700 tn). With this device a pressure up to 25 GPa and a temperature up to 2500 °C could be realized.

The basic equation for the generation of the pressure is

$$p = \frac{F}{a}; \text{units } [Pa = \frac{N}{m^2} = \frac{kg}{ms^2}]$$

By this equation it's obvious that there are two ways to increase the pressure. The first way is to increase the force which is applied on the parts of the press. Due to the maximum load of 700 tn of the press this method is limited. The other way to increase the pressure is to minimize the area of the sample on which the pressure is applied. Therefore a smaller octahedron in which the sample is localized can be chosen. This way is common because only a few facilities in the world have several presses in use.

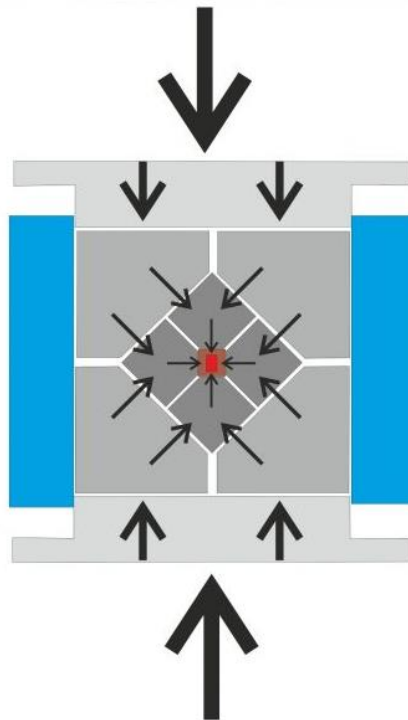


Figure 1: Schematic way of pressurize the sample in a multi anvil press

As mentioned above the module on which the force is applied is divided in three stages. The first stage are the so called wedges which are made up by hardened steel and are the host for the second stage. During the transformation of the force the area on which this is applied is shrinking so that the contact area between the ram and the wedges is larger than the area from where the force is transferred from the wedges to the second stage.

The second stage contains the so called anvils which are made of tungsten carbide which is well-known for its high hardness. For an experiment eight of these anvils are combined so that they form a cube. The corners of these anvils are truncated what creates an octahedral shaped cavity in which the sample is nested. The truncations of an anvil differ so that the same anvil can be used for different experimental set ups. Before the experiment can be started this cubes have to be insulated against each other and the Walker module (with Teflon foil and epoxide plates) to avoid a short circuit because the current which is necessary to heat the sample is delegated by them (Fig. 2). The black material around the cavity (Fig. 2) is phyrophyllite. This material forms a gap between the anvils because otherwise they would break during the pressurization. Additional phyrophyllite behaves ductile during the pressurization so that it fills the gap during the experiment and avoids the outflow of the MgO octahedron.

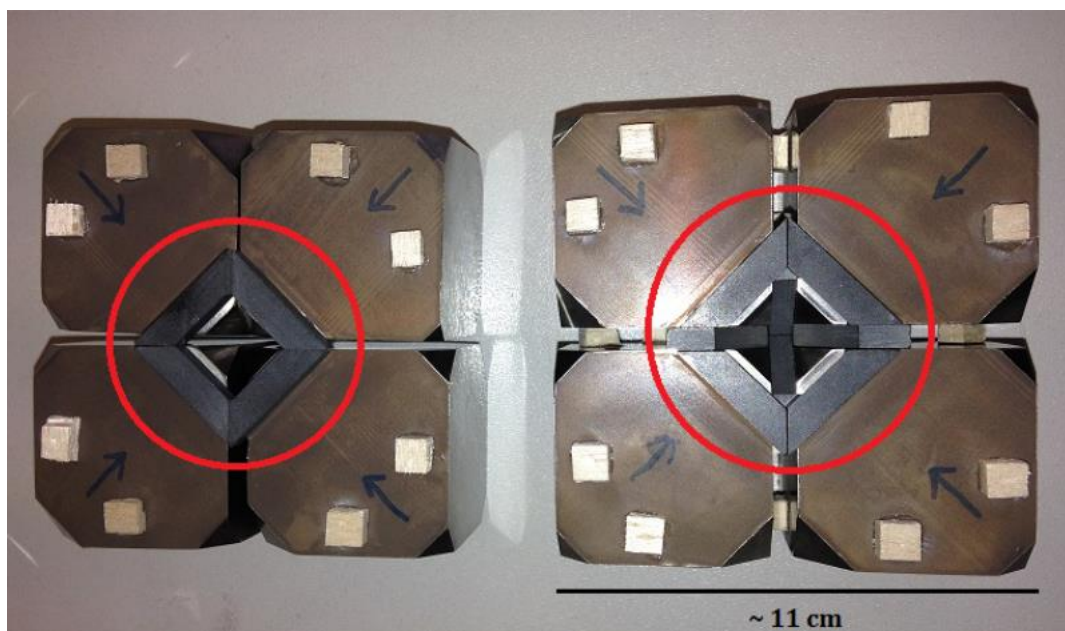
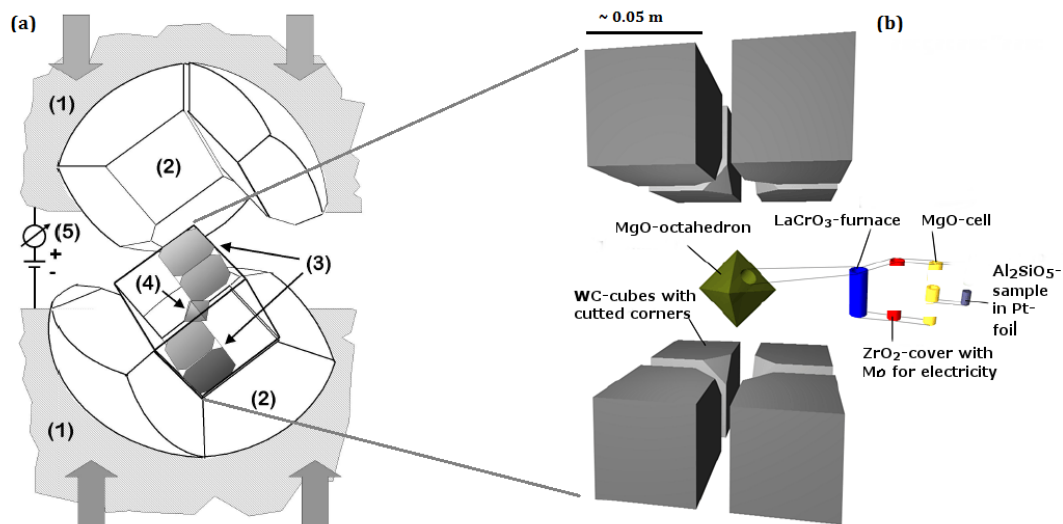


Figure 2: The eight insulated anvils. Indicated by the red circles is the cavity in which the MgO octahedron is located [Gaida, 2014]

The last stage is the magnesium oxide octahedron in which the sample and the furnace are located. Magnesium oxide is the perfect material to host the sample and all the other parts because it has a high hardness to prevent the sample of destruction but is still compressible enough to create high pressures. By using material with such properties it's possible to

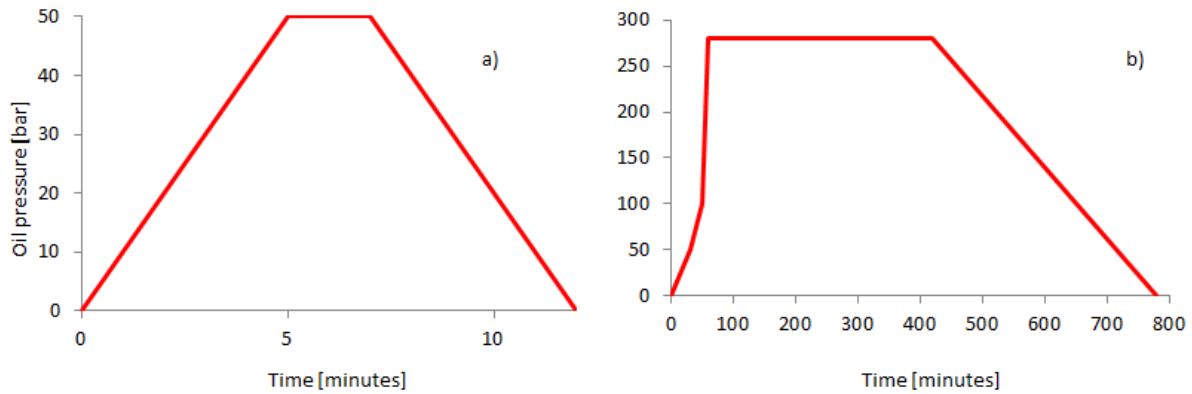
assume a hydrostatic pressure without any gradients. Furthermore magnesium oxide doesn't show any transformations under the applied conditions (transformation at pressures of several hundreds of GPa). The size of the octahedron is slightly larger than the formed cavity so that it can be compressed during the experiment. The size of the octahedron is given by the expression  $18/11$  where 18 show the length of the edges of the octahedron and 11 the length of the truncation of the tungsten carbide anvils.



**Figure 3: Experimental set up of multi anvil press experiments. (a) shows how the wedges form a half sphere in which the eight inner anvils are located ((1) Walker module, (2) wedges, (3) inner anvils, (4) MgO octahedron). (b) shows the cavity of the inner anvils in which the MgO octahedron is located [Gaida, 2014].**

Experiments with the multi anvil press were performed in four phases. The first one was the wedge alignment. The goal of this phase was to test if the insulation of the Walker module works and to align the lower three wedges. Therefore a test cube was installed inside the wedges and resistance measurements were performed. In the case that the resistance wasn't high enough (lower than 15 MOhm) the insulation had to be renewed. During the alignment a pressure of 50 bar was applied and was hold for two minutes (Fig.4a). Afterwards the test cube was removed and the anvils with the sample inside were placed. The pressurization was carried out in several steps with increasing velocity. When the final pressure was reached the heating was performed in 100 Watt steps till the final temperature was reached. In dependence of the desired result the temperature was kept for 30 to 60 minutes. The heating phase was then followed by the decompression. For this phase it was

necessary to choose one of two options. The first one was used when the resulting material should be crystalline. In this case the temperature was decreased during decompression in several steps. This way ensures that the formed crystals had enough time to grow. When the resulting material should be densified silica glass decompression without heating but a longer decompression time was used.



**Figure 4: (a) shows the pressure curve during the wedge alignment and (b) the pressure curve during compression and heating**

## 2.2 Cell assembly

All parts for the cell assembly were hand-made to ensure a high precision with a maximum deviation of 0.02 mm. Also the cell had to be perfectly symmetric because otherwise pressure gradients could occur. The dimensions and the materials of the commonly used 18/11 cell are shown in figure 5.

Beside the sample the furnace is the most important part and is made by lanthanum chromite. Lanthanum chromite is a resistance heater so that the shape has to be perfectly without any unevenness or cracks. The current is transferred by molybdenum wires and disks to the furnace.

To avoid contamination by the other parts of the cell assembly for which the temperature and the pressure are favorable the sample is encapsulated in platinum.

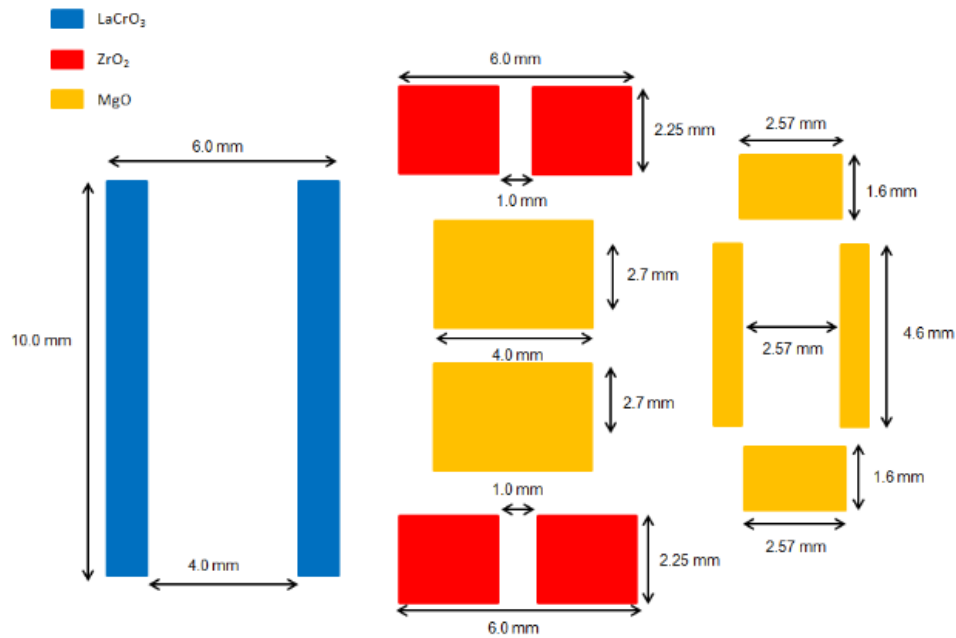


Figure 4: Dimension of the parts for the experimental set up commonly used during the summer school program (Cell 18/11) [Gaida, 2014]

Figure 5: Illustration of the installed sample during the experiment [Gaida, 2014]

### 2.3 Temperature and pressure calibration

Because it's not possible to measure the pressure directly during the experiment it's necessary to do calibrations. Therefore phase transformations of different chemical compounds are used which leads to a measurably feedback in the resistance. In figure 6 a calibration for different cell sizes at the 5000 tn press in Bayreuth is shown. Additionally the used materials for the different pressure ranges can be found. For the calibration up to 9 GPa commonly bismuth is used which transforms at 2.55 GPa from phase I to phase II and at 7.8 GPa from phase III to phase V which is marked by a significant drop in the resistance. At higher pressures chemical compounds such as ZnTe and ZnS can be used which also show phase transformations at certain pressures.

Beside the pressure calibrations temperature calibrations were used for the press at DESY. The temperature can be measured by thermocouple during the pressurization of the sample. The reason why temperature calibrations were used is that under high pressures the stress and strain state can change so that the wires can become sheared apart. Because of this



additional measurements with thermocouples and without samples were performed so that it was possible to relate the power supply to the measured temperature and control the temperature by the power supply during the experiment.

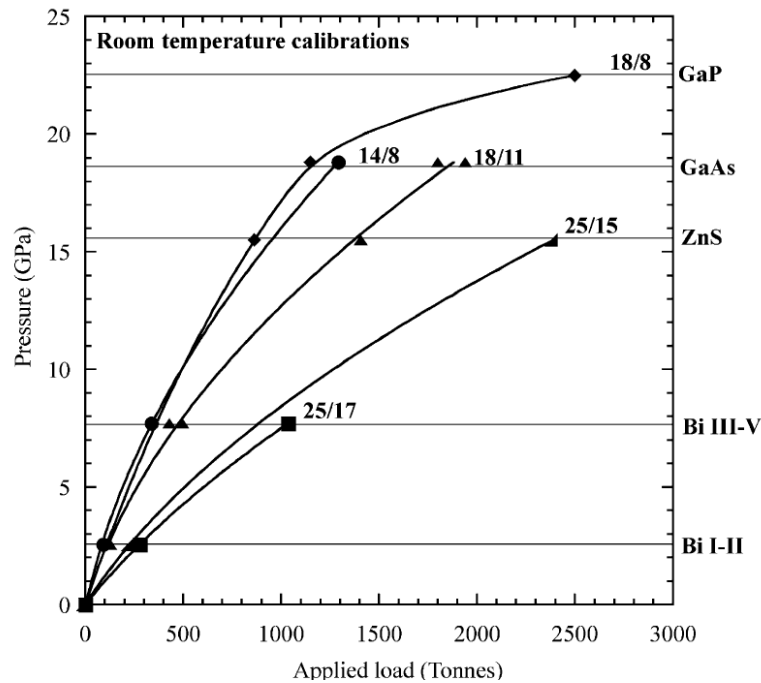


Figure 6: Example of a pressure calibration for the 5000 tn press in Bayreuth [Frost et al, 2004]

### 3 Experiments

During the summer school program experiments with different starting materials and resulting materials were performed. The first idea was to synthesize the gamma phase of  $\text{Si}_3\text{N}_4$  which is believed to be one of the hardest ceramics. The goal was to proof the theoretical phase transformation of  $\alpha\text{-Si}_3\text{N}_4$  to  $\gamma\text{-Si}_3\text{N}_4$  which is based on thermodynamic calculations. Unfortunately these experiments weren't successful what was probably related to the extreme conditions of the experiments in respect to temperature and pressure. Due to this the topic was changed to synthesize densified glass and coesite by using the starting material SK-1310 (pure silica glass). The main goal of this series of experiments was to see how the mechanical properties and the structure of the material will change under different temperatures (pressure was fixed at 8 GPa). Afterwards XRD, hardness and density measurements were performed.

Additionally we performed two experiments with kyanite which decompose under application of high temperature and pressure to stishovite and corundum. For this samples only XRD measurements were done but further investigations will be execute during an ongoing PhD thesis.

Sample	Starting material	Resulting material	Temperature [°C]	Pressure [GPa]	Success
<b>1</b>	Silicon nitride ( $\alpha$ -Si <sub>3</sub> N <sub>4</sub> )	Silicon nitride ( $\gamma$ -Si <sub>3</sub> N <sub>4</sub> )	2000	12	Failed
<b>2</b>	Silicon nitride ( $\alpha$ -Si <sub>3</sub> N <sub>4</sub> )	Silicon nitride ( $\gamma$ -Si <sub>3</sub> N <sub>4</sub> )	1800	12	Failed
<b>H164</b>	SK-1310 (pure silica glass)	Coesite (SiO <sub>2</sub> )	1600	8	Successful
<b>H165</b>	Kyanite (Al <sub>2</sub> SiO <sub>5</sub> )	Stishovite (SiO <sub>2</sub> ) and Corundum (Al <sub>2</sub> O <sub>3</sub> )	1600	10	Successful
<b>H166</b>	SK-1310 (silica glass)	Densified silica glass (SiO <sub>2</sub> )	1200	8	Successful
<b>H167</b>	SK-1310 (silica glass)	Coesite (SiO <sub>2</sub> )	800	8	Successful
<b>H168</b>	SK-1310 (silica glass)	Coesite (SiO <sub>2</sub> )	1500	8	Successful
<b>H170</b>	SK-1310 (silica glass)	Coesite (SiO <sub>2</sub> )	1000	8	Successful
<b>H171</b>	SK-1310 (silica glass)	Coesite (SiO <sub>2</sub> )	RT	20	Successful
<b>H173</b>	SK-1310 (silica glass)	Coesite (SiO <sub>2</sub> )	1400	8	Successful
<b>H175</b>	Kyanite (Al <sub>2</sub> SiO <sub>5</sub> )	Stishovite (SiO <sub>2</sub> ) and Corundum (Al <sub>2</sub> O <sub>3</sub> )	2000	10	Failed

Table 1: Experiments during the summer school program 2015 at DESY

## 4 XRD measurements

### 4.1 Theory

For XRD measurements the samples were polished and installed in a Rigaku MiniFlex. During the measurement the sample is exposed to X-Ray radiation which is produced by a X-Ray tube. The energy of the X-Rays was 60 keV with a wavelength of 0.02 nm. In most of the cases the measurements were performed for a range of theta from 10 to 80° with a step width of 0.02° and a speed of 1° per minute.

The X-Rays became scattered at the electrons of the atoms of the crystal lattice. If the reflected ray followed Bragg's law

$$n\lambda = 2d * \sin\theta$$

constructive interference occurred. These emitted rays can then be detected and out of the location of the reflections the distance between the single layers of the lattice and the Miller indices can be determined. Due to this the crystal structure can be solved.

### 4.2 Results

Figure 7 and 8 show the results of the XRD measurements. In figure 7 the results of the densified silica glass samples are plotted. The starting material shows no reflections what is reasonable because of its amorphous structure. The highest intensity can be observed between 10 and 30° with a maximum around 21°. This elevation in the intensity is called glass hump.

The maximum intensity of the other samples is shifted to higher theta values. The reason for the shift of the glass hump is the densification of the glass during the pressurization. The lack of sharp reflections is related to the relative low temperatures which aren't high enough to overcome the thermodynamically barrier which is necessary to initiate the crystallization.

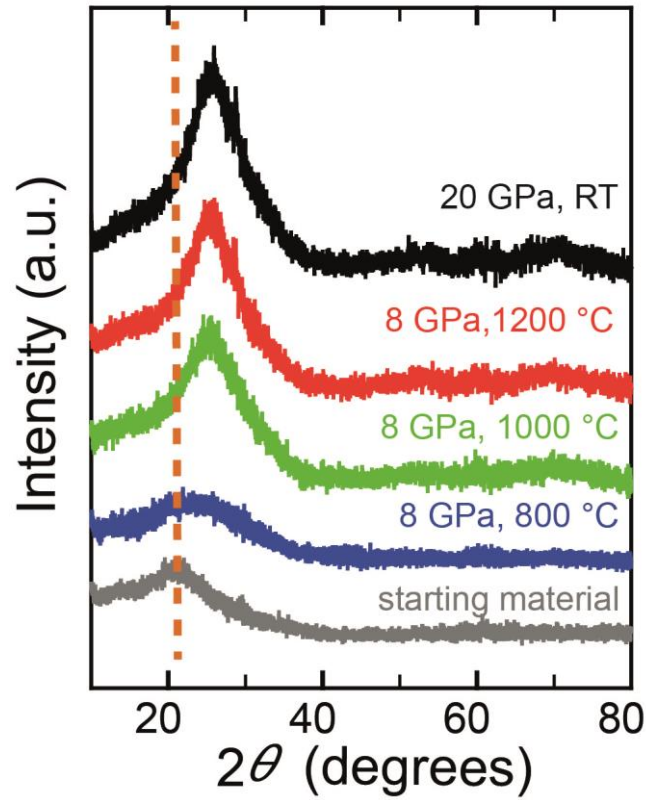


Figure 7: XRD measurements of the starting material and the densified glass samples

In contrast to the XRD measurements of the densified silica glass samples the measurements of coesite show reflections. This is due to the crystalline structure of coesite. At the different layers of the lattice the X-Rays became scattered and interfered constructively. With increasing temperature during the synthesis the intensity is increasing.

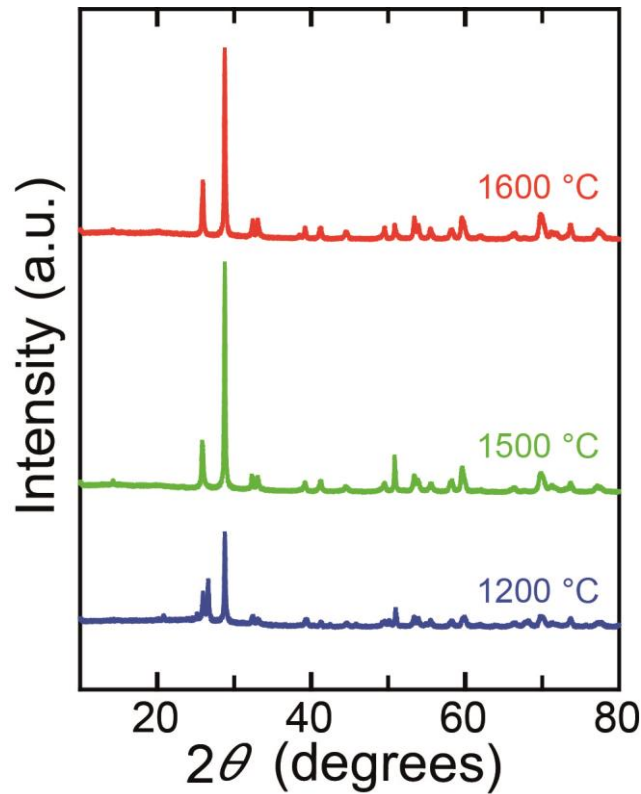


Figure 8: XRD measurements of the coesite

The same behavior can be observed for the experiments with kyanite which decompose to stishovite and corundum at higher temperatures (Fig. 9). The starting material shows clearly the mentioned glass hump. With increasing temperature reflections occur which are results of crystallization of the starting material.

In the plots of the coesite samples just one peak was observed. This is in contrast to the plots of the kyanite samples. This can be easily explained by the reaction which occurs under higher temperatures. During the pressurization of the silica glass only the structure is changing what differs from the processes which take place during the kyanite experiments. As mentioned above kyanite decompose during the experiment to stishovite and corundum which leads to two peaks.

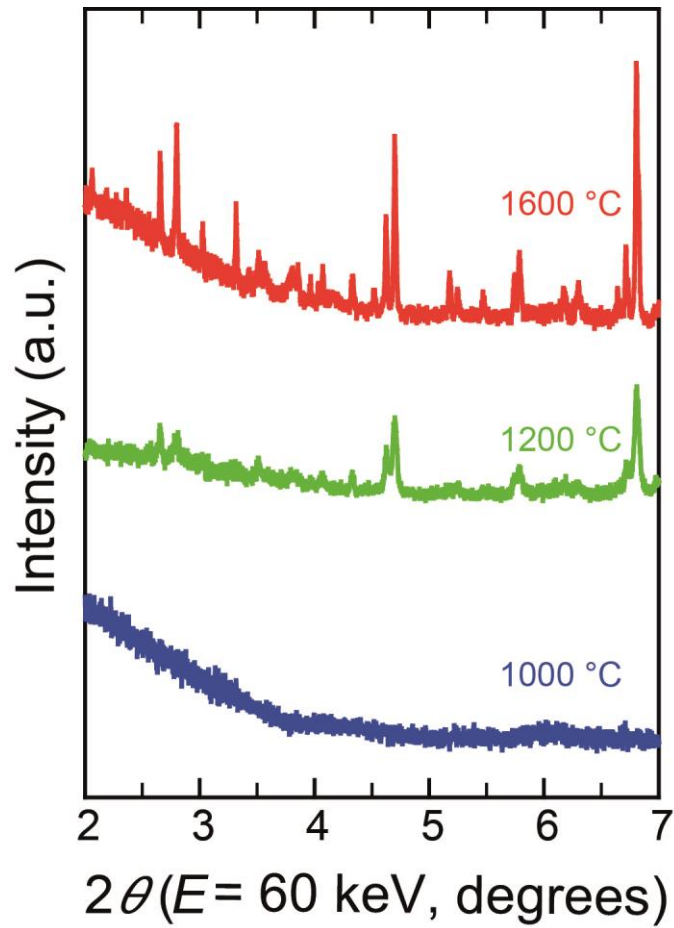


Figure 9: XRD measurements of kyanite glass and composite of stishovite and corundum

## 5 Hardness measurements

### 5.1 Theory

For the determination of the hardness of the densified silica glass and coesite the Knoop hardness test was used. An indenter applied a known load by a rhombohedral-shaped diamond on the sample which creates an imprint at the surface (Fig. 10).

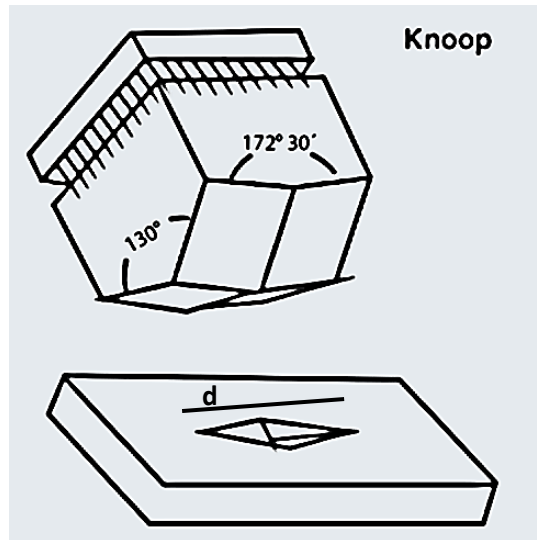


Figure 10: Knoop indenter and resulting imprint [Blau and Shives, 1985]

After the load was removed the length  $d$  of the imprint (Fig. 10) was measured and by using the equation of Knoop et al. (1939)

$$HK = \frac{14229 * L}{d^2}$$

where  $L$  is the applied load in gf (mass\*gravitational acceleration) and  $d$  the length of the imprint the hardness in GPa was calculated. The applied load depended on the structure of the sample because brittle samples tend to form fractures which can influence the calculated hardness. In the case of brittle samples loads between 100 and 500 g were applied whereas the load which was applied on not brittle samples ranged between 200 and 1000 g. To create reliable values three imprints per load were created and the length  $d$  was measured twice per imprint. In the case that fractures or asymmetries were formed during the application the imprint wasn't used to calculate values for the hardness (Fig. 11c).

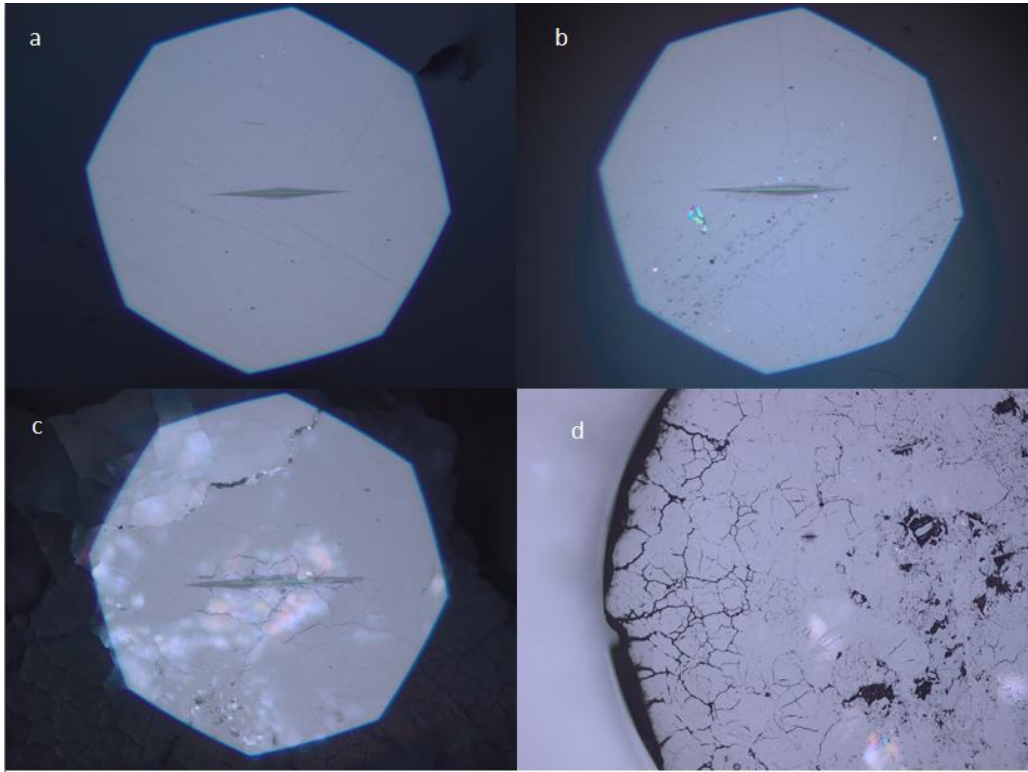


Figure 11: Indentation imprints for a load of 500 g and picture of sample H173. (a) show a perfect symmetric imprint whereas (b) show an asymmetric imprint. In (c) the sample H173 broke under the load so that this imprint couldn't be used for calculations of hardness. (d) shows a overview over sample H173 and shows that this sample was brittle and not well-sintered

## 5.2 Results

Figure 12 shows the results of the hardness measurements of the densified silica glass and coesite (values can be found in the appendix). The highest value ( $10.8 \pm 0.3$  GPa) for Knoop hardness was observed for sample H171 which was synthesized at room temperature and 20 GPa. In contrast sample H173 shows the lowest value ( $6.5 \pm 0.6$  GPa) for the hardness. All other samples are distributed around an average value of 8.5 GPa.

It was surprisingly that the hardness of the densified silica glass and coesite samples are relative similar. So far there weren't other surveys which deals with the hardness of coesite and densified silica glass what makes the interpretation of the values difficult. There are only speculations why the hardness of the densified is equal to the hardness of coesite. Maybe there are some polymorphs of silicon oxide in this normally amorphous densified silica glass which leads to an increased hardness. But



to answer the question if this leads to such a high hardness further analysis has to be performed.

The extreme low hardness of sample H173 can be easily explained by the brittle character of this sample (Fig. 11d). When the load was applied the sample broke which leads to a low estimation of the hardness.

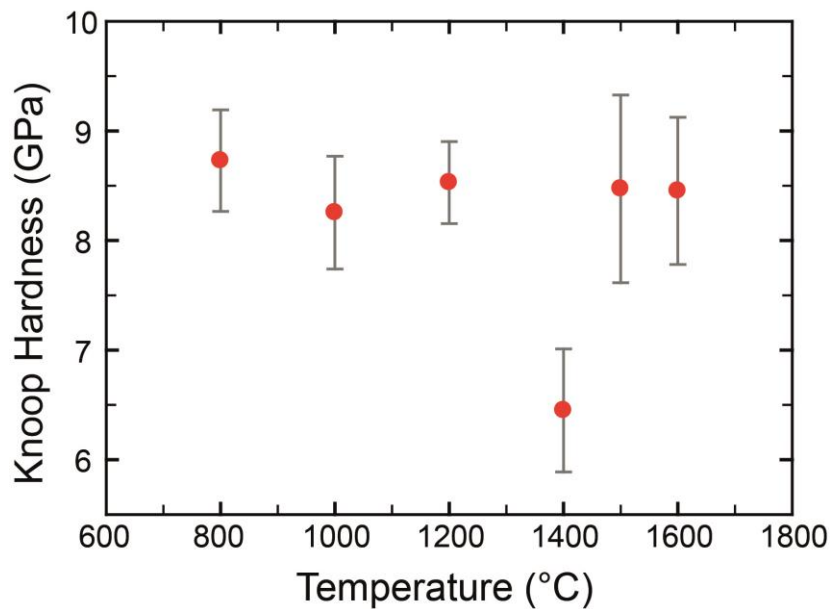


Figure 12: Results of the hardness measurements of the SiO<sub>2</sub> samples

## 6 Density measurements

### 6.1 Theory

The principle for the determination of the density is buoyant force weighing. Therefore the sample was weighted with a special installation (Fig. 13) inside ( $m_{air}$ ) and outside ( $m_{liq}$ ) toluene. By using the mass of the sample inside and outside the liquid and the following equation the density was calculated.

$$\rho = \frac{\rho_{toluene} * m_{air}}{m_{air} - m_{liq}}$$

Because the density of toluene depends on the ambient temperature it's necessary to measure it and correct the theoretical density of toluene.

$$\rho_{toluene} = 0.8852 \frac{g}{cm^3} - 0.0009 * T$$

To proof the reliability of the calculated values the mass of the sample were measured 10 times to determinate an average value. Furthermore a standard ( $SiO_2$ ) was measured and compared to the theoretical value (measured:  $2.211 \pm 0.006 \text{ g cm}^{-3}$ , theoretical:  $2.201 \text{ g cm}^{-3}$ ).

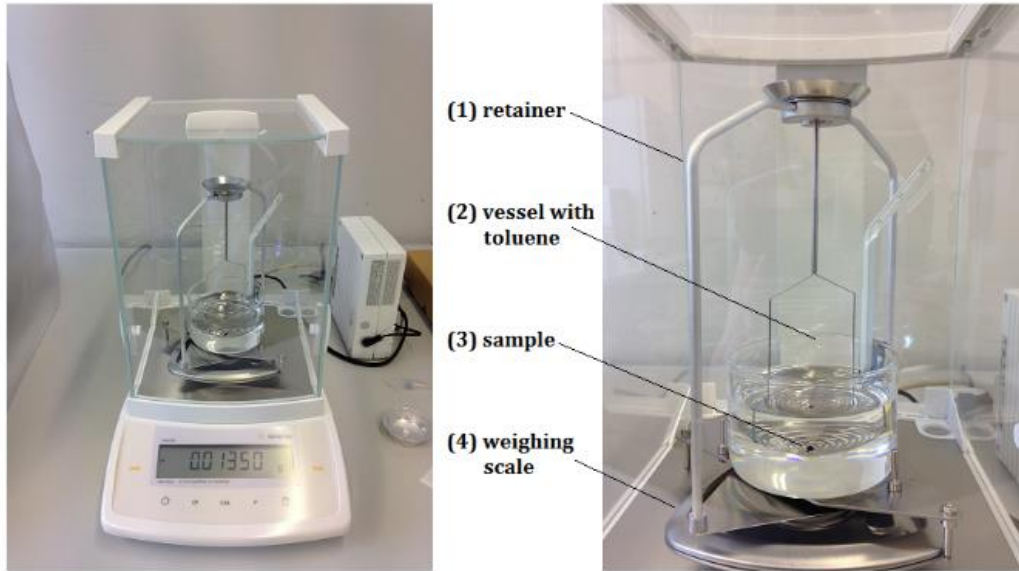


Figure 13: Installation for the measurement of the mass  $m_{air}$  and  $m_{liq}$  [Gaida, 2014]

## 6.2 Results

The results of the density measurements are shown in Figure 14. The samples which were identified as densified silica glass show densities from  $2.658 \text{ (800 } ^\circ\text{C)}$  to  $2.699 \text{ g cm}^{-3} \text{ (1000 } ^\circ\text{C)}$  whereas the samples which were synthesized at higher temperatures show higher densities of  $2.724 \text{ (1400 } ^\circ\text{C)}$  to  $2.923 \text{ g cm}^{-3} \text{ (1600} ^\circ\text{C)}$ .

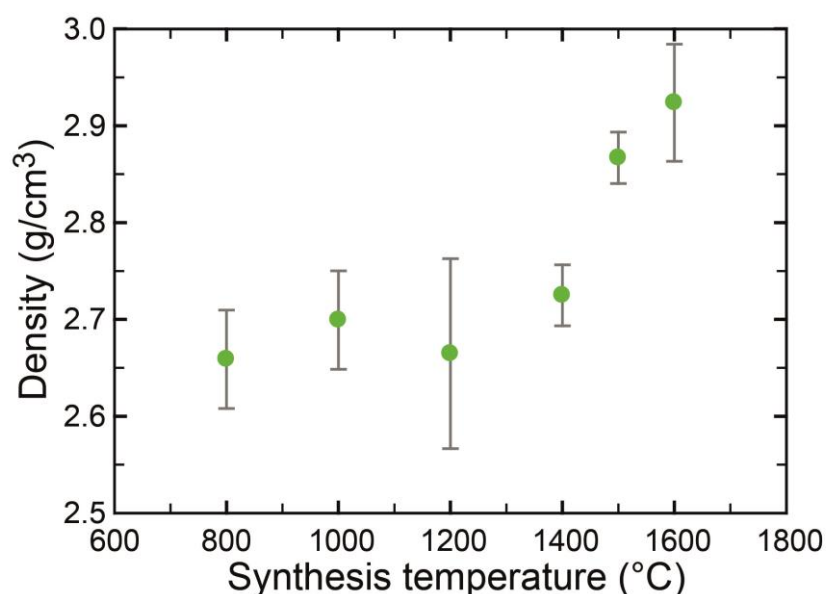


Figure 14: Results of the density measurements from 800 to 1600 °C

This can be easily explained by the sphere packing. The densified silica glass samples are amorphous so that the atoms in this material aren't well-ordered and show just a long-range order. Because of this the atoms in the densified silica glass aren't packed close to each other which decrease the density.

In contrast to this the crystalline samples have a denser package of atoms so that the same volume of sample contains a higher number of atoms which leads to a higher density. With higher temperatures the degree of crystallinity increases so that the portion of crystalline phases in contrast to the amorphous phases grows. The density of sample H164 (8 GPa and 1600 °C) is close to the theoretical density of coesite (measured:  $2.92 \pm 0.02 \text{ gcm}^{-3}$  vs theoretical:  $2.96 \text{ gcm}^{-3}$ ) what means that the sample has a high crystallinity and a low porosity.

## 7 Summary

During the time of the summer school program several experiments with the same starting materials were performed. In this series of experiment the pressure was fixed to 8 GPa in case of silica glass as starting material and just the temperature was changed between the different runs. XRD measurements showed that a certain temperature was necessary to

form crystalline phases because of the thermodynamically barrier which had to be overcome. If the temperature wasn't high enough for crystallization only densification of the material was observable. Measurements of hardness didn't show any differences between the densified silica glass and the coesite samples. During the stay at DESY it wasn't possible to explain this behavior and the reliability of the collected data so that further work is necessary.

Measurements of the density showed a clear trend of increasing density with increasing temperature which could be explained by the higher order of atoms in crystals in comparison to amorphous material.

## 8 References

Blau, P.J., Shives, T.R., 1985. Microindentation hardness testing. ASTM Stand. News, Vol. 13.1, 47-51

Frost, D.J., Poe, P.T., Trønnnes, R.G., Liebske, C., Duba, A., Rubie, D.C., 2004. A new large-volume multianvil system. Physics of the Earth and Planetary Interiors 143-144, 507-514

Gaida, N., 2014. Synthetic nanocrystalline composite ceramics – synthesis of tailored alternative materials of high pressure minerals. Master's thesis at the Christian-Albrechts-Universität zu Kiel

Kawai, N., Endo, S., 1970. The Generation of Ultrahigh Hydrostatic Pressures by a Split Sphere Apparatus. The Review of Scientific Instruments, Vol 41, Number 8, 1178-1181

Knoop, F., Peters, C.G., Emerson, W.B., 1939. A sensitive pyramidal-diamond tool for indentation measurements. Journal of research of the nation bureau of standards, Vol. 23, 39-61

Onodera, A., Suito, K., Kawai, N., 1979. Semisintered oxides for pressure-transmitting media. Journal of Applied Physics, 51 (1), 315-318

## 9 Appendix

	Oil pressure [bar]	Power supply [W]	Pressure [Gpa]	Temperature [dC]	Starting material	Heating duration [min]	Decompression [h]	Density [gcm <sup>-3</sup> ]	Knoop hardness [Gpa]
H164	280.6	1145.6	8	1600	SK-1310	30	12	2.92 ± 0.02	8.5 ± 0.7
H165	374.4	831.7	10	1600	Al <sub>2</sub> SiO <sub>5</sub> glass	30	3	-	-
H166	280.6	880.7	8	1200	SK-1310	30	12	2.67 ± 0.04	8.5 ± 0.4
H167	280.6	603.8	8	800	SK-1310	30	12	2.66 ± 0.02	8.7 ± 0.5
H168	235.1	1140.3	7	1500	SK-1310	30	2	2.87 ± 0.01	8.5 ± 0.9
H170	280.6	744	8	1000	SK-1310	30	12	2.70 ± 0.02	8.3 ± 0.5
H171	310	0	20	RT	SK-1310	0	15	2.70 ± 0.06	10.8 ± 0.3
H173	280.6	1013.8	8	1400	SK-1310	30	12	2.73 ± 0.01	6.5 ± 0.6
H175	374.4	1014.1	10	2000	Al <sub>2</sub> SiO <sub>5</sub> glass	30	3	-	-