## Report on Experiment # ES-485

### Scientific background

SiO2 is a dominant component of terrestrial planets. Although it is rarely present as a pure phase in the mineral assemblages (except in subducted basalts), it is an important component of almost all mantle minerals. Nevertheless, SiO2 plays a major role on melting relations, on defining the degree of partial melting as a function of pressure, temperature and composition, and also on the compositions of melts upon partial melting (e.g. [1]). Unfortunately, we still have a poor knowledge about the melting behavior of the SiO2 component at the P-T conditions of the deep Earth. On one hand, very high melting temperatures were previously reported based on experiments works; SiO2 melting temperature was reported as high as ~4250 K for a pressure of ~35 GPa [2]. Conversely, shockwave experiments suggest a melting point lower than 5000 K at the core-mantle boundary pressure of 135 GPa [3]. For conditions in between, a molecular dynamics calculation suggests a major change in the curvature of the melting curve at ~40 GPa [4]. Still, the different reports differ markedly from each other, for example with a melting temperature reported between ~4000 [3] and ~5250 [4] K at ~50 GPa. In order to model properly the melting behavior of the SiO2-bearing geological materials, it appears necessary to improve our knowledge on the melting behavior of the SiO2 end-member.

### Experimental techniques

We performed a new determination of the SiO2 melting curve up to ~100 GPa using the laser-heated diamond anvil cell coupled with *in situ* X-ray diffraction measurements at the ID-27 beamline of the ESRF. The experimental procedure has been very similar to our previous melting studies [1,5]. High pressures were provided by a membrane-driven DAC mounted with flat or beveled diamond anvils. We used pre-indented Re-gasket in which the sample chamber was drilled using a pulsed infrared laser. Samples consisted in small shards of pure SiO2 glass, typically of 20-50 μm across and 10-15 μm thick. To prevent adsorption of additional water, the glass was grinded in a glove bag under N2-flux where all subsequent steps of the DAC loading were performed. The sample pressure was derived from the equation of state of the KCl pressure medium.

Pressure at high temperature was corrected by $10^{-3}$ GPa/K compared to the nominal pressure measured at 300 K, to take into account the effect of thermal pressure [6]. Samples were heated alternatively using a CO2 laser or two fiber lasers, as we found that SiO2 absorbs relatively well the 1 μm radiation of the fiber laser after the sample was already heated to high temperatures. Temperature up to more than 6000 K have been measured based on spectro-radiometric measurements [7] (Fig. 1).



**Figure 2**: Thermal emission of the sample (blue) heated by two infrared lasers in the diamond anvil cell. The raw signal is corrected to the system response and fitted by a plank function (red). The fits provide experimental temperatures with a precision of ±50 K.

The sample behavior was monitored *in situ* using X-ray μ-diffraction. A monochromatic X-ray beam of 0.3738 Å wavelength was focused using two Kirkpatrick-Baez mirrors onto a spot of less than 2*2 μm² at the sample position. Based on the optical image produced by the fluorescence of the irradiated KCl, we adjusted the position of the entrance hole of the optical spectrometer to measure the temperature at the exact position of the X-ray beam. Diffraction patterns were acquired
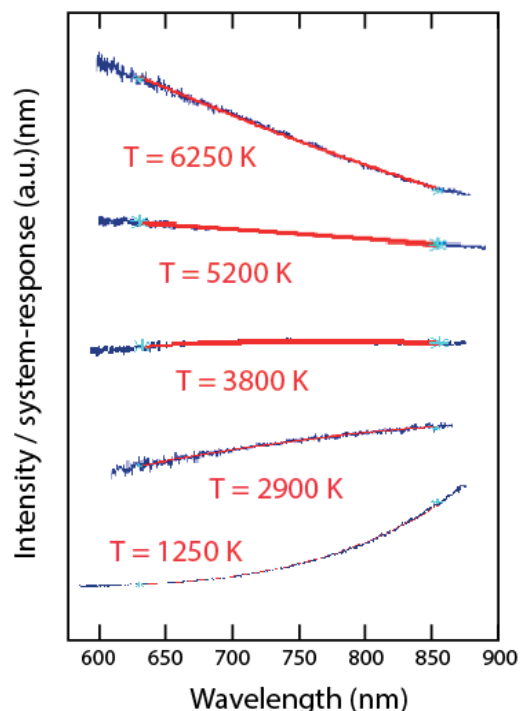
using a MAR-160 CCD detector, before integration and analysis using the Dioptas [8] and XRDUA [9] codes, respectively. At the ID27 beamline, high quality diffraction patterns can be recorded in ~10 seconds.

*Preliminary results:*

At room temperature, the diffraction pattern of the glassy $SiO_2$ did not presented a broad band of diffuse scattering. This lack of signal is explained by the use of very thin samples, which was intentional in order to minimize the axial thermal gradients in the sample. With increasing the sample temperature, we first observed crystallization of the glass. Resulting phases were typical stishovite, with the $CaCl_2$-distortion at above ~60 GPa [10].

With increasing temperature, the diffraction images evolve progressively; grain growth is evidenced by the apparition of diffraction spots of relatively higher intensities, which are superimposed on the continuous rings. At a given temperature, increasing more laser power does not result in an increase of the sample temperature anymore. Simultaneously, the texture of diffraction images becomes spottier, with a growing number of intense diffraction peaks. Also, the position of the diffraction spots on the 2D images changes rapidly with time, showing rapid grain rotation in the sample. Integrated diffraction patterns shows a clear decrease of the intensity of $SiO_2$ diffraction peaks, compared to those of the KCl pressure medium. Upon quenching, many large diffraction peaks reappear. All these experimental features are interpreted as the onset of sample melting. The reason why all diffraction peaks of $SiO_2$ do not disappear abruptly at the melting temperature is because temperature gradients cannot be totally avoided in the LH-DAC. Melting first occurs in the sample region where the temperature is the highest. Still, we are confident that the temperature measurement is appropriate to the molten region because (i) the spectrometer alignment is carefully checked before and after each experiments and (ii) the sample position at the highest temperature dominates the thermal emission of the sample, due to the form of Plank's (or Wien's) law.

*Conclusions:*

Our (still preliminary) melting curve of $SiO_2$ is compared with previous studies. We confirm the very steep Clapeyron slope above the coesite to stishovite transition, which was reported from both experiments [2] and *ab initio* calculations [4,11,12]. This feature is associated to the huge volume change of more than 35% at the transition [13]. Then, the melting curve remains very steep, until an abrupt flattening occurs in the melting curve. At high mantle pressures, we measure a melting curve with a Clapeyron slope only slightly more steep than previously reported based on shock wave experiments [14] and *ab initio* calculations [4,11,12]. The abrupt flattening of the melting slope may be produced by the Si coordination change from 4- to 6-fold in the liquid silicate with increasing pressure. Such behavior would produce an abrupt densification of the melt structure, which was already suggested based on *ab initio* calculations [4,15] and cold compression of glasses [16,17].

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