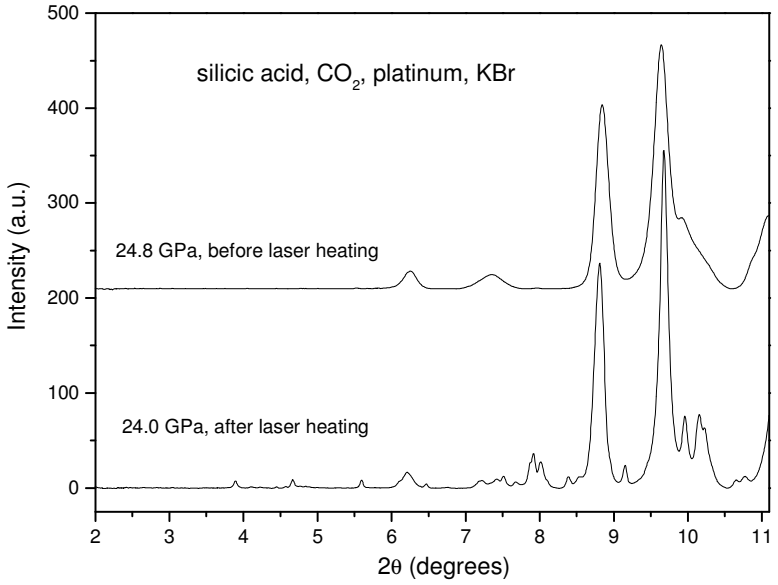
Study of the high pressure molecular-to-non-molecular transformation of CO_2, confined in nanoporous materials, by X-ray diffraction.

Carbon dioxide is one of the most important volatile systems. It is the dominant component of the atmospheres of terrestrial planets such as Mars and Venus, is commonly found in ice form in planets and asteroids, and it is an important volatile in volcanic activity. From the fundamental point of view it is one of the model systems involving the π bonding and the hybridization properties of the carbon atom, which are strongly affected by the high pressure conditions. Despite its simplicity, solid carbon dioxide undergoes a number of high pressure modifications, including the formation of non molecular, extended solids (P > 25-30 GPa) with carbon in 4-fold and 3-fold coordination by oxygen [1, 2, 3]. The non-molecular phases of CO_2 are hard materials. These phases were recovered, at room T, down to about 1 GPa, where they are most likely to be meta-stable. Below such pressures, the extended materials transform back to molecular CO_2. The discovery of extended, partially silica-like CO_2 structures, led us to the idea of searching for possible CO_2/SiO_2 compounds, to be obtained at high pressures, which in turn have been recently predicted by an *ab initio* molecular dynamics study [4]. These systems would represent an entirely new class of materials of high interest in diverse areas of both fundamental and applied sciences.

During the beam time of the experiment CH-3004 at the ESRF, we have obtained amorphous CO_2/SiO_2 compounds in DACs, at about 20 GPa using resisitive heating, by mixing together CO_2 with silicalite (a synthetic SiO_2 zeolite [5]). We studied silicalite-OH powder with silicone oil, dense CO_2 and Argon, respectively in order to determine the ambient-temperature, high-pressure behavior of this material and the corresponding mixtures. XRD patterns were measured upon increasing pressure, in the diamond anvil cell (DAC), up to about 20 GPa, at room temperature. The sample of silicalite with a non penetrating, pressure transmitting medium was found to become amorphous above a few gigaPascals as reported previously [6]. The chemical reaction of CO_2 with the silicalite-OH framework was induced and investigated at about 20 GPa, upon increasing the temperature by the restive heating of the DAC. The XRD diffraction patterns of the silicalite indicate the amorphization of this material along such a P-T path. The combination of the XRD data and IR spectroscopic data, collected along the same P-T path, shows this is not a true amorphisation and that silicalite reacts with CO_2 and a CO_2/SiO_2 compound is obtained. Data analysis is still in progress on these results.

During the CH-3004 beam time we tried laser heating in a DAC of a mixture of CO_2 and silicic acid, a hydrogen containing, highly reactive, silica based material. We used the Nd:YAG laser, combined with a fine Pt nano-powder, which was put inside the reacting sample and used as the laser absorber. KBr thin layers (1 micron) were also put on the anvils, in order to provide the necessary thermal insulation of the sample. The platinum powder was heated up to at least 2000 K. The XRD patterns of the laser heated sample resulted in much sharper Bragg peaks than the starting materials, still to be assigned (figure 1). Unfortunately, platinum participates to the reaction, producing unwanted compounds, as shown by extremely strong and sharp Raman peaks at 150-350 cm^{-1} (figure 2).



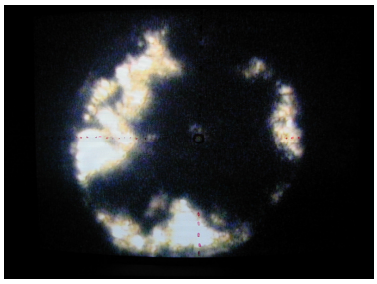


Figure 1: XRD patterns of the CO_2-silicic acid-Pt nanopowder sample, before and after the Nd:YAG laser heating (about 2000 K). Picture on the right: laser heated sample. The black material corresponds to the laser heated part of the sample. The XRD patterns have been averaged over a series, which was measured within this area.

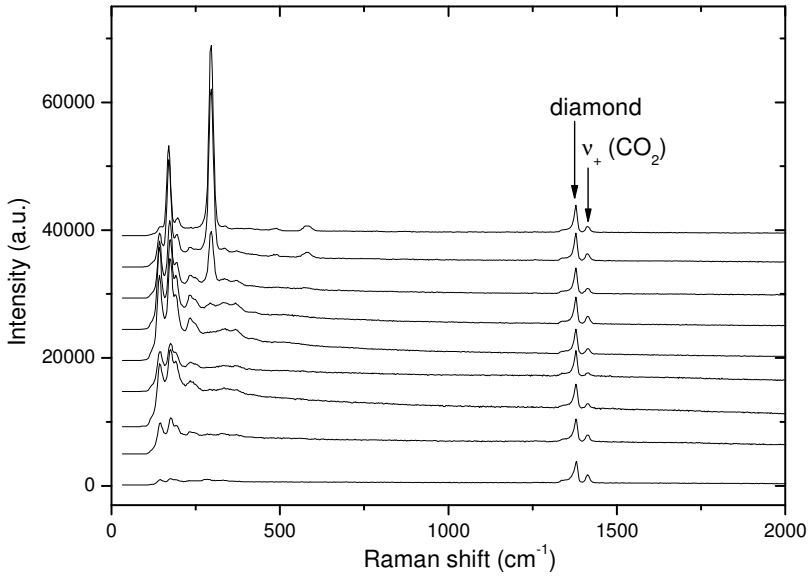


Figure 2: Raman spectra on the of the CO_2-silicic acid-Pt nanopowder sample, after the Nd:YAG laser heating (about 2000 K). The spactra have been measured in different points within the black, laser heated area of the sample.

References

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