Study of high pressure CO_2/SiO_2 compounds by X-ray diffraction.

During the experiment CH-3240 the potential formation at high pressures and temperatures of non molecular CO_2/SiO_2 alloys with the C and Si cations in tetrahedral coordination by oxygen was investigated by reacting CO_2 with various forms of SiO_2. This kind of alloy was predicted to exist by ab initio molecular dynamics simulations [1], and its discovery would give rise to a completely new class of oxides of great interest for fundamental chemistry, Earth science and materials science. We already discovered the high P-T formation of disordered carbonate compounds between CO_2 and SiO_2 (silicon carbonate), at 20-25 GPa and 300-700 K [2]. After this, it became soon clear that the formation of crystalline, tetrahedral alloys would have required more extreme P-T conditions. In fact, pressure in excess of 30-40 GPa and temperatures above 700 K are needed, where it is shown that CO_2 itself forms non molecular solids built up of CO_4 units [3].

We tryed to obtain tetrahedral CO_2/SiO_2 alloys under pressures and temperatures of 40-50 GPa and 1500-2000 K, respectively, using CO_2 laser heated DACs, by chemical reactions of CO_2 and various silica based solids such as silicalite (a pure SiO_2 zeolite), quartz nanopowder and silicic acid, $[SiO_x(OH)_{4-2x}]_n$. The temperature quenched samples were analyzed by the XRD on ID27. The CO_2 laser (10.6 microns wavelength, power of 60 W, 40 microns spot) resonates with IR absorption bands of silica and non molecular CO_2, therefore it is directly absorbed by the sample, not requiring the use of additional absorbing materials as otherwise needed with using NIR lasers (Nd:YAG). This allows to simplify the reaction environment and to avoid unwanted chemical reactions. Also, in order to make the environment very simple and clean we did not use coating on the diamond surface, which in turn limited the high temperatures actually achieved and the thermal stability of the sample.

In all the investigated samples we always got a macroscopic mixture of tetrahedrally coordinated CO_2 (phase V) and octahedral SiO_2, stishovite, whereas the expected CO_2/SiO_2 tetrahedral alloys where never observed. A possible rationale for this is that the P-T range where CO_2 is thermodynamically stable in the tetrahedral forms, as phase V, corresponds to P-T conditions where instead SiO_2 is stable in the octahedral form (SiO_6). In other words the P-T range where CO_2 and SiO_2 are tetrahedrally coordinated do not seem to overlap, which most likely prevents the formation of the alloy. Nevertheless, the formation of a metastable tetrahedral alloy could always be possible in some P-T intervals, maybe at intermediate temperatures between 700 K, where the silicon carbonate forms, and 1500 K where CO_2 and SiO_2 chemically separate each other and form CO_2-V and stishovite, respectively.

The experiment presented a very positive outcome. In fact, the very clean laser heating preocedure allowed us to prepare additional samples made of pure CO_2 in order to study the structure fo the remarkable phase V, whose determination was the matter of a long standing debate [3]. Based on high quality CO_2-V samples, we performed a very reliable Rietveld refinement of the structure of this material, which assessed phase V to be in a partially collapsed variant of SiO_2 beta-cristobalite, space group $I\bar{4}2d$, in which the CO_4 tetrahedra are tilted by 38.4° about the c-axis (figure 1). The existence of CO_4 tetrahedra (average O-C-O angle of 109.5°) is thus confirmed. The results add to the knowledge of carbon chemistry with mineral phases similar to SiO_2 and potential implications for Earth and planetary interiors [4].

Finally, we understood that a tetrahedral alloy including CO_4 groups could be obtained, in principle, by reacting CO_2 with other oxides which remain tetrahedral at high P-T conditions, such as BPO_4 [5]. We then prepared two samples made of a mixture of CO_2 and BPO_4 and performed laser heating (1500-2000 K) at pressures of 40-50 GPa. Although this run was very preliminary, we probably achieved some hint of the existence of a tetrahedral CO_2/BPO_4 alloy. We now think this study urgently needs a follow up in near future synchrotron XRD runs, that we intend to propose. It is likely that more extreme temperatures (2500-3000K) are required to complete the reaction between CO_2 and BPO_4. We are confident to achieve this temperature range by upgrading the laser heating procedure.

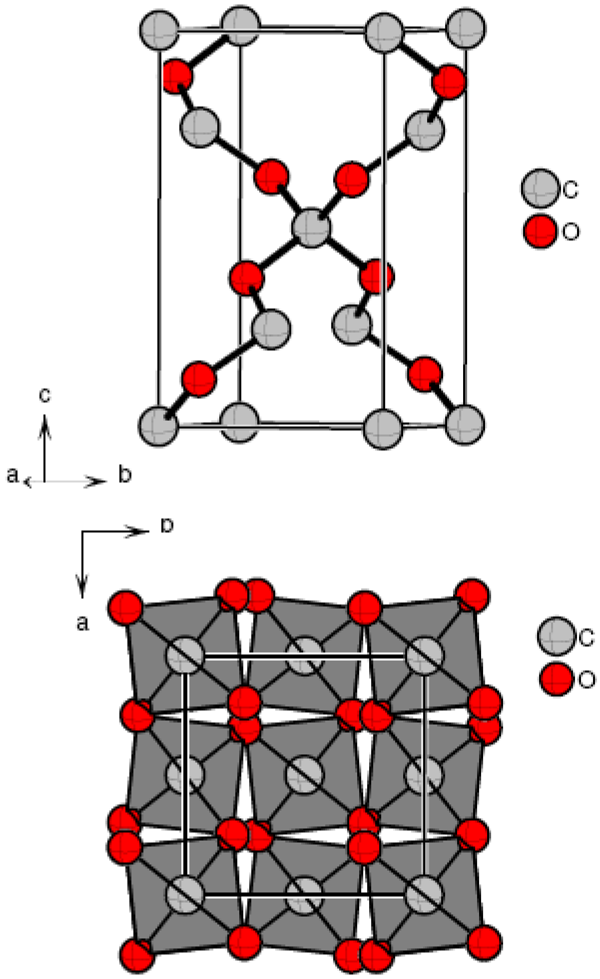

Figure 1. The structure of CO2-V at 43 GPa. The drawings show the $I\bar{4}2d$ structure obtained from the Rietveld refinement using the experimental XRD data.

References

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