New carbonic acid compounds in the H-C-O system at elevated pressures

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Abstract

Due to its great relevance for astrophysical research carbonic acid (H_2CO_3) and its monohydrate ($H_2CO_3 \cdot H_2O$) have recently been studied intensively [1-5]. However, no single-crystal structure determination of water-free H_2CO_3 had been reported, while for $H_2CO_3 \cdot H_2O$ a structural model based on single crystal diffraction data had been determined at 6.5 GPa [5]. Hence, no lattice dynamical calculations for H_2CO_3, needed for unambiguous vibrational spectrum assignment and, consequently, for remote sensing of its presence in meteorites or on icy bodies, could be carried out [1,2]. The high-pressure behaviour of H_2CO_3 has long been disputed [6-9]. At pressures between 1-44 GPa the crystal structure of H_2CO_3-*Pnma* has been predicted by density functional theory (DFT) calculations [6]. However, this structural model substantially differs from the structure of H_2CO_3-$P2_1/c$ derived from a combined neutron powder diffraction and DFT-based study at ~2 GPa [7].

In our studies we used a combination of single crystal X-ray diffraction, Raman spectroscopy and DFT-based calculations, in order to study the formation and crystal structure of H_2CO_3 at elevated pressures in laser-heated diamond anvil cells (LH-DAC). We determined for the first time the crystal structure of a H_2CO_3 phase ($P2_1/n$) using single crystal X-ray diffraction (Fig. 1R) and derived the positions of the hydrogen atoms experimentally [8]. Fig. 1L shows our 2D-Raman mapping before and after laser-heating a H_2O + CO_2 mixture at 8(1) GPa. Using the same approach, we confirmed that H_2CO_3-$Cmc2_1$ with polymerized [CO_4]-chains can be obtained at 40(2) GPa [9]. Its crystal structure was successfully refined from single crystal X-ray diffraction data, including the hydrogen position and is in agreement with a structural model predicted earlier [6]. Further experiments, carried out in the H-C-O system between 5-50 GPa, show that other novel carbonic acid phases can be obtained by laser-heating a H_2O + CO_2 mixture in this pressure range and that the phase diagram of carbonic acid is more complex than previously assumed.

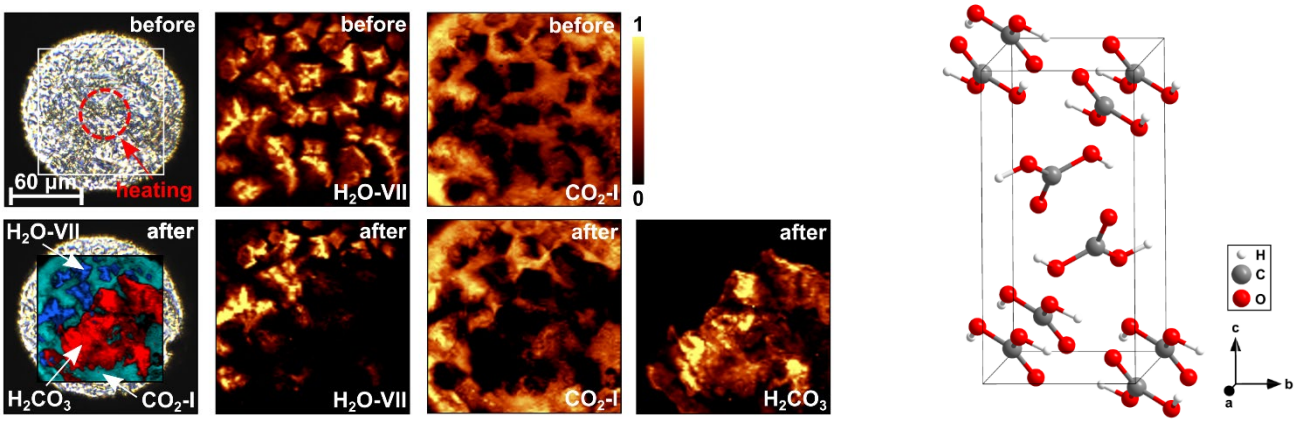

Fig. 1 (L): Synthesis of H_2CO_3 at 8(1) GPa from a H2O + CO2 mixture in a LH-DAC. **(R)** Structure of H_2CO_3-$P2_1/n$ [3].

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