Partially collapsed cristobalite structure in the non molecular phase V in CO₂

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Non molecular CO₂ has been an important subject of study in high pressure physics and chemistry for the past decade opening up a unique area of carbon chemistry. The phase diagram of CO₂ includes several non molecular phases above 30 GPa. Among these, the first discovered was CO₂-V which appeared silica-like. Theoretical studies suggested that the structure of CO₂-V is related to that of β -cristobalite with tetrahedral carbon coordination similar to silicon in SiO₂, but reported experimental structural studies have been controversial. We have investigated CO₂-V obtained from molecular CO₂ at 40–50 GPa and T > 1500 K using synchrotron X-ray diffraction, optical spectroscopy, and computer simulations. The structure refined by the Rietveld method is a partially collapsed variant of SiO₂ β -cristobalite, space group $I\bar{4}2d$, in which the CO₄ tetrahedra are tilted by 38.4° about the c-axis. The existence of CO₄ 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 SiO₂ and potential implications for Earth and planetary interiors.

carbon dioxide | material science

CO₂ is a simple system of paramount importance for a broad range of scientific problems. Carbon dioxide is found in the atmospheres of Earth-like planets, in the ices of outer planets and asteroids, and plays a role in volcanic and seismic activity. The double bonds of the molecule are dramatically altered at high pressures as revealed by the discovery of non molecular CO₂ that forms above 30 GPa in crystalline and amorphous forms, which has attracted great interest in the last decade (1–7). The high degree of metastability in these materials makes the study of the phase diagram of this archetypal substance difficult (8). The first non molecular phase discovered was CO₂-V, obtained by laser heating molecular CO₂-III to 1,800 K at about 40 GPa (3), but its structure has been the subject of controversy and has never been solved so far (1). Raman spectroscopy indicates that CO₂-V is non molecular and most probably characterized by C-O single bonds and carbon in tetrahedral coordination by oxygen as is silicon in silica (3, 9, 10).

Over the same period, several density functional theory (DFT) studies were performed. All of them support the existence of non molecular, tetrahedrally coordinated CO₂ (11–15). These studies took into account a variety of potential silica-like structures, including different types of quartz, tridymite, and cristobalite. A β -cristobalite-like structure was predicted to be the most stable among these structures and most likely the thermodynamically stable phase in the P-T range where CO₂-V is formed and temperature quenched (13–15). This structure is tetragonal, space group $I\bar{4}2d$, built up by corner sharing CO₄ tetrahedra with the carbon atoms forming a diamond network. CO₂-V was predicted

to be denser than molecular CO₂ (12, 16) and hard with bulk modulus of 149.1 GPa (14). The $I\bar{4}2d$ structure is adopted by tetrahedrally coordinated materials, for which the ratio between the lattice parameters c and a exhibits a close relationship to the open space between the tetrahedra: the lower the c/a value, the more open the structure (17, 18). At one end of this class, there is β -cristobalite ($Fd\bar{3}m$) found for SiO₂ and GeO₂, which is cubic and has the most open structure. The β -cristobalite-related structures with high c/a ratios are partially collapsed cristobalites. These compact structures are found in systems with a smaller average cation radius than Si⁴⁺, such as BPO₄, BaSO₄, and PON (18, 19). It is remarkable that the DFT Raman spectrum of $I\bar{4}2d$ CO₂ is in good agreement with the experimental spectrum of phase V (1, 13). Nevertheless, the structure of CO₂-V remains to be determined. An experimental X-ray diffraction (XRD) pattern study on what was considered to be CO₂-V was indexed based on a tridymite like structure (20). In contrast, DFT calculations predicted this structure to be highly metastable and even to give a remarkably different XRD pattern (14). One difficulty in these experiments is to get a clean laser heating procedure, often limited by the use of additional materials in order to absorb the laser beam, which can react with the substance under examination. A rather clean procedure was recently employed using a CO₂ laser with no additional absorbers (21). The resulting XRD pattern of CO₂-V was indexed based on a $I\bar{4}2d$ structural model. Unfortunately, neither structural refinements nor vibrational spectroscopy were performed.

Results and Discussion

CO₂-V was synthesized by clean, direct CO₂ laser ($\lambda = 10.6 \mu\text{m}$) heating of molecular CO₂-III in the diamond anvil cell (DAC) at 40–50 GPa and temperatures in excess of 1,500 K. A total of four different samples were prepared and studied at room temperature by synchrotron XRD [ID27, European Synchrotron Radiation Facility (ESRF)] and Raman and IR absorption spectroscopy. The crystal structure of CO₂-V was refined by the Rietveld method using the XRD data. The experimental results were compared to DFT simulations, which provide a detailed understanding of CO₂-V. The heated samples consist of β -cristobalite-

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Fig. 1. Room temperature, powder XRD pattern of phase V. Dots, and red line: experimental and calculated pattern from the Rietveld refinement, respectively. The difference between the two patterns is shown in green. Blue line: pattern obtained by DFT calculations, with line-width values adapted to the experimental ones. Miller indices for phase V and Bragg angles (vertical, red and blue lines) are also shown. An additional phase is included in the refinement, Rhenium, which is due to the far tails of the X-ray beam hitting the edge of the gasket.

like CO₂ with some remaining molecular CO₂ at some points in the sample. Additional details are given in *Methods* section.

A very good fit to the experimental XRD pattern at 43 GPa was obtained from the refined $I\bar{4}2d$ structure with slightly distorted CO₄ tetrahedra using the Rietveld method (Fig. 1). This result is in very good agreement with the DFT pattern. Experimental and DFT values of the structural parameters differ at most by 1–2% (Table 1). There is close agreement between the volumes of CO₂-V, which is about 23% denser than CO₃-III. These values are consistent with the DFT equation of state (16) with a predicted bulk modulus of 115.3 GPa. The reported experimental bulk modulus of 236 GPa yields similar volume values in the 40–100 GPa pressure range (21), but the experimental volumes diverge with respect to the DFT volumes upon extrapolating the measured Equation of state (EOS) down to ambient pressure. This range of values of the bulk modulus indicates that CO₂-V is a hard material as compared to β -cristobalite and quartz

Fig. 2. 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. In the lower part the view of the unit cell along the *c*-axis is presented, showing the partially collapsed arrangement of the CO₄ tetrahedra. This kind of arrangement is characterized by the values of the tilt angle, ϕ , around the *c*-axis and of the *c/a* ratio; in our case we have $\phi = 38.4^\circ$ and *c/a* = 1.655, whereas a full collapsed structure, with minimum open space between tetrahedra, corresponds to $\phi = 45^\circ$ and *c/a* = 2.

SiO₂, which have bulk moduli of 11 and 37 GPa, respectively (22, 23). The hardness of CO₂-V is related to the remarkable strength of the chemical bonds involving the small cation, giving rise to the short C-O distances and the stiff intertetrahedral bridging angle (13, 16). The experimental C-O distance of 1.353(2) Å (1.3538 Å in our DFT calculations) is much shorter than the values of about 1.59 Å reported for tetrahedrally coordinated SiO₂ up to 10 GPa (24). The C-O bond distance is even shorter than those in other materials with similar structures with smaller cations than Si⁴⁺, such as BPO₄ with bond distances of 1.46–1.51 Å at similar pressures (18). The bridging angles of CO₂-V [117.3(2)° in the experiment—116.4° in DFT calculations] and of these

Table 1. Structural parameters of CO₂-V

	Refined using exp. data	DFT simulations (this work)	DFT simulations (ref. 16)
Pressure (GPa)	43(1)	40	100
Unit cell			
Space group	$I\bar{4}2d$ (<i>Z</i> = 4)	$I\bar{4}2d$ (<i>Z</i> = 4)	$I\bar{4}2d$ (<i>Z</i> = 4)
<i>a</i> (Å)	3.5601(3)	3.523	3.2906
<i>c</i> (Å)	5.8931(9)	5.926	6.0349
<i>V</i> (Å ³)	74.69(1)	73.56	65.346 (76.006 at 43 GPa)
Agreement factors			
<i>R</i> _p (%)	9.9		
<i>R</i> _{wp} (%)	15.7		
<i>R</i> _{Bragg} (%) (for CO ₂)	2.9		
Fractional atomic coordinates			
C1 <i>x</i>	0	0	0
C1 <i>y</i>	0	0	0
C1 <i>z</i>	0	0	0
O2 <i>x</i>	0.1978(9)	0.20236	0.22610
O2 <i>y</i>	1/4	1/4	1/4
O2 <i>z</i>	1/8	1/8	1/8
C-O bond distance (Å)	1.353(2)	1.3538	1.3414
intra-CO ₄ O-C-O angle (°)	107.2(1)–114.0(1)	107.4–113.6	108.4–111.6
bridging C-O-C angle (°)	117.3(2)	116.4	112.6
ϕ angle (°), see text and Fig. 2	38.4(1)	39.0	42.1

materials (112.3° in BPO_4) are similar. Another important feature of materials with partially collapsed β -cristobalite structure is the tilt angle of the tetrahedra ϕ around the c -axis and the related c/a ratio (Fig. 2), which in the ideal uncollapsed structure ($Fd\bar{3}m$) have values of 0 and $\sqrt{2}$, respectively, corresponding to a body-centered cubic oxygen sublattice. In these materials, the dominant compression mechanism is the pressure induced tilting of the tetrahedra (increasing ϕ angle), which leads to a more compact crystal; i.e., to a decreased amount of open space between the tetrahedra. The fully collapsed structure exhibits values of ϕ and c/a of 45° and 2, respectively, corresponding to a cubic close packed oxygen sublattice (17, 18, 25). In $\text{CO}_2\text{-V}$, $\phi = 38.4^\circ$ and $c/a = 1.655$, whereas BPO_4 and BaSO_4 show an almost fully collapsed structure at similar pressures. Phase V thus has a partially collapsed structure, which may explain its remarkable hardness.

In addition to the structural investigation, a more complete description of $\text{CO}_2\text{-V}$ was obtained by Raman and IR spectroscopy. The expected optical modes of $\text{CO}_2\text{-V}$ and their activity are: $1A_1$ (Raman) + $2A_2$ (silent) + $2B_1$ (Raman) + $2B_2$ (Raman + IR) + $4E$ (Raman + IR). Each IR active mode (B_2 and E) is expected to split into a longitudinal (LO) and a transverse optical (TO) component; the LO-TO splitting being very large for modes with strong IR activity. We indeed observe all the expected modes (see Table S1). The experimental and DFT Raman and IR spectra agree well (Figs. 3 and 4). The Raman spectrum is dominated by the strong A_1 peak due to the intertetrahedral, symmetric C-O-C mode, which stretches the two C-O bonds and bends the C-O-C angle. Interestingly, the six expected LO-TO pairs are indeed found in the Raman spectrum. The two E pairs below

950 cm^{-1} exhibit small splitting of a few wave numbers, whereas the other pairs exhibit very high splitting of $50\text{--}160\text{ cm}^{-1}$ at 20 GPa, corresponding to the strongest IR activity. The IR spectra contain peaks with very high absorbance. We note that, although the LO components exhibit null intensity here (except that of a B_2 mode), they do affect the band shape of IR peaks. All the modes involve simultaneous stretching and bending. The intensity of the IR spectrum of $\text{CO}_2\text{-V}$ decreases upon decreasing pressure below 10 GPa and eventually vanishes at about 1 GPa, whereas peaks of molecular CO_2 become stronger, indicating the transition to molecular CO_2 .

The structure determination of $\text{CO}_2\text{-V}$ indicates that this material has a partially collapsed cristobalite structure ($I42d$) with slightly distorted tetrahedra corresponding to a more compact, tetragonal modification of the cubic β -cristobalite structure type. The investigation of optical vibrational modes adds to a rich physical description of this important material. In addition, the short C-O bond distance and the reduced open space between CO_4 tetrahedra gives an insight into the low compressibility of phase V. In conclusion, we obtained the quantitative proof of the existence of tetrahedral coordination in CO_2 , which definitely supports the close analogy between carbon and the other group IV elements in forming oxides, although the analogy is limited to the local structure for the moment because the currently known crystal structures differ. On the other hand, $\text{CO}_2\text{-V}$ exhibits the same structure of other oxides or oxynitrides such as BaSO_4 , BPO_4 , and PON, which transform to the well known quartz-type structure at high pressure. It is shown once again the capability of high pressures to remarkably reduce the chemical and physical differences among elements, ultimately reducing the rich variety of

Fig. 3. Raman spectra of $\text{CO}_2\text{-V}$. Experimental (red) and DFT (black) spectra are shown, along with symmetry mode assignment. DFT spectra have been calculated for random sample orientation. DFT line-width roughly resembles the experimental values. One can see six LO-TO pairs (mode symmetry B_2 and E). Note the intercrossing of the pressure shift of different modes between 700 and 950 cm^{-1} . Some remaining molecular CO_2 is seen in the experimental spectrum below 430 cm^{-1} .

Fig. 4. IR absorption spectra of $\text{CO}_2\text{-V}$. Experimental (red, measured upon pressure decrease) and DFT (black) spectra are shown along with symmetry mode assignment. Some remaining molecular CO_2 can be observed in the experimental spectra above 20 GPa. The transition to molecular CO_2 clearly occurs below 10 GPa. Stars indicate a peak of molecular CO_2 . DFT spectra have been calculated for random sample orientation. LO components exhibit null intensity (except that of a B_2 mode), whereas they do affect the band shape of IR peaks.