A New Molecular Solid Phase of Carbon Dioxide at High Pressure and Temperature

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We report the discovery of a new high-pressure molecular phase of carbon dioxide. The new polymorph, CO_2-IV, is formed by heating the high-pressure orthorhombic phase III to temperatures above 1000K at pressures between 12 and 33GPa. Analysis of the Raman spectrum of the new phase suggests a structure lacking inversion symmetry.
[carbon dioxide, molecular solids, phase transitions]

1. Introduction

The high-pressure phases of the CO_2 have been the object of several studies, both experimental and theoretical. Four molecular-solid polymorphs have been described at high-pressure (I-IV), and a room temperature phase diagram has been reported recently [1-5]. In addition, two non-molecular phases have been reported. An extended solid polymorph CO_2-V has been synthesized recently by laser heating CO_2-III to temperatures above 1800K at pressures above 40GPa [6]. In addition, an ionic form of CO_2, the $CO^{++}CO^{=}$ dimer, has been discovered from the direct elementary reactions between carbon and oxygen at high temperature and under pressure [7].

At room temperature and 1.5GPa, CO_2 crystallizes as *dry ice* (phase I), with a cubic *Pa3* structure. This phase has been characterized in detail both in Raman and X-ray diffraction [1] experiments. The Raman spectrum characteristic of the CO_2-I structure is shown in fig 1a.

Another low-pressure phase, CO_2-II, has been reported between 0.5 and 2.3GPa [3], but its existence could not be confirmed in later studies.

At pressures between 12 and 20GPa, CO_2-I transforms to an another molecular solid, labeled CO_2-III [4]. The structure of phase III has been determined to be orthorhombic (*Cmca*) from X-ray diffraction experiments up to 12GPa[2]. Its characteristic Raman spectrum consists of four bands, although nonhydrostatic smearing reduces the number of distinctive peaks at higher pressures (see figure 1 c). The domain of stability of CO_2-III has been established in Raman and IR vibrational studies to extend past 50GPa [5, 7].

The I→III phase transition is still incompletely understood. Early X-ray diffraction data suggests a sluggish transition, occurring between 12 and 20 GPa. Over this rather wide range of pressures, phases I and III have been found to coexist [2]. In fact, the crystal structure of CO_2-III has only been determined in studies of phase I and phase III mixture. Furthermore, a hysteresis effect has been reported. On decompression, the transition between III and I is abrupt (with no intermediary mixed phase) and occurs around 8-10GPa.

More recently, the existence of another phase IV was postulated in order to resolve the complex Raman spectra measured between 12-20GPa (fig 1b). However, this latter assumption was based on Raman studies of mixtures containing only 7% CO_2 in a solution of 80%He and 13%N_2 [5]. The dilution of the samples, together with doubts regarding reciprocal miscibility and peak assignments raise legitimate reservations about the validity of this assignment. Moreover, the existence of a phase IV between 12-20GPa at room temperature is not supported by previous X-ray diffraction results [2].

In an earlier paper, we describe the synthesis of an extended-solid phase of carbon dioxide by laser heating phase III to temperatures of 1800K at pressures above 40GPa [6]. In this study we report the results of similar laser-heating experiments on CO_2 samples at pressures below 40GPa.
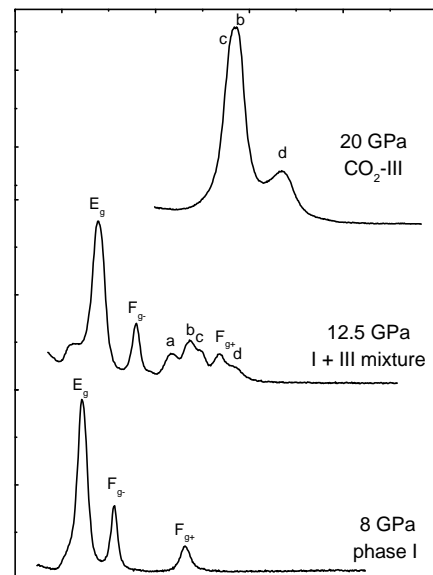

Fig 1. Raman spectra of CO_2-III at 22GPa (bottom) and 40GPa (top). Assignment follows ref. [5]. The significant broadening of the Raman bands at higher pressures indicates increased material strength, possibly the result of electron delocalization.

2. Experiments

Neat CO_2 samples were loaded the diamond anvil cell (DAC) from liquid phase, by condensing CO_2 gas at $-40^{\circ}C$ and 10bars. A few micron-size ruby chips were scattered inside the cell for in-situ pressure measurement [9].

The CO_2 samples were heated *in situ* at various pressures using the 1054nm IR line of a Nd:YLF laser operating in CW TEM_{00} regime. Since the CO_2 itself is transparent at this wavelength, heating was achieved via an indirect method by focusing the laser onto opaque objects imbedded in the CO_2 sample. A large number of experiments was conducted using alternately ruby chips or thin Pt foils placed inside the cell or the edge of the Re gasket to assist in sample heating. The results of our experiments were found to be independent of the heating method.

Sample temperature was determined by measuring the thermal radiation of the sample during heating and fitting its profile to a two-parameter gray-body radiation function. Room temperature Raman measurements were recorded before and after laser heating, using the 514nm line of an Ar^{++} ion laser and a 1/4m triple monochromator with a cooled CCD detector.

In addition to Raman measurements, an optical microscope fit with a CCD camera was used to observe and record the physical appearance of the sample before, during and after laser heating.

3. Results

Laser heating cubic CO_2-I to temperatures up to 2800K was not found to lead to any remarkable changes either in the physical characteristics of the sample or in the associated room temperature Raman spectrum.

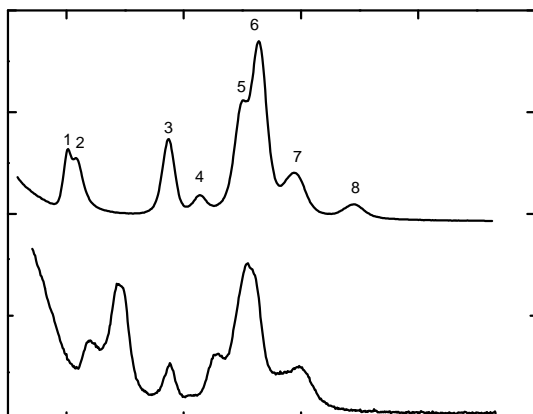However, at pressures between 12-20GPa (range of stability of the I+III phase mixture), laser heating to temperatures above 1000K results in dramatic changes both in the physical appearance of the sample and in the Raman spectrum. Before heating, the CO_2 I+III mixture is uniformly transparent to transmitted light, with fine lines delineating the grain boundaries. After laser exposure, the heated regions of the sample appear distinctly darker. This change in physical appearance suggests the formation of a new phase.

Figure 2 shows the corresponding changes in the Raman spectrum. The bottom trace was measured at 14.5GPa before any sample heating took place. It consists both of peaks characteristic of the cubic phase I and of bands attributed to the orthorhombic phase III. The top spectrum was measured under the same conditions after heating to 1000K. The obvious dissimilarity between the two spectra confirms the formation of a new phase, which we label CO_2-IV for convenience.

The conspicuous absence of the *Eg* band (characteristic of the cubic structure), in the top spectrum implies that there are no traces of phase I in the material quenched from high temperatures. Conversely, the fact that there are no peaks in the bottom Raman spectrum that would correspond to peak 8 (for example) indicates that the quenched material represents a new high-temperature phase and is not a component of the original mixed phase. Therefore, it is unlikely that this phase corresponds to the phase IV described in ref. [5].

We are confident that the Raman spectrum in figure 2 corresponds to a new molecular-solid phase of CO_2. The possibility of heat induced dissociation is discounted since the operating temperatures of around 1000K were too low to break the strong C=O double bonds [10]. In addition, no Raman lines corresponding to vibrations of C-C, O-O or single C-O bonds were observed. In a number of different experiments, our results were found to be independent of the heating method. Therefore, we also discount the possibility that the end product results from chemical reactions with the materials used for laser heating.
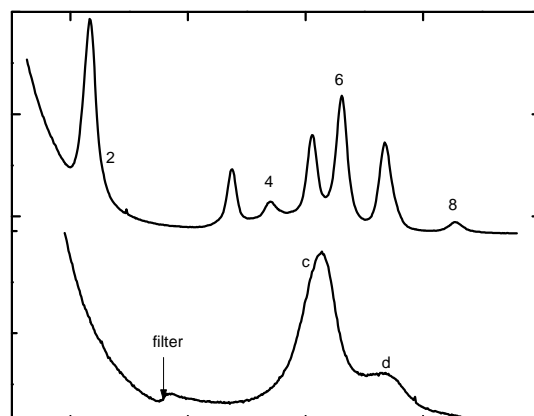

Fig. 2 Raman spectra of the CO_2 sample before (bottom) and after (top) laser heating to 1000K at 14.5GPa. The Raman features associated with the cubic *Pa3* phase disappear in the spectrum of the phase quenched from high temperature.

Fig. 3 Raman spectra of the CO_2 sample before (bottom) and after (top) laser heating to 1000Kat 28GPa. The material quenched from high temperature is CO_2-IV regardless of whether occurs in pure CO2-II or in I+III mixtures.
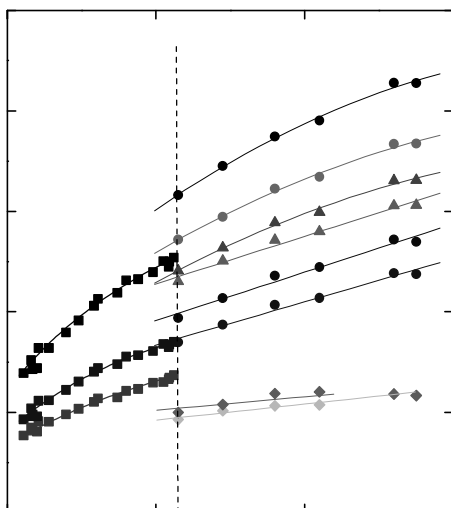
Fig. 4. The domain of stability of phase IV extends well above 20GPa, into the pressure range previously thought to stabilize phase III. The phase boundary between I and IV is well defined and no hysteresis is observed upon decompression.

Similar results are obtained by heating CO_2 at various pressures between 12 and 33GPa (fig. 3). Both the physical appearance of the quenched phase and its Raman spectrum indicate that the resulting phase is identical to the one obtained at 14.5GPa. The results did depend on whether the starting sample was pure phase III or a mixture of phases I and III.

By continuing to heat CO_2-IV at pressures above 33GPa, we observe the appearance in the Raman spectrum of the C-O-C symmetric vibration mode − the characteristic signature of the extended solid phase V [6]. In our previous study, heating phase III below 40GPa did not yield CO_2-V.

Figure 4 shows the pressure shifts of the characteristic Raman modes of phase IV. All the data points in the plot were taken by heating after each pressure increase. (If the pressure is increased with no heating, the Raman lines become progressively smeared due to nonhydrostaticity). The phase boundary between I and IV is abrupt, and no significant hysteresis is observed on pressure downloading. Furthermore, the plot shows that by heating the sample at each pressure point, phase III is completely bypassed as its usual stability field is shared by CO_2-IV (below 33GPa) and V (above 33GPa).

4. Discussion

There are four Raman active modes in CO_2-III (*Cmca*) which is centrosymmetric [5]. The presence of eight distinct Raman lines in the CO_2-IV spectrum suggests a loss of inversion symmetry from the *Cmca* structure. The effect of this presumed loss of inversion symmetry would be the activation of modes previously only active in the IR. For a structure with four molecules per unit cell, this would bring the total number of modes to eight, consistent with our measurements.

There are two possible alternatives to explain the loss of inversion symmetry observed in phase IV: (i) a non-centrosymmetric structure and (ii) bending of linear CO_2 molecules. The latter case would explain the observed lowering of the phase boundary for the synthesis of CO_2-V. A CO_2-IV phase with bent molecules, would act as a precursor to the extended-solid phase V by lowering the kinetic barriers for breaking the C=O double bonds [10]. Further X-ray diffraction experiments are necessary to settle this issue.

5. References

* The details of this work will be published elsewhere.

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