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Coesite-like CO_2: An analog to SiO_2

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We report recent findings of coesite-like carbon dioxide phases: coesite I phase (cI-CO_2) formed by laser-heating pseudo-six-fold phase VI above 50 GPa, a high-pressure form of coesite (cII-CO_2) by further compressing cI phase above 70 GPa, and an amorphous form above 100 GPa. The existence of coesite-like carbon dioxide, an important linkage between fourfold quartz and sixfold stishovite in SiO_2, underscores the periodic analogy between SiO_2 and CO_2, which has been in a recent controversy. Its pressure-temperature stability field signifies the possibility of volatile CO_2 incorporated in silicate minerals in the Earth's lower mantle.

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Compressed carbon dioxide displays a structural similarity via its transformations to SiO_2-like extended solids with interesting properties such as superhardness, optical nonlinearity, high thermal conductivity, and high-energy density.[1–8] As a result, the phase diagram of carbon dioxide is rather intricate with an array of polymorphs exhibiting great diversity in crystal structure, chemical bonding, and collective interaction. The thermal-path-dependent phases and phase boundaries underscore the metastability and kinetics over a large pressure-temperature domain, which give rise to interesting yet often controversial results regarding: if compressed CO_2 is linear or bent,[9,10] how does an extended solid melt or disassociate,[11] what is the nature of bonding and how does it evolve,[12,13] and what is the origin of lattice strain and structural distortion.[4,7,14] These questions are commonly shared in many other molecular systems such as nitrogen,[15] oxygen,[16] and carbon,[17] posing both theoretical and experimental challenges in understanding the phase diagram, phase transitions, transition mechanisms, properties, and the periodic systematic.

Linear CO_2 molecule is an important greenhouse gas, which crystallizes into a typical molecular solid (phase I, $Pa3$) at $\sim$1 GPa and 300 K (see Fig. 1). The intermolecular interaction of CO_2 molecules rapidly increases with increasing pressures, which results in large lattice strains and phase metastability in the intermediate pressure range of 20–40 GPa.[2,18] At high pressures above $\sim$40 GPa, carbon dioxide transforms to various forms of nonmolecular SiO_2-like extended solids, which include fourfold tridymite-like CO_2-V,[2,3] pseudo-six-fold stishovite-like CO_2-VI,[4] cristoballite-like CO_2-IV,[5] and silica-like a carbonia.[6]

To a first approximation, the crystallographic similarities between these extended CO_2 and SiO_2 polymorphs seem to indicate a periodic analogy between CO_2 and SiO_2. Yet, there exist subtle significant differences; for example, stishovite-like CO_2-VI still maintains largely sp^3 hybridization with carbon atom rattling within highly distorted octahedron.[4] Theory predicts that sixfold carbon atom is stable above 900 GPa,[19,20] and the structure of a carbonia may be a mixture of threefold and fourfold structure.[8] Phase IV is isostructural with cristobalite ($P4_12_12$),[5] yet its intermolecular bonding is still far from being fully covalent. In fact, a single crystal, grown near the triple point of liquid-phase VII-phase IV at around 830 K and 15 GPa and quenched to 11.7 GPa and 300 K,[14] suggests a different crystal structure R-$3c$, a distorted structure of phase I ($Pa3$), which is evident for molecular nature of this phase at relatively low pressures below 20 GPa. Furthermore, the presence of intermediate phases II, III, and IV between 20 and 40 GPa are not unique[21] but different from SiO_2; although the observed metastability of CO_2 phases, except phase I, are common as all SiO_2 polymorphs exist at ambient conditions.

The strong covalence in carbon-oxygen bonds and the rigidity of sp^3-bond angles are the primary reasons precluding the formation of higher coordination configuration such as sixfold coordinated carbon units. Furthermore, the large energy and spatial separation of d orbital in carbon makes spd hybridization unlikely in CO_2, adding to the disparity between CO_2 and SiO_2. Accordingly, total-energy calculations predict fourfold cristoballite and/or layered carbonate structures to be among the most stable configurations in the pressure range of 100 GPa.[22,23]

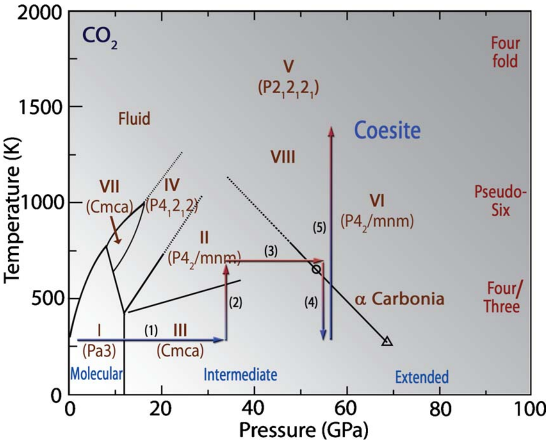

FIG. 1. (Color online) The phase/chemical transformation diagram of carbon dioxide. Solid lines indicate measured phase boundaries. The line between phases III and II is a kinetic line. The broken melting line of phase IV has not been measured. The figure also indicates a typical experimental pathway of the present study to obtain coesite-I-like CO_2. The blue arrows indicate room-temperature compression of the sample (path 1), the blue-red or red-blue arrows indicate isobaric heating (2 and 5) or cooling (4) of the sample and the red arrow indicates high-temperature compression of the sample (3). The corresponding Raman spectra are shown in Fig. 2.

Fundamental structures of SiO_2 stable at high pressures and ambient temperatures are quartz, coesite, and stishovite, important planetary minerals discovered at ambient conditions with two most fundamental building blocks of SiO_4 tetrahedra and SiO_6 octahedra. Recently, the pyrite structure of SiO_2 was also discovered by laser heating above 268 GPa around 1800 K.[24] While the pyritelike CO_2 phase may be stabilized at the formidably high pressures, it is significant to recognize that coesite-like CO_2 has not been found. Because coesite occupies a large stability field between fourfold quartz and sixfold stishovite, it is particularly important to understand the structural evolution from fourfold to sixfold structures in both SiO_2 and CO_2.

Coesite is the highest density tetrahedrally coordinated form, built in a fully polymerized three-dimensional network different from those of one-dimensional spiral tetrahedral in quartz and two-dimensional layered tetrahedral in cristobalite or tridymite.[25,26] It is the form that transforms into sixfold coordinated stishovite in SiO_2 but is absent in GeO_2.[27] Coesite-like CO_2 has not been found nor predicted, previously.

In this Brief Report, we present experimental evidences for coesite-like carbon dioxide, formed by laser-heating pseudo-six-fold CO_2-VI above 50 GPa, following a pressure-temperature path illustrated in Fig. 1. The corresponding Raman spectra are in Fig. 2. Note that coesite-like carbon dioxide was made only by laser-heating phase VI, not by heating any other phases including II, III, IV, V, and *a* carbonia.

Because of the metastability and irreversible nature of transformations of CO_2 phases, it is important to perform the experiments along well-defined pressure-temperature paths with freshly loaded CO_2 samples. At least eight experiments were performed with freshly loaded CO_2 samples (from liquid CO_2 at -35 °C and 15 atm using a gas-loading device), using both external and laser-heating methods to synthesize coesite-like CO_2, and the results were reproducible and independent of the heating material. The external heating was done using a resistive heater (Chromalox) wrapped around the cell and a *K*-type thermocouple mounted on the back of diamond and the laser heating was done using a Nd:YLF (yttrium lithium fluoride) laser focused on a Pt foil or a ruby particle. However, because of the indirect heating and the heat of transformation, the temperature uncertainty in laser-heated CO_2 samples can be substantially larger, and the measured transition temperature ($\sim$1300 °C) should be considered as an upper bound of the transformation. The Raman spectra of the transformed samples were spatially resolved in a confocal arrangement with a backscattering geometry using the 514.5 nm line of the Ar^+ laser having a spot size of about 6–8 μm.

The sample was initially compressed to phase III at $\sim$35 GPa (1 in Fig. 1, a in Fig. 2) and ohmically heated to phase II at 580 K (2, b). At this high temperature, phase II was isothermally compressed to phase VI (3, c) at $\sim$60 GPa, which occurred slowly over a few hours. During these external heating and compression processes, the Raman spectra were collected as close as every 10 K and a few gigapascals to find out the exact point of transformation (shown in the solid line in Fig. 1). The presence of phase VI was confirmed by its characteristic Raman peaks at 625, 1000, and 2000 cm^{-1} (not shown).[4] After producing an appreciable amount of phase VI, the temperature of sample was reduced slowly (25–30°/h) to the ambient temperature. During this cooling process, we observed a pressure drop of about 10% and phase VI was stabilized at around 55 GPa and ambient temperature (4, d). The phase VI was then laser heated to obtain the currently reported form of carbon dioxide at $\sim$1300 °C ($\pm$30 °C). The Raman spectrum of quenched phase (5, e) was similar to that of coesite-I previously reported in SiO_2 (graph on top).[25] All characteristic Raman features of coesite-I were observed in CO_2, consisting of four major vibration peaks at around 160 (80), 360 (280), 640 (425), and 830(520) cm^{-1} in CO_2 (SiO_2). Thus, we denoted this phase as coesite-I-like (or *cI*-) CO_2. Following similar arguments, while assigning the modes for comparison with SiO_2-based coesite, we assigned the most dominant 870 cm^{-1} mode to be due to symmetric C-O-C bending mode. Based on the pressure dependence [Fig. 3(c)], this mode should be around 720 cm^{-1} at ambient conditions. We also observed a large pressure increase ($\sim$5–10 %) after the laser heating, which suggests that the discovered phase, *cI*-CO_2 is less dense than its parent phase VI.

The pressure dependence of the Raman spectra indicates that *cI* phase further undergoes a displacive phase transfor-

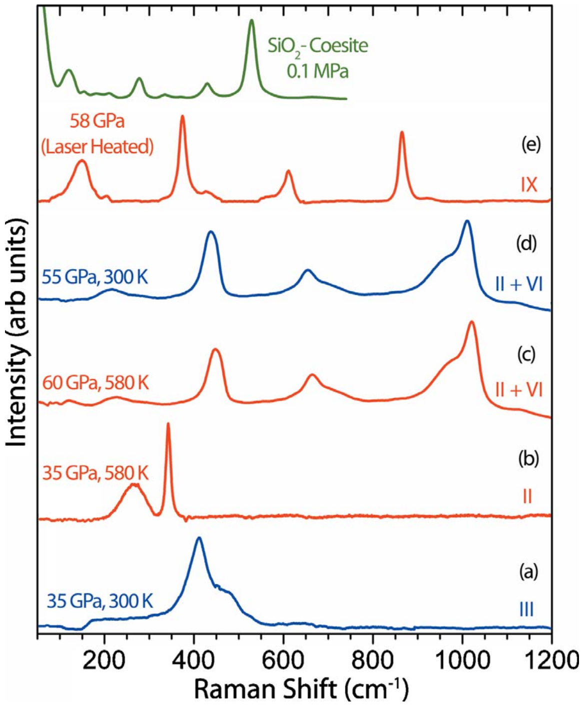

FIG. 2. (Color online) Raman spectra of CO_2 phases along the pressure-temperature path in Fig. 1, resulting in coesite-I-like CO_2. (a) Room-temperature compression of phase I produces phase III, path 1 in Fig. 1; (b) Isobaric external heating of phase III produces phase II, path 2; (c) high-temperature compression of phase II produces a mixture of phases II and VI above 50 GPa, path 3; (d) room-temperature stabilization of the mix of Phases II and VI, path 4; and (e) laser heating of this phase to obtain coesite-I-like CO_2, path 5. The top graph shows the reproduced Raman spectrum of SiO_2-coesite at 0.1 MPa reproduced from Ref. 25 for comparison.

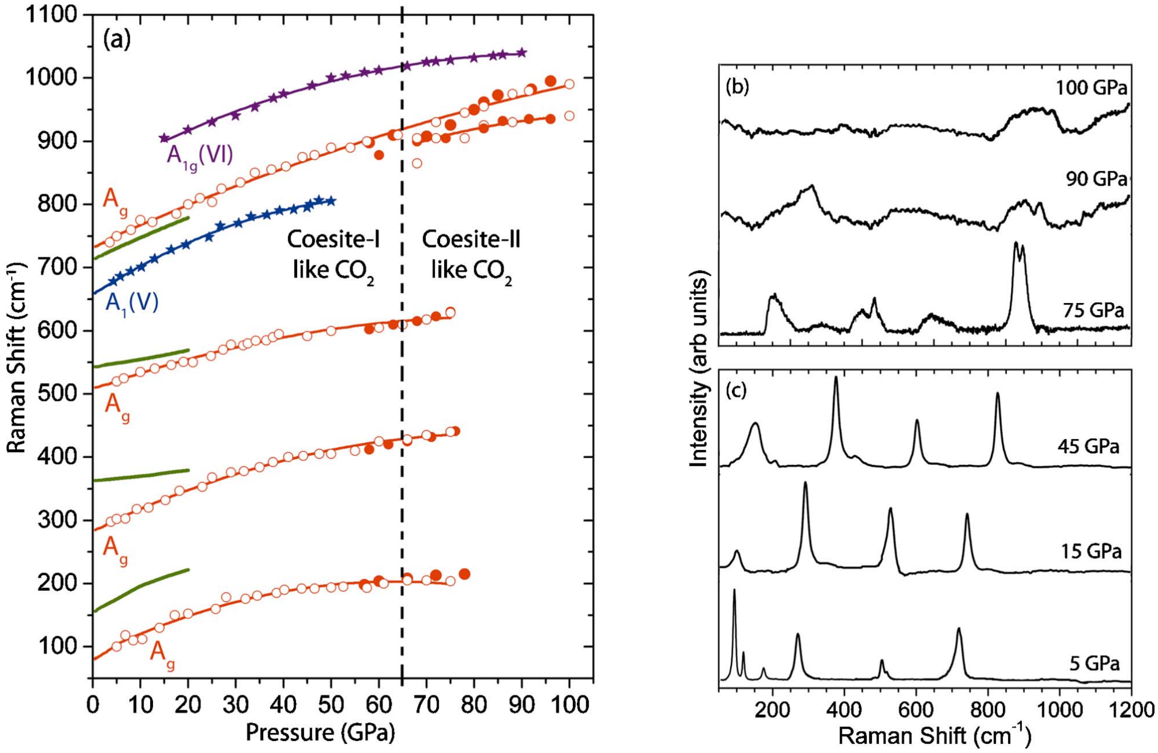

FIG. 3. (Color online) The pressure dependences of the Raman spectra of coesite-like CO_2 phases, showing (a) the coesite I (*cI*) to coesite II (*cII*) phase transition at 65 GPa; (b) an irreversible amorphorization of *cII* phase above 90 GPa; and (c) the *cII*-to-*cI* phase transition at around 45 GPa and the stability of *cI* phase at low pressures. The *cI*-to-*cII* phase transition is evident from the splitting and broadening of the Raman modes in (b), which occurs abruptly and reversibly with a relatively large pressure hysteresis of 10–20 GPa. The *cI* phase slowly transforms back to phase I below 10 GPa but it can be observed at pressures as low as 1 GPa where it rapidly transforms into liquid.

mation into coesite-II-like (or *cII*-) phase above ~65 GPa, as shown in Fig. 3(a). At this pressure, the most characteristic singlet of the phase *cI*-CO_2 around 870 cm^{-1} splits into a doublet while other peaks in lower frequencies broaden. Similar changes were previously observed in SiO_2 above 20 GPa. The *cII* phase eventually amorphizes above ~90 GPa, evident from a complete loss of Raman peaks and an optically isotropic and transparent appearance of the sample. No further changes are discernible to 105 GPa, the maximum pressure of the present study [Fig. 3(b)]. Upon pressure cycling, the *cI*-to-*cII* transition occurs reversibly within a pressure hysteresis of 10–15 GPa, yet the *cII*-to-amorphous transition occurs irreversibly. Both *cI* and amorphous phases transform back to phase I below 10 GPa and ultimately to fluid around 1 GPa [Fig. 3(c)]. Upon laser heating of the *cI* phase at around 20 GPa, no further phase transformation was observed.

The phase VI to *cI* transition is sensitive to strains and temperatures of the laser-heated area above 50 GPa, as illustrated in Fig. 4. As we probe further away from the hot spot (that is, as the temperature decreases),[28] we observe phase V, possibly a distorted structure of *cI* phase, *cI* phase, and the mixture of phases II, VI, and *cI*. It indicates that the stability field of *cI*-CO_2 is at higher pressures and, to a less degree, lower temperatures than that of phase V. The transition temperature measured at the center was around 1300 °C, which is independent of pressure and likely represents a kinetic

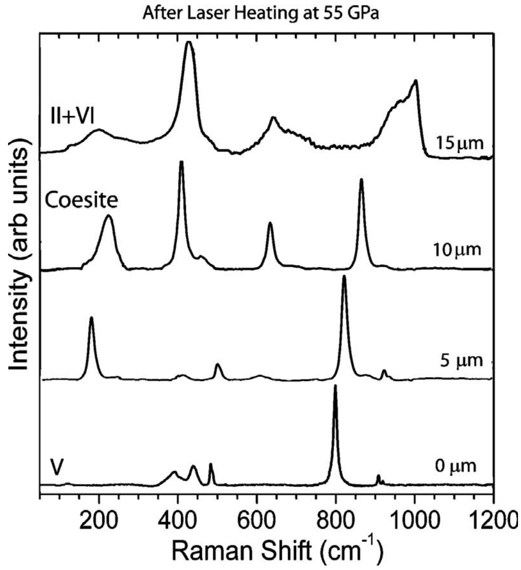

FIG. 4. Spatially resolved Raman spectra of laser-heated CO_2-VI, showing the transitions to phase V, distorted coesite-like, coesite-I-like CO_2, and a mixture of phase II and untransformed phase VI as moving away from the laser-heated spot by the distance marked. Phases V and VI are evident by their characteristic C-O-C bending mode at 800 cm^{-1} and 1000 cm^{-1}, respectively. A similar mode of coesite-like CO_2 appears at 870 cm^{-1}, displaying an intermediate force field between fourfold CO_4 of phase V and pseudo-six-fold CO_6 of phase VI.

barrier of phase VI transformation to phase V (Refs. 3 and 29) or to *cI* phase. In fact, the transition from phase VI to *cI* phase does not occur to about 90 GPa at ambient temperature, suggesting the existence of a large activation barrier for the transition.

In conclusion, we have reported the discovery of coesite-like *cI*-CO_2 and its high-pressure modification *cII*-CO_2, synthesized by laser-heating stishovitelike CO_2-VI above 55 GPa. The presence of coesite-like phase between fourfold phase V and pseudo-six-fold phase VI is similar to the phase diagram of SiO_2, which underscores the periodic analogy between SiO_2 and CO_2 (or Si and compressed C) in their local and crystal structures despite the significant difference in their electronic structures at low pressures.

The presence of coesite-CO_2 offers distinctive insights into how CO_2 can be incorporated into carbonate minerals originating from the Earth's interior[30] as well as for the high-temperature origin of carbonates in Martian meteorites.[31] Its presence at the pressure-temperature condition of 50–100 GPa and 1000–2000 K signifies the possibility of existence of volatile chemical species such as CO_2 even in the lower mantle. The absence of extended CO_2 in Earth's surface minerals could simply reflect the volatility of CO_2 below 1 GPa.

Finally, the stability of coesite-CO_2, which has not been predicted previously, calls attention for more theoretical studies such as metadynamics calculations[32] that can describe the stability and transitions of structure well beyond thermodynamic constraints to kinetics and phase metastabilities.

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