PHYSICAL REVIEW B **79**, 144102 (2009)

Thermodynamic stability of layered structures in compressed CO_2

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(Received 4 March 2009; published 2 April 2009)

The crystal structures of the recently discovered nonmolecular phases of CO_2 are still the subject of intense debate. Based on density-functional theory calculations, we show that a layered structure (space group $P4_2/nmc$) with carbon in tetrahedral coordination is thermodynamically stable between 200 and 900 GPa. The Raman spectrum for this phase agrees with that measured for CO_2-VI. Contrary to SiO_2, where octahedral coordination for silicon starts with stishovite at about 10 GPa, we find that structures with carbon in octahedral coordination are unlikely to be thermodynamically stable in CO_2 at pressures currently reachable in the laboratory. We attribute the exceptional stability of tetrahedral structures in CO_2 to the small atomic size of the carbon atom, which allows it to occupy the tetrahedral interstitial sites of the close-packed oxygen sublattices.

DOI: 10.1103/PhysRevB.79.144102 PACS number(s): 81.40.Vw, 61.50.Ks, 64.30.Jk, 78.30.−j

The recent discovery that molecular CO_2 transforms under compression into extended nonmolecular phases that are structurally similar to the ambient-pressure phases of silica[1] has generated considerable interest in the potential technological applications and geochemical implications that the nonmolecular phases of CO_2 may have if they could be recovered to ambient conditions.[2] From a fundamental point of view, the discovery opens unique scenarios on the solid-state chemistry of carbon oxides. In particular, the structural analogy of nonmolecular CO_2 with isoelectronic compounds SiO_2 and GeO_2 raises important questions regarding the tetrahedral or octahedral nature of the carbon coordination with oxygen. In SiO_2 the transition between the two local coordinations takes place at around 10 GPa in the crystal and in the 10–40 GPa pressure range in the amorphous phase.[3] Crystalline GeO_2 has octahedral coordination at ambient pressure[4] but the amorphous phase is tetrahedral up to 5 GPa.[5] In CO_2, the transition between tetrahedral and octahedral carbon coordinations is still the subject of considerable controversy. Vibrational and diffraction spectra of CO_2-V, the first reported nonmolecular crystalline phase of CO_2, suggest structural similarities between CO_2-V and two tetrahedral phases of silica: cristobalite and tridymite.[1,6–13] The analogy with silica has been recently extended to include a new crystalline form, phase VI,[14] which has been proposed to be isostructural to stishovite and thus with carbon in octahedral sixfold coordination with oxygen.[14] Among a number of silicalike crystal structures including tridymite and several cristobalite polymorphs, first-principles calculations find a β-cristobalite structure with $I\bar{4}2d$ space group as the most stable phase of CO_2 in the pressure range of synthesis of CO_2-V and CO_2-VI (Refs. 6 and 7) and do not support the presence of sixfold-coordinated carbon in that pressure range.[6–9] Static calculations predict a transition from β-cristobalite to stishovite only at a pressure of 400 GPa,[8] and first-principles molecular-dynamics (MD) simulations up to 120 GPa and at two different temperatures (1000 and 2000 K) did not yield any evidence of octahedral coordination.[9] The combination of metadynamics, an advanced method for structural search, and first-principles calculations yields for phase VI a partially disordered layered structure with carbon in tetrahedral coordination.[15] A similar structure has also been proposed for phase VI based on transition-path geometrical considerations.[16] To summarize, theory has been so far unable to substantiate the experimental claim that carbon in phase VI is octahedrally coordinated.

Failure by theory to predict a structure with octahedral coordination may in principle be due to intrinsic limitations of the theoretical approaches used so far. Static calculations have only considered a stishovitelike structure as a candidate for hypothetical octahedral phases, and search for octahedral coordination in dynamical simulations might have been hampered by large energy barriers in plain molecular dynamics or by the choice of the collective variables in metadynamics simulations.

In this work we present an extended search for high-pressure phases of CO_2 by considering the thermodynamical stability of a larger set of candidate octahedral structures. We conclude that octahedral coordination is unlikely in carbon dioxide up to at least 900 GPa, i.e., at much higher pressure than predicted before. We also find that the tetrahedral-layered structure found in first-principles MD simulations[9] is thermodynamically stable in the pressure range between 200 and 900 GPa over all other crystal structures proposed so far.

Calculations were performed with the QUANTUM ESPRESSO package[17] employing density-functional theory and the Perdew-Burke-Ernzerhoff exchange-correlation functional.[18] Vanderbilt ultrasoft pseudopotentials were used together with a plane-wave basis set for the electronic wave functions and a kinetic-energy cutoff of 50 Ry. The validity of the ultrasoft pseudopotential approximation is fully justified as the shortest C-O bond length at the highest pressure calculated in this work (910 GPa) is in the range of values characteristic of the C=O double bond at ambient pressure (1.2 Å). Brillouin-zone integration was found to be converged with a uniform grid of $7\times7\times7$ points for the small unit cells (up to 2 f.u.) and $5\times5\times5$ points for 4 f.u. cells. Structural optimizations were performed on lattice parameters and atomic coordinates at several different pressures.

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TABLE I. Lattice and internal parameters at 410 GPa. Cell parameters are in Å. Atomic positions are in crystal coordinates.

Structure	Space group	a	b	c	Atom	Positions (x,y,z)
β-cristobalite	$I\bar{4}2d$	2.8436	2.8436	5.7651	C($4a$)	(0.0000, 0.0000, 0.0000)
					O($8d$)	(0.2605, 0.2500, 0.1250)
layer-AB	$P4_2/nmc$	2.0386	2.0386	5.5706	C($2b$)	(0.7500, 0.2500, 0.2500)
					O($4d$)	(0.2500, 0.2500, 0.1171)
layer-AA	$P\bar{4}m2$	2.0292	2.0292	2.8158	C($1c$)	(0.5000, 0.5000, 0.5000)
					O($2g$)	(0.0000, 0.5000, 0.2353)
α-PbO_2	$Pbcn$	3.1827	3.9879	3.4673	C($4c$)	(0.0000, 0.1617, 0.2500)
					O($8d$)	(0.2555, 0.3856, 0.4224)
$CaCl_2$	$Pnnm$	3.1690	3.3890	2.0581	C($2a$)	(0.0000, 0.0000, 0.0000)
					O($4g$)	(0.2627, 0.3393, 0.0000)
Stishovite	$P4_2/mnm$	3.2530	3.2530	2.1025	C($2a$)	(0.0000, 0.0000, 0.0000)
					O($4f$)	(0.3008, 0.3008, 0.0000)
Pyrite	$Pa\bar{3}$	3.5092	3.5092	3.5092	C($4a$)	(0.0000, 0.0000, 0.0000)
					O($8c$)	(0.3478, 0.3478, 0.3478)
Anatase	$I4_1/amd$	2.8541	2.8541	5.5354	C($4a$)	(0.0000, 0.0000, 0.0000)
					O($8e$)	(0.0000, 0.5000, 0.2414)

Vibrational frequencies at the Brillouin-zone center, infrared (IR), and Raman intensities were calculated using state-of-the-art density-functional perturbation theory[19] with norm-conserving pseudopotentials and a kinetic-energy cutoff of 100 Ry.

We considered in this work four crystal structures borrowed from the silica phase diagram and characterized by octahedral or quasioctahedral coordination: α-PbO_2, $CaCl_2$, stishovite, and pyrite structures. To these four structures we added anatase, an octahedral crystal structure not seen in silica and characterized by a face-centered-cubic (fcc) oxygen sublattice (contrary to stishovite and $CaCl_2$ where the oxygen sublattice is hexagonal close packed) and predicted to appear under nonhydrostatic conditions.[20] Among the tetrahedral structures, we considered β-cristobalite as well as two layered structures discussed in recent theoretical works[9,15,16] and formed by tetrahedral layers stacked in a $ABAB\ldots$ order (space group $P4_2/nmc$) and $AAAA\ldots$ order (space group $P\bar{4}m2$). We call hereafter these structures "layer AB" and "layer AA," respectively.

The optimized structural parameters of all the structures at 410 GPa are given in Table I. We report the calculated relative enthalpies of all structures considered in this work, with respect to β-cristobalite, in Fig. 1. Because our goal is to search for thermodynamically stable phases, we do not report enthalpies for all those tetrahedral structures that have been shown in Ref. 7 to be systematically higher in enthalpy with respect to β-cristobalite.

We notice that all octahedral structures become thermodynamically stable over tetrahedral structures only above 900 GPa. This is much above the calculated transition pressure of 400 GPa reported in Ref. 8, which was however the result of an extrapolation of calculations carried out at much lower pressure. Our calculations have been carried out for volumes corresponding to pressures in excess of 900 GPa, so we believe that our estimate of the transition pressure is more reliable. A transition pressure to octahedral phases of 900 GPa is largely above the pressure that can be currently achieved statically in the laboratory. Enthalpy differences between the octahedral structures and the most stable tetrahedral structure at 60 GPa (β-cristobalite), i.e., close to the experimental conditions of synthesis of all extended phases reported so far, are substantially above 2 eV/CO_2, far too high to justify their metastable synthesis in experiments. In addition, most of the octahedral structures considered in this work are dynamically unstable at 60 GPa.[21] Among the structures with octahedral coordination, the α-PbO_2 structure has the lowest enthalpy. However, full atomic and lattice relaxation of a α-PbO_2-like CO_2 structure yields, below 290 GPa, the layer-AB structure found in first-principles MD

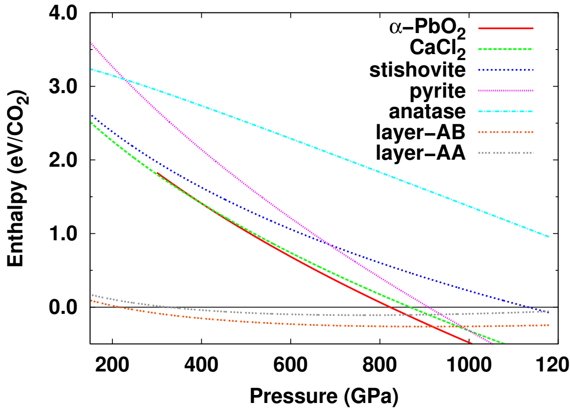

FIG. 1. (Color online) Calculated relative enthalpies per CO_2 molecular unit for all the CO_2 structures considered in this work with respect to β-cristobalite.

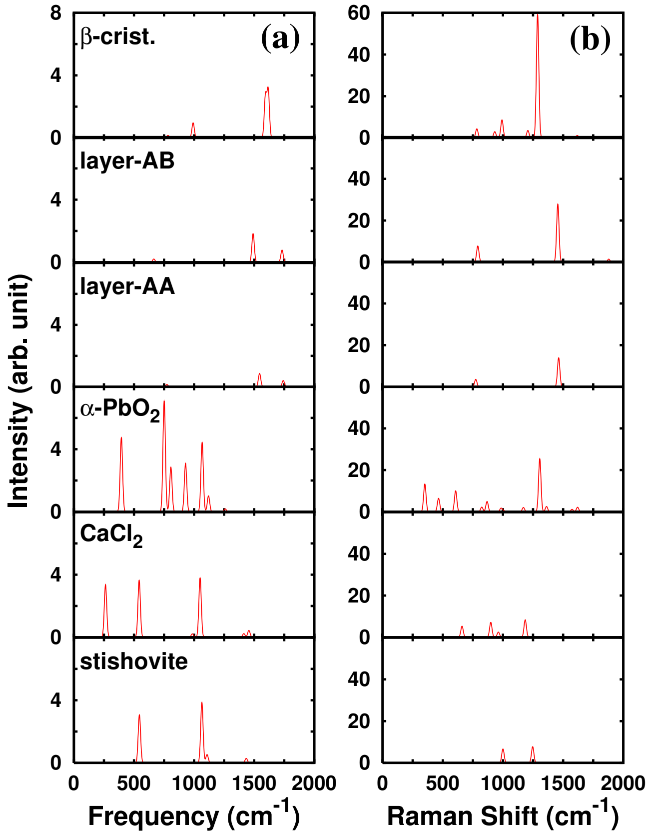

FIG. 2. (Color online) (a) Calculated infrared spectra of the β-cristobalite, layered, α-PbO$_2$, CaCl$_2$, and stishovite structures at 410 GPa. (b) Calculated Raman spectra of the β-cristobalite, layered, α-PbO$_2$, CaCl$_2$, and stishovite structures at 410 GPa and 300 K.

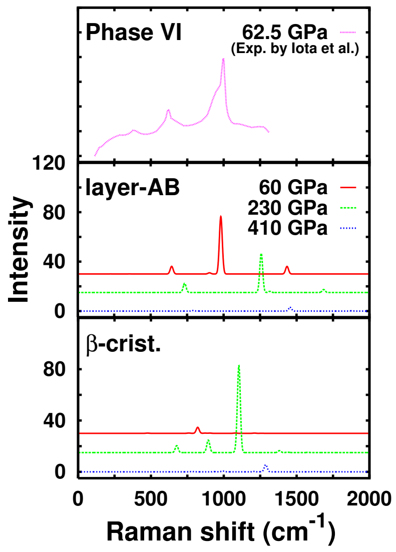

FIG. 3. (Color online) Calculated Raman spectra at different pressures for layer *AB* and β-cristobalite, the two thermodynamically stable structures according to our calculations. Notice that β-cristobalite is stable at 60 GPa, layer *AB* is stable at 410 GPa, and 230 GPa is close to the pressure of transition between the two phases. The experimental spectrum of phase VI at 62.5 GPa (Ref. 14) is also shown for comparison.

simulations by Serra *et al.*,[9] indicating that α-PbO$_2$-like CO$_2$ is mechanically unstable at pressures below at least 290 GPa. The enthalpy of layer-*AB* CO$_2$ is lower than that of β-cristobalite above 200 GPa, and its stability range extends up to 900 GPa, where the octahedral phases become favored.

We calculate IR and Raman spectra of β-cristobalite, layered, α-PbO$_2$, CaCl$_2$, and stishovite structures, which are shown in Figs. 2(a) and 2(b), respectively. We carried out our calculations at 410 GPa, i.e., well within the stability range of the layered phases but not too far from current experimental limits. Temperature effects are included in the Raman spectra using the Placzek approximation.[22] The main IR peaks of the octahedral structures are at lower frequencies than in tetrahedral structures, which can be explained by the reduction in the force constants induced by the increase in coordination, similar to silica. Contrary to silica, however, the distinction between octahedral and tetrahedral coordinations is less evident in the Raman spectra. The Raman spectrum of α-PbO$_2$-like CO$_2$ is accidentally similar to that of β-cristobalite, although their IR spectra differ noticeably.

Having ruled out the presence of octahedral phases at pressures closer to the experimental conditions of synthesis of phases V and VI, we focus now on differences between the Raman spectra of β-cristobalite and of the layer-*AB* structures, the two most stable structures of CO$_2$ according to our calculations (Fig. 3). A single peak dominates both Raman spectra, but the frequency of the main peak in the layered phase is systematically 10% higher than in β-cristobalite. The Raman spectra of both layered structures at 60 GPa match the experimentally reported Raman spectrum for phase VI much better than any other structure con-

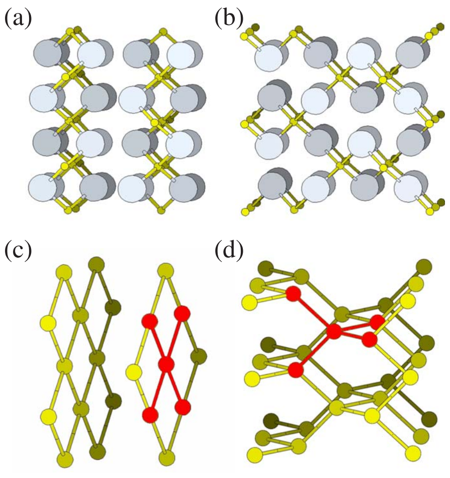

FIG. 4. (Color online) Atomic arrangement in layer-*AB* and β-cristobalite structures. The big spheres represent oxygen atoms and the small spheres represent carbon atoms. Notice, in (a) and (b), the fcc close-packed structure of the oxygen sublattice. Panels (c) and (d) show the carbon sublattice in the two structures. The connections between nearest-neighbor carbon atoms in (c) and (d) do not represent chemical bonds rather they are a guide to visualize their three-dimensional (3D) arrangement. The red (dark)-colored connection in (c) and (d) is representative of the only two types of local arrangement of carbon atoms in a fcc oxygen sublattice (see text).

sidered so far, as already noted.[15,16] Our finding that layered phases are increasingly favored enthalpically with increasing pressure and become thermodynamically stable above 200 GPa suggests that phase VI may be observed over a considerably larger pressure range than reported so far.

The remarkable difference between the transition pressure from tetrahedral to octahedral coordination in SiO_2, where the transition occurs around 10 GPa, and that in CO_2, where it takes place at 900 GPa, calls for a couple of remarks. Because of the larger size of the oxygen ion with respect to both cations,[23] oxygen packing plays an important role in determining structural stability in both SiO_2 and CO_2. In SiO_2 the transition from tetrahedral to octahedral structures coincides with the transformation of the oxygen sublattice from a body-centered-cubic (bcc) to a close-packed lattice.[20] When the close-packed oxygen sublattice forms in SiO_2, Si moves away from the tetrahedral interstitial sites of the oxygen lattice to occupy the larger octahedral interstitial sites. On the contrary, a nearest-neighbor analysis of β-cristobalite CO_2 and of the layered structures shows that carbon fourfold coordination coexists with an almost ideal fcc close-packed oxygen sublattice in CO_2. The smaller size of carbon atoms makes it possible for them to occupy the tetrahedral interstitial sites of the oxygen close-packed sublattice, which explains the remarkable stability of tetrahedral phases in CO_2. It is also interesting to remark that only two local nearest-neighbor arrangements of carbon atoms are possible, which are consistent both with carbon residing in tetrahedral sites of the fcc oxygen lattice and twofold coordination for oxygen. When the two arrangements, schematically illustrated in Fig. 4 with red (dark) color, are extended to form an infinite solid, they give rise to β-cristobalite and to the layer-*AB* phase, respectively, which are the two thermodynamically stable structures according to our calculations. It would be interesting to verify whether carbon sublattices composed of a mixture of the two local structures shown in Fig. 4 with red (dark) color are also energetically competitive with β-cristobalite and layer-*AB*.

In summary, we have shown that a tetrahedral-layered phase becomes thermodynamically stable over all structures considered so far for CO_2 between 200 and 900 GPa. Together with the similarity between calculated and experimental Raman spectra, our findings support the interpretation of experiments on phase VI as evidence for a layered tetrahedral phase. Our calculations further show that octahedral coordination is unlikely to be present in the thermodynamical stable crystal structures of CO_2 below 900 GPa. We attribute the exceptionally broad range of stability of fourfold-coordinated carbon in CO_2 to the small size of carbon atoms which allows them to retain fourfold coordination within the tetrahedral interstitial sites of the close-packed oxygen sublattice.

We thank M. Santoro, F. Gorelli, and R. Martoňák for discussions, and we acknowledge support from INFM-CNR through "Iniziativa di Calcolo Parallelo."

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[23] Pauling's ionic radii for the three ions are O(-II)=1.24 Å, Si(IV)=0.40 Å, and C(IV)=0.16 Å. These radii are consistent with the measured Si-O bond lengths of 1.6 Å (our calculated value is 1.62 Å) in tetrahedral silica at ambient pressure and also with our calculated C-O bond length of 1.40 Å in β-cristobalite at ambient pressure.