

Amorphous silica-like carbon dioxide

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Among the group IV elements, only carbon forms stable double bonds with oxygen at ambient conditions. At variance with silica and germania, the non-molecular single-bonded crystalline form of carbon dioxide, phase V, only exists at high pressure^{1–9}. The amorphous forms of silica (a-SiO₂) and germania (a-GeO₂) are well known at ambient conditions; however, the amorphous, non-molecular form of CO₂ has so far been described only as a result of first-principles simulations⁹. Here we report the synthesis of an amorphous, silica-like form of carbon dioxide, a-CO₂, which we call ‘a-carbonia’. The compression of the molecular phase III of CO₂ between 40 and 48 GPa at room temperature initiated the transformation to the non-molecular amorphous phase. Infrared spectra measured at temperatures up to 680 K show the progressive formation of C–O single bonds and the simultaneous disappearance of all molecular signatures. Furthermore, state-of-the-art Raman and synchrotron X-ray diffraction measurements on temperature-quenched samples confirm the amorphous character of the material. Comparison with vibrational and diffraction data for a-SiO₂ and a-GeO₂, as well as with the structure factor calculated for the a-CO₂ sample obtained by first-principles molecular dynamics⁹, shows that a-CO₂ is structurally homologous to the other group IV dioxide glasses. We therefore conclude that the class of archetypal network-forming disordered systems, including a-SiO₂, a-GeO₂ and water, must be extended to include a-CO₂.

High pressure can change substantially the microscopic interactions in condensed phases, and can lead to unexpected transformations. This is even the case in simple molecular systems, where new materials are obtained as a result of dramatic changes of the molecular structure. Among paradigmatic molecular crystals such as those made of CO₂ and N₂, high pressure has been recently shown to lead to a transformation into non-molecular ordered structures^{1,2,10}, and also, in the case of nitrogen, into amorphous materials^{11–13}. Carbon dioxide is the dominant component of the atmospheres of Earth-like planets, is embedded in ice form in the outer planets and asteroids, plays an important role in volcanic and seismic activity¹⁴ and is used as a supercritical solvent in chemical reactions¹⁵. Its high natural abundance and chemical stability can be traced to the presence of a strong π bond, whose strength is however severely affected by pressure¹⁶. The recent discovery of a crystalline ‘super-hard’ phase of carbon dioxide (CO₂-V) composed of CO₄ tetrahedra indicates that the strong molecular bond is replaced, at high pressure, by an extended network of C–O single bonds, structurally similar to many ordered SiO₂ polymorphs. Naturally, the question therefore arises if there is the potential for non-molecular glassy phases and/or stishovite-like structures in carbon dioxide. The existence of an amorphous extended form of CO₂ would extend the class of network-forming systems, to which a-SiO₂

and water belong, to include a material with very high bond stiffness and thus probably remarkable mechanical properties. Stishovite-like ordered structures, with octahedral carbon coordination by oxygen, have been already considered in first-principles calculations^{8,9}. They were predicted to be very hard and ionic, and to be stable over a number of tetrahedral polymorphs above 400 GPa (ref. 8).

We studied modifications of carbon dioxide by conducting five separate experiments close to the recently determined⁴ transformation boundary from CO₂-III to CO₂-V, that is, at 40–76 GPa and 300–680 K (see Fig. 1b inset), by using an externally heated diamond anvil cell. Phase III was compressed at room temperature to between 40 and 48 GPa until a new, broad, infrared band (B_{IR} in Fig. 1a), composed of at least two components and centred at about 1,250 cm⁻¹, emerged. This strong band, which saturates the absorption when the transformation is enhanced by increasing temperature, is not due to molecular CO₂ and therefore indicates a chemical transformation of the sample. Another band not belonging to molecular CO₂, A_{IR}, centred around 730 cm⁻¹, is also observed in the transformed sample. The width of band B_{IR} is a preliminary hint of disorder in the structure. The almost complete disappearance of the infrared molecular lines, Fig. 1, confirms that the transformation into a non-molecular phase (a-CO₂) is complete at 564 K and 64 GPa.

The temperature quenched a-CO₂ samples are transparent (see inset of Fig. 2), and were investigated by means of infrared (IR) and Raman spectroscopy, and X-ray diffraction techniques. At variance with a study of CO₂ at very high pressures and temperatures (above 2,000 K)³, where the presence of molecular oxygen, carbon clusters, and large spatial inhomogeneities were reported in the recovered samples, we did not find evidence of decomposition, probably owing to the milder temperature conditions of our experiments. We also did not find traces of carbonyl groups. The comparison of the IR spectrum of a-CO₂ with those of different silica polymorphs (Fig. 2) such as a-SiO₂, quartz, coesite and stishovite suggests a silica-like character for our non-molecular extended phase. When compressed to 25–35 GPa, both quartz and coesite amorphize¹⁷ and their IR spectra, along with that of a-SiO₂ compressed to similar pressures, tend to resemble that of stishovite^{18,19}. By shifting the frequencies according to the reduced mass ratio between Si–O and C–O pairs, the overall spectral shapes of all dense silica polymorphs are found to resemble closely that of a-CO₂. The shifted silica band at about 650 cm⁻¹ appears to be related to band A_{IR} of a-CO₂, which we therefore assign to a deformation of the carbon–oxygen framework. The broad feature lying between 800 and 1,700 cm⁻¹ in the SiO₂ shifted spectrum can be related to band B_{IR} of a-CO₂; this feature corresponds, in SiO₂, to stretching and O–Si–O bending vibrations within SiO₆ octahedra (between 800 and 1,300 cm⁻¹), and to SiO₄ tetrahedral stretching vibrations (above 1,300 cm⁻¹). On the basis

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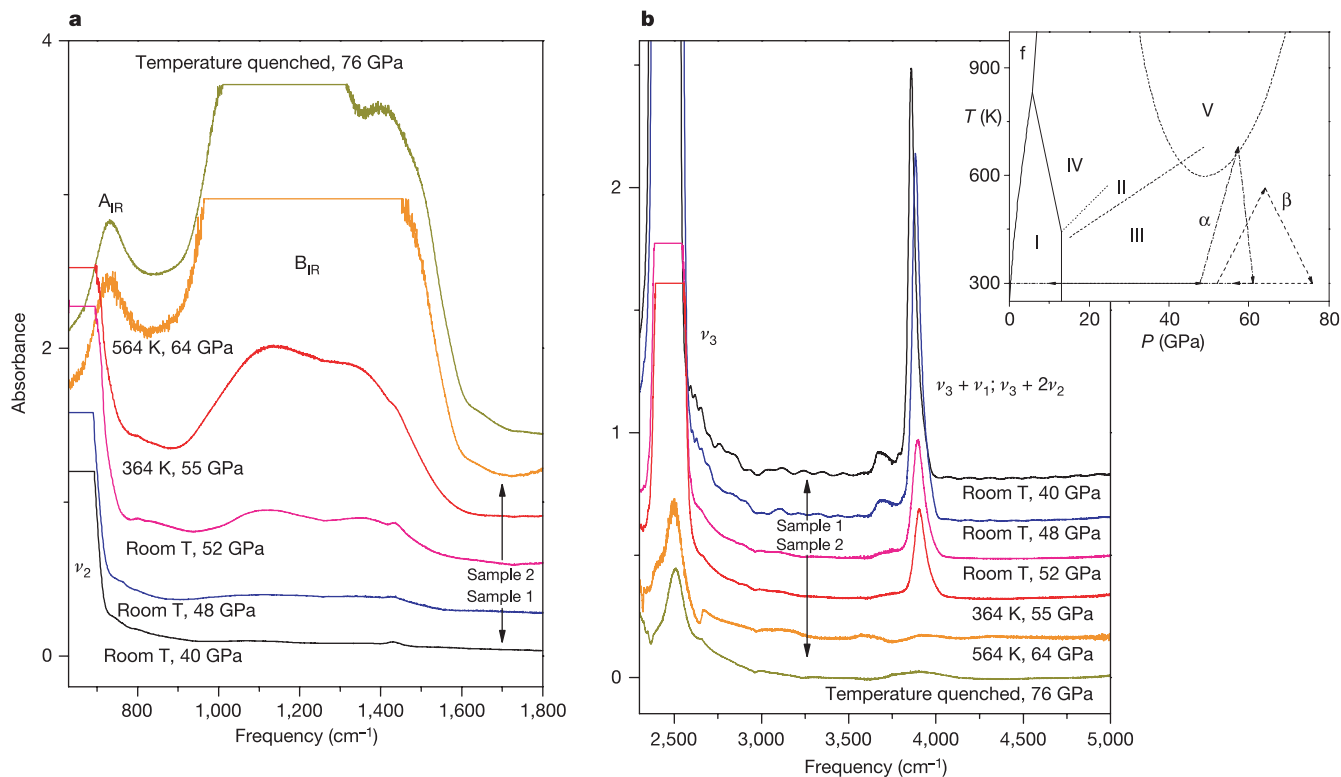
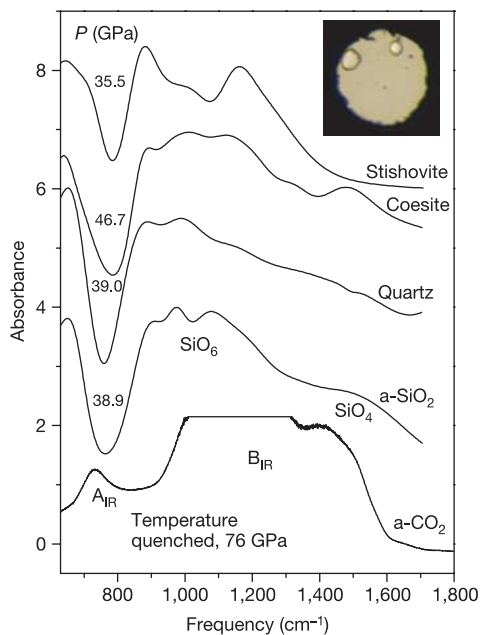


Figure 1 | Infrared spectra showing the transformation of the molecular solid, CO₂-III, into a-CO₂ for two different samples. In **a**, the initial spectrum, at room temperature and 40 GPa, is dominated by the saturating ν_2 band of CO₂ below 800 cm⁻¹. A new broad band, B_{IR}, formed by at least two components, appears on increasing pressure from 40 to 52 GPa. At 564 K, the intensity of band B_{IR} saturates and the absorption in the spectral region between 965 and 1,450 cm⁻¹, and another new band, A_{IR}, is observed around 730 cm⁻¹. Pressure changes were not compensated along the heating cycle. In **b**, the spectral region of the saturating molecular ν_3 line and of the $\nu_3 + \nu_1$ and $\nu_3 + 2\nu_2$ combination bands is shown in reverse order versus temperature, for the sake of visual clarity. Just a remnant of the ν_3 line is evident in spectra of the transformed sample. In the inset, we report the

state-of-the-art phase diagram of CO₂ (refs 4, 24): I, II, III, IV, molecular crystalline phases; f, fluid phase; V, non-molecular crystal. Dashed lines are kinetic barriers. The apparent quadruple point that seems to connect phases I, IV, II and III does not imply any thermodynamic paradox, as the line between CO₂-II and -III is a kinetic barrier rather than a phase boundary. Arrows schematically indicate the *P*-*T* paths of our five separate experiments: paths α (dot dashed) and β (dashed). Spectra in this figure are relative to path β , while similar IR spectra were obtained in synthesizing a-CO₂ along path α . Spectra were measured by means of a Fourier transform infrared spectrometer (Bruker IFS-120 HR), equipped with an optical beam condenser system²⁵. Starting sample thickness and diameter at ambient pressure were about 40 and 100 μm , respectively.

Figure 2 | Comparison of a-CO₂ IR spectrum with mass-shifted spectra. Shown are the IR spectrum of a-CO₂ and mass-shifted spectra of a-SiO₂, pressure amorphized quartz and coesite, and stishovite^{18,19}. Mass shift was obtained by multiplying the frequency scale relative to SiO₂ by $(\mu_{\text{Si-O}}/\mu_{\text{C-O}})^{0.5}$, where $\mu_{\text{Si-O}}$ and $\mu_{\text{C-O}}$ are reduced masses of the Si-O and C-O pair, respectively. Inset, typical temperature quenched a-CO₂ sample (*P* = 61 GPa, sample diameter about 80 μm ; two ruby chips are close to the gasket). The broad feature lying between 800 and 1,700 cm⁻¹ in the SiO₂ shifted spectra corresponds to stretching and O-Si-O bending vibrations within SiO₆ octahedra (between 800 and 1,300 cm⁻¹), and to SiO₄ tetrahedral stretching vibrations (above 1,300 cm⁻¹).



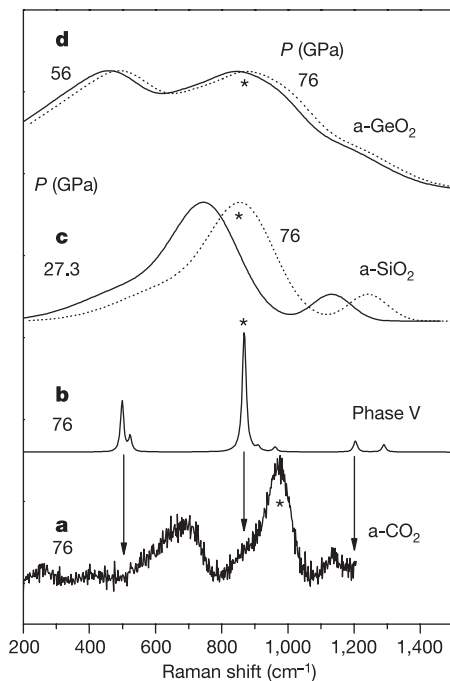


Figure 3 | Comparison of a-CO₂ Raman spectrum with phase V spectra and mass-shifted spectra. **a**, Spectrum of temperature quenched a-CO₂ at 76 GPa, as obtained along the synthesis path β (Fig. 1b inset); **b**, pattern fitted to spectra of temperature quenched phase V (ref. 4), measured up to 66 GPa, and pressure shifted to 76 GPa. Arrows point out the correspondence of phase V lines to band edges of a-CO₂. **c**, **d**, Mass (continuous lines) and mass and pressure (dotted lines) shifted spectra of a-SiO₂ and a-GeO₂, respectively; spectra of glassy SiO₂ and GeO₂ are from refs 20 and 21, respectively. Stars indicate bands assigned to symmetric X–O–X (X = C, Si or Ge) stretching modes. The shifted spectrum of a-GeO₂ exhibits a broad feature centred around 470 cm⁻¹, which was suggested to be related to the high pressure octahedral modification of amorphous germania²¹. Raman measurements on a-CO₂ were performed by using the 752.5 nm line of a Kr⁺ laser as excitation source. The backscattering geometry was used, and the unpolarized signal was detected by a single monochromator (Acton/SpectraPro 2500i) equipped with a CCD detector (Princeton Instruments Spec-10:100BR).

of the analogy between the IR spectra of CO₂ and SiO₂, we infer that a-CO₂ and dense silica have similar local structures.

The Raman spectrum of a-CO₂ is characterized by broad features (Fig. 3), which confirm the amorphous character of the new phase. In particular, we find an asymmetric band at around 690 cm⁻¹, a narrower band at 970 cm⁻¹ with a shoulder at 870 cm⁻¹ and a weak band at 1,135 cm⁻¹. The spectrum of crystalline phase V (ref. 4) exhibits much narrower lines, shifted slightly with respect to that of a-CO₂. The Raman lines of CO₂-V are close to the a-CO₂ band edges, so we speculate that the broad bands observed in a-CO₂ reflect vibrational density-of-states features of CO₂-V. This also supports the notion that a-CO₂ is the glassy counterpart of phase V. Comparison with the Raman spectra of a-SiO₂ (ref. 20) and a-GeO₂ (ref. 21), available up to 27.3 and 56 GPa, respectively, points to the homology between those glasses and a-CO₂. Spectra of a-Si(Ge)O₂ were properly shifted by considering the different masses (as for IR spectra) and pressures (according to the measured pressure shifts) with respect to those of a-CO₂. The shifted spectra of a-SiO₂ and a-GeO₂ exhibit prominent broad bands peaked at around 845 and 880 cm⁻¹, respectively, corresponding to symmetric Si(Ge)–O–Si(Ge) stretching modes that overlap with the spectral region of the C–O–C stretching modes of phase V and a-CO₂ (peaks at 868 and 970 cm⁻¹, respectively).

As a final test of structural disorder in the new material, we

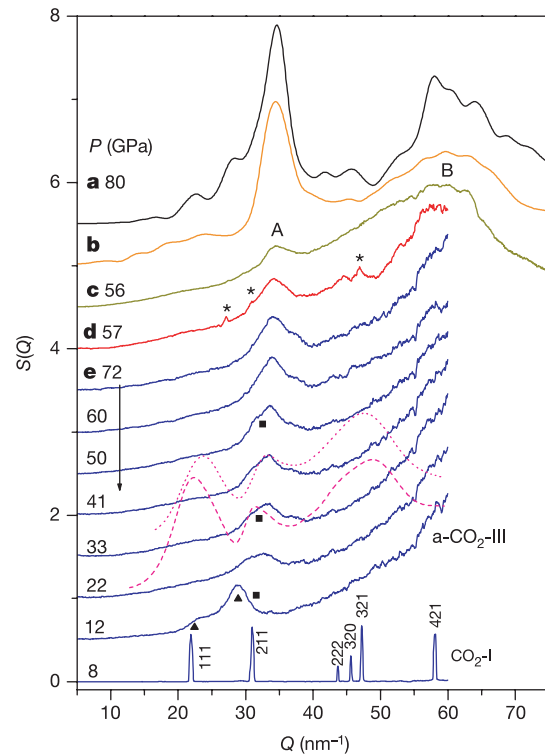


Figure 4 | Static structure factor, $S(Q)$, of a-CO₂. **a**, **b**, Theoretical $S(Q)$ for CO₄ and higher (up to octahedral) carbon coordination, respectively; **c**, **d**, temperature quenched samples synthesized along path α (see Fig. 1b), and **e**, along path β . The structure factor of sample **e** has been measured upon decreasing pressure. At about 16 GPa, a-CO₂ transforms into a new amorphous material, a-CO₂-III, that is suggested to be the glassy counterpart of phase III (see text). Below 10 GPa, the amorphous material recrystallizes into phase I (dry ice), whose peaks are indexed. The shorter Q range relative to sample **d** and **e** was due to the smaller access angle of the cell. The experimental $S(Q)$ of a-SiO₂ is also reported at 42 GPa (dotted line) and 28 GPa (dashed line)²². Symbols indicate diffraction peaks of: (stars) rhenium gasket, (squares) phase V² (the closest line to peak A of a-CO₂), and (triangles) phase III²³. Angle dispersive X-ray diffraction patterns have been measured at the ID27 beam line of the European Synchrotron Research Facility, with monochromatic beam ($\lambda = 0.3738 \text{ \AA}$), and image plate detection. The nominal size of the focal spot was equal to $6 \times 6 \mu\text{m}^2$. The diffraction patterns were analysed and integrated using the FIT2D computer code²⁶. The structure factor $S(Q)$ was obtained as: $S(Q) = [I(Q) - I_b(Q)]/Nf^2$, where $I(Q)$ and $I_b(Q)$ are the polarization-corrected total and empty-cell X-ray diffraction intensities, respectively, N is a normalization factor, and f is the CO₂ molecular form factor. See Supplementary Information for further details. Pattern **a** was obtained by means of *ab initio* molecular dynamics simulations of CO₂, after compression of phase III to 80 GPa at 2,000 K, where a-CO₂ was found to contain only tetrahedral sites. Pattern **b** was obtained by classical molecular dynamic simulations of a-SiO₂, brought to 28 GPa, which we find to contain similar proportions of four-, five-, and six-fold coordinated Si (ref. 27), by scaling its volume to that of simulated a-CO₂, and by artificially replacing the atomic form factor of Si with that of C.

measured its static structure factor, $S(Q)$ (Fig. 4), where Q is the exchanged wave-vector. The $S(Q)$ at 56 GPa is dominated by a broad peak centred around 34.3 nm⁻¹ (peak A), which corresponds to a length scale $2\pi/Q \approx 1.83 \text{ \AA}$, and a much broader peak around 58 nm⁻¹ (peak B). The theoretical $S(Q)$, calculated on a fully tetrahedral atomic structure obtained by first-principles molecular dynamics⁹, reproduces both experimental peaks A and B, although peak A exhibits a higher intensity in the theoretical pattern. However, similar agreement with the measured $S(Q)$ can be obtained by considering a theoretical sample containing carbon in higher coordination (see Fig. 4 legend). The similarity between the structure

factors calculated with different local environments (from tetrahedral to octahedral) shows that, even though the first-principles molecular dynamics simulations give a fully tetrahedral phase for a-CO₂, the measured structure factor cannot be used to discriminate between differently coordinated local atomic environments.

Network-forming disordered systems like a-SiO₂ are characterized by a peculiar first diffraction peak at considerably lower *Q* than expected on the basis of nearest-neighbour atomic distances, which has been attributed to the existence of correlation over medium length scales. It is thus interesting to compare the *S(Q)* of a-CO₂ with that of a-SiO₂ (ref. 22) to check if a similar peak exists in a-CO₂. At 42 GPa, the length scale related to peak A in a-SiO₂ (1.86 Å) compares well with the expected O–O distance at that pressure, while the peak at lower *Q* corresponds to a length approximately 30% longer. Peak A in a-CO₂ corresponds also to the theoretical O–O distance, but no peak can be found at lower *Q*. However this is not a consequence of lack of medium range order, but rather of a sort of cancellation among the partial structure factors. As a matter of fact, if we replace artificially the atomic form factor of C used to calculate *ab initio* the *S(Q)*, with that of Si, we recover a peak at lower *Q* similarly to a-SiO₂.

We notice that peak A is very close to the strongest peak of crystalline CO₂-V (ref. 2), whose intensity has been suggested to be enhanced by disorder², indicating once again that a-CO₂ is the amorphous counterpart of phase V. The *S(Q)* was also measured upon decreasing pressure, showing a positive pressure shift of peak A ($\Delta Q = 1.63 \text{ nm}^{-1}$ for $\Delta P = 50 \text{ GPa}$), consistent with pressure induced densification. The pressure shift is, however, very small and parallels that of the strongest CO₂-V peak², suggesting that the two materials have similar and very small compressibilities. At about 16 GPa a-CO₂ transforms into a new amorphous material, whose diffraction features appear to be related to the strongest Bragg peaks of phase III (ref. 23). We therefore suggest this to be the amorphous molecular counterpart of phase III. Below 10 GPa, phase I is formed by recrystallization of the amorphous material.

With the discovery of 'a-carbonia', a new, extended analogy emerges between the structures of CO₂ and those of the known SiO₂/GeO₂ polymorphs. CO₂ transforms under pressure into a three-dimensional amorphous network, similar to, but most probably harder than, a-SiO₂ and a-GeO₂. Amorphous carbonia is the disordered parent of tetrahedral quartz-like CO₂-V, though some carbon sites having higher coordination, at least in the sense of coordination defects, may also be included in such a material. This point seems to be specifically supported by the general agreement between IR spectra of a-CO₂ and those of densified a-SiO₂/GeO₂ systems, which are known to be composed by tetrahedral up to octahedral sites. The X-ray diffraction analysis is not conclusive in this respect, and further investigation is needed to definitely assess the possible existence of high coordination sites in carbonia. Our findings demonstrate that non-molecular CO₂ is the stable form of the important compound CO₂ at high pressure and room temperature, as already suggested on the basis of thermodynamic arguments⁴. We hope that the discovery of a-carbonia will stimulate further studies on the high-pressure phase diagram of CO₂, which could extend our understanding of network-forming systems and strengthen the notion of pressure-induced amorphous states.

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Supplementary Information is linked to the online version of the paper at www.nature.com/nature.

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