

Six-fold coordinated carbon dioxide VI

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Under standard conditions, carbon dioxide (CO_2) is a simple molecular gas and an important atmospheric constituent, whereas silicon dioxide (SiO_2) is a covalent solid, and one of the fundamental minerals of the planet. The remarkable dissimilarity between these two group IV oxides is diminished at higher pressures and temperatures as CO_2 transforms to a series of solid phases, from simple molecular to a fully covalent extended-solid V, structurally analogous to SiO_2 tridymite. Here, we present the discovery of an extended-solid phase of CO_2 : a six-fold coordinated stishovite-like phase VI, obtained by isothermal compression of associated CO_2 -II (refs 1,2) above 50 GPa at 530–650 K. Together with the previously reported CO_2 -V (refs 3–5) and a-carbonia⁶, this extended phase indicates a fundamental similarity between CO_2 (a prototypical molecular solid) and SiO_2 (one of Earth's fundamental building blocks). We present a phase diagram with a limited stability domain for molecular CO_2 -I, and suggest that the conversion to extended-network solids above 40–50 GPa occurs via intermediate phases II (refs 1,2), III (refs 7,8) and IV (refs 9,10). The crystal structure of phase VI suggests strong disorder along the c axis in stishovite-like $P4_2/mnm$, with carbon atoms manifesting an average six-fold coordination within the framework of sp^3 hybridization.

Carbon dioxide is a prototypical molecular system, with strong covalent bonds within the $\text{O}=\text{C}=\text{O}$ molecules and rather weak quadrupolar interactions between them. At high pressures and temperatures, CO_2 transforms to a series of solid polymorphs with differing intermolecular interactions, chemical bonding and crystal structures (Fig. 1). Phase V, in particular, consists of a network of corner-sharing CO_4 tetrahedra, structurally similar to SiO_2 tridymite. Thus, CO_2 -V is a fundamentally new material that exhibits extremely low compressibility⁵ and strong optical nonlinearity³. The large disparity in chemical bonding between the extended network and molecular CO_2 results in a broad metastability domain for phase V, to room temperature and almost to ambient pressure^{3,5}.

The other CO_2 phases, II (refs 1,2), III (refs 7,8) and IV (refs 9–11) (formed in the intermediate pressure–temperature regime) exhibit strong intermolecular interactions, enhanced substantially over those of typical quadrupolar molecular solids¹². The strong interactions lead to enhanced collective behaviour of molecules, and result in strong associations of neighbouring molecules in phase II, strain-induced disorder in phase III and molecular bending in phase IV. Accordingly, these phases have been considered as intermediates between the simple molecular phase I and the fully extended phase V.

The crystallographic similarities between CO_2 and SiO_2 polymorphs^{2,5,10,13} suggest the existence of other CO_2 extended solids, including six-fold stishovite. The strong covalence in C–O

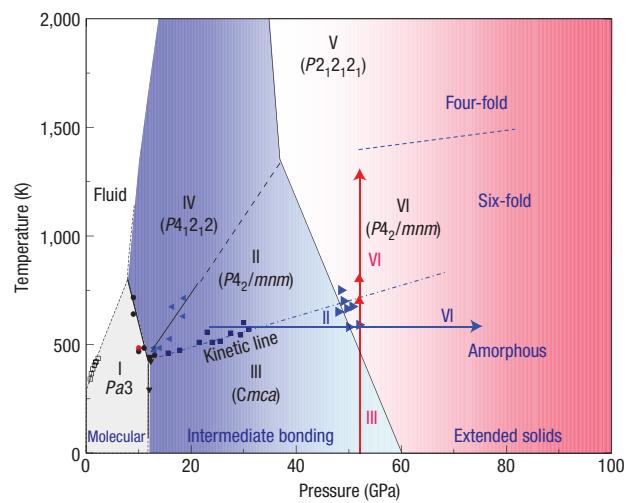


Figure 1 Phase diagram of carbon dioxide illustrating the molecular to non-molecular phase transitions to four- and six-fold coordinated carbon atoms. The arrows represent two typical experimental paths: isothermal compression of phase II to 90 GPa or isobaric heating of phase III to 1,200 K, shown together with the observed phase transformations. Phase V was synthesized by laser heating the quenched phase VI well above $\sim 1,500$ K (marked as a dashed line). The dash-dot line between phases II and III indicates a kinetic line, whereas the broken melting line of phase IV was not measured. The grey, blue and red colours, respectively, signify the stability fields of molecular, intermediate and extended phases and the electron delocalization occurring gradually in CO_2 , via the intermediate phases II and IV.

bonds and the rigidity of sp^3 -bond angles, however, seem to hamper the formation of six-fold coordinated carbon units¹⁴. Total-energy calculations predict four-fold cristoballite¹⁴ and/or layered carbonate⁴ structures to be among the most stable configurations, whereas six-fold CO_2 are thought to stabilize only at ultrahigh pressures above 400 GPa (ref. 15).

Here, we report the discovery of fully extended stishovite-like CO_2 phase VI, formed at pressures below 100 GPa (Fig. 1). On the basis of a large number of resistive- and laser-heating experiments using membrane diamond-anvil cells (mDACs), we propose the relationship between the molecular and extended phases in the pressure–temperature domain shown in Fig. 1.

CO_2 -VI is stabilized by isothermal compression of phase II to pressures above 50 GPa at temperatures 530–650 K. As shown in

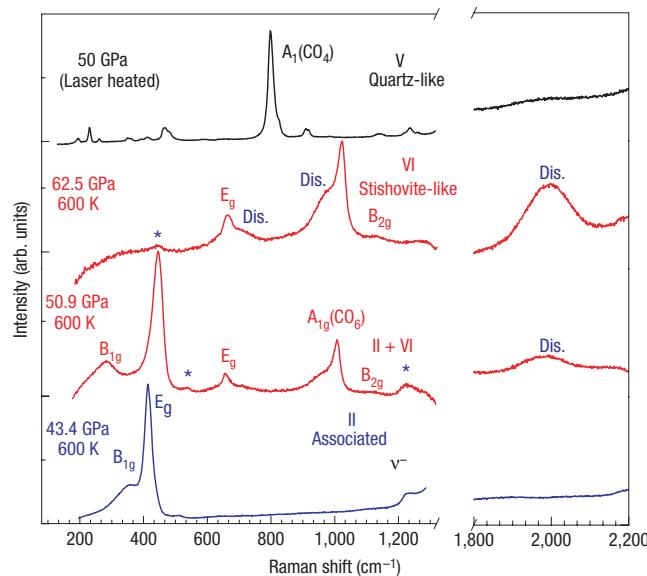


Figure 2 Raman spectra of carbon dioxide phases at high temperatures and pressures, representing the phase transition from strongly associated phase II to fully extended, stishovite-like phase VI at 600 K and 51 GPa. Note that residual phase II (marked by an asterisk) still apparent at this pressure gradually weakens and eventually disappears above \sim 65 GPa, whereas the features of phase VI are enhanced. CO₂-VI is quenchable at ambient temperature, and laser heating the quenched phase VI to above 1,500 K transforms it to CO₂-V. The peaks labelled ‘Dis.’ are assigned to disorder within the stishovite structure as described in text.

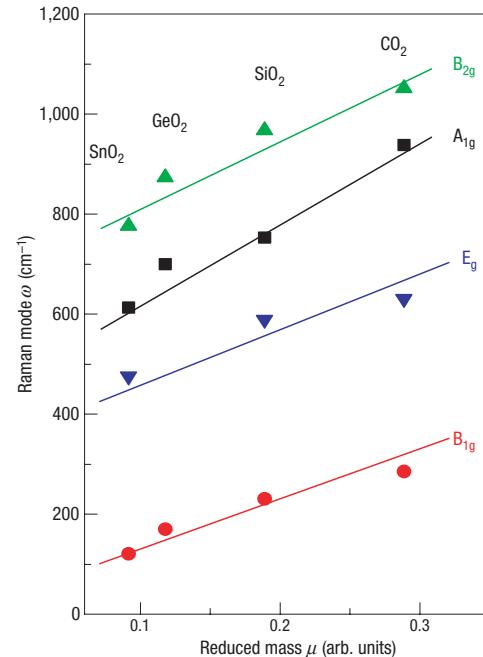


Figure 3 Raman mode frequencies of CO₂-VI compared with those of other group IV dioxides in rutile structures. We find a near-linear scaling of the four principal Raman bands with the reduced mass, strongly supporting our stishovite-like assignment for phase VI.

Table 1 Comparison of the major Raman frequencies observed in extended CO₂ phases and corresponding SiO₂ polymorphs in four- and six-fold configurations. The numbers indicate the Raman shift in cm⁻¹ at ambient pressure, obtained by extrapolation from Fig. 4 for CO₂ phases and from ref. 16 for SiO₂ phases.

Four-fold		Six-fold	
SiO ₂	CO ₂ -V	SiO ₂	CO ₂ -VI
464	660	967	1,051
206	285	753	905
128	240	589	620
		231	285

Fig. 2, the most notable Raman feature of CO₂-VI is the emergence of a strong band around 1,010 cm⁻¹ at 50 GPa. This mode frequency is substantially higher than that of four-fold coordinated carbon in CO₂-V (\sim 800 cm⁻¹) (ref. 3), indicating that it probably originates from six-fold coordinated carbons in octahedral sites—similar to the A_{1g} mode of stishovite¹⁶. Following this assignment, we further associate the peaks at 300 cm⁻¹ to B_{1g}, 680 cm⁻¹ for E_g, and a weak, but measurable band at 1,100 cm⁻¹ to B_{2g}, thus accounting for all four Raman-active modes reported in stishovite¹⁶. Importantly, the frequencies of these modes scale very well to those observed in SiO₂ polymorphs (see Table 1). In addition, in Fig. 3 we compare the observed Raman spectra of CO₂-VI with those of other group IV dioxides in rutile structures. We find that the frequencies of all four Raman-active modes scale linearly with the reduced mass, strongly supporting the present assignment of phase VI as stishovite-like. The data for SiO₂, GeO₂ and SnO₂ are from previous studies¹⁷.

Figure 4 summarizes the pressure dependence of the Raman modes of the new material. In addition to the four modes assigned

to the stishovite-like structure, we observe a number of broad Raman features in CO₂-VI, centred at \sim 2,000, 950 and 700 cm⁻¹ at 65 GPa, which we assign to disorder in the stishovite structure. In fact, the 950 and 700 cm⁻¹ Raman bands are very similar to those of amorphous CO₂ (ref. 6). Although the 2,000 cm⁻¹ band is well within the overtone range of the A_{1g} band, we note that the C–O stretching mode of carbosonium¹⁸ or a theoretically suggested ring dimer¹⁹ also appear in this frequency range.

The II-to-VI transition is strongly affected by kinetics, requiring slow compression over several hours in a wide pressure range. Although the conversion to CO₂-VI starts at \sim 50 GPa (530 K), residual CO₂-II is observable to 60–65 GPa. In this pressure range, the A_{1g} mode of phase VI gradually increases, whereas the E_g mode of phase II gradually decreases in intensity and eventually disappears above 60–65 GPa, as shown in Fig. 2. CO₂-VI can also be produced by isobaric heating of phase III to \sim 700–900 K above 50 GPa, although this method typically leads to a less crystalline phase. Once CO₂-VI is formed at high pressures and temperatures, it remains stable in a wide pressure range, from 90 GPa (the maximum pressure applied in the present study), down to 20 GPa, below which it transforms back to phase II. CO₂-VI is also stable in a wide temperature range from ambient to at least 1,200 K at 50 GPa, the maximum temperature reached in our resistive heating experiments. Further heating CO₂-VI to above 1,500 K using a Nd:YLF laser converts the sample to CO₂-V (Fig. 2).

The stability of six-fold coordinated carbon dioxide at around 50 GPa is remarkable. It has not been reported in any other carbon compounds, and theory has predicted its existence only at substantially higher pressures above 400 GPa at 0 K (ref. 15). We attribute its low-pressure stability to the crystal structure of phase II (ref. 2) in which each carbon atom already has six quasi-nearest-neighbour oxygen atoms, facilitating the formation of the six-fold C–O single-bond configuration observed in phase VI. In fact, our

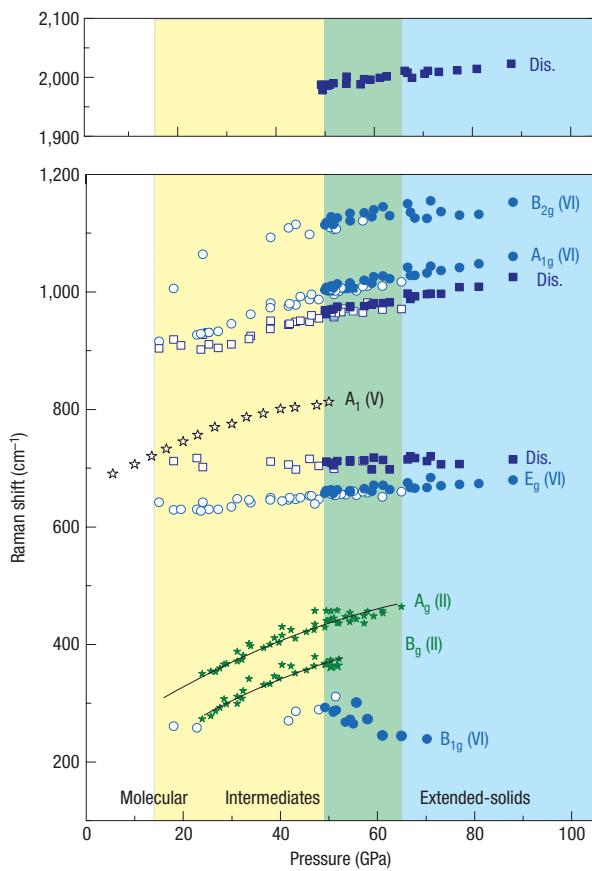


Figure 4 Pressure-dependence of the Raman modes observed in the extended phases of CO_2 -VI (in blue) and V (in black from ref. 3), overlaid with those of CO_2 -II (in green) for comparison. The broad features arising from the disorder in phase VI are also shown (in dark blue, labelled as 'Dis'). Open and filled symbols signify the data obtained during pressure upstroke and downstroke, respectively.

X-ray diffraction data confirm the close similarity between the crystal structures of phases II and VI (Fig. 5).

Figure 5 shows the X-ray diffraction data of phases II and VI obtained at elevating pressures at 600 K. Phase II diffraction pattern is well described in terms of stishovite-like $P4_2/mnm$; $a = 3.5430(5)$ Å, $c = 4.1544(7)$ Å, C:2a(0,0,0) and O:2f($x, x, 0$) $x = 0.247(1)$. Small differences observed in the 110 and 101 reflections represent a minor, less than 0.1%, lattice distortion in the ab plane².

Figure 5 shows a remarkable similarity between the diffraction patterns of phases II and VI, confirming the structural similarity between the two phases. Indeed, the diffraction patterns of phase VI are reasonably well refined in terms of the same space group $P4_2/mnm$; $a = 3.4284(3)\{3.363(1)$ Å, $c = 4.0259(7)\{3.973(4)$ Å at 59{70} GPa. Furthermore, all observed pressure-induced diffraction changes occur smoothly and continuously across the phase transition. The two most characteristic changes are a gradual diminution of the 002/111 intensity ratio and an overall broadening of all reflection lines. However, in $P4_2/mnm$, carbon atoms in the 2(a) sites can contribute only to the hkl reflections matching $h + k + l = 2n$, whereas oxygen atoms in the 4(f) do not have any additional reflection conditions. Therefore, to describe the observed diffraction changes in phase VI, it is necessary to introduce the movement of atomic positions away from the ab plane, by either allowing carbon atoms to deviate from 2a(0, 0, 0)

along the c axis to 4e(0, 0, z) (shown in Fig. 5b) or oxygen atoms from 4f($xx0$) to 8m(xxz) or more generally 16k(xyz) (not shown), reducing the atomic occupancy correspondingly. In this model, we found that the value of the displacement z increases gradually above 50 GPa, approaching $z = 0.095\{0.170\}$ at 59{70} GPa (see Supplementary Information, Fig. S1 inset). This results in all carbon atoms well within carbon–oxygen single-bond distances, 1.45–1.71 Å, having six quasi-nearest oxygen atoms in a highly distorted octahedral configuration as illustrated in Fig. 5b.

Alternatively, the observed diffraction changes may also be described in terms of large-amplitude thermal vibrations. The best refinements of the X-ray data in Fig. 5a, however, result in relatively large thermal displacement parameters; $0.16(1)\{0.110(8)\}$ Å² for carbon and $0.11(1)\{0.096(8)\}$ Å² for oxygen at 59{70} GPa, two–three times those previously obtained in phase II at similar temperatures. Therefore, we prefer the static-disorder model described above, with the fixed initial displacement parameters at 0.058 Å² for both C and O. Nevertheless, we found that the latter refined thermal displacement parameters become larger again; $0.109(8)$ Å at 59 GPa and $0.115(7)$ Å at 70 GPa or actual thermal motion of ~ 0.33 – 0.34 Å. These values are quite comparable to the displacement of carbon atoms along the c axis, 0.4 – 0.6 Å (see Fig. 5b). In this regard, it is difficult to differentiate the static disorder from the dynamic thermal model. In either case, carbon atoms remain on average six-fold coordinated with oxygen atoms.

Although the present X-ray data confirms the stishovite-like $P4_2/mnm$ structure for phase VI, there is a subtle difference from stishovite. That is, the CO_6 octahedron in phase VI is made of two edge-sharing CO_4 units that share a single carbon atom. Nevertheless, the similarity in the Raman spectra between phase VI and stishovite clearly indicates that up to 90 GPa the amount of disorder is relatively small to maintain an average coordination of six. The short interatomic oxygen–oxygen contact distance in the ab plane of phase II, 2.1–2.4 Å depending on the pressure–temperature conditions, is well in the repulsion regime and thus leads to mechanical instability^{14,20} and the observed structural frustration on pressure increase. This results in a configuration of carbon atoms manifesting six-fold coordination while maintaining the frame work of sp^3 hybridization at elevated pressures.

We point out that the proposed disordered $P4_2/mnm$ model cannot be uniquely determined based on the limited number of reflections observed in the present powder X-ray diffraction patterns. Nevertheless, in addition to its close similarity to the parent phase II, the present model is consistent with all of our other experimental observations. First, it explains the increased ionicity of C–O bonds in phase VI, as observed in the Raman spectra and also predicted by theory¹⁵. Second, it accounts for the significant temperature dependence of the specific volume of phase VI (see Supplementary Information, Fig. S1). At 70 GPa, the specific volume of phase VI is $0.305 \text{ cm}^3 \text{ g}^{-1}$ at 600 K but collapses to ~ 0.290 – $0.220 \text{ cm}^3 \text{ g}^{-1}$ at 300 K, well within the range of fully extended solids (for example, $0.265 \text{ cm}^3 \text{ g}^{-1}$ for phase V at 300 K)⁵. Third, the proposed structural disorder is consistent with the emergence of the broad Raman bands in phase VI (marked as 'Dis' in Figs 2 and 4). Finally, it provides a mechanism for the stability of phase VI at moderate pressures and temperatures (above 50 GPa and 550 K), in contrast to the extreme pressures (400 GPa) predicted by theory¹⁵.

Finally, considering the rich abundance of carbon, oxygen and silicon in the Earth's mantle, the new high-density form of six-fold carbon dioxide may offer new concepts in geo- and mineral chemistry. For example, CO_2 could exist in the Earth's mantle as four- and six-fold covalent solids and within alloys or solid solutions with SiO_2 and/or other minerals. The structural similarities between CO_2 and SiO_2 polymorphs would

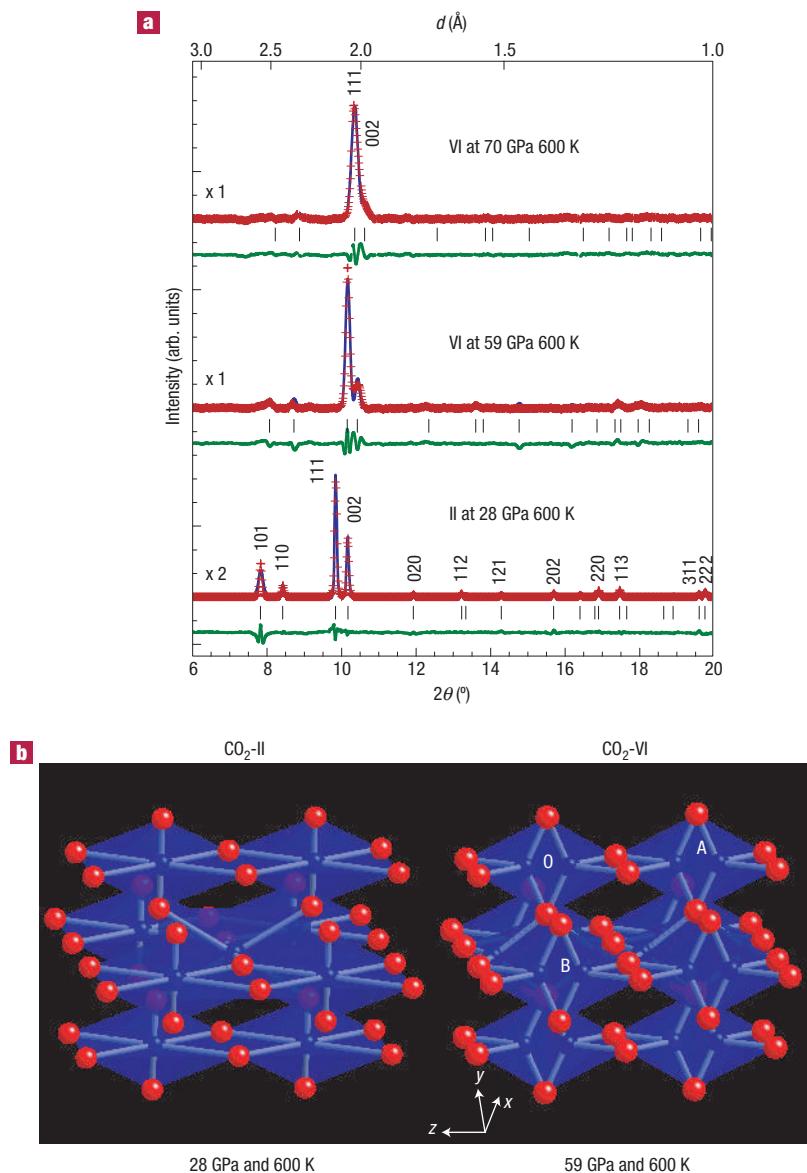


Figure 5 Structural model for CO₂-VI based on *in situ* X-ray diffraction measurements. **a**, ADXD patterns of CO₂-II and VI (red plus symbols), shown together with the refined (blue lines) and difference (green lines) patterns. The X-ray wavelength was 0.3682 \AA , and the hkl reflection lines are also marked. **b**, Crystal structures of phases II and VI in a stishovite-like $P4_2/mnm$ structure. Note that carbon atoms in phase VI are disordered but maintain an average six-fold coordination within the carbon framework of sp^3 hybridization.

presumably enhance their mutual solubility and chemical reactivity at the pressure–temperature conditions of the Earth's mantle. The structural instability of six-fold CO₂ at low pressures and its enhanced ionic character on decompression, would help account for the carbonate minerals originating from the Earth's interior²¹ as well as for the high-temperature origin of carbonates in martian meteorites²².

METHODS

Samples were loaded into an externally heated He gas mDAC by condensing 99.99% pure CO₂ gas at 10 MPa and 233 K in a sealed pressurized vessel. The use of resistively heated mDACs provided precise control over both pressure (± 2 GPa up to 100 GPa) and temperature (± 10 K up to 1,200 K). Furthermore, the mDAC applies a constant load by He gas to the sample during external

heating to 1,200 K at a given pressure, thus allowing isobaric heating experiments. Precise control over the experimental pressure–temperature path was crucial considering the significant metastability observed in CO₂ phases. The sample temperature was measured by a K-type thermocouple attached in close proximity to the diamond-anvil, and the pressure was determined by measuring the R_1 luminescence of several micrometre-size rubies (Al₂O₃/Cr) placed around the sample. We carried out *in situ* Raman measurements using both 514.5 nm and 488.8 nm lines of an Ar⁺ laser. For laser-heating experiments, we used the 1,054 nm line of a Nd:YLF laser to heat the CO₂ samples indirectly by heating either the ruby or the Re gasket edge as an absorber.

Angle-dispersive X-ray diffraction (ADXD) data were obtained at the microdiffraction beamline of the High Pressure Collaborative Access Team at the Advanced Photon Source by using focused (~ 0.01 – 0.02 mm) monochromatic X-rays ($\lambda = 0.3682 \text{\AA}$) and a high-resolution image plate detector. The recorded two-dimensional diffraction images (Debye–Scherrer's

rings) were then integrated to produce high-quality ADXD patterns using FIT2D and analysed with the XRDA and GSAS programs.

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Author contributions

Project planning: V.I., C.S.Y., samples and Raman measurements: V.I., Z.J., XRD measurements: V.I., C.S.Y., W.E., H.C., data analysis: V.I., C.S.Y., J.H.K.

Competing financial interests

The authors declare that they have no competing financial interests.

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