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A novel crystalline SiCO compound

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Ab initio evolutionary structural searches have been performed on $Si_xC_yO_{2(x+y)}$ compounds. A novel structure, with SiC_2O_6 stoichiometry and $P2_1/c$ space group is calculated to be stable against decomposition in a wide pressure window from 7.2 to 41 GPa, and metastable under ambient conditions. It consists of CO_3 units, linked to SiO_6 octahedra, supporting previous experimental studies. The evolution of the carbon environment towards tetrahedral CO_4 units, thus resembling the crystal chemistry of silicon, is predicted at higher pressures.

1 Introduction

Understanding the processes involved in the complex global carbon cycle and its coupling to other elemental cycles (oxygen, nitrogen, iron, silicon...) remains a challenge. A vital step is unveiling the structure, bonding and phase stability of the carbon-bearing compounds in the Earth's mantle conditions[1]. On the other hand, the critical influence of atmospheric CO_2 (main greenhouse gas) on Earth's climate and the increasing concern on global warming have led to a renewed interest on this area with the development of different CO_2 sequestration techniques[2]. Nowadays, it is assumed that calcium and magnesium carbonates are the dominant oxidized carbon species in the mantle[3]. Most importantly, CO_2 is produced through decarbonating reactions with silica in subducted basalts and released into the oceans and atmosphere during volcanic activity[4,5]. Therefore, the importance of the analysis of the CO_2-SiO_2 reactivity is clear.

Although CO_2 and SiO_2 do not react at ambient conditions, their structural analogies at high pressure raise the question whether any Si-C-O crystalline phase may exist. An interface consisting of unknown SiCO compounds has been in fact attributed to the oxidized silicon carbide[6] and previous *ab initio* studies proposed hypothetical $Si_{(1-x)}C_xO_2$ structures generated by replacing silicon atoms by carbon atoms on the α-quartz and the distorted-β-cristobalite-like ($I\bar{4}2d$) SiO_2 reference structures[7,8]. However, none of the generated structures was found to be thermodynamically stable. Also, recent experiments performed by Santoro *et al.* at 18-26 GPa and 600-980 K by reacting silicalite, a microporous zeolite, and molecular CO_2 filling the pores claimed the synthesis of a silicon carbonate phase with CO_3 units[9]. Even more recently, at 16-22 GPa and temperatures in excess of 4000 K, the same authors have claimed the synthesis of a solid solution with an average chemical formula of $C_{0.6}Si_{0.4}O_2$[10]. X-ray diffraction showed that carbon and silicon atoms were randomly distributed in the cationic site of an α-cristobalite-type structure. Therefore, both, carbon and silicon atoms were fourfold coordinated to oxygen atoms.

Interestingly, we had already proposed the SiC_2O_6 ($\approx C_{0.6}Si_{0.4}O_2$) stoichiometry as the most plausible one for silicon carbonate compounds based on stability studies on the UB_2O_6-type structure[11]. Subsequent structural searches with the Universal Structure Predictor: Evolutionary Xtallography (USPEX) code at 20 GPa confirmed the stability of the SiC_2O_6 stoichiometry, with a $P\bar{3}$ structure consisting of SiO_6 and CO_3 units as the lowest enthalpy structure[12].

In this paper, we explore the existence of cationic-ordered crystalline systems containing just C, Si and O in a wide pressure range, from 0 GPa to 100 GPa. It opens the way for a new class of stable carbonate compounds at pressures close to the Earth's mantle conditions, with possible implications in the understanding of the deep carbon cycle and the carbon storage[13,14].

2 Methods

We present here results from extensive structural searches of crystalline systems containing only these three elements within the general stoichiometric formula $Si_xC_yO_{2(x+y)}$, with x and y varying between 1 and 3, and up to 4 formula units in the simulation cell. These searches have been performed with the USPEX[15] code at selected pressures from 0 to 100 GPa. This code has successfully predicted the crystal structures of a large number of different systems, including carbonates[16–18].

Each generation contains $40\times Z$ structures, Z being the number of formula units per cell, 60% of which are generated by heredity,

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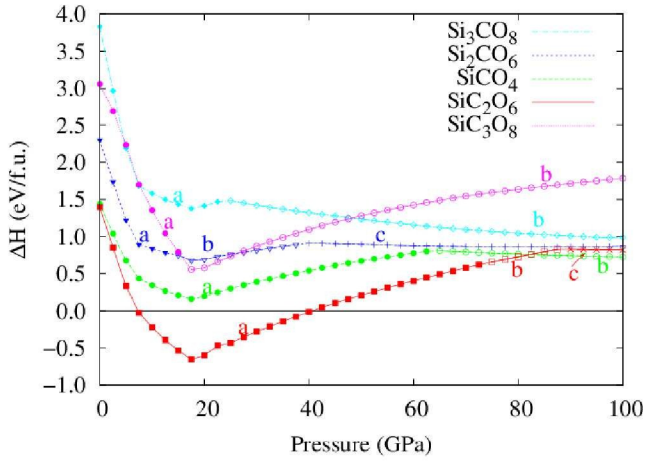

Fig. 1 Calculated enthalpies of formation as a function of pressure for the lowest enthalpy structures corresponding to each stoichiometry. Both, cell parameters and internal coordinates were relaxed at each pressure. The enthalpy of the stable SiO_2 and CO_2 polymorphs at the corresponding pressure is taken as the reference enthalpy. $\Delta H = H(Si_xC_yO_{(2x+2y)}) - xH(SiO_2) - yH(CO_2)$. Different symbols and labels for each stoichiometry correspond to different structures. Specifically, the lowest enthalpy structures on increasing pressure have been labelled following the alphabetic order, a), b), (and c)).

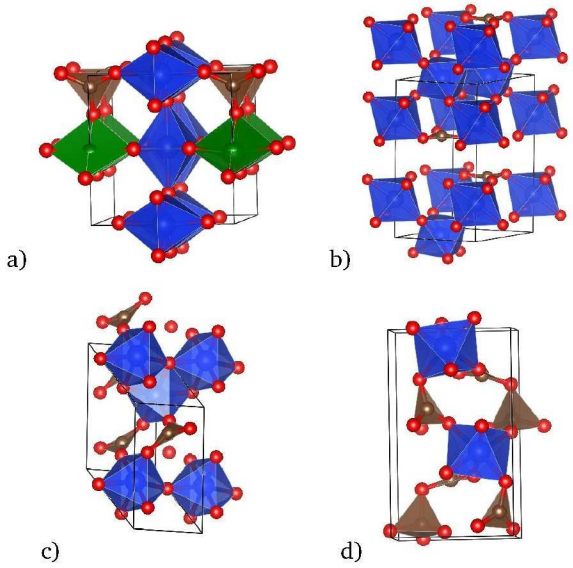

Fig. 2 Unit cells of the lowest enthalpy polymorphs corresponding to the a) Si_3CO_8, b) Si_2CO_6, c) $SiCO_4$, and d) SiC_3O_8 stoichiometries at the minima region. Coordination polyhedra for silicon and carbon atoms in blue and brown, respectively. In Si_3CO_8, coordination polyhedra for 5-coordinated silicon atoms in green.

and the others by random choice. We followed 30-60 generations (depending on the size of the system) to achieve the converged structure. Apart from randomly generated cationic-ordered crystalline structures, the initial search space of some of the searches also included structures derived from known SiO_2 and CO_2 polymorphs as well as others containing CO_4, SiO_4, CO_3 and SiO_6 units, potential constituents of the SiCO compounds. The underlying DFT *ab-initio* calculations were performed with the VASP code[19]. We used the Perdew-Burke-Ernzerhof generalized gradient (GGA) exchange-correlation functional[20] and the projector augmented wave (PAW) all-electron description of the electron-ion-core interaction[21]. Brillouin zone integrals were approximated using the method of Monkhorst and Pack[22], and the energies converged with respect to k-point density (k-point grid spacing of $2\pi \times 0.03$ Å^{-1}) and to the plane wave kinetic energy cutoff (600 eV). Phonons were calculated within density-functional perturbation theory[23] as implemented in the QUANTUM-ESPRESSO code[24].

3 Results and discussion

3.1 Phase stability

The enthalpies of the formation reaction, $xSiO_2 + yCO_2 \rightarrow Si_xC_yO_{2(x+y)}$, for the most stable phases of the different stoichiometries at their corresponding pressure stability ranges are plotted in Fig. 1. We have considered the structures for SiO_2 and CO_2 at 0 K in their corresponding stable pressure ranges, i.e, SiO_2 in the α-quartz (0 - 4.8 GPa), coesite (4.8 - 8.5 GPa), stishovite (8.5 - 55 GPa), $CaCl_2$-type (55 - 85 GPa) and PbO_2-type (85 - 100 GPa) structures and CO_2 in the $Pa\bar{3}$ (0 - 13 GPa), $P4_2/mnm$ (13 - 18.2 GPa), and tetragonally-distorted β-cristobalite-like, $I\bar{4}2d$ (18.2 - 100 GPa) structures. A maximum of two formula units per cell was enough to obtain the lowest enthalpy structures associated to each stoichiometry, with a number of generations between 30-50. The problem becomes much more complex when the number of formula units is four. It forced us to repeat simulations several times to achieve the same structures obtained when Z=2. At ambient conditions, none of the SiCO phases was found to be energetically stable versus decomposition. It agrees with the reported abscence of reactivity between SiO_2 and CO_2 at those conditions. In fact, the structural searches at pressures below 5 GPa lead to structures with exceedingly big volume and molecular CO_2 units, a signpost of the expected dissociation. Therefore, the graph only includes the lowest enthalpy structures for each stoichiometry found above 5 GPa. On pressure increase, the positive enthalpies of formation for all the stoichiometries decrease, presenting a minima region in the experimental range of stability of the previously synthesized SiCO phases.

3.2 Si_3CO_8, Si_2CO_6, $SiCO_4$, and SiC_3O_8

Structurally, the lowest enthalpy structures in the minima enthalpic region consist of SiO_6 and CO_3 units, differing in the distortion, arrangement and the connectivity between them (see Fig. 2).

For instance, in Si_3CO_8, 2/3 of the Si atoms (blue) form almost regular octahedra, whereas the coordination of the remaining Si atoms (green) is rectangular piramidal (5-coordinated Si atoms). The almost planar CO_3 units are corner-connected to the octahedra. There is also edge-sharing by the octahedra. For Si_2CO_6, the lowest enthalpy structure is laminar, with slabs consisting of two external layers of C atoms and 3 internal layers of Si atoms. The distribution of the O atoms on the layers of C atoms and between the Si layers generates an octahedral coordination for the

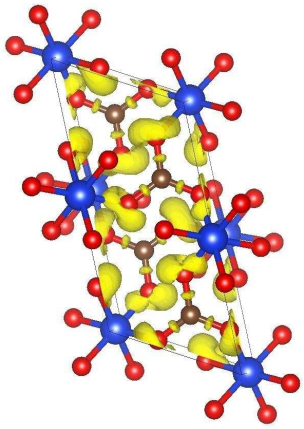

Fig. 3 $P2_1/c$ structure. Blue, brown and red spheres correspond to Si, C and O atoms. ELF isosurface (ELF=0.8) in yellow.

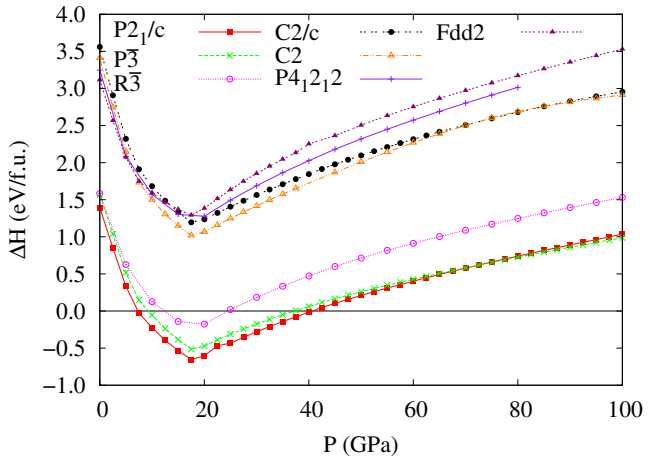

Fig. 4 Calculated enthalpies of formation as a function of pressure for several structures with SiC_2O_6 stoichiometry. The enthalpy of the stable SiO_2 and CO_2 polymorphs at the corresponding pressure is taken as the reference enthalpy: $\Delta H = H(SiC_2O_6) - H(SiO_2) - 2H(CO_2)$.

Si atoms and a triangular planar coordination for the C atoms. There is sharing of edges by octahedra. The CO_3 units are corner-connected to SiO_6 polyhedra. For $SiCO_4$ each distorted SiO_6 ochahedron shares two edges with two adjacent SiO_6 octahedra and is connected through three CO_3 units to three extra octahedra. For SiC_3O_8, 1/3 of the C atoms adopt a strongly distorted tetrahedral coordination, with 2 elongated C-O distances. Each SiO_6 octahedron is then corner-connected to 4 CO_3 and 2 CO_4 units. However, for all these stoichiometries, the formation enthalpies are positive. Therefore, and according to the convex hull formalism, the corresponding structures are not metastable.

3.3 SiC_2O_6: A stable $P2_1/c$ structure

Interestingly enough, only in a wide pressure range between 7.2 and 41 GPa, the SiC_2O_6 stoichiometry emerges as thermodynamically stable against the decomposition into the corresponding stable SiO_2 and CO_2 polymorphs at those conditions (see Fig. 1). The most stable SiC_2O_6 phase is monoclinic, spacegroup $P2_1/c$ with Si atoms located on 2*a* sites (0.0,0.0,0.0), C atoms on 4*e* sites (0.662,0.662,0.755) and tree non-equivalent oxygen atoms on 4*e* sites, at (0.684,0.316,0.287), (0.850,0.052,0.245), and (0.519,0.350,0.735) at 27.5 GPa. The corresponding lattice parameters are a=8.492 Å, b= 4.264 Å, c = 4.306 Å, with γ=119.992°. Given that $a \approx 2b$, it can be also described as a 2x1x1 supercell of a pseudohexagonal phase. The predicted phase consists of almost planar triangular CO_3 carbonate groups connecting slightly distorted SiO_6 octahedra through the oxygen atoms.

An electron localization function (ELF) analysis (see Fig. 3) reveals the covalent bond basin associated to the C-O bond (small ring, signature of a double bond) and confirms the partial ionic character of the Si-O bonds (superanionic basin around the oxygen atoms consisting of two lone pairs and a bond basin displaced towards the oxygen atom)[25]. The mixed covalent-ionic character is also clear from the quantum theory of atoms in molecules (QTAIM) charges associated to the Si, C and O atoms, +3.12e, +1.75e and -1.10e, respectively. In contrast to the other structures, it does not present neither edge-sharing of octahedra nor corner-sharing of CO_3 units. Therefore, it does not violate the 3rd Pauling rule.

3.4 SiC_2O_6: other proposed structures

In a previous study[11], we proposed a candidate UB_2O_6-type structure ($C2/c$, Z=4) with carbonate units when substituing U and B for Si and C, respectively. After analysing the stability of different SiCO configurations generated replacing U and B′ for Si, and B for C in the conventional reference structure $U_4[B_nB'_{8-n}]O_{24}$ (n=1-8), the SiC_2O_6 stoichiometry was indeed found to be the most plausible one. However, this potential UB_2O_6-type structure is clearly unstable with respect to the one found after evolutionary searches in the current study.

A detailed analysis of the structural searches performed on the SiC_2O_6 stoichiometry (Fig. 4) reveals that whereas all the low enthalpy structures ($P2_1/c$, $P\bar{3}$, $R\bar{3}$) present SiO_6 octahedra corner-connected through almost-planar CO_3 units, the $C2/c$ structure shows SiO_4 and distorted CO_4 units after optimization. To further analyze the stability of potential structures with tetrahedral coordination for both, C and Si atoms, we have calculated the enthalpy of structures derived from known tetrahedrically-coordinated polymorphs of SiO_2 and CO_2. In particular, and to reproduce the SiC_2O_6 stoichiometry, (3x3x1), (1x1x3) and ($\sqrt{2}$x$\sqrt{2}$x1) supercells of the α-cristobalite , tetragonally-distorted β-cristobalite-like and α-cuartz structures have been generated. Cationic sites have been substituted by Si and C atoms. The resulting space groups of the configurations with the lowest enthalpies for the three derived structures are $P4_12_12$, $Fdd2$ and $C2$, respectively (see Fig. 5).

Interestingly, all the phases derived from the α-cristobalite, β-cristobalite, and α-quartz $Si(C)O_2$ polymorphs, ($P4_12_12$, $Fdd2$, $C2$) consist of the same tetrahedral structural units than $C2/c$ and are similar in enthalpy. Also, their formation enthalpy curves versus pressure show a minima region in the same pressure range indicated before. Therefore, there is a favourable pressure range

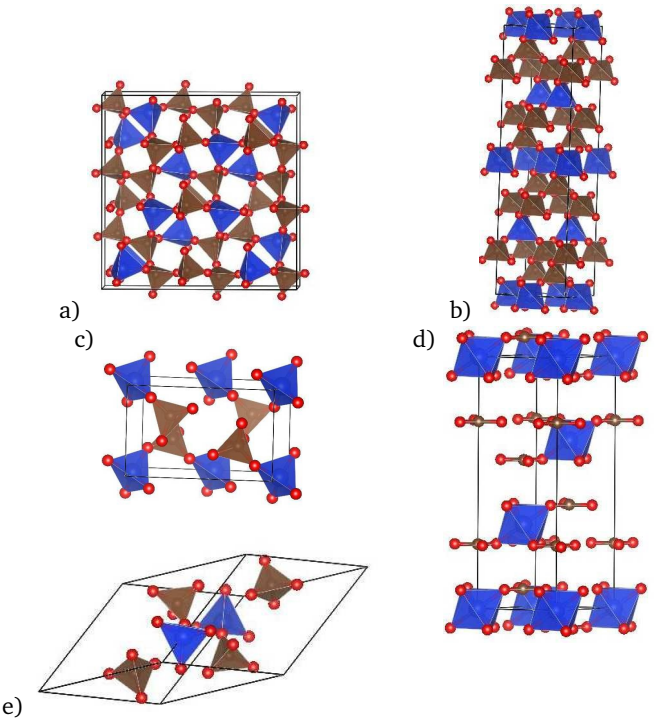

Fig. 5 Unit cells of the a) $P4_12_12$, b) $Fdd2$, c) $C2$, d) $R\bar{3}$ and e) $C2/c$ phases of the SiC_2O_6 stoichiometry. Coordination polyhedra for silicon and carbon atoms in blue and brown, respectively.

for their formation. Still, the 4-coordinated phases are 1.67-1.95 eV/SiC_2O_6 unit higher in enthalpy than the most stable $P2_1/c$ phase at the minimum of the enthalpy curves. It implies that the possible temperature-driven stabililization of these phases would require at least 2200 K. It is also in agreement with the recent paper by Santoro *et al* where temperatures higher than 4000 K are needed for the synthesis of a solid solution with an α-type cristobalite structure[10]. This unstabilization is mainly energetically-related since the energies differ by 1.66-1.99 eV/SiC_2O_6 unit at the same pressure (17.5 GPa). Mechanically, all these phases are less compressible than the $P2_1/c$ phase, in the order $C2 < C2/c < P4_12_12 < Fdd2$.

A preference towards the formation of carbonate CO_3 units is then unveiled. Moreover, the most stable $P2_1/c$ structure (Fig. 3) resembles the calcite structure found in some carbonates such as $CaCO_3$[26], with planar CO_3 units and metals octahedrically coordinated to oxygen atoms. But whereas in the calcite structure each octahedra share corners with other six octahedra, no direct linkage of SiO_6 octahedra appears in the monoclinic structure, with intercalated CO_3 units in between. Besides, a pseudo-calcite structure ($R\bar{3}$, see Fig. 5d) generated by occupying only 3/4 of the cation sites turns to be unstable with respect to the $P2_1/c$ structure. Looking at the cationic (SiC_2) framework of the $P2_1/c$ structure at 27.5 GPa, it can be described as a distorted $CaCl_2$-type structure, with the orthorhombic *Pnnm* space group, a=7.355 Å, b = 4.306 Å, c= 4.264 Å, Si atoms on 2a sites (0.0,0.0,0.0) and C atoms on 4g sites (0.338,0.245,0.0), where C atoms form a hcp arrangement, and Si atoms fill octahedral sites in alternated layers.

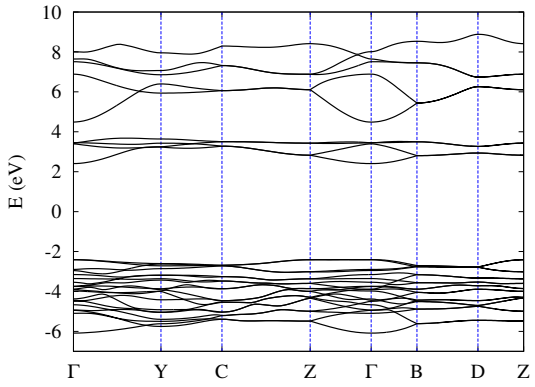

Fig. 6 Band structure for the $P2_1/c$ structure at ambient pressure.

3.5 Mechanical, electronic and vibrational properties of $P2_1/c$-SiC_2O_6

In analogy with the calcite-type compounds, the compressibility of the $P2_1/c$ structure is clearly anisotropic. This is due to the fact that the C-O bonds are less compressible than the Si-O bonds (the average interatomic C-O and Si-O distances shorten by 1.78 % and 4.11 %, respectively, betweeen room pressure and 50 GPa). Since the CO_3 units dispose on planes almost perpendicular to the c axis, the compressibility along this axis is greater (κ_c=0.053 GPa^{-1}, being κ_b=0.002 GPa^{-1}). From 0 to 8 GPa, the axis a is subjected to a negative lineal compressibility, related to the deviation of the CO_3 units from the plane axial to the c axis. This modulation dissappears when increasing pressure, being the axis a even less compressible than the b axis. This pressure-driven tendency to the coplanarity of the CO_3 units on planes perpendicular to the c axis is also accompanied by a simetrization of the SiO_6 units. A polynomial fitting of the volume-pressure data leads to a bulk modulus of 34.98 GPa (B_0'=3.60) at ambient conditions, increasing to 192.43 GPa at 27.5 GPa. The anisotropy also manifests in the elastic constants, with $C_{22} \approx 2C_{33}$ (C_{33}=240.95 GPa at 27.5 GPa).

It must be also noted that the stishovite structure of SiO_2 (the one with the lowest enthalpy in the pressure range where the SiC_2O_6 structure appears as thermodynamically stable) also shows SiO_6 polyhedra and, what is more interesting, similar Si-O distances are observed for the SiO_2 polymorph and the SiCO compound at the same pressure.

At ambient conditions, the electronic band structure of the stable $P2_1/c$ structure (see Fig. 6) shows an insulator character with a high band gap of 4.8 eV, and negligible variation under pressure. Although the highest occupied state appears on the middle of the Γ-Z line, its energy is almost identical at the Γ point. Specifically, the difference between the formally indirect band gap and the direct band gap is of only 2 meV.

The phonon dispersion curves present three well diferentiated regions, all with positive frequencies, confirming its dynamically stability (see Fig. 7). The modes with frequencies lower than 900 cm^{-1} mainly correspond to bending and Si-O stretching, the modes with frequencies around 1200 cm^{-1} can be associated to C-O symmetric stretching modes, and the higher fre-

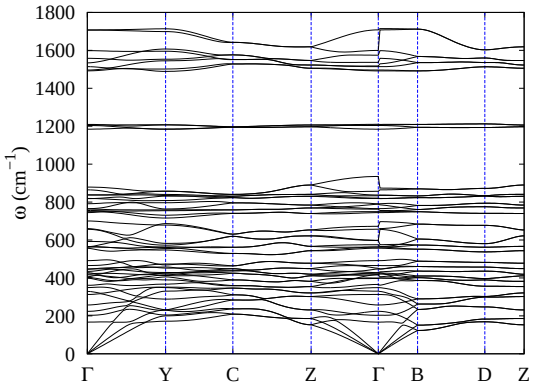

Fig. 7 Phonon dispersion curves for the $P2_1/c$ structure at 27.5 GPa

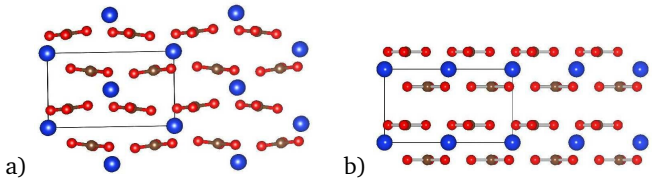

Fig. 8 Crystal structures for the (a) $P2_1/c$ and (b) $P\bar{3}$ structures. Larger blue spheres represent Si atoms, smaller brown and red ones correspond to C and O atoms, respectively

quency modes, with frequencies higher than 1490 cm^{-1} and up to 1708 cm^{-1} can be assigned to C-O asymmetric stretching modes. The reported experimental infrared spectra of the disordered silicon carbonate phase with CO_3 units assigned two peaks between 1500 and 1700 cm^{-1} to the C-O antisymmetric stretching[9]. Curiously enough, the calculated infrared frequencies for the C-O antisymmetric stretching range between 1518-1599 cm^{-1} in good agreement with the experimental data. It must be noted that PBE frequencies tend to be subestimated. It is also interesting to note that in spite of being unstable against decomposition, this phase remains dynamically stable at ambient pressure. It might be then possible to recover it as metastable.

3.6 $P\bar{3}$-SiC_2O_6 and potential structures at higher pressure

The previously proposed $P\bar{3}$ structure (Z=1)[12] appears as thermodynamically stable against decomposition in a slightly smaller pressure range than the $P2_1/c$ structure, from 9.4 to 37.3 GPa (see Fig. 4). Structurally, both structures are similar as their representation in a common $P\bar{1}$ subgroup shows (see Fig. 8). The main difference comes from the displacement of the silicon atoms located on the center of the faces to the middle of the edges, going from the $P2_1/c$ towards the $P\bar{3}$ structure. It generates a multislab structure, consisting each slab of two layers of carbonates and a layer of silicon atoms in between. Also, as a consequence of the higher symmetry of the $P\bar{3}$ structure, the modulation of the CO_3 units dissappears, and the SiO_6 octahedra has six equal Si-O distances. Then, at 22.5 GPa, the only Si-O distance is 1.75 Å, whereas the Si-O distances for the $P2_1/c$ structure take three values, 2x1.74 Å, 2x1.75 Å, and 2x1.76 Å. In analogy with the $P2_1/c$ structure and since the CO_3 units dispose in planes perpendicular to the c axis, the compressibility along the c axis is considerably higher. What is more, the formation of empty space between the slabs intensifies this effect (κ_c=0.09 GPa^{-1}, κ_b=0.0003 GPa^{-1}), resulting in a lower bulk modulus at ambient conditions of 10.4 GPa. However, it must not be forgotten that the $P2_1/c$ structure has the lowest enthalpy in all the thermodynamically stable pressure range. In particular, it is 166.9 meV/SiC_2O_6 unit lower in enthalpy at 10 GPa, and although there is a stabilization of the P$\bar{3}$ structure at higher pressures (the own simmetrization of the $P2_1/c$ structure signposts it), the $P2_1/c$ structure is still 90.13 meV/SiC_2O_6 unit lower in enthalpy at 35 GPa.

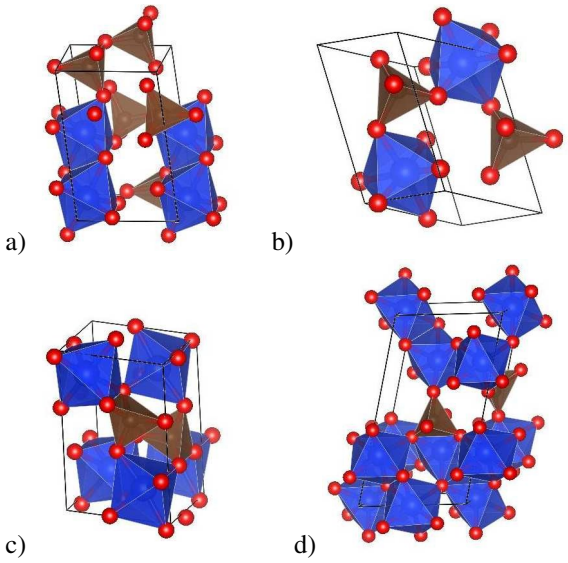

Fig. 9 Unit cells of the lowest enthalpy polymorphs corresponding to the a) SiC_2O_6, b) $SiCO_4$, c) Si_2CO_6 and d) Si_3CO_8 stoichiometries, at 100 GPa. Coordination polyhedra for silicon and carbon atoms in blue and brown, respectively.

The layered character of the P$\bar{3}$ structure also suggests the possible influence of van der Waals effects in its stabilitization. But, the inclusion of these effects does not alter the relative stability of the phases. For instance, at 20 GPa, 130 meV favors the $P2_1/c$ structure against the hexagonal structure, reduced to 120 meV with the inclusion of van der Waals effects. Moreover, the inclusion of the vibrational effects leads to an extra stabilization of the monoclinic structure versus the hexagonal one. In fact, even at 0 K, slightly lower frecuencies for the $P2_1/c$ structure lead to a zero point energy (phonon contribution to the Helmholtz free energy at 0 K) 2.84 meV lower than that of the P$\bar{3}$ structure . The stabilization is significantly enhanced when temperature, and therefore, entropic contributions are included. For instance, at 1000 K, the phonon contribution to the Helhmoltz free energy is lower by 26.83 meV.

Finally, at considerable higher pressures (above 86 GPa), another structure with tetrahedral CO_4 units appears to be more favourable energetically (note the change of symbols in Fig. 1 associated to a different structure for the SiC_2O_6 stoichiometry and see Fig. 9a)). Therefore, a change of the carbon hybridization

from sp^2 to sp^3 is predicted in close resemblance to the observed in other ionic carbonates[27,28]. The searches performed on the rest of stoichiometries do not reveal any structure stable against decomposition at any pressure. However, in analogy with the SiC_2O_6 stoichiometry, there is a preference for the formation of CO_3 and SiO_6 units at low pressures and CO_4 and SiO_6 units at high pressure (see Fig. 1 and Fig. 9).

4 Conclusions

In summary, extensive evolutionary algorithm searches lead to the prediction of the first SiCO-based stable crystal structure in a wide pressure range from 7.2 to 41 GPa. The structure of this novel phase with SiC_2O_6 stoichiometry and $P2_1/c$ space group has been fully characterized and proved to be dynamically stable. It is a strongly anisotropic insulator with a wide band gap, consisting of SiO_6 units corner-connected to CO_3 units. Crystal structures consisting of tetrahedral CO_4 and SiO_4 units are only accesible in this pressure range at temperatures above 2200 K. However, a 4-fold coordination for carbon is predicted at higher pressures for all the stoichiometries. The identification of this new class of stable carbonates at pressures close to the Earth's mantle represents a step forward towards the understanding of the oxide chemistry and opens the way for solving issues in the deep carbon cycle. We hope that our findings will encourage further experimental and theoretical work.

5 Acknowledgements

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