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First-principles study of structure and stability in Si–C–O-based materials

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Abstract The decomposition of silicon–carbon–oxygen (SiCO)-based materials into their binary oxides is studied at different pressure conditions by first-principles total energy calculations. We evaluate how the influence of pressure modifies the enthalpy of this reactive process as the carbon concentration increases for a number of compounds with variable stoichiometries within the general chemical formula $Si_xC_yO_{24}$ ($x = 4$–11, $y = 1$–8, $x + y = 12$). At low carbon content, pressure destabilizes all SiCO structures examined, whereas at high carbon content, pressure tends to reduce the exothermic character of the decomposition reaction. After the evaluation of the equation of state parameters for these crystals, we found a similar trend for the bulk modulus with the highest values found for the richest carbon compounds. According to our results, we propose SiC_2O_6 as the most plausible stoichiometry.

Keywords First-principles · SiCO-based materials · High pressure · Decomposition enthalpy

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1 Introduction

The analogies and differences between the stability and reactivity of CO_2 and SiO_2 polymorphs have been the subject of several investigations [1–3]. Although both compounds belong to the group IV oxides, they are remarkably different under ambient conditions: CO_2 is a molecular gas, and SiO_2 is a crystalline solid. However, such differences progressively vanish at extreme conditions. Thus, although isolated CO_2 molecules are characterized by double bonds, the bonding pattern changes dramatically in the solid state at extreme conditions of pressure (p) and temperature (T). Non-molecular CO_2 crystalline phases in close resemblance to high-pressure SiO_2 polymorphs have been discovered above 30 GPa [4–7].

Such structural similarities suggest the possible existence of exotic mixed oxides based on silicon and carbon, which will be referred to as SiCO compounds. Only few theoretical efforts have been invested to face this attractive, yet difficult challenge. Considering α-quartz (SiO_2) as the reference structure, da Silva et al. [8] carried out a molecular dynamics study with the aim of proposing crystalline structures for SiCO-based compounds. A hypothetical α-quartz silicon oxycarbide ($Si_{1-x}C_xO_2$) was then generated by replacing Si atoms with C ones. This strategy provided two potential and competing crystalline phases, though an ab initio study of the (meta)stability of these compounds was not undertaken. Other density functional theory calculations were performed by Aravindh et al. [9] by assuming that SiO_2, CO_2, and their alloys took a β-cristobalite-like structure. In that work, the authors found that, despite mixed SiO_2–CO_2 alloys do not appear to be thermodynamically stable at ambient pressure, it might be possible to create them in metastable forms. They observed some tendency for C atoms in polymeric phases

to prefer threefold coordination rather than fourfold coordination.

Recently, Santoro et al. [7] succeeded in the synthesis of a silicon carbonate phase, which was obtained by reacting silicalite and fluid CO_2 in a diamond anvil cell at 18–26 GPa and 600–980 K. Interestingly, their spectroscopic results were in agreement with the observations of Aravindh et al. predictions. These experiments definitively reveal a unique oxide chemistry at extreme conditions, which can be summarized in the chemical equation $xSiO_2 + yCO_2 \rightarrow Si_xC_yO_{2(x+y)}$, thus opening routes for the synthesis of a novel class of chemical compounds of interest in different scientific areas, from geochemistry to materials science.

In this article, we study the stability of SiCO-based materials under pressure, with specific emphasis on the decomposition reaction of these hypothetical compounds into their simple oxides: SiO_2 and CO_2. Since no clues about the possible structure of potential SiCO compounds are available, we choose a monoclinic (space group $C2/c$, $Z = 4$) reference structure for our first-principles electronic structure calculations. This choice is justified by the expected analogy with the structure of UB_2O_6 [10] using well-established crystal-chemistry concepts based on the Zintl-Klemm concept applied to oxides [11]. This reference structure has been selected after a careful and systematic search among simple lattices of ternary compounds compatible with the carbonate-like environment proposed for C in the new synthesized SiCO compound [7]. Several U/Si and B/(C,Si) substitutions have been considered, as detailed in the following section.

This crystal modeling allows us to understand the different role played by Si and C in the stabilization of SiCO-based materials. The carbon content, along with the influence of hydrostatic pressure in the decomposition enthalpy, are the two variables considered in our study. After presenting the crystallographic models and the computational details, we evaluate and discuss the calculated decomposition enthalpies for several compounds within the stoichiometries involved in the general chemical formula $Si_xC_yO_{24}$ ($x = 4$–11, $y = 1$–8, $x + y = 12$). Our analysis is completed with the calculation of the static equations of state (EOS) for all the optimized structures. The conclusions are summarized at the end of the paper.

1.1 Modeling stoichiometries

The cell parameters and atomic positions of the reference UB_2O_6 structure are listed in Table 1 [10]. Our calculations are performed making use of the conventional monoclinic cell containing 4 formula units. With the aim of extending the number of potential stoichiometries and atomic environments for C and Si in this monoclinic lattice, it is pertinent to substitute the eight B sites for C and Si atoms. Boron atoms are in threefold coordination with oxygen (BO_3), and the uranium atoms are in sixfold coordination (UO_6) (see Fig. 1).

Since the experiments of Santoro et al. [7] suggested the existence of carbonate units (CO_3), the reference structure should be rewritten as $U_4[B_nB'_{8-n}]O_{24}$ ($n = 1$–8), where we have distinguished two types of boron atoms: B and B'. The SiCO configurations are built just substituting U and B' for Si and B for C. Notice that n stands for the number of carbon atoms in the chemical formula above. Therefore, up to eight different stoichiometries involving different content of threefold coordinated carbon are to be considered (see Table 2). These structures can be generalized in the following carbon silicate or silicon carbonate chemical formula: $Si_xC_yO_{24}$, $x = 4$–11, $y = 1$–8, with $x + y = 12$. In addition, for some of these stoichiometries, more than one isomeric structure is compatible depending on the specific B and B' atoms chosen to be replaced by C and Si, respectively. This results in C–D, E–F and G–H isomers for $Si_4[C_3Si_5]O_{24}$, $Si_4[C_4Si_4]O_{24}$ and $Si_4[C_5Si_3]O_{24}$, respectively. Although the stoichiometries are the same for each pair of isomers, the environments are different, leading to energetically non-equivalent structures with the same carbon content. As a result, the final number of different SiCO-based compounds examined is eleven, covering a carbon content (defined as the ratio $n/8$) ranging between 0.125 and 1.

1.2 Calculation details

We perform first-principles enthalpy calculations within the framework of the density functional theory (DFT) with a plane-wave pseudopotential approach, as implemented in the Vienna ab initio simulation package (VASP) [12]. We use the projector augmented wave (PAW) all-electron description of the electron–ion–core interaction [13] and the Perdew-Burke-Ernzerhof generalized gradient exchange–correlation functional (PBE) [14]. Brillouin zone integrals were approximated using the method of Monkhorst and

Table 1 Lattice parameters and internal coordinates of the UB_2O_6 structure

Atom type	Wyckoff positions	x	y	z
U	4e	0	0.2407	0.25
B	8f	0.3013	0.1484	0.2509
O	8f	0.1026	0.2433	0.7562
O	8f	0.2983	0.1830	0.7614
O	8f	0.0893	0.2439	0.4487

Space group $C2/c$, $Z = 4$. $a = 12.504$ Å, $b = 4.183$ Å, $c = 10.453$ Å, and $\beta = 122.18°$
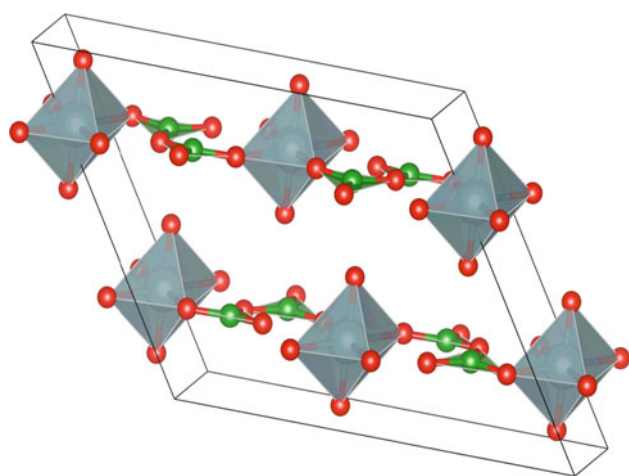
Fig. 1 Reference structure, UB_2O_6. *Gray*, *green* and *red* spheres represent uranium, boron and oxygen atoms, respectively. Boron (Uranium) atoms are tri(hexa)-coordinated to oxygen atoms

Table 2 Chemical formula and number and type of symmetry-inequivalent SiCO configurations for each carbon content

Carbon atoms	Structure	Carbon content	Structures (Fig. 3 nomenclature)
1	$Si_4[CSi_7]O_{24}$	0.125	1 (A)
2	$Si_4[C_2Si_6]O_{24}$	0.250	1 (B)
3	$Si_4[C_3Si_5]O_{24}$	0.375	2 (C–D)
4	$Si_4[C_4Si_4]O_{24}$	0.500	2 (E–F)
5	$Si_4[C_5Si_3]O_{24}$	0.625	2 (G–H)
6	$Si_4[C_6Si_2]O_{24}$	0.750	1 (I)
7	$Si_4[C_7Si]O_{24}$	0.875	1 (J)
8	$Si_4[C_8]O_{24}$	1.000	1 (K)

Carbon content = Carbon atoms/8

Pack [15], and the energies were converged with respect to the k-points density and the plane-wave cutoff (600 eV).

Guided by the experimental conditions under which the silicon carbonate phase was stabilized [7] and the known overestimation of pressure by the PBE functional, we restricted our calculations to a hydrostatic pressure window between 22.5 and 30 GPa. It is expected that temperature plays a crucial role in the kinetics (energy barrier) but not in the thermodynamics of the decomposition reaction. Therefore, only static (zero temperature and zero point vibrational contributions neglected) results will be presented here.

Due to the consideration of static conditions, enthalpy, $H = E + pV$, is the most suitable thermodynamic potential in our study, where E is the energy and V the volume, and all the quantities are considered per formula unit. We perform enthalpy calculations for the different SiCO configurations as well as for SiO_2 stishovite and the so-called phase III of solid CO_2, since they are the thermodynamically stable phases in the proposed pressure range. In
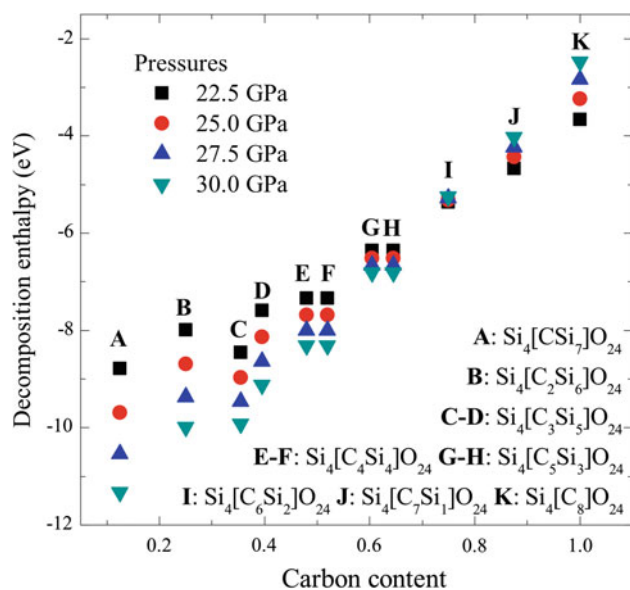

Fig. 2 Decomposition enthalpy versus carbon content for all the SiCO configurations at selected pressures. For sake of clarity, although the C and D structures have the same carbon content, the corresponding enthalpy values are slightly shifted to the *left/right*. The same applies to the E–F and G–H structures

particular, $4\times8\times4$, $6\times6\times8$ and $6\times6\times6$ k-meshes were employed for the SiCO structures, SiO_2-stishovite and CO_2-III, respectively. Full structural relaxations of both lattice parameters and atomic coordinates at each pressure were performed via a conjugate-gradient minimization of the enthalpy using the Hellmann–Feynman forces on the atoms and stresses on the unit cell. The geometry relaxation was considered to be complete when the total force on atoms was less than 1 meV/Å.

Additionally, the (p,V) calculated points have been described using the Murnaghan equation of state [16]:

$$V(p) = V_0 \left(1 + B_0' \frac{p}{B_0}\right)^{-\frac{1}{B_0'}} \tag{1}$$

where V_0 is the zero-pressure volume, and B_0 and B_0' are the bulk modulus and its pressure derivative, respectively, both evaluated at zero pressure. The results are summarized in Table 4. The pressure derivative of the bulk modulus has been fixed to 3.5 and 4, which are typical values observed in oxides [17]. This option minimizes the relative uncertainty in the numerical determination of B_0 since large covariance terms between B_0 and B_0' are usually present in the fitting procedure.

2 Results and discussion

In order to study the stability of the optimized structures summarized in Table 2, the decomposition enthalpy into

Table 3 Unit formula volumes of stishovite (SiO_2), phase III (CO_2), $Si_4[C_4 Si_4]O_{24} \equiv Si_2CO_6$, $Si_4[C_6 Si_2]O_{24} \equiv SiCO_4$ and $Si_4[C_8]O_{24} \equiv SiC_2O_6$, at selected pressures

p (GPa)	SiO_2 ($Z = 2$)	CO_2 ($Z = 4$)	$Si_4[C_4 Si_4]O_{24}$ (E–F)		$Si_4[C_6 Si_2]O_{24}$ (I)		$Si_4[C_8]O24$ (K)	
	V (Å³/Z)	V (Å³/Z)	V (Å³)	ΔV (%)	V (Å³)	ΔV (%)	V (Å³)	ΔV (%)
22.5	22.450	26.875	309.57	7.8	293.20	-0.93	277.35	−9.0
25.0	22.305	26.265	304.26	7.3	288.65	-0.95	273.51	−8.6
27.5	22.160	25.720	299.82	7.0	284.86	-0.84	270.36	−8.2
30.0	22.025	25.227	295.66	6.7	281.29	-0.78	267.37	−7.8

The volume changes (ΔV (%)) involved in the formation of the SiCO compounds (inverse reaction to the decomposition process) are also indicated
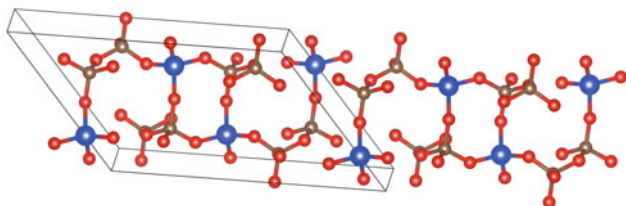

Fig. 3 SiC_2O_6 monoclinic structure. Lattice parameter: $a = 12.651$ Å, $b = 4.133$ Å, $c = 8.011$ Å, $\beta = 129.9°$. Wyckoff positions: Si(4e) (0, 0.9808, 0.75), C(8f) (0.3270, 0.2274, 0.3145) and O(8f) × 3 (0.1219, 0.1970, 0.7886) (0.2971, 0.1177, 0.7741) (0.0738, 0.2465, 0.4634). *Brown*, *red* and *blue* spheres represent carbon, oxygen and silicon atoms, respectively

Table 4 Zero-pressure bulk modulus (B_0) and first pressure derivative of the bulk modulus (B_0') for all the structures

Carbon atoms	Structures (Fig. 3 nomenclature)	B_0 (GPa)	B_0'
1	A	44.9–31.9	3.5–4
2	B	52.7–39.7	
3	C–D	65.3–52.3	
4	E–F	71.9–58.9	
5	G–H	80.1–67.1	
6	I	89.7–76.7	
7	J	101.4–88.4	
8	K	113.7–100.6	

B_0' is fixed at 3.5 and 4. The range of B_0 comes from different parameters and uncertainties in the fitting procedure

their binary oxides has been calculated. We consider the general chemical reaction $Si_xC_yO_{2(x+y)} \rightarrow xSiO_2 + yCO_2$ and evaluate $\Delta H_r = xH_{SiO_2} + yH_{CO_2} - H_{Si_xC_yO_{2(x+y)}}$ at four different pressures: 22.5, 25, 27.5 and 30 GPa. The decomposition enthalpy of the different SiCO structures as a function of the carbon content is plotted in Fig. 2. Specific pressure–volume data for SiO_2 stishovite, CO_2-III and SiCO structures with Si_2CO_6, $SiCO_4$ and SiC_2O_6 stoichiometries, along with the associated volume changes involved in their formation are also collected in Table 3. Analysis of these results allows us to draw some

conclusions regarding the role played by pressure and carbon content in the chemistry of SiCO-based materials.

The first general remark to emphasize is the exothermic character ($\Delta H_r < 0$) of the decomposition process, regardless the stoichiometry of the SiCO compound and the pressure involved in the reaction. As a result, these structures are not thermodynamically stable, releasing between 100 and 250 kcal/mol after decomposition into SiO_2 stishovite and CO_2–III. This fact agrees with the difficulty in finding crystalline forms containing simultaneously C, Si and O, and reinforces the well-known fact that CO_2 presents difficulties to become part of a solid solution [18].

It is now interesting to explore the combined influence of pressure and carbon content on ΔH_r. Bringing together these two factors in our simulations allows us to explore the existence of potential SiCO-based materials, since at the Earth depths corresponding to the pressure window of our simulations, traces of carbon have been found, and Si and O are common elements of many minerals [19, 20]. The results are summarized in Fig. 2.

It is observed that in those structures with carbon content below 0.75, a pressure increase favors the decomposition process, but the effect is reversed as the carbon content increases. Thus, it is predicted that pressure has negligible influence on ΔH_r in the structure with a carbon content of 0.75 (I configuration: $Si_4[C_6Si_2]O_{24} \equiv SiCO_4$), whereas for the J and K stoichiometries ($Si_4[C_7Si]O_{24}$ and $Si_4[C_8]O_{24} \equiv SiC_2O_6$), where the carbon content is higher, the role of pressure makes ΔH_r to increase around 35 kcal/mol from 22.5 to 30 GPa. Globally, it is interesting to condense the combined action of the two factors in these general rules: (1) the effect of increasing pressure changes from favoring to disfavoring the decomposition reaction as the carbon content increases, and (2) the decomposition reaction is less exothermic ($|\Delta H_r|$ decreases) as the carbon content increases for a given pressure. As a result, we found that SiC_2O_6 is the most plausible stoichiometry with the lowest value for $|\Delta H_r|$. Figure 3 shows this structure with the unit cell description given in the caption.

These results can be explained taking into account that pressure favors processes encompassing volume reductions [21], and these can be achieved by increasing the carbon content, as illustrated in Table 3. For each of the pressures examined, there is a continuous tendency to reduce the total volume involved in the reaction of formation of the SiCO compound (ΔV) as the carbon content increases. Thus, the highest volume reduction is found for the formation of SiC_2O_6.

The reason why is not difficult to understand has to do with the compressibilities of the three compounds involved in the reaction. In Table 4, we collect B_0 values corresponding to all the SiCO stoichiometries examined in this work. For CO_2-III and SiO_2 stishovite, our computed values are 7.6 GPa and 260 GPa, respectively. Since CO_2-III is the most compressible reactant, a high y stoichiometric coefficient for CO_2-III favors a great reduction of volume in the formation of a given SiCO compound: $\Delta V = \frac{V_{Si_xC_yO_{(2x+2y)}} - (xV_{SiO_2} + yV_{CO_2})}{xV_{SiO_2} + yV_{CO_2}} \times 100$. Besides, those compounds with higher carbon content are the ones with higher B_0 values (see Table 4), thus also favoring the reduction of volume in the reaction. Both factors make SiC_2O_6 to be the compound with highest volume reduction.

For a given stoichiometry, pressure variations from 22.5 to 30 GPa play a lower role on ΔV values. If we look, for example, at the sequence of ΔV in SiC_2O_6, it is found a slightly lower reduction of volume at the highest pressure compared with the value at 22.5 GPa. This fact does not contradict the result shown in Fig. 2. In energetic terms, we should consider the product $p\Delta V$, and this is greater in absolute value as the pressure increases making the decomposition reaction to be less favorable, in agreement with our discussion above.

3 Conclusions

In the search for relative stability of in SiCO-based compounds at high pressure, we have carried out a computational study of the chemical decomposition of eleven structures with varying stoichiometries into the binary oxides SiO_2 stishovite and CO_2-III. We have evaluated how the influence of pressure and carbon content modify the enthalpy of the reactive process: $Si_xC_yO_{(2x+2y)} \rightarrow xSiO_2 + yCO_2$. Although we found $\Delta H_r < 0$ for all SiCO structures analyzed, at high carbon content pressure tends to reduce their exothermic character. According to the results of our investigation, SiC_2O_6 is the most plausible stoichiometry. This agrees with the fact that this SiCO structure with the highest carbon content is less compressible than the corresponding decomposition products, due to the great concentration of the molecular CO_2-III phase. This behavior suggests new synthetic routes of this family of materials.

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