$Si_xC_{1-x}O_2$ alloys: A possible route to stabilize carbon-based silica-like solids?

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Abstract

Novel extended tetrahedral forms of CO_2 have been synthesized recently under high-pressure conditions. We perform *ab initio* density functional theory calculations to investigate whether doping with Si can extend the stability range of such tetrahedral forms of CO_2 to ambient pressure. Calculations are performed with a simple cubic cell containing eight formula units in a β-cristobalite-like structure. Though we find that all the $Si_xC_{1-x}O_2$ structures considered by us are thermodynamically unstable with respect to decomposition into the end members at ambient pressures, the energy differences are small, suggesting that it might be possible for such phases to exist in metastable forms. At higher pressures, the heat of formation is found to be negative. The bonding between C and O atoms is more covalent than that between Si and O atoms. We also find indications that some C atoms may prefer three-fold coordination at low pressure.
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1. Introduction

CO_2 is one of the most stable molecules in the universe and is held together by a pair of strong double bonds (O=C=O). On the other hand, its isoelectronic counterpart, SiO_2, exists only as an ionic solid, with many crystalline polymorphs (quartz, cristobalite, coesite, etc. [1]) and an amorphous form (silica

glass), all of them characterized by interlinked tetrahedral units (SiO_4), at least at low pressure. It has been shown recently [1–3] that such a "chemical" difference between CO_2 and SiO_2 disappears at high pressures, where the CO_2 units transform from molecular to tetrahedral, giving rise to extended solids presumably very similar to the low-pressure SiO_2 polymorphs. A glassy and a crystalline six-fold coordinated form of CO_2 has also been obtained very recently [5,6]. Unfortunately, applications of such extended forms of CO_2 are limited by the fact that none of them has been yet recovered at ambient pressure, where CO_2 transforms back to the molecular state. In view of the extended stability range of the tetrahedral forms of SiO_2, in this paper we wish to address two questions: (i) whether mixing SiO_2 and CO_2 tetrahedral structures would stabilize an extended carbon-based oxide compound at ambient conditions (ii) whether such structures might be thermodynamically favored at high pressures (where SiO_2 and CO_2 are both stable in tetrahedral forms) from where one could hope to recover them at ambient conditions. In this work we employ *ab initio* theoretical methods to study these issues, by determining the relative stability of hypothetical $Si_xC_{1-x}O$ alloys, with respect to the end members SiO_2 and CO_2.

2. Method

We have performed calculations within the framework of density functional theory, making use of the local density approximation (in the form parametrized by Perdew and Zunger [7]). We have used a plane wave expansion of the electronic wave functions, with a cut-off of 30 Ry, and a pseudopotential description of the ion–electron interaction [8] as implemented in the Quantum-ESPRESSO codes [9]. The crystal structure of non-molecular CO_2 is not known [4]. The SiO_2-like trydimite crystal structure gives the best fit to X-ray patterns, but vibrational spectroscopy is instead consistent with a cristobalite-like crystal structure [4]. According to first-principles calculations [10], the structure of non-molecular CO_2 with lowest energy is isostructural to β-cristobalite (space group I-$42d$). In order to be consistent with previous theoretical studies, in this work we will assume that SiO_2, CO_2, and their alloys take the I-$42d$ β-cristobalite structure. The β-cristobalite primitive cell is body-centered tetragonal with c/a ratio very close to $\sqrt{2}$, and contains two AO_2 units ($A = Si, C$). The structure can be approximated by a diamond sublattice of A atoms, with O atoms placed close to the centres of the A–A connecting lines, slightly displaced from the high symmetry positions. Though our calculations were performed making use of a conventional cubic cell containing eight AO_2 units (see Fig. 1), we have found that the stress tensor after atomic relaxation is nearly isotropic, suggesting that the error introduced by working with a cubic unit cell is small. Brillouin zone integrations were carried out using a single special point. Convergence with respect to plane wave cut-off and reciprocal space sampling was carefully established.

3. Results and discussion

First, we calculated the total energy as a function of lattice constant for the end members SiO_2 and CO_2. Upon fitting to the
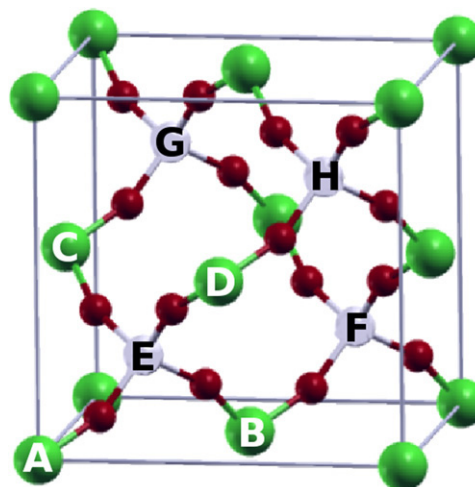

Fig. 1. Example of a conventional cubic unit cell for I-$42d$ cristobalite. The small dark spheres (red online) indicate O atoms, while the large grey (green online) and small light (white online) spheres represent Si and C atoms respectively. The positions of C/Si atoms are labeled A–H (see also Table 1); the figure shows a representative structure (g) at a 50-50 Si–C concentration. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1
Convention used in labelling structures

Config.	x	A	B	C	D	E	F	G	H
a	0.0	C	C	C	C	C	C	C	C
b	0.125	Si	C	C	C	C	C	C	C
c	0.25	Si	Si	C	C	C	C	C	C
d	0.25	Si	C	C	C	Si	C	C	C
e	0.375	Si	Si	Si	C	C	C	C	C
f	0.375	Si	Si	C	C	Si	C	C	C
g	0.5	Si	Si	Si	Si	C	C	C	C
h	0.5	Si	Si	Si	C	Si	C	C	C
i	0.5	Si	Si	C	C	Si	C	Si	C
j	0.5	Si	Si	C	C	Si	Si	C	C
k	0.625	Si	Si	Si	Si	Si	C	C	C
l	0.625	Si	Si	Si	C	Si	Si	C	C
m	0.75	Si	Si	Si	Si	Si	Si	C	C
n	0.75	Si	Si	Si	C	Si	Si	Si	C
o	0.875	Si	Si	Si	Si	Si	Si	Si	C
p	1.0	Si	Si	Si	Si	Si	Si	Si	Si

Lower case letters label inequivalent structural configurations, while upper case letters label sites in the unit cell, following the convention depicted in Fig. 1. x indicates the $[Si]/([Si] + [C])$ ratio.

Birch–Murnaghan equation of state [11], we obtained values for the equilibrium volume per formula unit V_0 and bulk modulus B_0 ($V_0 = 46.5$ Å^3, $B_0 = 20.9$ GPa for SiO_2, and $V_0 = 22.4$ Å^3, $B_0 = 155$ GPa for CO_2). These results are in good agreement with previous theoretical studies, both for SiO_2 ($V_0 = 46.2$ Å^3, $B_0 = 22.6$ GPa for SiO_2, [12]; $V_0 = 45.6$ Å^3 [1,13]), and for CO_2 ($V_0 = 22.3$ Å^3, $B_0 = 149.1$ GPa for CO_2 [10]).

In order to investigate the effects of doping carbonia with Si atoms, we obtained representative structures at a range of compositions by considering all symmetry-inequivalent substitutions of Si atoms by C atoms in the ideal eight-formula-unit cell of space group $Fd\bar{m}d$ (Table 1 and Fig. 1). We then distorted the structures according to space group I-$42d$,
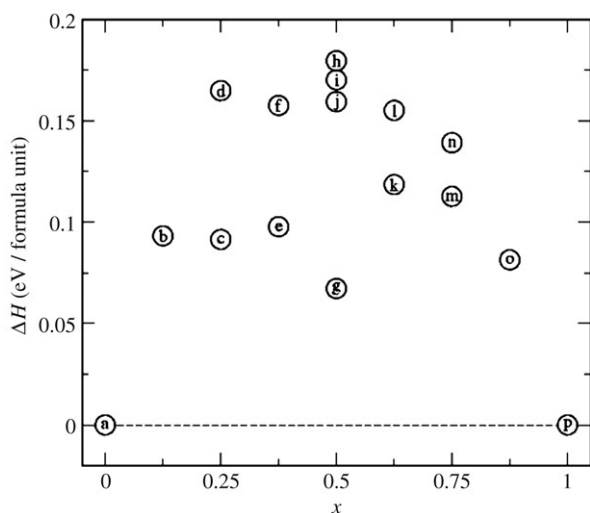
Fig. 2. Heats of formation ΔH for alloys of the form $Si_xC_{1-x}O_2$, plotted as a function of x. Data points are labeled 'a' through 'p', to indicate inequivalent structures and compositions, following the convention set out in Table 1 and Fig. 1.

and optimized all internal parameters. The resulting structures possess no symmetry because of chemical disorder. In this way, we have considered a total of 16 different configurations at 9 different concentrations, as summarized in Table 1. In order to obtain the equilibrium volume at each configuration, calculations were performed at different lattice constants, and the results were fitted using a Birch–Murnaghan equation of state [11].

In Fig. 2, we have shown how the alloy excess energy ΔH, i.e. the energy of the alloy referred to the weighted sum of the end members $x * SiO_2 + (1 - x) * CO_2$, varies with x, at ambient pressure. We find that, under these conditions, the excess energy of the alloy is never negative, indicating that the alloy is in principle thermodynamically unstable with respect to its end members. The excess energy, at ambient conditions, reaches a value as low as 0.07 eV/formula unit for the ordered alloy with 50% concentration (configuration "g" in Table 1). As can be seen from Fig. 1, upon removing oxygen atoms, this configuration becomes isostructural to the SiC cubic polytype, just as β-cristobalite is the analogue of the cubic diamond structure. Being the configuration that is most ordered, elastic considerations tend to favor this structure, since all Si atoms and all C atoms possess the same environment, and thus bond-length mismatches can be completely accommodated.

Upon examination of all the equilibrium structures obtained by us, we find that, in general, C–O and Si–O bond lengths do not change significantly as a function of composition, and that these preferred bond lengths are accommodated at the expense of distorting cation–O–cation angles.

In Fig. 3, we have plotted the results obtained for the equilibrium lattice constant, under ambient conditions, as a function of x, the [Si]/([Si] + [C]) ratio. Vegard's Law [14] is an approximate empirical rule, which suggests that the lattice constants should vary linearly with x, and we find that this is approximately true (despite the large difference in the lattice constants of the end members); however it
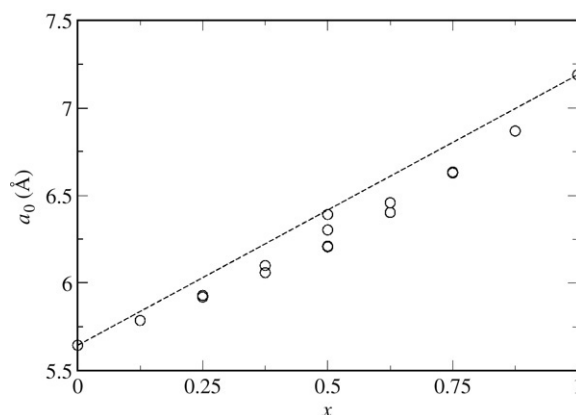

Fig. 3. The variation of lattice constant a_0 with Si concentration x. The dashed line shows the linear interpolation predicted by Vegard's Law. The various points at a given value of x correspond to a variety of inequivalent structures at that concentration, as given in Table 1.
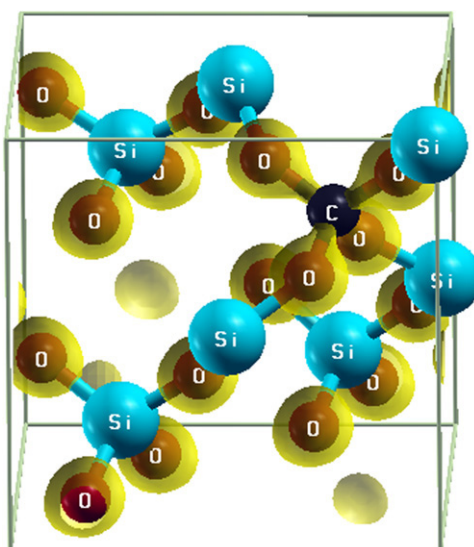

Fig. 4. Charge density for the structure "o", which contains 7 Si atoms, one C atom and 16 O atoms in the unit cell. The small black sphere depicts the C atom, small dark spheres (red online) depict O atoms, and the large spheres (light blue online) indicate Si atoms. The grey lobes (yellow online) show an isosurface of the electronic charge density. The coordination is seen to remain tetrahedral throughout, and the bond between C and O is seen to be more covalent than that between Si and O. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

overestimates lattice constants slightly as one moves away from the end members. (Note: If the volumes rather than the lattice constants varied linearly with concentration, one would expect an underestimation of lattice constants, rather than the overestimation observed by us.)

The local stability of the equilibrium structures can be inferred from the analysis of the local coordination of the tetrahedral units in the equilibrium structures. Upon analyzing the relaxed structures obtained by us, we find that almost all the equilibrium structures have Si and C in tetrahedral coordination with O. This indicates that tetrahedral units are local minima, at least within the set of distortions compatible with the periodicity of the simulated cells. In Fig. 4, we have

plotted the valence electron charge density for the system "o", whose unit cell contains seven Si atoms, one C atom and sixteen O atoms. From this figure, we can see that the system is tetrahedrally coordinated throughout, and the bonding is mainly ionic (note that the charge is localized on the O atoms). However, the bonding between O atoms and the C atom appears to be more covalent than that between O and Si atoms (the yellowish lobes of charge density in the figure can be seen to be extended towards the C atom).

However, we found that in a few configurations, at large, negative strains, a small number of C–O bonds starts to break, indicating a preference for the carbon atoms to be coordinated with only three O atoms. This is consistent with the idea that three-fold coordinated carbon may be a microscopic precursor to the formation of tetrahedral CO_2 units [15].

Returning to Fig. 2, we notice that the excess energies, though positive, are systematically rather low and never exceed 0.2 eV/formula unit, which is in the range of values for III–V semiconductor alloys [16], themselves metastable but widely employed in electronics. One should however keep in mind that in our case, one end member, extended CO_2, is itself unstable with respect to its gaseous form at ambient conditions. Since it does, however, become stable at pressures above 20 GPa [17], we next examine enthalpies of formation at high pressures, restricting our analysis to the structure with configuration "g", since it seems the best candidate for a stable mixed compound. Upon using the *ab initio* equations of state we found that configuration "g" becomes thermodynamically more stable than the end members at 6 GPa, and remains stable with respect to the end members at 20 GPa, where both SiO_2 and CO_2 are stable in their tetrahedral forms. This suggests that it should be possible to form this phase, in thermodynamic equilibrium, at high pressures. When combined with the observation that large energy barriers are presumably required to induce phase segregation at ambient conditions, this suggests that it may be possible to recover this phase, in a metastable form, also at ambient conditions.

In summary, we have found that though mixed SiO_2–CO_2 alloys do not appear to be thermodynamically stable at ambient pressure, their excess energies are small, suggesting that it may be possible to create them in metastable forms. We have also observed some tendency for C atoms in extended solids to prefer three-fold coordination to four-fold coordination.

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