Reduction of solid silicon monoxide by elemental metals

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Received (in Strasbourg, France) 14th February 2001, Accepted 3rd May 2001
First published as an Advance Article on the web 28th June 2001

Reaction of solid SiO with calcium in various ratios at 900 °C results in the formation of a mixture of CaO, CaSi and Ca_5Si_3. When the reaction (in a 1:3 ratio) is carried out at 750 °C, CaO and Ca_3SiO are formed. The structure of the latter compound, which is erroneously described in the literature as "cubic Ca_2Si", was determined from powder diffraction data. In the reaction mixtures of solid SiO with strontium or titanium, SrSi, $SrSi_2$ and Ti_5Si_3 were identified. Reaction with aluminium did not result in the formation of a silicide, but of elemental silicon instead.

Solid SiO is an amorphous solid that is industrially prepared from Si and SiO_2 at high temperatures *via* gaseous (molecular) SiO. Despite its technical uses[1] and many physical investigations, the structure of SiO is still controversial. The reason for the sometimes inconsistent results is probably that samples with a different thermal history have been used.

With the plausible assumption that all silicon atoms in SiO are tetrahedrally co-ordinated, 50% of the bonds must be Si–Si and 50% Si–O. The bonding model that best accounts for the observed spectroscopic results and the chemical reactivity is the "mixed-phase model",[2] according to which, Si and SiO_2 regions of a few nm diameter are connected by a region with an intermediate stoichiometry. We recently suggested a modification of this model and postulated regions with an accumulation of Si–Si bonds and other regions rich in Si–O bonds.[3]

SiO is metastable with regard to disproportionation into silicon and SiO_2. However, this reaction only proceeds at reasonable rates at temperatures >1000 °C.[3] The dependence of the properties of SiO on the annealing conditions after condensing SiO from the gas phase is consistent with the mixed-phase model, as the structure of the metastable solid can approach the thermodynamic equilibrium ($Si + SiO_2$) to different degrees by a more or less extensive rearrangement of Si–Si and Si–O bonds.

Little is known about the reactivity of solid SiO, although this might allow conclusions on the basic units from which its structure is composed. The current knowledge suggests that in most reactions SiO behaves like highly dispersed silicon in silica (although SiO definitely is not a mixture of silicon and silica phases). For example: (i) SiO can be used for the preparation of organosilicon chlorides instead of elemental silicon;[4] (ii) SiO is oxidised to Si(IV) compounds under similar conditions to those employed for the oxidation of elemental silicon;[5,6] (iii) reaction of solid SiO with CuI, AgI, AgCl or AgF results in the formation of the silicon tetrahalides SiX_4, elemental silver or copper, and silica.[7]

We have recently shown that reaction with elemental magnesium results in the formation of Mg_2Si.[3] While investigating this reaction in more detail, we found one of the few cases in which SiO shows a unique reaction behaviour, not paralleled by reactions of Si or SiO_2. We observed a comproportionation reaction between Mg_2Si and SiO to give nanosized silicon particles.[3] This reaction with magnesium is the only reduction reaction of solid SiO discovered so far. From the extension of the reduction reaction to other elemental metals, which are reported in the present paper, we expected information on the magnitude of the oxidation potential of SiO, and additional information on how much SiO and Si resemble each other in their redox reactions.

Results and discussion

We used commercially available SiO (Patinal®),[8] a dark brown amorphous powder, as a physically well-defined starting compound with a defined preparation history. The reaction products were analysed by powder XRD, and the crystalline compounds were identified by comparison with the data in the JCPDF database or with diffraction patterns calculated from entries in the ICSD database.[9] This methodology implies that any amorphous by-products cannot be detected and therefore that there is no information on how quantitative the observed reactions are.

The reaction with elemental aluminium was investigated to find out whether the formation of silicides is a driving force for the reaction of SiO. The reactivity of elemental aluminium is similar to that of magnesium; however, in contrast to magnesium, aluminium does not form silicides. When solid SiO was reacted with aluminium in an 8:3 ratio at 650 °C for 24 h, the powder diffractogram of the reaction products showed the reflections of elemental silicon, weak reflections of alumina and reflections of unreacted aluminium. The latter was extracted from the reaction mixture by aqueous HCl. The XRD of the remaining mixture is given in Fig. 1. Silica is reduced by aluminium under similar conditions, and elemental silicon and alumina are formed.[10] Thus, solid SiO behaves like silica in the reaction with elemental aluminium. Boron, gallium and indium did not react with solid SiO.

The known silicides of titanium are TiSi, $TiSi_2$ and Ti_5Si_3.[11] After reaction of a 1:1 mixture of titanium and silicon monoxide at 900 °C for 24–48 h, the reflections of hexagonal Ti_5Si_3 were clearly identified (Fig. 2). A few weak reflections could not be assigned unambiguously; however, some of them indicate the presence of elemental silicon. An interesting aspect of this reaction is that no crystalline TiO_2 phase was obtained. The fate of the oxygen in this reaction therefore remains unclear.

DOI: 10.1039/b101503f

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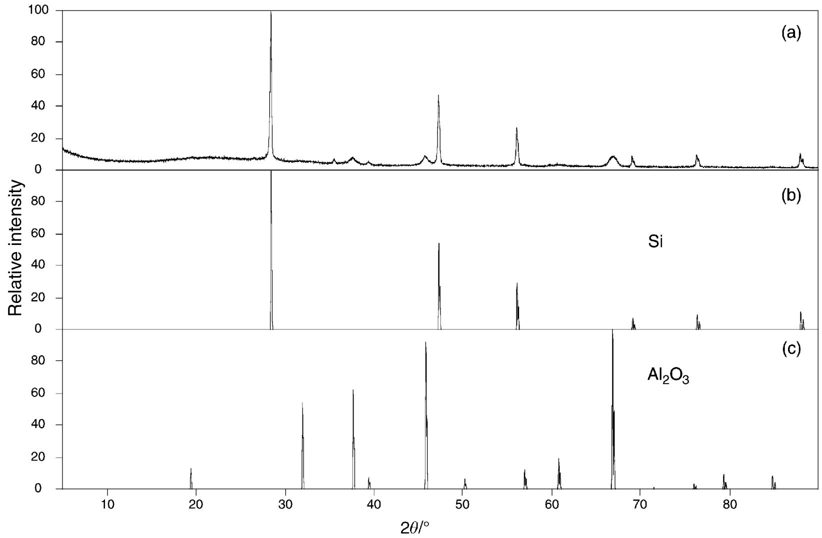

Fig. 1 (a) Powder XRD pattern of the products from the reaction of aluminium and SiO (8:3 ratio) at 650 °C after leaching with aqueous HCl. Calculated powder XRD patterns of silicon (b) and alumina (c).

To increase the reactivity of the metal, we also used the higher alkaline earth metals. When a 3:1 mixture of calcium and SiO was heated to 750 °C, two crystalline phases were identified in the product mixture. One was clearly identified as CaO. Part of the remaining reflections corresponded to a compound that is described in the JCPDF database as cubic Ca_2Si with a lattice constant of 4.702 Å.[12] The structure of this compound is unknown and, apart from the JCPDF data

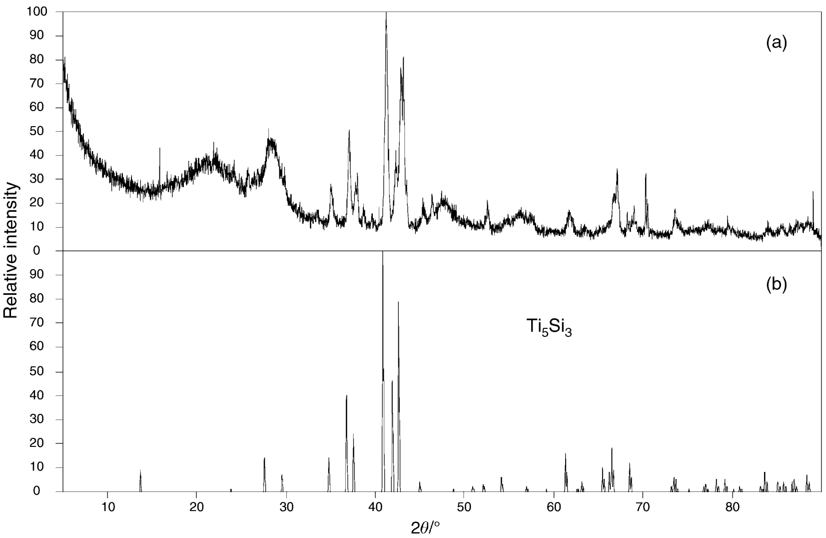

Fig. 2 (a) Powder XRD pattern of the products from the reaction of titanium and SiO (1:1 ratio) at 900 °C. (b) Calculated powder XRD pattern of Ti_5Si_3.

Table 1 Observed reflections for "Ca_2Si", their indexing and their intensities, compared with the values reported by Dow Chemical[12]

h k l		2θ/°			Intensity (a.u.)		*d*/Å		
This work	Dow	Obs.	Calc.	Diff.	This work	Dow	d_{obs}	d_{calc}	d_{Dow}
2 0 0		18.833	18.807	0.0259	31.8		4.7081	4.7145	
3 1 1		31.468	31.441	0.0266	12.5		2.8406	2.8430	
2 2 2	1 1 1	32.899	32.878	0.0205	100.0	100	2.7203	2.7219	2.71
4 0 0	2 0 0	38.165	38.146	0.0188	79.3	83	2.3562	2.3573	2.35
3 3 1		41.730	41.721	0.0091	6.8		2.1627	2.1632	
4 2 0		42.871	42.858	0.0137	13.8		2.1078	2.1084	
4 4 0	2 2 0	55.067	55.049	0.0171	42.6	42	1.6664	1.6668	1.66
5 3 1		57.820	57.803	0.0167	6.3		1.5934	1.5938	
6 0 0		58.711	58.703	0.0088	3.9		1.5713	1.5715	
5 3 3		64.795	64.783	0.0119	3.8		1.4377	1.4379	
6 2 2	3 1 1	65.638	65.626	0.0120	27.0	33	1.4213	1.4215	1.42
4 4 4		68.914	68.942	−0.0286	10.5		1.3615	1.3610	
7 1 1		71.371	71.382	−0.0103	1.0		1.3205	1.3203	
7 1 1		71.424	71.382	0.0425	1.0		1.3197	1.3203	
7 3 1		77.690	77.732	−0.0427	3.6		1.2281	1.2276	
8 0 0	4 0 0	81.609	81.620	−0.0111	6.0	3	1.1788	1.1786	1.18
8 2 0		84.693	84.701	−0.0086	1.0		1.1435	1.1400	

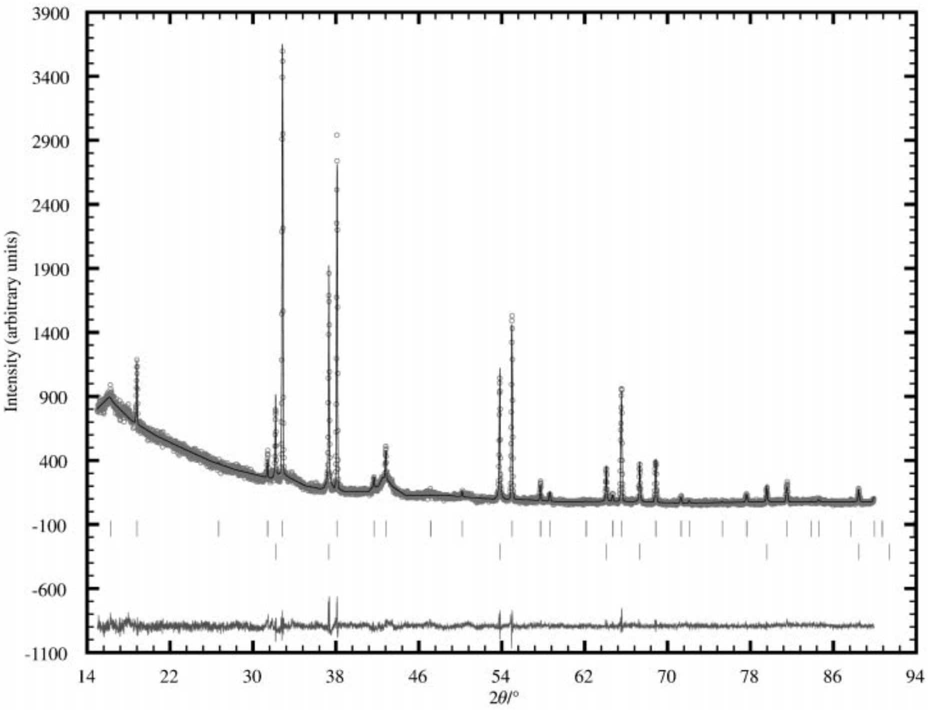

Fig. 3 Powder XRD pattern of the products from the reaction of a 3:1 mixture of calcium and SiO at 750 °C (top) and the difference between the calculated and observed intensities (refined relative weight of Ca_3SiO and CaO: 33:67) (bottom). Ca_3SiO: R_{Bragg} (R_F): 5.9 (11.7); CaO: R_{Bragg} (R_F): 5.2 (3.7).

base entry, "cubic Ca_2Si" has not been mentioned in the literature. In the Ca/Si system, orthorhombic Ca_2Si, tetragonal Ca_5Si_3, orthorhombic CaSi, rhombohedral/tetragonal $CaSi_2$ and rhombohedral $Ca_{14}Si_{19}$ are known.[11,13] The silicides are mostly prepared from the elements at high temperatures; $CaSi_2$ was also obtained from elemental calcium and silica.

Table 2 Atomic positions of Ca_3SiO. Space group $R\bar{3}m$, $a = 6.6727(13)$, $b = 16.347(3)$ Å. Ca–O(1) 2.37(3), Ca–O(2) 2.35(3), Ca–Si 3.24(4), 3.35(3), 3.48(4) Å

Atom	x/a	y/b	z/c	B_{iso}
Si	0	0	0.265(2)	0.5(5)
Ca	0.163(5)	−0.163(5)	0.089(2)	1.89(15)
O(1)	0	0	0	1.0(4)
O(2)	0	0	0.5	1.0(4)

All the strong reflections of the compound obtained from the reaction of solid SiO with Ca can be indexed by the reported cell of "cubic Ca_2Si". However, the diffractogram obtained from the reaction product of SiO with Ca contained additional weak reflections, which do not originate from CaO. When the lattice constant was doubled to $a = 9.4291(8)$ Å (refined by least squares and pattern fitting), we were able to index all reflections of the reaction mixture not belonging to CaO (Table 1).[14] The systematically absent reflections indicate a face-centred cell, a possible space group being $Fm\bar{3}m$. We suppose that the weak reflections were not observed by the previously used recording technique, which led to the erroneous assignment of the unit cell.

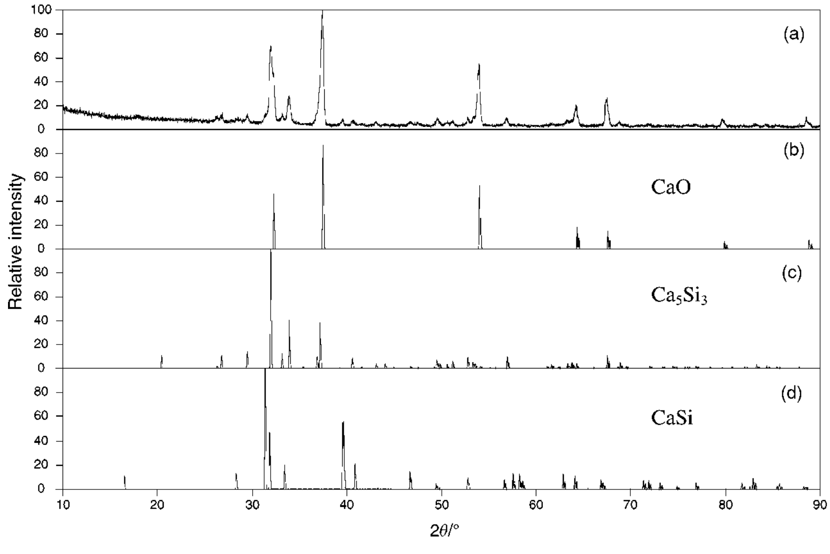

Fig. 4 (a) Powder XRD pattern of the products from the reaction of calcium and SiO (3:1 ratio) at 900 °C. Calculated powder XRD patterns of CaO, (b) Ca_5Si_3 (c) and CaSi (d).

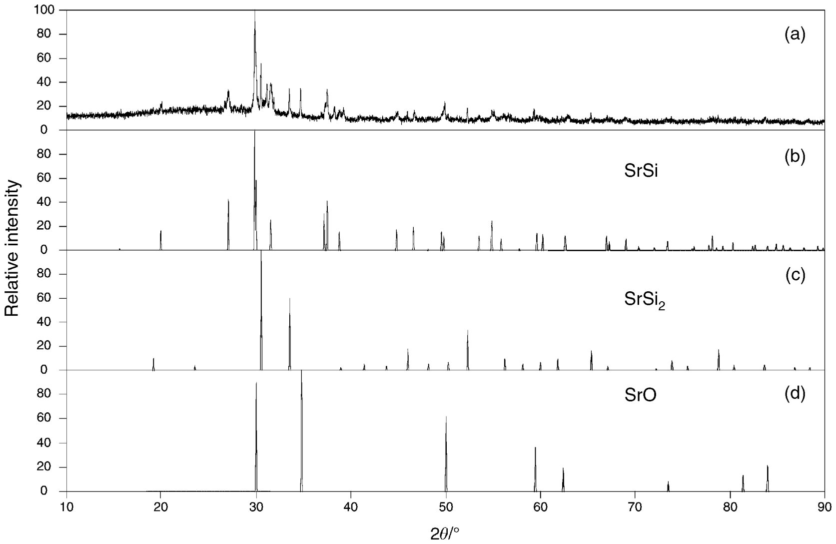

Fig. 5 (a) Powder XRD pattern of the products from the reaction of strontium and SiO (3:2 ratio) at 900 °C. Calculated powder XRD patterns of SrSi (b), $SrSi_2$ (c) and SrO (d).

A reasonable refinement of the structure (Xtal 3.2[15,16] on extracted intensities from the FullProf[17] powder diffraction analysis package) was possible in the space group $R\bar{3}m$, a subgroup of $Fm\bar{3}m$ (Table 2, Fig. 3). The composition of the compound turned out to be Ca_3SiO with a distorted anti-perovskite structure similar to that of Ca_3GeO.[18] Ca_3GeO was refined in the cubic space group; it should be mentioned, however, that for Ca_3GeO a rather high atomic displacement factor was observed for the Ca atom, which also indicates some distortion.

Ca_3SiO is not stable at higher temperatures. When the 3:1 mixture of calcium and SiO was heated to 900 °C instead of 750 °C, this phase was no longer observed, and a mixture of CaSi, Ca_5Si_3 and CaO was obtained (Fig. 4). Reaction of mixtures of Ca and SiO with lower molar Ca:SiO ratios (8:3, 2:1, 1:1) at 900 °C also resulted in the formation of this mixture, which apparently are the most stable compounds in this system. The ready formation of this mixture could explain why CaO is formed at 750 °C, together with Ca_3SiO, starting from the 3:1 mixture; the silicide phases are possibly not sufficiently crystalline at this temperature.

The formation of an oxide silicide phase—as in the reaction of SiO with calcium— was not observed with the more reactive strontium, at least not as a major reaction. Upon reaction of strontium with solid SiO at 900 °C in a 3:2 ratio, SrO, SrSi and $SrSi_2$ were formed (Fig. 5). We cannot exclude the presence of a minor fourth phase, which could not be identified. The structurally characterised silicides of strontium are Sr_4Si_7, cubic and tetragonal Sr_2Si, SrSi, Sr_4Si_7 and $SrSi_2$.[11]

The alkali metals also reacted with solid SiO. However, the products obtained did not crystallise very well and were difficult to handle. The product obtained from the reaction with lithium gave strong reflections, which, however, could not be assigned to a known lithium silicide or elemental silicon. In the reaction products of SiO and Na, K or Rb, the known silicides RbSi and M_8Si_{46} (M = Na, K) were identified by comparison of the powder diffractograms.

Conclusions

While a number of reactions are known in which SiO is oxidised to Si(IV) compounds, little is known about reduction reactions. The reactions reported previously[3] and in this article show that SiO can also be reduced to form either elemental silicon or metal silicides. The metals that react with SiO have redox potentials less than -1.6 V, while metals that did not react have less negative potentials. For example, zinc ($E^{\circ}_{\mathrm{Zn/Zn2+}}$ -0.76 V) did not react. Although other factors certainly influence the reduction behaviour of SiO as well, this result allows the prediction that only compounds with a potential of less than -1.2 ± 0.4 V will be able to reduce SiO.

The outcome of these reactions mainly mirrors the behaviour of elemental silicon. While calcium, strontium, the alkali metals and titanium form silicides upon reaction with silicon, aluminium does not. The experiments described herein do not allow a conclusion on how the silicides are formed. The first possibility is that silicon is formed first, which then, in a faster reaction, reacts with excess metal to give the silicides. An alternative would be the intermediate formation of ternary metal, oxygen, silicon phases. This possibility is suggested by the identification of Ca_3SiO as a product of the reaction of a 3:1 Ca:SiO mixture at 750 °C.

The successful structure refinement of Ca_3SiO with a distorted anti-perovskite structure clearly shows that the diffraction data reported for "cubic Ca_2Si" must instead be assigned to Ca_3SiO.

Experimental

Small pieces of Ca were used and strontium was mechanically ground in an inert gas atmosphere. Aluminium and titanium was employed as fine powders. Commercially available SiO (Patinal®)[8] was used as received. All reactions were carried out in corundum crucibles to avoid reaction of quartz vessels with the metal. The corundum boat was charged with the reaction mixtures in an inert gas atmosphere. The boat was then placed in a quartz ampoule. After sealing under vacuum, the ampoules were slowly (12–24 h) heated to the desired temperature, held at this temperature for 1–2 days and then slowly cooled to room temperature. The subsequent operations were performed under an argon atmosphere. The reaction products were transferred from the ampoules to quartz capillaries under argon, sealed again and analysed by powder XRD.

The powder diffraction data were collected in transmission geometry on Siemens D5000, Stoe Stadi P and Philips PW 1710 instruments with Cu-Kα radiation (Ge monochromator).

Acknowledgements

We thank the "Fonds zur Förderung der wissenschaftlichen Forschung"(FWF), Vienna, for supporting this work. We thank Prof. H. J. Deiseroth, H. Hirt and T. Nilges, Siegen, E.

Halwax and M. Weil, Vienna University of Technology, and C. Lengauer, University of Vienna, for the powder XRD measurements.

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