Formation of Mg₂Si from Solid Silicon Monoxide, and Solid-State Comproportionation between Mg₂Si and SiO

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Solid (amorphous) SiO is technically prepared from Si and SiO_2 at high temperatures via gaseous (molecular) SiO, which is isoelectronic to CO. There is still no unambiguous structural model for solid SiO, despite a variety of physical–chemical investigations. Their results are sometimes controversial, possibly due to the use of ill-defined and differently treated samples. With the plausible assumption that all silicon atoms in SiO are tetrahedrally coordinated, 50% of the bonds must be Si–Si and 50% Si–O. Limiting models are a statistical mixture of Si–Si and Si–O bonds ("random bonding" model[1]) on one hand and the homogeneous 1:1 mixture of small Si and SiO_2 particles on the other hand. The chemical and spectroscopic properties of solid SiO rule out the latter model. To account for some of the spectroscopic properties, a mixed-phase model was proposed,[2] in which Si and SiO_2 regions of a few nanometers in diameter are connected by a region with an intermediate stoichiometry.

The various models differ by the percentage of the tetrahedral units $Si(Si_4)$ (central silicon surrounded by four other silicon atoms), $Si(Si_3O)$, $Si(Si_2O_2)$, $Si(SiO_3)$, and $Si(O_4)$. The local distribution of the Si–Si and Si–O bonds (i.e. the tetrahedral units) must additionally be discussed. A modification of the mixed-phase model would be that there are regions with an accumulation of Si–Si bonds and other regions rich with Si–O bonds. The available spectroscopic evidence suggests that the distribution of the different units varies depending on the annealing conditions after solid SiO has been formed from the gas phase.

Little is known about the chemical reactivity of solid SiO. In most reactions, SiO was oxidized to Si(IV) compounds, such as SiO_2, silicates, or $SiCl_4$.[3,4] The only other known reactions are with aqueous HF, which yields elemental silicon and a mixture of mono- to hexasilanes,[5] and with solutions of alkaline glycolates in ethylene glycol, which results in the degradation of the solid and the formation of pentacoordinate silicon compounds.[6]

The reduction of solid SiO was not investigated so far. If the arrangement of the silicon atoms of the mixed-phase model could be preserved during reduction, it appears possible that silicon or silicide nanoparticles or amorphous silicon would be obtained. In this paper we report the reaction between solid SiO and elemental magnesium which was in situ followed by high-temperature XRD. We used commercially available SiO (Patinal), a dark brown amorphous powder without a XRD pattern, to have a physically well-defined starting compound with a defined preparation history.[7]

Prior to that we checked the thermal behavior of SiO to find the limiting conditions for high-temperature reactions. There was no reaction below 900 °C in air according to DTA and TG. When SiO was heated in pure O_2 to higher temperatures, thermogravimetric analysis showed a slow weight increase above 1000 °C. However, the total weight increase up to 1500 °C was only 15% (instead of 36.3% for the complete oxidation). Thus, exhaustive oxidation was not observed at this temperature. The thermochemical behavior of elemental silicon was similar. Weiss and Weiss reported the exhaustive oxidation of SiO with O_2 at temperatures above 1200 °C;[4] this is obviously again due to the use of a sample of different origin.

When a sample of SiO was held at 1300 °C in air for 48 h, crystalline Si and SiO_2 (cristobalite) were observed by XRD. This experiment shows that disproportionation in Si and SiO_2 is much faster than oxidation at this temperature. We are aware that XRD only allows the observation of crystalline phases, with diameters larger than about 1.5–2 nm. Thus, we cannot totally exclude that disproportionation already starts at lower temperatures and the higher temperatures just favor the crystallization process of both phases. Nevertheless, the conclusion from these experiments is that solid-state reactions of SiO must be carried out at temperatures below 1000 °C to exclude that the observed products originate from the oxidation product SiO_2 or from the disproportionation mixture of elemental Si or SiO_2 instead of SiO.

When a stoichiometric mixture of SiO and Mg was heated to 700 °C under argon (to prevent Mg from oxidation by air), elemental silicon and MgO were observed as the only crystalline phases by XRD. The average Si particle size was 11 nm, as calculated from the line width of the Si(111) reflection ($2\theta = 28.44°$).

However, the reaction is more complex than it may appear. When a 1:1 mixture of Mg and SiO was heated and X-ray diffractograms taken in situ at different temperatures (Figure 1), another crystalline compound was observed at intermediate temperatures. At 200 °C and below, only the reflections of Mg were found. The

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(7) SiO powder (Merck Patinal, particle size < 0.044 mm, as received) and Mg powder were mixed in a glovebox under argon (H_2O < 2 ppm, O_2 < 1 ppm) and intimately ground in an agate mortar. The size of the Mg particles has to be very small (below 0.1 mm) to get sufficient reaction rates. The mixture was filled into a SiO_2 Mark tube which was then sealed. The high-temperature experiments were performed on a STOE STADI P powder diffractometer (Cu Kα radiation, $\lambda = 154.06$ pm).
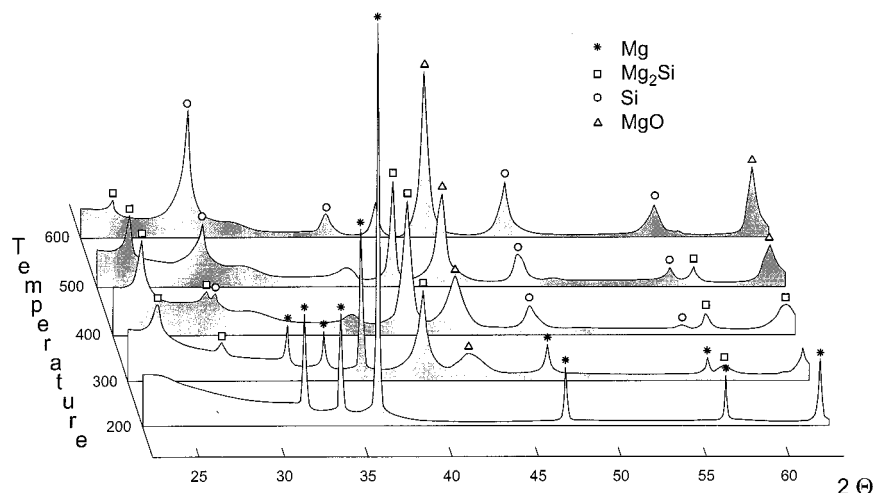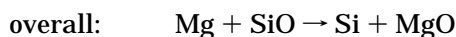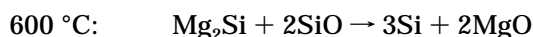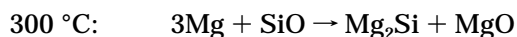
Figure 1. Temperature-dependent in situ X-ray diffractograms of the reaction of SiO with Mg.
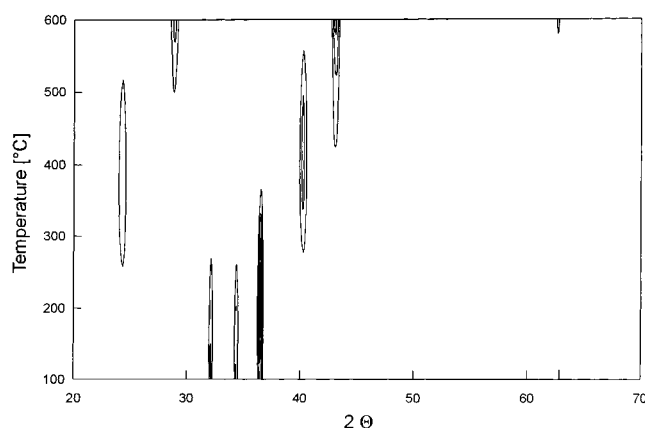
Figure 2. Contour plot of the observed reflections vs temperature. An intensity cutoff was applied to the reflections; therefore, reflections with lower intensity appear in the plot in a more narrow temperature range than reflections with higher intensities.

new reflections first observed at 300 °C at $2\theta = 40.1°$ and 42.8° belong to the Zintl phase Mg_2Si and MgO, respectively.[8] Between 300 and 400 °C, the XRD patterns of Mg_2Si and MgO fully developed, while the reflections of Mg disappeared completely. Weak reflections of elemental Si were already observed at 400 °C too, which increased in intensity at higher temperatures, while that of the Mg_2Si reflections decreased. At $T > 600$ °C, only elemental Si and MgO was eventually observed. The appearance and disappearance of the individual reflections is shown in Figure 2.

This suggests the following sequence of reactions:

300 °C: $3Mg + SiO \rightarrow Mg_2Si + MgO$

600 °C: $Mg_2Si + 2SiO \rightarrow 3Si + 2MgO$

overall: $Mg + SiO \rightarrow Si + MgO$

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(8) JCPDS numbers of the observed compounds: Mg, [350821]; MgO, [040829]; Si, [271402]; Mg_2Si, [350773].

The alternative reaction

$$2Mg + 2SiO \rightarrow Mg_2Si + SiO_2$$
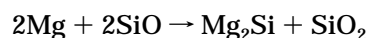
appears less likely because we observed MgO more or less simultaneously with Mg_2Si.

We performed several control experiment which support the proposed mechanism:

(i) Mg_2Si, independently prepared from elemental Si and Mg at 300 °C (1:1 or 2:1 ratio),[9] did not react with quartz powder in the applied temperature range.

(ii) Heating of Mg_2Si to 700 °C did not change its XRD pattern, i.e., it is stable at this temperature.

(iii) When a mixture of Mg_2Si and SiO (to simulate the second part of the overall reaction) was heated under identical conditions, the reflections of Mg_2Si disappeared at about 500 °C. However, no new crystalline phase was formed between 500 and 700 °C. We attribute this observation to the larger crystallite size of the independently prepared Mg_2Si.

In conclusion, SiO exhibits the same reactivity toward Mg as elemental silicon. The Zintl phase Mg_2Si is formed in both cases under identical conditions. This chemical behavior supports the "mixed-phase" model of the SiO structure. We observed the first reduction reactions of SiO: Mg as the reductant gives Mg_2Si, while Mg_2Si as the reductant gives elemental silicon. The overall reaction (formation of silicon particles and a metal oxide) could be a method to prepare silicon nanocrystallites in an oxide matrix. We will transfer this reaction to a preparative scale.

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