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A novel pressure-induced polymorphic transition from fumed silica to transparent amorphous SiO₂ at room temperature

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Abstract

We show that when we use highly dispersed oxides called fumed silica, a pressure-induced structural transition occurs at lower pressures (2–8 GPa) than would normally be expected for bulk a-SiO₂ (over 10 GPa). Furthermore, this transition finally results in a transparent monolith at 6–8 GPa, accompanied by densification, even at room temperature. We suggest that this novel polymorphic modification of a-SiO₂ results from the highly reactive nature surface strained Si–O bonds that are formed particularly in the compressed fumed silica samples.

1. Introduction

The structure and properties of amorphous silicon dioxide (a-SiO₂) have been the focus of many investigations because of its importance in modern technological applications. It is accepted that a-SiO₂ exhibits well defined first-coordination shells consisting of SiO₄ tetrahedra; however, at elevated pressure their local configurations are expected to change, showing a number of interesting and anomalous properties [1]. Recently, several new experimental and theoretical techniques have been developed to study the structure and properties of a-SiO₂ at high pressure [1–7]. When a-SiO₂ is subjected to a pressure up to ~30 GPa, permanent densification is induced, indicating that the original local structure is not completely recovered at ambient pressure [8]. Such irreversible nature of the densification is often referred to as polymorphism of a-SiO₂ [9]. It has commonly been believed that the irreversible changes of a-SiO₂ only take place above ~10 GPa under hydrostatic pressures [1–9].

These measurements have been performed mainly for bulk forms of a-SiO₂ such as rods, plates, and powders produced by crushing rods. To our knowledge, however, there have been no high-pressure measurements for very fine-particle oxides such as fumed silica. In contrast to bulk a-SiO₂, amorphous fumed silica, which is usually synthesized with SiCl₄ in an oxygen/hydrogen flame at 1100–1400 °C, has a high surface area (~100–400 m² g⁻¹) and highly reactive defect sites [10]. Such reactive sites in fumed silica will comprise rather strained

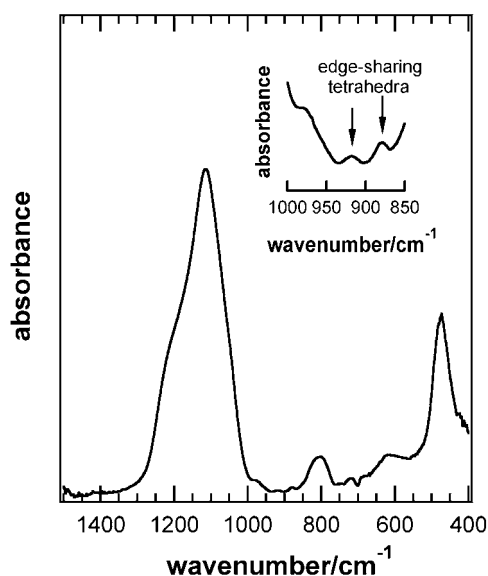


Figure 1. The Fourier transform infrared absorption spectrum (KBr disc) of non-compressed fumed silica dehydroxylated at 1000 °C. The inset shows the spectrum in the wavenumber region from 850 to 1000 cm^{-1} .

Si–O–Si bonds. In particular, the most reactive surface defect consists of siloxane bonds in the edge-sharing tetrahedral dimer that is formed by dehydroxylation of adjacent silanol groups at temperatures over 900 K. These highly strained Si–O–Si bonds in the dimers are reportedly destroyed via dissociative chemisorption reactions with, for example, water, ammonia, and methanol [11]. It is hence quite likely that when dehydroxylated fumed silica is compressed, bond breaking and/or forming may occur at these strained sites at lower pressures than would normally be expected for bulk α -SiO₂, and accordingly different compression mechanisms may take place.

Thus, in this study, we compress dehydroxylated fumed silica between 2 and 8 GPa, and possible structural changes in these compressed samples are investigated.

2. Experiment

The fumed silica (Sigma) used in this work is an extremely fine powder (particle size: 7 nm; surface area: $390 \pm 40 \text{ m}^2 \text{ g}^{-1}$ (product specification)). The powder sample was heated to 1000 °C in air prior to compression in order to oxidize any hydrocarbon impurities and to dehydroxylate surface OH groups. The sample was filled into a boron nitride cell and was pressed at room temperature almost isostatically at 2, 5.5, 6, and 8 GPa for 30 min using a cubic-anvil-type apparatus.

3. Results and discussion

It has been found that opaque and translucent samples were obtained when the fumed silica sample was compressed at 2 and 5.5 GPa, respectively. It should further be emphasized that at higher pressures (6 and 8 GPa), we obtained transparent silica samples. These results clearly indicate that a pressure-induced structural change does occur at the interface between the silica particles even at room temperature. It is hence quite likely that as for fumed silica, irreversible or anelastic compression takes place in the pressure regime (below ~ 10 GPa) in which compression is believed to be reversible for normal α -SiO₂.

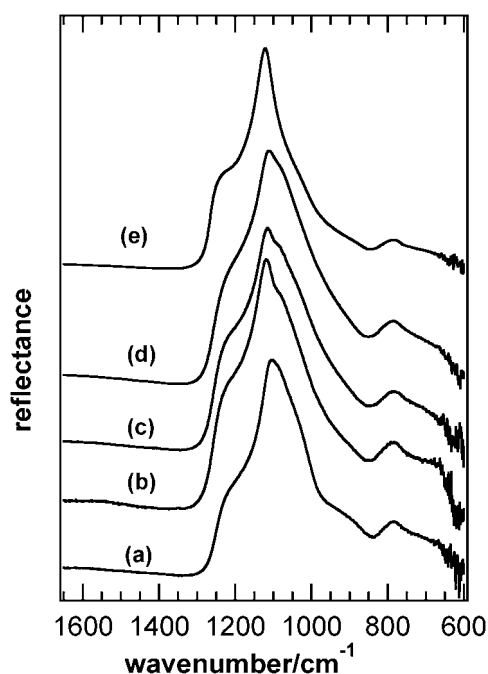


Figure 2. Fourier transform infrared microreflectance spectra of compressed fumed silica ((a) 2, (b) 5.5, (c) 6, and (d) 8 GPa) along with normal non-compressed a-SiO₂ (e). The wavenumber region below $\sim 600\text{ cm}^{-1}$ was not recorded because of the limitation of the MCT detector.

To get a better knowledge of such a pressure-induced structural change in fumed silica, we measured the infrared microreflectance spectra of the compressed samples. The rod samples obtained were mounted on a gold mirror, and infrared microsampling was carried out in the reflection mode of a Bio-Rad Model UMA 500 Fourier transform infrared microscope. We also measured the infrared absorption spectrum of the non-compressed fumed silica employing the conventional KBr disc technique. Figure 1 shows the infrared absorption spectrum of the non-compressed sample. In accordance with the previous experiments [10–12], the infrared spectrum of non-compressed fumed silica dehydroxylated at $1000\text{ }^{\circ}\text{C}$ exhibits two small bands at 917 and 878 cm^{-1} which have been assigned to edge-shared tetrahedral surface defects as mentioned earlier. This spectrum is also accompanied by a weak shoulder at $\sim 980\text{ cm}^{-1}$ which is due to the bending vibration of the residual Si–OH groups [13]. Figure 2 shows the infrared reflectance spectra of the compressed samples. We see from figure 2 that the spectral feature depends strongly on pressure. At 2 GPa, the main Si–O–Si stretching band is located at 1107 cm^{-1} and is accompanied by a broad lower-frequency component. At 5.5 GPa, the band is shifted to a higher frequency (1118 cm^{-1}), and a shoulder appears on the lower-frequency side ($\sim 1090\text{ cm}^{-1}$) of the band. At still higher pressures, the Si–O–Si stretching band is then shifted to lower frequencies again; the $\sim 1090\text{ cm}^{-1}$ shoulder tends to overlap with this main band, showing a very broad feature in the 8 GPa spectrum as in the case of the 2 GPa spectrum. It should be noted that the 6 and 8 GPa spectra (figures 2(c) and (d)) are much broader and are shifted to lower frequencies than the infrared spectrum of bulk non-compressed a-SiO₂ (figure 2(e)). Thus, we can conclude that the transparent SiO₂ glass obtained in this study is structurally different from normal a-SiO₂; that is, polymorphic modification occurred in the present compression process.

The changes observed in the infrared peak frequency with pressure will give information on mean Si–O–Si angle variations since the frequency ω of the $\sim 1100\text{ cm}^{-1}$ infrared band and

the Si–O–Si bond angle θ are related via the relation [14]

$$\omega = \alpha \sqrt{2(\alpha \sin^2 \theta/2 + \beta \cos^2 \theta/2)/m}$$

where α and β are the central and non-central force constants, respectively, and m is the atomic mass of the oxygen. According to this relation, higher- and lower-frequency shifts in the Si–O–Si stretching band correspond to an increase and a decrease in the mean Si–O–Si bond angle, respectively.

With this knowledge, the seemingly complicated frequency variations in the infrared $\sim 1100 \text{ cm}^{-1}$ band can be interpreted as follows. At 2 GPa, the Si–O–Si bonds in each fumed silica particle are expected to be highly deformed to yield rather a small mean Si–O–Si bond angle since its peak frequency (1107 cm^{-1}) is substantially smaller than the corresponding frequency (1122 cm^{-1}) of normal a-SiO₂. As has been pointed out before, a pressure of 2 GPa is not enough to induce the irreversible structural change in bulk a-SiO₂. As for fumed silica, however, the situation may be different because of its specific surface state which can accommodate the applied pressure by decreasing, in particular, the surface Si–O–Si bond angles. It is reasonable to expect that with elevating pressure such highly strained bonds become close together at the interface between the particles, and, accordingly, the strain energy of the surface of each silica particle will then be relaxed by forming the inter-particle siloxane bonds. We consider that this pressure-induced inter-particle reaction accounts for the lower-frequency shift of the Si–O–Si stretching band from 2 to 5.5 GPa, resulting in the corresponding transition from an opaque to a translucent sample. When the reaction at the interface is completed at still higher pressures (6–8 GPa), the sample will eventually become transparent. However, as further pressures will again induce the strain bonds in the Si–O–Si random network, the higher-frequency shift of the infrared band will occur as we go from 5.5 to 8 GPa. Thus, we suggest that the pressure-induced structural transformation of fumed silica at room temperature is triggered by the formation of the highly strained Si–O bonds in the respective silica particles. Its subsequent pressure-induced reaction forming the inter-particle Si–O–Si linkages will cause novel polymorphic modification of a-SiO₂.

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