

Transformation of SiO₂ to the amorphous state by shearing at high pressure—Reply

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Nasdala et al. have taken time to read our paper (Furuichi et al. 2003; vol. 88, 926–928, 2003), and I am grateful for that. I am, however, afraid that there are misunderstandings in the discussion. Let me explain essential points.

The main conclusion, transformation of SiO₂ to the amorphous state based on a structure with *Fd3m* space group by shearing at high pressure, could be drawn only by X-ray diffraction. The Raman spectra were not used to analyze the sheared structure but presented as reference data.

Although the rings in the transmission X-ray pattern are extremely vague and faint, they were distinguishable with the naked eye. The legend for Figure 3 “they may not be clearly seen in this print” does not mean that we could not distinguish the rings from the other part of the pattern on the original imaging plate. This does mean that it is difficult for present-day printing techniques to reproduce the rings as clearly as those on the original pattern.

As written in the paper being discussed, we determined the densest radii. We used an image processor that can demonstrate diametrical density distribution of the rings. In the process of determining the radii, we did not find any rings invisible to the naked eye.

We removed noise from the imaging plate before taking the diffraction pattern; unlike an X-ray film, noise can be removed from an imaging plate (Miyahara 1992). We did not find any noise in the diffraction pattern in the paper being discussed.

The proportionality between the amount of X-ray and density (this corresponds to darkness in the case of an X-ray film) on an imaging plate is at least one thousand times as high as that of an X-ray film (Miyahara 1992). The former is much more sensitive to X-ray than the latter. It seems inadequate, therefore, to condemn the X-ray diffraction pattern in the paper being discussed as unreliable. If we take the undetectable rings into consideration, we have to cast doubt on all the structures determined by X-ray diffraction.

The interplanar spacings that correspond to the rings in the pattern being discussed are 283.0, 172.7, 145.6, 129.8, and 112.9 cm. Their ratios correspond to a structure with the space group *Fd3m*. These facts give little possibility to the thought that the pattern corresponds to other space groups than *Fd3m*.

We mildly polished the sheared SiO₂ before the diffraction. The thickness of the affected layer in α -quartz polished in the

usual way is considered to be several micrometers, judging from those of materials with almost the same hardness, e.g., silicon (Matsunaga 1971). The diffraction pattern in the paper being discussed was the transmission one. The X-ray used was MoK α . The mass absorption coefficient of MoK α with SiO₂ is roughly one tenth of that of the most used CuK α (e.g., Cullity 1956, appendix). The decrease in the intensity of X-ray by the affected layer is estimated to be a few percent (e.g., Guinier 1952).

Sheared SiO₂ was severely damaged. Materials scientists and mechanical engineers who specialize in plastic deformation have seen that diffraction patterns taken from severely damaged solids show broad rings (e.g., Kuzel and Klimanek 1969). Intensity of these rings is attenuated little by the affected layer, as mentioned above. It seems unreasonable, therefore, to ascribe the broadening of the rings only to the polishing.

It is the extreme vagueness and faintness of the rings in the diffraction pattern that positively demonstrates the amorphous state and that exclude the possibility of a crystalline structure. Sheared SiO₂ was severely damaged.

We were mistaken in the discussion related to Scherrer's equation. The rings are closely located near the direct spot and the difference between the radii of the second and the third smallest ring is small. The broadening of the rings, however, ought to be small considering the small difference in the Bragg angle. This small difference may not bring about a much broader ring than the second smallest one and does not affect our main conclusion.

We obtained the Raman spectrum of the used quartz before shearing and some spectra after shearing. We pasted the former to the latter using a personal computer. Because of a defect in the software, it was impossible to paste the former to the exact corresponding position of the latter. This caused a slight shift of the peaks of the former. The cause of the peak shift of the former is not a calibration problem. The peak position of the Raman spectra after shearing, therefore, is exact and reliable.

In spite of the fact that the Raman spectrum before shearing and the spectra after shearing were obtained using the same apparatus under the same condition (in triple subtractive mode using a spectroscope with resolving power 100 μ m), the former consists of sharp peaks and the latter widened dull ones. This shows that the cause of the widening of the peaks of the Raman spectra after shearing was not the spectral resolution. Instead, the widening of the peaks of the Raman spectra indicates a disordered crystalline structure or an amorphous state.

The peak position of the Raman spectra of sheared SiO₂

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differ from previously reported ones except that of α -quartz (e.g., Hemley 1987).

The main strong diffraction from α -quartz corresponds to the interplanar spacings of 425.7(22), 334.2(100), 181.7(14), 154.18(9), 245.7(8), 228.2(8), 137.18(8) pm; figures in parentheses indicate the relative intensity (Nat. Bur. Stand. USA 1981). These interplanar spacings largely differ from those presented in the paper being discussed. This shows that even the strongest ring that ought to appear from α -quartz was not detected. It is impossible, therefore, to produce the diffraction pattern of α -quartz by adding undetectable rings to the observed rings.

Crystalline structures are definitely classified in usual textbooks (e.g., Kittel 1956). A face-centered cubic structure is not a hexagonal one. It is indispensable to get the pattern corresponding to a hexagonal structure with interplanar spacings of α -quartz by adding undetectable rings to claim that the X-ray diffraction pattern in the paper being discussed is that of α -quartz.

Accordingly, the Raman spectra of the sheared specimen ought to be those of other structures or states than α -quartz.

The Raman spectra presented in the paper being discussed were taken from SiO_2 severely sheared in one direction. It has been accepted that unidirectional shearing preferentially orients grains in a sheared specimen, irrespective of their initial orientation (e.g., Cullity 1956). The sheared SiO_2 therefore cannot be an "unoriented" crystalline structure. The above spectra are almost identical irrespective of the scattering geometry. This shows that the sheared state is not crystalline.

The Raman spectra presented in the paper being discussed did not show notable band shift as claimed by Nasdala et al. (e.g., Ostroumov et al. 2002), unlike those of disordered α -quartz. This does show that the sheared SiO_2 presented in the paper being discussed has transformed to another structure or state other than disordered α -quartz.

We do not claim that the sheared SiO_2 is strongly disordered α -quartz.

The X-ray diffraction pattern of SiO_2 glass (Bridgman et al. 1953) is quite different from that of sheared SiO_2 in the paper being discussed. The amorphous state of SiO_2 glass and its Raman spectrum, therefore, ought to differ from those of the sheared SiO_2 mentioned above. The amorphous state is not unique.

Severe shearing ought to have generated high internal residual strain in α -quartz. Transformation decreases internal residual strain of solids to decrease strain energy (e.g., Mayer and Mayer 1940). This may decrease the broadening of peaks in Raman spectra. The small broadening of the peaks in the Raman spectra of sheared SiO_2 , therefore, indicates the transformation of α -quartz to another structure or state.

Raman spectra of amorphous ceramics sometimes consist of slightly widened peaks (e.g., Praver et al. 2000). We cannot deny the existence of amorphous SiO_2 with a Raman spectrum consisting of slightly widened peaks.

We examined the quartz before shearing and found no trace

of a twin.

The expression in the paper by us does not necessarily mean that TEM should be applied to confirm XRD results. We wanted to add a TEM diffraction pattern as one of the reference data.

Severely sheared solids are liable to recrystallize when heated (Yoshida 1957). Electron beam heats a specimen. Heat conductivity of quartz is not so high.

Specimens for the observations under TEM must be extremely thin. High internal stress generated by severe shearing may plastically deform a specimen in the process of thinning. These facts make a TEM diffraction pattern somewhat unreliable.

The study of limiting state is very difficult. As far as I know, X-ray diffraction is one of the most useful methods to determine the structure of severely damaged specimens. Diffraction patterns become vague and faint with the disorder of atomic arrangement. The presented diffraction pattern was taken with the most advanced equipment by a specialist after many trials. There is no way but to use vague and faint diffraction patterns to study the extremely disordered state. The vagueness and the faintness, however, inform us of essential information on the structure of solids.

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