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Transformation of SiO_2 to the amorphous state by shearing at high pressure—Comment

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In a recent letter, Furuichi et al. (2003) described transmission X-ray diffraction (XRD) and Raman spectroscopic results of a shearing experiment of an α-quartz crystal. The authors claim that shearing at high pressure causes different structural changes than does treatment at high hydrostatic pressure and it was concluded that shearing has transformed crystalline α-quartz to an amorphous state derived from a face-centered cubic lattice. We disagree with this conclusion and see serious problems with the interpretation of the experimental work it was based on. The goal of the present paper is to critically evaluate and discuss the results of Furuichi et al. (2003) and their interpretation.

Furuichi et al. (2003) concluded from a single XRD measurement of the shearing product that the treatment had caused α-quartz to transform to largely disordered SiO_2, and they claim to have some indication for a structure corresponding to the cubic space group *Fd*3*m*. This conclusion and the accompanying discussion are questionable for the following reasons: (1) Based on the ratios of the radii of five observed extremely vague and faint halo rings, Furuichi et al. (2003) interpreted the rings as representing five (*hkl*) planes of a cubic lattice. There is no reason, however, to assign them to the $Fd\bar{3}m$ space group since a phase belonging to another face-centered cubic group, such as $Fm\bar{3}m$, would yield almost the same pattern. (2) Considering the low signal-to-noise ratio of the XRD pattern even after 10 h exposure time, it seems likely that further low intensity rings may also exist that could not be observed. Therefore, the apparent absence of additional rings does not exclude other space groups, for example those corresponding to a face-centered tetragonal or orthorhombic structure. (3) The low intensity and large width of the rings is reminiscent of patterns observed from minerals whose structure has been surficially disordered by polishing or thinning (e.g., Libowitzky 1994). Potential effects of the thinning procedure after the shearing experiment should, therefore, be thoroughly checked. (4) Furuichi et al. (2003) state that the observation of the third-smallest ring being broader than the second-smallest ring is in conflict with Scherrer's equation. By contrast, it follows from $\beta = K\lambda/D\cos\Theta$ that the broadening of the rings (β) should increase with their diameter. Thus, there is nothing in conflict with the above observation, especially if a plane imaging plate was used. (5) Finally, only the shearing product but not the starting material was analyzed. Since natural quartz crystals are typically affected by structural twinning, it is mandatory to prove that the starting material was actually a single crystal. The existence of twin domains in the unsheared specimen needs to be excluded, before the behavior of a genuine single crystal during the shearing process can be discussed.

Our above criticism is substantiated when we evaluate the Raman results presented by Furuichi et al. (2003). Based on their Raman spectra, Furuichi et al. (2003) claimed that sheared α-quartz has transformed to a previously unreported form of disordered SiO_2. This conclusion is neither supported by their presented Raman spectra nor by the relevant literature, which seems to have been inappropriately considered by Furuichi et al. (2003). To support our criticism, we compare in Figure 1 the Raman spectra published by Furuichi et al. (2003) with our spectra of natural and synthetic α-quartz, as well as SiO_2 glass. The Raman spectra of the shearing product (Fig. 1e) uniformly show the typical pattern of (unoriented) α-quartz (Scott and Porto 1967; Etchepare et al. 1974; Sato and McMillan 1987; see our Fig. 1d). Most of the apparently significant difference of the Raman spectra of SiO_2 before and after shearing as reported by Furuichi et al. (2003) is probably caused by the effect of different crystallographic orientations. We suspect that only the starting material was analyzed under (XZ) or (ZX) scattering geometry, because *A*-type vibrational modes are suppressed in such a scattering geometry (Scott and Porto 1967; compare Figs. 1a, 1b, and 1c). We agree with Furuichi et al. (2003) that the spectrum of their shearing product is not that of SiO_2 glass (Sharma et al. 1981; see our Fig. 1f). There is also no indication for the presence of coesite, any of the other known SiO_2 polymorphs, or an unknown cubic SiO_2 phase. In fact, there is no indication of any other phase but α-quartz (compare again Figs. 1d and 1e). Consequently, their Raman spectra do not support the existence of a previously unreported form of disordered SiO_2, as was claimed by Furuichi et al. (2003).

Admittedly, Raman bands in the spectra of Furuichi et al. (2003) appear slightly more broadened than expected for highly crystalline quartz, which potentially could indicate structural disorder. This, however, is only a qualitative observation, limited by the low quality of the spectra and the lack of any detailed information on the Raman spectrometer used by Furuichi et al. (2003). Since low spectral resolution also can account for broad Raman bands (e.g., Verma et al. 1995), no sound inference can be made about any real, i.e., structurally caused, broadening of the bands. In addition, extremely disordered α-quartz is likely not only to show strong band broadening, but also notable band shifts toward lower relative wavenumbers (e.g., Ostroumov et al. 2002), which is in apparent contrast to the assumption the shearing product consisted of strongly disordered α-quartz. This, however, was not observed by Furuichi et al. (2003). The upshifted peak positions observed by Furuichi et al. (2003) for the starting material (Fig. 1a) are probably due to some calibration

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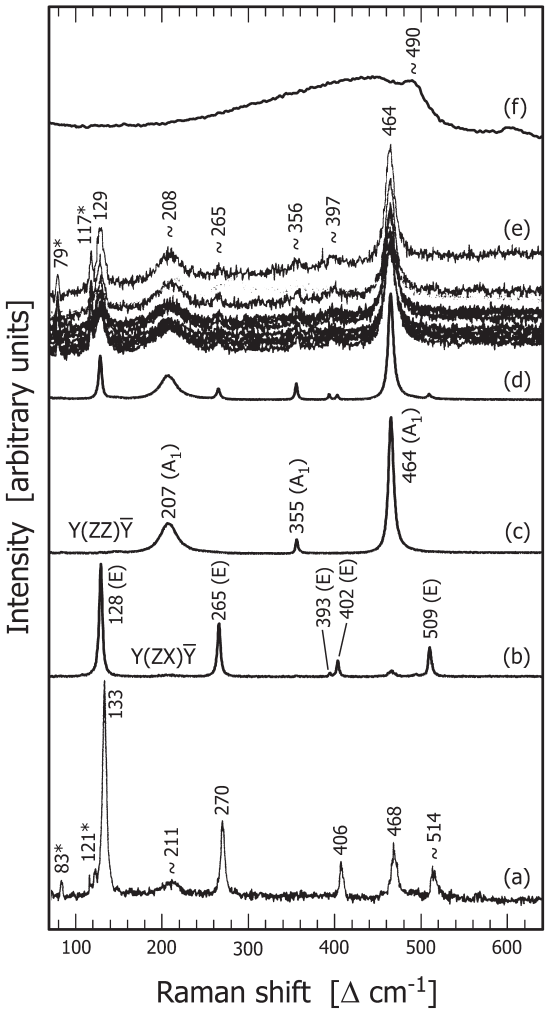

FIGURE 1. Raman spectra of Furuichi et al. (2003) in comparison with reference spectra. **(a)** Unsheared SiO_2 as obtained by Furuichi et al. **(b)** Synthetic α-quartz crystal, $Y(ZX)\bar{Y}$ scattering geometry. **(c)** Same crystal, $Y(ZZ)\bar{Y}$ scattering geometry. Scattering geometries are described using the so-called Porto notation (compare Damen et al. 1966). **(d)** Natural α-quartz, powdered (unpolarized analysis). **(e)** Spectra of the sheared SiO_2 sample as obtained by Furuichi et al. **(f)** SiO_2 glass produced by melt quenching. Since there are no peak positions explicitly given in Furuichi et al. (2003), the band positions in spectra (**a**) and (**e**) are labeled with Raman shifts that the present authors graphically interpolated from Furuichi et al.'s original figure. Bands marked with an asterisk are most probably artifacts (plasma lines emitted by the Ar^+ laser).

problem, because not only the quartz bands but also the plasma lines in this spectrum have peak positions that are ~4–5 cm^{-1} higher than what they are supposed to be.

High hydrostatic pressure or shock compression can transform α-quartz to the non-crystalline state (Hazen et al. 1989, Champagnon et al. 1996). We do not know whether the SiO_4 tetrahedrons of α-quartz form a stable cubic arrangement during a high-pressure shearing experiment. This hypothesis, however, is decidedly not supported in a convincing way by the results of Furuichi et al. (2003). It must be questioned cautiously why the X-ray pattern indicated an amorphous shearing product derived from a cubic structure, without any indication for α-quartz, whereas Raman spectra of this same shearing product revealed only the presence of α-quartz, without any indication for the presence of a cubic SiO_2 polymorph. In addition to these doubts, Furuichi et al. (2003) failed to propose a structural model for the cubic symmetry they claimed to have found in the sheared sample. For future work, it will be necessary to subject a well characterized (i.e., unambiguously not twinned) single α-quartz crystal to X-ray and Raman measurements before and after shearing. To provide comparability of results, these measurements should be done with starting material and shearing product under the very same experimental conditions. Finally, we agree with Furuichi et al. (2003) that transmission electron microscopy (TEM) should be applied to confirm any future XRD and Raman results that propose to have found a previously unreported, cubic form of SiO_2.

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