

A new high-pressure silica phase obtained by molecular dynamics—Discussion

MASAMI KANZAKI,¹ YOSHITO MATSUI,¹ AND MASANORI MATSUI²

¹Institute for Study of Earth's Interior, Okayama University, Misasa, Tottori 682-01, Japan

²Department of Earth and Planetary Sciences, Faculty of Science, Kyushu University, Hakozaki, Fukuoka 812-81, Japan

Belonoshko et al. (1996) argued that they found a new high-pressure silica phase (which they denoted SBAD) with space group *Pnc2* from molecular dynamics (MD) simulations. However, we noticed that a simple cell transformation for the reported structural data of the SBAD phase results in a structure that is virtually the same as the well known α -PbO₂ type SiO₂ structure with space group *Pbcn*, as previously described by Matsui and Kawamura (1987) and Matsui and Matsui (1988). To compare the two structures, we transformed the coordinates of the SBAD (*Pnc2*) in accord with those of the α -PbO₂ (*Pbcn*) structure as follows:

$$x' = -y, y' = z + 0.014, \text{ and } z' = x + 0.25$$

The origin along *z* is arbitrary for the *Pnc2* lattice. The resulting revised structural data for the SBAD (now *Pb2n*) are $a' = 3.8900$, $b' = 4.7225$, $c' = 4.2275$ Å; Si1 = (0.0, 0.1590, 0.25); Si2 = (0.0, 0.8411, 0.75); O1 = (0.7364, 0.3820, 0.0822); O2 = (0.2414, 0.1190, 0.9172). The original structural data and notation of sites are from Belonoshko et al. (1996).

The revised structure becomes the α -PbO₂ structure with space group *Pbcn*, when $y(\text{Si2}) = 1 - y(\text{Si1})$, $x(\text{O2}) = 0.5 + x(\text{O1})$, $y(\text{O2}) = 0.5 - y(\text{O1})$, and $z(\text{O2}) = 1 - z(\text{O1})$. Deviations from these conditions are only 0.0001, 0.0050, 0.0010, and 0.0006 in fractional coordinate for $y(\text{Si2})$, $x(\text{O2})$, $y(\text{O2})$, and $z(\text{O2})$, respectively. Therefore, the SBAD structure cannot be considered to be "intermediate between the α -PbO₂ and baddeleyite structures" as described in their paper. To clarify whether this small difference in coordinate is significant or not, we performed MD calculations at 100 and 150 GPa and 300 K with the MS-1 (Matsui and Matsui 1988) and TTAM (Tsuneyuki et al. 1988) potentials. The SBAD structure immediately converged to the α -PbO₂ structure; the time-average and fractional coordinates are simulated to deviate less than 0.0001 from the α -PbO₂ structure.

The stability of the SBAD relative to the α -PbO₂ structure might ultimately be checked by first-principles electronic structure calculation. Recently, Karki et al. (1997) performed such calculations for the *Pnc2* (SBAD) SiO₂ phase, as well as the CaCl₂ and *Pa3* phases. In their calculations, they have optimized the SBAD structure at 80 to 140 GPa and 0 K (see Table 2 of the paper for structural parameters at these pressures). However, the same coordinate transformation described above reveals that the structure is identical to the α -PbO₂ structure. Unlike the case of Belonoshko et al. (1996), no deviation from

the α -PbO₂ structure is detected.

We also noted that the X-ray diffraction patterns presented in Table 1 of Belonoshko et al. (1996) contain errors. As shown above, the coordinate differences between the SBAD and the α -PbO₂ structures are so small that they should yield similar calculated X-ray patterns. Nevertheless, completely different patterns were given for the two structures in Table 1 of their paper. We recalculated the X-ray patterns for the two structures and found them to be virtually identical and similar to the pattern for the SBAD given in Table 1 of the paper. The pattern for the α -PbO₂ phase in Table 1 of their paper is thus erroneous. For example, the 3.8260 Å peak listed for the α -PbO₂ phase can be indexed as the 100 reflection, which (*h*00 with *h* = odd) is not allowed by the space group *Pbcn* of the α -PbO₂ phase.

Finally, we address the importance of the α -PbO₂ type SiO₂ phase in the Earth's deep mantle. Although the presence of this phase was first claimed by German et al. (1973) in recovered product of shock compression (1973), its powder X-ray diffraction pattern did not match that from computer simulations (Matsui and Kawamura 1987). However, the results of our MD simulation and those of the first-principles calculation of Karki et al. (1997) suggest that the α -PbO₂ phase might be stable in the deep mantle. Recently, Saxena et al. (1996) reported its occurrence in the decomposed products of MgSiO₃ perovskite above 60 GPa, although these authors attributed it to the SBAD phase. Therefore, the α -PbO₂ type SiO₂ is a candidate for post-stishovite phase at the lower mantle conditions.

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