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

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Kanzaki et al. (1997) argue that SBAD structure cannot be considered to be intermediate between α-PbO_2 and baddeleyite structures. The similarity between SBAD and α-PbO_2 at high pressure was emphasized by Belonoshko et at. (1996); for example, in Figure 1 we showed an octahedron with an arrangement similar to α-PbO_2 structure and explained this in the figure caption. To obtain possible high-pressure silica phases with molecular dynamics (MD) or lattice dynamics (LD) simulations (Belonoshko et al. 1996a, 1996b; Dubrovinsky et al. 1996), we started from different ideal structural types: fluorite, α-PbO_2, modified α-PbO_2 (with space group *I*2/*a*), α-$PbCl_2$, and baddeleyite ZrO_2. Starting from zero pressure and 300 K with 10 GPa steps, we calculated equilibrium configurations of atoms. The structure obtained on a previous step was used as the initial configuration for the next step. Table 1 shows such configurations calculated at 10 and 90 GPa (at 300 K) in the case of baddeleyite as the initial structure (Wells 1986). It is clear that at 10 GPa the structure is much closer to baddeleyite than to α-PbO_2. As described by Belonoshko et al. (1996a, 1996b) and Dubrovinsky et al. (1996), this proves our point that SBAD is intermediate between α-PbO_2 and baddeleyite structures.

TABLE 1. Calculated structures at 10 and 90 GPa and 300 K with baddeleyite as starting configuration

	10 GPa			90 GPa		
	x	*y*	*z*	*x*	*y*	*z*
a (Å)		4.418			4.275	
b (Å)		4.285			3.927	
c (Å)		5.111			4.757	
α		90.00			90.00	
β		94.33			90.00	
γ		90.00			90.00	
Si1	0.2528	0.0224	0.1709	0.2502	0.0112	0.1479
Si2	0.7472	0.5224	0.3291	0.7502	0.5112	0.3241
Si3	0.2528	0.4776	0.6709	0.2502	0.5112	0.6479
Si4	0.7472	0.9776	0.8291	0.7502	0.0112	0.8241
O1	0.0791	0.2862	0.3830	0.0836	0.2746	0.3690
O2	0.4321	0.7430	0.3591	0.4168	0.7478	0.3690
O3	0.9209	0.7862	0.1170	0.9176	0.7764	0.1054
O4	0.5679	0.2430	0.1409	0.5828	0.2460	0.1054
O5	0.0791	0.2138	0.8830	0.0836	0.2478	0.8690
O6	0.4321	0.7570	0.8591	0.4168	0.7746	0.8690
O7	0.9209	0.7138	0.6170	0.9176	0.7460	0.6054
O8	0.5679	0.2570	0.6409	0.5828	0.2764	0.6054

Note: At 90 GPa, the structure can be described by *Pnc*2 space group after transformation $x' = x - 0.2502$, $y' = y - 0.0112$.

SBAD and α-PbO_2 structures are different from formal criteria, because they have different symmetry, and it does not matter how much the positions of the atoms deviate from symmetry positions—what is important is that they do deviate. The structure obtained by Karki et al. (1997) is closer to the ideal α-PbO_2 than to the one calculated by Belonoshko et al. (1996). But still, from a theoretical point of view, deviation in positions of the atoms from symmetrical positions even as small as ~0.00045 Å [e.g., at 80 GPa and 0 K (Karki et al. 1997)] decreases the symmetry of the ideal structure from *Pbcn* to *Pnc*2. In our calculations at pressures higher than 120 GPa at a temperature of 300 K, the energy of silica with the SBAD structure is lower than the energy of stishovite or $CaCl_2$-like structure. Karki et al. (1997) also found that the structure with the *Pnc*2 space group has the lowest energy at pressures higher than 93 GPa at 0 K. At the same time, the ideal α-PbO_2 structure was found less stable than stishovite in MD calculations [ab initio interatomic potential (Tse et al. 1992)] and in ab initio calculations in the same pressure range [periodic Hartree-Fock (Sherman 1993)].

When we started from ideal α-PbO_2, at 10 GPa, we got a distorted structure, and the degree of distortion increased with pressure. As a result, at 100 GPa we obtained a local minimum with a 20 kJ/mol higher energy than that of stishovite and with a configuration of atoms having low symmetry, which caused the appearance of additional reflections on the calculated diffraction pattern (Table 1 in Belonoshko et al. 1996).

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