

Appendix I

Thermo-chemical and thermo-physical properties of the high-pressure phase anhydrous B ($\text{Mg}_{14}\text{Si}_5\text{O}_{24}$): An ab-initio all-electron investigation **G. Ottonello,^{1,*} B. Civalleri,² J. Ganguly,³ W.F. Perger,⁴ D. Belmonte,¹ and M. Vetusch Zuccolini¹**

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Computational details on the adopted all-electron LCAO DFT/B3LYP procedure

Computations were carried out with developmental version of the CRYSTAL06 program (Dovesi et al. 2006). All-electron calculations were performed within the LCAO (Linear Combination of Atomic Orbitals) approach within the Kohn-Sham formalism by using the hybrid B3LYP functional (Becke 1993; Stephens et al. 1994) which contains a hybrid Hartree-Fock and density functional exchange-correlation functional that combines the Becke three-parameter exchange functional and the LYP (Lee et al. 1988) correlation functional. The adopted basis set expansions have been utilized previously in the ab-initio investigation of thermodynamic properties of the Mg_2SiO_4 polymorphs and stishovite (Ottonello et al. 2009a, 2009b). These consist of a 88-31G(d) contraction for silicon and a 8-411(d) set for oxygen, as proposed by Nada et al. (1996). For Mg we adopted the full reoptimization of the basis set proposed by Harrison et al. (1992), McCarthy and Harrison (1994). Core electrons were described using atomic like orbitals resulting from a combination of 8 GTOs (Gaussian Type Orbitals). A combination of 5 GTOs described the valence region closer to the nuclei and two individual GTOs described the outer valence electrons in a split-valence basis set arrangement. A diffuse *d*-type function was added to better reproduce the anisotropic distortion of the valence shells. Both coefficients and exponents of the various GTO were further reoptimized to better account for the periodicity of the investigate systems.

Cut-off limits in the evaluation of Coulomb and exchange series appearing in the SCF equation for periodic systems were set to 10^{-6} for coulomb overlap tolerance, 10^{-6} for coulomb penetration tolerance, 10^{-6} for exchange overlap tolerance, 10^{-6} for exchange pseudo-overlap in the direct space, and 10^{-12} for exchange pseudo overlap in the reciprocal space (see Dovesi et al. 2006). The DFT exchange-correlation contribution is evaluated by numerical integration over the cell volume (Pascale et al. 2004). Radial and angular points of the atomic grid are generated through Gauss-Legendre and Lebedev quadrature schemes and grid pruning has been applied, as discussed by Pascale et al. (2004), that contains M radial points and a variable number of angular points, with a maximum of N points on the Lebedev surface in the most accurate integration region that is, henceforth, referred to as (M,N)p. A preliminary investigation of the effect of the sampling grid on the static and vibrational features of stishovite, while keeping constant the structural parameters, shows a negligible overall effect on the computed energies. We adopted the grid (75,434)p for all calculations. The pruned (75,434)p grid spans the radial

range as proposed by Gill et al. (1993) with five shells with different angular points. The reciprocal space is sampled according to a regular sublattice with a shrinking factor IS equal to 4 (Dovesi et al. 2006) corresponding to 27 k points in the irreducible Brillouin zone.

The gradient with respect to the atomic coordinates and lattice parameters was evaluated analytically (Doll 2001; Doll et al. 2001, 2004). The equilibrium structure was determined (Civalleri et al. 2001) by using a modified conjugate gradient algorithm as proposed by Schlegel (1982). Convergence in the geometry optimization process was tested on the root-mean-square (RMS) and the absolute value of the largest component of both the gradients and nuclear displacements. The threshold for the maximum and the RMS forces and the maximum and the RMS atomic displacements were set to 0.00045 and 0.00030 a.u. and 0.00180 and 0.00120 a.u., respectively.

For calculation of frequencies, we refer to a previous paper (Pascale et al. 2004) for a detailed formulation of the method. Here, we simply note that, within the harmonic approximation, frequencies at the Γ point ($\mathbf{k} = 0$) are obtained by diagonalizing the mass-weighted Hessian matrix W , whose (i, j) element is defined as $W_{ij} = H_{ij}/(M_i M_j)^{1/2}$, where M_i and M_j are the masses of the atoms associated with the i and j coordinates, respectively. For the calculation of vibrational frequencies, the tolerance on the energy convergence of the SCF cycles was set to 10^{-10} a.u. LO/TO splitting was computed by including a non-analytical correction to the Hessian matrix elements (see Born and Huang 1954). It depends essentially on the electronic (clamped nuclei) dielectric tensor ϵ_∞ and on the Born effective charge tensor associated to each atom. ϵ_∞ was evaluated by using a saw-tooth finite field approach (see Darrigan et al. 2003). The Born effective charge tensor was calculated through the use of well-localized Wannier functions (Noel et al. 2002; Baranek et al. 2001; Zicovich-Wilson et al. 2001, 2002).

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