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Ab initio thermal expansion and thermoelastic properties of ringwoodite (γ-Mg_2SiO_4) at mantle transition zone conditions

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Table S1. Computed vibrational frequencies in this work by ab initio B3LYP (ν_{TO}, wavenumbers in cm^{-1}) as compared to experimental results obtained by IR (Exp.1, Akaogi et al., 1984; w = weak, sh = shoulder) and Raman spectroscopy (Exp. 2 – McMillan & Akaogi, 1987; Exp. 3 – Chopelas et al., 1994). Other DFT calculations are also shown for comparison (Calc. 1 – GGA plane-wave calculations with ultrasoft pseudopotentials, Piekarz et al., 2002; Calc. 2 – GGA plane-wave calculations with the PAW, Projector Augmented Wave method, Hernandez et al., 2015; Calc. 3 – LDA plane-wave calculations with pseudopotentials, Yu & Wentzcovitch, 2006; Calc. 4 – LDA plane-wave calculations with pseudopotentials, Li et al., 2009). Longitudinal optic modes (LO) are in italics. The statistical index $|\bar{\Delta}| = M^{-1}\sum_{i=1}^{M}\left|{\nu_{TO}}^{calc} - {\nu_{TO}}^{exp}\right|$ is the mean absolute difference between experimental and ab initio values, as defined on the wavenumbers of 12 Raman-active modes (see text for details).

Mode	Activity	ν_{TO} (cm^{-1}) (B3LYP)	Exp. 1 (IR)	Exp. 2 (Raman)	Exp. 3 (Raman)	Calc. 1 (GGA-PP)	Calc. 2 (GGA-PAW)	Calc. 3 (LDA)	Calc. 4 (LDA)
T_{2u}	Silent	199.3				223	194		
T_{2g}	Raman	305.2		302	302	282	281	309	306
E_u	Silent	338.5				355	335		
T_{1u}	IR	341.3	350 w			350 / *350*	333	345	345
T_{1g}	Silent	344.7				317	329		
E_g	Raman	371.8		370	372	343	357	375	372
T_{1u}	IR	396.0	395 sh - 445			396 / *447*	389	423	418
T_{2u}	Silent	438.9				407	421		
T_{1u}	IR	545.3	510 sh – 545 w			475 / *561*	502	549	545
E_u	Silent	566.5				523	531		
A_{2u}	Silent	573.7				563	560		
T_{2g}	Raman	619.4		600	600	571	574	586	585
T_{2g}	Raman	791.2		794	796	778	765	817	811
T_{1u}	IR	802.4	785 sh – 830			761 / *896*	768	829	823
A_{2u}	Silent	810.2				790	781		
A_{1g}	Raman	831.2		836	834	805	795	831	828
$\overline{\lvert\Delta\rvert}$		7	-	-	-	24	25	12	10

Table S2. Pressure dependence of vibrational frequencies (dv_i/dP, in cm^{-1}/GPa) and mode Grüneisen parameters (γ_i) as calculated in this work by ab initio B3LYP. Ab initio mode Grüneisen parameters are compared to experimental results (Exp. – Chopelas et al., 1994) and other DFT calculations (Calc. 1 – GGA plane-wave calculations with ultrasoft pseudopotentials, Piekarz et al., 2002; Calc. 2 – GGA plane-wave calculations with the PAW, Projector Augmented Wave method, Hernandez et al., 2015). $<\gamma>$ is the average mode Grüneisen parameter.

Mode	Activity	dv_i/dP (B3LYP)	γ_i (B3LYP)	Exp. (Raman)	Calc. 1 (GGA-PP)	Calc. 2 (GGA-PAW)
T_{2u}	Silent	0.95	1.774		1.697	3.47
T_{2g}	Raman	1.89	1.446	1.54	1.506	1.68
E_u	Silent	1.89	1.704		1.573	1.99
T_{1u}	IR	0.54	0.768		0.937	1.26
T_{1g}	Silent	1.93	1.168		1.279	1.23
E_g	Raman	1.81	1.011	0.985	1.049	1.12
T_{1u}	IR	3.50	1.806		1.559	1.64
T_{2u}	Silent	3.56	1.650		1.808	1.66
T_{1u}	IR	2.97	1.235		0.880	1.26
E_u	Silent	3.11	1.016		1.183	1.15
A_{2u}	Silent	2.20	0.890		1.038	0.95
T_{2g}	Raman	1.75	0.590	0.661	0.721	0.75
T_{2g}	Raman	4.98	1.395	1.26	1.349	1.37
T_{1u}	IR	4.75	1.274		1.228	1.30
A_{2u}	Silent	4.42	1.173		1.120	1.14
A_{1g}	Raman	4.12	1.108	0.926	0.951	1.11
$<\gamma>$			1.19	1.11	1.18	1.39

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