

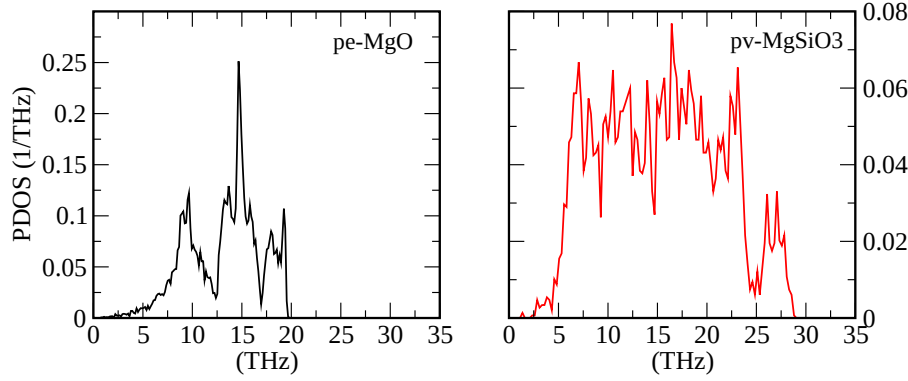


Fig. 1 Phonon density of states for periclase-MgO (pe) and perovskite-MgSiO₃ (pv) at the pressure $p=20$ GPa.

Supplementary material

Post-spinel phases

The structures of perovskite (MgSiO₃) with the orthorhombic lattice and periclase (MgO) with the cubic lattice have been constructed similarly to other studied phases. The supercell for MgSiO₃ has been chosen to be $1 \times 2 \times 2$ with the $Pmnb$ (#62) symmetry and $Z=4$ and for the MgO $2 \times 2 \times 2$ with the $Fm\bar{3}m$ (#225) symmetry and $Z=4$. The energies per formula unit for these compounds have been calculated in the range of pressures from -20 to 50 GPa. Lattice constants and unit cell volumes of considered post-spinel crystals at zero external pressure, obtained by the optimization procedure, are summarised in Table 1. The PDOSes characterizing the post-spinels lattice dynamics at critical pressure 20 GPa are described in Fig. 1.

The character of the β -Mg₂SiO₄ to γ -Mg₂SiO₄ phase transition

During the structural phase transition the crystal symmetry changes. To determine character of the transition between wadsleyite and ringwoodite, we have studied the space group relationships between the β -Mg₂SiO₄ and γ -Mg₂SiO₄

Table 1 Lattice constants and unit cell volumes obtained from the structural optimization at zero external pressure compared with the experimental data: ^a (Hazen 1976), ^b (Kojitani et al. 2007), ^c this work

Structure	symmetry	a[Å]	b[Å]	c[Å]	$V_{cell}[\text{\AA}^3]$	Ref.
MgO(pe)	$Fm\bar{3}m$	4.242	-	-	76.31	^c
		4.211	-	-	74.67	^a
MgSiO ₃ (pv)	$Pmnb$	6.970	4.971	4.819	166.95	^c
		6.906	4.779	4.933	162.81	^b

phases. Using the ISOTROPY program (Stokes et al. 2007), we have found that the $Imma$ symmetry is not a subgroup of $Fd\bar{3}m$. Therefore, a usual displacive phase transition accompanied by a soft mode cannot occur, and the phase transition must be a first order type with no group-subgroup relationship. The phase transition mechanism can, however, use the transition path, which would locally put the atomic configuration described by a common space group, being a subgroup to the $Fd\bar{3}m$ and $Imma$ space groups. A possible common space subgroup is $I4_1/amd$. This finding is consistent with the experimental observations of the $\beta \rightarrow \gamma$ transformation, that the transition mechanism includes grain boundary nucleation (Brearley et al. 1991) and intra-crystalline nucleation of ringwoodite within wadsleyite, where differential stress generated dislocations act as nucleation sites (Kerschhofer et al. 1998).

Complete phase diagram with dissociation into post-spinels

The total Gibbs energy for the $(MgO(pe) + MgSiO_3(pv))$ mixed system is obtained by the sum of energies per unit cell for pe and pv separately:

$$G_{pe+pv}(T, P) = 2 \cdot G_{pe}(T, P) + 2 \cdot G_{pv}(T, P). \quad (1)$$

The mixing entropy term in the Gibbs energy of this mixture can be omitted since the $(MgO(pe) + MgSiO_3(pv))$ system is considered to be formed at $P \approx 25$ GPa and $T \geq 1573$ K from separate grains grown in the aggregates of periclase and perovskite (Yamazaki et al. 1996).

For the wadsleyite to ringwoodite transition (i.e. between β and γ phases), the obtained Clapeyron slope is 0.0051 GPa/K (see Fig. 2), at the temperatures up to 1400 K and pressures between 14 and 22 GPa. This value is very close to 0.005 ± 0.0004 GPa derived by (Chopelas et al. 1994), using experimental thermochemical parameters and the Raman spectra, and experimental value of 0.0052 GPa/K at 18.7 GPa and 1600 K published by (Akaogi et al. 2007).

The calculated dissociative boundary slopes of β -, γ -($MgO(pe) + MgSiO_3(pv)$) are negative. For the dissociation process of ringwoodite: γ - Mg_2SiO_4 to $(MgO(pe) + MgSiO_3(pv))$ the slope is -0.0022 GPa/K, in agreement with results of Chopelas et al.: -0.0025 ± 0.0004 GPa/K and Akaogi -0.0026 ± 0.0002 GPa/K. For the wadsleyite to $MgO(pe) + MgSiO_3(pv)$ transition, the slope is -0.0008 GPa/K, which is again in good agreement with -0.0007 ± 0.0003 GPa/K published by Chopelas et al. (Chopelas et al. 1994).

Three phase boundaries meet at the triple point of chemical equilibrium of phases β -, γ - Mg_2SiO_4 and the system consisted of $MgSiO_3(pv)$ and $MgO(pe)$. The equilibrium triple point of all considered phases is located at the temperature $T = 1400$ K and pressure $P = 21.6$ GPa, as shown in Fig. 2, with comparison to (2260 K, 22.9 GPa) (Chopelas et al. 1994) calculated from the Raman spectra of γ - Mg_2SiO_4 taken at 20 GPa and the result from *ab initio* calculations (2020 K, 22.8 GPa) of (Yu et al. 2008). The value of pressure of the triple point from our study 21.6 GPa is in good agreement with these

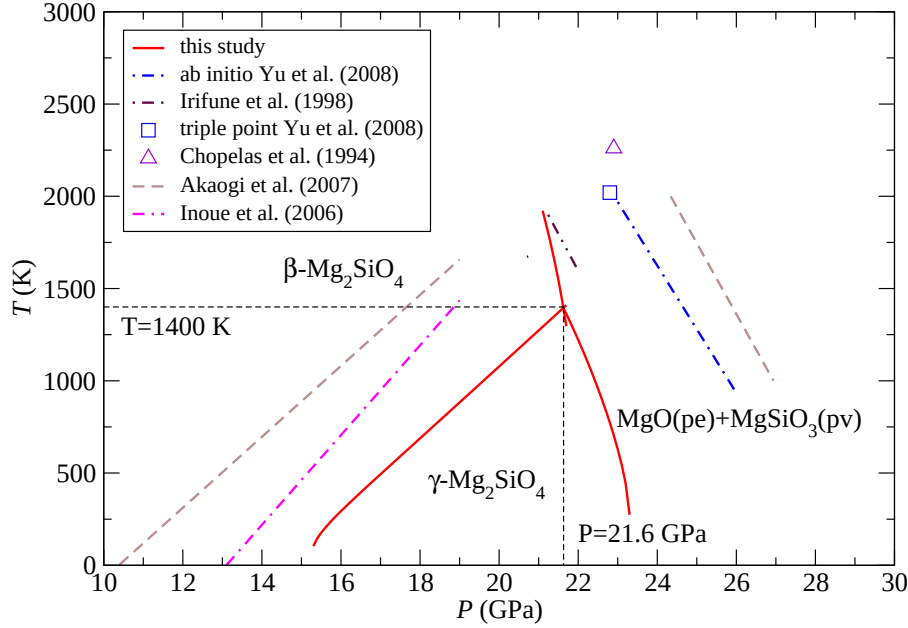


Fig. 2 The phase diagram for β - γ Mg_2SiO_4 phases and periclase+perovskite system with triple equilibrium point of all the considered phases at $T = 1400$ K and $P = 21.6$ GPa, their boundaries are described by solid lines. The left dashed line (Akaogi et al. 2007) and dotted line (Inoue et al. 2006) represent experimentally determined β - γ boundaries. The dashed and dashed-two-dotted line depict the experimental boundary for the γ to $\text{MgO(pe)} + \text{MgSiO}_3(\text{pv})$ dissociation (Akaogi et al. 2007; Irifune et al. 1998), triangle up is the triple point from (Chopelas et al. 1994) – thermochemical calculation from Raman spectra, dashed-dotted line and square represent the boundary and the triple point from the *ab initio* calculation by (Yu et al. 2008).

data, also the Clapeyron slopes of the phase boundaries are in good agreement with experimentally determined values. The temperature of the triple point is about 600 K lower in comparison with temperature at the triple point from other works (Chopelas et al. 1994; Yu et al. 2008). The temperature discrepancy between our *ab initio* phase diagram and experimentally determined phase transition data may be explained by the presence of pressure shift due to the GGA approximation used. In this approximation, the geometric parameters of the lattice and cell volume of the crystal are often overestimated (e. g. see comparison in Tab. 1) and this shift may be different for different phases. The occurrence of such phenomenon is well known and have been reported and debated in several theoretical works (Li et al. 2006; Ottonello et al. 2009; Oganov et al. 2001; Lee and Wan 2008). Unfortunately, the temperature of the triple-point is very sensitive to these changes, which may explain mentioned discrepancy.

References

- Akaogi M, Takayama H, Kojitani H, Kawaji H, Atake T (2007) Low-temperature heat capacities, entropies and enthalpies of Mg_2SiO_4 polymorphs, and $\alpha - \beta - \gamma$ and post-spinel phase relations at high pressure. *Phys Chem Mineral* 34:169–183
- Brearley AJ, Rubie DC, Ito E (1991) Mechanisms of the transformations between the α , β and γ polymorphs of Mg_2SiO_4 at 15 GPa. *Phys Chem Mineral* 18:343–358
- Chopelas A, Boehler R, Ko T (1994) Thermodynamics and behavior of γ - Mg_2SiO_4 at high pressure: Implications for Mg_2SiO_4 phase equilibrium. *Phys Chem Min* 21:351–359
- Hazen RM (1976) Effects of temperature and pressure on the cell dimension and X-ray temperature factors of periclase. *Am Mineral* 61: 266–271
- Inoue T, Irifune T, Higo Y, Sanehira T, Sueda Y, Yamada A, Shinmei T, Yamazaki D, Ando J, Funakoshi K, Utsumi, W (2006) The phase boundary between wadsleyite and ringwoodite in Mg_2SiO_4 determined by in situ X-ray diffraction. *Phys Chem Mineral* 33, 2:106–114
- Irifune T, Nishiyama N, Kuroda K, Inoue T, Isshiki M, Utsumi W, Funakoshi K, Urakawa S, Uchida T, Katsura T, Ohtaka O (1998) The postspinel phase boundary in Mg_2SiO_4 determined by in situ X-ray diffraction. *Science* 279, no. 5357:1698–1700
- Kerschhofer L, Dupas C, Liu M, Sharp TG, Durham WB, Rubie DC (1998) Polymorphic transformations between olivine, wadsleyite and ringwoodite; mechanisms of intracrystalline nucleation and the role of elastic strain. *Mineralogical Magazine* 62, (5):617–638
- Kojitani H, Katsura T, Akaogi M (2007) Aluminium substitution mechanisms in perovskite-type MgSiO_3 : an investigation by Rietveld analysis. *Phys Chem Min* 34, 4:257–267
- Lee SH, Wan JTK (2008) Pressure correction in density-functional calculations. *Phys Rev B* 78:224103
- Li L, Weidner DJ, Brodholt J, Alf D, Price GD (2006) Elasticity of Mg_2SiO_4 ringwoodite at mantle conditions. *Phys Earth Planet Int* 157:181–187
- Oganov AR, Brodholt J, Price GD (2001) The elastic constants of MgSiO_3 perovskite at pressures and temperatures of the Earth’s mantle. *Nature* 411, 6840:934–937
- Ottonello G, Civalleri B, Ganguly J, Vetushi Zuccolini M, Noel Y (2009) Thermophysical properties of the α - β - γ polymorphs of Mg_2SiO_4 : a computational study. *Phys Chem Mineral* 36, 2:87–106
- Stokes HT, Hatch DM, Campbell BJ (2007) ISOTROPY. Brigham Young University, Provo, Utah
- Yamazaki D, Kato T, Ohtani E, Toriumi M (1996) Grain growth rates of MgSiO_3 perovskite and periclase under lower mantle conditions. *Science* 274, 5295:2052–2054
- Yu YG, Wu Z, Wentzcovitch RM (2008) α - β - γ transformations in Mg_2SiO_4 in Earth’s transition zone. *Earth Planet Sci Lett* 273:115–122