



Ab initio thermodynamics and phase stability of MgSiO₃ pyroxene polymorphs: new insights on protoenstatite

Mattia La Fortezza and Donato Belmonte

(Donato.Belmonte@unige.it) Department of Sciences of Earth, Environment and Life, University of Genova, Genova, Italy

Pyroxene minerals are key to understand the structure and composition of Earth and rocky exoplanets interiors. Nevertheless, the full details of the MgSiO₃ phase diagram still remain unclear, in particular in the high temperature region. Protoenstatite (PEn) is one of the HT polymorphs of MgSiO₃ pyroxene, having stability range from ~1200 to 1800 K at ambient pressure. Its importance has been recognized by many authors, since PEn is regarded as a precursor phase of low-clinoenstatite (LP-CEn)/ortho-enstatite (OEn) intergrowths in some cometary samples [1] and in calcium-aluminum-rich inclusions (CAIs) from CV3 chondrites [2]. Moreover, PEn is the liquidus phase of pyroxene in the MgO-SiO₂ binary system and may have played a role in gas solar nebula condensation processes [3]. Very little is known about the thermodynamics and phase relations of protoenstatite. This is due for the most part to its unquenchable nature, meaning that even if PEn can be synthesized at high temperature conditions, it doesn't preserve at ambient conditions since it very rapidly reverts either to OEn or LP-CEn. The difficulty to perform measurements on samples of PEn prevents to obtain complete information on its thermodynamic properties, which are in turn fundamental for the investigation of phase equilibria of this mineral. In that sense, *ab initio* calculations based on quantum-mechanical theory are one of the most reliable methods available to obtain information on thermodynamics and phase relations of minerals at HT conditions.

We present a DFT based *ab initio* B3LYP computational study on MgSiO₃ PEn. All the relevant thermophysical and thermodynamic properties of PEn (e.g. heat capacity, vibrational entropy, thermal expansion, EoS) have been calculated in the framework of the quasi-harmonic approximation (QHA) by a full phonon dispersion calculation. This allowed to obtain original insights into protoenstatite thermodynamics and enabled to retrieve a complete set of physically consistent thermodynamic properties, that are in good agreement with the very few experimental data currently available [4]. The computed properties have been tested by predicting relevant phase equilibria involving PEn up to melting conditions, in particular the OEn – PEn phase transition. The P-T location of the phase boundary and its Clapeyron slope ($dP/dT = 2.04$ MPa/K) are consistent with previous piston-cylinder experiments ([5],[6]). Theoretical modelling of the melting curve of MgSiO₃ polymorphs reveals a change of the melting behavior from incongruent to congruent due to the onset of the OEn – PEn transition in the phase diagram.

[1] Schmitz, S., and Brenker, F.E (2008) *Astrophys. J.*, 681, L105-L108.

[2] Che, S., and Brearley, A.J. (2021) *Geochim. Cosmochim. Acta*, 296, 131-151.

- [3] Nagahara, H.. (2018) *Rev. Mineral. Geochem.*, 84, 461-497.
- [4] Thiéblot, L., Téqui, C., and Richet, P. (1999) *Am. Mineral.*, 84, 848-855.
- [5] Boyd, F. R., England, J. L., and Davis, B. T. (1964) *J. Geophys. Res.*, 69, 2101-2109.
- [6] Chen, C. H., and Presnall, D. C. (1975). *Am. Mineral.*, 60, 398-406.