Ab initio study of the relative stability under pressure of MgSiO$_3$-ilmenite, -perovskite, and (periclase + stishovite)

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The study of mantellic phases is challenging the experimentalist. Experimental difficulties emphasize the importance of theoretical approaches which should provide not only good calculated geometries, but also consistent sets of thermochemical data. Two high-pressure polymorphs of MgSiO$_3$ adopt the ilmenite (*Il*) and perovskite (*Pv*) structures.

We present the first *ab initio* study of the relative stability of these two polymorphs, and of the assemblage MgO-periclase (*Pe*) + stishovite (*St*) as a function of pressure.

Computational method

The calculations were performed with CRYSTAL92, an *ab initio* Hartree-Fock Self Consistent Field Crystalline Orbital linear combination of Atomic Orbitals program. The basic basis set (BS0) is 8-5-1G, 8-6-1G and 5-1-1-1G* for O, Mg and Si, respectively, derived larger and more flexible basis sets have been used.

Results and discussion

For the first time, the structure of MgSiO$_3$-ilmenite was fully optimized. BS0 reproduces with reasonable accuracy the experimental geometry; the calculated volumes of ilmenite, perovskite, and stishovite are underestimated by 1.32 %, 0.14 %, 1.40 %, respectively with reference to room temperature data.

The HF energy differences at the static limit are reported in Table 1. At the BS0 level, ilmenite is more stable than perovskite by 38.1 kJ/mol, but the (*Pe* + *St*) assemblage is more stable than ilmenite (2.6 kJ/mol). It turns out that the addition of *d* orbitals and the split of the contracted inner valence shell of oxygen and magnesium (entry BS5) were necessary to stabilize ilmenite with respect to perovskite and the oxydes assemblage by 62.2 and 33.8 kJ/mol, respectively.

In order to interpretate these values, approximations implicit in the present calculations 1) the basis set is not complete, 2) the HF Hamiltonian does not take into account correlation effects, 3)

TABLE 1. Energy differences (δE), pressure transition (p_t), and volume difference at p_t (ΔV). p_t values without arrow correspond to 'metastable'' phase transitions. Entries BS0, BS5, and BS5+C refer to calculated values, whereas entries Fei90, and Nav89, refer to experimental data quoted by Fei *et al.*, 1990 and Navrotsky, 1989, respectively; *: values corrected for zero-point energy

	Il ⇌ *Pv*			*Il* ⇌ *St* + *Pe*			*Pv* ⇌ *St* + *Pe*		
	δE	p_t	ΔV	δE	p_t	ΔV	δE	p_t	ΔV
BS0	38.1	22.9	−1.61	−2.6	⟶	−1.11	−40.7	⟵	0.50
BS5	62.2	39.2		33.9	36.0		−28.3	45.0	
BS5+C	47.8	28.6		30.2			−17.6		
Fei90	43.2		−1.85	25.4		−1.099	−17.6		0.76
Fei90*	36.2			15.2			−21.8		
Nav89	50.0		−1.91						
Nav89*	43.0								

temperature effects and zero-point energy are disregarded, are discussed. Test calculations indicate that further improvements of the basis set would not significantly change the relative stabilities as calculated at the BS5 level.

The correlation energy (CE) was estimated by using an *a posteriori* scheme based on correlation-only density functional formulas. After correction for CE, ilmenite is more stable than perovskite by about 47.8 kJ/mol (entry BS5 + C).

The zero-point energy cannot be calculated within the scheme used. For comparison, the experimental data (entries 4,6) have been reduced to the static limit (entries 5, 7). The agreement between calculated 'static (BS5) and corrected for correlation' and experimental 'reduced to the static limit' energy differences is reasonable.

The EOS of the four phases have been used to calculate transition pressure for the three possible reactions. At BS5 level and taking into account the CE, ilmenite transform to perovskite at about 29.4 GPa, and the oxides assemblage is never stable. The obtained phase diagram agree qualitatively and to some extend quantitatively with experimental data.

References

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