Available online at www.sciencedirect.com

Physics of the Earth and Planetary Interiors 156 (2006) 108–116

PHYSICS
OF THE EARTH
AND PLANETARY
INTERIORS

www.elsevier.com/locate/pepi

Phase transformations between garnet and perovskite phases in the Earth's mantle: A theoretical study

L. Vitos[a,b,c,*], B. Magyari-Köpe[d], R. Ahuja[c], J. Kollár[b], G. Grimvall[d], B. Johansson[a,c]

[a] Applied Materials Physics, Department of Materials Science and Engineering, Royal Institute of Technology, SE-10044 Stockholm, Sweden
[b] Research Institute for Solid State Physics and Optics, H-1525 Budapest, P.O. Box 49, Hungary
[c] Condensed Matter Theory Group, Physics Department, Uppsala University, SE-75121 Uppsala, Sweden
[d] Theory of Materials, Physics Department, Royal Institute of Technology, Stockholm Center for Physics, Astronomy and Biotechnology, SE-106 91, Stockholm, Sweden

Received 19 October 2005; received in revised form 30 January 2006; accepted 3 February 2006

Abstract

Using first-principles theories, we show that the stability of garnet and perovskite phases in an Al-free system is strongly influenced by both pressure and temperature, giving rise to a sequence of phase changes. Around 17 ± 3 GPa pressure, the $(Mg_{1-y}Ca_y)_3(MgSi)Si_3O_{12}$ majorite garnet dissociates into Ca- and Mg-perovskites. This divariant transition is associated with structural, density and elastic changes, and for $y \approx 0.13$ it has a width of ∼0.6 GPa. In $CaSiO_3$ plus $MgSiO_3$ aggregate, a (Mg, Ca)SiO_3 solid solution with an intermediate orthorhombic perovskite structure can be formed. The $(Mg_{1-x}Ca_x)SiO_3$ solid solution with $x \approx 0.04$–0.06 is calculated to be stable at the transition zone base and uppermost lower mantle conditions, and with increasing pressure it separates into perovskite end-members. The pressure–temperature stability limit for the perovskite solid solutions is close to the mantle geotherms, suggesting the appearance of structural and chemical inhomogeneities driven by temperature anomalies within the Earth's lower mantle.

Keywords: Earth's lower mantle; Majorite garnet; Ca-perovskite; Mg-perovskite; Perovskite solid solutions; Seismic inhomogeneity; Density Functional calculation

---

1. Introduction

Seismic discontinuities in the Earth's mantle have significant impact on geodynamics. Extensive experimental and theoretical efforts focus on understanding their physical and chemical origin. Today there exists a universal view of the nature of the global velocity changes in the upper part of the mantle. The two main 410 and 660-km discontinuities result from isochemical phase transitions in the olivine (olivine-wadsleyite) and ringwoodite (ringwoodite-perovksite plus magnesiowüstite) (Helffrich and Wood, 2001). The less pronounced 520-km discontinuity (Shearer and Flanagan, 1999; Shearer, 1990) has been proposed to be due to a phase change from wadsleyite to ringwoodite (Helffrich and Wood, 2001), or, alternatively, to the exsolution of the calcium silicate perovskite from majorite garnet (Canil, 1994; Ita and Stixrude, 1992). The observed splitting of the mid-transition zone discontinuity (Deuss and Woodhouse, 2001) supports the existence of both olivine and non-olivine transitions. The origins of discontinuities in the lower mantle are less clearly understood (Helffrich and Wood, 2001; Vinnik et al., 2001; Kaneshima and Helf-

---

[*] Corresponding author. Tel.: +46 8 790 8356; fax: +46 8 100 411.
E-mail address: levente.vitos@fysik.uu.se (L. Vitos)

0031-9201/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.pepi.2006.02.004

frich, 1999). They are possibly related to transitions in the most abundant minerals from this region produced by the breakdown of ringwoodite (Vinnik et al., 2001; Badro et al., 2003): $MgSiO_3$-rich perovskites and (Mg, Fe)O. Indeed, it was found that $MgSiO_3$ perovskite transforms to the post-perovskite phase above 125 GPa and 2500 K, corresponding to conditions near the base of the mantle (∼2700 km depth) (Murakami et al., 2002). Apart from this deep mantle transformation, no other phase transformations in Mg-perovskites have been observed so far (Sergiou et al., 1998; Dubrovinsky et al., 1998; Stixrude and Cohen, 1993; Kiefer et al., 2002). Most recent theoretical data on thermoelastic properties of $(Mg, Fe)SiO_3$ plus (Mg, Fe)O pyrolite aggregates give evidence for a radially heterogeneous lower mantle and suggest the presence of another, still unknown mineral phase in this region (Wentzcovitch et al., 2004).

The proportion of Ca-perovskite at mantle conditions is estimated to be about 10–20% of mineral materials from this region (Ita and Stixrude, 1992). In the upper mantle calcium is present in pyroxene, which is gradually dissolved in the garnet structure within the transition zone. At larger pressures majorite garnet transforms into $MgSiO_3$-rich perovskite plus $CaSiO_3$ perovskite (Canil, 1994). Despite the similarities between the electronic structures, Mg and Ca are predicted to be incorporated in separate perovskite phases throughout lower mantle conditions (Irifune et al., 2000; Ahmen-Zaid and Madon, 1995). Based on first-principles theories (Vitos et al., 2001; Blöchl, 1994), here we present an insight into the phase diagram of Ca-bearing garnet and perovskite phases and the interaction between Mg- and Ca-perovskites. We show that the garnet-perovskite transition occurs near 17 ± 3 GPa, and for an average 10% Ca on Mg + Ca sites, it has a width of ∼35 km. Furthermore, we find that a $Mg - Ca$ perovskite solid solution is stable at the transition zone base and uppermost lower mantle conditions, and it can be formed near high temperature anomalies throughout the lower mantle.

2. The thermodynamic model

We investigate the thermodynamics of the dissociation reactions

$$\begin{aligned} &\text{MgCa-gt} \rightarrow \text{Mg-pv} + \text{Ca-pv} \\ &\text{MgCa-pv} \rightarrow \text{Mg-pv} + \text{Ca-pv} \end{aligned} \tag{1}$$

By considering these transformations we model the exsolution of the $MgSiO_3$ and $CaSiO_3$ *perovskites* (abbreviated by Mg-pv and Ca-pv) from the $(Mg_{1-x}Ca_x)SiO_3$ *perovskite* (MgCa-pv) and $(Mg_{1-y}Ca_y)_3(MgSi)Si_3O_{12}$ *garnet* (MgCa-gt) phases, respectively. Here, and throughout the paper the concentrations are expressed in atomic fraction (specified by x and y) or atomic percentage (%). In the Earth's mantle, both majorite garnet and Mg-perovskite contain significant amount of Al and Fe. In the present study, however, we neglect this elements and consider only Al- and Fe-free systems.

The crystal structure of $MgSiO_3$ has the orthorhombic *Pbnm* symmetry (Stixrude and Cohen, 1993). Recent experiments (Shim et al., 2002; Ono et al., 2004; Kurashina et al., 2004) predict a tetragonal crystal structure as the stable phase of $CaSiO_3$. However, the exact space group is not specified in these experiments. Our investigations based on ab initio methods (Section 3.1) show that at high pressure $CaSiO_3$ crystallizes in a tetragonal $I4/mcm$ structure. In all the dissociation reactions considered in this work, we use this tetragonal structure as the reference state for $CaSiO_3$.

The unit cells of the *Pbnm* and $I4/mcm$ structures contain four ABO_3 formula units (f.u.), and they can approximately be described by the average degree of BO_6 octahedral tilt (Θ): $\Theta = 0$ for the ideal cubic perovskite structure, and increases with distortion. For the garnet structure we use the tetragonal lattice with $I4_1/a$ symmetry, observed in $(Mg_{0.84}Ca_{0.16})_3(MgSi)Si_3O_{12}$ majorite garnet (Hazen et al., 1994). The unit cell of garnet contains 32 ABO_3 f.u., with randomly distributed Mg and Ca atoms on dodecahedral sites (Hazen et al., 1994). For $(Mg, Ca)SiO_3$ perovskite we assume an orthorhombic *Pbnm* symmetry. The possible occurrence of such an intermediate phase in high pressure and temperature Ca-bearing assemblages has been reported in experiments on mid-ocean ridge basalt (MORB) (Funamori et al., 2000).

At pressure P and temperature T the stable phase of a mineral with volume V is determined by the minimum of the Gibbs free energy $G(P, T) = E + PV - TS$, where E is the internal energy and S is the entropy. In the present application, we approximate the entropy by the configurational entropy. We expect that this approximation has only a minor effect on the energy balance ΔG, because the neglected vibrational terms appear on both sides of the reaction and thus they, to a large extent, cancel each other (Grimvall, 2001). For the configuration entropy we use the mean-field expression $S_{\text{mix}} = -k_B[(1-x)\ln(1-x) + x\ln(x)]$, valid for a fully disordered state. Here, k_B is the Boltzmann constant. At temperatures characteristic for the transition zone and lower mantle ($T \gtrsim 1600$ K) and for small x values, this is a reasonable approximation.

The considered gt-pv and pv-pv phase transitions (1) are not univariant and, therefore, the $\Delta G = 0$ condition leads to a finite pressure–temperature phase loop