LETTER

Stability of the MgCO$_3$ structures under lower mantle conditions

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ABSTRACT

The presence of carbon in the Earth makes the search for high-pressure carbon-containing phases essential for our understanding of mineral compositions of the Earth’s mantle. In a recent study Ishiki et al. (2004) demonstrated that magnesite transforms into a new phase at lower mantle pressures. However, the structure of the emerging phase remained unknown. Here we show, by means of first principles calculations, that MgCO$_3$ magnesite can transform into a pyroxene structure at 113 GPa, which further transforms into a CaTiO$_3$-type structure at about 200 GPa.

INTRODUCTION

Carbon can be delivered to the lower mantle in two ways. The first is through subduction of oceanic crust and sediments (e.g., Becker and Altherr 1992). We note, however, that this possibility is a matter of debate (Domanik and Holloway 2000; Hammouda 2003) and should be considered with caution. Second, it has been suggested that carbon might be present in the Earth’s inner core (Alfe et al. 2003). Therefore, carbon could enter the lower mantle through the liquid outer core and the core-mantle boundary (D’), although the total amount of carbon delivered in this way might be rather insignificant. Finally, primordial carbon might be present in the lower mantle. Regarding these possibilities, it seems important to determine the high-pressure host phases for carbon at lower-mantle conditions.

Recent experiments (Ishiki et al. 2004) have demonstrated that magnesite (MgCO$_3$) transforms into a new phase at 115 GPa and 2100 K. The exact structure of the new phase has not been refined and its unit cell parameters have been determined only tentatively. In particular, it has been estimated to be 17% denser than the initial magnesite phase (Ishiki et al. 2004). Here we present the results of a theoretical search for possible high-pressure phases of MgCO$_3$, which suggests the stabilization of two new MgCO$_3$ phases at 113 GPa and 200 GPa.

It is known that carbon at high pressure forms compounds which are structurally similar to those of silicon. For example, CO$_2$ at high pressure transforms into silica-like polymorphs (Iota et al. 1999; Holm et al. 2000; Yoo et al. 2002). The newly discovered MgCO$_3$ phase (Ishiki et al. 2004) has been proposed to have a similar density to that of the MgSiO$_3$ perovskite, which is believed to be the major mineral in the Earth’s mantle. [We note that there are different opinions regarding the stability of MgSiO$_3$-perovskite at lower mantle conditions, based on contradictory experimental data (Saxena et al. 1996; Serghiou et al. 1998)]. These similarities suggest that phases found for MgSiO$_3$ could also exist for MgCO$_3$. This prompted us to closely investigate the stability of about 10 perovskite and pyroxene structures for MgCO$_3$ over a wide pressure range.

DETAILS OF CALCULATIONS

The study was done using the projector augmented-wave method (PAW) (Blochl 1994) within the density functional theory (DFT) as implemented in VASP (Kresse and Furthmüller 1996a, 1996b; Kresse and Joubert 1999). The electronic exchange-correlation effects were described within the generalized gradient approximation (GGA) (Perdew et al. 1992). The following orbitals were treated as valence states: 2$s$ and 2$p$ for Mg; 2$s$ and 2$p$ for C; and 2$s$ and 2$p$ for O. Convergence of the total energies (within 0.001 eV/atom) with respect to the cut-off energy, which determines the number of plane-waves included in the basis set, and the number of $\mathbf{k}$-points used for the integration over the Brillouin zone was achieved for each studied structure. Final calculations were done with a cut-off energy of 800 eV and sampling of 11 $\times$ 11 $\times$ 11 $\mathbf{k}$-points for the orthorhombic perovskite unit cells consisting of 20 atoms, and 6 $\times$ 6 $\times$ 6 $\mathbf{k}$-points for the 40 atom pyroxene unit cell. During the calculations Hellmann-Feynmann forces were systematically calculated and the nuclei were steadily relaxed to equilibrium positions. The shape of the unit cell was allowed to fully relax as well.

RESULTS AND DISCUSSION

The calculated properties of magnesite (Fig. 1) are in good agreement with both experimental data (Fiquet et al. 2002; Fiquet and Reynard 1999) and earlier calculations (Vocadlo 1999).