New high-pressure phase relations in CaSnO$_3$

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ABSTRACT

High-pressure phase stabilities of the CaSnO$_3$ system were investigated using density functional theory static lattice energy calculations. We have identified six phase changes in this system: perovskite-post-perovskite, post-perovskite-B$_2$+cotunnite in CaSiO$_3$, B$_1$-B$_2$ in CaO, cassiterite-pyrite, pyrite-orthorhombic-I, and orthorhombic-I-cotunnite in SnO$_2$. Our results demonstrate a new high-pressure phase sequence of perovskite $\rightarrow$ post-perovskite $\rightarrow$ B$_2$ + cotunnite. The post-perovskite transformation occurs at $\sim$12 GPa with $\sim$2.5% volume reduction and then it decomposes into the oxide mixture of B$_2$ CaO and cotunnite SnO$_2$ at $\sim$70 GPa with 8.1% volume reduction. The results also predict a few percent bulk velocity variations across these phase changes.

Keywords: CaSnO$_3$, perovskite, post-perovskite, density functional calculation

INTRODUCTION

Calcium stannate CaSnO$_3$ crystallizes in the GdFeO$_3$-type orthorhombic perovskite (hereafter called pv) structure at ambient condition (Vegas et al. 1986). According to recent experimental studies on the high-pressure behavior of CaSnO$_3$ perovskite (Kung et al. 2001; Zhao et al. 2004), this pv is a good structural analog of MgSiO$_3$ pv, which is believed to be a major component in the Earth’s lower mantle (e.g., Helffrich and Wood 2001). The discovery of the post-perovskite (ppv) phase transition in MgSiO$_3$ to the CaIrO$_3$ structure under P-T conditions near those of the lowermost mantle (e.g., Murakami et al. 2004; Tsuchiya et al. 2004a) could account for some of the observed properties in the D’ layer, such as small velocity discontinuities, shear wave anisotropy, and their large lateral variations (Lay et al. 2004). As a result the interest in this phase change has rapidly increased. While the ppv transitions in some other oxide compounds such as MgGeO$_3$ (Hirose et al. 2005) and Al$_2$O$_3$ (Caracas and Cohen 2004) could account for some of the observed properties in the D’ layer, such small velocity discontinuities, shear wave anisotropy, and their large lateral variations (Lay et al. 2004). As a result the interest in this phase change has rapidly increased. Although the ppv transitions in some other oxide compounds such as MgGeO$_3$ (Hirose et al. 2005) and Al$_2$O$_3$ (Caracas and Cohen 2004) have been found since the discovery of the ppv in MgSiO$_3$, it is still difficult to determine detailed properties such as the equation of state, elasticity, rheology, and phase boundaries experimentally because of the very high transition pressures $P$. Therefore, the investigation of a good oxide analog for this phase is of great importance. Although it has not been found experimentally to date, one such analog is CaSnO$_3$ pv, which is expected to transform to the ppv phase under high pressure.

Possibility of the decomposition of silicate pv into oxides under high pressure has been long argued (e.g., Meade et al. 1995; Saxena et al. 1996). Therefore, we have investigated further the evolution of high-pressure phase relations in the CaSnO$_3$ system beyond ppv. For these purposes, the energetics of not only CaSnO$_3$ pv and ppv but also oxide phases of CaO and SnO$_2$ were calculated using density functional theory, yielding predictions for the relative enthalpies of each phase. In this paper we report new high-pressure phase relations in CaSnO$_3$, structural properties, and the compression behavior of phases in the CaSnO$_3$ system.

CRYSTAL STRUCTURES

CaSnO$_3$

The pv structure of CaSnO$_3$ (Fig. 1a) belongs to the orthorhombic $Pbnm$ space group and is isostructural with MgSiO$_3$ pv. The unit cell contains four CaSnO$_3$ formula units with Ca at $(x, y, 0.25)$, Sn at $(0, 0.5, 0.5)$, O1 at $(x, y, 0.25)$, and O2 at $(x, y, z)$. Each Sn ion is surrounded by six O ions forming an almost regular SnO$_6$ octahedron, which is connected to other octahedra by sharing corners. These octahedra tilt from the crystallographic axes and the cell is strained to orthorhombic. The orthorhombic distortion of the pv lattice increases with increasing pressure. Due to this distortion, the first coordination shell of the larger cation includes 8 O atoms, in contrast to 12 in the ideal cubic pv. Some experiments have shown that the compression mechanism of CaSnO$_3$ pv is very similar to that of MgSiO$_3$ pv (Kung et al. 2001; Zhao et al. 2004).

To the authors’ knowledge, no high-pressure transition of CaSnO$_3$ pv has been reported to date. Here, we investigate using theoretical calculations the enthalpy relations between pv and ppv and explore a possible phase change of pv to CaIrO$_3$-type ppv in CaSnO$_3$. The CaIrO$_3$ structure (Fig. 1b) is base-centered orthorhombic with space group $Cmmn$ (Hyde and Andersson 1989). There are four CaSnO$_3$ formula units in the conventional $Cmmn$ unit cell. In this structure, Ca and Sn are located at $(0, y, 0.75), (0, 0, 0), O1$ at $(0, y, 0.25)$, and $O2$ at $(0, y, z)$. Sn is sixfold-coordinated to O as is the case in pv. However, unlike pv, SnO$_6$ octahedra share edges and form the rutile-like chains. This manner of octahedra connectivity in the CaIrO$_3$ structure is clearly more suitable under high pressure than the pv structure. These chains form SnO$_2$ layers in the a-c plane by sharing corners. Although the ppv structure seems to be a layered structure, it has been suggested that the concept of a layered structure is not simply applicable to MgSiO$_3$ ppv at high pressures (Tsuchiya...