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ScienceDirect
Earth and Planetary Science Letters 260 (2007) 201–211
EPSL
www.elsevier.com/locate/epsl

A computational study of ionic vacancies and diffusion in $MgSiO_3$ perovskite and post-perovskite

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Received 14 February 2007; received in revised form 9 May 2007; accepted 19 May 2007
Available online 26 May 2007
Editor: G.D. Price

Abstract

We have performed first-principles simulations within density functional theory to investigate the effects of pressure on the formation of defects (ionic vacancies) and ionic diffusion in the perovskite (pv) and post-perovskite (ppv) phases of $MgSiO_3$. Our results show that the predicted formation enthalpies of three Schottky (MgO, SiO_2 and $MgSiO_3$) defects are similar between the two phases at high pressures (100 to 150 GPa) with MgO Schottky defect being the most favorable. However, the calculated activation enthalpies and activation volumes of diffusion are shown to differ substantially between them. In particular, the activation enthalpies for Mg and Si diffusion in ppv are smaller than the corresponding values for pv, for example, by factors of 2.2 and 3.4, respectively, at 120 GPa, whereas the O migration enthalpy of ppv is only slightly larger than that of pv. The easy migration paths of the cations in ppv are shown to take place along the ⟨100⟩ direction in which Si–O octahedra share the edges. Visualization of the simulation data reveals that the vacancy defects and migrating ions induce substantial distortions in the atomic and electronic structures around them. It is suggested that diffusion is equally easy for all three species in ppv and is likely to occur through extrinsic processes near the bottom of the lower mantle.
Published by Elsevier B.V.

Keywords: defects; diffusion; high pressure; $MgSiO_3$; first-principles simulation; scientific visualization

1. Introduction

Recent experimental and computational studies have shown that $MgSiO_3$ transforms from the perovskite (pv) phase to the post-perovskite (ppv) phase under lower mantle conditions (Murakami et al., 2004; Oganov and Ono, 2004; Tsuchiya et al., 2004a) suggesting that the D″ region consists primarily of the ppv phase. Possible implications of the transition and of the properties of the new phase for the deep lower mantle, particularly, for the D″ region are being studied extensively. For instance, the equations of state (Oganov and Ono, 2004; Tsuchiya et al., 2004a), elastic wave velocities and anisotropy (Tsuchiya et al., 2004b; Iitaka et al., 2004; Oganov et al., 2005; Wookey et al., 2005) and phonon spectra (Tsuchiya et al., 2005) of ppv have previously been calculated using the first-principles methods. The two phases of $MgSiO_3$ are found to have several interesting differences in their physical properties, which are used/expected to explain key seismic observations of the D″ region such as velocity

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0012-821X/$ - see front matter. Published by Elsevier B.V.
doi:10.1016/j.epsl.2007.05.031

discontinuities, lateral heterogeneities and anisotropy (Murakami et al., 2004; Oganov and Ono, 2004; Iitaka et al., 2004; Tsuchiya et al., 2004a,b; Oganov et al., 2005; Wookey et al., 2005; Tsuchiya et al., 2005; Ono and Oganov, 2005; Wentzcovitch et al., 2006; Hirose, 2006), and also to model mantle electrical conductivity (Oganov et al., 2005; Ono et al., 2006).

Among several physical properties of the pv and ppv phases of $MgSiO_3$ that need to be better understood are rheological properties at high pressure. Knowledge about the defect energetics (formation and migration), and related atomic and electronic structures is critical to our understanding of mantle rheology because defects control diffusion and creep processes. For instance, the dominant diffusion mechanism may be vacancy-hopping and even the dominant deformation mechanism may be diffusion creep or diffusion-controlled dislocation climb. Ionic diffusion also determines electrical conductivity in minerals, which is important in modeling mantle conductivity (Hermance, 1995). In recent years, first principles studies of defective crystals have become common (e.g., Brodholt, 1997; Brodholt and Refson, 2000; Braithwaite et al., 2003; Carrasco et al., 2004; Alfe et al., 2005). To obtain reasonably accurate results for defects require quantum mechanical simulations of a relatively large atomic system. We have recently studied, from first principles, vacancy defects and migration in MgO (Karki and Khanduja, 2006a), and also studied vacancy defects in $MgSiO_3$ pv (Karki and Khanduja, 2006b) as a function of pressure. To the best of our knowledge, only simplified model calculations of defects and diffusion in pv were previously performed (Wall and Price, 1989; Wright and Price, 1993; Watson et al., 2000). Also, a relatively few experimental studies of ionic diffusion in pv at high pressures currently exist (e.g., Yamazaki et al., 2000; Dobson, 2003; Holzapfel et al., 2005).

In this paper, we report important results on the energetics, geometry, and electronic structure of defects and diffusion in the pv and ppv phases of $MgSiO_3$ at geophysically relevant pressures using the first-principles computational method based on density functional theory. The defects studied are ionic vacancies with charge states of 2+, 4+ and 2−, respectively, on cationic (Mg and Si) and anionic (O) sublattices, which allow us to study Schottky defects of different types as in the previous studies (Wall and Price, 1989; De Vita et al., 1992; Wright and Price, 1993; Watson et al., 2000; Walker et al., 2003; Alfe et al., 2005; Karki and Khanduja, 2006a,b). Our focus is on defect migration (diffusion) in pv and on both defect formation and migration in ppv to understand how defects and diffusion compare between the two phases at deep mantle pressures.

2. Methodology

Calculations are performed using the parallel code PWscf (Plane-Wave Self-Consistent Field), which is an implementation of density functional theory within the local density approximation (Baroni et al., 1987; Giannozzi et al., 1991). A plane wave basis set with cutoff of 70 Ry is used to expand the valence electronic wave function and Brillouin Zone summations of electronic quantities are performed on $2\times2\times2$ k-mesh (Monkhorst and Pack, 1976). Other computational details can be found elsewhere (Karki and Khanduja, 2006a,b). Supercells containing 80 and 60 atoms are used, respectively, for $MgSiO_3$ pv and ppv. They are large enough to get fully converged results, as also tested previously (Karki and Khanduja, 2006b). The defective cell contains only one charged defect of given type at a time. Two types of cation vacancy are created; one by removing an Mg core leaving two valence electrons in the system and other by removing an Si core leaving 4 electrons in the system. An anion vacancy is formed by removing an O core together with eight valence electrons. There are two distinct O sites in the orthorhombic structure; however, their vacancy formation energies are within 1% for both pv and ppv so we consider only one O vacancy without making a distinction between them. Thus, the net charges of the Mg, Si and O vacancies are −2e, −4e and 2e, respectively. These ionic vacancies form the Schottky defects — the dominant point defects. Such defects were previously studied in silicate phases (Wall and Price, 1989; Wright and Price, 1993; Watson et al., 2000, 2003; Karki and Khanduja, 2006b). Other charge states including F center (neutral O vacancy) are also possible; however, they are not of interest here.

Due to a net defect charge (q) associated with the supercell used, two treatments are needed to obtain acceptable results. The first is to use the Ewald sum for the long-range columbic interactions by assuming that there is a counter-charge, which is distributed uniformly throughout the simulation cell (Leslie and Gillan, 1985). The second is to make appropriate correction for defect–defect interactions arising from a periodic array of defective cell because we are interested in the energy of an infinite lattice containing only one defect. The defect–defect correction (Leslie and Gillan, 1985; Brodholt, 1997; Lento et al., 2002) is given by $\Delta E=-\alpha^* q^2/\varepsilon$. The value of α^* varies from 2.266 at zero pressure (the largest supercell) to 2.513 at 150 GPa (the smallest