First-principles simulations of MgO tilt grain boundary: Structure and vacancy formation at high pressure

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ABSTRACT

Three \{n10\}/[001] tilt grain boundaries (n = 2, 3, and 4) of MgO were studied as a function of pressure from first principles within density functional theory. Our results show that the physical properties of the grain boundary are very distinct from the bulk properties. The predicted symmetric boundary containing well-defined dislocation pipes at zero pressure transforms to asymmetric boundaries with denser structures at higher pressures. The asymmetric boundary structure stable at 50 GPa can be associated with a shear in the boundary plane, whereas the asymmetric boundary structure stable at 100 GPa can be associated with an additional shear in the direction perpendicular to the boundary plane. Unlike in the bulk, several nonequivalent sites exist for vacancy formation in the boundary regions, and the calculated Schottky defect formation enthalpy varies among different boundaries with the \{310\} and \{410\} boundary values at zero pressure being similar to the bulk value. Pressure increasingly stabilizes the boundary vacancies relative to the bulk thereby causing an enhancement in the vacancy concentration, which is further enhanced due to high-binding energy for cation-anion vacancy pairs in the interfacial regions. Also, the grain boundary was shown to induce electronic states in the band gap below the conduction band, which can trap the electrons inside the free space at the interface. Additional states with strong electron localization character appear at the boundary in the presence of the vacancies. Our results are expected to be useful to understand how grain boundaries can serve as primary storage sites for defects and high-diffusion pathways.

Keywords: Grain boundaries, structure, point defects, diffusion, first-principles calculations

INTRODUCTION

Real materials including minerals and ceramics are, in general, polycrystalline and the presence of the boundaries (interfaces) between different grains influences their physical properties. For instance, grain boundaries serve as high-diffusivity paths, thus controlling electrical conductivity, sintering, and solid-solid reactions, and also act as nucleation sites for corrosion, precipitation, fracture, and plastic deformation (e.g., Duffy 1986). The study of grain boundaries of MgO is of substantial interest from theoretical, technological, and geological viewpoints. It is a prototype oxide with a wide pressure stability field. It is a major component in MgO+FeO+SiO$_2$ system that makes up 90% of the Earth’s mantle, so its polycrystalline properties are crucial in interpreting seismic and geodynamical data of the deep interior.

A wide variety of grain boundaries can form in a polycrystal depending on factors such as growth conditions and thermal treatment though a few well-defined interfaces are usually studied. They include [001] tilt grain boundaries for MgO experimentally observed as atomic resolution Z-contrast images (Yan et al. 1998; Kizuka et al. 1998; Browning et al. 1999). Grain boundaries are considered as the hotbed of formation of point defects such as vacancies and impurities. The segregation of Ca to particular atomic columns in the MgO grain boundary was confirmed by electron energy loss spectroscopy (Yan et al. 1998). Experimental studies have shown that grain boundary diffusivity of oxygen in MgO (Hashimoto and Hama 1971) is considerably higher than the bulk value (Oishi and Kingery 1960; Van Orman et al. 2003). High grain boundary diffusion was measured for several siderophile elements in polycrystalline MgO (Hayden and Watson 2007).

Unlike point defects (e.g., De Vita et al. 1992; Alfe and Gil- lan 2005; Karki and Khanduja 2006, 2007; Verma and Karki 2009), grain boundaries (planar defects) in minerals including MgO are yet to be studied in detail using the first-principles method. Previous studies of the grain boundary were primarily based on atomistic models (e.g., Duffy 1986; Ita and Cohen 1997; Harris et al. 1999, 2001; Karki and Kumar 2007), which permit much faster computation, but their forms are uncertain. The first-principles approach is more accurate, and the required intensive computations involving a relatively large number of atoms and optimization of electronic configurations have now become feasible. Recently, the \{310\}/[001] tilt grain boundary in MgO at zero pressure has been studied using the embedded cluster method in which only a small part of the supercell was treated with the first-principles method, whereas the larger part of the supercell was modeled with polarizable shell potentials (McKenna and Shluger 2008, 2009). Here, we simulate the \{n10\}/[001] tilt grain boundaries (n = 2, 3, and 4) of MgO within the framework of density functional theory to study their atomic...