New high-pressure phases in MOOH (M = Al, Ga, In)

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ABSTRACT

A unique phase, belonging to an orthorhombic crystal system (Pbca, Z = 8), is proposed in AlOOH using crystal structure searches based on an evolutionary genetic algorithm method, combined with density functional theory. This phase features a nonlinear asymmetric doubly covalent hydrogen-bond and metal cations that are sixfold oxygen coordinated. Unlike the earlier proposed monoclinic phase, the stability region of Pbca (166–189 GPa) lies well below the pressure of decomposition to \( \text{Al}_2\text{O}_3 + \text{ice X} \) (287 GPa). In GaOOH the \( \text{Pbca} \)-type phase is not energetically favorable at any pressure. In the course of evaluating the breakdown of GaOOH to its constituent oxides, we have found a new phase of \( \text{Ga}_2\text{O}_3 \) (\( U_2\text{S}_3 \)-type). In InOOH, \( \text{Pbca} \) is energetically favorable over a narrow pressure interval (12–17 GPa). Also in InOOH, we find a new tetragonal structure (\( P\bar{4}_2_1_2 \), \( Z = 4 \)) stable above 51 GPa. This phase has nonlinear asymmetric hydrogen-bonds and metal cations that are sevenfold oxygen coordinated. Phonon calculations confirm the vibrational stability of the new phases and show that the high-pressure polymorphs of AlOOH are likely to be important carriers of water into the deep lower mantles of Earth and rocky super-Earths.

Keywords: High pressure, first-principles, phase transitions, AlOOH; Water in Nominally Hydrous and Anhydrous Minerals

INTRODUCTION

Hydrogen is an important component of the solid Earth, where even in small concentrations it can have a major effect on physical properties including the melting temperature, rheology, and seismic wave velocities (Williams and Hemley 2001). The hydrogen contained in minerals is an important part of the long-term water cycle: there may be more hydrogen bound in the mantle than there is in the surface ocean. Hydrogen bound in minerals is likely to be an important part of the water cycle on rocky exoplanets as well, including super-Earths (Tikoo and Elkins-Tanton 2017).

Despite its importance, our knowledge of where hydrogen is stored throughout most of the pressure range of planetary mantles is still very limited, particularly at conditions of the Earth’s lower mantle (24–136 GPa; 1000–4000 K) and beyond: the mantle of a 2 Earth-mass super-Earth may extend to 270 GPa (Stixrude 2014). A key question is whether hydrous minerals: minerals in which hydrogen is present in stoichiometric quantities, rather than merely as defects, can be stable in the deep interiors of rocky planets.

The AlOOH component appears to be essential for stabilizing hydrous phases at lower mantle conditions. The stability field of phase H is much wider in the MgO-SiO\(_2\)-Al\(_2\)O\(_3\)-H\(_2\)O (MASH) system than in the MSH system and encompasses the ambient lower mantle geotherm up to the pressure of the core-mantle boundary (Nishi et al. 2014; Walter et al. 2015). In contrast, the stability fields of hydrous phases in the MgO-SiO\(_2\)-H\(_2\)O system found so far are limited, and none are stable at conditions of the ambient lower mantle (Nishi et al. 2014; Walter et al. 2015).

The greater stability of phase H in aluminous systems has a structural origin. Phase H has composition MgSi(OOH)\(_2\) and a structure commensurate with that of the \( \delta \)-phase of AlOOH. In aluminous systems, phase H is found to consist of a near complete solid solution between these two end-members. The alumina content of phase H in a typical mantle bulk composition is estimated to be 40% (Walter et al. 2015). The \( \delta \)-AlOOH phase is also commensurate with the post-stishovite CaCl\(_2\)-type phase of silica with which it may form a solid solution (Panero and Stixrude 2004) that could be an important hydrous phase in more silica-rich compositions such as subducted oceanic crust. Studies of the AlOOH solid solutions are limited to the pressure range of Earth’s mantle and their stability at the high-pressure and high-temperature conditions expected in deep super-Earth mantles is unknown.

Because of its crucial role in stabilizing hydrous phases in the lower mantle and the structural relationship with the H phase and CaCl\(_2\)-type silica, end-member AlOOH serves as an ideal model system for understanding the nature of hydrous phases that may occur in Earth’s mantle and super-Earth mantles. Experimentally, the only known high-pressure phase is \( \delta \)-AlOOH (\( P2_1_2_1_2 \), \( Z = 4 \)), first synthesized at 21 GPa and 1000 °C (Suzuki et al. 2000), and subsequently observed up to 120 GPa (Sano et al. 2008). The phase has a wide temperature stability field up to conditions comparable to those present in Earth’s mantle (2000 K at 70 GPa). The \( \delta \)-phase also serves as a paradigm for the fundamental changes to hydrogen bonding that occur at high pressure. On compression, the hydrogen bond symmetrization raise the symmetry to \( Pnnm \) and produce large anomalies in elastic and vibrational properties (Tunega et al. 2011; Cedillo et al. 2016). The stability field, symmetry, and physical properties of this...