High-pressure phase stability and elasticity of ammonia hydrate

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ABSTRACT

Phase stability and elasticity of ammonia hydrate have been studied using Raman spectroscopy and Brillouin scattering in diamond-anvil cells up to 53 GPa at 300 K. Here we have established the high-pressure phase diagram of ammonia hydrate in three different compositions, including ammonia monohydrate (AMH, NH₃·H₂O), dihydrate (ADH, NH₃·2H₂O), and trihydrate (ATH, NH₃·3H₂O). In contrast to previous experimental results, our Raman and Brillouin measurements at 300 K have shown that all three ammonia hydrates start to dehydrate at 2.1–2.2 GPa. Dehydration of the ammonia hydrate leads to the formation of single-crystal ice-VII and an increase in the concentration of NH₃ in the residual liquid. The residual liquid finally turns into solid ammonia hemihydrate phase II (AHH-II) at 4–4.6 GPa, leading to a 28% jump in the compressional-wave velocity (Vₚ). Considering a 10–15 vol% NH₃ in the mantle of ice giants, AHH should thus be the dominant form of NH₃ coexisting with H₂O-ice in the ice giants. Further Brillouin measurements provide crucial constraints on the Vₚ of AHH and the single-crystal elasticity of ice-VII at high pressures and 300 K. Vₚ of AHH increases smoothly with pressure. No anomalous change in Vₚ of AHH was identified up to 39 GPa, although a solid to solid phase transition was noted to occur at ~18 GPa by Raman measurements. In addition, the elasticity of single-crystal ice-VII, which was the dehydration product of ammonia hydrate, has been determined up to 53 GPa at 300 K. The deviation of C₁₂ from C₄₄ observed at 11.4 and 14.6 GPa could be caused by the hydrogen bond symmetrizations or the ordering of dipole of single-crystal ice-VII. An abnormal softening in the elastic moduli C₁₁, C₁₂, and the adiabatic moduli K₃ together with stiffening in C₄₄ was observed between 42 and 53 GPa, which should be caused by the transition from ice-VII to its pre-transitional state. Of particular interest is the dramatic increase in the anisotropy of ice-VII with increasing pressure. Combining the sound velocity of AHH and ice-VII, we have modeled the Vₚ of ice giants with a volume ratio of 20% AHH and 80% ice-VII in the mantle. The obtained high-pressure phase diagram and elastic properties of ammonia hydrate could contribute to understanding the structure of the mantle in the ice giants and satellites.

Keywords: Ammonia hydrate, AHH, single-crystal ice-VII, elasticity, phase transition, ice giants

INTRODUCTION

Hundreds of ice giants with a mean density of ~1 g/cm³ and up to 10 times of Earth’s mass have been discovered by recent astronomy observations (e.g., Helled et al. 2010; Rauer et al. 2014; Sohl et al. 2007; Valencia et al. 2007). The mantle of these ice giants, including Neptune and Uranus as well as their large satellites, is expected to be composed of the water-ammonia-methane mixture (e.g., Brown and Calvin 2000; Sohl et al. 2003; Fortes 2012; Nettelmann et al. 2016). High-pressure studies on the physical properties of the related water mixtures, particularly the phase diagram, density, and elasticity, etc., are thus essential in understanding the structure, composition, and evolution of these ice giants and satellites (Grasset and Pargamin 2005; Kurnosov et al. 2006; Dong et al. 2009; Choukroun and Grasset 2010).

As one of the potential mantle components in the ice giants, ammonia hydrate, especially regarding its phase stability, has been of particular research interest for many years (e.g., Sill et al. 1981; Johnson and Nicol 1987; Lunine and Stevenson 1987; Cynn et al. 1989; Grasset and Pargamin 2005; Fortes et al. 2007, 2012a; Wilson et al. 2012). The high-pressure phase diagram of ammonia hydrate is complicated and strongly depends on the path-compression and the ammonia to water ratio (Loveday and Nelmes 1999, 2004; Ujike and Tominaga 2002; Fortes et al. 2007, 2009; Loveday et al. 2009; Wilson et al. 2012). Below 140 K, both ammonia monohydrate (NH₃·H₂O, AMH) and dihydrate (NH₃·2H₂O, ADH) crystalize into a single solid phase at high pressures (Loveday and Nelmes 2004; Fortes et al. 2007; Fortes et al. 2009; Loveday et al. 2009; Wilson et al. 2012, 2015). Between 140 and 300 K, at least five stable phases have been identified for AMH or ADH at high pressures (Loveday and Nelmes 2004; Fortes et al. 2007; Loveday et al. 2009; Wilson et al. 2015). Since the mantle of ice giants is at high pressures and...