Ammonia hydrates under high pressure and high temperature: a new route to synthesize ionic/superionic compounds ?

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Water and ammonia are simple molecules with large abundances in the universe. In particular, they are thought to be, together with methane, the main constituents of the internal layers of the giant icy planets Uranus and Neptune and several exoplanets such as GJ 436b or HAT-P-11b, where extreme pressure (P)-temperature(T) conditions exist. The properties of these astronomical bodies are thus expected to be largely influenced by the behavior of these high P ice mixtures. In particular, an ionized ice layer is suspected to be the source of the unusual magnetic fields measured by the Voyager II spacecraft. Constraining the interior structure of these planets thus require precise information on water/ammonia mixtures over a large range of P-T conditions.

Up to now, most high pressure studies have been devoted to the pure systems and have shown that very high pressure (100 GPa = 1 Mbar) favors the creation of ions : in pure ammonia, our group have shown that at 300 K, ammonia transforms into an ionic compound [1] and at high P-High T into superionic ice [2]. On contrary, up to 2017, the presence of ionic species in ice mixtures had not been experimentally evidenced whereas ab initio calculations predict ionic/superionic phases in the ammonia hydrates.

We have thus started an experimental program to determine the properties of ammonia hydrates at high P-T, for which very few information existed. At room P, the ammonia/water mixtures crystallize at T into three stoechiometric compounds: ammonia monohydrate (AMH), ammonia dihydrate (ADH) and ammonia hemihydrate (AHH). We have performed an extensive study (XRD, neutrons, Raman and Infrared experiments, *ab initio* calculations) of AMH up to 80 GPa and demonstrate that AMH spontaneously converts into an unusual crystalline state above 7 GPa, where H_2O and NH_3 molecules coexist with OH^- and NH_4^+ ions into a Disordered Ionico-Molecular Alloy [3]. The relatively low-pressure onset for static ionization contrasts with the extreme P required in the pure ices. The stability of this partial ionic ammonia hydrate was then investigated at high T (700 K - 30 GPa) and reveals the existence of a new high T phase potentially superionic. More recently, we have extended our investigations to the phase diagram of AHH and ADH to understand the influence of the O/N compositions on the proton transfer which occur at high pressure and leads to ionic/superionic phases.

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