

Anion effects on the crystal structures and thermodynamics of ionic clathrate hydrates

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Clathrate hydrate is a sort of ice materials which can capture a large amount of gas molecules (~170 vol/vol) in hydrogen-bonded water framework. As a particular species in this category, ionic clathrate hydrates are materials that contain hydrophobic cationic or anionic guests in counterion-incorporated clathrate framework. Tetramethylammonium hydroxide (Me₄NOH) hydrate is a widely known ionic clathrate hydrate that Me₄N⁺ is enclathrated in a hydroxide-doped water framework and that can form structure II (sII) binary hydrate in the presence of secondary gaseous molecules such as N₂ or O₂. In this work, we synthesized binary clathrate hydrates of tetramethylammonium fluoride (Me₄NF) with N₂ or O₂ and identified their crystal structures by using powder X-ray diffraction pattern analysis. The phase equilibria of synthesized samples were also investigated so as to check the effects of anions incorporated in the framework on the thermodynamics of ionic clathrate hydrates.