Structural Diversity and Stabilization of Substituted Silicon and Carbon Clathrates

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Beyond the guest/host compounds formed by water and small molecules, clathrate structures are also found in tetrahedral systems involving the group-14 elements, predominantly silicon, germanium, and tin. For the case of filled, usually metallic, silicon-based frameworks, several clathrate and clathrate-like structure types are known, typically involving alkali or alkaline-earth guest ions. In some cases, these guests may be removed to produce electron-precise semiconductors with potentially useful optoelectronic properties. Chemically similar to silicon, carbon has been predicted to form isostructural clathrate materials, yet the realization of such compounds remains a synthetic challenge. This presentation will review recent developments in binary-host clathrate frameworks predominantly comprised of silicon and carbon and accessed using high-pressure synthesis methods. For the case of silicon, framework doping with boron and germanium enables a wide range of clathrate and clathrate-like compounds with varying physical properties. Boron substitution is critical to stabilizing carbon clathrate frameworks, wherein hexagonal-ring substitution alleviates tetrahedral bond strain and enables thermodynamic stability at high pressure. Diamond-like, carbon-based clathrates with high strength and hardness possess tunable electronic structures ranging from insulators to metals and superconductors.