# Formation of Type II Silicon Clathrate with Lithium Guests

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Silicon clathrates are inclusion compounds composed of silicon cages surrounding guest atoms, typically alkali metals. Theoretical studies have predicted type II Si clathrate to have a direct or nearly direct bandgap near 2.0 eV. Synthesized in the presence of Na, Si clathrates with Na guests have been extensively investigated, particularly at low Na concentrations where type II Si clathrate can be viewed as a heavily doped semiconductor with Na acting as shallow donors. Previous work showcased the exciting optoelectronic and spin properties of Na-doped type II Si clathrate films. However, to truly understand the role of the guests and realize the potential of these materials, studying Si clathrates with other guest species is critical.

Here we explore thermal diffusion of Li into a nearly empty clathrate framework to synthesize $Li_xSi_{136}$. Starting with an extremely low-Na-content type II Si clathrate film ($Na_{0.009}Si_{136}$), Li diffusion experiments were performed at a range of temperatures. Confirmation of Li diffusion into the film and estimation of the effective Li diffusion constant were achieved through TOF-SIMS. Raman scattering spectroscopy and XRD were employed to study the interaction of Li with the Si framework. EPR results suggest Li tends to form pairs with Na and other Li atoms in the lattice, indicating multiple occupancy and cluster formation.

Our findings underscore the feasibility of incorporating Li into the Si clathrate structure via thermal diffusion, offering new insights into the structural and electronic transformations as Li integrates into the crystal lattice. The results are relevant to the potential utilization of Si clathrate as an anode material in Li-ion batteries. Furthermore, the procedures and techniques unveiled present a novel approach to filling Si clathrate cages, potentially enabling studies involving a broad range of other guest atoms in Si clathrates. This work was supported by NSF Award 1810463 and 2114569.