

## Efficient route to phase selective synthesis of type II silicon clathrates with low sodium occupancy

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Electronic Supplementary Information:

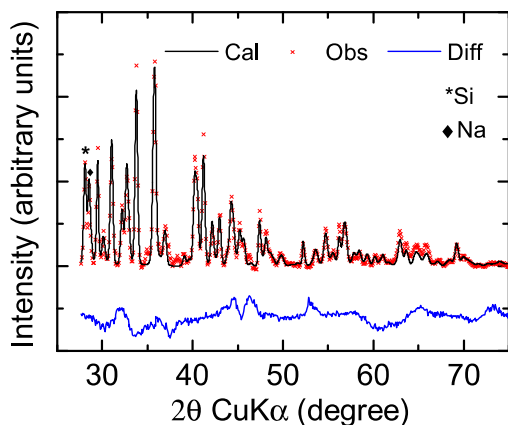


Fig. S1. XRD pattern, Rietveld refinement, and difference profile of NaSi synthesized and annealed at 250 °C for 3 h. Kapton tape was used to prtect the NaSi sample during measurement; this leads to large background that was subtracted during refinement.

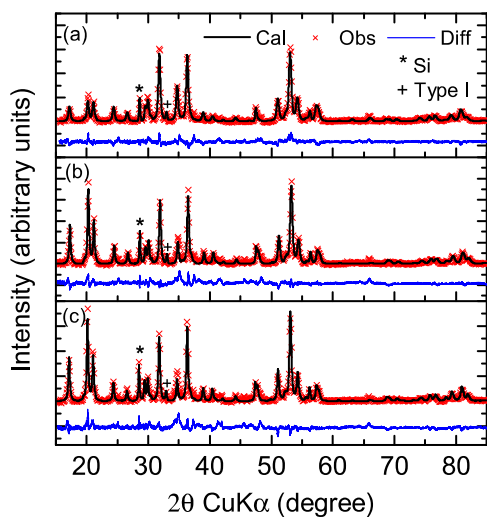


Fig. S2. XRD patterns from thermal decomposition of 0.5 g NaSi decomposed at 370 °C in the cold plate reactor for (a) 24 h, (b) 48 h, and (c) 72 h. Rietveld refinement include  $\text{Na}_x\text{Si}_{136}$ ,  $\text{Na}_8\text{Si}_{46}$  and d-Si. Less than 5 wt. % type I is obtained using this approach.

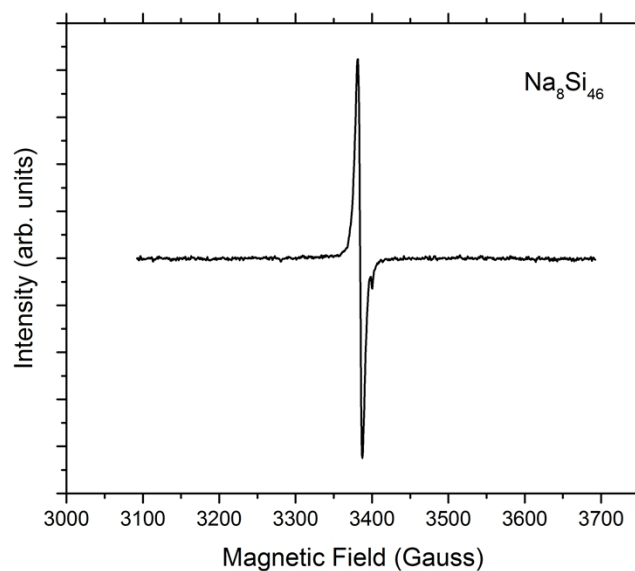


Fig. S3. ESR spectrum of type I clathrate ( $\text{Na}_8\text{Si}_{46}$ ) acquired at 10 K. Only prominent feature is the conduction electron peak. This sample approximately has 10 % type II clathrate ( $\text{Na}_{14}\text{Si}_{136}$ ) phase.

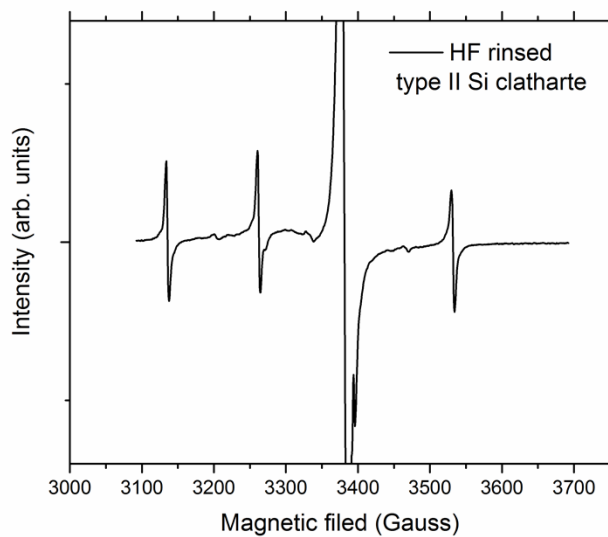


Fig. S4. ESR spectrum of type II clathrate ( $\text{Na}_x\text{Si}_{136}$ ;  $x \sim 5$ ) acquired at 10 K. The sample is rinsed with HF to get rid of sodium oxide phases.

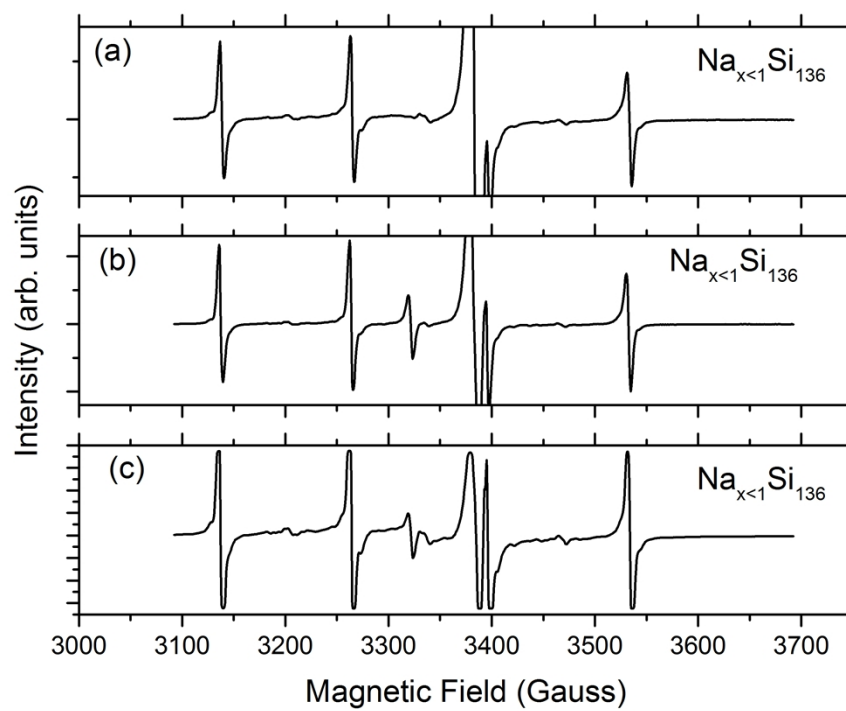


Fig. S5. The ESR spectra of Fig.8 in the manuscript are re plotted here where all the quartet peaks are normalized. The fourth septet feature can be seen in all the panels (a, b and c).