Electronic Supplementary Information

y	Wt% $NaSi_{1-y}Ge_y$	Wt% Na	Wt% *d*-SiGe	R_{wp}	a (Å)	b (Å)	c (Å)	β°
0	90	1	9	0.0494	12.16	6.55	11.14	118.9
0.1	97	3	0	0.0553	12.19	6.58	11.17	119.1
0.25	96	4	0	0.0397	12.19	6.58	11.18	119.0
0.5	96	4	0	0.0592	12.21	6.62	11.22	119.0
0.75	96	4	0	0.0840	12.32	6.66	11.38	119.7
1	100	0	0	0.0367	12.38	6.66	11.50	120.2

Table S.1 Rietveld refinment data for $NaSi_{1-y}Ge-y$ samples.

R_{wp} represents the weighted R-factor, which is an indication of goodness of fit between the modeled crystal structure and the experimental data. For powder X-ray diffraction data, values of $R_{wp} \leq 0.1$ are preferrable. For more information, please see:

1. Toby, B. H. "R factors in Rietveld analysis: How good is good enough?" *Powder Diffraction* **21** (1), 2006.
2. McCusker, L. B., Von Dreele, R. B. Cox, D. E., Louer, D., and Scardi, P. "Rietveld refinement guidelines" *J. Appl. Cryst.* (1999) **32**, 36-50.

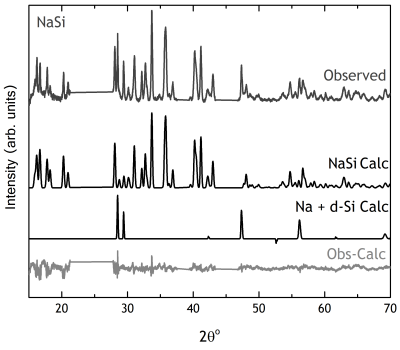

Fig. S.1 Rietveld refinement of NaSi.

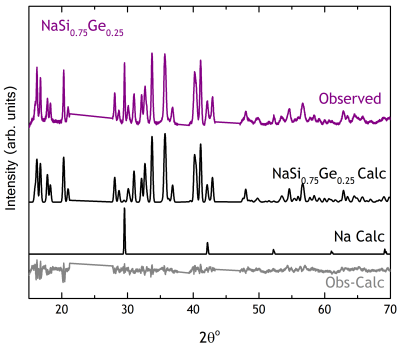

Fig. S.2 Rietveld refinement of $NaSi_{0.75}Ge_{0.25}$.

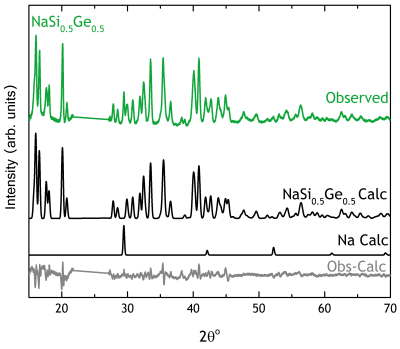

Fig. S.3 Rietveld refinement of $NaSi_{0.5}Ge_{0.5}$.

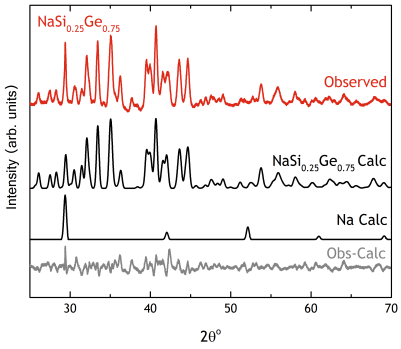

Fig. S.4 Rietveld refinement of $NaSi_{0.25}Ge_{0.75}$.

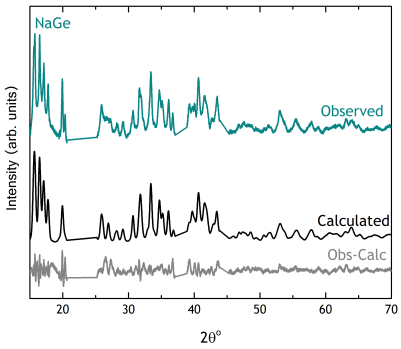

Fig. S.5 Rietveld refinement of NaGe.

y	Wt% type II	Wt% type I	Wt% d-SiGe	R_{wp}	Type II lattice parameter (Å)	Na1 F	Na2 F	Total Na
0	88	8	4	0.0967	14.64	0.16	0.03	1.85
0.1	99	0	1	0.0792	14.69	<0.01	0.01	0.16
0.25	100	0	0	0.0538	14.77	0.80	0.58	15.62
0.5	99	0	1	0.0451	15.08	<0.01	0.17	2.78
0.75	99	0	1	0.0777	15.10	0.04	0.04	0.98
1	90	0	10	0.0838	15.22	0.22	0.17	4.52

Table S.2 Rietveld refinment data for clathrate samples.

Notes on this table:

- For samples with significant amorphous fractions (y=0.25, 0.5), the Wt% of each phase applies only to the crystalline fraction of the sample. The amorphous fraction was not quantified.
- "Na1 F" and "Na2 F" represent the fractional occupancy (0-1) on the two distinct Na site in the type II crystal structure.
- The "Total Na" represents the value of x in $Na_x(Si_{1-y}Ge_y)_{136}$.

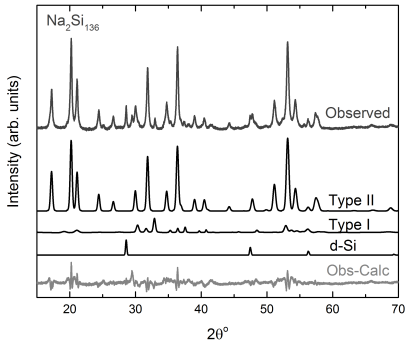

Fig. S.6 Rietveld refinement of Na_2Si_{136}.

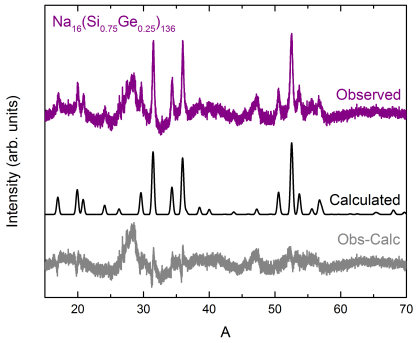

Fig. S.7 Rietveld refinement of $Na_{16}(Si_{0.75}Ge_{0.25})_{136}$. The amorphous background was subtracted, so that the crystalline portion of the sample could be better analyzed.

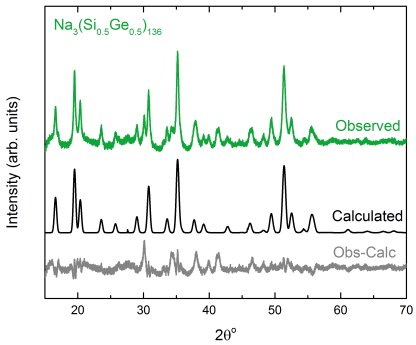

Fig. S.8 Rietveld refinement of $Na_3(Si_{0.5}Ge_{0.5})_{136}$. The amorphous background was subtracted, so that the crystalline portion of the sample could be better analyzed.

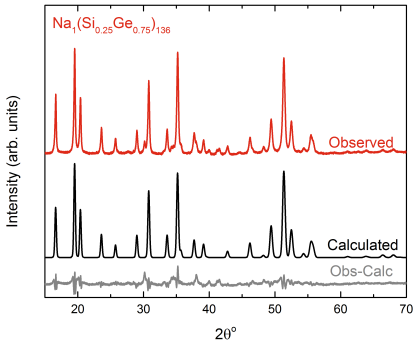

Fig. S.9 Rietveld refinement of $Na_1(Si_{0.25}Ge_{0.75})_{136}$.

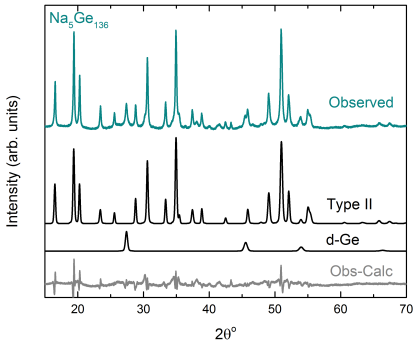

Fig. S.10 Rietveld refinement of Na_5Ge_{136}.

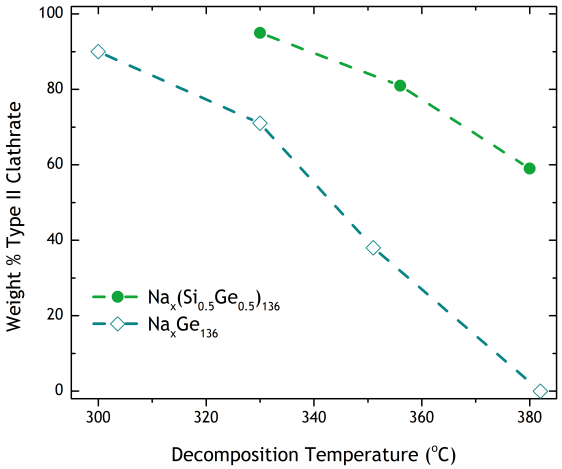

Fig. S.11 Temperature is a key parameter in controlling the phase competition between type II Si-Ge clathrates and the diamond cubic phase.

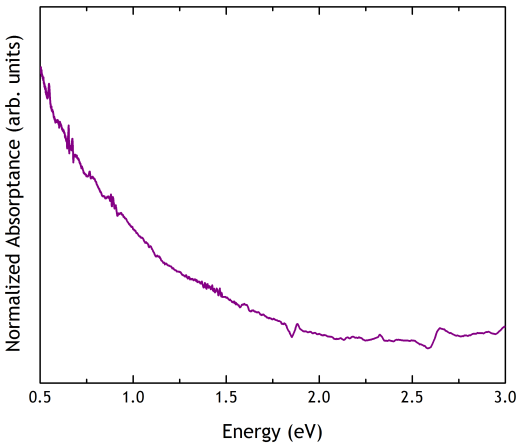

Fig. S.12 Normalized absorptance spectra for the mostly amorphous sample at y=0.25. The spectrum is dominated by free carrier absorption due to the ∼20 at% Na content of the sample.