Supporting Information

The temperatures highlighted are the one at which the phase changes are observed.

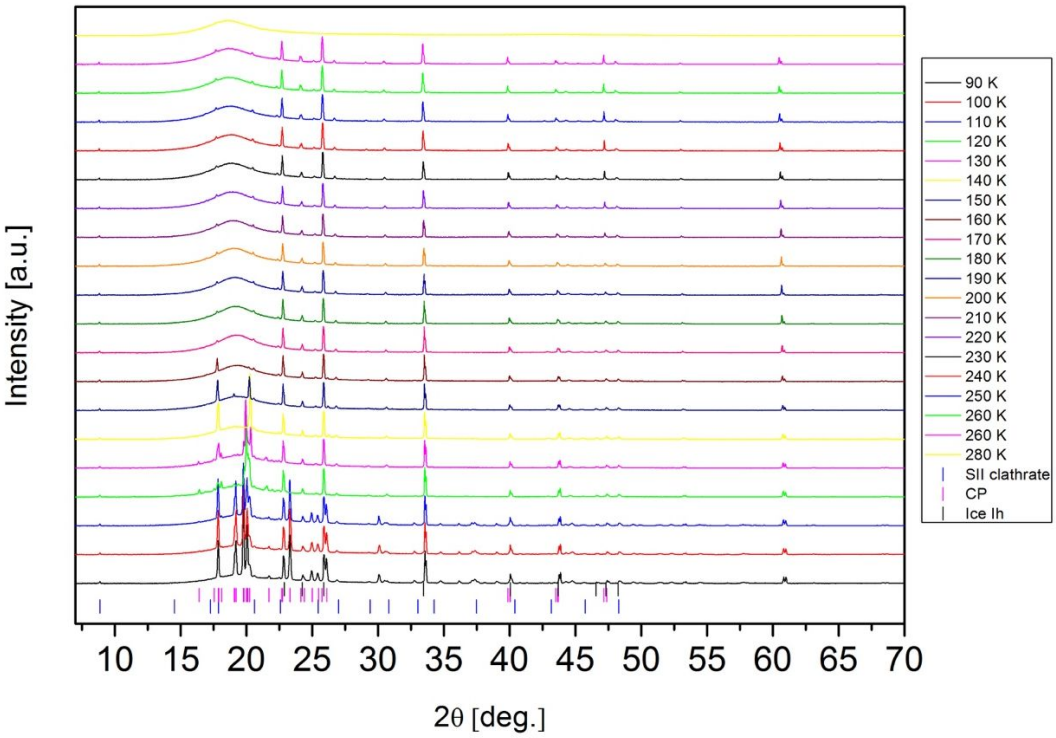

Figure S1. Full-range XRD patterns of CP clathrate hydrate.

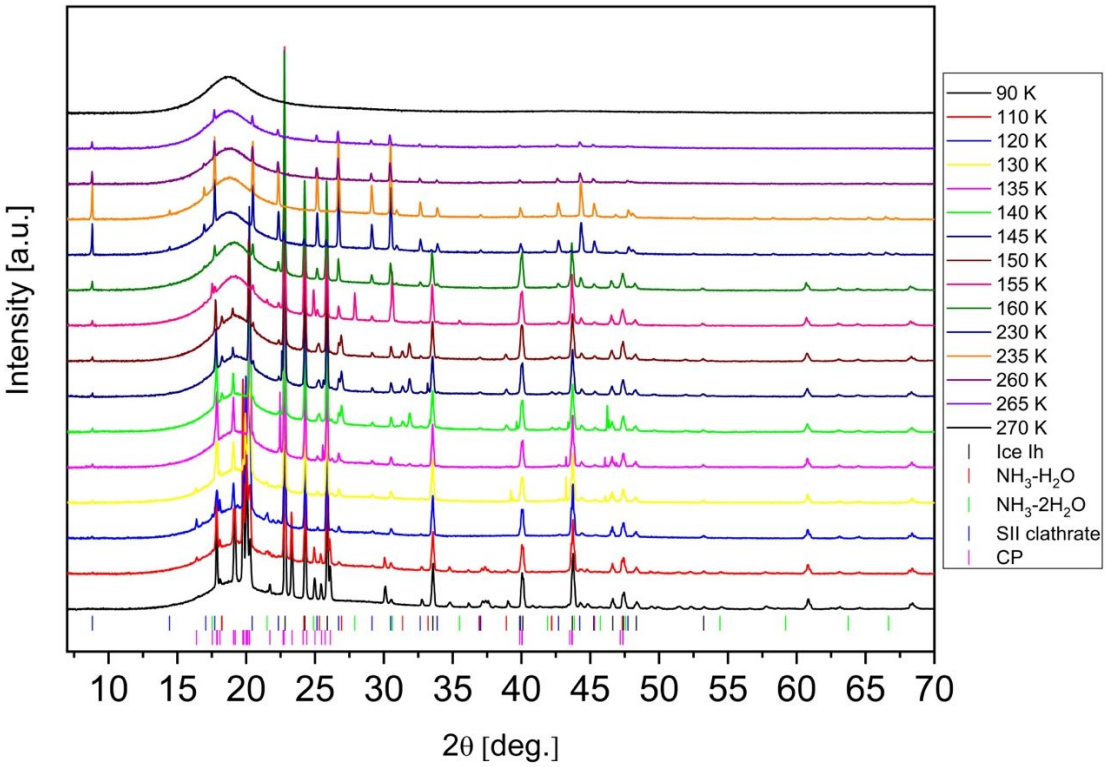

Figure S2. XRD patterns of CP clathrate formed in 10 wt% ammonia solution. CP clathrate melts at 270 K. Ammonia monohydrate is formed at 140 K, and then transformed into the dihydrate at 155 K which disappears at 160 K.

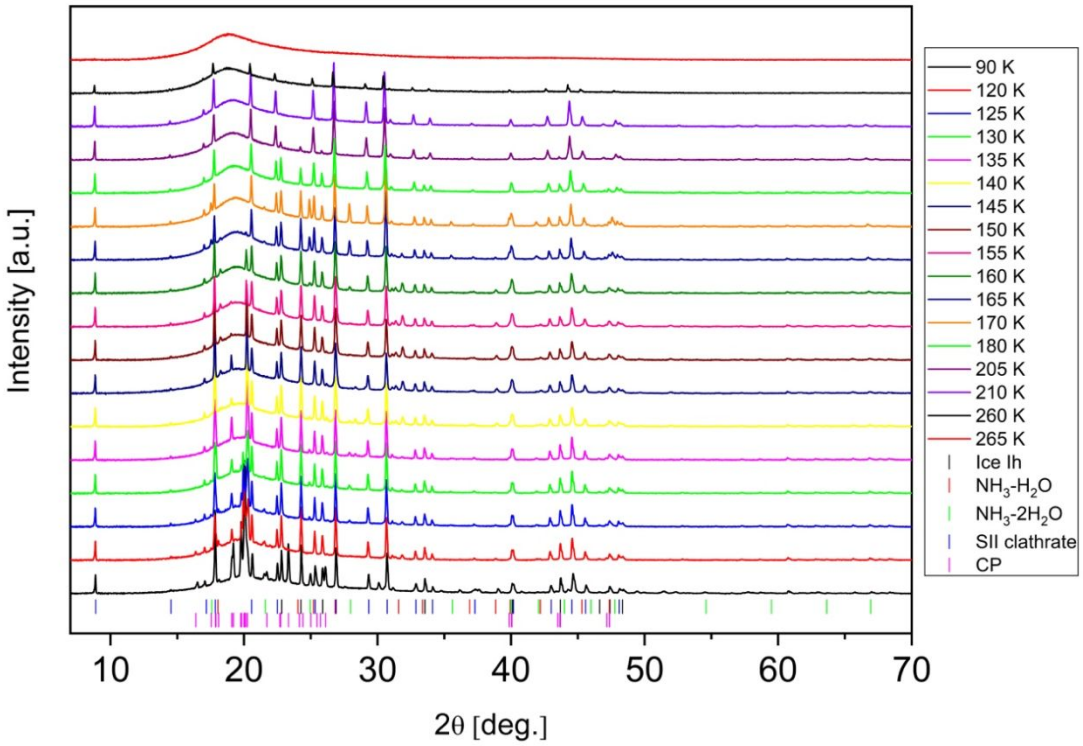

Figure S3. XRD patterns of CP clathrate grown in a 17 wt% ammonia solution overnight. CP clathrate is present at 90 K and melts at 265 K. The increase of the temperature with a smaller step (every 5 K) allows to have a more precise temperature of dissociation. It seems that the ammonia dihydrate is formed between 125 K and 140 K and then at 160 K until 175 K. There is no signature of ammonia monohydrate.

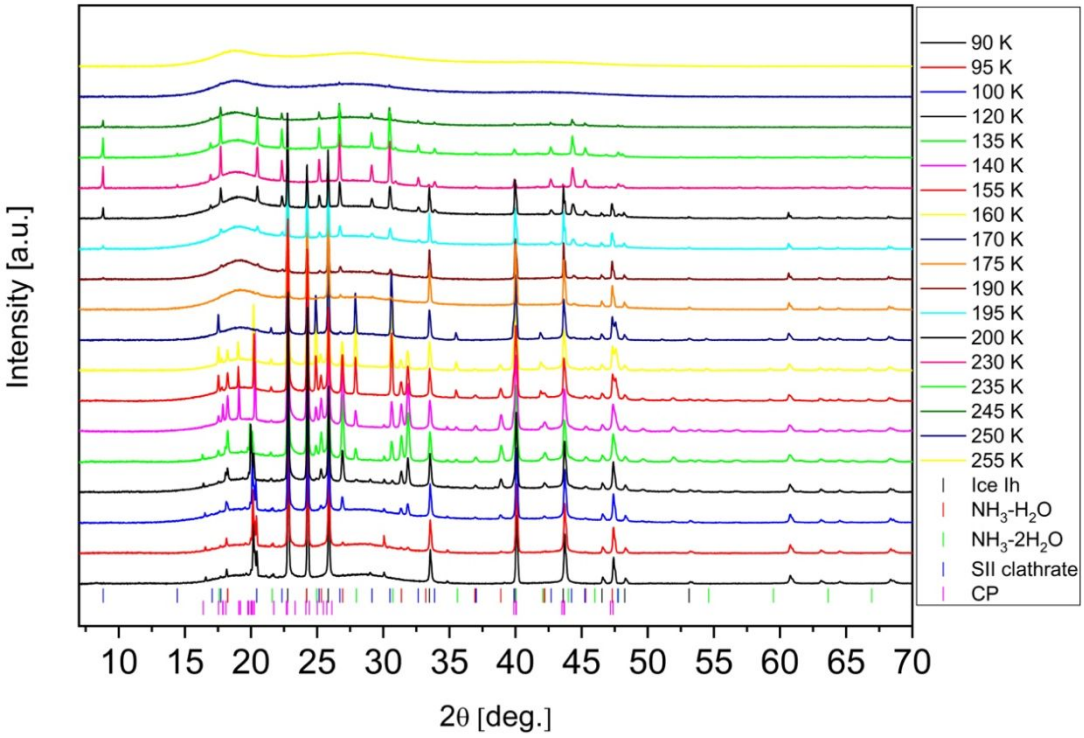

Figure S4. XRD patterns of CP clathrate formed in a 20 wt% ammonia solution. The CP clathrate is formed at 175 K and dissociated at 250 K. The ammonia monohydrate is formed from 95 K and melts at 170 K. The ammonia dihydrate is formed at 120 K to 170 K and melts at 175 K.

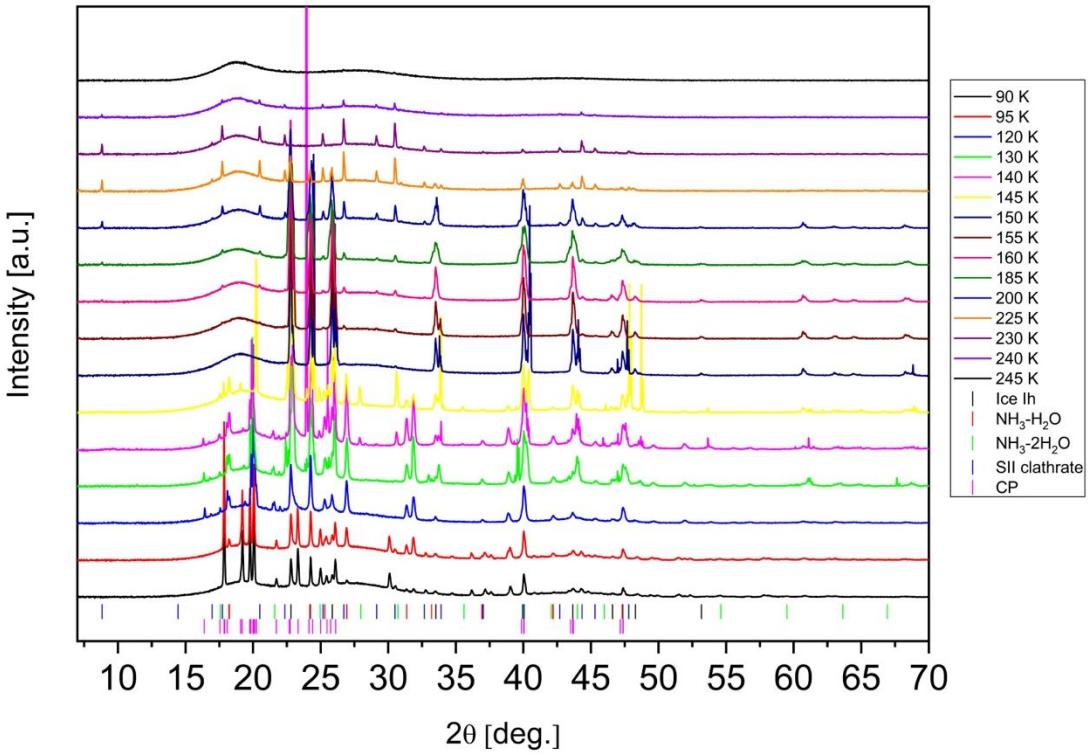

Figure S5. XRD patterns of CP clathrate formed in 23 wt% ammonia solution. The CP clathrate hydrate is formed at 160 K and dissociated at 245 K. The ammonia monohydrate is present between 95 K and 150 K, and ammonia dihydrate between 140 K and 150 K.

It is important to note that the behavior of ammonia hydrate phases varies significantly depending on the ammonia concentration. This could be due to the fact that the system may not be at the thermal equilibrium. Yarger et al.[1] mentioned this thermal equilibrium in their work showing that if the increase of the temperature is too fast (2 degrees/min) during a DSC experiment with ammonia-water system, the data are not reproducible. Moreover, a heating rate that is too slow can also cause the outgassing of ammonia from the sample. However, during DSC experiments a heating rate of 1K/min has been used and the same results have been observed about ammonia hydrates phases without no change on the CP clathrate sample. In our XRD sample, the heating rate is higher than the DSC experiments, with 10 min of stabilization at each temperature.

(1) Yarger, J.; Lunine, J. I.; Burke, M. Calorimetric Studies of the Ammonia-Water System with Application the the Outer Solar System. *J. Geophys. Res.* **1993**, *98*, 13109-13117.

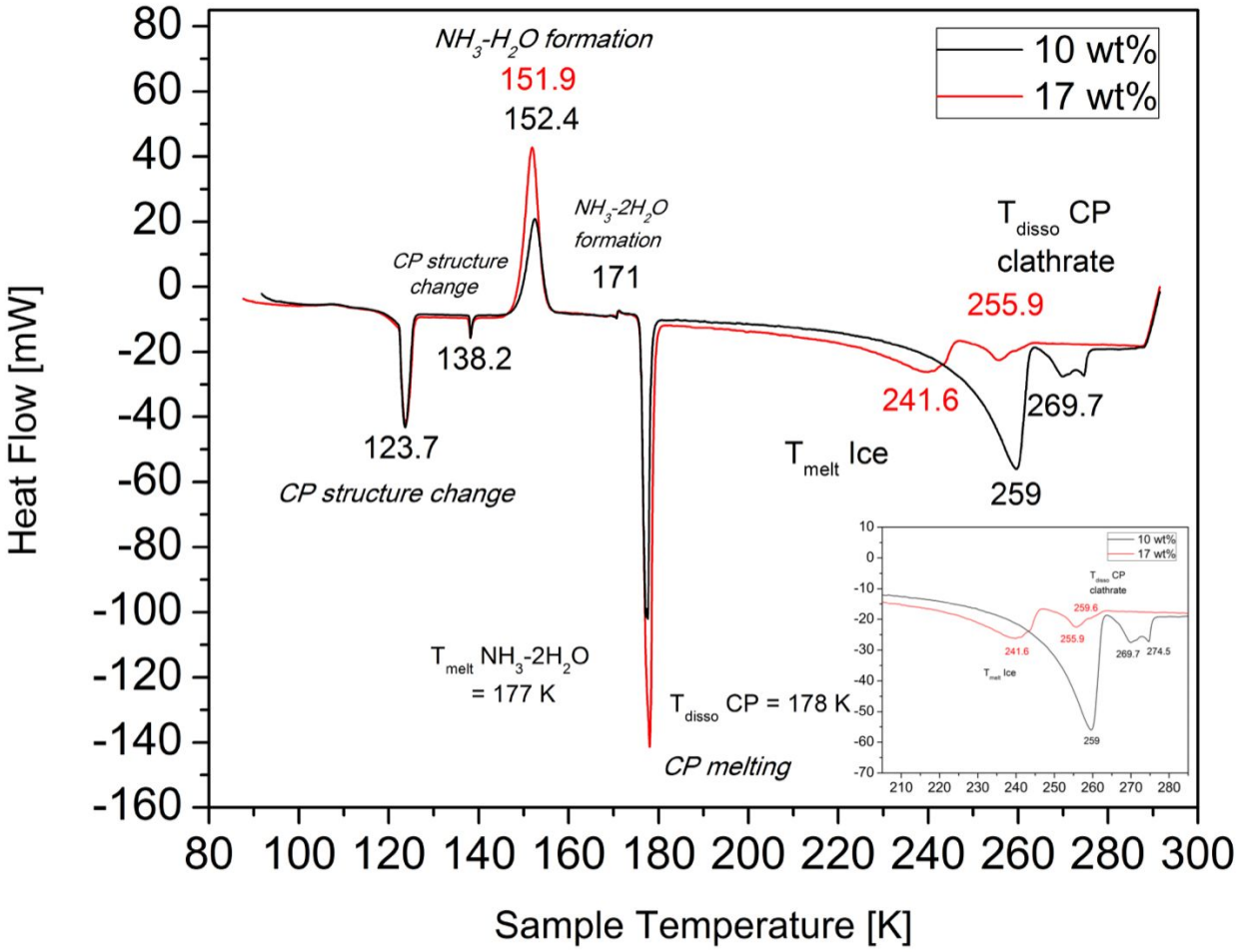

Figure S6. DSC thermograms of the CP clathrate formed within ammonia solution concentrated at 10 wt% and 17 wt %. These two samples were first equilibrated at 254 K and 264 K, respectively, to limit the isolation of regions with different NH_3 concentrations within the samples. This clearly shows the impact of sample growth temperature on the intensities of the dissociation peaks in the thermograms.

2θ	CP-H2O	NH_3 10%	NH_3 17%	NH_3 17% (growth)	NH_3 20%	NH_3 23%
	8.852	8.835	8.835	8.852	8.836	8.835
	14.48	14.452	14.452	14.48	14.429	14.452
	16.997	16.963	16.963	16.997	17.062	16.963
	17.758	17.724	17.724	17.758	17.719	17.724
	20.533	20.493	20.493	20.533	20.436	20.493
	22.398	22.354	22.354	22.398	22.333	22.354
	25.217	25.167	25.167	25.217	25.149	25.167
	26.774	26.721	26.721	26.774	26.719	26.721
	29.198	29.14	29.14	29.198	29.139	29.14
	30.568	30.507	30.507	30.568	30.502	30.507
	32.736	32.671	32.671	32.736	32.644	32.671
	33.977	33.909	33.909	33.977	33.878	33.909
	37.109	37.034	37.034	37.109	37.027	37.034
	40.028	39.947	39.947	40.028	39.89	39.947
	42.78	42.693	42.693	42.78	42.692	42.693
	44.43	44.339	44.339	44.43	44.231	44.339
	45.396	45.303	45.303	45.396	45.246	45.303
	47.9	47.801	47.801	47.9	47.742	47.801

h, k, l	CP-H2O	NH_3 10%	NH_3 17%	NH_3 17% (growth)	NH_3 20%	NH_3 23%
	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1
	2,2,0	2,2,0	2,2,0	2,2,0	2,2,0	2,2,0
	3,1,1	3,1,1	3,1,1	3,1,1	3,1,1	3,1,1
	2,2,2	2,2,2	2,2,2	2,2,2	2,2,2	2,2,2
	4,0,0	4,0,0	4,0,0	4,0,0	4,0,0	4,0,0
	3,3,1	3,3,1	3,3,1	3,3,1	3,3,1	3,3,1
	4,2,2	4,2,2	4,2,2	4,2,2	4,2,2	4,2,2
	3,3,3	3,3,3	3,3,3	3,3,3	3,3,3	3,3,3
	4,4,0	4,4,0	4,4,0	4,4,0	4,4,0	4,4,0
	5,3,1	5,3,1	5,3,1	5,3,1	5,3,1	5,3,1
	6,2,0	6,2,0	6,2,0	6,2,0	6,2,0	6,2,0
	5,3,3	5,3,3	5,3,3	5,3,3	5,3,3	5,3,3
	7,1,1	7,1,1	7,1,1	7,1,1	7,1,1	7,1,1
	7,3,1	7,3,1	7,3,1	7,3,1	7,3,1	7,3,1
	7,3,3	7,3,3	7,3,3	7,3,3	7,3,3	7,3,3
	6,6,0	6,6,0	6,6,0	6,6,0	6,6,0	6,6,0
	5,5,5	5,5,5	5,5,5	5,5,5	5,5,5	5,5,5
	7,5,3	7,5,3	7,5,3	7,5,3	7,5,3	7,5,3

Table S1. Miller indices and 2θ positions of each sample used to calculate lattice parameters.