Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Non-typical sequence of phase transitions in $(NH_4)_3GeF_7$: Optical and structural characterization

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Table 1S. Fractional atomic coordinates and isotropic displacement parameters (Å^2) of $(NH_4)_3GeF_7$

	x	*y*	*z*	B_{iso}
*P*4/*mbm* (G_1 phase) at T = 303 K				
Ge1	0	0.5	0	1.4 (2)
F1	0	0	0.5	6.2 (2)
F2	0.3556 (7)	0.8556 (7)	0	6.2 (2)
F3	0.1019 (6)	0.6019 (6)	0.2112 (9)	6.2 (2)
N1	0	0	0	4.2 (3)
N2	0.2832 (7)	0.7832 (7)	0.5	4.2 (3)
Pbam (G_2 phase) at T = 273 K				
Ge1	0	0.5	0	2.0 (2)
Ge2	0	0	0	2.0 (2)
F1	0.250 (1)	0.257 (1)	0.5	6.4 (2)
F2	-0.057 (1)	0.136 (1)	0	6.4 (2)
F3	0.1456 (9)	0.498 (2)	0	6.4 (2)
F4	-0.007 (1)	0.4057 (8)	0.227 (1)	6.4 (2)
F5	0.1026 (6)	0.0302 (9)	0.194 (1)	6.4 (2)
N1	0.245 (2)	0.227 (1)	0	3.1 (2)
N2	-0.016 (1)	0.211 (2)	0.5	3.1 (2)
N3	0.213 (1)	0.492 (2)	0.5	3.1 (2)
$P2_1/c$ (G_3 phase) at T = 243 K				
Ge1	0	0	0	1.7 (1)
Ge2	0	0.5	0	2.0 (1)
F1	0.522 (2)	0.260 (1)	0.2656 (8)	4.03 (8)
F2	-0.016 (3)	0.1431 (7)	0.023 (1)	4.03 (8)
F3	-0.029 (2)	0.5612 (9)	0.1412 (8)	4.03 (8)
F4	0.177 (2)	0.392 (1)	0.049 (1)	4.03 (8)
F5	0.186 (2)	0.026 (1)	-0.108 (1)	4.03 (8)
F6	0.238 (2)	0.591 (1)	-0.027 (1)	4.03 (8)
F7	0.256 (2)	-0.008 (1)	0.0841 (9)	4.03 (8)
N1	-0.046 (2)	0.275 (1)	0.251 (1)	1.9 (2)
N2	0.493 (4)	0.206 (1)	-0.007 (2)	1.9 (2)

N3	0.506 (3)	0.018 (1)	0.285 (1)	1.9 (2)
$Pa\bar{3}$ (G_4 phase) at T = 143 K				
Ge1	0	0	0	1.26 (6)
Ge2	0.5	0	0	1.16 (6)
F1	0.1533 (2)	-0.0071 (3)	0.0120 (4)	2.33 (8)
F2	0.3880 (3)	0.0920 (3)	0.0527 (2)	1.30 (8)
F3	0.2537 (3)	0.2537 (3)	0.2537 (3)	1.97 (7)
N	0.2412 (4)	0.2324 (5)	0.4810 (4)	2.3 (1)
H1	0.2793 (4)	0.1701 (5)	0.5064 (4)	4
H2	0.2581 (4)	0.2444 (5)	0.4066 (4)	4
H3	0.1652 (4)	0.2210 (5)	0.4887 (4)	4
H4	0.2622 (4)	0.2941 (5)	0.5225 (4)	4

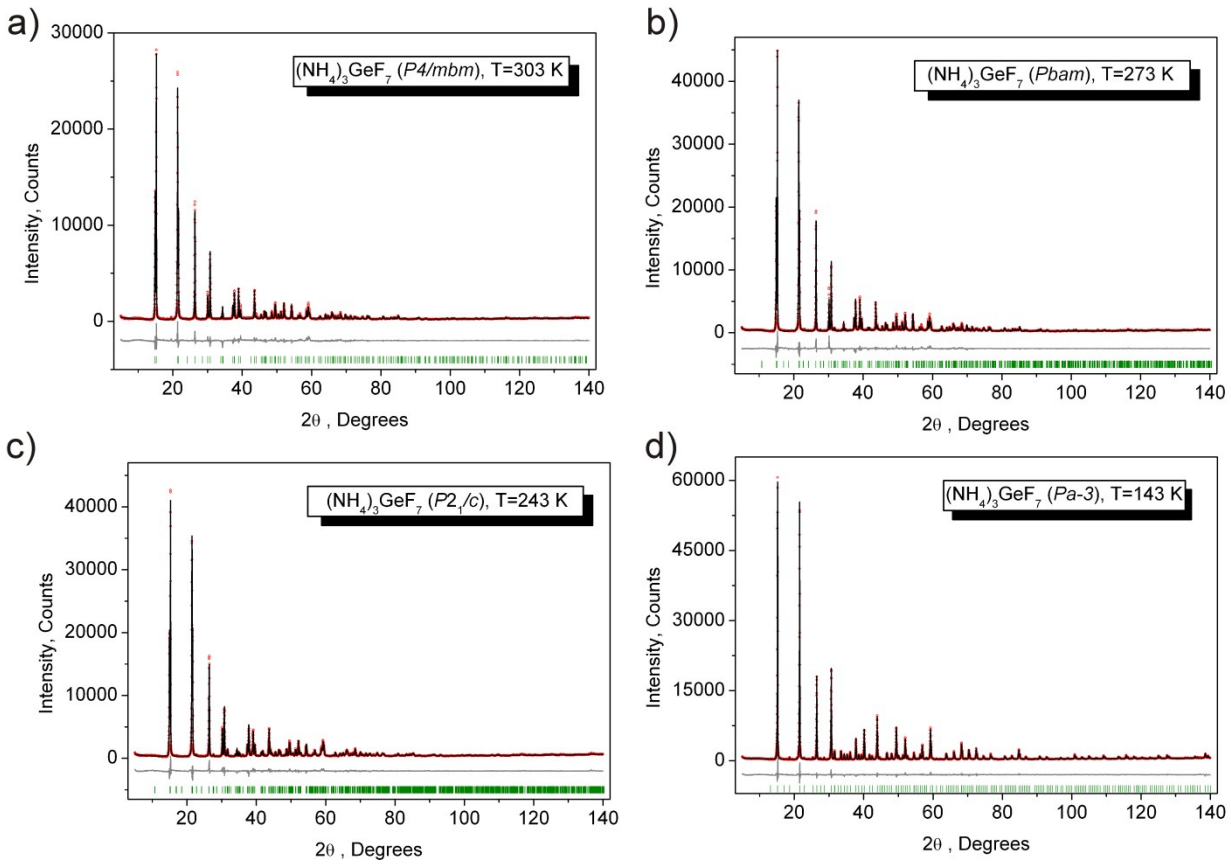

Figure 1S. Difference Rietveld plot of $(NH_4)_3GeF_7$ at: a) T = 303 K in G_1 phase (*P4/mbm*); b) T = 273 K in G_2 phase (*Pbam*); c) T = 243 K in G_3 phase ($P2_1/c$); d) T = 143 K in G_4 phase ($Pa\bar{3}$).

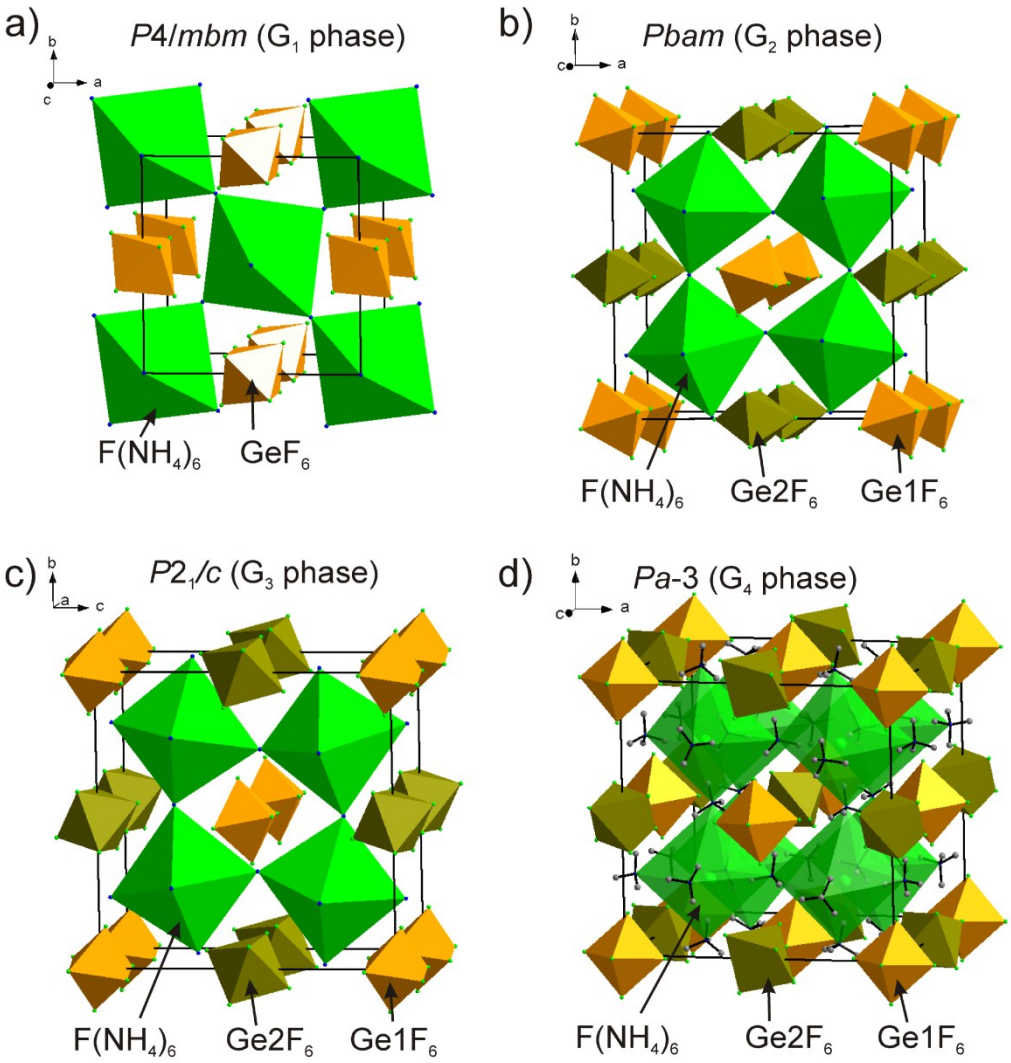

Figure 2S. Crystal structures of $(NH_4)_3GeF_7$: a) G_1 phase (*P4/mbm*) at T = 303 K; b) G_2 phase (*Pbam*) at T = 273 K, c) G_3 phase ($P2_1/c$) at T = 243 K; d) G_4 phase ($Pa\bar{3}$) at T = 143 K.

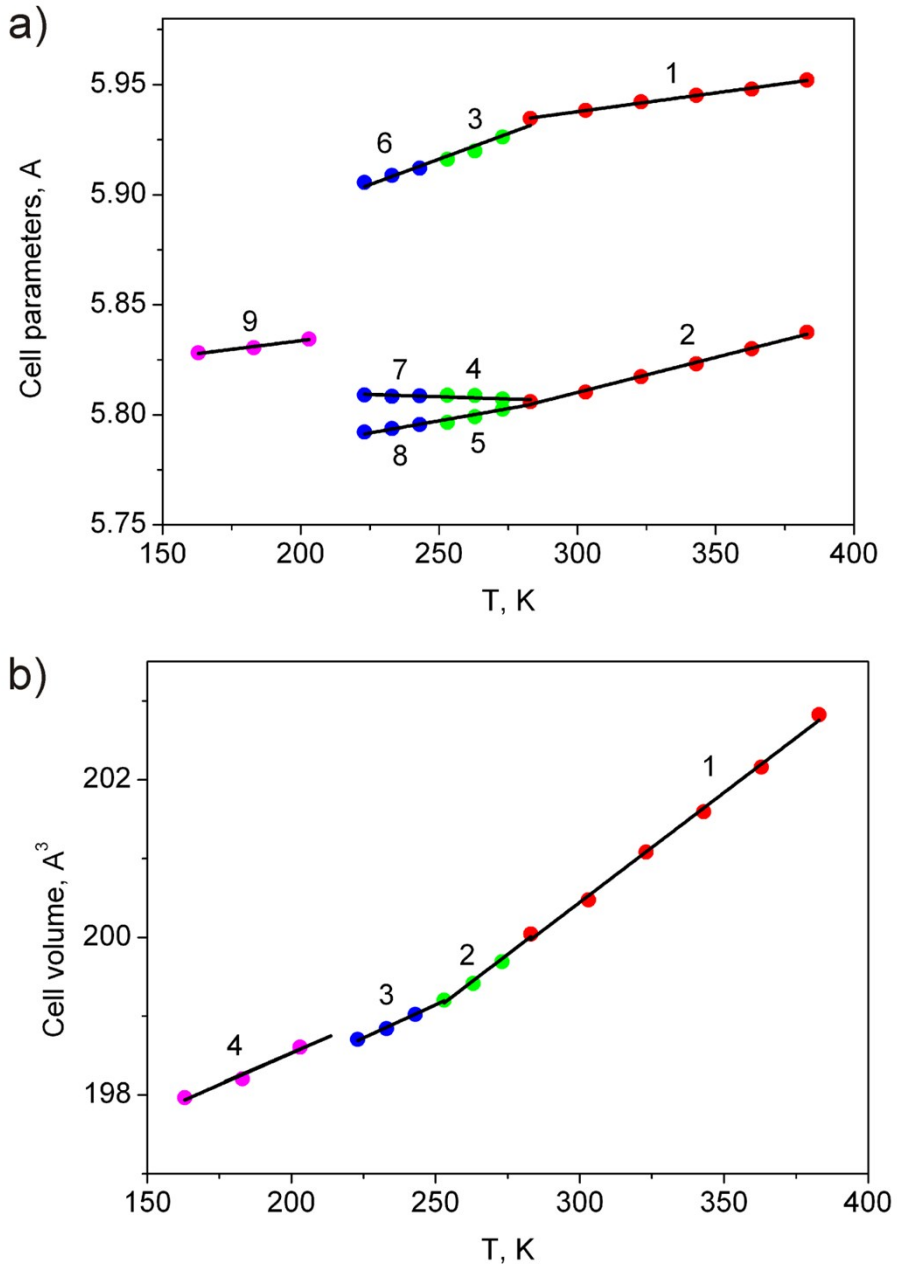

Figure 3S. Temperature dependence of: a) the cell parameters c (1) and $a/2^{1/2}$ (2) in G_1 phase, c (3), $a/2$ (4) and $b/2$ (5) in G_2 phase, a (6), $c/2$ (7) and $b/2$ (8) in G_3 phase, $a/2$ in G_4 phase; b) the cell volume of formula unit $V/2$ (1) in G_1 phase, $V/4$ (2) in G_2 phase, $V/4$ in G_3 phase, $V/8$ in G_4 phase.