Supporting Information:

A Germanate with a Collapsible Open-Framework

A. Ken Inge,[,†] Kirsten E. Christensen,[‡] Tom Willhammar,[†] and Xiaodong Zou[*,†]*

†Inorganic and Structural Chemistry and Berzelii Center EXSELENT on Porous Materials, Stockholm University, SE-106 91 Stockholm, Sweden, ‡Department of Chemistry, University of Oxford, OX1 3TA, United Kingdom

Email: xzou@mmk.su.se (X.D.Z.), andrew.inge@mmk.su.se (A.K.I.)

Contents:

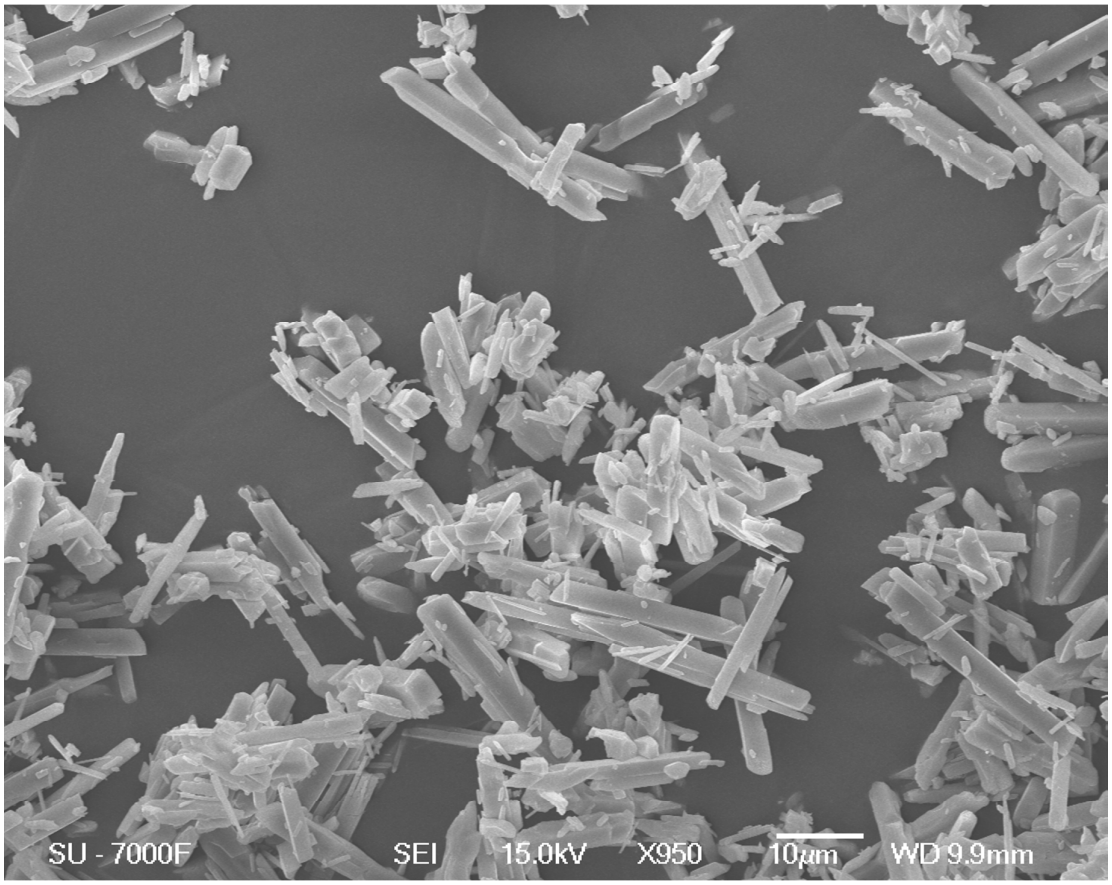

Figure S1. A scanning electron micrograph of SU-65 crystals.

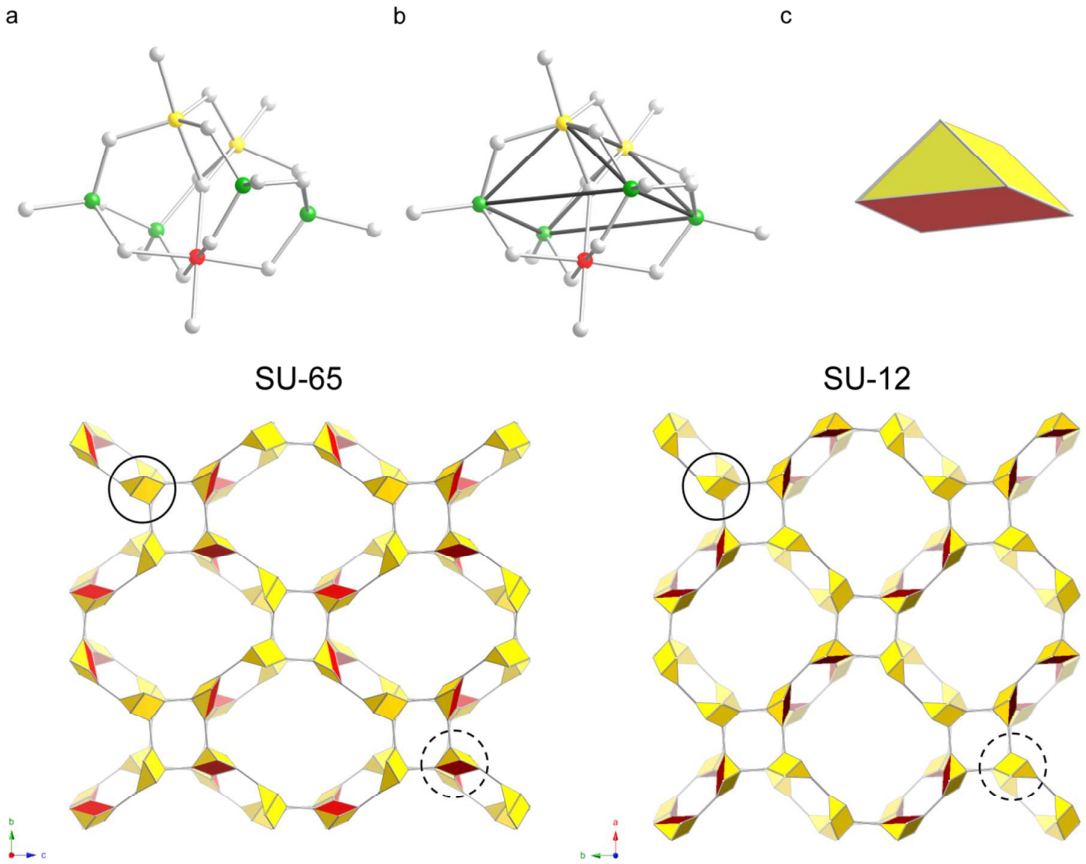

Figure S2. (Top) Simplification of the Ge_7 cluster into a trigonal prism. (a) Ball-and-stick model of the Ge_7 cluster. Oxygen and fluorine atoms are shown in white while tetrahedral, trigonal bipyramidal and octahedral germanium atoms are shown in green, yellow and red respectively. (b) Transformation of the ball-and-stick model to the trigonal prism representation. (c) Vertices of the trigonal prism correspond to germanium atoms, however the octahedrally coordinated germanium atom has been omitted for clarity in the framework models. (Bottom) The framework structures of SU-65 and SU-12 with the trigonal prism representation. Half of the clusters/trigonal prisms in SU-65 have the same orientation as in SU-12. Ge_7 clusters with the same orientation in both structures are outlined by solid circles, while dashed circles outlines Ge_7 clusters with different orientations.

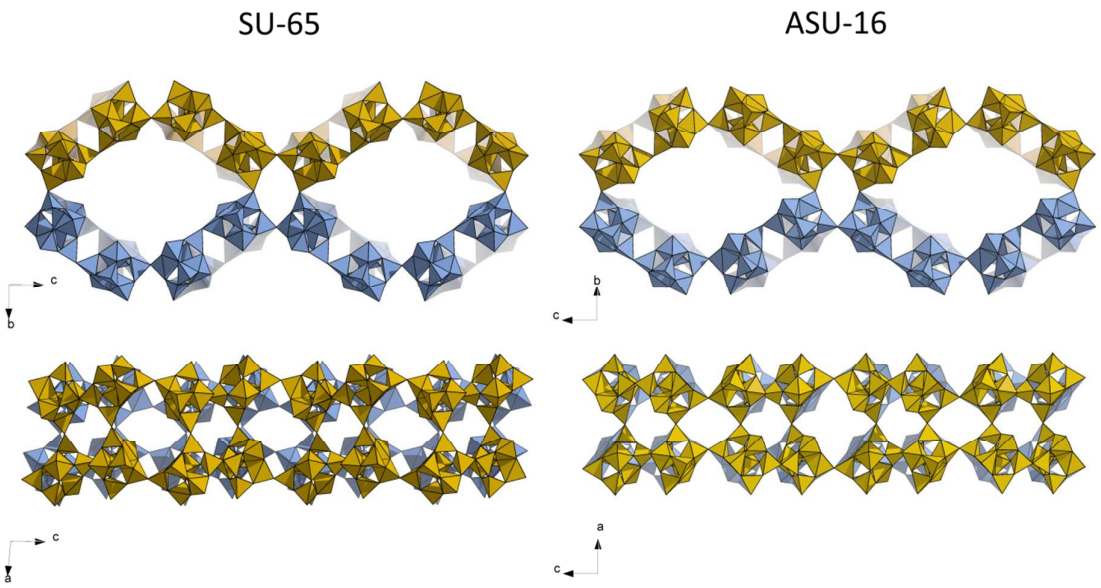

Figure S3. Framework symmetry and rings of SU-65 compared to ASU-16. (Top) Projection down the 24-ring channels. (Bottom) Projection perpendicular to the 24-ring channels. In SU-65 12-rings overlap 8-ring down this projection. In ASU-16, rings of the same size overlap down this projection and are related by a 2-fold rotation along the 24-ring channel. Regions of the frameworks are colored to clarify overlying and underlying layers.

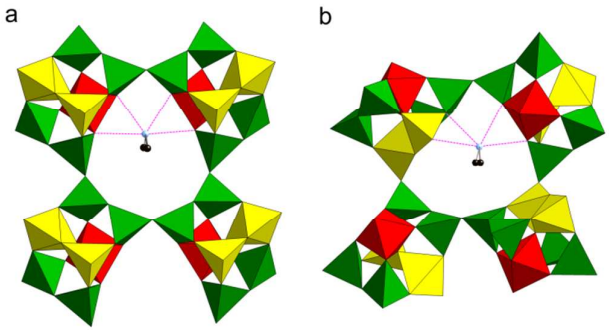

Figure S4. Comparison of 10-rings formed by Ge_7 clusters and the location of dimethylammonium cation in the 10-ring a) ASU-12 and b) SU-65.

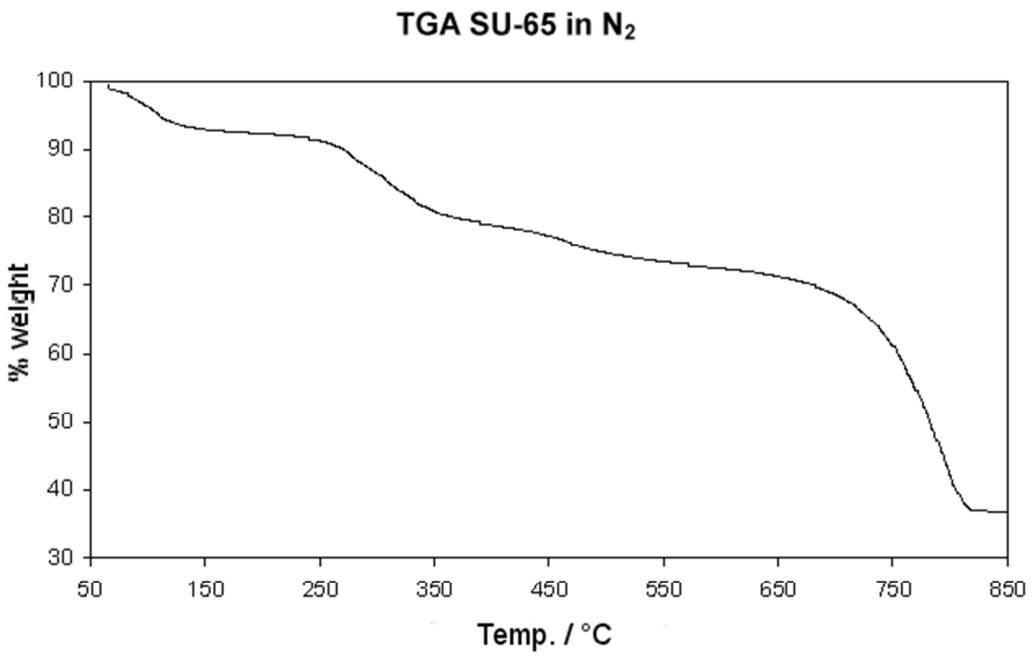

Figure S5. TG trace of SU-65 in nitrogen.

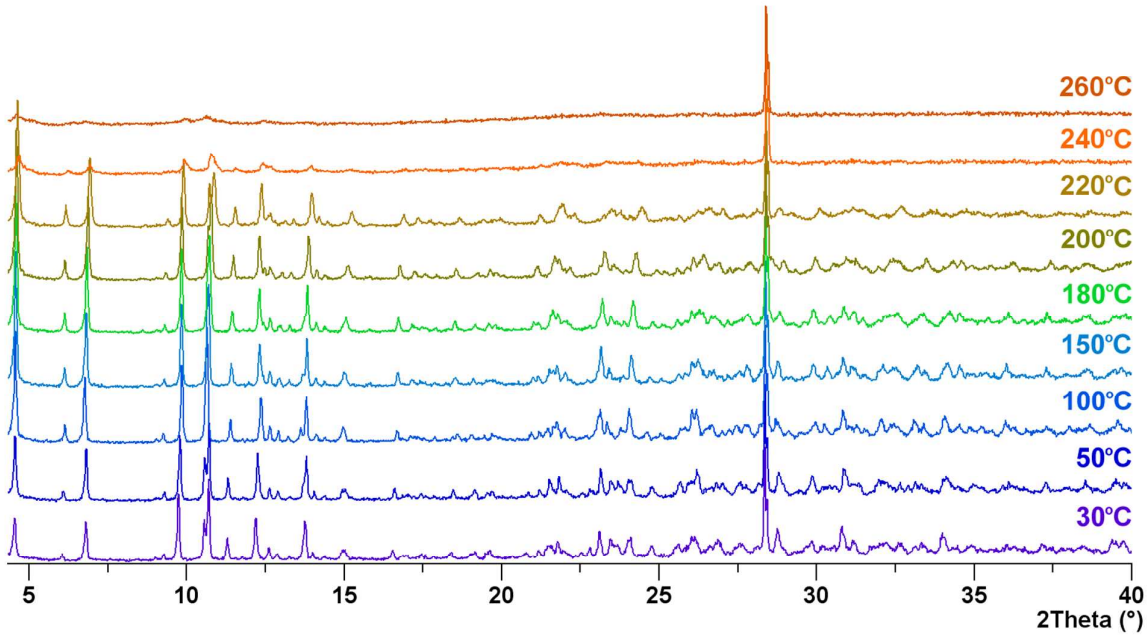

Figure S6. *In situ* XPD patterns of SU-65 collected in air with divergent slits and a silicon standard (strong peak at 2θ = 28.35°).

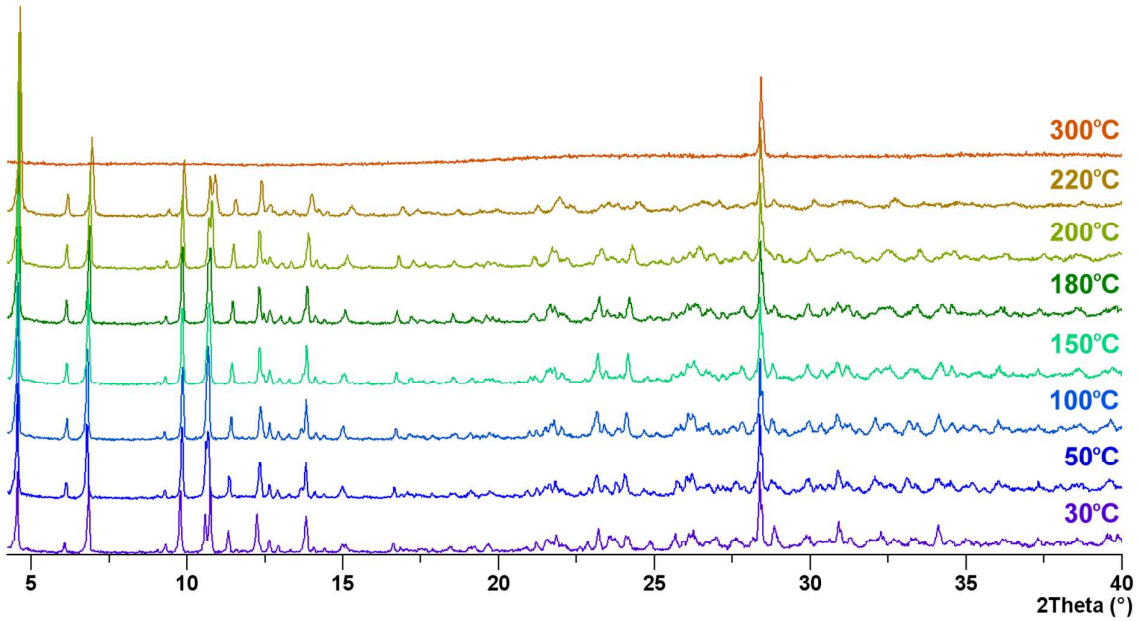

Figure S7. *In situ* XPD patterns of SU-65 collected in nitrogen with divergent slits and a silicon standard (strong peak at 2θ = 28.35°).

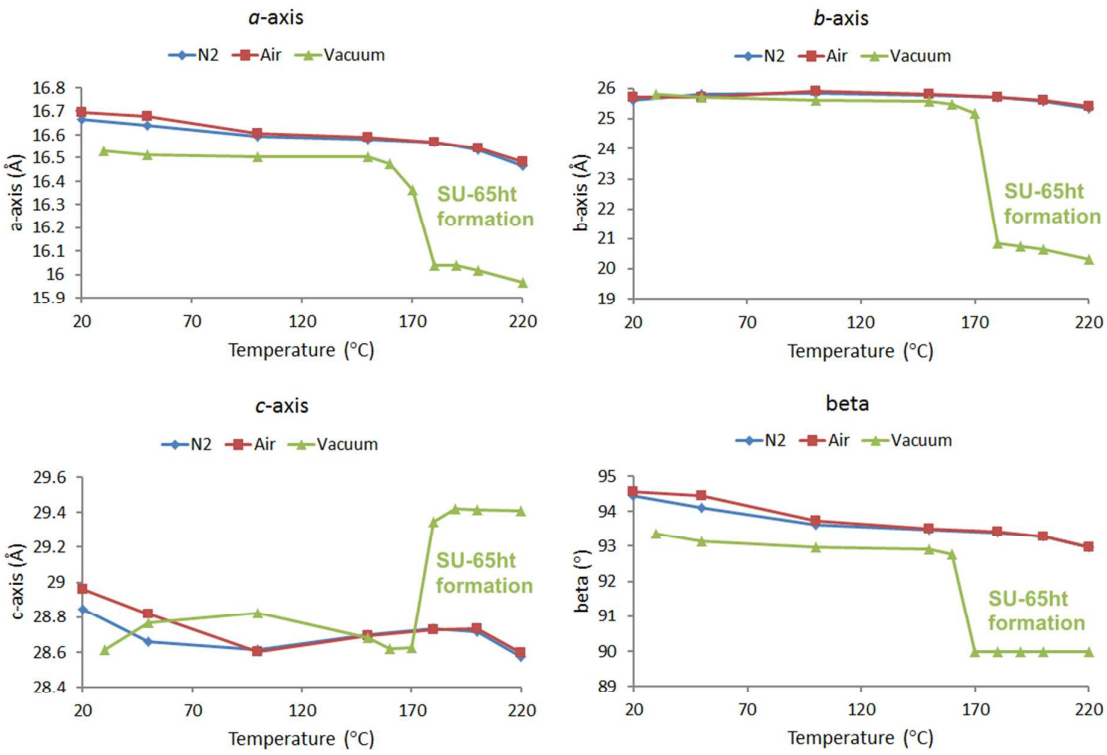

Figure S8. Comparison of the lattice parameters of SU-65 and SU-65ht in nitrogen, air and under vacuum at various temperatures as determined by the Le Bail method from *in situ* XPD data. SU-65ht forms between 170 - 180 °C under vacuum.

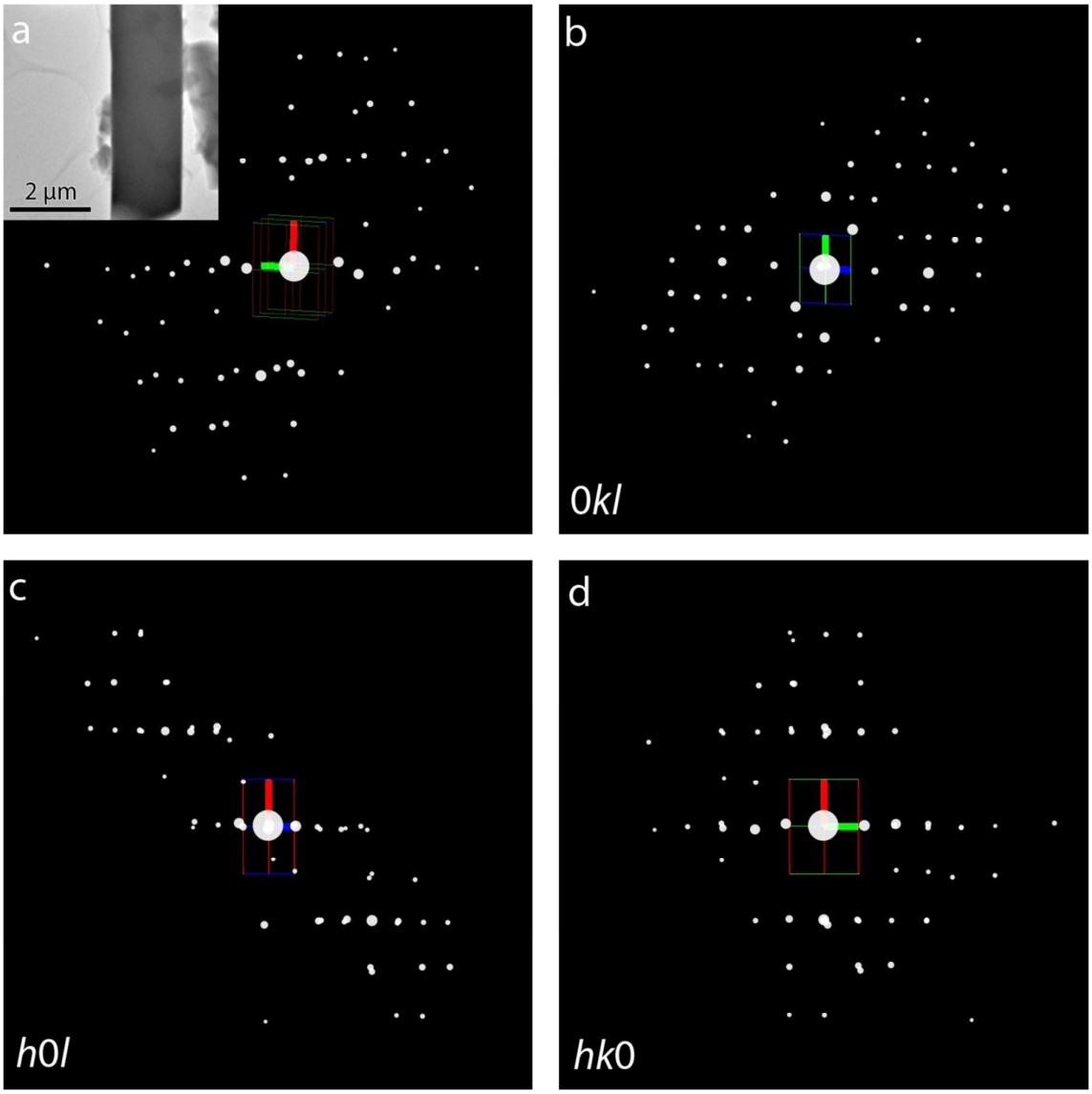

Figure S9. (a) The 3D reciprocal lattice of SU-65ht reconstructed from the RED data, from which the unit cell parameters of SU-65ht were deduced. Inset is the crystal from which the RED data was collected. (b-d) 2D sections cut from the reconstructed 3D reciprocal lattice shown as (b) 0*kl* (c) *h*0*l* and (d) *hk*0. Projected views of 2 x 2 x 2 unit cells shown in each of the panels with color coding *a** (red), *b** (green) and *c** (blue).

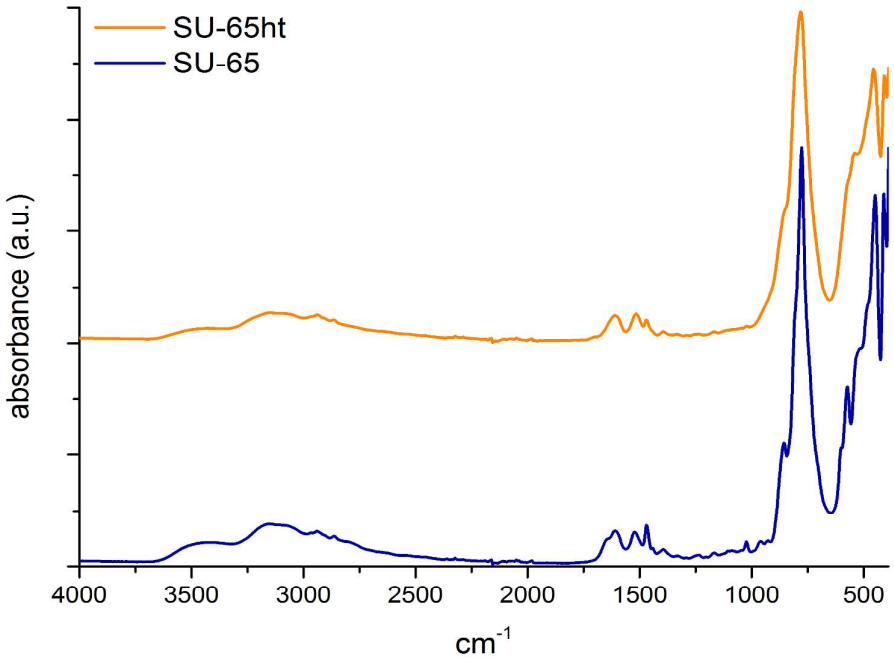

Figure S10. FT-IR spectra of SU-65 and SU-65ht. Bands below 1000 cm^{-1} correspond to Ge-O framework vibrational modes.

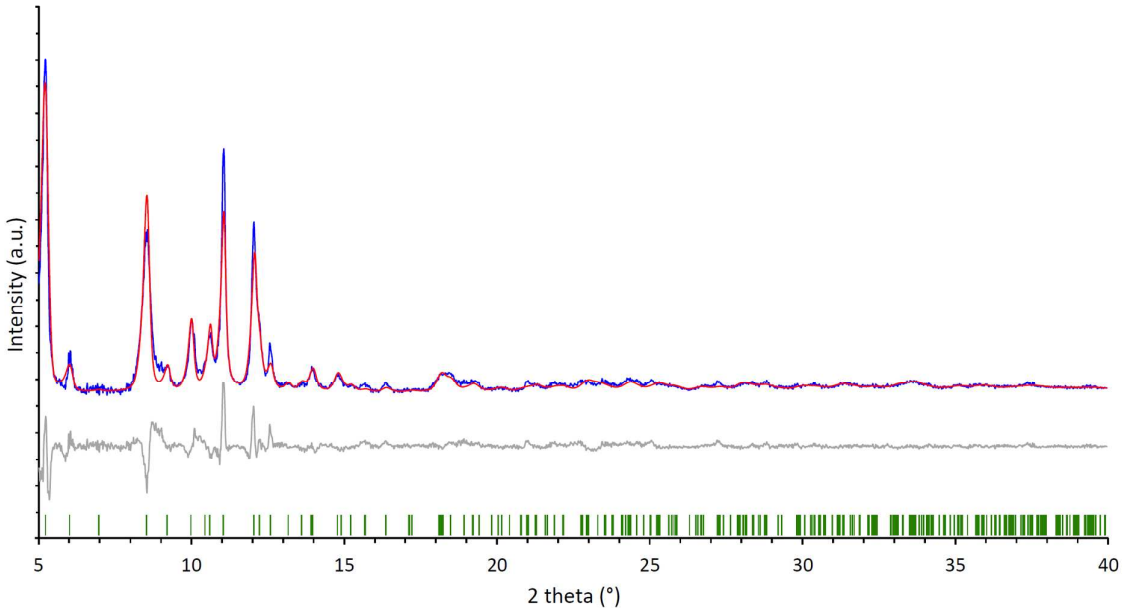

Figure S11. Observed, calculated and difference XPD patterns for the Rietveld refinement of SU-65ht shown in blue, red and grey respectively.

Table S1. Crystallographic data and refinement details on SU-65.

identification code	SU-65
empirical formula	$\|NC_2H_8\|\|N_2C_6H_{18}\|[Ge_7O_{14.5}F_2]\cdot 4H_2O$
formula weight	1528.26
temperature	100 K
wavelength	0.6889 Å
crystal system	monoclinic
space group	*I*2/*a* (No. 15)
unit cell dimensions	a = 16.7771 (4) Å
	b = 25.4780 (4) Å
	c = 29.3361 (9) Å
	β = 94.501 (3) °
volume	12501.0 (5) $Å^3$
Z	16
density (calculated)	1.862 g/cm^3
absorption coefficient	6.006 mm^{-1}
$F(000)$	6632
crystal size	0.020 × 0.005 × 0.005 mm^3
θ range for data collection	0.919 to 24.52°
index ranges	$-20\leq h\leq 17$, $-30\leq k\leq 30$, $-35\leq l\leq 25$
reflections collected	34715
independent reflections	10517 [R(int) = 0.1222]
absorption correction	Multi-scan
max. and min. transmission	0.517 and 1
data / restraints / parameters	10517 / 36 / 481
goodness-of-fit on F^2	0.962
final R indices [$I>2\sigma(I)$]	$R1$ = 0.0768, w$R2$ = 0.1792
largest diff. peak and hole	1.894 and –1.655 e/$Å^3$

Table S2. Crystallographic data and Rietveld refinement details on SU-65ht.

identification code	SU-65ht
empirical formula	$\|NC_2H_8\|\|N_2C_6H_{18}\|[Ge_7O_{14.5}F_2]$
formula weight	1423.94
temperature	463 K
wavelength	1.541874 Å (Cu $K\alpha_{1,2}$)
2θ range	4.9730 – 39.9998 °
step size	0.0167 °
crystal system	monoclinic
space group	*I*2/*a* (No. 15)
unit cell dimensions	a = 16.006 (5) Å
	b = 20.693 (8) Å
	c = 29.346 (9) Å
	β = 90.00 (8) °
volume	9719 (6) $Å^3$
Z	16
Observations	2096
Contributing reflections	463
Geometric restraints	187
Positional parameters	141
R_{wp}	0.21288
R_{exp}	0.10949
R_{Bragg}	0.07703
GoF	1.944