Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Revealing the Slow Decomposition Kinetics of Type-I clathrate $Ba_8Ga_{16}Ge_{30}$

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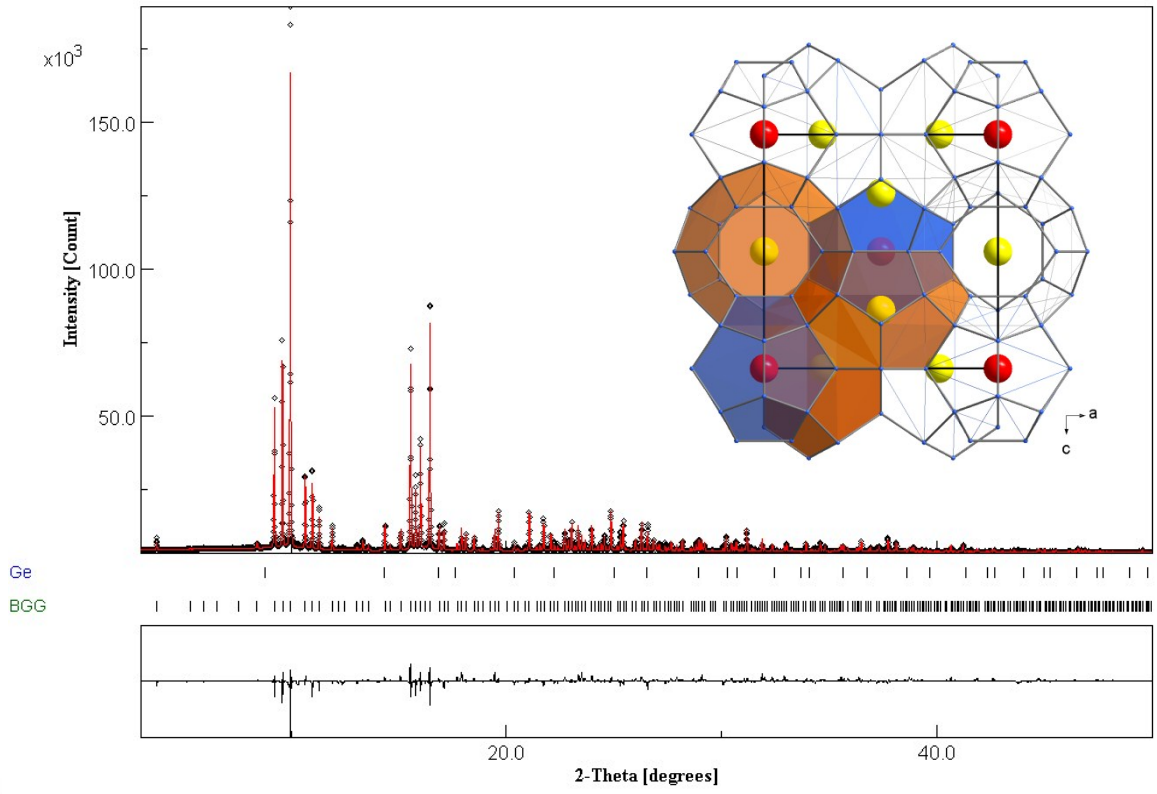


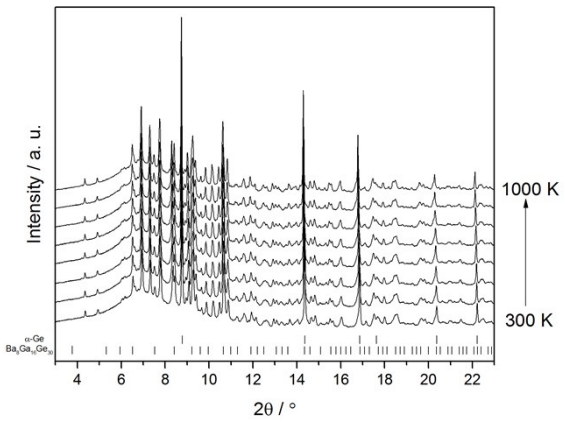
Sample / Chemical Formula	MS_1 / $Ba_8Ga_{16}Ge_{30}$
Crystal System	Cubic
Space Group	$Pm\bar{3}n$ (223)
Z	1
a / Å	10.7832(1)
V / Å^3	1247.12
Formula Weight / g	4393.084
Density, ρ_x / g cm^{-3}	5.82
Refinement Parameters	17
R_{wp}	7.12
R_p	4.32
Goodness of Fit	4.82

SI.1 Rietveld refinement plot, structure representation and information for 1_MS (SXRD data collected at SPring-8 using λ = 0.500493(7) nm); black circles represent actual data, the red line shows the calculated plot, and the difference between actual and calculated data is shown as a continuous black plot below the

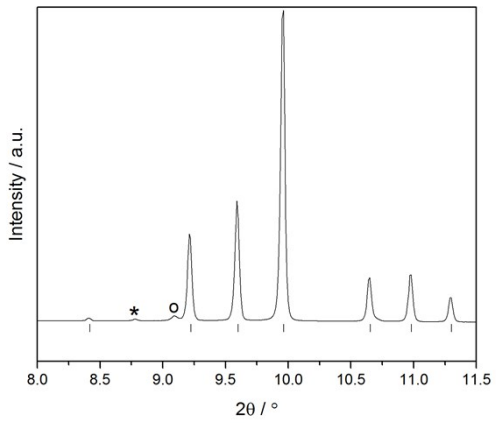
tick marks for the two phases. Inset: Representation of BGG structure viewed along the b axis showing the Ba1 (red spheres) and Ba2 (yellow spheres) atoms residing in the dodecahedron (blue) and tetrakaidecahedron (orange) cages, respectively. (Ga and Ge atoms are given as small blue spheres, and the unit cell edges are highlighted as bold lines.) The table provides the key Rietveld refinement output data. Two phases: BGG (ICSD 153737) and α-Ge (ICSD 76146), were included in the refinements, where the phase fraction of α-Ge was found to be <1% in MS_1.

Sample	**2_MS_300a**	**3_MS_400a**	**4_MS_500a**	**5_MS_600a**	**7_MS_730v**
Crystal System	Cubic				
Space Group	$Pm\bar{3}n$ (223)				
Z	1				
a / Å	10.77923(8)	10.7763(2)	10.7776(3)	10.7680(7)	10.77680(9)
Phase Fraction / %	99.9(9)	99.5(1)	59.8(2)	43.4(5)	99.5(1)
R_{wp} / %	5.76	3.63	1.62	2.20	6.34
R_p / %	3.64	2.35	1.02	1.33	3.85
R_{exp} / %	1.23	1.21	1.18	0.79	1.50
Goodness of Fit	4.69	2.99	1.37	2.80	4.24

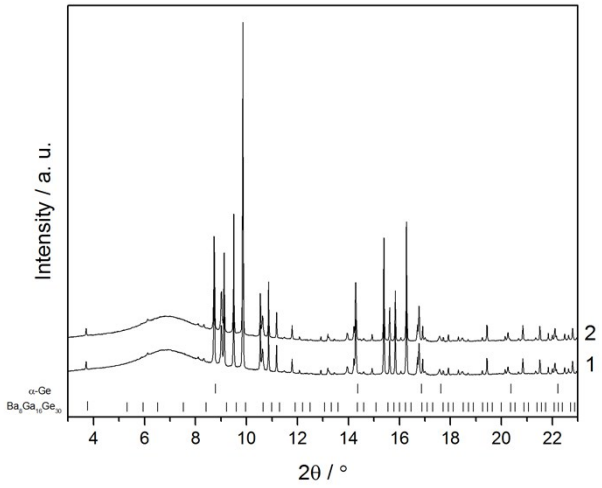
SI.2 Table of Rietveld refinement results for the BGG phase in the annealed samples. SXRD data were collected at SPring-8; λ = 0.500179(1) nm. Two phases: BGG (ICSD 153737) and α-Ge (ICSD 76146), were included in the refinements and the phase fraction of BGG is given relative to the α-Ge phase.



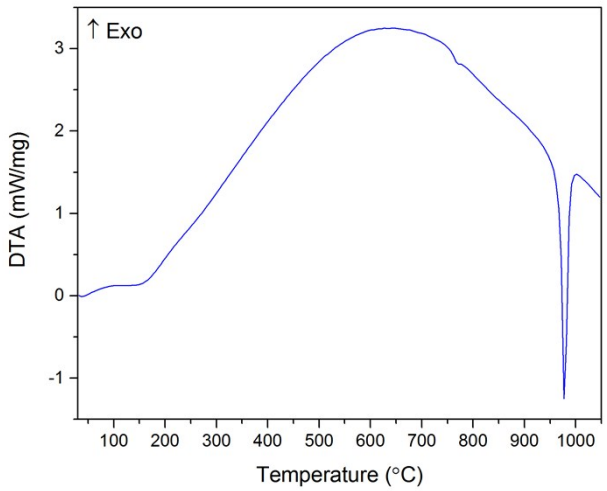
SI.3 Overlay of the variable temperature SXRD patterns collected for 7_MS_730a, where the upper and lower tick marks indicate reflection positions for α-Ge and BGG, respectively.



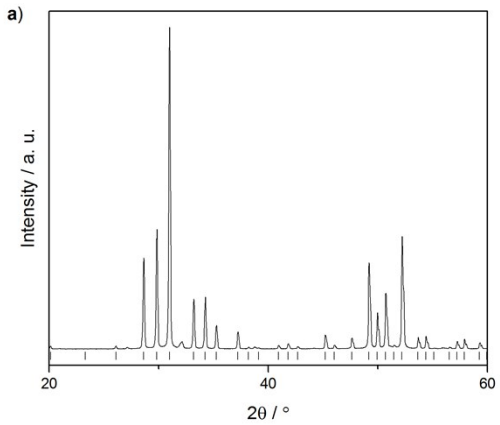
SI.4 Focussed view of the SXRD pattern for 7_MS_730v. The asterisk and circle indicate the reflections for the α-Ge and unknown impurity, respectively.



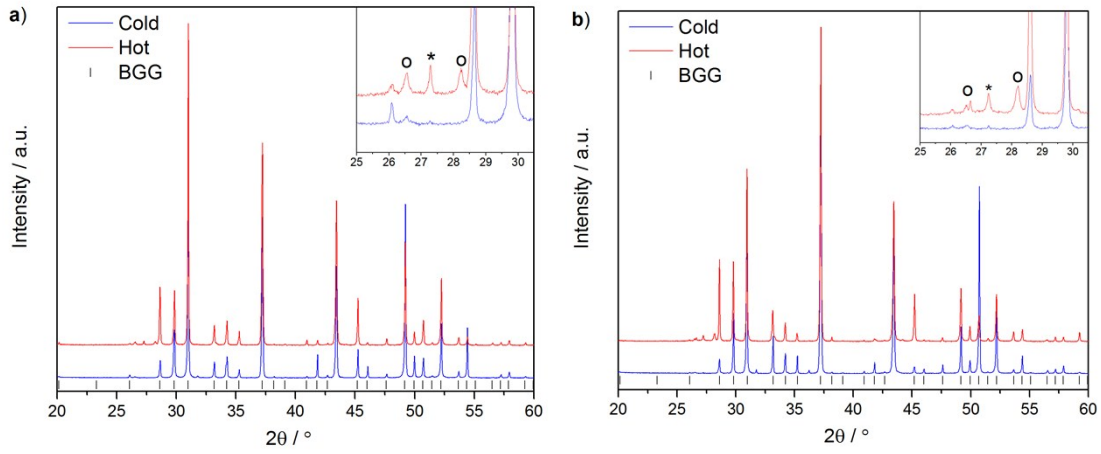
SI.5 SXRD patterns collected at 1000 °C for 7_MS_730v, where lower and upper tick marks indicate the reflection position for BGG and α-Ge phases respectively.



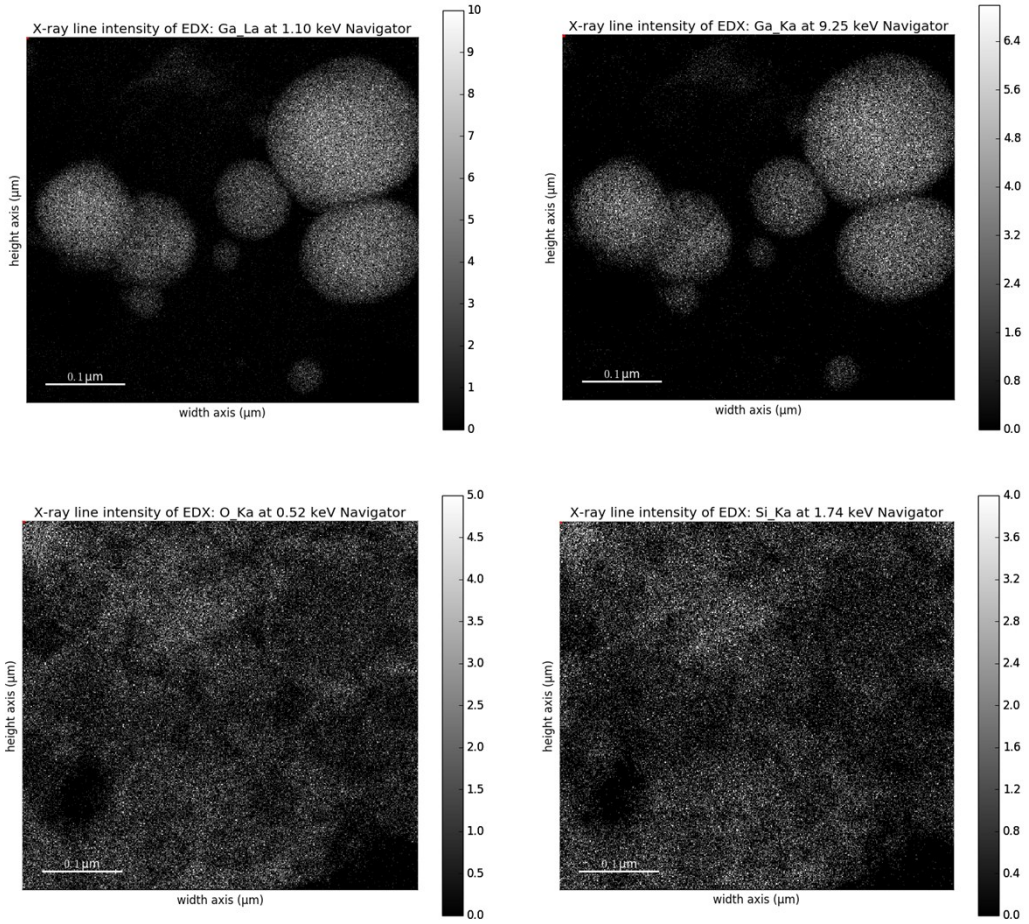
SI.6 DTA data collected for 7_MS_730v.



SI.7 a) PXRD and DTA data collected for 8_SPS. (Collected using the in-house Rigaku diffractometer (λ = 0.154056 nm.)



SI.8 Selected region of the diffraction patterns for the cold (blue) and hot (red) sides of the bulk pellet for a) 9_MS_SPScyc and b) 10_MS_SPSsus, where asterisks indicate reflections from the α-Ge phase and the circles represent those arising from unknown phase. (Collected using the in-house Rigaku diffractometer (λ = 0.154056 nm.)



SI.9 The TEM-EDS maps obtained from the ground protrusion for Ga (L_a and K_a), O (K_a) and Si (K_a).