Table S1. Atomic coordinates and isotropic displacement parameters U_{iso} for $Ba_8Al_{6.9}Si_{39.1}$ (a = 10.4647(2) Å) from multiphase Rietveld refinement (see Fig. 1 in the main text) using synchrotron X-ray diffraction data (λ = 0.43046 Å) and applying the model Ba_8Si_{46} (space group $Pm\bar{3}n$).

Atom	Site	x	y	z	U_{iso} / Å^2
Ba1	2*a*	0	0	0	0.0053(5)
Ba2	6*d*	¼	½	0	0.0161(3)
Si1	6*c*	¼	0	½	0.0154(13)
Si2	16*i*	0.1845(2)	*x*	*x*	0.0046(8)
Si3	24*k*	0	0.3023(3)	0.1173(3)	0.0088(7)

The refinement was finished at R_p = 0.114 and R_i(clathrate) = 0.065. The refinement included $BaSi_2$ and α-Si, for which profile and lattice parameters as well as the phase fractions (see Table 1 in the main text) were refined. For α-Si, the isotropic displacement parameter of the silicon site was refined to a value of U_{iso} = 0.0048(5) Å^2. For $BaSi_2$, the isotropic displacement parameters for all atoms were fixed to U_{iso} = 0.0063 Å^2, and the positional parameters were fixed to literature values.[A] The estimated standard deviations (e.s.d.) were calculated using the Bérar method, which takes into account correlations of the errors in the profile fit for the individual data points of the diffraction pattern.[B] The Bérar factor was calculated to 2.26.

Table S2. Interatomic distances in $Ba_8Al_{6.9}Si_{39.1}$ calculated from the structural parameters obtained by Rietveld refinement of XRPD data (Table S1) in comparison with those obtained from refinement of the X-ray single crystal diffraction data (cf. Tables 2-4 in the main text).

Distance		Rietveld refinement		Refinement of single crystal data	
		d / *a*	*d* / Å	*d* / *a*	*d* / Å
Ba1(2*a*)	– Si2(16*i*) (8×)	0.3196(3)	3.344(4)	0.3204(1)	3.353(1)
	– Si3(24*k*) (12×)	0.3243(3)	3.393(3)	0.3241(2)	3.391(2)
Ba2(6*d*)	– Si1/Al1(6*c*) (4×)	¼√2	3.69983(7)	¼√2	3.69976(7)
	– Si2(16*i*) (8×)	0.3713(1)	3.886(1)	0.37105(4)	3.8828(4)
	– Si3(24*k*) (8×)	0.3396(2)	3.554(2)	0.3395(1)	3.5522(1)
	– Si3(24*k*) (4×)	0.3863(3)	4.042(3)	0.3868(2)	4.047(2)
Si1/Al1(6*c*)	– Si3(24*k*) (4×)	0.2381(3)	2.492(3)	0.2384(2)	2.495(2)
Si2(16*i*)	– Si2(16*i*) (1×)	0.2269(7)	2.374(7)	0.2252(3)	2.356(3)
	– Si3(24*k*) (3×)	0.2290(2)	2.396(2)	0.2294(1)	2.400(1)
Si3(24*k*)	– Si1/Al1(6*c*) (1×)	0.2381(3)	2.492(3)	0.2384(2)	2.495(2)
	– Si2(16*i*) (2×)	0.2290(2)	2.396(2)	0.2294(1)	2.400(1)
	– Si3(24*k*) (1×)	0.2346(6)	2.455(6)	0.2336(4)	2.445(4)
	mean (framework)	0.2319(2)	2.427(2)	0.2319(1)	2.427(1)

Table S3. Space groups, occupancy factors (*Occ*), optimized atomic coordinates (*xyz*) and lattice parameter (*a*) used for the electronic structure calculations of $Ba_8Al_6Si_{40}$, Ba_8Si_{46} and Ba_7Si_{46}.

Composition	Space group	*a* / Å	Atom	Site	*x*	*y*	*z*	*Occ*
$Ba_8Al_6Si_{40}$	$Pm\bar{3}n$	10.375	Ba1	2*a*	0	0	0	1
			Ba2	6*d*	¼	½	0	1
			Al1	6*c*	¼	0	½	1
			Si2	16*i*	0.1851	*x*	*x*	1
			Si3	24*k*	0	0.3024	0.1168	1
Ba_8Si_{46}	$Pm\bar{3}n$	10.262	Ba1	2*a*	0	0	0	1
			Ba2	6*d*	¼	½	0	1
			Si1	6*c*	¼	0	½	1
			Si2	16*i*	0.18514	*x*	*x*	1
			Si3	24*k*	0	0.30699	0.12002	1
Ba_7Si_{46}	$Pm\bar{3}$	10.221	Ba11	1*a*	0	0	0	1
			Ba12	1*b*	½	½	½	0
			Ba2	6*g*	0.24560	½	0	1
			Si1	6*f*	0.2550	0	½	1
			Si21	8*i*	0.18674	*x*	*x*	1
			Si22	8*i*	0.31768	*x*	*x*	1
			Si31	12*j*	0	0.30737	0.12209	1
			Si32	12*k*	½	0.38154	–0.19557	1

References used in the supplementary information.

[A] T. Goebel, Yu. Prots, F. Haarmann, *Z. Kristallogr. NCS 224* (2009) 7.
[B] J.-F. Bérar, P. Lelann, *J. Appl. Crystallogr. 24* (1991) 1.