Supporting Information

Completing the Ba–As Compositional Space: Synthesis and Characterization of Three New Binary Zintl Arsenides, Ba_3As_4, Ba_5As_4, and $Ba_{16}As_{11}$

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Table S1. Refined atomic coordinates and equivalent isotropic displacement parameters (U_{eq}[a], Å^2) for Ba_3As_4 in the orthorhombic space group *Fdd2*.

Atom	Site	*x*	*y*	*z*	U_{eq}
As1	16*b*	0.0829(1)	0.5002(1)	0.0009(2)	0.0052(1)
As2	16*b*	0.0899(1)	0.1712(1)	0.0019(2)	0.0058(1)
Ba1	16*b*	0.5008(1)	0.1676(1)	0.0107(1)	0.0057(1)
Ba2	8*a*	0	0	0.0003(1)	0.0065(1)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{IJ} tensor.

Table S2. Refined atomic coordinates and equivalent isotropic displacement parameters (U_{eq}[a], Å^2) for Ba_5As_4 in the orthorhombic space group *Cmce*.

Atom	Site	*x*	*y*	*z*	U_{eq}
Ba1	16*g*	0.1469(1)	0.3315(1)	0.1639(1)	0.0066(1)
Ba2	4*a*	0	0	0	0.0067(3)
As1	8*f*	0	0.1055(1)	0.3952(1)	0.0067(3)
As2	8*d*	0.1976(1)	0	0	0.0065(3)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{IJ} tensor.

Table S3. Refined atomic coordinates and equivalent isotropic displacement parameters (U_{eq}[a], Å^2) for $Ba_{16}As_{11}$ in the tetragonal space group $P\bar{4}2_1m$.

Atom	Site	*x*	*y*	*z*	U_{eq}
Ba1A[b]	8*f*	0.0738(7)	0.1965(3)	0.1869(3)	0.031(1)
Ba1B[b]	8*f*	0.0844(9)	0.2174(8)	0.2102(11)	0.031(1)
Ba2	8*f*	0.2076(1)	0.0961(1)	0.4988(1)	0.019(1)
Ba3A[b]	8*f*	0.5802(1)	0.2931(1)	0.2100(2)	0.019(1)
Ba3B[b]	8*f*	0.5741(5)	0.3094(5)	0.1743(6)	0.0185(4)
Ba4	4*e*	0.1247(1)	*x* + 1/2	0.0011(1)	0.015(1)
Ba5A[b]	2*c*	0	1/2	0.3412(8)	0.029(1)
Ba5B[b]	2*c*	0	1/2	0.3022(14)	0.029(1)
Ba6A[b]	2*c*	0	1/2	0.6945(5)	0.018(1)
Ba6B[b]	2*c*	0	1/2	0.6505(14)	0.018(1)
As1A[c]	4*d*	0	0	0.0342(2)	0.020(1)
As1B[c]	8*f*	0.037(3)	0.088(3)	0.012(4)	0.020(2)
As2	4*e*	0.1698(1)	*x* + 1/2	0.2615(1)	0.013(1)
As3	4*e*	0.1751(1)	*x* + 1/2	0.7413(1)	0.013(1)
As4	4*e*	0.6271(1)	*x* − 1/2	0.0047(2)	0.019(1)
As5A[b]	4*e*	0.6420(2)	*x* − 1/2	0.4751(6)	0.0120(1)
As5B[b]	4*e*	0.6396(5)	*x* − 1/2	0.5252(12)	0.0120(1)
As6A[b]	4*d*	0	0	0.3901(2)	0.009(1)
As6B[b]	4*d*	0	0	0.3374(3)	0.009(1)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{IJ} tensor.

[b] Refined occupancies for split atomic sites: 0.738(7)Ba1A+0.262Ba1B=1; 0.738(7)Ba3A+0.262Ba3B=1; 0.72(2)Ba5A+0.28Ba5B=1; 0.767(14)Ba6A+0.233Ba6B=1; 0.681(10)As5A+0.319As5B=1; 0.534(3)As6A+0.466As6B=1.

[c] Site Occupancy Factors (SOF) for partially occupied As atomic sites: As1A=0.468(7); As1B=0.034(4).

Table S4. Bond distances for Ba_3As_4.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
As1	As1	2.5484(14)	As2	Ba1	3.3437(11)
As1	As2	2.4674(11)	As2	Ba1	3.3767(16)
As1	Ba1	3.3486(11)	As2	Ba1	3.3301(9)
As1	Ba1	3.3995(9)	As2	Ba	3.4955(8)
As1	Ba1	3.4199(11)	As2	Ba2	3.2669(11)
As1	Ba1	3.3837(9)	Ba1	Ba1	4.4078(8)
As1	Ba2	3.3931(18)	Ba1	Ba1	4.4078(8)
As1	Ba2	3.3857(18)	Ba1	Ba2	4.4167(7)
As2	Ba1	3.4776(16)	Ba1	Ba2	4.3971(9)

Table S5. Bond distances for Ba_5As_4.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Ba1	Ba1	4.0309(13)	Ba1	As1	3.4333(13)
Ba1	Ba1	3.7860(15)	Ba1	As1	3.7202(13)
Ba1	Ba1	4.5201(8)	Ba2	As2	3.3353(18)
Ba1	Ba1	4.5201(8)	Ba2	As2	3.3353(18)
Ba1	Ba2	4.0186(8)	Ba2	As1	3.5211(16)
Ba1	Ba2	4.0741(8)	Ba2	As1	3.4875(16)
Ba1	As2	3.3108(15)	Ba2	As1	3.4875(16)
Ba1	As2	3.3446(9)	Ba2	As1	3.5211(16)
Ba1	As2	3.2767(9)	As1	As1	2.550(3)
Ba1	As1	3.4466(13)			

Table S6. Select bond distances for $Ba_{16}As_{11}$.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Ba1A	Ba3B	3.770(6)	Ba3B	As6A	3.667(6)
Ba1A	Ba3B	3.799(7)	Ba3B	As1B	3.113(8)
Ba1A	As1B	3.764(4)	Ba3B	As6B	3.266(6)
Ba1A	As1B	3.256(4)	Ba3B	As1A	3.46(4)
Ba1A	As6A	3.621(4)	Ba3B	As1A	3.51(4)
Ba1A	As6B	3.242(4)	Ba3B	As1A	2.61(4)
Ba1A	As1A	2.53(4)	Ba5A	Ba6A	4.174(12)
Ba1A	As1A	3.76(4)	Ba5A	As5A	3.378(8)
Ba1A	As1A	3.83(4)	Ba5A	As5A	3.378(8)
Ba1B	Ba1B	3.614(19)	Ba5A	As5B	2.995(12)
Ba1B	Ba3B	4.021(12)	Ba5A	As5B	2.995(12)
Ba1B	Ba5B	3.955(13)	Ba5A	Ba6B	3.65(2)
Ba1B	As1B	3.656(12)	Ba5B	As5A	3.691(14)
Ba1B	As5B	3.698(18)	Ba5B	As5A	3.691(14)
Ba1B	As6A	3.682(11)	Ba5B	As5B	3.261(16)
Ba1B	As6B	3.362(10)	Ba5B	As5B	3.261(16)
Ba1B	As1A	2.93(4)	Ba5B	Ba6B	4.11(2)
Ba2	Ba2	3.5795(14)	Ba6A	As5A	3.274(6)
Ba2	Ba3A	4.072(3)	Ba6A	As5A	3.274(6)
Ba2	As5A	3.6414(13)	Ba6A	As5B	3.636(13)
Ba2	As5A	3.496(4)	Ba6A	As5B	3.636(13)
Ba2	As5B	3.531(9)	Ba6A	Ba6B	0.520(12)
Ba2	As5B	3.635(3)	As1B	As1B	0.809(6)
Ba2	As6A	3.2177(13)	As1B	As1A	1.36(4)
Ba2	As6A	3.2289(14)	As1B	As1A	1.27(4)
Ba2	As6B	3.5129(19)	As1B	As1A	1.27(4)
Ba2	As6B	3.5281(19)	As1B	As1A	1.36(4)
Ba3A	Ba3A	3.883(4)	As5A	As5B	0.594(9)
Ba3A	As1B	3.535(3)	As5A	Ba6B	2.984(10)
Ba3A	As5A	3.774(7)	As5B	Ba6B	3.284(16)
Ba3A	As6A	3.565(2)	As6A	As6A	2.598(5)
Ba3A	As6B	3.233(2)	As6A	As6B	0.622(3)
Ba3A	As1A	3.09(4)	As1A	As1A	2.48(7)
Ba3A	As1A	3.87(4)	As1A	As1A	1.78(5)
Ba3B	As1B	3.609(9)	As1A	As1A	1.78(5)

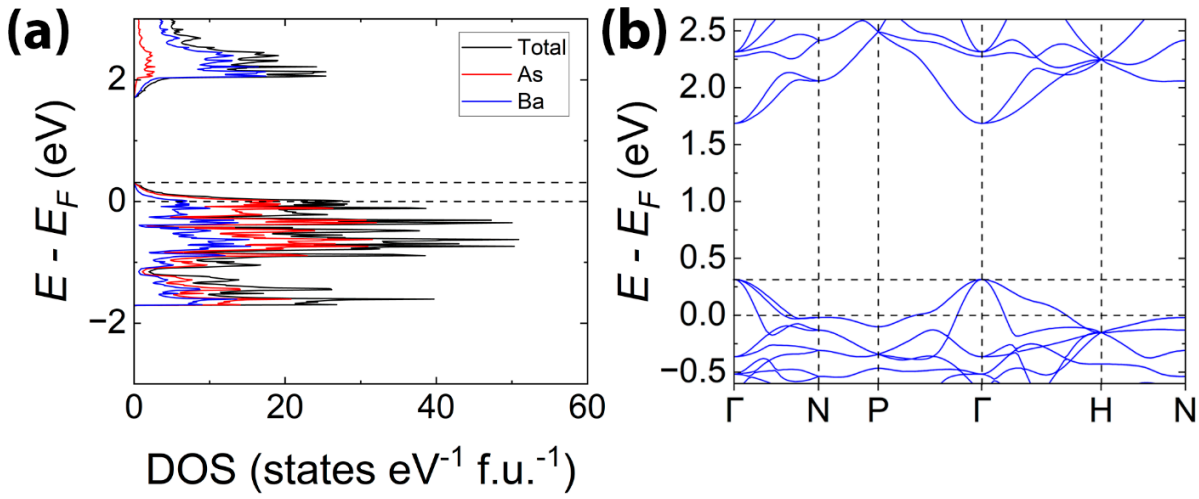


Figure S1. (a) Density of states (DOS) plot and (b) band structure for Ba_4As_3. The Fermi level is the energy reference at 0 eV. An additional dashed line indicates a 1-electron shift per formula unit justifying a deficient Ba_4As_{3-x} composition.