$Ba_4AgGa_5Pn_8$ (n=P, As): New Pnictide-Based Compounds with Nonlinear Optical Potential

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Supporting Information

Contents

10. Figure S10. Model structure of $Ba_4AgGa_5Pn_8$ used for electronic structure calculations. Due to the arbitrary arrangement of mixed atoms, the space group is lowered to C2 (No.5). The Ba, Ga, Ag and Pn atoms are indicated as purple, green, yellow and pink spheres, respectively.

11. Figure S11. Coordination geometry plot for Ba cations in $Ba_4AgGa_5P_8$, related atoms are labeled in graph.

12. Figure S12. (a) Ball and stick structure view of $Ba_4AgGa_5P_8$, viewed down the c-axis. The Ba, Ga and P atoms are represented by pink, blue and red spheres, respectively. The mixed $(Ag/Ga)P_4$ tetrahedra are plotted in yellow colors. (b) An expanded view of the $^1_\infty[AgGa_5P_{10}]$ column along the a-axis.

13. EDX analyses on the composition of a single crystal for (a) $Ba_4AgGa_5P_8$ and (b) $Ba_4AgGa_5As_8$.

14. Table S1. Refined atomic coordinates and isotropic displacement parameters for two polymorphs of $Ba_4AgGa_5Pn_8$ (Pn = P, As).

15. Table S2. The selected important interatomic distances (Å) in $Ba_4AgGa_5Pn_8$ (Pn=P, As).

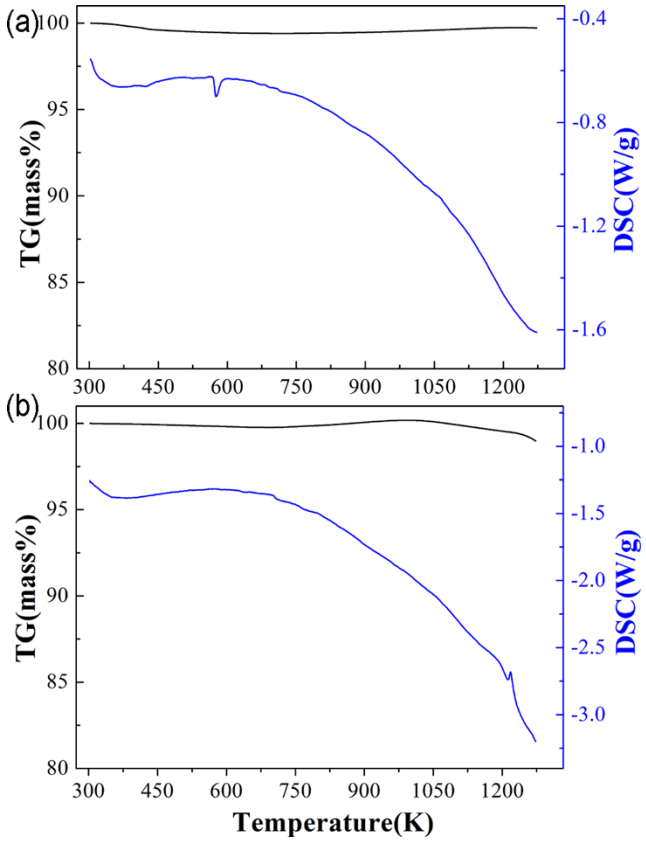


Figure S1. TG-DSC measurements on (a) $Ba_4AgGa_5P_8$ and (b) $Ba_4AgGa_5As_8$, conducted in an inert atmosphere of argon.

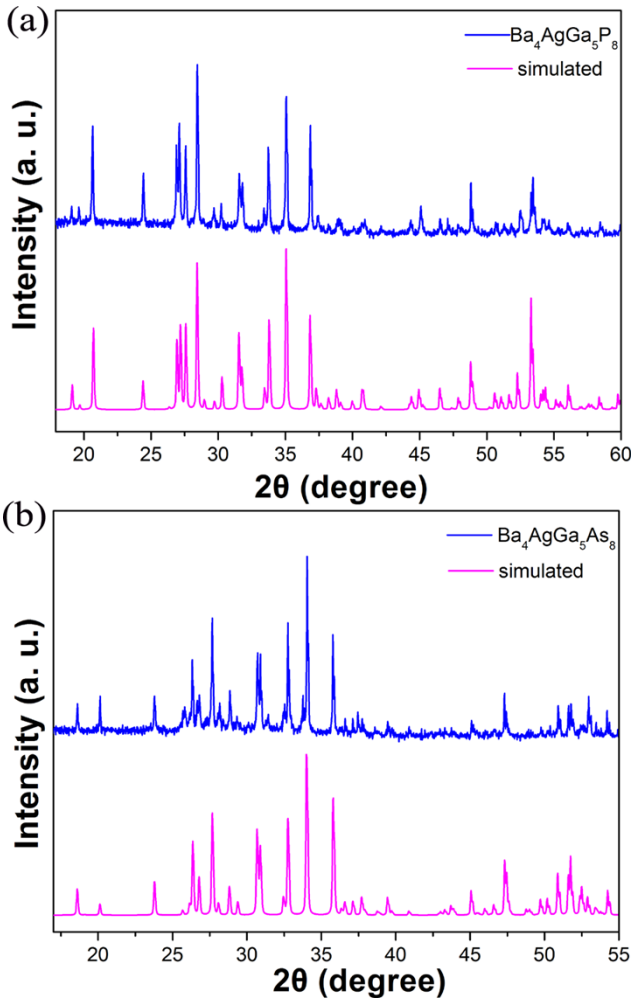


Figure S2. Powder XRD patterns of (a) $Ba_4AgGa_5P_8$ and (b) $Ba_4AgGa_5As_8$ recorded at room temperature. The theoretical calculated patterns are provided for comparison as well. A small amount of GaPn impurity is found in both compounds.

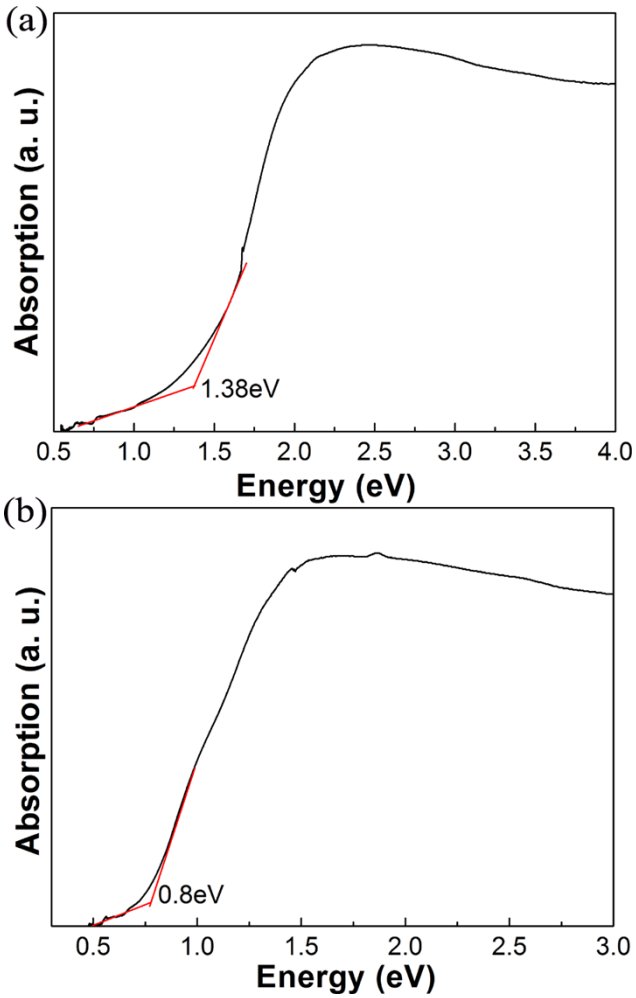


Figure S3. Optical absorption spectra measured on the polycrystalline samples of (a) $Ba_4AgGa_5P_8$ and (b) $Ba_4AgGa_5As_8$.

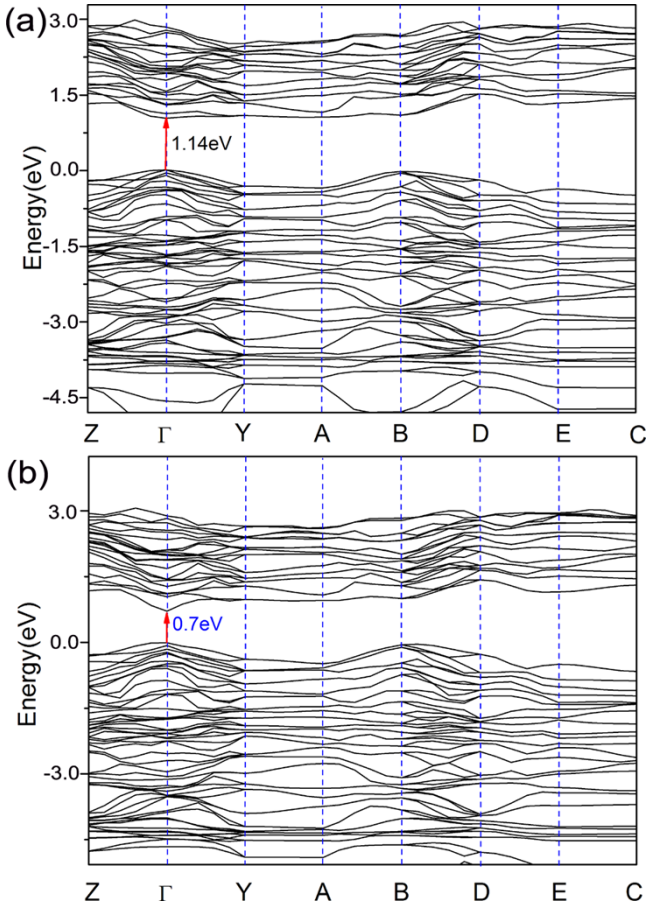


Figure S4. Electronic band structures calculated on (a) $Ba_4AgGa_5P_8$ and (b) $Ba_4AgGa_5As_8$.

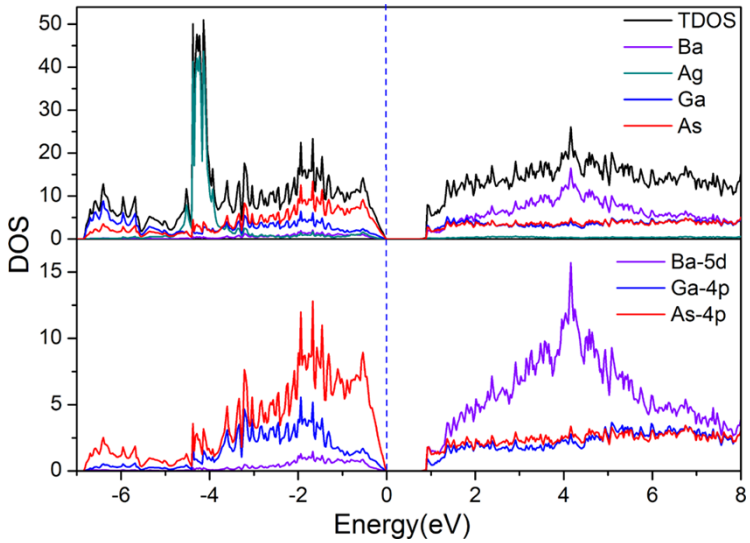


Figure S5. Calculated total DOS and projected DOS for $Ba_4AgGa_5As_8$. The dotted line marked the Femi level.

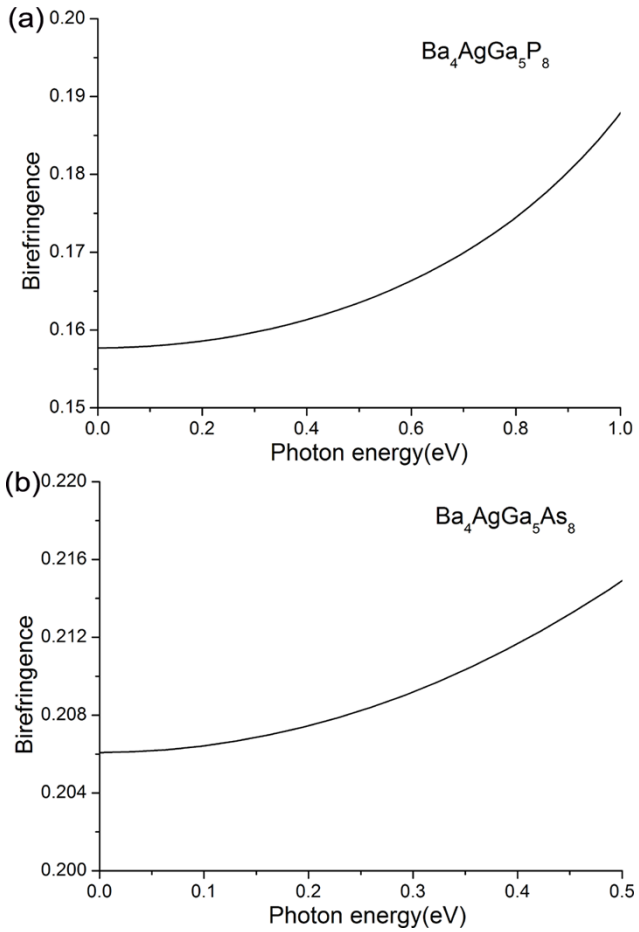


Figure S6. The calculated birefringence (Δn) for (a) $Ba_4AgGa_5P_8$ and (b) $Ba_4AgGa_5As_8$.

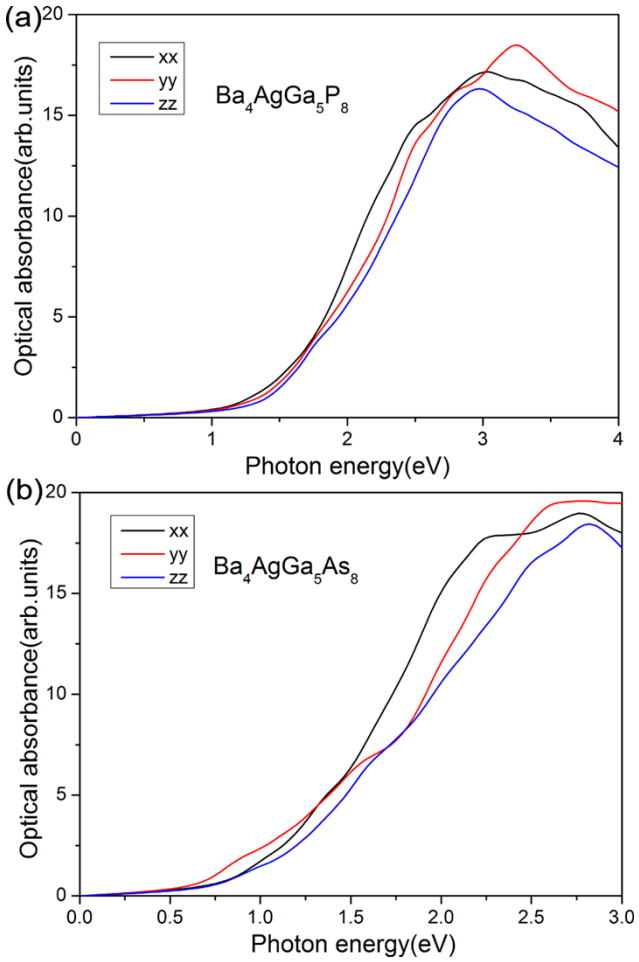


Figure S7. Calculated absorption coefficients of (a) $Ba_4AgGa_5P_8$ and (b) $Ba_4AgGa_5As_8$.

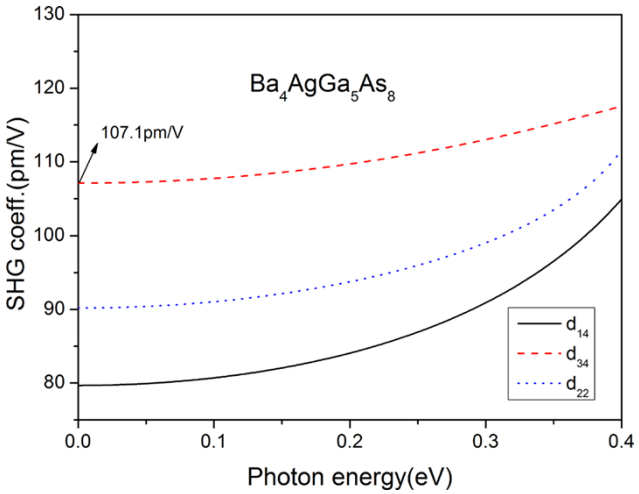


Figure S8. Calculated frequency-dependent second harmonic generation coefficients for $Ba_4AgGa_5As_8$.

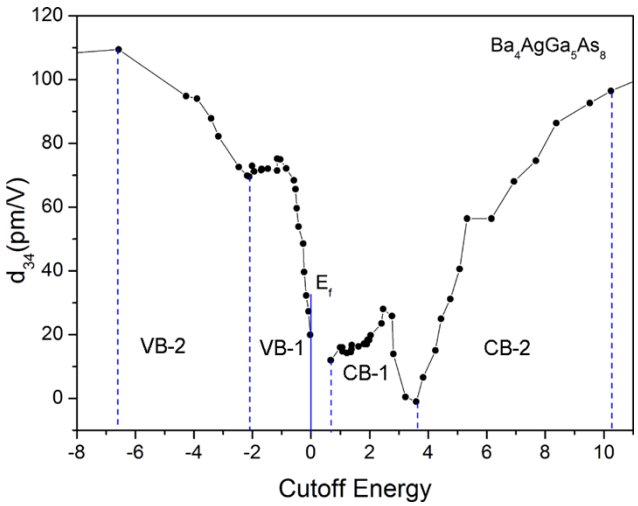
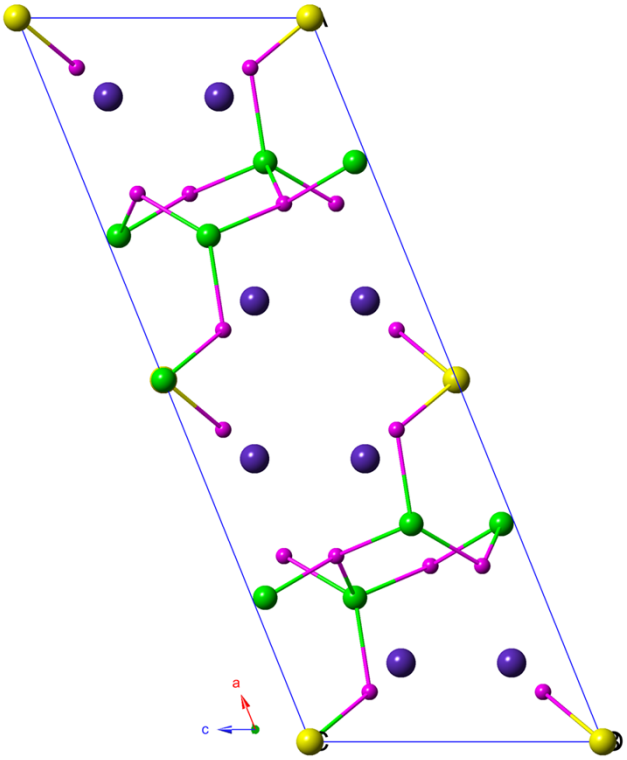


Figure S9. Cutoff-energy-depending static SHG coefficients for $Ba_4AgGa_5As_8$. The dotted lines mark the different regions in VB and CB.



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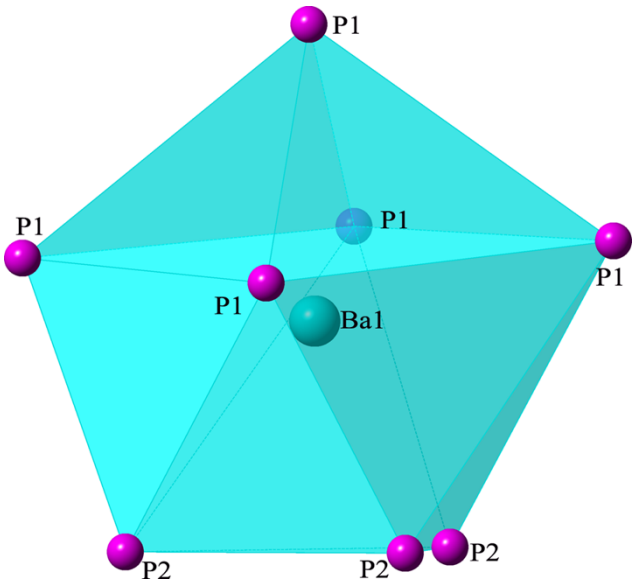

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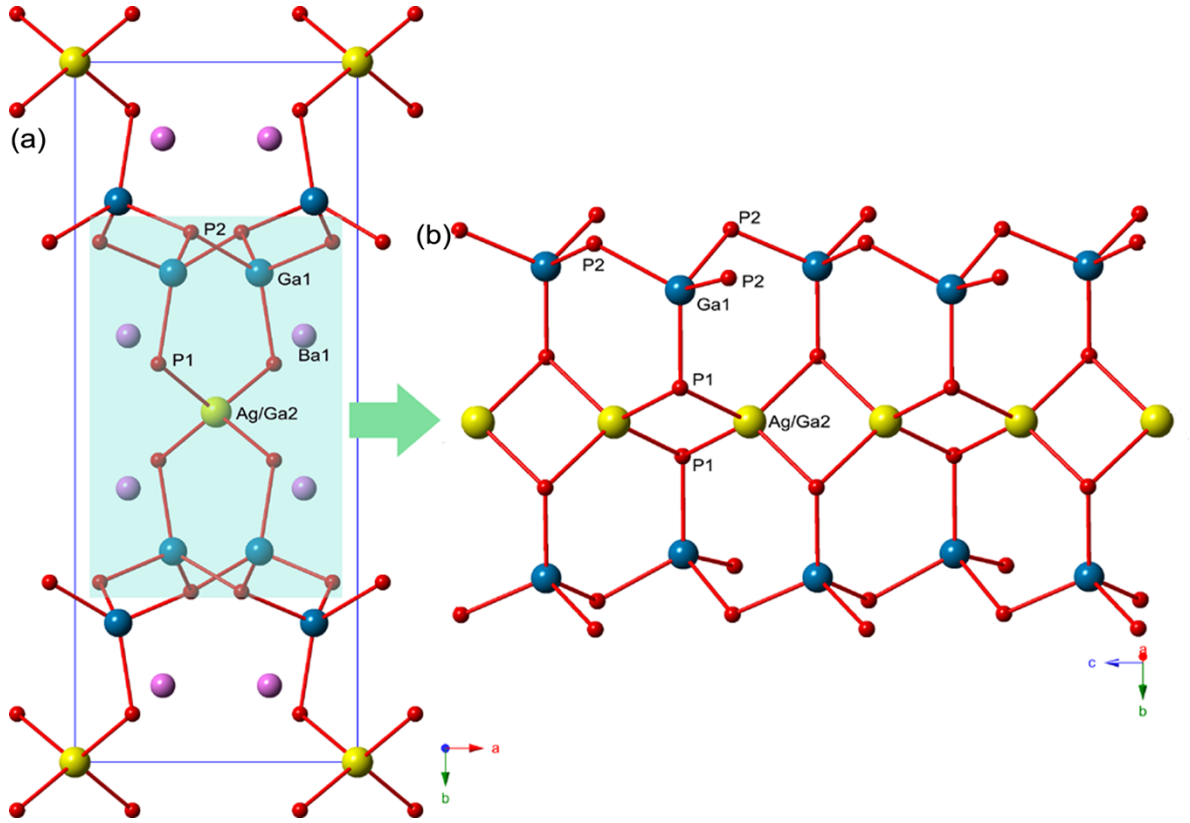


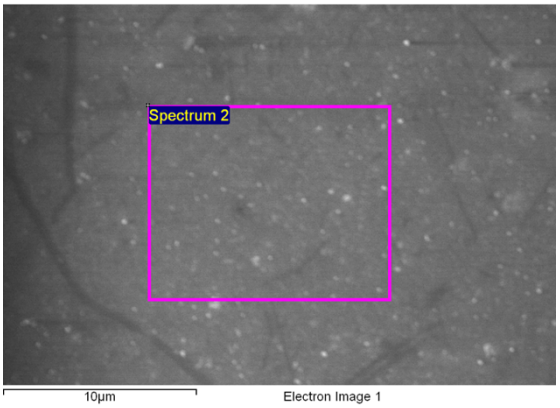
Figure S12. (a) Ball and stick structure view of $Ba_4AgGa_5P_8$, viewed down the c-axis. The Ba, Ga and P atoms are represented by pink, blue and red spheres, respectively. The mixed $(Ag/Ga)P_4$ tetrahedra are plotted in yellow colors. (b) An expanded view of the $^{1}_{\infty}[AgGa_5P_{10}]$ column along the a-axis.

13. EDX analyses on the composition of a single crystal for (a) $Ba_4AgGa_5P_8$ and (b) $Ba_4AgGa_5As_8$.

(a) $Ba_4AgGa_5P_8$

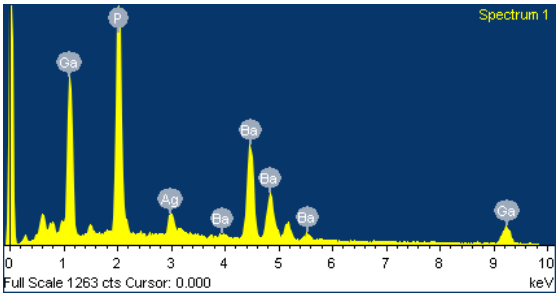
Point 1

Element	Weight%	Atomic%	Composition
P K	21.68	47.36	8.54
Ga L	27.90	27.07	4.88
Ag L	5.41	3.40	0.61
Ba L	45.01	22.18	4



Point 2

Element	Weight%	Atomic%	Composition
P K	21.89	47.54	8.76
Ga L	28.43	27.43	5.05
Ag L	5.34	3.33	0.61
Ba L	44.33	21.71	4

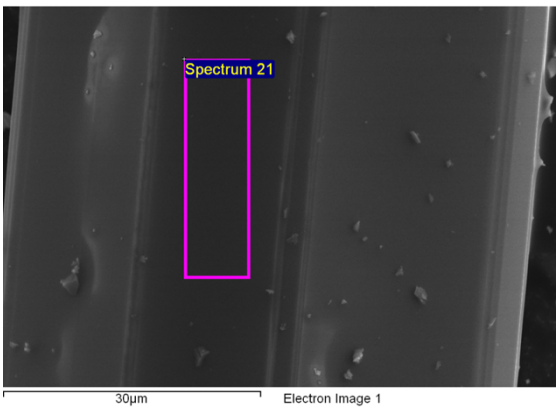


Averaged Composition: $Ba_4Ag_{0.61}Ga_{4.97}P_{8.65}$

(b) $Ba_4AgGa_5As_8$

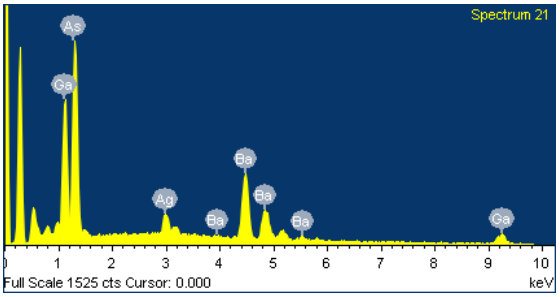
Point 1

Element	Weight%	Atomic%	Composition
As L	36.32	43.33	7.56
Ga L	22.43	28.76	5.02
Ag L	6.02	4.99	0.87
Ba L	35.23	22.93	4



Point 2

Element	Weight%	Atomic%	Composition
As L	36.46	43.39	7.70
Ga L	22.65	28.97	5.14
Ag L	6.18	5.11	0.91
Ba L	34.70	22.53	4



Averaged Composition: $Ba_4Ag_{0.89}Ga_{5.08}As_{7.63}$

Table S1. Refined atomic coordinates and isotropic displacement parameters for two polymorphs of $Ba_4AgGa_5Pn_8$ (Pn=P, As).

Atoms	*Wyckoff site*	*x*	*y*	*z*	*Ueq (Å²)*
$Ba_4AgGa_5P_8$					
Ba1	*8(c)*	0.81096(10)	0.60903(4)	0.7542(2)	0.0204(2)
Ga1	*8(c)*	0.84356(15)	0.80091(6)	0.7492(4)	0.0088(3)
Ag/Ga2[b]	*4(a)*	1	1	1	0.0190(4)
P1	*8(c)*	0.7961(4)	0.93114(16)	0.7481(13)	0.0210(7)
P2	*8(c)*	0.5889(5)	0.7568(2)	0.9334(6)	0.0121(7)
$Ba_4AgGa_5As_8$					
Ba1	*8(c)*	0.80368(4)	0.61010(2)	0.75587(6)	0.01815(12)
Ga1	*8(c)*	0.84459(7)	0.80115(3)	0.74621 (13)	0.01073(14)
Ag/Ga2[b]	*4(a)*	1	1	1	0.01522(17)
As1	*8(c)*	0.79006(8)	0.93160(3)	0.74750(15)	0.02013(16)
As2	*8(c)*	0.58454(8)	0.75922(3)	0.93462(10)	0.01127(15)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

[b] Ag or Ga2 occupancy are both constrained to 50% at the mixing sites.

Table S2. The selected important interatomic distances (Å) in $Ba_4AgGa_5Pn_8$ (Pn=P, As).

Atom pairs		Distances (Å)	Atom pairs		Distances (Å)
$Ba_4AgGa_5P_8$					
Ba1–	P1	3.301(5)	Ga1 –	P1	2.376(4)
	P1	3.409 (9)		P2	2.365(5)
	P1	3.485(9)		P2	2.371(4)
	P1	3.612 (5)		P2	2.380(4)
	P2	3.287(5)	Ag/Ga2–	P1 × 2	2.529(7)
	P2	3.331(5)		P1 × 2	2.546(6)
	P2	3.367(4)			
$Ba_4AgGa_5As_8$					
Ba1–	As1	3.3896(7)	Ga1–	As 1	2.4575(8)
	As1	3.4833(11)		As 2	2.4441(10)
	As1	3.5914(11)		As 2	2.4514(9)
	As1	3.7187(7)		As 2	2.4694(9)
	As2	3.3625(8)	Ag/Ga2–	As 1 × 2	2.6223(10)
	As2	3.4297(7)		As 1 × 2	2.6440(10)
	As2	3.4377(7)			