Electronic Supplementary Material (ESI) for CrystEngComm.

Uncovering New Transition Metal Zintl Phases by Cation Substitution: The Crystal Chemistry of Ca_3CuGe_3 and $Ca_{2+n}Mn_xAg_{2-x+z}Ge_{2+n-z}$ (n = 3, 4)

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Electronic Supporting Information

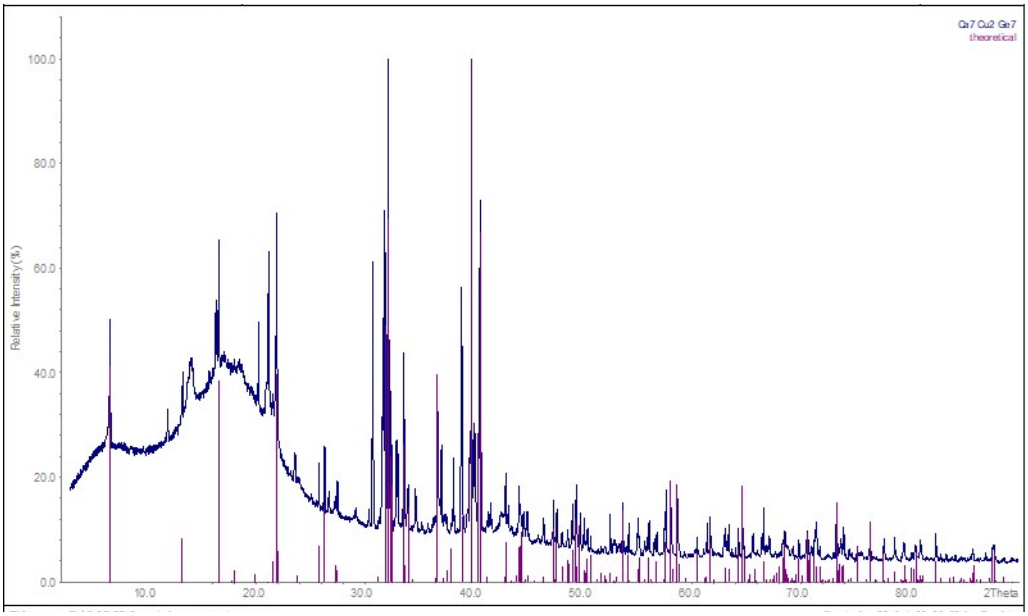

Figure S1: Experimental Powder XRD pattern for Ca_3CuGe_3 obtained from a sample with nominal composition "$Ca_5Cd_2CuGe_5$" compared with the expected calculated from SXRD analysis.

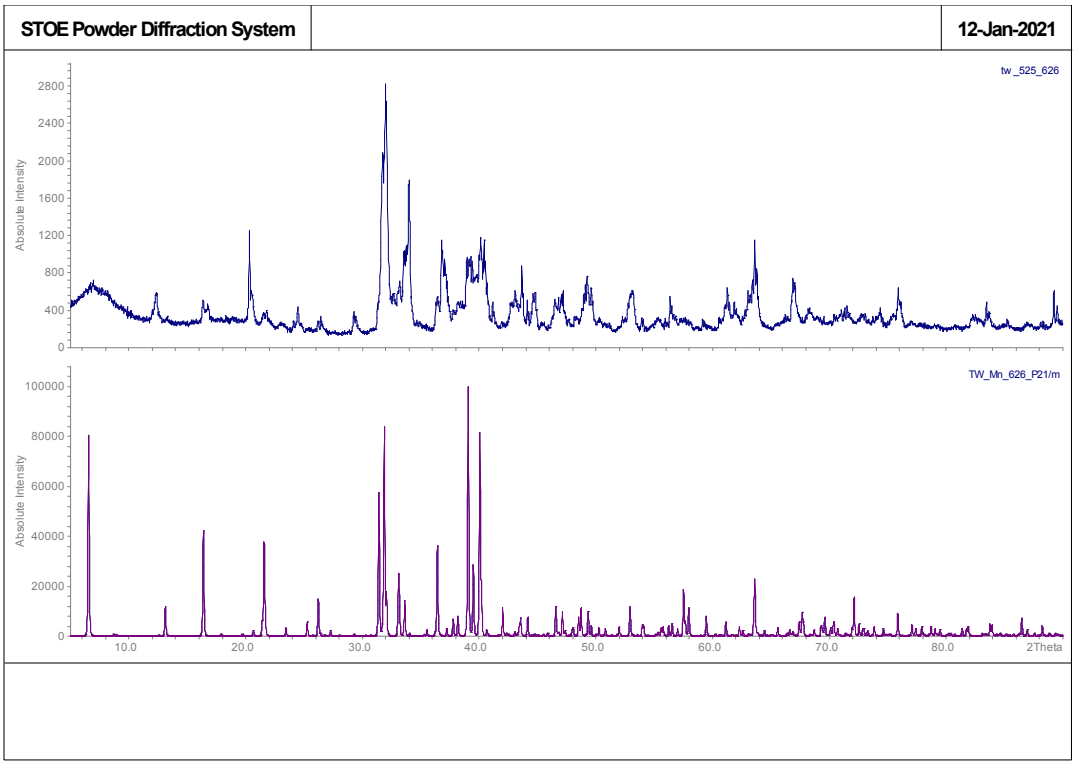

Figure S2: Experimental Powder XRD pattern obtained from a sample with nominal composition for "$Ca_{12}Mn_5Ag_3Ge_{11}$" compared with the calculated pattern using SXRD analysis of the monoclinic structure of $Ca_6Mn_xAg_{2-x}Ge_{6-z}$ ($P2_1/m$).

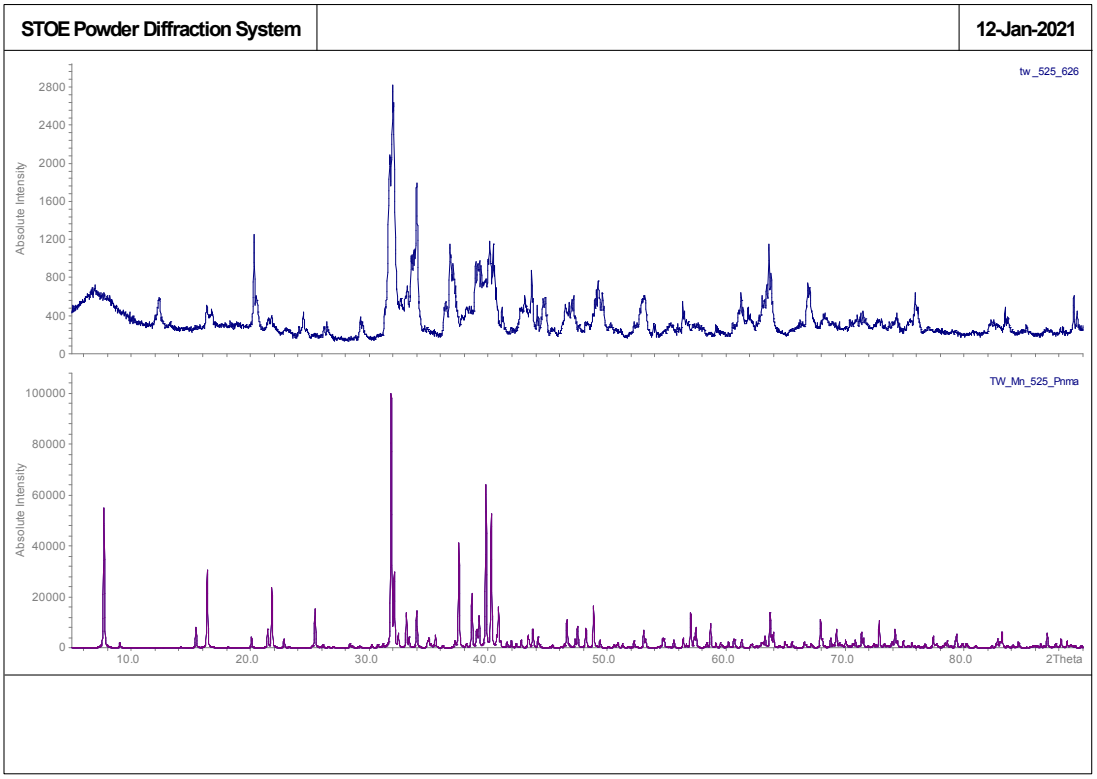

Figure S3: Experimental Powder XRD pattern obtained from a sample with nominal composition for "$Ca_{12}Mn_5Ag_3Ge_{11}$" compared with the calculated pattern using SXRD analysis of the orthorhombic structure of $Ca_5Mn_xAg_{2-x}Ge_{5-z}$ (*Pnma*).

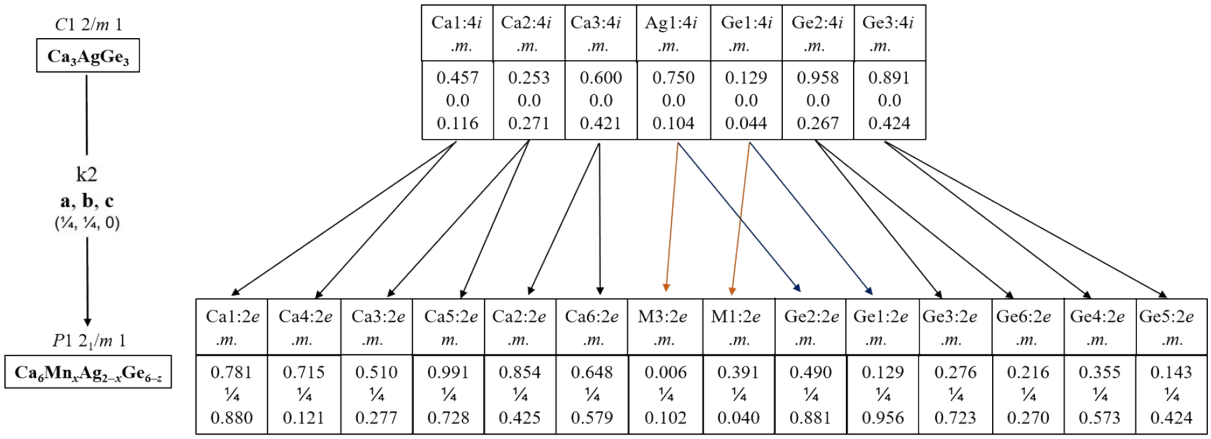

Figure S4. Tree of group-subgroup relations for $Ca_3Ag_{1+x}Ge_{3-x}$ ($C2/m - c^7$) and its Mn-substituted derivative $Ca_6Mn_xAg_{2-x+z}Ge_{6-z}$ ($P2_1/m - e^{14}$).

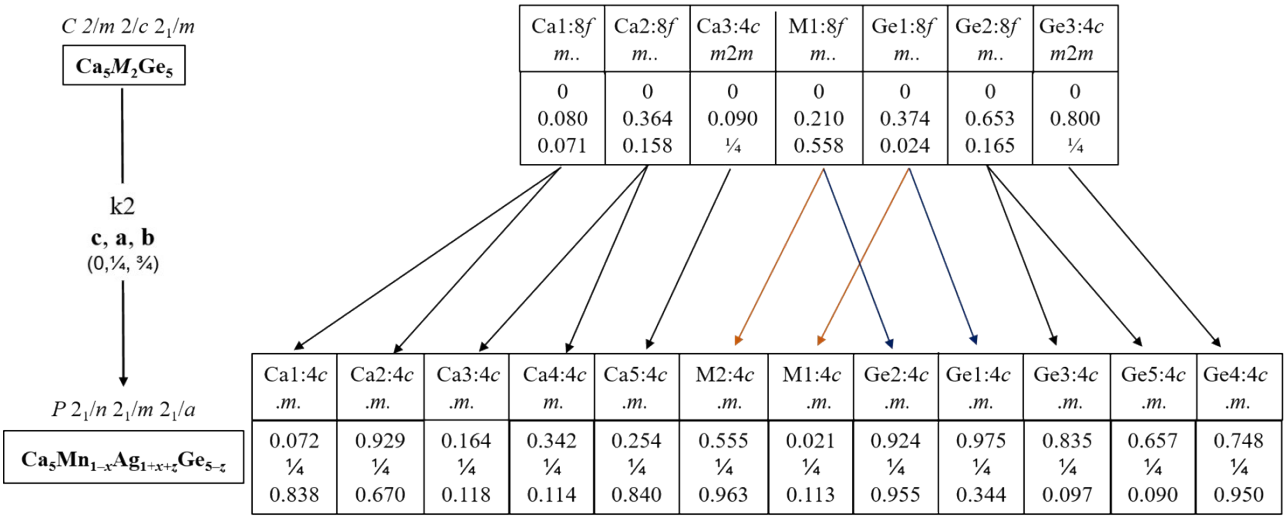

Figure S5. Tree of group-subgroup relations for imaginary "$Ca_5M_2Ge_5$ ($Cmcm - f^5c^2$)" and the experimentally observed quaternary derivative $Ca_5Mn_xAg_{2-x+z}Ge_{5-z}$ ($Pnma - c^{12}$). The space group ($Cmcm - f^5c^2$) was originally predicted by Zhao and Parthé,[1] and the coordinates are deduced by from refined model in *Pnma*, by adding the additional symmetry using the program JANA2006.[2]

[1] J. T. Zhao, E. Parthé, $Sc_3Ni_2Si_3$ with $Hf_3Ni_2Si_3$-type structure, an intergrowth of CrB-, $ThCr_2Si_2$-and W-type slabs, *Acta Crystallogr., Sect. C*, 1989, **45**, 1853–1856.

[2] V. Petříček, M. Dušek and L. Palatinus, JANA2006. The Crystallographic Computing System, Institute of Physics, Praha, Czech Republic, 2006.

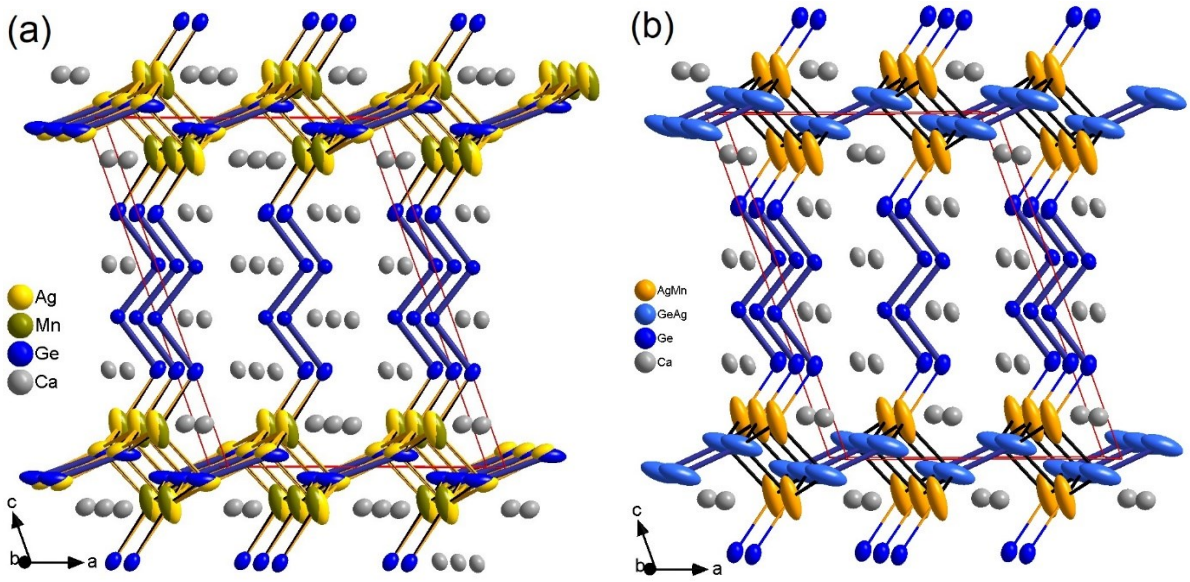

Figure S6. View of the structure of "$Ca_3Mn_xAg_{1-x+z}Ge_{3-z}$" in (a) the Sc_3NiSi_3 type ($C2/m - i^7$) in a tentative split model. The refined composition in this model is "$Ca_3Mn_{0.27}Ag_{1.15}Ge_{2.58}$", i.e. $x = 0.27$, and $z = 0.42$. In (b) a mix-occupied model also shows elongated thermal ellipsoids, which is a clear sign of symmetry breaking and can be assigned to unfavorable Mn–Ag interactions. The refined composition in this model is "$Ca_3Mn_{0.37}Ag_{1.03}Ge_{2.60}$", i.e. $x = 0.37$, and $z = 0.40$. The thermal ellipsoids are drawn at 99% probability level.

However, these models resulted in significant systematic violation of the C centering systematic extinction. The statistics were as followed:

- For the first crystal: 3048 Systematically absent reflections rejected

6033 Reflections read, of which 3048 rejected
-12 =< h =< 16, -6 =< k =< 5, -21 =< l =< 19, Max. 2-theta = 63.77
1374 Systematic absence violations (I>3sig(I)) before merging
17 Inconsistent equivalents
1178 Unique reflections, of which 0 suppressed
R(int) = 0.0231 R(sigma) = 0.0255 Friedel opposites merged

- Another crystal from the same batch give the data statistic:

7444 Reflections read, of which 3754 rejected
-15 =< h =< 11, -6 =< k =< 6, -18 =< l =< 21, Max. 2-theta = 64.51
1808 Systematic absence violations (I>3sig(I)) before merging
8 Inconsistent equivalents
1200 Unique reflections, of which 0 suppressed
R(int) = 0.0317 R(sigma) = 0.0314 Friedel opposites merged

In the alternative model in the space group $P2_1/m - e^{14}$, (Figure S5) almost all reflections could be modelled with no significant violation of the systematic extinction and, the following statistics:

6033 Reflections read, of which 6 rejected
-12 =< h =< 16, -6 =< k =< 5, -21 =< l =< 19, Max. 2-theta = 64.28
2 Systematic absence violations (I>3sig(I)) before merging

29 Inconsistent equivalents
2349 Unique reflections, of which 0 suppressed
R(int) = 0.0285 R(sigma) = 0.0338 Friedel opposites merged

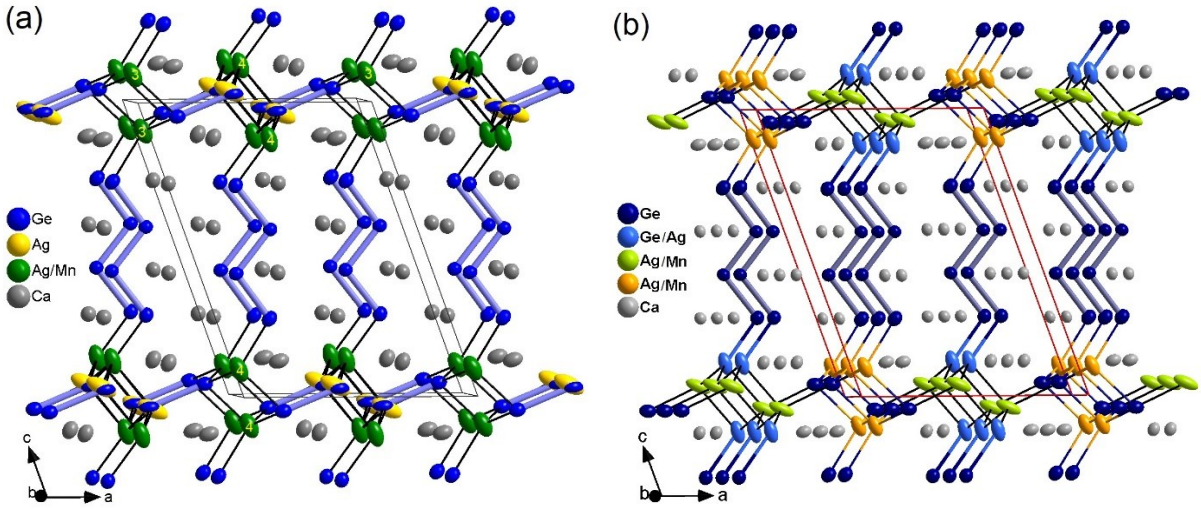

Figure S7. View of the structure of "$Ca_3Mn_xAg_{1-x+z}Ge_{3-z}$" in the alternative space group ($P2_1/m - e^{14}$) and a tentative split model. (a) When the mixed occupied position are refined as Ga/Ag and Mn/Ag, the refined composition in this model is "$Ca_3Mn_{0.41}Ag_{0.89}Ge_{2.70}$", i.e. $x = 0.41$, and $z = 0.30$. However, this model doesn't explain the symmetry breaking, since only one end of the Ge_2 dumbbells is substituted (unreasonable) with the Ge–Ge bond distance of 2.746 Å, longer than the Mn–Ge bond distances (between 2.609 and 2.705 Å) at the interface. In addition, Ge position is found in similar tetrahedral coordination than the Mn-occupied position. (b) The final model discussed in the manuscript is also supported by the implementation of the Zintl-Klemm concept alongside more reasonable bond distances and coordination geometries.

Discussion: There are two Mn/Ag mixed position in the model (a) with significantly different Mn–Ge bond distances and, also different coordination geometry since Mn4/Ag4 is nearly trigonal planar as expected for anionic Ge species. This suggested that an alternative model similar to $Ca_5MgAgGe_5$ model may be applicable here to reconcile the symmetry breaking, the bond distances and the coordination geometry with well-established chemical principles and structure directing rules.

Table S1. Wyckoff Sites, atomic coordinates, and equivalent isotropic displacement parameters for $Ca_5Mn_{0.64(1)}Ag_{1.42(1)}Ge_{4.94(1)}$ (**3_Mn**: $Ca_5Mn_xAg_{2-x+z}Ge_{5-z}$)

Atom	*Site*	*Occupancy.*	*x*	*y*	*z*	*Ueq*(/Å²)
Ge1	4*c*	1	0.97463(2)	¼	0.34373(5)	0.0104(1)
Ge2/Ag	4*c*	0.943/0.057(6)	0.92393(2)	¼	0.95477(5)	0.0105(2)
Ge3	4*c*	1	0.83494(2)	¼	0.09700(5)	0.0084(1)
Ge4	4*c*	1	0.74769(2)	¼	0.94975(5)	0.0083(1)
Ge5	4*c*	1	0.65723(2)	¼	0.08989(5)	0.0094(1)
Ag1/Mn1	4*c*	0.83/0.17(1)	0.02136(2)	¼	0.11273(4)	0.0146(2)
Mn2/Ag2	4*c*	0.47/0.53(1)	0.55503(2)	¼	0.96294(4)	0.0147(2)
Ca1	4*c*	1	0.07209(4)	¼	0.83804(9)	0.0112(2)
Ca2	4*c*	1	0.92922(4)	¼	0.67001(9)	0.0113(2)
Ca3	4*c*	1	0.16338(4)	¼	0.11759(9)	0.0094(2)
Ca4	4*c*	1	0.34188(4)	¼	0.11440(9)	0.0100(2)
Ca5	4*c*	1	0.25376(4)	¼	0.83953(9)	0.0097(2)

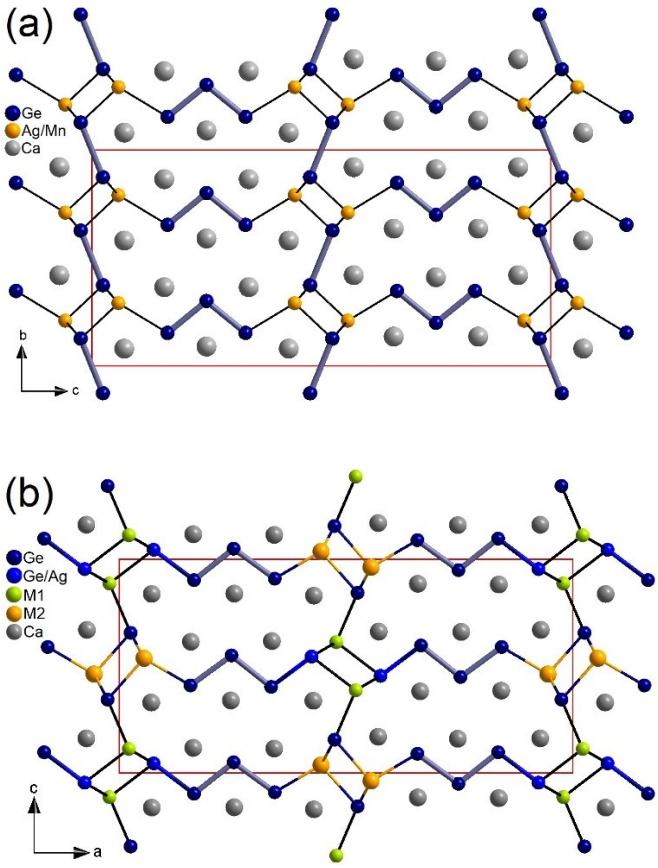

Figure S8. Comparative view of the projected structures of imaginary ternary "$Ca_5M_2Ge_5$" (*Cmcm* – f^5c^2) and the experimentally observed quaternary derivative $Ca_5Mn_xAg_{2-x+z}Ge_{5-z}$ (*Pnma* – c^{12}).

Table S2. Calculated –iCOHP (/eV) values for Selected bond distances (/Å) and in "Ca_3AgGe_3" (**4_Ag**)

Atom pairs		Distances	–iCOHP	Atom pairs		Distances	–iCOHP
Ag1	–Ge1 (×2)	2.657(1)	1.99	Ge1	–Ge1	2.588(1)	2.51
	–Ge2	2.689(1)	1.94		–Ag1 (×2)	2.657(1)	
	–Ge1	2.894(1)	1.24		–Ag1	2.894(1)	
	–Ca1 (×2)	3.151(5)	0.37		–Ca2	3.0468(6)	0.78
	–Ca1	3.225(1)	0.49		–Ca1 (×2)	3.162(1)	0.65
	–Ca1	3.305(1)	0.30		–Ca1 (×2)	3.275(1)	0.61
	–Ca2 (×2)	3.280(1)	0.40		–Ca1	3.417(1)	0.35
Ge2	–Ge3	2.581(1)	2.36	Ge3	–Ge3	2.544(1)	2.53
	–Ag1	2.689(1)			–Ge2	2.581(1)	
	–Ca1 (×2)	3.155(1)	0.88		–Ca2 (×2)	3.124(1)	0.84
	–Ca3 (×2)	3.105(5)	0.92		–Ca3	3.133(1)	1.03
	–Ca2	3.121(1)	1.01		–Ca3 (×2)	3.135(1)	0.87
	–Ca2 (×2)	3.121(1)	0.74		–Ca3 (×2)	3.212(1)	0.58