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Supporting Information

Nine Hexagonal $\text{Ca}_5\text{Pb}_3\text{Z}$ Phases in Stuffed Mn_5Si_3 -Type Structures with Transition Metals
 Interstitial Atoms Z. Problems with Classical Valence States in Possible Zintl Phases

INORG CHEM

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Table S1. Data collection and refinement parameters

Compound	$\text{Ca}_5\text{Pb}_3\text{Mn}$	$\text{Ca}_5\text{Pb}_3\text{Fe}$	$\text{Ca}_5\text{Pb}_3\text{Cu}$
f.w.	876.93	877.84	885.54
Space group, Z	$P6_3/mcm$ (No. 193), 2	$P6_3mcm$ (No. 193), 2	$P\bar{3}c1$ (No. 165), 2
Cell parameters $\text{\AA}^a$			
$a =$	9.3580(3)	9.3554(5)	9.4130(3)
$c =$	7.009(1)	7.009(1)	7.052(1)
V	531.6(1)	531.3(1)	541.0(3)
Dens., g cm^{-3}	5.46	5.49	5.44
Crystal dimen. (mm)	0.05–0.05–0.20	0.07–0.07–0.18	0.05–0.05–0.15
2θ max.	70.2°	70.2°	50.0°
no. of octants	4 ($\pm h, k, \pm \ell$)	4 ($\pm h, k, \pm$)	4 ($\pm, k, \pm \ell$)
Reflections. ^b			
measured	4909	4909	1996
observed ($I > 3\sigma$)	1666	1692	1044
independent	221	232	152
$R_{\text{ave}} (I > 0)$, %	6.1	5.0	11.1
Abs. coeff. (Mo $K\alpha$), cm^{-1}	757	787	550
Rel. transm. coeff. range	0.311 – 1.00	0.301 – 1.00	0.640 – 1.00
no. of parameters	14	14	14
R , %	3.7	3.2	3.0
R_w , %	3.9	3.5	4.3
G.O.F.	1.15	1.10	1.08
Largest param. shift/ σ	0.00	0.00	0.01
Sec. extinct. coeff. (10^{-7})	6.62(3)	6.96(3)	12.8(2)
Largest resid. peaks, $\text{e}^-/\text{\AA}^3$	+2.06, -2.32	+2.00, -2.12	+3.32, -3.19

^a Guinier data, 22 °C, $\lambda = 1.54056 \text{ \AA}$.^b All data collected with Rigaku AFC6R diffractometer, 295 K.^c $R = \sum ||F_o| - |F_c|| / \sum |F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w(F_o)^2]^{1/2}$; $w = \sigma/F^2$.

Table S2. Anisotropic Displacement Parameters for $\text{Ca}_5\text{Pb}_3\text{Z}$, Z = Mn, Fe, Cu

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
<u>$\text{Ca}_5\text{Pb}_3\text{Mn}$</u>						
Pb1	0.0304(4)	0.054(5)	0.076(1)	$U_{22/2}$	0	0
Ca1	0.024(2)	0.024	0.040(3)	$U_{22/2}$	0	0
Ca2	0.031(2)	0.052(2)	0.075(4)	$U_{22/2}$	0	0
Mn	0.047(2)					
<u>$\text{Ca}_5\text{Pb}_3\text{Fe}$</u>						
Pb1	0.0401(3)	0.044(5)	0.066(1)	0.003	0	0
Ca1	0.026(2)	0.026	0.045(3)	0.012	0	0
Ca2	0.041(2)	0.046(2)	0.072(4)	0.002	0	0
Fe	0.049(2)					
<u>$\text{Ca}_5\text{Pb}_3\text{Cu}$</u>						
Pb1	0.024(1)	0.024(1)	0.062(2)	$U_{22/2}$	-0.001(1)	$2U_{13}$
Ca1	0.0246(1)	U_{11}	0.051(1)	$U_{11/2}$	0	0
Ca2	0.026(4)	0.021(2)	0.042(1)	$U_{22/2}$	-0.07(7)	$2U_{13}$
Cu	0.036(1)	U_{11}	0.057(1)	$U_{11/2}$	0.0	0.0

Figure S1. Gram magnetic susceptibility of $\text{Ca}_3\text{Pb}_3\text{Ag}$.

Figure S2. Molar susceptibility of $\text{Ca}_5\text{Pb}_3\text{Cu}$.