SUPPLEMENTARY INFORMATION

Narrowing the gap: From semiconductor to semimetal in the homologous series of rare-earth zinc arsenides $RE_{2-y}Zn_4As_4 \cdot n(REAs)$ and Mn-substituted derivatives $RE_{2-y}Mn_xZn_{4-x}As_4 \cdot n(REAs)$ (RE = La–Nd, Sm, Gd)

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Table S1. EDX analyses of $RE_{2-y}Mn_xZn_{4-x}As_4 \cdot n(REAs)$ (RE = La–Nd, Sm, Gd; n = 2, 3, 4) crystals. [a]

Compound	No. of analyses	at. % *RE*	at. % Mn	at. % Zn	at. % As
$Ce_{3.3}Mn_{1.1}Zn_{2.9}As_6$	16	25(1)	13(1)	20(2)	41(2)
		25	*8*	*22*	*45*
$Pr_{3.5}Zn_4As_6$	16	29(1)		30(2)	41(2)
		26		*30*	*44*
$Nd_{3.3}Mn_{0.9}Zn_{3.1}As_6$	15	25(2)	4(1)	28(1)	44(3)
		25	*7*	*23*	*45*
$Nd_{4.4}Zn_4As_7$	19	31(1)		26(1)	43(1)
		29		*26*	*45*
$Sm_{4.4}Zn_4As_7$	16	33(2)		26(2)	41(2)
		29		*26*	*45*
$Nd_{5.4}Zn_4As_8$	16	30(1)		23(1)	47(1)
		31		*23*	*46*
$Sm_{5.4}Zn_4As_8$	15	35(1)		22(1)	43(1)
		31		*23*	*46*
$Sm_{5.3}Mn_{0.6}Zn_{3.4}As_8$	16	35(2)	5(1)	20(1)	40(3)
		31	*3*	*20*	*46*
$Gd_{5.3}Mn_{0.6}Zn_{3.4}As_8$	16	34(1)	6(1)	17(1)	42(2)
		31	*3*	*20*	*46*

[a] Expected compositions are indicated in italics.

Table S2. Crystallographic data for $RE_{2-y}Mn_xZn_{4-x}As_4 \cdot n(REAs)$ (n = 2, 3, 4).

Formula	$Ce_{3.32(1)}Mn_{1.1(1)}Zn_{2.9(1)}As_6$	$Pr_{3.46(1)}Zn_4As_6$	$Nd_{3.34(1)}Mn_{0.92(6)}Zn_{3.08(6)}As_6$	$Nd_{4.41(1)}Zn_4As_7$	$Sm_{4.39(1)}Zn_4As_7$
Formula mass (amu)	1162.27	1197.14	1182.07	1420.58	1447.46
Space group	$R\bar{3}m1$ (No. 166)	$R\bar{3}m1$ (No. 166)	$R\bar{3}m1$ (No. 166)	$P\bar{3}m1$ (No. 164)	$P\bar{3}m1$ (No. 164)
a (Å)	4.218(3)	4.2067(7)	4.1788(7)	4.197(3)	4.1703(6)
c (Å)	62.11(4)	62.637(10)	61.727(10)	24.204(15)	23.981(3)
V (Å^3)	957.0(13)	959.9(4)	933.5(3)	369.2(5)	361.19(12)
Z	3	3	3	1	1
ρ_{calcd} (g cm^{-3})	6.050	6.213	6.308	6.390	6.654
Crystal dimensions (mm)	0.05 × 0.03 × 0.02	0.09 × 0.04 × 0.02	0.04 × 0.03 × 0.02	0.08 × 0.05 × 0.03	0.06 × 0.06 × 0.02
Radiation	graphite monochromated Mo $K\alpha$, λ = 0.71073 Å				
μ(Mo $K\alpha$) (mm^{-1})	33.34	35.57	36.14	37.49	39.96
Transmission factors	0.277–0.519	0.176–0.558	0.334–0.636	0.153–0.452	0.207–0.453
2θ limits	3.93–51.16°	3.90–66.47°	3.96–66.35°	3.37–66.26°	3.40–66.44°
Data collected	$-5 \le h \le 5$, $-5 \le k \le 5$, $-75 \le l \le 75$	$-6 \le h \le 6$, $-6 \le k \le 6$, $-94 \le l \le 95$	$-6 \le h \le 6$, $-6 \le k \le 6$, $-93 \le l \le 93$	$-6 \le h \le 6$, $-6 \le k \le 5$, $-36 \le l \le 36$	$-6 \le h \le 6$, $-6 \le k \le 6$, $-36 \le l \le 36$
No. of data collected	2373	4546	4476	4144	5171
No. of unique data, including $F_o^2 < 0$	297 (R_{int} = 0.080)	564 (R_{int} = 0.031)	546 (R_{int} = 0.049)	647 (R_{int} = 0.055)	631 (R_{int} = 0.042)
No. of unique data, with $F_o^2 > 2\sigma(F_o^2)$	216	509	440	480	544
No. of variables	27	27	28	30	30
$R(F)$ for $F_o^2 > 2\sigma(F_o^2)$ [a]	0.032	0.021	0.026	0.029	0.028

$R_w(F_o^2)$ [b]	0.058	0.045	0.056	0.051	0.067
Goodness of fit	1.06	1.16	1.08	1.06	1.11
$(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$ (e Å^{-3})	1.74, –1.58	3.60, –2.78	2.05, –2.88	2.75, –3.55	4.07, –3.34

Formula	$Nd_{5.43(1)}Zn_4As_8$	$Sm_{5.40(1)}Zn_4As_8$	$Sm_{5.33(1)}Mn_{0.58(1)}Zn_{3.42(1)}As_8$	$Gd_{5.27(1)}Mn_{0.62(1)}Zn_{3.38(1)}As_8$
Formula mass (amu)	1644.54	1672.73	1656.80	1682.59
Space group	$R\bar{3}m1$ (No. 166)	$R\bar{3}m1$ (No. 166)	$R\bar{3}m1$ (No. 166)	$R\bar{3}m1$ (No. 166)
a (Å)	4.2038(11)	4.1689(4)	4.1691(9)	4.1398(12)
c (Å)	82.97(2)	82.103(9)	81.965(17)	81.17(2)
V (Å^3)	1269.8(7)	1235.8(3)	1233.8(6)	1204.8(8)
Z	3	3	3	3
ρ_{calcd} (g cm^{-3})	6.452	6.743	6.690	6.957
Crystal dimensions (mm)	0.05 × 0.04 × 0.03	0.06 × 0.06 × 0.03	0.06 × 0.04 × 0.01	0.05 × 0.04 × 0.02
Radiation	graphite monochromated Mo $K\alpha$, λ = 0.71073 Å			
μ(Mo $K\alpha$) (mm^{-1})	37.38	40.53	39.97	43.15
Transmission factors	0.284–0.411	0.127–0.406	0.238–0.675	0.261–0.499
2θ limits	2.95–66.23°	2.98–66.04°	2.98–66.53°	4.52–66.31°
Data collected	$-6 \le h \le 6$, $-6 \le k \le 6$, $-123 \le l \le 124$	$-6 \le h \le 6$, $-6 \le k \le 6$, $-123 \le l \le 123$	$-6 \le h \le 6$, $-6 \le k \le 6$, $-124 \le l \le 124$	$-6 \le h \le 6$, $-6 \le k \le 6$, $-123 \le l \le 123$
No. of data collected	5860	5971	6025	5634
No. of unique data, including $F_o^2 < 0$	741 (R_{int} = 0.066)	715 (R_{int} = 0.038)	726 (R_{int} = 0.039)	705 (R_{int} = 0.051)
No. of unique data, with $F_o^2 > 2\sigma(F_o^2)$	530	595	621	568

No. of variables	33	33	33	32
$R(F)$ for $F_o^2 > 2\sigma(F_o^2)$ [a]	0.040	0.026	0.025	0.033
$R_w(F_o^2)$ [b]	0.094	0.053	0.053	0.088
Goodness of fit	1.08	1.12	1.11	1.09
$(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$ (e Å^{-3})	4.37, –3.72	2.46, –3.53	2.33, –3.34	3.99, –5.18

[a] $R(F) = \sum||F_o| - |F_c|| / \sum|F_o|$.

[b] $R_w(F_o^2) = [\sum[w(F_o^2 - F_c^2)^2] / \sum wF_o^4]^{1/2}$; $w^{-1} = [\sigma^2(F_o^2) + (Ap)^2 + Bp]$, where $p = [\max(F_o^2,0) + 2F_c^2] / 3$.

Table S3. Atomic coordinates and equivalent isotropic displacement parameters for $RE_{2-y}Mn_xZn_{4-x}As_4 \cdot n(REAs)$ (n = 2, 3, 4).

Atom	Wyckoff position	Occupancy	*x*	*y*	*z*	U_{eq} (Å^2) [a]
$Ce_{3.32(1)}Mn_{1.1(1)}Zn_{2.9(1)}As_6$						
Ce1	6*c*	1	0	0	0.39010(2)	0.0187(4)
Ce2	3*b*	0.323(9)	0	0	1/2	0.038(3)
Ce3	3*a*	1	0	0	0	0.0170(5)
*M*1a	6*c*	0.721(7) Zn	0	0	0.13028(8)	0.0332(13)
*M*1b	6*c*	0.279(7) Mn	0	0	0.1478(3)	0.0332(13)
*M*2	6*c*	0.75(6) Zn, 0.25(6) Mn	0	0	0.23276(5)	0.0265(13)
As1	6*c*	1	0	0	0.08679(4)	0.0186(6)
As2	6*c*	1	0	0	0.19204(5)	0.0271(7)
As3	6*c*	1	0	0	0.30451(4)	0.0173(6)
$Pr_{3.46(1)}Zn_4As_6$						
Pr1	6*c*	1	0	0	0.38893(2)	0.0079(1)
Pr2	3*b*	0.461(3)	0	0	1/2	0.0105(3)
Pr3	3*a*	1	0	0	0	0.0072(1)
*M*1a	6*c*	0.879(3) Zn	0	0	0.12902(2)	0.0237(3)
*M*1b	6*c*	0.121(3) Zn	0	0	0.14966(15)	0.0237(3)
*M*2	6*c*	1 Zn	0	0	0.23482(2)	0.0165(2)
As1	6*c*	1	0	0	0.08505(2)	0.0088(2)
As2	6*c*	1	0	0	0.19442(2)	0.0116(2)
As3	6*c*	1	0	0	0.30502(2)	0.0079(1)
$Nd_{3.34(1)}Mn_{0.92(6)}Zn_{3.08(6)}As_6$						
Nd1	6*c*	1	0	0	0.38917(2)	0.0106(1)
Nd2	3*b*	0.339(4)	0	0	1/2	0.0234(8)
Nd3	3*a*	1	0	0	0	0.0092(2)
*M*1a	6*c*	0.722(4) Zn	0	0	0.12967(3)	0.0259(5)
*M*1b	6*c*	0.279(4) Mn	0	0	0.14757(12)	0.0259(5)
*M*2	6*c*	0.82(3) Zn, 0.18(3) Mn	0	0	0.23396(2)	0.0186(4)
As1	6*c*	1	0	0	0.08504(2)	0.0119(2)
As2	6*c*	1	0	0	0.19321(2)	0.0169(2)
As3	6*c*	1	0	0	0.30506(2)	0.0097(2)
$Nd_{4.41(1)}Zn_4As_7$						
Nd1	2*d*	1	1/3	2/3	0.07145(2)	0.0072(1)
Nd2	2*c*	1	0	0	0.21498(2)	0.0082(1)

Nd3	1*b*	0.410(4)	0	0	1/2	0.0112(6)
*M*1a	2*d*	0.830(4) Zn	1/3	2/3	0.40538(10)	0.0279(5)
*M*1b	2*d*	0.170(4) Zn	1/3	2/3	0.4550(5)	0.0279(5)
*M*2	2*d*	1 Zn	1/3	2/3	0.67457(6)	0.0169(3)
As1	2*d*	1	1/3	2/3	0.28933(5)	0.0087(2)
As2	2*d*	1	1/3	2/3	0.57088(5)	0.0116(2)
As3	2*d*	1	1/3	2/3	0.85542(4)	0.0067(2)
As4	1*a*	1	0	0	0	0.0067(3)
$Sm_{4.39(1)}Zn_4As_7$						
Sm1	2*d*	1	1/3	2/3	0.07017(2)	0.0085(1)
Sm2	2*c*	1	0	0	0.21375(2)	0.0094(1)
Sm3	1*b*	0.385(4)	0	0	1/2	0.0127(6)
*M*1a	2*d*	0.804(4) Zn	1/3	2/3	0.40566(10)	0.0313(5)
*M*1b	2*d*	0.196(4) Zn	1/3	2/3	0.4551(4)	0.0313(5)
*M*2	2*d*	1 Zn	1/3	2/3	0.67521(6)	0.0183(3)
As1	2*d*	1	1/3	2/3	0.28737(4)	0.0101(2)
As2	2*d*	1	1/3	2/3	0.57084(5)	0.0135(2)
As3	2*d*	1	1/3	2/3	0.85646(4)	0.0083(2)
As4	1*a*	1	0	0	0	0.0082(3)
$Nd_{5.43(1)}Zn_4As_8$						
Nd1	6*c*	1	0	0	0.29167(2)	0.0072(2)
Nd2	6*c*	1	0	0	0.41684(2)	0.0084(2)
Nd3	3*b*	0.429(5)	0	0	1/2	0.0088(7)
Nd4	3*a*	1	0	0	0	0.0069(2)
*M*1	6*c*	1 Zn	0	0	0.11573(2)	0.0182(5)
*M*2a	6*c*	0.848(5) Zn	0	0	0.19440(4)	0.0268(7)
*M*2b	6*c*	0.152(5) Zn	0	0	0.1799(2)	0.0268(7)
As1	6*c*	1	0	0	0.06309(2)	0.0071(3)
As2	6*c*	1	0	0	0.14598(2)	0.0121(3)
As3	6*c*	1	0	0	0.22807(2)	0.0092(3)
As4	6*c*	1	0	0	0.35437(2)	0.0072(3)
$Sm_{5.40(1)}Zn_4As_8$						
Sm1	6*c*	1	0	0	0.29186(2)	0.0072(1)
Sm2	6*c*	1	0	0	0.41644(2)	0.0082(1)
Sm3	3*b*	0.400(4)	0	0	1/2	0.0113(5)
Sm4	3*a*	1	0	0	0	0.0070(1)
*M*1	6*c*	1 Zn	0	0	0.11549(2)	0.0169(3)

*M*2a	6*c*	0.819(4) Zn	0	0	0.19437(3)	0.0286(5)
*M*2b	6*c*	0.181(4) Zn	0	0	0.17988(12)	0.0286(5)
As1	6*c*	1	0	0	0.06272(2)	0.0068(2)
As2	6*c*	1	0	0	0.14601(2)	0.0122(2)
As3	6*c*	1	0	0	0.22865(2)	0.0088(2)
As4	6*c*	1	0	0	0.35424(2)	0.0070(2)
$Sm_{5.33(1)}Mn_{0.58(1)}Zn_{3.42(1)}As_8$						
Sm1	6*c*	1	0	0	0.29173(2)	0.0089(1)
Sm2	6*c*	1	0	0	0.41670(2)	0.0104(1)
Sm3	3*b*	0.332(4)	0	0	1/2	0.0212(7)
Sm4	3*a*	1	0	0	0	0.0088(1)
*M*1	6*c*	1 Zn	0	0	0.11598(2)	0.0197(3)
*M*2a	6*c*	0.710(4) Zn	0	0	0.19445(3)	0.0255(4)
*M*2b	6*c*	0.290(4) Mn	0	0	0.18086(9)	0.0255(4)
As1	6*c*	1	0	0	0.06290(2)	0.0086(2)
As2	6*c*	1	0	0	0.14657(2)	0.0157(2)
As3	6*c*	1	0	0	0.22834(2)	0.0107(2)
As4	6*c*	1	0	0	0.35430(2)	0.0089(2)
$Gd_{5.27(1)}Mn_{0.62(1)}Zn_{3.38(1)}As_8$						
Gd1	6*c*	1	0	0	0.29192(2)	0.0112(2)
Gd2	6*c*	1	0	0	0.41624(2)	0.0134(2)
Gd3	3*b*	0.271(5)	0	0	1/2	0.0292(13)
Gd4	3*a*	1	0	0	0	0.0109(2)
*M*1	6*c*	1 Zn	0	0	0.11600(2)	0.0252(4)
*M*2a	6*c*	0.692(5) Zn	0	0	0.19511(4)	0.0276(6)
*M*2b	6*c*	0.308(5) Mn	0	0	0.18112(11)	0.0276(6)
As1	6*c*	1	0	0	0.06269(2)	0.0108(3)
As2	6*c*	1	0	0	0.14706(2)	0.0189(3)
As3	6*c*	1	0	0	0.22855(2)	0.0128(3)
As4	6*c*	1	0	0	0.35423(2)	0.0107(3)

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

Table S4. Interatomic distances (Å) for $RE_{2-y}Mn_xZn_{4-x}As_4 \cdot n(REAs)$ (n = 2, 3, 4).

	$Ce_{3.32(1)}Mn_{1.1(1)}Zn_{2.9(1)}As_6$	$Pr_{3.46(1)}Zn_4As_6$	$Nd_{3.34(1)}Mn_{0.92(6)}Zn_{3.08(6)}As_6$
*RE*1–As3 (×3)	2.991(2)	2.970(1)	2.952(1)
*RE*1–As1 (×3)	3.067(2)	3.050(1)	3.012(1)
*RE*1–*M*2 (×3)	3.652(3)	3.623(1)	3.611(1)
*RE*2–As2 (×6)	2.901(2)	2.987(1)	2.917(1)
*RE*2–*M*1b (×6)	2.702(8)	2.652(4)	2.685(3)
*RE*2–*M*1a (×6)	3.324(4)	3.385(1)	3.322(2)
*RE*3–As3 (×6)	3.023(2)	3.008(1)	2.978(1)
*M*1a–As2 (×3)	2.530(2)	2.507(1)	2.497(1)
*M*1a–As1	2.698(6)	2.754(2)	2.755(2)
*M*1a–*M*2 (×3)	3.053(4)	3.090(1)	3.053(2)
*M*1b–As2 (×3)	2.469(3)	2.520(3)	2.456(2)
*M*1b–As2	2.747(18)	2.804(10)	2.817(8)
*M*1b–*M*1b (×3)	3.38(2)	3.231(13)	3.374(10)
*M*2–As2	2.529(5)	2.530(1)	2.515(2)
*M*2–As1 (×3)	2.581(2)	2.571(1)	2.570(1)
*M*2–*M*1a (×3)	3.053(4)	3.090(1)	3.053(2)
	$Nd_{4.41(1)}Zn_4As_7$	$Sm_{4.39(1)}Zn_4As_7$	
*RE*1–As4 (×3)	2.977(1)	2.950(1)	
*RE*1–As3 (×3)	3.001(2)	2.969(1)	
*RE*2–As3 (×3)	2.962(2)	2.938(1)	
*RE*2–As1 (×3)	3.018(2)	2.986(1)	
*RE*2–*M*2 (×3)	3.608(2)	3.590(1)	
*RE*3–As2 (×6)	2.969(2)	2.947(1)	
*RE*3–*M*1b (×6)	2.657(5)	2.638(4)	
*RE*3–*M*1a (×6)	3.334(2)	3.304(2)	
*M*1a–As2 (×3)	2.490(2)	2.473(1)	
*M*1a–As1	2.809(3)	2.837(3)	
*M*1a–*M*2 (×3)	3.101(2)	3.092(2)	
*M*1b–As2 (×3)	2.502(3)	2.487(3)	
*M*1b–As2	2.805(12)	2.776(11)	
*M*1b–*M*1b (×3)	3.259(16)	3.231(14)	
*M*2–As2	2.510(2)	2.503(2)	
*M*2–As1 (×3)	2.576(2)	2.570(1)	

*M*2–*M*1a (×3)	3.101(2)	3.092(2)
	$Nd_{5.43(1)}Zn_4As_8$	$Sm_{5.40(1)}Zn_4As_8$
*RE*1–As4 (×3)	2.970(1)	2.940(1)
*RE*1–As1 (×3)	3.008(1)	2.973(1)
*RE*2–As1 (×3)	2.960(1)	2.931(1)
*RE*2–As3 (×3)	3.025(1)	2.989(1)
*RE*2–*M*1 (×3)	3.611(2)	3.586(1)
*RE*3–As2 (×6)	2.973(1)	2.944(1)
*RE*3–*M*2b (×6)	2.665(7)	2.640(4)
*RE*3–*M*2a (×6)	3.344(2)	3.312(2)
*RE*4–As4 (×6)	2.989(1)	2.956(1)
*M*1–As2	2.510(3)	2.506(2)
*M*1–As3 (×3)	2.578(1)	2.565(1)
*M*1–*M*2a (×3)	3.098(2)	3.084(2)
*M*2a–As2 (×3)	2.496(1)	2.475(1)
*M*2a–As2	2.793(3)	2.815(2)
*M*2a–*M*1 (×3)	3.098(2)	3.084(2)
*M*2b–As2 (×3)	2.504(4)	2.483(2)
*M*2b–As2	2.818(17)	2.780(10)
*M*2b–*M*2b (×3)	3.28(2)	3.240(13)
	$Sm_{5.33(1)}Mn_{0.58(1)}Zn_{3.42(1)}As_8$	$Gd_{5.27(1)}Mn_{0.62(1)}Zn_{3.38(1)}As_8$
*RE*1–As4 (×3)	2.942(1)	2.913(1)
*RE*1–As1 (×3)	2.973(1)	2.949(1)
*RE*2–As1 (×3)	2.934(1)	2.899(1)
*RE*2–As3 (×3)	2.989(1)	2.978(1)
*RE*2–*M*1 (×3)	3.598(1)	3.596(2)
*RE*3–As2 (×6)	2.917(1)	2.871(1)
*RE*3–*M*2b (×6)	2.674(3)	2.662(4)
*RE*3–*M*2a (×6)	3.314(2)	3.323(2)
*RE*4–As4 (×6)	2.958(1)	2.931(1)
*M*1–As2	2.507(2)	2.522(2)
*M*1–As3 (×3)	2.570(1)	2.558(1)
*M*1–*M*2a (×3)	3.053(2)	2.995(2)
*M*2a–As2 (×3)	2.488(1)	2.495(1)
*M*2a–As2	2.778(3)	2.715(3)

*M*2a–*M*1 (×3)	3.052(2)	2.995(2)
*M*2b–As2 (×3)	2.455(2)	2.426(2)
*M*2b–As2	2.811(7)	2.764(9)
*M*2b–*M*2b (×3)	3.348(10)	3.349(13)

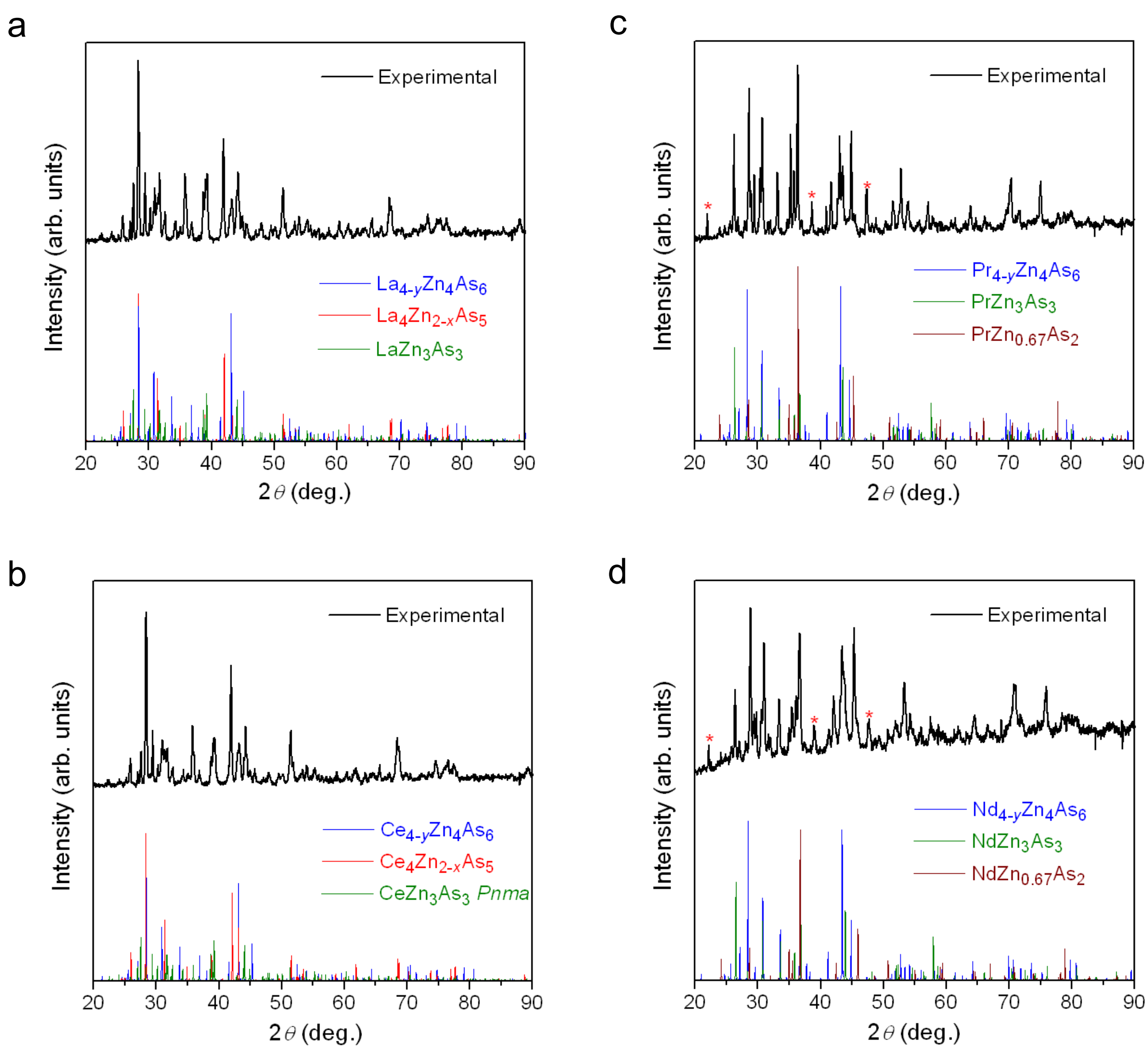

Figure S1. Powder XRD patterns for $RE_{4-y}Zn_4As_6$ (RE = La–Nd).

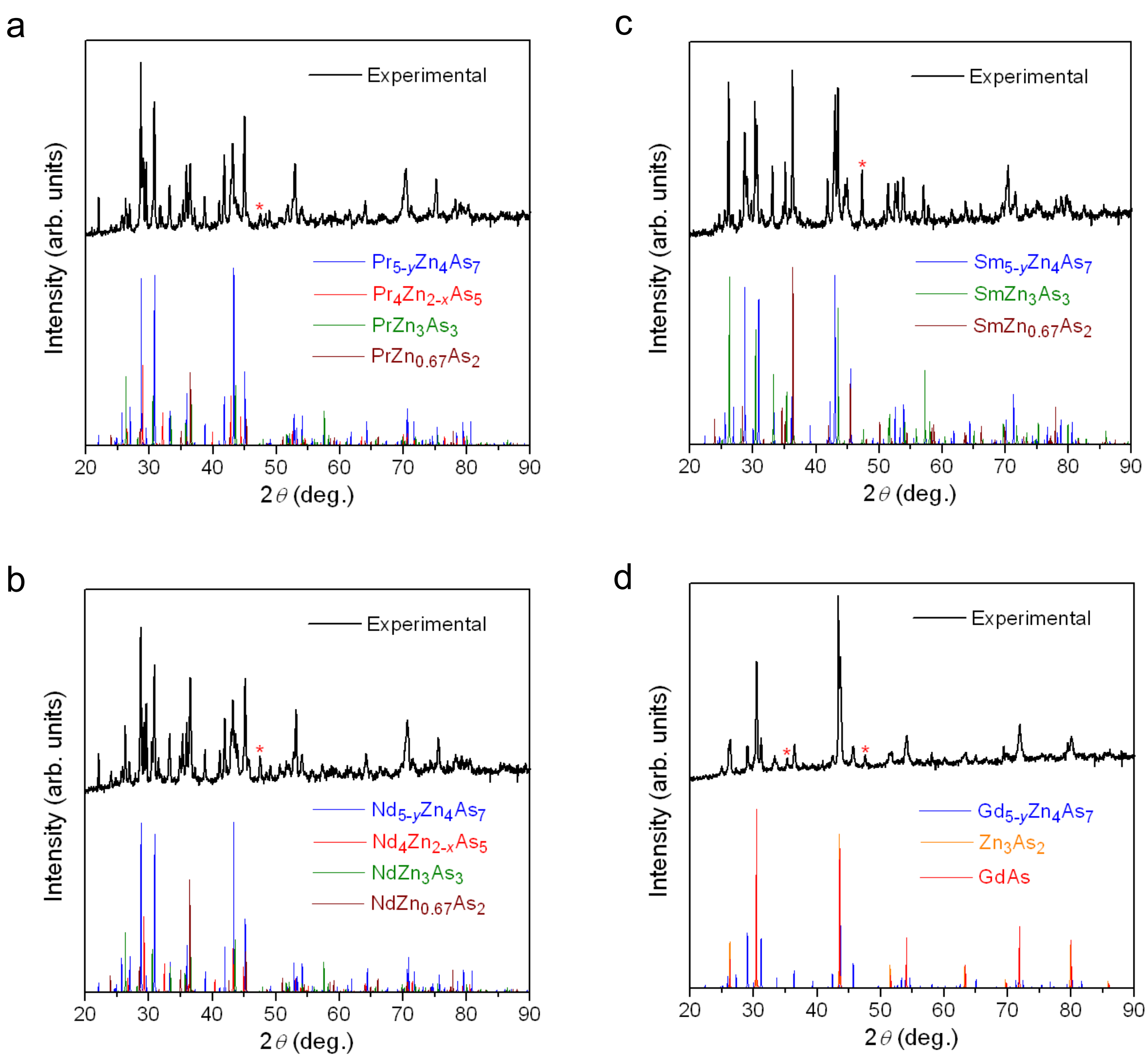

Figure S2. Powder XRD patterns for $RE_{5-y}Zn_4As_7$ (RE = Pr, Nd, Sm, Gd).

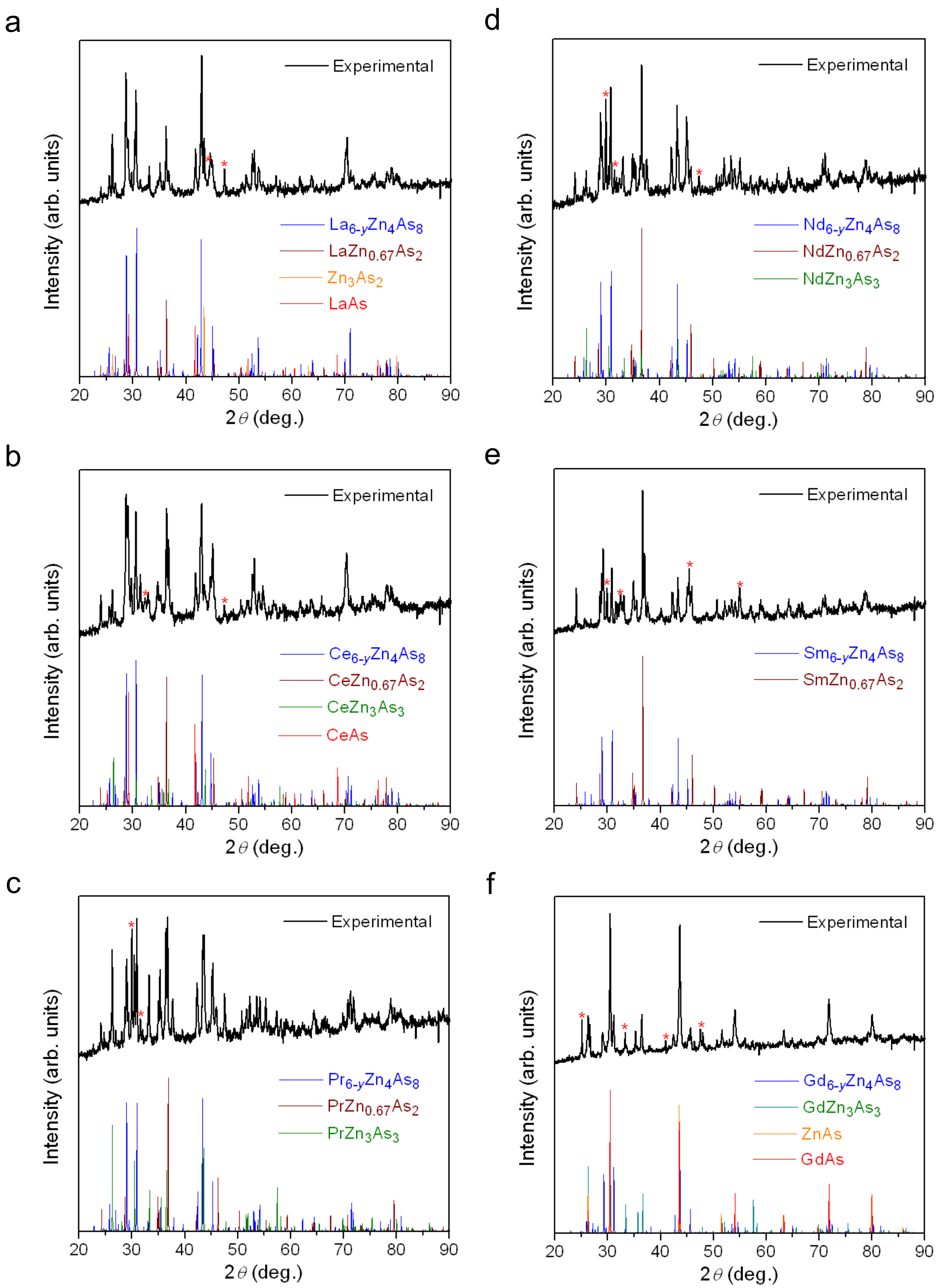

Figure S3. Powder XRD patterns for $RE_{6-y}Zn_4As_8$ (RE = La–Nd, Sm, Gd).