Supporting Information

Crystal chemistry and magnetic properties of the solid solutions $Ca_{14-x}RE_xMnBi_{11}$ (*RE* = La–Nd, Sm, Gd–Ho; $x \approx 0.6$–0.8)

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Table S1 Atomic coordinates and equivalent isotropic displacement parameters for $Ca_{13.18}Ce_{0.82}MnBi_{11}$

Atom	Site	*x*	*y*	*z*	U_{eq} [a]
Ca1/Ce1[b]	32*d*	0.0412(1)	0.0736(1)	0.17164(8)	0.0146(7)
Ca2/Ce2[b]	32*d*	0.02286(9)	0.37639(9)	0.00273(8)	0.0179(7)
Ca3/Ce3[b]	16*e*	0.3532(2)	0	1/4	0.015(1)
Ca4/Ce4[b]	32*c*	0.3411(1)	0.0727(1)	0.09276(8)	0.0189(8)
Mn1	8*a*	0	1/4	3/8	0.0142(6)
Bi1	16*f*	0.13835(2)	0.38835(2)	1/8	0.0132(1)
Bi2	32*g*	0.35865(2)	0.25576(2)	0.05972(2)	0.0141(1)
Bi3	32*g*	0.12967(2)	0.02732(2)	0.04677(2)	0.0146(1)
Bi4	8*b*	0	1/4	1/8	0.0134(2)

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

[b] Refined occupancies: Ca1/Ce1 = 0.958(4)Ca + 0.042Ce; Ca2/Ce2 = 0.878(4)Ca + 0.122Ce; Ca3/Ce3 = 0.982(5)Ca + 0.018Ce; Ca4/Ce4 = 0.967(4)Ca + 0.033Ce.

Table S2 Atomic coordinates and equivalent isotropic displacement parameters for $Ca_{13.34}Pr_{0.66}MnBi_{11}$

Atom	Site	*x*	*y*	*z*	U_{eq}[a]
Ca1/Pr1[b]	32*d*	0.0412(1)	0.0738(1)	0.17178(7)	0.0109(6)
Ca2/Pr2[b]	32*d*	0.0234(1)	0.37642(9)	0.00310(7)	0.0135(6)
Ca3/Pr3[b]	16*e*	0.3533(2)	0	1/4	0.0112(8)
Ca4/Pr4[b]	32*c*	0.3412(1)	0.0723(1)	0.09272(7)	0.0148(6)
Mn1	8*a*	0	1/4	3/8	0.0100(6)
Bi1	16*f*	0.13842(2)	0.38842(2)	1/8	0.0088(1)
Bi2	32*g*	0.35868(2)	0.25588(2)	0.05973(2)	0.0099(1)
Bi3	32*g*	0.12963(2)	0.02732(2)	0.04683(2)	0.0104(1)
Bi4	8*b*	0	1/4	1/8	0.0091(2)

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

[b] Refined occupancies: Ca1/Pr1 = 0.954(4)Ca + 0.046Pr; Ca2/Pr2 = 0.920(4)Ca + 0.080Pr; Ca3/Pr3 = 0.974(5)Ca + 0.026Pr; Ca4/Pr4 = 0.973(4)Ca + 0.027Pr.

Table S3 Atomic coordinates and equivalent isotropic displacement parameters for $Ca_{13.36}Nd_{0.64}MnBi_{11}$

Atom	Site	*x*	*y*	*z*	U_{eq}[a]
Ca1/Nd1[b]	32*d*	0.04120(9)	0.07361(9)	0.17157(8)	0.0083(5)
Ca2/Nd2[b]	32*d*	0.0234(1)	0.3766(1)	0.00356(9)	0.0123(6)
Ca3/Nd3[b]	16*e*	0.3529(2)	0	1/4	0.0098(9)
Ca4/Nd4[b]	32*c*	0.3413(1)	0.0723(1)	0.09254(9)	0.0135(7)
Mn1	8*a*	0	1/4	3/8	0.0098(6)
Bi1	16*f*	0.13848(2)	0.38848(2)	1/8	0.0077(1)
Bi2	32*g*	0.35876(2)	0.25588(2)	0.05959(2)	0.0087(1)
Bi3	32*g*	0.12964(2)	0.02733(2)	0.04689(2)	0.0090(1)
Bi4	8*b*	0	1/4	1/8	0.0082(2)

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

[b] Refined occupancies: Ca1/Nd1 = 0.947(4)Ca + 0.053Nd; Ca2/Nd2 = 0.935(4)Ca + 0.065Nd; Ca3/Nd3 = 0.970(5)Ca + 0.030Nd; Ca4/Nd4 = 0.973(4)Ca + 0.027Nd.

Table S4 Atomic coordinates and equivalent isotropic displacement parameters for $Ca_{13.38}Sm_{0.62}MnBi_{11}$

Atom	Site	*x*	*y*	*z*	U_{eq}[a]
Ca1/Sm1[b]	32*d*	0.0410(1)	0.0736(1)	0.1716(8)	0.0135(6)
Ca2/Sm2[b]	32*d*	0.0236(1)	0.3766(1)	0.0036(1)	0.0159(7)
Ca3/Sm3[b]	16*e*	0.3530(2)	0	1/4	0.013(1)
Ca4/Sm4[b]	32*c*	0.3414(1)	0.0728(1)	0.0926(1)	0.0178(8)
Mn1	8*a*	0	1/4	3/8	0.0132(6)
Bi1	16*f*	0.13854(2)	0.38854(2)	1/8	0.0115(2)
Bi2	32*g*	0.35861(2)	0.25598(2)	0.05957(2)	0.0127(1)
Bi3	32*g*	0.12966(2)	0.02744(2)	0.04697(2)	0.0133(1)
Bi4	8*b*	0	1/4	1/8	0.0120(2)

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

[b] Refined occupancies: Ca1/Sm1 = 0.930(4)Ca + 0.070Sm; Ca2/Sm2 = 0.956(5)Ca + 0.044Sm; Ca3/Sm3 = 0.962(6)Ca + 0.038Sm; Ca4/Sm4 = 0.977(4)Ca + 0.023Sm.

Table S5 Atomic coordinates and equivalent isotropic displacement parameters for $Ca_{13.38}Gd_{0.62}MnBi_{11}$

Atom	Site	*x*	*y*	*z*	U_{eq}[a]
Ca1/Gd1[b]	32*d*	0.04102(9)	0.07380(9)	0.17134(7)	0.0099(6)
Ca2/Gd2[b]	32*d*	0.0237(1)	0.3766(1)	0.00386(9)	0.0134(7)
Ca3/Gd3[b]	16*e*	0.3527(1)	0	1/4	0.0092(8)
Ca4/Gd4[b]	32*c*	0.3413(1)	0.0724(1)	0.09259(8)	0.0129(7)
Mn1	8*a*	0	1/4	3/8	0.0099(6)
Bi1	16*f*	0.13857(2)	0.38857(2)	1/8	0.0084(1)
Bi2	32*g*	0.35854(2)	0.25602(2)	0.05952(2)	0.0096(1)
Bi3	32*g*	0.12972(2)	0.02748(2)	0.04704(2)	0.0101(1)
Bi4	8*b*	0	1/4	1/8	0.0089(2)

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

[b]Refined occupancies: Ca1/Gd1 = 0.917(4)Ca + 0.083Gd; Ca2/Gd2 = 0.970(4)Ca + 0.030Gd; Ca3/Gd3 = 0.948(5)Ca + 0.052Gd; Ca4/Gd4 = 0.982(4)Ca + 0.018Gd.

Table S6 Atomic coordinates and equivalent isotropic displacement parameters for $Ca_{13.30}Tb_{0.70}MnBi_{11}$

Atom	Site	*x*	*y*	*Z*	U_{eq}[a]
Ca1/Tb1[b]	32*d*	0.0406(1)	0.0738(1)	0.17141(7)	0.0115(6)
Ca2/Tb2[b]	32*d*	0.0239(1)	0.3768(1)	0.00400(9)	0.0145(8)
Ca3/Tb3[b]	16*e*	0.3526(2)	0	1/4	0.0092(9)
Ca4/Tb4[b]	32*c*	0.3412(1)	0.0724(1)	0.09239(9)	0.0147(8)
Mn1	8*a*	0	1/4	3/8	0.0102(7)
Bi1	16*f*	0.13858(2)	0.38858(2)	1/8	0.0088(2)
Bi2	32*g*	0.35846(2)	0.25600(3)	0.05936(2)	0.0102(1)
Bi3	32*g*	0.12974(3)	0.02751(2)	0.04712(2)	0.0109(1)
Bi4	8*b*	0	1/4	1/8	0.0091(2)

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

[b]Refined occupancies: Ca1/Tb1 = 0.893(4)Ca + 0.107Tb; Ca2/Tb2 = 0.977(4)Ca + 0.023Tb; Ca3/Tb3 = 0.948(5)Ca + 0.052Tb; Ca4/Tb4 = 0.982(4)Ca + 0.018Tb.

Table S7 Atomic coordinates and equivalent isotropic displacement parameters for $Ca_{13.31}Dy_{0.69}MnBi_{11}$

Atom	Site	*x*	*y*	*Z*	U_{eq}[a]
Ca1/Dy1[b]	32*d*	0.04058(8)	0.07382(8)	0.17117(6)	0.0137(5)
Ca2/Dy2[b]	32*d*	0.0240(1)	0.3767(1)	0.00383(9)	0.0171(7)
Ca3/Dy3[b]	16*e*	0.3525(1)	0	1/4	0.0109(7)
Ca4/Dy4[b]	32*c*	0.3416(1)	0.0726(1)	0.09256(8)	0.0156(7)
Mn1	8*a*	0	1/4	3/8	0.0129(6)
Bi1	16*f*	0.13856(2)	0.38856(2)	1/8	0.0114(1)
Bi2	32*g*	0.35839(2)	0.25605(2)	0.05932(2)	0.0130(1)
Bi3	32*g*	0.12981(2)	0.02767(2)	0.04723(2)	0.0137(1)
Bi4	8*b*	0	1/4	1/8	0.0115(2)

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

[b]Refined occupancies: Ca1/Dy1 = 0.883(3)Ca + 0.117Dy; Ca2/Dy2 = 0.983(3)Ca + 0.017Dy; Ca3/Dy3 = 0.944(4)Ca + 0.056Dy; Ca4/Dy4 = 0.990(3)Ca + 0.010Dy.

Table S8 Atomic coordinates and equivalent isotropic displacement parameters for $Ca_{13.36}Ho_{0.64}MnBi_{11}$

Atom	Site	*x*	*y*	*Z*	U_{eq}[a]
Ca1/Ho1[b]	32*d*	0.04043(8)	0.07392(8)	0.17117(6)	0.0132(5)
Ca2/Ho2[b]	32*d*	0.0236(1)	0.3767(1)	0.00387(9)	0.0169(7)
Ca3/Ho3[b]	16*e*	0.3527(1)	0	1/4	0.0120(7)
Ca4/Ho4[b]	32*c*	0.3411(1)	0.0726(1)	0.09245(8)	0.0173(7)
Mn1	8*a*	0	1/4	3/8	0.0131(6)
Bi1	16*f*	0.13861(2)	0.38861(2)	1/8	0.0114(1)
Bi2	32*g*	0.35832(2)	0.25605(2)	0.05947(2)	0.0130(1)
Bi3	32*g*	0.12990(2)	0.02769(2)	0.04723(2)	0.0137(1)
Bi4	8*b*	0	1/4	1/8	0.0114(2)

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

[b] Refined occupancies: Ca1/Ho1 = 0.896(3)Ca + 0.104Ho; Ca2/Ho2 = 0.988(3)Ca + 0.012Ho; Ca3/Ho3 = 0.944(4)Ca + 0.056Ho; Ca4/Ho4 = 0.986(3)Ca + 0.014Ho.

Table S9 Atomic coordinates and equivalent isotropic displacement parameters for $Ca_{13.83}Er_{0.17}MnBi_{11}$

Atom	Site	*x*	*Y*	*Z*	U_{eq}[a]
Ca1/Er1[b]	32*d*	0.0408(1)	0.0740(1)	0.17166(8)	0.0118(6)
Ca2/Er2[b]	32*d*	0.0237(1)	0.3766(1)	0.0033(1)	0.0138(8)
Ca3/Er3[b]	16*e*	0.3531(2)	0	1/4	0.0100(9)
Ca4/Er4[b]	32*c*	0.3411(1)	0.0726(1)	0.09269(9)	0.0141(7)
Mn1	8*a*	0	1/4	3/8	0.0099(6)
Bi1	16*f*	0.13869(2)	0.38869(2)	1/8	0.0095(1)
Bi2	32*g*	0.35835(2)	0.25615(2)	0.06014(2)	0.0107(1)
Bi3	32*g*	0.12992(2)	0.02754(2)	0.04706(2)	0.0112(1)
Bi4	8*b*	0	1/4	1/8	0.0099(2)

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

[b] Refined occupancies: Ca1/Er1 = 0.968(3)Ca + 0.032Er; Ca2/Er2 = 0.999(3)Ca + 0.001Er; Ca3/Er3 = 0.985(4)Ca + 0.015Er; Ca4/Er4 = 0.998(3)Ca + 0.002Er.

Table S10 Selected interatomic distances (Å) for $Ca_{14-x}RE_xMnBi_{11}$

	Ce	Pr	Nd	Sm	Gd	Tb	Dy	Ho	Er
Ca1/RE1—Bi2	3.236(2)	3.236(2)	3.237(2)	3.231(2)	3.230(2)	3.229(2)	3.227(1)	3.227(1)	3.233(2)
Ca1/RE1—Bi4	3.262(2)	3.257(2)	3.260(2)	3.256(2)	3.247(2)	3.249(2)	3.244(1)	3.243(1)	3.251(2)
Ca1/RE1—Bi2	3.266(2)	3.260(2)	3.268(2)	3.262(2)	3.263(2)	3.261(2)	3.264(1)	3.265(1)	3.265(2)
Ca1/RE1—Bi3	3.273(2)	3.268(2)	3.271(2)	3.269(2)	3.263(2)	3.270(2)	3.267(1)	3.269(1)	3.270(2)
Ca1/RE1—Bi3	3.287(2)	3.285(2)	3.285(2)	3.281(2)	3.273(2)	3.280(2)	3.272(1)	3.274(1)	3.281(2)
Ca1/RE1—Bi1	3.301(2)	3.298(2)	3.300(2)	3.294(2)	3.289(2)	3.286(2)	3.281(1)	3.279(1)	3.294(2)
Ca2/RE2—Bi2	3.208(2)	3.201(2)	3.207(2)	3.204(2)	3.201(2)	3.204(2)	3.198(2)	3.206(2)	3.206(2)
Ca2/RE2—Bi3	3.231(2)	3.232(2)	3.230(2)	3.228(2)	3.225(2)	3.228(2)	3.229(2)	3.226(2)	3.237(2)
Ca2/RE2—Bi3	3.344(2)	3.337(2)	3.342(2)	3.339(2)	3.337(2)	3.336(2)	3.338(2)	3.344(2)	3.342(2)
Ca2/RE2—Bi1	3.391(2)	3.376(2)	3.373(2)	3.367(2)	3.359(2)	3.357(2)	3.359(2)	3.362(2)	3.370(2)
Ca2/RE2—Bi4	3.518(2)	3.509(2)	3.508(2)	3.503(2)	3.495(2)	3.500(2)	3.500(2)	3.499(2)	3.506(2)
Ca2/RE2—Bi2	3.859(2)	3.866(2)	3.872(2)	3.873(2)	3.872(2)	3.881(2)	3.877(2)	3.876(2)	3.883(2)
Ca3/RE3—Bi3 × 2	3.205(2)	3.203(2)	3.201(2)	3.200(2)	3.193(2)	3.195(2)	3.193(2)	3.196(2)	3.203(2)
Ca3/RE3—Bi2 × 2	3.320(2)	3.314(2)	3.321(2)	3.313(2)	3.311(2)	3.313(2)	3.311(2)	3.310(2)	3.314(2)
Ca3/RE3—Bi1 × 2	3.4014(2)	3.396(4)	3.4016(3)	3.3968(3)	3.3932(3)	3.3975(3)	3.3961(3)	3.3955(3)	3.3912(3)
Ca4/RE4—Bi2	3.222(2)	3.226(2)	3.228(2)	3.219(2)	3.222(2)	3.224(2)	3.219(2)	3.220(2)	3.225(2)
Ca4/RE4—Bi1	3.245(2)	3.233(2)	3.236(2)	3.238(2)	3.227(2)	3.230(2)	3.230(2)	3.232(2)	3.234(2)
Ca4/RE4—Bi3	3.275(2)	3.270(2)	3.273(2)	3.273(2)	3.270(2)	3.272(2)	3.275(2)	3.274(2)	3.269(2)
Ca4/RE4—Bi3	3.305(2)	3.304(2)	3.311(2)	3.305(2)	3.301(2)	3.307(2)	3.305(2)	3.302(2)	3.298(2)
Ca4/RE4—Bi2	3.466(2)	3.461(2)	3.469(2)	3.460(2)	3.459(2)	3.468(2)	3.458(2)	3.464(2)	3.450(2)
Ca4/RE4—Bi3	3.830(2)	3.826(2)	3.827(2)	3.826(2)	3.816(2)	3.816(2)	3.819(2)	3.810(2)	3.819(2)
Mn1—Bi2 × 4	2.8247(4)	2.8209(4)	2.8240(4)	2.8234(4)	2.8215(4)	2.8272(4)	2.8269(4)	2.8269(4)	2.8208(4)
Bi1—Bi4	3.3355(5)	3.3335(6)	3.3365(5)	3.3349(6)	3.3312(5)	3.3334(6)	3.3308(5)	3.3330(5)	3.3412(5)