Electronic Supplementary Information (ESI)

Synthesis and structural study of a new group of trigermanates, $CaRE_2Ge_3O_{10}$ (*RE* = La–Yb)

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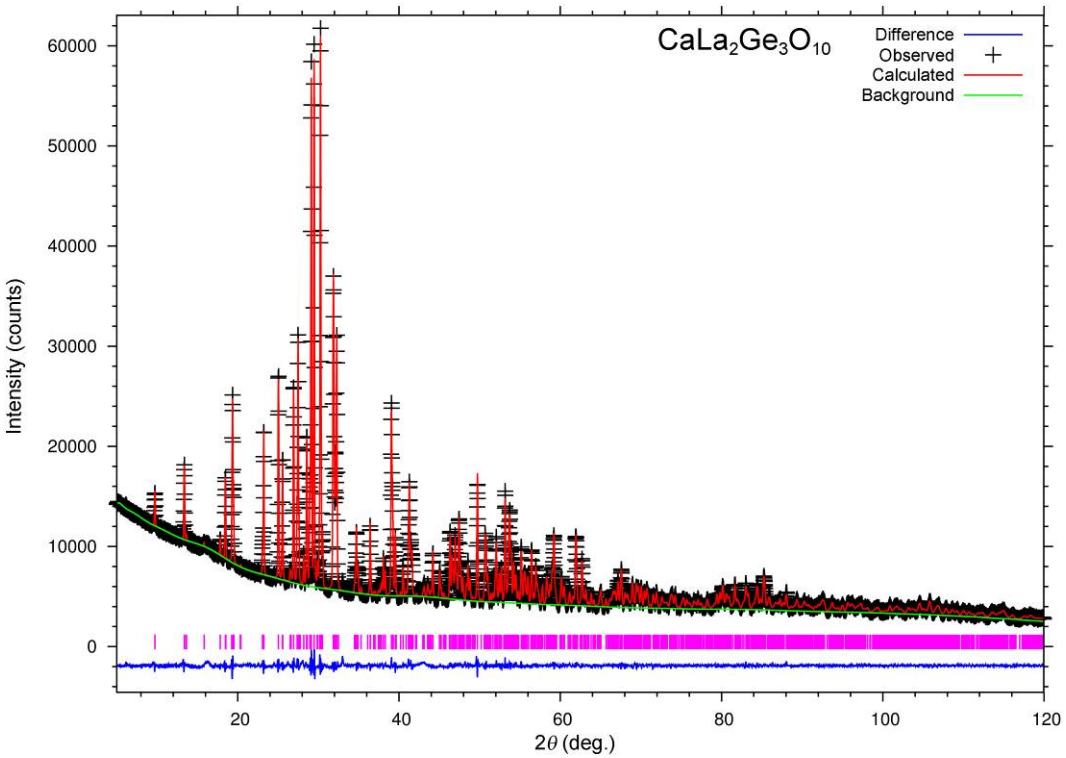

Fig. S1 Rietveld refinement of $CaLa_2Ge_3O_{10}$ from the powder XRD data.

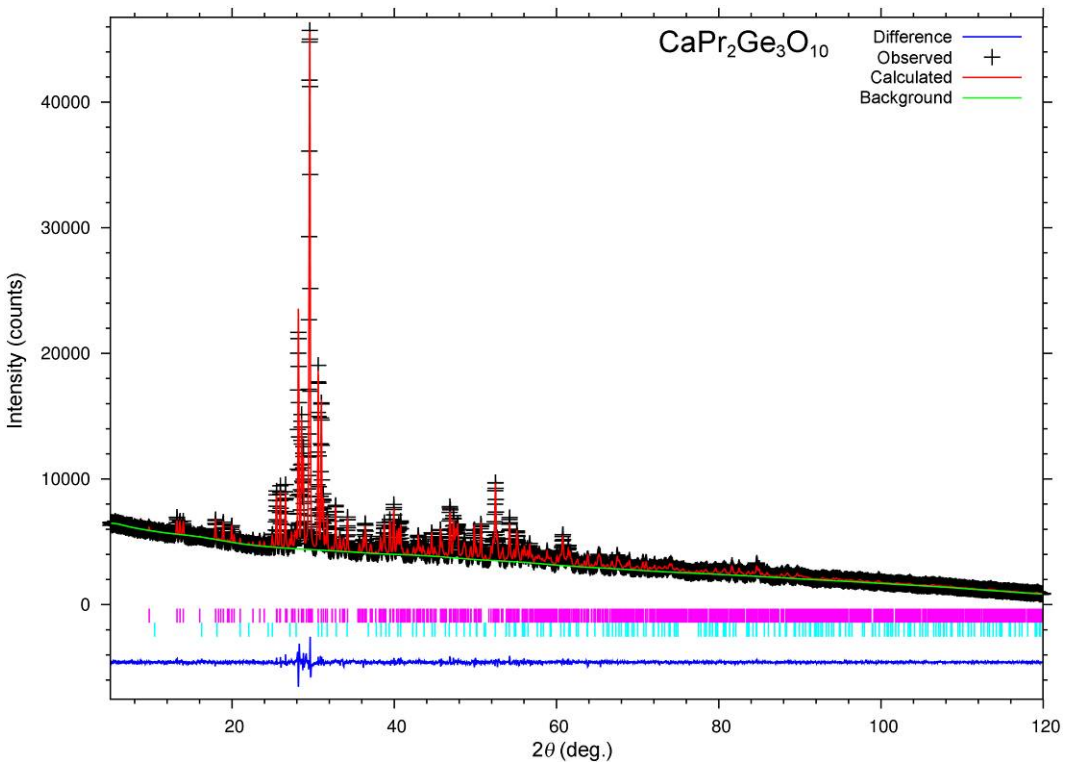

Fig. S2 Rietveld refinement of $CaPr_2Ge_3O_{10}$ from the powder XRD data.

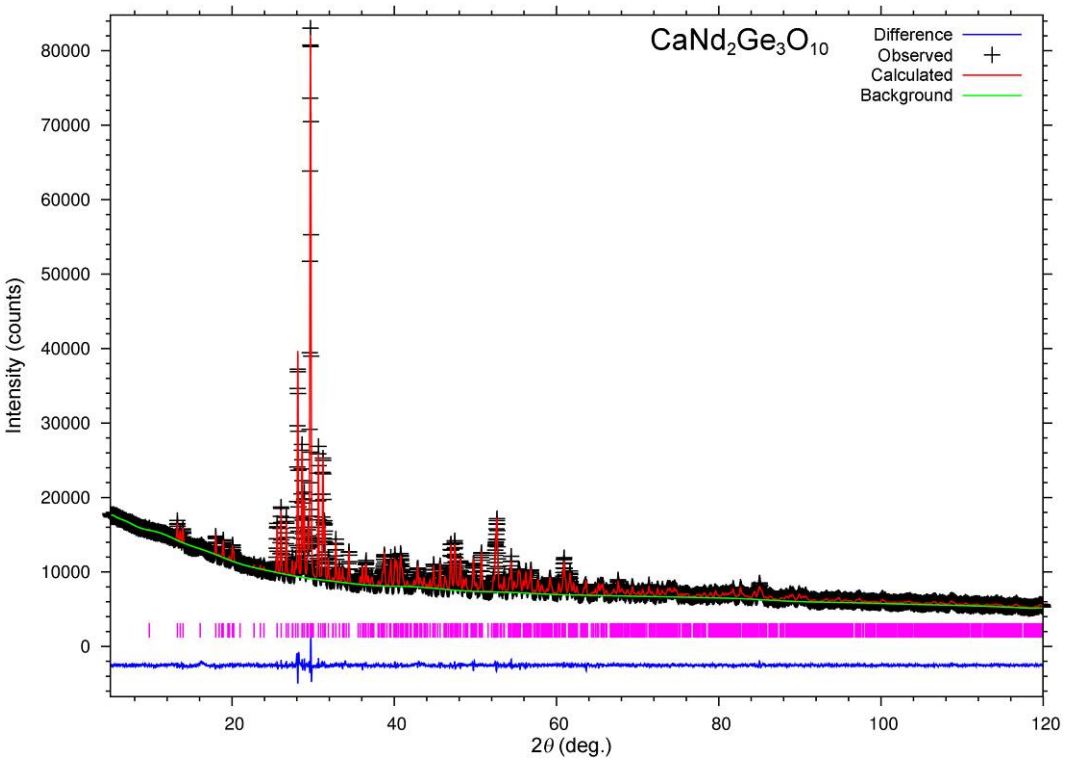

Fig. S3 Rietveld refinement of $CaNd_2Ge_3O_{10}$ from the powder XRD data.

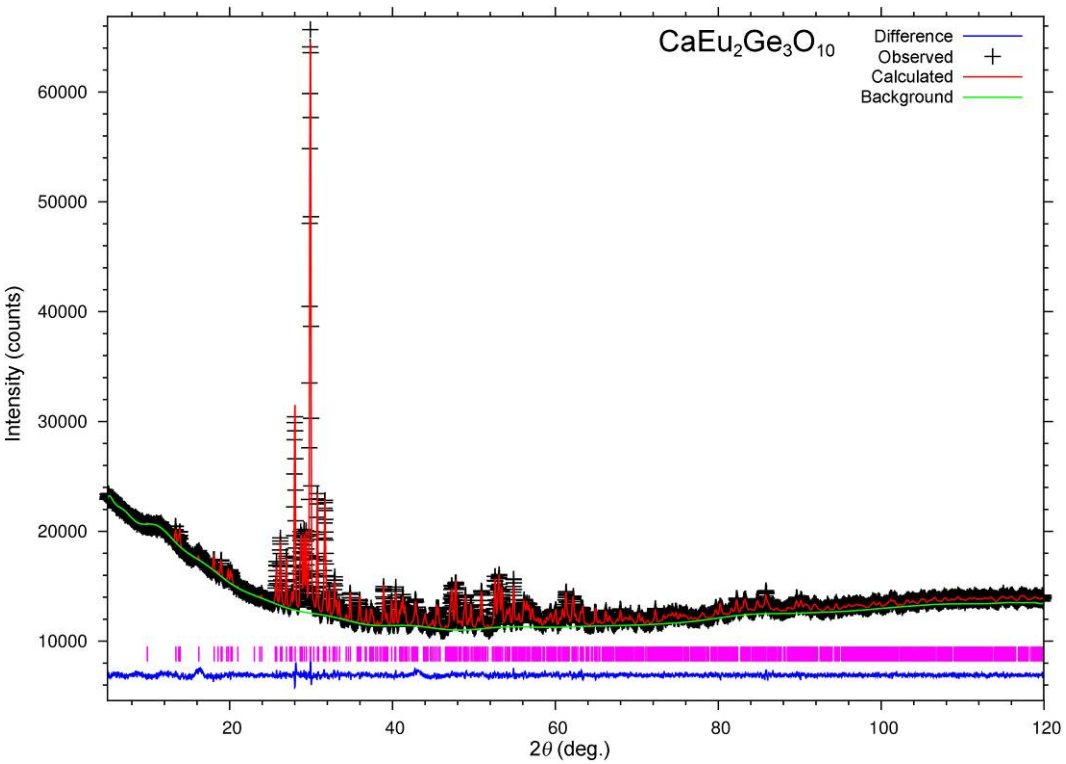

Fig. S4 Rietveld refinement of $CaEu_2Ge_3O_{10}$ from the powder XRD data.

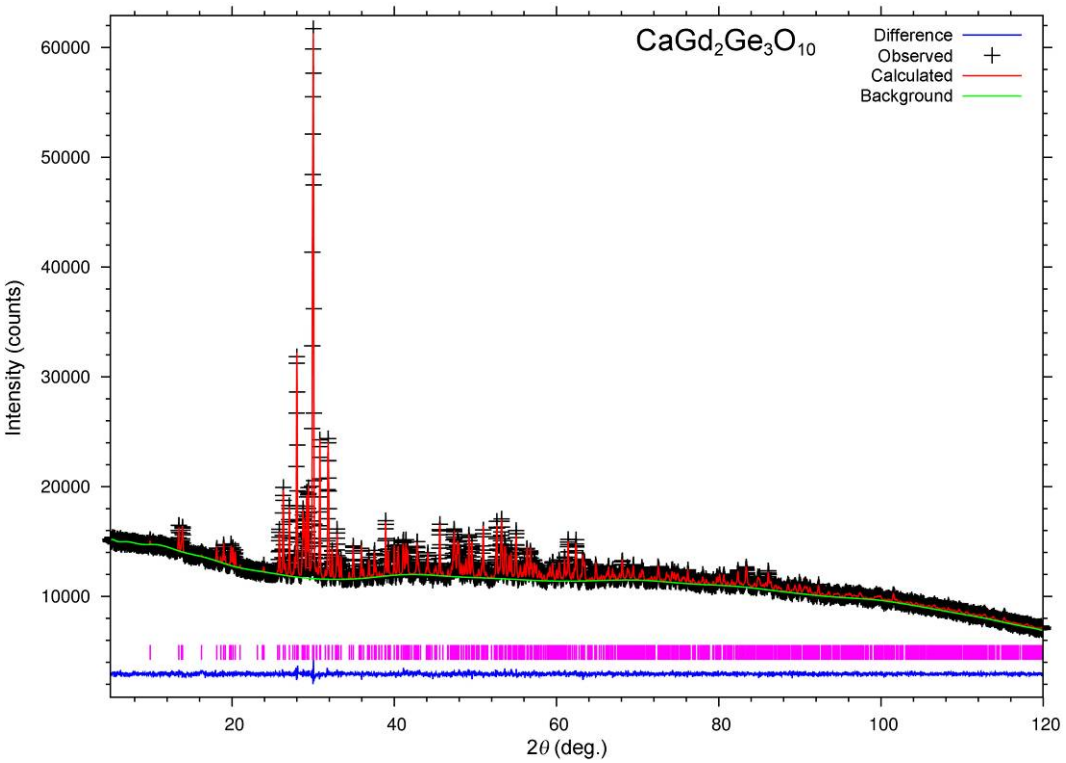

Fig. S5 Rietveld refinement of $CaGd_2Ge_3O_{10}$ from the powder XRD data.

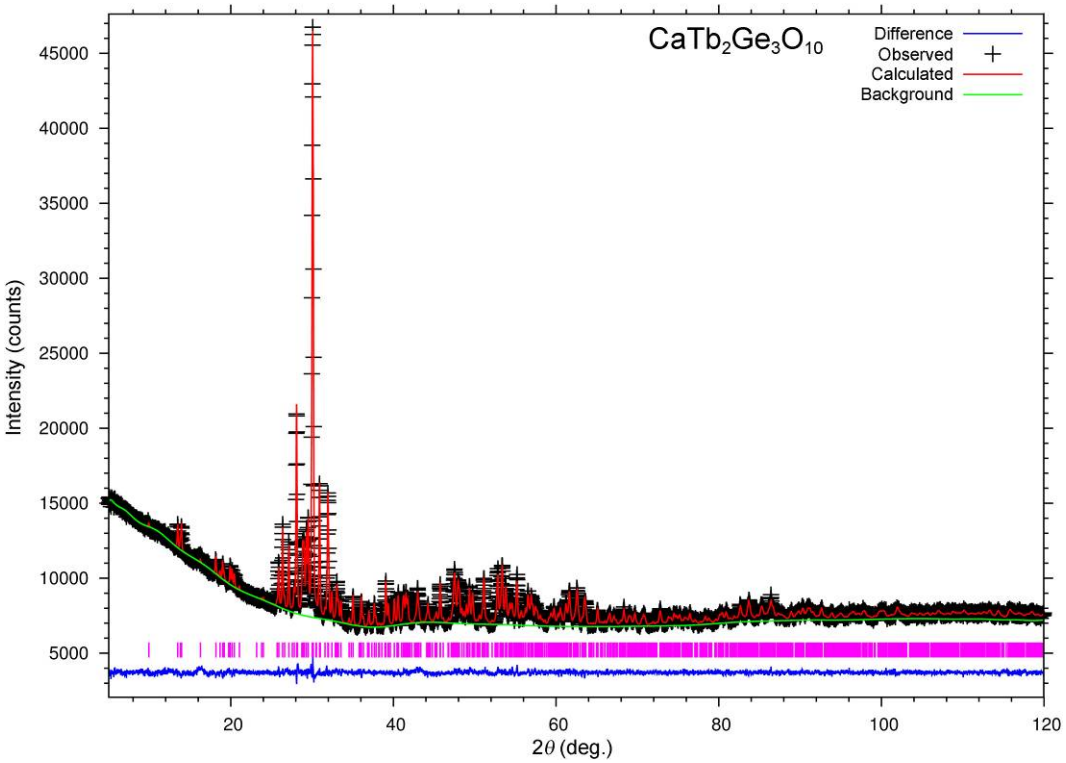

Fig. S6 Rietveld refinement of $CaTb_2Ge_3O_{10}$ from the powder XRD data.

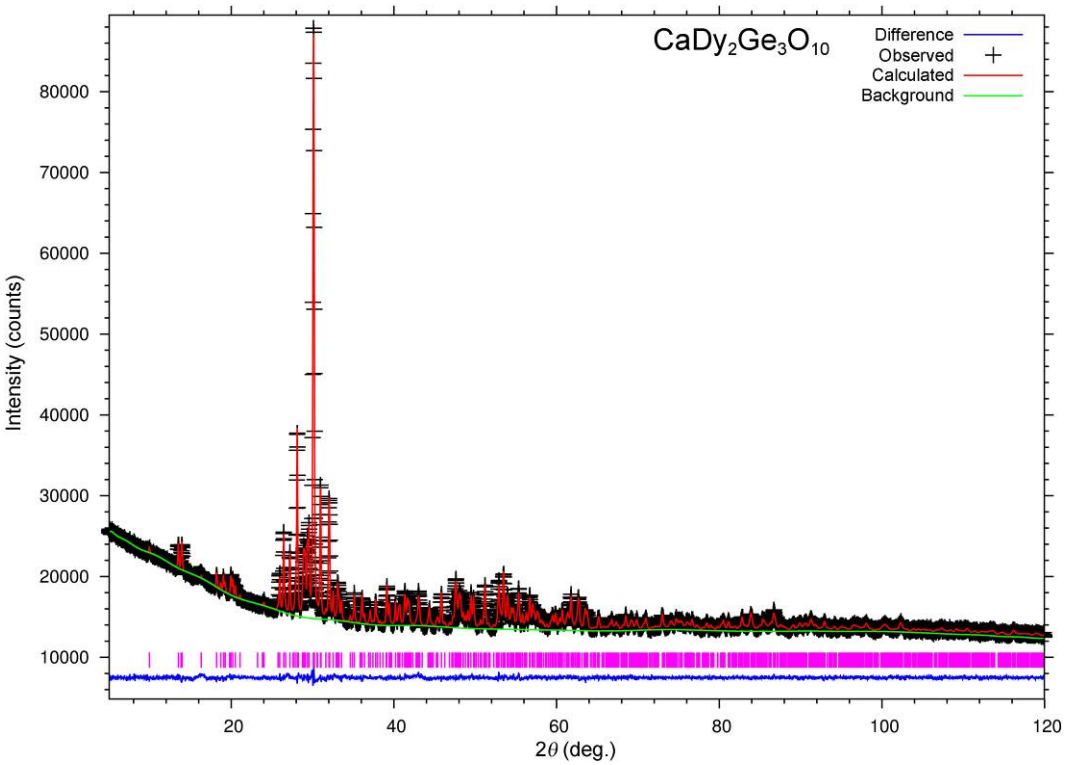

Fig. S7 Rietveld refinement of $CaDy_2Ge_3O_{10}$ from the powder XRD data.

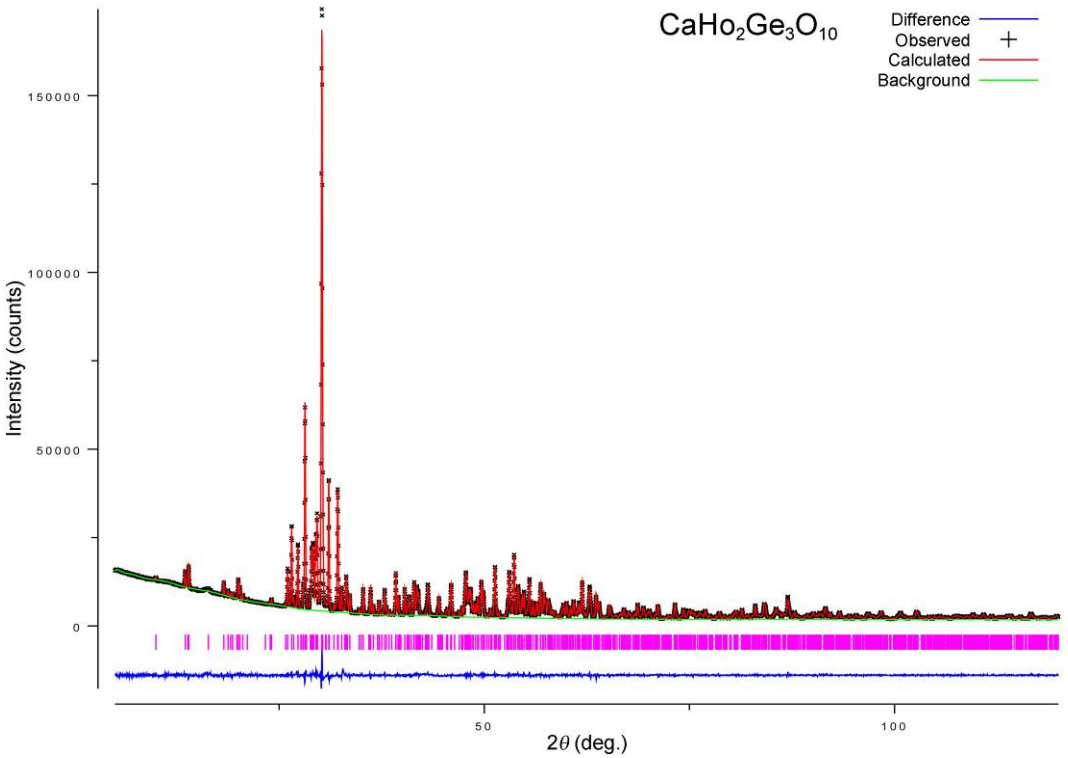

Fig. S8 Rietveld refinement of $CaHo_2Ge_3O_{10}$ from the powder XRD data.

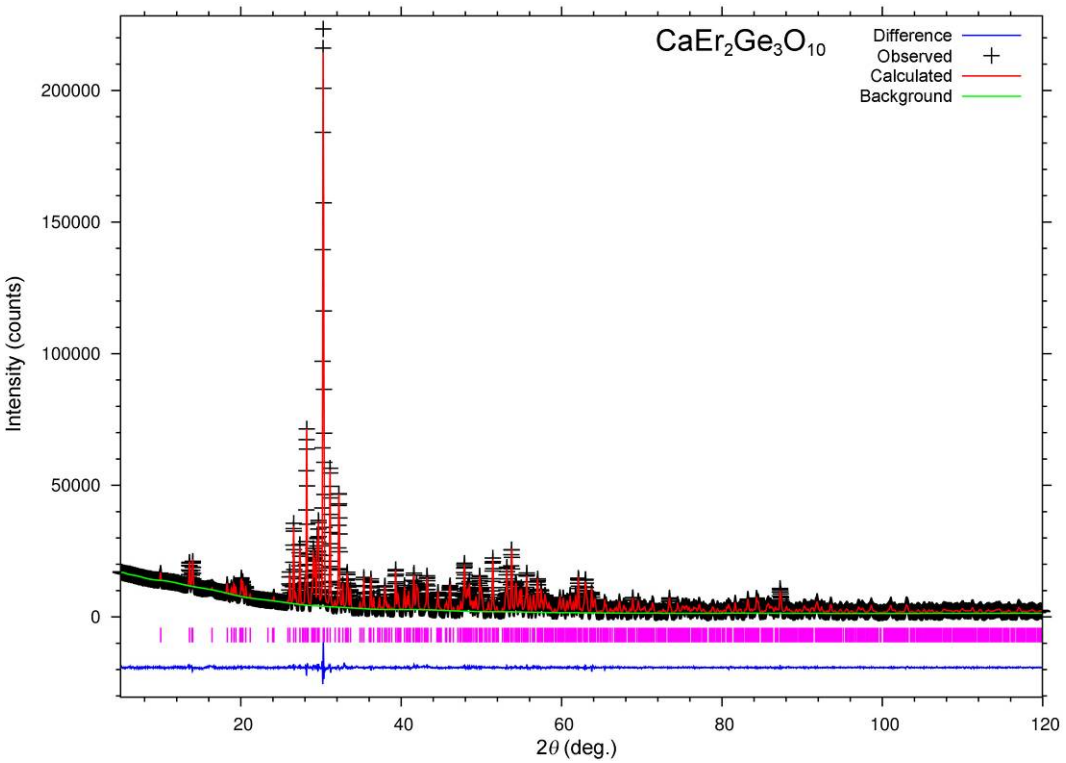

Fig. S9 Rietveld refinement of $CaEr_2Ge_3O_{10}$ from the powder XRD data.

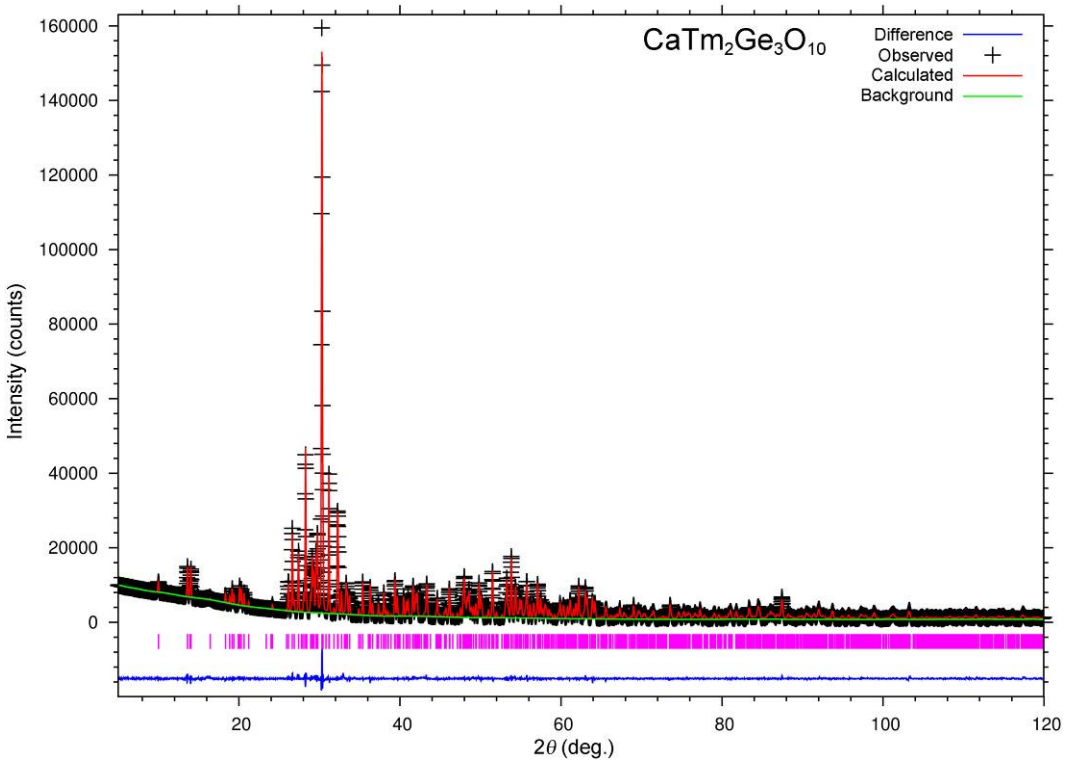

Fig. S10 Rietveld refinement of $CaTm_2Ge_3O_{10}$ from the powder XRD data.

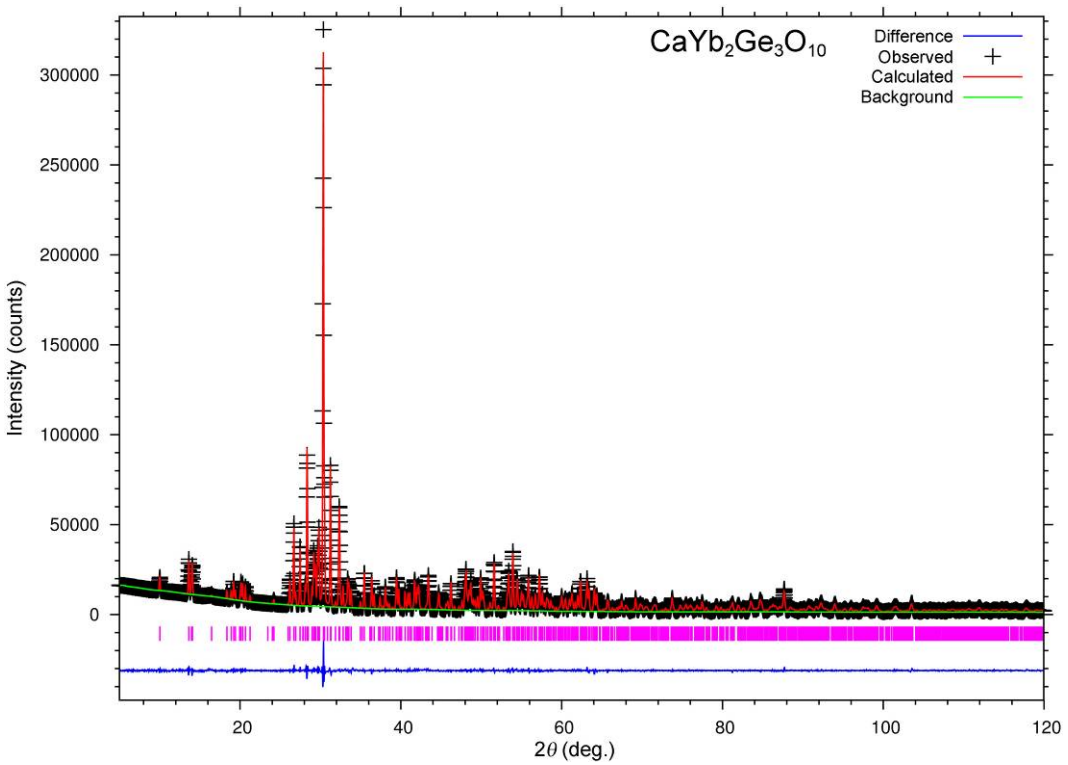

Fig. S11 Rietveld refinement of $CaYb_2Ge_3O_{10}$ from the powder XRD data.

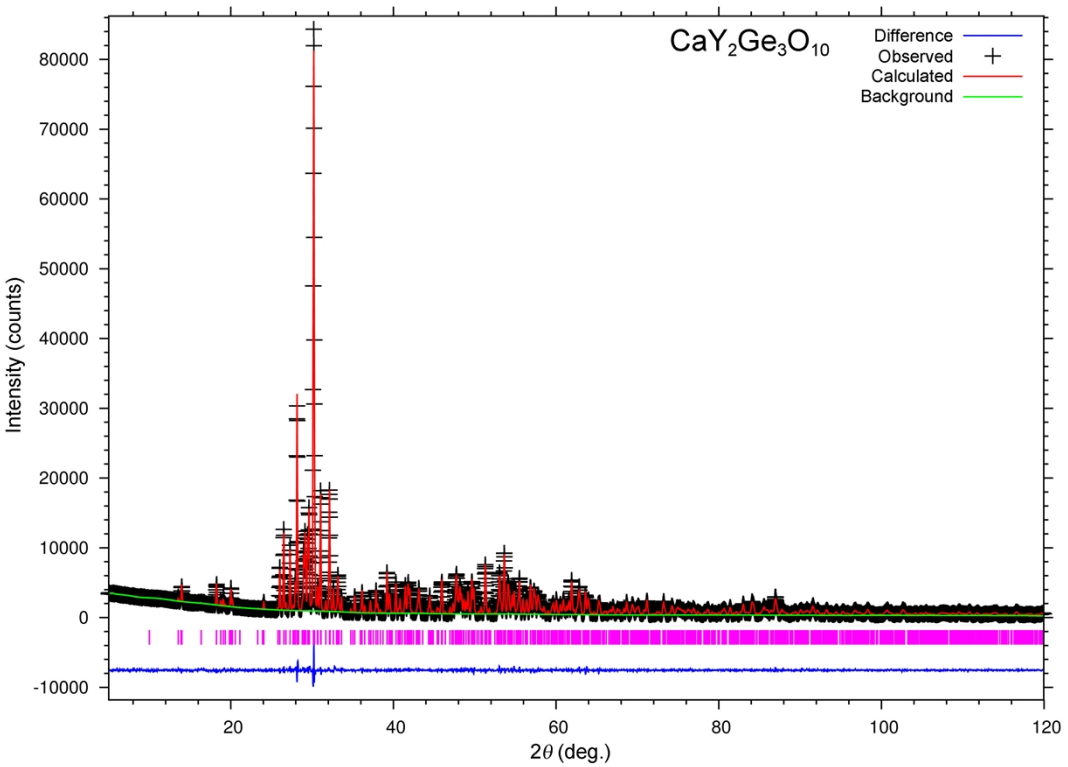

Fig. S12 Rietveld refinement of $CaY_2Ge_3O_{10}$ from the powder XRD data.

Table S1 Atomic coordinates and thermal parameters (Å^2) for CaRE_2Ge$_3$O$_{10}$ (*RE* = La–Tb)

Atom		La	Pr	Nd	Eu	Gd	Tb
Ca(1)/*RE*(1)	*x/a*	0.9296(6)	0.0397(5)	0.0358(4)	0.0305(6)	0.0306(5)	0.0280(6)
	y/b	0.0516(5)	0.8987(4)	0.8992(4)	0.9014(5)	0.9042(4)	0.9012(5)
	z/c	0.5771(2)	0.4110(2)	0.4115(2)	0.4141(2)	0.4156(2)	0.4151(2)
	U_i/U_e*100	3.9(2)	3.0(3)	2.5(1)	2.6(1)	2.9(1)	3.2(1)
Ca(2)/*RE*(2)	*x/a*	0.6384(2)	0.5814(5)	0.5838(5)	0.5823(6)	0.5814(5)	0.5790(6)
	y/b	0.1758(2)	0.2312(4)	0.2341(4)	0.2384(5)	0.2373(4)	0.2357(5)
	z/c	0.90843(8)	0.4131(2)	0.4137(2)	0.4139(2)	0.4150(2)	0.4139(2)
	U_i/U_e*100	2.89(6)	2.2(3)	2.3(1)	3.4(2)	2.6(1)	3.4(1)
Ca(3)/*RE*(3)	*x/a*	0.8416(2)	0.1417(5)	0.1376(4)	0.1316(4)	0.1301(4)	0.1288(4)
	y/b	0.2762(2)	0.1331(5)	0.1315(4)	0.1328(4)	0.1309(4)	0.1299(4)
	z/c	0.73952(7)	0.2513(2)	0.2521(2)	0.2536(2)	0.2525(2)	0.2529(2)
	U_i/U_e*100	3.02(6)	2.1(3)	2.0(1)	2.3(1)	2.80(8)	2.98(9)
Ge(1)	*x/a*	0.1738(4)	0.0977(8)	0.1010(7)	0.0999(7)	0.0973(6)	0.0997(7)
	y/b	0.0650(3)	0.3678(7)	0.3681(6)	0.3728(7)	0.3702(6)	0.3697(7)
	z/c	0.9217(1)	0.4274(3)	0.4264(3)	0.4234(3)	0.4262(3)	0.4237(3)
	U_i/U_e*100	2.89(9)	3.0(3)	2.8(1)	2.7(2)	3.1(1)	3.0(1)
Ge(2)	*x/a*	0.4128(4)	0.4463(8)	0.4426(7)	0.4473(8)	0.4499(7)	0.4470(8)
	y/b	0.1787(4)	0.2268(6)	0.2253(5)	0.2293(7)	0.2290(6)	0.2294(7)
	z/c	0.5731(1)	0.0732(3)	0.0722(3)	0.0726(3)	0.0729(3)	0.0722(3)
	U_i/U_e*100	3.22(9)	2.3(3)	2.1(1)	3.3(2)	2.7(1)	3.7(2)
Ge(3)	*x/a*	0.2970(3)	0.6603(7)	0.6589(6)	0.6569(7)	0.6582(6)	0.6537(7)
	y/b	0.2751(3)	0.1264(7)	0.1253(6)	0.1201(7)	0.1223(6)	0.1206(7)
	z/c	0.7160(1)	0.2352(3)	0.2354(2)	0.2411(3)	0.2413(2)	0.2408(3)
	U_i/U_e*100	2.92(7)	1.9(3)	2.3(1)	2.8(1)	2.8(1)	3.4(1)
O(1)	*x/a*	0.870(2)	0.029(3)	0.022(3)	0.013(3)	0.010(3)	0.022(3)
	y/b	0.136(1)	0.067(3)	0.067(3)	0.074(3)	0.085(2)	0.083(3)
	z/c	0.0335(6)	0.125(1)	0.123(1)	0.133(1)	0.124(1)	0.131(1)
O(2)	*x/a*	0.968(2)	0.066(3)	0.059(3)	0.063(3)	0.066(3)	0.070(3)
	y/b	0.227(1)	0.708(3)	0.709(3)	0.717(3)	0.719(3)	0.710(3)
	z/c	0.8890(5)	0.045(1)	0.045(1)	0.048(1)	0.043(1)	0.048(1)
O(3)	*x/a*	0.140(2)	0.150(3)	0.154(3)	0.159(3)	0.145(3)	0.157(3)
	y/b	0.445(1)	0.457(3)	0.463(3)	0.464(3)	0.450(2)	0.452(3)
	z/c	0.7319(6)	0.222(1)	0.223(1)	0.228(1)	0.217(1)	0.226(1)
O(4)	*x/a*	0.537(1)	0.194(3)	0.188(3)	0.192(3)	0.184(3)	0.175(3)
	y/b	0.250(2)	0.800(3)	0.813(2)	0.826(3)	0.817(2)	0.818(3)
	z/c	0.7787(5)	0.288(1)	0.279(1)	0.265(1)	0.2722(9)	0.266(1)
O(5)	*x/a*	0.300(2)	0.233(3)	0.217(3)	0.220(3)	0.216(3)	0.225(3)
	y/b	0.032(2)	0.213(3)	0.207(3)	0.209(3)	0.205(2)	0.193(3)
	z/c	0.8603(6)	0.384(1)	0.382(1)	0.380(1)	0.378(1)	0.381(1)
O(6)	*x/a*	0.380(2)	0.304(3)	0.302(2)	0.299(3)	0.312(2)	0.303(3)
	y/b	0.307(1)	0.062(3)	0.054(3)	0.061(3)	0.047(2)	0.051(3)
	z/c	0.4912(5)	0.001(1)	0.001(1)	0.006(1)	0.004(1)	0.005(1)
O(7)	*x/a*	0.235(2)	0.300(3)	0.297(3)	0.285(3)	0.302(2)	0.296(3)
	y/b	0.999(1)	0.408(3)	0.418(3)	0.433(3)	0.422(2)	0.431(3)
	z/c	0.5459(6)	0.090(1)	0.086(1)	0.079(1)	0.0841(9)	0.084(1)
O(8)	*x/a*	0.132(2)	0.485(3)	0.495(3)	0.486(4)	0.485(3)	0.479(3)
	y/b	0.081(1)	0.175(3)	0.184(2)	0.178(3)	0.166(2)	0.165(3)
	z/c	0.6970(6)	0.280(1)	0.279(1)	0.278(1)	0.287(1)	0.280(1)
O(9)	*x/a*	0.667(1)	0.502(3)	0.520(3)	0.534(3)	0.527(3)	0.531(3)
	y/b	0.663(2)	0.063(3)	0.067(3)	0.063(3)	0.054(2)	0.054(3)
	z/c	0.3695(6)	0.141(1)	0.144(1)	0.144(1)	0.150(1)	0.149(1)
O(10)	*x/a*	0.663(2)	0.616(3)	0.626(3)	0.639(3)	0.626(3)	0.636(3)
	y/b	0.101(2)	0.307(3)	0.325(2)	0.327(3)	0.313(3)	0.312(3)
	z/c	0.6173(6)	0.041(1)	0.043(1)	0.040(1)	0.040(1)	0.036(1)
	U_i/U_e*100[a]	2.8(1)	1.9(3)	2.2(2)	1.8(2)	1.8(2)	1.7(2)

[a] The thermal vibration parameters of oxygen atoms have been constrained as a single variable.

Table S2 Atomic coordinates and thermal parameters (Å^2) for CaRE_2Ge$_3$O$_{10}$ (*RE* = Y, Dy–Yb)

Atom		Dy	Y	Ho	Er	Tm	Yb
Ca(1)/*RE*(1)	*x/a*	0.0267(5)	0.0249(3)	0.0259(3)	0.02453(20)	0.0238(2)	0.0229(2)
	y/b	0.9008(4)	0.9009(3)	0.9003(2)	0.90048(18)	0.8997(2)	0.8988(2)
	z/c	0.4152(2)	0.4149(1)	0.4151(1)	0.41485(7)	0.41479(9)	0.41475(7)
	U_i/U_e*100	2.9(1)	2.2(1)	2.58(6)	2.485(45)	2.58(6)	2.48(5)
Ca(2)/*RE*(2)	*x/a*	0.5801(5)	0.5821(3)	0.5815(3)	0.58133(21)	0.5813(3)	0.5797(2)
	y/b	0.2353(4)	0.2343(3)	0.2349(2)	0.23391(19)	0.2323(2)	0.2295(2)
	z/c	0.4140(2)	0.4148(1)	0.4148(1)	0.41467(8)	0.4144(1)	0.41421(8)
	U_i/U_e*100	2.8(1)	2.0(1)	2.30(6)	2.215(49)	2.20(7)	2.30(6)
Ca(3)/*RE*(3)	*x/a*	0.1280(3)	0.1292(2)	0.1291(2)	0.12881(14)	0.1283(2)	0.1281(1)
	y/b	0.1296(4)	0.1290(2)	0.1290(2)	0.12831(13)	0.1274(2)	0.1258(1)
	z/c	0.2532(2)	0.25331(9)	0.25332(8)	0.25352(6)	0.25337(7)	0.25340(6)
	U_i/U_e*100	2.37(8)	1.79(9)	2.02(4)	2.023(28)	1.99(4)	1.99(3)
Ge(1)	*x/a*	0.0980(6)	0.0971(3)	0.0975(3)	0.09699(26)	0.0961(3)	0.0958(3)
	y/b	0.3715(6)	0.3718(3)	0.3716(3)	0.37084(24)	0.3710(3)	0.3697(3)
	z/c	0.4241(3)	0.4243(1)	0.4243(1)	0.42393(10)	0.4234(1)	0.4231(1)
	U_i/U_e*100	2.6(1)	2.39(9)	2.15(5)	2.29(5)	2.28(6)	2.22(5)
Ge(2)	*x/a*	0.4479(7)	0.4520(3)	0.4523(3)	0.45326(26)	0.4539(3)	0.4542(3)
	y/b	0.2287(6)	0.2279(3)	0.2266(3)	0.22628(23)	0.2262(3)	0.2251(3)
	z/c	0.0719(2)	0.0720(1)	0.0722(1)	0.07203(10)	0.0718(1)	0.0716(1)
	U_i/U_e*100	2.6(1)	2.2(1)	1.95(5)	2.08(5)	2.00(6)	2.06(5)
Ge(3)	*x/a*	0.6543(6)	0.6560(3)	0.6561(3)	0.65645(25)	0.6556(3)	0.6555(3)
	y/b	0.1174(6)	0.1170(3)	0.1175(3)	0.11641(25)	0.1149(3)	0.1132(3)
	z/c	0.2412(2)	0.2411(1)	0.2413(1)	0.24133(9)	0.2408(1)	0.2408(1)
	U_i/U_e*100	2.5(1)	1.95(9)	1.70(5)	1.92(4)	1.90(6)	1.86(5)
O(1)	*x/a*	0.017(3)	0.016(1)	0.016(1)	0.0148(12)	0.014(2)	0.017(1)
	y/b	0.076(2)	0.075(1)	0.079(1)	0.0768(11)	0.076(1)	0.077(1)
	z/c	0.130(1)	0.1289(5)	0.1269(5)	0.1275(5)	0.1280(6)	0.1293(5)
O(2)	*x/a*	0.072(3)	0.068(1)	0.065(1)	0.0635(12)	0.066(2)	0.066(1)
	y/b	0.711(2)	0.719(1)	0.715(1)	0.7162(11)	0.717(1)	0.714(1)
	z/c	0.0505(9)	0.0459(4)	0.0488(5)	0.0467(5)	0.0485(6)	0.0470(5)
O(3)	*x/a*	0.160(3)	0.147(1)	0.148(1)	0.1462(12)	0.147(2)	0.147(1)
	y/b	0.448(2)	0.450(1)	0.449(1)	0.4494(10)	0.446(1)	0.445(1)
	z/c	0.227(1)	0.2171(4)	0.2199(5)	0.2176(4)	0.2188(6)	0.2195(5)
O(4)	*x/a*	0.180(2)	0.184(1)	0.1864(12)	0.1876(11)	0.187(2)	0.188(1)
	y/b	0.812(2)	0.813(1)	0.815(1)	0.8109(11)	0.808(1)	0.808(1)
	z/c	0.2642(9)	0.2677(4)	0.2663(5)	0.2660(4)	0.2665(6)	0.2665(5)
O(5)	*x/a*	0.218(3)	0.217(1)	0.220(1)	0.2177(13)	0.215(2)	0.216(1)
	y/b	0.198(2)	0.202(1)	0.201(1)	0.2001(11)	0.197(1)	0.195(1)
	z/c	0.380(1)	0.3795(5)	0.3815(5)	0.3807(5)	0.3787(6)	0.3787(5)
O(6)	*x/a*	0.307(2)	0.308(1)	0.309(1)	0.3088(11)	0.309(2)	0.304(1)
	y/b	0.055(2)	0.053(1)	0.055(1)	0.0570(11)	0.058(1)	0.057(1)
	z/c	0.004(1)	0.0059(5)	0.0056(6)	0.0056(5)	0.0045(6)	0.0039(5)
O(7)	*x/a*	0.299(2)	0.308(1)	0.303(1)	0.3040(11)	0.303(1)	0.302(1)
	y/b	0.425(2)	0.419(1)	0.420(1)	0.4175(11)	0.416(1)	0.411(1)
	z/c	0.0838(8)	0.0876(4)	0.0864(4)	0.0862(4)	0.0870(5)	0.0870(4)
O(8)	*x/a*	0.480(3)	0.473(1)	0.478(1)	0.4772(12)	0.478(2)	0.474(1)
	y/b	0.158(2)	0.168(1)	0.165(1)	0.1651(10)	0.162(1)	0.161(1)
	z/c	0.282(1)	0.2843(5)	0.2848(5)	0.2843(4)	0.2845(6)	0.2841(5)
O(9)	*x/a*	0.532(3)	0.525(1)	0.529(1)	0.5272(12)	0.529(2)	0.529(1)
	y/b	0.059(2)	0.048(1)	0.052(1)	0.0484(11)	0.048(1)	0.045(1)
	z/c	0.147(1)	0.1458(5)	0.1476(6)	0.1460(5)	0.1451(6)	0.1452(5)
O(10)	*x/a*	0.632(2)	0.636(1)	0.638(1)	0.6371(11)	0.634(2)	0.636(1)
	y/b	0.317(3)	0.320(1)	0.324(1)	0.3236(11)	0.322(1)	0.322(1)
	z/c	0.036(1)	0.0387(5)	0.0380(5)	0.0387(5)	0.0375(6)	0.0389(5)
	U_i/U_e*100[a]	1.8(2)	1.7(1)	1.63(8)		1.8(1)	1.73(8)

[a] The thermal vibration parameters of oxygen atoms have been constrained as a single variable.

Table S3 The Ca^{2+}–RE^{3+} fractions in three metal cation sites in the structures of $CaRE_2Ge_3O_{10}$ (*RE* = La–Tb)

Atom	La	Pr	Nd	Eu	Gd	Tb
Ca(1)	0.928(0)	0.227(2)	0.276(4)	0.395(5)	0.404(4)	0.390(5)
RE(1)	0.072(0)	0.773(2)	0.724(4)	0.605(5)	0.596(4)	0.610(5)
Ca(2)	0.073(3)	0.427(3)	0.424(1)	0.418(5)	0.473(3)	0.453(4)
RE(2)	0.927(3)	0.573(3)	0.576(1)	0.582(5)	0.527(3)	0.547(4)
Ca(3)	0.000(3)	0.346(5)	0.300(5)	0.187(1)	0.123(1)	0.157(1)
RE(3)	1.000(3)	0.654(5)	0.700(5)	0.813(1)	0.877(1)	0.843(1)

Table S4 The Ca^{2+}–RE^{3+} fractions in three metal cation sites in the structures of $CaRE_2Ge_3O_{10}$ (*RE* = Y, Dy–Yb)

Atom	Dy	Y	Y[a]	Ho	Er	Tm	Yb
Ca(1)	0.399(4)	0.447(4)	0.450(3)	0.415(3)	0.421(2)	0.418(2)	0.416(2)
RE(1)	0.601(4)	0.553(4)	0.550(3)	0.585(3)	0.579(2)	0.582(2)	0.584(2)
Ca(2)	0.476(3)	0.464(4)	0.462(4)	0.481(2)	0.499(2)	0.518(2)	0.524(2)
RE(2)	0.524(3)	0.536(4)	0.538(3)	0.519(2)	0.501(2)	0.482(2)	0.476(2)
Ca(3)	0.125(1)	0.089(1)	0.088(4)	0.104(1)	0.080(2)	0.064(2)	0.060(1)
RE(3)	0.875(1)	0.911(1)	0.912(3)	0.896(1)	0.920(2)	0.936(2)	0.940(1)

[a] Data for the $CaY_2Ge_3O_{10}$ compound taken from Ref. [1].

References

1 H. Yamane, R. Tanimura, T. Yamada, J. Takahashi, T. Kajiwara and M. Shimada, *J. Solid State Chem.*, 2006, **179**, 289–295.