Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supplementary Information (ESI)
Structural and spectroscopic characterization of new $Ba_2RE_2Ge_4O_{13}$ (*RE* = Pr, Nd, Gd, Dy) and $Ba_2Gd_{2-x}Eu_xGe_4O_{13}$ tetragermanates

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Table S1 Atomic coordinates and isotropic thermal parameters (Å^2) for $Ba_2RE_2Ge_4O_{13}$ (*RE* = Pr–Dy)

			Pr	Nd	Eu[a]	Gd	Dy
Ba	8*f*	x	0.15698(10)	0.15676(8)	0.15677(8)	0.15689(10)	0.15700(9)
		y	0.5035(5)	0.5031(4)	0.5035(4)	0.5029(4)	0.5032(4)
		z	0.33231(7)	0.33256(5)	0.33266(6)	0.33266(7)	0.33263(6)
		U_{iso}×100	2.63(6)	2.49(9)	3.06(4)	2.56(12)	3.39(4)
RE	8*f*	x	0.11713(10)	0.11615(8)	0.11467(9)	0.11428(10)	0.11297(9)
		y	0.5112(4)	0.5106(3)	0.5101(3)	0.5104(4)	0.5099(4)
		z	0.08758(7)	0.08719(5)	0.08656(5)	0.08652(6)	0.08598(5)
		U_{iso}×100	2.49(6)	2.30(9)	2.71(5)	2.14(12)	2.94(5)
Ge(1)	8*f*	x	0.06606(18)	0.06640(14)	0.06551(14)	0.06559(17)	0.06542(14)
		y	0.0463(7)	0.0457(5)	0.0432(6)	0.0449(7)	0.0421(6)
		z	0.18570(15)	0.18567(11)	0.18386(11)	0.18393(13)	0.18260(11)
		U_{iso}×100	2.43(10)	2.32(11)	2.98(8)	2.28(14)	2.92(7)
Ge(2)	8*f*	x	-0.11945(22)	-0.11998(17)	-0.12123(16)	-0.12124(21)	-0.12221(18)
		y	-0.0312(8)	-0.0307(6)	-0.0308(6)	-0.0289(8)	-0.0342(6)
		z	0.04059(15)	0.04035(12)	0.03864(12)	0.03839(15)	0.03705(12)
		U_{iso}×100	2.33(9)	2.63(10)	2.72(7)	2.38(13)	2.69(7)
O(1)	8*f*	x	0.0752(11)	0.0756(8)	0.0758(8)	0.0780(10)	0.0789(9)
		y	-0.2727(25)	-0.2726(18)	-0.2831(18)	-0.2824(23)	-0.2870(19)
		z	0.1921(9)	0.1899(6)	0.1885(6)	0.1897(7)	0.1890(6)
		U_{iso}×100	2.2(5)	1.3(4)	2.22(14)[a]	1.84(20)[a]	2.01(14)[a]
O(2)	8*f*	x	0.1749(11)	0.1726(8)	0.1738(9)	0.1743(11)	0.1783(9)
		y	0.2338(21)	0.2300(16)	0.2360(16)	0.2296(19)	0.2395(16)
		z	0.1990(8)	0.1978(6)	0.1967(6)	0.1944(7)	0.1938(6)
		U_{iso}×100	1.7(5)	1.6(3)	2.22(14)[a]	1.84(20)[a]	2.01(14)[a]
O(3)	4*e*	x	0	0	0	0	0
		y	0.1803(33)	0.1725(26)	0.1747(25)	0.1628(31)	0.1745(26)
		z	¼	¼	¼	¼	¼
		U_{iso}×100	1.8(6)	2.4(5)	2.22(14)[a]	1.84(20)[a]	2.01(14)[a]
O(4)	8*f*	x	-0.0178(11)	-0.0175(8)	-0.0199(8)	-0.0190(10)	-0.0214(9)
		y	0.1732(22)	0.1652(17)	0.1769(16)	0.1703(20)	0.1727(17)
		z	0.0951(7)	0.0965(6)	0.0967(6)	0.0968(7)	0.0948(6)
		U_{iso}×100	1.4(4)	1.6(4)	2.22(14)[a]	1.84(20)[a]	2.01(14)[a]
O(5)	8*f*	x	-0.1620(10)	-0.1635(7)	-0.1615(8)	-0.1602(9)	-0.1621(8)
		y	0.1023(23)	0.1019(17)	0.1071(16)	0.1140(19)	0.1072(17)
		z	-0.0482(8)	-0.0507(6)	-0.0524(5)	-0.0509(7)	-0.0546(5)
		U_{iso}×100	2.7(5)	1.9(4)	2.22(14)[a]	1.84(20)[a]	2.01(14)[a]
O(6)	8*f*	x	-0.2037(8)	-0.2053(6)	-0.2101(6)	-0.2084(7)	-0.2106(6)
		y	-0.0428(34)	-0.0485(22)	-0.0539(19)	-0.0536(24)	-0.0563(20)
		z	0.0983(6)	0.0986(4)	0.0964(4)	0.0956(5)	0.0947(4)
		U_{iso}×100	2.8(5)	1.4(4)	2.22(14)[a]	1.84(20)[a]	2.01(14)[a]
O(7)	8*f*	x	-0.0669(9)	-0.0694(7)	-0.0667(7)	-0.0689(9)	-0.0707(8)
		y	-0.3419(24)	-0.3391(20)	-0.3441(18)	-0.3343(23)	-0.3466(18)
		z	0.0346(7)	0.0354(6)	0.0337(5)	0.0329(7)	0.0339(6)
		U_{iso}×100	2.2(5)	2.6(4)	2.22(14)[a]	1.84(20)[a]	2.01(14)[a]

[a] The data for the $Ba_2Eu_2Ge_4O_{13}$ compound was taken from ref. [29]. The thermal vibration parameters of oxygen atoms have been constrained as a single variable for the $Ba_2RE_2Ge_4O_{13}$ (*RE* = Eu–Dy).

Table S2 Selected interatomic distances (Å), angles (°) and degree of distortion/asymmetry, *D*, for $Ba_2RE_2Ge_4O_{13}$ (*RE* = Pr–Dy)

	Pr	Nd	Eu[a]	Gd	Dy
			Interatomic distances		
Ba–O(1)	2.756(14)	2.792(10)	2.782(10)	2.762(12)	2.754(10)
Ba–O(1)	3.233(14)	3.231(10)	3.187(10)	3.206(12)	3.193(10)
Ba–O(2)	2.880(14)	2.900(10)	2.899(10)	2.949(12)	2.941(10)
Ba–O(2)	2.745(13)	2.751(10)	2.719(11)	2.675(13)	2.633(11)
Ba–O(3)	2.824(11)	2.844(9)	2.823(8)	2.858(11)	2.808(9)
Ba–O(4)	3.103(13)	3.104(10)	3.020(10)	3.042(13)	3.021(11)
Ba–O(5)	2.828(13)	2.786(10)	2.780(10)	2.809(12)	2.740(10)
Ba–O(6)	3.211(18)	3.232(12)	3.263(10)	3.256(13)	3.268(10)
Ba–O(6)	2.755(17)	2.725(11)	2.706(10)	2.709(12)	2.697(10)
Ba–O(7)	3.071(12)	3.033(10)	3.057(9)	3.066(12)	3.008(10)
Ba–O[b]	**2.941**	**2.940**	**2.924**	**2.933**	**2.906**
Expected[c]	*2.898*	*2.898*	*2.898*	*2.898*	*2.898*
D	0.058	0.057	0.057	0.058	0.062
RE–O(1)	2.409(14)	2.372(11)	2.314(10)	2.319(12)	2.287(10)
RE–O(2)	2.464(13)	2.462(10)	2.429(10)	2.422(12)	2.390(10)
RE–O(4)	2.592(14)	2.609(10)	2.556(10)	2.565(11)	2.545(10)
RE–O(5)	2.340(12)	2.333(9)	2.279(8)	2.246(10)	2.261(9)
RE–O(6)	2.354(10)	2.340(7)	2.285(8)	2.308(10)	2.286(8)
RE–O(7)	2.506(13)	2.520(10)	2.448(10)	2.481(12)	2.451(10)
RE–O(7)	2.317(12)	2.327(9)	2.274(9)	2.280(11)	2.256(9)
***RE*–O**[b]	**2.426**	**2.423**	**2.369**	**2.374**	**2.354**
Expected[c]	*2.435*	*2.423*	*2.387*	*2.377*	*2.347*
D	0.033	0.038	0.039	0.041	0.039
Ge(1)–O(1)	1.735(14)	1.727(10)	1.761(10)	1.766(13)	1.770(11)
Ge(1)–O(2)	1.732(13)	1.690(10)	1.725(10)	1.703(13)	1.777(11)
Ge(1)–O(3)	1.785(7)	1.770(5)	1.787(5)	1.756(6)	1.796(6)
Ge(1)–O(4)	1.848(12)	1.815(9)	1.820(9)	1.798(11)	1.824(9)
Ge–O[b]	**1.775**	**1.751**	**1.773**	**1.756**	**1.792**
Expected[c]	*1.770*	*1.770*	*1.770*	*1.770*	*1.770*
D (Ge–O)	0.023	0.024	0.017	0.015	0.010
Ge(2)–O(4)	1.820(13)	1.807(10)	1.838(9)	1.817(11)	1.820(10)
Ge(2)–O(5)	1.712(13)	1.746(9)	1.751(9)	1.733(11)	1.763(9)
Ge(2)–O(6)	1.722(10)	1.737(7)	1.758(7)	1.730(9)	1.738(8)
Ge(2)–O(7)	1.838(13)	1.809(11)	1.842(10)	1.791(12)	1.807(10)
Ge–O[b]	**1.773**	**1.775**	**1.797**	**1.768**	**1.782**
Expected[c]	*1.765*	*1.765*	*1.765*	*1.765*	*1.765*
D (Ge–O)	0.032	0.019	0.024	0.021	0.018
			Angles		
Ge(1)–O(3)–Ge(1)	132.0(11)	134.4(9)	133.3(8)	137.7(11)	133.5(9)
Ge(1)–O(4)–Ge(2)	115.9(7)	118.7(5)	116.1(5)	118.5(6)	116.9(5)
O(1)–Ge(1)–O(2)	122.3(8)	122.5(6)	122.9(6)	120.8(7)	121.3(6)
O(1)–Ge(1)–O(3)	113.6(8)	113.5(6)	114.1(6)	111.9(7)	113.9(6)
O(1)–Ge(1)–O(4)	116.4(7)	114.4(5)	117.2(5)	116.8(6)	117.8(5)
O(2)–Ge(1)–O(3)	102.0(6)	103.1(5)	101.3(5)	104.9(6)	102.2(5)
O(2)–Ge(1)–O(4)	100.8(7)	101.4(5)	100.2(5)	100.6(6)	100.2(5)
O(3)–Ge(1)–O(4)	98.0(5)	98.6(4)	97.1(4)	99.1(5)	97.9(4)
O(4)–Ge(2)–O(5)	105.2(6)	107.4(4)	105.7(4)	105.6(5)	105.3(4)
O(4)–Ge(2)–O(6)	101.7(6)	101.9(4)	101.4(4)	101.6(5)	101.0(5)
O(4)–Ge(2)–O(7)	110.6(6)	109.6(5)	110.6(4)	109.7(6)	111.3(5)
O(5)–Ge(2)–O(6)	118.5(6)	119.1(4)	120.0(4)	120.4(5)	120.4(4)
O(5)–Ge(2)–O(7)	111.6(7)	111.6(5)	111.6(4)	112.2(6)	112.9(5)
O(6)–Ge(2)–O(7)	108.7(7)	106.7(5)	106.8(5)	106.5(6)	105.3(5)

[a] The data for the $Ba_2Eu_2Ge_4O_{13}$ compound was taken from ref. 29.

[b] The average values are given in boldface.

[c] The expected values were calculated as the sum of crystal radii according to ref. 44: Ba^{+2} (X) – 1.66 Å, Pr^{+3} (VII) – 1.198 Å, Nd^{+3} (VII) – 1.186 Å, Eu^{+3} (VII) – 1.15 Å, Gd^{+3} (VII) – 1.14 Å, Dy^{+3} (VII) – 1.11 Å, Ge^{+4} (IV) – 0.530 Å, O^{-2} (III) – 1.22 Å, O^{-2} (IV) – 1.24 Å.

Table S3 Crystallographic data for $Ba_2Gd_{2-x}Eu_xGe_4O_{13}$, x = 0.1–0.8 (space group *C*2/*c*, Z = 4).

x	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8
a, Å	13.0764(2)	13.0773(2)	13.0799(2)	13.0796(2)	13.0810(1)	13.0849(1)	13.0852(3)	13.0866(2)
b, Å	5.3679(1)	5.3694(1)	5.3696(1)	5.3700(1)	5.3707(1)	5.3711(1)	5.3715(1)	5.3719(1)
c, Å	17.9920(4)	17.9934(3)	17.9932(4)	17.9947(3)	17.9937(2)	17.9946(2)	17.9945(4)	17.9947(4)
β, °	105.112(1)	105.133(1)	105.130(1)	105.140(1)	105.147(1)	105.136(1)	105.135(1)	105.151(1)
V, Å³	1219.24(4)	1219.64(4)	1219.92(4)	1220.02(4)	1220.23(2)	1220.80(2)	1220.92(4)	1221.06(4)

Table S4 Crystallographic data for $Ba_2Pr_2Ge_4O_{13}$ and $Ba_2Gd_2Ge_4O_{13}$ at selected temperatures.

T, K	*a*, Å	*b*, Å	*c*, Å	*β*, °	*V*, Å³
			$Ba_2Pr_2Ge_4O_{13}$		
100	13.2391(21)	5.4112(8)	18.0022(31)	105.535(8)	1242.55(34)
200	13.2590(11)	5.4164(4)	18.0235(16)	105.505(4)	1247.28(18)
300	13.2783(13)	5.4218(5)	18.0467(18)	105.448(5)	1252.30(21)
473	13.3318(12)	5.4397(5)	18.1176(18)	105.392(5)	1266.79(21)
673	13.3729(14)	5.4525(5)	18.1701(21)	105.285(5)	1278.01(23)
TEC, K⁻¹	1.85×10^{-5}	1.42×10^{-5}	1.74×10^{-5}		5.25×10^{-5}
			$Ba_2Gd_2Ge_4O_{13}$		
298	13.0787(11)	5.3716(4)	17.9969(17)	105.143(5)	1220.44(18)
373	13.0894(12)	5.3748(5)	18.0112(18)	105.116(5)	1223.30(20)
473	13.1043(14)	5.3803(5)	18.0311(21)	105.081(6)	1227.49(23)
673	13.1369(12)	5.3907(5)	18.0763(19)	104.998(5)	1236.52(21)
873	13.1662(13)	5.4004(5)	18.1097(21)	104.919(5)	1244.24(22)
1073	13.1972(11)	5.4108(4)	18.1472(18)	104.819(5)	1252.74(20)
TEC, K⁻¹	1.17×10^{-5}	0.94×10^{-5}	1.09×10^{-5}		3.43×10^{-5}

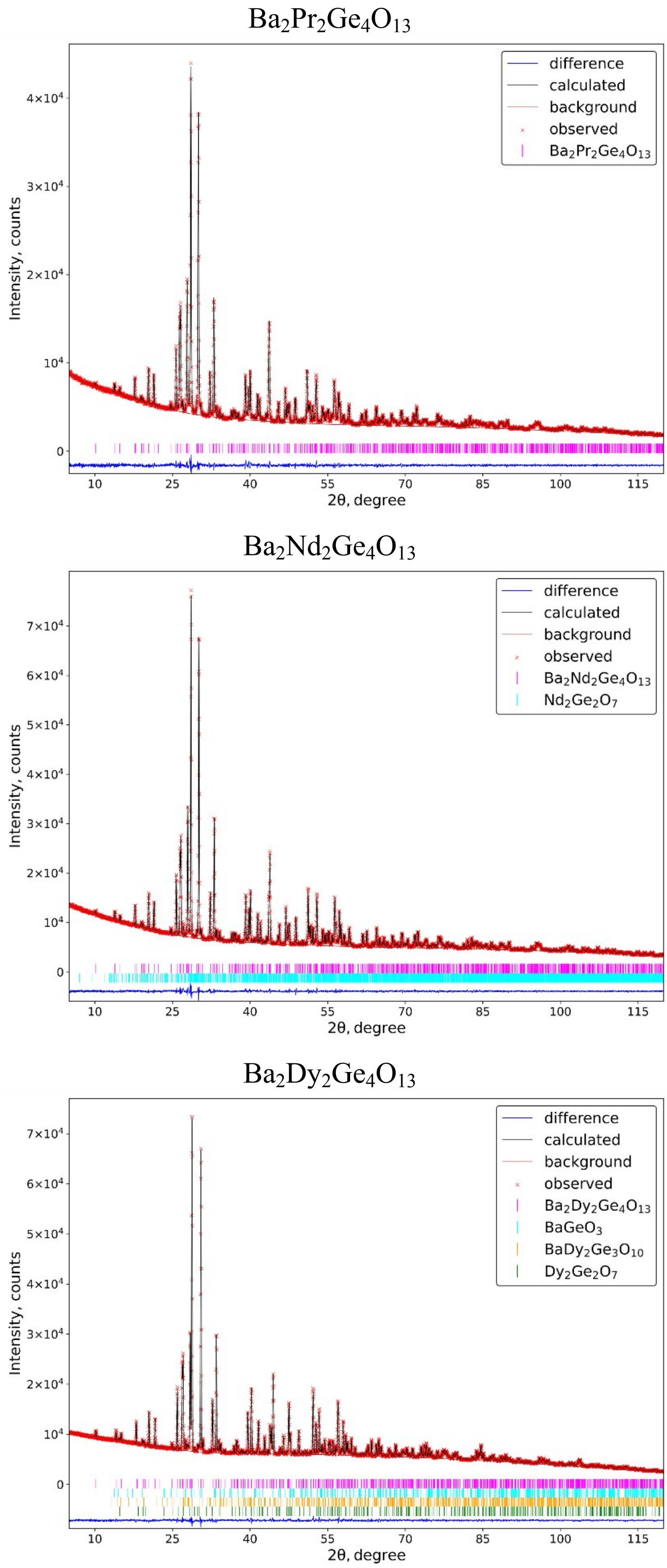

Fig. S1 The Rietveld refined XRPD patterns of $Ba_2\mathit{RE}_2Ge_4O_{13}$ (*RE* = Pr, Nd, Dy).

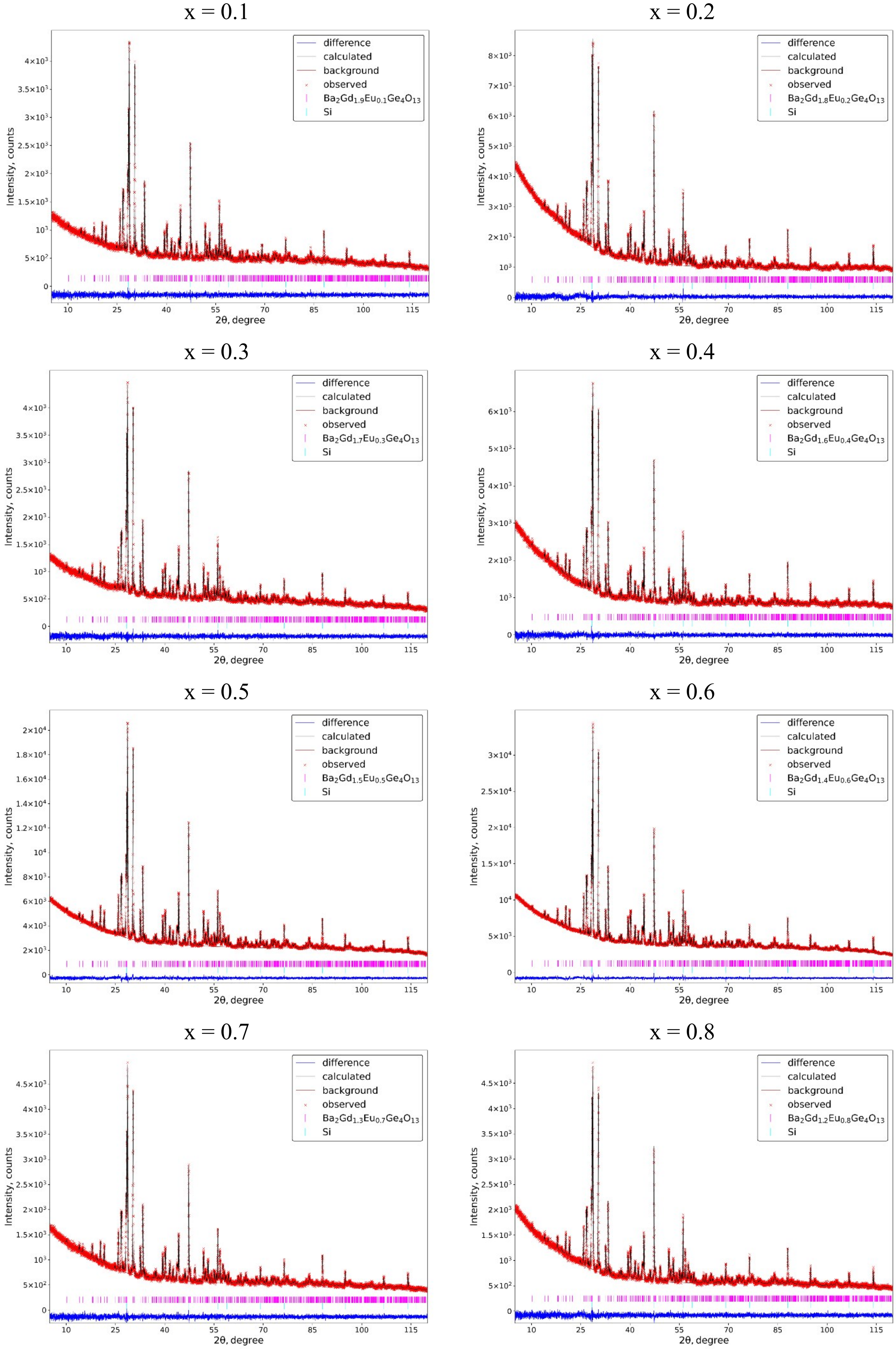

Fig. S2 The Rietveld refined XRPD patterns of $Ba_2Gd_{2-x}Eu_xGe_4O_{13}$ (x = 0.1–0.8).

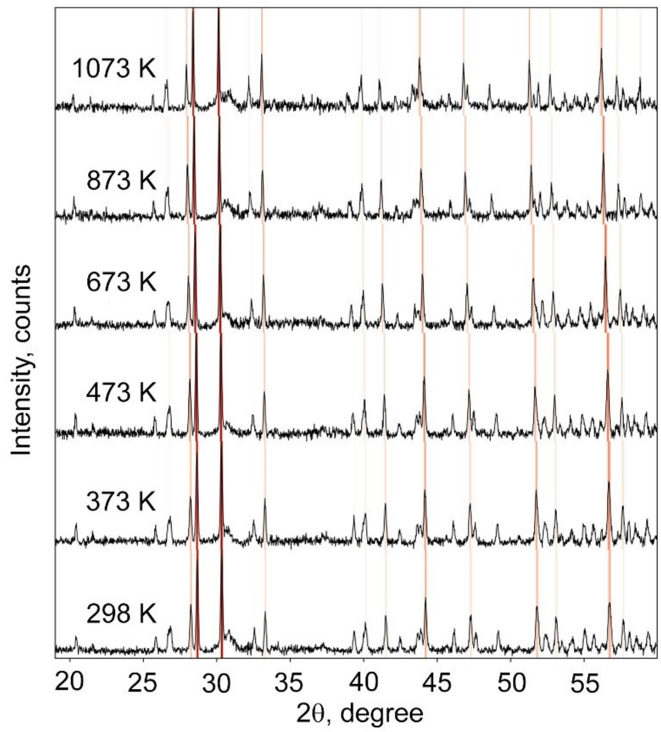

Fig. S3 XRPD patterns of $Ba_2Gd_2Ge_4O_{13}$ measured at different temperatures.

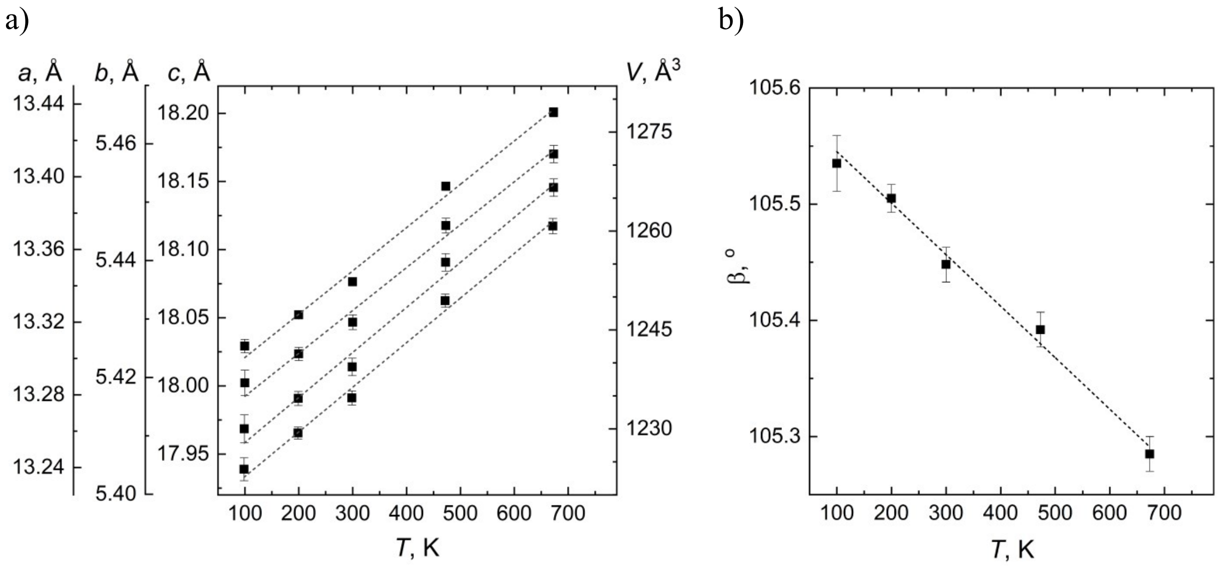

Fig. S4 Temperature dependences of the unit cell parameters, volume (a) and β angle for $Ba_2Pr_2Ge_4O_{13}$ (the error is equal to three standard deviations).

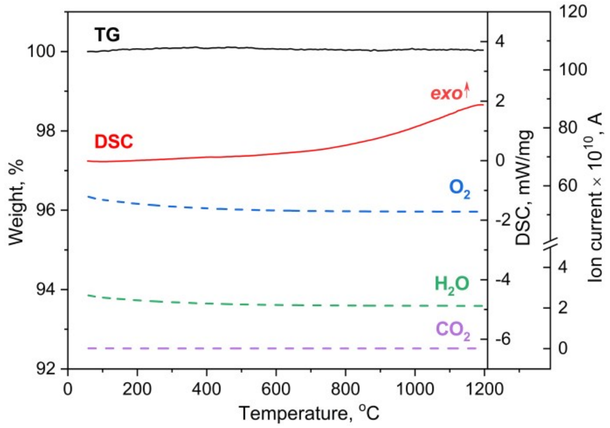

Fig. S5 Simultaneous thermal analysis of $Ba_2Nd_2Ge_4O_{13}$: solid lines - TG and DSC, dashed lines – ion currents of gases.

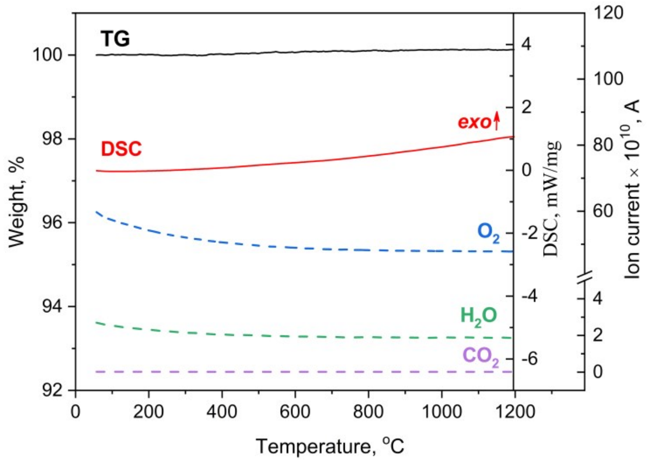

Fig. S6 Simultaneous thermal analysis of $Ba_2Gd_2Ge_4O_{13}$: solid lines - TG and DSC, dashed lines – ion currents of gases.

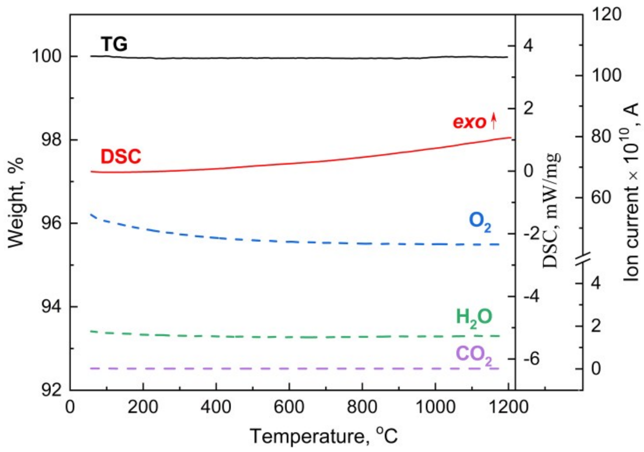

Fig. S7 Simultaneous thermal analysis of $Ba_2Dy_2Ge_4O_{13}$: solid lines - TG and DSC, dashed lines – ion currents of gases.

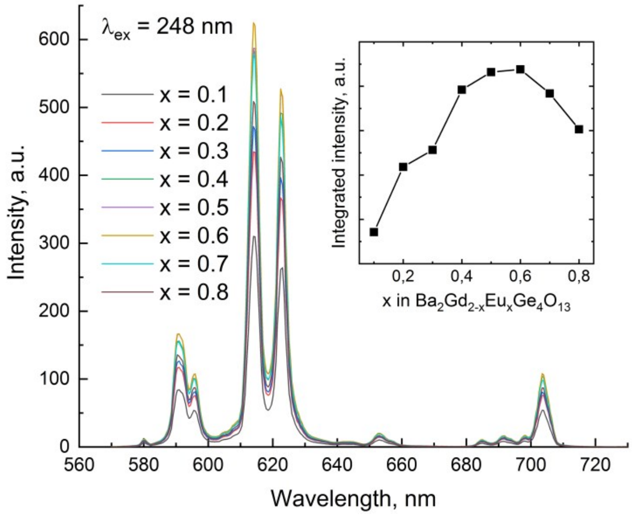

Fig. S8 The PL spectra (λ_{ex} = 248 nm) of $Ba_2Gd_{2-x}Eu_xGe_4O_{13}$. The inset shows the integrated luminescence intensity vs. Eu^{3+} concentration.

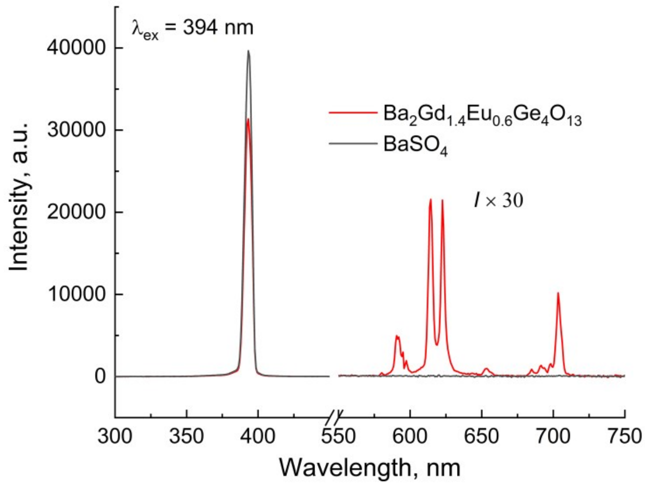

Fig. S9 The results of the measurement of the external quantum efficiency for $Ba_2Gd_{1.4}Eu_{0.6}Ge_4O_{13}$ phosphor (λ_{ex} = 394 nm).