Electronic Supplementary Material (ESI) for CrystEngComm.

Structure, magnetic and optical properties of $Sr_3RE_2(Ge_3O_9)_2$ cyclogermanates (*RE* = La – Gd)

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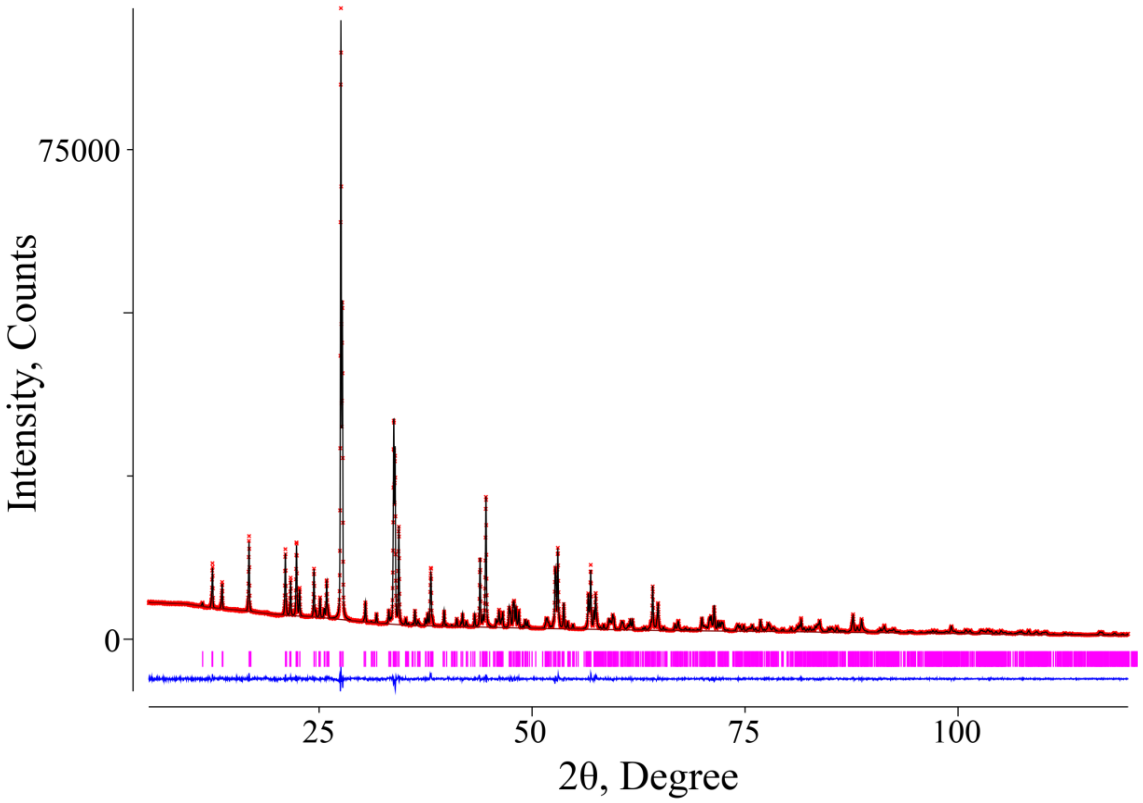

Fig. S1 Experimental (crosses), calculated (solid line), and difference (bottom line) XRPD patterns for $Sr_3La_2(Ge_3O_9)_2$. Series of tick marks correspond to the Bragg reflection.

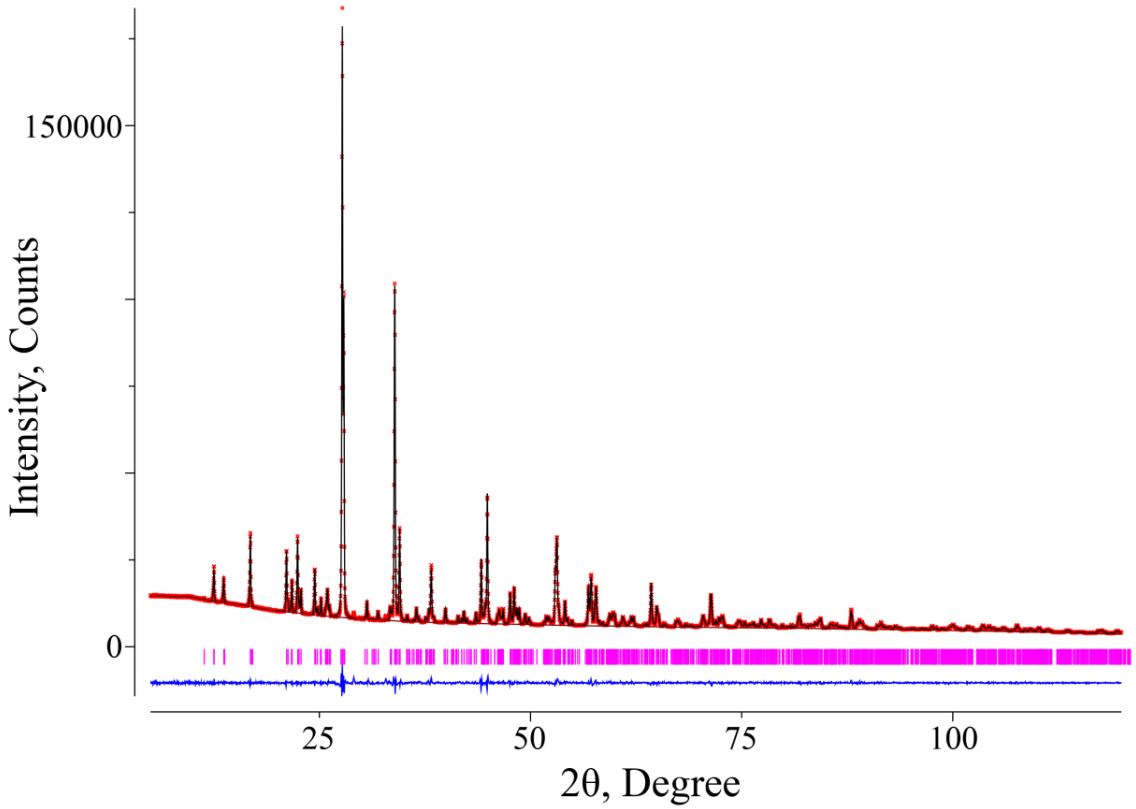

Fig. S2 Experimental (crosses), calculated (solid line), and difference (bottom line) XRPD patterns for $Sr_3Pr_2(Ge_3O_9)_2$. Series of tick marks correspond to the Bragg reflection.

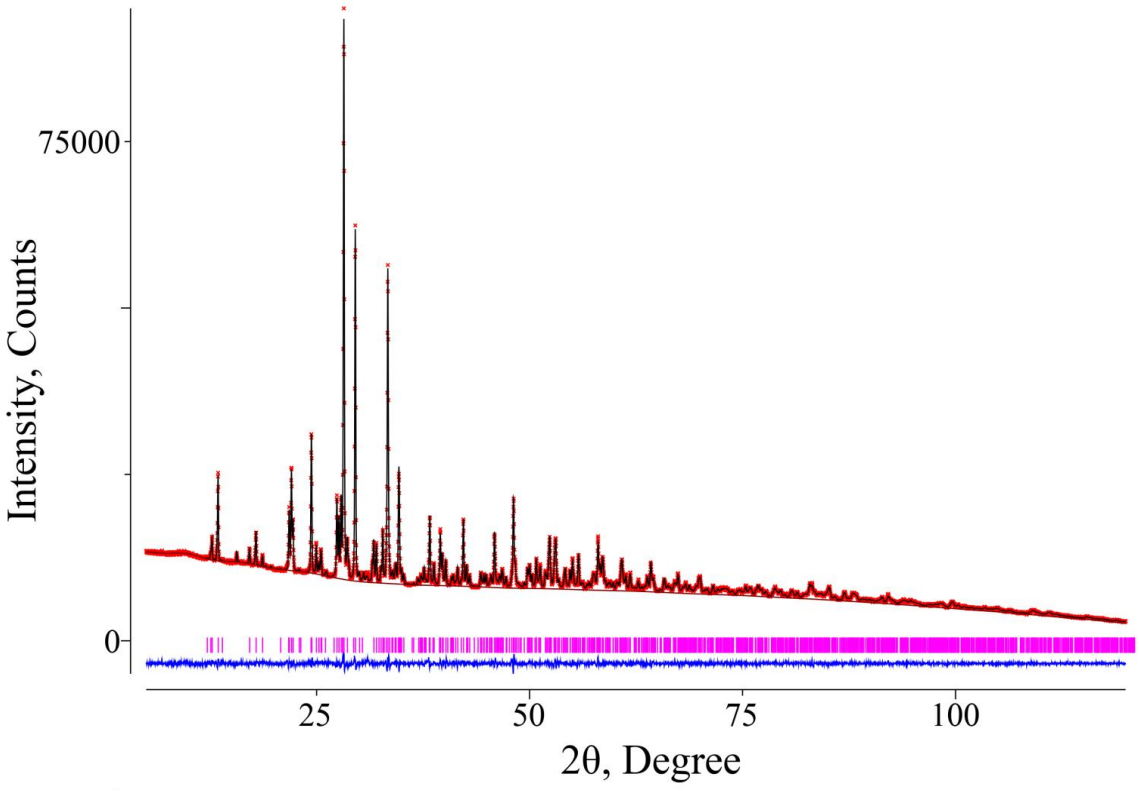

Fig. S3 Experimental (crosses), calculated (solid line), and difference (bottom line) XRPD patterns for $Sr_3Sm_2(Ge_3O_9)_2$. Series of tick marks correspond to the Bragg reflection.

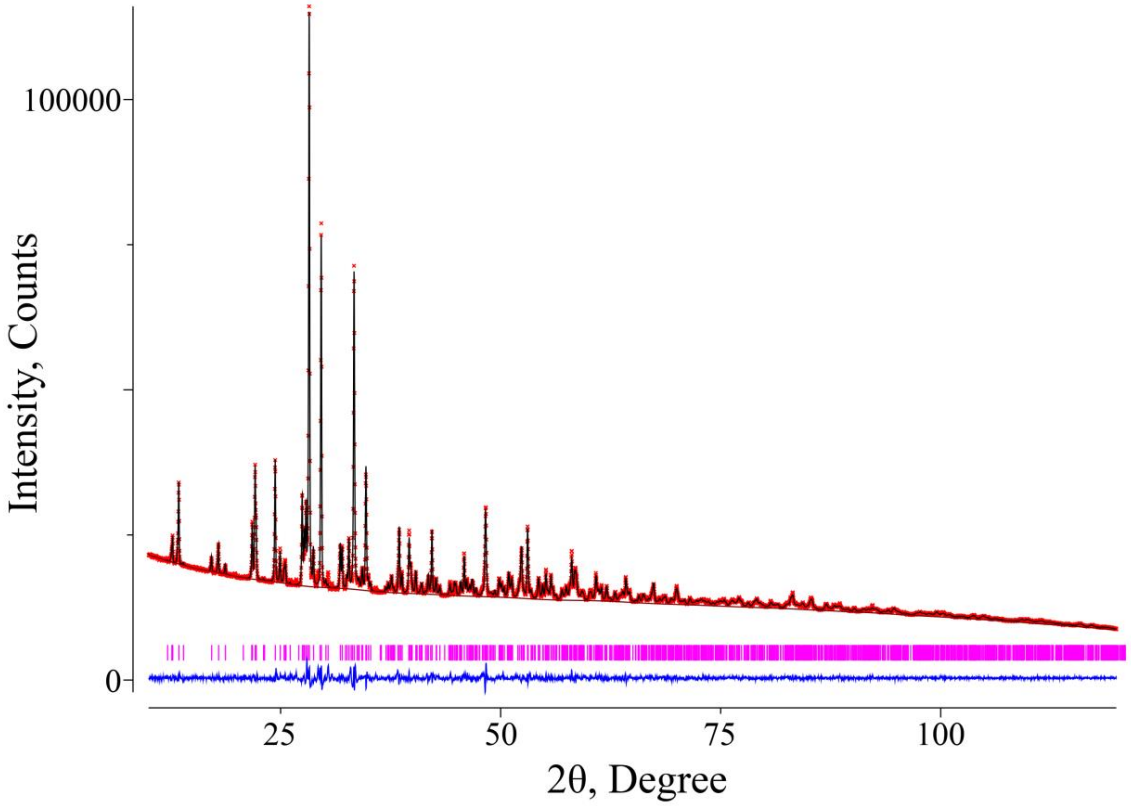

Fig. S4 Experimental (crosses), calculated (solid line), and difference (bottom line) XRPD patterns for $Sr_3Eu_2(Ge_3O_9)_2$. Series of tick marks correspond to the Bragg reflection.

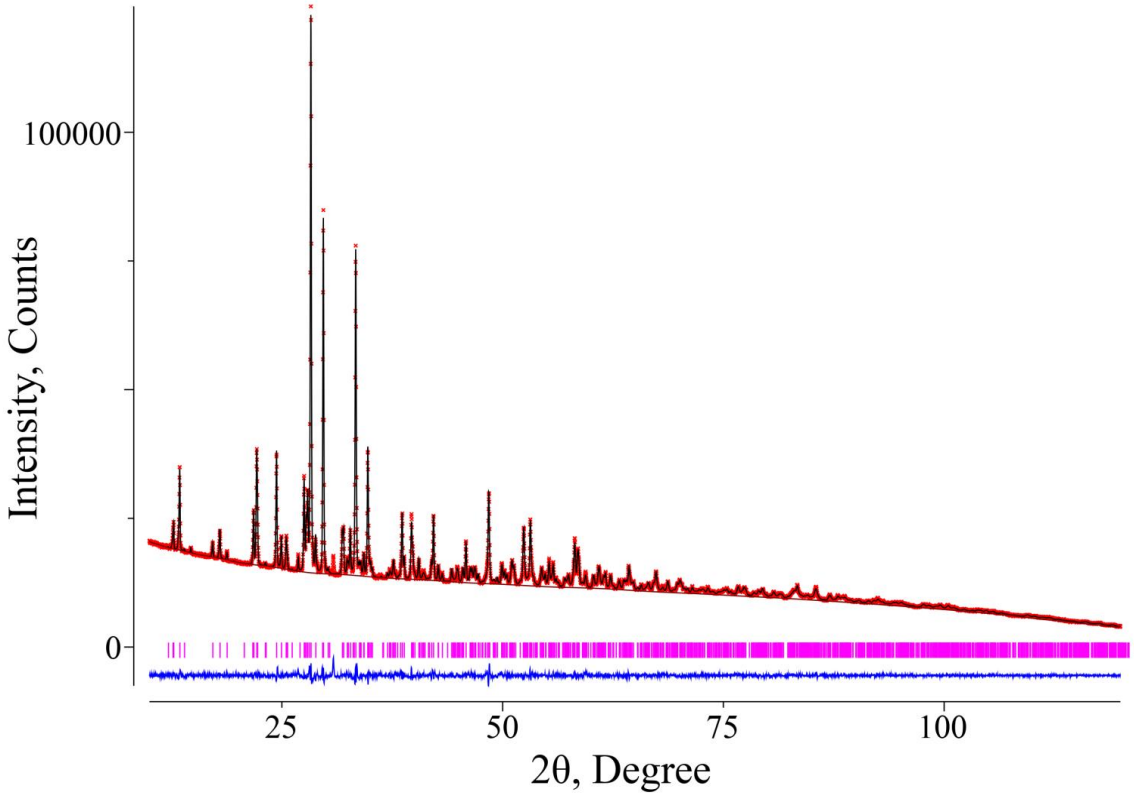

Fig. S5 Experimental (crosses), calculated (solid line), and difference (bottom line) XRPD patterns for $Sr_3Gd_2(Ge_3O_9)_2$. Series of tick marks correspond to the Bragg reflection.

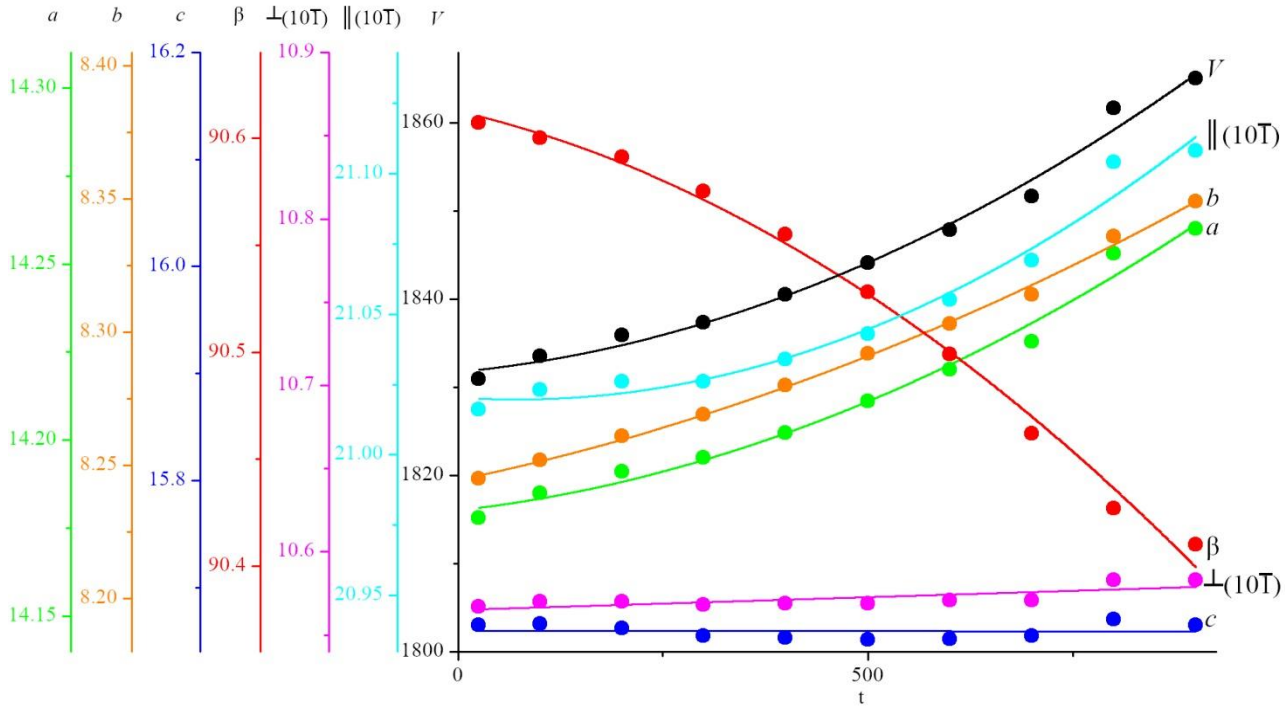

Fig. S6 Temperature dependence of the unit cell parameters and distances along the normal (⊥) and parallel (∥) to (10$\bar{1}$) plane for $Sr_3La_2(Ge_3O_9)_2$.

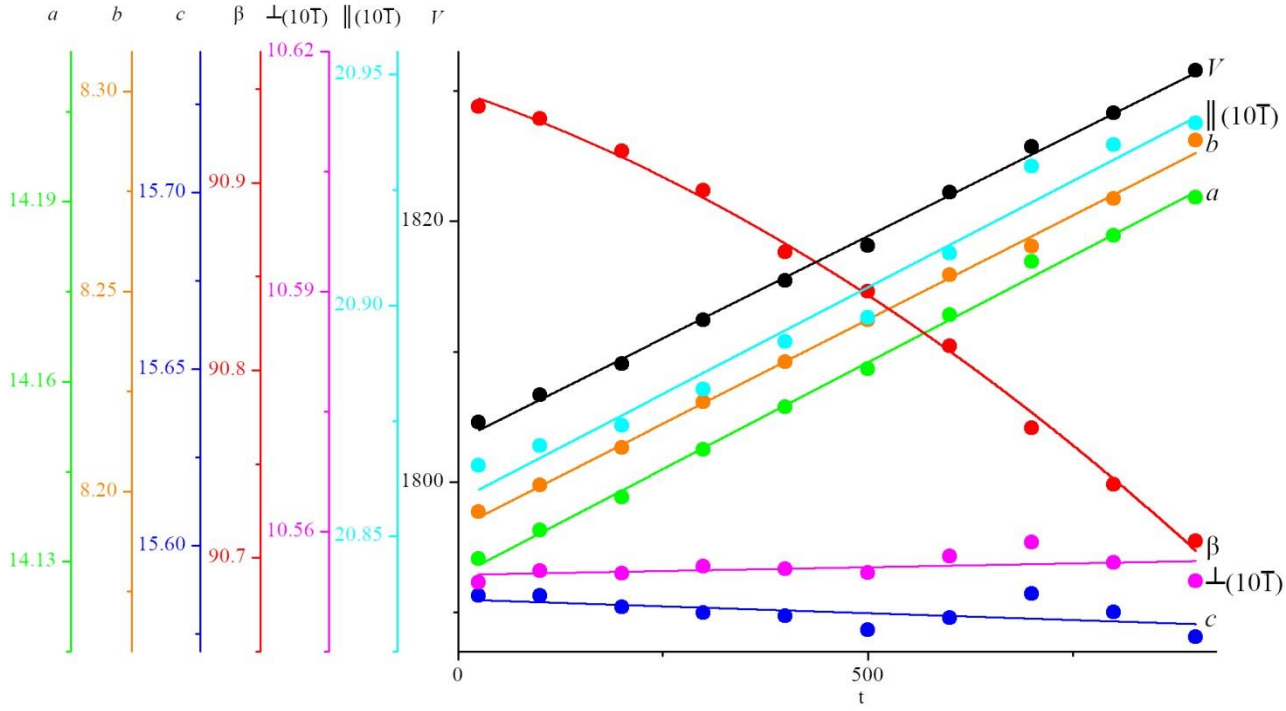

Fig. S7 Temperature dependence of the unit cell parameters and distances along the normal (⊥) and parallel (∥) to (10$\bar{1}$) plane for $Sr_3Pr_2(Ge_3O_9)_2$.

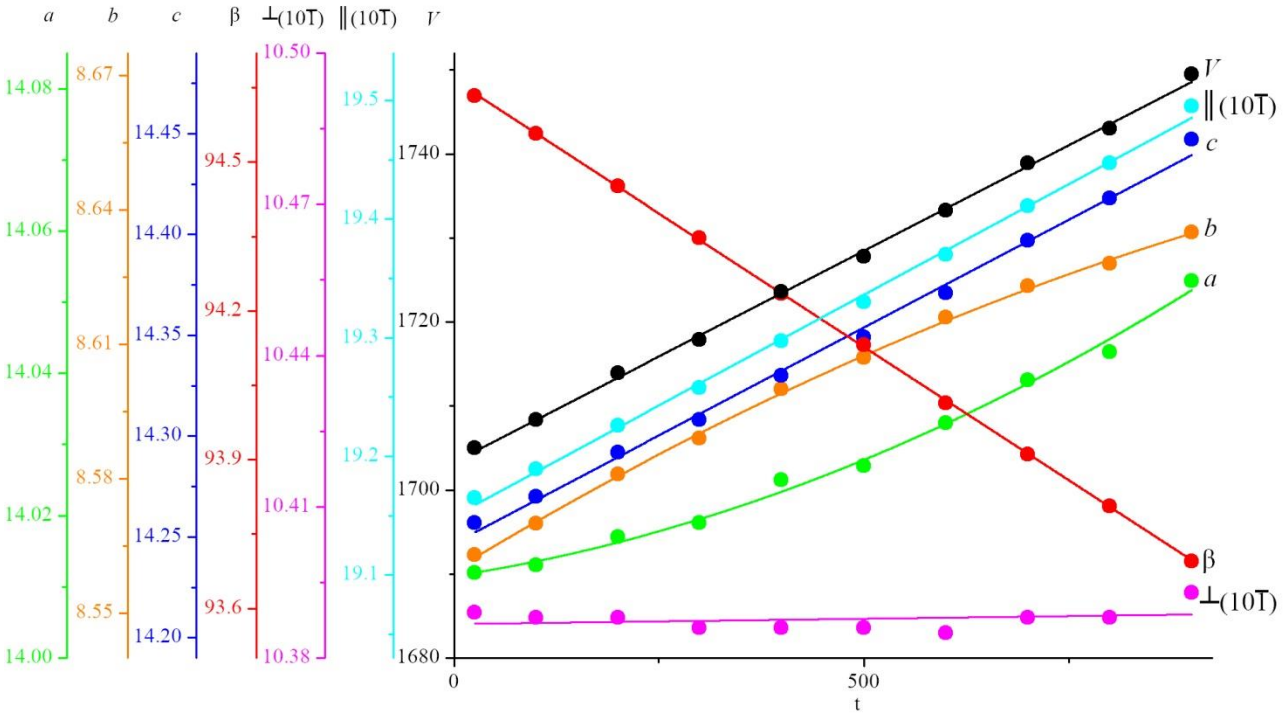

Fig. S8 Temperature dependence of the unit cell parameters and distances along the normal (⊥) and parallel (∥) to (10$\bar{1}$) plane for $Sr_3Nd_2(Ge_3O_9)_2$. Given for structure type after MPT.

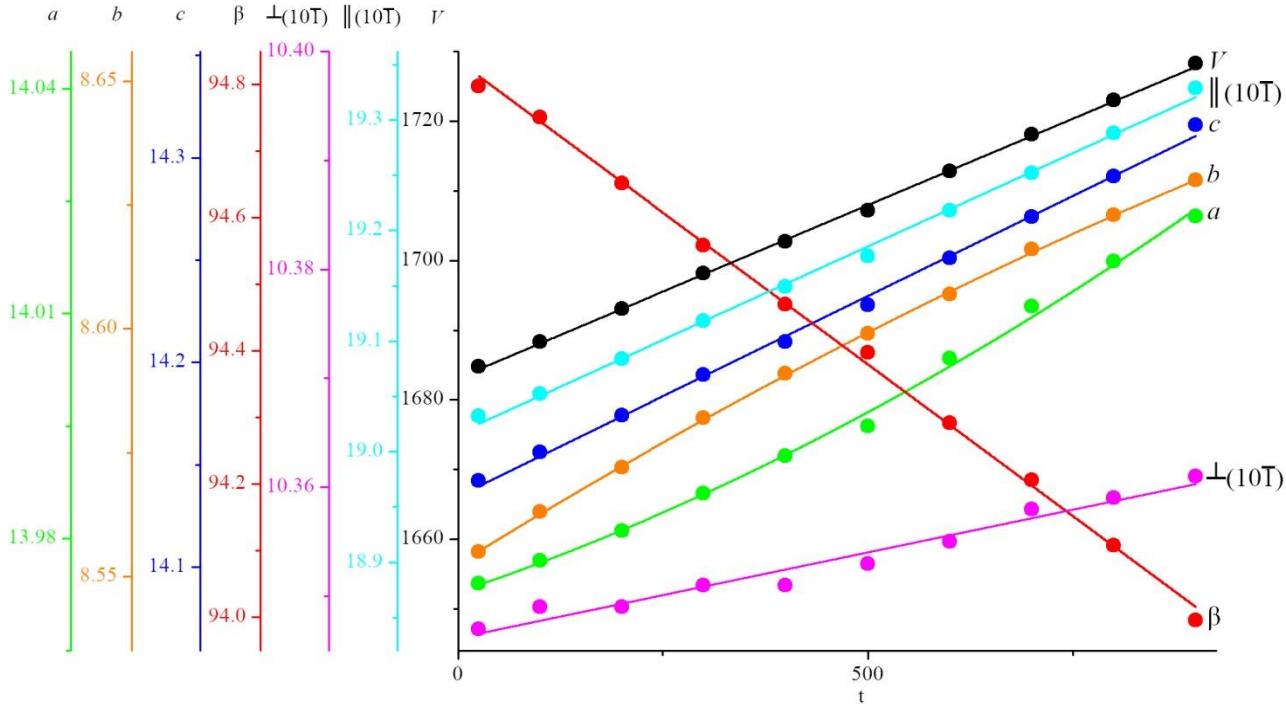

Fig. S9 Temperature dependence of the unit cell parameters and distances along the normal (⊥) and parallel (∥) to (10$\bar{1}$) plane for $Sr_3Sm_2(Ge_3O_9)_2$.

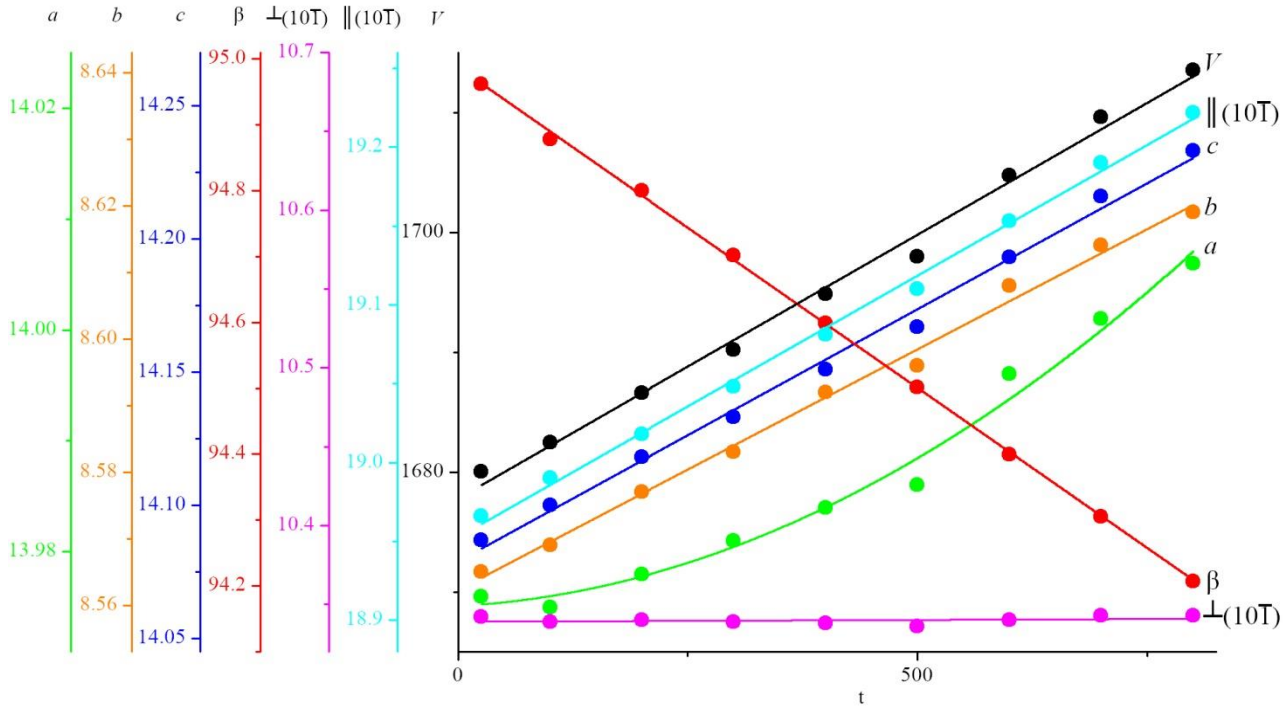

Fig. S10 Temperature dependence of the unit cell parameters and distances along the normal (⊥) and parallel (∥) to (10$\bar{1}$) plane for $Sr_3Eu_2(Ge_3O_9)_2$.

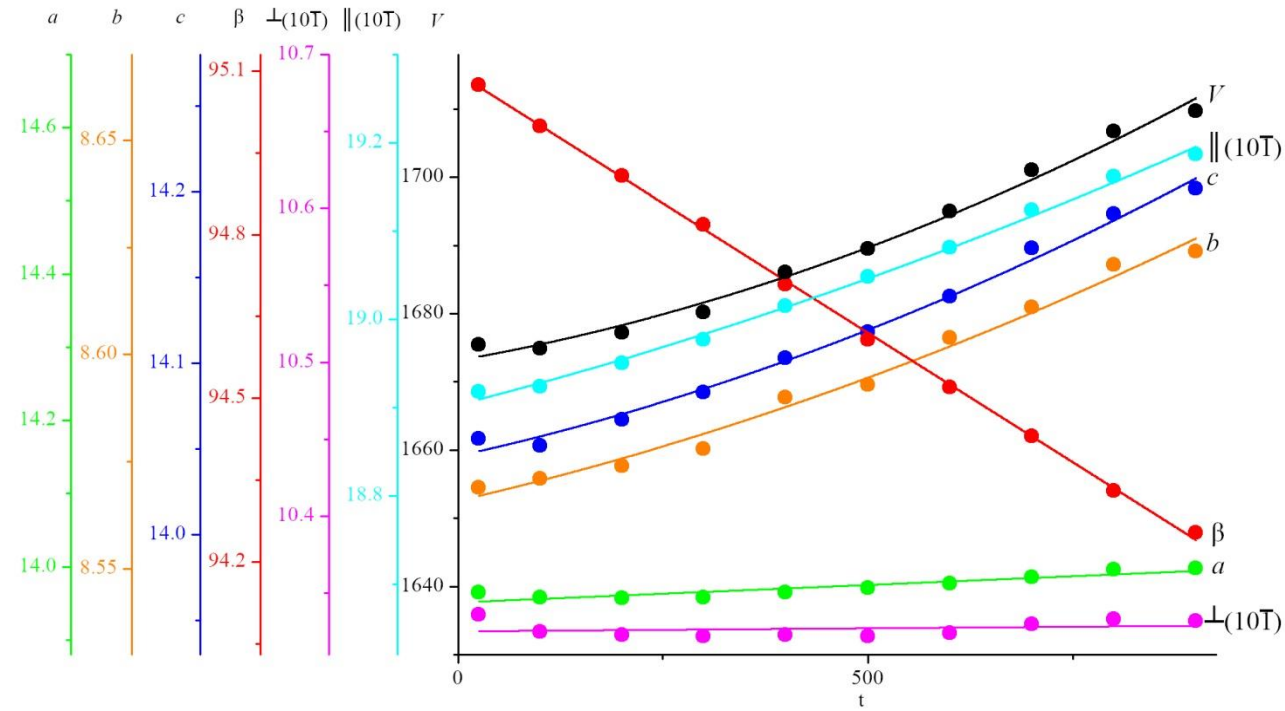

Fig. S11 Temperature dependence of the unit cell parameters and distances along the normal (⊥) and parallel (∥) to (10$\bar{1}$) plane for $Sr_3Gd_2(Ge_3O_9)_2$.

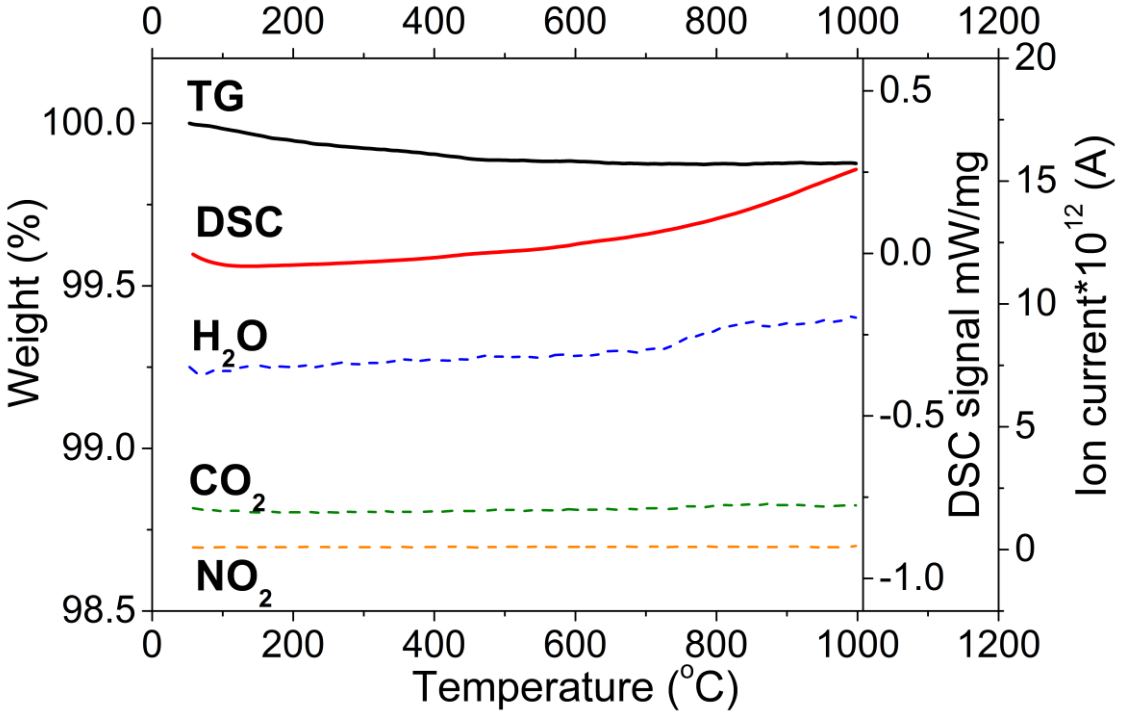

Fig. S12 Simultaneous thermal analysis of the $Sr_3La_2(Ge_3O_9)_2$: solid lines - TG and DSC, dashed lines – ion currents of gases.

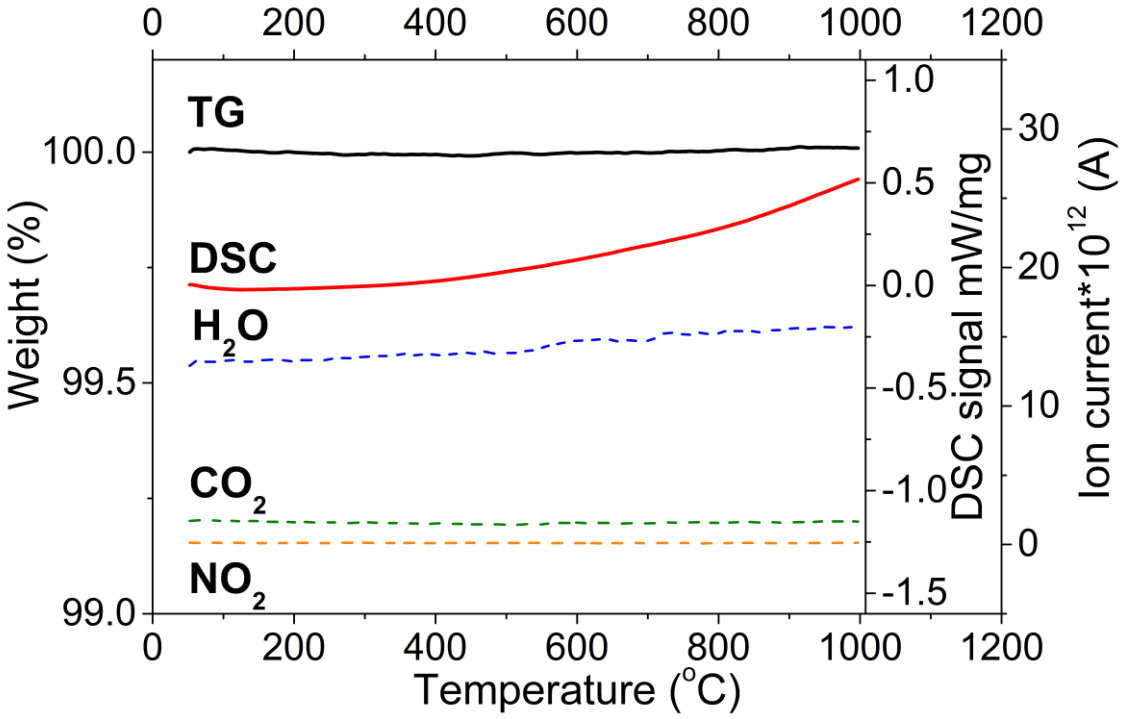

Fig. S13 Simultaneous thermal analysis of the $Sr_3Gd_2(Ge_3O_9)_2$: solid lines - TG and DSC, dashed lines – ion currents of gases.

Table S1 Selected bond lengths (Å), angles (°) for $Sr_3RE_2(Ge_3O_9)_2$ (*RE* = La, Pr, Sm, Eu, Gd) not included in Table 2

	La	Pr	Sm	Eu	Gd
Ge(1)-O(1)	1.743(14)	1.826	1.750(15)	1.799(20)	1.846(16)
Ge(1)-O(2)	1.752(14)	1.784(18)	1.788(18)	2.054(22)	1.934(20)
Ge(1)-O(4)	1.809(11)	1.751(13)	1.709(14)	1.696(20)	1.714(17)
Ge(1)-O(5)	1.794(11)	1.701(15)	1.783(17)	1.661(22)	1.703(20)
Average	**1.775**	**1.765**	**1.757**	**1.803**	**1.799**
Expected	*1.75*	*1.75*	*1.75*	*1.75*	*1.75*
Ge(2)-O(3)	1.774(11)	1.751(13)	1.774(12)	1.794(18)	1.766(15)
Ge(2)-O(5)	1.816(11)	1.860(15)	1.774(18)	1.791(25)	1.781(21)
Ge(2)-O(6)	1.736(10)	1.643(13)	1.686(12)	1.713(17)	1.695(15)
Ge(2)-O(7)	1.758(12)	1.703(14)	1.771(17)	1.615(22)	1.702(19)
Average	**1.771**	**1.739**	**1.751**	**1.728**	**1.736**
Expected	*1.75*	*1.75*	*1.75*	*1.75*	*1.75*
Ge(3)-O(2)	1.811(14)	1.881(18)	1.775(19)	1.703(22)	1.706(20)
Ge(3)-O(7)	1.778(12)	1.811(15)	1.764(16)	1.815(22)	1.758(20)
Ge(3)-O(8)	1.703(12)	1.801(15)	1.728(13)	1.813(18)	1.768(15)
Ge(3)-O(9)	1.779(12)	1.700(14)	1.717(16)	1.549(22)	1.621(19)
Average	**1.768**	**1.798**	**1.746**	**1.720**	**1.713**
Expected	*1.75*	*1.75*	*1.75*	*1.75*	*1.75*
Ge(1)-Ge(2)	3.232(4)	3.251(5)	3.124(6)	3.141(8)	3.130(6)
Ge(1)-Ge(3)	3.2249(23)	3.2417(28)	3.088(4)	3.132(6)	3.089(5)
Ge(2)-Ge(3)	3.223(4)	3.229(5)	3.150(6)	3.106(9)	3.153(8)
Average	**3.227**	**3.240**	**3.121**	**3.126**	**3.124**
Bond angles					
O(1)-Ge(1)-O(2)	108.9(5)	106.2(7)	106.6(9)	104.3(10)	103.5(8)
O(1)-Ge(1)-O(4)	119.0(6)	130.0(10)	118.7(7)	122.4(10)	117.1(9)
O(1)-Ge(1)-O(5)	107.5(5)	109.6(6)	110.1(8)	116.1(10)	118.4(9)
O(2)-Ge(1)-O(4)	104.0(5)	98.7(8)	105.8(7)	99.2(9)	102.9(8)
O(2)-Ge(1)-O(5)	112.0(5)	113.2(6)	105.8(7)	101.0(9)	104.8(9)
O(4)-Ge(1)-O(5)	105.4(5)	98.8(6)	108.9(8)	109.6(12)	108.1(10)
Average	**109.5**	**109.4**	**109.3**	**108.7**	**109.1**
O(3)-Ge(2)-O(5)	105.2(6)	99.9(7)	117.3(7)	119.6(10)	119.7(8)
O(3)-Ge(2)-O(6)	120.6(5)	123.9(6)	120.3(6)	122.9(9)	121.1(8)
O(3)-Ge(2)-O(7)	100.9(6)	105.5(8)	106.6(8)	107.0(11)	104.9(9)
O(5)-Ge(2)-O(6)	109.3(6)	110.5(8)	101.3(8)	101.4(11)	104.6(9)
O(5)-Ge(2)-O(7)	110.7(4)	106.6(5)	101.6(6)	94.7(9)	96.1(7)
O(6)-Ge(2)-O(7)	109.8(6)	109.2(8)	108.1(8)	107.2(12)	107.0(11)
Average	**109.4**	**109.3**	**109.2**	**108.8**	**108.9**
O(2)-Ge(3)-O(7)	109.0(5)	108.7(6)	106.6(6)	111.6(11)	107.2(9)
O(2)-Ge(3)-O(8)	101.1(6)	109.2(7)	112.2(7)	107.3(11)	109.5(10)
O(2)-Ge(3)-O(9)	108.0(5)	103.1(7)	107.4(8)	107.7(11)	109.0(10)
O(7)-Ge(3)-O(8)	100.5(5)	108.1(7)	105.2(8)	110.8(10)	112.1(8)
O(7)-Ge(3)-O(9)	109.9(5)	108.8(7)	108.9(7)	104.6(11)	105.0(9)
O(8)-Ge(3)-O(9)	127.3(7)	118.6(7)	116.1(8)	114.8(12)	113.8(10)
Average	**109.3**	**109.4**	**109.4**	**109.5**	**109.4**
Ge(1)-O(2)-Ge(3)	129.7(5)	124.3(6)	120.2(7)	112.7(10)	116.0(8)
Ge(1)-O(5)-Ge(2)	127.0(6)	131.7(8)	122.8(9)	131.0(14)	127.9(12)
Ge(2)-O(7)-Ge(3)	131.4(7)	133.5(8)	126.1(8)	129.7(13)	131.3(11)

Table S2 Atom coordinates and thermal parameters ($Å^2$) for the $Sr_3RE_2(Ge_3O_9)_2$ (*RE* = La, Pr, Sm, Eu, Gd) compounds

Atom		La	Pr	Sm	Eu	Gd
Sr/*RE*(1)	*x*/*a*	0.16218(14)	0.16159(17)	0.16691(17)	0.16789(26)	0.16804(20)
	y/*b*	0.1174(5)	0.1232(10)	0.1237(4)	0.1278(6)	0.1269(5)
	z/*c*	0.41319(12)	0.41301(15)	0.40876(15)	0.40878(22)	0.40900(19)
	U_i/U_e*100	3.16(7)	3.22(7)	2.02(15)	3.55(27)	2.92(22)
	Fraction	0.652(8)/0.348(8)	0.721(5)/0.279(5)	0.445(1)/0.555(1)	0.459/0.541(12)	0.442/0.558(9)
Sr/*RE*(2)	*x*/*a*	0.33451(13)	0.33582(17)	0.34232(20)	0.34282(30)	0.34262(25)
	y/*b*	0.1264(4)	0.1287(9)	0.1265(6)	0.1275(8)	0.1272(7)
	z/*c*	0.08156(11)	0.08226(13)	0.05086(18)	0.05242(26)	0.05419(23)
	U_i/U_e*100	2.59(7)	2.79(8)	2.34(16)	4.10(27)	3.54(22)
	Fraction	0.665(7)/0.335(7)	0.657(6)/0.343(6)	1/0	0.983/0.017(5)	0.977/0.023(3)
Sr/*RE*(3)	*x*/*a*	0	0	0	0.000000	0.000000
	y/*b*	0.3827(4)	0.3815(5)	0.3820(4)	0.3829(6)	0.3790(6)
	z/*c*	0.25	0.25	0.25	0.250000	0.250000
	U_i/U_e*100	2.85(7)	2.30(7)	0.92(16)	1.68(30)	1.85(24)
	Fraction	0.365(1)/0.635(1)	0.245(2)/0.755(2)	0.109(1)/0.891(1)	0.116/0.884(14)	0.162/0.838(12)
Ge(1)	*x*/*a*	0.09427(20)	0.09466(24)	0.08735(29)	0.0871(4)	0.08620(31)
	y/*b*	0.07120(31)	0.0726(4)	0.0476(4)	0.0478(6)	0.0441(5)
	z/*c*	0.10012(20)	0.10058(22)	0.12210(29)	0.12390(40)	0.12477(35)
	U_i/U_e*100	3.16(9)	3.32(12)[a]	1.77(19)	2.75(31)	2.68(27)
Ge(2)	*x*/*a*	0.27338(17)	0.27218(20)	0.26283(24)	0.2622(4)	0.26081(30)
	y/*b*	0.37129(54)	0.3696(8)	0.3650(9)	0.3572(11)	0.3611(10)
	z/*c*	0.26763(14)	0.26511(16)	0.24393(23)	0.24436(35)	0.24203(30)
	U_i/U_e*100	3.19(8)	3.28(10)[a]	1.57(18)	3.32(31)	2.79(26)
Ge(3)	*x*/*a*	0.40331(21)	0.40301(24)	0.40992(30)	0.4085(4)	0.40947(36)
	y/*b*	0.18030(32)	0.1772(4)	0.1871(4)	0.1824(7)	0.1840(5)
	z/*c*	0.40456(22)	0.40344(24)	0.38653(27)	0.38515(40)	0.38590(35)
	U_i/U_e*100	2.88(9)	3.10(13)[a]	1.88(20)	4.39(34)	3.73(28)
O(1)	*x*/*a*	-0.0033(9)	-0.0059(12)	-0.0016(11)	-0.0095(15)	-0.0134(12)
	y/*b*	0.1785(15)	0.1839(21)	0.1889(19)	0.1855(26)	0.1861(22)
	z/*c*	0.1363(8)	0.1435(9)	0.1326(12)	0.1299(14)	0.1230(12)
O(2)	*x*/*a*	0.0571(6)	0.0491(7)	0.0265(8)	0.0194(13)	0.0215(10)
	y/*b*	0.1195(19)	0.1179(24)	0.1339(24)	0.1601(28)	0.1524(25)
	z/*c*	0.5638(6)	0.5630(7)	0.5988(9)	0.5895(13)	0.5965(10)
O(3)	*x*/*a*	0.1549(8)	0.1570(9)	0.1610(9)	0.1598(14)	0.1603(12)
	y/*b*	0.3674(20)	0.3680(28)	0.3570(23)	0.3463(29)	0.3420(24)
	z/*c*	0.3026(6)	0.3047(8)	0.3105(9)	0.3125(13)	0.3092(11)
O(4)	*x*/*a*	0.1611(8)	0.1672(9)	0.1637(12)	0.1634(15)	0.1623(13)
	y/*b*	0.1520(18)	0.1193(31)	0.0683(17)	0.0536(24)	0.0590(23)
	z/*c*	0.0120(7)	0.0140(8)	0.0347(10)	0.0366(14)	0.0358(12)
O(5)	*x*/*a*	0.1767(8)	0.1799(10)	0.1563(14)	0.1475(19)	0.1542(17)
	y/*b*	0.0558(13)	0.0521(17)	0.0229(18)	0.0021(26)	0.0130(23)
	z/*c*	0.1875(7)	0.1782(9)	0.2329(12)	0.2269(16)	0.2299(14)
O(6)	*x*/*a*	0.2989(7)	0.2969(9)	0.2491(8)	0.2530(12)	0.2481(11)
	y/*b*	0.3617(18)	0.3774(28)	0.3669(23)	0.3631(34)	0.3550(28)
	z/*c*	0.1596(6)	0.1626(8)	0.1245(9)	0.1224(13)	0.1209(11)
O(7)	*x*/*a*	0.3193(8)	0.3267(12)	0.3358(13)	0.3308(17)	0.3352(15)
	y/*b*	0.1996(14)	0.2044(16)	0.2029(19)	0.2114(25)	0.2116(21)
	z/*c*	0.3200(8)	0.3100(9)	0.2798(10)	0.2765(15)	0.2794(13)
O(8)	*x*/*a*	0.3312(7)	0.3327(10)	0.3321(11)	0.3383(16)	0.3423(13)
	y/*b*	0.1322(23)	0.0952(23)	0.1585(21)	0.1526(31)	0.1548(28)
	z/*c*	0.4870(7)	0.4885(8)	0.4736(10)	0.4860(13)	0.4854(11)
O(9)	*x*/*a*	0.4969(9)	0.4984(11)	0.5070(12)	0.5263(15)	0.5218(13)
	y/*b*	0.0696(14)	0.0740(18)	0.0422(18)	0.0432(29)	0.0379(24)
	z/*c*	0.1312(7)	0.1261(9)	0.1254(11)	0.1373(16)	0.1357(13)
	U_i/U_e*100[a]	2.19(9)[a]	3.08(12)[a]	1.53(19)	2.53(33)	2.15(29)

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

Table S3 Thermal expansion coefficients $Sr_3RE_2(Ge_3O_9)_2$ (*RE* = La, Pr, Nd, Sm, Eu, Gd)

$\alpha_L \times 10^6$, °C^{-1}															
T, °C	$Sr_3La_2(Ge_3O_9)_2$					$Sr_3Pr_2(Ge_3O_9)_2$					$Sr_3Nd_2(Ge_3O_9)_2$				
	a	*b*	*c*	*β*	*V*	*a*	*b*	*c*	*β*	*V*	*a*	*b*	*c*	*β*	*V*
100	6.7	11.3	1.0	-0.9	19.0	4.5	10.9	-0.1	-0.9	15.4	1.3	10.7	12.6	-10.7	26.1
200	4.7	11.1	-2.8	-1.0	13.0	3.9	11.4	-2.1	-1.9	13.3	3.1	12.7	15.1	-11.1	32.3
300	2.3	9.5	-4.0	-1.7	7.7	5.6	13.9	-1.1	-2.3	18.4	1.1	9.2	11.6	-11.1	23.3
400	5.4	13.2	-1.2	-2.3	17.3	5.0	12.1	-0.5	-3.6	16.7	4.0	12.6	15.1	-12.0	33.1
500	6.1	14.7	-1.3	-2.9	19.5	4.5	12.6	-2.5	-2.3	14.7	2.1	7.8	13.2	-10.9	24.4
600	6.6	13.2	0.3	-3.3	20.2	6.4	13.8	2.2	-3.2	22.4	4.1	10.8	15.0	-12.4	31.3
700	5.4	13.5	1.7	-4.0	20.7	6.3	8.6	4.3	-4.8	19.3	4.5	8.6	18.3	-11.0	32.6
800	17.6	26.4	9.8	-3.9	53.7	3.0	14.3	-3.3	-3.3	14.1	2.3	5.6	14.4	-11.2	23.6
900	5.2	15.8	-3.1	-1.9	18.0	4.5	17.7	-4.5	-3.3	17.8	7.1	8.1	20.5	-11.8	36.9
T, °C	$Sr_3Sm_2(Ge_3O_9)_2$					$Sr_3Eu_2(Ge_3O_9)_2$					$Sr_3Gd_2(Ge_3O_9)_2$				
	a	*b*	*c*	*β*	*V*	*a*	*b*	*c*	*β*	*V*	*a*	*b*	*c*	*β*	*V*
100	3.4	11.2	12.7	-6.7	14.2	-1.0	6.5	12.3	-11.9	19.6	-6.4	3.6	-3.5	-10.7	-4.8
200	2.4	11.3	12.8	-10.4	17.0	2.1	8.4	12.7	-8.2	24.4	-0.7	3.0	10.4	-9.5	14.1
300	3.8	10.7	14.1	-9.8	17.7	1.8	7.3	10.8	-10.3	21.3	0.2	4.8	11.5	-9.5	17.8
400	3.8	10.5	11.3	-9.4	16.0	2.4	10.5	13.1	-10.9	27.5	5.4	13.5	14.0	-11.5	34.5
500	3.0	9.5	12.8	-7.6	14.8	1.2	4.8	10.9	-10.3	18.3	4.4	4.1	10.4	-10.8	20.4
600	6.1	9.4	16.0	-11.3	21.2	6.8	13.4	18.0	-10.8	39.6	3.8	12.8	14.7	-9.2	32.5
700	4.9	10.9	13.9	-9.1	17.5	3.8	7.1	16.5	-10.1	28.7	6.6	7.8	20.3	-9.5	35.9
800	4.7	7.9	14.3	-10.4	18.8	3.5	6.0	11.8	-10.4	22.6	7.2	11.3	13.6	-10.6	33.4
900	3.9	8.2	17.0	-12.0	21.2						1.8	4.2	10.5	-8.2	17.5