Electronic Supplementary Information (ESI)

Structural, electronic and optical studies of $BaRE_2Ge_3O_{10}$ (*RE* = Y, Sc, Gd–Lu) trigermanates with a special focus on the $[Ge_3O_{10}]^{8-}$ geometry

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Table **S1**. The results[a] of quantitative energy-dispersive X-ray analyses for $BaRE_2Ge_3O_{10}$ (*RE* = Y, Sc, Gd–Lu)

	Mass. % of Ba		Mass.% of *RE*		Mass.% of Ge	
Compound	Calculated	Experimental	Calculated	Experimental	Calculated	Experimental
$BaY_2Ge_3O_{10}$	25.8	25.0±0.8	33.4	34.4±1.0	40.8	40.6±0.8
$BaSc_2Ge_3O_{10}$	30.8	31.0±1.1	20.2	20.0±0.4	49.0	49.0±1.4
$BaGd_2Ge_3O_{10}$	20.5	19.8±1.9	47.0	48.7±1.7	32.5	31.5±2.0
$BaTb_2Ge_3O_{10}$	20.4	19.4±1.5	47.2	48.9±1.5	32.4	31.7±1.0
$BaDy_2Ge_3O_{10}$	20.2	19.1±2.2	47.8	49.5±2.8	32.0	31.4±0.9
$BaHo_2Ge_3O_{10}$	20.0	20.3±0.9	48.1	47.8±1.0	31.8	31.9±1.1
$BaEr_2Ge_3O_{10}$	19.9	19.3±0.7	48.5	51.5±2.6	31.6	29.2±2.8
$BaTm_2Ge_3O_{10}$	19.8	21.1±1.9	48.8	49.2±2.5	31.4	29.7±2.6
$BaYb_2Ge_3O_{10}$	19.6	21.5±1.8	49.4	48.7±2.2	31.1	29.8±2.1
$BaLu_2Ge_3O_{10}$	19.5	20.0±1.4	49.6	48.9±1.7	30.9	31.1±1.4

[a] Random errors of direct measurements shown in the table were determined according to the formulas:

$\Delta a_r = t_{St} \cdot S(\bar{a})$

and

$$S(\bar{a}) = \sqrt{\frac{\sum_{i=1}^{n}(a_i - \bar{a})^2}{n \cdot (n-1)}}$$

where $\bar{a}$ is an arithmetic mean value of all measurement results,

$n = 5$ is amount of measurements,

$t_{St} = 2.776$ is the Student's coefficient ($n = 5$ and $\alpha = 0.95$).

Table **S2**. Atomic coordinates and thermal parameters ($U_{iso}\times100$, Å^2) for Ba*RE*$_2$Ge$_3$O$_{10}$ (*RE* = Y, Gd–Ho)

			Gd	Tb	Dy	Ho	Y
Ba	2*e*	*x*	0.7675(4)	0.7689(4)	0.7666(3)	0.7655(1)	0.7652(1)
		y	0.25	0.25	0.25	0.25	0.25
		z	0.0117(3)	0.0127(3)	0.0130(2)	0.0138(1)	0.0135(1)
		$U_{iso}\times100$	3.09	2.46(9)	2.49	1.76	2.62
RE	4*f*	*x*	0.1593(4)	0.1551(3)	0.1545(2)	0.1531(1)	0.1531(1)
		y	0.0991(1)	0.1000(1)	0.10018(7)	0.10083(5)	0.10088(5)
		z	0.6795(2)	0.6783(2)	0.6766(1)	0.67621(9)	0.67599(9)
		$U_{iso}\times100$	2.48	2.38(7)	2.36	2.03	2.30
Ge(1)	2*e*	*x*	0.5862(9)	0.5849(8)	0.5829(5)	0.5799(3)	0.5808(2)
		y	0.25	0.25	0.25	0.25	0.25
		z	0.4760(7)	0.4733(6)	0.4759(4)	0.4759(2)	0.4763(2)
		$U_{iso}\times100$	2.70	2.06(13)	2.13	1.61	2.36
Ge(2)	4*f*	*x*	0.3026(6)	0.3038(5)	0.3059(4)	0.3046(2)	0.3040(2)
		y	0.0548(2)	0.0531(2)	0.0534(1)	0.05289(7)	0.05294(6)
		z	0.2019(4)	0.2012(4)	0.2014(3)	0.2020(1)	0.2012(1)
		$U_{iso}\times100$	2.78	2.27(11)	2.57	1.62	2.44
O(1)	2*e*	*x*	0.361(3)	0.3503(31)	0.3468(19)	0.3414(12)	0.3428(10)
		y	0.25	0.250000	0.25	0.25	0.25
		z	0.6003(21)	0.6038(23)	0.5975(13)	0.5923(8)	0.5919(7)
		$U_{iso}\times100$	2.2(7)	2.71(20) [a]	0.59(33)	1.49(20)	2.49(16)
O(2)	2*e*	*x*	0.895(4)	0.9035(39)	0.8838(25)	0.8804(13)	0.8797(10)
		y	0.25	0.250000	0.25	0.25	0.25
		z	0.6402(27)	0.6510(27)	0.6466(17)	0.6394(9)	0.6409(8)
		$U_{iso}\times100$	3.1(8)	2.71(20) [a]	2.43(45)	1.19(21)	1.42(16)
O(3)	4*f*	*x*	0.5740(23)	0.5683(22)	0.5840(13)	0.5722(8)	0.5673(7)
		y	0.1385(10)	0.1364(9)	0.1366(6)	0.1382(3)	0.1380(3)
		z	0.3152(18)	0.3216(18)	0.3145(11)	0.3166(6)	0.3160(6)
		$U_{iso}\times100$	2.8(5)	2.71(20) [a]	2.27(26)	1.83(14)	2.52(11)
O(4)	4*f*	*x*	0.4303(21)	0.4276(21)	0.4348(13)	0.4411(8)	0.4437(7)
		y	-0.0715(11)	-0.0692(10)	-0.0731(6)	-0.0695(3)	-0.0698(3)
		z	0.1713(20)	0.1761(18)	0.1763(11)	0.1775(6)	0.1809(6)
		$U_{iso}\times100$	2.9(5)	2.71(20) [a]	1.98(30)	2.03(16)	2.59(12)
O(5)	4*f*	*x*	0.1308(20)	0.1610(21)	0.1323(14)	0.1312(8)	0.1335(7)
		y	0.1225(10)	0.1267(10)	0.1211(7)	0.1186(3)	0.1193(3)
		z	-0.0187(19)	-0.0091(19)	-0.0160(11)	-0.0134(6)	-0.0160(6)
		$U_{iso}\times100$	1.2(4)	2.71(20) [a]	2.08(27)	1.16(13)	2.35(11)
O(6)	4*f*	*x*	0.1115(24)	0.0974(24)	0.1164(15)	0.1142(9)	0.1168(8)
		y	0.0450(10)	0.0471(10)	0.0428(6)	0.0428(3)	0.0407(3)
		z	0.3651(17)	0.3652(18)	0.3662(11)	0.3616(6)	0.3605(6)
		$U_{iso}\times100$	1.8(4)	2.71(20) [a]	1.43(26)	1.44(14)	2.36(11)

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

Table **S3**. Atomic coordinates and thermal parameters ($U_{iso}\times100$, Å^2) for Ba*RE*$_2$Ge$_3$O$_{10}$ (*RE* = Sc, Er–Lu)

			Er	Tm	Yb	Lu	Sc
Ba	2*e*	*x*	0.7649(2)	0.7671(2)	0.7664(1)	0.7656(3)	0.7744(1)
		y	0.25	0.25	0.25	0.25	0.25
		z	0.0148(1)	0.0161(1)	0.0169(1)	0.0173(2)	0.0304(1)
		$U_{iso}\times100$	1.90	2.53	2.92	2.49	2.48
RE	4*f*	*x*	0.1514(1)	0.1502(1)	0.14936(9)	0.1477(2)	0.1420(3)
		y	0.10127(5)	0.10157(4)	0.10185(3)	0.10212(7)	0.1039(1)
		z	0.67552(9)	0.67465(8)	0.67390(7)	0.6733(1)	0.6684(3)
		$U_{iso}\times100$	1.79	2.37	2.70	2.16	2.17
Ge(1)	2*e*	*x*	0.5789(3)	0.5781(3)	0.5771(3)	0.5757(5)	0.5658(3)
		y	0.25	0.25	0.25	0.25	0.25
		z	0.4759(2)	0.4759(2)	0.4762(2)	0.4764(4)	0.4799(3)
		$U_{iso}\times100$	1.69	2.29	2.61	2.09	2.18
Ge(2)	4*f*	*x*	0.3037(2)	0.3045(2)	0.3037(2)	0.3041(4)	0.3009(2)
		y	0.05200(9)	0.05142(8)	0.05090(7)	0.0504(2)	0.04452(7)
		z	0.2013(2)	0.2007(2)	0.2008(1)	0.2011(3)	0.1999(2)
		$U_{iso}\times100$	1.78	2.37	2.73	2.36	2.26
O(1)	2*e*	*x*	0.3380(15)	0.3328(14)	0.3337(11)	0.3333(24)	0.3029(12)
		y	0.25	0.25	0.25	0.25	0.25
		z	0.5928(10)	0.5904(9)	0.5878(8)	0.5911(16)	0.5715(10)
		$U_{iso}\times100$	1.69(25)	2.01(23)	2.47(20)	1.66(40)	2.22(20)
O(2)	2*e*	*x*	0.8877(17)	0.8827(16)	0.8808(11)	0.8831(28)	0.8793(12)
		y	0.25	0.25	0.25	0.25	0.25
		z	0.6487(12)	0.6456(11)	0.6471(8)	0.6450(21)	0.6486(10)
		$U_{iso}\times100$	1.59(26)	1.63(23)	1.36(18)	2.43(45)	1.82(19)
O(3)	4*f*	*x*	0.5715(10)	0.5679(9)	0.5689(8)	0.5714(18)	0.5593(8)
		y	0.1386(4)	0.1371(4)	0.1387(3)	0.1414(8)	0.1371(4)
		z	0.3160(8)	0.3163(7)	0.3182(6)	0.3166(13)	0.3115(7)
		$U_{iso}\times100$	1.83(17)	2.18(16)	2.64(14)	2.89(31)	2.08(15)
O(4)	4*f*	*x*	0.4487(10)	0.4477(10)	0.4541(8)	0.4559(19)	0.4702(10)
		y	-0.0704(4)	-0.0716(4)	-0.0709(3)	-0.0710(7)	-0.0774(3)
		z	0.1839(8)	0.1836(8)	0.1822(6)	0.1848(15)	0.1960(8)
		$U_{iso}\times100$	1.58(18)	2.23(18)	2.58(15)	3.24(34)	2.14(15)
O(5)	4*f*	*x*	0.1319(11)	0.1371(10)	0.1311(8)	0.1327(16)	0.1184(8)
		y	0.1167(5)	0.1182(4)	0.1149(4)	0.1151(8)	0.1084(4)
		z	-0.0185(8)	-0.0198(7)	-0.0219(6)	-0.0208(13)	-0.0305(8)
		$U_{iso}\times100$	1.81(17)	1.69(15)	2.82(13)	1.89(27)	2.09(15)
O(6)	4*f*	*x*	0.1206(11)	0.1153(10)	0.1166(8)	0.1170(18)	0.1067(9)
		y	0.0412(4)	0.0382(4)	0.0401(3)	0.0380(7)	0.0360(4)
		z	0.3652(8)	0.3605(8)	0.3652(6)	0.3637(12)	0.3684(8)
		$U_{iso}\times100$	1.03(17)	1.96(16)	2.29(14)	1.21(28)	2.43(14)

Table **S4**. Anisotropic thermal parameters[a] (U×100, Å^2) of metal atoms for Ba*RE*$_2$Ge$_3$O$_{10}$

		Gd	Tb	Dy	Ho	Y
Ba	U_{11} × 100	2.87(28)	1.55(22)	2.67(14)	1.96(6)	2.58(5)
	U_{22} × 100	2.64(28)	2.14(22)	2.30(12)	1.67(5)	2.72(4)
	U_{33} × 100	3.62(27)	3.55(22)	2.50(12)	1.68(5)	2.53(4)
	U_{12} × 100	0	0	0	0	0
	U_{13} × 100	1.03(16)	0.69(15)	0.86(9)	0.62(4)	0.85(4)
	U_{23} × 100	0	0	0	0	0
RE	U_{11} × 100	2.66(21)	2.36(14)	2.37(8)	1.91(5)	2.41(4)
	U_{22} × 100	2.47(20)	2.48(12)	2.50(7)	2.11(4)	2.41(4)
	U_{33} × 100	2.33(21)	3.13(14)	2.25(7)	2.06(4)	2.15(4)
	U_{12} × 100	-0.36(11)	0.15(11)	-0.12(7)	-0.09(4)	-0.16(4)
	U_{13} × 100	0.86(10)	1.25(10)	0.85(6)	0.71(4)	0.853(34)
	U_{23} × 100	-0.25(10)	0.26(10)	-0.07(6)	-0.04(4)	-0.051(33)
Ge(1)	U_{11} × 100	1.50(39)	1.16(36)	1.28(21)	1.30(10)	2.26(8)
	U_{22} × 100	3.13(39)	2.31(33)	2.16(20)	1.68(10)	2.18(8)
	U_{33} × 100	3.13(37)	2.82(34)	2.76(20)	1.76(10)	2.57(8)
	U_{12} × 100	0	0	0	0	0
	U_{13} × 100	0.53(28)	0.19(27)	0.67(17)	0.46(8)	0.80(6)
	U_{23} × 100	0	0	0	0	0
Ge(2)	U_{11} × 100	2.55(32)	2.03(27)	2.89(17)	1.60(8)	2.42(6)
	U_{22} × 100	2.84(27)	2.68(21)	2.29(13)	1.81(6)	2.49(5)
	U_{33} × 100	2.84(30)	2.57(25)	2.56(15)	1.42(7)	2.36(5)
	U_{12} × 100	-0.40(19)	-0.34(17)	-0.04(11)	-0.02(6)	-0.03(5)
	U_{13} × 100	0.83(20)	0.94(20)	0.94(13)	0.47(6)	0.75(5)
	U_{23} × 100	-0.06(18)	-0.13(17)	0.13(11)	-0.07(6)	-0.01(5)
		Er	Tm	Yb	Lu	Sc
Ba	U_{11} × 100	1.92(8)	2.52(8)	3.05(6)	2.68(13)	2.63(8)
	U_{22} × 100	1.89(8)	2.78(7)	2.90(6)	2.54(13)	2.50(8)
	U_{33} × 100	1.90(7)	2.40(7)	2.90(6)	2.41(12)	2.41(8)
	U_{12} × 100	0	0	0	0	0
	U_{13} × 100	0.68(6)	1.05(5)	1.19(4)	1.10(9)	1.04(5)
	U_{23} × 100	0	0	0	0	0
RE	U_{11} × 100	1.85(5)	2.44(4)	2.721(29)	2.26(7)	2.44(12)
	U_{22} × 100	1.74(5)	2.42(4)	2.627(27)	2.15(7)	2.00(11)
	U_{33} × 100	1.75(5)	2.20(4)	2.720(28)	2.03(6)	1.99(12)
	U_{12} × 100	-0.33(4)	-0.245(34)	-0.103(27)	-0.08(6)	-0.46(8)
	U_{13} × 100	0.57(4)	0.724(33)	0.926(21)	0.69(5)	0.63(9)
	U_{23} × 100	-0.11(4)	-0.070(32)	-0.101(25)	-0.05(5)	0.07(8)
Ge(1)	U_{11} × 100	1.67(12)	2.02(11)	2.70(9)	1.90(19)	2.09(11)
	U_{22} × 100	1.90(12)	2.79(12)	2.47(9)	2.40(19)	1.92(11)
	U_{33} × 100	1.43(12)	1.93(11)	2.70(9)	1.83(19)	2.41(11)
	U_{12} × 100	0	0	0	0	0
	U_{13} × 100	0.43(9)	0.50(8)	1.03(7)	0.46(15)	0.73(8)
	U_{23} × 100	0	0	0	0	0
Ge(2)	U_{11} × 100	1.78(10)	2.18(9)	2.50(7)	2.08(15)	2.20(9)
	U_{22} × 100	1.63(8)	2.31(8)	2.44(6)	2.03(13)	2.28(8)
	U_{33} × 100	1.76(9)	2.46(9)	2.92(7)	2.73(15)	2.25(9)
	U_{12} × 100	-0.17(7)	0.02(6)	-0.07(5)	-0.26(11)	0.14(6)
	U_{13} × 100	0.38(8)	0.64(7)	0.51(6)	0.63(12)	0.78(6)
	U_{23} × 100	-0.22(6)	0.06(6)	-0.19(5)	-0.37(10)	0.01(6)

[a] Anisotropic thermal factors are defined by $T = e\,[-2\pi^2(u_{11}h^2a^{*2} + \ldots + 2u_{12}hka^*b^* + \ldots)]$

Table **S5**. The bond–valence sums (BVS) for the cations and oxygen anions, and global instability indexes (*GII*) for Ba*RE*$_2$Ge$_3$O$_{10}$ (*RE* = Y, Sc, Gd–Lu)

		Gd		Tb		Dy		Ho		Y	
Atom	Assumed oxidation state	BVS	% dev.	BVS	% dev.	BVS	% dev.	BVS	% dev.	BVS	% dev.
Ba	+2	2.079	4	1.861	7	2.155	8	1.986	1	1.952	2
RE	+3	2.977	1	3.135	4	2.889	4	3.087	3	3.010	0
Ge(1)	+4	3.743	6	3.537	12	3.618	10	3.921	2	3.926	2
Ge(2)	+4	3.516	12	3.784	5	3.600	10	3.909	2	3.927	2
O(1)	-2	2.013	1	1.939	3	1.974	1	2.081	4	2.066	3
O(2)	-2	1.869	7	1.863	7	1.919	4	2.020	1	2.010	0
O(3)	-2	1.849	8	1.948	3	1.784	11	1.942	3	1.950	3
O(4)	-2	1.838	8	1.962	2	1.852	7	1.971	1	1.930	4
O(5)	-2	1.879	6	1.957	2	1.889	6	1.979	1	1.947	3
O(6)	-2	1.897	5	1.85	7	1.904	5	2.007	0	2.011	1
GII		0.20		0.19		0.21		0.06		0.05	

		Er		Tm		Yb		Lu		Sc	
Atom	Assumed oxidation state	BVS	% dev.	BVS	% dev.	BVS	% dev.	BVS	% dev.	BVS	% dev.
Ba	+2	1.945	3	1.947	3	1.947	3	1.955	2	2.123	6
RE	+3	2.974	1	2.884	4	2.956	1	3.053	2	2.808	6
Ge(1)	+4	3.750	6	3.776	6	3.990	0	4.044	1	3.982	0
Ge(2)	+4	3.844	4	3.901	2	3.811	5	3.811	5	3.864	3
O(1)	-2	1.998	0	1.958	2	2.013	1	2.039	2	1.994	0
O(2)	-2	1.899	5	1.925	4	1.944	3	1.976	1	1.937	3
O(3)	-2	1.919	4	1.960	1	1.982	1	1.985	1	2.074	4
O(4)	-2	1.912	4	1.894	5	1.902	5	1.934	3	1.902	5
O(5)	-2	1.924	4	1.916	4	1.934	3	1.948	3	1.914	4
O(6)	-2	1.962	2	1.935	3	1.939	3	1.989	1	1.869	7
GII		0.11		0.10		0.08		0.07		0.11	

Table **S6**. Theoretical lattice parameters, relative energies ΔE and band gap BG for representative set of $BaY_2Ge_3O_{10}$ and $BaLa_2Ge_3O_{10}$ polymorphic modifications. DFT calculations.

Compound	Lattice type	Lattice parameters in Å or °	ΔE, eV/st.unit	BG, eV
$BaY_2Ge_3O_{10}$	$BaY_2Ge_3O_{10}$	*a* = 5.64, *b* = 12.45, *c* = 7.01, *β* = 104.9	±0.0000	3.4
	$CaY_2Ge_3O_{10}$	*a* = 7.00, *b* = 7.08, *c* = 19.23, α = 89.4, *β* = 104.2, γ = 88.7	+0.4232	3.1
	$CaLa_2Ge_3O_{10}$	*a* = 7.05, *b* = 20.71, *c* = 7.14, *β* = 114.6	+0.5797	3.2
	$SrY_2Si_3O_{10}$	*a* = 7.07, *b* = 7.15, *c* = 9.76, α = 71.0, *β* = 86.9, γ = 87.8	+0.0680	3.5
$BaLa_2Ge_3O_{10}$	$BaY_2Ge_3O_{10}$	*a* = 5.81, *b* = 12.13, *c* = 7.27, *β* = 104.5	+0.6933	3.0
	$CaY_2Ge_3O_{10}$	*a* = 7.19, *b* = 7.21, *c* = 19.47, α = 91.1, *β* = 106.0, γ = 90.5	+0.5762	3.1
	$CaLa_2Ge_3O_{10}$	*a* = 7.02, *b* = 21.00, *c* = 7.26, *β* = 115.9	+0.5559	3.2
	$SrY_2Si_3O_{10}$	*a* = 7.11, *b* = 7.11, *c* = 9.80, α = 71.6, *β* = 87.2, γ = 90.4	±0.0000	3.1

Table **S7**. IR wavenumbers (cm^{-1}) for the Ba$RE_2Ge_3O_{10}$

Gd	Tb	Dy	Y	Ho	Er	Tm	Yb	Lu	Sc	Assignment
836	838	843	848	846	848	849	851	852	857	ν_{as} Ge-O-Ge
805	810	808	812	812	814	816	819	822	823	ν_s GeO_3
	776	780	782	782	783	786	785	791		
	743	747	752	751	753	755	758	757	768	ν_{as} GeO_3
735	729	727	727	727	727	724	715	722	713	
511	515	515	517	519	519	521	523	522	536	ν_s Ge-O-Ge
							488	492	488	
466	467	471	462	477	482	480	475	475	469	δ O-Ge-O
437	439			443	444		449	450	447	
				414	415	418	420	426		

Table **S8**. Raman wavenumbers (cm^{-1}) for the Ba$RE_2Ge_3O_{10}$

Tb	Dy	Y	Tm	Yb	Lu	Assignment
828	829	829	830	831	833	ν_s GeO_3
787	787	790	791	793	796	
765	768	770	771	775	763	ν_{as} GeO_3
742	743	757	750	761	754	
505	505	506	509	511	512	ν_s Ge-O-Ge
		458			454	
432	429	431	430	433	432	δ O-Ge-O
		389	374	389	391	
366	368	366		371	373	

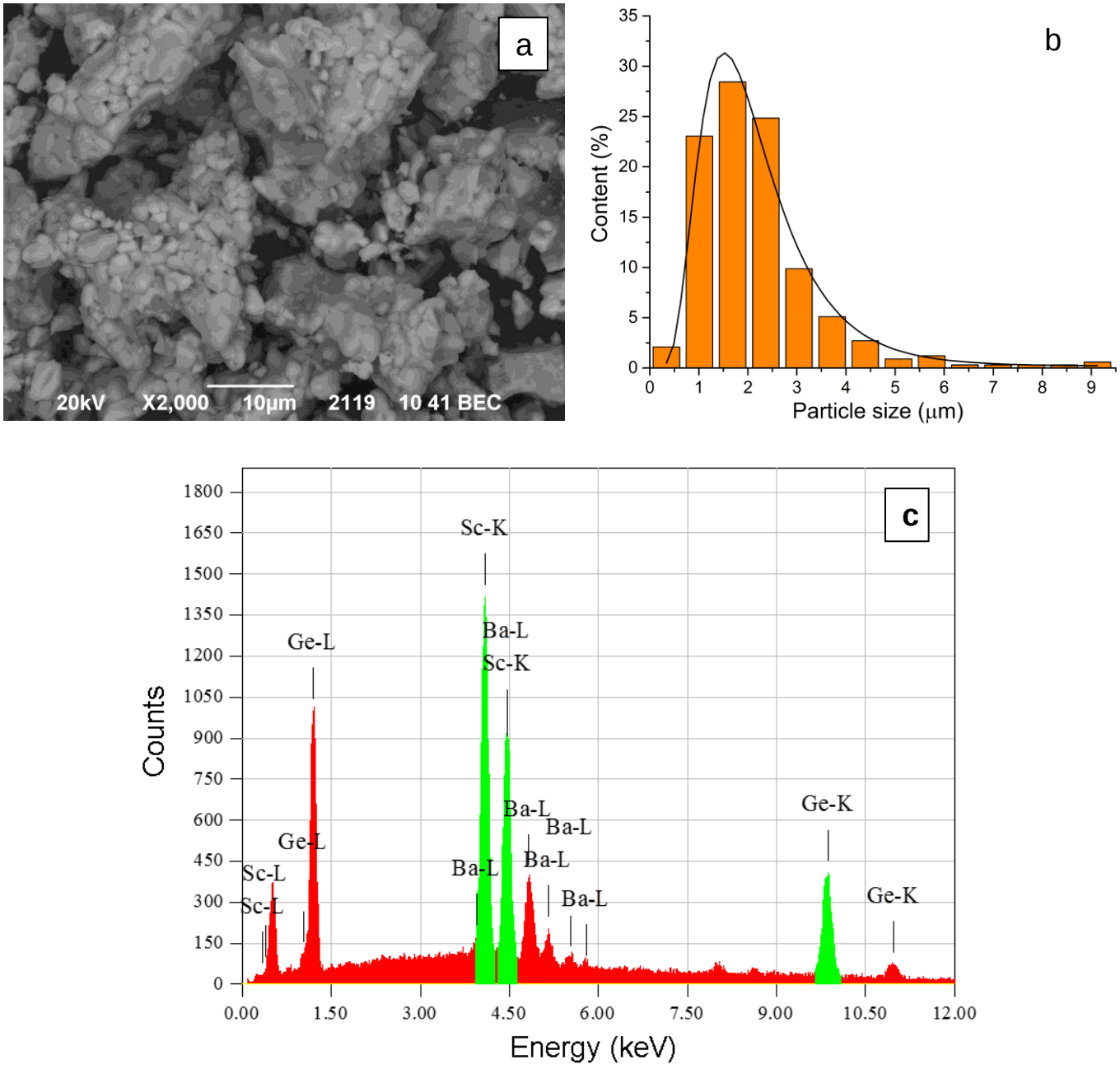

Fig. S1 The typical SEM image of $BaSc_2Ge_3O_{10}$ powder (a), the particle size distribution histogram with a log-normal distribution fit (b) and the spectrum of $BaSc_2Ge_3O_{10}$ acquired at 20 kV (c).

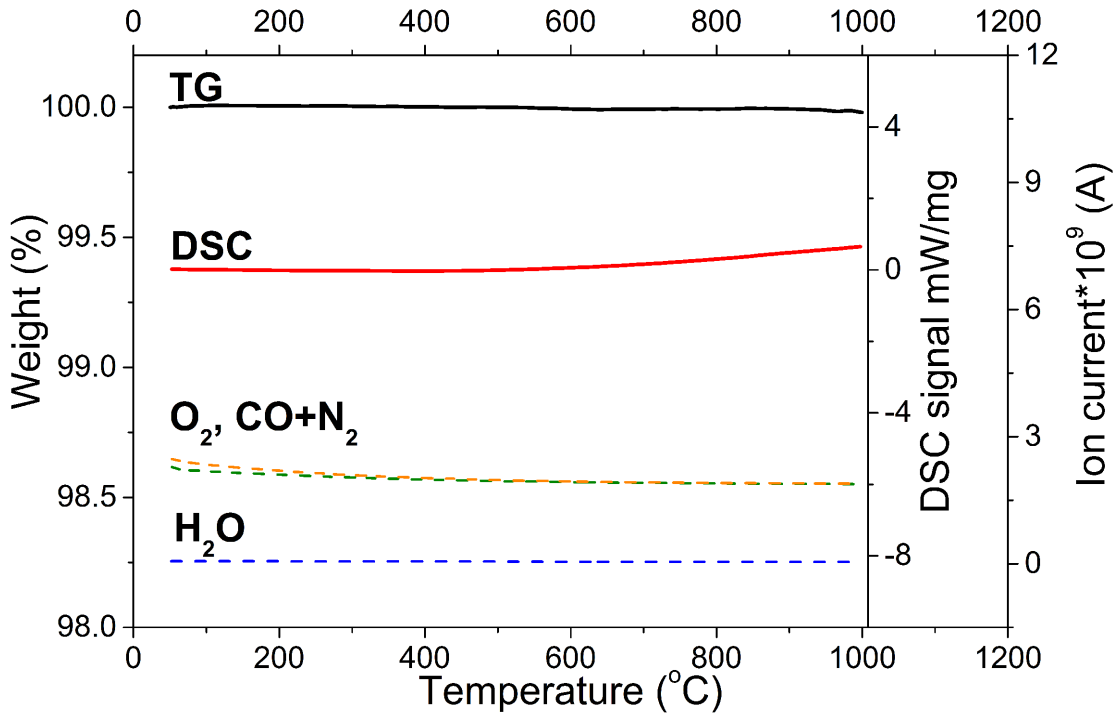

Fig. S2 Simultaneous thermal analysis of the $BaYb_2Ge_3O_{10}$: solid lines - TG and DSC, dashed lines – ion currents of gases.

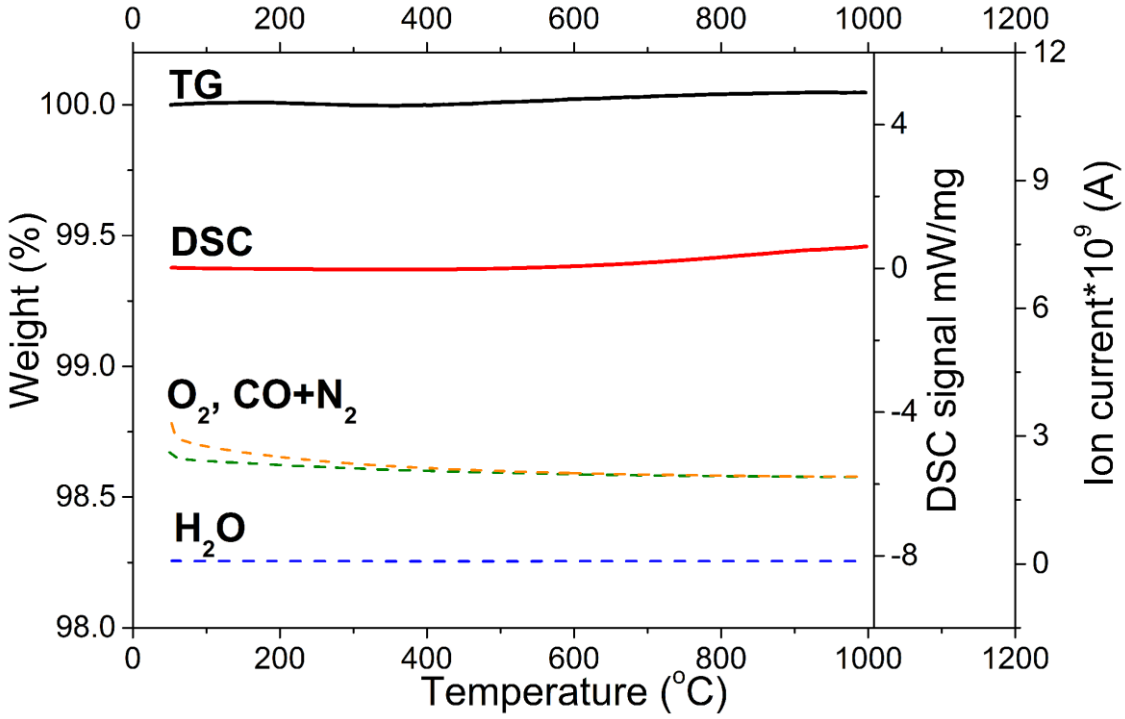

Fig. S3 Simultaneous thermal analysis of the $BaY_2Ge_3O_{10}$: solid lines - TG and DSC, dashed lines – ion currents of gases.

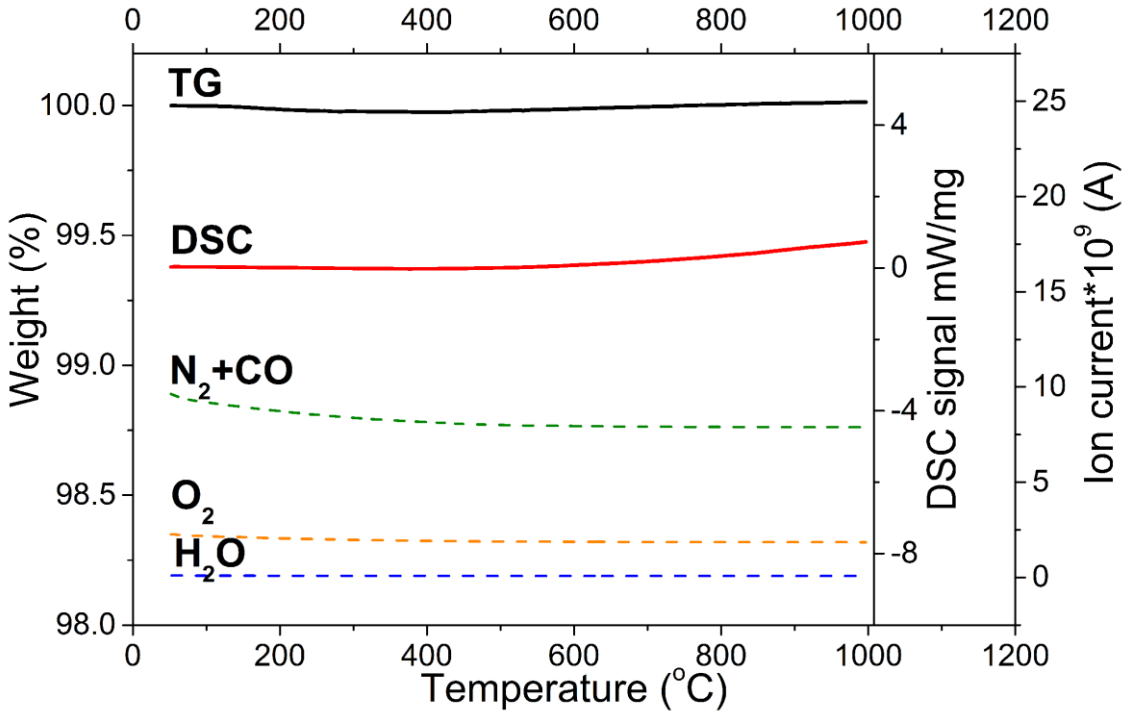

Fig. S4 Simultaneous thermal analysis of the $BaGd_2Ge_3O_{10}$: solid lines - TG and DSC, dashed lines – ion currents of gases.

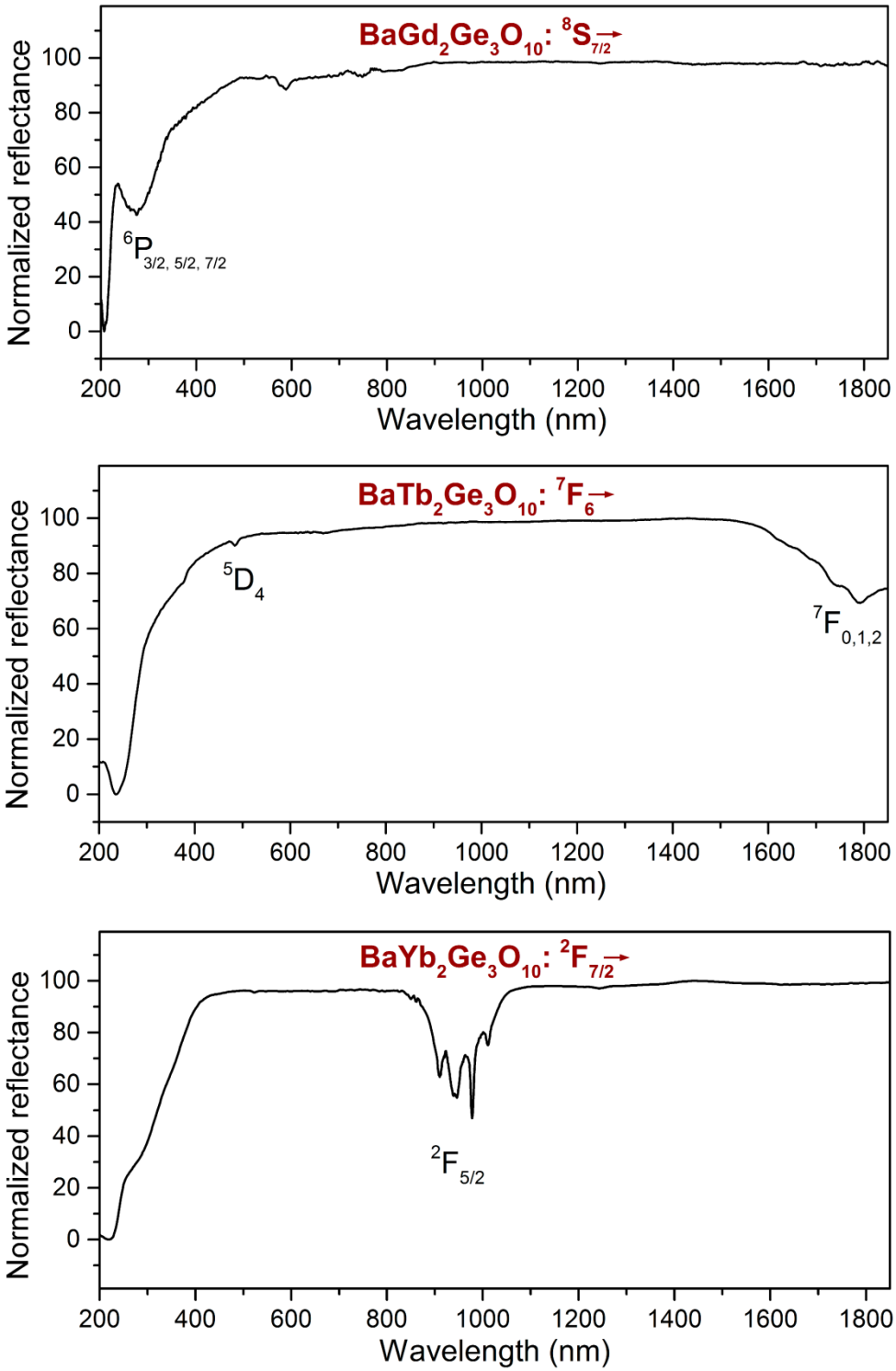

Fig. S5 Diffuse reflectance spectra of Ba*RE*$_2$Ge$_3$O$_{10}$ (*RE* = Gd, Tb, Yb)

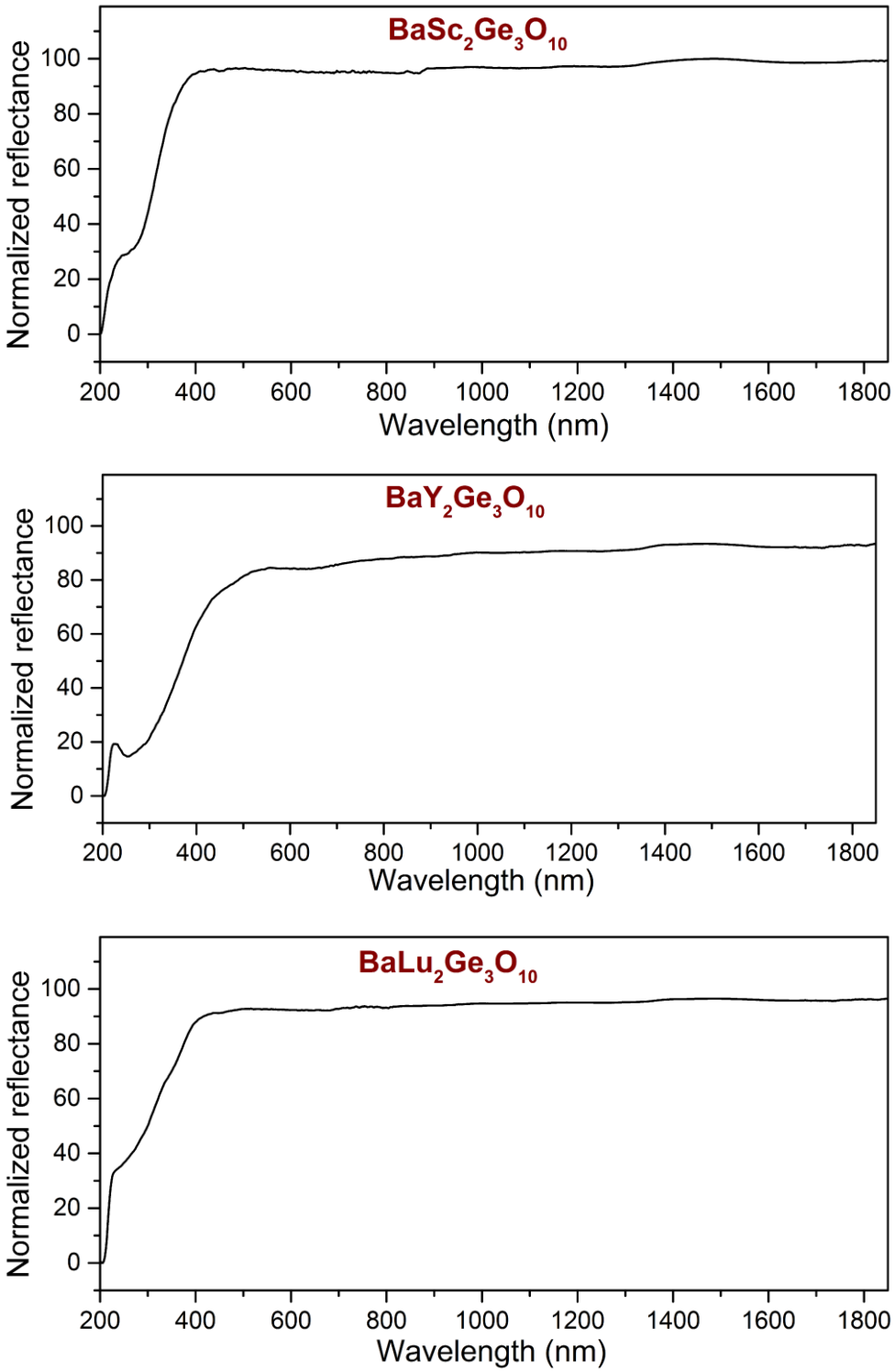

Fig. S6 Diffuse reflectance spectra of Ba$RE_2Ge_3O_{10}$ (*RE* = Y, Sc, Lu)