Electronic Supplementary Information (ESI)

Structural, electronic and optical properties of $BaRE_6(Ge_2O_7)_2(Ge_3O_{10})$ (*RE* = Tm, Yb, Lu) compounds and $BaYb_6(Ge_2O_7)_2(Ge_3O_{10}):Tm^{3+}$, $BaLu_6(Ge_2O_7)_2(Ge_3O_{10}):Yb^{3+},Tm^{3+}$ phosphors: potential applications in temperature sensing

O. A. Lipina,* L. L. Surat, A. Yu. Chufarov, I. V. Baklanova, A. N. Enyashin, M. A. Melkozerova, A. P. Tyutyunnik, and V. G. Zubkov

Institute of Solid State Chemistry, UB RAS, 620990 Ekaterinburg, Russia

* Corresponding author. E-Mail: LipinaOlgaA@yandex.ru

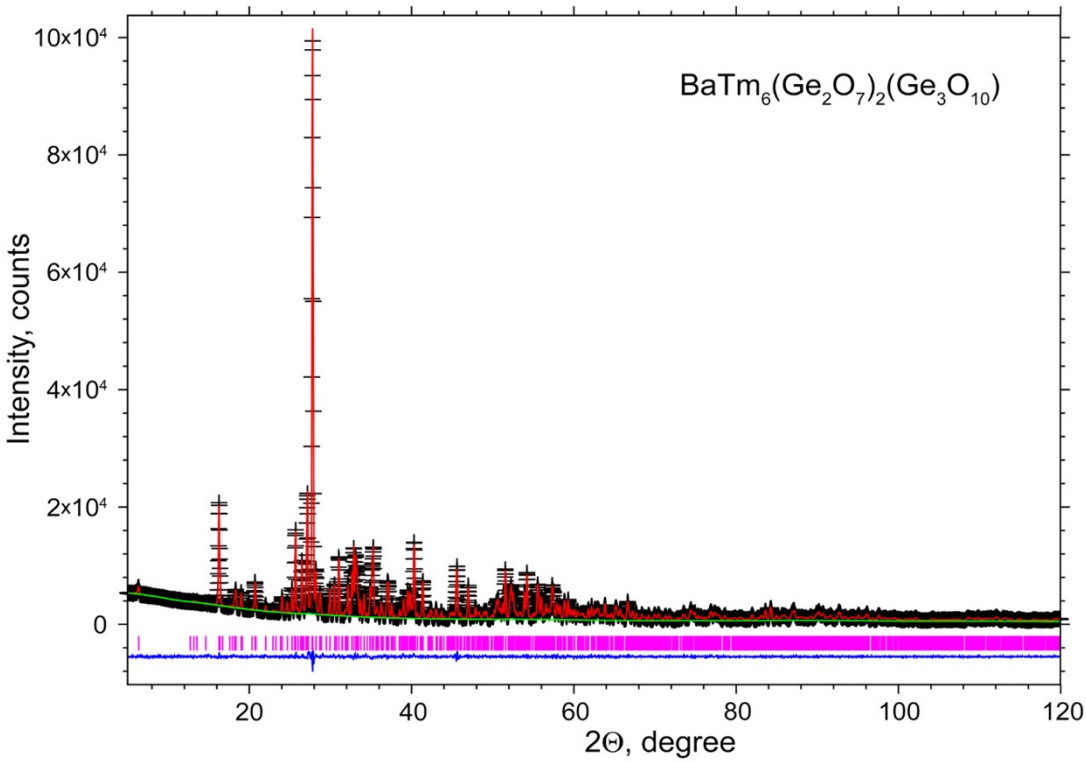

Fig. S1 Experimental (crosses), calculated (solid line), and difference (bottom line) XRPD patterns for $BaTm_6(Ge_2O_7)_2(Ge_3O_{10})$. Series of tick marks correspond to the Bragg reflection.

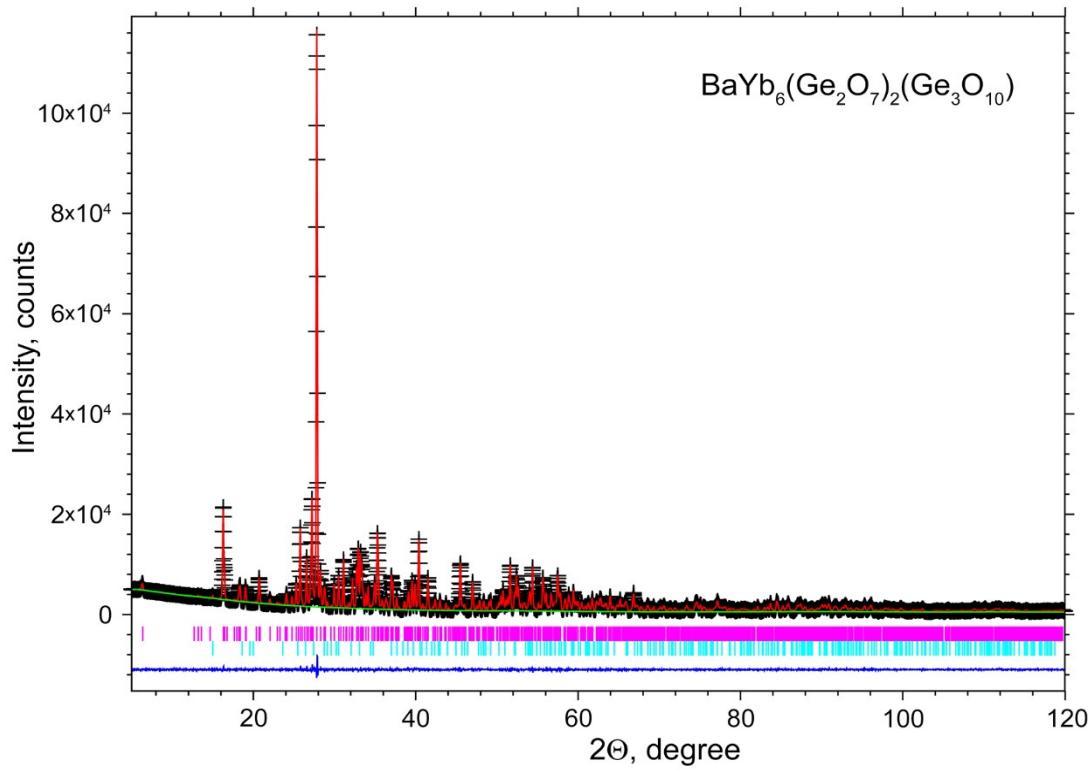

Fig. S2 Experimental (crosses), calculated (solid line), and difference (bottom line) XRPD patterns for $BaYb_6(Ge_2O_7)_2(Ge_3O_{10})$. Series of tick marks correspond to the Bragg reflection of the main phase and $Yb_2Ge_2O_7$ impurity.

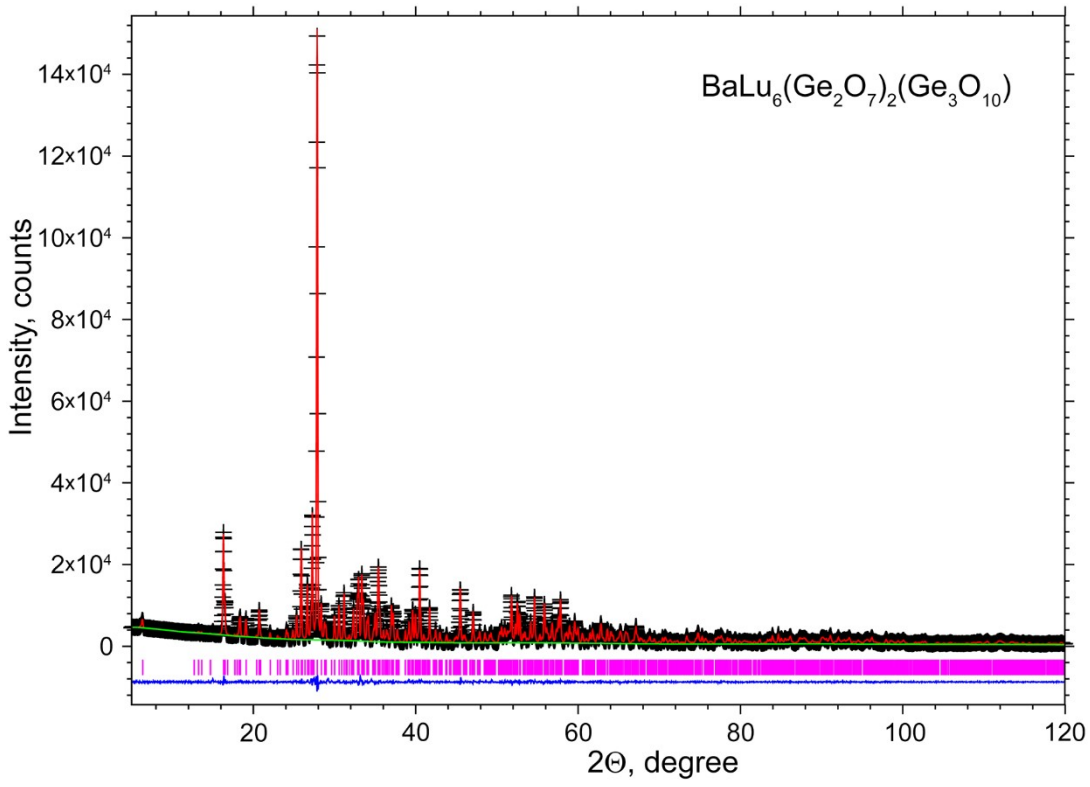

Fig. S3 Experimental (crosses), calculated (solid line), and difference (bottom line) XRPD patterns for $BaLu_6(Ge_2O_7)_2(Ge_3O_{10})$. Series of tick marks correspond to the Bragg reflection.

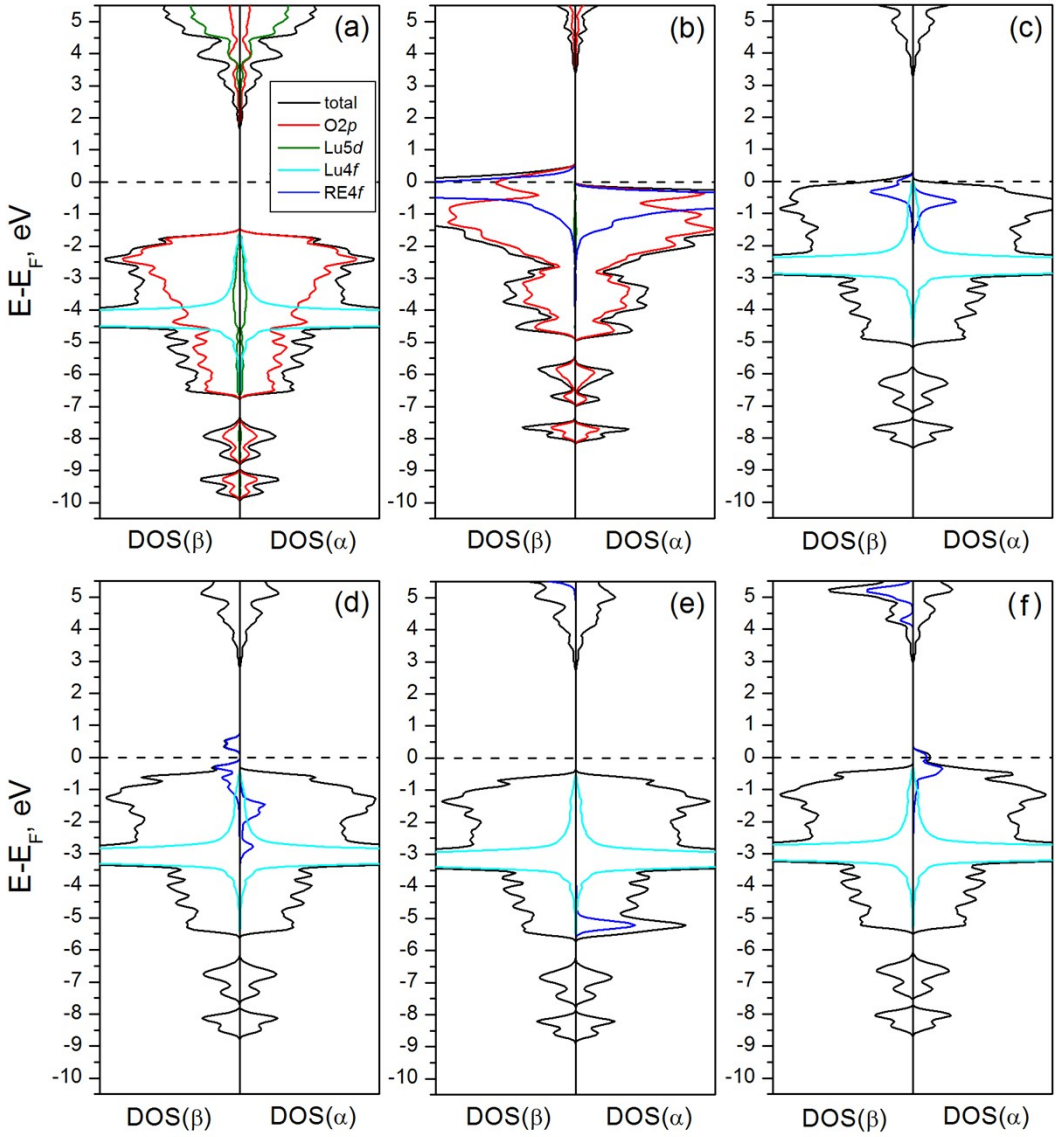

Fig. S4 Total and partial densities of electronic states for pristine $BaLu_6(Ge_2O_7)_2(Ge_3O_{10})$ (a) and $BaYb_6(Ge_2O_7)_2(Ge_3O_{10})$ compounds (b) as well as for $BaLu_6(Ge_2O_7)_2(Ge_3O_{10})$ matrix doped by single atoms of Yb (c), Tm (d), Gd (e) or Eu (f) in amount of ~8%. DFT calculations.

Table S1 Atomic coordinates and isotropic thermal parameters (Å^2) for Ba*RE*$_6$(Ge$_2$O$_7$)$_2$(Ge$_3$O$_{10}$) (*RE* = Tm, Yb, Lu)

Atom			Tm	Yb	Lu
Ba	2*e*	x	0.7128(4)	0.7107(4)	0.7086(4)
		y	0.25	0.25	0.25
		z	0.07181(31)	0.07143(27)	0.06900(32)
		U_{iso}×100	2.63(6)	2.56(6)	2.85(7)
RE(1)	4*f*	x	0.87495(25)	0.87893(20)	0.88195(24)
		y	0.68508(5)	0.68530(4)	0.68530(5)
		z	0.25188(20)	0.25531(16)	0.25827(19)
		U_{iso}×100	2.32(4)	2.253(35)	2.38(4)
RE(2)	4*f*	x	0.21662(26)	0.21792(22)	0.21864(25)
		y	0.60063(5)	0.60028(4)	0.60010(4)
		z	0.60186(21)	0.60411(18)	0.60525(19)
		U_{iso}×100	2.33(4)	2.521(36)	2.53(4)
RE(3)	4*f*	x	0.80857(26)	0.81133(21)	0.81145(23)
		y	0.54061(6)	0.54110(5)	0.54158(5)
		z	0.82162(19)	0.82371(16)	0.82399(19)
		U_{iso}×100	2.44(4)	2.234(34)	2.40(4)
Ge(1)	4*f*	x	0.2723(6)	0.2710(5)	0.2704(6)
		y	0.47539(12)	0.47580(10)	0.47531(11)
		z	0.6936(4)	0.69227(33)	0.6908(4)
		U_{iso}×100	2.51(9)	2.67(8)	2.25(9)
Ge(2)	4*f*	x	0.3117(5)	0.3130(4)	0.3133(5)
		y	0.61248(11)	0.61319(9)	0.61316(11)
		z	0.1200(4)	0.12314(35)	0.1238(4)
		U_{iso}×100	2.91(9)	2.67(7)	2.72(9)
Ge(3)	4*f*	x	0.7602(5)	0.7601(4)	0.7647(5)
		y	0.66542(11)	0.66583(9)	0.66510(11)
		z	0.7346(4)	0.73836(34)	0.7403(4)
		U_{iso}×100	2.59(9)	2.26(7)	2.20(8)
Ge(4)	2*e*	x	0.5532(8)	0.5468(6)	0.5436(7)
		y	0.25	0.25	0.25
		z	0.5447(5)	0.54185(48)	0.5415(5)
		U_{iso}×100	2.87(12)	2.98(11)	2.64(13)
O(1)	4*f*	x	0.1031(23)	0.1039(20)	0.0938(23)
		y	0.4481(5)	0.4507(5)	0.4499(5)
		z	0.4605(18)	0.4666(15)	0.4635(17)
O(2)	4*f*	x	0.4100(24)	0.4159(21)	0.4118(24)
		y	0.5293(5)	0.5299(4)	0.5278(5)
		z	0.6733(18)	0.6696(15)	0.6773(18)
O(3)	4*f*	x	0.5299(23)	0.5307(20)	0.5339(23)
		y	0.4429(4)	0.4408(4)	0.4425(5)
		z	0.7969(18)	0.8030(16)	0.7974(18)
O(4)	4*f*	x	0.0933(22)	0.0917(19)	0.0894(22)
		y	0.4819(5)	0.4795(4)	0.4798(5)
		z	0.8548(19)	0.8535(17)	0.8505(19)
O(5)	4*f*	x	0.4837(25)	0.4889(21)	0.4923(24)
		y	0.6600(5)	0.6618(4)	0.6614(5)
		z	0.1112(17)	0.1126(16)	0.1161(19)
O(6)	4*f*	x	0.1214(24)	0.1195(21)	0.1168(24)
		y	0.5957(5)	0.5974(4)	0.5973(5)
		z	-0.1116(19)	-0.1173(16)	-0.1090(18)
O(7)	4*f*	x	0.1415(22)	0.1402(19)	0.1581(21)
		y	0.6248(5)	0.6237(4)	0.6265(5)

		z	0.2935(18)	0.2985(16)	0.3101(18)
O(8)	4*f*	x	0.9144(21)	0.9117(18)	0.9122(21)
		y	0.6949(5)	0.6941(4)	0.6959(5)
		z	0.9491(17)	0.9486(15)	0.9482(17)
O(9)	4*f*	x	0.6170(23)	0.6249(21)	0.6242(24)
		y	0.6120(4)	0.6126(4)	0.6129(5)
		z	0.7530(17)	0.7554(15)	0.7603(18)
O(10)	4*f*	x	0.9408(25)	0.9504(21)	0.9504(23)
		y	0.6655(5)	0.6648(4)	0.6638(5)
		z	0.5646(18)	0.5712(15)	0.5713(17)
O(11)	4*f*	x	0.4722(23)	0.4800(20)	0.4896(23)
		y	0.7012(5)	0.7006(4)	0.7008(5)
		z	0.6210(16)	0.6262(14)	0.6271(16)
O(12)	2*e*	x	0.3351(29)	0.3399(25)	0.3283(27)
		y	0.25	0.25	0.25
		z	0.6876(24)	0.6844(21)	0.6871(24
O(13)	2*e*	x	0.8621(34)	0.8605(28)	0.8520(32)
		y	0.25	0.25	0.25
		z	0.6910(26)	0.6968(22)	0.6988(25)
		$U_{iso}\times100$[a]	1.71(9)	2.07(9)	1.61(10)

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

Table S2 The bond valence sums (BVS) for the cations and oxygen anions, and global instability indexes (*GII*) for Ba$RE_6(Ge_2O_7)_2(Ge_3O_{10})$ (*RE* = Tm, Yb, Lu)

		Tm		Yb		Lu	
Atom	Assumed oxidation state	BVS	% dev.	BVS	% dev.	BVS	% dev.
Ba	+2	1.780	10	1.792	10	1.861	7
RE(1)	+3	3.146	5	2.990	0	2.937	2
RE(2)	+3	3.155	5	3.154	5	3.060	2
RE(3)	+3	3.102	3	2.941	2	2.840	5
Ge(1)	+4	4.161	4	4.131	3	4.347	9
Ge(2)	+4	4.108	3	3.968	1	3.984	0
Ge(3)	+4	3.810	5	4.086	2	4.125	3
Ge(4)	+4	3.761	6	3.724	7	3.689	8
O(1)	-2	2.013	1	2.041	2	2.025	1
O(2)	-2	2.151	8	2.070	3	2.154	8
O(3)	-2	2.044	2	2.008	0	2.002	0
O(4)	-2	2.051	3	2.015	1	1.975	1
O(5)	-2	1.985	1	1.882	6	1.883	6
O(6)	-2	2.029	1	1.957	2	1.983	1
O(7)	-2	2.067	3	2.036	2	2.061	3
O(8)	-2	2.027	1	2.107	5	2.055	3
O(9)	-2	2.139	7	2.154	8	2.162	8
O(10)	-2	1.926	4	1.838	8	1.879	6
O(11)	-2	1.800	10	1.904	5	1.892	5
O(12)	-2	2.038	2	2.102	5	2.044	2
O(13)	-2	2.003	0	1.930	4	1.950	3
GII		0.13		0.12		0.14	

Table S3 IR and Raman wavenumbers (cm^{-1}) for Ba$RE_6(Ge_2O_7)_2(Ge_3O_{10})$, *RE* = Tm, Yb, Lu.

Tm		Yb		Lu		Assignment
IR	Raman	IR	Raman	IR	Raman	
946		956		963		ν_{as}(Ge-O-Ge)
853	860	854	863	856	860	ν_s(Ge-O)
	834		835		832	
805	799	806	799	809	795	ν_{as}(Ge-O)
752	768	752	772	755	769	
734		727		732		
548		549		551		ν_s(Ge-O-Ge)
504	503	504	505	506	501	
463		469		468		δ_{as}(O-Ge-O)
438	436	441	438	440	435	
394	409	395	408	397	407	δ_s(O-Ge-O)
	368		367		365	ρ_r(O-Ge-O)
	346		345		344	
	307		305		305	